Granulated Biochar Derived from Chicken Manure as an Alternative Fertiliser for Cereals

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Summary

A three-year field experiment tested single (2021) and double (2022, 2023) tillage with powdered and granular biochar (B, gB, B2x, gB2x) and annual mineral fertiliser (diammofoska, KF). Biochar in powder (B) and granular (gB) forms was produced from chicken manure by slow pyrolysis using silicosol as a binder. Untilled soil served as a control (K). Barley, wheat and oats were cultivated in 2021, 2022 and 2023, respectively. Both tillage regimes with biochar increased soil nutrient contents to levels comparable to triple mineral fertilisation. Pyrolysis decreased total carbon (TC) and total nitrogen (TN) contents by 37% and 24%, respectively, while available phosphorus (AP) and available potassium (AK) increased by 3.4 and 3-fold. Granulation did not significantly alter elemental content or biochar toxicity, which was reduced during pyrolysis, as shown by tests with *Paramecium caudatum* Ehrenberg, 1833 and *Daphnia magna* Straus, 1820. A single biochar application increased barley yield by 50–54%, wheat by 30–34%, and oats by 19–30% relative to the control, producing yields similar to those under KF. Double tillage further raised wheat yields by 60–85% over the control and by 8–24% over KF. In the third year without biochar application, oat yields matched those in the KF treatment. Powdered and granular biochar showed comparable effectiveness in improving crop yields, supporting the use of either form depending on equipment availability.

Key words

powdered biochar, granulated biochar, crop yield, chicken manure, slow pyrolysis

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Introduction

Improving soil fertility is one of the most important current challenges in modern agriculture. One way to increase crop productivity is the use of mineral and/or organic fertilisers. Fertilisers such as urea are the most commonly used traditional nitrogen source. However, urea is rapidly hydrolysed with the release of NH_4^+, and only a small proportion of the nitrogen remains in the soil for a long time (Kamau et al., 2019; Prommer et al., 2014; Sun et al., 2019; Zhang et al., 2021). Often, the lack of nitrogen in the soil is compensated by applying increased doses of fertiliser, which can decrease crop quality, cause eutrophication of surface waters, pollute groundwater and increase emissions of N_2O, a greenhouse gas. Other greenhouse gases (e.g. CO_2, CH_4) can also be emitted by the use of organic residues (manure or litter), originally intended to increase soil organic carbon (González et al., 2015; Hagemann et al., 2018; He et al., 2021; Kour et al., 2020; Pokharel and Chang, 2019; Shi et al., 2020; Sun et al., 2019; Thangarajan et al., 2013). These consequences dictate the need to use fertilisers, from which there is a slow release of organogenic elements. Biochar is an example of such fertilisers, the advantages of the biochar potential as a non-conventional fertiliser are well described in a wide range of publications (Asai et al., 2009; Cornelissen et al., 2013; Ding et al., 2017; J. Gao et al., 2019; Glazunova et al., 2018; Goldan et al., 2022; Juriga et al., 2018; Li et al., 2019; Pokharel and Chang, 2019; Zhang et al., 2012). Biochar is a product of high-temperature oxygen-free decomposition (pyrolysis) of an organic substrate (Kuzyakov et al., 2009; Lehmann, 2007; Lehmann et al., 2011, 2006; Lehmann and Joseph, 2009). Biochar is characterized as a highly porous pyrolysis product rich in macronutrients (C, N, P) and trace elements, which, when applied to the soil, increases crop yield (Bashir et al., 2018; Huggins et al., 2016; Kammann et al., 2015; Sun et al., 2019). It is noted in the literature that biochar is able to increase the porosity and, accordingly, the aeration of soils, which contributes to the retention of moisture in the soil and, in general, improves its hydrological properties (Agegnehu et al., 2017; Andrenelli et al., 2016; Bass et al., 2016; Dumroese et al., 2011; Goldan et al., 2022; Liang et al., 2014). In addition, the use of biochar as a fertiliser helps to mitigate the effects of global warming through carbon sequestration (Kinney et al., 2012; Roy and Dias, 2017; Singh et al., 2010; Tahir et al., 2019; Woolf et al., 2010). Most often, biochar with fertilising properties is obtained in the process of slow pyrolysis from plant biomass, in particular, waste from wood processing, from rice husks, corn cobs, wheat straw, peanut shells, coffee husks, cotton waste, grain waste (Agyarko-Mintah et al., 2017; Amin and Eissa, 2017; Andrenelli et al., 2016; Chintala et al., 2014; Feng et al., 2021; Lau et al., 2017; Li et al., 2017; Nguyen et al., 2010; Pandit et al., 2018; Peng et al., 2011; Saha et al., 2019; Van Zwieten et al., 2009; Zhou et al., 2019). However, such a product is characterized by a rather low nitrogen content, which leads to the need for its modification (Zhang et al., 2021). A more balanced fertiliser is biochar, obtained from animal or poultry waste - manure or litter (Cely et al., 2015; S. Gao et al., 2019; Glazunova et al., 2018; Ilyas et al., 2021; Kuryntseva et al., 2022; Zhao et al., 2016). Obtaining biochar from such a substrate not only contributes to an increase in nitrogen content, but also prevents some environmental problems: the leaching of nitrates from the original waste into groundwater, the entry of nitrates into plants, the emission of greenhouse gases, the spread of unpleasant odors, as well as the occurrence of risks to human and animal health due to pathogenic microorganisms, antibiotic resistance genes and toxic compounds present in the initial waste (Haider et al., 2022; Pokharel and Chang, 2019; Zhang et al., 2019, 2018). It is believed that all pyrolysis products can be divided into "nutritional" biochar, which supply plants with nutrients (biochar from manure and litters) and "structuring" biochar, which are obtained from plant biomass (Jeffery et al., 2017; Pokharel and Chang, 2019).

