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Biochar Derived from the Dry, Solid Fraction of Pig Manure as Potential Fertilizer for Poor and Contaminated Soils

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Abstract

Pig manure results in the release of NH_3, NO_x, volatile organic compounds and odour nuisance. Pyrolysis of dried pig manure can be considered as an economical viable approach converting this agricultural waste into value added products. The produced amendment biochar can be used as a slow release fertilizer with high concentration of N, K and P and has beneficial effects as carbon sequester and improver of soil quality and crop productivity. It is proved that a 2 wt.% blending of biochar with a poor soil affects positively plant growth and crops (dwarf beans), and worm (*Eisenia fetida*) survival and production. Additional, available heavy metals are immobilised in the biochar and not leachable. The resulting biochar therefore offers prospects as low cost, slow release soil conditioner and fertiliser for a long term effect.

Keywords: agricultural waste, manure, biochar, slow release fertilizer, pyrolysis, Phaseolus vulgaris, Eisenia fetida

1. Introduction

Nowadays handling of pig manure due to their increased amounts together with a stricter environmental regulation increases the search for economic viable and environmental friendly treatments. The storage of pig manure has an impact on the quality of air, groundwater and surface water. Manure also results in the release of NH_3, N_2O and volatile organic compounds and has an odour nuisance (European Environment Agency [EEA], 2009). Many techniques such as anaerobic and aerobic digestion, composting and flocculation have been studied for the treatment of pig manure. These techniques have some drawbacks, and in some cases contribute to pollution of the environment. A very interesting alternative is a thermochemical conversion using pyrolysis. The first results of this treatment described in literature are promising, although pyrolysis of pig manure has not been thoroughly investigated yet (Cantrell, Hunt, Uchimiya, Novak, & Ro, 2012); (Xiu, Shahbazi, Shirley, & Cheng, 2010). Pyrolysis as thermochemical conversion method for pig manure entails different benefits such as: a shorter conversion time compared to composting, the absence of non-biodegradable and toxic substances destroying pathogens that can be found in manure and of course the conversion to value-added products (Ro, Cantrell, & Hunt, 2010).

The thermal conversion of biomass residues and waste streams in absence of oxygen into products with added value is a well-known process. These streams can be converted at relatively low temperatures via pyrolysis into three fractions: biochar, bio-oil and bio-gas. Each pyrolysis product has its own valorisation route and products with unique properties (Demirbas, 2001); (Tuck, Perez, Horvath, Sheldon, & Poliakoff, 2012). The biochar can be used as an alternative for fertilizers as it contains not only C, but also relative high amounts of N, P and K or as precursor for the production of activated carbon (AC) (Azargohar & Dalai, 2006); (Dias, Alvim-Ferraz, Almeida, Rivera-Utrilla, & Sanchez-Polo, 2007). Many studies have reported beneficial effects of biochar as a soil amendment for improving soil quality and crop productivity (Schulz & Glaser, 2012); (Zhang et al., 2010). Amendment biochar can restore soil fertility and could be used to replenish soil carbon pools and sequester CO_2 as a double win option. These biochar management systems can be seen as modern analogues of this Amazonian

phenomenon, *terra preta de Indio*, where aboriginal cultures boosted soil productivity of highly weathered tropical soils mainly through the incorporation of biochar and nutrients into the soil.

A further advantage is that biomass waste streams, present on a large scale around the world, have a low economic value, and do not contribute significantly to the final price of the products obtained. Pyrolysis of biomass waste streams leads to sustainable, environmentally friendly and economically attractive products with added value. Manure processing via pyrolysis is rather limited focused on the bio-oil and biochar. However, the latter can be used, because of its composition, as an alternative for chemical fertilizers (Cantrell et al., 2012); (Uchimiya, Bannon, Wartelle, Lima, & Klasson, 2012). Recently production of AC from biochar as an effective valorisation route is also investigated (Galinato, Yoder, & Granatstein, 2011); (Tuck et al., 2012). The low economic value of the manure together with low production cost and the advantages of the biochar makes it a very interesting economical pathway (Kuppens, Van Dael, Maggen, et al., 2014); (Kuppens, Van Dael, Vanreppelen, et al., 2014).

This study will prove that implementing amendment biochar from pig manure to a soil has a positive effect on soil properties and on cultivating beans.

2. Materials and Methods

2.1 Materials and Soil Preparation

The dry, solid fraction of pig manure was obtained as pellets with a dry-matter content of 32 wt.%. and dried overnight (110 ℃) to increase the dry-matter content. After drying, the pellets were ground (< 2mm) for further pyrolysis and analysis. The manure was sent to Schwerin (Germany) were a pilot pyrolysis installation from Renovia enterprise was used to obtain high amounts of biochar. Renovia enterprise is a company that is investing in the valorisation of manure and other biomasses via pyrolysis and fermentation. The installation was equipped with an automated feeder and uses a unique patented heating system consisting of a horizontal reactor tube with a double hollow screw system filled with a liquid salt and working at an operating temperature of 450 ℃. The residence time of the manure is about 1 h.

This biochar is evaluated as a soil improver mixed with a sandy (88% sand, 8% silt and 4% clay) contaminated soil from a testing field in Lommel (Belgium) which is located 500 m from a metal processing plant (smelter). This soil is chosen due to multiple studies in upgrading this soil suffering from historical contamination (Bouwman & Vangronsveld, 2004). The soil was first air-dried and sieved to remove stones and plant residues. Afterwards, the biochar was added to create the blended soils. Sandy soils were blended with 2, 5 and 10 weight percentage (wt.%) of biochar from pyrolysed swine manure and mixed for 5 minutes. Tests and analysis were performed after the soil was conditioned for three months.

2.2 Chemical Analysis of Swine Manure and Derived Biochar

For the thermogravimetric analysis (TGA) of overnight dried samples a DuPont 951 TGA instrument device was used to determine moisture, volatile matter, fixed carbon and ash content. The standard ASTM methods for the analysis of chars were applied (International, 2011). Elemental analysis of carbon (C), nitrogen (N), hydrogen (H), sulphur (S) and oxygen (O) was carried out with a Thermo Electron Flash EA1113 element analyser with BBOT (2, 5-bis(5-tert-butyl-benzoxazol-2-yl) thiophene with formula $C_{26}H_{26}N_2O_2S$) as standard for calibration. Concentration of metals and non-metals were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) after microwave digestion. Since there are no specific standard procedures described or developed for the decomposition of manure, several standard procedures were tested. The best procedure applied was the standard "microwave digestion of plants in a closed vessel" and uses 5 ml of concentrated nitric acid (HNO_3, suprapur) and 3 ml of hydrogen peroxide (H_2O_2, 30%) followed by a single step microwave treatment (Table 1) (Milestone MLS 1200-Mega) (Araujo, Gonzalez, Ferreira, Nogueira, & Nobrega, 2002). The char produced from pyrolysis was digested in two steps rather than in one step as described above for the pig manure. In a first step, 3 ml HNO_3 suprapur and 2 ml H_2O_2 30% were used. In the second step, 2 ml HNO_3 supra pure and 1 ml H_2O_2 30% were added again. Finally, the obtained solutions were filtered and diluted with Milli-Q water in a volumetric flask. The determination of element concentrations in the solution was done using a Perkin Elmer Optima 3000 DV ICP-AES device with an axial plasma configuration.

Table 1. Microwave program for the digestion of manure and biochar

Step 1	Time (min)	Power (W)
	2	200
	1	0
	5	200
	5	340
	5	400
	20	340
Step 2	5	200
	5	340
	5	400
	5	500
	15	340

To use amendment biochar as a natural soil improver and fertilizer, the impact of the leachability of the metals and the nutrients is a key parameter. Leachability will indeed provide insight on the mobility of the major nutrients (N, K and P) and a number of heavy metals present. It is favourable that nutrients are released slowly while the metals remain in the biochar. Therefore, Milli-Q water or a solution of $CaCl_2$, HNO_3, KCl or NH_4OAc, respectively, was added to the char as described by Faridullah et al. (2012). The solution was filtered through a 0.45 micron Millipore filter and analysed with ICP-AES. This extraction was also executed dynamically for the Milli-Q and KCl solutions: the solution was replaced every 24 hours by a "fresh" solution to estimate how much material could be leached within a certain period of time and to determine its maximum limit of leaching. This 24 hours' cycle was repeated 4 times. A first outcome on a one step leaching can be formed via conductivity measurements. Each solution is selected to examine the change in conductivity at a different level. The change in conductivity for Milli-Q water is based on the solubility of metals present. For HNO_3 this change is based on acid-base reactions. The change in conductivity using $Ca(NO_3)_2$ and $CaCl_2$ is based on exchangeable ions while with KCl as indifferent electrolyte the change is based on ionic strength.

