HENRYK RYSZARD PARZENTNY[1]

The role of mineral matter in the concentration of phosphorus in bituminous coal seams from the Lublin Formation in the Lublin Coal Basin in Poland

Introduction

In non-organic sedimentary rocks, phosphorus occurs mainly in the minerals of the apatite group (e.g., Stamatakis 2004; Khan et al. 2012; Baioumy 2007). However, in the rocks surrounding coal strata and in the coal seams, the sources of phosphorus apart from these minerals are also: crandallite, goyazite, gorcexite (e.g. Kokowska-Pawłowska and Nowak 2013; Muszyński and Wyszomirski 1998; Rao and Walsh 1999; Ward 2002; Ward et al. 1996). Studies the of contents and mode of minor elements binding in coal are important to understand the causes and sites of their accumulation in the coal deposits. The arrangement of the elements in a deposit is the result of processes associated with the accumulation of organic matter, coalification, as the interactions between organic matter and syn- and epigenetic solutions, and volcanic interference.

Recently, the object of the geochemical studies of Polish coal-bearing formations were mainly coals from the Upper Silesian Coal Basin (USCB), and Lover Silesian Coal Basin (LSCB) and, rarely, from the Lublin Coal Basin (LCB). The increasing share of LCB coals in the total weight of the annual coal production in Poland encourages its deeper geochemical recognition. Geochemical investigation of these coals began in 1978 in the Polish Geological Institute in Warsaw (PGI). In cooperation between the Upper Silesian Branch of the PGI in

✉ Corresponding Author: Henryk Ryszard Parzentny; e-mail: hr.parzentny@vp.pl

[1] University of Silesia in Katowice, Poland; e-mail: hr.parzentny@vp.pl

Sosnowiec; the Central Mining Institute in Katowice; and the Department of Earth Sciences, the University of Silesia, covered under the "Fund of Maria Curie-Skłodow-ska", program the contents of 25 minor elements and trace elements were determined in the coal from the boreholes in the Chełm seam. In these investigations it was found, among others, that the content of most elements in the coal decreases with the depth of the deposit; and Be, Cu and Zn are bonded with organic matter; and Li, Mo, Cd, Cr, V, Pb and Zn are associated with the mineral substance (Bojakowska and Pasieczna 2007; Cebulak 1983; Cebulak and Różkowska 1983; Marczak 1985; Marczak and Lewińska 1982; Marczak and Parzentny 1985, 1989).

The phosphorus occurrence in the LCB coal has been described so far in two publications. Firstly Cebulak (1983) calculated the ratio of coal enrichment in P relative to the Earth's crust (equal to 0.21), and then Staniek (1985) described the P_2O_5 content in coal ash from the 382 seam (0.87 wt. %) and the 383 seam (4.87 wt. %) in the Bogdanka mine and ash derived from coal from 10 boreholes (1–4 wt. %) adjacent to this mine.

In the current study there is an opportunity for determining previously ungratified information about the mode of phosphorus binding in the LCB coal. This information can be used in the prediction of this element contents in the furnace waste, sometimes used as an additive to soils improving their properties. The author previously determined the content and mode of binding of Ag, Sn and W – in the mineral matter of coal from the LCB (Parzentny 2009). The aim of the present paper is to define the role of mineral and organic matter on the concentration of phosphorus in coal from the Lublin Formation, the most coal-bearing strata being the best developed and recognized in terms of the mining parts of the LCB.

1. Material and methods

The study included 30 samples of bituminous coal taken from the Bogdanka and Chełm deposits. The geological characteristics of the researched areas in the LCB (after Porzycki and Zdanowski 1995) and the location of the places from where samples were taken were presented in the previous article (Parzentny 2009). The simplified scheme of the geological structure of the researched areas is shown in Figure 1. The Chełm samples come from the 378, 382, 385, 387, 389, 391, and 394 seams, which PGI identified in the seven cores of the 7 boreholes (the Cyców IG-5, Cyców IG-6, Dorohucza IG-4, Dorohucza IG-6, Dorohucza IG-8, Syczyn IG-2, and Syczyn IG-3), sampled and transferred or investigation. In the Bogdanka seam, eight coal seam samples were taken, with four samples from the 382 and 385 seams by means of cutting out a column of coal in the seam, starting from the floor to the roof of the seam.

Maceral and mineral compositions were determined using a Zeiss Axio Imager D1m microscope (40 × objective, 10 × oculars, 546-nm interference filters, non-polarized reflected light, oil immersion with the refractive index n = 1.5176 at 23°C) and a D8 Discover X-ray Diffractometer (iron-filtered CoKα radiation, Ni filter and Lynxeye detector). The results are shown in Table 1. The ash content in coal was found in 525°C. The contents of P, Si, Al, Fe,
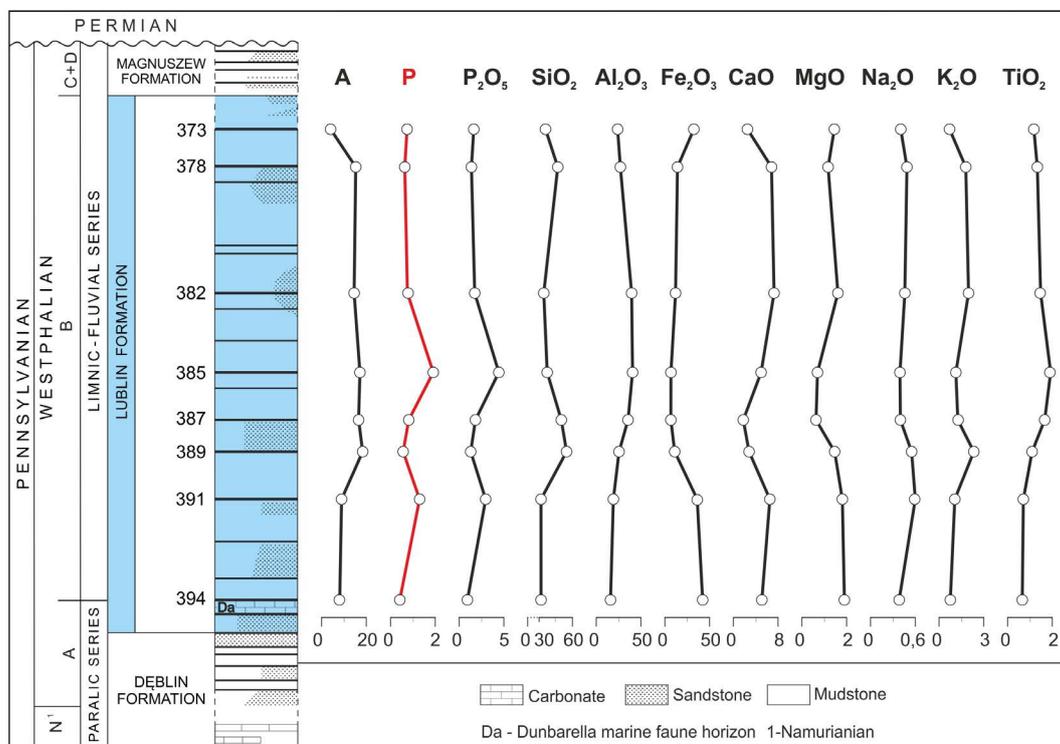
Fig. 1. Contents (wt. %) of ash and phosphorus in coal and P_2O_5, SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O and TiO_2 contents in coal ash in vertical profile of the Lublin Formation

