WATERAGRI

D4.5: Advanced Use of Biochar for Nutrient Retention

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WP 4 Nutrient Recovery from Streams

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Author(s)/Organisation(s)	Mona Arnold /VTT Eriona Canga /ALCN Nora Hatvani / BZN Attila Hargitai / BZN
Contributor(s)	Rolf Larsson Sebastian Puculek
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Abstract:	This work assesses various commercially available biochars' capacity to adsorb nutrients from a solution and their potential to act as a substrate for retaining nutrients from runoff water. The biochar materials are pyrolysis products of various organic materials, wood and agricultural sidestreams. Most biochar showed some capacity to retain NH_4-N. The capacity to retain NO3-N again varied between not considerable to ca 0.34 mg/g NO_3-N. Thermal activation of biochar increases the number of adsorption sites and thus also improves the adsorption efficiency. Commercial biochars did not show any significant affinity towards phosphate, but only after being coated with $Mg(OH)_2$. Instead, the natural phosphorous content of biochar seems to leach into a solution easily. However, phosphorous leaching did not have any noticeable fertilising effect, neither that of NO_3-N nor NH_4 -N.

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1. Table of Contents

List of tables

List of figures

List of Abbreviations and Acronyms

BET	Brunauer-Emmett-Teller
NH_4-N	The nitrogen content of the ammonium ion. 18 mg/l NH4 ammonium is equivalent to 13 mg/l NH_4-N
NO_3-N	The nitrogen content of the nitrate ion. Nitrate Nitrogen = Nitrate x 0.226
S	Sweden

1. Introduction

Agricultural runoff and wastewater can contain considerable nutrient loads released to the environment without precaution and lack of treatment. Capturing and reusing these nutrients in agriculture can have significant economic and environmental potential.

One of the objectives of WP4 (Nutrient Recovery from Streams) was to develop and assess individual nutrient recovery technologies, among others, biochar (solutions B6 and C4). Biochar has been shown to increase both soil water holding capacity and available water capacity, but it also has the potential to recover nutrients from runoff. However, the biochar's efficiency depends on its properties, soil texture, the raw material(s) and processing conditions. Char activation increases the char's specific surface and active sites and will likely improve the nutrient adsorptive efficiency.

Various types of biochar produced from sidestreams were assessed for nutrient uptake. These same materials were later tested in pilot environments in selected drainage systems. These demonstrations are reported in deliverables 3.4 and 4.2.

Moreover, the potential of reusing saturated biochar as fertiliser was included in the test scheme to demonstrate how the fertiliser can be managed in a closed loop, following the ideology of a circular economy.

2. Methodology and test setup

The work included the assessment of several commercially available biochars produced by pyrolysis of various agro sidestreams. **Error! Reference source not found.** shows the test setup and performing organisations. **Error! Reference source not found.** gives the commercial characteristics of the tested biochars.

Two biochar types were also thermally activated at VTT to produce a material with a larger specific surface and more adsorption sites. These materials' nutrient retaining capacity was assessed similarly with spiked water and compared to the capacity of non-treated biochar. More details on the procedure have been given in D4.7.

Table 1. Test setup

Test / Biochar / Substrates	Nutrient adsorption test /organisation	Fertilisation test of nutrient-saturated biochars	Tested also in the pilot (D4.1)
Pflanzenkohle (Sonnenerde GmbH)	VTT, ALCN (Del 4.7)	BZN	
Thermally activated Pflanzenkohle	VTT	BZN	
Draingarden(R) (Zenebio GmbH)	BOKU, ALCN		Mistelbach (Austria II)
$Mg(OH)_2$-coated Pflanzenkohle (<2 mm) (Sonnenerde GmbH) two types	ALCN		Mistelbach (Austria II), Gleisdorf (Austria III)
$Mg(OH)_2$-coated Pflanzenkohle from cherry (0.1-4 mm) (Sonnenerde GmbH) (named hereafter $Mg(OH)_2$ -coated cherry biochar)	ALCN		Gleisdorf (Austria III)
Güllekohle (Charline GmbH)	VTT, BOKU/ALCN*	BZN	Mistelbach (Austria II)
Thermally activated Güllekohle	VTT*	BZN	
Biokol (S)	VTT		

**reported in D4.7.*

2.1 Adsorption tests

The nutrient loading technique on biochar at a small scale was developed by conducting nutrient adsorption batch experiments of phosphorous, nitrogen and ammonia solutions in several concentrations in the range of 0-50 mg l^{-1}. Pflanzenkohle and Güllekohle biochars were also analysed by VTT using the same nutrient loading technique provided by ALCN. ALCN, VTT and BZN used the same method for nutrient loading (substrate:solute ratio of 1:25). Details of the methodology have been given in D4.7.

Substrates investigated

- Bio-Pflanzenkohle, is a biochar (grain size: 0-2 mm) derived from grain husks, fruit sludge and wood shavings, which are heated to high temperatures (600 °C) in the absence of air and then extinguished with water (Sonnenerde GmbH). It is used in agriculture not as a nutrient per se but in conjunction with fertiliser. It provides an optimal habitat for desired microorganisms due to its large surface area (Sonnenerde GmbH). It has also been tested for nutrient adsorption in wastewater and agricultural drainage water treatment because of the high specific surface area.

- Güllekohle is a carbon-rich (88.6%) material, provided in a grain size fraction (0-2mm) and produced by CharLine from wood shavings. It has a high specific surface area of 292 m^2/kg), with an alkaline pH of 8.9, high electrical conductivity, and a high specific surface area of 292 m^2/kg (Table 2).

- Biokol is a biochar by a local producer in Sweden, with grain size fractions of 5-10 mm and, as advertised by the producer, is sustainably produced from sidestreams and aimed to improve soil and climate.

Table 2 represents the main characteristics of these materials measured by the producers.

Table 2. Tested biochars. Elemental Composition of two biochars, Pflanzenkohle and Bio-Güllekohle (Data from the producers)[1,2,3]

Commercial name (Producer)	Pflanzenkohle[1] (Sonnenerde GmbH)	Güllekohle[2] (Charline GmbH)	Biokol[3] (S)
pH	8.7	8.9	10.1
Electrical conductivity (µS/cm)	n.a	2010	n.a
Specific area (BET) (m^2/kg)	247	292	91.1-117
Max. Pyrolysis temperature (°C)	600	n.a.	750
Bulk density (kg/m^3)	178	218	150
Water content	32.2%	29.8%	24.6
H/C_{org} Ratio	0.24	0.06	0.25
C (%)	69.1	88.8	70.2
N – as (Na_2O) (%)	0.5	0.3	2.65
P – as (P_2O_6) (%)	0	0.1	1.1
K – as (K_2O) (%)	1.4	0.7	2.7
Ca (%)	2.5	n.a	1.3
Mg (%)	0.1	n.a	0.63
Grain size (mm)	0-2	0-2	5-10
Raw material	Grain husks, fruit sludge and wood shavings	Wood shavings	Seed and grain residuals

[1] Source: Product data sheet. Bio Pflanzenkohle. Sonnenerde GmbH. www.sonnenerde.at (Accessed on 18.02.2022).
[2] Source: Product data sheet. Bio Güllekohle, CharLine GmbH. Version v2020_1. Website: www.char-line.com/at-en/ (Accessed on 17.02.2022)
[3] Source: Biokol, label of the product picture.

