Research Article

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Addition of biochar to acidic boreal podzolic soils enhances micronutrient availability and crop productivity

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Abstract: Results of a recent multiyear experiment conducted on an agricultural plot that was recently converted from boreal forest (Labrador, Canada) suggested that NPK fertilizers contributed to better crop establishment and higher yield but only when it was applied along with biochar. The failure of fertilizer only treatments to allow crop establishment and desirable growth and yield could be related to the deficiency of one or more micronutrients. Consequently, a missing element trial with a number of micronutrients (Mn, Cu, Zn, and Mo) was initiated on the same soil to investigate whether biochar can facilitate the availability of one or more of these micronutrients, contributing to crop growth and yields. Results show that the incorporation of chemical fertilizers with biochar produced significantly higher yields than in the absence of biochar. Furthermore, in the absence of biochar, the addition of micronutrients (i.e., Mn, Cu, Zn, and Mo) did not significantly increase yield. On the other hand, among the treatments that included biochar, the absence of a micronutrient (i.e., only three of the four micronutrients included) had either no effect (e.g., absence of Mn or Zn) or was associated with the increased yields (i.e., absence of Cu or Mo). Thus, it is proposed that while all tested micronutrients were present in the podzolic soil, with Cu and Mo possibly oversupplied, co-application with biochar enhanced both macronutrient and micronutrient utilization by plants. The data on the availability of micronutrients in the soil, their concentration in plants, and total uptake also support this conclusion. Thus, biochar facilitates the plant uptake of

both naturally occurring and added micronutrients, and associated crop productivity, in a podzolic soil typical for lands converted from forest to agricultural use in the boreal ecoregion of Labrador. These results also challenge the view that micronutrients must always be added to Podzols to achieve maximum productivity; biochar-mediated micronutrient plant uptake deserves consideration when managing Podzols.

Keywords: boreal, soil, biochar, nutrients, micronutrients, fertility, yield, soil quality, beet, wheat

1 Introduction

To increase local food security, there is no sustainable alternative other than producing more affordable and quality foods locally. The Government of Newfoundland and Labrador (NL) decided to boost food security by implementing policies that support expansion of farmlands on Crown lands (Government of Newfoundland and Labrador 2017). This implies the conversion of boreal forests into agricultural lands. The primary soil type in the boreal forest is Podzol (Sanborn et al. 2011; Walker 2012), a soil with many physical and chemical limitations that lead to its low fertility. Agriculture on the land converted from the boreal forest is the representative for the Happy Valley-Goose Bay (HV-GB) region of Labrador, Canada. The principal issues with the converted Podzols are low soil organic matter (SOM), acidic pH, and sandy soil texture (St Croix 2002). The stores and the availability of essential plant nutrients, which are commonly associated with clay, SOM, and neutral pH, are consequently very low (Curtin and Rostad 1997).

The SOM content is a key soil property that influences the physical, chemical, and biological properties of soil (Ferreras et al. 2006; Bhogal et al. 2009; Johnston et al. 2009; Diacono and Montemurro 2010; Bouajila and Sanaa 2011). In sandy soils SOM, much of it in microbial biomass, is the main reservoir of essential nutrients

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(Hassink et al. 1993; Hassink 1994). SOM facilitates soil aggregates' stability, which increases the soil water holding capacity and aeration (Murphy 2014; Oldfield et al. 2018; Rasool et al. 2008). Soil pH is the governing parameter for all chemical and biochemical reactions in soils, thus controlling both the inorganic and the organic soil chemistry (Brady 1990). The availability of N, S, Ca, and Mg in soils decreases at pH <5.5 (Fernández and Hoefft 2009). On the other hand, phosphorus availability is affected by both excessive acidic or excessive alkaline pH range, with a maximum availability around a pH of 6.5 (Hopkins and Ellsworth 2005; Devau et al. 2009). The availability of Fe, Mn, Zn, Cu, and B is generally greater at lower pH (Mccauley et al. 2017). Nevertheless, Podzols are considered to have a naturally low availability of micronutrients, and thus, often addition of micronutrients is recommended for crop production on Podzols (Carter and Gupta 1997). Practically, maintaining a soil pH level of at least 6.0 seems to be a realistic target for maximizing the availability of most nutrients (Fernández and Hoefft 2009). Thus, maintenance of an adequate soil pH for enhanced soil fertility and crop productivity is a primary goal of the agricultural management of Podzols. The low pH is routinely corrected with the application of limestone materials; however, in the HV-GB region, limestone must be imported from great distances at significant costs, usually provided as government subsidies. Therefore, alternative amendments or changes in crop management practices must be considered to ensure viability of farm production.

