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ORIGINAL ARTICLE

Assessing the impact of biofuel ash on agricultural crops: ecotoxicity and risk index evaluation

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Abstract
Biofuel ash is a heterogeneous solid matrix, which improves agricultural areas, as it contains a considerable amount of nutrients: K, Ca, P, and Mg. Therefore, they can be used to make fertilizer products (liquid or granules). The study utilized raw materials, biofuel ash (BA) identified as BA1, BA2, and BA3, along with spent coffee grounds (SCG), either individually or in different combinations. Three experiments were conducted: one assessing phytotoxicity and two pot experiments aimed at evaluating the suitability of BA for agricultural applications. Additionally, simulation models were used to estimate the heavy metal accumulation risk in soil and to evaluate the potential ecological risk to the environment following BA application. Despite containing the highest levels of heavy metals and benz-α-pyrene, BA3 positively affects spring wheat seed germination and shows no phytotoxicity. The results from the phytotoxicity tests (conducted at 10 days) generally indicated low toxicity levels across all tested products, except for BA1 leachate after 2 h of extraction, which exhibited moderate phytotoxicity, and SCG leachate after 4 h, which showed high phytotoxicity. BA3, whether used alone or in combination with SCG, does not affect root biomass, while shoot biomass increases with different amendments, though not statistically significant. The overall potential ecological risk to the environment, as indicated by the risk index (RI) values of BA samples, revealed a moderate risk for BA2, a considerable risk for BA1, and a very high risk for BA3. Notably, the potential environmental risk increased primarily due to the high cadmium (Cd) concentration in the BA samples and the high toxicity factor of Cd.

Keywords Ash · Spent coffee grounds · Fertilizer products · Germination · Phytotoxicity · Risk index

1 Introduction

Biofuel ash contains a complex and heterogeneous mixture of inorganic crystalline and amorphous minerals in combination with organic substances [1–3]. Most of the ash is stored in landfills [4, 5]. However, such ash storage is expensive, so sustainable biofuel ash management is very important [6, 7]. In the Lithuanian state waste prevention and management plan, it should be noted that in 2020, about 398,000 tons of waste were burned, and about 96,000 tons of ash and slag were formed from them. It is predicted, that in the future, when all power stations (Klaipeda, Kaunas, and Vilnius) will be operating, the amount of incinerated waste may reach about 615,000 tons and ash and slag waste about 154,000 tons per year [8]. The amount of waste will increase even more if waste prevention measures are not taken. Ash and slag are currently being used for experimental road surfacing [9]. It is planned to expand this activity and the possibilities of practical use of this waste [8].

The properties and components of the ash used may vary depending on the nature and origin of the raw materials being burned [10]. They may contain toxic elements such as chromium (Cr), cadmium (Cd), nickel (Ni), and lead (Pb) [11] and polycyclic aromatic hydrocarbons (PAHs) [12]. Which can cause danger to the environment and people even at low concentrations [13, 14]. Water-soluble elements can contaminate the soil, groundwater, and endanger living organisms. However, zinc (Zn) and copper (Cu) are essential microelements for living organisms, but their excess is dangerous. Phytotoxic effects may occur at high levels of these elements [15]. Ash can be used for fertilization, which does

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not exceed the maximum allowable limits (MAL) [16]. Such ashes improve agricultural and forest areas, as they contain a considerable amount of potassium (K), calcium (Ca), phosphorus (P), and magnesium (Mg) [1, 17, 18].

In addition to biofuel ash, another waste is spent coffee grounds (SCG). Coffee is a very common drink all over the world. According to the *International Coffee Organization*, about 178 million 60-kg bags of coffee (102.2 *arabica* and 75.8 *robusta*) are produced in the last year [19]. Various wastes are generated during coffee making: husks and skins. However, the largest amount of waste consists of spent coffee grounds, which remain after brewing coffee. Spent coffee grounds consist of hemicellulose, lignin, and cellulose: lipids, polysaccharides, polyphenols, and proteins [20–22]. Most of the spent coffee grounds are discharged into landfills and incinerated. However, such waste management is resource-intensive and unsustainable [23]. One of the alternatives is to granulate biofuel ash together with organic waste (SCG) and obtain fertilizing products. During granulation, water is usually used as a binder. The resulting granules should be mechanically strong for easy transport and spreading in the fields [24]. Moreover, such granules at the same time should be easily decomposed in the soil.

This study aims to investigate the chemical composition of biofuel ashes and spent coffee grounds, assess their phytotoxicity on spring wheat, and evaluate the environmental pollution risk associated with their application. The most contaminated biofuel ashes have been selected for pellet production by mixing them with spent coffee grounds to determine whether heavy metal contamination directly affects the length and biomass of plant roots and shoots. The conclusions obtained from this assessment will be valuable for the management and quality control of biofuel ash. Additionally, this study will provide insights into both the agronomic value and pollution levels of biofuel ash, as well as its potential use in agriculture.

2 Materials and experimental methods

2.1 Biofuel ash (BA) and spent coffee ground (SCG)

Biofuel ash samples were collected from different bioboilers operating in Lithuania. Five kilograms of each biofuel ash was taken. Five kilograms of spent coffee ground was collected from household coffee machines. The coffee used for coffee machines was 100% *arabica*, medium roasted. The waste particle size distribution was determined using a Retsch AS 200 (Retsch, Germany). This is a set of sieves stacked vertically. Sieves size from < 0.036 to 3.15 mm. The ash and spent coffee ground were sieved for 10 min, the vibration frequency was configured at 60 amplitude, and the amount in each sieve was weighed with a Radwag AS 60/220/C/2 (Radwag, Poland) analytical balance (Fig. 1).

2.2 Physicochemical properties of BA and SCG

- Determination of pH: 10 g of the sample is mixed with 50-ml deionized water. The resulting mixture is shaken for 1 h. Then pH is measured using a pH meter PC 8 + DHS (XS Instruments, Italy) [25].
- Determination of electrical conductivity (EC): One part raw material and five parts water were poured into a glass (1:5 ratio). The resulting mixture is shaken for 1 h and filtered. The filtrate is measured using pH meter PC 8 + DHS (XS Instruments, Italy) with an electrical conductivity electrode [26, 27].
- Determination of organic carbon (C_{org}): 0.2 g of the dried and homogenized sample is weighed in a crucible. A total of 4 mol of HCl solution is added to the crucible to wet the samples. If the sample foams, more acid is added until the foaming stops. The prepared samples are dried for 16 h at a temperature of 64–66 °C. The samples are measured with a Multi EA 4000 analyzer (Analytik Jena, Germany) [28, 29].
- Determination of total nitrogen (N_{total}): The raw materials are sieved through a 0.25-mm sieve. A total of 0.2 g of sample is weighed for analysis. The prepared sample is placed in the nitrogen analyzer Vario EL Cube (Elementar, Germany). The firing temperature is 1150 °C. The results were processed using the program [28, 30].
- Analysis of metals and nutrients: The determination of metals: Ni, Cr, Cd, Pb, Cu, Zn, As, Al, Mn, and Fe and nutrients: K, P, Ca, and Mg in biofuel ash and spent coffee grounds was carried out according to the methodology prepared in the laboratory. First, 0.3 g of the sample is weighed into Teflon mineralization vessels and added 2 ml of HCl and 10 ml of HNO_3 (1:5). The