In addition to the Sonnenerde and Charline basic biochars (Table 2, Figure 1b and 1c), ALCN performed sorption experiments for the following filter materials (two biochar types and zeolite) used in the pilot site in Gleisdorf, while Draingarden was analysed from a Master student work (BOKU) (Kupelwieser, 2022) Zeolite was included due to its larger grain size, 4-8 mm, which can provide good hydraulic conductivity, and its known properties to adsorb nitrogen forms (Canga et al., 2011).

- $Mg(OH)_2$ coated biochar, fine grain size fraction 0 – 2 mm, produced by Sonnenerde GmbH (0-2 mm). This is the same material as Pflanzenkohle, except it was enriched with 20% by weight with magnesium hydroxide ($Mg(OH)_2$) during production. This material was used in Mistelbach and the Gleisdorf setup (1st and 2nd trials). From the previous deliverable 3.4, the biochar by Sonnenerde was found to leach both phosphorous and nitrate, but both chars adsorbed ammonia well. Here we repeated the sorption experiments to see any differences.

- $Mg(OH)_2$ coated biochar produced from cherry seeds (0-4 mm grain size), Sonnenerde GmbH. This biochar was produced especially out of ALCN request to ensure a biochar with larger particle grain-size, but following the same procedure of coating with $Mg(OH)_2$ as for the fine biochar. The idea was that cherry seeds, being round granular media, would produce higher grain-size fractions and, therefore, better hydraulic conductivity.
- Zeolite 4 – 8 mm grain size (*Boden 4-8)*, from Buchrucker-Hygeine GmbH. This substrate is a natural aluminium silicate containing Al, Si, Na, K, Ca, Mg and trace elements. The starting material is natural clinoptiolite. Zeolite was used in Gleisdorf, and adsorption tests were performed following the same method of sorption experiments as for the biochar materials.
- Drain Garden® (Figure 1 a) (named hereafter 'Draingarden') is a mixture of mineral and organic components. The elemental composition is not made public by the producer Zenebio GmbH. However, the texture of Draingarden is described as loamy sand, and its basic properties are 73% sand, 16.2% silt, and 10.5% clay (Kupelwieser, 2022). Draingarden® was tested for nutrient retention in the lab and was used as the main layer in one of the pilot multi-layer systems in the Mistelbach pilot site. One of the filter systems consisted of two layers of Draingarden alone and Draingarden mixed with 5% biochar.

Figure 1. a) Draingarden substrate, b) CharLine Güllekohle, c) Sonnenerde Bio Pflanzenkohle

The use of nutrient-saturated chars as a fertiliser was further assessed. The release of nutrients for plant uptake in soil was evaluated by BZN, who assessed the efficiency of the nutrient-saturated biochar as a fertiliser by laboratory-scale cultivation tests. The nutrients: nitrogen, phosphorus and potassium in the soil and plants were also analysed.

2.2 Laboratory-scale cultivation tests for nutrient-saturated biochars

The saturation process of the different biochars was done at BZN to ensure that the chars were fully loaded. Four types of biochar were received from VTT and used in the experiments:

- plant biochar ('Pflanzenkohle' / Sonnenerde GmbH) - original
- manure biochar ('Güllekohle' / CharLine) - original
- plant biochar ('Pflanzenkohle' / Sonnenerde GmbH) - activated by VTT
- manure biochar ('Güllekohle' / CharLine) - activated by VTT

Loading (saturation) of biochar was carried out according to the method provided by VTT, having a substrate-to-solution ratio of 1:25. Three 5-gram aliquots of each biochar sample were added to 125 ml of 25 mg/l KNO_3, NH_4Cl or KH_2PO_4 solutions, in order to load the biochar with potassium, nitrogen and phosphorus, respectively. The solutions were mixed with a circular shaker for 24 hours (*Figure 2).* Biochar samples were filtered from the solutions with filter paper and dried at room temperature before the pot experiments. The nutrient adsorption process of the biochar samples was monitored by measuring the pH and concentration of NH_4Cl, KH_2PO_4 and KNO_3 in the loading solutions.

Pot experiments were carried out with eight different samples: unsaturated and saturated samples of the four types of biochars. 1-gram aliquots of biochars were mixed into the top 2 cm layer of sandy soils in 7x7 cm pots (*Figure 3*).

Figure 2. Nutrient loading of biochars

Figure 3. Preparation of pot experiment with biochars.

Two seeds of 'Lollo Bionda' lettuce were sown into each pot. Pots were watered and put under artificial light (8^{00}-18^{00}). Four pots were used for each experimental setting and control without biochar. Germination of seeds was followed, and the number of leaves was recorded daily. The macronutrient (N, P, K) content of the soil and plant leaves was determined at the end of the experiment.

3 Results

3.1 Nutrient adsorption tests

The results of comparing the nutrient recovery capacity of thermally activated and commercial biochars have been reported in detail in D4.7. The nutrient loading technique using a char-to-solution ratio of 1:25 with shaking at 200 rpm for 24 hours showed that phosphorous is adsorbed in small quantities by the Güllekohle and CharLine biochar. The Pflanzenkohle biochar by Sonnenerde leached phosphorous and nitrogen, but both chars adsorbed ammonia well. Thermal activation improved the adsorption rate significantly.

This chapter describes additional results. These are nutrient loading tests on biochar by Skånefrö AB (VTT) and $Mg(OH)_2$ coated biochars (fine fraction 0-2 mm, and cherry biochar 0-4 mm fraction) (ALCN), Draingarden (BOKU) and Zeolite (ALCN).

The nutrient retaining capacity was assessed with spiked water and compared to the capacity of non-treated biochar. The tests were repeated for the negative results to ensure the outcome. Nutrient concentrations were analysed with DR3900 (VTT and DR1900 (ALCN) (Hach Lange), and the results are given in Table 3**Error! Reference source not found.**. Spectrophotometry methods were followed for testing Draingarden and Draingarden+5% Güllekohle substrates, and the results are the outcome of a Master's student thesis from BOKU (Kupelwieser, 2022).

Table 3. Results of the nutrient sorption batch tests. Values are given in mg retained / g material. (Min, Max values in brackets). Negative values for initial concentration 0 mg/L were excluded. (Average removal rates in %)

Parameter	Biokol (S)	$Mg(OH)_2$ fine*	$Mg(OH)_2$-cherry biochar*	Zeolite *	Draingarden*	Draingarden+5% Güllekohle*
NO_3-N	0.004 (0-0.02)	0.13 (0.04-0.22)	0.341 (0.013-0.920) 74%	0.277 (0.013-0.640) 63%	Data not available	Data not available-
NH_4 -N	0.04 (0-0.09)	0.105 (0.084-0.134) 34%	0.162 (0.001-0.302) 45%	0.360 (0.021-0.940) 78%	0.095 (0.005-0.234) 33%	0.109 (0.006-0.292) 35%
PO_4	< 0 (released PO_4 to the solution)	0.15 (0.04-0.25)**	0.252 (0.025-0.615) 98%	0.013 (0.0001-0.038) 3.5%	< 0 (released PO_4 to the solution)	< 0 (released PO_4 to the solution)

*** Inlet concentration tested: 0, 0.5, 3.75, and 12.5 mg/L NO_3-N.*

Of the studied materials, NO_3-N was best retained by $Mg(OH)_2$ cherry biochar with an average retention of 0.341 mg N / g substrate, followed by zeolite (0.277 mg N/g) and fine biochar (0.13 mg N/g) of NO_3-N. Biokol had the lowest nitrogen-nitrate retention rate of 0.016 mg/g.