In recent years biochar (BC), a product obtained from combustion of biomass via pyrolysis, has attracted huge attention within agricultural communities. It is recommended for its positive effects on soil physical and chemical properties. In the HV-GB region, the development of large hydroelectric projects lead to significant availability of large amounts of waste wood material, a result of clear-cutting in forests to prepare reservoirs for flooding and construction of transmission lines. This offers a locally available source of feedstock for biochar production.

Biochar applications were reported to increase soil organic carbon levels (Mchenry 2011; Tian et al. 2016) and improve soil structure (Glaser et al. 2002; Burrell et al. 2016). Biochar was also reported to improve soils' ability to retain moisture (Steiner et al. 2007; Laird et al. 2010; Liu et al. 2016), mitigate nutrient leaching (Ding et al. 2010; Taghizadeh-Toosi et al. 2012; Yuan et al. 2016), and also increase cation exchange capacity (Liang et al. 2006; Atkinson et al. 2010; Clough and Condon 2010; Yao et al. 2012; He et al. 2017). In acidic soils, biochar increased soil pH (Yuan et al. 2011; Deal et al. 2012; El-Naggar et al. 2018; Pandit et al. 2018; Obia et al. 2019), reducing aluminum toxicity (van Zwieten et al. 2010; Qian et al. 2013; Lin et al.

2018) and the bioavailability of heavy metals (Méndez et al. 2012; Rinklebe et al. 2016). Biochar increased the efficiency of using plant macronutrients (Glaser et al. 2002; Bird et al. 2011; Angst and Sohi 2013; Biederman and Harpole 2013; Ding et al. 2016; Bornø et al. 2019) and micronutrients (Patel 2018; Jatav et al. 2018; Ali et al. 2019), thereby decreasing the need for chemical fertilizers, an effect relevant for both the economic and the environmental sustainability of farming in the North. All these consequences of biochar utilization on soils' abiotic parameters are echoed in an improved biological state of soils (Clough and Condon 2010; Kwapinski et al. 2010; Lehmann et al. 2011; Tian et al. 2016), with an increases in soil microbial biomass and microbial activity (Lehmann et al. 2011; Domene et al. 2014; Gul and Whalen 2016; Xu et al. 2018; Ge et al. 2019).

A multi-year field trial, initiated in 2013 on a permanent plot layout in HV-GB, evaluated whether biochar could be applied to soil as a single amendment option or combined with fish meal or inorganic fertilizers to manage both SOM and pH problems. The results of the first 3 years of experimentation suggested that the biochar application could only contribute to better crop establishment and higher yield when it was applied along with NPK fertilizers or fishmeal (Abedin 2018). The failure of fertilizer or fishmeal only treatments to establish crop and desirable growth could be traced to the deficiency of one or more micronutrients.

This combination of putative advantages of biochar, local opportunity, i.e., local potential for biochar production, and the known micronutrient availability limitations of cool climate podzolic soils leads us to the design of the current experiment.

Consequently, it was hypothesized that the addition of biochar to a podzolic soil will enhance the plant uptake of added micronutrients, with measurable effects on yield. It is expected that these effects are most notable for the plough layer where the biochar is incorporated.