Fourier Transform Infrared Spectroscopy (FTIR) was carried out for the initial biomass and char to characterize the bulk composition using a Bruker Vertex 70 FTIR spectrometer equipped with a DTGS detector. The dried samples are pressed into a KBr pellet. The spectrum was recorded in transmission between 4000 to 480 cm^{-1} (number of scans: 32, resolution: 4 cm^{-1}).

2.3 Physicochemical Analysis of Biochar Blended Soils

The acidity of the char gives an idea about the mobility of metals in the soil and plant growth. Therefore, Milli-Q water was added to the blended soil (Carter, 1993). This procedure was also used to determine the pH of the soils. This is also done after cultivating. Metal concentrations were determined by wet digestion of the blended soils followed by ICP-AES as described in §2.3. $Ca(NO_3)_2$ was used for the determination of the exchangeable metals in soil. Using this method, phyto-toxic heavy metals for plants are exchanged with Ca-ions. In addition to the metal concentration, different key parameters such as pH, organic matter, chemical bonding of the metals and intrinsic plant parameters have to be taken into account, all of which have an effect on the availability and therefore the uptake of metals by the plant (Gleyzes, Tellier, & Astruc, 2002).

The Cation Exchange Capacity (CEC) a good indicator of soil quality and productivity (Extension & United States. Cooperative State Research, 1995). It measures the quantity of negatively charged positions on soil surfaces. The Water Holding Capacity (WHC) is a parameter for determining the amount of water that soil can hold relative to its dry mass. The WHC can be calculated from the equation:

$$WHC\ (as\ a\ percentage\ of\ the\ dry\ weight)\ = \frac{(S-T-D)}{D}\ x\ 100 \quad (1)$$

Here S is the mass of the tube, the filter paper and the water-saturated blended soil; T is the mass of the tube and the filter paper; D is the mass of the dried blended soil (Standardization, 2012).

In order to evaluate salt stress on worms (Eisenia fetida) an extra washing step procedure with deionized water

was needed based on preliminary worm test experiments. The soil was mixed with distilled water in a 1/2 (g/v) ratio. The slurry was stirred for 1 minute and kept aside for 15 minutes; this procedure was repeated 4 times. The slurry was left to settle for 24 h before decantation. Samples of the washing water were analysed using ICP-AES, conductivity and pH measurements. The remaining wet soil was left 4 weeks to dry at ambient temperature.

2.4 Plant Grow Tests with Beans

The dwarf beans (*Phaseolus vulgaris*), also called "Limburgse vroege", were sown on the stabilized soils blended with amendment biochar and on a soil without this biochar for control. The soils with beans were placed in a specially designed growth chamber which mimics natural conditions. (Vanassche & Clijsters, 1990). The plants were carefully removed from the soil after the growth period of 15 days. The roots were washed gently to remove the grains of biochar and soil. The plant is then separated into 3 parts: the leaves, roots and stem according reference (Vanassche & Clijsters, 1990). The analysis of the bean plant takes place in three steps. First, all parts of plants are weighted separately. Further, the length of the stem is also measured. Second, the enzymatic activity is examined for every plant. Samples are stored in a freezer at -80 ℃ prior to analysis. Thirdly, the metal concentration in the leaves of every plant is determined using 200 mg of dried leaves digested in pure, warm nitric acid (HNO_3). After digestion suprapur HCl and Milli-Q water was added. The metal concentrations in these solutions are determined by ICP-AES (Vanassche & Clijsters, 1990). The roots are not used for the analysis of metal concentrations due to remains of soil that cannot be washed off.

2.5 Soil Toxicity Tests with Worms

The worms (*Eisenia fetida*) were obtained from synchronized cultures and fed with cow manure. The untreated Lommel soil was chosen as reference. Tap water was added to these containers and humidity was monitored during the test and adjusted if necessary (Standardization, 2012). Survival, growth (biomass) and number of cocoons were used as endpoint. Small bait portions consisting of oatmeal and activated carbon were fixed in holes pierced in PVC strips (Bait lamina). These strips with ten holes each were placed in the soils of the containers mentioned above. The worms added to the soils progressively feed on the bait placed in the soil substrate. The disappearance of the bait material after one week was directly associated with the feeding activity of the worms (Kratz, 1998). Analysis is done by weighing the worms before and after the soil toxicity test. The worms and their produced cocoons are also counted after 4 weeks for a first indication of the toxicity of the soils. The number of open holes in the PVC strips is counted and expressed in percentage for comparison. All the results are then statistically analysed (Kruskal-Wallis, Mann-Whitney U) to see if there is a significant difference between the soils blended with amendment biochar and the reference. The independent samples Kruskal-Wallis test was used to check if there is a significance for the cocoons, mortality, growth and bait lamina not taking into account the different blends. The Mann-Whitney U test was used to check if there are significant differences between the 0, 2 and 5 wt.% soils within the cocoons, mortality, growth and bait lamina. If the significance is less than 0.05 the difference is regarded as significant (Solutions)

3. Results and Discussion

3.1 Characterization of the Manure and Biochar

The major part (± 77 wt.%) of the manure consists of volatile matter (45%) and ash (32%). The rest of the manure consists of fixed carbon (± 18 wt.%) and moisture (± 4 wt.%). The composition of the biochar shows significant differences as a result of pyrolysis. A temperature of up to 450 ℃ is reached during the pyrolysis process, causing the volatile matter to drop under 5 wt.% increasing simultaneously the amounts of ash and fixed carbon. The amount of fixed carbon doubled to about 43 wt.% and the ash content shows an increase of 66 % to about 52 wt.%. These results are summarized in Table 2.

Table 2. Thermogravimetric and elemental analysis of the manure and biochar

Sample	W^{ad}	Ash^{db}	VM^{db}	$C_{fix}{}^{db}$	C	H	N	S	O^{diff}
Virgin Manure	4.1	32.4	45.4	18.1	30.1	4.0	2.7	0.5	30.3
Amendment Biochar	1.4	51.6	4.4	42.8	33.0	1.1	1.8	0.1	12.4

^{db}dry basis; ^{ad}air dried, O^{diff}=100-(C+H+N+S+Ash), db

Element analyses are also shown in Table 2. The biggest difference between the virgin manure and amendment biochar can be found in the O content. The virgin manure has an O content of 30.3 wt.% while the amendment biochar has only 12.4 wt.% of O content. This decrease in O content can be explained by the conversion of

compounds in the virgin manure resulting in volatile matter (NO_x, SO_x, H_2O, …) leaving the material and thus, beside a decrease in O, also a decreasing N and S content.

The results of the ICP-AES analyses indicate a broad distribution of metal concentrations in the virgin manure (Table 3). High concentrations (> 20 $mg.g^{-1}$) of Ca, K and Mg are present. Na and P are present in moderate concentrations (> 10 $mg.g^{-1}$) while Al, Cu, Fe, Mn and Zn are present in low concentrations (< 3 $mg.g^{-1}$). Other (heavy) metals were not detected. Since most metals are not volatilized during pyrolysis under the given conditions, they are not found back in the bio-oil or gas. (Tack, Van Ranst, Lievens, & Vandenberghe, 2006) This leads to a concentration increase in the biochar as visualised in Table 3. Elements present in the biochar are doubled in concentration compared with the starting material.

Table 3. Elemental composition of the virgin manure and amendment biochar

Sample	**Ca**	**K**	**Mg**
	$mg.g^{-1}$	**$mg.g^{-1}$**	**$mg.g^{-1}$**
Manure	35.18 (0.55)	35.03 (0.31)	21.13 (0.33)
Biochar	68.18 (1.90)	25.22 (2.18)	36.05 (4.04)
Sample	**Na**	**P**	**Fe**
	$mg.g^{-1}$	**$mg.g^{-1}$**	**$mg.g^{-1}$**
Manure	14.90 (0.14)	19.84 (0.39)	2.13 (0.04)
Biochar	6.51 (0.53)	57.27 (5.39)	14.48 (2.68)
Sample	**Mn**	**Al**	**Cu**
	$mg.g^{-1}$	**$mg.g^{-1}$**	**$mg.g^{-1}$**
Manure	0.55 (0.01)	0.72 (0.08)	0.44 (0.01)
Biochar	1.39 (0.09)	2.86 (0.16)	1.19 (0.11)
Sample	**Zn**	**Cr**	**Ni**
	$mg.g^{-1}$	**$mg.g^{-1}$**	**$mg.g^{-1}$**
Manure	0.64 (0.01)	< 0.01	< 0.1
Biochar	2.75 (0.20)		
Sample	**Pb**	**As**	
	$mg.g^{-1}$	**$mg.g^{-1}$**	
Manure	< 0.1	< DL	
Biochar			

DL: below detection limit, standard deviation between brackets

FTIR spectra of the virgin manure and biochar are shown in Figures 1. The spectrum of the virgin manure clearly shows absorption bands of amides (3280, 1650, 1544 cm^{-1}), carbonates (2500 (overtone), 1440, 873, and 714 cm^{-1}), phosphates (1080 cm^{-1}) and nitrates (1385 cm^{-1}). The FTIR spectrum of the biochar shows clearly that the organic fraction in the biochar is almost completely carbonized by the absence of a significant response in the spectral range for CH absorptions (2800-3000 cm^{-1}). Dominant IR absorption bands that are present can be related to the mineral fraction (carbonates, phosphates and nitrates).

