

# BPA – an endocrine disrupting compound in water used for drinking purposes, a snapshot from South Poland

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**Abstract:** Bisphenol A (BPA) is a chemical produced in large quantities for use primarily in the production of polycarbonate plastics and epoxy resins. As an endocrine disrupting compound, it has been included in the list of substances requiring special supervision as a very high-risk substance due to its toxic influence on reproduction. BPA with a reference value of 0.01 µg/L was included in the Drinking Water Directive revision (DWD 2018). This paper presents the results of preliminary studies aimed at identifying the occurrence of BPA in different types of water, i.e. groundwater captured with house wells or flowing wells in a selected location in southern Poland. These waters are commonly used as a source of water intended for human consumption and their quality is not regularly controlled. Additional tests were carried out for surface water, as well as water from springs used for drinking purposes. The authors also analysed tap water from various sources, i.e. surface and groundwater, as the final product of the drinking water production cycle.

The results indicate the presence of BPA in water and the necessity of a detailed study on the risk of the BPA occurring in groundwater, especially in domestic wells.

**Keywords:** emerging contaminants, endocrine disrupting compounds, groundwater protection, groundwater domestic wells, bisphenol A

## INTRODUCTION

The increasing use of pharmaceuticals, both for humans and animals, also results in a growth in the concentration of endocrine disrupting compounds and products of their metabolism in sewage, and thus in surface water, groundwater (i.e. domestic

wells) and tap water, which are subsequently consumed by humans (Loos 2012, 2015). The seriousness of the problem is documented by the rich literature devoted to emerging contaminants (EC) and endocrine disrupting compounds (EDCs) in the aquatic environment, e.g.: Cunningham et al. (2006), Kümmerer (2009), Loos et al. (2010),

Snyder & Benotti (2010), Sanderson (2011), Kozisek et al. (2013), Rocha et al. (2013), Webb et al. (2013), Küster & Adler (2014), Schaidler et al. (2014), Corrales et al. (2015), Lin et al. (2015), Baranauskaitė-Fedorova et al. (2016), Clayton (2016), Paxéus et al. (2016), Yan et al. (2016), Bilal et al. (2018), Rasheed et al. (2019), Wazir & Mokbel (2019).

According WHO (2012) an endocrine disruptor “is an exogenous substance or mixture that alters function(s) of the endocrine system and consequently causes adverse health effects in an intact organism, or its progeny, or (sub)populations” and a potential endocrine disruptor “is an exogenous substance or mixture that possesses properties that might be expressed to lead to endocrine disruption in an intact organism, or its progeny, or (sub)populations”.

EDCs enter into the environment and groundwater through many routes: human or animal excreta, wastewater effluent, treated sewage sludge, industrial waste (also pharmaceutical), medical waste from health-care and veterinary facilities, landfill leachate, surface runoff biosolids, as well as indirectly through the process of groundwater–surface water exchange (Lapworth et al. 2012, WHO 2012). Groundwater, especially that from shallow aquifers, is intensively supplied by the infiltration of atmospheric precipitation. Precipitation transports different pollutants by washing dumping grounds, urban-industrial agglomerations, areas of crops, etc. Migration of these substances is a major threat to groundwater resources (Witczak et al. 2013). The domestic wells capturing shallow groundwater are most liable to pollution. EDCs and their metabolites undergo natural attenuation by adsorption, dilution or degradation in the environment, depending on their hydrophobicity, biodegradability and the temperature. Therefore, these compounds in water sources and drinking water are often present in trace concentrations, as they would have undergone metabolism and removal through natural processes and, if applicable, wastewater and drinking water treatment processes (WHO 2012).

The Water Framework Directive (WFD 2000) established a strategy for the prevention of water pollution covering i.a. identification of priority substances among those which represent a significant risk to the aquatic environment or through

it at the European Union level. In 2013, the European Commission introduced the obligation to draw up the so-called watch lists, covering such substances (EU 2013). Watch lists (EU 2015) concern only surface waters. The Groundwater Directive (GWD 2006) aims to prevent and combat groundwater pollution in the EU. In a document “Developing a groundwater watch list for substances of emerging concern: a European perspective” almost 280 compounds are considered as hazardous for humans, however, in most European countries only 31 of them were examined (Lapworth et al. 2019). Bisphenol A (with a limit reference value of 0.01 µg/L) was included in Part B of Annex 1 of the Drinking Water Directive revision (DWD 2018). This regulation will also be applied for groundwater, including domestic wells often used as a source of drinking water without regular quality control and treatment. The paper presents the results of preliminary studies aimed at identifying bisphenol A – an endocrine disrupting compound – in some sites in southern Poland.

Bisphenol A (BPA) is a chemical produced in large quantities for use primarily in the production of polycarbonate plastics and epoxy resins. It is mainly used in combination with other chemicals to manufacture plastics and resins (Pubchem 2017). It has been included in the list of substances requiring special supervision as a very high-risk substance due to its toxic influence on reproduction (ED/01/2017, ED/01/2018). Its endocrine disrupting activity is associated with cardiovascular disease, diabetes, obesity, and liver dysfunction (EU 2010).

BPA has been proven to have estrogenic activity even at concentrations below 1 ng/L (Rykowska & Wasiak 2006). The effects of exposure to BPA can be particularly harmful to i.a. infants and young children because of a lack of feedback regulating the activity, synthesis, and elimination of hormones (Rykowska & Wasiak 2006, Careghini et al. 2015).

Endocrine disrupting compounds are more widely determined in water bodies. However, it turns out that EDCs, like alkylphenols and bisphenol A, are emitted into the atmosphere during fuel combustion, mainly because of technical reasons (since many domestic stoves are defective) and economic ones (since in many cases waste combustion is much cheaper than burning ecological fuel)

(Alliot et al. 2014, Lyons et al. 2014, Vorkamp et al. 2014, Salgueiro-González et al. 2015). Many studies have been conducted on BPA in soil and aquatic environments as well as the widespread and continuous human exposure to bisphenol through food, drinking water, dental sealants, cell phones and inhalation of indoor dust (Wilson et al. 2001, Rudel et al. 2003, Vandenberg et al. 2007, Fu & Kawamura 2010). Bisphenol A is not likely to occur in the gas phase of the atmosphere as its vapor pressure is very low. But as atmospheric releases of bisphenol are reported during production, an association with aerosols particulates is possible. Bisphenol has attracted considerable public attention due to its potential association with adverse health effects such as prostate cancer, obesity, neurobehavioral and reproductive problems (Krishnan et al. 1993, Vogel 2009, Fu & Kawamura 2010). BPA was detected in 40% of groundwater bodies identified as drinking water sources investigated in Europe (Loos et al. 2010, Arnold et al. 2013, Postigo & Barceló 2015).

The achievements of Polish researchers on the scope of this form of pollution as an emerging group of contaminants are significant. Literature studies of the occurrence of the pharmaceuticals, EDCs and their residues in Poland have focused mainly on sewage, surface water, and water intended for human consumption. However, there is little information about groundwater pollution caused by these substances. A comprehensive study on the occurrence, removal, mass loading, and environmental risk assessment of 19 multi-class emerging organic contaminants (i.a. bisphenol A) in groundwater from two MSW landfill sites located in northeast Poland is presented in Kapelewska et al. (2018). BPA was found in all of the analyzed samples. Its concentrations in groundwater were at the level of  $<0.003$ – $6.88$   $\mu\text{g/L}$ . In 2016 Polish Geological Institute-National Research Institute (PGI-NRI) conducted pilot studies on the amounts of the pharmaceuticals in groundwater in Poland (Kuczyńska 2017). Among the analyzed parameters were compounds belonging to the group of endocrine disruptors, i.e. estrone, estriol, 17- $\alpha$ -ethinylestradiol, 17- $\beta$ -estradiol, but they were found only in selected areas. BPA was not analyzed during this research study. Preliminary results of the pharmaceutical

residues in the groundwater of southern Poland were presented by the authors of the work at several worldwide conferences (Kmieciak et al. 2017a, 2017b, 2018, Wątor et al. 2017).

In this paper, the results of simple tests are presented. The aim of the research was the determination of the occurrence of BPAs in different kinds of water which are used for drinking purposes. Also, samples of total amounts of BPAs suspended in air particles and soils were tested to indicate possible routes of BPA migration in the environment.

## MATERIALS AND METHODS

During the first sampling campaign (in February 2017) grab water samples were collected. The location of sampling points is presented in Figure 1.

Samples of water intended for human consumption were collected from taps from different sources (surface water, groundwater and domestic wells in the vicinity of agricultural areas) (Tab. 1 on the interleaf). The samples of flowing surface water (rivers) and groundwater (wells and spring) were also taken from areas where they are used for drinking purposes.

**Water samples** were collected in accordance with the procedures given in the 5667 series ISO standards (*Water quality – Sampling*) and transferred into 500 mL glass bottles. Samples were stored in a fridge and transported to the laboratory in a short time (a few hours).

Solid phase extraction (SPE) was used for the extraction of the BPA from the aqueous samples. SPE was carried out with a System BAKER spe 12G. Oasis HLB extraction cartridges were conditioned with  $\text{CH}_3\text{OH}$  (2 mL) and  $\text{H}_2\text{O}$  (2 mL). Samples (1 L) were spiked with 200 ng of internal standard (bisphenolA-D16) and then passed through the HLB cartridge at a rate of 6 mL/min. After the extraction was completed, the cartridges were dried under full vacuum for 20 min. The elution was performed using 4 mL of  $\text{CH}_3\text{OH}$ . The extracts were dried to dryness under argon at  $35^\circ\text{C}$  and then dissolved in 200  $\mu\text{L}$  of derivatization reagent. The silylation process with BSTFA+1% TMCS was carried out at  $65^\circ\text{C}$  for 35 min in a thermo-block. Solutions were then analyzed by GC-MS/MS (Nosek et al. 2014).