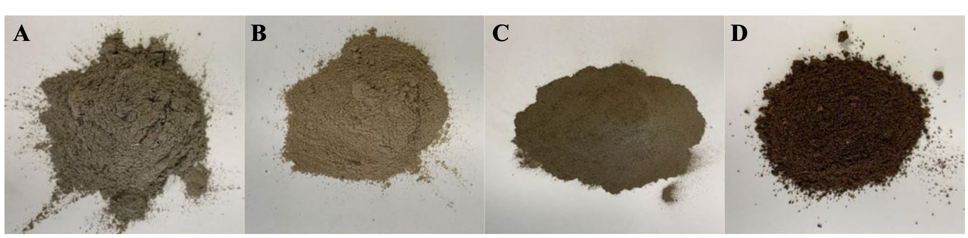

Fig. 1 Biofuel ashes. **A** BA1, **B** BA2, **C** BA3, and **D** SCG used in experiments

vessels were covered and left to stand for ~ 15 min and then placed in the MARS6 (CEM, US) automatic sample mineralization system at 180 °C, 800-Pa pressure, and 800-W power. Later, the mineralized mixture was cooled and diluted to the meniscus in a 100-ml volumetric flask with 2% HNO_3 solution. The resulting solution is analyzed by inductively coupled plasma mass spectrometry (ICP – MS) (ThermoFisher Scientific, USA). Standards are prepared together with the test samples for each analysis, and a calibration curve is obtained [31].

- Analysis of polycyclic aromatic hydrocarbons (PAHs): Polycyclic aromatic hydrocarbons in biofuel ash and coffee grounds were determined by following [32] with slight modifications. Approximately, 6 g of the homogenized sample was weighed into the centrifugal tube. Two-stage extraction was carried out using 20-mL cyclohexane: acetone mixture at equal parts and shake on the orbital shaking (Biosan, Latvia) for 30 min at 130 rpm, after being treated with an ultrasonic bath (VWR, UK) for 30 min, centrifugated (Hettich, Germany) for 10 min at 250 rpm, and filtrated using paper filter 90 g m^2. The solvent after both extractions was collected to the same flask and evaporated until dryness using a rotary evaporator (Heidolph Instruments, Germany) under the following conditions: rotating speed 140 rpm and temperature 40 °C. The residue dissolved in acetone and analyzed using gas chromatography mass spectrometry (GC–MS) (Shimadzu, Japan). The separation of 16 PAHs was carried out using a RXi-5 ms (30 m × 0.25 mm inner diameter, 0.25-μm film thickness) capillary column (Restek, USA). Pure helium was used as the carrier gas at a constant ramped flow rate of 2.0 ml/min. Two microliters of samples was introduced using AOC-5000 Plus autosampler (Shimadzu, Japan) under spitless mode and 280 °C injection temperature. The GC oven temperature was programmed from 60 °C hold for 1 min, then at a rate 25 °C/min raised to 180 °C, and at a rate 5 °C/min raised to 320 °C and held for 10 min. Further, the MS operational conditions were as follows: ion source temperature 220 °C, interface temperature 280 °C, electron impact (EI) ionization at 70 eV, data acquisition was performed at scanning mode from 127 to 300 m/z at a speed 625, and selective ion monitoring (SIM) mode with characteristic molecular ions of each PAH.

2.3 Soil and plant sampling

The soil was taken in 2023 from the organic experimental fields of the Agricultural Institute of the Lithuanian Research Centre for Agriculture and Forestry, where no fertilizers are used (Akademija, Kėdainiai district, Lithuania). Before the experiment, plant remains, and stones were separated, and the soil was homogenized.

2.4 Ecotoxicity experiment

Germination rate was determined based on a modified methodology of Italian scientists [33]. A total of 25 g of the sample (BA, SCG, or granular products) was added to 100 ml of distilled water. The suspensions were shaken for 2, 4, and 24 h. Petri dishes were prepared, each containing 25 spring wheat seeds placed upon 2 sheets. Each filter paper was pre-treated with 10 ml of the prepared solution. The dishes were stored in a controlled climate chamber (temperature 20 °C). In the case of dry dishes, irrigation was performed with 2 ml of solution. The experiment was performed in four replicates. The number of germinated seeds was counted after 3, 6, 8, and 10 days.

During the processing of the obtained data, two toxicity indices were calculated: SG — seed germination and RE — radicle elongation [34, 35]:

$$SG = \frac{G_E(i) - G_C}{G_C} \tag{1}$$

$$RE = \frac{R_E(i) - R_C}{R_C} \tag{2}$$

$G_E(i)$ — average number of germinated seeds in extract (i), G_C — average number of germinated seeds in the control, $R_E(i)$ — average radicle length of the seedling in extract (i) (mm), and R_C: average radicle length of the seedling in the control (mm).

SG and RE values range from − 1 to > 0. Negative SG and RE values indicate phytotoxicity, while positive values indicate stimulation of germination or radicle growth. The degrees of phytotoxicity are presented in Table 1. The degrees are classified into four groups: low, moderate, high, and very high [34, 35].

2.4.1 *Root and shoot length and mass*

Root and shoot lengths were measured manually with a ruler. Mass was measured on an analytical balance Radwag AS 60/220/C/2 (Radwag, Poland).

Table 1 Classification of phytotoxicity according to SG or RE values

Low	0 > SG or RE > − 0.25
Moderate	− 0.25 > SG or RE > − 0.5
High	− 0.5 > SG or RE > − 0.75
Very high	− 0.75 > SG or RE > − 1

Table 2 The treatments of the pot experiment with ash and spent coffee grounds

Treatments	Application rate of P kg/ha
1. Control	0
2. BA3	40
3. SCG	40
4. BA3SCG pellets	40
5. BA3SCG pellets	20
6. BA3SCG pellets	60

BA3 biofuel ash no. 3, *SCG* spent coffee grounds, *BA3SCG* biofuel ash no. 3, and spent coffee ground pellets

2.5 Description of pot experiment with ash and spent coffee ground pellets

The pot experiment was conducted in 2023, and the treatment design used in the experiment is shown in Table 2.