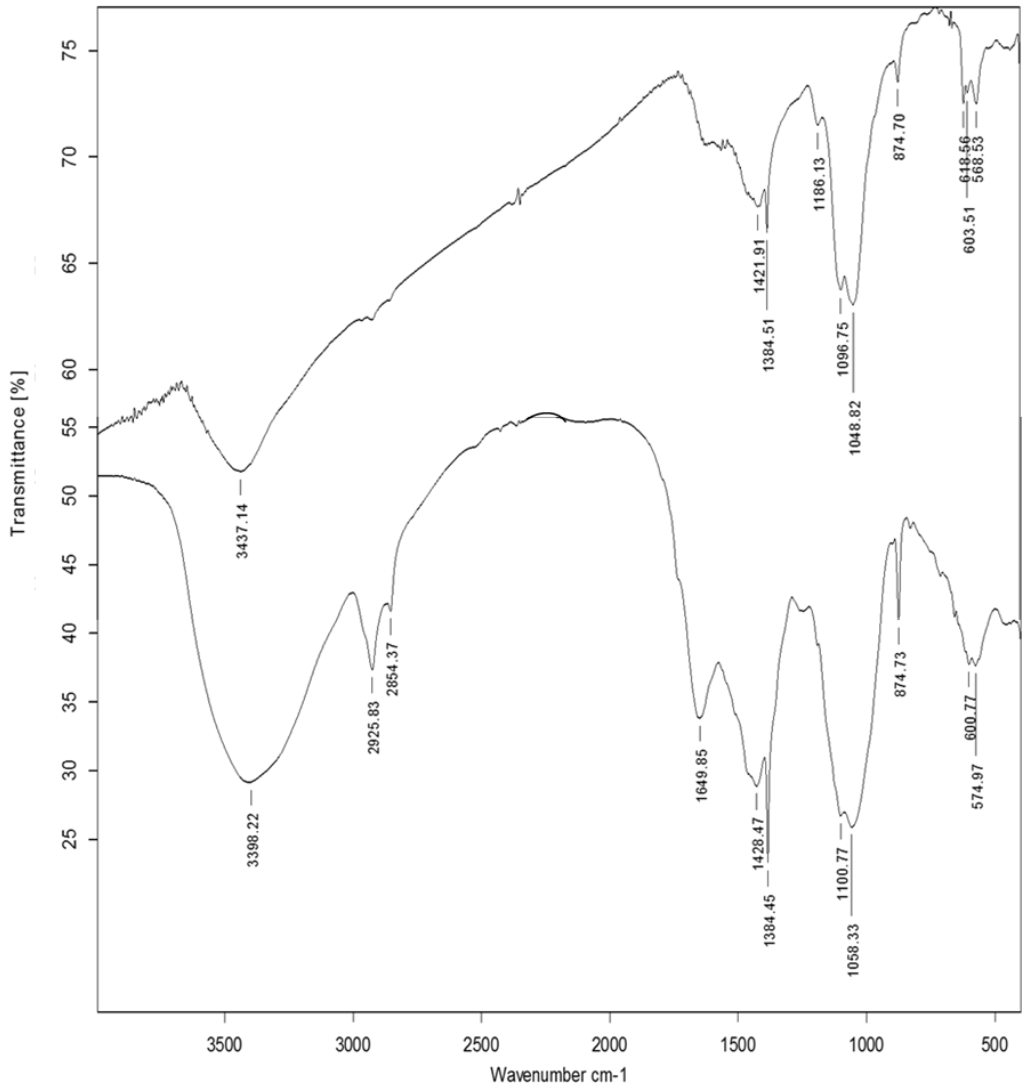

Figure 1. FTIR spectrum of the virgin manure (bottom) and fertilizer like biochar (top)

3.2 Leachability of the Amendment Biochar

The conductivity (Table 4) of the solution increased the most for the biochar mixed with KCl solution and Milli-Q water, the last because of its initial absence of ions and Milli-Q water is considered as a strong leaching agent. An increase in conductivity is also found for $CaCl_2$ and $Ca(NO_3)_2$ stating that the Ca^{2+} presence will be exchanged with other ions present in the biochar. Table 4 also shows a sharp drop in conductivity for 0.1 and 0.5M HNO_3 solutions. This decrease in conductivity can be explained by the neutralisation reaction of the biochar. This neutralisation reaction by carbonate and phosphate explains the buffering action of the char. For 0.01M HNO_3, NH_4OAc and NH_4OAc/EDTA treatments it can be stated that leaching of the biochar is rather limited.

Table 4. Conductivity of the solution before and after immersion of amendment biochar for 24h

	Milli-Q	HNO_3 (0.5M)	HNO_3 (0.1M)
Conductivity of biochar ($mS.cm^{-1}$)	3.23	35.20	11.15
Conductivity control solution ($mS.cm^{-1}$)	< 0.01	148.50	31.20
Difference	3.23	-113.30	-20.05
	HNO_3 (0.01M)	KCl (1M)	$Ca(NO_3)_2$ (0.1M)
Conductivity of biochar ($mS.cm^{-1}$)	4.40	96.17	18.07
Conductivity control solution ($mS.cm^{-1}$)	3.10	92.40	16.00
Difference	1.30	3.77	2.07
	$CaCl_2$ (0.1M)	NH_4OAc (1M)	NH_4OAc (0.5M) / EDTA (0.02M)
Conductivity of biochar ($mS.cm^{-1}$)	5.28	57.30	35.05
Conductivity control solution ($mS.cm^{-1}$)	2.60	56.60	33.60
Difference	2.68	0.70	1.45

A better insight in the change in conductivity and leaching mechanisms can be obtained using dynamic leaching procedure. A 1x 96h test is performed to see if saturation is reached between 24h and 96h. The conductivity increase of the 1M KCl solution shows a decrease after 48h and remains constant the next 24 and 48h at a somewhat lower value compared to the first 24h leaching while the increase in conductivity in Milli-Q water decreases with each 24h fresh leaching treatment (Figure 2). This can be interpreted as a limited leachability of the biochar in Milli-Q water in contrast to KCl where the ionic strength will affect solubility and conductivity.

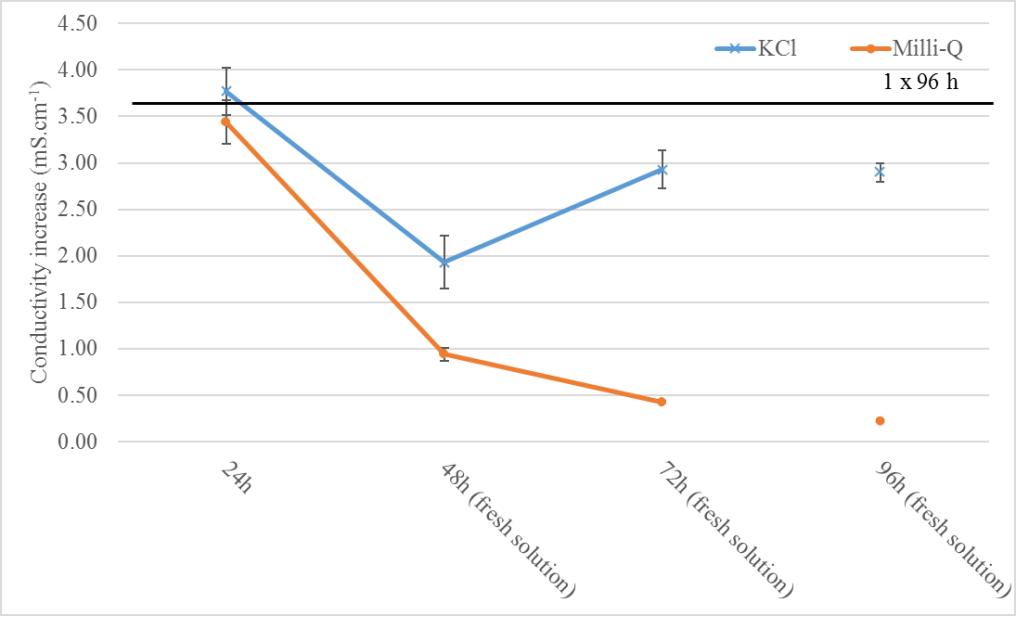

Figure 2. Conductivity increase in function of dynamic leaching of the amendment biochar in Milli-Q water and KCl solution (1M)

Figure 3 shows the trend of the pH change as a function of the same dynamic leaching procedure. For the 1M KCl leaching an almost constant pH of 8.00 is reached for each fresh KCl treatment and this indepently for the n x 24H or 1 x 96h application. For Milli-Q water pH increases steadily for each leaching treatment until almost the PZC of the amendment biochar is reached, being 9.4. For the 1 x 96h treatment this pH is not reached for Milli-Q water, a maximum of 8.4 can be noticed. The amendment biochar has the strong ability to buffer the

solution due to the presence of carbonates and phosphates. As Milli-Q water is more aggressive this buffering effect is not perfectly compensated.