Rys. 1. Zawartość (% wag.) popiołu węgla i fosforu w węglu oraz zawartość P_2O_5, SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O i TiO_2 w popiele węgla w profilu pionowym formacji Lublina

Ca, Mg, Na, K, and Ti in coal ash were determined by inductively coupled plasma-emission spectrometry (ICP-ES); next recalculated to the phosphorus contents in the coal and the oxides contents of other elements in the coal ash (Table 2, Figs. 1–3). A scanning electron microscope with energy dispersive X-ray (SEM/EDS) was used to determine the mineral and phosphorus contents in the grains of macerals and mineral matter. The analytical conditions were as follows: Acc. voltage = 15.0 kV, bse-comp = 30Pa, image resolution = 1024 × 768, image pixel size = 0.04–0.27 μm, magnification = 90–5000×). The results are shown in Fig. 4.

2. Calculations

Based on Pearson's chi-square test and the Kolmogorov-Smirnov and Shaphiro-Wilk tests (at the $\rho = 0.05$ significance level) it was found that the contents of petrographic and

Table 1. Petrographic composition (% vol.), coal ash content (wt. %) and vitrinite reflectance (%) of coal from Lublin Formation

Tabela 1. Skład petrograficzny (% vol.), zawartość popiołu węgla (% wag.) i refleksyjność witrynitu (%) węgla z formacji Lublina

Component	Content
Vitrinite	57.3
	(63.7)*
Liptinite	23.1
	(25.7)*
Inertinite	9.6
	(10.6)*
Mineral matter	10.0
Kaolinite	2.4
Illite+muscovite	1.9
Montmorillonite	0.3
Quartz	1.9
Chalcedony	0.2
Feldspar	0.3
Siderite	0.2
Dolomite+ankerite	0.8
Jarosite	sg
Gypsum	sg
Pyrite+marcasite	1.8
Chalcopyrite	sg
Galena	sg
Sphalerite	sg
Crandallite ?	0.1
Apatite ?	0.1
Coal ash content	13.9
Vitrinite reflectance	0.64

* Petrographic composition in terms of coal without mineral matter; sg – single grain.

geochemical components show a normal distribution, and the arithmetical mean value estimates the average value well. In order to find the relationship between the ash content and the phosphorus content in the coal and coal ash, and between the phosphorus content in the coal and the contents of 26 other elements in the investigated coal (Ag, As, Ba, Be, Bi, Cd, Co, Cr, Cu , La, Mn, Mo, Nb, Ni, Pb, Sb, Sc, Sn, Sr, Th, U, V, W, Y, Zn, and Zr) values of the Pearson correlation coefficient were calculated. Only statistically significant value of this factor of > ± 0.35 are given in Table 3.

Significant information concerning the trace-element affinity to organic- and inorganic coal fractions can be obtained from the data given by the concentration-distribution (*CD*) function of Marczak (1985) given below:

$$CD = C_A = C_0 \frac{A-1}{A} + KA + C_m$$

- A – ash content expressed as a mass fraction;
- C_A – trace element concentration (g/Mg) in ash;
- C_0 – average trace-element concentration (g/Mg) in organic coal substance;
- K – proportionality factor expressing a concentration increase (g/Mg) in ash;
- C_m – trace element concentration (g/Mg) in coal ash for a limit value $A = 0$.

The value A is determined empirically as the ash content in coal. Values of C_0, K, and C_m are determined mathematically by solving a system of three equations with three variables. $C_0 (1 - A)/A$ in the above equation determines that part of the content of an element in coal ash that is associated with organic matter. $KA + C_m$ involves the part which results from the presence of an element in the mineral matter. It has been previously shown that the *CD* function is useful in determining which part of a given trace-element concentration is associated with the organic fraction in coal, and which with the inorganic fraction (Lewińska-Preis et al. 2009; Parzentny 1994). The results obtained are given in Table 3.

3. Results

3.1. Petrographic characteristics of coal seams

The petrographic composition of the tested coal, when recalculated as coal without mineral matter (Table 1), is similar to that of Palaeozoic coals in the North Atlantic region (Vt = 68%, L = 12%, I = 20%) as determined by Vasconcelous (1999). In the coal seams there are accumulations of mineral matter, most commonly as veins in claystones and polimorphs FeS$_2$ veins. The 382 and 385 coal seams in the Lublin Coal Bogdanka Mine have a layer of tonstein (2.0–4.0 cm thick) and claystone, whereas in cores intersecting 387 and 391 seams

Table 2.   Phosphorus content in researched coal compared to the results of other authors

Tabela 2.   Zawartość fosforu w badanym węglu w porównaniu z wynikami badań innych autorów

