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Influence of hydrochar from hydrothermal carbonisation (HTC) on plant growth aspects and soil improvement

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Abstract

Hydrochar (HC), produced by hydrothermal carbonisation (HTC), offers technical advantages compared to biochar (BC) produced by pyrolysis, and is suitable for soil amelioration, carbon (C) sequestration, and enhanced plant growth. However, this suitability is dependent on the feedstock, HTC process conditions, application rate, and environmental and soil conditions. BC grain size has shown to influence, inter alia, nutrient retention, microbial colonisation and aggregate formation, however, such research for HC's is lacking. This study conducted pot trials to investigate the influence of HC grain size (coarse (6.3-2 mm), medium (2-0.63 mm) and fine (<0.63 mm)), produced from biogas digestate, for soil improvement in three soils: loamy Chernozem, sandy Podzol, and clayey Gleysol, at a 5% HC application rate. All soils, including two controls (with and without plants) were analysed for germination and biomass success, pH, and plant available nutrients, namely phosphate (PO_4), potassium (K) and mineral nitrogen (Nmin) content using standard laboratory methods. Results showed no germination inhibition using Chinese cabbage seeds at a 5% HC application rate, while its influence on biomass production was mostly insignificant. Soil pH showed a compensatory shift toward the pH of the HC, based on the initial pH of the soils and the HC. This effect was most pronounced in the fine grained HC treatments. The HC served as a short-term source of nutrients, namely PO_4, K (both nutrients showing the greatest effect in the fine grained HC treatments) and ammonium (NH_4^+) due to the relatively more easily mineralized fraction of the HC, which allowed for the quick release of these nutrients. However, the duration of this contribution is dependent on the presence of this particular fraction in the soil. A relationship between HC and nitrate (NO_3^-) content was indeterminable due to the variable results between controls and HC grain size over the course of the study. In conclusion, the 5% HC application rate was insufficient to induce substantial changes to those soil properties affecting plant growth, nor to sustain a longer-term supply of nutrients.

Keywords

Biochar, biomass, germination, grain size, hydrochar, Hydrothermal Carbonization, nutrients, pH

Introduction

Biochar (BC); a carbon (C) - rich product produced by the process of pyrolysis for the intended purpose of soil amelioration, has long been suggested as a potential solution to soil degradation and for climate change mitigation through C sequestration, as well as substituting for peat and minimising the requirement for fertilizer;

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thereby reducing the adverse environmental impacts associated with the excessive use thereof. Pyrolysis mimics the natural formation of charcoal, whereby a variety of biomass types (such as manure, crop residues etc.) is heated in a closed system at temperatures between 400- 850˚C, under limited oxygen and dry conditions. A large proportion of the source materials C content remains in the final product, which is highly recalcitrant in soils, due mainly to its resistance to microbial decomposition and mineralization (Steiner et al., 2009a). This recalcitrance essentially lowers the rate at which C fixed by photosynthesis is returned to the atmosphere and increases the soil C stocks. This net increase subsequently improves soil properties such as aggregate stability, water holding capacity (WHC), cation exchange capacity (CEC), and nutrient dynamics, which essentially stimulates plant growth and improves plant health. There are several disadvantages of pyrolysis, such as, ~ 50% of the biomass C is released back into the atmosphere during production (Steiner et al., 2009b); and it is restricted to dry biomass, which makes it energy intensive if pre-drying the biomass is deemed necessary. As an alternative to BC by pyrolysis is hydrochar (HC) by hydrothermal carbonisation (HTC). This thermochemical conversion method takes place in a closed, water-saturated system, at temperatures between 180-230˚C and under elevated pressure (~20-60 bar) to produce a material similar to peat and charcoal, called hydrochar (Busch and Glaser, 2015).

Limited existing studies show the suitability of HC as a soil amendment varies widely depending on the feedstock, process conditions, soil and plant types used, HC application rate, and environmental conditions; making it difficult to get a consensus on its effectiveness for soil amelioration. However, the alternate use of HC over BC is worth serious consideration given the advantages HTC offers over pyrolysis. For example, the lower temperatures used for HTC, compared to pyrolysis, ensures that no combustion takes place, making it a relatively C- neutral process. Also, importantly, it is capable of processing wet feedstocks (with water content ≥ 70%), (as well as dry feedstocks within a single system) and it utilises heat released during the conversion process, which means that minimal additional energy is required after the closed system is initially heated. HC differs from BC in its physical and chemical structure, which holds implications for its intended purposes (Steiner et al., 2009b; Libra et al., 2011; Kambo and Dutta, 2015). However, it is presumed that HC should exhibit similar beneficial properties to BC for soil amelioration, as both have a particularly high C content. Due to HTC being a relatively novel carbonisation method compared to pyrolysis; research pertaining to BC for soil improvement and enhanced plant growth far exceeds similar research for HC. Consequently, knowledge regarding HC suitability for soil amendment is lacking. Hence, the aim of this study was to analyse the influence of grain size of a HC produced from biogas digestate on germination success, biomass production and soil improvement.

