

Field evaluation of a boron recycling fertiliser

OLIVIER DUBOC^{1,2*}, KONRAD STEINER³, FRANK RADOSITS¹, WALTER W. WENZEL¹,
WALTER GOESSLER⁴, ALEXANDRA TIEFENBACHER⁵, PETER STRAUSS⁵, HERBERT EIGNER⁶,
DIETMAR HORN⁷, JAKOB SANTNER^{2*}

¹University of Natural Resources and Life Sciences, Vienna, Institute of Soil Research, Tulln, Austria

²University of Natural Resources and Life Sciences, Vienna, Institute of Agronomy, Tulln, Austria

³Höhere Bundeslehranstalt für Landwirtschaft Ursprung, Elixhausen, Austria

⁴University of Graz, Institute of Chemistry, Graz, Austria

⁵Federal Agency for Water Management, Institute for Land and Water Management Research, Petzenkirchen, Austria

⁶Agrana Research & Innovation Center GmbH, Tulln, Austria

⁷Bodengesundheitsdienst GmbH, Ochsenfurt, Germany

*Corresponding authors: olivier.duboc@boku.ac.at; jakob.santner@boku.ac.at

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Abstract: Boron (B) is a plant nutrient and a limited mineral resource. Therefore, secondary B sources such as end-of-life cellulose fiber insulation (CFI) should be preferred for B fertiliser production over primary borates. In addition, crop B fertilisation is challenging because B is only weakly adsorbed in soils and prone to leaching in particular if the soil pH is below 7. The objectives of this study were to assess the effect of pyrolysed CFI (B-Biochar) on crop B uptake in the field and on B leaching in a lysimeter study. B-Biochar was pyrolysed at 600 °C and tested (1) in a field experiment with maize (*Zea mays* L.) and sunflower (*Helianthus annuus* L.), and (2) in a lab microlysimeter experiment to study B leaching under simulated rainfall. In the field experiment, B concentration in plant tissue increased by up to 100% with B-Biochar compared to the control (from 29.6 to 61.6 mg B/kg in young sunflower leaves) and was only slightly lower (–10% to –20%) than with water-soluble Na-tetraborate (Borax). This lower uptake was attributed to the slow-release properties of the B-Biochar. In the lysimeter experiment, 41% and 55% of added B through B-Biochar was leached below 16 cm depth when fertilised with 1 and 2 kg B/ha, respectively, but B concentration of the leachate remained below the 1 mg B/L threshold value for drinking water in the European Union. In conclusion, CFI has a strong potential as a secondary B source for fertiliser production, and pyrolysis appears to be a suitable process for that purpose. During the processing of CFI to fertiliser, more focus should be given to slow B release in the future in order to reduce losses by leaching.

Keywords: bioeconomy; circular economy; critical raw material; nutrient availability

Boron (B) is a plant micronutrient which has been listed as critical raw material (CRM) in the European Union (EU) since 2014 (European Commission 2014). Glass accounts for 70% of B used in the EU, followed by fertilisers (12%), frits and ceramics (11%) and other applications (18%) (BIO by Deloitte 2015). Beyond supply risks of geopolitical nature, the global borate reserves are limited and must be used sustainably to secure supply in the long-term (Henckens et al. 2014,

BIO by Deloitte 2015, Schlesinger and Vengosh 2016, European Commission 2017, Duboc et al. 2019). It is therefore important to use secondary resources, when available, instead of continuously mining non-renewable minerals.

One such secondary resource is borate-impregnated biobased insulation material. In a previous study, Duboc et al. (2019) estimated that approximately 1 100 t B, as boric acid, is used as a fire retardant in

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cellulose fiber insulation (CFI) in Europe annually. This is equivalent to ~ 25% of the annual B fertiliser application in Europe, which amounts to 3 000–5 000 t B annually (Shorrocks 1997, BIO by Deloitte 2015). At the European level, the total amount of B that was applied to CFI since the 1980's represents roughly 10 years of B fertilisation. Assuming a lifespan of ca. 40 years until building renovation, CFI is expected to increasingly accrue as a waste in the coming years. These considerations make this material a relevant source of secondary B for agriculture.

When developing and testing B fertilisers, the specific challenges of plant B nutrition must be accounted for. In particular, (1) the optimum B soil fertility level (i.e., above deficiency and below toxicity thresholds) is in a narrow range, and (2) B is mainly present as uncharged H_3BO_3 , which only adsorbs weakly on soil particles, increasing the risk of leaching (Degryse 2017). Apart from decreasing the agronomic B use efficiency, B leaching into groundwater bodies may be problematic given common drinking water thresholds (1 mg/L) in the EU. To solve these issues, much attention is directed to slow-release B fertilisers (Abat et al. 2015a,b, Degryse 2017).