2 Materials and methods

2.1 Experimental design and treatments

In 2016, a missing element trial with four micronutrients (Mn, Cu, Zn, and Mo) was initiated on a sandy Podzol in the Happy Valley-Goose Bay. The experiment was set up in a randomized block design. There were 3 blocks with a block-to-block distance of 1 m. Each block contained 9 plots (plot dimensions were of 3 m × 4 m; 1 m spacing between plots), where the 9 treatments were randomly

distributed. All experimental treatments except the absolute control (i.e., where neither biochar nor fertilizer was applied) received a basal fertilization of N, P, and K (fertilizer). The treatments were as follows:

T1. Ctrl, absolute control (no NPK fertilizer and no biochar)

T2. F, NPK fertilizer only, without micronutrients or biochar

T3. F + Micr, NPK fertilizer and all micronutrients (Cu, Mn, Zn, and Mo), but no biochar

T4. BC + F, biochar and NPK fertilizer

T5. BC + F + Micr, biochar, NPK fertilizer, and all micronutrients

T6. BC + F + Micr-Cu, biochar, NPK fertilizer, and all micronutrients except Cu

T7. BC + F + Micr-Mn, biochar, NPK fertilizer, and all micronutrients except Mn

T8. BC + F + Micr-Zn, biochar, NPK fertilizer, and all micronutrients except Zn

T9. BC + F + Micr-Mo, biochar, NPK fertilizer, and all micronutrients except Mo

2.2 Fertilizer and biochar dosing

Each year (2016, 2017, and 2018), all experimental plots except Ctrl received a basal chemical fertilizer dose of 196, 132, and 143 kg ha⁻¹ of N, P₂O₅, and K₂O, respectively.

At the start of 2016 cropping season, Mn, Cu, Zn, and Mo were applied at the rates of 30, 10, 9, and 1.4 kg ha⁻¹ in forms of MnSO₄·H₂O, CuSO₄·5H₂O, ZnSO₄·H₂O, and Na₂MoO₄, respectively.

Cement kiln-derived hardwood biochar (4% moisture and 70% C; pyrolysed at 550°C) produced principally from maple (*Acer saccharum*) and yellow birch (*Betula alleghaniensis*) was applied once, in 2016, at a rate of 15 t C ha⁻¹. This biochar was produced and supplied by Basques Hard Wood Charcoal (Rimouski, Quebec, Canada). This dose was selected according to previous field trials conducted on the same soil type that evaluated a wide range of biochar doses, between 0 and 80 t C ha⁻¹.

2.3 Experimental site

The soil is a “Humo-Ferric Podzol” developed on alluvial sand deposits. The experimental site (53°19′09″ N; 60°14′18″ W) was selected to be representative of the agricultural soil found in Happy Valley-Goose Bay, Labrador, Canada.

Most of the agricultural lands in the area are flat to nearly flat (0–2% slope), well to moderately well drained, moderately permeable, and have slow surface runoff. The elevations range between 1 and 20 m above the sea level.

According to the information provided by the farmer, the site was converted to agricultural use from the boreal forest in the fall of 2011 by removing large trees and incorporating smaller shrubs and ground level organic materials directly into the top 30 cm of the soil profile. Limestone was added in 2012 and 2014 at the rate of 2,500 kg ha⁻¹ to increase the soil pH. However, the soil pH data before the start of the experimentation (i.e., from 2011 to 2016) were not available. The land did not receive any other amendment, and no cropping activity happened before 2016.

2.4 Crop

Beet (*Beta vulgaris* L., variety Red Ace) was grown in 2016 and 2017. Beet seeds were sown during second to third week of June depending on the weather condition. The seeds were sown using a 2-rows hand seeding device (JP-3/Jang Automation Co., Ltd) with an interrow spacing of 30 cm. The seeds were placed at a depth of approximately 2 cm, with the rate of 16–20 seeds per linear meter. Thinning was done to adjust the population to the final desired 8–10 plants per meter of row at the four-leaf stage. Weeds were physically removed, and the standard organic methods of pest management practices were followed. Wheat (*Triticum aestivum* L. variety AAC Scotia) was grown in 2018. The wheat seeds were sown at the rate of 200 kg ha⁻¹ using a “Brillion” seeder mounted on a tractor. The crops under this study were grown under rainfed conditions, without supplemental irrigation. The total rainfall measured for the growing period (June 20 to August 31) was of 259, 277, and 319 mL, respectively for 2016, 2017, and 2018.

