Chemical and mineral composition of fly ashes from home furnaces, and health and environmental risk related to their presence in the environment
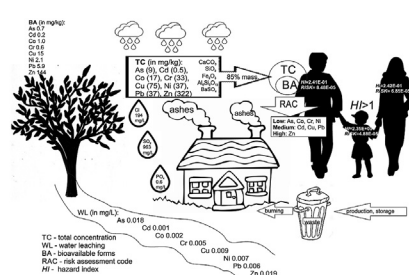
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HIGHLIGHTS

- The ashes exhibit high variability in terms of morphology as well as phase and chemical composition.
- Mobility of pollutants expressed in the leaching potential of toxins released from ashes is important parameter.
- The established risk assessment code was: *Low* for As, Co, Cr, Ni, *Medium* for Cd, Cu and Pb, and *High* for Zn.
- Calculated *Risk* and *HI* indicators point to the existence of a health risk, especially for children.

GRAPHICAL ABSTRACT

ABSTRACT

The study presents the results of an analysis of fly ashes produced from burning of solid fuels mixed with municipal waste and assesses the environmental and health risk associated with infiltration of the selected metals to the environment. The phase composition suggests that the material is extremely mixed and diverse. Low-temperature components were mixed with substances formed in high temperatures. The variable composition of waste from different home furnaces with high content of the amorphous phase (which dissolves in water more easily than its crystalline equivalents) may be harmful to the environment and for the people. The dominant elements were silicates and aluminosilicates, such as: quartz, feldspar and plagioclase (albite). Clay minerals (kaolinite and mullite), carbonates (calcite), oxides/oxidehydroxides of iron and sulfate minerals (gypsum and anhydrite) were also abundant. The particles' major constituents were Si, Al, Ca and Fe oxides (85.5%), while S, Mg, Na, K and Ti oxides accounted for 12.6% of the total content. The risk assessment code suggested: Low Risk for As, Co, Cr, Ni, Medium Risk for Cd, Cu and Pb, and High Risk for Zn. Hazard Index (*HI*) calculated for non-cancerogenic substances for children was 2.35E+00. The total *Risk index* for children was 4.88E-05. As for adults, *HI* was 2.42E-01 for women, and 2.89E-01 for men, while the *Risk index* value was 6.85E-05 for women, and 8.48E-05 for men. The value HI > 1 points to the risk of adverse health impact on children exposed to fly ashes.

1. Introduction

Fly ashes are a fine particle fraction of the material produced through combustion of solid fuels (coal, wood and other high-energy substances), which usually takes place in furnaces (boilers) constructed for this purpose. The composition of ashes depends directly on the type of incinerated material and the boilers used in the process (Matsui et al., 2003; Wyrzykowska et al., 2009, Tsiridis et al., 2012; Kicińska and Mamak, 2017). As well as the quality of fuel, the efficiency of the devices which capture and store combustion products is of utmost importance (Reinik et al., 2013; Yanda et al., 2015; Takaoka et al., 2005). In commercial power generation, most hazardous compounds are collected by electrostatic precipitators, which eliminate the emission of these substances to the atmosphere. This is beneficial for the environment, minimizing the concentration of pollutants settling on soil, vegetation and surface waters (Kabata-Pendias and Pendias, 1999; Kicińska et al., 2017).

The situation is quite different, however, when it comes to home furnaces, particularly in rural areas (Kicińska and Mamak, 2017). Residents of small towns and villages tend to buy low-quality coal and fine coke known as "koksik", often combining it with all kinds of waste produced in their households. Klojzy-Karczmarczyk and Staszczak (2017) have shown in their study that about 50% of waste from rural areas may originate from home furnaces. Thus, it can be assumed that waste is used as a free, additional type of fuel.

The incinerated mass contains all kinds of substances: plastic, paper, cleaning products containers, disposable nappies, food leftovers and many other unwanted items, such as clothes, toys or waste from home workshops — for instance leather and carpentry materials. In the Polish legislation this kind of waste is termed municipal waste (Waste Catalogue, 2014, Minister of the Environment, 2016). It refers to any waste produced in households, trade, catering industry, education and service industries, often containing green waste, i.e. branches, mowed grass, tree leaves, and even street litter.

The problem of burning municipal waste in home furnaces exists in many countries (Czop and Kajda-Szcześniak, 2013; Yanda et al., 2015). It stems mainly from lack of common knowledge about the harmfulness of this practice or simply from ignoring the fact. Another important factor is the popular habit of burning waste, passed on from generation to generation. For many people, the financial factor is important as well — burning rubbish saves money they would have to spend on solid fuels such as coal.

The effects of these practices are easy to predict. The illusory thrift and cultivation of shameful habits increase pollution and ultimately result in higher incidence of respiratory diseases, cardiovascular diseases and cancer among residents of those regions (Kabata-Pendias and Pendias, 1999; Pan et al., 2013; Kicińska, 2016).

Particularly hazardous substances produced in the course of municipal waste burning include: dusts, carbon oxides, nitric oxides, sulphur dioxides, ozone, hydrogen chloride, hydrogen fluoride, polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and multinuclear aromatic hydrocarbons (Reinik et al., 2013). The list would not be complete without heavy metals such as chromium, nickel, lead, cadmium and mercury (Hansen et al., 2001; Wang et al., 2007, 2017). Storage of furnace ash in a landfill is one of the ways of its disposal as provided for in the Polish legislation (The Act, 2001). However, due to high fees for the disposal of thermally processed waste, many land and furnace owners scatter the ashes over pavements and roads in winter, or spread them over the soil in their kitchen gardens or agricultural land. Moreover, these individuals are convinced that by doing so

they do not exceed the maximum permissible values of pollutants for organic and organic-mineral plant growth enhancers.

The problem of pollution caused by combustion of municipal waste is particularly serious in agricultural and high nature value areas. Given the above-listed facts, we have decided to investigate the severity of this social and health problem in an agricultural region protected by law. We have collected samples of fly ashes disposed of without any safety measures taken in illegal landfills in the area of Beskid Sądecki (southern Poland), which is legally protected as a landscape park and Natura 2000 area, and we: (*1*) determined the chemical and phase composition of the samples, (*2*) studied the level of leaching of selected metals into water and their bioavailability to plants (*3*) used the data to assess health risk associated with the presence of fly ashes in the environment for 6-year-old and 70-year-old inhabitants of the region (*4*) assessed the environmental risk associated with infiltration of the selected metals to the environment.

2. Materials and methods

Nine 9 independent samples of ashes collected from illegal landfills were analyzed (Fig. 1). The limited amount of material collected was due to the difficulties in locating illegal landfills and irregular dumping of ashes in them. Each sample weighed approx. 0.5 kg and consisted of several smaller extracted portions. The original samples were dry and came from the so-called home furnaces, which was indicated by objects found in close proximity to the ashes, such as paper and unburned waste remains.

The study used instrumental methods (XRF, XRD, SEM) to determine the chemical and phase composition of the material collected. In addition, pH and the total content of As, Cd, Co, Cr, Cu, Hg, Ni, Pb and Zn were determined in a chemical analysis. The leaching potential was determined with the use of water solutions (solid/solution ratio 1:10), and the amount of elements bioavailable to plants was determined with 0.11 M of EDTA solution.

X-ray fluorescence method (Rigaku WD-XRF ZSX Primus II spectrometer, X-ray tube) was used for elemental analysis of the fragmented material by identifying spectral lines and detecting any coincidence of these lines. The analysis was conducted within the fluorine-uranium range (F-U) using SQX Calculation software (fundamental parameters method). Sample compositions were normalized to 100%.

The phase composition of crystalline components was carried out using a Rigaku MiniFlex 600 XRD diffractometer. The measurement parameters were as follows: CuK_α radiation, reflection graphitic monochromator, lamp voltage 40 kV, lamp current 20 mA, recording range 2-72°2Θ; step 0.05°2Θ, impulse count rate 1 sek/step. The interplanar distances obtained from the X-rays patterns were used for identifying crystalline phases based on the data of the ICDD (International Centre for Diffraction Data) catalogue and the XRAYAN software.

Scanning electron microscopy SEM-EDS (a FEI Quanta model 200 FEG unit) was used for observing the morphology of the grains in all the fractions and conducting spot analyses. The observations were extended by chemical analyses of microareas applying an EDS detector (SEM-EDS method) conducted in the high vacuum mode. The resolution power of the microscope was increased by covering the samples with carbon prior to analysing. The accelerating voltage was 20 kV.

The chemical determinations of the quasi-totals of elements were made by dissolving the samples in *aqua regia* (HCl + HNO₃, at the ratio 3:1) in a microwave oven SCP SCIENCE, DigiPREP HT type, at 130 °C. The mass of the analytical samples was 0.5 g.