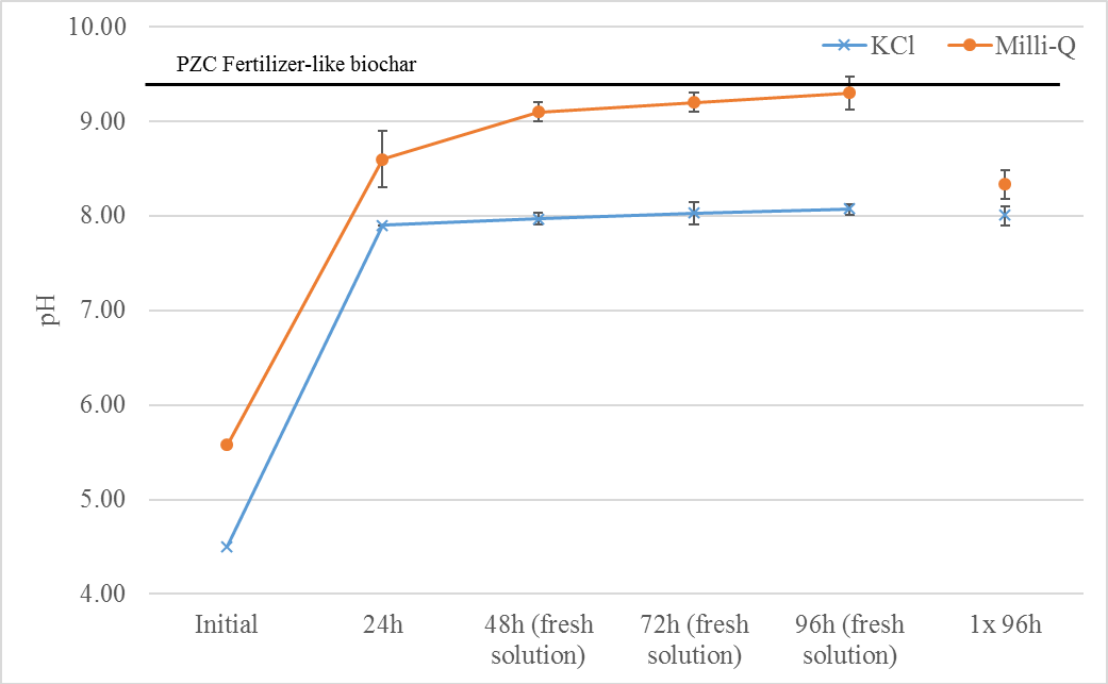

Figure 3. pH in function of dynamic leaching of the amendment biochar in Milli-Q water and KCl solution (1M)

Furthermore, we examined the ionic composition of the solutions after dynamic leaching of the amendment biochar. In the case of Milli-Q water (Figure 4), all analysed elements show a decreased concentration in function of leaching repeatability over a constant time. Figure 5 shows that 40% of K present in the biochar is leached after 96h. Ca and Mg with 3% and 2% removal are less leached in contrast to Na with 22% removal. Only 0.26% of P present in the biochar is leached, which is important in view of its plant availability suggesting a less soluble P species stronger bound in the biochar. This is an indication that P is present as calcium phosphate ($Ca_3(PO_4)_2$) and that most of the released Ca is coming from calcium carbonate ($CaCO_3$). Al, Cu, Zn and Fe were not detected in the leaching solutions. Also this is an important fact in view of its environmental friendly and save use as soil amendment. The outcome is rather different for leaching with KCl (Figure 5) where the leaching is more or less constant in function of leaching repeatability over a constant time. K is not taken into account because of the matrix (KCl solution). 48% of Na present in the biochar is leached after 96h. Ca, Mg and P are leached for respectively 2%, 7% and 4% of the amount present in the biochar. Al, Cu, Zn and Fe were not detected in the leaching solutions.

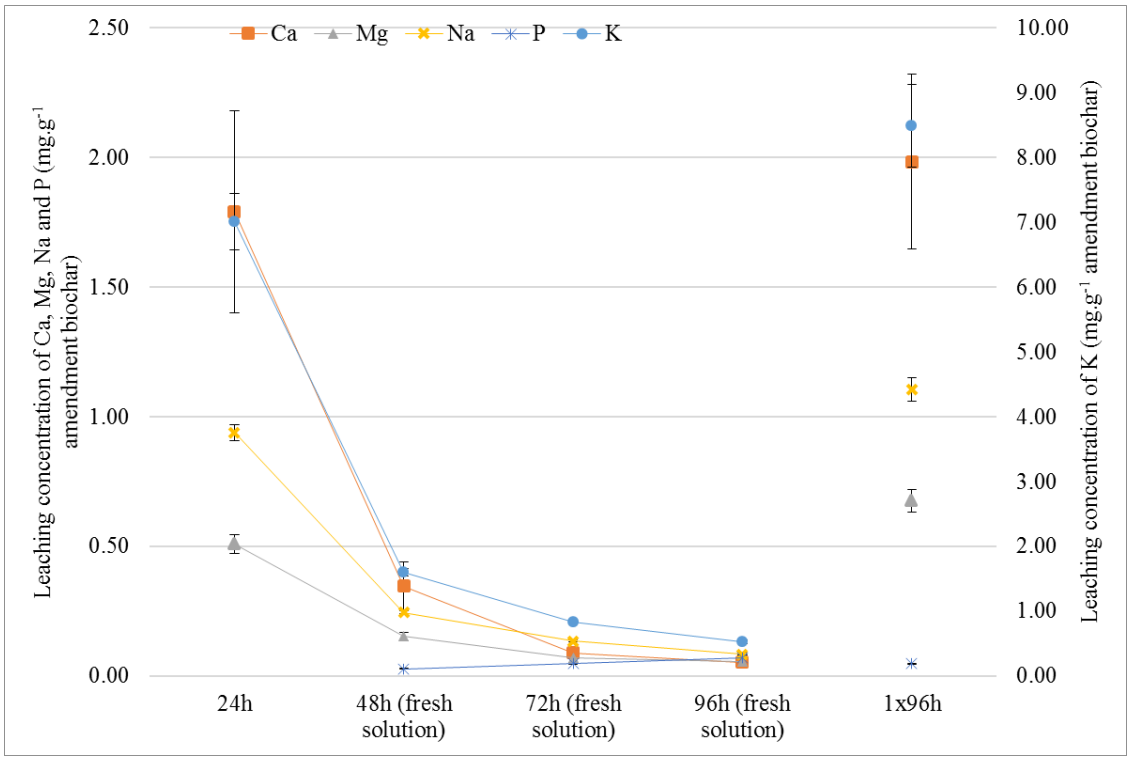

Figure 4. Elemental analysis of solution after dynamic leaching of the amendment biochar with Milli-Q water

