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ORIGINAL PAPER

Nitrogen Use Efficiency and Crop Yield in Four Successive Crops Following Application of Biochar and Zeolites

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Abstract

Two soil amendments, biochar and zeolites, were evaluated in their potential for increasing crop productivity and agro-system sustainability. The effect of biochar and zeolites, in combination with four nitrogen (N) rates [0 (N0), 50 (N50), 100 (N100), and 200 (N200) kg ha^{-1}], on crop yield, N use efficiency, and soil properties was evaluated in a cropping system of irrigated forage maize (*Zea mays* L.) grown in summer and oats (*Avena sativa* L.) grown in winter as a catch crop. Biochar increased soil organic carbon (C), pH, cation exchange capacity (CEC), and extractable phosphorus (P), but strongly reduced N recovery in the set of the four cropping cycles. In biochar-amended plots, N50 had a negative apparent N recovery (− 21%), indicating that less N was recovered by the plants than in the N0 treatment without biochar. Biochar reduced maize dry matter (DM) yield by 15.6% in comparison to the untreated control, indicating N immobilization by biochar at low N rates (N0 and N50). Zeolites did not influence crop productivity or soil properties, except for the increase in extractable K, probably the result of its initial K content. N application to maize significantly increased the productivity of both crops, including that of the non-fertilized oats. Under the conditions of this experiment, biochar and zeolites did not prove to be useful soil amendments to increase crop DM yield in the short-term. The use of biochar increased soil organic C, which associated to a high N rate can enable the dual objective of maintaining productivity and the sustainability of the agro-system. The results stressed also the important role of oats as a cover crop to reduce the risk of nitrate leaching and denitrification during winter.

Keywords Soil conditioners · *Zea mays* · *Avena sativa* · Carbon sequestration · Crop nutritional indices · Soil properties

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1 Introduction

Nitrogen is the most important nutrient in crop fertilization taking into account the regularity of application and the rates usually applied. It is estimated that 109 × 10^6 t of N were applied in the world in 2017 (FAOSTAT 2020). However, most of the applied N (50 to 60%) is not used by plants, due to its high dynamic in the soil, and nutrient loss from the soil/plant system, contributing to environmental pollution (Werner 2007). Given all the associated implications of using N, from the effect on productivity and product quality, to aspects of nutrient use efficiency and environmental issues, its use in agriculture has been investigated more than any other essential nutrient (Havlin et al. 2014). In recent years, great importance has been given to soil amendments, fertilizing materials that can help regulate the bioavailability of nutrients in soils, which may have a relevant role in increasing the sustainability of agricultural systems. Biochar and zeolites are two of the most widely studied (Bernardi et al. 2010; Gao et al. 2019; Yu et al. 2019; Guaya et al. 2020; Wei et al. 2020).

Biochar is a C-based material that can be used as a soil amendment. It can be obtained from a range of biomass feedstock and a variety of methods, from which pyrolysis, under limited oxygen supply, is the most widely adopted (Bian et al. 2019; Jin et al. 2019). Biochar is highly recalcitrant in soils, due to its high molar H/C ratio, presenting also other important physical properties such as high porosity and low bulk density relative to soil (Kavitha et al. 2018; Shaaban et al. 2018). The application of biochar to the soil can change microbial community structures and many other relevant soil properties such as pH, CEC, or nutrient bioavailability (Shaaban et al. 2018; Palansooriya et al. 2019). In recent years, several studies have been carried out to evaluate the effect of applying biochar on soil properties and crop productivity, and on the regulation of greenhouse gas emissions. Although positive effects of the application of biochar on soil quality and crop productivity have not always been recorded, most review papers (Kavitha et al. 2018; Palansooriya et al. 2019; Yu et al. 2019) and meta-analyses (Jeffery et al. 2011; Gao et al. 2019) generally suggest positive results, especially when studies are conducted on poorly structured soils, such as acid, alkaline, nutrient-limited, salt-affected, or metal-contaminated ones.

Zeolite minerals are hydrated aluminosilicates, built from tetrahedral AlO_4 and SiO_4, whose rings join in a system of canals, cavities, and pores (Bernardi et al. 2010; Litaor et al. 2017). Negative charges appear due to the isomorphic substitutions of Si^{4+} by Al^{3+} in the silica framework. These minerals are characterized by the ease of retaining and releasing water and exchanging cations (counterions) without structural changes (Santasnachok et al. 2015). The use of zeolites as a soil amendment may explore their ion-exchange, adsorption, and catalytic properties in the soil. Nutrient-enriched zeolites have been used for soil application where some nutrients (NH_4^+, K^+) can be exchanged and slowly released for plant uptake, reducing their loss from the soils (Bernardi et al. 2010; Palanivell et al. 2016; Guaya et al. 2020). It seems that zeolites can also improve P availability from phosphate rocks, with Ca^{2+} exchanging onto the zeolite in response to plant uptake of other cations (NH_4^+, K^+), enhancing the dissolution of the rock phosphate (Pickering et al. 2002), and reduce the uptake of metals by plants (Golia et al. 2017).

Given the importance of N fertilization for agricultural crops, the environmental impact of N forms which are released from the soil/plant system, and the increasing presence of the soil amendments biochar and zeolites in the market, the working hypothesis set for this study was that the use of biochar and/or zeolites, in combination with N, can improve the productive performance of forage maize and oats and the N use efficiency, in an irrigated intensive farming system where high rates of the nutrient are usually applied. Before a widespread use of biochar and zeolites, farmers need to know about their effects on crops and also if they affect the rates of N to apply.

2 Materials and Methods

2.1 Site Characterization

The field experiment was carried out in Bragança, NE Portugal, in the experimental farm of Poulão (41° 47′ N; 6° 46′ W; 750 m a.s.l.) from May 2018 to May 2020. The plot where the experiment took place is organized as an 8-year rotation where 4 years of a double crop, forage maize in summer and oats in winter, is followed by a temporary (4-year) pasture. The experiments of this study were carried out after the second year of maize in the crop rotation, corresponding to the third and fourth years of maize, just before the pasture phase.

The region benefits from a Mediterranean type climate, where average annual air temperature and accumulated precipitation are 12.7 °C and 772.8 mm, respectively. Data of average monthly temperature and precipitation recorded during the experimental period are shown in Fig. 1. The soil is a Eutric Fluvisol (WRB 2015), developed in fluvial deposits, sandy clay loam textured (soil separates are 54% sand, 25% silt, and 21% clay). Other soil properties, from samples taken when the experiment started, were $pH_{(H2O)}$ 5.54, organic C 12.6 g kg^{-1}, extractable P 26.0 mg (P_2O_5) kg^{-1}, extractable K 63.0 mg (K_2O) kg^{-1}, and CEC 17.6 $cmol_c$ kg^{-1}.

2.2 Experimental Design

The experiment included two experimental factors, soil amendments (at three levels) and N fertilization (at four levels). Soil amendments were biochar, zeolites, and a non-treated control (mineral fertilization only). The N rates were 0 (N0), 50 (N50), 100 (N100), and 200 (N200) kg ha^{-1} and were applied to maize. These N rates were selected to create a gradient in the response of plants to N high enough to facilitate the interpretation of the effect of the soil amendments. N fertilization was split into two applications, 50% at pre-plant and 50% at side-dress timing. Thus, N50, for instance, represents a treatment where 25 kg N ha^{-1} were applied at planting and 25 kg N ha^{-1} were applied as side dressing.

