The Effect of Digestate from Biogas Plants Alone and with the Addition of Biochar and Zeolite on Soil Properties and Sorghum Yield

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This article examines the effect of digestate from biogas plants, as well as its combinations with biochar and zeolite, on soil properties, sorghum yield, and heavy metal accumulation. The experiment was carried out in an experimental field in Czeslawice (Poland). The results showed that the incorporation of digestate increased the organic matter content, improved the availability of nutrients (nitrogen, phosphorus, potassium), and improved the soil pH. The addition of biochar was demonstrated to support the stabilization of nutrients and limit the bioavailability of heavy metals. In contrast, zeolite has been observed to enhance the mineral content of the soil, although it has also been noted that this can result in an increase in sodium and heavy metal content. The highest sorghum biomass production was obtained in soils with digestate from biogas plants and biochar, while the addition of zeolite reduced the yield. Therefore, the study confirmed that natural additives have different effects on the soil. The utilization of waste material in agriculture requires monitoring of soil quality and the judicious selection of organic waste additives. The results indicate the potential of these additives to promote sustainable agriculture and the circular economy.

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INTRODUCTION

In the context of the increasing challenges posed by climate change and environmental degradation, the notion of a circular economy is of paramount importance. This concept is based on the principles of minimizing waste and optimizing the recycling of waste. Consequently, there has been significant progress in the management of organic waste.

Moreover, the European Council Directive on waste landfilling stipulates that the European Union countries must formulate a strategy for the gradual reduction of the amount of organic waste in landfills. This directive is underpinned by the overarching objective of mitigating the adverse environmental impacts of organic waste, with a particular emphasis on reducing greenhouse gas emissions (Council of the European Union

1999). The most common methods of managing organic waste are methane fermentation and composting. However, these processes also produce a significant amount of waste: digestate and compost. As the number of biogas and composting plants increases, so does the amount of digestate and compost (Wei *et al*. 2021). Agriculture plays the most important role in the management of fermentation and composting residues. The utilization of diverse organic waste materials in agriculture, including digestate, plant residues, manure, and kitchen waste, or their combinations as soil fertilizers, has been evaluated. The use of digestate, a nutrient rich by-product characterized by its abundance in nitrogen, phosphorus, calcium, potassium, and magnesium compounds, has been shown to improve the soil nutrient content. Mayerová *et al.* (2023) demonstrated that the incorporation of digestate into the soil resulted in a reduction in bulk density and an improvement in water retention capacity. As demonstrated by Möller and Müller (2012), digestate has been shown to increase the organic matter content to a degree comparable to that of commonly used pig and cow manure.

However, the carbon content of digestates (from 30 to 50% dry matter) is lower than that of manure (from 20 to 40% dry matter) because manure contains unprocessed organic matter, while digestates are a product of fermentation, where some of the carbon has been converted into biogas (methane and carbon dioxide). Consequently, research is underway to investigate the potential for incorporating carbon-rich waste into digestates. One such waste material that has been identified as a potential additive is biochar. Biochar is produced from biomass through a process known as pyrolysis. Biochar has been demonstrated to possess exceptional sorption properties. The presence of organic carbon in biochar makes it a suitable soil additive. Biochar has been shown to improve soil structure, increase its capacity to retain water and nutrients, and promote the proliferation of soil microorganisms. Furthermore, the use of biochar in soil has the potential to contribute to carbon sequestration, that is, long-term storage of carbon, which is a favorable outcome from the perspective of climate change (Osman *et al*. 2022).

However, field experiments have shown mixed results. For instance, Udall *et al.* (2017) obtained lower wheat yields with the addition of biogas and digestate compared to fields where only digestate was used (Kizito *et al.* 2019). These outcomes may be influenced by the chemical variability of organic waste, which remains a significant limitation in its agricultural use. Organic waste can contain heavy metals or pesticide residues that may accumulate in soils and crops (Seo *et al.* 2019; Ma *et al.* 2020).

A significant limitation in the utilization of organic waste is its variable chemical composition; it can contain heavy metals or pesticide residues that can accumulate in soils and crops (Seo *et al.* 2019; Ma *et al.* 2020). The solution to this problem may be found in the addition of other wastes that are characterized by high porosity, such as biochar or zeolites. In a study by Głąb *et al.* (2021), the effects of biochar and zeolite used to remediate soils contaminated with toxic heavy metals were examined. The study demonstrated that biochar produced from willow biomass at 550 °C (B550) exhibited a higher specific surface area (2.01 $m^2 \cdot g^{-1}$) and carbon content (795 $g \cdot kg^{-1}$ DM) compared to biochar produced at 350 °C (B350), which had a surface area of 1.36 $m^2 g^{-1}$. Furthermore, the study revealed that while biochar alone had limited effect on grass productivity, the application of zeolite (15 $t \cdot ha^{-1}$) significantly enhanced aboveground biomass yields, particularly in contaminated soils, with the highest yield of tall fescue reaching up to 0.485 $kgDM \cdot m^{-2}$ annually under the B550 treatment, and up to 0.519 $kg \cdot DM \cdot m^{-2}$ when combined with zeolite (Głąb *et al.* 2021). Zheng *et al.* (2020) showed that the incorporation of rice husk biochar (pyrolyzed at 400 °C) in conjunction with natural zeolite in a 1:1 weight ratio serves as an effective remediation technique for the stabilization and reduced bioavailability of cadmium, lead, arsenic, and tungsten in contaminated soils, decreasing their bioavailability by 57.4%, 62.7%, 56.4%, and 22.5%, respectively.

The incorporation of organic waste has been shown to enhance soil quality while concomitantly increasing the yield and quality of cultivated plants. Numerous studies have shown that the use of digestates leads to improved crop productivity compared to the application of animal fertilizers. Witoroec-Piechnik *et al.* 2021 showed that the application of digestate (90 kg N ha^{-1}) significantly increased the fresh matter yield of sorghum up to 85.4 Mg ha^{-1} compared to 69.3 Mg ha^{-1} under mineral fertilization (70 kg N ha^{-1}), while its effect on maize and triticale fresh yields was not statistically significant (). Baróg *et al.* (2020) showed that, compared to mineral nitrogen fertilization (NPK), the use of digestate (20 t ha^{-1} FM annually) led to an increase in the elements N, S, Na, Zn, and Fe in wheat grains. For instance, the annual nutrient input from digestate included approximately 36.6 kg N ha^{-1}, 5.6 kg S ha^{-1}, 4.6 kg Na ha^{-1}, 344 g Zn ha^{-1}, and 3.43 kg Fe ha^{-1}, which were higher than the respective levels in NPK treatments

While there is a wealth of research focusing on the direct impact of organic waste on soil and plants, a more detailed understanding of how these wastes affect long-term soil fertility and plant productivity is needed. Moreover, it is imperative to understand the interplay between the incorporation of organic waste and the presence of heavy metals in soil, which have the potential to accumulate and exert an influence on the quality of crops and the safety of food.

This publication presents the findings of research conducted to assess the impact of digestate from biogas plants, both as a standalone substance and in conjunction with biochar and zeolite, on soil characteristics, sorghum yield, and the presence of heavy metals in both mixtures and plants. The objective of this study is to understand the potential of these additives in fostering more sustainable and ecological agricultural practices.

EXPERIMENTAL

The following materials were added to the soil: digestate from biogas plants, biochar, and zeolite, the proportions of which were selected based on a review of the relevant literature. The experiment was carried out in a random block design with three replications (Fig. 1). Four soil variants with the additives were tested. The research was carried out in the year 2021 at the experimental farm located in Czeslawice, which is affiliated with the University of Life Sciences of Lublin (51°18 '23' N, 22°16'02'), located 30 kilometers from Lublin in western Poland. The experiment included planting sorghum (*Sorghum bicolor* L. Moench ssp. *bicolor*) on the same day the fertilizer was applied, with the initial harvest on 11 May, followed by the sorghum harvest on 15 September.

Replications/Plots	ST – control, soil without additives DT – soil + digestate 5% w/w DT+B – digestate 5% w/w + biochar 1% w/w DT+Z – digestate 5% w/w + zeolit 1% w/w				
Rep. 1	ST	DT	DT+B	DT+Z	
Rep 2	ST	DT	DT+B	DT+Z	10 m
Rep. 3	ST	DT	DT+B	DT+Z	
	1.5 m	1.5 m	1.5 m	1.5 m	

Fig. 1. The randomized block design utilised in this research study

The characteristics of the additives and soil used are presented in Table 1 (Cardelli *et al*. 2018). The study utilised digestate originating from the Piaski Biogas Plant, which is situated in the town of Piaski in the Lublin Voivodeship. The digestate production utilized raw materials such as maize silage (70%), sugar beet pulp (15%), fruit pomace (5%), dairy waste (5%), and manure (5%). (Szaja *et al*. 2021). This installation, owned by Wikana Bioenergia Sp. J. has been in operation since 2011. The technological process is carried out in mesophilic conditions, at a temperature of approximately 35 to 40°C. The biogas plant has an installed capacity of 999 kWe (electric) and 1039 kWt (heat), and its annual biogas production is approximately 4.25 million m^3. It is evident that this process also yields a sub-par outcome (Koszel *et al.* 2020).

The experiment utilised biochar produced by Fluid S.A. (Poland). The material under discussion was formed by means of rapid pyrolysis at a low temperature (300 °C). This process was carried out on wood chips derived from pine and spruce. The calorific value of biochar was determined to be 25 $MJ \cdot kg^{-1}$. The production capacity of the plant was 24 m^3 of chips per hour, which is equivalent to the production of up to 2 mg of biochar per hour per unit (Gruss *et al.* 2019) The natural zeolite known as clinoptilolite was sourced from the Dylgówka deposit (Poland). Dylgówka zeolite has constituted clinoptilolite material which was a result of laboratory treatment of clinoptilolite-montmorillonite clay (Franus 2002).