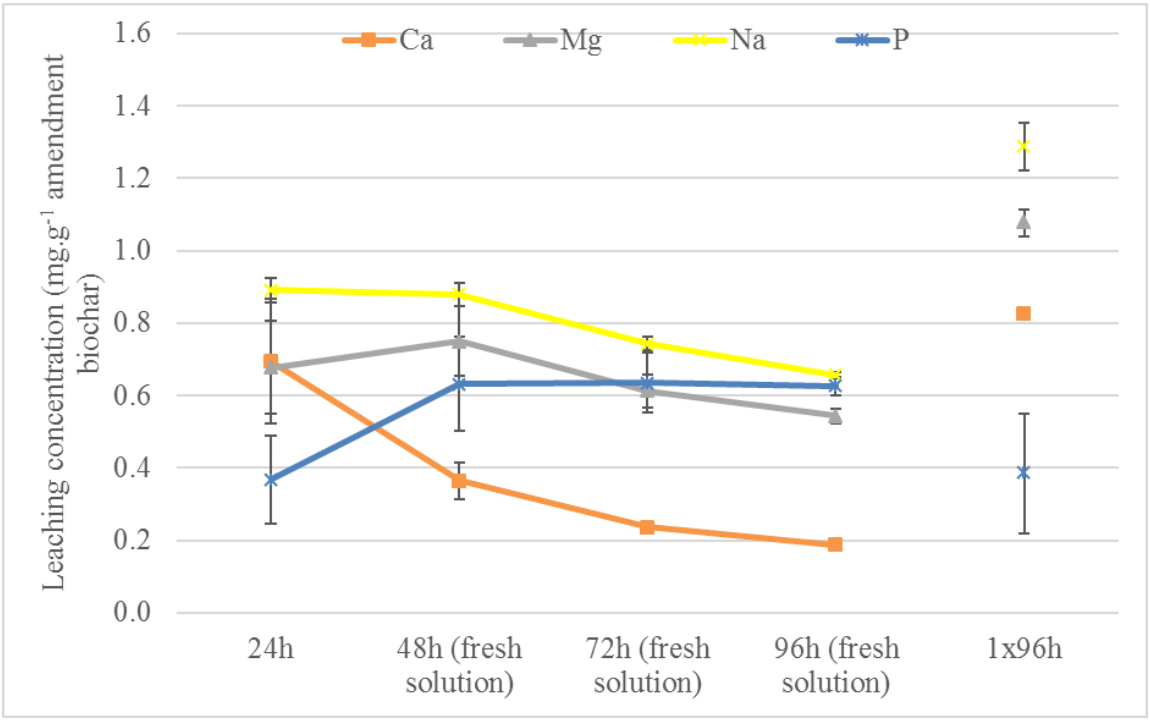

Figure 5. Elemental analysis of the solution after dynamic leaching of the amendment biochar with KCl solution (1M)

3.3 Characterization of the Amendment Biochar Blended Soils

3.3.1 Characterization of the Amendment Biochar Blended Soils

Only the 2 wt.% and 5 wt.%, besides the virgin sandy soil, are researched in more detail because of the positive plant growth. For the 10 wt.% blending very negative plant growth results were obtained. The element concentrations of K, Al, Cu, Zn, Mg, Na, Fe, and P in the soils are presented in Figure 6. This graph shows that the concentration of the elements increases with increasing content of biochar except for Al and Fe, because of their high amounts already present in the virgin sandy soil and the relative small amount added via the amendment biochar. The pH values for the soils are 6.3, 7.0 and 7.3 for 0 wt.%, 2 wt.% and 5 wt.% respectively (Table 5). This increase in pH can be explained by its high PZC and the buffering capacity of the amendment biochar due to the carbonates and phosphates present in the biochar.

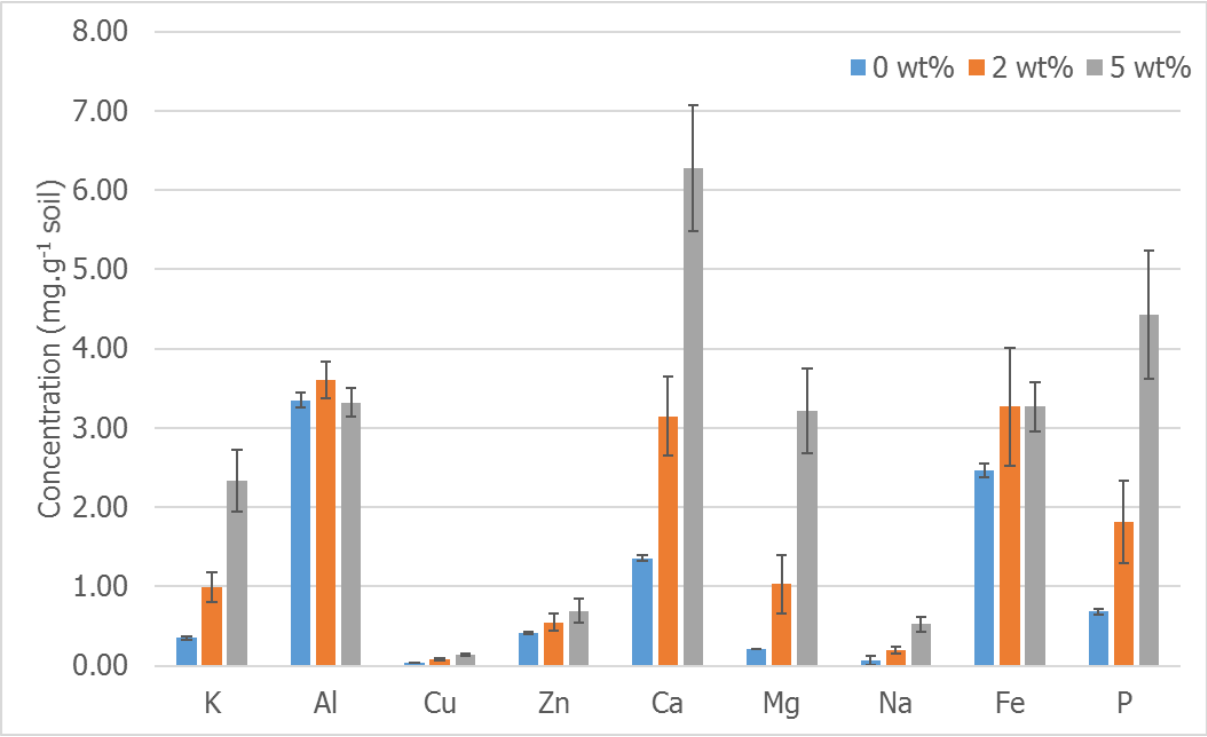

Figure 6. Elemental analysis of the soils with different wt.% of amendment biochar

Table 5. pH, Water Holding Capacity, Cation Exchange Capacity and conductivity of the biochar blended soils (not washed)

Sample	pH (before)	WHC (%)	CEC (cmol.kg^{-1})	Conductivity (µS.cm^{-1})
0 wt% biochar	6.3	42.8	5.9	143.7
2 wt% biochar	7.0	54.0	7.3	422.3
5 wt% biochar	7.3	57.2	8.2	1088.7

The WHC increases with increasing biochar content from about 43% for the soils without biochar till about 57% for the soils with 5 wt.% biochar (Table 5). The difference between 2 wt.% and 5 wt.% is rather small. This shows that soils containing biochar can retain more water than those without which is ideal for sandy soils that dry out easily. The same trend is found for the CEC (Table 5) which increases with increasing content of biochar and can be related with the adsorptive character of the biochar. The more biochar in the soil the more it tends to retain positively charged ions in the soil. The difference between 2 wt.% and 5 wt.% amendment biochar is however more expressed. The CEC rises with almost 24% when 2 wt.% amendment biochar is added to the soil and with an additional 12% when 5% is added.

In contrast to the conductivity, it increased dramatically by adding the amendment biochar. This is the reason why a washing step of the 2 wt.% and 5 wt.% blended soils is executed for the worm experiments. Indeed, it was

found that in case of the worm experiments, the conditions for reproduction and bait lamina test were rather negative.

3.3.2 Effect of Cultivation on Biochar Amendment Soil

The results can be found in Figure 7 for all plant parts showing that plant uptake of these elements increases with increasing biochar content. K, Ca, Mg and P concentrations increase very strongly for the 2 wt.% blend and even with the same tendency, except perhaps for Fe, for the 5 wt.% blend while the increase for the other elements is rather moderate. The change in exchangeable dedicated elements is also checked. These results can be found in Figure 8 in terms of leachable elements without and with cultivation. The range for the 0 wt. % blended soil is between 0 and 0.07 mg/g soil, for the 2 wt.% blended soil it is between 0 and 0.35 mg/g soil, while for the 5 wt.% blended soil it has a range between 0 and 0.56 mg/g soil. What stand out is that the range of the increases with increase percentage of biochar. This observation coincides with the increasing cation exchange capacity as discussed in §3.3.1. For the soil without biochar the leachability before and after planting changed only slightly in favour of the cultivated soil for K, Zn, Mg and Na; for P the change is negligible. The soils with 2 wt.% and 5 wt.% biochar show that K, Mg and P are released more after harvesting. However, Zn is less released than before planting. The released amounts of Al, Cu and Fe are below 0.01 mg/g. Ca cannot be measured due to the use of $Ca(NO_3)_2$ for the determination of exchangeable metals.