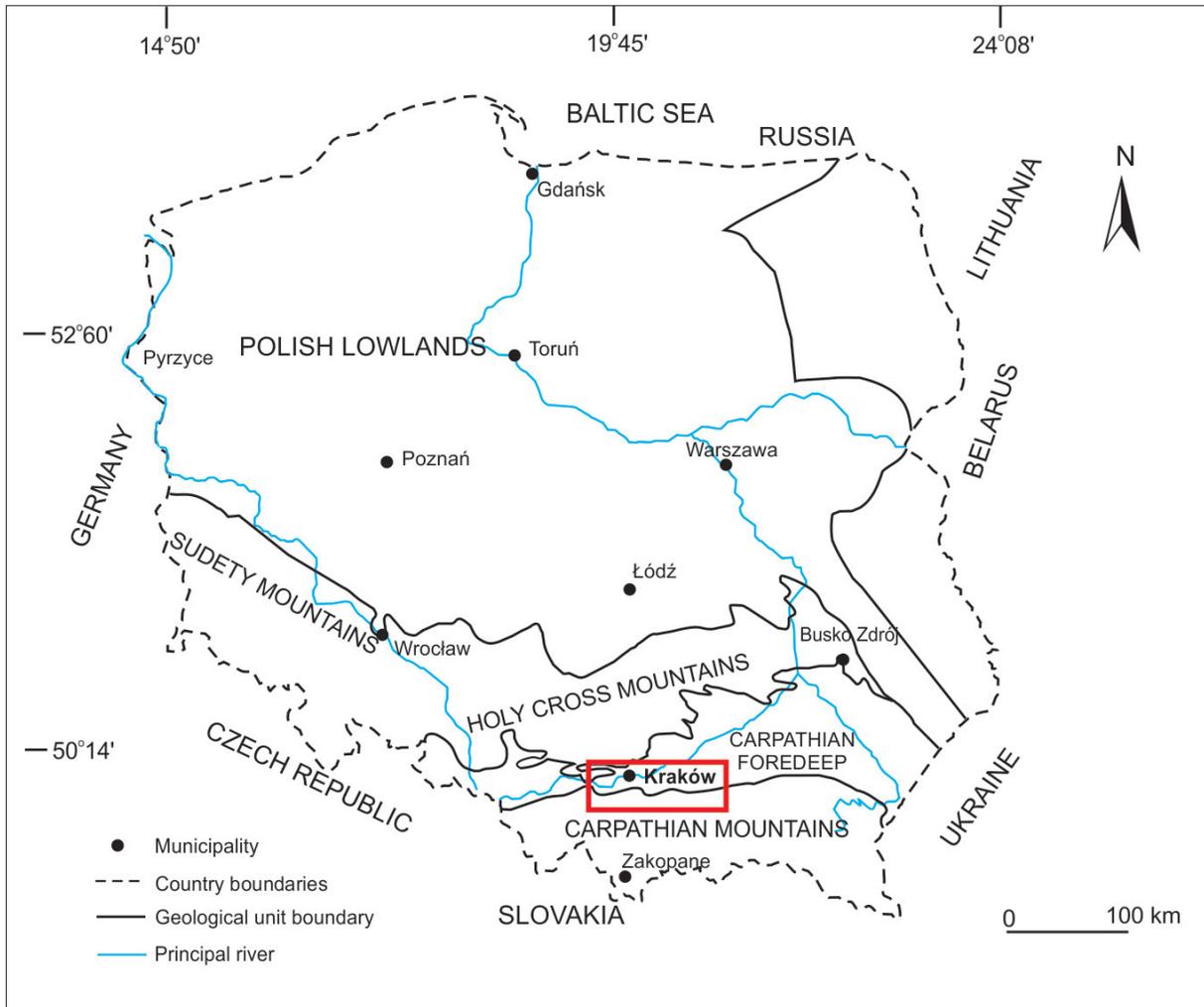


Fig. 1. Location of sampling points P1–P8

**Table 1**  
Characteristic of sampling sites and summary of sampling series

| Sampling point Id | Kind of water       | Characteristics   | Sampling series           |                                       |                                     |
|-------------------|---------------------|---|---------------------------|---------------------------------------|-------------------------------------|
|                   |                     |   | 1 <sup>st</sup> (II 2017) | 2 <sup>nd</sup> (XI 2017)             | 3 <sup>rd</sup> (II 2018)           |
| P1                | surface water       | The stream flows parallel to the road, between houses and farms where not all farms are connected to the sewage system (cesspool), farmlands and numerous forest areas are found around the farms   | water (glass containers)  | –                                     | –                                   |
| P2                |                     | It flows between the houses and farms through the areas where not all of the farms are connected to the sewage system (cesspool) and near to the farmlands  |                           | water (plastic container)             | water (plastic and glass container) |
| P3                | spring/ground-water | The spring flows from the slope of the mountain, the intake is enclosed by stone slabs, water flows in a continuous stream along a rocky grove, forest areas are mostly found around as well as farmlands, farms and house where not all farms are connected to the sewage system (cesspool). The water is a source of drinking water for residents |                           | water (plastic container)<br>soil     | –                                   |
| P4                | ground-water        | Domestic well, connection at home, galvanized steel pipes, 30-year-old installation, the well is located about 50 km from the bank of river P2  |                           | water (plastic container)<br>soil air | water (plastic container)           |
| P5                |                     | Domestic well, the connection at home, galvanized steel pipes, 30-year-old installation   |                           | water (plastic container)             | –                                   |
| P6                | tap water           | Treated surface water, central installation which is about 60-year-old, 5-year-old installation at home, plastic and steel  |                           | –                                     | –                                   |
| P7                |                     | Treated surface water, central installation is about 15-year-old, 15-year-old installation at home, plastic and steel   |                           | –                                     | –                                   |
| P8                |                     | Groundwater intake, central installation which is about 20-year-old, 1-year-old installation at home, steel   |                           | –                                     | –                                   |

The analysis was carried out with the usage of Thermo Scientific GC Trace 1300 gas chromatography coupled to a ITQ 900 ion trap mass spectrometer and a TriPlus RSH autosampler. The flow of helium through a GC column was constant and set at 1 mL/min. The programmable temperature of the vaporization injector was maintained at 250°C, the transfer line at 250°C and the ion source at 250°C. The injector was operated at splitless conditions for 2 min. The volume of injections was 1 µL. All the compound separations were performed on a TG-SQC capillary column from Thermo Scientific that had a 30 m × 0.25 mm inner diameter and a film thickness of 0.25 µm (5% phenyl 95% dimethylpolysiloxane). The temperature program was as follows: 70°C for 2 min, from 70 to 320°C at 20°C min<sup>-1</sup>, and finally 5 min at 320°C. The analyses

were performed in a positive mode, an electron energy 70 eV and emission current 250 µA. Helium (99.999%) was used as a collision gas with a flow of 0.3 mL/min. Mass spectrometry analyses were performed in the multiple reaction monitoring (MRM) mode measuring the fragmentation of the precursor ions. Data was collected, analyzed and processed using a Thermo Xcalibur. Limits of detection and quantification were calculated based on signal to noise ratios (S/N) of 3 and 10, respectively (Tab. 2). Deuterated internal standard (bisphenol A-D16) was added before SPE extraction to compensate for losses or enhancement of compounds during both the sample preparation procedure and resulting from matrix effects. The correlation coefficient ( $r^2$ ) of the calibration curve was 0.9987 for the concentration range studied (0–500 ng/mL).

**Table 2**

GC-MS/MS method parameters for the analysis of BPA (calculated during method validation)

| Retention time [min] | m/z for characteristic ions (for quantification) | Method detection limit MDL [ng/L] | Method quantification limit MQL [ng/L] |
|----------------------|--|-----------------------------------|--|
| 13.37                | 357 → 191,267                                    | 0.15                              | 0.5                                    |

The recovery of BPA was 88%. The estimated measurement uncertainty is 30% (Kmiecik et al. 2018). During the second series (November 2017) water samples from selected points were collected where the highest BPA concentrations were observed in the first series (P2–P5).

In parallel, **soil samples** from the investigated areas were also taken (points P3, P4). Topsoil samples from the depth 0–20 cm (about 10 primary samples) were placed in a container from randomly selected points around the well/spring using an Egner's stick. All primary samples were mixed and averaged, and a bulk sample of approximately 0.5 kg was separated. Such collected samples were immediately delivered to the laboratory in a string bag. Soil samples were frozen and dried by lyophilisation, sieved through a 2 mm sieve and stored at 4°C until analysis. Dried soil samples of 5 g were spiked with 100 ng of BPA D16 and extracted with 10 mL of methanol for 1 h using horizontal shaker at 50 rpm, and centrifuged. The final extracts were evaporated to dryness and reconstituted in 100 µL of BSTFA+1% TMCS and derivatized at 65°C for 35 min. The recovery of BPA was 61%. The estimated measurement uncertainty is 19%.