Table 1. Characteristics of Materials

Trait Tested	Biochar	Digestage	Zeolite
pH	6.6	6.91	7.2
TOC (%)	53.8	4.80	0.5
TN (%)	0.12	0.61	0.09
K^+ (cmol · kg-^{1})	5.10	12.48	-
Mg^{2+} (cmol · kg-^{1})	1.80	0.62	-
Ca^{2+} (cmol · kg-^{1})	30.5	0.75	-
Pb (mg · kg-^{1})	1.57	0.5	-
Mn (mg · kg-^{1})	29.7	2.05	-
Cu (mg · kg-^{1})	0.50	0.45	-
Zn (mg · kg-^{1})	13.04	1.94	-
Cd (mg · kg-^{1})	2.0	0.05	-

The determination of selected parameters was carried out in soil samples and sorghum leaves, according to the standards delineated in Table 2.

Table 2. Research Methods Used in this Study

Parameter	Soil	Leaves	Device	Standard
pH	+	-	ORION multimeter model: VERSA STAR	PN-ISO 10390: 1997 P Soil Quality, Determination of pH 1997
Electrical Conductivity (EC)	+	-	ORION multimeter model: VERSA STAR	PN-EN 27888:1999 Water quality - Determination of electrical conductivity
Organic matter (OM)	+	-	Electric muffle furnace FCF 2,5S made by Czylok with SM-946 electronic controller and temperature display (Warsaw, Poland)	PN–EN 15935:2013-02 Sludge, treated biowaste, soil and waste - determination of loss at ignition 2013
Total organic carbon (TOC)	+	-	RC 62 LECO apparatus (LECO, St Joseph, MO, USA)	
Total nitrogen (TN)	+	-	KjeltecTM 8200 Foss Tecator system (Foss, Hogans, Sweden)	Kjeldahl method
Available Phosphorus P_2O_5 / avilable	+	-	ICP MS Triple Quad spectrophotometer (Agilent 8900)	PN-R-04023:1996 - Soil Agricultural Chemical Analysis - Determination of available phosphorus in mineral soils
Available Potassium K_2O / avilable	+	-	ICP MS Triple Quad spectrophotometer (Agilent 8900)	PN-R-04022:1996 Chemical and agricultural analysis – Determination of the content of potassium available in mineral soils
Available Magnesium Mg/avilable	+	-	ICP MS Triple Quad spectrophotometer (Agilent 8900)	PN-R-04020:1994 / Az1:2004 Agricultural chemical analysis of the soil: determination of available magnesium

Metals: Cd and Cr. Cu. Ni, Pb, Zn	+	+	ICP MS triple quad spectrophotometer (Agilent 8900)	Direct calibration models. The samples of homogenized soil (1 g) and sorghum leaves (0.1 g) were digested in an acid mixture of HNO_3: HCl (1:3) were digested in HNO_3 (3 mL) in a microwave system (Multiwave 3000, Anton Paar). The digestion process lasted for about 45 min at 180 °C and at a pressure of 18 bars.

The yield assessment was carried out during the last week of September. The dryer method was used to determine the dry mass yield of the plants. At the end of September, the sorghum was harvested in the milky maturity stage (after 160 days of BBCH 73-77 vegetation), at a stubble height of approximately 10 cm. Samples for laboratory determination were taken from an area of 1 m^2 of each plot, in 3 repetitions (corresponding to approximately 8 to 10 sorghum plants). The samples were weighed in their fresh state and subsequently dried in the vegetation hall to a dry mass state of approximately 13%. At this point they were weighed once more. In the laboratory, the plant samples were categorized into stem, leaf, and panicle, and the resulting material was subjected to crushing for the purpose of laboratory analysis.

Assessment of the accumulation of specific heavy metals translocated from the soil to the plant was carried out using the bioconcentration factor (BCF), according to Eq. 1,

$$BCF = \frac{PC}{SC} \tag{1}$$

where PC denote the concentration of the heavy metals on within the leaf tissue of sorghum (mg $\cdot$kg^{-1})), and SC represents the concentration metals within the soil matrix (mg$\cdot$ kg^{-1}) (Abreu *et al.* 2012).

Netty (2013) defined the following classification of BCF values: values greater than 1 are indicative of hyperaccumulation of a particular element within a plant; values between 0.1 and 1 indicate moderate accumulation; and values ranging from 0.01 to 0.1 reflect a low level of accumulation.

Statistical Analysis

The data underwent statistical analysis using a parametric test, namely one-way analysis of variance (ANOVA) with Tukey's test. The Statistica 13.1 software package (Lublin University of Technology license) was used for this purpose. The letter indicators provided at the average value of particular parameters considered in the ANOVA test indicate statistically homogeneous groups (Tukey homogeneous groups). The presence of the same indicator is indicative of the absence of statistically significant differences between them.

RESULTS AND DISCUSSION

Soil pH and Electrical Conductivity (EC) Changes

The introduction of waste material induced statistically significant alterations in the pH and conductivity of soil samples (Table 3). Incorporation of digestate (DT) was observed to result in a notable increase in the pH level to 6.7. After the addition of waste, a shift in the pH of the solution was evident, with the pH of the application becoming slightly acidic. The pH values recorded in this study ranged from 5.5 to 6.5, indicating conditions that were conducive to the growth of plants that are able to tolerate slightly acid environments (Kunhikrishnan *et al.* 2016).

In the case of the pH value for digestate addition, the highest conductivity value was recorded, reaching a maximum of 52.7 $\mu S \cdot cm^{-1}$. The addition of biochar to the digestate has been shown to reduce the EC value to 24 $\mu S \cdot cm^{-1}$. In contrast, digestate with zeolite exhibited an EC value of 34.8 $\mu S \cdot cm^{-1}$. The results of the Tukey test indicate that all EC values were statistically significant. The CE value on the plots after taking into account soil salinity according to Jackson allowed for the classification of these as "moderately saline" (22 to 64 $\mu S \cdot cm^{-1}$) (Nkoh *et al.* 2022). It is imperative to select plants with a high frequency for salinity, as waste plots may pose a threat to plant life (Muhammad *et al.* 2024).

Table 3. Characteristics of Materials EC and pH Values in Tested Plots

Plots	pH	EC ($\mu S \cdot cm^{-1}$)
ST	6.1a	19.24±0.12a
DT	6.7b	52.7±1.07b
DT+B	6.6b	24±1.20c
DT+Z	6.4c	34.8±0.10d

The presence of the same indicator is indicative of the absence of statistically significant differences between them.

The increase in soil pH and electrical conductivity (EC) can be attributed to the high organic carbon content. The decomposition of organic matter has been shown to result in the release of organic acids and other compounds, which in turn can influence the pH of the soil. As demonstrated by Pinheiro *et al.* (2014), the incorporation of organic residues, such as those derived from chicken and quail manure, has been shown to possess considerable potential in correcting soil acidity, thus resulting in an increase in pH levels.

Organic Carbon, Nitrogen, and C:N Ratio in Tested Plots

Statistical analysis indicates that the values of carbon and nitrogen in the soil in the plots studied vary significantly depending on the type of waste used (Fig. 3). The content of organic carbon in the soil is a crucial indicator of its quality and its ability to sequester carbon, and the content of organic matter is a fundamental indicator of soil fertility. Higher levels of organic matter are generally associated with improved soil quality, which in turn supports increased plant growth.

The highest concentrations of carbon (1.76%) and organic matter (2.34%) were observed in soil with digestate and biochar. The Tukey test revealed that the carbon and organic matter concentration in the soil without additives did not differ significantly from the carbon concentration in the DT and DT+Z plots, but it was significantly lower than in the DT+B plot. The values of the waste plots were approximately 1.2 times higher than in the non-additive plot. Here the carbon content was 1.45% and OM = 2.03%. Incorporation of digestate and digestate with biochar led to the achievement of values for organic matter and organic carbon in the recommended plots for arable soils, defined as SO=2-2.6%, C=1.3-1.5%. The carbon content in the soil with digestate and biochar confirmed that the addition of biochar increased the content of stable forms of carbon in the soil.

Subsequent analysis of the nitrogen content revealed that the soil sample with the highest nitrogen concentration was the one treated with digestate, as determined by Tukey's test. This concentration was found to be statistically different from the nitrogen values obtained in the other plots. For agricultural soils, the recommended nitrogen content is as follows: >0.15% in fertile soils, <0.1% in other soils. The incorporation of digestate into soils was shown to result in a substantial increase in nitrogen content (1.59%), which exceeds the requirements for fertile soils. This finding serves to confirm that digestate from biogas plants is a substantial source of nitrogen while simultaneously indicating a low nitrogen content. The incorporation of biochar and zeolite was found to result in a decrease in nitrogen content, reaching levels lower than those found in soils without additives. Soils with digestate and biochar (0.095%) and digestate and zeolite (0.09%) demonstrated a remarkably low nitrogen content.