2.5 Soil sampling, handling, and analysis

2.5.1 Initial soil

Twenty soil samples were randomly collected from a depth of 0–15 cm (*topsoil*) and 15–30 cm (*subsoil*) from the entire experimental area using an AMS regular step probe. Sampling, in 2016, was done before the application of any soil amendments. The samples were thoroughly mixed to obtain composite sample for each depth. Composite samples were air dried and sieved through a 2-mm sieve.

2.5.2 Season end soil

At the end of each cropping season, soil samples from both *topsoil* and *subsoil* were similarly collected. Nine subsamples from each plot at each depth were randomly collected and mixed to get a composite sample for each depth and plot. The composite samples were air dried and sieved using 2-mm sieve before shipping to the lab.

A portion of composite samples (both top and subsoil) were analyzed for organic matter content (loss on ignition method), pH (soil water at 1:1), CEC (calculated at the laboratory from the Mehlich-3 extracted K, Ca, and Mg concentrations), and Mehlich-3 extractable concentrations of P, K, Ca, Mg, Fe, Mn, Zn, Cu, S, and B at the Soil, Plant and Feed Laboratory managed by the government of the province of Newfoundland and Labrador.

2.6 Initial soil properties

The *topsoil* had a loamy sand texture (82% sand, 14% silt, and 4% clay), near neutral pH, moderate levels of SOM, and low CEC (Table 1). The *subsoil* had a slightly coarser texture (86% sand, 11% silt, and 3% clay), higher acidity, and lower SOM and CEC. The Mehlich-3 extractable concentrations of S, Ca, Mg, K, Fe, Cu, Mn, and Zn were also lower in the *subsoil* than that in the *topsoil*. Only Fe and B contents were higher in the *subsoil* than that in the *topsoil* (Table 1).

2.7 Harvesting and plant sample preparation for analysis

At maturity, whole beet plants, from a 2 m² area of each experimental plot, were harvested. However, for treatments resulting in little biomass, the entire plot was harvested instead. After harvesting, the beet plants were separated into leaf and root (beet) portions and

weighed separately. Due to the short growing period, wheat crop did not mature; wheat plants from 2 m² area were harvested for biomass yield and elemental analysis. All experimental plots in each year were harvested at the same time. Yields were expressed as ton per hectare (t ha⁻¹). Leaf and root subsamples for beet and whole plant samples for wheat were preserved for chemical analyses.

All plant samples were washed thoroughly with the tap water to remove any dirt and rinsed with the deionized water. Thereafter, the beet roots were thinly sliced with a knife and kitchen slicer. Plant samples from both beet and wheat were oven dried at 60°C before being ground with a Thomas T4276M steel Wiley mini mill (115 V, 60 H). Ground samples were then shipped to the same laboratory for total elemental analyses.

2.8 Statistical analyses

Statistical analyses were performed using Minitab 18 and the “*agricolae*” package in Rstudio. The general approach was to first carry out exploratory analyses that allowed for a general visualization of the dataset. For this, the data were commonly standardized as *z*-scores (i.e., units of standard deviation around the mean). For example, when yields from different years and crops were compared, a *z*-score based approach removed the year- or crop-related difference in means, allowing for a direct comparison of the proportional effect of the treatment. When soil parameters were employed for full dataset-integrated exploratory analyses (i.e., PCA), the use of *z*-scores standardized data removed the undue effects associated with the variability in magnitudes due to the distinct measurement scales (i.e., units) across the tested parameters. Single-parameter correlative analyses using Pearson’s coefficients were carried out using either the absolute data or the standardized data as appropriate. Data normality, homogeneity of variance testing, and subsequent GLM analyses were carried out in

Table 1: Initial soil properties (before applying any soil amendments)

Soil depth	Texture	pH	O.M. (%)	CEC (cmol kg ⁻¹)	Ca	Mg	K	P	S	Fe	Cu	Mn	Zn	B
mg L ⁻¹ (Mehlich-3, extractable)														
0–15 cm	Loamy sand	6.4	3.10	8.46	745	271	30	38	14.1	552	0.75	6.1	1.7	1.5
15–30 cm	Sand	5.3	2.01	5.21	140	56	18	15	10.2	710	0.39	3.0	1.4	2.0

“agricolae” as necessary. *Post hoc* tests were carried out as appropriate; while not all are reported in detail, the relevant information is mentioned in Sections 3 and 4. Descriptive graphic summaries of data (e.g., bar graphs) can be found in the Supplementary Data.