From point (P4), an additional sample of the **total suspended in the air particles** (TSP) was collected. A low volume sampler was equipped with a filter holder, needle valve, membrane pumps and gas meters. The sampler worked with an air flow of 1.4 m<sup>3</sup>/h. Samples were collected on quartz fibre filters (Pallflex, Pall Life Sciences) with a 47 mm diameter. Before sampling, the filters were thermally pre-cleaned at 550°C for 5 h, cooled and equilibrated to constant humidity. Two samples of TSP were collected, in 70 h. The sampled filters were equilibrated for 24 h to achieve conditions comparable with the conditions of the weighing of empty filters. The mass of the particulate matter was obtained as an average of the three subsequent weighing results of each filter. The OHAUS Discovery DV215CD balance with an accuracy of ±0.01 mg was used for

weighing. The circular filter aliquots with a diameter of 22 mm were cut from the filters and then spiked with 10 µL (10 ng/µL) BPA D16 solution, after that extracted twice with 3 mL dichloromethane and 2 mL cyclohexane, for 40 min. The volume of combined extracts was reduced to 250 µL, using a gentle stream of argon at 35°C. The 100 µL of concentrate was finally transferred into the chromatographic vial, derivatized with BSTFA+1% TMCS (65°C, 35 min) and analyzed with GC-MS/MS. The recovery of BPA was 67%.

During the third series of samples collection (February 2018), water samples from points P2 and P4 were collected. In the case of P2, they were placed in plastic (p – BPA free) and glass (g) containers.

## RESULTS AND DISCUSSION

Bisphenol A was found in all samples tested during the 1<sup>st</sup> series (Fig. 2). Their concentrations range from 6 ng/L (P7) through 351–427 ng/L in surface water (P1, P2) to 629 ng/L in spring water (P3). The lower concentration of bisphenol A in the tap water (P6–P8 – 6–53 ng/L) confirms their removal during the water treatment process. The highest concentrations of bisphenol A were found in the sample of spring water (P3 – 629 ng/L) and groundwater from domestic wells (P4 – 518 ng/L, P5 – 255 ng/L) located in villages where the sewage system is not very common and surface runoff is possible. BPA concentrations in all samples except P7 exceed the maximum permissible limit sets in the drinking water directive (DWD 2018).

Bisphenol A was one of the most relevant compounds detected in European groundwater described in the study of Loos et al. (2010) (autumn sampling series, the maximum measured concentration of BPA 2.3 µg/L). In groundwater, higher BPA concentration levels were also observed than in surface water. Environmentally significant concentrations of EDCs are being detected in

groundwater globally (Lapworth et al. 2012) but concentrations of these compounds change over time. The data from the literature indicate that the highest concentrations are observed in winter (Daneshvar et al. 2010, Baker & Kasprzyk-Hordern 2013, Boleda et al. 2013, Paxéus et al. 2016, Petrie et al. 2016). The results of the first series concern only the instantaneous concentrations of bisphenol A in single water samples collected in February and therefore may be higher than in other seasons. It may be related to rainfall, temperature, etc. What is more, this series of samples was collected during the height of the heating season, after several months of the intensive combustion of various fuels in domestic boiler rooms, which may affect the results obtained for the determination of bisphenol A. Therefore, at the beginning of the heating season in November 2017, a second series of tests was carried out. Samples were collected in plastic containers (BPA free) from those points in which high concentrations of bisphenol A had been found in February (P2–P5). In parallel, soil samples were also taken (points P3, P4)

and from point (P4) an additional sample of the total suspended in the air particles was collected. The results for water samples are also presented in Figure 2. This time, BPA concentrations in the surface water sample (P2) and groundwater samples (P3–P5) were at a very low level, about 1 ng/L.

In the soil samples, BPA was determined at the level of 4 ng/g (P4) and 10 ng/g (P3). In the literature, there is only a little information about BPA in soil samples. For example, researchers have proven that the contamination of industrial soil with BPA was higher (mean concentration 11.28 ng/g) than for agricultural soil (mean concentration 2.42 ng/g) (Sánchez-Brunete et al. 2009, Fischer et al. 2014). BPA concentrations for landfill soil ranged from <0.1 to 2.8 ng/g (Hansen & Lassen 2008, Sánchez-Brunete et al. 2009, Fischer et al. 2014). The results of the analysis performed for soil samples at points P3 and P4 are relatively high. Research provided by Styszko (2016) indicated that bisphenol A had relatively poor sorption properties which were dependent on the type of sediments/soils.

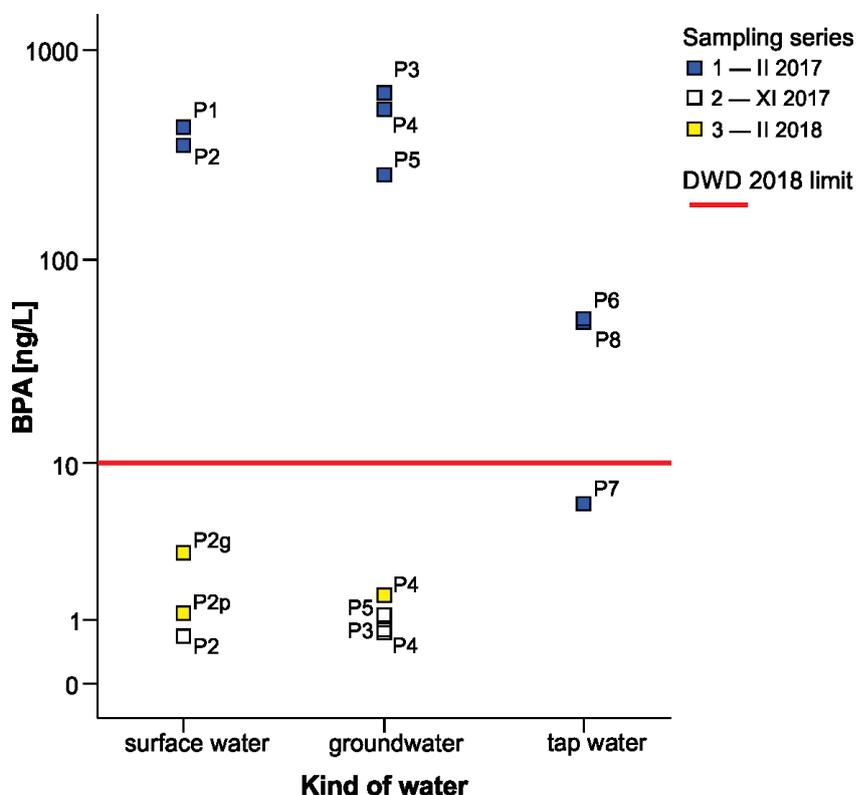


Fig. 2. The results of bisphenol A determination in the analyzed samples

In the sample of air particulate matter from point P4, 2.83 ng/m<sup>3</sup> of BPA was determined. Fu & Kawamura (2010) showed that in the agricultural areas of China, BPA concentration in the air does not exceed 0.240 ng/m<sup>3</sup>, while in urban areas it reaches concentrations ranging from 0.020 to 2.340 ng/m<sup>3</sup> (Kryłów & Rezka 2017). A positive correlation was found in urban regions between BPA and 1,3,5-triphenylbenzene, a tracer for the burning of plastic, indicating that the open burning of plastics in domestic waste should be a significant emission source of atmospheric BPA (Fu & Kawamura 2010). The concentration of BPA in the air particulate matter from point P4 suggests that one of the possible sources of this compound in the investigated areas, where neither industry nor high traffic occurs, is the burning of plastics in domestic waste. From the air, BPA can migrate to the soils and water – surface and groundwater.

During the third series of sampling (February 2018) samples from points P2 and P4 were collected. In the case of P2, these were placed in plastic (p – BPA free) and glass (g) containers. BPA was identified in all samples, also in small concentrations (Fig. 2), but higher than in the second series. In sample P4, BPA was measured at the level 1.61 ± 0.37 ng/L. There was a difference in BPA determination in sample P2 from the plastic (1.13 ± 0.17 ng/L) and glass containers (3.17 ± 0.92 ng/L), probably occurring during the sorption processes. The research will be expanded to explain the behavior of BPA under different conditions. Column and batch experiments are planned (Okońska & Pietrewicz 2018, Okońska et al. 2019a, 2019b, 2019c).

In 2015, the European Food Safety Authority reduced the tolerable daily intake (TDI) for BPA from 50 to 4 µg/kg BW/day. TDI is “the maximum amount of a substance to which any individual can be exposed every day of his/her life, through all possible sources, without any risk to his/her health” (EFSA 2019). Maximum Allowable Dose Level (MADL) is the exposure level at which a chemical would have no observable reproductive effect even if a person were exposed to 1000 times that level. Goodman et al. (2017) estimated this parameter at the level of 157 µg/day. Drinking water equivalent level (DWEL, µg/L) can be

calculated from TDI, multiplying by the default adult body weight (about 70 kg) and divided by average daily water consumption (2 L):

$$\begin{aligned} \text{DWEL} &= 4 \mu\text{g/kg BW/day} \times 70 \text{ kg BW} / 2 \text{ L} = \\ &= 140 \mu\text{g/L}. \end{aligned}$$

In the Health Based Guidance for Water Health Risk Assessment Unit (MDH 2015) there are other BPA limits:

- Short-term Non-Cancer Health Risk Limit (nHRLShort-term) = 100 µg/L,
- Subchronic Non-Cancer Health Risk Limit (nHRLSubchronic) = 20 µg/L,
- Chronic Non-Cancer Health Risk Limit (nHRLChronic) = nHRLSubchronic = 20 µg/L.