Author	Deposits, Beds	Content	
		P (g/Mg) in coal	P$_2$O$_5$ (wt %) in coal ash
Ketris and Yudivich (2009)	Coal Clarke values	250±10	0.15±0.01
Coal from LSCB			
Jęczalik (1970)	dpcs*	120**	
Pendias (1964)	Wałbrzych + Biały Kamień	48**	0.080**
Pendias (1966)	Żacler	54***	0.089**
	Arithmetic mean	74.0	0.085
Coal from USCB			
Bouśka (1981)	Ostrava		0.953**
	Karvina		0.877**
Fleck (1865)	Anticlinal Member	185	0.356**
Gabzdyl (1967)	Jastrzębie	205**	0.764**
Grundmann (1861)	Anticlinal Member	108***	0.191**
Hajdus et al. (1981)	Jaworzno–Mikołów	36**	0.046**
Jensch (1886)	Pokój	578**	0.985**
Jęczalik (1970)	dpcs*	322**	0.619
Krzyżanowska (1960) – citation after Kuhl and Dąbek (1961)	Bielszowice	677**	5.22
Kuhl (1961)	Marcel	582**	1.305**
Kuhl and Dąbek (1961)	Bielszowice	1055**	1.06
Kuhl and Aleksa (1967)	Pokój	358**	0.47
Kuhl and Widawska-Kuśmierska (1978)	Marcel		0.92
Kuśmierska (1978)	Zofiówka		4.71
Marcisz (2014)	Pniówek + Zofiówka	83***	0.147**
Mielecki et al. (1963)	dpcs*	318**	0.545**
Morga (2007)	Pniówek	86***	0.151**
Olkuski et al. (2010)	Jastrzębie Revier	53***	0.094**
Róg (2005)	dpcs*	356**	0.81**
Różkowska (1993)	dpcs*	412	0.792**
Różkowska and Parzentny (1990)	22 boreholes	404	0.808**
Widawska-Kuśmierska (1975)	Brzeszcze + Wesoła		0.28–1.20
Widawska-Kuśmierska (1981)	dpcs*		0.1–5.0
Wnękowska and Czubek (1951)	dpcs*	515**	0.907***
	Arithmetic mean	352.0	1.032
Coal from LCB			
Staniek (1985)	16 borehole and Bogdanka	1098***	1.696**
Researched area average		1375	2.267
range		0.077–2.644	0.206–6.055
	Arithmetic mean	1236.5	1.982

  * Different places and coal seams.
 ** Calculated by the author based on results by authors cited.
*** Calculated by the author based on the results authors cited and average content of ash in coal from LSCB (14.00%, by Bossowski 1995), USCB (13.00%, by Jureczka and Kotas 1995), LCB (14.82%, by Porzycki and Zdanowski 1995).

other authors found both layers and lenses of sediment of the origin pyroclastic (Lipiarski et al. 1993; Muszyński and Wyszomirski 1998; Porzycki and Zdanowski 1995). The composition of this matter mineral is dominated by pyrite and lower amounts of kaolinite and illite, and sporadically occurring phosphate minerals (probably crandallite and apatite).

On the basis of vitrinite reflectance ($R_{o\ average}$ = 0.64%, Table 1) the studied coal was included into ortho-bituminous coal of medium rank (type C).

3.2. Phosphorus content in coal seams

The average content of phosphorus in the Lublin Formation investigated coal is significantly higher than hard coal Clarke values (Table 2). There are significant differences in the content of phosphorus in coal and in coal ash in the Lublin Formation profile (Fig. 1). These changes are accompanied by similar changes in the content of Al_2O_3 (Pearson's correlation coefficient r = 0.50, Table 3) and TiO_2 in the coal ash (r = 0.47), and ash content in coal (r = 0.37), as well as the lack of such dependence in the distribution of the SiO_2, CaO, MgO, Fe_2O_3, Na_2O, and K_2O contents in ash coal. Particularly high levels of phosphorus in coal and coal ash were found in the currently exploited 385 and 391 coal seams in the mining area of the Lublin Coal Bogdanka Mine and its SE neighborhood (Cyców IG-5, Cyców IG-6, Dorohucza IG-4 boreholes, Fig. 2). The difference between the maximum and the minimum value of the phosphorus content in the coal between the coal sampling regions is high and decreases in the order of the following seams: 385 (1.97%), 391 (1.72%), 389 (1.15%), 387 (0.05%), 382 (0.92%), 394 (0.89%), and 378 (0.87%). The large difference in phosphorus contents in coal and high phosphorus content in 382, 385, 387, and 391 coal seams coincide with tonstein and claystone layers within these seams.

The high levels of phosphorus in coal and coal ash are most common in coal seams with a thickness of 1.20 m to 1.80 m (Fig. 3), i.e. the seams included into the economic LCB seams. This variability in P contents in coal is often accompanied by similar trends in ash content in coal and Al_2O_3 and TiO_2 contents in coal ash.

3.3. The role of organic and mineral matter in the concentration of phosphorus in coal

The following values of the Pearson correlation coefficient: 0.39 (rA-P in coal), 0.50 (rAl-P in coal), and 0.47 (rTi-P in coal) show the relationship between the increase of phosphorus content in coal and the content of mineral matter in coal (Table 3). The solution of the *CD* functions indicates a decisive influence of mineral matter on the P contents in coal and coal ash. SEM/EDS analysis showed a high phosphorus content in kaolinite aggregates of pyroclastic origin in the 382 and 385 coal seams (Fig. 4). Isometric grains (size 5–25 microns) of phosphates, probably crandallite and apatite are quite often present in these aggregates.
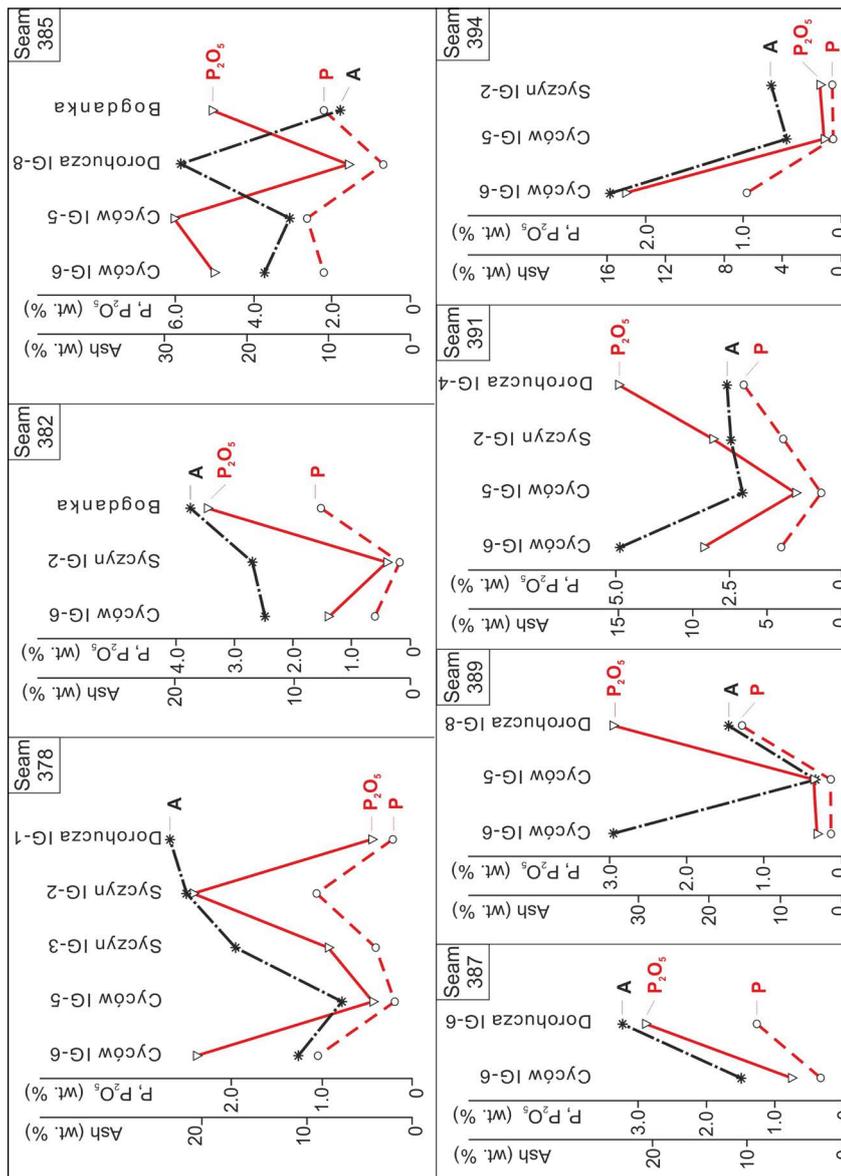
Fig. 2. Contents (wt. %) of ash and phosphorus in coal and P$_2$O$_5$ content in coal ash shown along the ranges of some coal seams of the Lublin Formation (the order of the boreholes is random)

