The replacement of mineral fertilizers with chicken manure biochar significantly decreases the carbon footprint of wheat

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Abstract. Biochar is a product of oxygen-free thermal decomposition of biomass and refers alternative fertilizers. Data on the carbon footprint of agricultural products obtained using different types of biochars are not enough to date. The purpose of this study was to compare the carbon footprint of wheat of the grade "Yoldyz-Elita", grown using mineral fertilizers "Diamofoska" and biochar. Biochar was received from chicken manure, the pyrolysis process was at 400°C, for 2 hours. Biochar was added in an amount of 30 t/ha, mineral fertilizers "Diamofoska" in an amount of 300 kg/ha, respectively. Calculations the carbon footprint included data on fuel consumption and N2O emission from mineral fertilizers, CO₂ emission from soil (respiration activity), data on C fixation in biomass of wheat plants and in biochar. It was demonstrated that the use of biochar led to an increase in total soil carbon by 28% by the end of the field experiment. The application of biochar led to an increase in wheat yield by 2.5 times that was similar to the yield with application of mineral fertilizers. It was found that the main contribution to the carbon footprint of wheat was the respiration activity of the soil (up to 95%). The volume of CO₂ from fuel used by agricultural machinery was insignificant (0.5% of the total CO₂ emissions), soil cultivation with mineral fertilizers increased CO₂ emissions by 3%. The use of biochar as an organomineral fertilizer led to a 79% decrease in the carbon footprint of wheat. Thus, biochar from chicken manures may be recommended to reduce the carbon footprint of wheat.

1 Introduction

Agriculture affects all components of the environment. The use of large quantities of organic and mineral fertilizers, chemical pesticides leads to soil, surface and groundwater pollution and contributes to an increase greenhouse gas emission. In addition, the use of agricultural machinery compacts the soil, as well as increases greenhouse gas emissions. Land use change, for example, deforestation, drainage of swamps, leads to soil erosion and landscape changes. Also, the expiation of agricultural land requires more water for

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melioration. Today, the degree of impact of agriculture on the environment is comparable to the petrochemical sector [1].

The ongoing climate change requires international cooperation. The KC-21 agreement was adopted in Paris at the 21st United Nations Conference on Global Climate Change in 2015. The agreement aims to substantially reduce global greenhouse gas emissions and limit global temperature rises this century to 2°C. Russia, together with 194 countries, has joined the Paris Agreement and committed to take into account and reduce greenhouse gas emissions and work on adaptation to the effects of climate change [2].

Within the framework of this conference, it was decided to increase the content of organic carbon in the world's soils by 4 % per year (Soil carbon 4 per mille) to compensate for the emission of greenhouse gases from anthropogenic sources [3]. Today, there are groups of technologies aimed at the development and implementation of methods that contribute to the capture and removal of CO₂. These technologies are called negative emissions technologies (NETs) or greenhouse gas removal (GGR) technologies.

In recent decades, the use of biochar has become one of NET's promising carbon sequestration technologies [4], [5]. Biochar derived from crop and livestock waste has become one of the resource-saving agricultural technologies that promote carbon sequestration and improve soil quality. Biochar is a highly condensed semi-oxide with high aromaticity and low O/C/N/C ratio. Also, biochar is resistant to microbial degradation, biochar sequestration period could be more than 100 years [6]. There is constant search for new technologies that combine the optimization of the mineral nutrition of plants, the regulation of the water-physical properties of the arable layer, the increase in humus, and the provision of high plant productivity. Often the use of mineral fertilizers is associated with the lack of a long-term accumulative effect. Also, mineral fertilizers can have an ambiguous effect on plant productivity on various soils [7]. An alternative to mineral fertilizers can be biochar, that can increase plant productivity [8]. In addition, the use of biochar in soils can contribute to the reduction of N₂O and CH₄ emissions, especially in waterlogged and acidic soils [9].

