Arsenic, cadmium, lead and thallium in coal ash from individual household furnaces

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Abstract
52 coal ash samples from individual households were analyzed to determine the pH and the concentrations of four toxic elements: arsenic, cadmium, lead and thallium. The method used was atomic absorption spectrometry with graphite-furnace atomization. The ash samples originated from various coal grades and statistical analysis showed existing correlations between the concentrations of studied elements, pH and the coal grades. The maximum concentrations of arsenic, cadmium, lead and thallium were 50,900, 43,500, 128,900, and 6660 µg/kg, respectively. The results were compared with the published data for the ash of industrial origin.

Keywords Coal ash · Atomic absorption spectrometry · Arsenic · Lead · Cadmium · Thallium

Introduction
Hard coal has been widely used as a heat source in Poland as well as worldwide. Despite the fact that in recent years more attention has been given to renewable energy sources, demand for hard coal still remains remarkable, despite certain environment-related drawbacks [1]. The hard coal consumption in 2018 in Poland was 74.2 million tons in total, and 13.5% of this amount (which is 10.0 million tons) was consumed by individual households [2]. In comparison, in the European Union, the hard coal consumption in 2018 reached 226 million tons (and 370 million tons of brown coal) [3]. There is a wide variety of coal present on the market in Poland. It comes mostly from domestic mining but the imported one is also available. The calorific value, which is considered the most important parameter for household use, strongly depends on the coal composition (mainly on the ash, sulphur and moisture content). The more expensive coal types have higher calorific values and lower ash content. Also, thicker coal grades are usually more favourable due to the easier handling (especially, for furnaces with manual loading), but they are also more expensive than the thinner grades. As a result, a wide variety of coal is being used by individual users.

The amount of residual ash in coal depends on many factors (e.g. type and quality of the coal, burning conditions, etc.) and in high-ash coal can exceed 50% [4]. According to recent regulations in Polish law, most of the coal grades being sold in Poland must not exceed the ash content of 12% (with few exceptions) [5].

For industrial purposes, usually large coal-burning boilers equipped with pulverizers are being used and the coal used as a fuel is finely ground to optimize the burning rate and heat production efficiency [6]. The amount of coal combustion products from the industry have been used as an auxiliary material, e.g. in road construction or concrete production [6, 7]. For heating purposes in individual households, however, a much thicker grade of coal is usually used and the resulting ash has virtually no application due to a lower amount being produced and potentially high costs of its collection.
According to Polish law, coal ash produced in individual households is a municipal waste and no special procedure for its disposal exists (hence, it should be disposed of together with other municipal waste) [8]. However, it can be observed, that coal ash is being disposed of illegally in the fields, on the local countryside roads as well as in the roadside ditches. Due to the very limited data, the range of toxic metals content in this material is not well known, as opposed to the industrial-origin coal ash, which is a well-recognized material and it is stored in the dedicated landfills. Combined with inappropriate storage, toxic metals contained in the ash could possibly have a hazardous impact on the environment, although in this study we focus on the ash only and no leaching behavior was studied.

There are no specific rules for toxic metals content in the municipal waste and thus they are not controlled from this point of view as it is assumed that under normal circumstances, no toxic metals should be found in this type of material. In our research, we focused on the elements generally considered toxic ones. Among them, several have been extensively studied for the past decades as the elements of the environmental concern, including arsenic, lead, mercury and cadmium [9]. For our study, we chose the elements for which we had proper analytical tools (graphite-furnace atomic absorption spectrometry). Thus, the choice of arsenic, cadmium and lead. Thallium was also included as it has not been studied as often as the other elements and thus could make a valuable contribution.

In environment-related publishing, much more attention has been given to the coal ash originating from the industry rather than the one from individual households. Thus, the goal of the present study was to evaluate the content of four toxic elements (namely: arsenic, cadmium, lead and thallium) in the coal ash from individual households and to compare the results with the available literature data. Statistical analysis was employed to evaluate the possible correlation structure of the results which could help in further characterization of the household-origin coal ash. By organizing and testing the results statistically, we aimed at the further characterization of the coal ash of the household origin based on the obtained data, particularly to see if the factors such as coal grade have any influence on the trace levels of toxic metals. For complete coal characterization, also major components (e.g. Al, Si) should have been studied, but we decided to focus on the toxic elements as their environmental impact is predominant.