Rys. 2. Zawartość (% wag.) popiołu i fosforu w węglu oraz zawartość P$_2$O$_5$ w popiele węgla po rozciągłości niektórych pokładów węgla w formacji Lublina (kolejność odwiertów jest losowa)
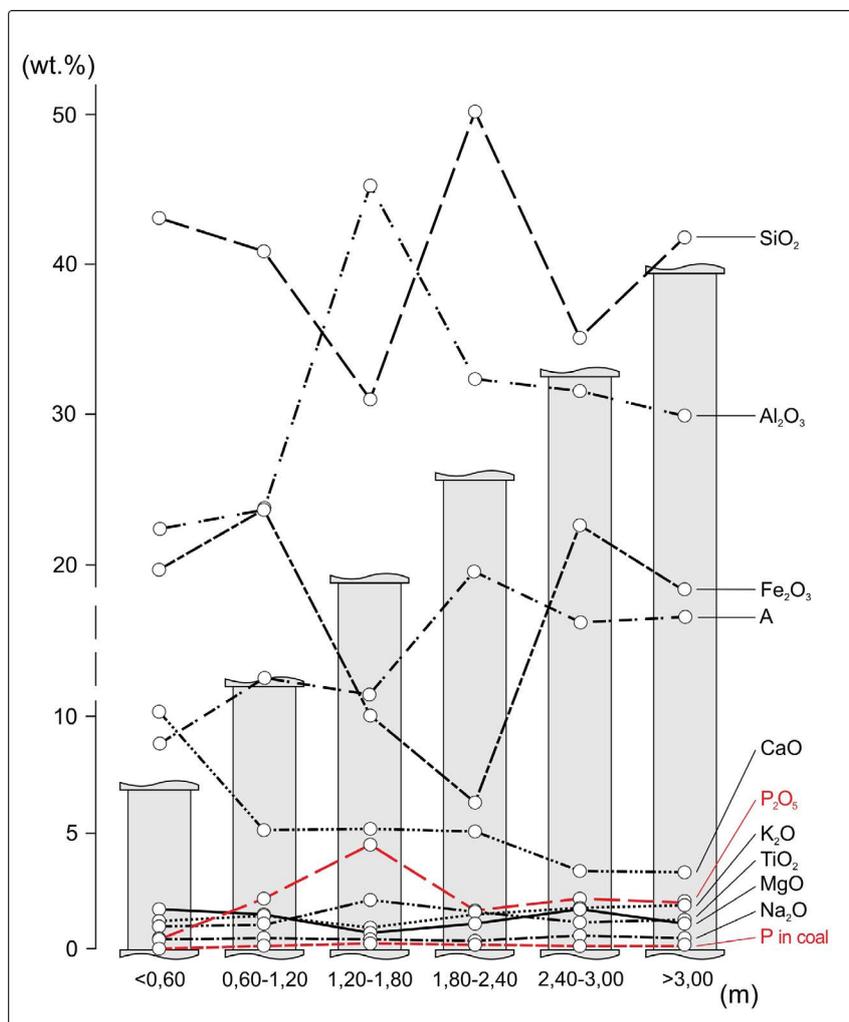
Fig. 3. Contents (wt. %) of ash and phosphorus in coal and P_2O_5, SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O, and TiO_2 contents in coal ash in coal seams of varying thickness in Lublin Formation

Rys. 3. Zawartość (% wag.) popiołu i fosforu w węglu oraz zawartość P_2O_5, SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O i TiO_2 w popiele węgla w zależności od grubości pokładów węgla w formacji Lublina