The concentrations of BPA observed in the analyzed samples are lower than the above limits, therefore they do not pose a threat to the health of the people drinking this water.

## CONCLUSIONS

Pollution of the environment by means of endocrine disrupting substances is an emerging problem. There is a lack of knowledge about the presence of many of them in the environment (i.a. in groundwater) and about the levels that could be harmful for human health. The main goal of the presented preliminary research was to identify the risk from exposure to BPA – an important endocrine disrupting compound – through consumption of drinking water from different sources, including groundwater from house (private) wells. These wells take water from Quaternary formations, so they are most exposed to contamination, also by EDCs. The problem is that the quality of groundwater taken from small domestic wells is not controlled and, even if it is, EDCs are not determined.

As the results of the conducted research show, BPA occurs in shallow groundwater in Poland, including water captured by small domestic wells. There is a need for regular research on the scope of the presence of BPA in groundwater. Meanwhile, the lack of analytical procedures constitutes a limitation to the reliable quantification of EDCs in groundwater, especially those occurring in very low concentrations, and affects the estimation of

human exposure to the discussed pollutants. Although studies and reviews can be found in the literature on sources, occurrence, environmental behavior, and the fate of BPA, the pathway of this pollutant from sources to receptors should be subject to advanced research. This is because the information is still insufficient, mainly due to the complexity of the environmental systems which may determine an unexpected behavior of the BPA in the air, water, or soil. The consequences of BPA in aquatic ecosystems are of particular concern since living organisms are subjected to exposure, with potential consequences for future generations.

The research presented in this paper is ongoing. Samples are being collected with different frequencies, allowing us to determine the trends/fluctuations of bisphenol in groundwater used for human consumption. The presented preliminary results indicated that there are changes in BPA concentrations during the course of a year. The influence of weather conditions such as precipitation, wind or temperature should be taken into account during the interpretation of results. The use of passive sampling or collection of composite samples (daily/week), column and batch experiments can give more reliable results which will help to identify the migration routes of bisphenol A into the tested groundwater.

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# Variation of lignite ash in vertical and horizontal sections of mining walls in the Konin Lignite Mine, central Poland

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**Abstract:** This paper focuses on the variations of lignite ash along selected sections and mining walls from three lignite opencast mines in central Poland. They are owned by the Konin Lignite Mine, where the first Mid-Polish lignite seam is being mined to produce electricity. Ash content in lignite is important because ash lowers the calorific value of the lignite. The results obtained are based on 266 samples of lignite collected from the Drzewce, Tomisławice, and Józwin IIB opencasts. All samples were tested according to ISO 1171 standard procedures, that is, they were first burned at a temperature of 850°C, then the ash content was determined on a dry basis ( $A^d$ ), before the basic statistical parameters were calculated. The studied lignite seam is characterised by a variable distribution pattern of ash both along selected vertical sections and lignite walls, as well as between the three opencasts. The ash content of individual samples ranged from 6.5 to 69.8 wt%, while the average content in opencast mines varied from 9.7 to 17.6 wt%. The coefficient of variation is large (80.23–96.33%) in the case of the Drzewce and Tomisławice, and low to average (14.53–37.75%) in the case of Józwin IIB. Significant ash enrichment of some beds is interpreted in this article as a consequence of floods occurring in a Mid-Miocene mire (backswamp), but also of chemical precipitation. When lignite is burned to generate electricity, a relatively large amount of ash is produced. Therefore, recognition of ash content in lignite, in addition to the chemical composition and phase of ash, is recommended to better protect the environment. At the first stage of protection, it can be best achieved by analysing field samples for ash content.

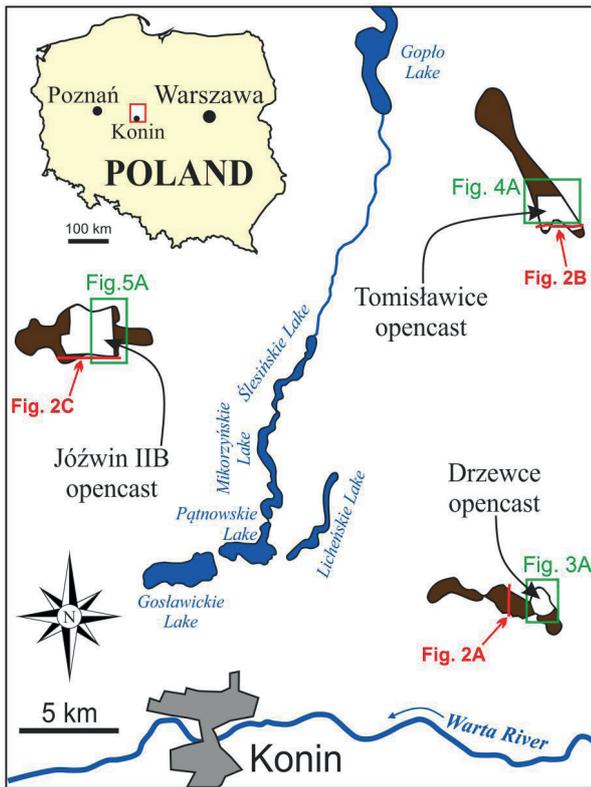
**Keywords:** Middle Miocene, backswamp, inorganic matter, coefficient of variation

## INTRODUCTION

Approximately 30–35% of the electricity in Poland is generated from lignite (Tajduś et al. 2014, Polskie Sieci Elektroenergetyczne 2019). This is the second-most abundant raw material, after bituminous coal (hard coal), used in the Polish energy mix; about 20% of electricity is produced from renewable energy sources: solar, hydro, geothermal, wind, and biomass (Tajduś et al. 2014, Widera et al. 2016). Therefore, the composition of lignite, its ash content, as well as chemical and

phase composition, is important during mining and combustion activities.

Parameters such as organic matter, water content and ash content affect fuel quality. The values of these parameters are especially useful in evaluating the suitability of lignite for combustion in lignite-fired power plants (e.g. Kozula & Mazurek 1996, Kwiecińska & Wagner 1997, Kozula 2001, Naworyta 2008, Naworyta & Mazurek 2010, Mastej et al. 2015, Pawelec & Bielowicz 2016). According to Polish norms, the ash content in lignite must be lower than 40 wt%, on a dry basis (Rozporządzenie 2001).



**Fig. 1.** Location map of the lignite opencast mines currently operating in the vicinity of Konin, central Poland

In the context of this study, the research question arose as to how the ash content in the lignite seam changes spatially. Hence, the main goals of the current study are (1) to present the quantitative ash content in the first Mid-Polish lignite seam from Drzewce, Tomiślawice, and Józwin IIB opencasts (Fig. 1), which belong to the Konin Lignite Mine, (2) to calculate and compare basic statistical parameters for the ash content results obtained, and (3) to briefly discuss the impact of ash on the combustion of lignite and its environmental ramifications.

## GEOLOGICAL BACKGROUND

Geologically, the research area is situated in the Szczecin–Miechów Synclinorium in the eastern part of the Mogilno–Łódź Segment (Żelaźniewicz et al. 2011). According to an older division of Poland into tectonic units, this region is located in the central part of the Mogilno–Łódź Basin, above the south-eastern slope of a deeply-rooted salt structure called the Gopło Anticline (Dadlez et al. 2000). The lignite deposits fill graben-like tectonic depressions that are up to several dozen metres

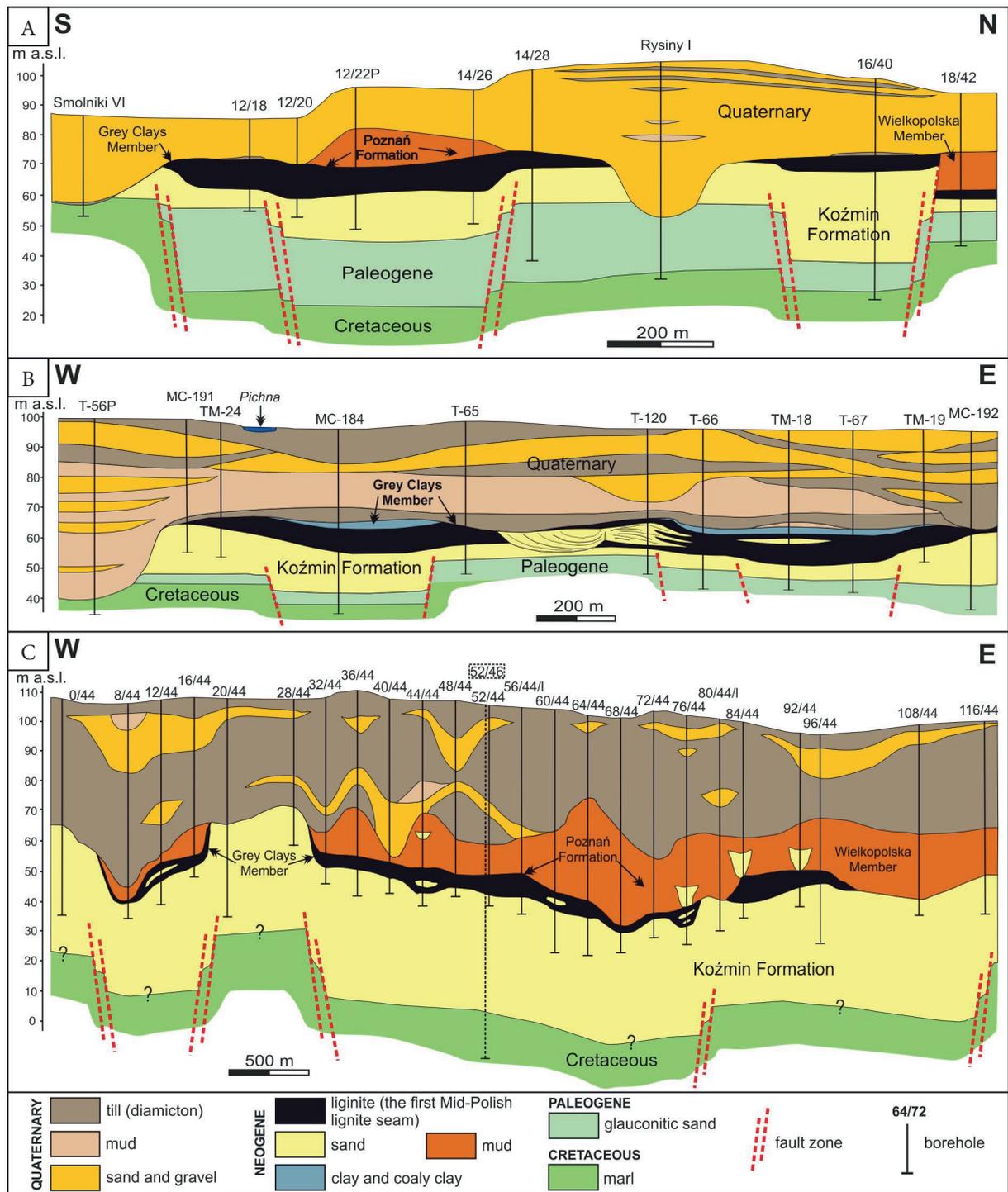
deep. These grabens began to develop at the turn of the Eocene/Oligocene or the Oligocene/Miocene transition as evidenced by the age of these deposits (Fig. 2, Widera & Kita 2007, Widera 2014).