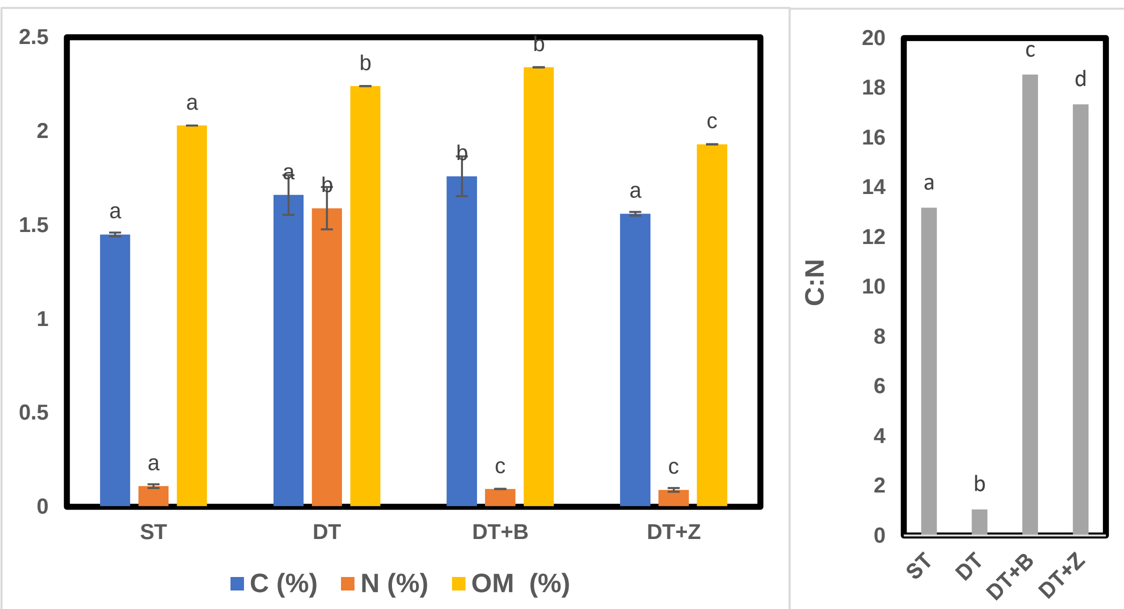

Fig. 2. Carbon, nitrogen, organic matter, and C:N ratio values in the studied plots. The presence of the same indicator is indicative of the absence of statistically significant differences between them.

Sepaskhah and Yousefi (2007) demonstrated that zeolite, through the adsorption process of ammonium ions, reduced the availability of nitrogen for microorganisms responsible for nitrification. Biochar can bind nitrogen in its structure, reducing its amount in mineral form (available for plants easily) (Zhang *et al*. 2021a). However, due to the limitation of nitrogen availability, such mixtures may be less effective in short-term soil improvement. The low nitrogen content of these mixtures underscores the necessity for the application of additional nitrogen fertilizers.

The carbon to nitrogen ratio is a critical factor in determining the balance of nutrients within the soil. The soil with the addition of digestate showed the lowest C:N ratio of 1.04 compared to the soil without additives. Such a low C:N ratio may indicate an excess of nitrogen in relation to carbon, which may lead to its rapid mineralization and nitrogen losses, as well as disturbances in the dynamics of nutrient decomposition (Jackowska and Olesiejuk 2004). However, the C:N ratio in the DT+B and DT+Z plots was approximately 1.5 times higher than in the soil without additives, where it reached a value of 13.2. The carbon to nitrogen (C:N) ratio in well humified organic matter is approximately 10 (Hoffmann *et al.* 2019). The addition of biochar and zeolite resulted in an elevated ratio, indicating a higher proportion of stable carbon, which promotes long-term soil improvement, but in the short term can limit nitrogen availability (Leite *et al.* 2017).

Assessment of nitrogen availability and interpretation of the carbon-to-nitrogen ratio in soils enriched with biochar requires special consideration due to the specific nature of the carbon present in biochar. Conventional composting methodologies place considerable emphasis on the regulation of the C:N ratio, with the objective of maximizing microbial activity and facilitating decomposition. However, when biomass is converted to biochar through pyrolysis, most of its carbon content becomes resistant, chemically stable, and largely unavailable for use by microorganisms in the short- and medium-term timeframes (Lehmann *et al*. 2011; Bolan *et al*. 2024). While biochar has been demonstrated to contribute substantially to an increase in total carbon, a significant proportion of this carbon is not bioavailable. Consequently, the actual C:N ratio relevant to microbial processes is lower than that calculated from total concentrations of C and N alone. Research by Bolan *et al*. (2024) highlights that unstable carbon fractions, such as dissolved organic carbon and volatile organic compounds, play a more significant role in microbial dynamics than total carbon content. A high C:N ratio in biochar-containing mixtures has been shown to yield erroneous conclusions regarding nitrogen deficiency, given that the actual bioavailable C:N ratio is considerably lower. Furthermore, biochar has been demonstrated to stabilize natural organic matter in the soil, thereby reducing the rate of mineralization (negative priming effect) (Weng *et al*. 2020). It is evident that biochar has a substantial impact on total soil organic carbon, though its effect on the bioavailable carbon pool is constrained and subject to variation.

Availability of Nutrients: Phosphorus, Potassium, and Magnesium in Tested Plots

The application of additives has been shown to exert a statistically significant effect on the content of bioavailable phosphorus, potassium, and magnesium in the soil (Fig. 3). The highest recorded value of available phosphorus was observed in soil treated with digestate, 30.9 $mg \cdot kg^{-1}$. The results obtained were then compared to the soil richness standards specified by the Institute of Cultivation, Fertilization, and Soil Science (IUNG) in Pulawy (Hoffmann *et al*. 2019). The digestate soil can be classified as soils with high phosphorus content (according to IUNG P >30 $mg \cdot kg^{-1}$). Soil samples treated with digestate in combination with biochar and zeolite exhibited phosphorus levels of 28.4 and 26.5 $mg \cdot kg^{-1}$, respectively. These plots can be classified as soils with medium phosphorus content (according to IUNG 15-30 mg kg^{-1}).

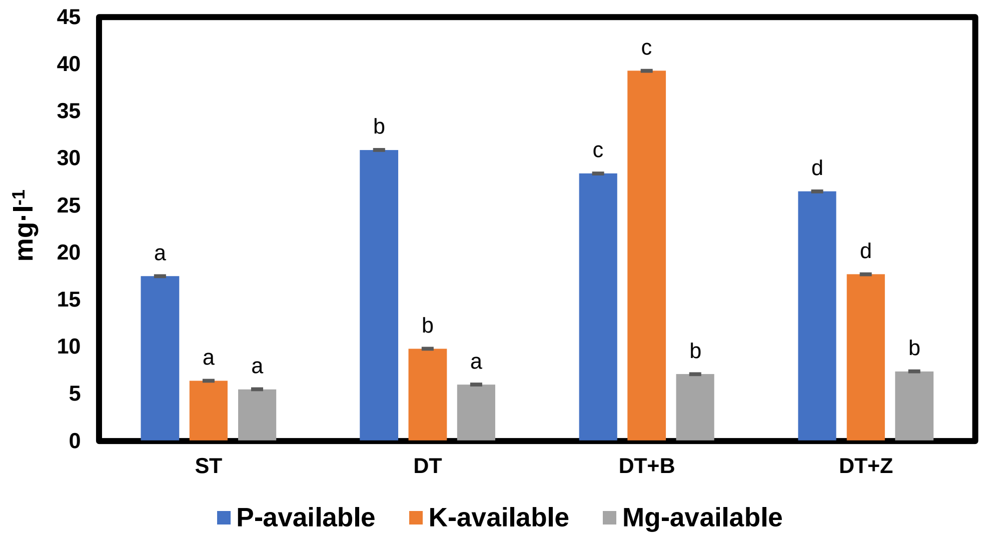

Fig. 3. Nutrient availability in the studied plots. The presence of the same indicator is indicative of the absence of statistically significant differences between them.

Soil with the addition of biochar digestate demonstrated the highest bioavailable potassium value (39.3 mg·kg^{-1}). The soil treated with digestate and digestate in conjunction with zeolite exhibited bioavailable potassium concentrations approximately double those observed in soil lacking additives, reaching 9.8 and 17.7 mg·kg^{-1}, respectively. Tukey's test revealed statistically significant differences in the values of bioavailable phosphorus and potassium among the tested plots. Consequently, it can be concluded that soil containing digestate and biochar is classified as soil with elevated potassium levels (according to IUNG >20 mg·kg^{-1}). In contrast, soil containing digestate and zeolite exhibited medium potassium levels (IUNG 10-20 mg·kg^{-1}). The remaining mixtures tested were found to have a low potassium content (less than 10 mg·kg^{-1}) (Hoffmann *et al.* 2019).

The soil with the addition of post-fermentation with zeolite exhibited the highest concentration of bioavailable magnesium (7.4 mg·kg^{-1}), and a similar value (7.1 mg·kg^{-1}) was recorded for the soil with the addition of post-fermentation and biochar. Tukey's test confirmed that the magnesium concentrations in these mixtures were statistically significantly different from those in the others. The magnesium content in all the tested plots (an average of 5 to 10 mg·kg^{-1} according to IUNG) is sufficient; however, none of the additives was able to significantly increase magnesium levels (Hoffmann *et al.* 2019).

Studies indicate that incorporating additives like biochar and zeolite into digestate applications boosts their efficiency by enhancing the availability of nutrients such as phosphorus, potassium, and magnesium. According to research conducted by Sharma *et al.* biochar can improve the absorption of nutrients by plants, leading to significant increases in biomass yields in crops like wheat (Sharma *et al.* 2023). In a similar study conducted by Kocatürk-Schumacher *et al.* (2019), the potential for nutrient recovery from the liquid part of digestate using zeolite and biochar enriched as nitrogen fertilizers was explored. The findings suggest that digestate supplies nutrients, whereas biochar aids in their gradual release. The research shows that zeolite improves nutrient retention, leading to better plant growth and nitrogen absorption when compared to digestate nutrients enhanced with biochar (Kocatürk-Schumacher *et al.* 2019).

Content of Alkaline Elements in Tested Plots

Figure 4 shows the content of alkali metals in the tested soil mixtures. The application of soil additives resulted in a substantial increase in the concentrations of Mg, Na, K, and Ca in the treated plots compared to the control soil, which may be attributable to dilution or leaching of nutrients. The concentration of alkali metals was approximately 1.5 times higher in the soil treated with additives compared to the control soil. Statistical analysis reveals that the content of alkali metals in the tested plots differed significantly from each other.