Additionally, there was a correlation between the phosphorus content and the content of Ba, Sn, Sr, Th, and Zr in coal, indicating the possibility of the coexistence of these elements in mineral substances of LCB coal. The presence of these elements in the vicinity of phosphate minerals was not confirmed by SEM/EDS, which does not exclude the coexistence of Ba and P, Sn, Sr, Th, and Zr in other forms of aggregates of mineral matter.
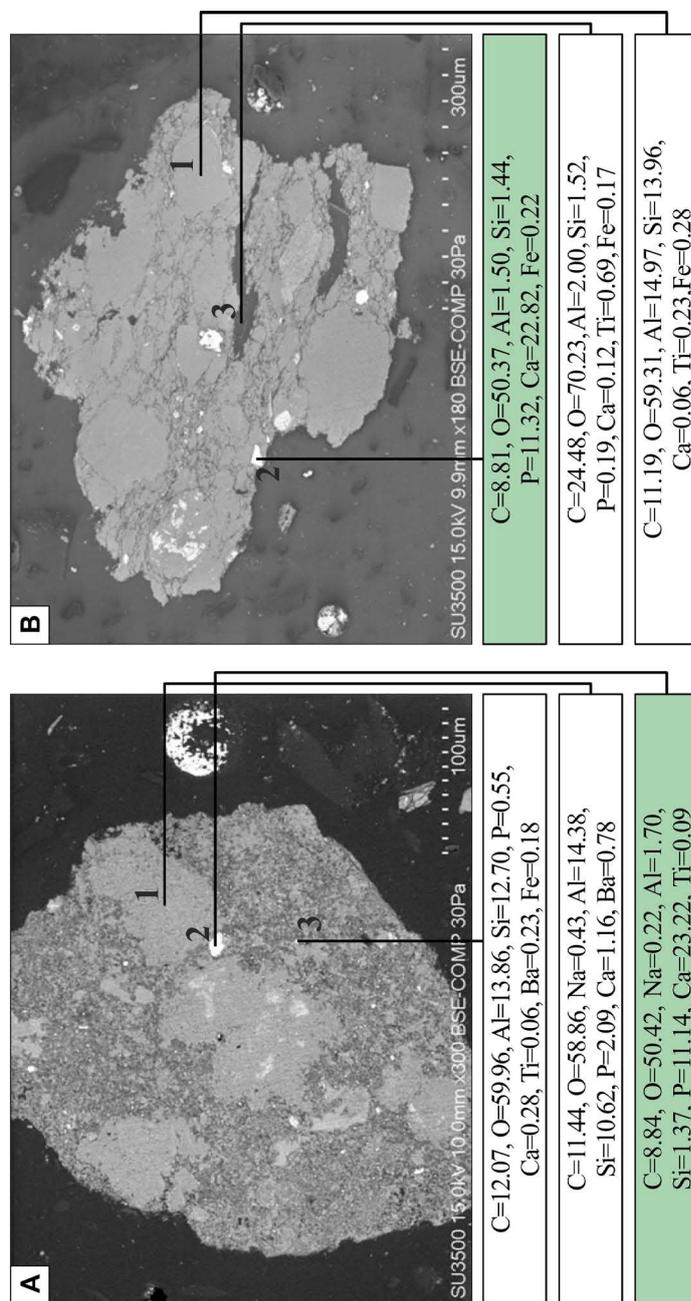
Fig. 4. SEM/EDS analysis of the: A – kaolinite aggregates (1, 3), and phosphorus minerals (2) in coal from coal seams 382; B – kaolinite aggregates (1), phosphorus minerals (2), and vitrinite streak (3) in tonstein from coal seams 385 in the Lublin Formation

Rys. 4. SEM/EDS analiza: A – agregatów kaolinitu (1, 3) i mineralów fosforanowych (2) w węglu z pokladu 382; B – agregatów kaolinitu (1), mineralów fosforanowych (2) i smugi witrynitu (3) w tonsteinie z pokladu 385 w formacji Lublina

Table 3.   Phosphorus distribution between the organic and mineral matter of coal from the Lublin Formation, determined using the *CD* function

Tabela 3.   Dystrybucja fosforu między organiczną i mineralną materią węgla z formacji Lublina, określona przy użyciu funkcji *CD*

Phosphorus	Organic matter		Mineral matter	
	wt. %	%	wt. %	%
In coal ash	0	0	1.503	100.0
In coal*	0	0	0.134	100.0

* Pearson correlation coefficients (r) of phosphorus (P) in coal with coal ash (A), and some elements: rA – P = 0.39, rP – Al = 0.50, rP – Ti = 0.47, rP – Ba = 0.38, rP – Sn = 0.40, rP – Sr = 0.81, rP – Th = 0.40, rP – Zr = 0.32.

From the SEM/EDS analysis, it was found that the content of phosphorus in coal macerals from coal seams, which do not have tonstein layers and macerals occurring at a greater distance from tonstein (> 20 cm) is low or lower than the detection limit of SEM/EDS (Fig. 4). In contrast, the phosphorus content of vitrinite being in direct contact with tonstein (<20 cm) or in a maceral dissecting a tonstein layer is greater than 0.10 wt. %.

4. Discussion

In order to assess the geochemistry of the investigated coal geochemically and compare it to LSCB and USCB coals, an average P content in the coal and coal ash were calculated using previously published results of other authors. The comparison, summarized in Table 2, indicated that the average P content in coal from the Lublin Formation is significantly higher than that in coal from the LSCB and the USCB. A large value difference and an extremely high content of P in coal and coal ash has been previously reported in the coal ash from USCB (ca 5 wt. % P_2O_5 in coal ash) by several authors (Kuhl and Dąbek 1961; Kuhl and Widawska-Kuśmierska 1978; Różkowska and Parzentny 1990; Widawska-Kuśmierska 1981). The highest P_2O_5 content in coal ash, up to 20 wt. %, was found in the Cook Inlet coals in Alaska (Rao and Walsh 1999).

The large differences in P contents in the coal investigated is not justified in increasing or decreasing P content in coal, depending on the stratigraphic affiliation of coal seams in the Lublin Formation (Fig. 1), or the thickness of the seams (Fig. 3). No trend in changes of P contents in coal was reported earlier in USCB coals (Marcisz 2014; Morga 2007; Różkowska and Parzentny 1990) and in coal beds from Alaska (Rao et al. 1999) and Australia (Ward et al. 1996).

The high average P contents and their high variability in hard coal from the Lublin Formation probably result from a different genesis of this element in some coal seams in different

areas of their occurrence in LCB. The largest source of phosphorus in the 382, 385, 387, and 391 coal seams is probably from pyroclastic sediments, and in coal seams without tonsteins (378, 389, 394) – plant and animal remains. The observed weak correlation between increased P content and a reduced content of Fe_2O_3 in the coal from the 382, 385, and 387 seams (Fig. 1) indicates the increased rate of phosphorus transition from organic matter to solutions of paleo-peatbog, which was indicated by Patric and Khalid (1974). Phosphorus of this origin is usually sorbed by clay minerals. A large P content in the coal and coal ash from the 394 seam (formed under paralic conditions) from the Cyców IG-6 borehole and the simultaneous relatively low P content in the coal from the Cyców IG-5 and Syczyn IG-2 boreholes (Fig. 3) indicate no effect of the marine fauna on the content of this element in the LCB paleo-peatbog.

According to Yudovich et al. (1985) in the coal of low and medium P content and low ash content, the major fraction of phosphorus in coal is bound to organic matter. At the same time, the organic phosphorus main source are phosphorus compounds adsorbed on peat and the secondary source are the remains of plants and animals. In contrast, in coals with above-the average and high P contents, the larger fraction of this element is present in the mineral matter as phosphates of aluminum, iron, and calcium. A large part of organic phosphorus is transformed to mineral phosphorus during coalification, resulting in the weight ratio of these two forms of phosphorus in lignite it is higher than in bituminous coal. There are autogenous apatite, gyoazite, gorceixite, and crandallite in the vitrinite vicinity (Ward et al. 1996). However, the main source of inorganic phosphorus in coal veins are pyroclastic materials (Kokowska-Pawłowska and Nowak 2013; Lipiarski et al. 1993; Muszyński and Wyszomirski 1998; Rao and Walsh 1999; Ward 2002).