The experiment was arranged as a split-block (Little and Hills 1978), since the operations involved make it difficult to handle all the factor combinations in the same manner. Soil amendments were assigned to whole plots in a randomized complete block with three replications (tree blocks) and N rates were assigned to subplots. The size of each experimental unit was 12 m^2 (4 m × 3 m).

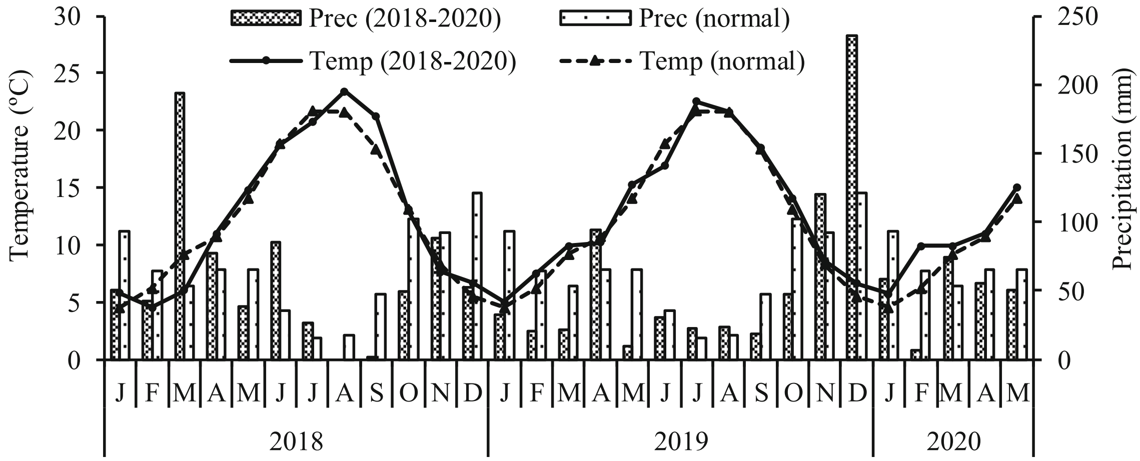

Fig. 1 Average air monthly temperature and precipitation during the experimental period and data of the climate normal of the region

Biochar and zeolites are commercial products which composition is provided in Table 1. N was applied as ammonium nitrate (27% N, 50% as NH_4^+, and 50% as NO_3^-). Biochar was used at a rate of 10 t ha^{-1} and zeolite at a rate of 5 t ha^{-1} as recommended by vendors. All the plots received also P and K in the rates recommend by the local advisory system, based on soil testing, to complement the fertilization program of maize. P was applied at a rate of 65.5 kg ha^{-1} (as superphosphate, 18% P_2O5) and K at a rate of 124.5 kg ha^{-1} (as potassium chloride, 60% K_2O).

2.3 Installation and Maintenance of the Field Trial

The experiment involved two summer growing seasons of forage maize and two winter growing seasons of oats. The experiment started in the spring of 2018. The soil was moldboard plowed to a depth of 25 cm, which was followed by a pass of cultivator to level the ground. Subsequently, the amendments and fertilizers were spread manually in the respective plots. All pre-plant fertilizers were then incorporated with a final pass of cultivator. Soil preparation and fertilizer application took place on May 15th 2018. The next day, on May 16th, maize was sown. Seeding density was 80,000 seed ha^{-1}, with seeds spaced at 0.70 and 0.18 m between and in the rows, respectively. Maize cultivar was the mid-season (FAO 500) hybrid Monero. The crop received an herbicide treatment in the phenological stage 14 (four unfolded leaves) (Meier 2001), on July 7th 2018. The active ingredients were isoxadifen-ethyl (22 g L^{-1}) and tembotrione (44 g L^{-1}) and the herbicide was applied at a concentration of 0.5 L hL^{-1} (2 L ha^{-1}). Side dress N was applied also on July 7th 2018. During the summer, the maize was sprinkled irrigated with a

Table 1 Properties of biochar and zeolite used in this study as provided by the manufacturers

Biochar (from *Acacia dealbata*)		Natural zeolite (cliptolinolite)	
Particle size (mm)	0.1–10	Particle size (mm)	0.4–3.0
Bulk density (kg m^{-3})	350–400	Water holding capacity (%)	15.5
Moisture (%)	≤30.0	Cation exch. Capacity (cmol$_c$ kg^{-1})	157
Conductivity (μS cm^{-1})	948	pH	7.6
pH	<9	Bulk density (kg m^{-3})	980
Total organic C (%)	≥90.0	SiO_2 (%)	63.00
Ash (%)	≤5.0	TiO_2 (%)	0.45
Volatile (%)	≤5.0	Al_2O_3 (%)	11.57
Total N (g kg^{-1})	≤5.0	Fe_2O_3 (%)	1.87
Cd (mg kg^{-1})	<0.05	FeO (%)	0.81
Pb (mg kg^{-1})	0.05	MgO (%)	0.92
Fe (mg kg^{-1})	99.5	CaO (%)	5.78
As (mg kg^{-1})	<0.10	Na_2O (%)	2.39
Hg (mg kg^{-1})	<0.10	K_2O (%)	1.49
		P_2O_5 (%)	0.09
		H_2O (%)	3.44

central pivot. The harvest took place on September 7th 2018, in the growth stage 73 (early milk).

On October 23rd 2018, oat crop (cv. Boa Fé) was established after a brief soil preparation with cultivator. Oat crop was not fertilized to better highlight the residual effect of maize fertilization and its role as a catch crop. The sowing rate was 130 kg ha^{-1} of seed. No other cropping operations were carried out on oat crop until harvest on May 7th 2019. At harvest, the plants were in the growth stage 65 (full flowering).

In 2019, maize was installed in the same way with the exception of the soil amendments biochar and zeolites which were only applied in 2018. The date of sowing was on May 27th, 2019. The applications of herbicide and N as a side dress were performed on July 17th. The harvest of maize took place on September 19th. Oats was sown on October 30th 2019 and harvested on 12th May 2020.

2.4 Data Acquisition in the Field and Tissue and Soil Sampling

Leaf greenness was estimated by using the portable SPAD (Soil and Plant Analysis Development)-502 Plus chlorophyll meter. Thirty readings for each measurement were taken from the middle of the blade of the youngest fully expanded leaves. The measurements were performed on 3rd August 2018 and 8th August 2019 (34/35 growth stage; 4 to 5 nodes detectable).

The hand-held FieldScout CM 1000 was used to estimate a normalized difference vegetation index (NDVI). To estimate the NDVI, the meter senses and measures the ambient light at the wavelength of 660 nm and the reflected light (non-absorbed by leaf chlorophyll) at 840 nm wavelength. The NDVI values (between − 1 and 1) are calculated from the equation [(%near infrared − %Red) / (%near infrared + %Red)]. The measurements were taken in the same leaf part and dates as SPAD readings.

The OS-30p+ chlorophyll meter was used to estimate chlorophyll *a* fluorescence and OJIP transient through the dark adaptation protocols F_V/F_M, F_V/F_0, and the advanced OJIP test. F_M, F_0, and F_V are, respectively, maximum, minimum, and variable fluorescence from dark adapted leaves. The variables F_V/F_M and F_V/F_0 were estimated as $F_V/F_M = (F_M\text{-}F_0)/F_M$ and $F_V/F_0 = (F_M\text{-}F_0)/F_0$. The OJIP test gives origin fluorescence at 20 μs (O), fluorescence at 2 ms (J), fluorescence at 30 ms (I), and maximum fluorescence (P, or F_M). Measurements were taken from the middle of the blade of the youngest fully expanded leaves, after a period of dark adaptation longer than 35 min, in the dates mentioned above.