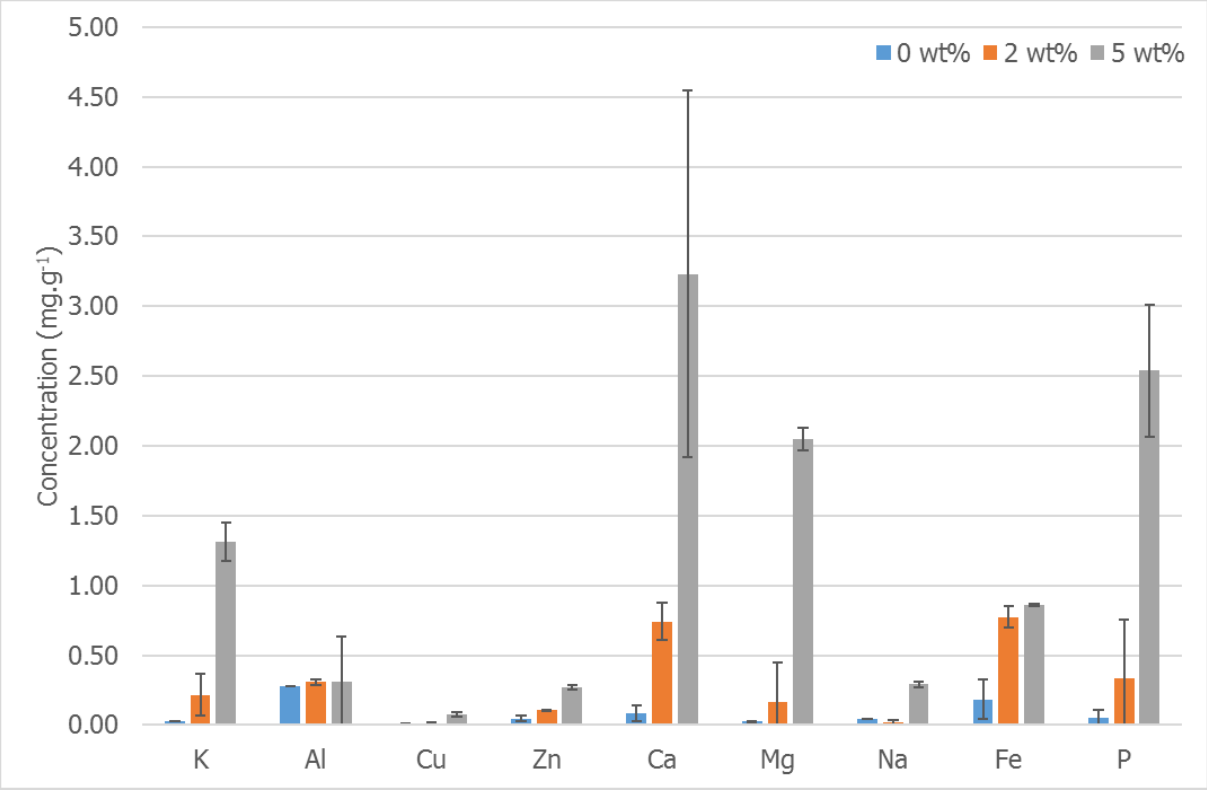

Figure 7. Analysis of the uptake of different elements by the plant

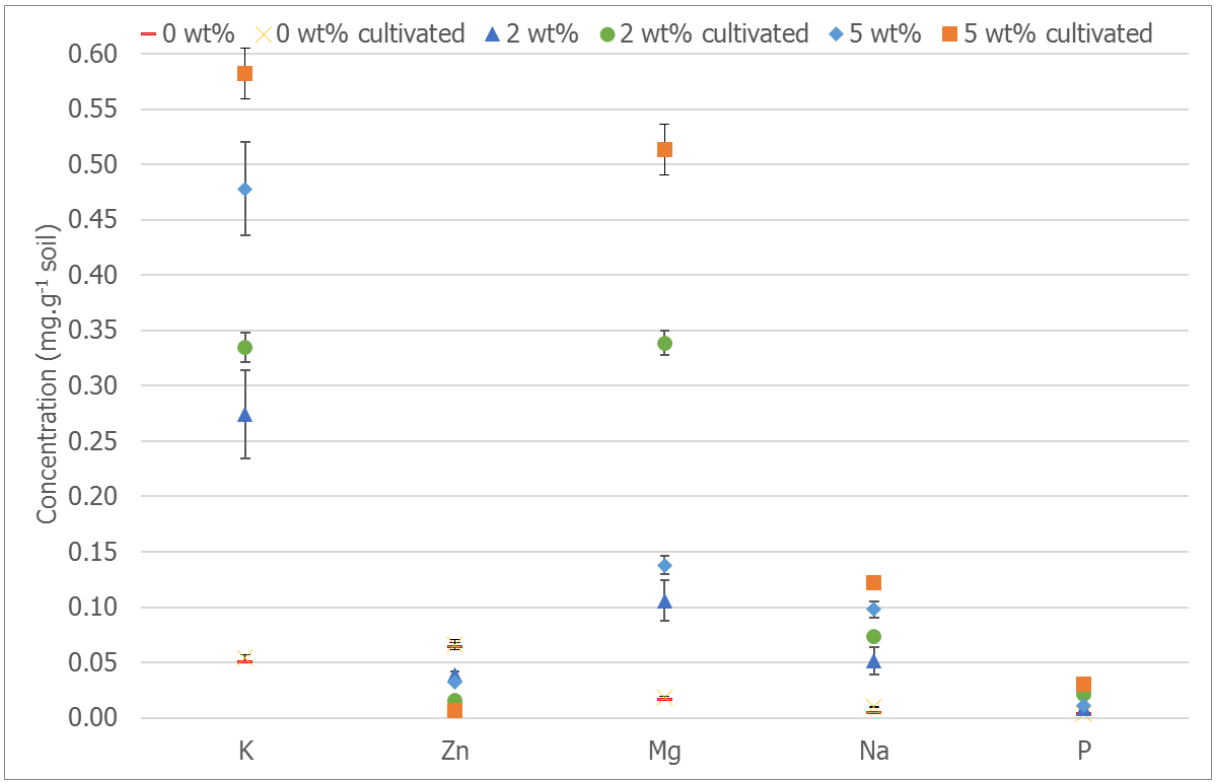

Figure 8. Elemental analysis of the leaching (24h) from 0, 2 and 5 wt.% biochar blended soil before and after harvesting

There is no general trend for the conductivity (Figure 9) between the different soils. Conductivity increases after harvesting for the 0 wt.% en 2 wt.% blended soils stating that there are more soluble present due to the amendment biochar. However, for the 5 wt.% soils a drop in conductivity is found. The initial pH value for the soils (Figure 10) is between 6.3 and 7.3. The pH in the soils without amendment biochar drops 0.6 pH units after harvesting in contrast to the soils with amendment biochar which drop only 0.2 and 0.1 pH units for the 2 wt.% and 5 wt.% respectively. This confirms again the buffering capacity of the biochar in the soil.

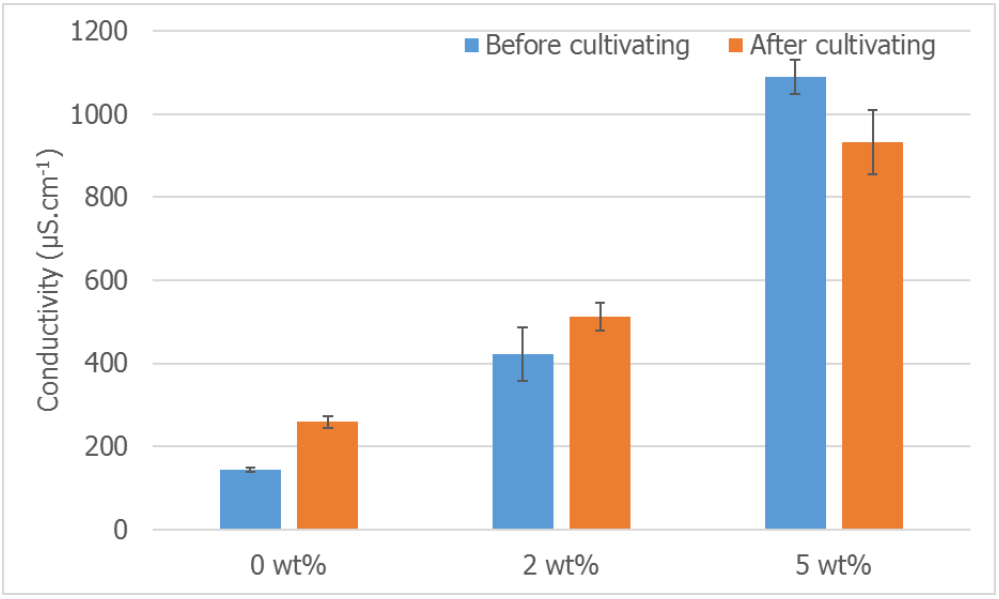

Figure 9. Conductivity before and after harvesting (24h) of the biochar blended soils

