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Odour reduction of manure through addition of boracic charcoal

G. Hampejs[1,*], A. Jäger[1], S. Steiner[1] and K. Steiner[2]

[1]University of Applied Sciences Upper Austria, Faculty of Engineering, Department of Bio & Environmental Technology, Stelzhamerstr. 23, AT4600 Wels, Austria
[2]HBLA Ursprung, Ursprungstraße 4, AT5161 Salzburg Austria
[*]Correspondence: g.hampejs@fh-wels.at

Abstract: Odours released during the land application of manure results from different gases released from the liquid phase. These gases do create objectionable odours in the vicinity of the land-applied manure. In order to reduce the intensity of odour during manure application, we investigated the effectiveness of combining Borkohle with manure during land application.
Boracic acid is widely used as a flame retardant in cellulose insulation. During demolition of existing buildings, this insulation is sorted into its own residual waste fraction. The cellulose fibres are extracted and pelletized on site. Subsequently, the pellets are charred in a pyrolysis furnace. The resulting Borkohle – charcoal containing boron in various compounds - can be used as a soil enhancer and provides the trace element Boron to the fields. Furthermore, Borkohle provides long-term storage of carbon in the soil. Initial trials of combining boracic charcoal with manure additionally showed that odour emissions seemed to be significantly lower when manure was combined with Borkohle.
This work presents methods to quantify the odour reductions resulting from the addition of Borkohle to manure as well as first results. Parameters like the influence of the amount of charcoal added and exposure time have been investigated.
Charcoal was added at concentrations between 5 and 250 g L^{-1}. While applying typical amounts of charcoal, a reduction of odour concentration of up to 85% was observed. A positive correlation between odour reduction and the amount of charcoal added was observed. Charcoal has a negligible effect when exposure times are less than 30 minutes.

Key words: Olfactometer, charcoal, insulation materials, demolition materials, manure.

INTRODUCTION

Demolishing or renovating a building unavoidably produces a range of waste materials. These can include insulating materials made from cellulose fibres. In order to minimise the risk of a fire, they are mixed with boric acid, which acts as a natural fire retardant (Wieland & Bockisch, 2006). When these cellulose fibres are no longer needed, they are sucked away without producing any dust and pelletized on site to simplify transportation (Bode et al., 1993). In a further step, the pellets are pyrolised in a technical process. This gives rise to boron-laden charcoal, hereinafter referred to as 'Borkohle' (Abbrev. BC). In order to be able to use this charcoal made from waste materials for other purposes, the valuable properties of the product must be investigated and proven and their compliance with relevant limit values demonstrated. The boron-laden organic charcoal – or 'Borkohle' – produces in this way can be spread on fields by farmers together with manure as a soil improver and as a source of the trace element boron (Glaser et al., 2015; Schulz et al, 2013). Initial field trials for the spreading of biochar on maize fields indicated that the odour emissions of manure mixed with biochar are lower than the odour emissions of manure applied without additives (Isocell, 2017).

The objective of this project at Upper Austria University of Applied Science / Campus Wels is to investigate the extent of odour reduction due to the charcoal and the underlying modes of action. The first step, which is reported on here, should involve the development of suitable test methods and the investigation of the influences of important constraints, in particular the quantity of charcoal and the reaction time.

MATERIALS AND METHODS

The manner in which the experiments for obtaining representative samples are conducted in the laboratory is explained below. To this end, the three applied trial methods are described in more detail.

Preparation of odour samples

Three different approaches were selected in order to simulate the odour of manure in the laboratory. (1) Direct application on the pasture (2) Desorption using a scrubber (3) Direct method in the bag

(1) In this trial, the manure is applied directly to a piece of pasture measuring 0.24 m x 0.24 m located in a capture hood. In order to simulate a standard spreading quantity of, for example, 30 m³ manure per ha for maize, 172 mL of manure is added to the pasture located in the hood. Next, an odour sample is taken after a certain reaction time. Before the pasture is treated with manure, the intensity of its inherent odour is determined.

(2) The application of manure is simulated by conveying the manure in a sealed circuit to a packed-bed scrubber, where it is brought into contact with the air also being moved around the circuit, and then returned to the collection tank. This simulates the intense contact experienced during conventional manure spreading through scattering. The odour-laden air is passed through a capture hood, from which the air samples can be taken. First, the storage tank located at the scrubber is filled with manure. Then, the process described above starts. The sample is taken after the scrubber has run for a set time.