Ammonia-nitrogen NH3-N was best retained by zeolite with an average retention of 0.36 mg N / g substrate, followed by $Mg(OH)_2$ cherry biochar that retained (0.162 mg N/g). Draingarden, fine biochar, and Draingarden+5% biochar substrates performed similarly with retention rates of 0.095, 0.105, and 0.109 mg/g, respectively. Biokol showed the lowest retention capacity, 0.038 mg N/g.

Phosphate (PO_4) was best retained by $Mg(OH)_2$-coated cherry biochar (0.252 mg P / g substrate) and followed by fine $Mg(OH)_2$-biochar (0.15 mg P / g substrate). Both the Swedish biochar and Draingarden substrates released phosphate into the solution (negative retention rates), thus indicating the presence of phosphate in the original material. The phosphate retention capacity of Zeolite was rather low, i.e. 0.013 mg/g.

Compared to the retention rates of Pfanzenkohle and Güllekohle, as reported in Deliverable 4.7, the materials reported here performed better. Pflanzenkohle retained neither NO_3-N or PO_4, and modest amounts of NH_3-N (0.08 mg/g). Güllekohle's adsorptive capacity was better than Pflanzenkohle, 0.055 mg NO_3-N /g, 0.048 mg

NH_4-N /g and 0.026 mg PO_4/g). Thermal activation improved the adsorption capacity, especially that of Güllekohle.

3.2 Cultivation tests

This chapter gives the results of the nutrient loading of biochars followed by fertilisation tests using the nutrient-loaded biochars as fertilisers.

Biochar saturation experiments

Figure 4 and *Figure 8* present the pH values measured in loading solutions mixed with original and activated biochars, respectively. The effectivity of the nutrient adsorption process was monitored by comparing the macronutrient (N, P, K) content in the original loading solutions with the concentrations measured at the end of the 24 h saturation time. *Figure 5*-*Figure 7* and *Figure 9*-*Figure 11* present the results of the measurements with original and activated biochars, respectively. Changes in N, P, K content of the solutions used for the loading (saturation) process with original and activated biochars are summarised in *Table 4* and *Table 5*, respectively.

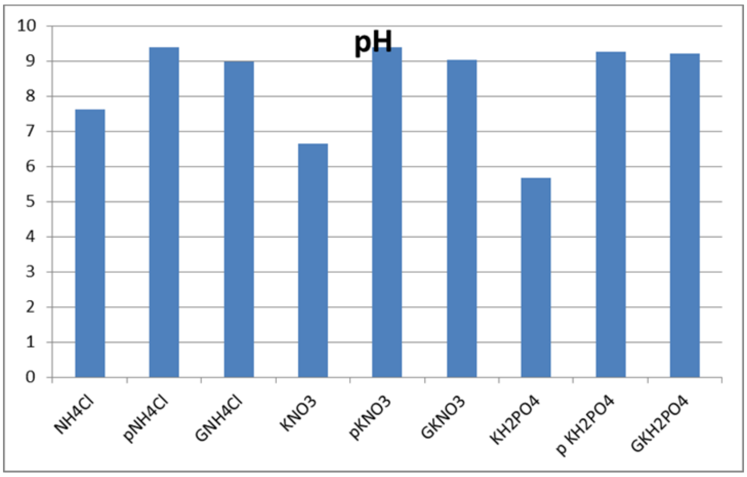

Figure 4. pH of NH_4Cl, KH_2PO_4 and KNO_3 loading solutions before and after mixing with original biochars (NH4Cl= original NH_4Cl solution; PNH4Cl= NH_4Cl solution after mixing with original 'Pflanzenkohle' biochar; GNH4Cl= NH_4Cl solution after mixing with original 'Güllekohle' biochar; KNO3= original KNO_3 solution, PKNO3= KNO_3 solution after mixing with original 'Pflanzenkohle' biochar; GKNO3= KNO_3 solution after mixing with original 'Güllekohle' biochar; KH2PO4= original KH_2PO_4 solution; PKH2PO4= KH_2PO_4 solution after mixing with original 'Pflanzenkohle' biochar, PKH2PO4= KH_2PO_4 solution after mixing with original 'Güllekohle' biochar)

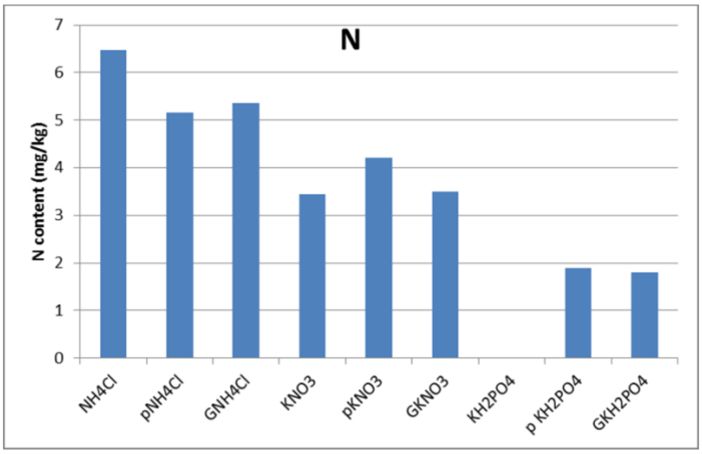

Figure 5. Nitrogen content of NH_4Cl, KH_2PO_4 and KNO_3 solutions before and after mixing with original biochars (sample codes are explained in the caption of *Figure 4*)

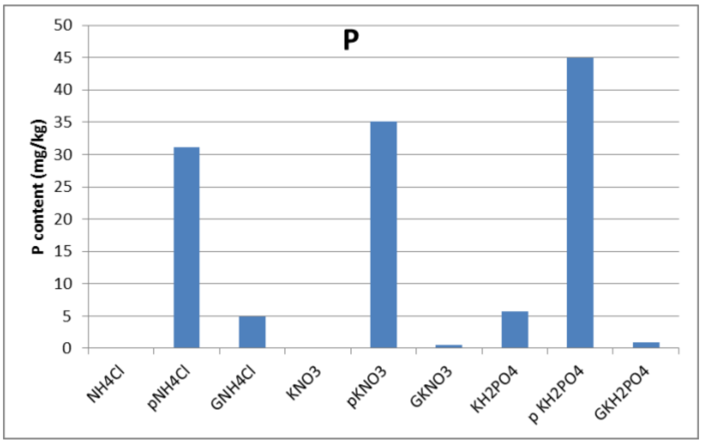

Figure 6. Phosphorus content of NH_4Cl, KH_2PO_4 and KNO_3 solutions before and after mixing with original biochars (sample codes are explained in the caption of *Figure 4*)

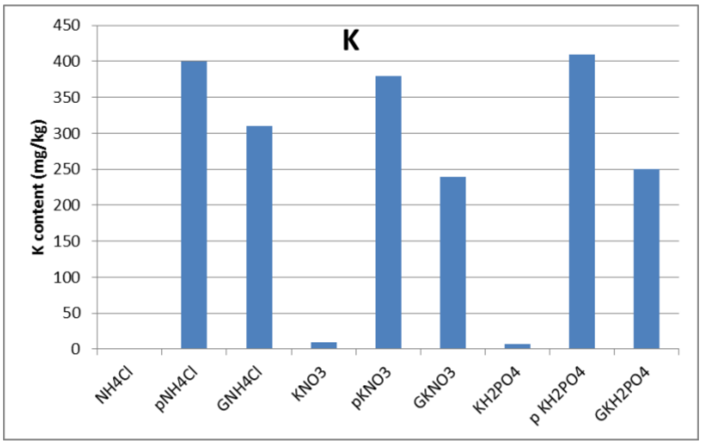

Figure 7. Potassium content of NH_4Cl, KH_2PO_4 and KNO_3 solutions before and after mixing with original biochars (sample codes are explained in the caption of *Figure 4*)