Samples of the youngest fully matured leaves were also taken on the same date of the use of portable devices to assess crop nutritional status. These samples were carried out to the laboratory, oven-dried at 70 °C, and analyzed for elemental composition.

Maize was harvested late in summer on September 7th and 19th in 2018 and 2019. Samples of 1 m linear (0.7 m^2) from the inner line of the plots were cut at soil level. The samples were weighed in fresh in the field. Still in the field, representative fresh sub-samples of the whole samples were weighed again and sent to the laboratory. After oven-dried at 70 °C, the sub-samples were weighed dry, to allow estimating the DM yield per unit area. From the initial maize samples, basal maize stalks, 15 to 35 cm above ground, were also taken and sent to the laboratory to perform the stalk nitrate test (SNT).

Oat crop was cut on May 7th 2019 and May 12th 2020. A square mesh of 0.5 m^2 was used to establish the size of the sample in each experimental unit. The field samples were oven-dried at 70 °C and weighed dry. These samples allowed to estimate the DM yield of the crop and the determination of the elemental composition of the tissues.

The soils were sampled at 0–30 cm depth, immediately before of the side dress N applications, to allow performing the pre-side dress soil nitrate test. The soils were also sampled at the end of the summer growing seasons of maize, on October 16th 2018 and October 21st 2019, and at the end of the field trial on May 20th 2020. Composite samples were collected from each experimental unit, consisting on sampling in six random points to create each composite sample.

2.5 Laboratory Analyses

The soil samples were oven-dried at 40 °C and sieved in a mesh of 2 mm. The samples were analyzed for (1) pH (H_2O, KCl) (soil: solution, 1:2.5); (2) cation-exchange capacity (ammonium acetate, pH 7.0) and exchange acidity (KCl extraction); (3) easily oxidizable C (wet digestion, Walkley-Black method); (4) total organic C (incineration); (5) extractable P and K (ammonium lactate); (6) extractable B (hot water extraction and azomethine-H methods); (7) extractable Fe, Mn, Zn, and Cu (ammonium acetate and EDTA, determined by atomic absorption spectrometry); (8) inorganic N (2 M KCl extraction). In the initial samples, there were also determined (9) soil separates (clay, silt, and sand fractions) (Robinson pipette method). Methods 1–4, 7, and 9 are fully described by Van Reeuwijk (2002), method 5 by Balbino (1968), method 6 by Jones (2001), and method 8 by Baird et al. (2017).

Elemental tissue analyses were performed by Kjeldahl (N), colorimetry (B and P), flame emission spectrometry (K), and atomic absorption spectrophotometry (Ca, Mg, Cu, Fe, Zn, and Mn) methods after nitric digestion of the samples (Temminghoff and Houba 2004). Nitrate concentration in basal maize stalks was determined according to Baird et al. (2017) by UV-vis spectrophotometry in a water extract (dry biomass:solution, 10:40).

2.6 Data Analysis

Data analysis was carried out using JMP software. Data was firstly tested for normality and homogeneity of variances using the Shapiro-Wilk test and Bartlett's test, respectively. In the split-block design, soil amendments (whole plots), N rates (subplots), and interaction (soil amendments × N rates) were treated as fixed and blocks as random factors. After ANOVA examination, the means with significant differences ($\alpha < 0.05$) were separated by Tukey HSD test ($\alpha = 0.05$). Some data plots were submitted to regression analysis by using N rates as independent variable and measured data as dependent variables. Linear and non-linear relationships were found and the model that better fit the data adopted. Apparent N Recovery (ANR) was used as an index of N use efficiency. ANR was estimated according to the equation:

Apparent N recovery (ANR, %) = 100 × [N recovered in the fertilized treatments – N recovered in the N0 (from the mineral plot) treatment]/N applied as a fertilizer).

3 Results

3.1 Maize Dry Matter Yield and Nitrogen Nutritional Status Indices

Maize DM yield varied significantly between soil amendments in 2018 and also in 2019 (Fig. 2). The plots amended with biochar produced less biomass than the plots treated with zeolites or the plots that received only mineral fertilizers. Maize DM yield increased significantly with N rate, the higher average values being found in the N200 treatment in both years. In 2019, maize DM yield tended to be lower than in 2018. The plots that did not receive N and those underfertilized were unable to maintain the crop productivity in the second growing season of maize.

For an easier interpretation of the DM yield results, data of N rates was presented separately from soil amendments, ignoring the global model of split-block. It can be seen clearly that the reduced maize DM yield found in the biochar plots was mainly due to the plots receiving lower N rates, particularly in 2019 (Fig. 3). In the biochar plots treated with a high N rate, the reduction in DM yield was not observed. The average DM yield in the biochar plot was 4.4 t ha^{-1} in the subplot N0 and reached 16.6 t ha^{-1} in the subplot N200, whereas average DM yields of zeolites and mineral treatments were 7.3 and 7.1 t ha^{-1} in the N0 treatment, reaching 17.6 and 14.2 t ha^{-1} in the subplot N200.

Leaf N concentration at 34/35 growth stage (4 to 5 nodes detectable) did not vary significantly with soil amendments in 2018 or 2019 (Table 2). Leaf N concentration increased significantly with N rate in 2018, the average values of the N100 and N200 treatments being higher than the average values of the N50 and N0 treatments. In 2019, a slight increase in leaf N concentration was observed as the N rate increased but the differences were not statistically significant. SPAD-readings showed a significant decrease in the plots amended with biochar in comparison to the other treatments. In 2018, the higher average values were found in the mineral treatment and in 2019 in the plots amended with zeolites. SPAD-readings also varied significantly with N rates in 2018, and the lower and the higher average values were found respectively in the N0 and N200 treatments. In 2019, SPAD-readings did not display significant differences between N treatments. NDVI showed little sensitivity to the experimental treatments. The values varied between 0.78 and 0.83 without significant differences