As part of this work, a comparison was made of the carbon footprint of wheat grown using mineral fertilizer and biochar. The carbon footprint is the quantity of greenhouse gas emissions and uptake resulting from the production of agricultural products [10] According to current research, the carbon footprint of biochar can range from positive emissions of 0.04 t eq CO₂ to negative 1.67 t eq CO₂ per ton of raw materials [11]. Such a wide range of carbon footprint values is due to different methodological approaches to assessing the life cycle (LCA) of products, using various technological modes, raw materials for the producing biochar. Therefore, the assessment of the carbon footprint with the refinement of calculation methodologies seems to be an urgent task.

2 Materials and methods

The purpose of this study was to compare the impact of biochar and mineral fertilizers on the carbon footprint of wheat. Vegetation experiments were carried out in which wheat was grown in fields with mineral fertilizers and biochar. The first field was treated with a biochar, in the second field was treated a mineral fertilizer. The third field was left as a control without the introduction of organogenic elements. The work determined changes in the activity of soil respiration during the vegetation experiment, harvesting and calculated the yield of wheat. The fuel used during agricultural work was fixed.

The biochar used for the experiment was produced from chicken manure obtained at a poultry farm in the Republic of Tatarstan. The pyrolysis was carried out in a rotary type unit at a peak 400°C temperature and a holding time of 2 hours. The resulting biochar was then ground and granulated using silicosol as a binding agent. The carbon content in the

biochar was determined to be 52% by the Dumas method on the analyzer Vario Max Cube (Elementar Analysensysteme GmbH, Germany), according to GOST 16634-1-2011.

The growing experiment was carried out on the experimental fields of the Kazan Federal University (55.64N 49.32E). As part of the experiment, three fields were laid, the area of each was 1 ha. Agrotechnical work included tillage, harrowing (soil sampling was carried out at the initial stage of the experiment - 0 days), application of fertilizers, sowing seeds (wheat of the "Yoldyz-Elita" variety), harvesting, mulching of soil.

The first field was a control field (variant K) without fertilization. A mineral fertilizer (Diammofoska) was applied into the second field in the amount of 300 kg/ha (variant – F). which corresponds to the application of 30, 34 and 65 kg of elementary N, P, K per 1 ha, respectively. Granulated biochar was introduced into the third field in an amount of 30 t/ha (variant - B). The duration of the experiment was 90 - days. To analyze the activity of soil respiration (RA), soil samples were taken on 0, 14, 30, 60, and 90 days of the experiment. To assess soil carbon, samples were taken on 0, 14 and 90 days of the experiment. RA was determined according to ISO 16072:2002 using a Nexis GC-2030 gas chromatograph (Shimadzu, Japan). The total carbon - according to GOST 16634-1-2011 using a Vario Max Cube analyzer (Elementar Analysensysteme GmbH, Germany). After the end of the growing experiment, a crop was harvested from each field and the wheat yield was estimated. To determine the CO₂ emission for the entire growing season, an integral indicator was used - the area under the curve formed by RA, measured on 0, 14, 30, 60, 90 days of the experiment. The calculation of the carbon footprint was carried out according to the IPCC methods based on data on fuel consumption, N₂O emissions from the application of mineral fertilizers, CO₂ emissions from soil respiration activity, data on C fixation in the biomass of wheat grains and in biochar. The calculations used data from GOST R ISO 14067-2021, GOST R ISO 14044-2019, orders of the Ministry of Natural Resources and Ecology of Russian Federation, reference and statistical data.

All parameters were measured at least fivefold. The tables show the mean and standard deviation values. The validity of the mean differences was assessed by Student's test (P < 0.05). Statistical processing was performed using Microsoft Excel.

3 Results

The field experiment was conducted in fields with gray forest soil type. This type of soil is characterized by a high humus content. The gray forest soil type has low soil aggregate stability, therefore, it often forms a crust after precipitation. The carbon content in the soil is one of the basic indicators characterizing soil fertility [12]. As can be seen from the data presented in Figure 1, the total carbon content of the samples studied ranged from 2.38 to 3.63%. The highest total carbon values were determined in the variant with the biochar (variant B) - 3.6%. The addition of biochar led to an increase in the total carbon content by 28% on the 14th and 90th day of the experiment (Figure 1).