The pots for the experiment were prepared as follows: the 1-L plastic containers (10-cm height, top diameter 12 cm, bottom diameter 10 cm) were filled with 1 L of soil, and according to the application rate of P, the equivalent amount of biofuel ash, spent coffee ground, and biofuel ash/spent coffee ground pellets, three replicates were tested ($n=3$). Also, three pots without any addition were used as a control. Spring wheat cultivar "Kalada" was grown in the pots, and 10 seeds of spring wheat were sown in each pot. The experiment for 28 days was conducted in controlled climate chambers where conditions were as follows: 16 h of the day and 8 h of the night, the relative humidity was $70 \pm 1\%$, and the temperature was set at 24.0 ± 1.0 °C during the day and 18.0 ± 1.0 °C at night. No additional fertilization and no pesticides during the vegetation of spring wheat were applied. Weeding was done manually, and pots were watered with deionized water as needed. The spring wheat was harvested after 28 days, and the following plant parameters were determined: root and shoot height, the mass of root and shoot, and biomass of the pot.

2.6 Pot experiment with ash and spent coffee ground liquid extracts

The pot experiment was conducted in controlled climate chambers in 2023. The experiment treatment design is shown in Table 3.

A total of 0.5-L plastic containers (9-cm height, top diameter 9.5 cm, bottom diameter 8.5 cm) were filled with 0.5 L of soil. Ten seeds of spring wheat cultivar "Kalada" were sown in the pots. Three replicates of each treatment were tested ($n=3$). Pots were watered with 10-ml ash or spent coffee ground extract and 40-ml deionized water mixture on the sowing day and every third day after sowing for 28 days.

Table 3 The treatments of the pot experiment with ash and spent coffee ground extracts

Treatments	Watering rate
1. Control (deionized water)	50-ml dH_2O
2. BA1 extract	10-ml extract + 40-ml dH_2O
3. BA2 extract	10-ml extract + 40-ml dH_2O
4. BA3 extract	10-ml extract + 40-ml dH_2O
5. SCG extract	10-ml extract + 40-ml dH_2O

BA1 biofuel ash no. 1, *BA2* biofuel ash no. 2, *BA3* biofuel ash no. 3, *SCG* spent coffee grounds

2.7 Potential risk of using biofuel ash and its derived products

The potential ecological risk of using biofuel ash and its derived products was estimated by previously described formulas [36]. Evaluation criteria of ash for individual heavy metals (E_r^i) and cumulative potential ecological risk of the environment *(RI)* are given elsewhere [36–38].

2.8 Time scale needed to double the heavy metal concentrations in soil from its background level after application of biofuel ash and its derived products

To present meaningful insights regarding the risk of six heavy metals (Cd, Cr, Cu, Ni, Pb, Zn) accumulation in soil resulting from BA and its derived products applications, Monte Carlo simulations were carried out. These simulations were employed to estimate the time necessary to increase twice the background level of six heavy metals after BA application following the formulas:

$$AI = C_c \cdot W_c \tag{3}$$

$$T = \frac{C_s \cdot W_s}{C_c \cdot W_c} \tag{4}$$

AI — annual input of heavy metal (g ha^{-1} year^{-1}); C_c — determined concentrations of heavy metal in BA (mg kg^{-1}), W_c — annual application rate of BA was selected according to annual maximum allowable phosphorus concentration (90 kg P_2O_5 per ha); C_s — background concentration of heavy metal in soil was taken from the hygienic norm (HN 60:2004) [16], which describes maximal permitted levels of dangerous substances in the soil and was calculated as an average background concentration for sandy and clay soils: Cr — 37 mg kg^{-1}, Zn — 31 mg kg^{-1}, Cd

— 0.18 mg kg^{-1}, Ni — 15 mg kg^{-1}, Pb — 15 mg kg^{-1}, and Cu — 9.55 mg kg^{-1}; and W_s — the weight of the soil plow layer (0–20 cm) soil per hectare (t ha^{-1}), and for an average soil bulk density of 1.3 t m^{-3}, Ws is 2600 t ha^{-1}.

2.9 Statistical analysis

The physical and chemical properties of the raw materials were calculated using MS Excel 2018 software as the arithmetic mean ± standard deviation of triplicates. Spring wheat root and shoot length and its mass were evaluated using Duncun's multiple range test in phytotoxicity and pot experiments. The statistical software package SAS, version 9.3, was used for analysis [39].

3 Results and discussion

3.1 Physical and chemical properties of biofuel ash (BA) and spent coffee grounds (SCG)

The pH and electrical conductivity (EC) were determined in BA and SCG. The pH of the biofuel ash was alkaline and varied within a very similar range: BA1 and BA2 were 14.0, respectively, while BA3 was13.7. In studies by other researchers, the pH in ash ranged from 12.5 to 13.3 [40]. In this study, the pH of the SCG was neutral, i.e., 7.7. However, Spanish and Korean researchers determined pH of about 5.0 in SCG [41–43]. Meanwhile, EC in biofuel ash was distributed differently: BA1 (14.9 ± 0.1), BA2 (10.4 ± 0.5), and BA3 (22.1 ± 1.0) mS/m. However, EC was significantly lower in spent coffee grounds 1.8 ± 0.0 mS/m. Nevertheless, a review of the literature studies found that used SCG with an electrical conductivity was 100 times higher than that found in this study [42, 43].

Table 4 shows the concentrations of 10 metals (Ni, Cr, Cd, Pb, Cu, Zn, As, Al, Mn, and Fe) in the raw materials. The last column of the table shows the maximum allowable limits (MAL) in biofuel ash [44]. The concentration of Cu and Zn in biofuel ash (BA1, BA2, and BA3) did not exceed the MAL. The content of Ni, Cr, Cd, Pb, and As in BA3 was found to exceed the maximum allowable limits (MAL), measuring a60.3 ± 0.3, 133 ± 3, 11.9 ± 0.2, 51.7 ± 0.1, and 15.2 ± 0.6 mg/kg, respectively. This finding of high-level metals in the BA3 sample correlates with previously described EC which usually is a reflection of various dissolved salt concentrations. It should be noted that the concentration of ash can be very diverse, and the values of ash can fluctuate in a very wide range. After evaluating the ash used in this experiment and comparing it with the data obtained by other researchers, the concentrations of Ni, Cr, Cd, Zn, Mn, and Fe obtained in this study are within the ranges determined in the previous experiment [45, 46].

Concentrations of six heavy metals were determined in spent coffee grounds (SCG): Ni, Cr, Cd, Pb, Cu, and Zn (Table 4), although these are not regulated. A small amount of hazardous metals was determined in SCG: 0.010 ± 0.000 mg/kg for Cd and 0.21 ± 0.09 mg/kg for Pb. Analyzing the studies of other scientists, the concentration for Cd was the same (0.01 ± 0.00 mg/kg), while Pb was found five times more (1.1 ± 0.1 mg/kg) [43]. Notable that the concentration of Zn reached only 14.0 ± 1.2 mg/kg (Table 4).