(3) With this method of making odour samples, the manure is added to a sample bag made from Nalophan® (approx. 15 litres). The bag is filled with synthetic air. After a dwell time of five minutes, the air is transferred to a sample bag. If the odour concentration is too great for an olfactometric evaluation, the odour sample must be pre-diluted. The dilution is made in a ratio of 1:7.3. The odour sample obtained in this way can be subsequently analysed without any problem with the aid of the olfactometer.

This method of sample creation was developed because the other methods used are very time-consuming and complex by comparison as well as being prone to errors. Less manure is needed than in trials with the scrubber.

Odour measurement with the olfactometer

There are various methods available for assessing odours. In order to assess emissions of the kind produced when spreading manure on agricultural land, the aim must be to determine the odour loads. In turn, the expected level of nuisance can be derived from this. As these loads are to be determined on the basis of quantity and concentration, particular importance is placed on determining the odour concentration.

The odour concentrations were determined by means of dynamic olfactometry with an Olfasense Olfactometer TO8, according to EN13725 – Odour. This involves diluting the air sample with clean, non-odorous air until none of the four to six test subjects are able to notice any more odour. The concentration of the diluted sample is increased in several steps by a factor of 2 or √2 until the perception threshold is significantly exceeded in all test subjects. The odour concentration is arithmetically determined from the odour thresholds of all test subjects whose results lie within the required tolerance. This correlates with the concentrations of the substances contained in the samples. (Hauschildt & Mannebeck, 2015)

Another way of presenting the odour concentrations is the unit of 'decibel odour' (dB_{od}). Due to the logarithmic relationship between concentration and intensity, which is analogous to the Fechner law for noise, this logarithmic scale is particularly suitable for comparing odours with each other and against specified limit values (Forrest, 2010).

Preparation of manure

Manure A was used in experiments A, B, C and D. Before the experiments, it was passed through a food mill to remove feed residues and other fibres and solids in order not to cause the pump to malfunction, as had been the case in preliminary tests.

Experimental setup

Experiment A: In this experiment, manure A was applied directly to the pasture. 0.8 g of biochar was added to the 172 mL of manure. This corresponds to a quantity of 5 kg of biochar per m^3 of manure. The biochar was allowed to react with the manure for four hours before spreading. Trials were done with 0.25 m^2 of natural grown pasture per trial which was taken from local meadows including 25 cm of sod. The treated manure was spread by hand, spreading drops of the liquor evenly over the pasture sample.

Experiment B: In experiment B, odour samples were taken using the scrubber. For the experiment without biochar, the storage tank was filled with 10 litres of manure A. The first sample was taken two minutes after starting the scrubber, the second after five minutes. Next, the scrubber was cleaned and the storage tank filled with 10 litres of manure A, which had been mixed five hours previously with 50 g of biochar. The sampling was conducted in the same as the sampling without charcoal. The measurements were outside of the measurement range for all samples, i.e. they were each more than 72,176 GE m^{-3}. Because of this, they could not be analysed and no results are available for experiment B.

Experiment C: In experiment C, the odour samples were also obtained with the aid of the scrubber. The difference from experiment B was that a larger quantity of biochar was used. Thus 150 g and 250 g of charcoal were added to 10 litres of manure respectively. The biochar was allowed to react for five hours. The samples were also taken after two and five minutes after starting the scrubber.

Experiment D: Experiment D involved the use of manure A, which had been pretreated in a food mill. The goal of this experiment was to find out whether the reaction time of biochar has an influence on the odour-reducing effect. To this end, 150 g of charcoal were added to 10 litres of manure. Thus three mixtures of manure and charcoal were made. The different reaction times of the charcoal were 30 min., 1 hr. and 2 hrs. Sampling was conducted after the respective reaction time in the scrubber. Two samples were taken for each mixture, two and five minutes respectively after the start of the scrubber. Samples BK-D01 and BK-D02 were made using the direct approach. The reason for this variation was that the other sampling methods are relatively complicated. This method requires much less manure, and the time taken to make the samples as well as the preparation and follow-up work can be reduced. To this end, 1 litre of manure with 150 g of biochar and 1 litre of manure without biochar were stored in a sample bag with 10 litres of synthetic air for 10 minutes. Next, the air was transferred into a fresh sample bag and analysed using the olfactometer.