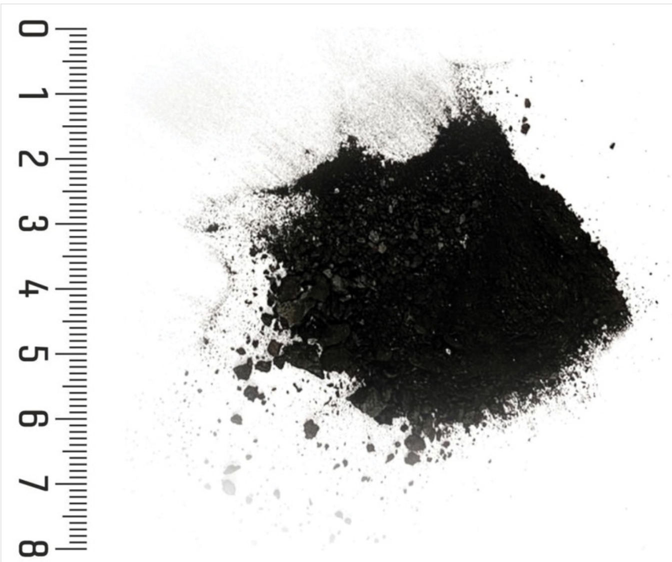
The traditional method of biochar application is to put it on the surface of the soil and then mix it. However, when using powdered biochar, this method of application can lead to its loss due to wind spraying at the stages of application and transportation (Reza et al., 2012). These losses can be overcome by using granulated or pelletised biochar. The use of granulated biochar is also supported by the fact that modern fertiliser spreaders are adapted for granulated materials. At the same time, there is an opinion that pelletised or granulated biochar, due to its size, cannot be evenly distributed in the soil, and therefore it is suitable for production mainly in greenhouses (Andrenelli et al., 2016; Dumroese et al., 2011; Vaughn et al., 2013). In addition to the fact that granulated and pelletised biochar are easier to apply to the soil, their use simplifies transportation and reduces losses during application.

The literature contains few publications devoted to the production of granulated and pelletised biochar. So, granulated biochar is obtained from corn cobs using clay (5%) as a binding agent. There is a method for production granules (pellets) by mixing biochar obtained from millet and lignin with potash and phosphate fertilisers, followed by granulation (pelletization) (Kim et al., 2014). To obtain biochar pellets used in nurseries as an additive to sfangum, biochar obtained from plant waste, wood flour, as well as polylactic acid and wheat starch, used to bind the components, are mixed. The resulting mixture is extruded to obtain pellets (Dumroese et al., 2011). In some cases, the process of biochar granulation is combined with the process of its enrichment with nitrogen (Zhang et al., 2021). There is a fertiliser granulation approach by coating urea particles with copolymers based on rice biochar (Chen et al., 2018). Granulated biochar can be used for wastewater treatment as a replacement for activated carbon (Huggins et al., 2016). In this case, the authors consider as granules only biochar particles ground to a size of 4.8-8 mm^3, obtained in a gasifier at a temperature of 1000 °C. However, simply crushing pieces of biochar will not allow it to be evenly distributed over the soil when applied as a fertiliser. At the same time, the mechanism of granulation of biochar with sufficient nitrogen content is not presented in the literature; data on the effect of granulated biochar on crop yields are also limited. At the same time, such data are interesting, since in the process of biochar granulation, its properties may change, for example, porosity, ecotoxicity, which will entail a decrease in the beneficial effect of the use of biochar. Based on this, the aim of this work was to carry out a comparative analysis of the effects of powdered and granulated biochar obtained from chicken manure on agrochemical soil parameters and crop yields during a three-year field trial.

Materials and Methods

Biochar production

The raw material for the production of biochar was chicken manure (CM) taken from a large poultry complex (Naberezhnye Chelny, Tatarstan, Russia 55.668788, 52.441136). It was produced with slow pyrolysis technology at a t_{max} = 400 °C and a retention time at peak temperature of 2 hours in a pilot pyrolysis oven with a 200L retort. The finished biochar was ground into powder (Fig. 1a). It was mixed with colloidal silica binder in an amount of 10% by weight. The moistened biochar mixture was granulated using a granulator (model ZLSP 120B, Pellet Press), which is a matrix with channels for pressing (diameter 5 mm) and rollers (Fig. 1b).



(a)

(b)

Figure 1. Powdered (a) and granulated (b) biochar used in the three-year field trial

Characteristics of the materials used in the field experiment

The contents of total carbon (TC) and total nitrogen (TN) were determined on an elemental analyser (Vario Max Cube, Elementar Analysensysteme GmbH, Germany) with the Pregl-Dumas method (ISO 10694:1995). The amount of available potassium (AK) and phosphorus (AP) was determined according to ISO 22036:2008 using an ICPE 9000 ICP spectrometer (Shimadzu, Japan) after extraction with acetate buffer.

The ecotoxicity of the biochar was determined using bioassays with the ciliate *Paramecium caudatum* (Kuryntseva et al., 2016; Miyoshi et al., 2003), and the crustacean *Daphnia magna* (ISO 6341:2012, 2012). For the test, eluate solutions were prepared – the sample was mixed with distilled H_2O (1:10 by weight) for 6 hours at room temperature, and then settled for 12 hours. Then it was centrifuged (30 min, 3500 rpm) and filtered. Sterile tap water was used as a control. A series of dilutions of the eluate was prepared (1, 1:1, 1:2, 1:3 w/v). Next, the number of dead individuals was calculated and mortality (I, %) was calculated as the ratio of this number to the initial number of individuals. Then the safe dilution factor was calculated (LID_{10}) (those dilutions that caused the death of less than 10% of individuals were taken into account).