The determined amounts of K, P, Ca, Mg, N_{total}, and C_{org} in BA and SCG are shown in Table 5. The obtained results show that BA3 was the most enriched with nutrients when evaluating biofuel ash samples. Other studies have found similar values, for example, P (0.37%) or Mg (2.7%) [47]. Also, the amount of N_{total} was estimated, and it is evident that it is minimal in BA but differently in spent coffee grounds containing approximately 2% N_{total} [41, 48, 49]. In

Table 4 Various metal concentrations in raw materials

	SCG	BA1	BA2	BA3	MAL, mg/kg
Ni, mg/kg	13.1 ± 0.1	14.3 ± 1.9	23.9 ± 0.3	60.3 ± 0.3	30
Cr, mg/kg	38.3 ± 2.68	18.5 ± 1.30	35.5 ± 4.6	133 ± 3	30
Cd, mg/kg	0.010 ± 0.000	2.34 ± 0.46	0.80 ± 0.10	11.9 ± 0.2	5
Pb, mg/kg	0.21 ± 0.09	23.9 ± 3.7	10.1 ± 0.3	51.7 ± 0.1	50
Cu, mg/kg	19.1 ± 3.1	32.3 ± 4.1	35.6 ± 1.2	81.2 ± 1.0	200
Zn, mg/kg	14.0 ± 1.2	460 ± 68	155 ± 12	501 ± 41	1500
As, mg/kg	–	7.03 ± 0.94	6.64 ± 0.12	15.2 ± 0.6	3
Al, mg/kg	–	1505 ± 211	2482 ± 127	18,988 ± 1072	–
Mn, mg/kg	–	2076 ± 346	514 ± 17	7491 ± 243	–
Fe, mg/kg	–	3711 ± 510	3756 ± 159	16,474 ± 4618	–

In the first column, the sign (–) indicates that these elements were not analyzed in the SCG. In the last column, the sign (–) indicates that these elements are not regulated (MAL — maximum allowable limits)

Table 5 Nutrient concentrations in raw materials

	SCG	BA1	BA2	BA3
K, %	0.39 ± 0.03	0.35 ± 0.05	0.61 ± 0.03	3.02 ± 0.05
P, %	0.068 ± 0.004	0.20 ± 0.01	0.27 ± 0.02	0.36 ± 0.01
Ca, %	0.11 ± 0.01	3.53 ± 0.46	2.52 ± 0.10	7.52 ± 0.37
Mg, %	0.10 ± 0.01	0.41 ± 0.06	0.35 ± 0.01	2.71 ± 0.18
N_{total}, %	2.73 ± 0.13	0.09 ± 0.01	0.04 ± 0.01	0.05 ± 0.01
C_{org}, %	39.6 ± 2.77	5.55 ± 0.39	5.20 ± 0.36	7.66 ± 0.54

this study, the N_{total} content was 2.73%. The amount of C_{org} in SCG reached 39.6%, although most studies have found higher C_{org} concentrations — 50% and above [41, 49, 50]. Meanwhile, the amount of C_{org} in biofuel ash was found to be 6–8 times lower than in the spent coffee grounds investigated in this study (Table 5). According to the literature, if the concentration of C_{org} is higher than 10% in ash, it indicates that the biofuel burns low quality and the combustion of the fuel in the power stations is considered inefficient [46]. In this experiment, C_{org} concentrations in different ashes were obtained < 10%, i.e., 5.55% for BA1, 5.20 for BA2, and 7.66% for BA3.

3.2 PAHs in raw materials

The distribution of PAHs according to benzene rings number is presented in Fig. 2. It was observed that PAHs with 5-benzene rings dominated in all BA samples followed by 4-benzene rings PAHs. 3-Benzene rings PAHs were determined in BA1 and BA3 while 6-benzene rings found only in BA2. All investigated PAHs in SCG were below the detection limit. The total amount of ∑16 PAHs in BA varied from 52.12 μg kg^{-1} (BA3) to 159.33 μg kg^{-1} (BA2) and were considerably lower than previously reported [12, 51]. Based on the national regulations, only the amount of benz-α-pyrene is required to be lower than 0.5 μg kg^{-1} (Lietuvos respublikos aplinkos ministerija, 2011). From all investigated BA, BA1 and BA2 meet this requirement with the determined benz-α-pyrene content which was 0.07 μg kg^{-1} and 0.15 ± 0.011 μg kg^{-1}, respectively, while the BA3 sample contained a much higher amount – 22.84 μg kg^{-1}. Mostly, higher organic carbon content leads to higher levels of total PAHs; however, results obtained in this study demonstrate an opposite trend. The primary disparities could be attributed to differences in the combustion process and the type of feedstock materials used.

3.3 Particle size distribution in raw materials

The sieving method is very common in powder technology [50]. It has also been used by other researchers to determine particle size in SCG. It has been reported that SCG has a particle size distribution of approximately 0.25 to 0.50 mm [52–54]. In this study, the largest fraction of SCG was particles of 0.36 mm in size. This accounted for about 55% of the total amount analyzed. SCG did not contain particles 0.036 mm or smaller (Fig. 3A). This is confirmed by the works of the previously mentioned scientists. Conversely, the finer fraction, characterized by particles measuring