The new EU fertiliser product regulation (EU 2019/1090) emphasises nutrient recycling, and new recycled fertiliser types are being defined together with specific requirements for processing (Huygens et al. 2018). In that context, thermo-chemical processes have a major role to play. Pyrolysis is a scalable thermo-chemical process providing a potential route to recycle CFI to a fertiliser. It was previously shown in lab and greenhouse experiments that pyrolysed CFI (B-Biochar) was an efficient B fertiliser, comparable to a conventional water-soluble Na-tetraborate, and that it also exhibited properties of slow-release fertiliser (Duboc et al. 2019). It was also shown in that study that no contamination is to be expected when applying (pyrolysed) CFI to soils, apart of polycyclic aromatic hydrocarbons (mainly naphthalene) that must be kept under control with appropriate process parameters.

To further assess the suitability of this new product as a B fertiliser, this study aimed at evaluating this material as a B-source for maize (*Zea mays* L.) and sunflower (*Helianthus annuus* L.) in a field trial. Moreover, the leaching behaviour of B from B-Biochar was studied in a 45-day microlysimeter experiment under simulated rainfall. This was done because a state government agency had advised to conduct an experimental risk assessment for the B-Biochar material before performing field trials.

MATERIAL AND METHODS

Field experiment

Design. The field experiment had 3 factors: B-application (5 levels), location (2 levels) and crop (2 levels). Within a location, each crop was grown on a separate field, but both fields were adjacent. The B-application treatments were completely randomised within a field, with four replications. This resulted in a total of 80 plots: 2 locations \times 2 crops \times 5 B-application treatments \times 4 replications. The plot size was 6 \times 6 m.

B-application treatments. B-biochar was prepared as described in Duboc et al. (2019). Briefly, a boric acid-impregnated CFI (Isocell GmbH, Neumarkt am Wallersee, Austria) was pelletised, mixed with spelt husks (*Triticum spelta* L.) and pyrolysed at 600 °C. The mixing ratio was 3 parts spelt husk + 1 part pelleted CFI by weight, equivalent to 1:1 by volume. The input materials contained 0.056 and 5.12 g B/kg, respectively. The resulting B-Biochar contained 9.35 g B/kg. Borax ($Na_2B_4O_7 \cdot 10 H_2O$; 115 g B/kg) was used as the positive control.

The fertiliser was applied at 1 kg B/ha ("B-Biochar-1" and "Borax-1", respectively). An additional B-Biochar application level of 2 kg B/ha was also established ("B-Biochar-2"). Application of 1 kg B/ha is the most common recommendation for deficient soils, with B fertiliser recommendations ranging from 0.4 to 1.5 kg B/ha depending on soil texture and crop. An application of up to 2.5 kg B/ha is recommended for crops with high B requirement (sugar beet, alfalfa) grown on heavy soils (BMLFUW 2017). Both fertilisers were applied to the soil as a powder.

Two control treatments were established: (1) an unfertilised control treatment ("Control"), which received no amendment and (2) a control biochar treatment ("C-Biochar"), in which commercial biochar produced from spelt husk and B-free cellulose was used ("Bio Pflanzenkohle" from Sonnenerde GmbH, Riedlingsdorf, Austria). In the C-Biochar treatment, the same amount of biochar was added to the soil as in the B-Biochar-1 treatment.

Location. The field experiment was conducted on the teaching farm of the HBLA Ursprung in Elixhausen (Salzburg, Austria), an agricultural high school, in 2018. Average precipitation (reference period: 1981–2019) at the site is 1 311 mm, whereas precipitation was 1 020 mm in 2018. The mean maximum daily temperature is 13.8 °C and was 15.7 °C in 2018.

Two fields, "Schachern" and "Spernegg", were selected. Both soils had similar properties: they were sandy loams with on average 284, 515 and 201 g/kg sand, silt, and clay, respectively (ÖNORM L 1061-2 2019), the pH was 6.15 in H₂O and 5.55 in CaCl₂ (1:2.5; w:v), and organic C content was 22.5 g/kg (dry combustion (ÖNORM L 1080 2013)).

Soil B availability was 0.494 ± 0.065 mg B/kg at Schachern and 0.417 ± 0.027 mg B/kg at Spernegg according to the hot water extraction method (ÖNORM L 1090 2010), while it was 0.211 ± 0.067 at Schachern and 0.231 ± 0.073 at Spernegg according to electro-ultrafiltration (sum of two fractions (VDLFA 2002)).

Crops. Maize (*Zea mays* L., cv. KWS STABIL) and sunflower (*Helianthus annuus* L., cv. ES Columbella) were selected for their contrasting B requirements: sunflower is known for its relatively higher B requirement and sensitivity to B deficiency (Shorrocks 1997) while maize does not have a high B demand (Bell 1997). Nevertheless, both crops have shown B deficiency – and response to B addition – in different parts of the world (Shorrocks 1997).