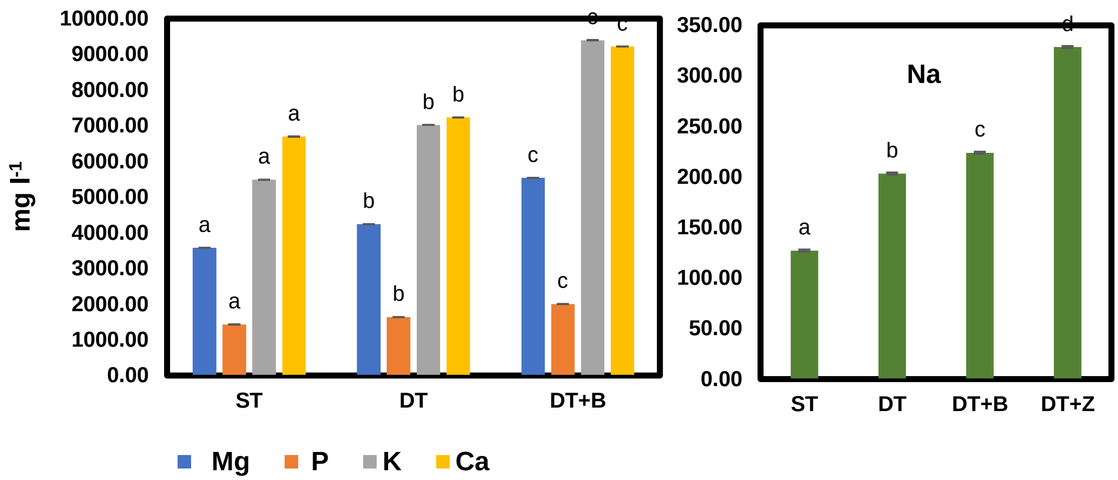

Fig. 4. Alkali metal content in the plots studied. The presence of the same indicator is indicative of the absence of statistically significant differences between them.

The incorporation of digestate into the soil increased the content of alkaline elements. Digestate was found to have a significant impact on the levels of calcium and phosphorus, with increases of 57.9% and 47.9%, respectively. However, the effect was found to be less pronounced in comparison to that observed in mixtures with biochar or zeolite. This phenomenon may be attributable to the accelerated mineralization of the components present within the digestate, thereby resulting in their immediate bioavailability.

The combination of digestate with biochar also significantly improved the levels of the alkaline elements analyzed. An increase in potassium content of 73.4% and in phosphorus content of 69.3% was observed in comparison with the control soil. Biochar has been shown to function as a nutrient reservoir, thereby stabilizing nutrients within the soil matrix and curtailing their leaching. It has been shown to improve the efficiency of fertilization and promote plant growth (Ding *et al.* 2016). The improved availability of Mg and K has a beneficial effect on photosynthesis, water management in plants, and strengthening their structure, which in turn results in higher yields and better plant quality (Tränkner *et al.* 2018).

The addition of zeolite (DT+Z) was found to exert the most significant effect on the increase in the concentration of alkaline elements, especially Na and K. The incorporation of zeolite resulted in a more than twofold increase in magnesium and phosphorus content in comparison with the control soil. A significant increase was observed in the levels of potassium (132.0%), calcium (117.4%), and sodium (158.3%).

Such substantial increases can be attributed to the sorption and exchange capacity of zeolite, which, due to its substantial specific surface area and microporous structure, effectively retains and makes available macronutrient ions. The present findings corroborate earlier reports that indicated the beneficial effect of zeolites on enhancing soil fertility and chemical quality (Głąb *et al*. 2021). Zeolite is characterized by its ability to retain water and nutrients in the soil, making them longer available to plants (Cataldo *et al.* 2021). The high K content supports plant metabolic processes, thus improving their resistance to environmental stresses, including drought and cold (Hasanuzzaman *et al.* 2018). In contrast, the increased amount of Ca improves soil structure, promotes root development, and increases the resistance of plants to diseases (Jing *et al.* 2024). However, the addition of zeolite resulted in an increase in sodium concentration (by 158% compared to soil without additives). An excess of sodium in soil is detrimental to plant life, as sodium competes with other cations, such as potassium, to participate in metabolic processes. This has the potential to disrupt the equilibrium of ions within the soil, which can hinder the growth and development of plants (Kronzucker *et al.* 2013). Therefore, it is vital to use the correct dose of zeolite when introducing it into soil, to avoid excessive sodium growth.

Heavy Metal Accumulation in Tested Plots

As demonstrated in Fig. 5, the application of these additives resulted in a substantial increase in the total metal content within the designated plots. It should be noted that the concentrations of these additives were lower than the specified concentration limits for mineral-organic substrates, as outlined in the Regulation of the Minister of the Environment of September 1, 2016, concerning the method of assessing the contamination of the earth's surface (Ministry of the Environment 2016). The concentration limits specified in this regulation are 50 $mg \cdot kg^{-1}$ for As, 600 $mg \cdot kg^{-1}$ for Ba, 5 $mg \cdot kg^{-1}$ for Cd, 300 $mg \cdot kg^{-1}$ for Cu and Ni, and 500 $mg \cdot kg^{-1}$ for Cr, Pb, and Zn.

Incorporation of digestate into the soil resulted in a statistically significant increase in the concentrations of the metals investigated compared to the soil that had not been treated with additives. The use of digestate alone resulted in a significant increase in the content of all analyzed metals: Pb by 72.7%, Zn by 80.0%, Ni by 35.3%, Cr by 45.5% and Cu by 20.5%. The most substantial increases in metal concentrations were observed for zinc and lead, while the least significant increases were observed for copper. Baldasso *et al*. (2023) demonstrated in their study that the use of digestate from unsegregated organic waste did not result in the elimination of heavy metals from the soil. However, due to their limited mobility and bioavailability, the majority of heavy metals remained bound to the surface layers of the soil, thus reducing the risk of contamination of its deeper layers (Baldasso *et al*. 2023). Nikolaidou *et al*. (2024) demonstrated that in digestate-fed soil, elevated concentrations of heavy metals such as copper and manganese were observed. However, these concentrations did not exceed acceptable standards for the agricultural environment, as evidenced by the present studies (Nikolaidou *et al*. 2024).

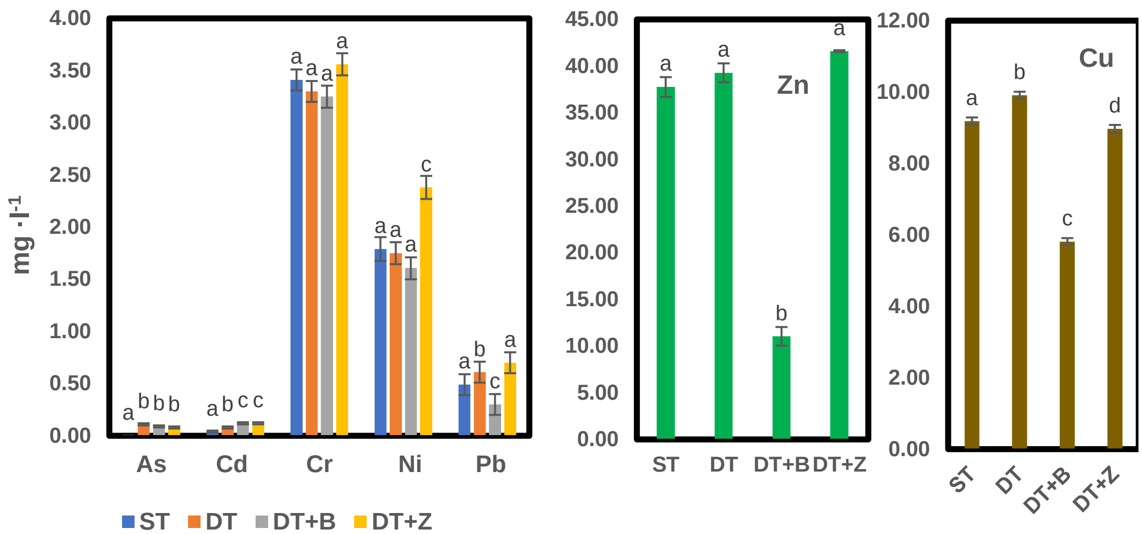

Fig. 5. Heavy metal content in the tested plots. The presence of the same indicator is indicative of the absence of statistically significant differences between them.

The addition of biochar did not result in a statistically significant alteration in the concentration of the metals under investigation compared to the soil containing digestate. Compared to the soil without additives, the addition of biochar with digestate showed an even higher increase in Cr (71.1%) and Ni (54.7%) contents, with a moderate increase in Pb (49.4%) and Cu (16.3%). The Zn value remained almost unchanged, suggesting that biochar can partially stabilize this element in the soil. Biochar, a widely recognized sustainable soil amendment, has been shown to be an effective tool for immobilizing heavy metals in soil through both direct mechanisms (*e.g.*, adsorption, ion exchange, complexation and precipitation) and indirect mechanisms (by altering soil properties) (Ali *et al.* 2019; Zhang *et al.* 2021b). The immobilization process of heavy metals is facilitated by the characteristics of biochar, including its substantial specific surface area and the presence of functional groups (*e.g.*, -COOH, -OH), which bind heavy metals in less bioavailable forms. Xue *et al.* (2021) demonstrated that the incorporation of biochar derived from fruit tree residues led to a reduction in the bioavailability of metals, including Cu, Zn, and Cd, a phenomenon attributable to immobilization processes. In the case of the highest doses: Specifically, the combination of 3 $kg·m^{-2}$ biochar and 8 $kg·m^{-2}$ digestate led to a 52.1% reduction in bioavailable cadmium, a 35.3% reduction in bioavailable copper, and a 22.6% reduction in bioavailable zinc compared to digestate alone (Xue *et al.* 2021). The effectiveness of biochar in the presented studies may be limited by the short duration of the studies. The extant literature suggests that the performance of biochar in heavy metal-contaminated soils may require a longer incubation period in order to facilitate a comprehensive evaluation of their sorption potential (Yaashikaa *et al*. 2020).