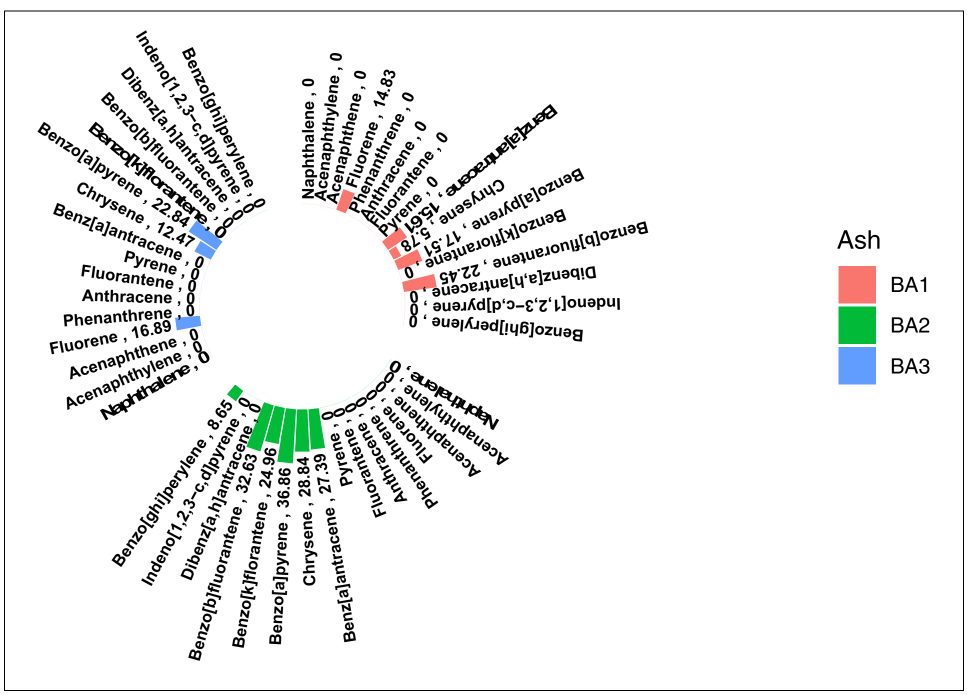

Fig. 2 The distribution of PAHs in biofuel ashes

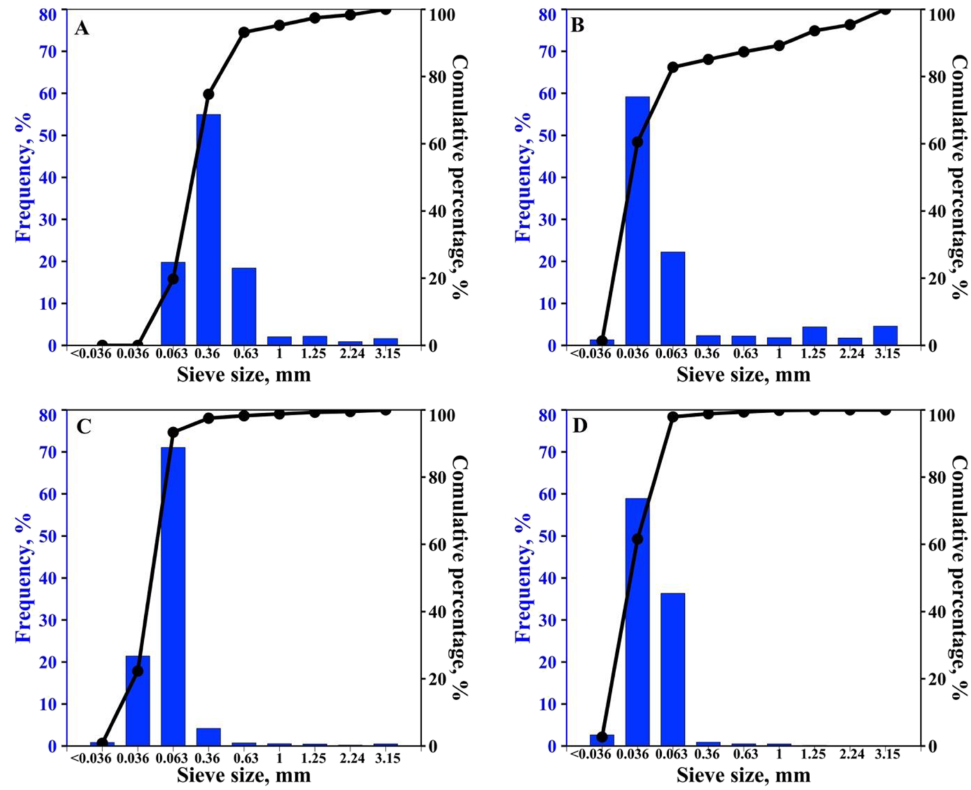

Fig. 3 The measured particle size distribution of **A** SCG, **B** BA1, **C** BA2, and **D** BA3

0.036 mm in size, prevailed in BA1 and BA3 (Fig. 3B, D), with particles smaller than 0.036 mm also being detected. BA2 was characterized by larger particles with a size of 0.063 mm (Fig. 3C). Figure 3 shows that ash BA1 had larger particles (< 0.36 mm) than ash BA2 and BA3. Granular fertilizer products were produced from the fraction with the highest amount, i.e., SCG — 0.36 mm, BA1 and BA3 — 0.036 mm, and BA2 — 0.063 mm.

3.4 Ecotoxicity experiment

Figure 4 shows the effects of different BA and SCG leachates on spring wheat germination rate. The results obtained with the BA1 showed that the lowest germination was determined when watering with filtrate which was shaken for 2 h. Spring wheat germination reached only 45% after 10 days. Meanwhile, when using BA2, germination was 65% after 3 days, and at the end of the experiment, it increased to 80%. Using the filtrate with SCG (also shaken for 2 h), the germination was highest and reached even 90% after 10 days.

The lowest germination was obtained using filtrates shaken with SCG for 4 h. After 6 and 8 days, the germination reached about 35%, and after 10 days, it increased only to 37%. Meanwhile, germination with BA2 and BA3 filtrates at the end of the experiment was 84% and 72%, respectively (Fig. 4).

The obtained results show that after shaking the raw materials for 24 h, the germination of spring wheat after 3 days was low, i.e., BA1 and BA3, 25%, respectively, BA2 — 20%, and SCG — 30% (control was 55%). However, at the end of the experiment, germination increased about four times, i.e., BA1 — 80%; BA2 and SCG, 85%, respectively; and BA3 — 90% (control was 85%) (Fig. 4). The increment in the percentage of seed germination treated with BA3 ash filtrate may be due to the presence of a higher amount of macro and micronutrients, such as Mn, Fe, Cu, and Zn [55].

The germination experiment was also carried out with granular products. Pellets were made by mixing ash and spent coffee grounds. When mixing BA1 ash with SCG, the granules did not bind tightly and fell apart. For this reason, the experiment was continued with only BA2 and BA3 ash. For the experiment, using the BA3SCG filtrate after 3 days, spring wheat germination was 60% and 20%, respectively, by shaking the filtrate for 2 and 4 h (Fig. 5). However, germination levelled off at the end of the experiment. During the experiment with BA2SCG filtrate, spring wheat germination was obtained the same as with BA3SCG filtrate, i.e., 60% after 3 days and 70% after 10 days (Fig. 5). After evaluating the influence of granular products, bulk ash, and spent coffee grounds on germination, it was found that better spring wheat germination is obtained by using bulk materials instead of granular ones. Shaking the bulk ash with water