Materials and Methods

Experimental design

Three soils, namely Chernozem, Podzol and Gleysol were collected from the upper 30 cm on conventionally operating farms in Saxony-Anhalt and Lower Saxony, Germany. The Chernozem is classified (USDA) as a silty loam, the Podzol a sandy loam, and the Gleysol a clay. The HC was produced from biogas digestate at

~200˚C, 18-20 bar, over ca. 6 hrs (Grenol GmbH). Pot trials were conducted over ~3 months, involving three HC grain sizes, namely coarse (6.3-2 mm), medium (2-0.63 mm), and fine (< 0.63 mm), at an application rate of 5% HC (w/w). Each soil – HC grain size mixture was sown with Chinese cabbage seeds to firstly exam the germination success and secondly, biomass production. Additionally, soil property analyses was performed, including pH, WHC, CEC, aggregate stability and plant available nutrients, namely phosphorous (P), potassium (K), and mineral nitrogen (Nmin). Only the results for pH and the plant available nutrients are presented here. Samples were collected and analysed at the beginning and end of the study (after ~ 3 months). Control samples absent of HC (with and without plants), were analysed at the beginning of the study and are referred to as T_0 samples, while soil-HC mixtures analysed at the beginning of the study are referred to as T_1 samples. The controls and soil-HC mixtures analysed at the end of the study are referred to as T_2 samples.

Germination success was calculated as the percentage of germinated seeds (25 seeds = 100%). Biomass production was determined from a single Chinese cabbage plant per pot at the end of the study, following a ~4 week growth period subsequent to the germination experiment. The above ground biomass was harvested and weighed before and after oven-drying to calculate the total biomass for each treatment and control.

Soil analyses

The pH was determined in a 1:2.5 (w/v) soil-to-distilled water solution, after manual stirring at 15 min intervals for 1 hour. Nmin in the form of ammonium (NH_4^+) and nitrate (NO_3^-), was determined according to DIN 19746 (VDLUFA A 6.1.4.1, 2002). The plant available P and K were determined using the calcium-acetate-lactate extraction method (VDLUFA A 6.2.1.1, 2012), at a concentration of 0.6%. This solution was buffered to a pH of 3.6. The P concentration was determined colorimetrically as phosphate (PO_4) using a coloring agent of 0.5% ascorbic acid and 1% ammonium heptamolybdate, measured by a spectrophotometer (Shimadzu UVmin-1240). The plant available K was measured by AAS.

Elemental analyses

The C, hydrogen (H), nitrogen (N), and sulfur (S) composition of the HC was determined using a Euro Elemental Analyzer (Schröter, 2018) and the ash content was determined according to DIN EN 14775:2010-04. The oxygen (O) content was calculated as the difference between 100% and the sum of the C, H, N, S and ash content (in %). The elemental composition of the HC is presented in Tab. 1.

Tab. 1. Elemental composition and ash content of the HC produced from biogas digestate (Schröter, 2018).

C	H	N	S	O	Ash
wt %					
35.2	3.8	2.7	0.9	10.2	47.2

Statistical analyses

The Kruskal-Wallis H test was applied for all residuals, following tests for normal distribution (Shapiro Wilk test) and homogeneity of variance (Levene's test). Significant differences between groups was determined by the pairwise comparisons post-hoc test, using the procedure prescribed by Dunn (1964), with a Bonferroni correction for multiple comparisons ($p < 0.05$) (Laerd Statistics, 2015). The biomass results underwent the ANOVA statistical test, and the normally distributed residuals further underwent a comparison of means post-hoc test (Scheffe test) to indicate significant differences ($p < 0.001$). To determine if the differences over the course of the study between HC grain size treatments and controls were statistically significant, the Independent-samples t-test was employed, following the Shapiro-Wilk test and Levene's test. If the assumption of homogeneity of variances was violated, the independent-samples t-test was calculated using separate variances and the Welch-Satterhwaite correction to the degrees of freedom (Laerd Statistics, 2015). Significant differences are based on mean values. Statistical analyses were performed using SPSS 25.

