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Article

Metallurgical Waste for Sustainable Agriculture: Converter Slag and Blast-Furnace Sludge Increase Oat Yield in Acidic Soils

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Abstract: The study is the first to examine the combined use of blast-furnace sludge as a source of microelements and converter slag as a soil-deoxidizing agent in oat (*Avena sativa* L.) cultivation in sod-podzolic soils. It has been established that blast-furnace sludge is a highly dispersed waste, which contains about 50% iron, 7% zinc, and a small amount of calcium, silicon, magnesium, aluminum, and sulfur. Hazardous components such as lead, arsenic, etc., are not detected. Converter slag comprises porous granules up to 3 mm in size, consisting mainly of calcium compounds (CaO, $Ca(CO)_3$, $CaSiO_3$, $CaFe_2O_4$) and a small amount of Mn, Al, and Mg trace elements. In a laboratory experiment, blast-furnace sludge increased the germination of oats by 5–10%, regardless of the addition of a deoxidizer (slag), but at the same time suppressed the growth of stem length by a maximum of 18% at 1 $g \cdot kg^{-1}$. The addition of slag raised substrate pH and increased the index by 8% at a sludge concentration of 0.1 $g \cdot kg^{-1}$. Root length in deoxidizer-free variants increased by 50–60% and with the addition of slag by 27–47%. Root dry mass also increased under the addition of sludge by 85–98%; however, the addition of slag reduced the indicator to the control level. In a field experiment with the combined application of waste, an increase in yield by more than 30% was shown. When soil was treated with slag and sludge, the height of plants increased by an average of 18%. It should be noted that the introduction of waste did not affect the quality of the grain. The use of slag increased the lead content in the soil, which is probably due to the sorption properties of calcium compounds in the slag, since lead was not found in the analyzed waste. Presumably, lead is sorbed by slag from the lower soil horizons, concentrating and immobilizing it in the upper layer. This version is supported by the absence of lead accumulation in straw and oat grain. The zinc-containing sludge increased the content of this element by 33% in the soil, as well as by 6% in straw and by 14% in grain. Thus, we found that the studied metallurgical wastes can be used as nutrients for agriculture, both individually and jointly. Overall, the proposed approach will contribute both to reducing the amount of accumulated waste and to improving the efficiency and sustainability of agricultural production and CO_2 sequestration. However, the features of the accumulation of heavy metals in soil and plants under the influence of the analyzed types of waste require more in-depth study, including within the framework of long-term field experiments.

Keywords: blast-furnace sludge; converter slag; acidic soils; crop production; micronutrient fertilizer; soil deoxidizer; *Avena sativa* L.

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1. Introduction

One of the key principles of sustainable agriculture is to increase resource efficiency [1]. The chemical production of fertilizers is a powerful source of environmental pollution, including greenhouse gasses [2]. Therefore, a promising sustainable approach is the use of industrial waste in agriculture [3].

The metallurgical industry is one of the most waste-intensive industries [4,5]. Among the main wastes of metallurgy slag, ash, sludge, scale, crumbs, shavings, cuttings, residues, etc., can be distinguished [6,7]. Because these wastes can pose a serious threat to ecosystems, their safe disposal is vital [5]. At the same time, metal-containing wastes are of great value for recycling [8,9]. For example, highly dispersed electric steel-smelting, converter, and open-hearth ash and sludge are characterized by a high content of iron (up to 40–50%), as well as metals such as zinc, copper, nickel, lead, cadmium, etc. However, these wastes, which are potentially iron-rich metallurgical raw materials, cannot be used in the blast-furnace sintering process without additional processing due to the high zinc content (more than 0.5%), which destroys the lining of blast furnaces [10]. In this connection, at many metallurgical enterprises, waste disposal is carried out by placing it in sludge collectors and dumps.

Metallurgical wastes, in particular blast-furnace sludge, have a rich elemental composition [11,12], which makes them a promising source of trace elements in crop production [13]. It is well known, for the proper development of a plant, N, P, S, K, Mg, and Ca macroelements and Fe, Zn, Mo, Cu, Mn, Cr, Ni, and B microelements are necessary. These elements play an important structural and physiological role in the vital activity of plant cells. In addition, they serve as a part of the compounds responsible for photosynthetic reactions and osmoregulation. The activity of bioelements is mainly associated with the regulation of biochemical processes at the cellular level and the activation of plant enzymes [14]. Blast-furnace sludge, which contains a number of elements important for plants such as Fe, Zn, Mn, Cu, etc., could become a cheap substitute for microelement fertilizers. However, despite the prospects of this topic, there are practically no works on the study of the effect of metallurgical sludge on plants. A small number of studies have shown the positive effects of metal-containing sludges on crops. For example, Anderson and Parkpian [13] showed that Fe-containing smelter residues reduce Fe chlorosis in sorghum grown in Fe-deficient calcareous soil [13]. Previously, we showed a positive effect of blast-furnace sludge at application rates of 0.5 and 2 $t \cdot ha^{-1}$ on the biological and economic productivity of spring and common flax rape in medium loamy soils [15,16].

Soil acidification is the process by which soil pH decreases over time. Among the factors contributing to soil acidification are the application of ammonium-based nitrogen fertilizers in large quantities on naturally acidic soils; the leaching of nitrate nitrogen, originally used as ammonium-based fertilizers; the collection of plant materials; etc. [17]. Traditionally, calcareous materials have been used to neutralize acidic soils and overcome problems associated with soil acidification [18]. The most commonly used liming materials are ground limestone, dolomitic ground limestone, chalk, ground chalk, burnt lime, and hydrated lime [19]. Among the materials used for soil deoxidation, steelmaking slag can also be distinguished [20], the main components of which are CaO, SiO_2, Al_2O_3, MgO, and iron oxides [21].

The application of slag helps to increase the pH and availability of nutrients such as Ca, Mg, and Si in soil, which leads to an increase in the uptake of these elements by plants, promoting crop growth and yield [22]. For example, Mohammadi Torkashvand and Shahram showed an increase in soil pH in proportion to the amount of slag used [23]. The authors also found a decrease in the availability of Fe in the pH range of 7.4–8.5 and an increase at higher pH. Also, the use of slag increased the availability of P and Mn. In greenhouse studies, applications of 1 and 2% (w/w) slag to different soil types (pH 4.1 and 6.7) increased the dry mass of corn shoots and the uptake of P and Mn. Fe and K uptake increased in soil with pH 6.7, while K uptake decreased in soil with pH 4.1 and Fe uptake did not change. Silica-based slag fertilizers applied to silicon-deficient soil improved rice growth and yield, as well as plant resistance to brown spots [24]. Other authors have shown an increase in base saturation and availability of Si and P in soil [25], as well as an increase in rice yield and Si content in rice straw [25,26] under the influence of silicon-containing slag. A pot experiment with nutrient-poor substrates and electric arc furnace slag found an improvement in soil mineral composition, an increase in aboveground corn biomass, and an improvement in photosynthesis parameters [27]. Slag silicon can increase plant resistance to excess Fe and Mn [28], as well as Cd, Zn, and Al [29]. The addition of 3% and 5% crushed granulated blast-furnace slag to silty gravel sand contaminated with 1.5 mg kg^{-1} Cd increased the *Pinellia ternata* leaf area index by 29% and 30%, and the root area index by 65% and 66%, respectively, compared to controls [30]. The soil with the addition of 3% and 5% slag showed a higher water retention ability and air-entry value.