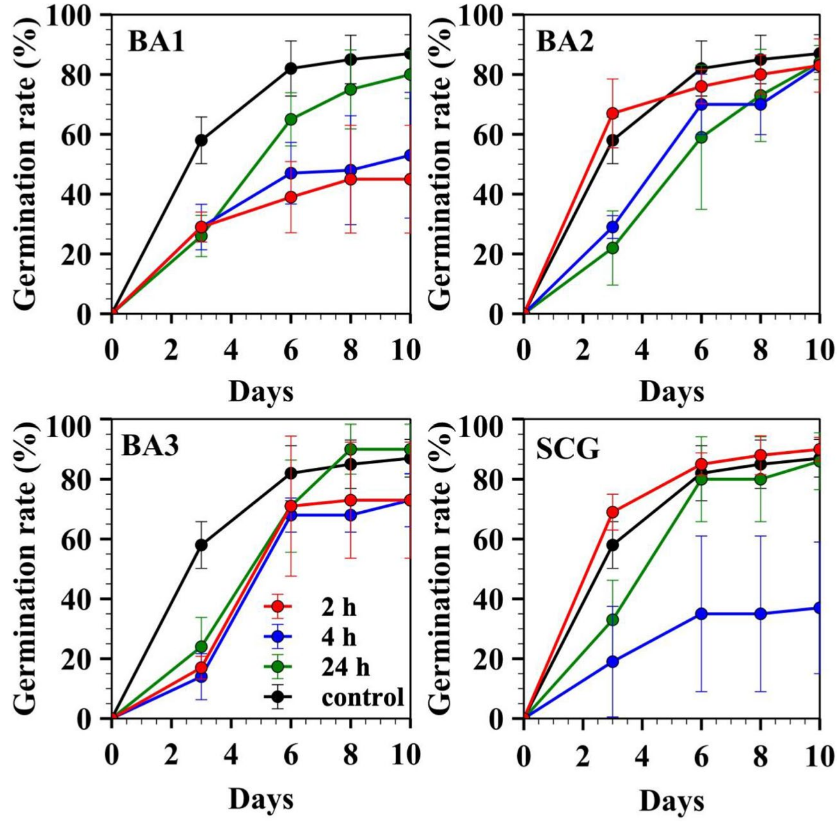

Fig. 4 Effect of different biofuel ashes and spent coffee ground leachates on spring wheat germination rate. Control (dH_2O), distilled water; SCG, spent coffee grounds; BA1, BA2, and BA3, biofuel ash

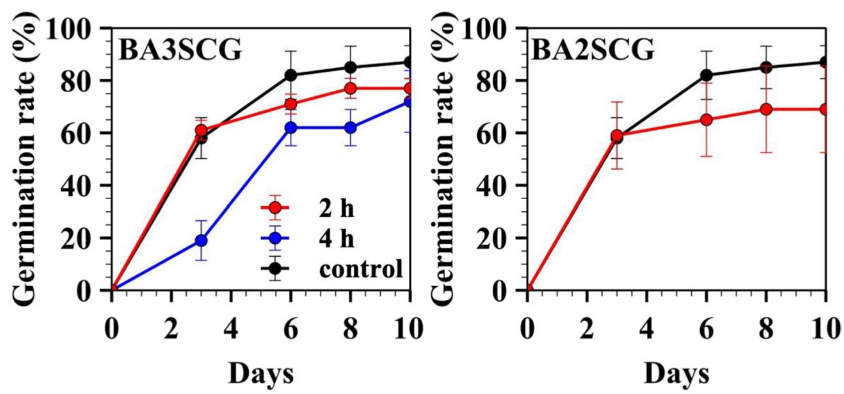

Fig. 5 Effect of different ashes and spent coffee ground product leachates on spring wheat germination rate. Control (dH_2O), distilled water; SCG, spent coffee grounds; BA1, BA2, and BA3, biofuel ash

probably transferred more nutrients to the filtrate than from the granular products [56].

Table 6 shows the calculated seed germination (SG) values for phytotoxicity [34, 35]. The calculated SG values correspond to the dependence of spring wheat germination presented in Figs. 4 and 5. The lower the germination percentage obtained, the higher the phytotoxicity. For example, the very high phytotoxicity degree was determined in two treatments: first − 0.78 (BA3 filtrate, which was shaken for 2 h) and second − 0.76 (SCG filtrate which was shaken for 4 h) after 3 days (Table 6). Spring wheat germination was only about 15–20% (Fig. 4). Meanwhile, SG values were − 0.19 and − 0.55, corresponding to low and high values in the same treatments (mentioned earlier) after 10 days (Table 6), and seed germination reached 72% and 37%, respectively, at the end of the experiment (Fig. 4). However, shaking the BA3 filtrate for 24 h and then watering the seeds with it showed a low and positive degree ($SG = 0.01$) of phytotoxicity after 8 and 10 days.

The obtained results show that BA1 filtrates had high and very high radicle elongation degrees of phytotoxicity in all different cases when the filtrates were shaken for 2, 4, and 24 h, and a moderate degree was obtained with BA2 filtrates: 2 h (− 0.36), 4 h (− 0.27), and 24 h (− 0.45) (Table 7). The degree

Table 6 Seed germination (SG) values for phytotoxicity

	2-h extraction time				4-h extraction time				24-h extraction time			
	Days				Days				Days			
	3	6	8	10	3	6	8	10	3	6	8	10
BA1	−0.63	−0.55	−0.49	−0.50	−0.26	−0.35	−0.38	−0.36	−0.54	−0.24	−0.16	−0.10
BA2	−0.15	−0.13	−0.09	−0.08	−0.26	−0.03	−0.09	−0.05	−0.61	−0.31	−0.18	−0.06
BA3	−0.78	−0.18	−0.17	−0.19	−0.64	−0.06	−0.12	−0.12	−0.58	−0.17	0.01	0.01
SCG	−0.13	−0.02	0.00	0.00	−0.76	−0.51	−0.55	−0.55	−0.42	−0.07	−0.10	−0.03
BA2SCG	−0.25	−0.25	−0.22	−0.23	-	-	-	-	-	-	-	-
BA3SCG	−0.23	−0.23	−0.13	−0.14	−0.51	−0.14	−0.19	−0.13	-	-	-	-

Low (0 > SG), moderate (−0.25 > SG), high (−0.5 > SG), and very high (−0.75 > SG)

Table 7 Radicle elongation (RE) values for phytotoxicity

Extraction time, h	BA1	BA2	BA3	SCG	BA2SCG	BA3SCG
2	−0.88	−0.36	−0.53	−0.18	−0.62	−0.58
4	−0.71	−0.27	−0.52	−0.70	-	−0.66
24	−0.82	−0.45	−0.45	−0.13	-	-

Low (RE > −0.25), moderate (RE > −0.5), high (RE > −0.75), and very high (RE > −1)

of phytotoxicity of low radicle elongation was not determined in any of the treatments. However, it is notable that BA3 ash exhibited higher levels of contamination compared to the other ash types (Table 4). Moreover, radicle elongation values for phytotoxicity with this ash were not as high as expected.

The length of the shoots and roots of spring wheat was measured after the experiment. The results are presented in Fig. 6. Shoot and root lengths were obtained shorter in treatments with ash or spent coffee ground filtrates than in the control. It is notable that the amount of most heavy metals in BA2 ash did not exceed the max allowable limits – only Cr and As values were determined slightly higher than MAL (Table 4). Therefore, it is likely that it had a positive effect on the length of roots and shoots compared to other ashes. BA1 ash filtrate (shaken for 2 and 24 h) significantly suppressed root growth and shoot growth (after shaken for 2 h) compared to the control. Root parameters of the other ashes (BA2 and BA3 filtrates) were similar to those of the controls and had no significant effect.