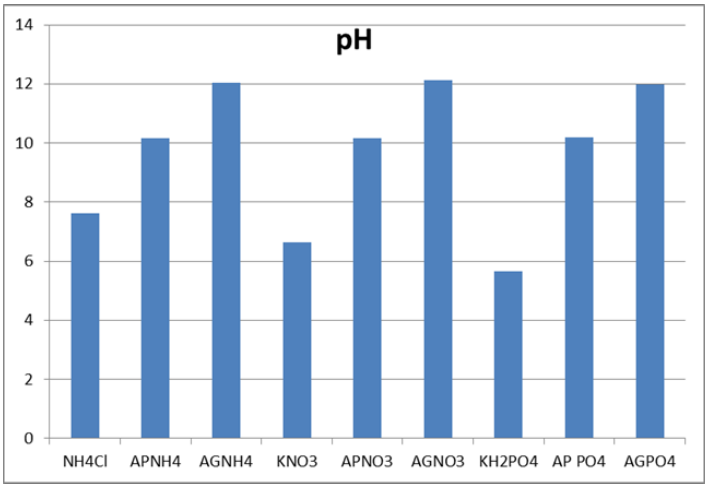

Figure 8. pH of NH_4Cl, KH_2PO_4 and KNO_3 solutions before and after mixing with activated biochars (NH4Cl= original NH_4Cl solution, APNH4= NH_4Cl solution after mixing with activated 'Pflanzenkohle' biochar, AGNH4= NH_4Cl solution after mixing with activated 'Güllekohle' biochar, KNO3= original KNO_3 solution, APNO3= KNO_3 solution after mixing with activated 'Pflanzenkohle' biochar, AGNO3= KNO_3 solution after mixing with activated 'Güllekohle' biochar, KH2PO4= original KH_2PO_4 solution, APPO4= KH_2PO_4 solution after mixing with activated 'Pflanzenkohle' biochar, AGPO4= KH_2PO_4 solution after mixing with activated 'Güllekohle' biochar)

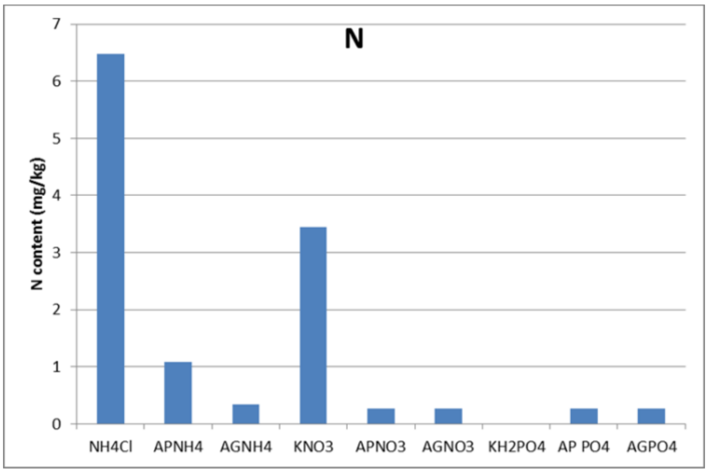

Figure 9. Nitrogen content of NH_4Cl, KH_2PO_4 and KNO_3 solutions before and after mixing with activated biochars (sample codes are explained in the caption of *Figure 8*)

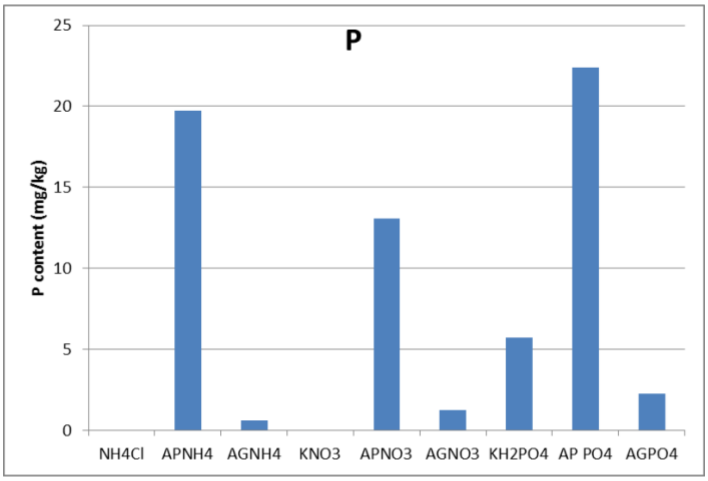

Figure 10. Phosphorus content of NH_4Cl, KH_2PO_4 and KNO_3 solutions before and after mixing with activated biochars (sample codes are explained in the caption of *Figure 8*)

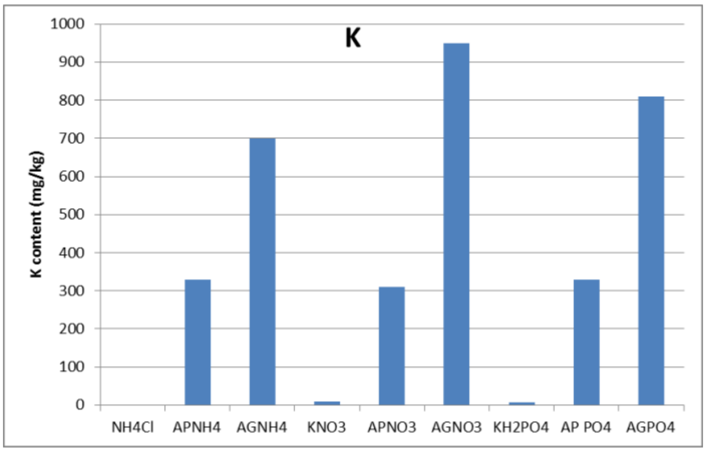

Figure 11. Potassium content of NH_4Cl, KH_2PO_4 and KNO_3 solutions before and after mixing with activated biochars (sample codes are explained in the caption of *Figure 8*)

Table 4. Changes in N, P, K content of the solutions used for the loading (saturation) process with original biochars. Cases where adsorption could be detected are highlighted with green letters.

Nutrient	The solution used for the loading process	Changes in the nutrient content of solutions after the loading (saturation) process	
		original 'Güllekohle' biochar	original 'Pflanzenkohle' biochar
Nitrogen content (*Figure 5*)	NH_4Cl	decreased (adsorption occurred)	decreased (adsorption occurred)
	KNO_3	did not change (no adsorption occurred)	slightly increased (nutrients released from the biochar into the solution)
	KH_2PO_4	increased (nutrients released from the biochar into the solution)	increased (nutrients released from the biochar into the solution)
Phosphorus content (*Figure 6*)	NH_4Cl	increased (nutrients released from the biochar)	largely increased (high amount of nutrient released from the biochar)
	KNO_3	increased (nutrients released from the biochar)	largely increased (high amount of nutrient released from the biochar)
	KH_2PO_4	decreased (adsorption occurred)	largely increased (high amount of nutrient released from the biochar)
Potassium content (*Figure 7*)	NH_4Cl	largely increased (high amount of nutrient released from the biochar)	largely increased (high amount of nutrient released from the biochar)
	KNO_3	largely increased (high amount of nutrient released from the biochar)	largely increased (high amount of nutrient released from the biochar)
	KH_2PO_4	largely increased (high amount of nutrient released from the biochar)	largely increased (high amount of nutrient released from the biochar)

Table 5. Changes in N, P, K content of the solutions used for the loading (saturation) process with activated biochars. Cases where adsorption could be detected are highlighted with green letters.