Field experiment

Field experiments were carried out at the experimental field of Kazan Federal University, Kazan, Russia (55.64N 49.32E) during the vegetation seasons of 2021-2023. The experimental field was located in the humid continental climatic zone of Russia. Precipitation patterns were modal with peaks in July. The annual precipitation in this area is about 600 mm and the average annual temperature is 6.1 °C. These data were taken from the reports of the Hydrometeorological Bureau of Kazan Federal University. The soil is classified as Alfisol, Oxic Haplustalf or Luvisol. The experimental site was prepared in October 2020. The stubble was loosened with an MTZ-1221 tractor with a BDM disc harrow to a depth of 10-12 cm to provoke the growth of weeds, destroy insect pest larvae and plow crop residues into the soil. After 2 weeks, the plowing was carried out, which made it possible to plow plant residues to a depth of 20-22 cm. At the end of April-May 2021, 2022 and 2023 (depending on the timing of snow melting), loosening of the upper soil layer on the experimental plot was carried out with BZTU-1 tooth harrows in two tracks with a C-11 hitch by an MTZ-1221 tractor. After repeated harrowing, the plots were broken up. Plots were randomly placed on the field, 8 replicates for each tillage variant. Each plot was the size of 10 m^2 (2 × 5 m). Protective strips with a width of 1 m were allocated between the plots, in addition, protective strips of 15 m from the experimental plot were created to move away from roads and other fields. In 2021, biochar (variant B), granular biochar (gB), complex NPK mineral fertilisers (Diammofoska), Falcon KE fungicide and Secateurs Turbo herbicide (KF) were applied to the plots, plots without additional treatments were used as control (K). The introduction of biochar was in the amount 30 $t{\cdot}ha^{-1}$, Diammofoska, which contains 30 $kg{\cdot}ha^{-1}$ of N, 34 $kg{\cdot}ha^{-1}$ of P and 65 $kg{\cdot}ha^{-1}$ of K was applied in the amount of 300 $kg{\cdot}ha^{-1}$, herbicides and fungicides in accordance with the manufacturer's instructions. Further cultivation was carried out by the MTZ-82 tractor with the KPS-4M cultivator to a depth of 6-8 cm.

The crop rotation included 3 crops: barley was grown in 2021, wheat in 2022, and oats in 2023. This is part of a four-field grain-forage crop rotation (peas-barley-wheat-oats). In 2021, seeds of the Raushan variety barley were sown on such prepared soil. Soil tillage after harvesting and pre-sowing treatment in subsequent years was carried out similarly to the first year of the experiment. In 2022, 4 plots out of 8 plots of variant B, were reapplied with biochar (B2x), similarly reapplied with granular biochar (gB2x). Mineral fertilisers and pesticides were introduced into the soil of plots of the KF variant as in 2021. The soil was sown with spring wheat variety "Yoldyz Elita". In 2023, plots B, B2x, gB and gB2x were not treated with biochar, but plots KF were treated with mineral fertilisers and pesticides. Sowing was carried out with oats variety "Concord".

Soil sampling and crop yield assessment

Soil for agrochemical analysis was sampled from each plot on the 1st and 90th days after sowing annually from the 0–25 cm layer with the envelope method. The crop was harvested in August after the full maturation of the crop with a special combine with a header width of 2 m, the straw was not returned to the soil. The harvest was collected from each plot separately. The collected samples of grain were cleaned from weeds on a separating column, the mass of the obtained grain was measured, its moisture was determined and, taking this into account, the yield in each sample was recalculated. The moisture content of wheat grain under the small-plot experimental conditions was 11.2 ± 0.5%, the moisture content of barley grain under the small-plot experimental conditions was 9.9 ± 0.3%, the moisture content of oats should not exceed 13.5–14.0% for harvesting and long-term storage according to GOST 28673-90.

Statistical analysis

Each measurement was carried out in triplicate; the results are expressed as mean ± standard deviation. To determine statistically significant differences ($P < 0.05$), we used the Mann–Whitney U test and the Kruskal–Wallis test in Statistica 10.0 (StatSoft Inc., USA).

Results

Characteristics of biochar

At the first stage, the chemical characteristics and ecotoxicity of the original chicken manure, powdered and granulated biochar were determined (Table 1). It was found that the content of TC and TN in powdered biochar was lower by 37 and 22%, respectively, compared to that in the original chicken manure. The content of AP and AK in biochar was 3.80 ± 0.24% and 4.10 ± 0.51%, which is 3.4 and 3.0 times higher compared to the original litter. The content of these elements in the granulated biochar did not differ significantly from that in the powdered one.

When determining the ecotoxicity of samples of the original litter, powder and granular samples using two test objects *P. caudatum* and *D. magna*, it was found that the most toxic sample is the original litter. To reduce the mortality of *P. caudatum* and *D. magna* to 10%, dilution of the extract obtained from the litter by 13 and 108 times, respectively, is required. Powdered biochar and granular biochar produced on its basis turned out to be less dangerous for organisms: LID_{10} in tests with *P. caudatum* and *D. magna* was 3.2 and 22.5, respectively.

Effect of biochar on soil agrochemical parameters

In 2021, a three-year experiment was established, including the variants for single (spring 2021) and double (spring 2021, spring 2022) application of two types of biochar and the variant of annual application of mineral fertilisers in the form of Diammofoska. In 2023, biochar was not used to assess its aftereffect, in the control variant and the variant with fertilisers, a similar treatment was carried out as in 2021 and 2022.

According to the theoretical calculation, such application of Diammofoska should lead to an increase in the content of N, P, K by 10, 11 and 22 mg·kg^{-1}, respectively (assuming that the fertiliser is evenly distributed in the arable layer with a depth of 20 cm, and the mass of 1 ha of the arable layer is 3000 tons). It has been established that in the control soil (K), which was not fertilised, the content of TC, TN, AK and AP varied during a three-year experiment in the ranges of 2.6-2.7%, 0.2-0.23%, 326-392 mg·kg^{-1} and 24-48 mg·kg^{-1}, respectively (Table 1, Fig. 1-4).