Large amounts of phosphorus in the Lublin Formation coal is very disadvantageous for this coal application as a possible component of coking coal mixtures. Almost all the phosphorus contained in coal passes to the coke produced from it, which then enters the steel, worsening its properties (Diez et al. 2002; Mahony et al. 1981; Michalik and Bronny 2001; Sakurovs et al. 2007). The LCB bituminous coal due to its adverse physico-chemical indicators of coal quality has not been so far used for coking (Michalik and Bronny 2001). However, the high content of phosphorus in hard coal and coal ash from the Lublin Formation appears to be beneficial to the environment in the case of using fly ash to improve the soil quality. In coal combustion with a high P content, a large part of the phosphorus is in the phosphate mineral relics and spheres (phosphospheres) and in coal fly ash (Valentim et al. 2016), which may be slowly leached into the soil (Ciećko et al . 2015; Seshadri et al. 2013), and lead to improved soil fertility.

Conclusions

1. It was found that there are high phosphorus contents in coal (1.38 g/Mg) and P_2O_5 in coal ash (2.27 wt%) of the Lublin Formation that are significantly higher than in USCB and

LSCB coals and coal ash, and much higher than Coal Clarke values. The P contents in coal and coal ash from the 385 and 391 coal seams in the area of the Lublin Coal Bogdanka Mine and in the area of its SE neighbor is the highest (max. 2.64 wt. % in coal and 6.06 wt. % of P_2O_5 in coal ash).

2. Phosphate minerals (probably apatite and crandallite) present in kaolinite aggregates in tonsteins contain the most phosphorus and have the greatest impact on the average P contents in coals of the Lublin Formation.

   ◆ In the coal seams containing tonsteins (382, 385, 387, 391) a number of isometric (5–25 μm) authigenic grains of phosphate minerals (probably apatite and crandallite) were found, which are the main source of phosphorus in coal, especially in the immediate vicinity of the tonstein veins.

   ◆ The secondary source of phosphorus in the above-mentioned coal seams (i.e. 382, 385, 387, and 391) and the main source of phosphorus in the coal from seams that contains mineral matter of pyroclastic origin (378, 389, 394) are probably clay minerals, which adsorbed phosphorus compounds derived from organic matter.

REFERENCES

Baioumy, H.M. 2007. Iron-phosphorus relationship in the iron and phosphorite ores of Egypt. *Chemie Erde – Geochemistry* 67, pp. 229–239.

Bojakowska, I. and Pasieczna, A. 2007. Arsenic and antimony in hard and brown coal from Polish deposits. *Ochrona Środowiska i Zasobów Naturalnych* 31, pp. 522–526 (*in Polish*).

Bossowski, A. 1995. Lower Silesian Coal Basin. Coal deposits [In:] Zdanowski, A. and Żakowa, H. Eds. The Carboniferous system in Poland. *Papers of the Polish Geological Institute* 148, pp. 173–175.

Bouška, V. 1981. *Geochemistry of coal*. Academia Prague. Czechoslovak Academy of Sciences, pp. 1–259.

Cebulak, S. 1983. *Determination of geochemical components of coal from the point of view of full utilization and environmental preservation* [In:] Bojkowski, K. and Porzycki, K. Eds. *Geological problems of coal basins in Poland*. Warszawa: Geological Institute, pp. 335–361.

Cebulak, S. and Różkowska, A. 1983. Correlate coal seams in the central coal region, Lublin Coal Basin, on the basis of geochemical data. *Kwartalnik Geologiczny* 27(1), pp. 25–40 (*in Polish*).

Ciećko, Z. et al. 2015 – Ciećko, Z., Żołnowski, A.C., Madej, M., Wasiak, G. and Lisowski, J. 2015. Long-Term Effects of Hard Coal Fly Ash on Selected Soil Properties. *Polish Journal of Environmental Studies* 24, pp. 1949–1957.

Diez, M.A. et al. 2002 – Diez, M.A., Alvarez, R., Barriocanal, C. 2002. Coal for metallurgical coke production: predictions of coke quality and future requirements for cokemaking. *International Journal of Coal Geology* 50, pp. 389–412.

Fleck, H. 1865. The chemical composition and chemical properties of coal [In:] Geinitz, H.B., Fleck, H. and Hartig, E. eds. Die Steinkohlen Deutschlands und anderer Länder Europas. Oldenbourgh R. Verlag, München 2, pp. 1–223 (*in German*).

Gabzdyl, W. 1967. Petrographical characteristics of coking coal from Jastrzębie Mine (ROW). *Przegląd Górniczy* 23, pp. 377–382 (*in Polish*).

Grundmann, F.W. 1861. Chemical analysis of the hard coal of Upper Silesia. *Zeitschrift für das Berg-Hütten und Salinenwesen in dem Preussischen Staate* 19, pp. 198–207 *(in German)*.

Hajdus et al. 1981 – Hajdus, D., Łoziński, J. and Steczko, K. 1981. Selected issues of laboratory tests of ash and slag byproducts of coal gasification process. *Koks Smoła Gaz* 26, pp. 243–247 (*in Polish*).

Jensch, E. 1886. About the metal content of Upper Silesian hard coal. *Chemie Industrie* 10, pp. 54–55 (*in German*).

Jęczalik, A. 1970. Geochemistry of uranium in uranium-rich hard coal in Poland. *Biuletyn Instutu Geologicznego* 224(4), pp. 103–195 (*in Polish*).

Jureczka, J. and Kotas, A. 1995. Coal deposits [In:] Zdanowski, A. and Żakowa, H. Eds. Upper Silesian Coal Basin: The Carboniferous system in Poland 148. *The works of Polish Geol. Institute*, Warsaw, pp. 164–173.

Ketris, M.P. and Yudivich, Ya.E. 2009. Estimations of Clarkes for Carbonaceous biolithes: World avarages for trace element contents in black shales and coals. *International Journal of Coal Geology* 78, pp. 135–148.

Khan et al. 2012 – Khan, K.F., Dar, S.A. and Khan, S.A. 2012. Geochemistry of phosphate bearing sedimentary rocks in parts of Sonrai block, Lalitpur District, Uttar Pradesh, India. *Chemie Erde – Geochemistry* 72, pp. 117–125.

Kokowska-Pawłowska, M. and Nowak, J. 2013. Phosphorus minerale in tonstein: coal seam 405 in Sośnica-Makoszowy coal mine, Upper Silesia, southern Poland. *Acta Geologica Polonica* 63, pp. 271–281.