Results and discussion

Seed germination

The germination success of the controls was, on average, 53% for the Chernozem, 84% for the Podzol, and 76% for the Gleysol. Although the different soils had a variable response to HC addition, and regardless of HC grain size, the average germination success for the HC amended soils over the course of the study was similar to the controls, being 56% for the Chernozem, 75 % for the Podzol and 60% for the Gleysol. Hence, on average, the addition of HC did not inhibit the germination of Chinese cabbage seeds in any soils. Literature states that the addition of non-pre-treated HC to soils delays or inhibits seed germination and plant growth due to organic contaminants in the HC (Bargmann et al., 2013; 2014; Röhrdanz et al., 2019). The HTC production conditions used for this study (~ 200˚C for ca. 6 hours) may have been sufficiently high and long in duration to remove the volatile compounds that are potentially harmful for germination and plant growth (Reza et al., 2014), or the open-air conditions of this study may also have allowed the release of these harmful substances. Additionally, the relatively low HC application rate (5%), and relatively older age and/or longer storage time for the HC may have negated the adverse impacts of the HC (Bargmann et al., 2013), however these details for the HC used in this study are uncertain.

Biomass

No significant differences in biomass production were observed between HC amended soils and controls, nor between grain sizes treatments, except for the Gleysol fine grained treatment ($Gleysol_{fine}$) (Fig. 1). Bargmann et al. (2014) postulate that microbial activity may act to decompose the harmful phytotoxic compounds in the HC, thereby allowing for favourable plant growth conditions and thus negating potentially negative effects of the HC. However, the lack of/ little influence of the HC in this study, may be due to the low application rate, and/ or the production conditions and age of the HC.

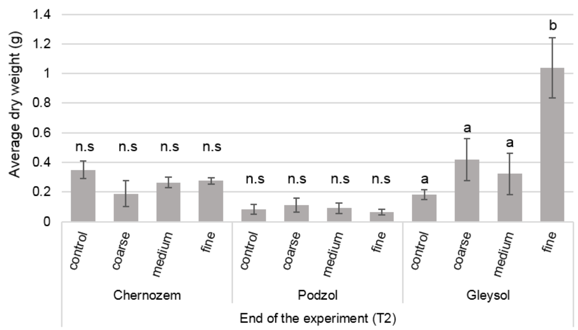

Fig. 1. Biomass production of Chinese cabbage for the controls and HC grain size treatments in a Chernozem, Podzol and Gleysol (expressed in mean dry weight (g), error bars represent 99% confidence level). Different letters indicate significant differences in means ($p < 0.01$); n.s = nonsignificant.

pH values

The initial average pH of the controls was slightly alkaline for the Chernozem (7.9 ± 0.1), and acidic for the Podzol (5.8 ± 0.1) and Gleysol (4.9 ± 0.0) (Fig. 2). A short period after the addition of HC with pH 7.2 ± 0.1 at T_1, pH increased slightly in the Podzol and Gleysol, most pronouncedly in the fine grained treatments, while the Chernozem pH remained relatively stable. At the end of the study (T_2), the pH of the HC amended Chernozem was lower than the controls, and the $Chernozem_{medium}$ and $Chernozem_{fine}$ had the same pH as the HC (7.2). At the same time, the increasing trend in the Podzol and Gleysol continued, with the HC amended soils having significantly higher pH values than the controls, particularly the $Podzol_{fine}$ (p = .040) and $Gleysol_{medium}$ (p = .010). As such, the addition of HC resulted in a shift in soil pH to the pH of the HC, and most prominently so in the fine grained fraction.

Similar findings are reported by Liao and Thomas (2019), who found the addition of small grained sieved BC (0.06-0.5 mm), which corresponds to the fine grained fraction in this study, had a greater increasing influence on the pH of a granitic sand, compared to larger BC grain sizes (2-4 mm), which showed no effect. They suggest this finding to be the result of increased physical contact between the soil and BC particles, as well as the improved liming ability of the BC due to its high ash content, which essentially buffers soil acidity (Domingues et al., 2017) and provides additional cations to the soil, which increases pH, particularly in sandy and loam textured soils (Glaser et al., 2002). Evinced by the Chernozem, it is also possible to lower the soil pH with the addition of a HC with a lower pH than the soil. Hence, the findings of this study confirm those of Biederman et al. (2013), which conclude that the response of soil pH to the addition of BC/HC is dependent on the initial pH of the soil, as well as the pH of the BC/HC material.