Nutrient	The solution used for the loading process	Changes in the nutrient content of solutions after the loading (saturation) process	
		activated 'Güllekohle' biochar	activated 'Pflanzenkohle' biochar
Nitrogen content (*Figure 9*)	NH_4Cl	largely decreased (high adsorption occurred)	largely decreased (high adsorption occurred)
	KNO_3	largely decreased (high adsorption occurred)	largely decreased (high adsorption occurred)
	KH_2PO_4	increased (nutrients released from the biochar)	increased (nutrients released from the biochar)

Nutrient	The solution used for the loading process	Changes in the nutrient content of solutions after the loading (saturation) process	
		activated 'Güllekohle' biochar	activated 'Pflanzenkohle' biochar
Phosphorus content (*Figure 10*)	NH_4Cl	increased (nutrients released from the biochar)	largely increased (high amount of nutrient released from the biochar)
	KNO_3	increased (nutrients released from the biochar)	largely increased (high amount of nutrient released from the biochar)
	KH_2PO_4	decreased (adsorption occurred)	largely increased (high amount of nutrient released from the biochar)
Potassium content (*Figure 11*)	NH_4Cl	largely increased (high amount of nutrient released from the biochar)	largely increased (high amount of nutrient released from the biochar)
	KNO_3	largely increased (high amount of nutrient released from the biochar)	largely increased (high amount of nutrient released from the biochar)
	KH_2PO_4	largely increased (high amount of nutrient released from the biochar)	largely increased (high amount of nutrient released from the biochar)

Near neutral or slightly acidic pH of the nutrient solutions increased to the alkaline range after mixing with the original and activated biochars (*Figure 4* and *Figure 8*, respectively). All three nutrient solutions became highly alkaline after mixed with activated 'Güllekohle' biochar.

The results listed in Table 4 and Table 5 are summarised as follows:

- In most cases, nutrients were released from the biochar into the loading solution. This experience aligns with the results gained by VTT and ALCN in similar adsorption tests (see sections 2.4.1 and 2.4.3 in deliverable D4.7).
- In their original form, both 'Güllekohle' and 'Pflanzenkohle' biochars can adsorb ammonium-N, which capacity seems to be enhanced by the activation process so does the adsorption capacity towards nitrate-N, which could be detected only with the activated forms.
- Only 'Güllekohle' biochar could adsorb phosphate, and the activation process did not enhance this capacity.
- Potassium concentrations were two orders of magnitude higher in the solutions after the saturation process, especially in the case of activated 'Güllekohle' biochar, which increased the pH of the solution to 12. This phenomenon is probably due to the biochars' ash (KOH) content, which leads to a high level of potassium and hydroxide ion release.
- Based on comparing the results with original biochars and activated ones, the following conclusions can be drawn:
  - the activation process applied by VTT increased the adsorption capacity towards both ammonium and nitrate;
  - the activation process did not affect the adsorption capacity towards phosphate and potassium.

Pot experiments

In the first experiment, a comparison was made between plantless pots and pots containing growing plants to see how significant the nutrient uptake is from the soils and whether there were any nutrient limitations by the end of the experiments. Although some differences could be observed in some cases, there was no significant difference between the nutrient content of the plantless and the plant-containing soils (*Figure 12*-*Figure 14*).

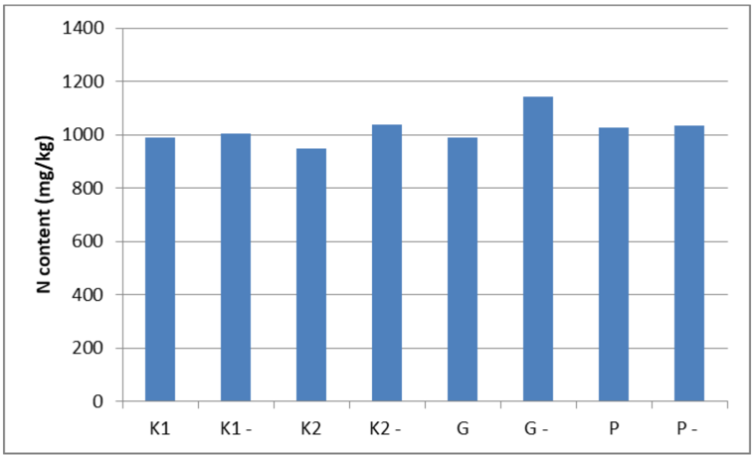

Figure 12. Nitrogen content of soils at the end of the pot experiments with or without plants (K1=control 1, K2=control2, P= original 'Pflanzenkohle' biochar mixed into the soil at a rate of 1 g/pot, G= original 'Güllekohle' biochar mixed into the soil at a rate of 1 g/pot. "-" signs indicate those pots that did not contain plants)

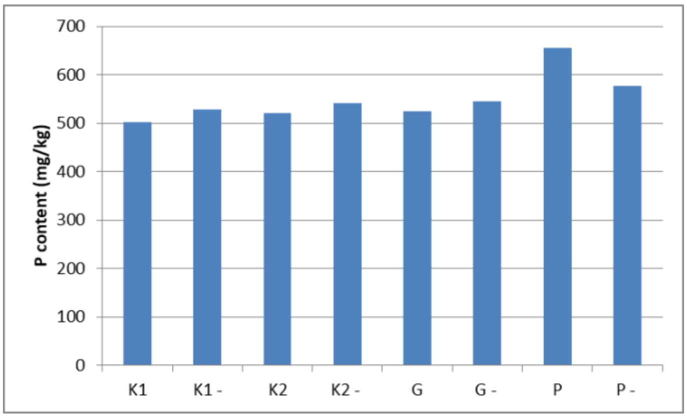

Figure 13. Phosphorus content of soils at the end of the pot experiments with or without plants (codes are explained in the caption of *Figure 12*)

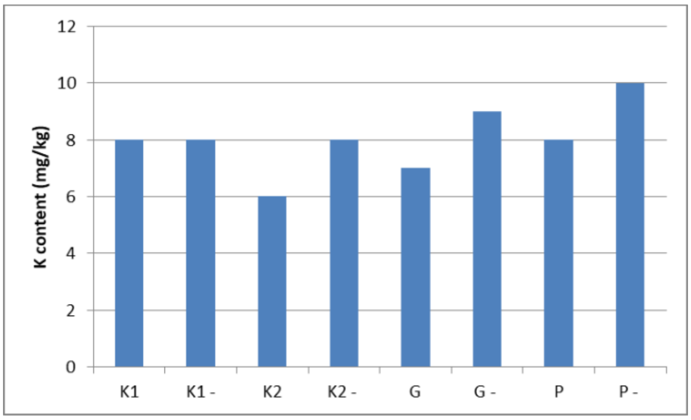

Figure 14. Potassium content of soils at the end of the pot experiments with or without plants (codes are explained in the caption of *Figure 12*)

In the later experiments, only **soil nutrient content with growing plants was** analysed. The addition of unsaturated (*Figure 12-Figure 14*) or saturated (*Figure 15-Figure 17*) original biochars did not have any positive effect on the macronutrient content of soils. The same results were obtained with the activated biochar versions as well.