Management, sampling dates and measured variables:

- (1) Fertilisation and sowing: The experiment was started on 9 May 2018. The fertiliser was spread by hand, homogenised with a rake and incorporated with a rotary harrow. The crops were sown on the same day.
- (2) Soil plant-available B: Soil samples (0–30 cm) were taken on 11 June (33 days after sowing (DAS)) to measure the effect of fertiliser addition on soil plant-available B. The soil samples were air-dried and extracted with hot water and electro-ultrafiltration as described further below.
- (3) B concentration in young leaves: The boron concentration in young leaves is a good indicator of a plant's B status (Bell 1997). Young leaves were harvested on 11 June (33 DAS) and on 22 August (105 DAS). The youngest leaves were harvested and pooled from 6 randomly selected plants per plot, except for sunflower at Schachern at 33 DAS (8 plants). For sunflower, the 2nd and 3rd leaves below the flower, and for maize, the youngest two leaves were harvested. Sampling took place on the inner 4 × 4 m of each plot. At 105 DAS, sunflower and maize had reached BBCH 71 and BBCH 73–75, respectively. Leaves were washed

with deionised water, dried at 65 °C and analysed for B concentration as described below.

- (4) Shoot biomass and B concentration: Eight plants were harvested from the inner 4 × 4 m of each plot on 22 August (105 DAS) to determine shoot dry biomass and B concentration. Sunflower biomass samples from the field Spernegg were not taken, as sunflower had suffered considerable wind damage on this site and might therefore not be representative. The plants were dried for 11 days at 80 °C in a wood dryer (compact dryer, BRUNNER-HILDEBRAND at Fachhochschule Salzburg, Campus Kuchl). This long drying period was necessary because the dryer was slightly overloaded. The whole shoots were shredded and homogenised. Subsamples were finely milled in a Retsch GM 200 at 8500 RPM and analysed for B concentration as described below.
- (5) Grain biomass: Grain was harvested from 8 plants per plot at maturity on 11 and 16 October (155–160 DAS). No sunflower grain biomass was measured at the site Spernegg due to the wind and bird damage.

Results of (4) shoot and (5) grain biomass were evaluated in g rather than converted to t/ha because only 8 plants per plot were harvested manually, which does not allow for reliable yield figures as would have been the case with a complete (mechanical) plot harvest.

Microlysimeter experiment

Soil core sampling and preparation of the experiment. Monolithic soil cores (Ap horizon; 0–16 cm, Ø 15 cm) were sampled from the site Schachern after seedbed preparation on 8. May. After sampling, soil cores were stored at 4 °C for two months.

The microlysimeter experiment used to monitor the fate of solutes percolating through the soil under constant tension (–60 hPa) was conducted in a controlled laboratory environment at 17 °C air temperature and 78% relative humidity. The cores were kept in the dark to prevent algal growth in the precipitation head, except during sampling.

Soil cores were placed in the lab at 17 °C for 24 h before starting the infiltration experiment. Prior to fertilisation, artificial raining of soil cores started with an intensity of 6 mm/day using deionised water (0.6 µg B/L; EC: 1–2 µS/cm). The chosen rainfall intensity equals the mean daily precipitation during the vegetation period (May–October, reference period 1981–2010 (BMNT 2018)). We used a peri-

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staltic pump connected to an 18-needle irrigation head to ensure homogeneous precipitation on the soil surface. More details about the lysimeter setup and hardware can be found in Tiefenbacher et al. (2020 (supplementary materials)).

Fertiliser addition and leachate collection. After constant leachate flow rates had been achieved, the B-biochar was applied at 1 and 2 kg B/ha, as for the field experiment. A non-fertilised treatment served as a control. The B-Biochar was mixed with 4 g air-dried, sieved soil from the upper soil layer to ensure homogenous fertilisation of the soil surface. The Control soil cores received 4 g of soil without B-biochar. Each treatment was repeated 3 times; for the whole experiment, 9 soil cores were used.

The duration of the experiment was chosen in order to exchange the soil pore volume 3 times (45 days; in total 5 L). Due to the low discharge of soil solution, the leachate samples had to be collected over longer time periods to collect enough volume for chemical analysis. In total, 10 leachate samples were taken (at 1, 3, 5, 9, 13, 17, 21, 28, 34 and 41 days after fertilisation) plus an initial sample prior to fertilisation. Immediately after sampling, the extracted leachate was filtered through 0.2 µm pore size filters (CROMAFIL® Xtra PA-20/13, Macherey-Nagel GmbH & Co. KG, Düren, Germany).

Soil, plant and leachate analysis

For extractions and sample analysis, Type I laboratory water (18 MΩ/cm) was used. Sample handling and storage was only done using polyethylene, polypropylene (PE, PP) or quartz vessels to avoid B contamination from borosilicate glass. Vessels were either new or soaked in a 5% (w:w) HNO₃ bath for ≥ 5 h and then rinsed with Type I water.

Soil "plant-available" B was assessed (1) with a hot-water extraction (ÖNORM L 1090 2010), abbreviated HWB hereafter and (2) with electro-ultrafiltration (VDLUFA 2002), abbreviated EUF hereafter. For HWB, 5 g soil was boiled in 50 mL H₂O for 5 min (after the onset of boiling) in quartz digestion tubes equipped with reflux condensers. After cooling and adding 0.2 mL 370 g/L CaCl₂ the solution was filtered through Munktell 14/N folded filter paper, acidified to 6% w/w HNO₃. For EUF, 5 g soil was suspended in 50 mL H₂O. An electric field was induced by platinum electrodes, and dissolved nutrients were permanently removed from the solution equilibrium. Positively dissolved charged cations migrate through the ultra-

membrane filter to the cathode, dissolved negatively charged anions to the anode. Ions were collected and analysed by ICP-OES. In the standard EUF procedure, two extraction steps are used: fraction 1 (30 min, max. 200 V, max. 15 mA, 20 °C) and fraction 2 (30–35 min, max. 400 V, max. 150 mA, 80 °C). For this study, the sum of fraction 1 and the following fraction 2 was evaluated.