The data obtained when using filtrates with SCG for irrigating show that the length of the roots (after 2 h of shaking) was 6 cm and after 24 h of shaking — 8 cm (Fig. 6) indicating not significantly different from the control ($p > 0.01$).

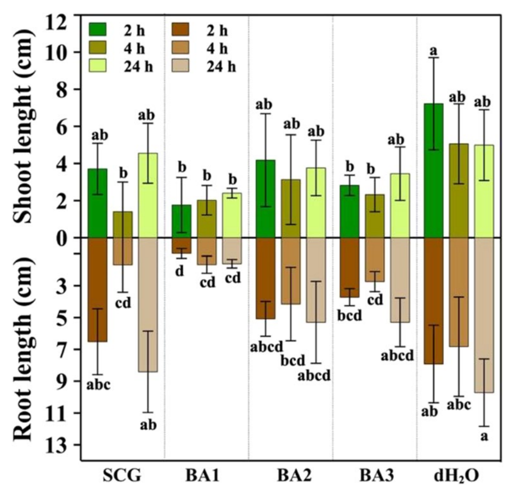

Fig. 6 Effects of different ashes and spent coffee ground leachates on spring wheat root and shoot length (dH_2O, distilled water; SCG, spent coffee grounds; BA1, BA2, and BA3, biofuel ash). Shoot: Extraction *F*-value – 0.5020, *p*-value – 0.4821; Fertilizer *F*-value – 7.7711, *p*-value – **6.826*e^{-5}**; Extraction x Fertilizer *F*-value – 1.0681, *p*-value 0.3829; Root: Extraction *F*-value – 10.7633, *p*-value – **0.001955**; Fertilizer *F*-value – 19.2885, *p*-value – **1.903*e.$^{-9}$**; Extraction x Fertilizer *F*-value – 0.9361, *p*-value – 0.3829. Note: Different lowercase letter indicate a significant difference according to Duncun' s multiple range test (DMRT $p \leq 0.01$)

3.5 Pot experiment with ash and spent coffee ground pellets

Regarding BA3 chemical composition, BA3SCG pellets were chosen to test for the pot experiment. Table 4 indicates that BA3 ash was the most contaminated. Therefore, it was decided to check whether it has a positive or negative effect on plant biomass. Figure 7A shows the root and shoot

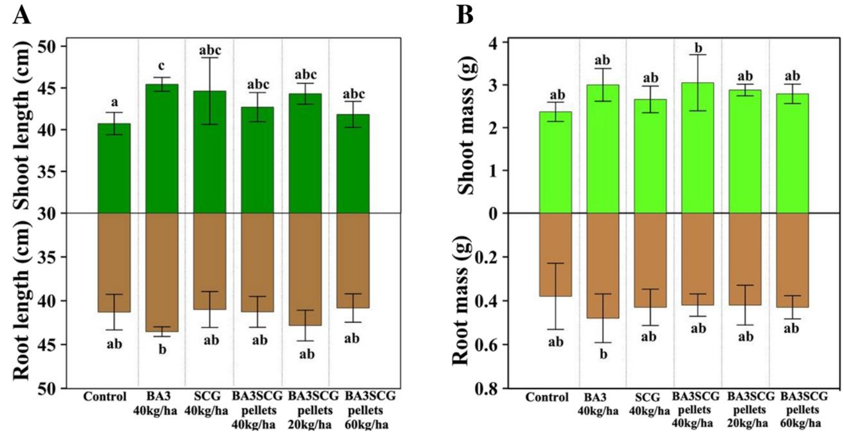

Fig. 7 **A** Root and shoot length of spring wheat. **B** Root and shoot mass of spring wheat. Different lowercase letters indicate a significant difference according to Duncun's multiple range test (DMRT $p \leq 0.01$)

lengths of spring wheat. Roots length was not statistically significantly different from the control ($p > 0.01$) which demonstrates no initial toxic effect. However, the length of shoots using BA3 ash differed. There are no significant differences between the treatments ($p > 0.01$) when evaluating the mass of spring wheat roots and shoots (Fig. 7B). Summarizing the obtained results, it was found that phytotoxicity did not occur when BA3, SCG, or BA3SCG pellets were used, although heavy metal concentrations exceeded the maximum allowable limits in BA3 (Table 4). Consideration emerges here, suggesting that the total heavy metal content determined may not adequately reflect the toxicity of the raw material or its resultant products. The decision for that could be the determination of bioavailable forms of metals.

3.6 Pot experiment with ash and spent coffee ground liquid extracts

The pot experiment was also performed with BA1, BA2, BA3, and SCG extracts, which were shaken for 2 h. The obtained results are presented in Fig. 8A and B. No significant differences ($p > 0.01$) were found between the length and mass of spring wheat roots and shoots. However, completely different results were obtained during the pot experiment compared to the germination watering experiment. During the watering experiment, the maximum length of roots and shoots was obtained by watering with distilled water (Fig. 6). However, the data from the pot experiment indicates that the roots and shoots had the smallest length in the control treatment (Fig. 8A).

In the pot experiment, the longest root and shoot lengths were obtained when watering with BA3 extract (Fig. 8A). Increased parameters when watering with these extracts may be signs of maximum absorption of micronutrients from ash. It is notable that BA3 ash had the highest amount of nutrients compared to BA1 and BA2 (Table 5).

3.7 Potential ecological risk to the environment

Estimated E_r^i and RI values for six heavy metals (Cd, Cr, Cu, Ni, Pb, Zn) are summarized in Fig. 9. The E_r^i values for Ni, Cr, Pb, and Zn in all tested BA varied from 1.0 to 20.1 indicating the low risk based on the classification of the risk level for individual heavy metals, while Cu risk varied from low to moderate respectively in BA1 (E_r^i = 16.9), BA2 (E_r^i = 18.6), and BA3 (E_r^i = 42.5). Ecological risks of Cd were found considerable in BA2 (E_r^i = 137.1) and high in BA1 (E_r^i = 401.1) and BA3 (E_r^i = 2040.0) samples. E_r^i