3 Results

3.1 Changes in soil properties

The relationships among *topsoil* properties as a function of treatment and year are summarized by a principal component analysis in Figure 1 (details on the raw data in Supplementary Data Figure 1.1). The treatments receiving biochar had generally higher soil pH ($p < 0.01$) than no biochar treatments (Table 2); the lowest soil pH was observed in the F + Micr treatment, which did not receive biochar. For most treatments, soil pH generally decreased over the 3 years of the experiment (Figure 1), but not necessarily statistically significant. On the other hand, SOM increased over time ($p < 0.01$) with the highest content measured in 2018. The SOM content

was not related to the biochar application (Table 2), but increased in time (Figure 1). In general, the soil's CEC (Tables 1 and 2) had no notable relationship to the soil amendment (Figure 1). Adding biochar was associated with the increased ($p < 0.01$) availability of certain nutrient elements (Ca, K, S, Mn, and Cu) (Figure 1) that were low in the initial soil (Table 2). There was a slight increase in the Ca content and decrease in the Mg content over years, but these changes were statistically not significant ($p > 0.05$). The extractability of Ca and Mg was lower in the F + Micr and BC + F + Micr-Zn treatments. The availability of K and P in all treatments except control increased in 2017 and 2018 over 2016 (Figure 1 and Supplementary Data Figure 1.1) significantly ($p < 0.001$). Available concentrations of Fe and Mn in soil decreased over years ($p < 0.001$) (Supplementary Data Figure 1.1). However, Fe content was unaffected by soil amendment.

At the end of experiment, the treatments that did initially receive Mn, Cu, and Zn had higher available concentrations of these elements than those that did not receive them (Figure 1 and Supplementary Data Figure 1.1). The concentration of a specific micronutrient decreased over years in the treatments where it was missing. It appears from the data that when a micronutrient was

Figure 1: The principal component analysis of topsoil parameters; data for each separate parameter was standardized as z-scores before the analysis. Sample year: dot = year 2016, square = year 2017, and x = year 2018. The labels show the treatment ID, with the year as superscript; each label is located at the centroid of the respective replicates. A similar analysis for subsoil can be found in the Supplementary Data Figure 2.1. A temporal shift can be observed in the distinct clustering of the 2016 (top left) and the 2017–2018 (bottom right). Directional eigenvectors indicate putative relationships.

[illegible]

Table 4: Correlation between the topsoil and subsoil parameters. Topsoil and subsoil data from all 3 years were included in the analysis.

	pH	SOM (%)	CEC (cmol kg ⁻¹)	Ca mg L ⁻¹	Mg (Mehlich-3, extractable)	K	P	S	Fe	Mn	Cu	Zn	B
Correlation (<i>r</i>)	0.53	0.39	0.22	0.49	0.36	0.73	0.33	0.41	0.21	0.55	0.41	0.47	0.89
<i>p</i> (<i>H</i> ₀)	<0.000	<0.000	<0.05	<0.000	<0.01	<0.000	<0.01	<0.001	NS	<0.000	<0.01	<0.000	<0.000

the soil micronutrient mix amendment was related to yield increases (Figure 2 and Table 5).

The pattern of the beet root-to-leaf ratios across treatments, for both 2016 and 2017 (Figure 3), was similar to the yield results (Figure 2). This indicated that, for beet, larger yields were associated with an increase in root yields in the biochar-treated plots (Supplementary Data Figure 3.1).

3.3 Nutrients in the biomass

Due to an analytical error, Mo values for the plant tissues are not available. Also, the control treatments (Ctrl) did not always produce sufficient biomass (Supplementary Data Figure 3.1) that could be used for chemical analysis, and thus they are not included in this section.