The determinations of the bioavailable (e.g. for plants and soil organisms) quantities of metals were conducted after a 2.5-h
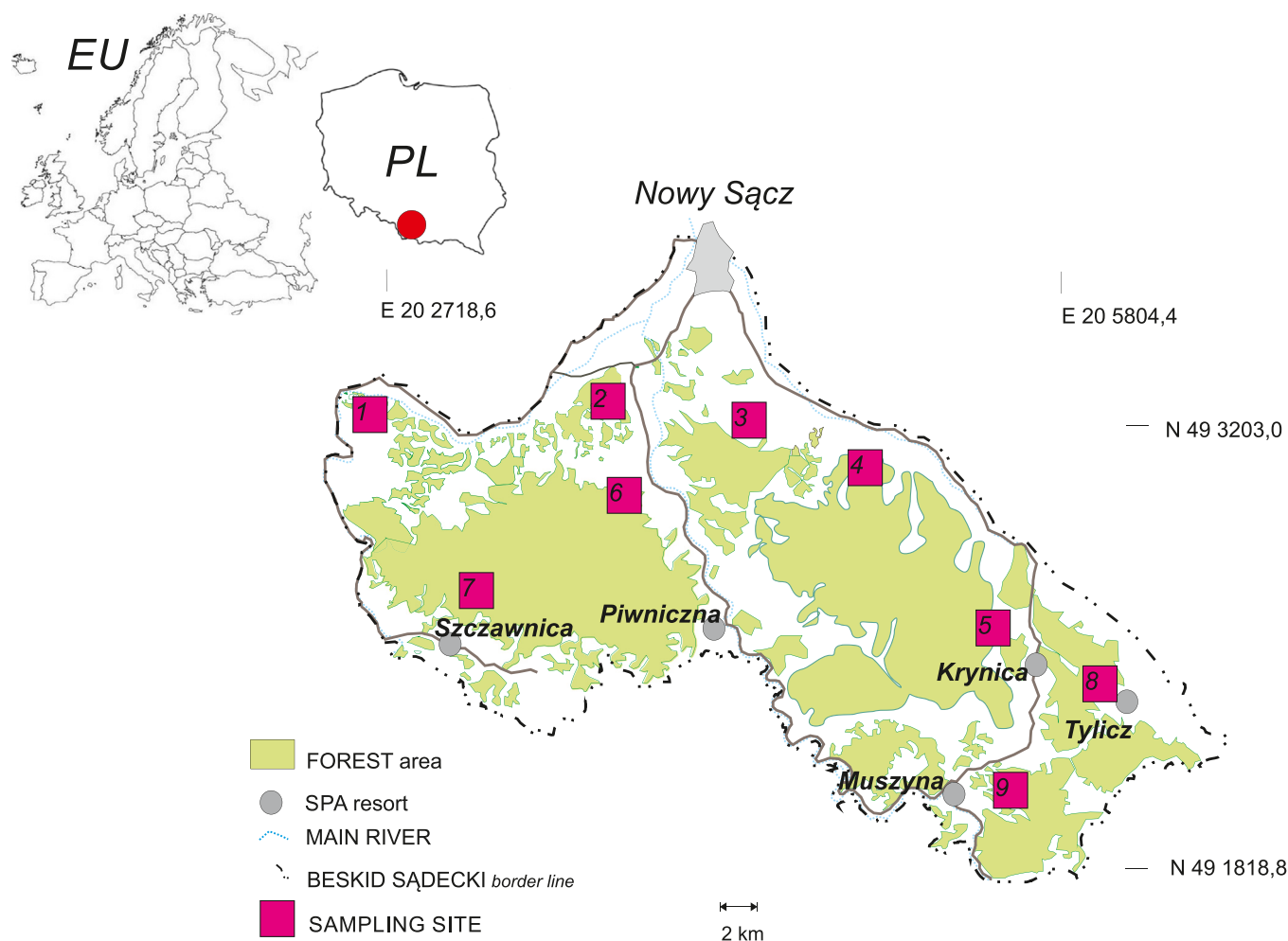
Fig. 1. Sampling sites.

extraction of the analytical samples with 0.11 M solution of EDTA at the solid to liquid ratio 1:10. EDTA is used extensively in soil sciences to determine the bioavailability of trace elements (including metals) and possible decontamination methods of polluted soils. Since the EDTA-leaching is of a non-selective nature, the co-dissolution of major elements also takes place (Lo and Yang, 1999; Manouchehri et al., 2006; Karczewska et al., 2009).

The total mercury content in the ash samples was determined by a modified classic AAS method, which measures low Hg concentrations in solid and liquid samples, ensuring minimal loss of mercury during the analysis. The analysis was performed with Altec AMA-254 Single-Purpose Atomic Absorption Spectrometer.

The chemical composition was determined using the method of induced coupled plasma mass emission spectroscopy (ICP-MS) at the certified geochemical laboratory (certificate no. AB1050) of the AGH University of Science and Technology in Krakow. The Certipur Certified Reference Material (HC69208280) was used as a standard. The precision of the determining Zn, Pb, As, Cd, Cu, Ni, Cr and Co was 10%, while the accuracies (AO) ranged between 95 and 104%. The limits of detection (LOD) and quantification (LOQ) parameters were calculated from the following equations:

$$LOD = X_b + 3\ SD_b, \tag{1}$$

$$LOQ = X_b + 10\ SD_b, \tag{2}$$

where:

X_b — mean concentration of the blank (zero concentration) sample;
SD_b — the standard deviation of the blank;
and their values are presented in Table 2.

The model used in this study to calculate human exposure to metals was adapted according to the US Environmental Protection Agency guidelines (US EPA, 1996; US EPA, 1997; US EPA, 2005). The health risk *HI* was calculated for three pathways: $HQ_{ingestion}$, $HQ_{inhalation}$, and HQ_{dermal} (De Miguel et al., 2007; Izquierdo et al., 2015). In the calculation of the $HQ_{inhalation}$ an older method was used (US EPA, 1986). Equation (3) was used to calculate exposure via oral route, resulting from accidental ingestion of ashes settled mainly on the hand surface. Exposure via inhalation route was calculated with equation (4). It is related to the inhalation of the finest particles of ashes, suspended in the air, and occurs mainly during activities like daily furnace cleaning, or scattering ashes over agricultural land or in kitchen gardens. In winter, especially during snowfall/freezing seasons, it is common practice to spread ashes from home furnaces over pavements and roads adjacent to houses, which is also a source of inhalation exposure. Equation (5) was used to calculate exposure via dermal route. In this case, the finest fraction adheres to the skin of the hands, arms and face during activities like daily furnace cleaning in enclosed spaces, and spreading ashes over

Table 1
Total content of oxides and elements of fly ashes determined by XRF and AMA analysis.

Oxides of Elements	DT	Min.	Max.	AV	SD	V
	[% wt.]					
SiO_2	0.011	27.568	65.535	42.141	16.70	0.40
Al_2O_3	0.016	12.869	27.830	21.242	6.23	0.29
CaO	0.009	9.840	18.706	13.533	3.76	0.28
Fe_2O_3	0.005	3.836	13.519	8.635	3.95	0.46
SO_3	0.006	0.435	7.875	4.240	3.03	0.71
MgO	0.016	1.126	4.585	3.132	1.46	0.47
Na_2O	0.025	0.627	3.793	2.289	1.29	0.56
K_2O	0.004	0.733	2.345	1.738	0.71	0.41
TiO_2	0.009	0.721	1.491	1.218	0.35	0.29
P_2O_5	0.004	0.240	1.464	0.725	0.53	0.73
MnO	0.005	0.090	0.519	0.323	0.17	0.53
Cl	0.006	0.013	0.655	0.249	0.28	1.12
BaO	0.037	0.092	0.195	0.129	0.04	0.31
ZnO	0.002	0.011	0.210	0.089	0.08	0.90
SrO	0.001	0.052	0.136	0.088	0.03	0.34
ZrO_2	0.011	0.054	0.078	0.065	0.01	0.15
V_2O_5	0.011	0.033	0.059	0.048	0.01	0.21
Cr_2O_5	0.006	0.013	0.04	0.030	0.01	0.33
PbO	0.003	0.026	0.028	0.027	0.001	0.04
CuO	0.002	0.009	0.033	0.023	0.01	0.43
NiO	0.002	0.014	0.023	0.019	0.01	0.53
Y_2O_3	0.001	0.011	0.012	0.012	0.001	0.08
Br	0.001	0.007	0.009	0.008	0.001	0.13
Rb_2O	0.001	0.004	0.013	0.008	0.003	0.38
Ga_2O_3	0.002	0.005	0.006	0.005	0.001	0.20
Hg*	0.001	0.007	0.028	0.017	0.009	0.53

DT – detection limit.
AV – average.
SD – standard deviation.
V – coefficient of variation (calculated as the ratio of SD to AV).
*determined by AMA Spectroscopy.

agricultural land without using protective gloves.

$$Dingestion = C \cdot \frac{IngR \cdot EF \cdot ED}{BW \cdot AT} \cdot CF1, \tag{3}$$

$$Dinhalation = C \cdot \frac{InhR \cdot EF \cdot ED}{PEF \cdot BW \cdot AT}, \tag{4}$$

$$Ddermal = C \cdot \frac{SA \cdot SL \cdot ABS \cdot EF \cdot ED}{BW \cdot AT} \cdot CF1, \tag{5}$$

where:

C – mean heavy metal concentration in all samples (mg/kg);
$IngR$ – conservative estimates of dust ingestion rates; for children 200 (mg per day) and for adults 50 (mg per day) (US EPA, 1997; US EPA, 2011);
$InhR$ – inhalation rate; in this study: 1.68 for children and 2.15 for adults (m^3/h) (US EPA, 2011);
EF – exposure frequency; calculated as: 245 days per year (heating season from October to May), 5 h per day = 1225 (hour/year);
ED – exposure duration; for children 6 (years) and for adults 70 (years);
BW – body weight; for children 3 to <6 years old 18.6 (kg), for adults 80 (kg) (US EPA, 2011);
AT – averaging time. In the case of non-carcinogens, for 6-year-old children its value is $6 \cdot 365 = 2190$ (days), while in the case of carcinogens, its value is $70 \cdot 365 = 25,550$ (days);
PEF – particle emission factor, 6.8E+08 (m^3/kg) after De Miguel et al. (2007);

Table 2
Content of elements (metals and a metalloid) in ashes determined by *aqua-regia* chemical extraction.