The most significant alterations were detected following the utilization of a combination of digestate and zeolite. A substantial increase in the content of Cr was observed, reaching 138.4% of the control group. Similar increases were noted for Ni (96.7%), Pb (100.4%), Cu (58.7%), and Zn (38.0%), indicating a significant enhancement in the presence of these additives. The findings of this study suggest that zeolite has the potential to complex and retain metals in soil, but they also indicate that it may increase the total availability of these metals. Further research is required to determine the extent of this effect. The concentration of metals in this plot was found to be statistically significantly higher than in the other plots. Zeolite is distinguished by its high ion exchange capacity and substantial specific surface area, suggesting that it can immobilize and restrict the mobility of heavy metals within soil solutions (Kukowska and Szewczuk-Karpisz 2024).

The findings indicate that the application of all combinations of additives results in an increase in the total content of the heavy metals analysed in the soil. This effect is most pronounced following the utilization of digestate and zeolite. The observed variations in remediation material effectiveness can be attributed to the diverse mechanisms of action exhibited by these materials, including sorption, complexation, and alterations in soil pH. However, it is important to note that the increase in the concentration of metals after the addition of materials to soil does not necessarily imply that these metals are fully bioavailable to plants. The experimental results corroborate these properties – despite the increase in the total content of heavy metals in the soil, the concentrations of metals in sorghum leaves were low and the BCF coefficient for sorghum remained below 1, which indicates the lack of significant bioavailability of these metals and their limited accumulation in plant tissues.

Sorghum Yield Response

The type of additive employed has a significant impact on the fresh and dry mass of sorghum plants, as illustrated in Table 3. Statistical analysis indicates that the maximum dry and fresh mass of sorghum plants was achieved in soils containing digestate and in soils containing digestate and biochar. In contrast, the lowest values for these parameters were recorded in soil with digestate and zeolite.

Table 3. Fresh and Dry Weight of Sorghum Plants Collected during Harvest from the Studied Plots

Plots	Fresh Mass ($kg\cdot m^{-2}$)	Dry Mass ($kg\cdot m^{-2}$)
ST	3.02b	1.32b
DT	5.44a	2.46a
DT-B	5.40a	2.40a
DT-Z	4.94b	2.24b

An examination of pertinent studies shows that utilizing diverse digestates from different origins has demonstrated an increase in crop yields (Jimenez *et al.* 2020; Bonet-Garcia *et al.* 2023). According to Walsh *et al.* (2012), grasses that were enhanced with liquid digestate achieved yields that were comparable to or exceeded those obtained with inorganic N or NPK fertilizers. Altering biochar derived from municipal sewage sludge enhances the fertility of poor urban soils as well as the nutrition and growth of turfgrass (Yue *et al.* 2017). The interaction between organic wastes introduced into the soil has been shown to contribute to increased yields. Notwithstanding the numerous benefits of using waste mixtures, the key challenge remains to optimize application rates and assess the long-term impact on both soil quality and crop productivity.

Heavy Metal Uptake by Sorghum and BCF Values

The introduction of digestate, biochar, and zeolite to soils results in increased mobility and accumulation of heavy metals in plants. Therefore, the concentration of heavy metals in the sorghum leaves was determined. The type of soil amendments significantly changed the content of heavy metals in plants (Fig. 6). Arsenic and chromium concentrations in sorghum leaves did not differ significantly between the soil mixtures tested, while barium, cadmium, copper, nickel, lead and zinc concentrations varied depending on the type of soil amendments. The lowest concentrations of chromium and copper were observed in sorghum leaves cultivated in soil with the incorporation of digestate. The highest concentrations of heavy metals were observed in leaves grown in digestate plots.

The addition of the tested materials to the soils resulted in an increase in the cadmium content of the sorghum leaves. Furthermore, the addition of digestate led to a twofold increase in cadmium concentration, while the other additives caused a threefold increase in the concentration of cadmium in the sorghum leaves. In sorghum leaves grown on a plot with digestate, the concentrations of Zn (up to 39.28 $mg \cdot kg^{-1}$) and Cu up to 9.91 $mg \cdot kg^{-1}$ increased slightly. A plot of digestate and biochar proved to be the most effective in reducing metal uptake by sorghum plants. The concentration of lead and copper in sorghum leaves on this plant decreased by about 35%, zinc by 71% and nickel by 10%, compared to the concentration of these metals in sorghum leaves grown on soil without additives. In sorghum leaves grown on a plot with digestate and zeolite, the highest concentrations of Zn (41.60 $mg \cdot kg^{-1}$), Pb (0.70 $mg \cdot kg^{-1}$) and Ni (2.38 $mg \cdot kg^{-1}$) were recorded, which may indicate increased mobility of these elements.

The metal accumulation capacity of sorghum was assessed using the BCF coefficient (Table 4). All BCF values are less than 1, suggesting that there is no excessive accumulation of heavy metals in the sorghum leaves in the tested soils compared to their concentrations in the soil. The BCF values of cadmium and lead do not differ statistically significantly from each other. The application of digestate in conjunction with biochar and zeolite resulted in a reduction in the BCF values for barium, chromium, and nickel. The soil treated with digestate, and biochar exhibited the lowest BCF values for the tested metals, suggesting its efficacy in reducing the bioavailability of heavy metals.

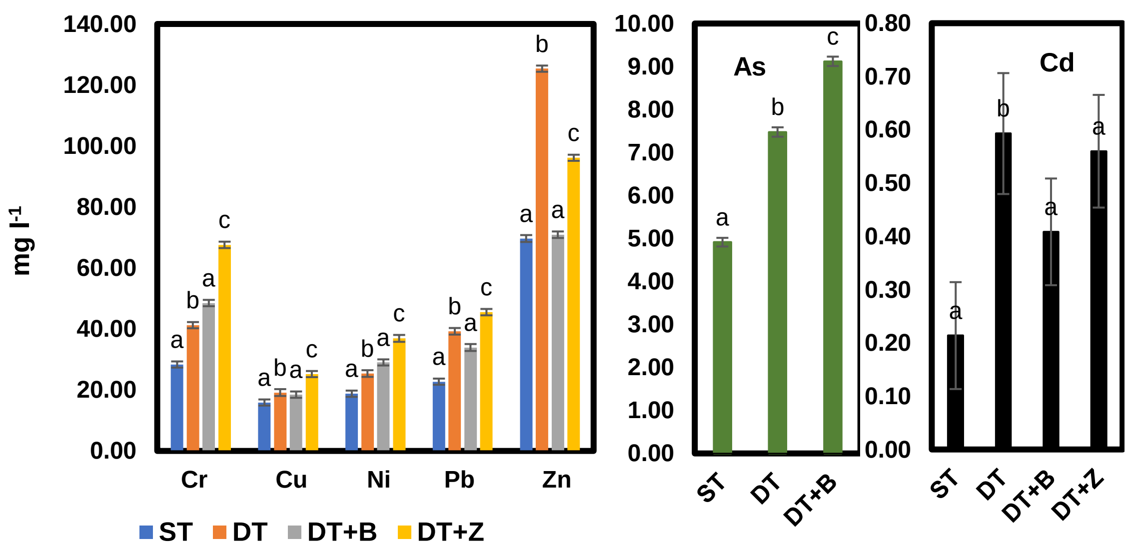

Fig. 6. Heavy metal content in sorghum leaves

Table 4. BCF Values Obtained in the Studied Plots

Plots	BCF As	BCF Cd	BCF Cr	BCF Cu	BCF Ni	BCF Pb	BCF Zn
ST	0a	0.46a	0.08a	0.48a	0.078c	0.012a	0.58a
DT	0.02b	0.30a	0.11a	0.62b	0.093b	0.027a	0.31b
DT+B	0.01b	0.29a	0.06b	0.31c	0.055c1	0.0088a	0.158c
DT+Z	0.009b	0.21a	0.05b	0.35c	0.064c	0.015a	0.39b

Plants cultivated in amended plots do not exhibit the characteristics of hyperaccumulators and do not pose a direct threat to the food chain, as indicated by BFC values below one. Afzal *et al.* (2024) investigated the effect of biochar, zeolite, and bentonite – used individually and in combination – on soil properties and Pb and Zn concentrations in *Zea mays* L. plants. The study findings indicated a substantial decrease in Pb and Zn concentrations in the soil after harvest, along with a low value of BCF in soils with elevated heavy metal content (Afzal *et al.* 2024).

DISCUSSION

The incorporation of biochar and zeolite into the soil has been shown to increase the total metal content but concomitantly to reduce the bioavailability of these metals in sorghum plants.

Consistent outcomes were attained in additional experiments, wherein, despite the documented surge in total concentrations of heavy metals in the soil following biochar application, metal fractions – encompassing water-soluble, exchangeable, and bound to organic matter – diminished, consequently curtailing their bioavailability and constraining metal uptake by plants.

For instance, in the study by Sun *et al.* (2020), which was conducted in columnar experiments using soils of varying types (sandy, clayey and chernozem), it was demonstrated that biochar was effective in reducing the content of Cd and Pb exchange fractions in the soil, while increasing their share in the residual fractions – which are considered the most stable. In the case of sandy soil, as much as 100% of Cd and 95% of Pb were transformed from exchangeable fractions to residual fractions, which clearly indicates a strong effect of metal immobilization. Of particular significance was the observation that the concentrations of Cd and Pb in water extracts diminished by 89 to 95.7% and 93.2 to 99.3%, respectively, in comparison with the control sample.

In contrast, Zhang *et al*. (2021) conducted a two-year field experiment on two types of tobacco-growing soils, using different doses of biochar (up to 40 $Mg \cdot ha^{-1}$). Despite the presence of cadmium (7.63 $mg \cdot kg^{-1}$) in biochar derived from tobacco stalks, no escalation in cadmium accumulation was observed in plant specimens. Furthermore, the content of mobile Cu, Ni and Pb forms in the soil decreased in a statistically significant way with the increase in the dose of biochar. The observed effects were attributed to the processes of adsorption, ion exchange, complexation, and precipitation of metals on the biochar surface. The authors also emphasize that the effectiveness of immobilization is contingent upon the pH of the soil – in acidic soil, the effect is more pronounced for Cu and Ni, while in soil with neutral pH, Pb stabilization is more effective.