Experiment E: Experiment E made use of two different methods for making the samples. Both the scrubber and the direct approach were used. In both cases, manure types B and D were used. In the case of the samples that were made in the experiment with the scrubber, the goal was to find out the extent to which a variation of the reaction time of the biochar in the manure has an impact on the odour concentration. Both manure types (B and D) were sampled. 10 litres of manure were used per sample for this. The amount of biochar used was 50 g per sample. An exception are the samples designated BK-E01 and BK-E02, as these were used to determine the odour concentration of the manure without charcoal. Each of the samples was taken five minutes after starting the scrubber. The reaction time of one and two hours respectively was investigated. For the samples made using the direct approach, the question of the extent to which an increase in the added quantity of biochar has an effect on the odour concentration was investigated. 1 litre of manure types B and D was used for each sample. The samples were taken five minutes after the addition of the synthetic air to the mixing bag. The reaction time of the charcoal was not changed and amounted to 30 minutes for all samples in this experiment setup. Samples were made with a charcoal quantity of 50, 150 and 250 g L^{-1}.

Experiment F: In experiment F, the samples were made with the aid of the direct approach method. All four available types of manure were used. 15 g of charcoal were added to each litre of manure. For each type of manure, two samples were made for which a charcoal reaction time of five and ten minutes respectively was selected.

Experiment G: The samples in experiment G was made according to the direct approach. To this end, 1 litre of manure was mixed with 50 and 150 g of biochar respectively. As this experiment was intended to more closely examine the effect of the reaction time of the charcoal on the odour concentration, only the reaction time was varied. Samples were taken after a reaction time of 5, 15, 30, 45 and 60 minutes.

RESULTS AND DISCUSSION

In the following diagrams, the results are summarised as far as possible in the form of the odour level. This achieves a better comparability of the various results and enables correlations to be identified more quickly. Here, too, a maximum measurement certainty of the odour level of ± 2 dBG is taken into consideration.

Results of the direct approach

The results were divided into two diagrams, as the various experiments involved varying the quantity of the charcoal added (Fig. 1) on the one hand, and varying the reaction time of the charcoal (Fig. 2) on the other. Fig. 1 shows the results of experiments D and E, in which the quantity of added charcoal was varied. It can be seen that the odour level of the manure reduces with the addition of the charcoal. It can also be concluded from this figure that the reduction in the odour level correlates to the increasing addition of charcoal.

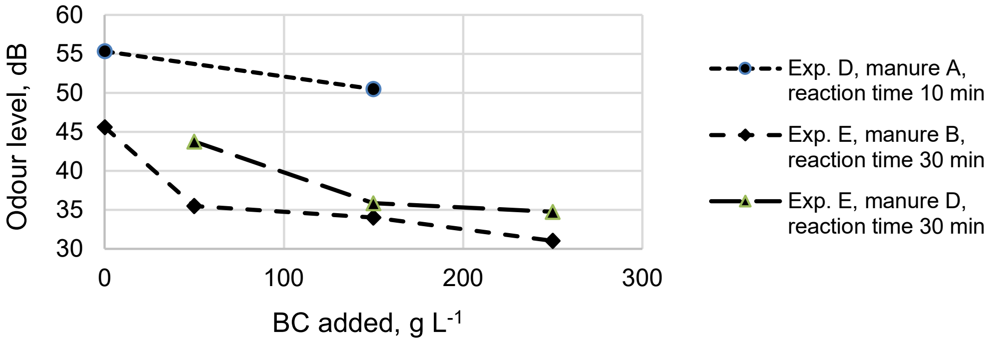

Figure 1. Variation of reaction time at different loads of BC applying experiment D and E showed an important effect at a reaction time of 30 minutes. positive effects were observed for BC loads of 50 gL^{-1}.