Parameters		As	Cd	Co	Cr	Cu	Ni	Pb	Zn
		[mg·kg⁻¹]							
CRM	reference values	98 ± 5	9.9 ± 0.5	9.9 ± 0.5	9.9 ± 0.5	9.9 ± 0.5	9.9 ± 0.5	9.8 ± 0.5	99 ± 5
	measured values (AO%)	92.88 (94.8)	9.53 (96.3)	9.82 (99.2)	10.16 (102.7)	9.64 (97.2)	10.16 (103.7)	10.07 (101.7)	102.6 (103.6)
LOD		0.0358	0.0013	0.0008	0.0039	0.0015	0.0064	0.0323	0.0473
LOQ		0.1552	0.0055	0.0036	0.0139	0.0064	0.0216	0.1198	0.2053
Sample									
1		10.50	0.89	18.95	48.51	117.84	45.31	51.05	812.12
2		10.84	0.25	23.71	35.78	94.2	44.54	40.98	135.13
3		5.72	0.19	6.35	12.04	15.87	19.01	17.45	41.58
4		11.25	1.25	21.52	55.55	68.62	43.56	45.69	255.69
5		3.49	0.79	14.61	21.86	59.89	36.89	58.59	221.36
6		6.82	0.56	15.98	46.28	79.89	38.45	26.41	469.87
7		12.32	0.45	8.79	18.98	88.69	39.38	36.69	198.56
8		8.75	0.38	21.91	36.78	96.35	22.56	45.78	287.89
9		9.28	0.15	25.30	25.68	56.87	47.89	12.36	481.45
for all samples									
Min.		3.49	0.15	6.35	12.04	15.87	19.01	12.36	41.58
Max.		12.32	1.25	25.30	55.55	117.84	47.89	58.59	812.12
Av.		8.77	0.55	17.46	33.50	75.36	37.51	37.22	322.63
SD		2.73	0.34	6.21	13.98	27.82	9.57	14.66	219.09
V		0.31	0.64	0.36	0.42	0.37	0.26	0.39	0.68
Upper limit determined for soil belong to II category[a] (% of samples upper this limit)		10 (44)	2 (0)	20 (33)	150 (0)	100 (11)	100 (0)	100 (0)	300 (33)

LOD – limit of detection.
LOQ – limits of quantification.
AO – analysis trueness (%).
CRM – certified research material.
[a] According to Minister of the Environment, 2016.

SA — exposed skin area calculated for head, arms and hands, for children 2550 (cm^2) and for adults 6840 (cm^2) (95% UCL, US EPA, 2011);

SL — skin adherence factor, calculated for activities involving soils, 0.27 for children and 0.22 for adults (mg/cm^2) (US EPA, 2011);

ABS — dermal absorption factor, 0.001 (all the elements with the exception of As, ABS for As = 0.03) after De Miguel et al. (2007);

*CF*1 — unit conversion factor of 10^{-6};

HQ$_{ing}$, *HQ$_{inhal}$*, and *HQ$_{dermal}$* values calculated by dividing the values of D$_{dermal}$, D$_{inhalation}$ and D$_{ingestion}$ by RfD$_{dermal}$, RfD$_{inhalation}$ oraz RfD$_{ingestion}$, respectively (US EPA, 2011).

The total hazard index (*HI*) was calculated as a sum of *HQ$_{ing}$*, *HQ$_{inhal}$*, and *HQ$_{dermal}$* values. It is accepted that at the *HI* ≤ 1 adverse health effects are of a low probability to occur, at the *HI* > 1 negative health effects are probable.

For carcinogens their doses were multiplied by the respective slope factors (SF) to produce a level of the cancer *Risk*. The toxicity values used in the analysis were taken from US EPA (2005). For Pb, the reference doses are those contained in the World Health Organization's Guidelines for Drinking Water Quality (WHO, 2004). The toxicity values of dermal absorption were taken from IRIS (US EPA, 2005).

Environmental risk assessment was calculated according risk assessment code (RAC), when the ratio of the elements concentration in exchangeable/in this case EDTA-extractable phase in less than 1% compared with the total metal concentration of this metal, that mean the metal has no adverse impact on the environment. If the ratio is between 1 and 10%, a low risk is defined, while medium risk is 11—30%, and 31—50% indicates a high risk. The values above 50% indicate a very high risk to the environment (Pan et al., 2013).

Statistical calculations and data presentations were conducted with the Statistica ver. 10 and Excel applications. The differences between means were detected by the Tukey's HSD test at a significance level of 0.05. Based on the statistical evaluation of the uncertainty of the parameters analyzed, the quantity and type of the material analyzed can be considered sufficient for a proper geochemical reasoning, although the obtained research results are of exploratory nature.

3. The studied area

Beskid Sądecki is a part of the Alpide belt of the Carpathians. This sparsely populated region is inhabited by over 196, 000 people, with 19% living in urban and 81% in rural areas. The area is characterized by high forest cover and natural wealth: beautiful landscapes, numerous spa resorts, abundance of mineral waters and a rich cultural heritage. Most of the area in Beskid Sądecki is protected by law as part of the Popradzki Landscape Park (Popradzki Park Krajobrazowy, PPK), which contains 14 nature reserves. PPK is one of the most biodiverse natural areas in Poland with some of the most beautiful landscapes in the country. Two mountain ranges — Jaworzyny and Radziejowej — determine the altitudinal climatic zones in the region: the moderately warm zone (up to 600—650 m a.s.) with the annual isotherm of 6 °C, moderately cold zone (up to 1100 m a.s.) with the annual isotherm of 4 °C, and cold zone with the annual isotherm of 2 °C. For 82% of the year, the weather is determined by polar air masses — maritime polar air for 60%, and continental polar air for 22% of days in the year. Settlements are concentrated mainly in river valleys and the heating season usually lasts from October to April.

4. Results

4.1. Phase composition of the ashes

4.1.1. XRD

X-ray diffraction, one of the basic methods for estimating the qualitative composition of materials, was used to identify the main mineral phases in the fly ashes (Fig. 2). Apart from common minerals, such as silicates and aluminosilicates: quartz, feldspar and plagioclase (albite), and mica (muscovite), the sample contained also clay minerals, such as kaolinite and high-temperature mullite. It is hardly possible that the latter two should occur in a primary environment due to the fact that kaolinite is commonly formed by weathering of feldspar and other aluminosilicates, while mullite occurs as a mineral in thermally metamorphosed rocks. Mullite has also been found in clay rocks sintered for instance during underground coal seam fires (Szponder and Trybalski, 2009).

Carbonates: calcite (CaCO$_3$) and common products of the oxidation of iron minerals — goethite (α-FeOOH) and hematite (α-Fe$_2$O$_3$) were abundant in the material studied. Sulfate minerals, such as gypsum (CaSO$_4$·2H$_2$O) and anhydrite (CaSO$_4$) were detected in nearly all samples. These are simple sulfates (hydrated in the case of gypsum, possibly as a result of anhydrite hydration), commonly occurring in the oxidation zone. They are common products of sulfide weathering found in limestone (carbonate) and marlstone. Hydrated calcium and iron silicates and aluminum oxides (α-AlOOH diaspores) were also detected in the spectra.

4.1.2. SEM

Scanning electron microscope images have shown that the material analyzed has a fine particle structure and is highly diversified in terms of granulometric and chemical composition. Microscope imaging revealed spindle-shaped, oval and highly irregular shapes of aggregate character (Fig. 3A and Fig. 4A). The size of most fly ash constituents falls within the range of 10—100 μm in length and 10—20 μm in width. They are made of large grains, tightly covered with very fine binder which often takes the form of multilayer coats. The aggregates take on convoluted forms resembling beads; typically, they are splayed and look very much like porous openwork (Fig. 3B, pt. 1, Fig. 4B, pt. 1 and 2). EDS analysis has shown that they are composed of iron oxides (hematite), where the proportion of Fe is almost 55 wt%. Other minerals found in abundance in the fly ashes were aluminosilicates (Fig. 3B, pt. 2, 3, 5, 6). Apart from typical alkaline aluminosilicates of potassium and aluminum, such as muscovite (KAl$_2$(OH,F)$_2$AlSi$_3$O$_{10}$), other detected components were potassium aluminosilicates (microcline KAlSi$_3$O$_8$) and sodium aluminosilicates (albite NaAlSi$_3$O$_8$). The EDS analysis has confirmed the presence of mullite Al$_6$Si$_2$O$_{13}$, a high-temperature clay mineral (Fig. 3B, pt. 2 and 3, Fig. 4B, pt. 3). As mentioned before, this aluminosilicate is a product of kaolinite dihydroxylation, formed in high-temperature processes (c. 950—1100 °C). The next image (Fig. 3C and D) presents a regular organic network structure. It is a fragment of a plant with clearly visible transverse tracheids and pits (Fig. 3D, pt. 1, 2). It is composed mostly of coal (c. 74—78 wt%). The small cube in the form of a regular-shaped reticulum (Fig. 3C, pt. 2) is probably calcium carbonate (CaCO$_3$). One can also see bright, irregular forms (Fig. 3E, pt. 1), which are barium sulfate — barite (BaSO$_4$), with 42 wt% of Ba and almost 11 wt% of S. We have also observed relatively large (c. 200 × 100 μm) plates of unburned coal covered with fine-particle material (Fig. 4C pt. 1—3).

