

Influence of biochar on nutrients dynamics in tropical soils of Burkina Faso

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INFLUENCE OF BIOCHAR ON NUTRIENTS DYNAMICS IN TROPICAL SOILS OF BURKINA FASO

CHLOÉ RAUW

**TRAVAIL DE FIN D'ÉTUDES PRÉSENTÉ EN VUE DE L'OBTENTION DU DIPLÔME DE MASTER
BIOINGÉNIEUR EN SCIENCES ET TECHNOLOGIES DE L'ENVIRONNEMENT**

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PROMOTEUR: PR. JEAN-THOMAS CORNÉLIS (ULIÈGE)

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Abstract

Agriculture is facing a major challenge in terms of fertilizer use whose efficiency is currently below 50%. Sustainable and more efficient alternatives to these fertilizers need to be found. In last decades, studies focusing on biochar reported improved soil properties particularly in highly weathered soils through modified physico-chemical characteristics. Recently, studies have demonstrated that biochar enhanced by organic or inorganic products prior its amendment to soils can serve as a slow-release fertilizer and improve nutrient cycling.

This study focuses on the nutrients dynamics of biochar-based fertilizers and on their potential use as slow-release fertilizers. Biochar enhanced with fertilizers, urine and through co-composting have been compared through serial nutrients extractions to assess their potential as substitutes to conventional chemical fertilizers. Furthermore, the effect of the duration of biochar incorporation in soils and its impact on nutrients dynamics have been assessed through the study of biochar remained in tropical soils for 6 and 18 months.

Results demonstrate that non-enhanced pristine biochar becomes rapidly depleted of nutrients whereas biochar enhanced by maceration in urine revealed improved nutrient cycling as far as potassium and magnesium are concerned. Biochar enhanced by maceration with a chemical fertilizer shows a good potential in terms of phosphorus release.

Biochar is thus a good support for slow-release fertilizers when macerated in cow urine or enhanced by maceration with phosphorus fertilizers.

Résumé

L'agriculture fait face à un défi majeur en termes d'usage de l'engrais dont l'efficience est aujourd'hui inférieure à 50%. Il est donc nécessaire de trouver des alternatives durables et plus efficaces à ces engrais. Ces dernières décennies, des études concernant le biochar ont montré une amélioration des propriétés des sols, particulièrement dans des sols très altérés, grâce à la modification de leurs caractéristiques physico-chimiques. Récemment des études ont démontré que le biochar amélioré par des composés organiques ou inorganiques peut être utilisé comme engrais à libération progressive et améliorer le cycle des nutriments.

Cette étude met l'accent sur la dynamique des nutriments pour des engrais à base de biochar et sur leur utilisation potentielle en tant qu'engrais à libération progressive. Des biochars améliorés par des engrais, par de l'urine et par co-compostage ont été comparés par des extractions de nutriments en série afin d'évaluer leur potentiel à remplacer les engrais chimiques. De plus, l'effet du temps d'incorporation du biochar dans les sols et son influence sur la dynamique des nutriments a été évaluée à travers l'étude de biochar ayant séjourné dans des sols tropicaux pendant 6 et 18 mois.

Les résultats ont démontré que le biochar pur perd rapidement son contenu en nutriments tandis que le biochar enrichi en nutriments par macération avec de l'urine montre une amélioration du cycle des nutriments en ce qui concerne le potassium et le magnésium. Le biochar chargé par macération avec de l'engrais chimique possède un potentiel important de libération progressive de phosphore.

Le biochar est donc un bon support pour des engrais à libération progressive lorsqu'il a macéré dans de l'urine ou lorsqu'il a été amélioré avec des engrais phosphatés.

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Abbreviations

BC: biochar

NH_4^+ : ammonium

NH_3 : ammoniac

NO_2^- : nitrite

NO_3^- : nitrate

N: nitrogen

P: phosphorus

K: potassium

Mg: magnesium

Si: silicon

O: oxygen

Al: aluminum

S: sulfur

Cl: chloride

Ca: calcium

OC: organic carbon

NPK: fertilizer containing nitrogen, phosphorus and potassium

BC-NPK: biochar enhanced with NPK fertilizer

BC-Urea: biochar enhanced with urea

BC-Compost: biochar activated by co-composting

BC-Urine: biochar enhanced by cow urine

M-6: Experimental plot in Massala

K-18: Experimental plot in Koumbia

ARTICLE

1. INTRODUCTION

Agriculture is facing a major challenge in terms of efficient fertilizer use. Loss of nutrients to the environment through irreversible retention in soils, volatilization, erosion and leaching (Diaz et al., 2008; Bouwman et al., 2013) decreases this efficiency. Since these losses represent an important production cost it is crucial to improve their efficiency (González et al., 2015).