The introduction of mineral fertiliser into the soil in 2021 led to an increase in the content of TN in the soil by 20% compared to the soil without tillage up to 0.24 (Fig. 2). The second and third application of mineral fertiliser (2022 and 2023) did not have a significant effect on the nitrogen content. In the variants with a single application of biochar (powdered and granulated) immediately after tillage, an increase in the content of TN to 0.26 and 0.27%, respectively, was revealed. During the next two vegetation seasons, its content decreased to 0.22 and 0.23%, but remained higher than the control variant. The re-introduction of biochar (in 2022) provided a fairly high level of nitrogen in the soil (0.27%), however, in this case, by the third year, the content of TN decreased to 0.22-0.23%. The third year of the experiment, evaluated as a follow-up, demonstrated that the granular biochar provided a higher level of nitrogen in the soil, which was 0.24% by the end of the third season.

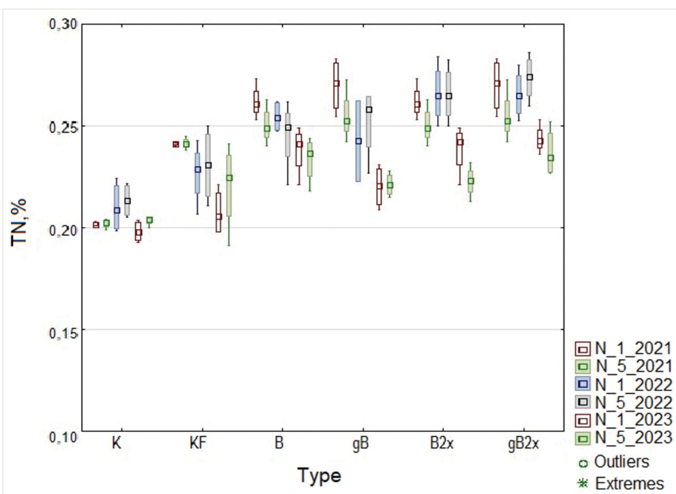


Figure 2. Change in total nitrogen (TN) content during the 2021–2023 field trial

Table 1. Characteristics of the chicken manure, biochar and soil used in the field trial

Sample	TC (%)	TN (%)	AP ($g \cdot kg^{-1}$)	AK ($g \cdot kg^{-1}$)	Ecotoxicity	
					P.c.*, LID_{10}	D.m.**, LID_{10}
Chicken manure	30.13 ± 0.50	3.42 ± 0.4	1.13 ± 0.10	1.4 ± 0.1	13	108
Biochar	18.85 ± 0.24	2.67 ± 0.04	3.80 ± 0.24	4.10 ± 0.51	3.8	18
Biochar granules	17.25 ± 0.33	2.31 ± 0.05	3.57 ± 0.21	3.95 ± 0.29	2.6	27
Soil	2.4 ± 0.50	0.22 ± 0.2	0.03 ± 0.01	0.36 ± 0.01	n/a	n/a

Note: *– *Paramecium caudatum*, ** – *Daphnia magna*; TC – total carbon content; TN - total nitrogen content; AP - available phosphorus content; AK - available potassium content; LID_{10} - safe dilution factor

Soil treatment in 2021 with biochar in both powder and granular form (variants B and gB) led to an increase in the content of TC in the soil to an average of 2.9% (Fig. 3). Soil analysis in subsequent years (2022, 2023) showed a decrease in its content, and in the third rotation of crops it turned out to be comparable to the control variant. In the variants with the repeated introduction of biochar in 2022 (B2x and gB2x), a significant increase in the content of TC up to 3.2% was noted, the level of which remained high until the end of the experiment. During the first two years of the experiment, significant difference between the variants with powdered and granulated biochar was not found, and only in the third year differences were revealed: in the gB2x variant, its content averaged 3.4%, while in the B2x variant it was 3.1%.

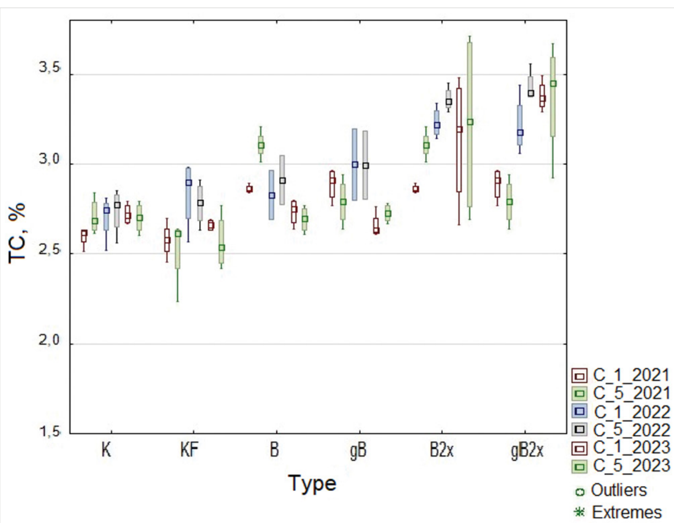


Figure 3. Change in total carbon (TC) content during the 2021–2023 field trial

The first application of mineral fertilisers to the soil led to an increase in the content of AK up to 414 $mg \cdot kg^{-1}$ (Fig. 4). In the second and third rotations of crops, despite the annual introduction of Diammofoska, the level of AK did not change significantly. In the case of a single application of powdered and granulated biochar, the content of AK increased to 744 and 593 $mg \cdot kg^{-1}$, respectively, and by the end of the experiment it was 572 and 601 $mg \cdot kg^{-1}$. With the repeated application of biochars (in 2022), an increase in the content of potassium was revealed both in comparison with the control soil and in comparison with a single application of biochar (B and gB) - up to 894 and 899 $mg \cdot kg^{-1}$ in the variants B2x and gB2x, respectively. It should be noted that the indicated content practically did not change during the third growing season.