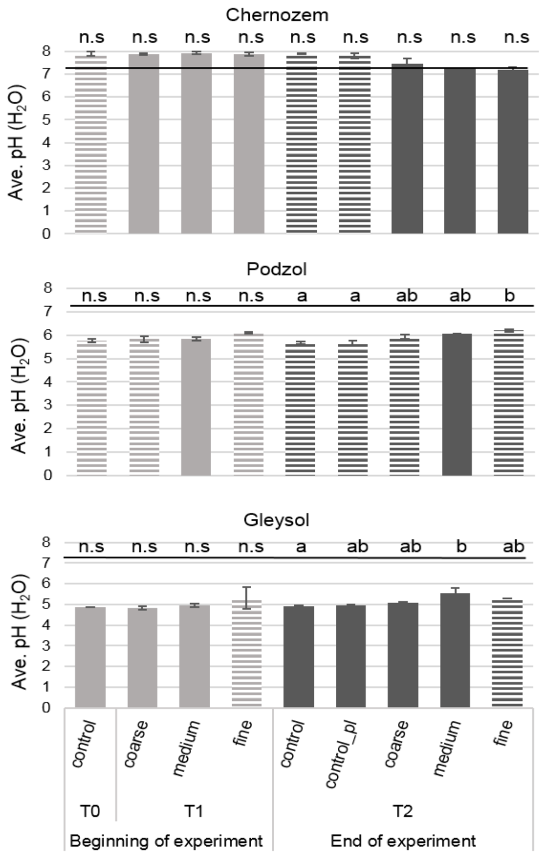

Fig. 2. Average pH (measured in H_2O) for the controls and HC grain size treatments in a Chernozem, Podzol and Gleysol over the course of the study. The solid line represents the pH of the HC (7.2). Different letters indicate significant differences in means at $p < 0.05$ level between treatments at the respective time periods (beginning and end). n.s = nonsignificant. Solid bars indicate significant differences in means ($p < 0.05$) between treatments over the course of the study. Patterned bars = nonsignificant. Control_pl = control with plant.

Phosphorous

The PO_4 content of the controls at the beginning of the study (T_0) was 172.4 ± 7.8 mg kg^{-1} for the Chernozem; 431.9 ± 8 mg kg^{-1} for the Podzol; and 20.9 ± 1.5 mg kg^{-1} for the Gleysol (Fig. 3). The initial PO_4 content of the HC was 2034.6 mg kg^{-1}. Shortly after the addition of HC (T_1), all HC amended soils had a higher PO_4 content than the controls, especially the fine grained treatments ($p < 0.05$) for all soils. Although most HC amended soils had higher PO_4 contents than the controls for all soils at the end of the study (at T_2), the only statistically significant increase was found in the $Gleysol_{fine}$ (p = .034). Over the course of the study (from T_1 to T_2), the PO_4

content mostly decreased for all soils in the controls, and was statistically significantly lower ($p < 0.05$) for all HC amended soils, except for the Chernozem$_{fine}$, Podzol$_{coarse}$, Gleysol$_{control_pl}$ and Gleysol$_{coarse}$. The results suggest the HC acted as a short-term source of PO_4 to the soils, with the greatest release of PO_4 occurring in the fine grained fraction.

Gronwald et al. (2015) found that a HC produced from digestate had a P content 10 times higher than the other feedstocks in the study. This finding is in line with those of this study, which indicates that the significant initial PO_4 increase is derived directly from the HC. The rapid release of PO_4 may be the result of the generally lower decomposition resistance of HC (compared to BC), as well as the liberation of P from iron and aluminium oxides in the char material and subsequent increasing soil pH (Alling et al., 2014; Marmiroli et al., 2018). However, the relative ease of HC mineralization, and the resultant temporary increase in microbial activity is suggested to only occur for the duration at which the easily mineralized fraction of HC (as dissolved OC) is present in the soil, typically only for a short-term (Gronwald et al., 2015).