The next figure (Fig. 4D) shows a large (c. 300 μm) oval grain. It is probably a grain of sand (silicon dioxide SiO$_2$, Fig. 4D pt. 1) covered
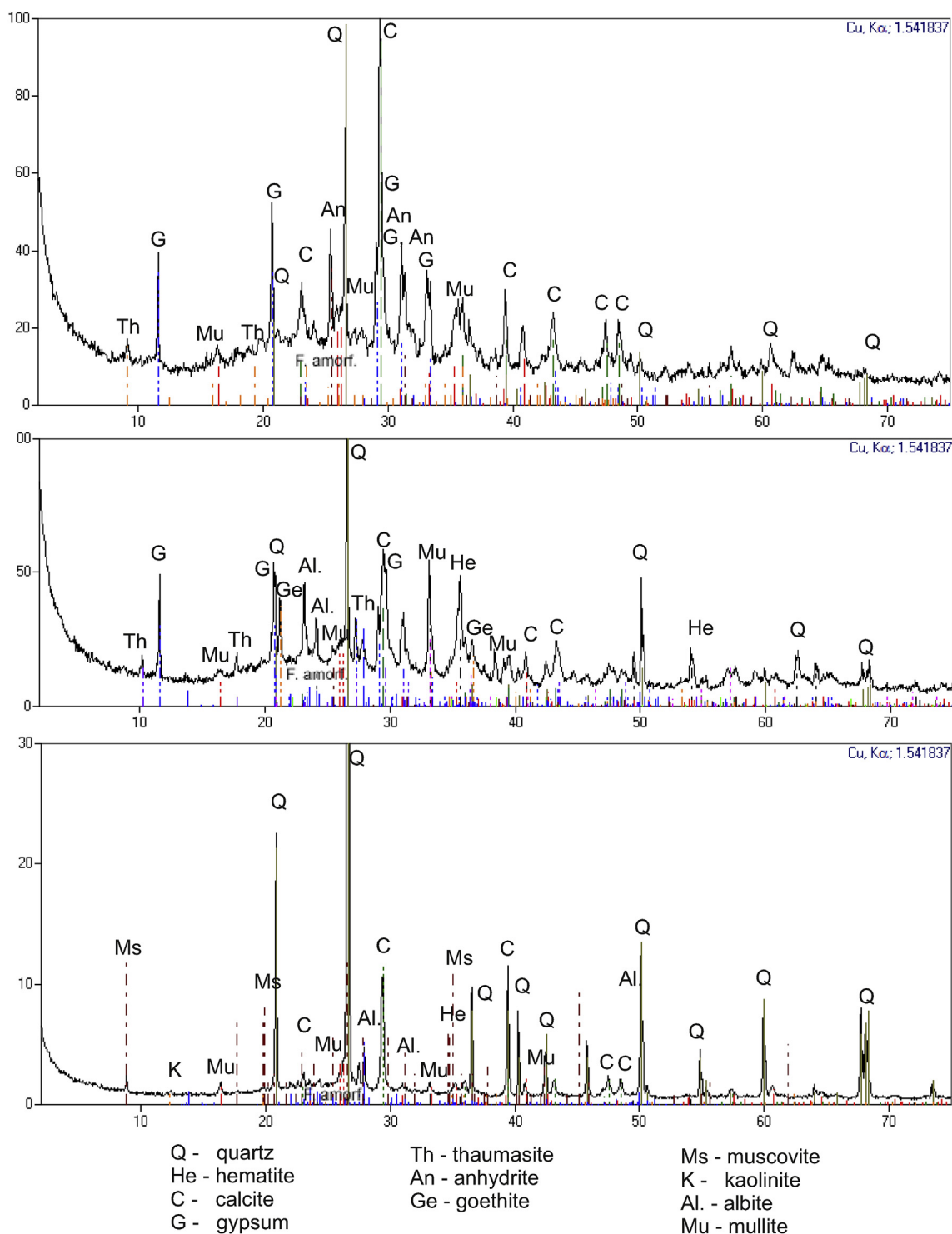
Fig. 2. XRD patterns of ashes samples collected in Beskid Sadecki region.

with fine material containing carbonates, probably gypsum (Fig. 4D pt. 2,3).

Microscope imaging also revealed sharp-edged fragments, oblong and pointed in shape (Fig. 4E). Chemical analysis revealed them to be a high-temperature mineral of the silicates group (mullite) with high Ca content, amounting to 24 wt%. The mineral composition determined corresponded precisely with the results obtained by Szponder and Trybalski (2009) and Wójcik and Smołka-Danielowska (2008).

4.2. Chemical composition of the ashes

4.2.1. XRF

Chemical composition of the ashes was determined with the use of direct WD-XRF (Table 1). We have observed that the dominant elements were: Si, Al, Ca and Fe. With regard to their oxides, the

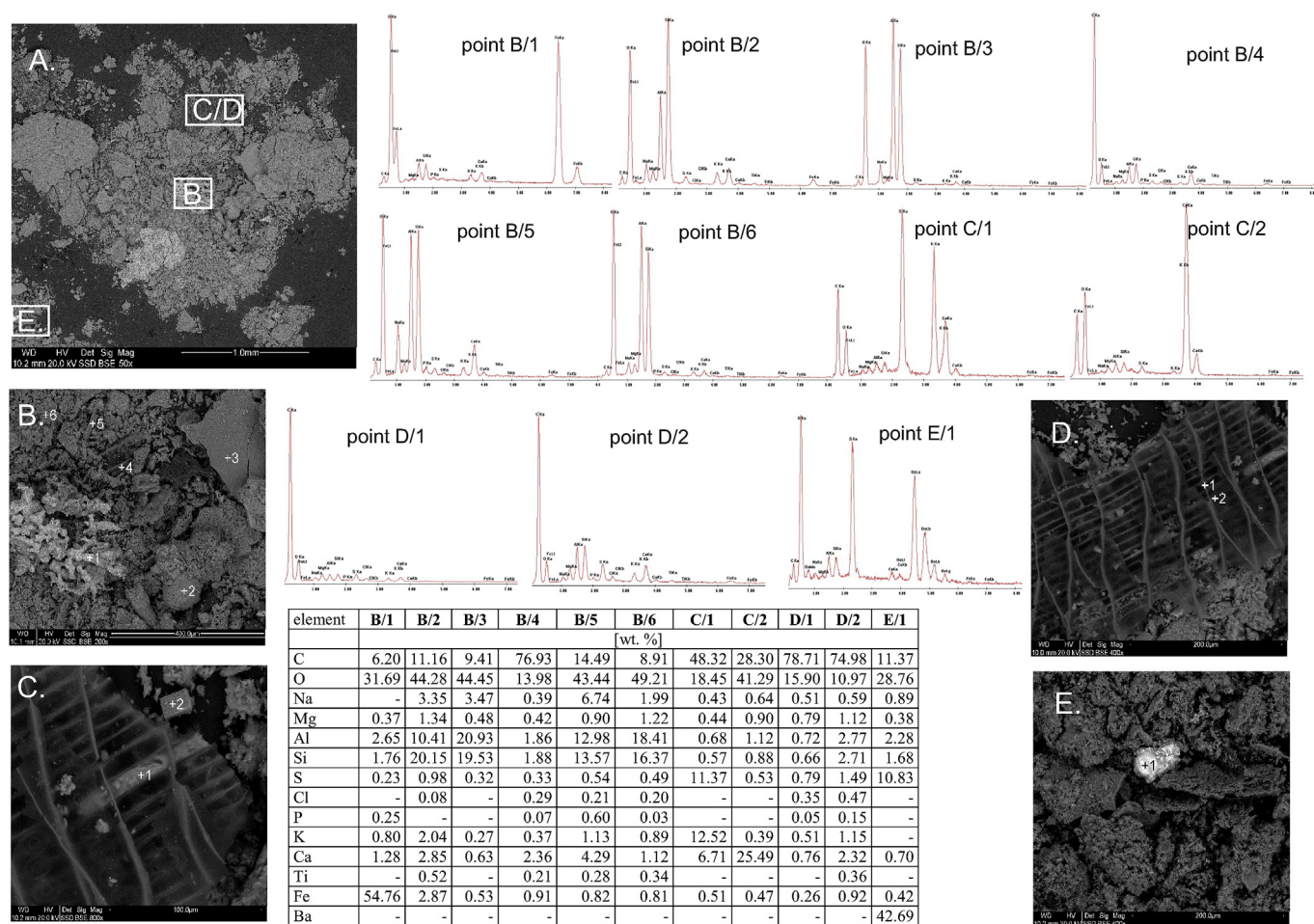| element	B/1	B/2	B/3	B/4	B/5	B/6	C/1	C/2	D/1	D/2	E/1
					[wt. %]						
C	6.20	11.16	9.41	76.93	14.49	8.91	48.32	28.30	78.71	74.98	11.37
O	31.69	44.28	44.45	13.98	43.44	49.21	18.45	41.29	15.90	10.97	28.76
Na	-	3.35	3.47	0.39	6.74	1.99	0.43	0.64	0.51	0.59	0.89
Mg	0.37	1.34	0.48	0.42	0.90	1.22	0.44	0.90	0.79	1.12	0.38
Al	2.65	10.41	20.93	1.86	12.98	18.41	0.68	1.12	0.72	2.77	2.28
Si	1.76	20.15	19.53	1.88	13.57	16.37	0.57	0.88	0.66	2.71	1.68
S	0.23	0.98	0.32	0.33	0.54	0.49	11.37	0.53	0.79	1.49	10.83
Cl	-	0.08	-	0.29	0.21	0.20	-	-	0.35	0.47	-
P	0.25	-	-	0.07	0.60	0.03	-	-	0.05	0.15	-
K	0.80	2.04	0.27	0.37	1.13	0.89	12.52	0.39	0.51	1.15	-
Ca	1.28	2.85	0.63	2.36	4.29	1.12	6.71	25.49	0.76	2.32	0.70
Ti	-	0.52	-	0.21	0.28	0.34	-	-	-	0.36	-
Fe	54.76	2.87	0.53	0.91	0.82	0.81	0.51	0.47	0.26	0.92	0.42
Ba	-	-	-	-	-	-	-	-	-	-	42.69

Fig. 3. SEM images (A—E) and EDS spectra of ashes samples collected in Beskid Sadecki region.

mean content of these elements was (in wt%): 42, 21, 13.5 and 8.6, respectively. The total share of these elements in the total content was 85.55%. The remaining 12.6% of the total content were oxides: S, Mg, Na, K and Ti. The percentage of the remaining elements detected with this method did not exceed 2 wt%. We consider the determined oxide composition to be typical of ashes (Szponder and Trybalski, 2009). What is noticeable, however, is the high concentration of sulfur oxides (0.43—7.87 wt%), which may have an adverse effect on nearly all components of the environment due to acidification processes. The WD-XRF analysis has also confirmed that the chemical composition of the material studied was highly diversified. The highest coefficient of variation V was calculated for Cl ($V = 1.12$), ZnO ($V = 0.90$) and P_2O_5 ($V = 0.73$). For other ash components it was $V < 0.5$.