The advantage of using metallurgical slags in agriculture is the reduction in greenhouse gas emissions due to carbonization processes in the soil [31]. In addition, the agricultural use of micronutrient-rich waste can contribute to solving the problem of mineral depletion in food products [32]. Generally, agricultural use of metallurgical waste is a sustainable approach. It is worth noting that the proposed by-products do not contain such dangerous heavy metals as Cd, As, Hg, and Pb [15,16,33,34]; however, as mentioned earlier, blast-furnace sludge contains Zn, which in high doses can have a phytotoxic effect, especially in acidic soils [35].

Since the joint effect of blast-furnace sludge as a source of trace elements and converter slag as a soil conditioner that increases the bioavailability of microelements has not yet been assessed on agricultural crops, we studied the effect of blast-furnace sludge on spring oat (*Avena sativa* L.) plants under conditions of an acidified substrate using converter slag as a lime.

2. Materials and Methods

2.1. Waste Characterization

Dried sludge from the wet gas cleaning of a blast-furnace shop and converter slag from metallurgical production were used in the work. To analyze the morphology and elemental composition of waste samples, a JEOL JCM-7000 scanning electron microscope (JEOL, Tokyo, Japan) was used. The elemental composition was determined using an energy dispersive analysis attachment based on a silicon drift detector (SDD) (JEOL, Tokyo, Japan).

The study of the qualitative phase composition was carried out by X-ray diffraction using a Difray 401 diffractometer (JSC Scientific Instruments, St. Petersburg, Russia). The interpretation of the diffraction patterns obtained during the study was carried out using Match! 3.0 software (Crystal Impact, Bonn, Germany) https://crystalimpact.com/match/download_previous_version.htm, accessed on 7 November 2024.

2.2. Laboratory Experiment

During the laboratory experiment, the influence of blast-furnace sludge as a source of microelements was studied under conditions of model acidified soil (sand), as well as during the neutralization of the substrate acidity with converter slag on spring oats (Lev variety, intensive type, recommended for cultivation in the North-Western region). Disinfection was carried out by calcining sand in a dry-heat oven, GP-40 SPU (JSC "Smolensk SDTB SMS" Smolensk, Russia). The sand was placed in 0.5 L plastic containers, where seeds were subsequently sown in the amount of 30 pcs. per container.

The introduction of waste was carried out by uniform spraying on the soil surface. Sludge concentrations were 0.01, 0.1, and 1 g·kg^{-1} (taking into account the maximum permissible concentrations (MPCs) for zinc in soil); slag's concentration was 0.8 g·kg^{-1} (up to an increase in the acidity of the aqueous extract of ~6). Sand was used as a control substrate (pH_{KCl}~4.5) without adding waste (for analyzing the effect of blast-furnace sludge in acidified soil) and sand (pH_{KCl}~4.5) with the addition of slag (for the analysis of the effect of blast-furnace sludge in the soil, neutralized by slag).

The studies were carried out in accordance with GOST R ISO 22030-2009 in laboratory conditions at +18 to 22 °C ambient temperature, 80 ± 5% relative air humidity, 84–106 kPa (630–800 mm Hg) atmospheric pressure, and 5000 lux illumination. The cultivation time was 14 days.

In the course of the laboratory experiment, the effect of blast-furnace sludge on germination rates, morphometric characteristics, and growth of spring oats' biomass was assessed. Chlorophyll fluorescence of plants has been used as an indicator of environmental stress. The photosystem II (PS II) Qy was measured with a PAM-fluorometer FluorPen FP S100 (Photon Systems Instruments, Drasov, Czech Republic) according to the manufacturer's protocol.

To assess the bioaccumulation of waste components, roots, and stems, an elemental analysis of the plants treated with sludge (1 $g \cdot kg^{-1}$) and sludge (1 $g \cdot kg^{-1}$) + slag was carried out. The samples were subjected to thermal annealing to determine the elemental composition of mineral compounds. Annealing was carried out in a muffle furnace at a heating rate of 2.5 $°C \cdot min^{-1}$ while maintaining a temperature regime of 600 °C for an hour. Samples were air-cooled and subjected to an integrated elemental analysis using energy dispersive X-ray spectroscopy (EDS) on a scanning electron microscope, Merlin (Carl Zeiss, GmbH, Germany), with an energy dispersion analyzer, "10 mm^2 SDD Detector—X-Act" (Oxford Instruments, Abingdon, Oxfordshire, Great Britain).

2.3. Field Experiment

This research was conducted in 2022 on the experimental field of the Vologda State Dairy Academy named after N.V. Vereshchagin, in a long-term agrochemical experiment (Figure 1). The soil of the plots was soddy-podzolic with the reaction of the soil medium of pH_{KCl}~4.5, 0.182% of total nitrogen content, 237 $mg \cdot kg^{-1}$ of the mass fraction of mobile phosphorus, 133 $mg \cdot kg^{-1}$ of mobile potassium, 1.9% of organic matter, more than 60 $mg \cdot kg^{-1}$ of the mass fraction of mobile sulfur, and 2.4% of humus.

The weather conditions during the research period were generally typical for the North-Western region of Russia. Thus, in May, the actual temperature was 12.5 °C, while the total precipitation was 65 mm (the norm is 48 mm). In June, according to observations, the temperature was 19.9 °C, and precipitation was 31 mm (49% of the norm). According to observations, the actual temperature in July was 19.8 °C, the norm of precipitation in July was 74 mm, and 27 mm of precipitation fell. The actual temperature in August was 16.3 °C, and precipitation was 139 mm, while the norm is 71 mm.

The seeds were sown on the date 31.05, and the seeding rate was 6 million seeds per hectare. The site was leveled prior to the commencement of work. The tillage included spring plowing, cultivation, and the application of mineral fertilizers ($N_{80}P_{40}K_{100}$). Before laying out the experiment, the soil was once again cultivated. The experimental area was divided into rectangles with an area of 100 m^2 (20 × 5 m), on which different doses of sludge were applied.