### Materials and methods

#### Samples collection and pretreatment

The samples were collected between January and April 2018 from individual households which were using coal-powered furnaces for heating purposes. The ash samples in this study consisted of waste material resulting from coal burning and they were collected from the furnace bottom. They contained coarse and fine particles as well as some slag. As this is the material which is considered the ash from the individual household, it was not further refined or separated, despite containing multiple fractions (as opposite to, e.g. fly ash from the industry, which is usually sourced from electrostatic precipitators and is much more homogenous material). Altogether 52 ash samples were collected, each one with the information about the size grade of the coal corresponding to the ash. Four grades of the coal were encountered at the furnace owners: lump coal (grade 1, approx. 120–200 mm in diameter); nut coal (grade 2, approx. 25–80 mm in diameter); pea coal (grade 3, approx. 8–30 mm in diameter) and culm (grade 4, below 6 mm in diameter). Prior to the analysis, the ash samples were ground and dried (105 °C, 3 h).

#### Chemicals and glassware

All chemicals were of ultrapure grade. Ultrapure water (< 0.055 µS/cm, purification system by Polwater, Poland) was used for all the operations. For wet digestion, quartz beakers with quartz watch glasses were used, while the dilutions were made in PMP (polymethylpentene) volumetric flasks.

#### pH measurements

The pH of water-soluble fraction was measured as follows: 5 g of the ash sample was mixed with 25 g of water and the mixture was shaken for 1 h. The suspension was left for 15 min and the supernatant was separated and filtered through the syringe filter (0.7 µm). The pH of the obtained solution was measured with a pH meter (Elmetron CP-551, Poland).

#### Wet digestion

For the determination of the four selected elements, wet digestion of the samples was performed. Approx. 3 g of each of the ash sample was placed in the beaker and 25 mL of nitric acid (1 + 1) was poured in. The mixture, covered with a watch glass, was heated just below the boiling point for approx. 15 min. Next, 5 mL of nitric acid (1 + 1) was poured in and the heating continued for another 30 min. At this point, the majority of the samples ceased to release red fumes which indicated the end of the process. For several samples, however, additional amounts of nitric acid and more heating time were required to complete the process. At this point, the watch glass was removed and the mixture was evaporated to a small volume (< 10 mL), diluted with water, filtered through filter papers (Whatman 54) directly...
to the volumetric flasks and filled to the mark. As we did not encounter any problems during the process, there was one digestion per sample (i.e. no replications).

**Measurements**

The concentrations of studied elements in the digested samples were determined using Agilent 240Z AA atomic absorption spectrometer with graphite-furnace atomizer and Zeeman background correction. Each measurement was executed in 4 replicates. High-purity argon was used as an inert gas. Working standards for calibration were prepared from stock solutions containing 1000 mg·L⁻¹ of each individual element (by Agilent).

**Quality assurance**

Together with the ash samples, two samples of the Certified Reference Material (CRM) were subjected to wet digestion (and further analysis) to provide quality assurance. Due to the lack of the coal-ash CRM, the material chosen was SS1 Contaminated Soil (SPC Science, Canada) since its matrix is reasonably comparable to the ash samples (complex and inorganic). Also, two blank samples were included in the analysis, to calculate the limit of detection (LOD) and limit of quantification (LOQ). Since the SS1 CRM does not provide certified value for thallium, another CRM was used (ESH3 Contaminated Water) to confirm the accuracy of thallium measurements. One of the risks during the process was losing the volatile elements (in our case mainly arsenic, which can be partly lost when the mixture is overheated). Using CRM, even if it differs in composition to a certain extent, gives us information, whether the applied procedure did not cause any losses.

The quality assurance results are presented in Table 1.

**Statistical approach**

Descriptive statistics were calculated for all parameters. For the means coming from non-Gaussian populations, data were transformed in logarithms and retransformed after calculations. The normality of the distribution of parameters was checked by Kolmogorov–Smirnov and Lilliefors tests. Between-group comparisons were performed using Kruskal–Wallis test with Dunn post hoc test. Differences with \( p < 0.05 \) were considered to be statistically significant.