A slow-release fertilizer is defined as “a fertilizer containing a plant nutrient in a form which delays its availability for plant uptake and use after application, or which extends its availability to the plant significantly longer than a reference ‘rapidly available nutrient fertilizer’ such as ammonium nitrate or urea, ammonium phosphate or potassium chloride” (Trenkel, 2010). This avoids important leaching of NO_3^- fertilizer and thus enhances their efficiency (Richards et al., 1993; Li et al., 2016).

Biochar is a carbon-rich product made by pyrolysis of organic matter. Biochar can be produced from various feedstock. The use of waste feedstock is an ideal way to produce biochar in order to keep a sustainable organic matter cycle. It is composed of condensed aromatic groups that are partially responsible for its high recalcitrance in soil (Guo et al., 2014). The presence of these aromatic groups implies a high density of functional groups at the surface of biochar particle that interact with nutrients (Glaser, 2007).

Soil scientists are looking for ways to increase soil productivity in highly weathered environments through more sustainable agronomical practices. In agroecosystems, biochar holds great potential for improving soil properties in tropical and subtropical environments (Glaser, 2007; Jeffery et al., 2011; Crane-Droesch et al., 2013). In these environments, biochar added in soils is oxidized, resulting in the formation of functional groups at the biochar surface at the beginning of the process, and then near the core of the particle (Lehmann et al., 2005). Those functional groups allow biochar to enhance its cationic exchange capacity. Nutrients can then interact with biochar surface and pores walls. Furthermore, application of biochar on acidic soils increases their pH through a liming effect (Jeffery et al., 2011). Finally through its high porosity, biochar can enhance soil water retention capacity (Verheijen et al., 2010). This aspect is closely related to the decrease of NO_3^- leaching while using biochar in soils. Indeed, NO_3^- ions can be kept in biochar by the way of hygroscopic water close to the biochar surface (Kammann et al., 2015).

However some studies have demonstrated that, at exceeding application rates, biochar can have negative effects on crop productivity. A 15 % (w/w) application induces a delay in plant growth (Prapagdee et al., 2014). Moreover an application rate of more than 50 t.ha⁻¹ diminishes the benefits that biochar can have in terms of shoot and total plant weight (Upadhyay, 2015).

Biochar properties can be improved by several activation or enhancing methods. Activation consists in modifying biochar surface structure to obtain new functional groups that can in turn capture nutrients and make them available for plants with a low need of uptake energy (Joseph et al., 2013). The enhancing of biochar allows the formation of an organic

coating at biochar surface that can increase the cationic exchange capacity of biochar (Schmidt et al., 2017). On the other hand, biochar can adsorb nutrients contained in organic or mineral matrix used to enhance it (Archanjo et al., 2017). In a context of sustainable development and help to producers in emerging countries, sources of activation and enhancing that are affordable and handy must be developed. Both organic and mineral ways are possible to enhance biochar.

Organic ways of biochar activation such as co-composting processes have been studied. A composting process including addition of biochar allows 1) a more intense decomposition of the compost and 2) nutrients fixation on biochar surface that can be available for plants when added into the soil (Hagemann, Joseph, et al., 2017). From a chemical point of view, high temperature in compost can enhance the oxidation of biochar and thus its capacity to retain nutrients (Thies et al., 2009). Maceration in urine has been studied as an organic way to enhance biochar. Biochar macerated with urine improves crop productivity and yields regardless of urine application doses (Schmidt et al., 2015, 2017).

Mineral ways of enhancing are also possible through maceration of biochar with ammonium (NH_4^+) (Wen et al., 2017), diammonium phosphate and potassium chloride (Qian et al., 2014), NPK fertilizers (Schmidt et al., 2017) or chemical urea (Joseph et al., 2013; Manikandan et al., 2013). New chemical functions appeared at biochar surface after such activation (Manikandan et al., 2013). Nitrogen (N) from mineral sources interacts mainly with carboxyl groups at the charcoal surface to form stable components such as amides or nitriles (Bimer et al., 1998).

Enhanced biochar has often been reported to induce crop yields equal or higher than these obtained with conventional chemical fertilizers (Schmidt et al., 2017). N adsorbed on biochar during enhancing processes acts like a source of available nutrients for plants during 20 days, which is longer than pure NH_4Cl (used as a chemical fertilizer) proving the slow release capacity of enhanced biochar (Wen et al., 2017).

Biochar enhancing by addition of urea has a positive impact in terms of N available for plants but also for the decrease in NO_3^- leaching. Biochar can play a role in decreasing NO_3^- loss, protecting urea from nitrification (González et al., 2015). This could possibly be the reason of a slower release of NO_3^- when urea is absorbed on biochar during an enhancing process.

Slow-release fertilizers made by maceration of biochar with NPK fertilizers release NO_3^- , K^+ and PO_4^{3-} at a lower rate than a chemical fertilizer (Gwenzi et al., 2018).