The experiment was conducted in an 8-field crop rotation, and the predecessor was potatoes. The experiment was repeated four times, and the plots were randomized.

For the study, 0.8 $g \cdot kg^{-1}$ (2.4 $t \cdot ha^{-1}$) slag and 1 $g \cdot kg^{-1}$ (3 $t \cdot ha^{-1}$) sludge were taken. The recalculation of waste application rates in $t \cdot ha^{-1}$ was carried out taking into account the average density of 1–1.5 $g \cdot cm^3$ podzolic soils prevailing in the Vologda region and a 30 cm arable layer depth. The application was carried out once before laying out the experiment. Absolute control soil was not treated with waste, and control soil was treated with slag.

Accounting indicators: yield, plant height, and net photosynthesis productivity (increase in dry weight of plants in grams per day); protein content was measured according to Kjeldahl [36].

An analysis of heavy metals' content in the soil and plants after the experiment was carried out by atomic absorption spectrometry on an MGA 1000 instrument (Lumex, St. Petersburg, Russia).

Figure 1. Experimental field.

2.4. Statistical Analysis

The descriptive statistics methods used included the estimation of the arithmetic mean (M) and standard deviation (S) calculated in Excel 2007 MS Office 2007 (Microsoft Corporation, Redmond, WA, USA). The ANOVA F-test was used to determine the statistical significance of differences between the qualitative variables of the study groups at significance level $p = 0.05$. The ANOVA F-test was selected because of its widespread use in agricultural research [37].

3. Results

3.1. Results of Waste Characterization

The electron microscopic analysis of blast-furnace sludge showed that the sample was a highly dispersed powder consisting of particles of various sizes and irregular shapes (Figure 2a). As it can be seen from the presented micrographs, the size of individual granules does not exceed 500 µm. It was noted that the surface of large particles is covered with a significant number of inclusions less than 1 µm. An integrated energy dispersive X-ray analysis (EDRS) was carried out in three different sites of the sample, and the results are presented in Figure 2a. As it can be seen in the table, iron (48.89 wt%) was the predominant element, in addition to carbon and oxygen. The sludge contained silicon (3.4 wt%), zinc (7.44 wt%), calcium (3.42 wt%), and other elements (1 wt%). The X-ray diffraction method was used to analyze the phase composition of the blast-furnace sludge. It was established that the sample contained phases of iron oxide (Fe_2O_3), zinc ferrite ($ZnFe_2O_4$), and carbon (C). These phases describe almost all reflections present in the diffraction pattern.

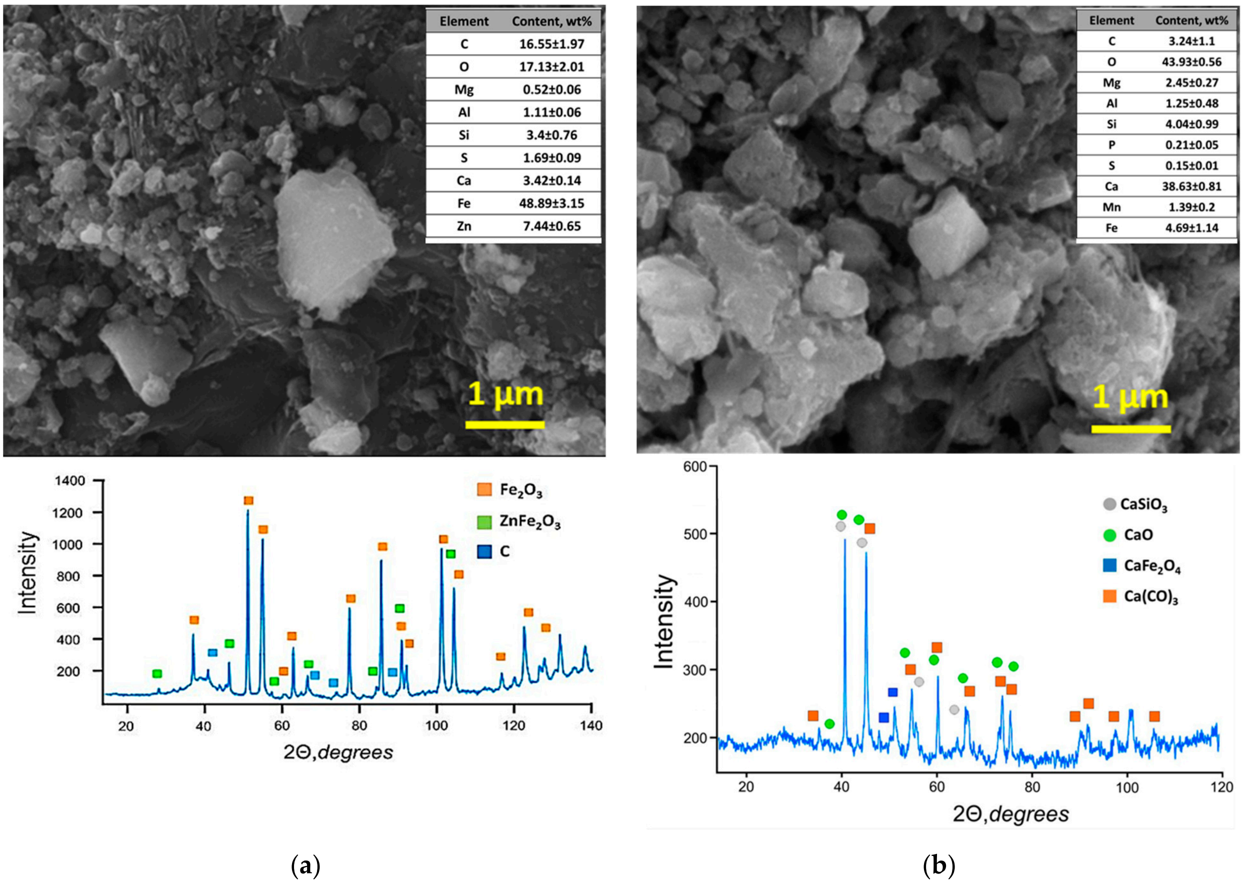

Figure 2. Waste characterization: (**a**) SEM micrograph with elemental composition and diffraction pattern of blast-furnace sludge sample; (**b**) SEM micrograph with elemental composition and diffraction pattern of converter slag.

In contrast to blast-furnace sludge, the microstructure of the slag sample was characterized by a large size of inclusions. Individual granules had an irregular shape, and objects less than 1 micron were observed on the surface of large particles (Figure 2b). The average particle size of the slag was in the range of 1–3 mm.