Principal component analysis (PCA) was applied to reveal the correlation structure between the parameters investigated and to find possible similarities between the samples. Before the use of this method, the variables were standardized. PCA model evaluation was performed with the criterion that the percentage of original variation of the predictor parameters explained by the model should exceed 50%, and the corresponding eigenvalues should be higher than 1. The parameters with large weights (absolute values > 0.3) in the PCA model were assumed to be correlated with one another. For the pairs of correlated parameters, obtained through PCA approach, the associations between them were quantified by calculating the correlation weights; i.e. for the pairs of considered parameters, the algebraic products of their coordinates and the cosines of the corresponding angles were calculated. The “corresponding angle” was determined by using the two lines connecting the origin of the coordinate system with the points representing both parameters on the PCA plot. Statistical analyses were performed using the following packages: Statistica v.12 (Statsoft, Tulsa, Oklahoma, USA; descriptive statistics, Kolmogorov–Smirnov and Lilliefors tests, PCA diagrams), GraphPad InStat v.3.05 (GraphPad Software Inc., San Diego, California, USA; Kruskal–Wallis test, Dunn test) and SIMCA-P v.9 (Umetrics, Umeå, Sweden; PCA analysis). The correlation weights were calculated using software delivered by MP System Co. (Chrzanów, Poland).

**Results and discussion**

Based on the results presented in Table 1, it was confirmed, that the method applied provided analytical data of high accuracy. Very good recoveries were obtained for all the
elements while limits of quantifications were much lower than any of the results.

The experimental results for arsenic, cadmium, lead and thallium concentrations in ash samples are presented in Table 2 together with the grade of the coal and pH of the ashes. Concentrations are stated with expanded uncertainties (k = 2).

As presented in Table 2, the pH of all samples was above 9 (what is rather typical for coal ash) and for 26 samples (50% of the total number) it was in the range of 12–13. The lowest pH (9.22) was found for sample 01 while the highest (13.24) for sample 27. Presented results are in line with existing literature data [10–13], though ashes with pH below 7 also exist [14].

For all studied elements, there was a large scatter of results except for arsenic, for which IQR/median ratio was below 1. For other elements this factor was above 1, being particularly high for Pb (1.43) and for Cd (1.86), and moderate for Tl (1.09). Arsenic and lead were found in relatively high concentrations (mean: 12 128 µg/kg and 27 912 µg/kg, respectively) while cadmium and thallium were less abundant (mean: 358.7 µg/kg and 592.1 µg/kg, respectively). There was no correlation between IQR/median ratios and mean values of the above-mentioned elements.

Table 3 presents a comparison of our results with the literature data, mostly focused on the ash of industrial origin. Either range of concentrations (if available) or mean concentrations of the studied elements are presented.

The results found in available literature, related to the ash of industrial origin (presented in Table 3), are scattered within a broad range and thus our results lie within respective ranges. However, some authors reported very high concentrations of lead (close to, or exceeding 1 g/kg) and arsenic (over 5 g/kg) and the results of our study are at least one order of magnitude lower than those maximum values. Levels of cadmium from our study are comparable with those found in industrial ashes, while thallium in household-produced ashes is clearly less abundant. Apparently, in all types of industrial ashes, arsenic and lead are the most abundant elements with cadmium and thallium being present in much lower concentrations. The number of results of other authors related to household-originating ashes is very limited, but still our results are comparable with those mentioned in Table 4 [15]. The study of the phase composition of the ash from individual domestic furnaces showed its multi-phase composition and a high amount of amorphous phase, which is hazardous to the environment due to its water-solubility [16]. In the present study, there was no leaching/elution investigation so we cannot directly state that the toxic elements can be eluted when in contact with water. The before-mentioned literature data, however, give a certain premise to that, which means that illegal disposal of the ash can pose a certain challenge for the environment.

We found certain statistically significant differences between parameters of ashes originating from different grades of coal and they are presented in Table 5. Namely, grade 1 differed from grade 3 in respect to pH, which was significantly higher for the latter group. Arsenic concentration discriminated between grade 1 and two other grades—grade 2 and grade 4, being significantly higher for the first grade. Cadmium concentration was lower for grade 4 as compared with grade 2. Similarly, lead concentration was lower for the same grade as compared with grade 1. Low number of samples of grade 4 presumably precluded to show other significant differences between this grade and others studied.