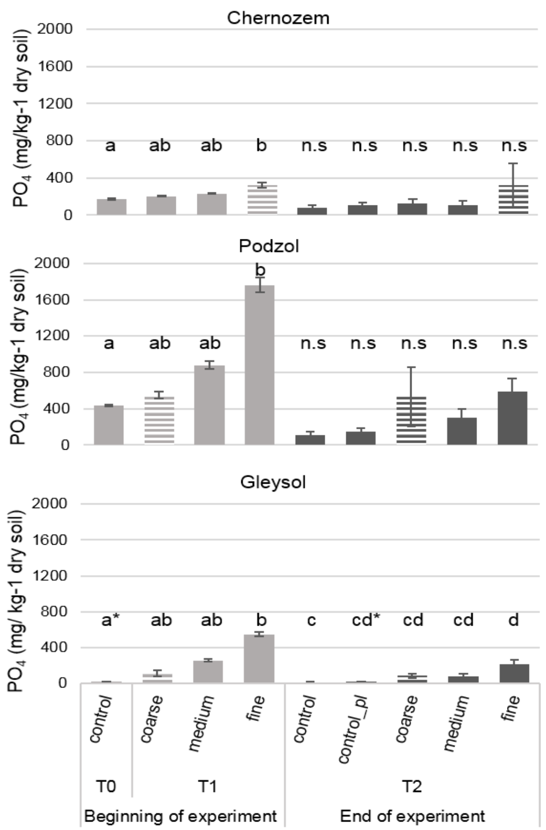

Figure 3. Average PO_4 content for the controls and HC grain size treatments in a Chernozem, Podzol and Gleysol over the course of the study. Different letters indicate significant differences in means at $p < 0.05$ level between treatments at the respective time periods (beginning and end). n.s = nonsignificant. Solid bars indicate significant differences in means ($p < 0.05$) between treatments over the course of the study. Patterned bars = nonsignificant. Control_pl = control with plant. *Statistically significantly different ($p < 0.05$) (not visible on graphic).

Potassium

The K content of the controls at T_0 was 565 ± 28.2 mg kg^{-1} for the Chernozem, 69.9 ± 14.2 mg kg^{-1} for the Podzol, and 43.9 ± 0.29 mg kg^{-1} for the Gleysol (Fig. 4). The HC K content was 2612.5 ± 268.7 mg kg^{-1}. Shortly after adding the HC (at T_1), the K content increased in all soils compared to the controls, but the only statistically significant difference was between the Podzol$_{control}$ and Podzol$_{medium}$ treatments ($p = .034$). At the end of the study (T_2), no significant differences were evident between treatments and controls and between HC grain sizes. Over the course of the study (T_1 to T_2) most treatments decreased significant in K content, except the Podzol$_{control}$ and both Gleysol controls (with and without plants). Therefore, as with the PO_4 content, the short-term initial increase in K content suggests the HC is a temporary K source. Similar findings by Alling et al. (2014) to those at T_1 corroborate these findings. As indicated for PO_4, it may be assumed that the quick release of K from the HC at T_1 of this study, is due to its relatively easily degradable fraction of the HC.