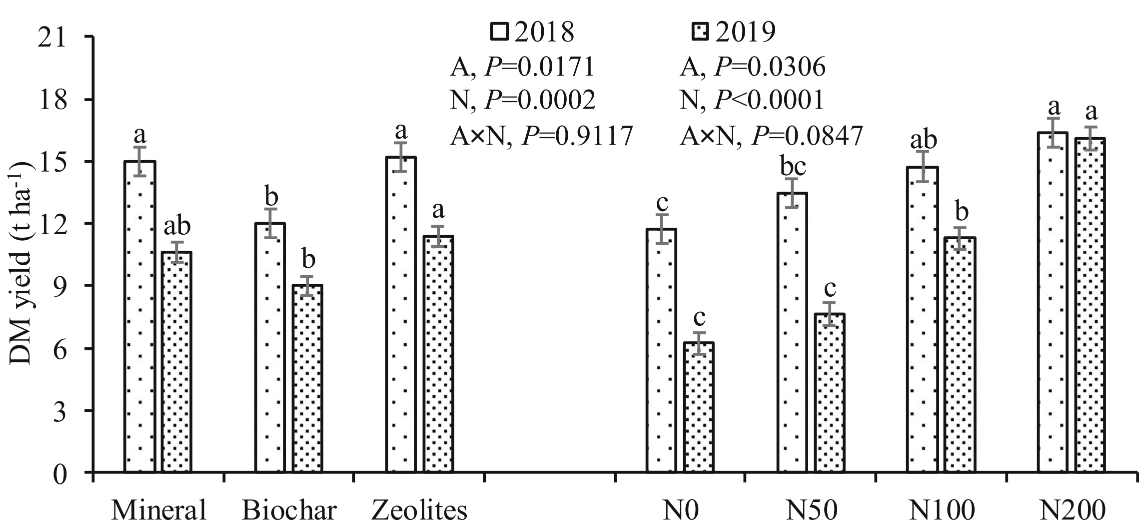

Fig. 2 Maize dry matter (DM) yield as a function of soil amendments as whole plots and nitrogen (N) rates [N0, 0 + 0 (pre-plant + side dress) kg ha^{-1}, N50, 25 + 25 kg ha^{-1}, N100, 50 + 50 kg ha^{-1}, N200, 100 + 100 kg ha^{-1}] as subplots and year. Analysis of variance, P (Prob > F), A (soil amendment), N (nitrogen rate), A × N (interaction). Means followed by the same letter (separated by soil amendment and N rate and year) are not significantly different by Tukey HSD test ($\alpha = 0.05$). Vertical bars are the standard errors

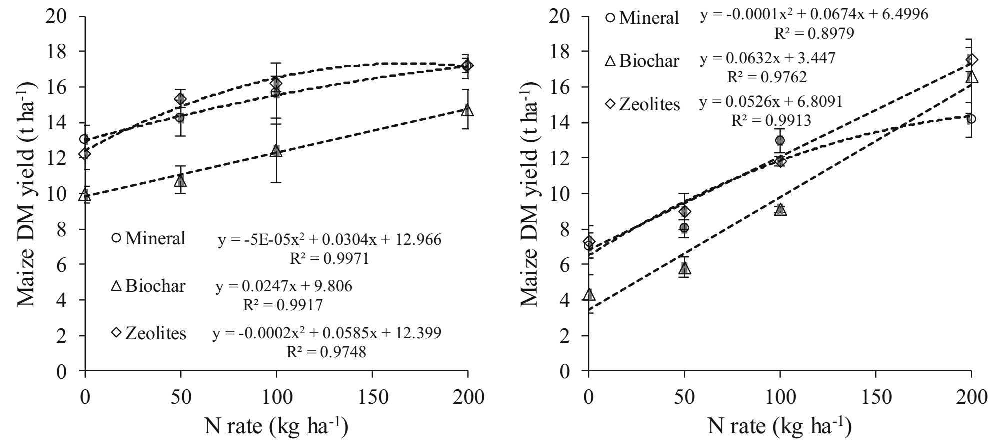

Fig. 3 Maize dry matter (DM) yield as a function of nitrogen (N) rate as subplots separated by soil amendments as whole plots and years. Vertical bars are the mean confidence intervals

between soil amendments or between N rates in both the years. The chlorophyll *a* fluorescence ratios (F_V/F_M and F_V/F_0) and OJIP transient are usually seen as important tests to assess stresses that can affect the function of photosystem II. However, in spite of the effects of the treatments in DM yield and plant nutritional status, most of these tests did not show significant differences between soil amendments and N rates. However, in 2019, F_V/F_M was significantly lower in the N0 in comparison to the N-fertilized treatments.

The concentration of N in the aboveground maize dry biomass at harvest did not vary significantly with soil amendments (Table 2). In 2018, average values varied from 11.8 to 12.3 g kg^{-1} and in 2019 from 7.5 to 8.0 g kg^{-1}. N fertilization, in turn, caused a significant effect on plant N concentration, the lower and the higher values to be found respectively in the N0 and N200 treatments. At harvest, basal stalk NO_3^- varied significantly with soil amendment in both the years. In 2018, the average value in the zeolite plots (1530.1 mg NO_3^--N kg^{-1}) was significantly higher than that in the other treatments (623.7 and 816.4 mg kg^{-1}, respectively in biochar and mineral treatments). In 2019, the average value of biochar treatment was significantly lower (654.8 mg kg^{-1}) than those of the other treatments (1174.3 and 945.4 mg kg^{-1} in the zeolites and mineral treatments). The higher the rate of N applied, the higher the stalk NO_3^--N levels at the end of the growing season in both the years. In 2018, they varied from 350.3 to 2180.6 mg kg^{-1} and in 2019 from 600.1 to 1592.8 mg kg^{-1}, respectively in N0 and N200 treatments.

Data of the effect of the soil amendments and N rates on the concentration of the other analyzed nutrients in the leaves was

Table 2 Nitrogen (N) nutritional status indices and chlorophyll *a* fluorescence as a function of soil amendments as whole plots and N rates [N0, 0 + 0 (pre-plant + side dress) kg ha^{-1}, N50, 25 + 25 kg ha^{-1}, N100, 50 + 50 kg/ha, N200, 100 + 100 kg ha^{-1}] as subplots and year. Analysis of variance, *P* (Prob > F), A (soil amendment), N (nitrogen rate), A × N (interaction), SE (standard error). In columns, means followed by the same letter, separated by soil amendment and nitrogen rate, are not significant different by Tukey HSD test (α = 0.05)

	Leaf N (g kg^{-1})		SPAD		NDVI		F_V/F_M		Plant N (g kg^{-1})		Stalk NO_3^--N (mg kg^{-1})	
	2018	2019	2018	2019	2018	2019	2018	2019	2018	2019	2018	2019
Mineral	26.3 a	30.9 a	59.3 a	59.1 ab	0.83 a	0.78 a	0.76 a	0.77 a	11.8 a	7.8 a	816.4 b	945.4 a
Biochar	26.6 a	30.1 a	56.5 b	56.1 b	0.83 a	0.79 a	0.75 a	0.76 a	11.8 a	7.5 a	623.7 b	654.8 b
Zeolites	28.3 a	30.0 a	58.0 ab	60.5 a	0.81 a	0.79 a	0.75 a	0.77 a	12.3 a	8.0 a	1530.1 a	1174.3 a
P (A)	0.0191	0.9056	0.0055	0.0376	0.1236	0.8007	0.6952	0.5064	0.6528	0.6081	0.0037	0.0020
SE (A)	0.07	0.16	0.23	0.99	0.01	0.01	0.01	0.01	0.03	0.03	115.47	53.49
N0	23.2 b	27.7 a	54.9 c	58.6 a	0.82 a	0.78 a	0.75 a	0.76 b	10.3 b	6.2 c	350.3 c	600.1 b
N50	25.6 b	31.0 a	55.9 c	58.0 a	0.82 a	0.80 a	0.75 a	0.78 a	12.6 a	6.4 c	494.2 bc	700.9 b
N100	29.8 a	31.5 a	59.1 b	57.9 a	0.83 a	0.80 a	0.76 a	0.78 a	12.2 a	8.1 b	973.0 b	803.9 b
N200	29.5 a	31.9 a	61.9 a	59.3 a	0.82 a	0.78 a	0.76 a	0.78 a	12.9 a	10.6 a	2180.6 a	1592.8 a
P (N)	0.0007	0.4856	<0.0001	0.8128	0.9052	0.4011	0.8293	0.0274	0.0001	<0.0001	<0.0001	<0.0001
SE (N)	0.08	0.18	0.27	1.14	0.01	0.01	0.01	0.01	0.04	0.03	133.33	61.74
P (A×N)	<0.0001	0.7715	0.0002	0.7880	0.5736	0.5368	0.4360	0.2121	<0.0001	0.2308	0.0254	0.6804
SE (A×N)	0.15	0.32	0.46	1.98	0.01	0.02	0.02	0.01	0.06	0.05	230.97	106.97

not provided in detail due to its extensity. In a brief summary, leaf P levels were significantly higher in the zeolite plots in 2018 in comparison to the other treatments, but in 2019 no significant differences between treatments were found. N rates also did not influence significantly leaf P levels. Leaf K levels did not vary significantly with soil amendments or N rates in any of the years. Biochar and zeolites significantly reduced leaf Ca levels in comparison to the non-amended plots in 2018 but not in 2019. Leaf Fe levels were significantly higher in the zeolites treatment in 2018 but in 2019, significant differences between treatments were not found. Leaf Mn levels were significantly lower in the biochar treatment in 2018 in comparison to the other treatments but not in 2019.