As expected, the application of mineral fertilizers did not lead to a significant change in the total carbon content - the content changed from 2.6 to 2.8, that corresponds to the data in the control soil without treatments.



Fig. 1 Total carbon content (C_{tot}) in soil samples on the 0, 14th, 90th day: without fertilizers (K), with mineral fertilizer (F), with biochar (B). "Compiled by the authors".

Determining the product's life cycle, study boundaries and level of detail is important in assessing the carbon footprint. To calculate the carbon footprint of wheat grown using mineral fertilizer and biochar, the following emitting components were isolated CO_2 – agrotechnical works (fuel consumption for tillage, harrowing, mulching, application of fertilizers, sowing seeds, harvesting, mulching of soil), emission of N₂O from the application of mineral fertilizers, emission of CO_2 from the arable soil layer (soil respiration activity during vegetation). In addition, the components of the wheat life cycle that contribute to CO_2 capture were determined. These are the introduction of biochar as a fertilizer and the increase in plant biomass, according to formula 1:

$$CF = RA + AW - H - B \tag{1}$$

Where: CF – carbon footprint with wheat growth, $kgCO_2/ha$; RA – respiration activity of soils, $kgCO_2/ha$; AW – agrotechnical works, including fuel consumption, use of mineral fertilizers, $kgCO_2/ha$; H – amount of CO_2 sequestered in wheat harvest, $kgCO_2/ha$; B – amount of SO2 sequestered by the biochar, $kgCO_2/ha$.

Soil respiration data are used to estimate CO_2 emission from soil. Soil respiration is an important indicator of soil microbial community stability. Changing the RA of soils can characterize the degree of stress impact of a particular factor. The main abiotic factors affecting the intensity of soil respiration are temperature and humidity [13]. Various biogenic elements and plant exudates also influence the dynamics of soil respiration [14], [15]. The soil RA data obtained during the experiment are presented in Figure 2a. The minimum values of respiration activity of the control sample were 0.0058 ± 0.0009 on day 90. This low level may be associated with the dry period before harvest. The maximum was 0.0271 ± 0.0079 on day 30 of the experiment. For samples with mineral fertilizer (sample F) and with biochar (sample B), a similar control trend of RA change with maximum RA values of 0.0296-0.0257 mgCO₂/g*h in the middle of growing season and RA decrease by the end of growing season to 0.009 ± 0.002 mgCO₂/g*h was established. The results obtained are consistent with the data of other authors. Thus, A. A. Larionova et al. (1998) demonstrated a similar range of RA (0.0013-0.0605 mgCO₂/g * h) for soils of the middle strip [16].

Further, cumulative RA values for the growing season were calculated to reveal the total CO_2 emissions from wheat cultivation. To do that, the area under the curve formed by

RA values measured on the 0, 14 $^{\text{th}}$, 30 $^{\text{th}}$, 60 $^{\text{th}}$, 90 $^{\text{th}}$ day of the experiment was estimated (Figure 2b).



Fig. 2 a) Respiration activity of the soil microbial community on the 0, 14th, 30th, 60th, 90th day of the vegetation experiment; b) integral values of soil respiration activity in samples K, F, B (control, fertilizer, biochar, respectively). "Compiled by the authors".