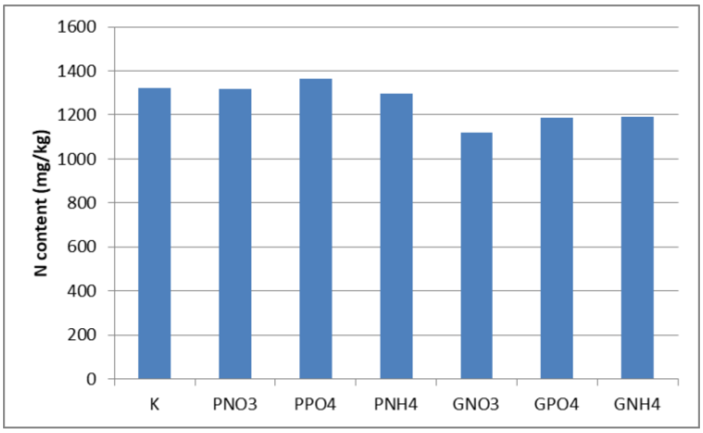

Figure 15. Nitrogen content of soils at the end of the pot experiments with saturated biochars (K=control, PNO3= original 'Pflanzenkohle' biochar saturated with nitrate, PPO4= original 'Pflanzenkohle' biochar saturated with phosphate, PNH4= original 'Pflanzenkohle' biochar saturated with ammonium, GNO3= original 'Güllekohle' biochar saturated with nitrate, GPO4= original 'Güllekohle' biochar saturated with phosphate, GNH4= original 'Güllekohle' biochar saturated with ammonium mixed into the soil at a rate of 1g/pot.)

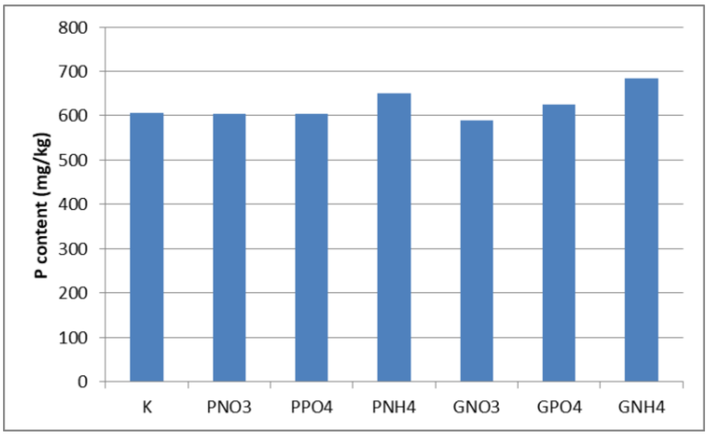

Figure 16. Phosphorus content of soils at the end of the pot experiments with saturated biochars (codes are explained in the caption of *Figure 15*)

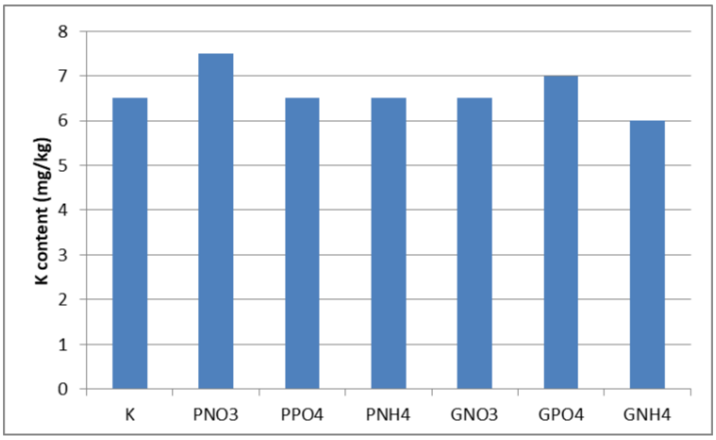

Figure 17. Potassium content of soils at the end of the pot experiments with saturated biochars (codes are explained in the caption of *Figure 15*)

The plant leaves' nutrient (N, P, K) content was determined at the end of the experiments. The addition of neither unsaturated (*Figure 18-Figure 20*) nor saturated (*Figure 21-Figure 23*) original biochars positively affected the macronutrient content of plants grown in the amended soil medium. The same results were obtained with the saturated activated biochar versions (*Figure 24-Figure 26*).

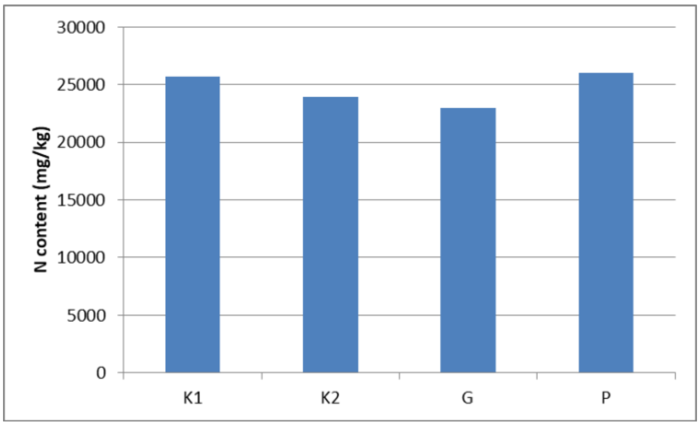

Figure 18. Nitrogen content of plants at the end of the pot experiments with unsaturated original biochars (K1=control 1, K2=control2, P= original unsaturated ‘Pflanzenkohle’ biochar, G= original unsaturated ‘Güllekohle’ biochar mixed into the soil at a rate of 1 g/pot.)

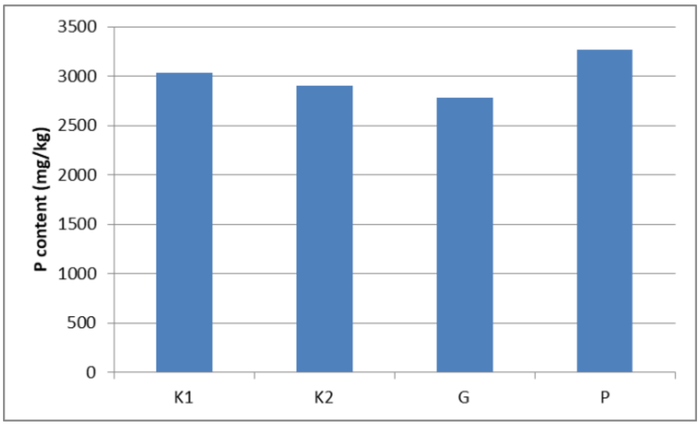

Figure 19. Phosphorus content of plants at the end of the pot experiments with unsaturated original biochars (codes are explained in the caption of *Figure 18*)

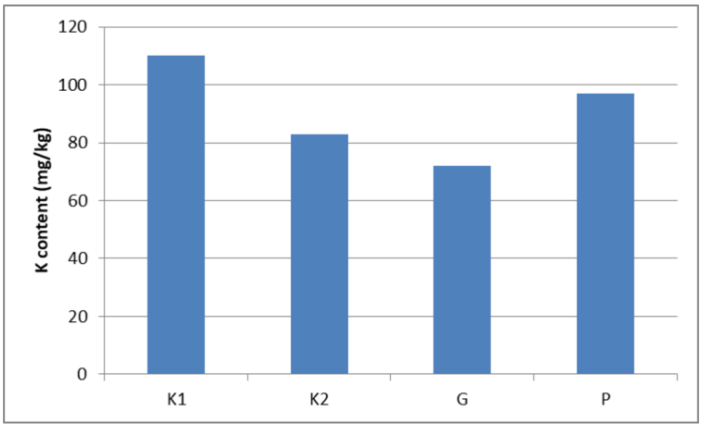

Figure 20. Potassium content of plants at the end of the pot experiments with unsaturated original biochars (codes are explained in the caption of *Figure 18*)