3.2 Oat Dry Matter Yield

In 2019, biochar decreased oat dry matter yield compared to mineral fertilization (Fig. 4). In 2020, DM yield of oats was similar among all treatments. N rate applied to maize grown in the previous season significantly increased oat DM yield. The unfertilized control and the N200 treatment produced respectively the lower and the higher average values in both years. The residual effect of maize N fertilization was strongly marked in the oat crop. The values in N200 were significantly higher than in N100 in 2018 and 2019. As observed to maize, DM yields for each treatment were lower in 2019 in comparison to 2018.

3.3 Nutrient Recovery by the Four Crops

Data on nutrient concentration in oat tissues were not provided due to the reduced effect of the soil amendments and N rates on plant elemental composition. These results appear reflected in the recovery of the nutrients by each crop after being multiplied by the production of dry biomass (Fig. 5).

Data on N recovery were presented by crop (or growing season) and as a sum of the four successive crops (maize 2018 + oats 2019 + maize 2019 + oats 2020) (Fig. 5). The crops grown in the plots amended with biochar gave significantly less N recovery than the crops grown in the non-amended and zeolite plots, which reflects the result observed in DM yield, particularly in maize, and less the result of tissue N concentration. The effect of the N rate on N recovery was very strong due to the combined effect on DM yield (Figs. 2 and 3) and on tissue N concentration (Table 2). In the N0 treatment, average N recovery was 197.9 kg N ha^{-1}, whereas in N200 was 446.2 kg N ha^{-1}.

Data on the recovery of the other nutrients analyzed was not provided in full due to its extensity. In a brief summary, significant differences between N treatments were found for almost all the nutrients with the exceptions of Fe and Zn. The N200 treatment gave the higher results, due to the great effect of the applied N on DM yield in comparison to the effect of N in the concentration of the other nutrients in plant tissues. The effect of the soil amendments on nutrient recovery was small. However, biochar tended to give lower values of K, Ca, Mg, Mn, and B, also mainly due to the detrimental effect on DM yield and less due to the effect on tissue elemental composition.

Estimates of apparent N recovery (ANR) as the four growing seasons succeed are presented in Table 3. In the non-amended (mineral) plots, ANR tended to decrease from the low to the higher N rates. In the final balance, after the second growing season of oats, the average values were 62.3, 43.5, and 46.6%, respectively in N50, N100, and N200 treatments. At this time, two fertilizations were already made (to maize

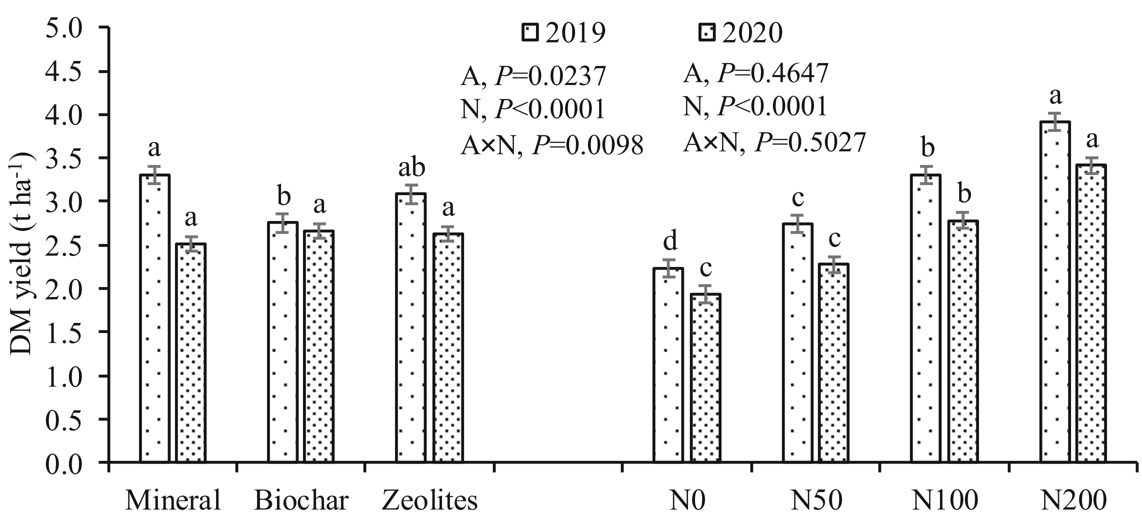

Fig. 4 Dry matter (DM) yield of oats as a function of soil amendments as whole plots and nitrogen (N) rates [N0, 0 + 0 (pre-plant + sidedress) kg ha^{-1}, N50, 25 + 25 kg ha^{-1}, N100, 50 + 50 kg ha^{-1}, N200, 100 + 100 kg ha^{-1}] as subplots and year. Analysis of variance, P (Prob > F), A (soil amendment), N (nitrogen rate), A × N (interaction). Means followed by the same letter (separated by soil amendment and N rate and year) are not significant different by Tukey HSD test ($\alpha = 0.05$). Vertical bars are the standard errors