The resulting volume of CO_2 was recalculated to 1 ha considering the soil density of 1.2 g/cm³ and the depth of the arable soil layer of 10 cm (Figure 2b). Interestingly, when observing differences in the dynamics of respiration activity of the samples, the total amount of CO_2 released from the soil during the growing season was similar for the variants K, F and B - 54.1, 54.3 and 57.1 tCO₂/ha, respectively. Next, they calculated the emission of greenhouse gases from agrotechnical work - the use of fuel for agricultural machinery and the application of nitrogen fertilizers. To grow wheat, the following works are carried out: tillage, harrowing, sowing seeds and applying fertilizers, harvesting, mulching of soil. Diesel fuel consumption for these activities was 23.97, 6, 10.6, 50 and 12.9 l/ha, respectively. Thus, the volume of fuel consumed during the growing season was 103 l/ha. Guidelines of the Ministry of Natural Resources and Ecology of Russian Federation No. 300 dated 30.06.2015 were used to calculate the emission of CO_2 from fuel combustion. The total volume of CO_2 released during the combustion of fuel used by agricultural machinery in variants K, F and B amounted to 254.4 kgCO₂/ha. In addition, for

variant F, the carbon footprint of the mineral fertilizer application was calculated according to the IPCC. To determine the emission of N₂O, it is necessary to take into account the nitrogen content in the fertilizer; in the used "Diammofoska" fertilizer, the nitrogen content is - 10%. According to Chapter 11 (IPCC method), the emission of N₂O from mineral fertilizer at a dose of 300 kg/ha in variant F is equivalent to 4.7 N₂O-N kg/ha, taking into account the emission factor from anthropogenic nitrogen application to soils equal to 0.01. Next, the carbon footprint of the mineral fertilizer was calculated using a coefficient that takes into account the degree of impact of N₂O on global warming (298). As a result, the carbon footprint from the mineral fertilize's application is 1,405 kg CO₂/ha [17].

At the next stage, CO_2 sequestration in wheat grains was taken into account during photosynthesis. The yield of wheat obtained on the field without fertilizers (variant K) was 17.6±4.59 c/ha (Figure 3a), the use of mineral fertilizers (variant F) led to an increase in yield by 2.54 times, and biochar (variant B) - 2.55 times.

It is known that the carbon content of wheat grains is about 45%. Taking into account the yield from each field, 808, 2,048, 2,063 kgC/ha were sequestered in carbon grains for variants K, F and B, respectively. That is an equivalent to 2,962, 7,510 and 7,565 kgCO₂/ha for variants K, F and B, respectively (Figure 3b).

For variant B, where biochar was added as fertilizer, sequestration C was calculated by processing chicken manures by pyrolysis into "slow" carbon and adding it to the soil as fertilizer. In this study, the biochar was prepared in an experimental rotary-type pyrolysis unit with pre-drying of chicken manures. The pyrolysis process is energy consuming, however, the energy for the pyrolysis in this unit is only necessary to start the pyrolysis furnace (natural gas). The gas released during the pyrolysis process is used to maintain combustion, excessive heat, to dry the raw materials [11, 18].



Fig. 3 a) Wheat yield; b) Amount of CO_2 kg/ha sequestered in wheat grains in samples grown without fertilizers (variant K) with mineral fertilizer (variant F), with biochar (variant B). "Compiled by the authors".

The following data were used to determine the amount of sequestered CO_2 in the biochar field. The carbon content of the biochar was 52%, it is assumed that 68% of the carbon of the biochar remains in the soil after 100 years [19]. Thus, the contributing of 1 t biochar from chicken manures into the soil promotes to the sequestration of 353.6 kg of carbon, which corresponds to 1,297 kg of CO_2 . A single contributing of 30 t/ha biochar from chicken manure promotes sequestration of 10,608 kg of carbon. Considering the atomic masses of carbon (12) and carbon dioxide (44), one kilogram of C will produce 3.67 kg of CO_2 . Therefore, depositing 10,608 kg of carbon at 30 tons of biochar is consistent with retaining 38,931 kg of CO_2 /ha in the soil. Further, according to formula 1, the carbon footprint from wheat grown in the Laishevsky district of the Republic of Tatarstan using biochar and mineral fertilizers was calculated. The results are presented in Figure 4.



Fig. 4 Carbon footprint of wheat (kgCO₂/ha) in various fertilization methods (K - absence, F - use of mineral fertilize, B - use of biochar). "Compiled by authors".