The elemental analysis of the converter slag sample showed that the predominant elements were calcium (38.63 wt%) and oxygen (43.93 wt%). It is known that calcium in the composition of the slag presented mainly in the form of an oxide. The presence of iron (Fe), silicon (Si), and magnesium (Mg) in 4.69, 4.04, and 2.45 wt%, respectively, was also shown. The diffraction pattern of the slag sample showed that calcium in the waste was present in the forms of oxide (CaO), carbonate ($Ca(CO)_3$), silicate ($CaSiO_3$), and ferrite ($CaFe_2O_4$).

Thus, the analysis of waste samples showed that blast-furnace sludge is a highly dispersed waste, which contains about 50% iron, 7% zinc, and a small amount of calcium, silicon, magnesium, aluminum, and sulfur. Hazardous components such as lead, arsenic, etc., were not found. Converter slag comprised porous granules up to 3 mm in size, consisting mainly of calcium compounds (CaO, $Ca(CO)_3$, $CaSiO_3$, $CaFe_2O_4$) and a small amount of Mn, Al, and Mg trace elements.

3.2. Results of Laboratory Experiment

The evaluation of spring oats' germination in a laboratory experiment showed a stimulating effect of the analyzed waste (Figure 3a). In the groups cultivated without the addition of slag, the germination increased in proportion to the decrease in the dose of sludge, reaching a maximum at 0.01 $g \cdot kg^{-1}$ (10% increase), while at 1 $g \cdot kg^{-1}$ of sludge in the substrate, germination increased only by 6%. When cultivating plants in a substrate containing converter slag, the germination rate increased by 10% at all sludge concentrations.

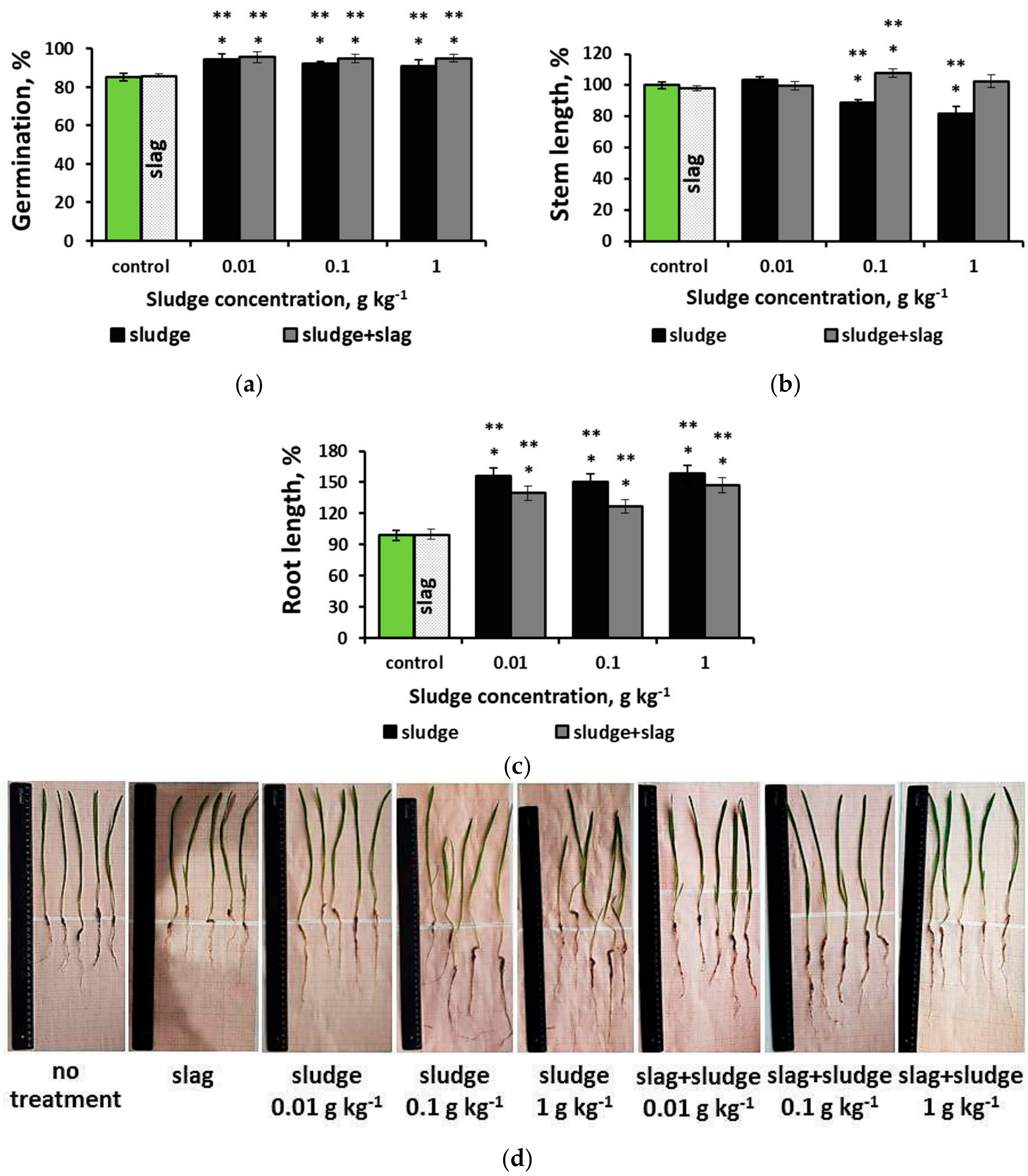

Figure 3. Morphophysiological parameters of oats: (**a**) germination; (**b**) average stem length; (**c**) average root length; (**d**) experimental plants. The * symbol marks significant differences with the control at a significance level of $p < 0.05$. *—differences from the untreated variant, **—differences from the slag-treated variant.

The development of oat stalks was suppressed by blast-furnace sludge, and the average length of the ground part of seedlings decreased by 11% when using 0.1 g·kg^{-1} and by 18% when using 1 g·kg^{-1} of sludge (Figure 3b,d). Against the background of slag, the length of the stem did not differ from the control at 0.01 and 1 g·kg^{-1} of sludge, but increased by 8% at 0.1 g·kg^{-1}. The growth of the root system was noticeably stimulated by blast-furnace sludge (Figure 3c,d). The maximum increase (+50–60%) was noted in deoxidizer-free variants. The introduction of slag reduced the difference with the control values to +27–47%.

An analysis of the biomass growth showed the absence of a pronounced effect of the analyzed metallurgical waste on the average weight of the stems (Figure 4a).