For plant analysis, a 150 mg sample was digested in 3 mL 65% HNO₃ + 0.76 mL 30% H₂O₂ in a MARS 6 microwave system (CEM Corporation, Matthews, USA). After digestion, 40 mL H₂O was added (final sample: 43.75 mL at 6% HNO₃), and the solutions were measured by ICP-OES at 249.677 nm.

Certified reference material was used for plant analysis. No such material was available for soil plant-available B. Measurement of soil HWB, fertiliser and plant digests were performed on ICP-OES at 249.677 nm with Y as internal normalisation standard. Certified reference solutions (Inorganic Ventures, Inc., Christiansburg, USA) were used as quality check and measured every 20 samples.

For the analysis of leachate (lysimeter experiment), certified reference solutions (Merck KGaA, Darmstadt, Germany) were used. The accuracy and precision of the measurements were monitored continuously by internal standards, laboratory replicates, matrix samples, reference material and standard solutions. The maximum allowable relative standard deviation between analytical replicates was set to 5%.

Data evaluation

For the field experiment, data evaluation and figures were done with the software "R", version 3.6.1 (R Core Team 2019). Analysis of variance (ANOVA) was conducted with main and interaction effects. The data were analysed for each crop separately ($n = 40$) because the crops were grown on adjacent fields at each location, rather than randomised, as the objective of the study was not to compare the crops but to focus on the B-application treatment effects. Soil HWB was analysed for the whole experiment ($n = 80$) because it is independent of the crop factor, and the plots were randomised within a location.

Data transformation (natural logarithm) was used, if necessary, to improve homogeneity and normality of residual variance (assessed visually after plotting). Log transformation was required for soil HWB and young leaves B concentration, but values displayed in the figures are the untransformed data. Because

the focus of the study was on fertiliser treatment (B-application factor), the results are shown averaged across the location and crop factors where suitable. It was mostly the case since there were no strong factor interactions in the ANOVA. Pairwise comparisons were performed with the functions *emmeans* and *pairs* of the "emmeans" package (Lenth 2019). The results are reported as mean \pm standard deviation of the mean (standard error) averaged over each model. Following recent recommendations, we avoid tagging results as "statistically significant" (or not) (Amrhein et al. 2019, Wasserstein et al. 2019). Instead, we report actual *P*-values where possible and discuss the magnitude and uncertainty of the effects. For convenience, we use a compact letter display with *P* thresholds in figures, but we report treatment groupings at $P < 0.05$, $P < 0.01$ and $P < 0.001$ (with Tukey adjustment) to increase the information content about the statistical evidence for the differences. The compact letter display groupings were produced with the function *cld* from the R package "multcomp" (Hothorn et al. 2008) executed on the *emmeans* object from above (`multcomp::cld(emmeans_object)`).

For the lysimeter experiment, total leached fertiliser B was calculated by subtracting the amount of B leached in the unfertilised control from the amount of B leached in the fertilised treatments. Uncertainties were propagated, accounting for the variability in the control treatment and a 3% analytical uncertainty on

each measurement of the leachate. Due to outlier correction, one soil core fertilised with B-Biochar-1 had to be excluded from the analyses.

RESULTS

Field experiment

Soil plant-available B (HWB and EUF). Fertiliser addition increased soil HWB from < 0.50 mg B/kg in the two control treatments to about 0.8 mg B/kg with B-Biochar-1 and Borax-1 ($P = 0.99$ between these both treatments) (Figure 1, left panel). B-Biochar-2 further increased HWB to 1.05 mg B/kg. *P*-values between unfertilised and fertilised plots were < 0.001 . Very similar results were obtained with EUF, but with lower concentrations (Figure 1, right panel).

Young leaf B concentration. In line with the results of soil extractable B, B concentration increased in young leaves of maize and sunflower at both harvests (Figure 2) due to B fertilisation. Concentrations were higher in sunflower (19.9 to 39.9 and 26.9 to 90.5 mg/kg at 33 and 105 DAS, respectively) than in maize (4.3 to 17.9 and 32.4 to 50.5 mg/kg at 33 and 105 DAS, respectively).