Presence of biochar in soil allows the limitation of NH_3 emissions that are the main factor of N-based fertilizers losses in agricultural soils (Macnack et al., 2013). Mechanisms driving these effects are the adsorption of NH_3 (Clough et al., 2013) and NH_4^+ (Chen et al., 2013) on biochar. Furthermore, adsorption of NH_4^+ on biochar can decrease the amount of NH_4^+ available for nitrifying bacteria, resulting in a lower rate of nitrification in soils amended with biochar (Taghizadeh-Toosi et al., 2012). Biochar induces an increase in biological fixation of N_2 (Mia et al., 2014) related to a decrease in N_2O emissions (Zheng et al., 2012). Since N_2O can be retained in micropores in soil (Maag et al., 1996) and then be converted into N_2 , biochar

porosity could also play a role in the longer sequestration of N_2O in soil since it increases the bulk soil porosity (Gul et al., 2015). Similarly, phosphorus (P) and potassium (K) cycles are also impacted by biochar as a result of increased microbial activity (Lehmann et al., 2011) responsible for the mineralization of P (Masto et al., 2013) and an increase in K content in soils (van de Voorde et al., 2014).

Biochar has also an impact on organic matter stabilization. Analyzes on old charcoal remained in soils for different periods of time show an increase in oxygen (O), silicon (Si), aluminum (Al) and iron (Fe) at surface of charcoal particles with residence time in soils (Hardy et al., 2017). Kramer (2012) and Kleber (2015) suggest that oxygen is the element on which those inorganic elements can be fixed since carboxyl groups formed at the biochar surface with time are highly involved in the stabilization of organic matter process (Kramer et al., 2012; Kleber et al., 2015). This precipitation of organo-mineral associations can occur at the biochar surface but also in pores (Hardy et al., 2017) which offer an important specific surface. Organic coating is formed by organo-mineral associations ranging in size from a few nanometers to 50 nm (Archanjo et al., 2017).

Biochar seems to be a good support in the production of slow release fertilizers because of its important specific surface. Biochar size influences nutrients release dynamics. Smaller biochar particles tend to release a higher amount of nutrients such as K, P and Mg (Angst et al., 2013). That can be explained by the larger surface in contact with the solution during the extraction experiment.

Today the use of enhanced biochar to increase yields has been largely studied (Schmidt et al., 2015, 2017). However the nutrients release from enhanced biochar deserves a better understanding. Its potential to be used as a slow-release fertilizer needs to be explored. In our study, we aim to study the nutrients dynamics interacting with biochar activated by different processes. More specifically, we will study (1) the dynamic of nutrient retention and release from activated biochar in order to highlight its ability to substitute chemical fertilizers; (2) the microscopic distribution of chemical elements on biochar surface after being remained in soil and after enhancement processes.

2. MATERIAL AND METHODS

2.1. Biochar

Biochar used in this study was produced by pyrolysis of cotton stalks in a Kon Tiki flame curtain pyrolyzer (650-700 °C) (Schmidt, Taylor, et al., 2014) and a top-lift updraft (TLUD) (400-500 °C) batch (Roth, 2013).

2.2. Mineral fertilizers, co-compost and cow urine

Cow urine was collected the day before the enhancement. Mineral fertilizers used in this study were NPK (14-23-14%), NPK (12-4-10%) containing nitrates and urea (47 % N). The compost used in this study was set by Lucie Blondiau. It was composed of 20% of biochar, 20% of old manure and 60% of fresh manure. After 5 days during which compost had remained at rest, compost was turned over every three days during 24 days (Maqbool et al., 2015). Water was added to the system when compost was not wet enough to maintain good humidity levels as is commonly done in Burkina Faso. After this process compost remained 2 weeks without being turned over before the sampling.

2.3. Field sampling

Experimental sites were sampled to extract biochar particles from cultivated soils in Burkina Faso. The first one is in the department of Koumbia (11°14'57.7" N 3°40'31.7" W) in the province of Tuy, and the second one in the department of Massala (12°27'00.9" N 3°28'08.1" W) in the province of Mouhoun. Samples of biochar were taken from plots that have been cultivated for 6 months (Massala, named M-6) and for 18 months (Koumbia, named K-18).

Only one treatment from previous experiments was studied. As far as the biochar concentration is concerned, it has been argued that 30 t.ha⁻¹ had no interest in terms of organic matter recycling on a large scale (Burgeon, 2017). That is why we focused on an application of 10 t.ha⁻¹. NPK concentration (15-15-15%) was set to 150 kg.ha⁻¹ (value of national recommendations).