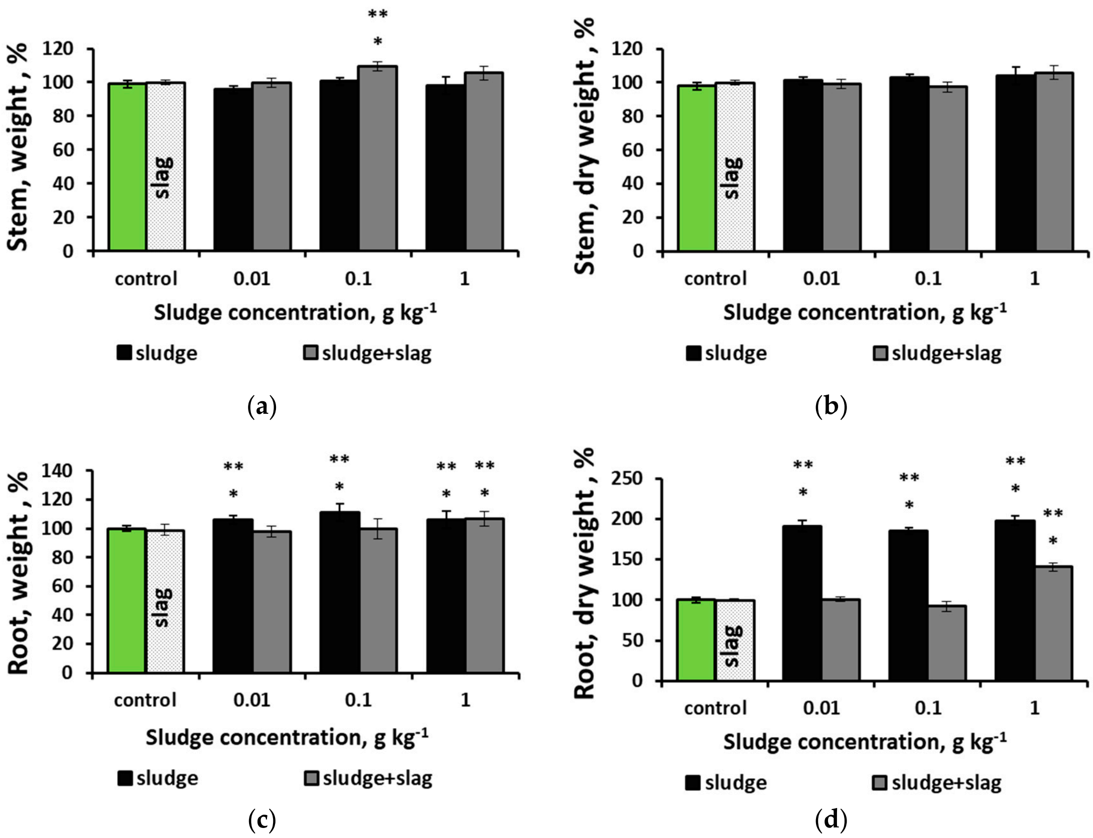

Figure 4. Weight of spring oat: (**a**) raw stem weight; (**b**) dry stem weight; (**c**) raw root weight; (**d**) dry root weight. The * symbol marks significant differences with the control at a significance level of $p < 0.05$. *—differences from the untreated variant, **—differences from the slag-treated variant.

However, as can be seen from the diagrams presented in Figure 4b, blast-furnace sludge stimulated an increase in root mass, and the maximum indicators were noted in the options without the addition of slag. The root raw mass index increased by 6–11% (Figure 4c), and the root dry mass index increased almost two times (Figure 4d). For the medium containing 1 g·kg^{-1} of sludge, the increase was 40% compared to slag.

Assessment of the effect of metallurgical waste on the efficiency of PS II (Fv/Fm parameter) did not reveal significant differences from control values, which can serve as one of the indicators of the absence of stress for plants when sludge and slag are introduced into the substrate.

The preliminary analysis of the bioaccumulation of hazardous waste components, in particular zinc, showed the presence of the element (highlighted with a red circle) in the roots of plants grown with the addition of sludge in the maximum concentration (Figure 5c). Moreover, as can be seen from the figures, the intensity of the X-ray peak of Zn is significantly higher in the option treated with sludge only. That is, it can be assumed that under the influence of sludge, the bioaccumulation of Zn decreases. Also, the presence of aluminum (highlighted with a red circle) was recorded in the roots of plants of the sludge + sludge group (Figure 5e).

Summarizing the results of assessing the impact of metallurgical waste on the spring oat crop in a laboratory experiment, the following can be distinguished. Blast-furnace sludge increases the germination of oats by 5–10%, regardless of the application of the ameliorant. At the same time, the growth of stem length was suppressed by 11% and 18% with the application of 0.1 and 1 g·kg^{-1} sludge, respectively. The introduction of a deoxidizer increased the index by 8% at a sludge concentration of 0.1 g·kg^{-1}. With some suppression of shoots' aerial part development, the blast-furnace sludge had a favorable effect on the development of the oat root system. Thus, root length in the deoxidizer-free variants increased by 50–60%, the introduction of slag reduced the difference with the control to +27–47%, and treatment with sludge increased root mass by 6–11%. For dry biomass, a similar trend was observed. The introduction of sludge increased the dry root biomass by 85–98%, and the introduction of an ameliorant reduced the positive effect of sludge on the growth of oat roots. It is worth noting that it was in the roots of plants grown in the presence of sludge that zinc accumulation was recorded, while the addition of sludge reduced the amount of Zn in the roots.

