agronomy

Section S1

1. Field experiment conditions

The study of the impact of fly ash from biomass combustion (BAs) on changes in the chemical speciation and total forms of trace elements present in chernozem soil (*Gleyic Chernozem*) with the granulometric composition of silty loam (SiL) [25] was carried out for 3 years (2019-2021) in a field experiment established in autumn 2018. The experiment was conducted on a farm in Korzenica in the south-eastern part of Poland (50°02′22″N 22°55′20″E) (Fig. S1).

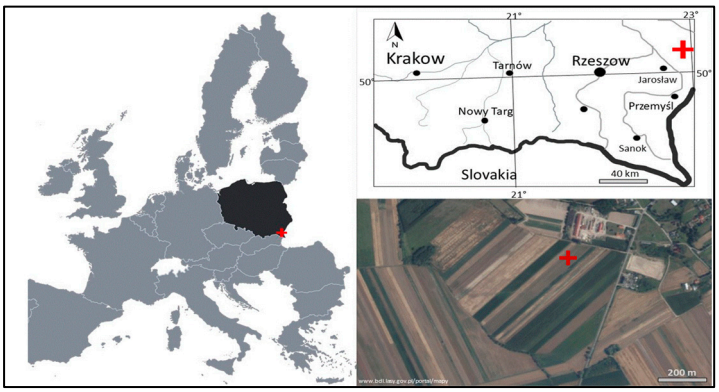

Figure S1. Localization of the field experiment [26].

Before the experiment, the soil was characterized by slightly acidic reaction (pH_{KCL}=5.89) and low content of available P and K forms (2.56 mg $100g^{-1}$ and 23 mg $100g^{-1}$). The one-factor field experiment was carried out on chernozem soil. It was conducted in a compact strip divided into 21 blocks, each with an area of 162 m^2, representing different fertilization variants - variable factor of the experiment. During the study, winter oilseed rape, spring barley, and potatoes were grown in the crop rotation system (7 blocs for every plant). In the study, the impact of biomass combustion ashes on changes in the chemical speciation of trace elements and their total forms was analyzed only in the soil under the winter oilseed rape cultivation. Winter oilseed rape (*Brassica napus* L. var. *napus*) cv. Mandril (from Syngenta) was sown at a density of 45 plants m^{-2} in each study year starting from August 20, 2018. To assess the impact of BAs on changes in the fractional composition and total concentration of trace elements, soil samples were collected from the 30-cm soil layer each year after plant harvest.

The doses of BAs were determined based on the content of potassium in the ash, which was its most abundant component. The field experiment variants were established on the basis of an earlier pot experiment, whose results are described in Szostek et al. (2023) [11]. The following doses of biomass combustion ashes were applied in the field experiment: 0.5 (D1), 1.0 (D2), 1.5 (D3), 2.0 (D4), and 2.5 (D5), which corresponded to the following doses of potassium applied as K_2O: 100, 200, 300, 400, and 500, respectively. Every year of study in autumn, the relevant plots were fertilized with ash from biomass combustion and this was mixed with the soil during pre-winter ploughing (approx. 25-30 cm). In spring, pre-sowing mineral fertilizers were applied and mixed with the soil using a cultivator. Mineral fertilization with nitrogen and phosphorus was constant (the same doses in all variants of the experiment). Nitrogen was used in the form of RSM® 32% N (aqueous solution of urea ammonium nitrate, density 1.32 kg dm^{-3}) and monoammonium phosphate (MAP) $NH_4H_2PO_4$ (12% N-NH_4), while phosphorus was introduced into the soil in the form of monoammonium phosphate (MAP, 22.7% P) [10]. The analysis of changes in the fractional composition of trace elements and their total content was carried out via comparison with the control (without K fertilization) and soil fertilized with

traditional NPK mineral fertilizers. In this variant, the soil was fertilized with a dose of 175 kg ha^{-1} of 60% potassium salt, which was determined based on the nutritional requirements of the plants. Changes in the chemical speciation of trace elements were also estimated via comparison with the soil analyzed before the experiment (0). Additionally, changes in the accumulation of trace elements in various parts of the winter oilseed rape plants were analyzed during the 3-year study.