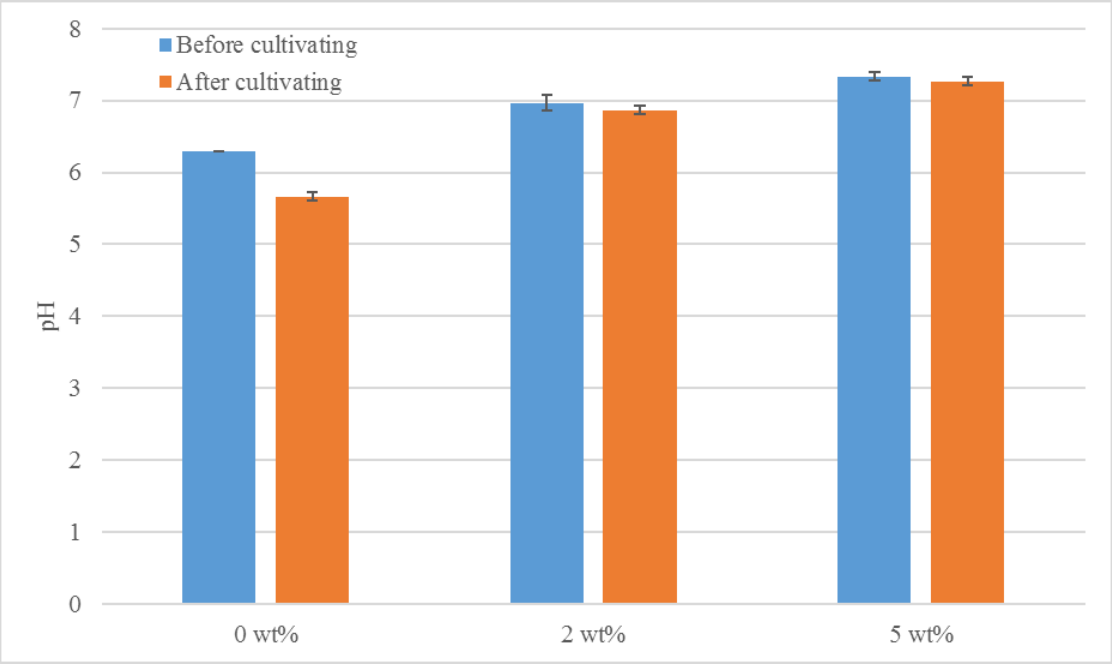

Figure 10. pH before and after harvesting of the biochar blended soils

3.3.3 Effect of Char on Plant Properties

The growth results of the plants after 2 weeks in the growth chamber can be seen in Table 6. The effect on a soil with or without biochar is clearly demonstrated. Initially it was thought that a higher content of biochar would be beneficial for plant growth, but this test shows the opposite. Soils with 10 wt.% biochar have a negative impact on plant growth. The explanation for this is that biochar tends to retain the water and thus higher biochar content increases the water holding capacity of the soil which becomes too wet and the bean plants become mouldy. Soils with 10 wt.% biochar are therefore not included in the further analyses. Minor visual differences between plants grown on soils with 2 wt.% and 5 wt.% biochar are observed and these plants grow 2 times faster than plants on soils without biochar. Length of the stems is measured and the leaves, roots and total plant are weighed for verification of the visual differences. These values are presented in Table 6 showing that plants grown on soils with 2 wt.% and 5 wt.% biochar are almost 2 times heavier compared to plants cultivated on the same soils without biochar. Additional it was found that crop yields were also much higher for the 2 wt.% biochar blending then in the case of the native soil but these results are not published yet.

The enzymatic activity in the root and the leaf is examined in order to have a better view on which soil is best for bean cultivation. The enzymatic activity can be considered as a measure of the stress induced in the plants. The higher the stress in the root and the leaf, the smaller the plant reflects an increased phytotoxicity in the soil. The results of the enzymatic activity in leaves and roots are also included in Table 6. From the enzymatic activity in the leaf, we see a significant decrease for a higher percentage of biochar in the soil. The enzymatic activity decreases by 50% for ME and ICDH, for GPOD this is even 75%. The enzymatic activity in the roots behaves differently from the trends found in leafs. For example, the data show that a minimum is reached for soils with 2 wt.% biochar while for the soils with 5 wt.% biochar the enzymatic activity decreases for ME and GPOD. The enzymatic activity also decreases by 50% compared to the soils without biochar. One can conclude that no significant differences between the soils with 2 wt.% and 5 wt.% biochar were found. However, improved enzymatic activities for these blends were measured compared to the 0 wt.% soil. The 2 wt.% char is better for the roots enzymatic activity; the 5 wt.% char is better for the leaves enzymatic activity. Economically, the 2 wt.% blending is more interesting than the 5 wt.% due to the fact that with 2 wt.% more soil can be blended and the results are the same.

Table 6. Plant growth and enzymatic activity of plants grown on biochar blended soils

	0 wt%	2 wt%	5 wt%
Number of plants	9	11	10
Plant mass (g)	1.29 (0.34)	2.19 (0.35)	2.27 (0.43)
Leaf mass (g)	0.75 (0.27)	1.44 (0.28)	1.52 (0.25)
Root mass (g)	0.67 (0.32)	1.33 (0.27)	1.38 (0.43)
Length (cm)	6.49 (0.54)	11.37 (1.60)	11.50 (1.46)
Enzymatic activity roots ($mU.g^{-1}$)			
ME	77 (7)	42 (8)	48 (8)
GIDH	-31 (3)	-18 (3)	-20 (3)
GPOD	853 (66)	567 (230)	681 (111)
Enzymatic activity leafs ($mU.g^{-1}$)			
ME	118 (24)	60 (12)	53 (3)
ICDH	113 (10)	67 (14)	59 (3)
GPOD	311 (113)	77 (34)	48 (5)

Number of plants with respect to 12 beans planted, standard deviation between brackets

The elemental concentration of K, Al, Cu, Zn, Ca, Mg, Na, Fe and P in the leaves is shown in Figure 11. The concentration of K, Mg and P increases with increasing concentration of biochar. On other hand, Ca decreases with increasing concentration of biochar in the soils. The concentrations of Zn, Na and Fe are below 0.01 and Al and Cu are not detected in the leaves of the plant.

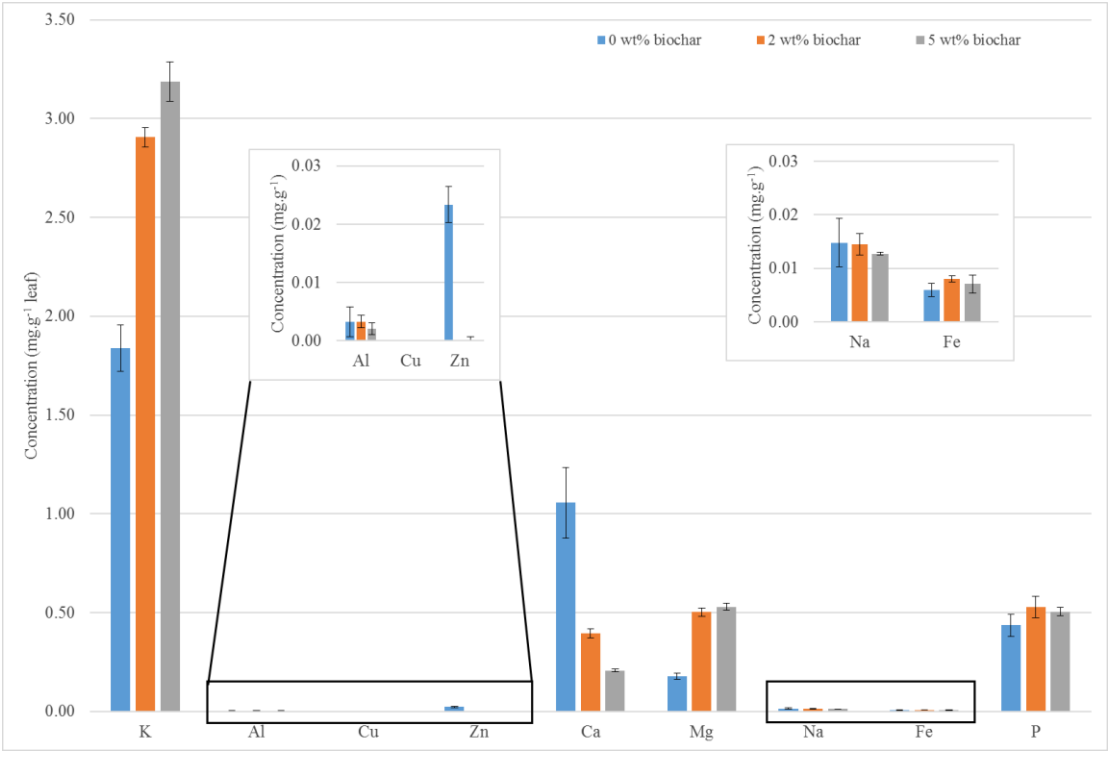

Figure 11. Elemental analysis of leaves from the plants grown on biochar blended soils