Sampling was carried out within 5 plots of this treatment (10 t.ha⁻¹ biochar and 150 kg.ha⁻¹ NPK) on each site. A composite sample coming from four random holes was taken on each plot on the 20 first centimeters of the soil. Soil was then sieved with a RETSCH AS 400 horizontal sieve shaker at 240 rpm. Different fractions were obtained according to the sieves (2 mm, 1 mm and 0.5 mm) in order to extract biochar particles of different sizes.

2.4. Soil properties

Physico-chemical properties of soil in Koumbia and Massala, before being amended with biochar, were analyzed by the provincial laboratory of La Hulpe. Methods used in this laboratory are described in APPENDIX 2: Laboratory analyzes.

2.5. Biochar enhancement

Biochar has been enhanced by maceration with dissolved NPK fertilizer (BC-NPK), dissolved chemical urea (BC-Urea) and in cow urine (BC-Urine). Biochar has been activated by co-composting (BC-Compost) (see above). All those enhanced biochar were compared with pristine biochar (Pristine BC).

The volume of liquid was chosen in order to respect a volume ratio of 1:1 with biochar (Schmidt et al., 2017). Maceration lasted 48 hours in ambient conditions and without stirring. After being filtered through a 50 µm sieve activated biochar was dried at 40 °C during 5 days until complete water evaporation.

For activation by addition of fertilizers, the weight of biochar and sources of nutrients were measured with an Acculab Atilon digital lab balance (accuracy of 0.01 g) to obtain a mass ratio of 1:1. Water was brought to a boil with a Heildolph MR 3001 hotplate and was then poured on the mix of biochar and fertilizer.

2.6. Nutrient dosage on enhanced biochar

Total nitrogen of biochar was measured by the Kjeldahl method. One gram of biochar was mineralized on a Buchi 430 digester with 20 mL of H₂SO₄ (95-97 %). The solution was then distilled in a Buchi B-324 distillation unit and total nitrogen was quantified with 1N or 0.1N hydrochloric acid (HCl) depending on the sample concentration.

Phosphorus was extracted from samples by heating 2 g of biochar on a Gemini BV Gerhardt hotplate with 20 mL of perchloric acid (HClO₄ 70 %). Quantification was made by colorimetric method with a Shimadzu UV-1205 Spectrophotometer at a wavelength of 880 nm. This quantification has not been done on cow urine since its color induced a bias during the coloring.

Potassium content was determined through tri-acid attack using nitric acid (HNO₃), HClO₄ and HCl to extract it from 0.5 g of biochar. Potassium content has been identified with an Atomic Absorption Spectrometer SpectrAA 220.

2.7. SEM/EDX analyzes

SEM/EDX analyzes were made with a Bruker e-Flash operating at 15 kV. Biochar was powdered to obtain particles between 200 and 2000 µm. Images were obtained by using the signal of backscattered electrons (BSE). A 50 µm diaphragm was used. Three areas have been observed using different zooms to have a large view of the BC and a more precise elemental mapping of BC's pores. Elemental mapping has been realized for aluminum (Al), carbon (C), calcium (Ca), chlorine (Cl), potassium (K), magnesium (Mg), sodium (Na), oxygen (O), phosphorus (P), sulfur (S) and silicon (Si).

2.8. Serial extractions

Samples stirring was carried out with a Universal Shaker SM-30 Edmund Bühler at 200 rpm/min.

2.8.1. Nitrates extraction

Nitrates were extracted from activated biochar, using KCl. 4 g of biochar were mixed with 40 mL of a 2M KCl solution and stirred during six time steps. After each time step the solution was filtered. The same 4 g of biochar were then mixed with 40 mL of a pure solution of 2M KCl. Solutions were collected three times after 1 h and after a time step of 18 h, 48 h and 96 h. After a filtration with a Whatman 602 H ½ filter, nitrates were reduced to nitrites through

a cadmium column. 200 μ L of a reagent composed of sulfanilamide, phosphoric acid and N-(1-naphtyl)éthylènediamine chloride dehydrate (1:1:1 v/v) were added to the reduced solution and nitrites were then quantified with a spectrophotometer at a wave length of 543 nm.

2.8.2. *Phosphorus, magnesium and potassium extraction*

P, Mg and K were extracted by adding 200 mL of distilled water to 10 g of biochar. Solutions were stirred during 4 hours and then filtered through a Whatman 602 H $\frac{1}{2}$ filter. The retentate was then mixed with 200 mL of pure distilled water and then stirred during 4 h. Eight sequential extractions were done this way. Phosphorus quantification was made by colorimetric method with a Shimadzu UV-1205 Spectrophotometer. Potassium and magnesium contents were identified with an Atomic Absorption Spectrometer SpectrAA 220. Phosphorus quantification has not been done on biochar activated with cow urine since the color of the extraction solution induced a bias during the coloring.