4.2.2. Aqua-regia extraction

Extraction with a mixture of concentrated acids was used to determine the quasi-total element composition of the ash samples. Despite the fact that strong reagents break certain chemical bonds, it can be assumed that substances which cause stronger reactions do not occur in natural environment. Unlike XRF, this method allows for the determination of the content of elements which occur in low concentrations. It is of utmost importance for studying environmental trace-elements related to health and environmental risks. However, the method has a drawback. Namely, it may underestimate the amounts of certain substances (e.g. silica) due to the fact they are hardly soluble in the reagents used.

Using *aqua-regia* extraction allowed us to precisely establish the content of elements related to the so-called low emission, i.e. fuel combustion processes. The elements analyzed were: As, Cd, Co, Cr, Cu, Ni, Pb and Zn. Their concentrations fell within the following ranges (in $mg \cdot kg^{-1}$): As 3.49—12.32, Cd 0.15—1.25, Co 6.35—25.3, Cr 12.04—55.55, Cu 15.87—117.84, Ni 19.01—47.89, Pb 12.36—58.59 and Zn 41.58—812.12 (Table 2). The highest variation (V) was shown by Zn ($V = 0.68$) and Cd ($V = 0.64$). For the other elements, the calculated V coefficients were significantly lower, falling within the range of 0.3—0.4.

Due to the lack of regulations and standards regarding the assessment of the impact of ashes on the soil environment, the content of elements was compared with the limits set for agricultural soils (Minister of the Environment, 2016). For the majority of elements, the mean concentrations: As 8.77, Cd 0.55, Co 17.46, Cr 33.50, Cu 75.36, Ni 37.51, Pb 37.22, and Zn 322.63 were definitely below the maximum limit for lands of Category II according to the regulation of the Minister of the Environment (Minister of the Environment, 2016). The category includes arable land, orchards, permanent pastures, land under ponds and ditches, meadows and allotments. The limits (in $mg \cdot kg^{-1}$) are: As 10, Cd 2, Co 20, Cr 150, Cu, Ni and Pb 100, and Zn 300. The conditions in the area studied should be considered satisfactory. However, the analysis of all samples has shown that the acceptable concentrations (Minister of the Environment, 2016) were exceeded in 44% of the samples for As, in 33% of the samples for Co and Zn, and in 11% of the samples for Cu.
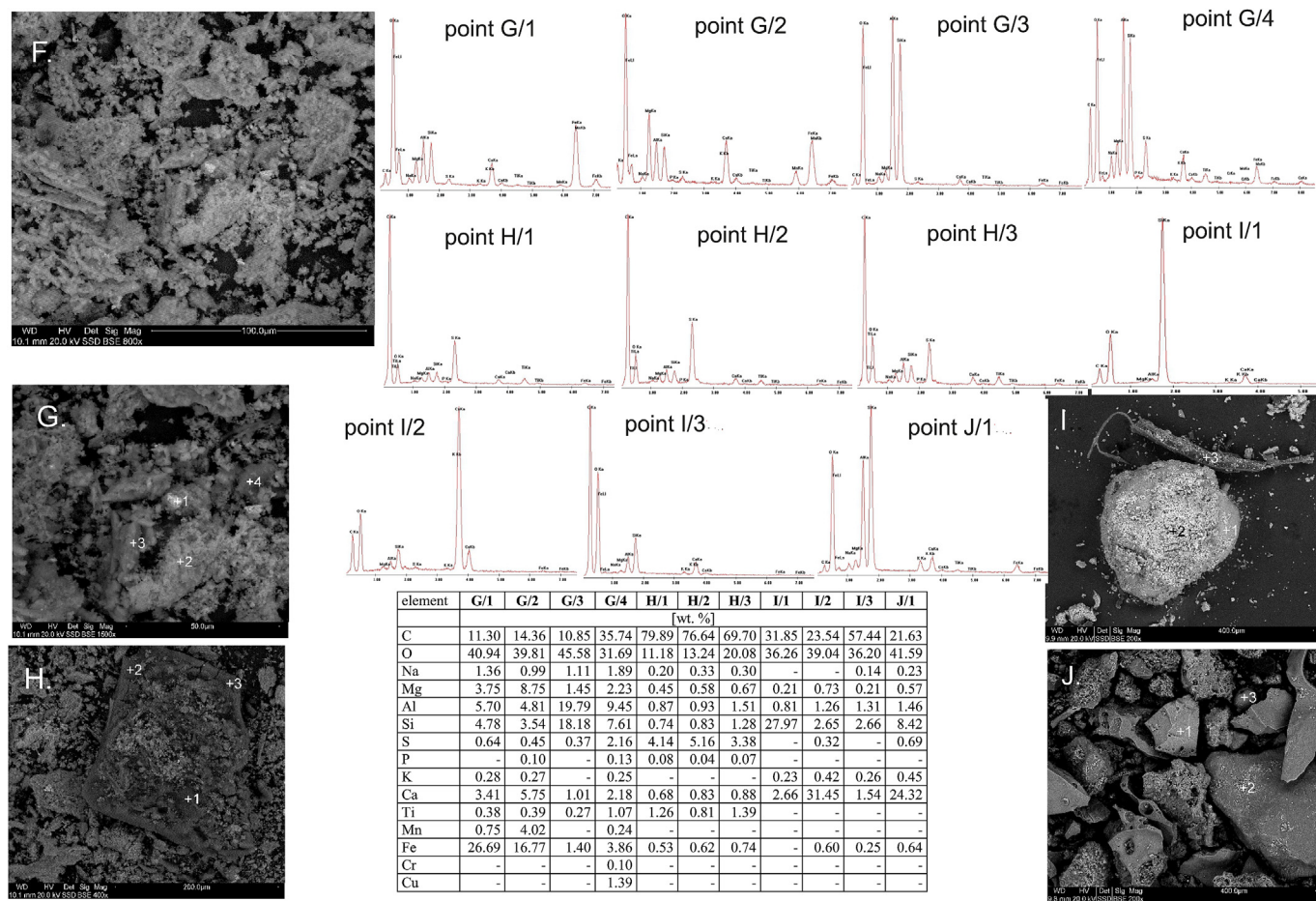
element	G/1	G/2	G/3	G/4	H/1	H/2	H/3	I/1	I/2	I/3	J/1
	[wt. %]										
C	11.30	14.36	10.85	35.74	79.89	76.64	69.70	31.85	23.54	57.44	21.63
O	40.94	39.81	45.58	31.69	13.24	13.24	20.08	36.26	39.04	36.20	41.59
Na	1.36	0.99	1.11	1.89	0.20	0.33	0.30	-	-	0.14	0.23
Mg	3.75	8.75	1.45	2.23	0.45	0.58	0.67	0.21	0.73	0.21	0.57
Al	5.70	4.81	19.79	9.45	0.87	0.93	1.51	0.81	1.26	1.31	1.46
Si	4.78	3.54	18.18	7.61	0.74	0.83	1.28	27.97	2.65	2.66	8.42
S	0.64	0.45	0.37	2.16	4.14	5.16	3.38	-	0.32	-	0.69
P	-	0.10	-	0.13	0.08	0.04	0.07	-	-	-	-
K	0.28	0.27	-	0.25	-	-	-	0.23	0.42	0.26	0.45
Ca	3.41	5.75	1.01	2.18	0.68	0.83	0.88	2.66	31.45	1.54	24.32
Ti	0.38	0.39	0.27	1.07	1.26	0.81	1.39	-	-	-	-
Mn	0.75	4.02	-	0.24	-	-	-	-	-	-	-
Fe	26.69	16.77	1.40	3.86	0.53	0.62	0.74	-	0.60	0.25	0.64
Cr	-	-	-	-	-	-	-	-	-	-	-
Cu	-	-	-	1.39	-	-	-	-	-	-	-

Fig. 4. SEM images (F–J) and EDS spectra of ashes samples collected in Beskid Sadecki region.

4.2.3. Water leaching

In the context of waste studies, the amount of elements leached by water solutions is of particular importance due to the fact that leached pollutants are easily transportable and generally easily absorbed by living organisms. Moreover, they quickly enter water ecosystems (surface and ground waters) if these are not sufficiently protected (Antonkiewicz et al., 2017). Water extraction provided data on the amount of fraction which is most easily released from ashes (Table 3). For water solutions of the ashes studied, we determined the following amount of elements: (in $mg \cdot dm^{-3}$): As

0.036, Zn 0.024, Cu 0.014, Cr, Ni and Pb 0.009, Co 0.003, and Cd 0.001. Comparing these results with the maximum permissible values of pollutants for industrial wastewater (Minister of the Environment, 2014), it can be noted that the limits were not exceeded for any of the elements. The situation was different with regard to sulfates, since SO_4^{2-} concentrations were above the allowed limit (500 $mg \, dm^{-3}$) in as much as 66% of the samples analyzed. This has an undoubtedly adverse effect on the acidification of water and soil environment as a result of ash being deposited on the ground surface. Such a risk was not noted for chlorides, whose concentrations in the material analyzed ranged from 63 to 439 $mg \, dm^{-3}$, while the acceptable level found by the legislation (Minister of the Environment, 2014) is 1000 $mg \, dm^{-3}$.

Received results may be compared with the study by Tsiridis et al. (2012), where leaching limit values for the analyzed elements in water extractions (with an L/S ratio of 10 $dm^3 \, kg^{-1}$) were: As 0.05, Cr 2.94, Cu 0.02, and Zn 0.35 $mg \, dm^{-3}$. These values are significantly higher than the results have obtained for fly ashes.