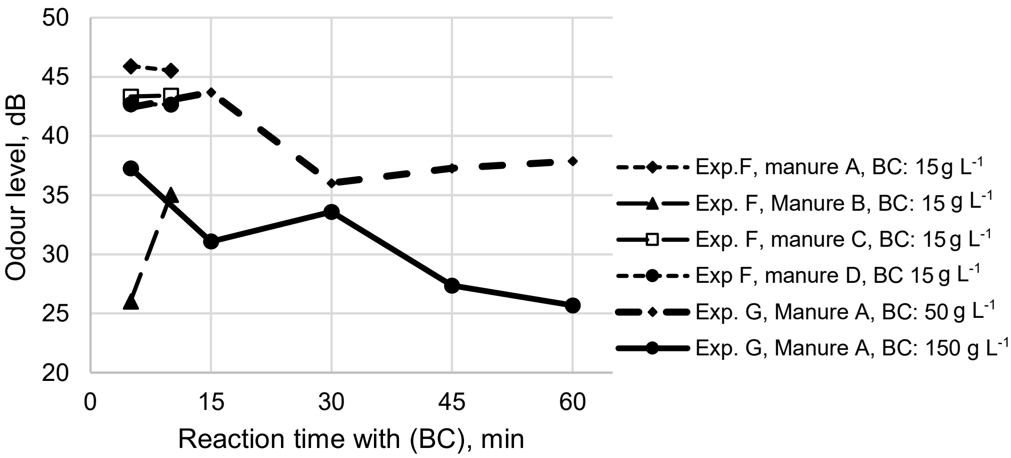

Figure 2. Results for influence of residence time on odor reduction in experiment F and G showed again that effects are poor or unclear at lower loads of BC. For higher loads of BC in experiment G, significant odor reduction could be observed at residence times of 30 to 60 minutes.

Fig. 2 shows the results of experiments F and G, in which the reaction time of the charcoal was varied. On the basis of the available data it is reasonable to conclude that there is hardly any change in the odour level when the reaction time is increased from five to ten minutes. However, if the reaction time is increased to up to one hour, the odour level also falls. It is likely that the combination of an increased quantity of added charcoal and an increased reaction time is responsible for this effect. This becomes clear when the results of experiment G are compared. In each case, manure A was used. The strongest reduction in the odour concentration of up to 12 dB_{OD} was observed with the addition of 150 g L^{-1} of biochar.

Results using the scrubber

The results obtained using the scrubber are presented below. The results were divided into two diagrams according to the varied parameter. On the one hand, the runtime of the scrubber was varied (Fig. 3) and on the other, the reaction time of the charcoal (Fig. 4). Fig. 4 presents the results of experiments C and D. These show that the runtime of the scrubber had a negligible effect on the odour level. The experiment setup proved to be insensitive to the parameter 'runtime of the scrubber'. The main factor here again is the added quantity of charcoal. In some cases (experiment D), no significant reduction in odour could be observed.

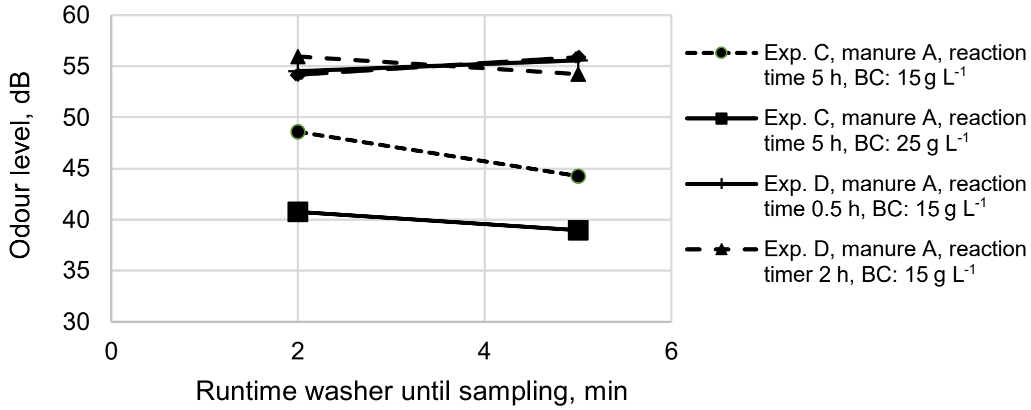

Figure 3. Experiment F and G were used to test if the scrubber experiment is sensitive to washer runtime. The answer is obviously negative. No significant influence of scrubber operation was observed.