The oldest sediments drilled in each of the three lignite deposits studied are predominantly marls of Late Cretaceous age (Fig. 2, Dadlez et al. 2000, Widera 2007). In the case of the Drzewce and Tomiślawice opencasts, Paleogene glauconitic sands, with their characteristic greenish colour, lie on top of Mesozoic bedrock (Fig. 2A, B). These glauconitic sands are obviously of marine origin (Widera & Kita 2007). In the Józwin IIB opencast, sediments of Paleogene age were not documented until the end of 2019 (Fig. 2C).

Neogene deposition started after a period of uplift and erosion during the Late Oligocene, when the area that is now central Poland began to undergo subsidence. During this time, mainly fluvial sedimentation occurred in this area. The Neogene succession began with the deposition of sand approximately 10–40 m thick, often containing organic matter. These deposits belong to the Koźmin Formation of Early to Mid-Miocene age (Fig. 2).

The Poznań Formation of Mid-Miocene to earliest Pliocene age ends the Neogene succession in the study area. This formation is divided into two lithostratigraphic members: the older Grey Clays Member and the younger Wielkopolska Member (Fig. 2, Piwocki & Ziemińska-Tworzydło 1997). The first Mid-Polish lignite seam belongs to the Grey Clays Member of Mid-Miocene age (Piwocki & Ziemińska-Tworzydło 1997, Kasiński & Słodkowska 2016). The thickness of this lignite seam reaches up to 19.8 m, but is less than 10 m on average (Fig. 2, Piwocki 1992, Widera 2007, 2014, Bechtel et al. 2019).

The Wielkopolska Member is the youngest lithostratigraphic unit in central Poland and is of late Mid-Miocene to earliest Pliocene age (Piwocki & Ziemińska-Tworzydło 1997). It consists predominantly of overbank muds (>95 vol.%) and channel-fill sands and muds (<5 vol.%). In the study area, these deposits are up to 30 m thick with evidence of glaciotectionic disturbances (Fig. 2). In recent years, the origin of this member has been connected with the environment of an upper Neogene anastomosing river system (e.g. Maciaszek et al. 2019, Widera et al. 2019).



**Fig. 2.** Geological cross-sections through the studied lignite deposits: A) Drzewce with Drzewce opencast (after Widera 2007, modified); B) Tomisławce with Tomisławce opencast (after Widera et al. 2017, modified); C) Pątnów IV with Józwin IIB opencast (after Widera 2014, modified); for the location of cross-sectional lines, see Figure 1

The Neogene succession is covered by Quaternary sediments such as glacial tills, fluvio-glacial gravels and sands, and glaciolacustrine muds. These deposits were strongly eroded and deformed

by the Scandinavian ice sheets and/or their melt waters. Therefore, the Quaternary thickness varies between 20 and 60 m of overburden on the first Mid-Polish lignite seam (Fig. 2).

## MATERIALS AND METHODS

### Fieldwork

Fieldwork was conducted in 2018–2019 at three operational opencasts belonging to the Konin Lignite Mine. A total of 266 samples of lignite were collected from three different lignite deposits and opencasts: “Drzewce” lignite deposit in the Drzewce opencast, “Tomisławice” lignite deposit in the Tomisławice opencast, and “Pątnów IV” lignite deposit in the Józwin IIB opencast (Fig. 1). The first Mid-Polish lignite seam was sampled in each of these opencasts along the vertical sections and walls exploited (Figs. 3–5).

In the case of the vertical sections, 33–36 samples were collected at an interval of 10–20 cm. On the other hand, samples taken along the lignite walls were collected at intervals of 1 m or more. The profiles were separated from each other by approximately 200 m. The obtained results are presented in graphical form in Figures 3–8.

### Laboratory analysis

All analyses of the ash content were made in accordance with the applicable ISO 1171:2010 standard and Polish equivalent PN-ISO 1171:2002 standard. They were conducted at the laboratory of the Institute of Geology in Poznań. Results from laboratory tests were subjected to basic statistical analysis using Microsoft® Excel. Several statistical parameters (mean, minimum, maximum values, and coefficients of variation) were calculated (Tabs. 1, 2), similar to the studies devoted to other Polish lignite deposits (e.g. Kasiński 1986, Naworyta & Mazurek 2010, Bielowicz 2013, Naworyta & Wasilewska-Błaszczuk 2014). In the case of ranges of the coefficient of variation, the classification according to Mucha (1994) was used.

Moreover, four histograms were prepared in order to sum up the distribution of the ash content results obtained. It was assumed that the sizes of the bins (intervals) were 5 wt% (Fig. 9).

## RESULTS

### Drzewce opencast

Ninety-one samples of lignite were collected from the Drzewce opencast, including 36 samples from the selected section D, and 55 from the exploitation fronts. The sampled lignite walls (sections) were 4.5–12.2 m high (Fig. 3). All these lignite samples were analysed for ash content.

In the case of section D, the arithmetic average ash content was 12.6 wt%, on a dry basis. However, it varies across a wide range from 6.7 to 66.0 wt% (Fig. 3B, Tab. 1). The highest values of ash content exceeded 30.0 wt% and were obtained from the lowermost beds of the lignite seam. The upper parts of this seam were characterised by a very even and relatively low ash content (<10 wt%), in which only 3 samples contained between 10.0 and 14.0 wt% (Fig. 3B). The coefficient of variation for these 36 samples was equal to 96.33% (Tab. 1).

The arithmetic average ash content along the lignite walls was 15.0 wt%, ranging from 6.5 to 69.8 wt% (Figs. 3C, 4, Tab. 2). Samples located close to the floor or roof of the seam had the highest ash content, exceeding 20–30 wt%. Similarly, sample number 52, situated in the middle part of the seam, was characterised by an ash content higher than 30 wt%. The remaining majority of the analysed lignite samples had an ash content below or slightly above 10.0 wt% (Fig. 4). Finally, in the case of these 55 samples, the coefficient of variation was 80.23% (Tab. 2).

**Table 1**

*Basic statistical parameters of ash content obtained for selected sections of the first Mid-Polish lignite seam from opencasts of the Konin Lignite Mine*

| Name of opencast mine | Average ash content ( $A^d$ ) [wt%] | Maximum ash content ( $A^d$ ) [wt%] | Minimum ash content ( $A^d$ ) [wt%] | Standard deviation | Coefficient of variation [%] |
|-----------------------|-------------------------------------|-------------------------------------|-------------------------------------|--------------------|------------------------------|
| Drzewce               | 12.6                                | 66.0                                | 6.7                                 | 12.09              | 96.33                        |
| Tomisławice           | 17.6                                | 71.4                                | 9.6                                 | 14.29              | 81.15                        |
| Józwin IIB            | 9.7                                 | 13.7                                | 7.4                                 | 1.41               | 14.53                        |