The effectiveness of biochar in reducing the bioavailability of metals has been corroborated by experimental research in planta. In their study, Ibrahim *et al*. (2022) demonstrated that biochar derived from Casuarina wood, utilized at a concentration of 4%, led to a reduction in metal concentrations in the aboveground parts of pumpkin plants by more than 80% in comparison with a control sample.

These results indicate that the addition of biochar to soil systems does contribute to a certain number of metals, but that these metals are converted into less bioavailable forms, thereby significantly reducing their toxic impact and the risk of transfer to plants.

As demonstrated by numerous studies, biochar has been shown to bind heavy metal ions effectively through a variety of physicochemical mechanisms, including surface adsorption, ion exchange, complexation, and precipitation (Kavitha *et al*., 2018). The structure of biochar facilitates robust electrostatic interactions with metal cations, while the presence of negatively charged functional groups fosters the formation of stable organometallic complexes, thereby resulting in the permanent immobilization of metals within the soil matrix. Furthermore, the alkaline nature of biochar (particularly produced at elevated pyrolysis temperatures) has been demonstrated to increase soil pH, thereby reducing the solubility of metals such as Cd, Pb, Zn, and Cu through the precipitation of these metals in the form of poorly soluble hydroxy- or carbonyl complexes. The high structural stability of biochar, coupled with its prolonged residence time in the soil environment, ensures the longevity of these effects, thereby contributing to a sustainable enhancement in the quality of degraded and heavy metal-contaminated soils (Kavitha *et al*. 2018; Subramanian *et al*. 2024). Furthermore, biochar functions not only as a sorbent of metals, but also exert an indirect effect on their availability by modifying the physicochemical properties of the soil. This results in an increase in the content of organic matter, an improvement in the structure of soil aggregates, and a stimulation of the activity of microorganisms that can promote the immobilization of metals through bioprecipitation and biosorption (Ibrahim *et al*. 2022; Sun *et al*. 2020).

In the case of natural zeolites, such as clinoptilolite, the immobilization efficiency of metals such as Pb, Cd, Ni, Zn, and Cu has been confirmed in numerous publications. The mechanisms responsible for metal immobilization in the presence of zeolites include ion exchange, surface sorption, as well as surface co-precipitation processes (Castaldi *et al*., 2005; Mondales *et al*. 1995; Belviso 2020). Li *et al*. (2009) demonstrated that the incorporation of 20 g kg^{-1} of zeolite into soil contaminated with Pb (2000 mg kg^{-1}) resulted in a reduction of lead concentration in rapeseed shoots by up to 30% in comparison with soil that is significantly contaminated.

Concurrently, the findings of certain studies remain inconclusive. Boros-Lajszner *et al*. (2017) observed the limited effectiveness of clinoptilolite in the remediation of nickel in silty soils, a phenomenon that may be associated with the selectivity of this mineral for various metals (Pb > Cd > Cs > Cu(II) > Co(II) > Cr(III) > Zn > Ni(II) > Hg(II)) and the textural characteristics of the soil.

The effectiveness of zeolites in metal immobilization can be enhanced by physicochemical modifications, such as the use of humic acids (Shi *et al*., 2009), or structural modifications. As demonstrated by Hasanabi *et al*. (2019), the implementation of a modified nano-zeolite resulted in a reduction of 33.2% and 46.7% in the concentrations of lead (Pb) and cadmium (Cd), respectively, in plant shoots.

In the presented studies, the amalgamation of digestate and zeolite has been found to result in an increase in metal concentrations within the soil matrix, a phenomenon attributable to the dissolution of heavy metal complexes. Digestate contains organic compounds, such as humic acids, which have the ability to dissolve metals from mineral particles in the soil or zeolite. Furthermore, an ion exchange process may occur. Specifically, the ammonium ions present in digestate could displace heavy metals that are adsorbed to the surface of the zeolite, thereby facilitating their migration into the soil solution (Kovai *et al.* 2022). The results demonstrated an increase in the total content of heavy metals in the soil (particularly in the zeolite plot), yet the BCF values for the sorghum plant cultivated in the plots with various additives were below 1, indicating the limited bioavailability of these metals and their minimal accumulation in plant tissues.

The results demonstrated an increase in the total content of heavy metals in the soil (particularly in the zeolite plot), yet the BCF values for the sorghum plant cultivated in the plots with various additives were below 1, indicating the limited bioavailability of these metals and their minimal accumulation in plant tissues.

The observed changes in soil properties and plant responses can be explained by the physicochemical characteristics and interactions of biochar and zeolite within the soil matrix.

Biochar, due to its porous structure, high surface area, and abundance of oxygen-containing functional groups (*e.g.*, –COOH, –OH), acts as a sorbent that retains nutrients and water. The immobilization of heavy metals is achieved through the mechanisms of adsorption, complexation and precipitation, thereby reducing their bioavailability. Furthermore, the contribution of this process to increasing soil pH and organic carbon supports microbial activity and nutrient cycling, thereby enhancing plant growth. Furthermore, biochar functions as a slow-release source of nutrients, thereby promoting the sustained availability of essential elements such as phosphorus and potassium over time.

Zeolite, a crystalline aluminosilicate with a high cation exchange capacity (CEC) and selective affinity for ammonium and heavy metal ions, has the capacity to act as a buffer and ion exchanger in the soil. The efficacy of the material in improving nutrient retention is attributable to its ability to trap cations within its lattice structure, thereby reducing nutrient leaching and enhancing nutrient use efficiency. However, due to its ion-exchange properties, zeolite has the capacity to release sodium into the soil, which may result in increased salinity. Furthermore, the interaction of zeolite with organic acids from digestate may facilitate the release of previously bound heavy metals.

The synergistic utilization of digestate from biogas plants, in conjunction with biochar or zeolite has been demonstrated to modulate nutrient dynamics and metal mobility. While digestate provides a readily available pool of nutrients and organic matter, biochar stabilizes these inputs, and zeolite enhances nutrient retention and availability. This interplay provides a satisfactory explanation for the enhanced plant performance and the varying degrees of heavy metal accumulation that were observed across the various treatments.

CONCLUSIONS

1. The use of additives, including digestate from biogas plants, biochar, and zeolite, has been shown to have a substantial positive impact on soil fertility. However, it is important to note that the efficacy of each additive varies depending on the specific characteristics of the soil, the type of crop being cultivated, and the prevailing environmental conditions. Consequently, precise adjustments are necessary to the additive dosage and application method to ensure optimal results.
2. The most optimal plot was identified as the post-fermentation plot, which has been

shown to increase the content of organic matter and the amount of available nutrients, such as nitrogen, phosphorus, and potassium. The addition of these substances resulted in an increase in the content of heavy metals in the soil. However, the accumulation of these metals in plants remained at a low level.

3. Research has shown that the incorporation of biochar in a plot of land, in conjunction with digestate, can facilitate the growth of plants that require greater nutrient resources. This finding is particularly relevant in soils that are deficient in minerals.
4. Research conducted on the plot demonstrated that post fermentation and zeolite increased soil richness in most elements. These findings suggest that the soil is suitable for crops that require greater mineral intake. However, it is imperative to note that the introduction of these waste mixtures into soils contaminated with heavy metals is not recommended.
5. Based on the experimental results, it is recommended to apply digestate at a dose of 5% w/w combined with 1% w/w biochar, which provided the most beneficial outcomes in terms of biomass yield and soil quality improvement. This mixture enhanced the stable organic carbon content and reduced heavy metal bioavailability, while supporting high plant productivity. In contrast, the addition of zeolite increased sodium levels in the soil and reduced yield, suggesting that zeolite should be used cautiously, particularly in sodium-sensitive soils. These findings may serve as a foundation for optimizing organic waste-based soil amendments in future applications.

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REFERENCES CITED

Afzal, S., Alghanem, S. M. S., Alsudays, I. M.., Malik, Z., Ghulam Hassan Abbasi, Ali, A., Noreen, S., Ali, M., Irfan, M., and Rizwan, M. (2024). "Effect of biochar, zeolite, and bentonite on physiological and biochemical parameters and lead and zinc uptake by maize plants (*Zea mays* L.) grown in contaminated soil," *J. Hazard. Mater.* 469(13), article 3927. DOI: 10.1016/j.jhazmat.2024.133927

Ali, N., Khan, S., Yao, H., and Wang, J. (2019). "Biochars reduced the bioaccessibility and (bio)uptake of organochlorine pesticides and changed the dynamics of the microbial community in agricultural soils," *Chemosphere* 224, 805-815. DOI: 10.1016/j.chemosphere.2019.02.163

Baldasso, V., Bonet-Garcia, N., Sayen, S., Guillon, E., Frunzo, L., Gomes, C. A. R., Alves, M. J., Castro, R., Mucha, A. P., and Almeida, C. M. R. (2023). "Trace metal fate in soil after application of digestate originating from anaerobic digestion of non-source separated organic fraction of municipal solid waste," *Front. Environ. Sci.* 10, article 1007390. DOI: 10.3389/fenvs.2022.1007390

Baróg, P., Hlisnikovsk, L., and Kunzová, E. (2020). "Effect of digestate on soil organic carbon and plant-available nutrient content compared to cattle slurry and mineral fertilisation," *Agronomy* 10(3), article 10030379. DOI: 10.3390/agronomy10030379

Belviso, C. (2020). "Zeolite for potential toxic metal uptake from contaminated soil: A brief review," *Processes* 8(7), article 827. DOI: 10.3390/pr8070827