4.2.4. Bioavailable forms

Apart from having an adverse effect on water and soil structure, ashes also affect plants and organisms living in the soil. In order to quantify bioavailability, we have performed 0.11 M EDTA extraction (Lo and Yang, 1999). The fraction determined with this method demonstrated bioavailability, i.e. phytoavailability (Manouchehri et al., 2006), of metals and As (which is a metalloid) (Table 4). It was determined the following amounts of bioavailable elements (in $mg \cdot kg^{-1}$): As 0.7–0.9, Cd 0.1–0.2, Co 0.4–1.3, Cr 0.4–1.0, Cu

Table 3
Water leaching of element from ashes samples.

Parameter	Min	Max	AV	SD	Allowed highest value[a]
Cations [mg·dm⁻³]					
As	0.005	0.036	0.018	0.013	0.1
Cd	0.001	0.001	0.001	0.0003	0.2
Co	0.002	0.003	0.002	0.0004	1
Cr	0.001	0.009	0.005	0.003	0.1
Cu	0.007	0.014	0.009	0.003	0.5
Ni	0.005	0.009	0.007	0.002	0.5
Pb	0.004	0.009	0.006	0.002	0.5
Zn	0.016	0.024	0.019	0.004	2
Anions [mg·dm⁻³]					
SO_4^{2-}	8.29	1877.19	963.36	763.53	500 (66%)[b]
Cl^-	63.81	439.58	193.79	173.89	1000

[a] According to Minister of the Environment (2014).
[b] Percent of samples above permitted limit.

Table 4
Bioavailable parts of elements extracted by 0.11 M EDTA solution from ashes.

Element	Min	Max	AV	SD	% of TC[a]	Content [b] [mg·kg^{-1}]			
	[mg·kg^{-1}]				[%]	Plants			Animal
						Toxic level	Grass	Fodder plants for animals	Different land species
As	0.675	0.866	0.744	0.086	7.7	>5	0.23–0.33	<50	<1.5
Cd	0.097	0.256	0.162	0.068	29.7	–	0.05–0.6	<0.5	0.1–1.5
Co	0.362	1.332	0.992	0.446	5.7	15–50	0.03–0.12	0.05	<0.5
Cr	0.428	0.970	0.634	0.240	1.9	5–30	0.6–3.0	3000	0.02–1.5
Cu	1.450	23.269	15.005	9.662	19.9	–	4–10	5–8	1–20
Ni	1.060	2.630	2.051	0.704	5.5	10–100	0.4–1.7	50–300	1–3
Pb	3.243	8.220	5.933	2.052	15.9	30–300	0.4–4.5	<30	0.2–2.0
Zn	15.577	380.583	144.161	167.390	44.7	100–400	12–72	<200	10–200

[a] Calculated for average content, as percent of content extracted by *aqua regia*.
[b] According to Kabata-Pendias and Pendias (1999).

1.4–23.3, Ni 1.1–2.6, Pb 3.2–8.2, and Zn 15.6–380.6. For As, Co, Cr and Ni the phytoavailable forms constituted less than 10% of their quasi-total content. For Cu and Pb the fraction did not exceed 20% of the total content, while for Cd it was almost 30%. The highest amount, nearly 45% of the total extracted content, was Zn. A comparison of the results with maximum toxicity levels for plants (Kabata-Pendias and Pendias, 1999) has shown that the norms were not exceeded for any of the elements analyzed. They are, however, worryingly high once compared with As, Co, Ni, Pb limits for grasses and Co and Pb limits for terrestrial animals.

4.3. Environmental risk and health risk

4.3.1. RAC

Calculation of the Risk Assessment Code (RAC) was based on the classification proposed by Pan et al. (2013). Each of the 5 categories (no, low, medium, high and very high) was assigned a percentage range calculated on the basis of the ratio of readily soluble/exchangeable amount (in the present study it was the amount extracted with 0.11 M EDTA solution) to the total (quasi-total) content of a given element.

Using the proposed values, the following ranges (expressed in %) were established for the material studied: *No Risk* <1, *Low Risk* 1–10, *Medium Risk* 11–30, *High Risk* 31–50 and *Very High Risk* >50. Based on the data presented in Table 5, we have established the following risk levels: *Low Risk* for As, Co, Cr and Ni, *Medium Risk* for Cd, Cu and Pb and *High Risk* for Zn.

4.3.2. Health risk

Another environmental index related to the presence of fly ashes is Hazard Index *HI* for non-cancerogenic substances and *Risk* index for cancerogenic substances, calculated for children and adults in the region. Calculations were performed with regard to 3 exposure pathways: ingestion, dermal contact and inhalation (Table 6).

For children living in the region studied, the total hazard index *HI* for non-cancerogenic substances was 2.35E+00. *HI* > 1 points to

the risk of adverse health impact on children exposed to fly ashes. The highest *HI* values were observed for the ingestion route ($HQ_{ing} = 2.01E+00$). They were slightly lower for dermal contact ($HQ_{der} = 3.39E-01$), and the lowest for inhalation ($HQ_{inh} = 1.83E-03$). The contribution of elements to the total *HI* decreased in the following order: As > Cr > Pb > Cu > Ni > Co > Cd > Zn. The total *Risk* index calculated for exposure of children to cancerogenic forms was 4.88E-05 and it was at the verge of the recommended limit, i.e. 10E-05. The *Risk* values were associated primarily with cancerogenic forms of As (99%), and to a much lesser extent with Cr > Co > Ni > Cd.

As for adult inhabitants of the region, the total *HI* was 2.42E-01 for women and 2.89E-01 for men. The results were different from those obtained for children, as the dominant exposure pathway was dermal contact ($HQ_{der} = 1.24E-01$ for women, $HQ_{der} = 1.72E-01$ for men). The values for ingestion were only slightly lower ($HQ_{ing} = 1.17E-01$ for both sexes), and very low for inhalation ($HQ_{inh} = 5.45E-04$ as previously). The Risk index value was 6.85E-05 for women and 8.48E-05 for men. Similarly to the results obtained for children, it was associated primarily with cancerogenic forms of As (99%).

The differences between *HQ* and *Risk* indices are due to different skin area values assumed in the calculations. The author believe that this factor is of utmost importance since women generally work less in the field and usually pay more attention to hygiene and careful hand washing, especially before meals.

The results obtained may be biased towards another underestimation. In spring and summer, people working in the field often do not wash their hands before meals. If we had assumed a significantly higher dose (the so-called pica behavior of 10 g rather than 50 mg), the *HI* index for men and women would be 2.35E+01 and the *Risk* index values would be 5.32E-03 for women and 5.34E-03 for men. In such a case, the acceptable (safe) levels: *HI* < 1 and *Risk*<10E-05 would be exceeded for both indices.

5. Discussion

The problem of chemical substances leaching from waste and entering water and soil environment in the form of salt or elements is extremely important not only in the context of environmental quality, but also safety of crops on arable land (Wyrzykowska et al., 2009). Toxic substances (including heavy metals) from fly ashes scattered over agricultural areas are introduced directly into soils and subsequently into waters, and thus might not only be incorporated into the food chain (Baran and Antonkiewicz, 2017) but also pose a health risk for people who work in the field or spend time in the open air (Kicińska, 2018). For this reason, good knowledge of the physical and chemical properties of waste

Table 5
Risk assessment category and classification of risk assessment code (RAC) values as well as environmental risk of metals and metalloid leaching by EDTA extraction from fly ahs.

Category	RAC [%]	Risk	Fly ash
I	<1	No Risk	–
II	1–10	Low Risk	As, Co, Cr, Ni
III	11–30	Medium Risk	Cd, Cu, Pb
IV	31–50	High Risk	Zn
V	>50	Very High Risk	–

Table 6
Hazard quotient (*HQi*) and *Risk* calculated for children and adults.

Element	RfD [$mg \cdot kg^{-1}$ per day]			3 to < 6 years old children					adults				
	ing	inhal	dermal	HQ_{ing}	HQ_{inh}	HQ_{dermal}	$\sum HQ_i$	*Risk*	HQ_{ing}	HQ_{inh}	HQ_{dermal}	$\sum HQ_i$	*Risk*
As-non cancer	3.00E-04	3.00E-04	1.23E-04	1.01E-00	1.25E-05	2.54E-01	1.26E+00		5.87E-02	3.71E-06	9.31E-02[1] 1.29E-01[2]	1.52E-01 1.88E-01	
As-cancer	1.50E+00	1.50E+01	3.66E+00	3.89E-05	4.81E-09	9.81E-06		4.87E-05	2.64E-05	1.67E-08	4.19E-05 5.82E-05		6.83E-05 8.46E-05
Cd-non cancer	1.00E-03	1.00E-03	1.00E-05	1.48E-02	1.82E-07	5.08E-03	1.98E-02		8.58E-04	5.42E-08	1.86E-03 2.58E-03	2.72E-03 3.44E-03	
Cd-cancer		6.30E+00			9.84E-11			9.84E-11		3.42E-10			3.42E-10 3.42E-10
Co-non cancer	2.00E-02	5.71E-06	1.60E-02	3.01E-02	1.30E-03	1.29E-04	3.15E-02		1.75E-03	3.87E-04	4.74E-05 6.57E-05	2.18E-03 2.20E-03	
Co-cancer		9.80E+00			6.24E-09			6.24E-09		2.17E-08			2.17E-08 2.17E-08
Cr-non cancer	3.00E-03	2.86E-05	6.00E-05	3.95E-01	5.11E-04	6.79E-02	4.63E-01		2.29E-02	1.52E-04	2.49E-02 3.45E-02	4.80E-02 5.76E-02	
Cr-cancer		4.20E+01			5.27E-08			5.27E-08		1.83E-07			1.83E-07 1.83E-07
Cu	4.00E-02	4.00E-02	1.20E-02	7.01E-02	8.66E-07	8.04E-04	7.09E-02		4.07E-03	2.58E-07	2.95E-04 4.09E-04	4.37E-03 4.48E-03	
Ni-non cancer	2.00E-02	2.00E-02	5.40E-03	6.69E-02	8.27E-07	8.54E-04	6.78E-02		3.89E-03	2.46E-07	3.13E-04 4.34E-04	4.20E-03 4.33E-03	
Ni-cancer		8.40E-01			1.19E-09			1.19E-09		4.13E-09			4.13E-09 4.13E-09
Pb	3.50E-03	3.50E-03	5.25E-04	3.84E-01	4.74E-06	8.80E-03	3.92E-01		2.23E-02	1.41E-06	3.22E-03 4.47E-03	2.55E-02 2.68E-02	
Zn	3.00E-01	3.00E-01	6.00E-02	4.05E-03	5.01E-07	6.97E-04	4.12E-04		2.36E-03	1.49E-07	2.55E-04 3.54E-04	2.61E-03 2.71E-03	
HI				2.01E+00	1.83E-03	3.39E-01	2.35E+00	4.88E-05	1.17E-01	5.45E-04	1.24E-01 1.72E-01	2.41E-01 2.89E-01	6.85E-05 8.48E-05

Data: [1] for female, [2] for male.

materials, the leaching processes they undergo, and the related health risk (Pöykiö et al., 2016) is extremely important. From the environmental perspective, the mobility of pollutants expressed in the leaching potential of toxins released from ashes is the most important parameter of the material analyzed.