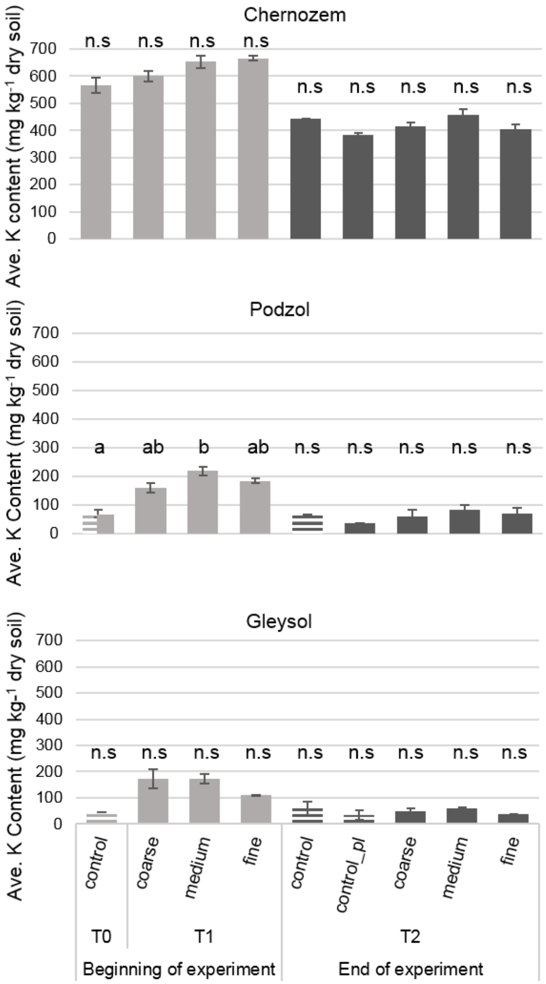

Figure 4: Average K content for the controls and HC grain size treatments in a Chernozem, Podzol and Gleysol over the course of the study. Different letters indicate significant differences in means at $p < 0.05$ level between treatments at the respective time periods (beginning and end). n.s = nonsignificant. Solid bars indicate significant differences in means ($p < 0.05$) between treatments over the course of the study. Patterned bars = nonsignificant. Control_pl = control with plant.

Nmin (ammonium and nitrate)

The Chernozem, Podzol and Gleysol controls had an average ammonium (NH_4^+) content of 1.7 ± 0.6 mg kg^{-1}, 3.1 ± 1.5 mg kg^{-1}, and 6.2 ± 0.3 mg kg^{-1}, respectively at the beginning of the study (T_0) (Fig. 5). The addition of HC resulted in the substantial increase in NH_4^+ at T_1 for all soils, however significance was limited to the Chernozem$_{medium}$ (p = .034), Podzol$_{fine}$ (p = .049), and Gleysol$_{coarse}$ (p = .034). At the end of the study (T_2), only the Gleysol$_{fine}$ was significantly different from the controls (p = .009), and the NH_4^+ content decreased significantly for all soils from T_1 to T_2, except for the Chernozem$_{control_pl}$ and Podzol$_{control_pl}$. These results indicate the HC acted as a short-term source of NH_4^+.

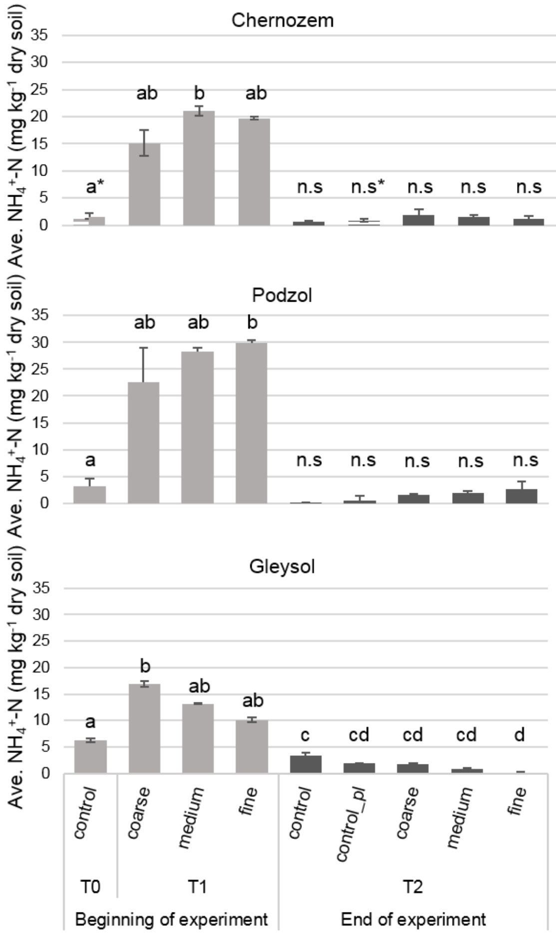

Figure 5: Average ammonium content (expressed as NH4+-N) for the controls and HC grain size treatments in a Chernozem, Podzol and Gleysol over the course of the study. Different letters indicate significant differences in means at $p < 0.05$ level between treatments at the respective time periods (beginning and end). n.s = nonsignificant. Solid bars indicate significant differences in means ($p < 0.05$) between treatments over the course of the study. Patterned bars = nonsignificant. Control_pl = control with plant. *Statistically significantly different (not visible on graphic).

The average nitrate (NO_3^-) content of the controls was 25 ± 2 mg kg^{-1} for the Chernozem; 17 ± 0.2 mg kg^{-1} for the Podzol; and 36.5 ± 0.6 mg kg^{-1} for the Gleysol (Fig. 6). The NO_3^- content varied for all soils after the application of HC at T_1, with no evident significant differences. The same varied response between controls and HC grain size treatments was observed at T_2. However, significant differences in NO_3^- content occurred from T_1 to T_2 for all soils, except for the $Chernozem_{coarse}$, $Podzol_{control\_pl}$ and $Gleysol_{fine}$. The response was however inconsistent, and hence, a relationship between NO_3^- content and HC was indistinguishable.