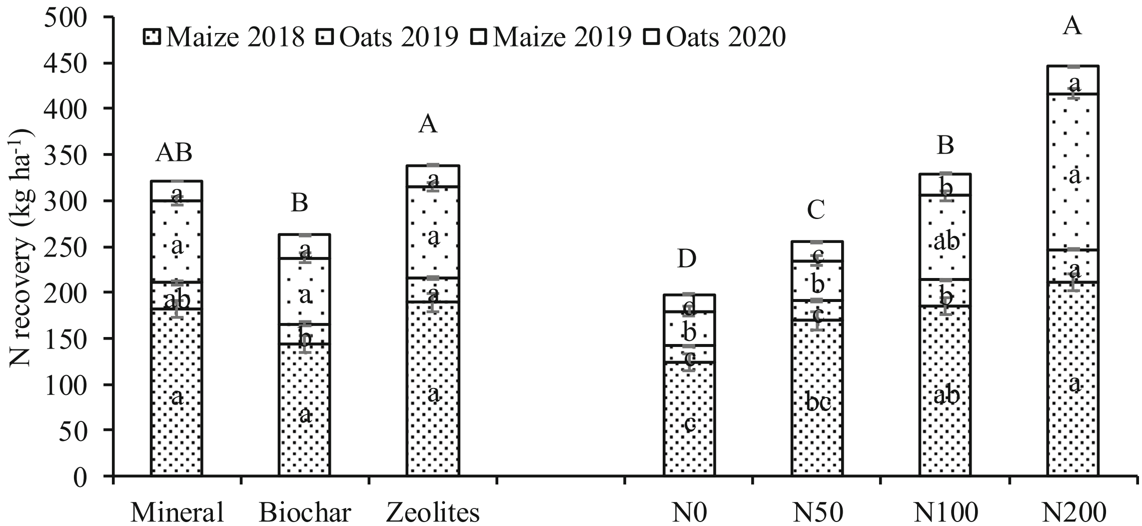

Fig. 5 Nitrogen recovery as a function of soil amendments as whole plots and nitrogen (N) rates [N0, 0 + 0 (pre-plant + sidedress) kg ha^{-1}, N50, 25 + 25 kg ha^{-1}, N100, 50 + 50 kg ha^{-1}, N200, 100 + 100 kg ha^{-1}] as subplots and year. To each crop (lowercase) and total (uppercase), means followed by the same letter (separated by soil amendment and N rate) are not significant different by Tukey HSD test ($\alpha = 0.05$). Vertical bars are the standard errors

crop), which means that the N200 plots, for instance, have received 400 kg N ha^{-1}. The use of low N rates (N50) in the biochar plots gave negative ANR, which means that less N was recovered than in the N0 plot of the mineral treatment. The results of zeolites showed an increase in ANR with N rate, contrarily to that observed in mineral plots.

3.4 Soil Inorganic Nitrogen and General Soil Properties

In 2018, soil NO_3^--N levels at pre-side dress N application (4 to 5 leaves unfolded) were significantly higher in the mineral treatment in comparison to the plots amended with biochar or zeolites (Table 4). The average values were 20.7, 8.0, and 8.3 mg kg^{-1}, respectively in mineral, biochar, and zeolites treatments. In July 2019, the biochar treatment presented significantly lower values of soil NO_3^--N and NH_4^+-N than the other treatments. After the harvest of maize, in October 2018 and 2019, no significant differences were found in soil NO_3^--N and NH_4^+-N levels between soil amendments. Soil NO_3^--N varied between 25.5 to 28.5 mg kg^{-1} and 12.9 to 16.9 mg kg^{-1}, respectively in 2018 and 2019. Also in May 2019 and 2020, after the harvest of oat crop, no significant differences were found between soil amendments in soil NO_3^--N and NH_4^+-N levels. Average NO_3^--N values varied between 4.5 to 4.8 mg kg^{-1} and between 6.4 and 7.8 mg kg^{-1}, respectively in 2019 and 2020. N rates significantly affected NO_3^--N levels in the soil in July 2018. The higher rate of N applied, N200 (at this time, only 100 kg N ha^{-1} had been applied at pre-plant), gave the higher average value of soil

Table 3 Apparent nitrogen recovery (ANR) (average ± standard deviation) after the harvest of the four consecutive crops as a function of soil amendments as whole plots and N rates [N0, 0 + 0 (pre-plant + sidedress) kg ha^{-1}; N50, 25 + 25 kg ha^{-1}; N100, 50 + 50 kg ha^{-1}; N200, 100 + 100 kg ha^{-1}] as subplots

		Maize 2018* (%)	Oats 2019*	Maize 2019**	Oats 2020**
Mineral	N50	48.0±30.8	57.8±20.9	52.7±15.2	62.3±7.6
	N100	15.3±12.8	20.2±11.4	37.8±16.5	43.5±12.5
	N200	23.2±11.9	32.6±14.3	42.6±6.0	46.6±7.2
Biochar	N50	−39.4±19.8	−42.1±19.6	−31.4±12.4	−21.0±10.3
	N100	13.3±17.0	20.9±15.7	21.7±14.5	29.2±12.5
	N200	15.4±7.9	20.5±8.3	40.6±6.8	46.1±6.8
Zeolites	N50	40.1±20.3	39.6±21.8	32.9±21.3	42.9±17.4
	N100	44.8±13.9	54.8±7.4	57.1±4.6	63.7±5.7
	N200	36.8±4.5	44.4±4.7	58.4±3.5	63.1±5.4

ANR (%) = [N recovery in fertilized treatments – N recovery in N0 (from mineral main plot) treatment)]/N applied as a fertilizer × 100. Estimated taking into account the N rates applied in the *first and **first plus second growing seasons of maize

Table 4 Soil inorganic nitrogen (N) at pre-side dress of maize, after the harvest of maize, and after the harvest of oats as a function of soil amendments as whole plots and N rates [N0, 0 + 0 (pre-plant + side dress) kg/ha, N50, 25 + 25 kg ha^{-1}, N100, 50 + 50 kg ha^{-1}, N200, 100 + 100 kg ha^{-1}] as subplots. Analysis of variance, *P* (Prob > F), A (soil amendment), N (nitrogen rate), A × N (interaction), SE (standard error). Means followed by the same letter in columns (separated by soil amendments and N rate) are not significant different by Tukey HSD test (α = 0.05)

	Pre-side dress soil N test				Soil residual N after maize				Soil residual N after oats			
	July 2018		July 2019		October 2018		October 2019		May 2019		May 2020	
	NO_3^--N (mg kg^{-1})	NH_4^+-N	NO_3^--N	NH_4^+-N	NO_3^--N (mg kg^{-1})	NH_4^+-N	NO_3^--N	NH_4^+-N	NO_3^--N (mg kg^{-1})	NH_4^+-N	NO_3^--N	NH_4^+-N
Mineral	20.7 a	1.9 a	10.8 a	1.7 a	25.5 a	4.4 a	16.9 a	5.0 a	4.8 a	1.2 a	6.4 a	1.0 a
Biochar	8.0 b	1.6 a	7.8 b	1.0 b	28.5 a	5.1 a	14.9 a	5.7 a	4.5 a	1.1 a	7.8 a	1.3 a
Zeolites	8.3 b	2.0 a	9.9 a	1.8 a	28.2 a	6.1 a	12.9 a	5.4 a	4.7 a	1.2 a	7.4 a	1.3 a
P (A)	<0.0001	0.0507	0.0035	0.0130	0.0929	0.0516	0.1636	0.6126	0.6449	0.2393	0.4441	0.1624
SE (A)	0.53	0.10	0.41	0.13	0.69	0.42	1.19	0.53	0.18	0.07	0.57	0.07
N0	10.6 b	1.9 a	7.3 b	0.9 c	18.1 d	4.1 b	11.2 b	4.3 b	4.4 a	1.2 a	6.7 a	1.2 a
N50	9.9 b	2.1 a	8.6 b	1.0 bc	21.9 c	3.4 b	10.9 b	4.7 b	4.7 a	1.2 a	7.3 a	1.2 a
N100	13.2 a	1.6 a	9.1 b	1.6 b	29.0 b	4.6 b	13.1 a	4.9 b	4.7 a	1.1 a	6.4 a	1.0 a
N200	15.1 a	1.7 a	12.7 a	2.4 a	49.0 a	8.6 a	24.9 a	7.6 a	4.8 a	1.2 a	8.6 a	1.4 a
P (N)	<0.0001	0.0600	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	0.0038	0.6230	0.5540	0.0679	0.0601
SE (N)	0.62	0.12	0.47	0.15	0.80	0.49	1.38	0.61	0.21	0.08	0.66	0.08
P (A×N)	<0.0001	<0.0001	0.0064	0.0319	0.3959	0.6110	0.0522	0.1191	0.0630	0.0675	0.0879	0.0510
SE (A×N)	1.07	0.20	0.59	0.26	1.39	0.84	2.39	1.05	0.37	0.13	1.14	0.15