The analysis has shown that the dominant minerals in the ashes collected were silicates and aluminosilicates, such as: quartz, feldspar and plagioclase (albite). Clay minerals (kaolinite and mullite), carbonates (calcite), oxides/oxide-hydroxides of iron and sulfate minerals (gypsum and anhydrite) were also abundant. In their respective studies, Oliveira et al. (2017), Pöykiö et al. (2016) and Wójcik and Smołka-Danielowska (2008) have also found that the dominant minerals in the bottom and fly ashes analyzed were quartz, feldspar (microcline) and albite. Wójcik and Smołka-Danielowska (2008) emphasize that aluminosilicates with variable content of Na, K, Ca and Fe were most abundant. Their forms were usually pointed or spherical and the particle size generally did not exceed 100 μm. Szponder and Trybalski (2009) have also concluded that silicates, such as quartz and mullite were the dominant constituents of fly ashes investigated in their study. The authors have emphasized that ashes gain fire-resistant properties due to the high content of mullite and may therefore be used in ceramics and construction. The authors believe that the presence of calcium and magnesium carbonates in ashes increases their binding potential, while substances such as hematite increase the value of ashes for potential industrial use. They can be used to produce clinker bricks, cement and construction ceramics. Wójcik and Smołka-Danielowska (2008) have also noticed an abundance of Fe oxides in the ashes studied, including hematite in a crystalline and amorphous form. In the case of crystalline forms, the Fe oxide particles are usually pointed, oval or spherical in shape (microspheres). In the amorphous form, particle surfaces are usually smooth, and their size is between 10 and 20 μm. They often form aggregates.

The phase composition determined suggests that the material is extremely mixed and diverse. Low-temperature components (such as calcite) were mixed with substances formed in high temperatures (such as mullite). Moreover, the entire material underwent the process of weathering, during which some of the mineral forms were hydrated and transformed. The variable composition of waste from different home furnaces with high content of the amorphous phase (which dissolves in water more easily than its crystalline equivalents) may be harmful to the environment.

The SEM images have confirmed that ashes are extremely fragmented, composed of smooth spherical particles (of the cenosphere and plerosphere type) and fine-particle aggregates. The average particle size was estimated at 40–60 μm. The particles were made of silicon, aluminum and oxygen, and the dominant mineral phases were quartz, mullite and glass. Particles of irregular shapes contained Ca, Mg, Al, K, Fe and Ti compounds. Similar observations were made by Oliveira et al. (2017) and Szponder and Trybalski (2009) for fly ash samples collected from power plants producing energy based on conventional coal combustion. The ashes contained also amorphous forms, the content of which may reach even 65%, according to Wang et al. (2017) and Wójcik and Smołka-Danielowska (2008). This has an effect on the solubility of components since the crystalline phases of e.g. silicon dioxide are hardly soluble in contrast to the amorphous ones. The size of ash particles determined in the analysis was 10–300 μm for oval grains. This corroborates the results obtained by Szponder and Trybalski (2009). In their study, the size range was 0–420 μm, with the majority (99%) of particles being smaller than 340 μm and 80% smaller than 150 μm.

Total contents of trace elements determined with *aqua-regia* extraction are comparable to the data presented by Pöykiö et al. (2016), especially for As, Cd, Cr and Ni, and by Reinik et al. (2013) for Cd, Cr and Ni (Table 7). Much higher concentrations of As, Cd, Cr, Cu, Pb and Zn in ashes were found by Kröppl and Lanzerstorfer

Table 7
Total concentration of elements in ashes measured by different authors.

Authors	Methods of extraction	As	Cd	Co	Cr	Cu	Ni	Pb	Zn
		[mg·kg^{-1}]							
Pöykiö et al. (2016) [a]	HNO$_3$+HCl (3:1)	7.6–13.0	0.5–2.9	3.2–6.6	33.2–66.9	21.1–63.6	12.0–32.4	4.9–28.7	401.0–295.3
Reinik et al. (2013) [b]	HNO$_3$	–	0.05–0.9	3.0–5.8	17–59	7.8–36	17–33	15–142	38–143
Yanda et al. (2015) [c]	HNO$_3$+HClO$_4$ (3:1)	–	2.9–7.9	–	–	94.6–206.7	49.7–87.0	–	590.1–2622.0
Kajda-Szcześniak (2014) [d]	–	3.5	2.65	–	–	–	6.7	1181	12406
Kajda-Szcześniak (2015) [e]	XRF	1.91–8.50	1.16–3.60	–	47.9–88.0	79.0–176.0	10.0–38.0	47.0–207.0	498.0–1738.0
Kröppl and Lanzerstorfer (2013) [f]	HNO$_3$+HCl (1:3)	20.3–39.8	0.24–55.7	–	40.2–75.0	92.7–221	15.6–34.3	<15–368	254–11200
this study [g] (min. – max.)	HNO$_3$+HCl (1:3)	3.49–12.32	0.15–1.25	6.35–25.3	12.04–55.55	15.87–117.84	19.01–47.89	12.36–58.59	41.58–812.12

"–" no data.
[a] Bottom and fly ash (respectively).
[b] Pulverized firing ashes (collected in 2004).
[c] Waste ashes.
[d] Ashes from fireplace.
[e] Ashes from combustion of wood derived boards.
[f] Fly ashes (coarse, cyclone and EP) of the biomass incinerator.
[g] Fly ashes.

(2013) and Takaoka et al. (2005). For Co, Cu and Zn, the values determined in the present study were higher than the results presented by Reinik et al. (2013) However, one should take into account the fact that the respective authors used different reagents and the results obtained may be biased towards certain underestimations.

Due to different combustion methods used, different fuel composition and different dynamics of thermal processes, the ashes studied exhibit high variability in terms of morphology as well as phase and chemical composition. This diversity is crucial in the search for possible ways of utilizing fly ash in different sectors of the economy (Gorazda et al., 2017).

6. Conclusion

The analysis has shown that:

1. The dominant minerals in the ashes collected were silicates and aluminosilicates, such as: quartz, feldspar and plagioclase (albite). Clay minerals (kaolinite and mullite), carbonates (calcite), oxides/oxide-hydroxides of iron and sulfate minerals (gypsum and anhydrite) were also abundant.
2. The phase composition determined suggests that the material is extremely mixed and diverse. Low-temperature components (such as calcite) were mixed with substances formed in high temperatures (such as mullite).
3. The ashes were composed of Si, Al, Ca and Fe oxides, which together accounted for 85.55% of the total content. S, Mg, Na, K and Ti oxides constituted 12.6% of the total content. The amount of the remaining elements detected with this method did not exceed 2 wt%.
4. With respect to water extracts of fly ashes, high concentrations of salts, mainly composed of sulfates (mean 963 mg/dm^3), may have an adverse effect on the soil and water environment as they are easily leached. In time, high content of Ca oxides (mean 13.5%) may trigger pozzolanic reactions related to the formation of weathering-resilient structures composed of hydrated calcium silicates.
5. Phytoavailable content accounted for: <10% for As, Co, Cr and Ni, <20% for Cu and Pb, <30% for Cd, and almost 45% for Zn. The values did not exceed the specified toxicity levels for plants. The waste material tested may pose a threat to plants as well as to the entire trophic chain.
6. The established risk assessment code (RAC) was: *Low Risk* for As, Co, Cr, Ni, *Medium Risk* for Cd, Cu and Pb, and *High Risk* for Zn. In

the study by Pöykiö et al. (2016), the RAC for bottom and fly ashes was: *Low Risk* for Co, Cr, Ni and Cu, *Medium Risk* for Zn and *High Risk* for As and Cd.
7. For children living in the region studied, the total hazard index *HI* for non-cancerogenic substances was 2.35E+00. The value *HI* > 1 points to the risk of adverse health impact on children exposed to fly ashes. The total *Risk* index for children was 4.88E-05, which is at the verge of the limit value, i.e. 10E-05.
8. For adults, the total *HI* was 2.42E-01 for women and 2.89E-01 for men. The *Risk* index value was 6.85E-05 for women and 8.48E-05 for men.

References

Antonkiewicz, J., Kolodziej, B., Bielinska, E., 2017. Phytoextraction of heavy metals from municipal sewage sludge by Rosa multiflora and Sida hermaphrodita. Int. J. Phytoremediation 19 (4), 309–318. https://doi.org/10.1080/15226514.2016.1225283.

Baran, A., Antonkiewicz, J., 2017. Phytotoxicity and extractability of heavy metals form industrial wastes. Environ. Protect. Eng. 43 (2), 143–155. https://doi.org/10.5277/epe170212.