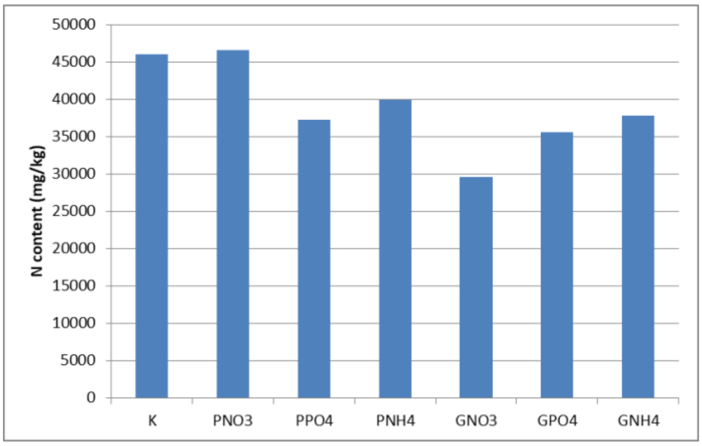

Figure 21. Nitrogen content of plants at the end of the pot experiments with saturated original biochars (K=control, PNO3= original ‘Pflanzenkohle’ biochar saturated with nitrate, PPO4= original ‘Pflanzenkohle’ biochar saturated with phosphate, PNH4= original ‘Pflanzenkohle’ biochar saturated with ammonium, GNO3= original ‘Güllekohle’ biochar saturated with nitrate, GPO4= original ‘Güllekohle’ biochar saturated with phosphate, GNH4= original ‘Güllekohle’ biochar saturated with ammonium mixed into the soil at a rate of 1 g/pot.)

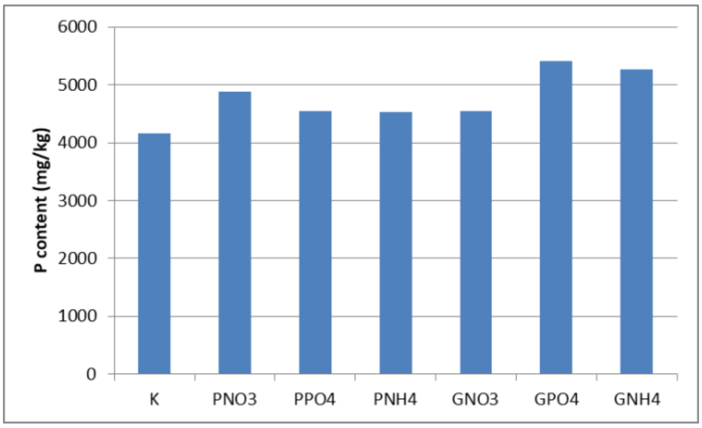

Figure 22. Phosphorus content of plants at the end of the pot experiments with saturated original biochars (codes are explained in the caption of *Figure 21*)

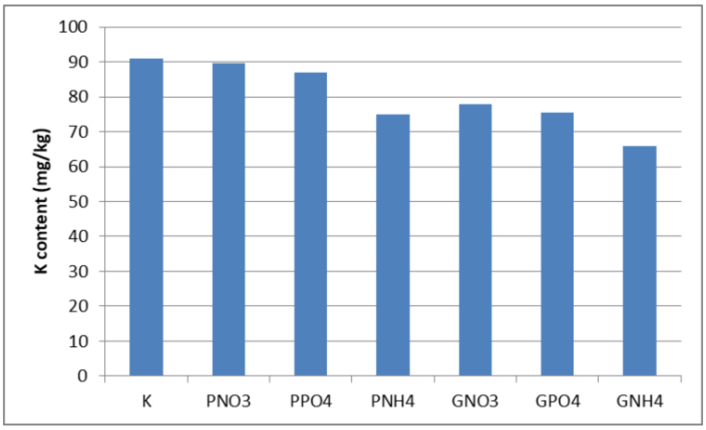

Figure 23. Potassium content of plants at the end of the pot experiments with saturated original biochars (codes are explained in the caption of *Figure 21*)

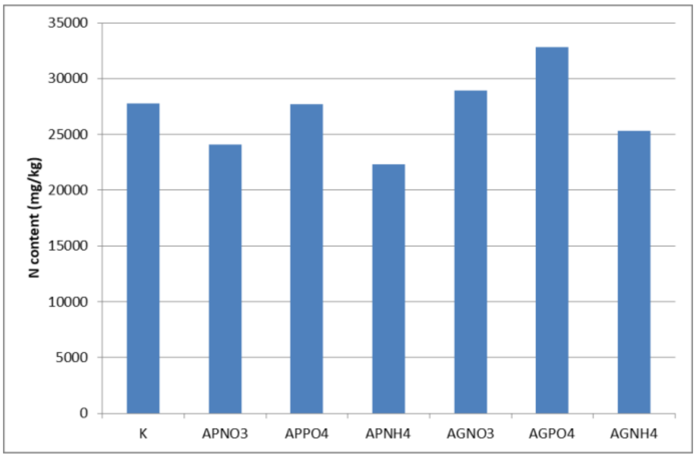

Figure 24. Nitrogen content of plants at the end of the pot experiments with saturated activated biochars (K=control, APNO3= activated ‘Pflanzenkohle’ biochar saturated with nitrate, APPO4= activated ‘Pflanzenkohle’ biochar saturated with phosphate, APNH4= activated ‘Pflanzenkohle’ biochar saturated with ammonium, AGNO3= activated ‘Güllekohle’ biochar saturated with nitrate, AGPO4= activated ‘Güllekohle’ biochar saturated with phosphate, AGNH4= activated ‘Güllekohle’ biochar saturated with ammonium mixed into the soil at a rate of 1 g/pot.)

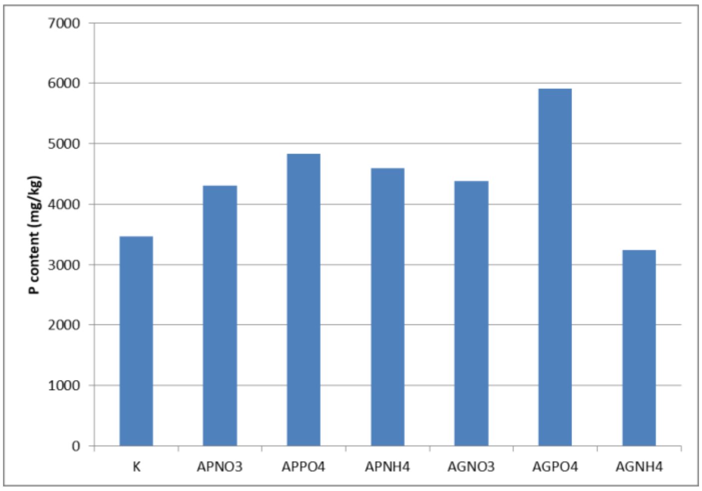

Figure 25. Phosphorus content of plants at the end of the pot experiments with saturated activated biochars (codes are explained in the caption of *Figure 24*)