When B-Biochar and Borax were added at 1 kg B/ha, the concentration in leaves was generally higher for Borax (+ ~ 20%), except for maize at the second harvest. An effect of increasing B fertilisation with

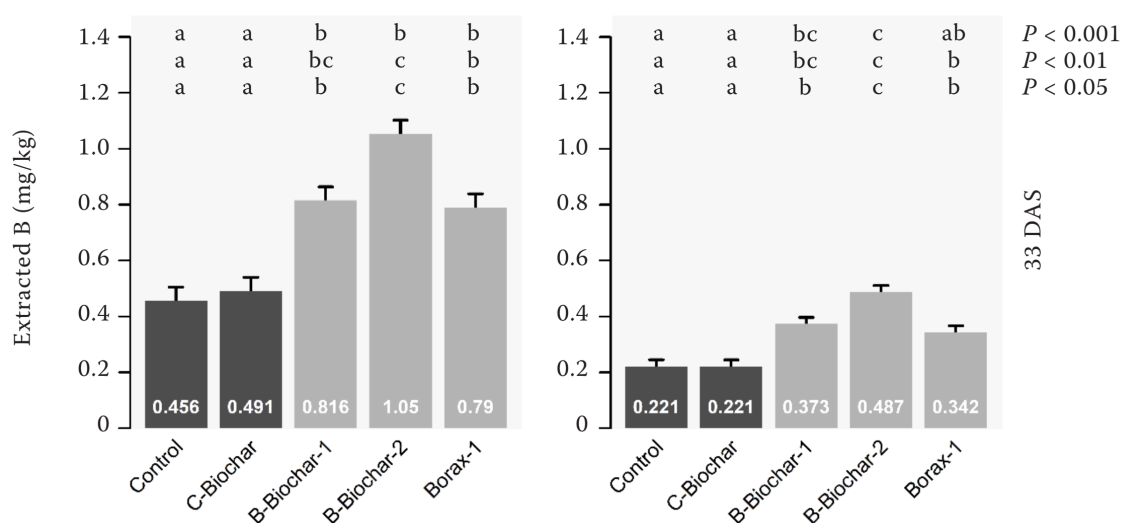


Figure 1. Soil plant-available boron (B) (mean + standard error) was assessed by hot water extraction (HWB, left) and by electro-ultrafiltration (EUF, right). Results averaged over location and crop factors to highlight the overall effect of B-application. *n* per group = 16. Different letters above the bars indicate differences between treatments at $P < 0.05$, $P < 0.01$ and $P < 0.001$ (Tukey-adjusted *P*-values). Numbers at the bottom of the bars are the respective mean values. Dark grey bars are the controls (no B applied), light grey bars are the treatments (B applied)

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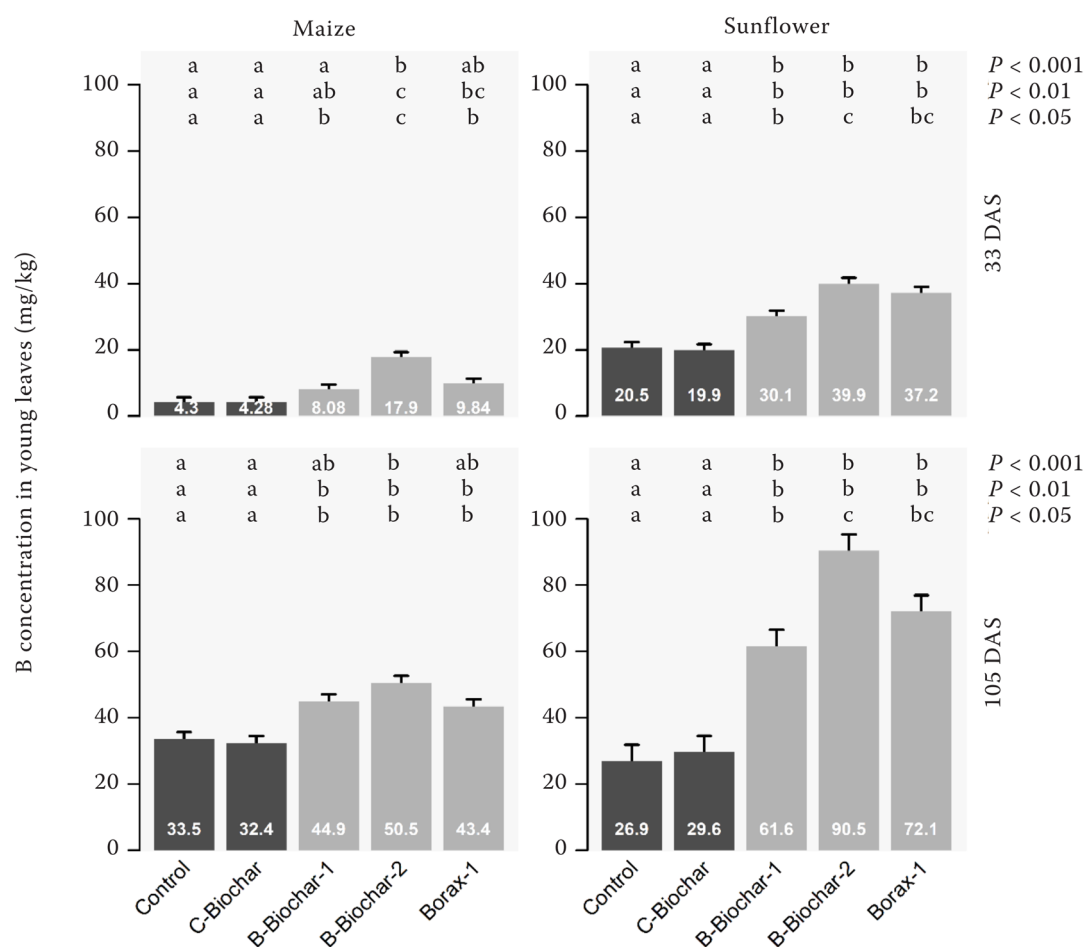