The reasons for the differences revealed above are not clear, though. The burning conditions certainly can be altered by the grade of coal, which may result in different ash composition. Higher coal grades (smaller pieces) are more likely to be burnt completely which can facilitate the evaporation of the volatile elements compared to the lower coal grade (thicker pieces). If it proved to be a true effect it would allow predictions on the toxic elements levels/ratios depending on the coal grade. Still, the composition of the coal seems to be the predominant factor affecting the ash composition. Ash samples analysed in this study originated from coal mined from various geological locations; thus, the coal composition could vary significantly and the coal-grade dependence should be considered a careful hypothesis only.

The content of the studied metals in the ash depends mostly on their initial concentration in the coal and the incineration conditions. However, it might also be dependent on the composition of the coal matrix, as its certain components might enhance or suppress the formation of volatile compounds during incineration, which alters the concentration of the toxic metals in the ash. On the other hand, as pH reflects the ash composition only to some degree (being not very sensitive parameter to composition changes in this case), and the link to the coal composition is even weaker, we are careful with drawing strong conclusions from these results.

To study pH-dependent differences among metal concentrations, the set of samples was divided into quartiles, according to the pH values. We found a statistically significant difference between the first pH quartile (pH below 11.22) and the third pH quartile (pH above 12.91) for lead concentration (median values of lead concentration for these quartiles: 77 606 µg/kg vs 26 895 µg/kg, respectively). Thus, the higher pH values were associated with lower concentrations of lead in the ash which might indicate, that at higher pH the formation of more volatile lead compounds and/or formation of higher amounts of such compounds, is preferable. The comparison of the pH of the supernatants and the lead content in the digested samples is difficult, as there are many other factors to include
Table 2 The experimental results for all ash samples ($U_{exp}$—expanded uncertainties; for all parameters which had non-Gaussian distribution, the means ± SD are based on the log-transformed data; IQR—inter quartile range)

| Sample code | Coal grade | pH | As [ug/kg] | $U_{exp}$ | Cd [ug/kg] | $U_{exp}$ | Pb [ug/kg] | $U_{exp}$ | Tl [ug/kg] | $U_{exp}$ |
|-------------|------------|----|------------|----------|-----------|----------|-----------|----------|-----------|----------|
| 01          | 1          | 9.22 | 14 384 | 978 | 417.9 | 7.7 | 92 380 | 2 446 | 432 | 13 |
| 02          | 1          | 11.20 | 15 447 | 2 182 | 39.9 | 2.2 | 14 667 | 1 534 | 183 | 2 |
| 03          | 1          | 11.11 | 30 187 | 868 | 1 264 | 76 | 119 838 | 4 958 | 6 557 | 669 |
| 04          | 1          | 10.49 | 13 421 | 105 | 1 893 | 139 | 128 907 | 1 920 | 2 331 | 69 |
| 05          | 1          | 12.14 | 31 711 | 1 327 | 246 | 30 | 39 534 | 1 701 | 2 865 | 142 |
| 06          | 1          | 12.89 | 7 536 | 710 | 778 | 20 | 14 652 | 242 | 466 | 46 |
| 07          | 1          | 12.95 | 16 894 | 619 | 373 | 20 | 37 854 | 2 318 | 464 | 18 |
| 08          | 1          | 12.98 | 19 688 | 1 030 | 181.1 | 7.1 | 25 541 | 1 141 | 335 | 34 |
| 09          | 1          | 10.31 | 11 560 | 1 391 | 80.9 | 4.7 | 23 448 | 504 | 580 | 18 |
| 10         | 1          | 10.31 | 18 964 | 1 091 | 75.4 | 3.4 | 24 032 | 437 | 507 | 1 |
| 11         | 1          | 12.39 | 15 352 | 602 | 7 739 | 243 | 57 192 | 1 609 | 1 345 | 42 |
| 12         | 1          | 12.80 | 25 597 | 469 | 1 262 | 76 | 52 802 | 6 117 | 655 | 27 |
| 13         | 1          | 9.98 | 25 956 | 679 | 357.5 | 8.4 | 66 617 | 3 197 | 1 618 | 127 |
| 14         | 1          | 12.39 | 19 076 | 2 295 | 139.8 | 4.8 | 21 913 | 1 705 | 865 | 36 |
| 15         | 1          | 10.88 | 24 919 | 782 | 1571 | 12 | 79 993 | 1 589 | 1 851 | 15 |
| 16         | 1          | 12.90 | 2 230 | 268 | 55.5 | 3.0 | 13 895 | 667 | 155 | 21 |
| 17         | 1          | 11.33 | 31 466 | 1 234 | 826 | 43 | 90 791 | 2 554 | 5 555 | 218 |
| 18         | 1          | 12.31 | 9 299 | 735 | 163.5 | 9.4 | 21 972 | 582 | 420 | 27 |
| 19         | 1          | 12.85 | 5 470 | 515 | 637.2 | 8.3 | 8 461 | 310 | 734 | 27 |
| 20         | 1          | 10.11 | 25 465 | 1 399 | 302 | 34 | 71 571 | 711 | 1 414 | 85 |