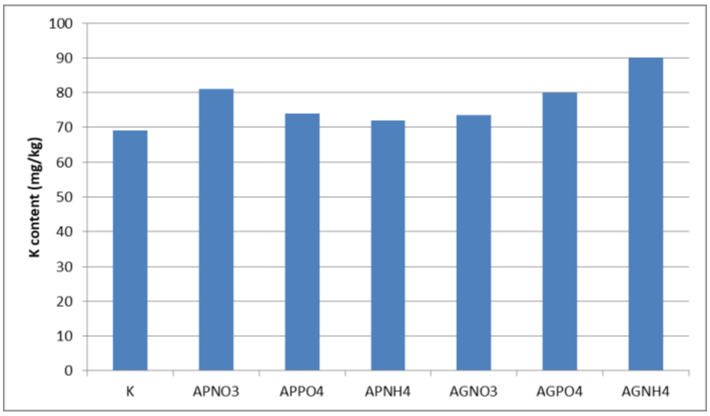

Figure 26. Potassium content of plants at the end of the pot experiments with saturated activated biochars (codes are explained in the caption of *Figure 24*)

The addition of original biochars to soils in the plant cultivation experiments did not have any positive effect on the germination of seeds neither regarding the time of germination nor the number of germinated seeds (*Figure 27*). Similarly, none of the original unsaturated biochars had a significant positive effect on the leaf number of the plants (*Figure 28*). The same results were obtained with the saturated original and activated biochars.

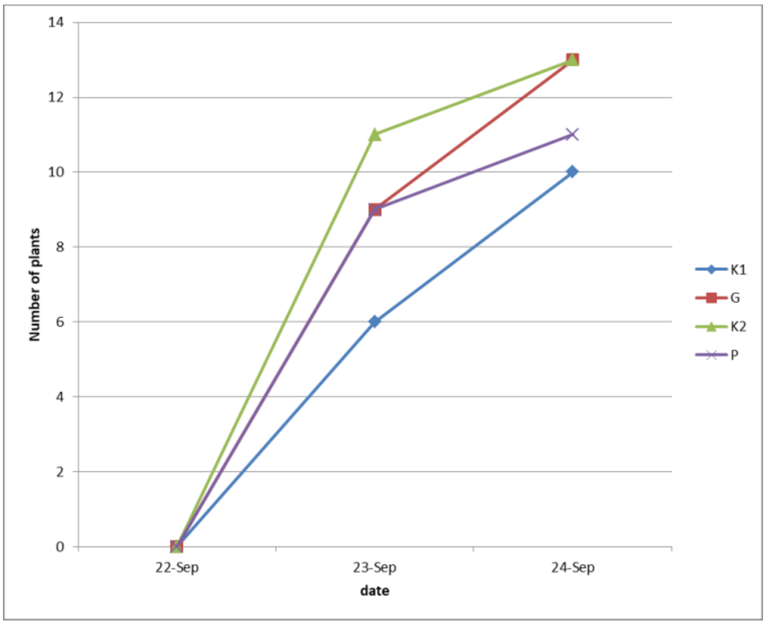

Figure 27. Germination of lettuce 'Lollo Bionda' seeds in a pot experiment (K1=control 1, K2=control 2, P= original 'Pflanzenkohle' biochar mixed into the soil at a rate of 1 g/pot, G= original 'Güllekohle' biochar mixed into the soil at a rate of 1 g/pot)

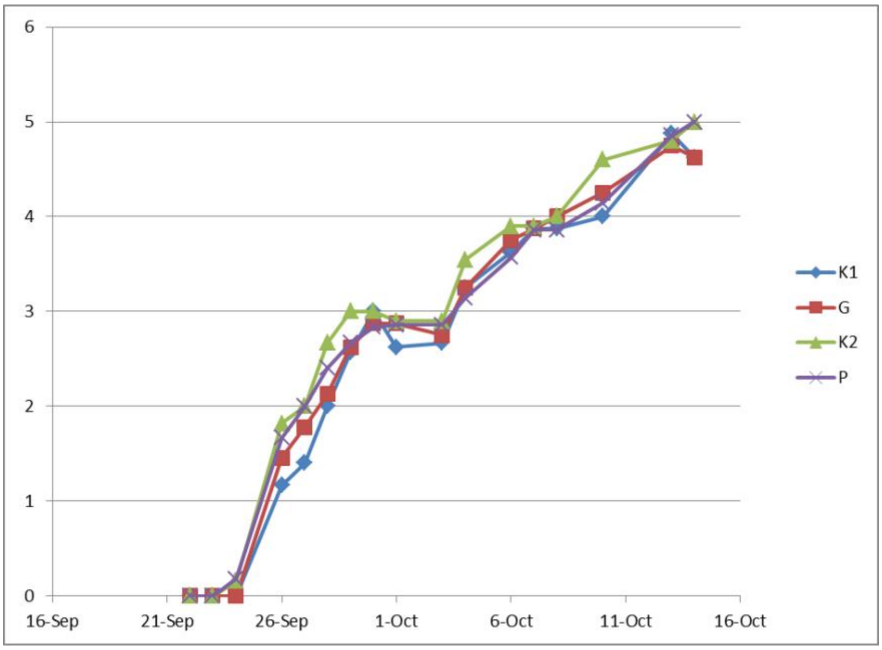

Figure 28. Average leaf number of lettuce 'Lollo Bionda' plants in a pot experiment (K1=control 1, K2=control2, P= original 'Pflanzenkohle' biochar mixed into the soil at a rate of 1 g/pot, G= original 'Güllekohle' biochar mixed into the soil at a rate of 1 g/pot)

The plant cultivation tests showed that none of the biochar samples (unsaturated/saturated original biochars, unsaturated/saturated activated biochars) had a significant effect on the soil and plant parameters (germination, average leaf number, soil nutrient content, and plant leaf nutrient content) investigated. A probable reason for this phenomenon is that the total amount of nutrients that could be released into the soil from the added biochars was not high enough to increase the already available nutrient content of the soil significantly.

4. Conclusion and outlook

This work assessed various commercially available biochars' capacity to adsorb nutrients from a solution and their potential to act as a substrate for retaining nutrients from runoff water. The biochar materials are pyrolysis products of various organic materials, wood and agricultural sidestreams.

The results indicate that most biochars have some capacity to retain NH_4-N. The capacity to retain NO_3-N again varied between not considerable (Pflanzenkohle) to ca 0.34 mg/g NO_3-N ($Mg(OH)_2$ cherry biochar). Thermal activation of biochar increases the number of adsorption sites and thus also improves the adsorption efficiency.

Commercial biochars did not show any significant affinity towards phosphate, but only after being coated with $Mg(OH)_2$. Instead, the natural phosphorous and potassium content of biochar seems to leach into a solution easily. However, phosphorous leaching did not have any noticeable fertilising effect, neither that of NO_3-N nor NH_4 -N.

In conclusion, $Mg(OH)_2$-coated biochar performed better than all other materials to retain NO_3-N (0.341 mg/g or 74% retention rate) and PO_4 (0.252 mg / g or 98% retention rate). Zeolite retained better NH_4-N (78%)

compared to all other materials, followed by coated cherry biochar (48% retention rate) and coated biochar (34% retention rate).

Biochar is a circular product which has been successfully applied as a soil amendment (Vijay et al., 2021; Kamali et al., 2020; Subedi et al., 2017), thereby improving the structure and water-retaining capacity of various soils (Alghamdi et al., 2020; Wang et al., 2019; Aslam et al., 2014). However, based on the results obtained here, tested substrates' role in contributing to the nutrient balance varies between nutrients and materials applied.

5. References

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