Figure 2. Boron concentration (mean + standard error) in young leaves at first (33 days after sowing (DAS)) and second harvest (105 DAS). Data in each panel is averaged over the location (n per group = 8). Different letters above the bars indicate differences between treatments at $P < 0.05$, $P < 0.01$ and $P < 0.001$ (Tukey-adjusted P -values). Numbers at the bottom of the bars are the respective mean values. Dark grey bars are the controls (no B applied), light grey bars are the treatments (B applied)

biochar (B-Biochar-2 compared to B-Biochar-1) was measured in all treatments, although the difference was sometimes small (Figure 2).

Shoot B concentration. Boron concentration in the shoots harvested at 105 DAS ranged from 3.35 to 4.81 mg/kg for maize and 23.4 to 35.5 mg/kg for sunflower. Response to fertiliser followed a trend similar to the young leaves, except that the magnitude of the fertiliser effect was less pronounced (increase factor ≤ 1.5). Nevertheless, all fertilised treatments had P -values < 0.05 compared to control (except Maize with B-Biochar-1) and up to < 0.001 in several treatments (Figure 3).

Shoot and grain biomass. Means of the shoot and grain biomass and respective summaries of ANOVA are given in Table 1. Neither shoot nor grain biomass

did show any effect of B-application. Overall, shoot and grain biomass were 25–30% larger at Spernegg than at Schachern.

Microlysimeter experiment

Boron concentration in leachate over time. Boron concentrations in the leachate samples were monitored continuously over time (Figure 4). Application of B-Biochar significantly increased leachate B concentration.

The B breakthrough times originating from the B-Biochar depended on the amount of applied B. The increase of B concentration in the leachate was first measured on day 13 for B-Biochar-2 and on day 17 for B-Biochar-1. The concentration peaked after 28

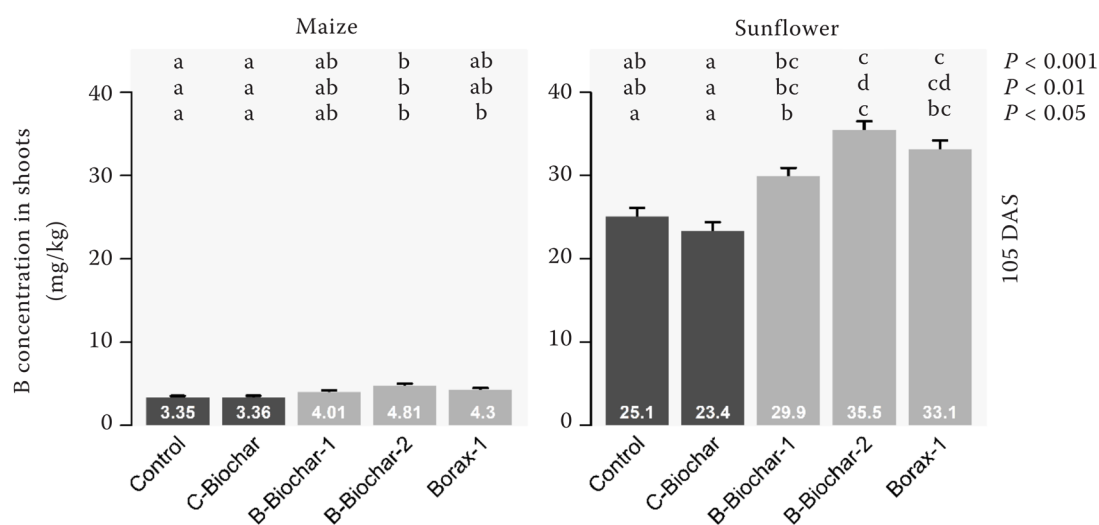


Figure 3. Shoot boron (B) concentration (mean + standard error) at 105 days after sowing (DAS). Results averaged over location (no location effect); n per group = 8. Different letters above the bars indicate differences between treatments at $P < 0.05$, $P < 0.01$ and $P < 0.001$ (Tukey-adjusted P -values). Numbers at the bottom of the bars are the respective mean values. Dark grey bars are the controls (no B applied), light grey bars are the treatments (B applied)

days ($1.8 \times$ exchanged pore volume), reaching 0.315 ± 0.004 mg B/L (B-Biochar-1) and 0.829 ± 0.095 mg B/L (B-Biochar-2). Subsequently, B concentration decreased until the end of the experiment ($2.67 \times$ exchanged soil pore volume), down to 0.227 ± 0.019 mg B/L (B-Biochar-1) and 0.387 ± 0.019 mg B/L (B-Biochar-2).