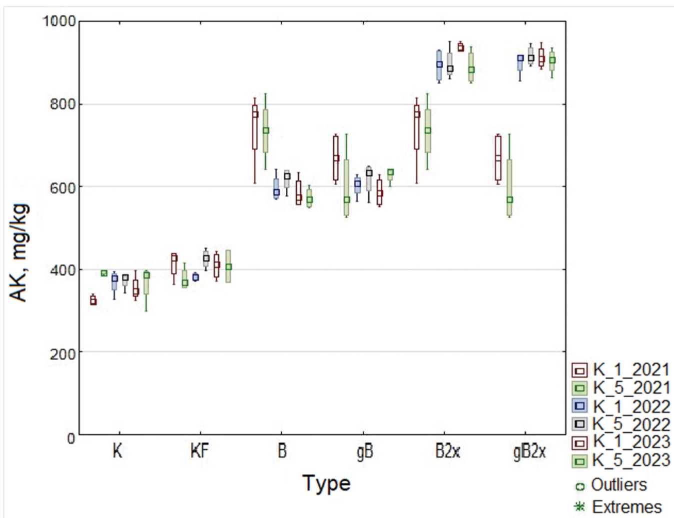


Figure 4. Change in available potassium (AK) content during the 2021–2023 field trial

An analysis of the content of AP in the dynamics of the field experiment showed that the annual application of mineral fertilisers did not lead to a significant change in its content compared to the control variant (K) (Fig. 5). A single application of biochar in powder (B) and granular (gB) form led to an increase in the amount of AP in the soil to 482 and 394 $mg \cdot kg^{-1}$, respectively. Further, its content decreased, by the end of the third growing season it amounted to 258 and 231 $mg \cdot kg^{-1}$. A double application of biochar led to an even greater increase in the element in the soil (up to 576 and 559 $mg \cdot kg^{-1}$). By the third year of the experiment, the content of AP in soils decreased significantly and amounted to 405 $mg \cdot kg^{-1}$ for both B2x and gB2x variants.

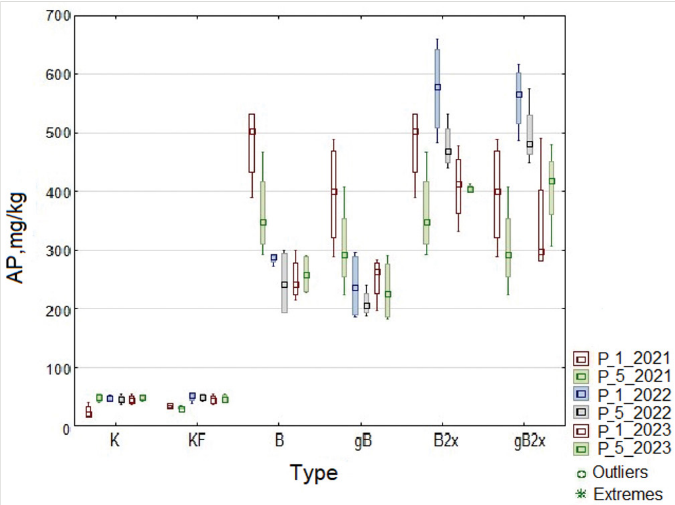


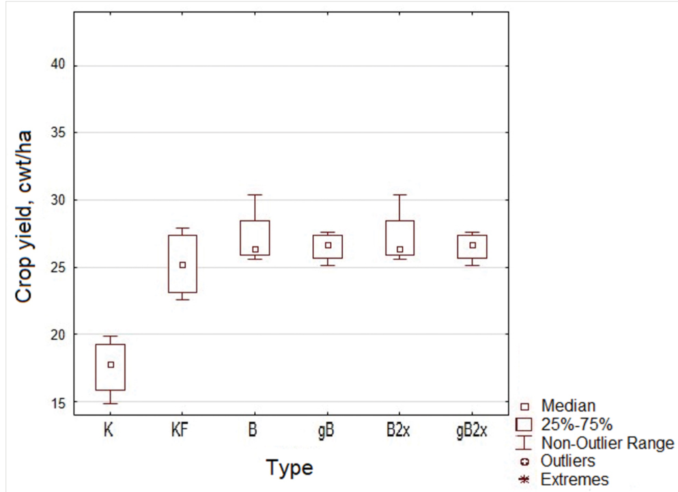
Figure 5. Change in available phosphorus (AP) content during the 2021–2023 field trial

Crop yield

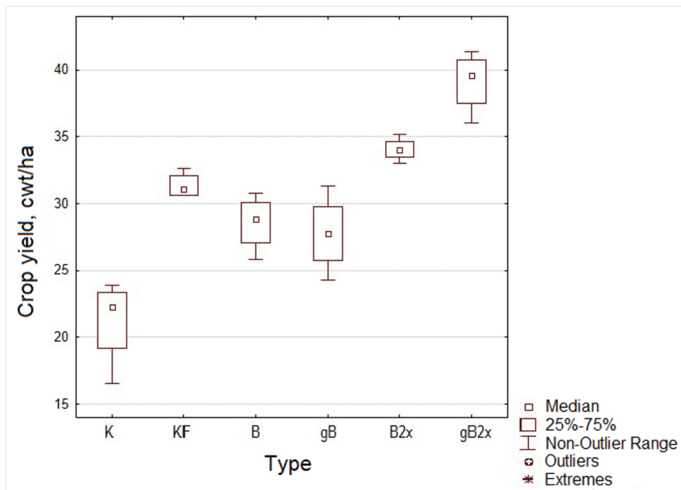
On the experimental plots, rotation of three types of grain crops was conducted - barley of the Raushan variety (2021), wheat of the Yoldyz Elita variety (2022) and oats of the Concord variety (2023). Data on crop yields are shown on Fig. 6.

In the first year of the experiment (2021), the minimum barley yield (1.8 t·ha^{-1}) was set for the control plots (variant K) (Fig. 5). Spring application of mineral fertilisers and both types of biochar (powdered and granulated) led to an increase in barley yield to 2.52, 2.72 and 2.65 t·ha^{-1}, respectively. There were no statistically significant differences ($P > 0.05$) in crop yield between the KF, B and gB variants.