Variant K (51.49 tCO₂/ha) had a large carbon footprint. The main contribution to the carbon footprint in this case is the burning of diesel fuel by agricultural machinery (Figure 4). The slightly lower carbon footprint (48.47 tCO₂/ha) of variant F is due to higher wheat yields, despite the emission of N₂O from the use of mineral fertilizers. The minimum carbon footprint (10.81 tCO₂/ha) is calculated for variant B, with a large negative contribution from sequestration of carbon in the biochar.

4 Discussion

Soil is a fundamental part of the terrestrial ecosystem affecting the global carbon cycle [20]. With modern intensive forms of agriculture, there is a decrease in the content of organic carbon in the soil [3]. In agricultural soils, soil carbon is less than 25 to 75% in the upper layers of the soil profile compared to the soils of natural ecosystems [21]. The recovery of lost organic carbon reserves in agricultural lands will hinder the increase in carbon concentration in the atmosphere [22]. The carbon content in soils can vary from a fraction of a percent in sandy soils poor in organic matter, up to 3-5%, sometimes up to 10% in rich humus chernozems or peat bogs [23]. In the control field (variant K) and in the mineral fertilizer field (variant F), the total carbon varied within 2.6-2.8. This content is typical for soils in this region. [24]. Biochar is a substrate rich in carbon (52%), the introduction of such a substrate in a large dose (30 t/ha) led to a significant increase in the carbon content in the soil - by 28% (variant B).

Soils are emitters of greenhouse gases, accurate quantification of soil respiration volumes is an important task contributing to the research and forecasting of global climate change [25]. Respiration activity is the sum of heterotrophic and autotrophic respiration of the soil microbial community, that depends on ambient temperature, soil moisture, biogenic elements, and plant exudates [26, 27]. In this work, at the beginning of the vegetation, RA was low in all three variants. That is probably due to low ambient temperature and the lack of abundant excretion of root exudates (fig. 2a). RA was high in all variants (from 0.0222 to 0.0296 mgCO₂/g * h) on the 14-60 days of the experiment. This is probably due to the background of high summer temperatures and the active release of root exudates. Interestingly, in variant B, the values were more stable during the growing season, and in variant F, the highest value of soil respiration was observed on 14th day. That could be due to the stress response of the microbial community to the application of mineral salts. RA values decreased in all samples on 90th day to initial values despite high air temperature values. Most likely, this decrease is due to both a lack of moisture in the soil and a

slowdown in the release of exudates by plants due to the end of the growing season and drying [28].

The application of mineral fertilizers should increase the content of nitrogen, potassium, phosphorus in the forms available to plants in the soil, that should ultimately lead to an increase in crop yields. Similarly, biochar tillage provides for the introduction of organogenic elements, and can also change other agrochemical characteristics of the soil. Wheat has a less developed root system compared to other cereals. At the same time, this crop is the most demanding for mineral nutrition, in this regard, fertilizers were added in the first half of the vegetation season [29].

Soil treatment with mineral fertilizer and biochar had the same positive effect on this indicator, the yield of variants F and B were 44.6 ± 2.39 c/ha and 44.9 ± 3.45 c/ha, respectively (Figure 2a). At the same time, the amount of sequestered CO₂ in the crop obtained in the corresponding fields (variants K, F and B) was 2.96, 7.51 and 7.56 tCO₂/ha, respectively (Figure 2b).