In the control treatment, leachate B concentration ranged from 0.015 to 0.037 mg B/L. It increased

slightly with the increasing amount of exchanged soil pore volume until day 20 and remained close to 0.03 mg B/L until the last measurement.

Total B leaching. While in the control treatment, 0.118 ± 0.038 mg B were leached, the fertilisation treatments B-Biochar-1 and B-Biochar-2 resulted in losses of 0.739 ± 0.019 and 1.77 ± 0.14 mg B (2.5-fold), respectively (Table 2). This corresponds to 41% (B-Biochar-1) and 55% (B-Biochar-2) of added B that

Table 1. Shoot and grain biomass from eight plants (mean \pm standard error)

		Schachern		Spernegg		ANOVA result for maize grain biomass
		biomass (g)	ANOVA results	biomass (g)	ANOVA results	
Shoot biomass (105 DAS)	maize	$1\,539 \pm 32$	$F = 1.16$ $P = 0.366$	$2\,090 \pm 70$	$F = 0.362$ $P = 0.832$	$F = 0.585$ $P = 0.676$
	sunflower	$1\,808 \pm 0.43$	$F = 1.42$ $P = 0.276$	$2\,662 \pm 84$	$F = 0.872$ $P = 0.504$	
Grain biomass (155/160 DAS)	maize	987 ± 35		$1\,425 \pm 35$		
	sunflower	636 ± 20	$F = 0.091$ $P = 0.984$	Ø		

For shoot biomass, ANOVA was conducted separately for each field due to unequal variances between locations. Because high P -values indicated no treatment effect, the results are shown for each field averaged over B-application treatments ($n = 20$) \pm residual standard error. For grain biomass, ANOVA was conducted at the crop level for maize (both locations, $n = 40$) since prerequisites were met and at the field level for sunflower (Schachern only, $n = 20$). No representative sunflower grain harvest could be estimated at Spernegg due to wind and bird damage

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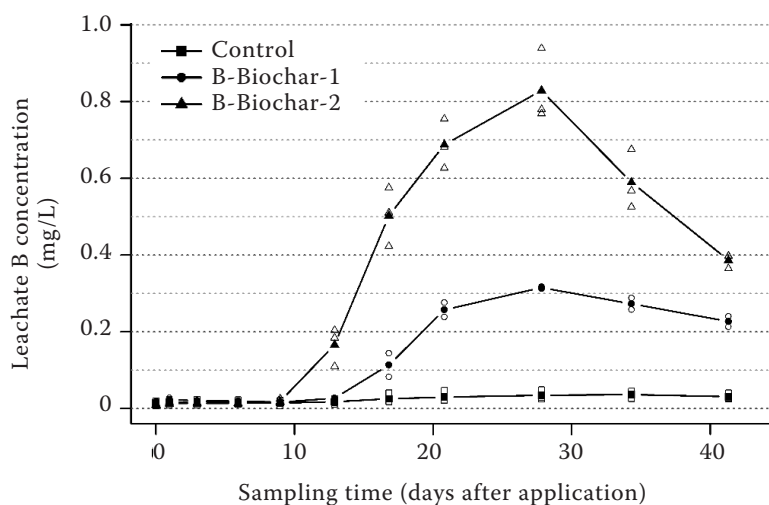


Figure 4. Boron (B) concentration in leachate percolating through a 16 cm deep soil core fertilised with 1 or 2 kg B/ha (B-Biochar-1 and -2, respectively). $n = 3$ ($n = 2$ for B-Biochar-1). Data points: concentration in individual lysimeters (white symbols) and mean concentration (black symbols)

percolated to below 16 cm soil depth. Therefore, in relative terms, B leaching also increased with the B application rate.

DISCUSSION

Soil and plant B concentration in relation to critical values

Hot-water soluble B in soil ranged from 0.45 to 1 mg B/kg in control and fertilised treatments (Figure 1). In Germany, 0.35 to 0.6 mg B/kg is considered adequate for crop growth in loamy and clay soils (Kerschberger et al. 2001, Sächsische Landesanstalt für Landwirtschaft 2007), but soil HWB threshold levels across Europe vary widely, from 0.3 to 1 and even 3 mg B/kg (Sinclair and Edwards 2008). This suggests that the soil in this study could provide adequate B for plant growth but that the unfertilised treatment was rather on the lower end of the optimal range of B availability. Boron extracted by EUF was on average 0.211 mg B/kg in the control treatments, and it increased up to 0.487 mg B/kg in the B-Biochar-2 treatment (Figure 1). According to

Austrian guidelines, EUF B concentrations < 0.65 mg B/kg are classified as low, and 0.65–0.95 mg B/kg as adequate (BMLFUW 2017). Thus, the experimental sites were low B soils according to EUF.