An analysis of the wheat harvest (sowing in 2022) showed that in the control plots it was 2.10 t·ha^{-1}, and in the areas with the application of mineral fertilisers – 3.16 t·ha^{-1}. On plots showing an aftereffect of biochars (B and gB) in the first year, the wheat yield was 2.80 and 2.70 t·ha^{-1}, respectively. At the same time, the double application of biochars led to an increase in the yield of wheat: on the plots of the B2x variant – 3.4 t·ha^{-1}, on the plots of the gB2x variant – 4.2 t·ha^{-1}. The third year of the experiment, in which oats were grown on plots, demonstrated that both on plots evaluating two-year and one-year aftereffects, the yield of this crop did not differ significantly and amounted to 2.64 (B), 2.44 (gB), 2.82 (B2x) and 2.54 t·ha^{-1} (gB2x). These values turned out to be significantly higher compared to the yield on the control plots (2.00 t·ha^{-1}) and comparable to the yield on the plots with the application of mineral fertilisers (2.35 t·ha^{-1}).



(a)



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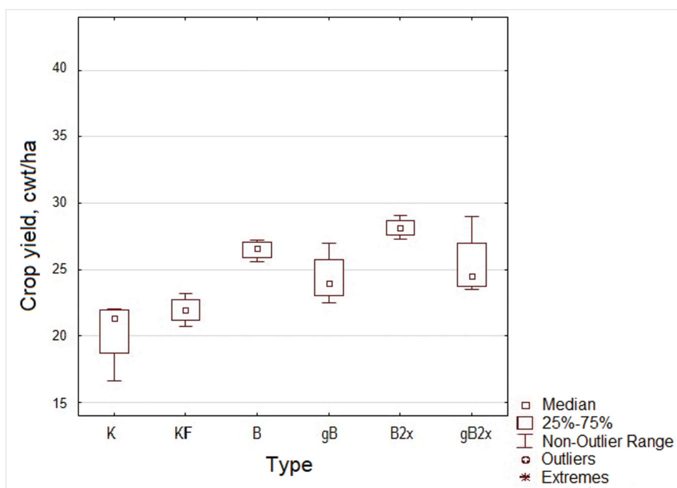

(c)

Figure 6. Change in crop yield during the field trial (a – 2021, b – 2022, c – 2023)

Discussion

An important characteristic of the pyrolysis product used as a fertiliser is the content of organogenic elements. In our case, the content of TC in the pyrolysis powder product was 18%, which made it possible to qualify it as a biochar (IBI, 2014). Comparative analysis of the content of TC in the powdered biochar and the original chicken manure revealed a decrease in its content by 37%. Such a decrease in the content of TC can be associated with losses due to volatilization, and the level of reduction in the carbon content in the pyrolysis product strongly depends on the temperature and duration of the pyrolysis process (IBI and Initiative, 2012). So, for example, a decrease in carbon content by 34 and 60% was observed by Cantrell et al., during the pyrolysis of poultry manure at temperatures of 350 and 700°C (Cantrell et al., 2012). However, the literature provides data on the absence of changes in the content of TC, while it should be noted that these data were obtained in closed systems in muffle furnaces under conditions without removal of pyrolysis gas (Hossain et al., 2021). The literature presents data on both an increase in the nitrogen content in biochar compared to the initial substrate, and a decrease in its content (Hossain et al., 2021). In our case, the content of TN during pyrolysis decreased from 3.4% in the original litter to 2.6% in the biochar, which is most likely due to the loss of NH4+-N during volatilization (El-Naggar et al., 2019). In general, the content of TC and TN in the resulting biochar corresponds to the level presented in the literature. (Brassard et al., 2018; Ding et al., 2017; Qambrani et al., 2017; Troy et al., 2013; Xu et al., 2017). A similar analysis of the content of AP and AK in the powdered biochar and the original chicken manure revealed that pyrolysis leads to an increase in AP by 3.4 and AK by 3 times, respectively. It is known that in the process of pyrolysis there is a loss of organic matter due to its volatilization, which leads to the concentration of such ash elements as P and K (He et al., 2018; Ilyas et al., 2021; Kuryntseva et al., 2022). In general, the revealed content of agrochemically valuable elements in biochar corresponds to the data presented in publications. So, in the biochar obtained from corn residues, the content of TC and TN varied at the level of 13.98-84.31% and 0.4-2.5% (Ding et al., 2017; Dume et al., 2015; Oh and Seo, 2016; Tan et al., 2017; Xu et al., 2017), from rice straw – 16-72.1% and 0.01-2.6 (Manickam et al., 2015; Oh and Seo, 2016; Tan et al., 2017; Xu et al., 2017; Yakout, 2017), from wheat straw – 41.8-75.8% and 0.47-1.58 (Ding et al., 2017; Tan et al., 2017; Wang et al., 2018; Xu et al., 2017), from wood of different species 50.9-96.1% and 0.12-1.2% (Baronti et al., 2010; Brassard et al., 2018; Ding et al., 2017; Tan et al., 2017; Troy et al., 2013; Xu et al., 2017), and in biochar from manure or litter – C 20.6-84.9% and N 0.12-4.9% (Brassard et al., 2018; Ding et al., 2017; Qambrani et al., 2017; Troy et al., 2013; Xu et al., 2017). It should be noted that in the process of pyrolysis, the C:N ratio decreases from 8.8 to 7.1, which is a positive effect, since subsequently such a biochar will have a beneficial effect on the yield (Sadaf et al., 2017). The formation of granules from powdered biochar did not lead to significant ($P < 0.05$) changes in the analyzed parameters.