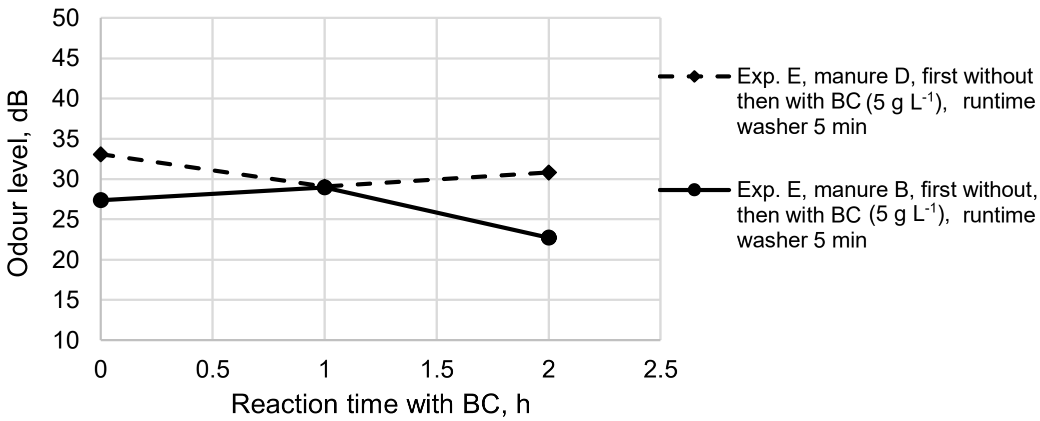

Figure 4. Reduction of odour level at low loads of BC is not clear, even with longer reaction times, applying experiment E.

However, if experiment C is compared with experiment D, the conclusion reached is that the reaction time does indeed have an influence on the odour level. There are concerns here that a reaction time of five hours is set relatively high. The intention in practice is to mix the charcoal with manure only immediately prior to spreading the mixture on the field. In practice, this would give a reaction time of between 30 minutes and one hour. Fig. 4 shows the results of experiment E, in which 2 manures were investigated under the same conditions. The odour level curve is different for the two types of manure used. The results for 2 different manures are an important aspect and require further investigation.

Results of direct spreading

Fig. 5 presents the results of experiment A in graphic form. It is evident that the odour level with added charcoal reduces constantly over time. In contrast, the odour level of the charcoal without additives first rises over time and then falls again towards the end of the observed period, although to a level that is higher than it was at the beginning of the measurement. The odour concentration of the manure treated with charcoal is also consistently at a lower level than the manure without added charcoal. The results of this measurement can be interpreted as an indication of a possible reduction in odour, depending on the manure. At the same time, in comparison to the easier to perform experiments, this complicated method of investigation is not deemed to be any more meaningful than others, but further results showed that the experiment with direct exposure was very sensitive to external influences (failure).

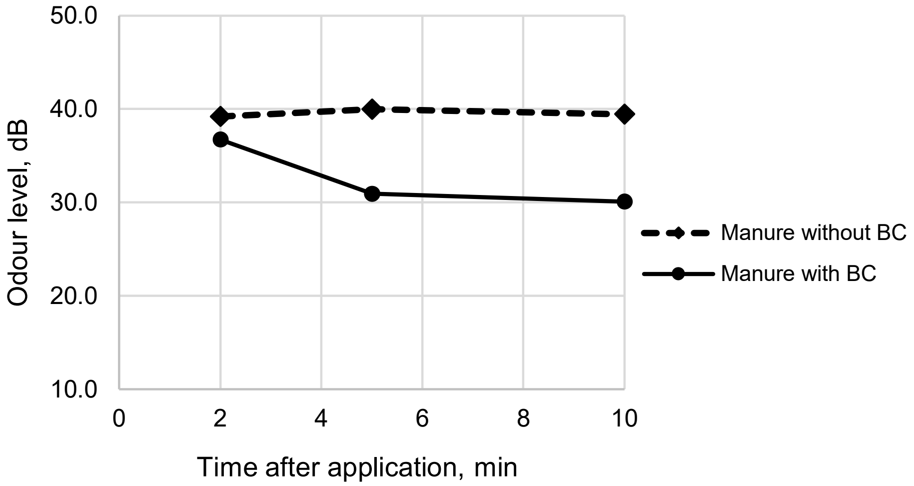

Figure 5. Results of direct spreading on pasture in experiment A showed promising results. With application of BC, odour level was sigificantly lower after a few minutes (> 4).