Czop, M., Kajda-Szcześniak, M., 2013. Environment impact of straw based fuel combustion. Arch. Environ. Protect. 39 (4), 71–80.

De Miguel, E., Iribarren, I., Chacon, E., Ordonez, A., Charlesworth, S., 2007. Risk-based evaluation of the exposure of children to trace elements in playgrounds in Madrid (Spain). Chemosphere 66, 505–513. https://doi.org/10.1016/j.chemosphere.2006.05.065.

Gorazda, K., Tarko, B., Wzorek, Z., Kominko, H., Nowak, A.K., Kulczycka, J., Henclik, A., Smol, M., 2017. Fertilisers production from ashes after sewage sludge combustion–strategy towards sustainable development. Environ. Res. https://doi.org/10.1016/j.envres.2017.06.008.

Hansen, H.K., Pedersen, A.J., Ottonsen, L.M., Villumsen, A., 2001. Speciation and mobility of cadmium in straw and wood combustion fly ash. Chemosphere 45, 123–128.

Izquierdo, M., De Miguel, E., Ortega, M.F., Mingot, J., 2015. Bioaccessibility of metals and human health risk assessmentin community urban gardens. Chemosphere 135, 312–318. https://doi.org/10.1016/j.chemosphere.2015.04.079.

Kabata-Pendias, A., Pendias, H., 1999. Biogeochemistry of Trace Elements. PWN.

Kajda-Szcześniak, M., 2014. Characteristic of ashes from fireplace. Arch. Waste Manag. Environ. Protect. 16 (3), 73–78.

Kajda-Szcześniak, M., 2015. Multielemental analysis of selected ashes from combustion of wood derived boards. Arch. Waste Manage. Environ. Protect. 17 (1), 105–110.

Karczewska, A., Gałka, B., Kocan, K., 2009. A carryover effect of the chelating agents EDTA and EDDS applied to soils on the uptake of copper and iron by maize in the second year of a pot experiment. J. Elementology 14 (4), 693–703.

Kicińska, A., 2016. Health risk to children exposed to Zn, Pb, and Fe in selected

urban parks of the Silesian agglomeration. Hum. Ecol. Risk Assess. 22 (8), 1687–1695. https://doi.org/10.1080/10807039.2016.1218271.

Kicińska, A., 2018. Health risk assessment related to an effect of sample size fractions: methodological remarks. Stoch. Environ. Res. Risk Assess. 32, 1867–1887. https://doi.org/10.1007/s00477-017-1496-7.

Kicińska, A., Mamak, M., 2017. Health risks associated with municipal waste combustion on the example of Laskowa commune (southern Poland). Hum. Ecol. Risk Assess. 23 (8), 2087–2096. https://doi.org/10.1080/10807039.2071.1364131.

Kicińska, A., Mamak, M., Skrzypek, M., 2017. Heavy metals in sands of sandboxes: health risk associated with their quantities and form of occurrence in some spas of Poland. Environ. Sci. Pollut. Control Ser. 24 (24), 19733–19748. https://doi.org/10.1007/s11356-017-9531-2.

Klojzy-Karczmarczyk, B., Staszczak, J., 2017. Estimation of the mass of Energy fractions in municipal waste produced in areas of different developmental character. Energy Policy J. 20 (2), 143–154.

Kröppl, M., Lanzerstorfer, C., 2013. Acidic extraction and precipitation of heavy metals from biomass incinerator cyclone fly ash. In: E3S Web of Conferences, 1, p. 16007. https://doi.org/10.1051/e3sconf/20130116007.

Lo, I.M.C., Yang, X.Y., 1999. EDTA extraction of heavy metals from different soil fractions and synthetic soils. Water Air Soil Pollut. 109, 219. https://doi.org/10.1023/A:1005000520321.

Manouchehri, N., Besancon, S., Bermond, A., 2006. Major and trace metal extraction from soil by EDTA: equilibrium and kinetic studies. Anal. Chim. Acta 559 (1), 105–112. https://doi.org/10.1016/j.aca.2005.11.050.

Matsui, M., Kashima, Y., Kawano, M., Matsuda, M., Ambe, K., Wakimoto, T., Doi, R., 2003. Dioxin-like potencies and extractable organohalogens (EOX) in medical, municipal and domestic waste incinerator ashes in Japan (2003). Chemosphere 53, 971–980.

Minister of the Environment, 2014. Regulation on the Conditions to Be Met for the Introduction of Sewage into Waters or to Land and on Substances Particularly Harmful to the Aquatic Environment. Dz. U. 2014, poz. 1800.

Minister of the Environment, 2016. Regulation on the Method of Conducting the Assessment of Surface Pollution. Dz. U. 2016, poz. 1395.

Oliveira, M.L.S., Navarro, O.G., Crissien, T.J., Tutikian, B.F., da Boit, K., Teixeira, E.C., Cabello, J.J., Agudelo-Castañeda, D.M., Silva, L.F.O., 2017. Coal emissions adverse human health effects associated with ultrafine/nano-particles role and resultant engineering controls. Environ. Res. 158, 450–455. https://doi.org/10.1016/j.envres.2017.07.002.

Pan, Y., Wu, Z.M., Zhou, J.Z., Zhao, J., Ruan, X.X., Liu, J.Y., Qian, G.R., 2013. Chemical characteristics and risk assessment of typical municipal solid waste incineration (MSWI) fly ash in China. J. Hazard Mater. 261, 269–276.

Pöykiö, R., Mäkelä, M., Watkins, G., Nurmesniemi, H., Dahl, O., 2016. Heavy metals leaching in bottom ash and fly ash fractions from industrial-scale BFB-boiler for environmental risks assessment. Trans. Nonferrous Metals Soc. China 26, 256–264. https://doi.org/10.1016/S1003-6326(16)64112–2.

Reinik, J., Irha, N., Steinnes, E., Urb, G., Jefimova, J., Piirisalu, E., Loosaar, J., 2013. Changes in trace element contents in ashes of oil shale fueled PF and CFB boilers during operation. Fuel Process. Technol. 115, 174–181. https://doi.org/10.1016/j.fuproc.2013.06.001.

Szponder, D., Trybalski, K., 2009. Determination of the properties of fly ash by using various research methods and devices. Kwartalnik Górnictwo i Geoinżynieria 33 (4), 287–298 [In Polish].

Takaoka, M., Yamamoto, T., Shiono, A., Takeda, N., Oshita, K., Matsumoto, T., Tanaka, T., 2005. The effect of copper speciation on the formation of chlorinated aromatics on real municipal solid waste incinerator fly ash (2005). Chemosphere 59, 1497–1505.

The Act on Environmental Protection Law of April 27, 2001. J. Laws Poland item 627.

Tsiridis, V., Petala, M., Samaras, P., Kungolos, A., Sakellaropoulos, G.P., 2012. Environmental hazard assessment of coal fly ashes using leaching and ecotoxicity test. Ecotoxicol. Environ. Saf. 84, 212–220. https://doi.org/10.1016/j.ecoenv.2012.07.011.

US EPA, 1986. Guidelines for Human Health Risk Assessment of Chemical Mixtures. Federal Register (51 FR 34014-34025), Washington.

US EPA, 1996. Soil Screening Guidance: Technical Background Document. EPA/540/R-95/128. Office of Solid Waste and Emergency Response. US Environmental Protection Agency, Washington. http://www.epa.gov/superfund/resources/soil/toc.htm#p1.

US EPA, 1997. EPA/600/P-95/002Fa. Exposure Factors Handbook – General Factors, vol. I. Office of Research and Development. National Center for Environmental Assessment. US Environmental Protection Agency, Washington. http://www.epa.gov/ncea/pdfs/efh/front.pdf.

US EPA, 2005. Integrated Risk Information System (IRIS). http://www.epa.gov/iris.

US EPA, 2011. Exposure Factors Handbook: 2011 Edition (EPA/600/R-09/052F). https://cfpub.epa.gov/ncea/risk/recordisplay.cfm?deid=236252.

Wang, T., Xue, Y., Zhou, M., Yuan, Y., Zhao, S., Tan, G., Zhou, X., Geng, J., Wu, S., Hou, H., 2017. Comparative study on the mobility and speciation of heavy metals in ashes from co-combustion of sewage sludge/dredged sludge and rice husk. Chemosphere 169, 162e170. https://doi.org/10.1016/j.chemosphere.2016.11.070.

Wang, J., Wang, T., Mallhi, H., Liu, Y., Ban, H., Ladwig, K., 2007. The role of ammonia on mercury leaching from coal fly ash. Chemosphere 69, 1586–1592. https://doi.org/10.1016/j.chemosphere.2007.05.053.

Waste Catalogue, 2014. Regulation of the minister of the environment on the catalogue of waste of december 9, 2014. J. Laws Poland item 1923.

Wójcik, M., Smołka-Danielowska, D., 2008. Phase minerals composition of wastes formed in bituminous coal combustion from individual domestic furnace in the Piekary Śląskie town (Poland), polish. J. Environ. Stud. 17 (5), 817–821.

World Health Organization. Water, Sanitation and Health Team, 2004. Guidelines for drinking-water quality. Recommendations, , 3rd ed.vol. 1. World Health Organization, Geneva http://www.who.int/iris/handle/10665/42852.

Wyrzykowska, B., Hanari, N., Orlikowska, A., Yamashita, N., Falandysz, J., 2009. Dioxin-like compound compositional profiles of furnace bottom ashes from household combustion in Poland and their possible associations with contamination status of agricultural soil and pine needles. Chemosphere 76, 255–263. https://doi.org/10.1016/j.chemosphere.2009.03.019.

Yanda, S.E., Tsado, M.J., Ndarubu, T.A., Chukwuma, M.R., 2015. Concentration of heavy metals in waste ashes from five sections of a major incineration ground at maikunkele, minna, Niger state, Nigeria. Sci. J. Anal. Chem. 3 (4), 39–42.