3.3.4 Effect Soil on Worm Population/Reproduction

The first test showed a significant lower growth in the soils with 5 % and 10 % biochar (both p= 0.02). Reproduction was significant lower in comparison with the original soil in all blended soils with biochar (resp. 0.02 (2%), 0.01 (5%) and 0.01 (10%)). The high values for conductivity indicate a potential impact of salt stress in biochar blended soils. Therefore, a washing step was included as described in §2.1. The results of this washing

step can be found in Table 7. A strong reduction in conductivity with respectively 72 %, 48 % and 66 % is noted for respectively 0wt%, 2wt% and 5wt% biochar. A heavy rain fall will have the same effect, so no extra washing procedure have to be included when blending this kind of char with poor soils properly mixed. Nevertheless, the soil was washed according §1.2.1 and it was found that washing with tap water resulted in a higher and neutral pH of the blended soil. Also a slight increase in pH is found for the blended soils. This increase can be explained as the result of a buffering effect of the biochar. The raise in pH is most pronounced in the untreated Lommel soil. Soils blended with 2% and 5 % biochar have a higher buffer capacity and show a reduced increase in soil pH in comparison to the untreated soil.

Table 7. Conductivity and pH before and after washing step

	0 wt% biochar	**2 wt% biochar**	**5 wt% biochar**
Conductivity before washing step	144 µS.cm^{-1}	422 µS.cm^{-1}	1089 µS.cm^{-1}
Conductivity after washing step	41 µS.cm^{-1}	218 µS.cm^{-1}	371 µS.cm^{-1}
pH before washing step	5.4	6.1	6.5
pH after washing step	7.2	6.8	6.9

The results of the reproduction and bait lamina test were collected and summarised in figure 12 and 13. Figure 12 shows the mass (before, after and increase) while figure 13 shows the number of cocoons (reproduction) of the worms (10 worms / container) and results of the bait lamina test. At first sight the results seem to be optimal for the soils with 2 wt.% biochar because of an increase in the numbers of cocoons and a higher % of empty bait lamina. However, a statistical analysis is a much more objective evaluation. Therefore, an independent samples Kruskal-Wallis test is done with a significance of 0.05. For the percent of mortality between the different samples no significant difference is found, which looks relevant. However, no significant difference between the percentages of empty bait lamina strips ($p > 0.05$) was found. The increase in weight of 0.095 has a significance which is still below 0.1, but relevant. This difference will be considered significant by increasing p to 0.1, though, the probability will be larger than another replica will fall outside the confidence interval. By keeping the significance here at 0.05, the difference here is not considered to be significant. Within the number of cocoons there is a significant difference. This requires other tests to be performed between the three sets (0-2, 0-5, 2-5). The Mann-Whitney test concludes that there is a significant difference between the 0% and 2% biochar. There is also a difference between the 2% and 5% biochar. Between 0% and 5% biochar there is no significant difference. There is a significant difference of 0.021 between 0% and 2% biochar similar to 2% and 5% biochar.

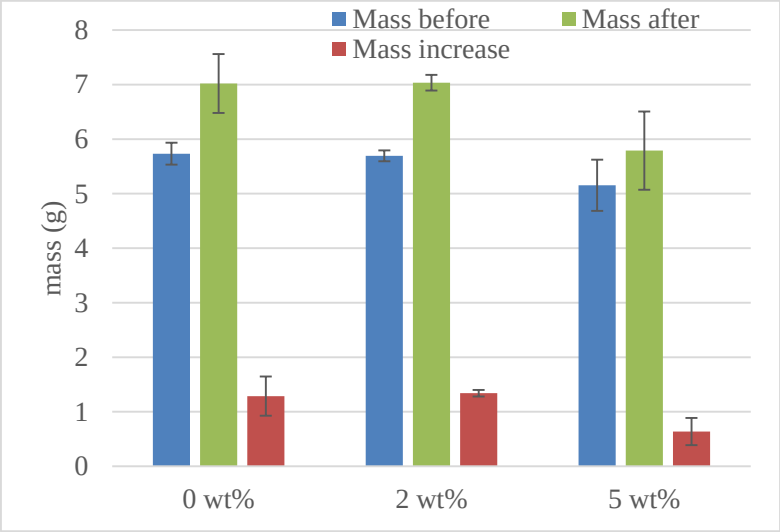

Figure 12. Effect of the blended soils on the mass of E. fetida

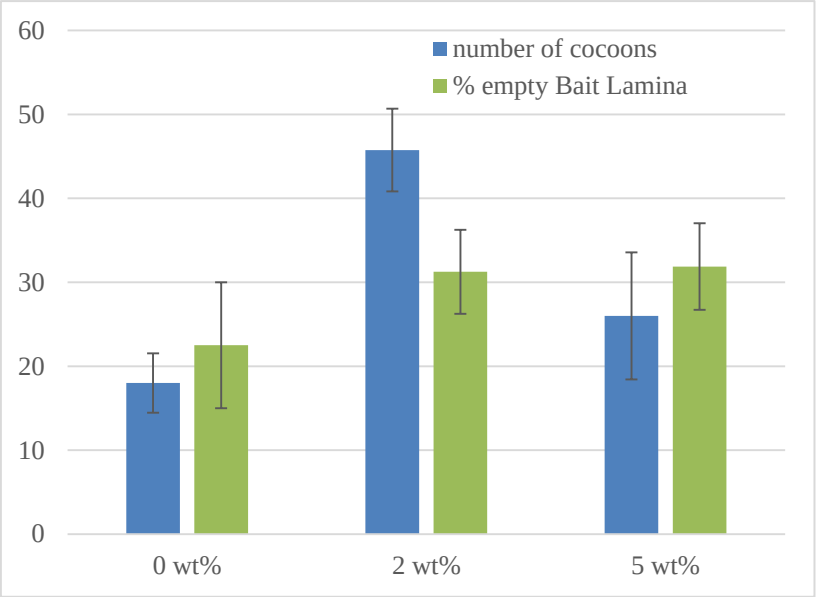

Figure 13. Effect of the blended soils on the reproduction and activity (bait lamina) of E. fetida

5. Conclusion

The dried thick fraction of the pig manure is a good starting material for the production of amendment biochar. The pyrolysis process was optimized to achieve a yield of 48.8%. The pyrolysis of the dried thick fraction of the pig manure also provides an additional 30% of biogas that can be used for the generation of electricity or the heating of the pyrolysis reactor itself. This produced biochar is suitable as alternative to the present chemical fertilizers due to the high concentrations of K and P. The total concentrations of Cu and Zn are too high compared to the environmental standards. However, blending this char with the char of another fraction of the pig manure, the thin fraction, increased also the concentration of N and at the same time lowers the total concentration of Cu and Zn (as its content is much lower) resulting in a total concentration below the Flemish Regulation on Environmental Authorisation (VLAREM) regulation. Nevertheless, the high ash content of this char, about 50%, it proves to be also suitable for the production of activated carbon (AC). This is confirmed by recently done studies. This char is also suitable for blending with a soil poor in nutrients. The soils with 2 wt.% and 5 wt.% biochar score much better than the reference soil. The soils in which 10 wt.% biochar was mixed held too much water which was detrimental to the plants. The blending of biochar in soils not only has a positive effect on plant growth but also on the immobilization of heavy metal ions preventing their release towards ground water. The cocoon production is the most sensitive endpoint for E. fetita. From these results it can be stated that the soil with 2% biochar scores the best. The resulting biochar therefore offers potential as low cost, slow release soil conditioner and better carbon sequester for a long term effect. The thermal conversion has a clear potential to market exploitable products. The effect of biochar is threefold: the buffering and beneficial WHC effect on the soil, inhibition of toxic elements which affect bioavailability and the release of nutrients in a more controlled manner favouring rapid plant growth.

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