Due to unique chemical and sorption properties, many authors note the positive effect of biochar on plant growth and development. L. Zwieten et al. 2015, a study of the effect of biochar on the productivity of beans (Vicia faba L., 1753) in acidic soil in the field determined a positive effect on crop yield. The authors of the study associate the obtained effects with the ability of biochar to reduce the pH of soils, increase the availability of phosphorus and boron [30]. Also, in the work of N. Rogovska et al. 2016 revealed the positive effect of biochar on corn yield (Zea mays) [31]. At the same time, many authors note that the effects of the use of biochar in agriculture depend on the properties of the starting substrate used for pyrolysis, the pyrolysis regime, the quality of the soil on which the biochar is used, the dose of the injected biochar [32–34]. For example, in an eight-year laboratory experiment analyzing the effect of different doses of biochar (15, 22, 45 t/ha) obtained from pine chips on sorghum yield Sorghum bicolor. The researchers established a significant increase in yield by 18% at a dose of 22 t/ha, and a decrease in sorghum biomass at a dose of biochar 45 t/ha [34]. In the work of M. Gonzaga et al, 2018, biochar in the amount of 30 t/ha from coconut husk provided an increase in the biomass of Zea mays corn by 90%. In a study by K. Uzoma et al, 2011 biochar derived from manure increased corn biomass by 98-150% [35, 36]. P. Kuryntseva et al., 2020, using 1% by weight of biochar, immobilized with free-living N-fixing bacteria, as fertilizer from chicken manure, determined an increase in the biomass of *Hordeum vulgare* barley to 84% compared with the control [37].

The use of biochar is considered as a resource-saving agricultural technology related to negative emissions technologies [9]. It is important to use crop or animal waste as raw materials in order to achieve negative values of the carbon footprint when using biochar. [19]. In Russia, there is a rapid increase in the production of mineral fertilizers and their use. That is associated with the transition to intensive agriculture and an increase in arable land. The assessment of greenhouse gas emissions from the agro-industrial complex in Russia in 2019 showed that the largest share (up to 60%) falls on agricultural production plus the industrial retail sector (according to the Food and Agriculture Organization of the United Nations -FAO). The researchers note, the intensification of agriculture and the rapid increase in the use of mineral fertilizers in Russia. Despite this, Russia occupies 42 (the last) place among European countries in terms of the amount of mineral fertilizers used. According to FAO statistics for 2018, on average, of 20.8 kg/ha of mineral fertilizers was applied. The first place belongs to Ireland was ured 1,544.9 kg/ha, on average European countries use 180.2 kg of fertilizers per hectare [38]. Thus, compared to European countries, Russia has a relative surplus in the use of fertilizers. However, the trend towards an increase in the volume of fertilizers and chemicals used is large. That will contribute to an increase in the carbon footprint of agricultural products. In this study, fuel consumption

from the operation of agricultural machinery accounted for 0.5% of the total CO₂ emissions, the use of mineral fertilizer increased the CO₂ volume to 3%. Calculated data showed use of biochar from chicken manure has the potential to reduce carbon footprint to 210%. In Russia, compared to European countries, a low level of mechanization is characteristic. For example: in Russia there are 30 units of equipment per 100 square meters, in Poland – 1,200 units of equipment per the same area. That helps to reduce the carbon footprint, but negatively affects the efficiency of the industry. Due to the difference in the structure of greenhouse gas emissions of the agriculture of developed and developing countries, it is necessary to standardize methods for estimating greenhouse gases. For example: an important point in the assessment of the carbon footprint is the methodological question: the calculation of greenhouse gases from the agro-industrial complex is carried out per unit of agricultural area or per unit of output. It is also necessary to introduce monitoring of the carbon footprint at various levels of economic organization, that will contribute to increasing the climate competitiveness of agricultural products.

5 Conclusion

Thus, the yield of wheat when fertilized with a biochar from chicken manures at a dose of 30 t/ha was similar to that of wheat grown with mineral fertilizers and 2.5 times higher than that on the control field. The use of biochar increased the content of soil carbon by 28% compared to the control. At the same time, biochar tillage had practically no effect on soil respiration activity, which is considered as a positive moment, since, apparently, there was no negative impact from biochar on the soil microbial community. The main contribution to the carbon footprint was made by soil respiratory activity. The use of biochar contributed to the compensation of greenhouse gas emissions, led to a decrease in the carbon footprint by 79%. The results obtained contribute to the pool of scientific data on the influence of different types of biochars on the yield of agricultural plants, as well as on the reduction of their carbon footprint. The data obtained can be used in the development of practical recommendations for agricultural producers to reduce carbon footprint, as well as in the development of climate projects.

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