Kuhl, J. 1961. Chemical-mineral structure of inorganic mineral matter in coal. *Kwartalnik Geologiczny* 5, pp. 801––813 (*in Polish*).

Kuhl, J. and Aleksa, H. 1967. The autoflotation of coal slurries. *Przegląd Górniczy* 23, pp. 363–365 (*in Polish*).

Kuhl, J. and Dąbek, H. 1961. The chlorine and phosphorus in the hard coal of Upper Silesia. *Przegląd Górniczy* 17, pp. 443–446 (*in Polish*).

Kuhl, J. and Widawska-Kuśmierska, J. 1978. *Composition of coals mineral substance and its influence on the utilizations processes* [In:] *Materials of analytical conservatory: Analytical methods for analyzing the carbonaceous resources.* Katowice: Polish Academy of Sciences, pp. 45–57 (*in Polish*).

Lewińska-Preis et al. 2009 – Lewińska-Preis, L., Fabiańska, M.J., Ćmiel, S.and Kita, A. 2009. Geochemical distribution of trace elements in Kaffioyra and Longyearbyen coals, Spitsbergen, Norway. *International Journal of Coal Geology* 80, pp. 211–223.

Lipiarski et al. 1993 – Lipiarski, I., Muszyński, M. and Stolecki, J. 1993. Tonstein from the coal seam no. 385 in the Lublin Formation (Lower Westphalian) from the Lublin Coal Basin. *Kwartalnik Geologiczny* 37, pp. 537–564.

Mahony et al. 1981 – Mahony, B., Moulston, I. and Wilkinson, H.C. 1981. Sudy of the relationship between the phosphorus content of coal and coke. *Fuel* 60, pp. 355–358.

Marcisz, M. 2014. Phosphorus content in deposits of Zofiówka Monocline (SW part of the Upper Silesian Coal Basin). *Gospodarka Surowcami Mineralnymi – Mineral Resources Management* 30, pp. 67–83 (*in Polish*).

Marczak, M. 1985. Genesis and regularities of the elements occurrence in the Chełm Coal Deposit at Coal Basin of Lublin. *Prace Naukowe Uniwersytetu* Śląskiego 748, pp. 1–109 (*in Polish*).

Marczak, M. and Lewińska, L. 1982. Molybdenum in hard coal of Chełm deposits, Lublin Coal Basin. *Prace Naukowe Uniwersytetu* Śląskiego, *Geologia* 6, pp. 22–32 (*in Polish*).

Marczak, M. and Parzentny, H. 1985. Geochemical and ecological evaluation of Pb-enriched coals from the Chełm deposits. *Przegląd Geologiczny* 33, pp. 680–683.

Marczak, M.and Parzentny, H. 1989. Concentration of cadmium as a criterion in ecological evaluation of coals from the Chełm deposits, Lublin Coal Basin. *Przegląd Geologiczny* 37, pp. 272–275 (*in Polish*).

Michalik, A. and Bronny, M. 2001. Quality parameters of coke fulfilling the requirements of blast furnace operators and the physico-chemical properties of the available coal base. *Karbo* 2, pp. 53–56 (*in Polish*).

Mielecki et al. 1963 – Mielecki, T., Chruściel, Z., Grayner, J., Karkosz, R. and Szulakowski, W. 1963. Research on the possibility of improving the quality of the national small coal energy. *Prace Głównego Instytutu Górnictwa w Katowicach seria B*, komunikat 331 (*in Polish*).

Morga, R. 2007. Structure of variability of phosphorus content in exploited seams of bituminous coal in the Pniówek Mine. *Gospodarka Surowcami Mineralnymi – Mineral Resources Management* 23, pp. 29–48 (*in Polish*).

Muszyński, M. and Wyszomirski, P. 1998. New occurrences of the crandallite group minerals in sedimentary rocks of Poland. *Mineralogia Polonica* 29, pp. 19–27.

Olkuski et al. 2010 – Olkuski, T., Ozga-Blaschke, U. and Stala-Szlugaj, K. 2010. Occurrence of phosphorus in hard coal. *Gospodarka Surowcami Mineralnymi – Mineral Resources Management* 26, pp. 23–35 (*in Polish*).

Parzentny, H. 1994. Lead distribution in coal and coaly shales in the Upper Silesian Coal Basin. *Kwartalnik Geologiczny* 38, pp. 43–58.

Parzentny, H. 2009. Silver, Tin and volframium in the Lublin Formation coal (westphal B) in the Lublin Coal Basin. *Gospodarka Surowcami Mineralnymi – Mineral Resources Management* 25, pp. 147–167 (*in Polish*).

Patric, W.H. and Khalid, R.A. 1974. Phosphate Release and Sorption by Soils and Sediments: Effect of Aerobic and Anaerobic Conditions. *Science* 186, pp. 53–55.

Pendias, H. 1964. Geochemical research of coal from Wałbrzych and Biały Kamień Member of Wałbrzych Basin. *Kwartalnik Geologiczny* 8, pp. 769–788 (*in Polish*).

Pendias, H. 1966. Geochemical research of coal from Żacler seam in Wałbrzych Basin. *Kwartalnik Geologiczny* 10, pp. 296–314 (*in Polish*).

Porzycki, J. and Zdanowski, A. 1995. Coal deposits, Lublin Coal Basin and Soudheastern Poland (Lublin Carboniferous Basin) [In:] Zdanowski, A. and Żakowa H. Eds. The carboniferous system in Poland. *Papers of the Polish Geological Institute* 148, pp. 102–109 and 159–164.

Rao, P.D. and Walsh, D.E. 1999. Influence of environments of coal deposition on phosphorous accumulation in a high latitude, northen Alaska, coal seam. *International Journal of Coal Geology* 38, pp. 261–284.

Róg, L. 2005. Natural radioactivity of hard coal and density fractions of different petrographic and chemical structure. *Research Reports Mining and Environment* 3, pp. 81–101 (*in Polish*).

Różkowska, A. 1993. Subordinate and trace elements in the deep-seated productive Carboniferous of the Upper Silesian Coal Basin. *Przegląd Geologiczny* 41, pp. 780–785 (*in Polish*).

Różkowska, A.and Parzentny, H. 1990. The contents of phosphorus in the Black coals from the Upper Silesian Coal Basin. *Kwartalnik Geologiczny* 34, pp. 611–622 (*in Polish*).