Relative change in the odour level

Table 1 shows the relative change of the odour level within the various experiments. Note that the change shown is the average change within the respective measurement series. Therefore, the starting value cannot be equated in all cases to the odour level of the untreated manure. It can also come from manure that has been pretreated with charcoal.

Comparing the results increasingly indicates that the reaction time of the charcoal in many instances leads to a reduction in the odour concentration when it lies in the range of about 30 minutes to 4 hours. Furthermore, there is a positive correlation between the reduction in odour and the quantity of charcoal.

Table 1. Relative reduction in the odour level

	Experimental setup	Variable	Odour change
A	direct Application, 4 h react.time, 5 g L^{-1}	amount of BC	- 17.5%
C	scrubber, react.time 5 h, 15 g L^{-1}	amount of BC	- 9.1%
	scrubber, react.time 5 h, 25 g L^{-1}	amount of BC	- 4.2%
D	scrubber, react.time 30 min, 15 g L^{-1}	react.time	+ 2%
	scrubber, react.time 1 h, 15 g L^{-1}	react.time	+ 3.3%
	scrubber, react.time 2 h, 15 g L^{-1}	react.time	- 3.2%
	direct applic., react.time 10 min, 150 g L^{-1}	amount of BC	- 8.7%
E	scrubber, manure D, react.time 1 und 2 h, 5 g L^{-1}	react.time	- 9.7%
	scrubber, manure B, react.time 1 und 2 h, 5 g L^{-1}	react.time	- 5.8%
	direct applic., manure B, react.time 30 min, 50, 150 and 250 g L^{-1}	amount of BC	- 26.5%
	direct applic., manure D, react.time 30 min, 50, 150 and 250 g L^{1}	amount of BC	- 19.3%
F	direct applic., manure A, react.time 5 and 10 min, 15 g L^{-1}	react.time	- 0.9%
	direct applic., manure B, react.time 5 and 10 min, 15 g L^{-1}	react.time	+ 34.6%
	direct applic., manure C, react.time 5 and 10 min, 15 g L^{-1}	react.time	+ 0.2%
	direct applic., manure D, react.time 5 and 10 min, 15 g L^{-1}	react.time	0%
G	direct applic., react.time 5, 15, 30, 45 and 60 min, 50 g L^{-1}	react.time	- 8.7%
	direct applic., react.time 5, 15, 30, 45 and 60 min, 150 g L^{-1}	react.time	- 21.2%

CONCLUSION

It was shown that the testing approaches are suitable for investigating the influence of different parameters on the release of odour when spreading manure. The 'direct approach' method offers the possibility to investigate the reduction in odour in very simple experiments. It was demonstrated that a reduction in the concentration of odour can be achieved by adding biochar to the manure. It was also shown that the measured odour concentration reduced further as the quantity of added charcoal increased. This effect occurred with all methods used. Quantities of charcoal ranging from five to 250 g L^{-1} were added. Important effects of odour reduction could be observed at BC loads of 50 g L^{-1} and higher. Moreover, it was found that, in particular, the differences between shorter reaction times of the charcoal in the manure can be ignored. Over the course of the project, there were increasing signs that where the charcoal has a positive effect, this occurs within the first 30 minutes and continues for several hours. It is therefore possible in practice to use biochar or other organic charcoals immediately before spreading the manure, e.g. when filling suction tankers with it. In conclusion, it can be said that the addition of biochar caused a reduction in odour in all types of manure used, although large differences were observed in the effect it had on various manures.

It can be assumed that odour reduction by 'Borkohle' and other charcoals is mainly related to adsorption of odorous substances and that the effect is reduced with higher residence times. First experiments are widely in accordance to this hypothesis.

In future experiments, an attempt should be made to explain the working mechanisms and to investigate further influencing parameters, such as different manures and manure temperatures. To this end, chemical analyses of the gas phase as well as the solid (charcoal) and liquid phase (manure) will be carried out in addition to odour measurements. This should also explain when – and for which manures – the addition of charcoal can be expected to have positive effects on the emission of odour during spreading. The extent to which the effects found in the laboratory setting can be achieved with standard agricultural equipment, i.e. investigated in field trials, will have to be clarified in a subsequent step. Further investigation of application is under progress. Not all crops need the same amount of boron or do need boron anyway so it will be part of future projects to investigate biochar and combinations of biochar with and without boron to be sure it can be applied due to the needs of different crops.

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