Mean ± SD for grade 1

| Sample code | Coal grade | pH | As [ug/kg] | $U_{exp}$ | Cd [ug/kg] | $U_{exp}$ | Pb [ug/kg] | $U_{exp}$ | Tl [ug/kg] | $U_{exp}$ |
|-------------|------------|----|------------|----------|-----------|----------|-----------|----------|-----------|----------|
| Mean ± SD   |            | 11.58 ± 1.22 | 18 231 ± 8 668 | 377.7 (98.7; 1446.1)* | 50 303 ± 36 705 | 870.7 (312.1; 2429)* |

21          | 2          | 11.50 | 9 335 | 461 | 1 051 | 47 | 41 665 | 1 724 | 782 | 67 |
| 22          | 2          | 11.70 | 7 865 | 1 214 | 1 284 | 20 | 18 303 | 303 | 905 | 28 |
| 23          | 2          | 12.93 | 4 476 | 663 | 56.0 | 3.8 | 12 634 | 899 | 231 | 25 |
| 24          | 2          | 11.79 | 13 842 | 1 738 | 319.0 | 9.2 | 55 336 | 2 106 | 1 057 | 55 |
| 25          | 2          | 11.49 | 5 105 | 801 | 239.5 | 6.3 | 42 400 | 1 193 | 748 | 16 |
| 26          | 2          | 12.62 | 4 722 | 469 | 566.3 | 7.4 | 19 740 | 947 | 312 | 49 |
| 27          | 2          | 13.24 | 9 967 | 1 173 | 563 | 65 | 22 198 | 588 | 490 | 60 |
| 28          | 2          | 10.55 | 10 254 | 724 | 43 482 | 4 094 | 77 606 | 1 541 | 864 | 34 |
| 29          | 2          | 12.81 | 4 943 | 517 | 368 | 11 | 10 248 | 724 | 234 | 14 |
| 30          | 2          | 12.98 | 24 021 | 1 696 | 316 | 11 | 28 717 | 1 046 | 574 | 47 |
| 31          | 2          | 13.18 | 6 899 | 812 | 490 | 26 | 19 944 | 1 056 | 301 | 3 |
| 32          | 2          | 11.41 | 7 839 | 759 | 67.0 | 3.5 | 21 273 | 1 303 | 380 | 26 |
| 33          | 2          | 12.96 | 20 495 | 1 930 | 868 | 70 | 52 055 | 2 154 | 859 | 58 |
Table 2 (continued)