NO_3^--N (15.1 mg kg^{-1} in comparison to 10.6 mg kg^{-1} in the N0 treatment). In that date, soil NH_4^+-N levels did not vary significantly with N rates. In July 2019, soil NO_3^--N and NH_4^+-N levels progressively increased with N rate, the higher values recorded in the N200 treatment (NO_3^--N varied from 12.7 to 7.3 mg kg^{-1} in N200 and N0 treatments). In October 2018 and 2019, significant differences were also found between N rates, in soil NO_3^--N and NH_4^+-N levels, the higher average values being found in both years in the N200 treatment. The highest average value of NO_3^--N was recorded in 2018 in the N200 treatment (49.0 mg kg^{-1}) and the lowest in 2019 in the N50 treatment (10.9 mg kg^{-1}). The effect of the N treatments in soil NO_3^--N and NH_4^+-N levels was not observed in May (2019 and 2020) after the harvest of oats. The average values of NO_3^--N varied from 4.4 (N0, 2019) to 8.6 (N200, 2020) mg kg^{-1}.

Soil analyses were performed three times during the experimental period, in October 2018, October 2019, and May 2020. Among several soil properties determined, those showing greater variation (usually with significant differences between soil amendments) are presented in Fig. 6. They are total organic C, easily oxidizable C, pH, extractable P and K, and CEC. N fertilization had a modest effect on most the soil properties determined (data not shown). Total organic C and easily oxidizable C were consistently higher over the experimental period in the biochar treatment. Soil pH was also higher in the biochar treatment, with significant difference to be found for the three sampling dates. Biochar plots also showed average higher values of extractable P, whereas higher extractable K values were found in the plots amended with zeolites. Biochar also significantly increased CEC.

4 Discussion

The application of biochar was found to reduce maize DM yield compared to zeolites and the untreated control. The lower productivity in the biochar treatment was due to the much reduced values in the N treatments that did not receive N (N0) or only received a little amount (N50). In the subplots of high N rates (N200), no reduction in maize DM yield was observed. Of all the plant nutritional status indices, the most sensitive to the treatments appeared to be the SNT. The plants treated with biochar showed the lowest values (623.7 and 654.8 mg kg^{-1} in 2018 and 2019 in comparison with 1530.1 and 1174.3 mg kg^{-1} observed in the mineral plot). The SNT was developed by Binford et al. (1990) and has been recognized as an index of high sensitivity to soil N availability, since N tends to accumulate as nitrate in the vacuoles of conductive tissues such as the maize stalks (Rodrigues et al. 2006; Isla et al. 2015; Yang et al. 2017). The ranges reported by Blackmer and Mallarino (1996) for the interpretation of results of SNT were < 250 (low N availability), 250–700 (marginal), 700–2000 (optimal), and > 2000 (excess). The results

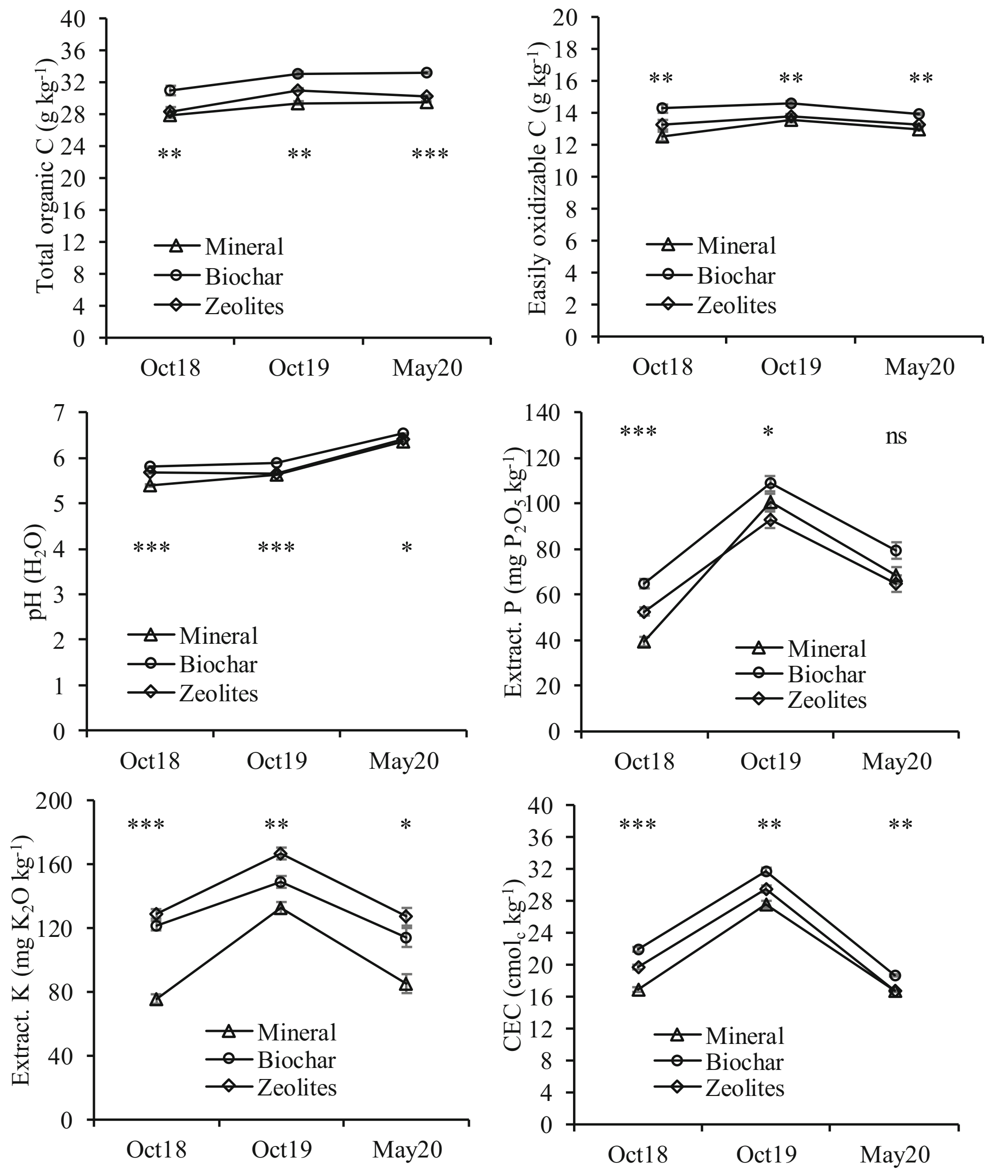

Fig. 6 Total organic carbon (C), easily oxidizable C, pH, extractable P and K, and cation exchange capacity (CEC) as a function of soil amendments (average values are from the whole plots, in the split-block model); *ns* not significant; $^{*}P < 0.05$; $^{**}P < 0.01$; $^{***}P < 0.001$). Error bars are the standard errors

clearly showed that in the biochar plot, low N availability might have been an important factor reducing maize DM yield. In oats, the reduction in DM yield occurred only in the first year, which may indicate that the depressive effect of biochar was temporary and not permanent. Regarding N recovery (the combined effect of DM yield and tissue N concentration), the values in the biochar treatment were the lowest. The estimation of ANR to the four growing seasons, based on the control treatment (N0) of the mineral whole plot, provided a good contribution to explain the effect of biochar. The N50 treatment (subplot), on the biochar treatment (as whole plot), showed negative ANR. This shows that the use of biochar deprived the plants of N, which explains the drop in DM yield. At high N rates (N200), ANR in the biochar treatment was equivalent to that of the mineral treatment. The presidedress soil nitrate test also revealed a reduction in soil inorganic N in the biochar treatment, mainly in 2019, whereas in autumn the effect was not evident.