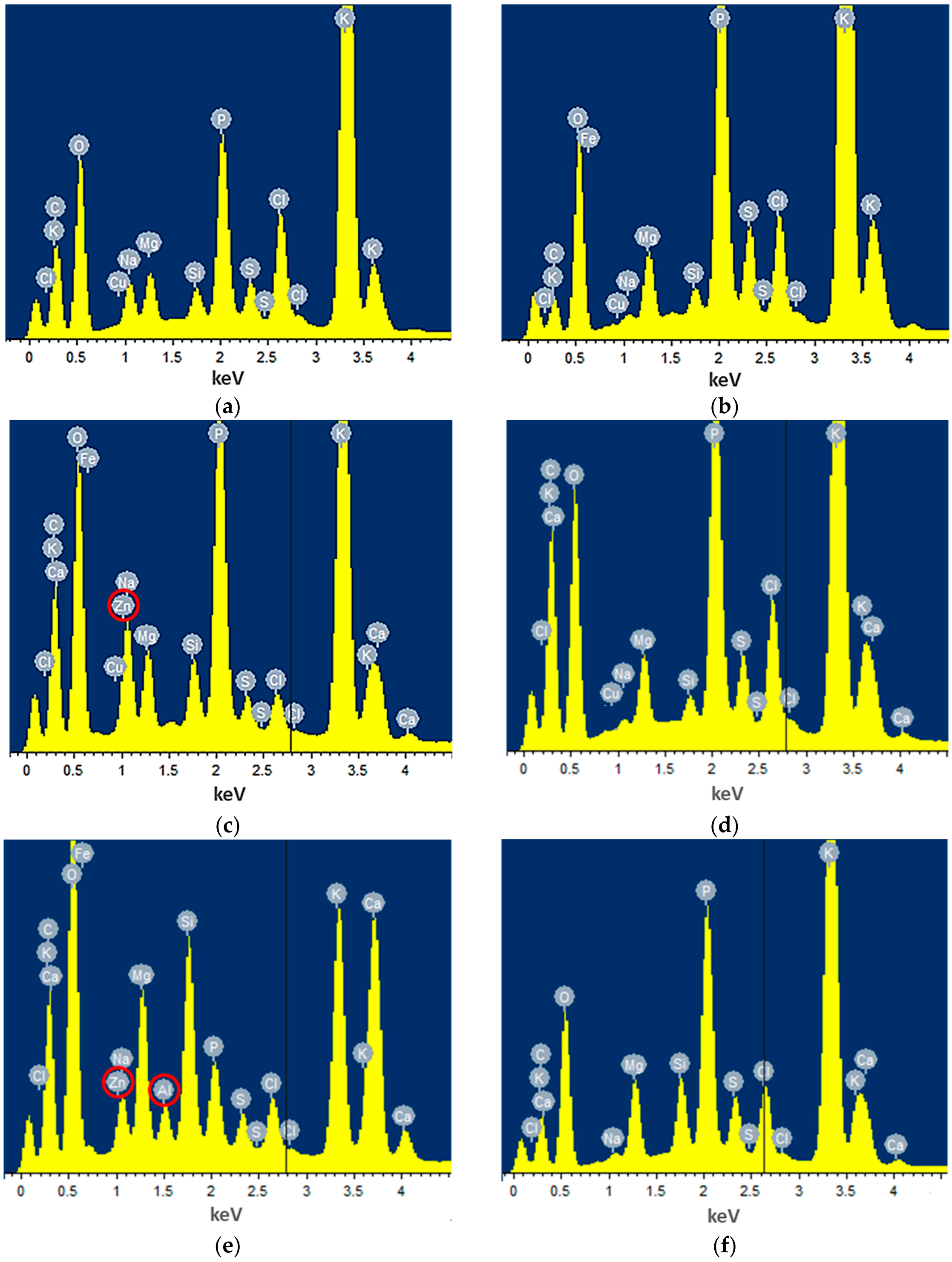

Figure 5. Elemental analysis of plants: (**a**) root, control; (**b**) stem, control; (**c**) root, sludge; (**d**) stem, sludge; (**e**) root, slag + sludge; (**f**) stem, slag + sludge.

3.3. Results of Field Experiment

The same duration and no deviations of the main development phases of spring oat plants were shown in all experimental variants. The evaluation of the crop yield showed high values in the control, 2.98 t·ha^{-1} (Figure 6a). Treatment with slag and sludge in various combinations increased the yield by 0.42–0.95 t·ha^{-1}. The maximum indicators were noted for the joint introduction of waste.

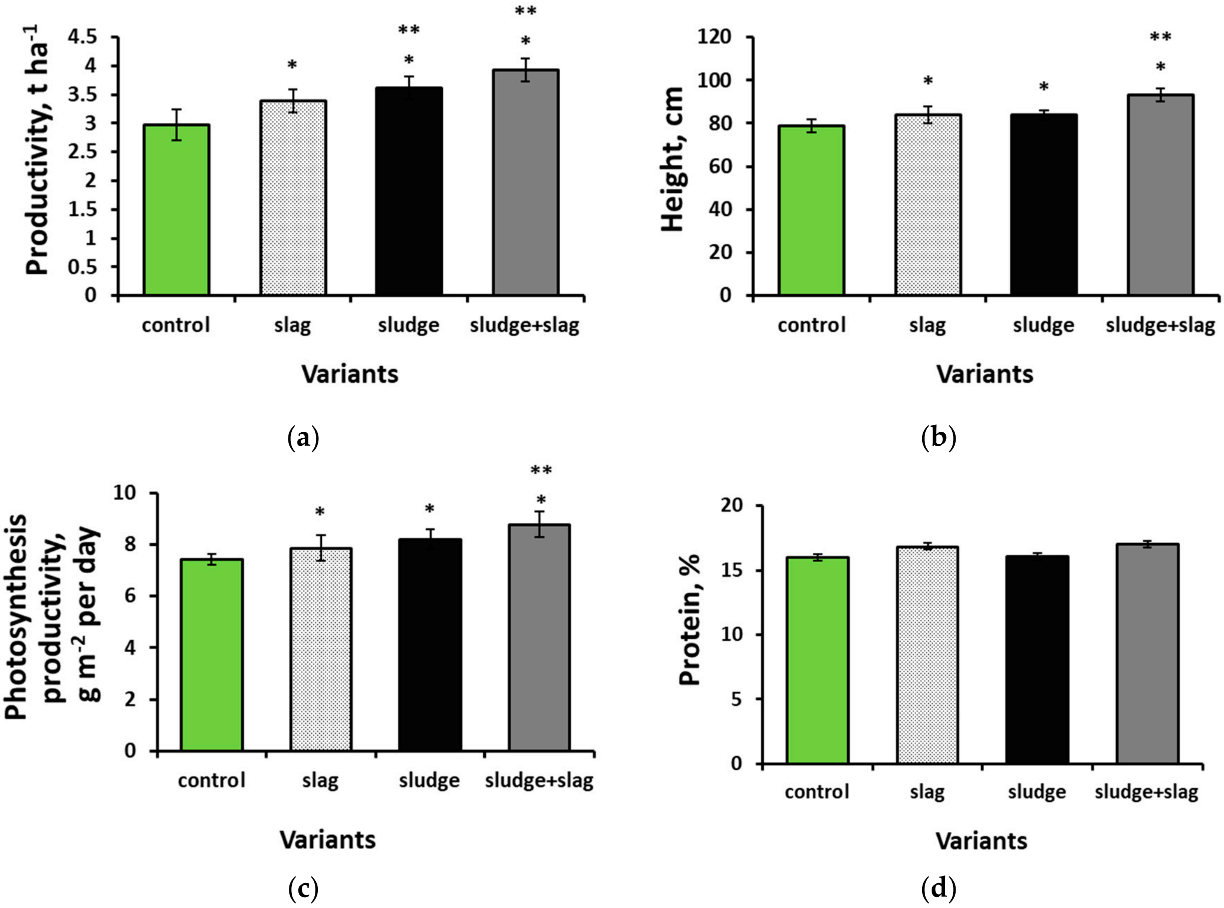

Figure 6. Productivity and crop quality indicators of spring oats: (**a**) yield; (**b**) height of plants; (**c**) net photosynthesis productivity; (**d**) protein content in grain. The * symbol marks significant differences with the control at a significance level of $p < 0.05$. *—differences from the untreated variant, **—differences from the slag-treated variant.