Bolan, S., Sharma, S., Mukherjee, S., Kumar, M., Rao, Ch. S., Nataraj, K. C., Singh, G., Vinu, A., Bhowmik, A., Sharma, H., El-Naggar, A., Chang, S. X., Hou, D., Rinklebe, J., Wang, H., Siddique, K. H. M., Abbott, L. K., Kirkham, M. B., and Bolan, N. (2024). "Biochar modulating soil biological health: A review," *Sci. Total Environ*. 914, article 169585. DOI: 10.1016/j.scitotenv.2023.169585

Bonet-Garcia, N., Baldasso, V., Robin, V., Gomes, C. R., Guibaud, G., Alves, M. J., Castro, R., Mucha, A. P., and Almeida, C. M. R. (2023). "Metal mobility in an anaerobic digestate amended soil: the role of two bioenergy crop plants and their metal phytoremediation potential," *Front. Environ. Sci.* 11, 1-21. DOI: 10.3389/fenvs.2023.1267463

Boros-Lajszner, E., Wyszkowska, J., and Kucharski, J. (2017). "Use of zeolite to neutralise nickel in a soil environment," *Environ. Monit. Assess*. 190, article 54. DOI: 10.1007/s10661-017-6427-z

Cardelli, R., Giussani, G., Marchini, F., and Saviozzi, A. (2018). "Short-term effects on soil of biogas digestate, biochar and their combinations," *Soil Res*. 56, 623-631. DOI: 10.1071/SR18017

Castaldi, P., Santona, L., Cozza, C., Giuliano, V., Abbruzzese, C., Nastro, V., and Melis, P. (2005). "Thermal and spectroscopic studies of zeolites exchanged with metal cations," *J. Mol. Struct*. 734, 99-105.

Cataldo, E., Salvi, L., Paoli, F., Fucile, M., Masciandaro, G., Manzi, D., Masini, C. M., and Mattii, G. B. (2021). "Application of zeolites in agriculture and other potential uses: A review," *Agronomy* 11(8), article 11081547. DOI: 10.3390/agronomy11081547

Council of the European Union. (1999). "Council Directive 1999/31/EC of 26 April 1999 on the landfill of waste," *Official Journal of the European Communities*, L182, pp. 1-19. Available at: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A31999L0031

De Abreu, C.A., Coscione, A. R., Pires, A. M., and Paz-Ferreiro, J. (2012). "Phytoremediation of a soil contaminated with heavy metals and boron using castor oil plants and amendments of organic matter," *J. Geochem. Explor*. 123, 3-7. DOI: 10.1016/j.gexplo.2012.04.013

Ding, Y., Liu, Y., Liu, S., Li, Z., Tan, X., Huang, X., Zeng, G., Zhou, L., and Zheng, B. (2016). "Biochar to improve soil fertility. A review, 'Agronomy for Sustainable Development," *Agron. Sustain. Dev*. 36(2), article 36. DOI: 10.1007/s13593-016-0372-z

Franus, W. (2002). "Geological and mineralogical study of clay rocks from the variegated shales formation of the Skole Unit," *Pr. Mineral*. 92 (in Polish).

Głąb, T., Gondek, K., and Mierzwa-Hersztek, M. (2021). "Biological effects of biochar and zeolite used to remediate soil contaminated with toxic heavy metals," *Sci. Rep.* 11(1), article 6998. DOI: 10.1038/s41598-021-86446-1

Gruss, I., Twardowski, J. P., Latawiec, A., Zaleski, T., and Bartkowiak, A. (2019). "Risk assessment of low-temperature biochar used as soil amendment on soil mesofauna," *Environ. Sci. Pollut. Res*. 26, 18230-18239. DOI: 10.1007/s11356-019-05153-7

Hasanuzzaman, M., Borhannuddin Bhuyan, M. H. M., Nahar, K., Md. Shahadat Hossain, Jubayer Al Mahmud, Md. Shahadat Hossen, Abdul Awal Chowdhury Masud, Moumita, and Fujita, M. (2018). "Potassium: A vital regulator of plant responses and tolerance to abiotic stresses," *Agronomy* 8(3), article 31. DOI: 10.3390/agronomy8030031

Hoffmann, C., Schulz, S., Eberhardt, E., Grosse, M., Stein, S., Specka, X., Svoboda, N., and Heinrich, U. (2019). "Data standards for soil and agricultural," *BonaRes Series* 2019/6, DOI: 10.20387/BonaRes-ARM4-66M2

Ibrahim, E. A., El-Sherbini, M. A. A., and Selim, E. M. (2022). "Effects of biochar on soil properties, heavy metal availability and uptake, and growth of summer squash grown in metal-contaminated soil," *Sci. Hortic*. 301, article 111097. DOI: 10.1016/j.scienta.2022.111097

ISO 10390 (1997). "Soil quality. Determination of pH," International Organization for Standardization, Geneva, Switzerland.

Jackowska, I., and Olesiejuk A. (2004). "Estimation of possible utilization of sewage sludge from municipal sewage treatment plant in Lubartów in agriculture," *Ann. Univ. Mariae Curie-Skłodowska, Lublin-Pol.* LIX(2), 1001-1006.

Jimenez, J., Grigatti, M., Boanini, E., Patureau, D., and Bernet, N. (2020). "The impact of biogas digestate typology on nutrient recovery for plant growth: Accessibility indicators for the first prediction of fertilisation," *Waste Manag.* 117, 1-38.

Jing, T., Li, J., He, Y., Shankar, A., Saxena, A., Tiwari, A., Maturi, K. C., Solanki, M. K., Singh, V., Eissa, M. A., Ding, Z., Xie, J., and Awasthi, M. K. (2024). "Role of calcium nutrition in plant physiology: Advances in research and insight into acidic soil conditions: A comprehensive review," *Plant Physiol. Biochem*. 210, article 108602. DOI: 10.1016/j.plaphy.2024.108602

Kavitha, B., Reddy, P. V. L., Kim, B., Lee, S. S., Pandey, S. K., and Kim, K. H. (2018). "Benefits and limitations of biochar amendment in agricultural soils: A review," *J. Environ. Manage*. 227, 146-154. DOI: 10.1016/j.jenvman.2018.08.082

Kizito, S., Luo, H., Lu, J., Bah, H., Dong, R., and Wu, S. (2019). "Role of nutrient-enriched biochar as a soil amendment during maize growth: Exploring practical alternatives to recycle agricultural residuals and to reduce chemical fertiliser demand," *Sustainability* 11(11), article 3211. DOI: 10.3390/su11113211

Kocatürk-Schumacher, N. P., Zwart, K., Bruun, S., Stoumann Jensen, L., Srensen, H., and Brussaard, L. (2019). "Recovery of nutrients from the liquid fraction of digestate: Use of enriched zeolite and biochar as nitrogen fertilisers," *J. Plant Nutr. Soil Sci*. 182(2), 187-195. DOI: 10.1002/jpln.201800271

Koszel, M., Parafiniuk, S., Szparaga, A., Kocira, S., Atanasov, A. Z., Bochniak, A., and Kovalyshyn, S. (2020). "Impact of digestate application as a fertilizer on the yield and quality of winter rape seed," *Agronomy* 10, article 878. DOI: 10.3390/agronomy10060878

Kovai., Lonari, Z., Jovi, J., Samac, D., Popovi, B., and Tama, M. (2022). "Digestate management and processing practices: A review," *Appl. Sci.* 12(18), article 9216. DOI: 10.3390/app12189216

Kronzucker, H. J., Coskun, D., Schulze, L. M., Wong, J. R., and Britto, D. T. (2013). "Sodium as a nutrient and toxicant," *Plant and Soil* 369(1-2), 1-24. DOI:

10.1007/s11104-013-1801-2
Kukowska, S., and Szewczuk-Karpisz, K. (2024). "Management of the soil environment using biochar and zeolite in various combinations: Impact on soil condition and economic aspects," *J. of Soils and Sediments* 25(1), 77-102. DOI: 10.1007/s11368-024-03927-2
Kunhikrishnan, A., Thangarajan, R., Bolan, N. S., Xu, Y., Mandal, S., Gleeson, D. B., Seshadri, B., Zaman, M., Barton, L., Tang, C., Luo, J., Dalal, R., Ding, W., Kirkham, M. B., and Naidu, R. (2016). "Functional relationships of soil acidification, lime and greenhouse gas flux," *Adv. Agron.* 139, 1-71. DOI: 10.1016/bs.agron.2016.05.001
Lehmann, J., Rillig, M. C., Thies, J., Masiello, C. A., Hockaday, W. C., and Crowley, D. (2011). "Biochar effects on soil biota – A review," *Soil Biol. Biochem*. 43(9), 1812-1836. DOI: 10.1016/j.soilbio.2011.04.022
Leite, M. F. A., Pan, Y., Bloem, J., Berge, H. T., and Kuramae, E. E. (2017). "Organic nitrogen rearranges both the structure and activity of the soil-borne microbial seedbank," *Sci. Rep.* 7, 1-11. DOI: 10.1038/srep42634
Li, P. J., Wang, X., Allinson, G., Li, X. J., and Xiong, X. Z. (2009). "Risk assessment of heavy metals in soil previously irrigated with industrial wastewater in Shenyang, China," *J. Hazard. Mater*. 161, 516-521. DOI: 10.1016/j.jhazmat.2008.03.130
Ma, J., Chen, Y., Antoniadis, V., Wang, K., Huang, Y., and Tian, H. (2020). "Assessment of heavy metal (loid) contamination risk and grain nutritional quality in organic waste modified soil," *J. Hazard. Mater*. 399, article 123095. DOI: 10.1016/j.jhazmat.2020.123095
Mayerová, M., Imon, T., Stehlk, M., Madaras, M., Koubová, M., and Smatanová, M. (2023). "Long-term application of biogas digestate improves soil physical properties," *Soil Tillage Res.* 231, article 105715. DOI: 10.1016/j.still.2023.105715
Mondales, K. D., Carland, R. M., and Aplan, F. F. (1995). "The comparative ion exchange capacities of natural sedimentary and synthetic zeolites," *Miner. Eng*. 8, 535-548.
Möller, K. and Müller, T. (2012). "Effects of anaerobic digestion on digestate nutrient availability and crop growth: A review," *Eng. Life Sci.* 12(3), 242-257. DOI: 10.1002/elsc.201100085
Ministry of the Environment. (2016). "Regulation of the Minister of the Environment of September 1, 2016, on the method of assessing soil contamination," *Journal of Laws*, item 1395. Available at: https://isap.sejm.gov.pl/isap.nsf/DocDetails.xsp?id=wdu20160001395
Muhammad, M., Waheed, A., Wahab, A., Majeed, M., Nazim, M., Liu, Y. H., Li, L., and Li, W. J. (2024). "Soil salinity and drought tolerance: An evaluation of plant growth, productivity, microbial diversity, and amelioration strategies," *Plant Stress* 11, article 100319. DOI: 10.1016/j.stress.2023.100319
Netty, S. (2013). "Bioaccumulation of nickel by five species of wild plants in nickel-contaminated soil," *IOSR J. Eng.* 03(05), 01-06. DOI: 10.9790/3021-03510106
Nikolaidou, C., Mola, M., Papakostas, S., Aschonitis, V. G., Monokrousos, N., and Kougias, P. G. (2024). "The effect of anaerobic digestate as an organic soil fertiliser on the diversity and structure of indigenous soil microbial and nematode communities," *Environ. Sci. Pollut. Res*. 0123456789. DOI: 10.1007/s11356-024-32850-9