Plant nutrient concentrations in leaf and beet samples are presented in the Supplementary Data, (Figure 4.1). Plant concentrations of most of the elements in beet leaf were much higher than that in beet root and wheat. In general, plant nutrient concentrations were higher in no biochar treatments than that of biochar treatments, but for a lower biomass yield. It can be noted that plant concentrations of all micronutrients in 2017 were generally lower than that of 2016. Soil application of Mn, Cu, and Zn increased plant concentrations of these elements in both beet root and leaf. On the other hand, plant concentrations also decreased in the treatments where any of these nutrients were missing from the BC + F + Micr treatment. Similar treatment effects were also observed for the total (i.e., for total yield of beet root and leaf) plant uptake, when expressed as g ha⁻¹ (the total plant uptake data were not presented).

Larger beet yields led to a proportional dilution of macronutrients (i.e., N, P, K, Ca, and Mg) and some micronutrients (Fe, and B); the absence of micronutrients (i.e., BC + F) was correlated with a slight direct relationship (not statistically significant) between yield and Mg and Ca proportions in biomass. On the other hand, the concentration of Mn in beet tissues was directly related to yield (Figure 4).

In the absence of biochar, the relationship between the yield of beet and pH or SOM was affected due to the presence (F + Micr) or the absence of micronutrients (F) amendments; for F + Micr, both pH and SOM were positively related to yield, while in the absence of micronutrients, i.e., F treatment, the relationship was negative (Figure 5). Larger soil stores of available P and K were linked to larger proportional uptake of most nutrients and micronutrients in the beet root; an exception was Mn, whose proportional uptake was mostly inversely related to soil P and K. Fe and Mn were inversely related to the uptake of any other macronutrient or micronutrient (Figure 6). In general, larger biomass yields were associated with lower elemental concentrations, with the exception of Mn, Zn, and Cu for which concentrations in plant tissues were larger with larger yields.

4 Discussion

Boreal forest Podzols converted to agricultural use is a particular scenario, rarely evaluated in the scientific literature. Nevertheless, these soils are critical in northern areas where agriculture expands. A particularity of Podzols is their acid nature and the accumulation of organic matter and metals in the spodic horizon underlying the eluviated E horizon (i.e., cheluviation). These two horizons are commonly brought to the surface and mixed during the conversion process. Moreover, the top LFH (litter, fibric, and humic) horizon is often lost during conversion. This puts the farmer in the situation to rebuild SOM while ensuring satisfactory productivity. Thus, the availability of nutrients and micronutrients is generally low. Acid soil is commonly recommended to receive micronutrients supplementation to overcome this (Lucas and Knezek 1972). This might happen even if the total store of some of these micronutrients is not necessarily small (Sillanpää 1982). Any management options that can overcome this limitation are of interest to the accelerated productivity enhancement during the first years after land use conversion.

Table 5: Significance of the impact of treatments on yield (beet and wheat) and beet root:leaf ratio

General linear models (GLM)															
Coefficients	Total biomass					Beet root:leaf ratio									
	Beet 2016 and 2017 nonstandardized data input					Beet (2016, 2017) & wheat (2018); standardized data input (z-scores)									
	Estim.	SE	t val.	Pr (> t)		Estim.	SE	t val.	Pr (> t)						
(Intercept)	29,479	4,227	6.97	<0.001	***	-1.46	162	-0.01	0.993	865	82	10.56	<0.001	***	
Year	-14.62	2.10	-6.97	<0.001	***	1.9×10^{11}	805	0	1	-0.43	0.04	-10.56	<0.001	***	
Biochar (BC)	19.71	3.14	6.27	<0.001	***	73.6	197	3.73	<0.001	***	0.50	0.06	8.28	<0.001	***
Fertiliser (F)	3.18	4.16	0.76	0.450		95.6	261	3.67	<0.001	***	0.18	0.08	2.24	0.030	*
BC + F + Micr-Cu	10.06	4.16	2.42	0.020	*	47.5	261	1.82	0.073	.	-0.043	0.08	-0.53	0.596	
BC + F + Micr-Mn	0.27	4.16	0.07	0.950		37.0	261	0.14	0.888		-0.034	0.08	-0.42	0.678	
BC + F + Micr-Mo	9.98	4.16	2.40	0.021	*	99.5	261	3.82	<0.001	***	-0.01	0.08	-0.11	0.916	
BC + F + Micr-Zn	2.42	4.16	0.58	0.563		17.9	261	0.69	0.494		-0.07	0.08	-0.86	0.394	
BC + F + Micr	-3.05	3.14	-0.97	0.337		-21.3	197	-1.08	0.284		-0.12	0.06	-1.89	0.065	.