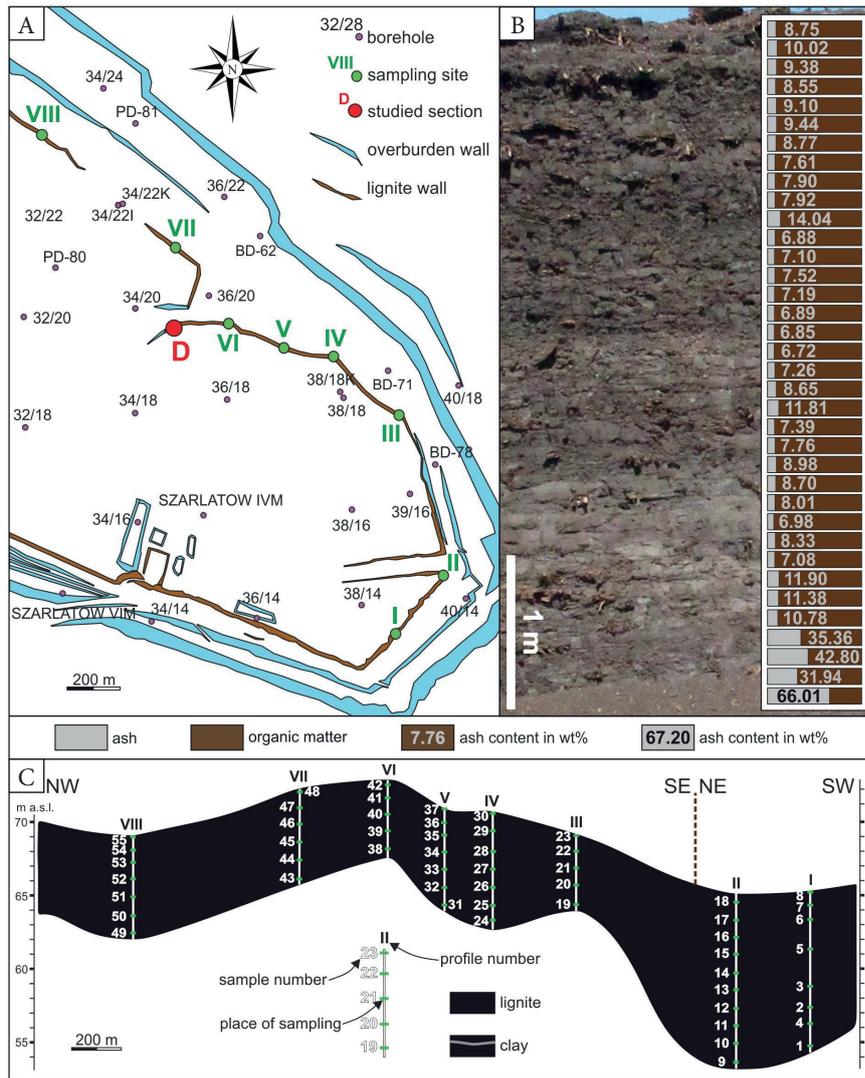


Fig. 3. Drzewce lignite opencast mine: A) location of the examined lignite walls with sampling sites I–VIII and the selected section D; B) broad view of the lignite seam with results of ash content tests; C) location of sampling sites along lignite walls; for the results of ash content tests see Figure 4

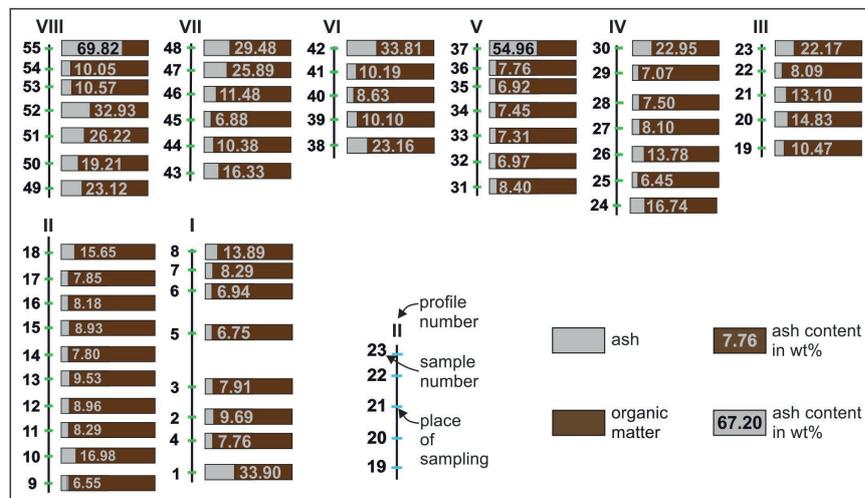


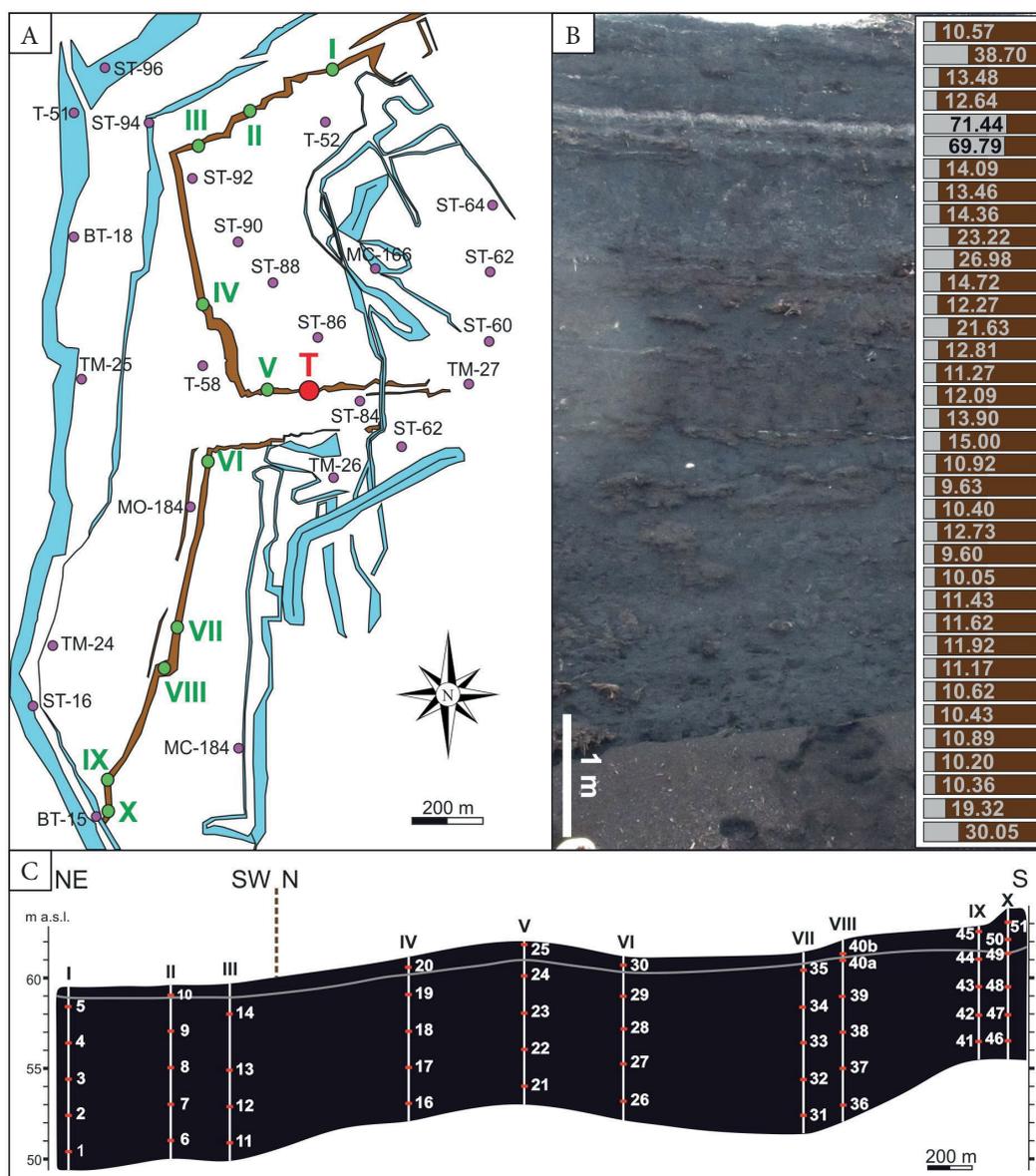
Fig. 4. Results of ash content tests obtained from lignite walls in the Drzewce opencast; for the location of sampling sites, see Figure 3A and C

## Tomisławice opencast

From the Tomisławice opencast, 87 samples of lignite were collected – 36 from section T and 51 from the lignite walls (Fig. 5). At the sampling sites, the first Mid-Polish lignite seam was thick, ranging from 7.4 to more than 10 m. The ash contents are shown graphically in Figures 5B and 6.

Section T contained 14.8 wt% (on a dry basis) of ash on average, but the variation in content was large, ranging from 6.9 to 71.4 wt% (Fig. 5B,

Tab. 1). Some samples contained an ash content 20–30 wt% higher in various parts of the lignite seam. These samples were found in floor, middle and roof layers of the seam, however, the most interesting two samples were situated about 1 m from the roof of the seam. These two samples contained an ash content of 69.8 and 71.4 wt%. In the middle part of this section, only two samples contained less than 10 wt% ash (Fig. 5B). For all 36 samples from section T, the coefficient of variation reached 81.15% (Tab. 1).