As shown in the present study, the use of biochar does not always improve crop productivity. In some studies, positive effects were recorded (Arif et al. 2017; Jin et al. 2019; Sun et al. 2020) while in others no, or even negative effects were observed (Rodrigues et al. 2019; Wei et al. 2020). Some review papers (Kavitha et al. 2018; Shaaban et al. 2018; Yu et al. 2019) and meta-analyses (Jeffery et al. 2011; Gao et al. 2019), recently published, have highlighted this controversy, but they tend to indicate a predominance of positive results in crop yield by the use of biochar as a soil amendment. Interference with the N cycle may be one of the most relevant aspects of the effect of biochar on crop productivity and sustainability of agro-systems. Several studies have been devoted to assessing the effect of biochar on greenhouse gas emissions. Also in this area, it is possible to find results showing a reduction in emissions (Singh et al. 2010; Spokas et al. 2012), an increase (Chen et al. 2015; Agegnehu et al. 2016), or where emissions have depended on the conditions of the biochar application (Wei et al. 2020). Studies evaluating the dynamic of inorganic N in the soil, and the risk of nitrate leaching, tend to show more coincident results, with lower values of inorganic N in the soil after the application of biochar (Sun et al. 2017; Li et al. 2019; González-Cencerrado et al. 2020). Currently, there seems to be no doubt about the effects of biochar on the dynamics of N in the soil. It has been suggested that the main mechanisms involved are adsorption, biological immobilization, and ionic exchange (Zornoza et al. 2016; Shaaban et al. 2018). In this study, biochar also increased soil organic C, pH, and CEC, which associated with its high porosity (aeration) and high surface area, may have stimulated soil biological activity, leading to biological N immobilization, and increased NO_3^- and NH_4^+ adsorption. In the treatments consisting of higher N rates, a reduction in soil available N was not observed, probably due to a faster immobilization-mineralization turnover.

The results of only one study cannot be generalized because results may depend on soil type (Zhu et al. 2015) and also on the characteristics of biochar, which may be dependent on feedstock, pyrolysis temperature, and holding time (Rajkovich et al. 2012; Zornoza et al. 2016). It is therefore still very difficult to predict in which specific agro-ecological conditions the effects prevail. Obtaining this information would be extremely useful so that biochar could be used without risks for the management of N in agrosystems. Furthermore, from the farmer's perspective, biochar is a production factor; if a net income cannot be obtained from its use, it will never be widely adopted by them.

The application of zeolites had virtually no positive or negative effect on soil properties or on the performance of plants. The only noticeable exception was the increase in soil extractable K. Studies using zeolites as a soil amendment are still noticeably fewer than with biochar. However, these materials have high CEC, high water holding capacity in the free channels, and high adsorption capacity (Bernardi et al. 2010). Under certain conditions, these properties can confer advantages to plants with their application to the soil, with improved efficiency in the use of water and nutrients (Bernardi et al. 2010; Villarreal-Núñez et al. 2015; Litaor et al. 2017), or in reducing metal uptake by plants (Golia et al. 2017). In particular situations, the application of zeolites may increase crop productivity as observed by Noori et al. (2007) in saline soils and by Assimakopoulou et al. (2020) through mixing zeolites with organic substrates. However, as in the present study, a lack of a significant effect on crop yield by the use of zeolites was reported by Litaor et al. (2017). The observed increase in K in the soil might have been due to the K content in the original material, but in this soil it was not found to increase crop productivity.

The higher N rates resulted in higher DM yields of maize and oats, as well as an increase in the most relevant indicators of plant nutritional status such as the SNT. Stalk NO_3^- levels, for instance, varied greatly with N rate, from 350.3 to 2180.6 mg kg^{-1} in 2018 and from 600.1 to 1592.8 mg kg^{-1} in 2019, respectively in the N0 and N200 treatments. The effect of N on highly demanding crops in intensive farming systems is well-known worldwide and is the result of the natural limitation of N in agro-systems (Rodrigues et al. 2005; Ferreira et al. 2020; Davies et al. 2020). In the most fertilized treatments, the SNT showed values within or close to the upper limit of the optimal range, as reported by Blackmer and Mallarino (1996). However, a situation of excessive fertilization did not seem to have occurred, since the maize DM continued to increase to the highest N rates. Probably, these relatively high stalk NO_3^- levels were the result of the application of half the rate of N as a side dress.

The residual effect of N applied to maize persisted for the oat crop, with an increase in DM yield for the higher N rates used in the previous maize crop, although oats had not been fertilized. High inorganic N levels in the soil were recorded in the autumn, before the start of the rainy season in this region. Average values varied from 18.1 to 49.0 mg kg^{-1} in 2018 and between 10.2 and 24.9 mg kg^{-1} in 2019, respectively in the N0 and N200 treatments. These values tended to be higher than those found by Sadeghpour et al. (2017) at maize harvest in the responsive years (8.9 to 23.3 mg kg^{-1}). Oats grown in the autumn/winter period recovered the excess of this residual N. The use of winter cover crops or catch crops is one of the most common advisable strategies to recover soil residual N, resulting from N applied in summer to the main crop, and may reduce the amount of N lost by leaching or denitrification due to winter rains (Rodrigues et al. 2002; Valkama et al. 2015; Notaris et al. 2018).

In this study, it was found that N fertilization had a reduced effect on the main soil properties. Organic C, pH, and some other soil properties can change with N fertilization. Organic C, for instance, can increase in highly productive plots due to the increased organic substrates entering the soil, and pH can decrease, for instance, following NH_4^+ nitrification (Havlin et al. 2014). However, this study ran for only 2 years and none of these effects were significant.

5 Conclusions

Biochar increased soil organic C, pH, CEC, and extractable P and greatly reduced soil available N. Under the conditions of these experiments, this resulted in a significant decrease in DM yield in both the cycles of maize and in the first cycle of oats. Great reductions in N recovery and ANR in the N treatments receiving the lower N rates (N50) were also observed. Even though the environmental benefit of C sequestration is unquestionable, the application of biochar to this type of soil is not advisable for farmers given the risk of crop productivity failure and the additional associated costs. However, to benefit from the increased soil organic C, farmers who decide to use biochar as a soil amendment should apply high N rates, at least in the first years, to compensate for the N make unavailable by biochar.

Zeolites had no measurable effect on soil properties or plant performance. There was only observed an increase in the extractable soil K that would have been a consequence of the presence of the element in the original material, and insufficient to justify its recommendation in this agro-system. N application significantly increased not only the DM yield of maize grown in the summer but also the DM yield of oats grown in the winter, although this crop had not been fertilized. The result highlights the risk of N loss in the winter season, and the importance of the sowing of a winter cover crop to recover residual N.

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Data Availability The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Conflict of Interest The authors declare no conflict of interest.

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