The fly ash from biomass combustion (BAs) used in the experiment was produced through the combustion of forest biomass (approx. 70%) and agricultural biomass (approx. 30%). The forest biomass comprised deciduous and coniferous trees (50/50), whereas cereal straw, sunflower husk, and willow were the components of the agricultural biomass. The characteristics of the ash used in the experiment are presented in Table S1 [11]. The BAs used in the experiment was characterized by alkaline reaction (pH=12.83) and high salinity (EC=8.81 mS cm^{-1}). Ash with the same properties was used throughout the experiment.

Table S1. Physicochemical properties of ash from biomass combustion used in the experiment (mean±standard error) (n=12).

Parameter	Units		Total concentration
pH	-	12.83±0.37	-
EC	mS cm^{-1}	8.81±0.24	-
C	%	-	2.99±0.21
N	mg kg^{-1}	-	10±0.52
S		-	4700±50
P		-	9244±65
K		-	165617±123
Mg		-	13512±78
Ca		-	145081±137
Na		-	1452±43
Fe		-	4351±16
Mn		-	1490±21

2. The BCR procedure scheme

Step 1 (exchangeable/extractable fraction F1)- acetic acid (40 ml, 0.11 M) was added to a 50 ml centrifuge tube containing approximately 1 g of dry sewage sludge and then shaken at room temperature for 16 h. The supernatant and solid were separated through centrifugation (10 min, 4500 rpm). Then, the supernatant was decanted into a polyethylene volumetric flask and kept for further analysis. The residual solid was rinsed twice with distilled water (2x10 ml) by shaking for 15 min. Following centrifugation, the liquid was decanted and discarded.

Step 2 (reducible fraction F2) – a hydroxylammonium chloride solution (40 ml, 0.5 M, pH 1.5) was added to the centrifuge tube containing the residue from step 1. The content was again shaken at room temperature for 16h and then centrifuged and treated as in step 1.

Step 3 (oxidizable fraction F3) – a hydrogen peroxide solution (10 ml, 8.8 M) was added to the Step 2 residue and the content was then digested at room temperature for 1 h with occasional manual shaking. A further digestion process was carried out at 85°C in a water bath for another 1 h; thereafter, the cover was removed to allow evaporation of the solution to about 1 ml. Ammonium acetate (45 ml, 1.0 M, pH 2.0) was added to the moist residue once it cooled down and shaken for 16 h at room temperature. The supernatant collected after centrifugation was kept for further analysis. The solid was rinsed as before and digested as described in step 4.

Step 4 (residue fraction F4) – 10 ml of HNO_3, 2.5 ml of $HClO_4$, and 0.5 ml of H_2SO_4 were added to the residue remaining after step 3. The contents were heated at 105°C for 1 h, 120°C for 2 h, and 160°C for 5 h. After cooling to room temperature, the residue was dissolved in ultra-pure water with a total volume of 50 ml.

The same procedure as that described in step 4 was performed to determine the total concentration of selected trace elements in the sewage sludge samples.

Section S2

Table S2. Percent share of BCR fractions in the total Zn content.

Variant	F1	F2	F3	F4
0	3.0	28.1	14.4	54.5
Control	6.7	39.6	14.6	39.1
NPK	4.1	33.3	17.1	45.6
D1	4.3	35.1	20.8	39.7
D2	3.9	34.4	17.9	43.9
D3	3.7	33.6	27.0	35.7
D4	4.0	32.7	17.9	45.4
D5	3.8	31.4	19.4	45.3

Explanation: 0 - soil before starting the experiment, D1-D5 - doses of BAs: 0.5, 1.0, 1.5, 2.0, and 2.5 Mg ha^{-1}, respectively. F1-exchangeable/extractable fraction, F2- reducible fraction, F3- oxidizable fraction, F4- residual fraction.