2.8.3. *Releasing capacity computation*

The releasing capacities of the BC's and the fertilizer were obtained by dividing the amount of nutrient released by the total content.

2.9. *Adsorption isotherms for NPK*

Five grams of pristine biochar were mixed during 72 h with 50 mL of solutions of increasing nitrates concentrations made by the dilution of NPK (12-4-10%) fertilizer. Solutions were prepared with respectively 1 g, 2 g, 3 g, 4 g, 5 g, 10 g and 20 g of NPK fertilizer. At the end of the reaction, samples were filtered through a Whatman 602 H $\frac{1}{2}$ filter. Nitrates were then measured in the solution to determine the amount of nitrates that was adsorbed on biochar. Adsorption isotherms were computed using Freundlich (1) and Langmuir (2) models:

$$Q_e = k * C_e^{\frac{1}{n}} \quad (1)$$

$$Q_e = \frac{Q_0 * K_L * C_e}{1 + K_L * C_e} \quad (2)$$

Where:

- Q_e : Concentration at equilibrium on biochar [mg/g]
- C_e : Concentration at equilibrium in solution [mg/L]
- k : Adsorption coefficient for Freundlich isotherm [mg/g]
- n : Freundlich exponent [-]
- Q_0 : Maximum concentration on biochar [mg/g]
- K_L : Adsorption coefficient for Langmuir isotherm [L/mg]

2.10. *Optimization of release curves*

The software RStudio (R 3.4.1) was used to optimize release curves of BC's and the chemical fertilizer. Each curve was approximated by an exponential growth curve (3):

$$C = A * e^{-kt} \quad (3)$$

Where:

- C: measured concentration in the extraction solution [mg/g of BC]
- t: time [h]
- A: concentration at t_0 [mg/g of BC]
- k: rate of growth

2.11. Statistical analysis

The software Minitab 18.1.0.0 was used to conduct statistical analyses. Before each analysis, a Levene test was applied on data to verify the equality of variance. Analyses of variance at one parameter (the type of component or the time of extraction) were applied on data. The significance threshold was fixed at $\alpha=0.05$. A Fisher test was used to classify the components on the basis of their nutrient concentration.

3. RESULTS

3.1. Duration of biochar amendment in soil

3.1.1. Soil physico-chemical properties

Table 1. Analytical results of soil physico-chemical properties in Koumbia and Massala before amendment with BC.

	P mg/100g	K mg/100g	Mg mg/100g	Ca mg/100g	pH_KCl	pH_H₂O	OC g/100g	Humus %	Total N %	C/N	Clay %	Silt %	Sand %
Massala 0-20 (M-6)	0.17	6.40	7.24	49.00	5.48	6.70	0.56	1.12	0.04	13.27	7.62	22.51	69.87
Koumbia 0-20 (K-18)	0.53	3.45	4.07	43.05	5.59	6.30	0.53	1.06			5.48	24.22	70.30

Table 1 shows the results of soil physico-chemical properties at K-18 and M-6 before being amended with BC. The site of M-6 has a higher nutrients content than the site of K-18, except in terms of bioavailable P content. The difference between pH_KCl and pH_H₂O is more important in M-6. In the first horizon of soil, the granulometric composition does not differ from one site to the other. Both soils are mainly sandy (69.87 % and 70.30 %).

3.1.2. Nutrients release according to BC age in soils

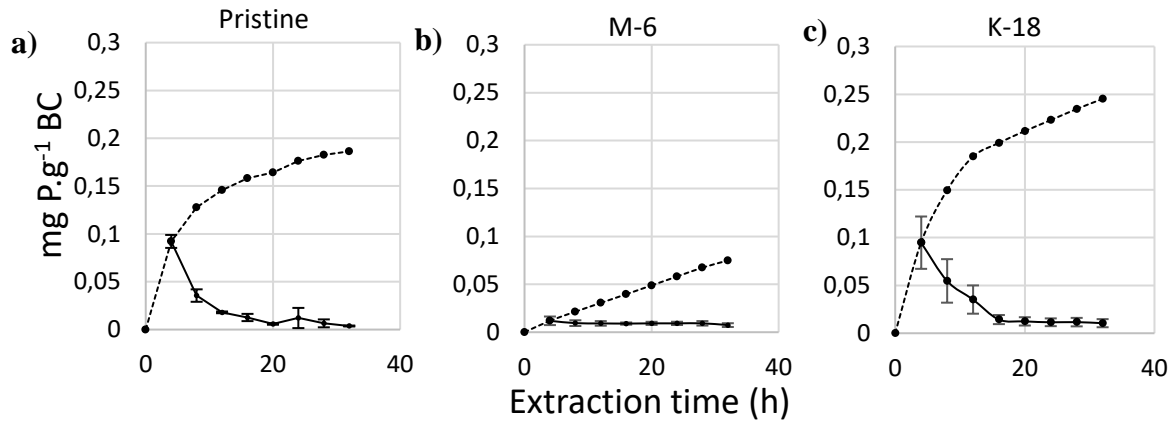


Figure 1. Amount of phosphorus released by a) Pristine, b) Massala (6 months) and c) Koumbia (18 months) BC's (mg.g⁻¹) as a function of time in hours. Continuous curve corresponds to the releasing rate of phosphorus (P_{rel}) and discontinuous curve to the cumulated amount of phosphorus released (P_{cum}).