Significance codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1

4.1 Effects of biochar on micronutrients availability in soil

Biochar addition to soils is not always seen as beneficial, and its effect vary with the biochar feedstock and pyrolysis procedures (Biederman and Harpole 2013), but this is mostly within the context of soils already fertile (Li et al. 2017). For lower fertility soils, biochar utilization is reported to have beneficial effects on soil quality, including soil microbiota, and yield (Glaser et al. 2002; Liang et al. 2006; Steiner et al. 2007; Lehmann et al. 2011; Biederman and Harpole 2013; Domene et al. 2014; Kätterer et al. 2019). Our biochar is not a significant source of micronutrients (Supplementary Data Figure 1.1), and it only compensated some of the Mn deficiency (availability increased by about 3 mg L^{-1}). When any of the three micronutrients (Mn, Cu, and Zn) were missing from the Micr treatments, the availability of the respective micronutrient reached to near the level of initial soil, which indicates the putative deficiency of these micronutrients in the studied Podzol. Despite these putative deficiencies, it was interesting to note the enhanced yield, nutrient and micronutrient uptake when biochar was supplemented. In the absence of biochar, the fertilizer applications (i.e., F and F + Micr) had an acidifying effects on soil (brought the pH down to about 5.3) and decreased the availability of soil Ca and Mg. The reduction of soil pH in the no biochar treatments (F and F + Micr) could be due to the acidification effects of chemical fertilizers (Barak et al. 1997; Du et al. 2010; Vigovskis et al. 2016). The addition of biochar alone, without fertilizer, did not increase the micronutrient content of soil, confirming that it is not a source of micronutrients. The increase in pH following biochar addition has been previously reported (Xie et al. 2016). The addition of biochar, even in the absence of micronutrient supplementation (i.e., BC + F), leads to an increased uptake of micronutrients in the plant biomass. Moreover, this led to an overall increase in the yield.

4.2 Effects of biochar on micronutrient uptake by crops

Micronutrient crop physiology and micronutrient uptake by plants have been extensively and repeatedly reviewed (Murphy et al. 1981; Clarkson 1985; Fageria 2001; Marschner 2012), and therefore, we will not speculate here on physiological processes, instead we will be focusing on accumulation of the soil-added

Figure 2: Total biomass yield; data standardized as z-scores, calculated separately for each year: white = beet 2016, gray = beet 2017, and black = wheat 2018.

Figure 3: Beet root-to-leaf biomass ratio; data standardized as z-scores, calculated separately for each year: white = 2016 and gray = 2017.

micronutrients into plant tissues (Clarkson 1985; Marschner 2012), which we applied. Micronutrient supplementation was clearly noticeable in their increased availability in soils.

Despite the year to year and crop-dependent differences in absolute biomass yield, an analysis employing within-year normalized yields has shown that the effects of the treatments on yield were constant

over years and crops. Such relatively uniform response profile to the treatments suggests a residual impact of the addition of micronutrients and biochar. The evidence suggests that while the positive effects of micronutrient application might be delayed in the absence of biochar, the presence of biochar micronutrient availability has the greatest effect on yields in the year of application with a decline in the subsequent years. While similar effects on available micronutrients have been previously reported for applications of organic wastes (Larney and Angers 2012), there is little information for the stability of mineral micronutrient amendments on recently converted Podzols. The removal of Mo from the micronutrient amendment mix led to best yields for both crop species in all years, a possible indication of toxicity (McGrath et al. 2010). The removal of Cu from the micronutrient amendment mix was also advantageous to beet production; however, the same effect was not noted for the wheat in year 3. Given that Cu is expected to be strongly complexed (Fageria 2001), the positive effect on yield when Cu was not added with the biochar suggests that biochar increased the uptake of both naturally occurring and added Cu, leading to possibly excess availability. While the change in Cu availability in the soil of the treatment that did not receive Cu as amendment was only marginally noticeable, its absence was noticeable in the yield shifts, suggesting that its addition was not needed for this soil. On the other hand, improved yield results after addition of micronutrients

Figure 4: Correlation between biomass production and elemental concentrations in beet leaf or root; the statistically relevant correlations are marked inside the respective box (significance codes: 0, “****”; 0.001, “***”; 0.01, “**”; 0.05, “*”; 0.1, “.”).

indicate that Mn and Zn might be deficient in the soil under this investigation.