Table S3. Percent share of BCR fractions in the total Cu content.

Variant	F1	F2	F3	F4
0	0.0	39.4	13.8	46.8
Control	0.5	34.3	11.9	53.4
NPK	0.2	33.5	16.9	49.5
D1	1.5	31.5	15.1	51.9
D2	0.4	35.2	14.6	49.8
D3	0.1	32.9	20.9	46.0
D4	0.1	31.6	14.6	53.6
D5	0.4	33.7	18.1	47.8

Explanation: 0 - soil before starting the experiment, D1-D5 - doses of BAs: 0.5, 1.0, 1.5, 2.0, and 2.5 Mg ha^{-1}, respectively. F1-exchangeable/extractable fraction, F2- reducible fraction, F3- oxidizable fraction, F4- residual fraction.

Table S4. Percent share of BCR fractions in the total Cr content.

Variant	F1	F2	F3	F4
0	0.0	4.2	15.9	79.9
Control	0.0	3.1	14.8	82.1
NPK	0.0	3.0	15.1	81.9
D1	0.0	2.8	16.1	81.1
D2	0.0	3.7	15.3	81.0
D3	0.0	5.0	19.8	75.3
D4	0.0	4.0	16.7	79.2
D5	0.0	3.6	17.4	79.1

Explanation: 0 - soil before starting the experiment, D1-D5 - doses of BAs: 0.5, 1.0, 1.5, 2.0, and 2.5 Mg ha^{-1}, respectively. F1-exchangeable/extractable fraction, F2- reducible fraction, F3- oxidizable fraction, F4- residual fraction.

Table S5. Percent share of BCR fractions in the total Ni content.

Variant	F1	F2	F3	F4
0	7.2	32.0	21.8	39.1
Control	7.2	29.2	18.2	45.4
NPK	6.5	22.6	17.6	53.3
D1	4.9	24.5	16.7	54.0
D2	4.5	28.0	16.9	50.6
D3	4.8	29.7	23.0	42.4
D4	5.3	23.6	19.8	51.4
D5	5.0	28.3	20.1	46.6

Explanation: 0 - soil before starting the experiment, D1-D5 - doses of BAs: 0.5, 1.0, 1.5, 2.0, and 2.5 Mg ha^{-1}, respectively. F1-exchangeable/extractable fraction, F2- reducible fraction, F3- oxidizable fraction, F4- residual fraction.

Table S6. Percent share of BCR fractions in the total Pb content.

Variant	F1	F2	F3	F4
0	0.0	61.3	6.1	32.5
Control	0.0	64.4	5.3	30.3
NPK	0.0	62.2	6.6	31.2
D1	0.0	59.7	6.5	33.8
D2	0.0	57.9	6.5	35.6
D3	0.0	62.3	8.1	29.6
D4	0.0	61.9	6.9	31.2
D5	0.0	62.8	7.4	29.9

Explanation: 0 - soil before starting the experiment, D1-D5 - doses of BAs: 0.5, 1.0, 1.5, 2.0, and 2.5 Mg ha^{-1}, respectively. F1-exchangeable/extractable fraction, F2- reducible fraction, F3- oxidizable fraction, F4- residual fraction.

Table S7. Percent share of BCR fractions in the total Cd content.

Variant	F1	F2	F3	F4
0	0.7	60.1	0.0	39.1
Control	1.1	59.3	0.0	39.6
NPK	1.4	67.6	0.0	31.0
D1	1.0	82.4	0.0	16.6
D2	1.4	89.7	0.0	8.9
D3	1.0	81.2	0.0	17.8
D4	1.0	79.6	0.0	19.4
D5	0.4	75.5	0.0	24.2

Explanation: 0 - soil before starting the experiment, D1-D5 - doses of BAs: 0.5, 1.0, 1.5, 2.0, and 2.5 Mg ha^{-1}, respectively. F1-exchangeable/extractable fraction, F2- reducible fraction, F3- oxidizable fraction, F4- residual fraction.