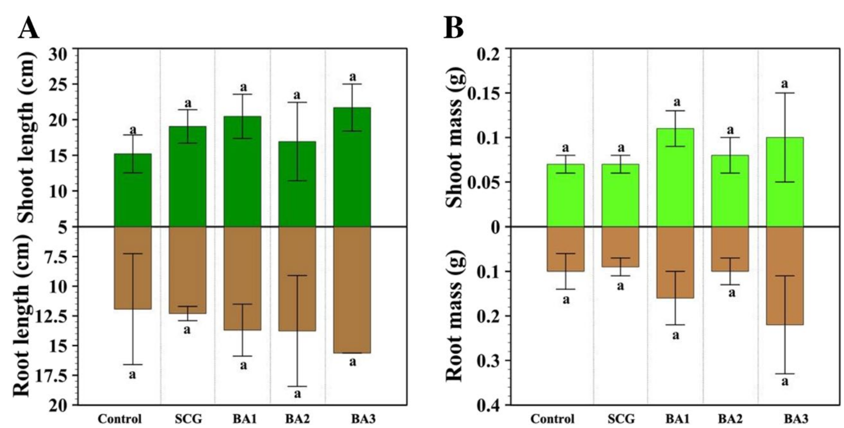

Fig. 8 **A** Root and shoot length of spring wheat. **B** Root and shoot mass of spring wheat. Note: Different lowercase letter indicate a significant difference according to Duncun's multiple range test (DMRT $p \leq 0.01$)

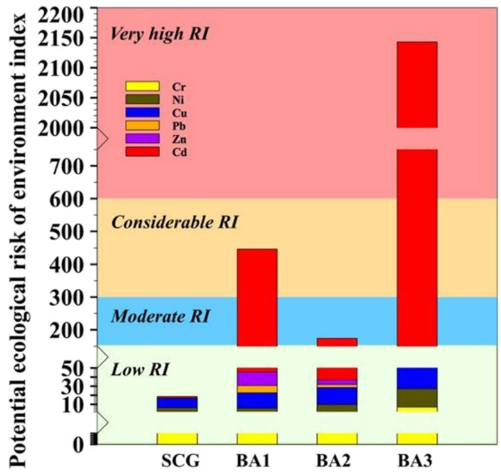

Fig. 9 Potential ecological risk of the environment index for biofuel ash (BA) and spent coffee grounds (SCG)

Table 8 Estimated annual maximum inputs of heavy metals (g ha^{-1} $year^{-1}$) and time (in years) needed to double heavy metals' background concentration in soil by continuous application of biofuel ash following phosphorous annual allowable rate (P_2O_5 = 90 mg/kg)

Heavy metals		BA1	BA2	BA3	SCG
Cd	Max. input	46.89	11.89	132.04	0.11
	Time	10	39	4	4218
Cr	Max. input	370.74	527.68	1464.63	2266.27
	Time	259	182	66	42
Cu	Max. input	647.29	529.17	900.97	211.93
	Time	38	47	28	117
Ni	Max. input	286.57	355.26	669.07	145.35
	Time	136	110	58	268
Pb	Max. input	478.96	150.13	573.65	0.23
	Time	81	260	68	167,375
Zn	Max. input	9218.44	2303.98	5558.95	828.40
	Time	9	35	14	97

could characterize the sensitivity of the local ecosystem to the toxic heavy metals and represent ecological risk resulting from the overall contamination if BA is utilized in the local agricultural land [57]. These findings demonstrate that BA requires treatment, to reduce the cadmium content before further application and to avoid environmental pollution. Previously performed studies agree with our findings that ash poses a high risk to the environment due to Cd [58, 59]. Compared to BA E_r^i of SCG for individual, heavy metals were much lower and classified as low risk.

The overall potential ecological risk to the environment (*RI*) values of BA samples was determined as moderate risk (BA2) followed by considerable risk (BA1) and very high risk (BA3), which Cd mainly influences. The main factor leading to a very high risk of BA is a high Cd toxicity rate [58].

3.8 Time scale needed to double the heavy metal concentrations in soil from its background level

The application of bioash leads to the risk of contaminating the soil. To determine the duration, in years, for the heavy metal content in agricultural soil to double from its baseline levels due to the use of BA and SCG raw materials, an assessment was performed. The annual application rate of BA and SCG input and the quantity of heavy metal incorporation were calculated based on the annual maximum allowable phosphorous concentration, and the results are summarized in Table 8. BA samples are distinguished by high Zn and Cd toxicity. Estimated predictions indicated that after 4 years of annual application of BA3, the background level of Cd will be doubled, respectively, and Zn requires 14 years. While using BA1 as soil amendment, only 9 years could be enough to double background levels of Zn, 10 years for Cd. However, the simulation results were somewhat overestimated as the calculations did not factor in trace metal outputs through processes such as leaching, runoff, and crop uptake. These outputs were deemed minor compared to the inputs [60]. Furthermore, the contribution of atmospheric deposition, which notably influences heavy metal accumulation in soil such as soil pH or/and organic matter content, was not considered in the calculations. Notably, it was proven that SCG did not show any significant contamination risk. There is a lack of studies which analyze the long-term heavy metals accumulation effect in the soil after BA application. Previously performed studies demonstrate that BA incorporation into the soil increases soil pH [1, 61, 62] which leads to lower heavy metals availability to plants [61, 63]. On the other hand, the total amount of heavy metals in the soil usually increases after using BA [64, 65]. Moreover, previously performed studies declare that heavy metal leachability from the soil does not increase [64, 66]. The findings mentioned above suggest that BA has potential as a soil amendment but should be used with careful monitoring.

4 Conclusions

Possible soil organic (SCG) and inorganic (BA1, BA2, BA3) amendments' chemical composition has been investigated in this study. It was determined that not all ash samples have a chemical composition that complies with the regulation for agricultural products: BA1 exceeds the maximum permissible limit for As, BA2 for As and Cr, and BA3 for As, Cr, Ni, Cd, and Pb. Nevertheless, the chemical composition and obtained values do not correlate with spring wheat seed germination for phytotoxicity. At the end of the experiment, the phytotoxicity for seed germination in most cases was low. Regardless of the chemical composition and determined parameters, the application of BA and SCG and their mixtures reduced spring wheat germination in all treatments, except when 24-h BA3 water extracts were used, which gave a positive effect compared to the control. No negative effects were recorded on plant root and shoot biomass after BA and SCG and their pellets incorporation into the soil. Monte Carlo simulations showed that after annual BA applications on soil, after a relatively short period (4–9 years), total concentrations of Cd and Zn would be doubled. An urgent need arises for the estimation of the impact resulting from the application of BA on soil. This necessity stems from the requirement to develop robust management practices and policies, which necessitate comprehensive information on the forms of bioavailable heavy metals present in BA. This need is underscored by a conducted study that unveiled no discernible phytotoxic effect on spring wheat even after BA application, despite containing significantly higher levels of heavy metals than the maximum allowable threshold.

Author contribution Kristina Bunevičienė, data analysis and writing an original draft. Donata Drapanauskaitė, data analysis and visualization, methodology, and editing original draft. Gabija Žilytė, investigation. Rimvydas Kamiskas, editing an original draft. Karolina Barčauskaitė, investigation, conceptualization, data curation, and editing of the original draft.

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Data availability The data are available upon request.

Declarations

Ethical approval The submitted work is original and should have not been published elsewhere in any form.

Consent to participate Not applicable.

Consent for publication All authors have consented to publish the article.

Conflict of interest The authors declare no competing interests.

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