The increased plant uptake of Mg, Ca, Fe, Zn, and B, and to a lesser extent Cu, was observed in direct relationship to P availability (Sillanpää 1982; Fageria 2001). Mg uptake is known to be directly linked to P uptake (Fageria, 2001). On the other hand, availability of Zn, Cu, Mo, Fe, and B to plants has been long reported to decrease with excessive P addition (Murphy et al. 1981).

These seemingly contradictory observations suggest that the addition of P led to the increased P uptake by plants, but that the added P was not available at rates leading to luxury uptake. Nevertheless, these observations were true only for the biochar treatments. Simple addition of P as fertilizer did not affect the micronutrient uptake rates. On the other hand, Mn uptake was not related to P uptake; Mn is rarely deficient in soils (Clarkson 1985), and its uptake was not affected by the fertilizer availability.

Figure 5: Correlation between elemental concentrations in the *topsoil* and beet leaf or root for no biochar treatments (2016 and 2017 beet crops). A similar analysis for subsoil can be found in the Supplementary Data Figure 5.1.

Figure 6: Correlations between elemental concentrations in the *topsoil* and beet leaf or root for all biochar treatments (2016 and 2017 beet crops). A similar analysis for subsoil can be found in the Supplementary Data Figure 6.1.

Nevertheless, Mn addition in the complete micronutrient mix did lead to enhanced uptake, more noticeable for the biochar treatments. Mn was reported to interfere with Zn uptake (Halder and Mandal 1981), a relationship also observed in our trials.

The assumption that biochars modify the soils' electrostatic parameters has led to biochars to be repeatedly evaluated for their capacity to retain elements, mainly in the context of soil contamination. However, many of these experiments reached a conclusion that linked the biochar's efficacy to retain elements to both the soil type and the type

of biochar (Shen et al. 2016; Wang et al. 2018). Any enhancement of the soil's CEC may be speculated to favor such retention. However, such CEC shift did not occur in our biochar plots, an observation supported by other reports on the minimal impact of biochar on CEC (Silber et al. 2010). Nevertheless, the enhanced solubilization of metals by biochars, especially in acid soils and for unactivated biochars, has been reported (Uchimiya and Bannon 2013), putatively a result of the formation of soluble complexes with biochar-borne dissolved organic carbon (Silber et al. 2010), a pH-dependent mechanism.

5 Conclusions

The addition of micronutrients, a common recommendation for acid soils, did increase yields. However, biochar amendments either with a full complement of micronutrient or with a missing micronutrient (i.e., minus Cu, Mn, Zn or Mo) led to productivities significantly above the no biochar fertilized and micronutrient-amended plots. The exclusion of Cu or Mo from the micronutrient amendment mix led to the improved yields, an indication of the capacity of biochar to mobilize the naturally occurring stores of these elements and thus leading to possible excess in the Cu- and Mo-amended plots. Thus, biochar facilitated the plant uptake of micronutrients, both added and naturally occurring in Podzol. These results suggest that recommendations for micronutrient supplementation of land-use converted acid boreal soils in Labrador, while enhancing plant uptake and yield are less effective than the micronutrient mobilization by biochar amendments. Moreover, repeated micronutrient addition, in no biochar-amended soils, can lead to excessive accumulation of micronutrients, which upon management-driven pH normalization might lead to toxicity issues and unnecessary costs. While the authors understand that biochar is not always locally available or cost-effective to import, biochar is a recommended soil and crop yield and quality enhancing amendment for boreal acid soil in regions where pyrolysis feedstock is easily available.

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