For field grown sunflower, 31–38 mg B/kg in the topmost mature leaf at flowering was reported as a critical threshold (Blamey et al. 1979), while for sunflower grown in a nutrient solution, 25 mg B/kg in the youngest opened leaf at 75 days after transplanting was determined as the critical concentration (Asad et al. 2002). The results from young leaf analysis in our field experiment (27.4 mg B/kg in control plots) therefore suggest that the sunflower crop was, if at all, only marginally B deficient. Rashid and Rafique (2005) determined B thresholds of 60 and 37 mg B/kg for 4- and 8-week old sunflower shoots in a pot experiment. While our measurement of the whole shoot (ca. 25 mg B/kg in control) was taken at a later stage (105 DAS) and is therefore not directly comparable, it can be expected that with ongoing crop growth, the optimal shoot B concentration decreases further due to dilution. There is less literature available for maize, but in a comparison of B concentrations of different crops grown at the same location (Bergmann

Table 2. Leached boron (B) during the infiltration experiment

	Applied B (mg)	Leached B (total, mg)		Leached fertiliser B (control subtracted; mg)		Leached fertiliser B (% of added B)	
	mean	mean	u	mean	u	mean	u
Control	0	0.118	0.038				
B-Biochar-1	1.51	0.739	0.019	0.621	0.042	41.1	2.8
B-Biochar-2	3.01	1.77	0.14	1.656	0.147	55.0	4.9

Data are shown as mean \pm u where u is the propagated uncertainty. $n = 3$ ($n = 2$ for B-Biochar-1)

1992), maize had 5 mg B/kg, which was at the low end compared to other crops. This is consistent with our data (Figure 3), where B concentrations (whole shoot) ranged from 3.35 to 4.81 mg B/kg.

The results of HWB and B concentration in plant tissue discussed above suggest that the unamended soil provided rather low but sufficient B to the crops for adequate growth. Boron fertilisation resulted in increasing HWB and EUF B concentrations in soil and in increasing B concentrations in young leaves and shoots. The absence of a yield response to B fertilisation further indicates that the B supply in the unfertilised control treatments was adequate for both crops. In spite of lower precipitation and higher temperatures compared to the average (see materials and methods), we consider it unlikely that the absence of yield response was due to water stress.

Effect of B-Biochar as B fertiliser. The results of this study are consistent with Duboc et al. (2019), confirming that the effect of B-Biochar on plant B nutrition is comparable to that of Borax. The fact that in most cases, B-Biochar-1 resulted in slightly lower concentrations in plant tissue than Borax-1 may be due to the slow release properties of B-Biochar. As shown by Duboc et al. (2019), B from B-Biochar was not completely soluble in a 0.01 mol/L CaCl_2 extract (1:50 w:v), but nearly 100% of the B could be extracted after 4–5 hot water extractions. This suggests the longer-term ("slow") release of B, meaning that less B would be available from B-Biochar in the initial growth phase compared to Borax, but also that the B leaching potential is reduced. Overall, this study shows the potential of biochar made from B-impregnated CFI as B fertiliser in the field.

Boron leaching. The lysimeter experiment was conducted in the lab with average precipitation and no/marginal evapotranspiration. This is therefore not representative for the particular year in which the field experiment was conducted but rather provides general information on potential B leaching.

As expected, the concentrations of B measured in the leachate varied according to the application rate of B-Biochar. At the application rate of 1 kg/ha (B-Biochar-1), 41% of applied B was leached, whereas this figure increased to 55% with B-Biochar-2 (Table 2). This large proportion of leached B can be expected because B leaching is more important in soils with pH < 7 (Degryse 2017), which is the case for this study with pH ~ 5.5 in CaCl_2 . Moreover, breakthrough

curves of the leached B were not recorded until the B concentration in the leachates decreased to the value of the unamended controls (Figure 4), suggesting that the total B losses of the different treatments are underestimated. However, the height of the soil columns was 16 cm, whereas the crop root zone extends well beyond that. Therefore, it can be expected that not all B leached during this experiment would be lost from the agricultural system.

Equally important, B leaching could result in exceeding the threshold value for drinking water, which is 1 mg B/L in the European Union (EC 1998). Boron concentration of the leachate remained below that threshold, reaching a maximum of 0.829 ± 0.095 mg B/L with the higher B addition (B-Biochar-2, Figure 4). Considering (1) the shallowness of the studied soil cores (16 cm), which did not even encompass the entire rooting zone depth; (2) that in this experiment, the soil was permanently saturated, thereby offering ideal conditions for leaching; and (3) that dilution of leachates with the existing groundwater body will take place, our data demonstrate that adding B-Biochar at recommended doses poses no threat to groundwater bodies. This result is important for regulatory bodies that require risk assessment before a new product can be placed on the market.

Even though the use of B-Biochar poses no environmental or health risk, B leaching still reduces agronomic B use efficiency, and by extension, the efficiency with which this limited resource is used. With ~ 50% of the added fertiliser B that percolated to < 16 cm within 45 days, alternative or complementary processes that further reduce B solubility from the CFI (e.g., Abat et al. 2014) would be beneficial to increase the fertiliser use efficiency (Abat et al. 2015b) and to reduce losses to the environment.

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