Nkoh, J. N., Ajibade, F. O., Atakpa, E. O., Baquy, M. A. Al, Mia, S., Odii, E. C., and Xu, R. (2022). "Reduction of heavy metal uptake from polluted soils and associated health risks through biochar amendment: A critical synthesis," *J. Hazard. Mater. Adv.* 6, article 100086. DOI: 10.1016/j.hazadv.2022.100086

Osman, A. I., Fawzy, S., Farghali, M., El-Azazy, M., Elgarahy, A. M., Fahim, R. A., Maksoud, M. I. A. A., Ajlan, A. A., Yousry, M., Saleem, Y., and Rooney, D. W. (2022). "Biochar for agronomy, animal farming, anaerobic digestion, composting, water treatment, soil remediation, construction, energy storage, and carbon sequestration: A review," *Environ. Chem. Lett.* 2385-2485. DOI: 10.1007/s10311-022-01424-x

Pinheiro, G. L., Silva, C. A., and Lima, J. M. de. (2014). "Soluble carbon in oxisol under the effect of organic residue rates," *R. Bras. Ci. Solo*. 38(3), 810-820. DOI: 10.1590/s0100-06832014000300012

PN-EN 27888 (1999). "Water quality – Determination of electrical conductivity," European Committee for Standardization, Brussels, Belgium.

PN-EN 15935: 2013-02 (2013). "Sludge, treated biowaste, soil, and waste - Determination of loss in ignition," European Committee for Standardization, Brussels, Belgium.

PN-R-04020:1994/Az1 (2004). "Agricultural chemical analysis of the soil: Determination of the available magnesium," Polish Committee for Standardization, Warsaw, Poland.

PN-R-04023 (1996). "Agricultural chemical analysis of soil - Determination of available phosphorus in mineral soils," Polish Committee for Standardization, Warsaw, Poland.

PN-R-04022 (1996). "Chemical and agricultural analysis - Determination of the content of potassium available in mineral soils," Polish Committee for Standardization, Warsaw, Poland.

Seo, B. H., Kim, H. S., Kwon, S. I., Owens, G., and Kim, K. R. (2019). "The accumulation and mobility of heavy metals in a soil profile depend on the type of organic waste applied," *J. Soils Sediments* 19(2), 822-829. DOI: 10.1007/s11368-018-2065-5

Sepaskhah, A. R., and Yousefi, F. (2007). "Effects of zeolite application on the retention of nitrate and ammonium in a loamy soil in saturated conditions," *Aust. J. Soil Res*., 45(5), 368-373. DOI: 10.1071/SR06069

Sharma, A., Swami, S., Pawaiya, A., Mishra, A., Chaudhary, M., Bhatt, N., Khan, A. A., Mutiyar, P. K., and Suthar, S. (2023). "Developing slow-release fertiliser based on the pyrolysis of domestic biogas digestate cake: A circular economy approach for rural farmers," *Biomass and Bioenergy* 178, article 106966. DOI: 10.1016/j.biombioe.2023.106966

Shi, W., Shao, H., Li, H., Shao, M., and Du, S. (2009). "Co-remediation of the lead-polluted garden soil by exogenous natural zeolite and humic acids," *J. Hazard. Mater.* 167, 136-140. DOI: 10.1016/j.jhazmat.2008.12.092

Subramanian, P., Pandian, K., Pakkiyam, S., Dhanuskodi, K. V., Annamalai, S., Chidambaram, P. P., and Mustaffa, M. R. A. F. (2024). "Biochar for heavy metal cleanup in soil and water: A review," *Biomass Convers. Biorefin*. DOI: 10.1007/s13399-024-05989-1

Sun, J., Cui, L., Quan, G., Yan, J., Wang, H., and Wu, L. (2020). "Effects of biochar on heavy metals migration and fractions changes with different soil types in column experiments," *BioResources* 15(2), 4388-4406. DOI: 10.15376/biores.15.2.4388-4406

Szaja, A., Montusiewicz, A., Lebiocka, M., and Bis, M. (2021). "A combined anaerobic digestion system for energetic application of beer spent grain in co-digestion with sewage sludge," *Waste Manag*. 135, 448-456. DOI: 10.1016/j.wasman.2021.09.034

Tränkner, M., Tavakol, E., and Jákli, B. (2018). "Functioning of potassium and magnesium in photosynthesis, photosynthete translocation, and photoprotection," *Physiol. Plant*. 163(3), 414-431. DOI: 10.1111/ppl.12747

Udall, D., Rayns, F., and Charlesworth, S. (2017). "The potential of biochar and anaerobic digestate use in a temperate conventional wheat production system," *Int. J. Res. Agric. For*. 4(10), article 44. http://www.ijraf.org/papers/v4-i10/6.pdf

Walsh, J. J., Jones, D. L., Edwards-Jones, G., and Williams, A. P. (2012). "Replacing inorganic fertiliser with anaerobic digestate may maintain agricultural productivity at less environmental cost," *J. Plant Nutr. Soil Sci*. 175(6), 840-845. DOI: 10.1002/jpln.201200214

Wei, Y., Wang, N., Lin, Y., Zhan, Y., Ding, X., Liu, Y., Zhang, A., Ding, G., Xu, T., and Li, J. (2021). "Recycling of nutrients from organic waste using advanced compost technology – A case study," *Bioresource Technol.* 337, article 125411. DOI: 10.1016/j.biortech.2021.125411

Weng, Z., Liu, X., Eldridge, S., Wang, H., Rose, T., Rose, M., Rust, J., Singh, B. P., Tavakkoli, E., Tang, C., Ou, H., and Van Zwieten, L. (2020). "Priming of soil organic carbon induced by sugarcane residues and its biochar control the source of nitrogen for plant uptake: A dual ^{13}C and ^{15}N isotope three-source-partitioning study," *Soil Biol. Biochem*. 146, article 107792. DOI: 10.1016/j.soilbio.2020.107792

Witrożec-Piechnik, A., Matyka, M., Wolszczak, P., and Oleszek, M. (2021). "Yield and selected physiological parameters of maize, sorghum, and triticale depending on the fertilisation system," *BioResources* 16(4), 7870-7883. DOI: 10.15376/biores.16.4.7870-7883

Xue, S., Chen, F., Wang, Y., Shao, Z., Zhang, C., Qiu, L., Ran, Y., and He, L. (2021). "Effects of co-applications of biochar and solid digestate on enzyme activities and heavy metal bioavailability in cd-polluted greenhouse soil," *Water, Air, and Soil Pollut*. 232(4), article 140. DOI: 10.1007/s11270-021-05089-0

Yaashikaa, P. R., Kumar, P. S., Varjani, S., and Saravanan, A. (2020). "A critical review on the biochar production techniques, characterization, stability and applications for circular bioeconomy," *Biotechnol. Rep*. 28, article e00570. DOI: 10.1016/j.btre.2020.e00570

Yue, Y., Cui, L., Lin, Q., Li, G., and Zhao, X. (2017). "Efficacy of sewage sludge biochar to improve the properties of urban soils and promote grass growth," *Chemosphere* 173, 551-556. DOI: 10.1016/j.chemosphere.2017.01.096

Zhang, S., Cui, J., Wu, H., Zheng, Q., Song, D., Wang, X., and Zhang, S. (2021a). "Organic carbon, total nitrogen, and microbial community distributions within aggregates of calcareous soil treated with biochar," *Agric. Ecosyst. Environ.* 314(12), article 107408. DOI: 10.1016/j.agee.2021.107408

Zhang, Y., Wang, J., and Feng, Y. (2021b). "The effects of biochar addition on soil physicochemical properties: A review," *Catena* 202, article 105284. DOI: 10.1016/j.catena.2021.105284

Zhang, J., Li, C., Li, G., He, Y., Yang, J., and Zhang, J. (2021). "Effects of biochar on heavy metal bioavailability and uptake by tobacco (*Nicotiana tabacum*) in two soils," *Agric. Ecosyst. Environ*. 317, article 107453. DOI: 10.1016/j.agee.2021.107453

Zheng, X. J, Chen, M., Wang, J. F., Liu, Y., Liao, Y. Q., and Liu, Y. C. (2020). "Assessment of zeolite, biochar, and their combination for stabilisation of multi-metal contaminated soil," *ACS Omega* 5(42), 27342-47288. DOI: 10.1021/acsomega.0c03710

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