| Sample code | Coal grade | pH   | As [ug/kg] | Uexp | Cd [ug/kg] | Uexp | Pb [ug/kg] | Uexp | Tl [ug/kg] | Uexp |
|-------------|------------|------|------------|------|------------|------|------------|------|------------|------|
| 34          | 2          | 12.72| 9 760      | 1 455| 90.2       | 1.9  | 14 601     | 153  | 235        | 23   |
| 35          | 2          | 12.92| 14 814     | 732  | 199        | 13   | 7 167      | 344  | 366        | 33   |
| 36          | 2          | 9.45 | 16 543     | 2 466| 768        | 80   | 110 191    | 2 371| 741        | 72   |
| 37          | 2          | 13.01| 6 449      | 911  | 1 752      | 23   | 28 075     | 2 643| 312        | 21   |
| 38          | 2          | 12.31| 19 569     | 512  | 1 134.8    | 5.9  | 54 951     | 546  | 348        | 40   |
| 39          | 2          | 12.78| 7 270      | 494  | 390        | 18   | 12 996     | 408  | 302        | 65   |
| 40          | 2          | 9.55 | 8 373      | 788  | 1 290      | 30   | 85 636     | 2 409| 582        | 27   |
| 41          | 2          | 11.23| 13 780     | 1 153| 185        | 15   | 22 757     | 1 243| 285        | 25   |
| Mean ± SD for grade 2 |          | 12.05 ± 1.14 | 10 777 ± 5 615 | 508.5 (124.2; 2082.3)* | 36 119 ± 27 680 | 519 ± 265 |
| 42          | 3          | 12.75| 9 981      | 418  | 123.3      | 3.2  | 44 217     | 1 025| 327        | 10   |
| 43          | 3          | 12.90| 50 924     | 7 325| 641        | 17   | 32 755     | 867  | 763        | 22   |
| 44          | 3          | 13.01| 13 257     | 416  | 236.4      | 8.7  | 31 889     | 1 001| 450        | 4    |
| 45          | 3          | 12.96| 11 911     | 966  | 181        | 17   | 10 353     | 651  | 313        | 7    |
| 46          | 3          | 11.31| 14 628     | 1 454| 486.2      | 3.8  | 35 956     | 1 845| 1 272      | 37   |
| 47          | 3          | 12.99| 13 888     | 1 525| 1 885      | 15   | 95 493     | 3 635| 1 541      | 113  |
| 48          | 3          | 12.78| 9 044      | 1 254| 185.6      | 8.3  | 17 095     | 1 073| 373        | 45   |
| 49          | 3          | 13.00| 40 775     | 2 559| 281        | 22   | 26 895     | 757  | 533        | 65   |
| Mean ± SD for grade 3 |          | 12.71 ± 0.58 | 20 551 ± 15 960 | 335.8 (139.3; 809.7)* | 36 831 ± 25 986 | 696 ± 467 |
| 50          | 4          | 10.82| 3 103      | 317  | 8.3        | 0.2  | 889        | 26   | 202        | 12   |
| 51          | 4          | 11.36| 5 551      | 232  | 34.5       | 0.8  | 5 297      | 131  | 226        | 53   |
| 52          | 4          | 12.00| 8 511      | 623  | 63.9       | 2.5  | 4 854      | 225  | 477        | 37   |
| Mean ± SD for grade 4 |          | 11.39 ± 0.59 | 5 722± 2 708 | 36 ± 28 | 3 680± 2 427 | 302± 152 |
| MEAN ± SD |          | 11.88 (10.71; 13.17)* | 12 128 (6 334; 23) | 358.7 (87.2; 1475.6)* | 27 912 (12.661; 61) | 592.1 (245.2; 1429.8)* |
| Median     |          | 12.35| 13 339     | 363.0| 27 485     | 8.3  | 889        | 155  | 665        | 155  |
| Min        |          | 9.22 | 2 230      | 8.3  | 889        | 155  | 665        | 155  | 665        | 155  |
| Max        |          | 13.24| 50 924     | 43 482| 128 906    | 39 263| 544.9      |      |            |      |
| IQR        |          | 1.70 | 11 470     | 675.0| 39 263     | 544.9|            |      |            |      |

*Calculated for data being transformed in logarithms and retransformed after calculations.
Thus, further study is required to generalize the conclusions. According to study from 2012, the alkalinity of fly ash attenuates the release of a large number of elements, including lead [17].

A statistically significant PCA model was constructed for the experimental data. First principal component of this model explained 44.6% and the second one 23.6% of the original variation. The eigenvalues for the first two principal components of the model were equal to 2.23 and 1.18, respectively. The correlation weights based on the PCA model are shown in Table 4 together with corresponding Spearman correlation coefficients, and the other results of the PCA analysis are shown in Figs. 1 and 2.

First principal component was mainly loaded by Pb, Tl, As (negatively) and pH (positively). Second principal component was determined predominantly by Cd (positively) and As and pH (negatively). Figure 1 and Table 4 show the positive correlation between Pb, As, and Tl, which formed a cluster of mutually positively correlated parameters. All of them were negatively correlated with pH, which is additionally negatively correlated with Cd. Moreover, Cd was strongly negatively correlated with As. The distribution of the examined samples in the space determined by the first two principal components (Fig. 2) showed that samples of grade 3 were all right to line “a”, which corresponded to higher values of pH. On the other hand, all samples of grade 2 and 4 were above the line “b”, which corresponded to higher concentrations of cadmium (in grade 2) and lower concentration of lead, arsenic and thallium (in both grades). As these differences were nonsignificant, none grade formed any strict separate cluster, Table 5.