An important characteristic of biochar is its ecotoxicity, since it is known that the initial substrate (chicken manure) undergoing pyrolysis has a negative effect on living organisms (Glazunova et al., 2018; Nowak et al., 2016; Ravindran et al., 2017). In addition, toxic components can be formed during the pyrolysis process; the use of a binding agent in the preparation of granules can also lead to an increase in ecotoxicity. The ecotoxicity of the original manure and biochar was assessed using two test objects, *P. caudatum* and *D. magna*. These test objects are traditional for assessing the hazard of waste and products of their processing (Dzabbarova et al., 2018; Flesch et al., 2019; Kuryntseva et al., 2016). Our results confirmed the data on the toxicity of the original chicken manure (Table 1), so the LID_{10} of this substrate was 13 and 108 for *P. caudatum* and *D. magna*, respectively. Powdered biochar, originally obtained from chicken manure, was characterized by lower ecotoxicity compared to the original chicken manure (3.4 times in relation to *P. caudatum* and 6 times in relation to *D. magna*). These data are consistent with the results of Zielińska and Oleszczuk (Zielińska and Oleszczuk, 2015), showing that biochar derived from sewage sludge significantly reduced its ecotoxicity to crustacean (*D. magna*), bacteria (*Vibrio fischeri*), and plants (*Lepidium sativum*) compared to the original substrate. As can be seen from the obtained data, both the chicken manure and the resulting biochar turned out to be more toxic for *D. magna*, which is consistent with the data of the authors, who note that *D. magna* is a more sensitive test object (Dzabbarova et al., 2018; Kuryntseva et al., 2016). Biochar granulation with the addition of silicosol as a binding agent resulted in an unreliable increase in ecotoxicity. Thus, biochar obtained from chicken manure has a lower ecotoxicity compared to the original manure, and the process of its granulation using silicosol as a binding agent does not lead to its increase.

According to the literature, the introduction of biochar into the soil is one of the ways to replenish the organogenic elements of the soil (Manolikaki and Diamadopoulos, 2016). That is why it is often used on rather poor soils (Ilyas et al., 2021). Based on this, the soil of the experimental plots was treated with biochar in powder and granular form, at a dose providing the application (equivalent) of 5655 and 5175 kg N·ha^{-1}, 114 and 107 kg P·ha^{-1}, 123 and 119 kg K·ha^{-1}, respectively. Equally important is that biochar is a carbon-rich material, so its application should provide an increase in carbon in the soil (Amoah-Antwi et al., 2020; He et al., 2021). Indeed, as can be seen from our data, a single application of powdered and granulated biochar leads to an increase in the carbon content by an average of 10% (Fig. 1). A decrease in the content of TC, due to the decomposition of organic matter, to the level of the control variant was observed by the end of the third growing season. In the variant with the re-introduction of biochar, the carbon content after the re-introduction of biochar increased to 3.2-3.4%, which amounted to 124-127% of the control variant. It should be noted that the content of TC did not decrease by the end of the third growing season, which confirms its resistance to microbial destruction. An increase in the content of organic carbon with the introduction of biochar was noted in the literature. Thus, Indian authors have shown that the use of a biochar prepared from the weed *Lantana camara* L. for the reclamation of a mine dump, on which *Zea mays* L. was grown for three months, led to an increase in soil organic carbon by 2.9 times (Ghosh et al., 2020). An increase in soil organic carbon is also evidenced by Ilyas et al. (Ilyas et al., 2021).

Comparison of the effects from the introduction of powdered and granulated biochar revealed that insignificant differences in the carbon content were observed only in the variants with a double application. Thus, by the end of the third growing season, which demonstrates the aftereffect of applying biochar, the content of TC in the variant with powdered biochar exceeded the control variant by an average of 19%, and with granulated biochar – by 25%. This may be in favor of the latter in terms of carbon sequestration in the soil, which is important both for the subsequent increase in soil fertility and the reduction of CO_2 emissions into the atmosphere. (Rafiq et al., 2020; Wang et al., 2020).

When analyzing the nitrogen content in the soil, the following regularities were observed. The first soil treatment with mineral fertiliser led to an increase in the content of TN in the soil by 16% compared to the original soil, however, despite the application of mineral fertilisers annually for each of the cultivated crops, no additional increase in nitrogen was observed in the soil, by the end of the experiment its content exceeded the control soil by 10%. Immediately after the first soil treatment with powder and granular biochar, the content of TN increased in the soil by 31 and 35% compared to the control soil, by 9 and 12% compared to the soil treated with Diammofoska. By the end of the first growing season, the content of TN decreased to the level of the soil treated with mineral fertiliser. Reapplication of biochars had a greater effect on nitrogen content compared to mineral fertiliser. So, if in the soil treated with mineral fertiliser in the spring of 2022, the content of TN turned out to be 8% higher than the control variant, then in the case of both types of biochar, the increase was 26%. Interestingly, despite the fact that biochars were applied twice in the B2x and gB2x variants, by the end of the third growing season, the nitrogen content in the soils turned out to be commensurate with the variants with a single application (B and gB). The fact that the content of TN in the soils of the variants with biochar was at the level of soils treated three times with Diammofoska indicates that biochar can serve as a substitute for mineral fertiliser, and the number of soil treatments can be reduced. The increase in the soil nitrogen content in the soil is due to the direct effect of biochar, since biochar prepared from chicken manure is rich in this element. It is known that an increase in C and N in the soil contributes to the subsequent formation of humus. (Prommer et al., 2014; Yang et al., 2021).

Potassium is a macronutrient that plays a critical role in increasing crop yields (Ilyas et al., 2021; Prajapati and Modi, 2012). In our study, a single application of biochar (variants B and gB) led to a significant increase in AK in the soil. Thus, its content was 128 and 82% higher compared to the control variant and 80 and 43% higher compared to the KF variant. In the future, its content decreased, which is associated with the removal of the element by plants (Ilyas et al., 2021). At the same time, by the end of the third growing season, its content in variants B and gB exceeded that in the KF variant by 40–47%, respectively. The fact that there was no decrease in the content of available potassium in a two-year experiment when growing maize using manure biochar and even its slight increase is presented in the literature (Ilyas et al., 2021). This is most likely due to the slow release of potassium from the biochar. At the same time, the authors suppose that the potassium released from the biochar is sufficient for plants, since an increase in the yield of maize was noted compared to the variant with mineral fertilisers.