Sakurovs et al. 2007 – Sakurovs, R., French, D. and Grigore, M. 2007. Quantification of mineral matter in commercial cokes and their parent coals. *International Journal of Coal Geology* 72, pp. 81–88.

Seshadri et al. 2013 – Seshadri, B., Bolan, N., Choppala, G. and Naidu, R. 2013. Differential effect of coal combustion products on the bioavailability of phosphorus between inorganic and organic nutrient sources. *Journal of Hazardous Materials* 261, pp. 817–825.

Stamatakis, W.G. 2004. Phosphate deposits of Neogene age in Greece. Mineralogy, geochemistry and genetic implications. *Chemie Erde – Geochemistry* 64, pp. 329–350.

Staniek, L. 1985. The report on phosphorus and beryllium in the Lublins coal. *Zeszyty Naukowe Politechniki* Śląskiej*, seria Górnictwo* 132, pp. 87–98 (*in Polish*).

Valentim et al. 2016 – Valentim, B., Flores, D., Guedes, A., Guimarães, R., Shreya, N., Paul, B. and Ward, C.R. 2016. Notes on the occurrence of phosphate mineral relics and spheres (phosphospheres) in coal and biomass fly ash. *International Journal of Coal Geology* 154–155, pp. 43–56.

Vasconcelos, L. 1999. The petrographic composition of world coals. Statistical results obtained from a literature survey with reference to coal type (maceral composition). *International Journal of Coal Geology* 40, pp. 27–58.

Ward, C.R. 2002. Analysis and significance of mineral matter in coal seams. *International Journal of Coal Geology* 50, pp. 135–168.

Ward et al. 1996 – Ward, C.R., Corcoran, J.F., Saxby, H.W. and Read, H.W. 1996. Occurrence of phosphorus minerals in Australian coal seams. *International Journal of Coal Geology* 30, pp. 185–210.

Widawska-Kuśmierska, J. 1975. Occerrence of gallium in coal fractions of different specyfic weight. *Bulletin de L'Academie Polonaice des Sciences, Serie Science de la Terre* 23, pp. 89–95.

Widawska-Kuśmierska, J. 1981. The presence of trace elements in the Polish hard coal. *Przegląd Górniczy* 37, pp. 455–459 (*in Polish*).

Wnękowska, L. and Czubek, S. 1951. Determination of phosphorus in hard coal. *Prace GIG w Katowicach* 83, pp. 1–12 (*in Polish*).

Yudovich et al. 1985 – Yudovich, Ya.E., Ketris, M.P. and Merc, A.W. 1985. *Trace elements in coals*. Leningrad: Izdatielstvo "Nauka", pp. 1–239 (*in Russian*).

THE ROLE OF MINERAL MATTER IN THE CONCENTRATION
OF PHOSPHORUS IN BITUMINOUS COAL SEAMS FROM
THE LUBLIN FORMATION IN THE LUBLIN COAL BASIN, POLAND

Abstract

The study included bituminous coal seams (30 samples coal from the Bogdanka and Chełm deposits) of the Lublin Formation, the most coal-bearing strata in the best developed and recognized in terms of mining parts of the Lublin Coal Basin in Poland. High phosphorus concentrations in coal of the Lublin Formation were found (1375 g/Mg) as well as P_2O_5 in coal ash (2.267 wt%). The phosphorus contents in coal and coal ash from the 385 and 391 coal seams in the area of the Lubelski Coal Bogdanka Mine and in the area of its SE neighbor is the highest (max. 2.644 wt. % in coal and 6.055 wt. % of P_2O_5 in coal ash). It has been shown that mineral matter effectively affects phosphorus contents in coal and coal ash. At the same time, phosphate minerals (probably apatite and crandallite) present in kaolinite aggregates of tonsteins contain the most of phosphorus and have the greatest impact on the average P content in the 382, 385, 387, and 391. The secondary source of phosphorus in these coal seams and main source of phosphorus in these coal deposits that do not contain mineral matter of pyroclastic origin (378, 389, 394) may be clay minerals, which absorbed phosphorus compounds derived from organic matter released during coalification. Phosphorus-rich ash from the combustion of the Lublin Formation coal tend to be environmentally beneficial to the environment and also useful for improving the soil quality. Due to the low degree of coalification and high content of phosphorus in coal, this coals of little use for coking.

K e y w o r d s : phosphorus, bituminous coal, coal seams, Lublin Coal Basin

ROLA SUBSTANCJI MINERALNEJ W KONCENTROWANIU FOSFORU
W POKŁADACH WĘGLA KAMIENNEGO Z FORMACJI LUBLINA
W LUBELSKIM ZAGŁĘBIU WĘGLOWYM W POLSCE

Streszczenie

Badaniami objęto pokłady węgla kamiennego (30 próbek ze złoża Bogdanka i złoża Chełm) z formacji Lublina, najbardziej węglonośnej i najlepiej pod względem górniczym rozpoznanej części Lubelskiego Zagłębia Węglowego (LZW). Stwierdzono dużą zawartość fosforu w węglu (1375 g/Mg) i P_2O_5 w popiele węgla (2,267 % wag.). Zawartość fosforu w węglu i w popiele węgla z pokładu 385 i 391 w rejonie kopalni Lubelski Węgiel Bogdanka i w obszarze z nią sąsiadującym od południowo-wschodniej strony jest najwyższa (max. 2,644% w węglu i 6,055% P_2O_5 w popiele węgla). Wykazano decydujący wpływ materii mineralnej na zawartość fosforu w węglu z formacji Lublina i w popiele węgla. Przy czym minerały fosforanowe (prawdopodobnie apatyt i crandallit), obecne w agregatach kaolinitu w tonsteinach, zawierają najwięcej fosforu i mają największy wpływ na średnią zawartość fosforu w węglu z pokładów 382, 385, 387 i 391. Drugorzędnym źródłem fosforu w węglu wymienionych pokładów oraz głównym źródłem fosforu w węglu z pokładów niezawierających materii mineralnej pochodzenia piroklastycznego (378, 389, 394) są prawdopodobnie minerały

ilaste, które zaabsorbowały związki fosforu pochodzące z materii organicznej, uwolnione w czasie uwęglania substancji roślinnej. Bogate w fosfor popioły pochodzące ze spalania węgla z formacji Lublina wydają się być ekologicznie korzystne dla środowiska i jednocześnie przydatne do poprawy jakości gleb. Ze względu na niski stopień uwęglenia i dużą zawartość fosforu w węglu, węgiel ten jest mało przydatny do koksowania.

Słowa kluczowe: fosfor, pokłady węgla, Lubelskie Zagłębie Węglowe