Table 3 Comparison of the experimental data with results of other authors

| References | Coal ash of industrial origin | As [µg/kg] | Cd [µg/kg] | Pb [µg/kg] | Ti [µg/kg] |
|------------|-------------------------------|------------|------------|------------|------------|
| [14]       | Fly ash                       | 11 500     | 1 200      | 41 100     | 2 100      |
| Bot. ash   | 1 800                         |            |            |            |            |
| [18]       | Fly ash                       | 110 000–141 800 | 18 600–34 900 | 20 100–1 192 500 | 28 100–64 500 |
| Bot. ash   | 239 100–572 200               | 2 500–5 500 | 70 500–165 900 | 6 700–13 200 |
| [19]       | Fly ash                       | 190–350    | 600–930    | 7 600–35 300 | –          |
| Bot. ash   | 100–300                       | 490–790    | 8 800–28 280 | –          |
| [20]       | Fly ash                       | 311 100–1 555 000 | 500–2 460 | 27 800–60 500 | 2 300–32 500 |
| Bot. ash   | –                             | <800–11 720 | 36 600–759 000 | 760–16 400 |
| [21]       | Fly ash                       | –          | –          | 41 000–276 000 | 2 000–11 000 |
| [22]       | Household-furnace residual ash | 10 200–28 000 | 900 | 30 000–97 000 | 500 |

Table 4 Correlation weights based on PCA model (only correlation weights with absolute values higher than 0.095 were shown). NS—not significant

| Pairs of correlated parameters | Correlation weights | Spearman correlation coefficients and significance level \((p)\) |
|-------------------------------|---------------------|----------------------------------------------------------|
| Pb Tl                         | 0.255               | 0.624 \((p<0.001)\)                                      |
| As Tl                         | 0.188               | 0.471 \((p<0.001)\)                                      |
| Pb As                         | 0.098               | 0.367 \((p<0.010)\)                                      |
| pH Pb                         | −0.130              | −0.542 \((p<0.001)\)                                     |
| pH Cd                         | −0.154              | NS                                                       |
| pH As                         | −0.159              | NS                                                       |
| pH Ti                         | −0.208              | NS                                                       |
| Cd As                         | −0.226              | NS                                                       |

Table 5 Comparison between ashes originating from different coal grades (the concentrations within each column marked with the same letter in upper index differ significantly, \(p<0.05\))

| Coal grade | Parameter (median and IQR\(^*\)) |
|------------|----------------------------------|
| pH         | As [µg/kg] | Cd [µg/kg] | Pb [µg/kg] |
| 1          | 11.7 (2.1) | 17,929 (13,040) | 365.1 (892.4) | 38,692 (21,942) |
| 2          | 12.6 (1.4) | 9335 (6943) | 489.9 (811.9) | 22,757 (33,752) |
| 3          | 12.9 (1.3) | 13,572 (5164) | 258.5 (297.0) | 32,322 (23,117) |
| 4          | 11.4      | 5551 | 34.5 | 4854 |

\(^*\)IQR was not calculated for coal grade 4, as there were only 3 samples of that grade

(e.g. amphoteric properties of lead). Thus, further study is required to generalize the conclusions. According to study from 2012, the alkalinity of fly ash attenuates the release of a large number of elements, including lead [17].

Conclusions

Statistical analysis showed certain correlations between the results, including correlations between the concentrations of studied metals and the grade of the source coal. The levels of concentrations of these metals found in the ash samples from individual households are comparable with those in
the ashes of industrial origin. Thus, from this point of view, household-origin ash does not seem to be more hazardous to the environment than the industrial one. On the other hand, the leaching characteristics, which can be an important factor, were not studied in this research. It is also worth noting that handling the ash (e.g. when unloading the furnace) poses the risk of ingestion, in which case also the phase composition and the total composition, apart from the toxic metal content, are of major importance.

Disclosure

Conflict interest The authors declare no conflict of interest.

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