The higher yield of oats with the use of ameliorants can be explained by the more powerful growth and development of crop plants in these variants. So, when the soil was treated with slag and sludge separately, the height of plants increased by an average of 5 cm, and with the combined use of sludge and slag by 14 cm (Figure 6b). According to the same regularity, the rate of net photosynthetic productivity increased (Figure 6c). The analysis of the protein content as one of the main indicators of oat grain quality showed a slight increase in slag-treated plants (Figure 6d).

At the end of the experiment, the acidity of the salt extract of soil from experimental plots treated with slag averaged ~5.5. The soils from the experimental plots were analyzed for the content of heavy metals and arsenic. The results of the study are shown in Table 1.

Table 1. The content of heavy metals and arsenic in waste-treated soil samples, mg·kg^{-1}.

Indicator	Cd	As	Hg	Pb	Zn	Cu	Mn	B ***
control	0.21 ± 0.06	3.10 ± 0.40	<0.02	3.19 ± 0.73	11.98 ± 3.93	3.0 ± 0.7	95.2 ±10.27	1.0 ± 0.32
slag	0.28 ± 0.07	2.87 ± 0.11	<0.02	4.08 ± 1	13.93 ± 4.6	3.17 ± 0.73	113 ± 12.9	0.52 ± 0.16
sludge	0.27 ± 0.05	3.0 ± 0.14	<0.02	3.42 ± 0.9	16.06 ± 4.4	5.02 ± 1.23	97.21 ± 11.23	0.91 ± 0.12
sludge + slag	0.29 ± 0.08	2.90 ± 0.38	<0.02	4.27 ± 1.11	15.90 ± 5.6	4.91 ± 1.36	108.43 ± 13.11	0.84 ± 0.16
MPC/APC * SanPiN 1.2.3685-21 **	-/1.0	-/5.0	2.1/-	-/65.0	-/110.0	-/66	1500/-	-

* MPC—maximum permissible concentration/APC—approximately permissible concentration. ** Sanitary and Epidemiological Norms, hygienic standards, and requirements for ensuring the safety and (or) harmlessness of environmental factors for humans [38]. *** Mobile.

The addition of metallurgical by-products to the soil did not affect the content of Cd, As, and Hg, but increased the content of elements present in their composition. Thus, the zinc content increased by 33% when adding blast-furnace sludge, and the amount of manganese increased by 18% when treating the soil with slag. It is worth noting a significant increase in the level of lead under the influence of slag and copper in the variants with sludge, and these elements were not found in the composition of the waste. Also, the analysis noted a decrease in the boron content when deoxidizing the soil with slag.

Generally, the use of waste did not cause the excess of Russian MPC/APC (SanPiN 1.2.3685-21) [38].

According to the results of the analysis of the bioaccumulation of hazardous waste components in plants grown in pots (laboratory experiment), zinc accumulation in plant roots was recorded. In the field experiment, the content of this element in straw and oat grains was analyzed. In addition, we analyzed the content of lead, cadmium, arsenic, and mercury (Table 2).

Table 2. Change in the content of heavy metals and arsenic in plants under the influence of waste, mg·kg^{-1}.

Element	Control		Slag		Sludge		Sludge + Slag		MPC
	Straw	Grain	Straw	Grain	Straw	Grain	Straw	Grain	
Pb	0.14 ± 0.04	0.15 ± 0.05	0.15 ± 0.05	0.15 ± 0.06	0.17 ± 0.07	0.16 ± 0.04	0.16 ± 0.08	0.16 ± 0.07	0.2 *
Cd	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.1 *
As	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.2 *
Hg	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.03 *
Zn	12.38 ± 0.6	15.86 ± 0.5	12.7 ± 0.3	16.01 ± 0.4	13.11 ± 0.6	18.16 ± 0.5	12.45 ± 0.5	16.73 ± 0.7	50 **

* Codex Alimentarius Commission (Codex) (1993, 2021) [39,40]. ** SanPiN 42–123–4089–86 (maximum permissible concentrations of heavy metals and arsenic in food raw materials and foodstuffs) [41].

The data obtained during the analysis of heavy metal accumulation did not show any significant increase in elements in straw and oat grain when cultivating plants in soils with metallurgical waste. As an exception, the content of zinc in grain increased by 14% relative to the control in the option with sludge. As in the laboratory experiment, the addition of slag reduced this indicator. In general, it should be noted that there were no excesses of heavy metal and arsenic content standards in plant products (according to Russian and international regulatory documents).

4. Discussion

The results we obtained generally showed a beneficial effect of treating substrates with metallurgical by-products on the growth and development of oat plants. The positive effect of blast-furnace sludge on plants can be explained by the content of iron, zinc, manganese, etc., trace elements important for plant development. Thus, iron is one of the most important nutrients for plants, and its absence dramatically affects the growth of crops [42]. Iron, as a significant cofactor for enzymes, plays an important role in the regulation of plant photosynthesis, mitochondrial respiration, nucleotide synthesis and repair, and metal homeostasis, especially in maintaining the structural integrity of various proteins [43,44]. Zinc is a cofactor located at the active site of chloroplast b-carbonic anhydrase (b-CA), which catalyzes the rapid reversible interconversion of HCO_3^- and CO_2 and supplies RuBisCO with CO_2 [45]. Zinc finger proteins, one of the largest families of transcription factors known for their finger-like structure and ability to bind Zn^{2+}, play an important role in plant resistance to abiotic stress [46]. Manganese is involved in a number of processes that regulate plant growth and development. Specifically, it initiates photosynthesis through the water splitting reaction in photosystem II [47–49]. The composition of slag can also contribute to better growth and development of plants. Calcium, which is the main element in the composition of the waste, is necessary to perform various structural functions in the cell wall and membranes [50,51]. Silicon mitigates the toxic effects caused by abiotic stresses and also increases plant viability [52,53]. There is evidence that silicon increases the availability of Ca, P, S, Mn, Zn, Cu, and Mo [54]. Magnesium is an essential nutrient for a wide array of fundamental physiological and biochemical processes in plants [55]. In our study, under laboratory conditions, the germination of oat seeds increased under the influence of sludge. As the elemental analysis of this by-product showed, it largely consists of iron compounds, which is a stimulator of plant growth and seed germination [56]. In addition, seed treatment with highly dispersed iron can not only affect seed germination, but also the strength of germination, growth rate, yield, and concentration of micronutrients and protect seedlings from the negative impact of unfavorable factors [57]. Other authors have shown that treatment with nanodispersed Fe_2O_3 particles at concentrations of 200 and 400 ppm significantly increased seed germination and growth of wheat seedlings [58], and the most favorable dose for the germination of alfalfa seeds was 50 ppm [59]. In addition, there is evidence that treating seeds with zinc can also increase germination [60]. Also, in our laboratory experiment, blast-furnace sludge significantly increased the growth of dry mass of roots in an acidified substrate, and the addition of slag neutralized the effect of the sludge, reducing the indicators to control values. The observed effects are probably related to the accumulation of zinc when applying the sludge. Similar effects were obtained on sugar beet plants, when the application of zinc fertilizers promoted the accumulation of dry matter in the roots with an increase in the Zn content in the root crops [61]. Soil deoxidation with slag reduced the zinc concentration in roots, which is probably due to a decrease in Zn bioavailability with increasing soil pH [62,63].