**Fig. 5.** Tomisławice lignite opencast mine: A) location of the examined lignite walls with sampling sites I–X and the selected section T; B) broad view of the lignite seam with results of ash content tests; C) location of sampling sites along lignite walls; for the results of ash content tests see Figure 6; for explanations see Figure 3

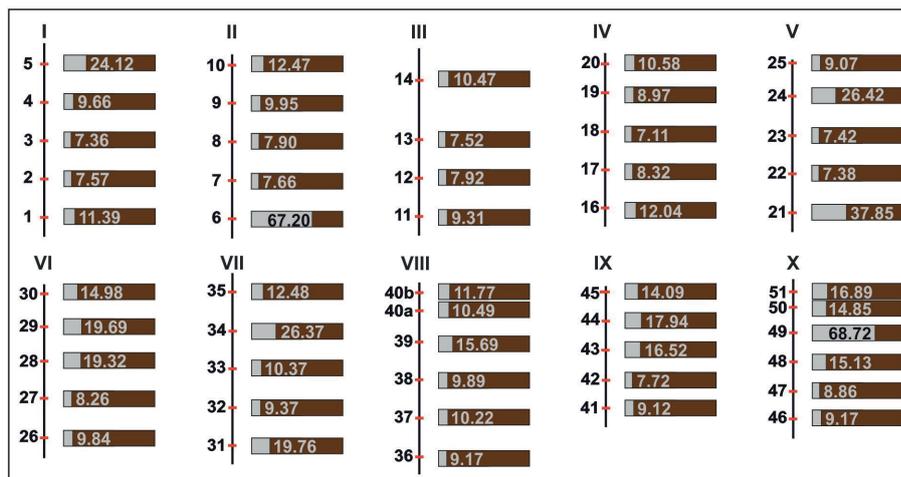


Fig. 6. Results of ash content tests obtained from lignite walls in the Tomisławice opencast; for location of sampling sites see Figure 5A and C; for explanations see Figure 4

Table 2

Basic statistical parameters of ash content obtained for exploited lignite walls of the first Mid-Polish lignite seam from opencasts of the Konin Lignite Mine

| Name of opencast mine | Average ash content ( $A^d$ ) [wt%] | Maximum ash content ( $A^d$ ) [wt%] | Minimum ash content ( $A^d$ ) [wt%] | Standard deviation | Coefficient of variation [%] |
|-----------------------|-------------------------------------|-------------------------------------|-------------------------------------|--------------------|------------------------------|
| Drzewce               | 15.0                                | 69.8                                | 6.5                                 | 12.01              | 80.23                        |
| Tomisławice           | 14.8                                | 68.7                                | 7.1                                 | 12.31              | 83.41                        |
| Józwin IIB            | 13.9                                | 30.5                                | 7.8                                 | 5.23               | 37.75                        |

In the case of 51 samples collected along the lignite walls, the average value of the ash content was 14.8 wt% and ranged from 7.1 to 68.7 wt% (Figs. 5C, 6, Tab. 2). The vertical and horizontal distribution of the ash did not show any regularity. Some floor and roof samples were characterised by clearly higher ash content (24.1–67.2 wt%), for example, samples 5, 6 and 24. Similarly, sample 49 contained very high ash content, reaching up to 68.7 wt% (Fig. 6). The coefficient of variation for these all samples was equal to 83.41% (Tab. 2).

### Józwin IIB opencast

Eighty-eight samples were collected from the Józwin IIB opencast and analysed for ash content. Thirty-three of the samples came from the 3-m high section J, while the remaining 55 samples were collected from the mine walls up to 8.5 m high (Figs. 7B, 8).

In the Józwin IIB opencast mine, the average arithmetic ash content of the first Mid-Polish lignite seam was 9.7 wt% for section J. In this case, the difference between the maximum (13.7 wt%) and minimum (7.4 wt%) ash content was only 6.3 wt% (Fig. 7B, Tab. 1). Excluding the two lowest samples from the floor of the lignite seam, the ash content and distribution along section J was relatively low and fairly even. For the majority of these samples, the ash content was in the range of  $10 \pm 2$  wt% (Fig. 7B). This is confirmed by the very low value of the coefficient of variation for 33 samples, which was only 14.53% (Tab. 1).

On the other hand, the arithmetic average ash content along the lignite walls was 13.9 wt% and ranged from 7.8 to 30.5 wt% (Figs. 7C, 8, Tab. 2). A few samples had ash contents greater than 20 wt%, and a dozen or so samples contained less than 10 wt% ash. Thus, most of the 55 samples had an ash content in the range of 10–20%, and the coefficient of variation is relatively low, only 37.75% (Tab. 2).

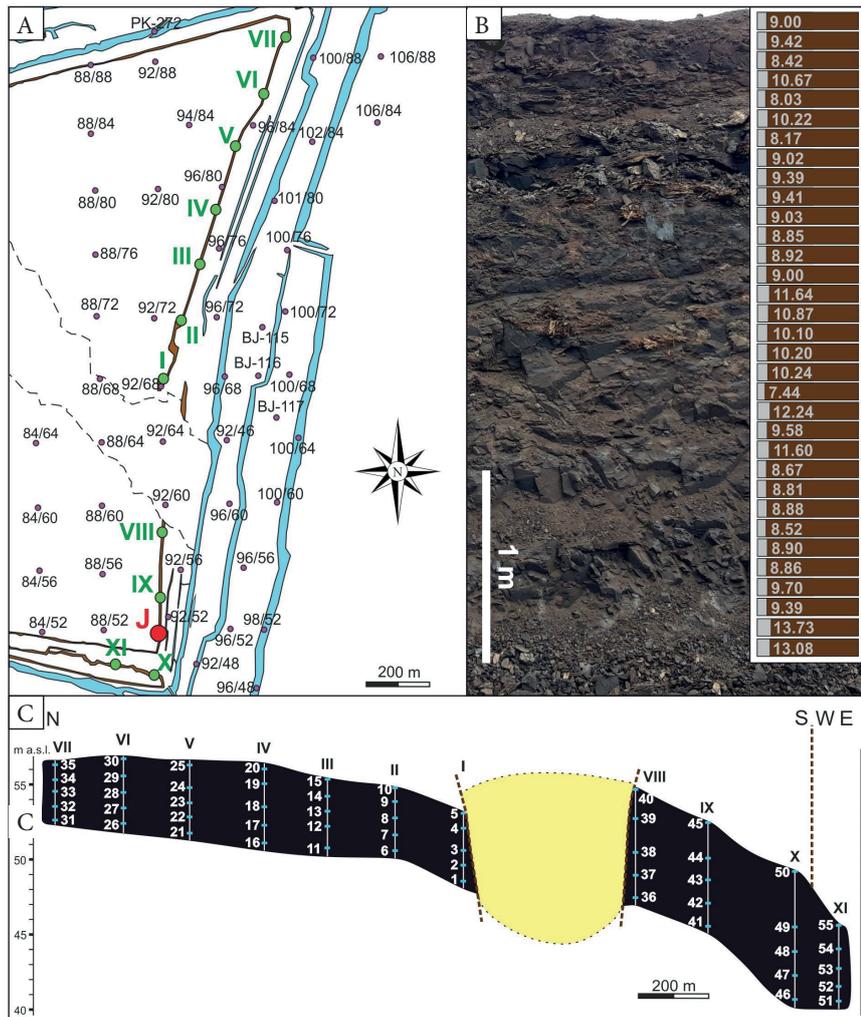


Fig. 7. Józwin IIB lignite opencast mine: A) location of the examined lignite walls with sampling sites I–XI and the selected section J; B) broad view of the lignite seam with results of ash content tests; C) location of sampling sites along lignite walls; for the results of ash content tests, see Figure 8; for explanations see Figure 3

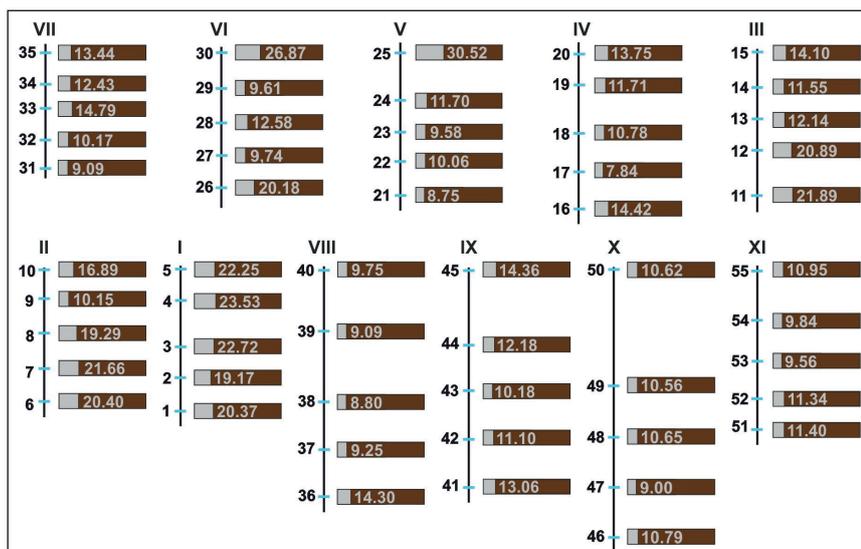


Fig. 8. Results of ash content tests obtained from lignite walls in the Józwin IIB opencast; for the location of sampling sites see Figure 7A and C; for explanations see Figure 4

## INTERPRETATION AND DISCUSSION

The variation of ash content in the first Mid-Polish lignite seam, along vertical and horizontal sections of mining walls, will be briefly interpreted and discussed. Taking into account previous studies of this lignite seam, an initial attempt to clarify some issues can be made. Thus, ash content is a parameter that is given in both geological documentation (e.g. Kozula 2001) and scientific studies devoted to lignite deposits owned by the Konin Lignite Mine (e.g. Kozula & Mazurek 1996, Naworyta 2008, Naworyta & Mazurek 2010, Pawelec & Bielowicz 2016). In these contributions, various geostatistical methods, both standard and modern, were used as summarised by Mucha (1994) and Jurek et al. (2013). Regardless of the method applied, they all use the same data source that was obtained during exploration and documentation of the lignite deposits. Moreover, the ash distribution is most often shown in plan view, that is, on maps plotted by the appropriate computer program in recent years (e.g. Naworyta & Mazurek 2010, Jurek et al. 2013, Mastej et al. 2015, Pawelec & Bielowicz 2016). On the contrary, the methodology proposed in this paper additionally allows to present the ash content in the vertical section of the lignite seam to be determined (cf. Figs. 3–8). Therefore, the current research can be considered as complementary to those already mentioned.