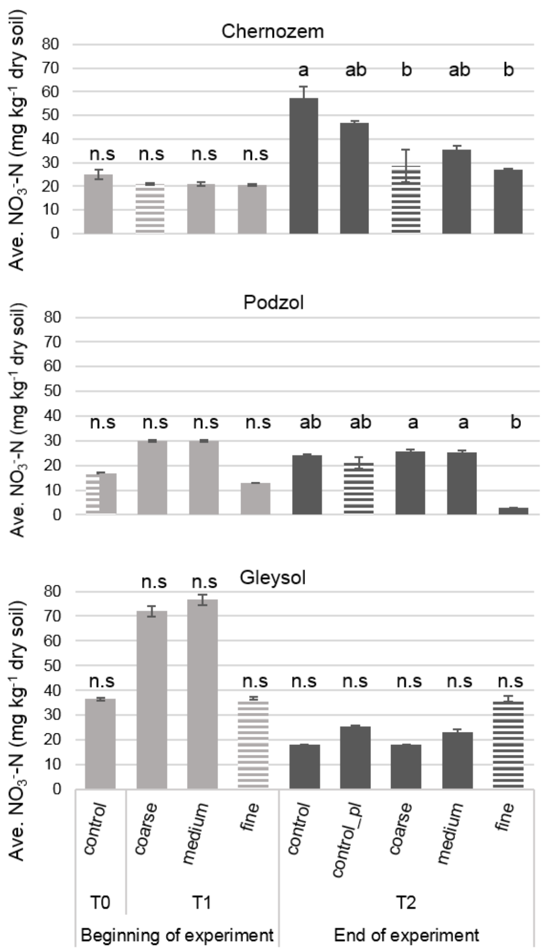

Figure 6: Average nitrate content (expressed as NO_3^--N) for the controls and hydrochar grain size treatments in a Chernozem, Podzol and Gleysol over the course of the study. Different letters indicate significant differences in means at $p < 0.05$ level between treatments at the respective time periods (beginning and end). n.s = nonsignificant. Solid bars indicate significant differences in means ($p < 0.05$) between treatments over the course of the study. Patterned bars = nonsignificant. Control_pl = control with plant.

Tambone and Adani (2017) found that a digestate feedstock had the highest N content compared to a compost and sewage sludge, of which ~80% comprised NH_4^+. Since the HC used in this study is produced from digestate, it is reasonable to assume that it may have a similarly high NH_4^+ content, which, as in the case for PO_4 and K, may have been directly released into the soil solution, and as such, substantially increased the NH_4^+ content of the HC amended soils at T_1. This is further implied by the C/N ratio of the HC used in this study (15.2), where a C/N ratio > 20 is indicative of HC decomposition (Dieguez-Alonso et al., 2018). However, as for the PO_4 and K contents, the direct source of nutrients from the relatively easily mineralized fraction of HC is short-lived, due to the rapid processing of the nutrients further within the food chain.

Tambone and Adani (2017) implicate nitrification as a likely cause for the decreasing NH_4^+ content in the soils, however, the corresponding NO_3^- findings in this study do not comply with this explanation. Rather, it is likely that although nitrification occurred from T_1 to T_2, the episodic analysis employed in this study resulted in nitrification going undetected. The results suggest that the variable NO_3^- content (according to soil type and HC grain size) was strongly responsive to the micro-environmental conditions existing within the pots, including the microbial communities and activity, temperature and moisture content, as well as the original SOM content of the three soils.

Conclusion

The findings of this study established that the addition of 5% HC produced from a digestate feedstock did not have inhibitory effects on the germination of Chinese cabbage seeds, despite contrary literature.

HC addition also caused a persistent compensatory migration in soil pH to the pH of the HC, most prominently in the fine grained treatments. Additionally, the HC acted as a short-term source of nutrients, namely PO_4, K, and NH_4^+, which was evident mostly in the fine grained treatments, regardless of soil type. The influence of HC on the biomass production of Chinese cabbage was minor, which indicates that the 5% application rate used in this study was insufficient to cause significant changes in certain soil properties or to sustain the supply of nutrients at quantities required to substantially promote plant growth.

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