We did not observe the suppression of photosystem II activity by metallurgical waste, which may indicate the absence of abiotic stress in plants [64–66]. Chlorophyll fluorescence is one of the most utilized ecophysiological techniques to study the photosynthetic process in plants [67]. Values of Fv/Fm range typically between 0.75 and 0.85 [68], which is comparable to the results of our measurements.

In field experiments, treatment with by-products increased the biological and economic productivity of oats, with the maximum increase in yield and plant height observed with the combined use of waste. In addition, our study noted an increase in net photosynthetic productivity under the influence of waste, which is important when using plants for CO_2 sequestration [69–71].

The treatment of soil with metallurgy waste had no effect on the content of Cd, As, and Hg. At the same time, we recorded a significant increase in the level of lead when treating the soil with slag, and in the option treated with sludge, copper was also detected. It is important to note that these elements were not detected in the composition of the waste. It can be assumed that the increase in the concentration of lead may be associated with the sorption properties of calcium compounds in the slag [72–74]; i.e., slag particles, sorbing lead ions, concentrate it in the upper soil layers. The most probable mechanisms for increasing the ability to immobilize heavy metals during CaO processing may be the adsorption and retention of heavy metals in newly formed aggregates [75]. It is also evident that lead accumulation in soil horizons depends on the acidity index. In the upper soil horizon, lead accumulates more intensively in a neutral and alkaline environment [76–78].

The soil firmly binds lead, which protects groundwater and vegetation from contamination, which is confirmed by our results of the analysis of lead accumulation in the organs of oat plants, where no increase in the metal content was noted when cultivating plants with waste. At the same time, the data obtained in the work on the lead content in the soil require further detailed study to identify the mechanisms of element migration in soil horizons depending on various factors, including acidity.

The analysis also showed an increase in the zinc content in the soil by 33% relative to the control when adding blast-furnace sludge; however, indicators within 16 mg·kg^{-1} (maximum values in our experiment) are not critical, since according to literary data, the natural concentration of Zn in soil ranges between 10 and 300 mg kg^{-1} with the mean level being 50 mg kg^{-1} [79]. And according to the Russian Sanitary and Epidemiological Norms, approximately permissible concentrations of zinc in acidic soils should not exceed 110 mg kg^{-1}.

Also, during the analysis, a decrease in the content of mobile boron in the soil was noted during deoxidation with slag, which may be due to a decrease in metal mobility with an increase in soil pH [80–82].

The elemental analysis of oat plants showed an increase in zinc content in oat plant organs when the soil was treated with sludge only, by 6% in straw and by 14% in grain. As in the laboratory experiment, an increase in soil pH reduced the bioavailability of zinc and, accordingly, its bioaccumulation. In general, it can be noted that the accumulated concentrations of zinc were very low. According to the Toxnet database of the U.S. National Library of Medicine, the oral LD50 for zinc is close to 3 g kg^{-1} body weight, more than 10-fold higher than cadmium and 50-fold higher than mercury [83].

Summarizing, the physiological effects noted in our study can be explained by the complex interaction of microelements in the composition of metallurgical waste, such as iron, zinc, manganese, calcium, magnesium, silicon, etc., taking into account the pH value of the soil environment.

5. Conclusions

Thus, for the first time, we conducted a study of blast-furnace sludge and converter slag influences on oat plants in laboratory and field experiments. It has been established that blast-furnace sludge is a highly dispersed waste (the size of individual particles is less than 1 μm), which contains about 50% iron, 7% zinc, and a small amount of calcium, silicon, magnesium, aluminum, and sulfur. Hazardous components such as lead, arsenic, etc., are not found. Converter slag comprises porous granules up to 3 mm in size, consisting mainly of calcium compounds (CaO, $Ca(CO)_3$, $CaSiO_3$, $CaFe_2O_4$) and a small amount of Mn, Al, and Mg trace elements.

In the laboratory experiment, blast-furnace sludge increased the germination of oats by 5–10%, regardless of the addition of a deoxidizer (slag), but at the same time suppressed the growth of stem length by a maximum of 18% at 1 g·kg^{-1}. The addition of slag raised substrate pH and increased the index by 8% at a sludge concentration of 0.1 g·kg^{-1}. By suppressing the development of stems, blast-furnace sludge had a beneficial effect on the development of oats' root system. Root length in deoxidizer-free variants increased by 50–60% and with the addition of slag by 27–47%. Root mass also increased under the addition of sludge by 6–11% (raw) and by 85–98% (dry). The addition of slag neutralized the positive effect of sludge on the growth of dry mass of oat roots.

In a field experiment with the combined application of waste, an increase in yield by more than 30% was shown. When soil was treated with slag and sludge, the height of plants increased by an average of 18%. It should be noted that the introduction of waste did not affect the quality of the grain, in particular the protein content.

The use of by-products did not increase the content of Cd, As, and Hg, while sludge treatment increased the content of lead, and slag treatment increased the amount of copper in the soil. It is important to note that lead and copper were not detected in the composition of the analyzed waste. The use of zinc-containing sludge increased the content of the element in the soil by 33%, and the amount of manganese increased when treating the soil with slag. We also noted a decrease in the content of boron when deoxidizing the soil with slag.

The elemental analysis of oat plants showed an increase in zinc content in oat plant organs when the soil was treated with sludge only, by 6% in straw and by 14% in grain.

Despite the recorded increase in the level of some heavy metals relative to the control, all indicators were within the limits of their maximum permissible concentrations in soil and plants.

Thus, we found that the studied metallurgical wastes can be used as nutrients for agriculture, both individually and jointly. In this case, specific soil and climatic conditions, as well as the biological characteristics of the species and variety of cultivated plants, will play an important role, which requires further research. Overall, the proposed approach will contribute to both reduce the amount of accumulated waste and improve the efficiency and sustainability of agricultural production and CO_2 sequestration. However, the characteristics of the accumulation of heavy metals in soil and plants under the influence of blast-furnace sludge require more in-depth study.

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