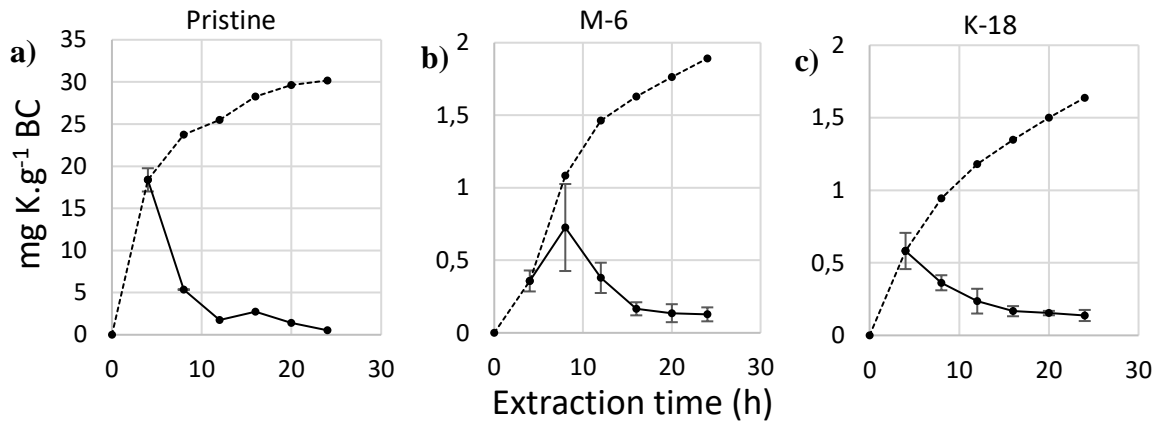


Figure 2. Amount of potassium released by a) Pristine, b) Massala (6 months) and c) Koumbia (18 months) BC's (mg.g⁻¹) as a function of time in hours. Continuous curve corresponds to the releasing rate of potassium (K_{rel}) and discontinuous curve to the cumulated amount of potassium released (K_{cum}).

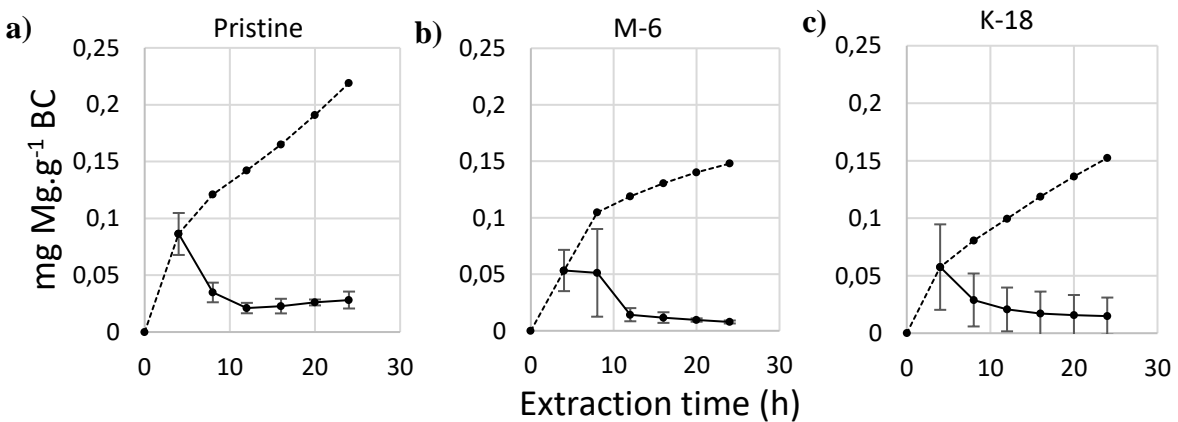


Figure 3. Amount of magnesium released by a) Pristine, b) Massala (6 months) and c) Koumbia (18 months) BC's (mg.g⁻¹) as a function of time in hours. Continuous curve corresponds to the releasing rate of magnesium (Mg_{rel}) and discontinuous curve to the cumulated amount of magnesium released (Mg_{cum}).