Most likely, the increased ash content in some samples is at least partially attributable to the floods that occurred during the accumulation of peat (Middle Miocene), which in turn transformed into the first Mid-Polish lignite seam. This interpretation is supported by the fact that this lignite seam, especially in the Tomisławice and Józwin IIB opencasts, is often split by sandy and clayey partings. These interbeddings are likely connected with flood events during which siliciclastics were supplied to the mire (Widera 2016, Widera et al. 2017, Chomiak et al. 2019a, 2019b, 2020, Chomiak 2020). The effects of floods on mires (backswamps) located in close proximity to river channels are often described in the geological literature (e.g. Gradziński et al. 1976, Horne et al. 1978, Kasiński 1986, Smith et al. 1989, Zieliński 2014, and references therein). It should be noted

that the relatively high content of CaO (~30 wt% on average) in the ashes tested additionally indicates their autogenic origin.

In this paper, a macroscopically visible bed of siliciclastics within the exploited lignite seam was documented in the Tomisławice opencast mine. This 10–30 cm thick layer of clay in the upper part of the seam was found in two samples (Fig. 5B), and in sample 49 at sampling site X (Fig. 6). In fact, this layer comprises a coaly clay containing about 30 wt% organic matter and 70 wt% mineral matter (i.e. ash) (Fig. 5B). Because the siliciclastic partings are not the subject of the present study, their origin is not discussed here. However, the impact of the clayey bed on the ash content of the entire seam may be significant, as was found to be the case for the “Tomisławice” lignite deposit (Chomiak et al. 2020).

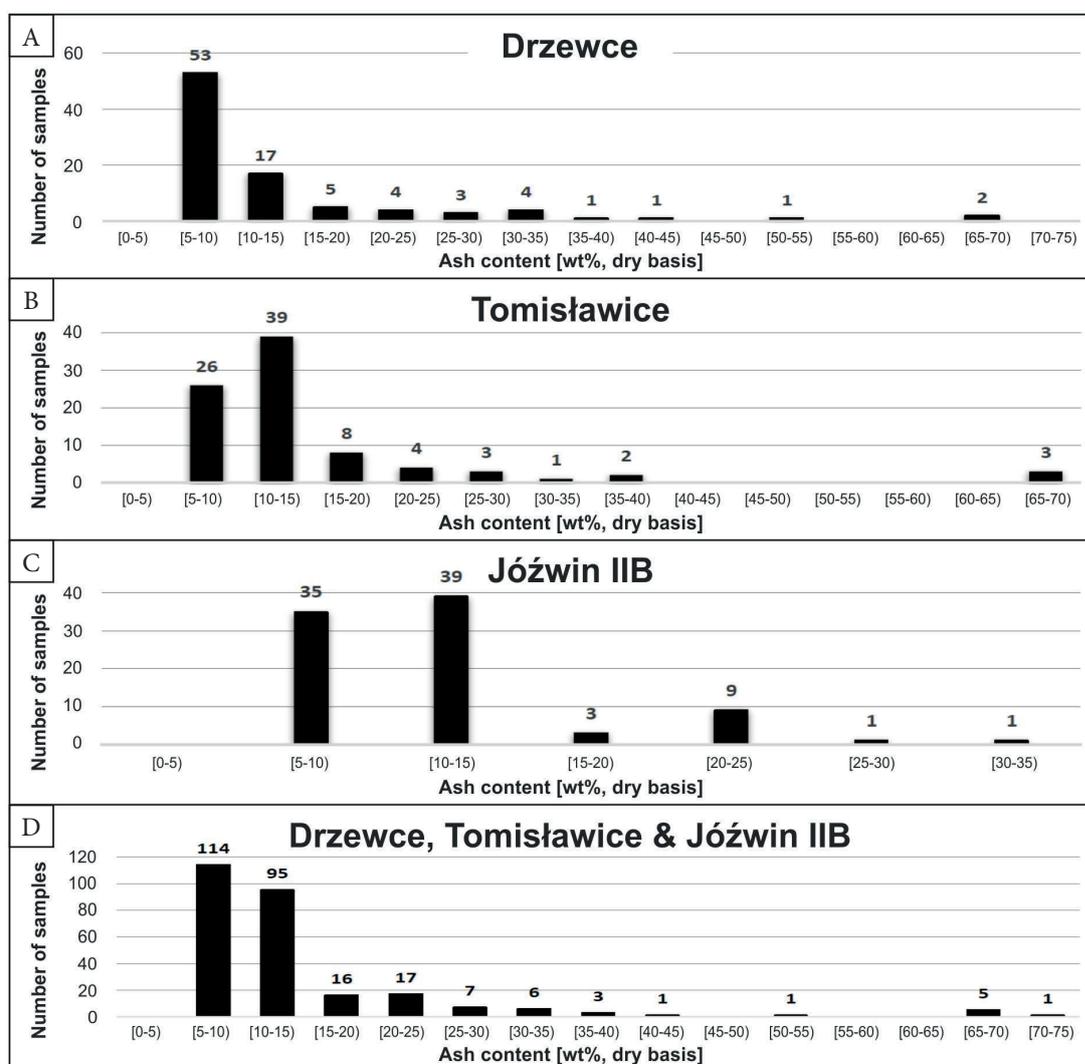
The distribution of ash content in the 266 lignite samples analysed from all currently operational opencasts belonging to the Konin Lignite Mine, is clearly visible on the histograms (Fig. 9). The shape of the statistical data is more similar in the case of lignite from the Tomisławice and Józwin IIB opencasts than from the Drzewce opencast. However, all these histograms are skewed right, that is, just like the histogram constructed for all samples (cf. Fig. 9A–D). This means that the largest number of lignite samples (>78.5%) is characterised by ash content in the range of 5–10 and 10–15 wt%, respectively. Consequently, only 8 samples analysed cannot be described as lignite because they contain >40 wt% of ash (Fig. 9D, Rozporządzenie 2001).

On the other hand, the statistically-calculated ash content within the first Mid-Polish lignite seam provides some interesting conclusions (Tabs. 1, 2). The values of the coefficients of variation obtained clearly show the similarity between the lignite seams in the Drzewce and Tomisławice opencasts. According to Mucha's classification (1994), this is expressed as a large variation in ash content (41–100%). In contrast to examples from the Drzewce and Tomisławice opencasts, the lignite seam from the Józwin IIB opencast is characterised by a low (<20%, in the case of section J) to an average (21–40%, in the case of the lignite walls) variation in ash content (Mucha 1994). At least two factors could have affected such significant

differences in ash content and its coefficient of variation. Firstly, the investigated lignite seam from the Józwin IIB opencast has the smallest thickness and is the least internally differentiated (Fig. 7B, C). Secondly, the sampled part of the seam only covers its upper bench, which rests above the sandy partings representing crevasse-splay sediments (Chomiak et al. 2019a, 2019b).

Finally, the ash (mineral matter) has a negative impact on the environment due to the combustion of lignite in power plants, as well as during other methods of its utilization, such as gasification, carbonisation, and liquefaction (e.g. Shirazi et al. 1995, Gülen 2007, Naworyta 2008, Bielowicz 2013,

and references therein). Therefore, the study of ash content in lignite seams is important, with many potential benefits for both industry and the environment. Detailed knowledge of the content and spatial distribution of ash in lignite deposits supplied to power plants can help reduce the amount of inorganic substance, and consequently less ash will be produced during combustion. This knowledge can help improve the quality of lignite used on an industrial scale, for example, by selective exploitation. Nevertheless, due to technological and financial limitations, this is practiced sporadically and only on a local scale by the Konin Lignite Mine (Chomiak et al. 2020).



**Fig. 9.** Distribution of ash content in lignites from opencasts belonging to the Konin Lignite Mine: A) the Drzewce opencast; B) the Tomisławice opencast; C) the Józwin IIB opencast; D) all currently operating lignite opencasts; for detailed data see Figures 3–8

## CONCLUSIONS

The results presented in this study summarize almost two years of fieldwork and laboratory analyses, as well as answering the research question posed in the introduction. Thus, the following conclusions can be drawn:

1. The examined first Mid-Polish lignite seam is relatively thin (<10 m on average) and contains a lot of ash (>10 wt% on average). The spatial distribution of the ash is highly diverse and ranges from 6.5 to 69.8 wt% (9.7–17.6 wt% on average). However, over 78.5% of analysed lignite samples contain 5–15 wt% of ash.
2. The coefficients of variation calculated for the results obtained (80.23–96.33%) indicate a large variation in ash content in lignites from the Drzewce and Tomisławice opencasts. The exceptions are lignites from the Józwin IIB opencast, where this coefficient is significantly lower (14.53–37.75%).
3. Such large differences in ash content make some parts of the first Mid-Polish lignite seam unsuitable for the production of electricity. Therefore, better knowledge of this seam, through detailed ash content analysis, could contribute to environmental protection by selected exploitation (avoiding the ash-rich parts) of the lignite seam and related lower ash production. But is it possible in light of the adopted method of mining?

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