Along with other macronutrients, biochar contains P, which is the limiting element in plant cultivation (Gao and DeLuca, 2018; Manolikaki and Diamadopoulos, 2016). An analysis of the content of AP in the dynamics of the field experiment showed that the application of mineral fertilisers did not change its content compared to the control variant. At the same time, the use of biochar in powder and granular form led to an increase in the amount of AP in the soil by 10 and 8 times (variants B and gB) compared with the control variant. The removal of the element by plants causes a decrease in the content of AP starting from the second growing season, however, it remained higher than the control variant by an average of 5 times even by the end of the third growing season. The re-introduction of biochar at the beginning of the second season led to a repeated increase in AP in the soil (on average, 12 times compared to the control). In this case, in the after-effect variants (third season), the phosphorus content was 8.5 times higher than both the control variant and the variant with mineral fertiliser. The fact that the use of biochar can increase the availability of phosphorus and reduce the need for phosphorus mineral fertiliser is also confirmed by other authors (Hong and Lu, 2018). A comparative analysis of the effects of applying powdered and granulated biochar allowed us to establish that granulation does not affect the behaviour of phosphorus in the soil. In general, increases in soil C, N, P and K contents after biochar application have also been reported by other authors, although most often the studies are of a more short-term nature (Oladele et al., 2019; Zhou et al., 2019). In our case, this result is quite natural, since it is biochars from manure that have the best potential for increasing soil phosphorus and potassium (Novak et al., 2018).

Plant productivity is an integral indicator that quantitatively reflects the change in soil fertility and the rate of absorption of nutrients by plants after the application of biochar (Mierzwa-Hersztek et al., 2017; Zhang et al., 2020). At the same time, it has been shown that treatment with biochar can have a positive effect on soil properties, but not increase productivity (Bass et al., 2016). In addition, some authors note that treatment with biochar may not only not affect the yield of agricultural plants, but even reduce it. Thus, the absence of any effect was found when growing maize (Borchard et al., 2014), papaya (Bass et al., 2016) using biochar.

A slight decrease in yield was shown in the cultivation of Suaeda salsa (Xu et al., 2016) and bananas (Bass et al., 2016). In our case, the introduction of biochar had a positive effect on the yield of all three crops grown both in the year of its introduction and when assessing the aftereffect. Thus, during the first soil treatment with biochar in powder (B) and granular (gB) form, there was an increase in barley yield by 54 and 50% compared to the variant without tillage and was comparable to the yield values in the variant with the application of mineral fertilisers (KF). When comparing the effect of the aftereffect of a single application of biochar with the control variant for two years, it was revealed that in the first year of the aftereffect, the wheat yield was 34 and 30% higher compared to that on the control soil and did not significantly differ from the yield on the plots with mineral fertiliser. The second year of the aftereffect assessment showed that the yield of oats, a crop of the third link in the crop rotation, was also higher than the control variant and was comparable to the effect of the use of mineral fertilisers. In the variant with double application of biochar, the following was revealed. The re-introduction of biochar led to a significant increase in wheat yield compared to the control variant (K) by 60 and 85% (variants B2x and gB2x) and with the variant with the application of mineral fertilisers (KF) by 8 and 24%, respectively. The third year of the experiment, in which biochar was not applied, demonstrated comparable yields of oats in biochar variants (B, gB, B2x, gB2x) with the yield in the KF variant. The data obtained by us are consistent with the information about the increase in crop yield when using biochar. So it is shown that biochar from manure, sugarcane cake and wood chips increased the yield of corn grain by 64% and 21% compared to control and treatment with chemical fertilisers, respectively (Ilyas et al., 2021). An increase in the yield of maize by 11.9% is shown when the soil is treated with biochar at a dose of 30 $t \cdot ha^{-1}$ (Feng et al., 2021). A number of authors have shown that biochar can increase soil fertility when growing rice (Rehman et al., 2015), wheat (Abbas et al., 2018), and lead to an increased formation of alfalfa biomass (Zhang et al., 2019). Numerous authors note that the main factors for increasing yields are an increase in soil organic carbon and the availability of key nutrients for plants (Adeniyan and Ojeniyi, 2005; Arif et al., 2021; Oguntunde et al., 2004; Ojeniyi, 2000).

Conclusion

The analysis of powdered biochar derived from chicken manure by slow pyrolysis at 400 °C, as well as its granular form produced using silicosol as a binder, demonstrated that pyrolysis caused a 37% decrease in carbon content and a 24% decrease in nitrogen content, while phosphorus content increased by 3.4 times and potassium content increased by 3 times. These changes are attributed to the volatilization of organic compounds during pyrolysis. Granulation did not significantly alter the final content of the analyzed elements. The pyrolysis process significantly reduced toxicity to *Paramecium caudatum* and *Daphnia magna*, and subsequent granulation of the biochar did not increase toxicity.

Single and double tillage with both biochar types resulted in increased soil contents of C, N, K, and P over a three-year experiment, reaching levels comparable to those achieved with triple mineral fertiliser applications. This suggests that biochar can potentially replace mineral fertilisers and reduce the frequency of soil treatments. Overall, there were no significant differences in changes in organogenic element content when comparing powdered and granular biochar, except under double tillage conditions. In this case, treatment with granular biochar consistently increased soil carbon throughout the entire experiment, indicating that granular biochar may be the most effective agent for carbon sequestration.

Biochar application positively affected the yields of barley, wheat, and oats both in the year of application and in subsequent assessments, increasing yields to levels comparable to those achieved with mineral fertilisers. Wheat exhibited the greatest response to biochar application, while barley and oats were less responsive. Comparison of the effects of powdered versus granular biochar on crop yields showed comparable effectiveness, allowing for the use of either biochar form. The choice between biochar types depends primarily on the availability of application equipment.

CredIT Authorship Contribution Statement

Polina A. Kuryntseva, Kamalya O. Karamova, Liliya R. Biktasheva, Natalia V. Danilova: Sampling, analysis of samples, plotting of graphs, processing the results. **Natalia A. Pronovich:** Manuscript design, proofreading of the final text. **Polina Y. Galitskaya:** Development of the idea of the experiment, planning and distribution of work tasks. **Svetlana Y. Selivanovskaya:** Development of the general concept of the work and search for funding.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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