The curves of P release show different trends (Figure 1). P_{tot} reaches a higher value for K-18 ($p=0.002$) and pristine ($p<0.001$) BC than M-6 BC. P_{cum} of K-18 BC and pristine BC do not reach significantly different values ($p=0.279$). Furthermore M-6 BC does not level off while the two others do.

The final value of K_{cum} (Figure 2) is almost twenty times higher for pristine BC than for BC's from K-18 ($p<0.001$) and M-6 ($p<0.001$). K_{cum} curve of K-18 and M-6 BC's reach the same value ($p=0.337$). M-6 BC has a different dynamics curve since K_{rel} increases significantly between 4 and 8 hours of extraction ($p=0.044$) before bottoming out.

Mg_{cum} (Figure 3) reaches a higher value for pristine BC than for M-6 BC ($p=0.048$). Final values of Mg_{cum} are the same for K-18 BC and pristine BC ($p=0.502$). M-6 BC dynamics curve does not have the same shape than the others. The two first value of Mg_{rel} of M-6 BC are not significantly different ($p=0.925$). However a high standard deviation is observed for the second value. Then a strong decrease is observed. The two others graphs show decreasing K_{rel} over time.

3.2. Nutrient loading on young biochar

3.2.1. Nutrients adsorption on biochar

3.2.1.1. Sorption isotherms

Experimental data of sorption isotherms were obtained by plotting the NO_3^- concentration on BC as a function of the concentration in solution (Figure 4). Freundlich and Langmuir models adjusted to experimental data show different trends. While Freundlich isotherm seems to grow continuously, Langmuir model highlights a later stabilization expressed by the Q_0 coefficient (Table 2).

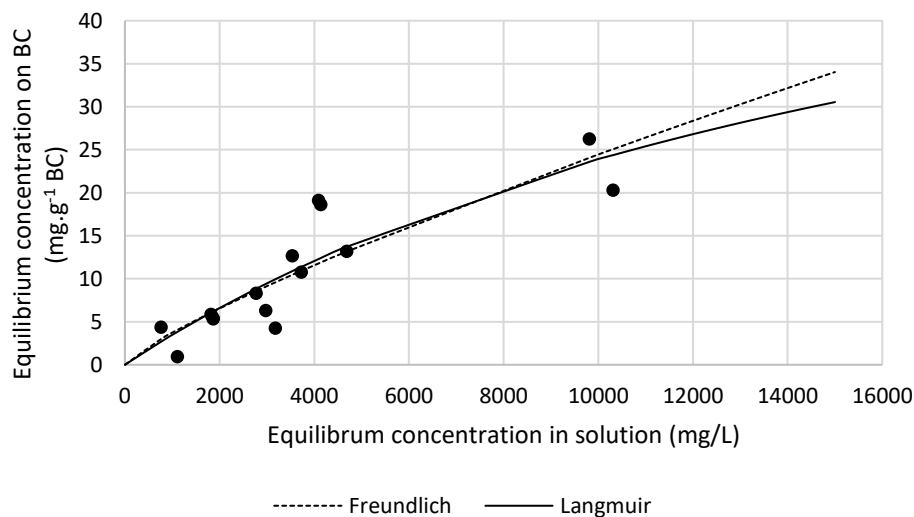


Figure 4. Sorption isotherms adjusted to experimental data by the way of Freundlich ($R^2=0.87$) and Langmuir ($R^2=0.88$) models.

Table 2. Coefficients of Langmuir and Freundlich isotherms adjusted to experimental data.

Langmuir		Freundlich	
Q ₀	K _L	k	n
[mg/g]	[L/mg]	[mg/g]	[-]
68.893	5.308E-05	0.013	1.225

3.2.1.2. Adsorbed nutrients after biochar loading

The total nutrient content of enhanced BC, pristine BC and chemical fertilizers used to load BC are shown in Table 3. After the loading process, BC-NPK contains almost twice as much N as pristine BC. It shows a higher content in P, K and Mg than pristine BC. BC-UREA has a N content more than seven times higher than pristine BC. BC-URINE contains more K and Mg than pristine BC. A decrease of N and P content is found in BC-URINE in comparison with pristine BC.

Table 3. Mean values of nutrients contents in BC's and fertilizers. Values on the same line that do not share the same letter are significantly different ($p < 0.05$).

		NPK Fertilizer	BC- NPK	Urea Fertilizer	BC- UREA	URINE	BC- URINE	Pristine BC
Total N (mg/g)	Mean	135.61 ^a	45.17 ^b	458.92 ^c	187.51 ^d	-	13.07 ^e	23.64 ^f
	Std	1.03	1.45	2.60	0.92	-	0.13	2.93
Total P (mg/g)	Mean	91.92 ^a	39.47 ^b	-	-	-	3.43 ^c	4.21 ^c
	Std	2.50	6.80	-	-	-	0.12	0.40
Total K (mg/g)	Mean	219.80 ^a	82.84 ^b	-	-	196.29 ^c	79.62 ^b	34.40 ^d
	Std	14.53	2.81	-	-	4.72	8.41	4.66
Total Mg (mg/g)	Mean	6.18 ^a	5.43 ^a	-	-	13.95 ^b	8.77 ^c	1.86 ^d
	Std	0.22	0.24	-	-	0.65	0.61	0.56

3.2.2. Potential release of nutrients

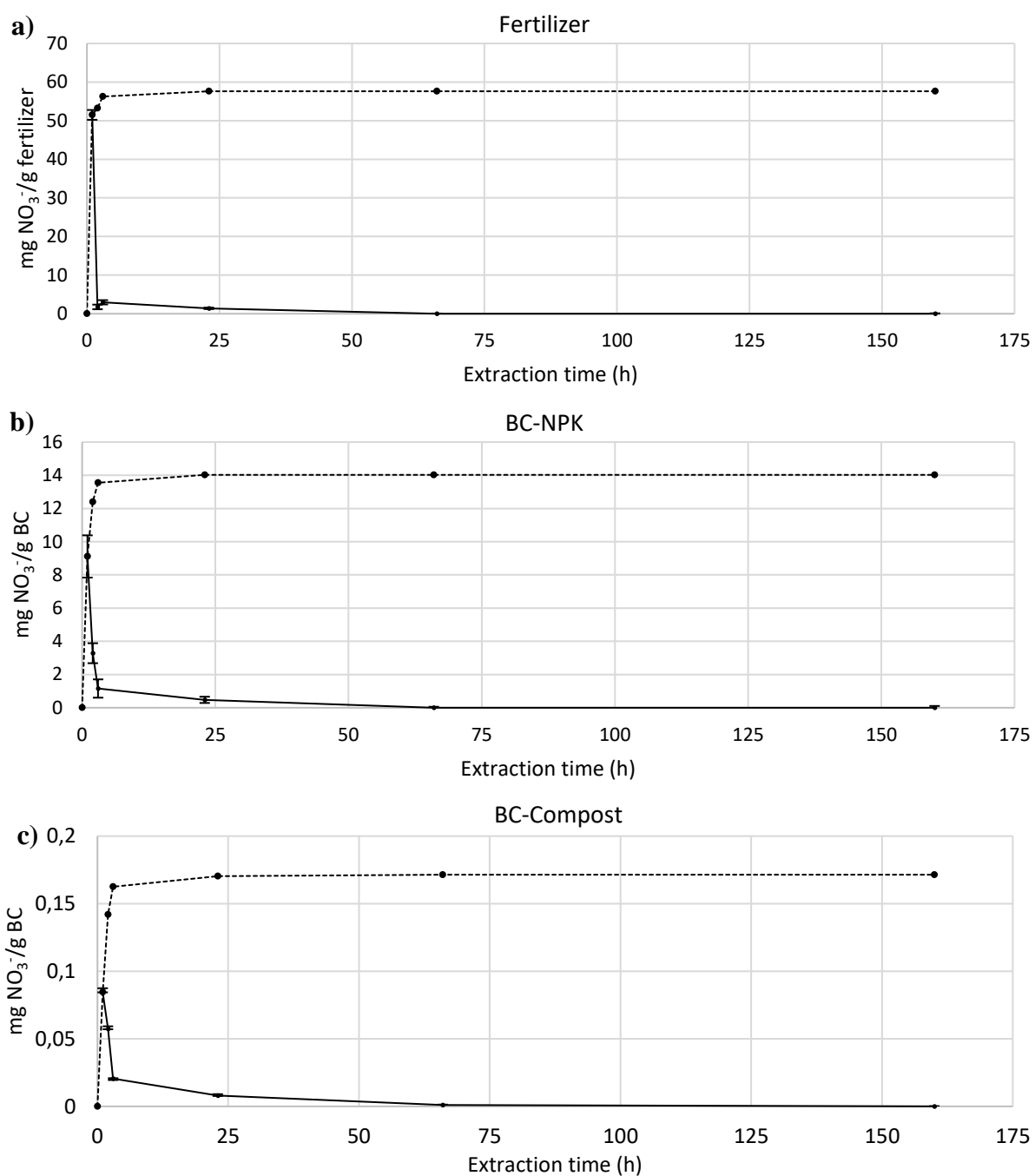


Figure 5. Nitrates release from a) Fertilizer b) BC-NPK and c) BC-Compost in mg per g of BC or fertilizer as a function of time in hours. Continuous curve corresponds to the releasing rate of nitrates ($\text{NO}_3^-_{\text{rel}}$) and discontinuous curve to the cumulated amount of nitrates released ($\text{NO}_3^-_{\text{cum}}$).

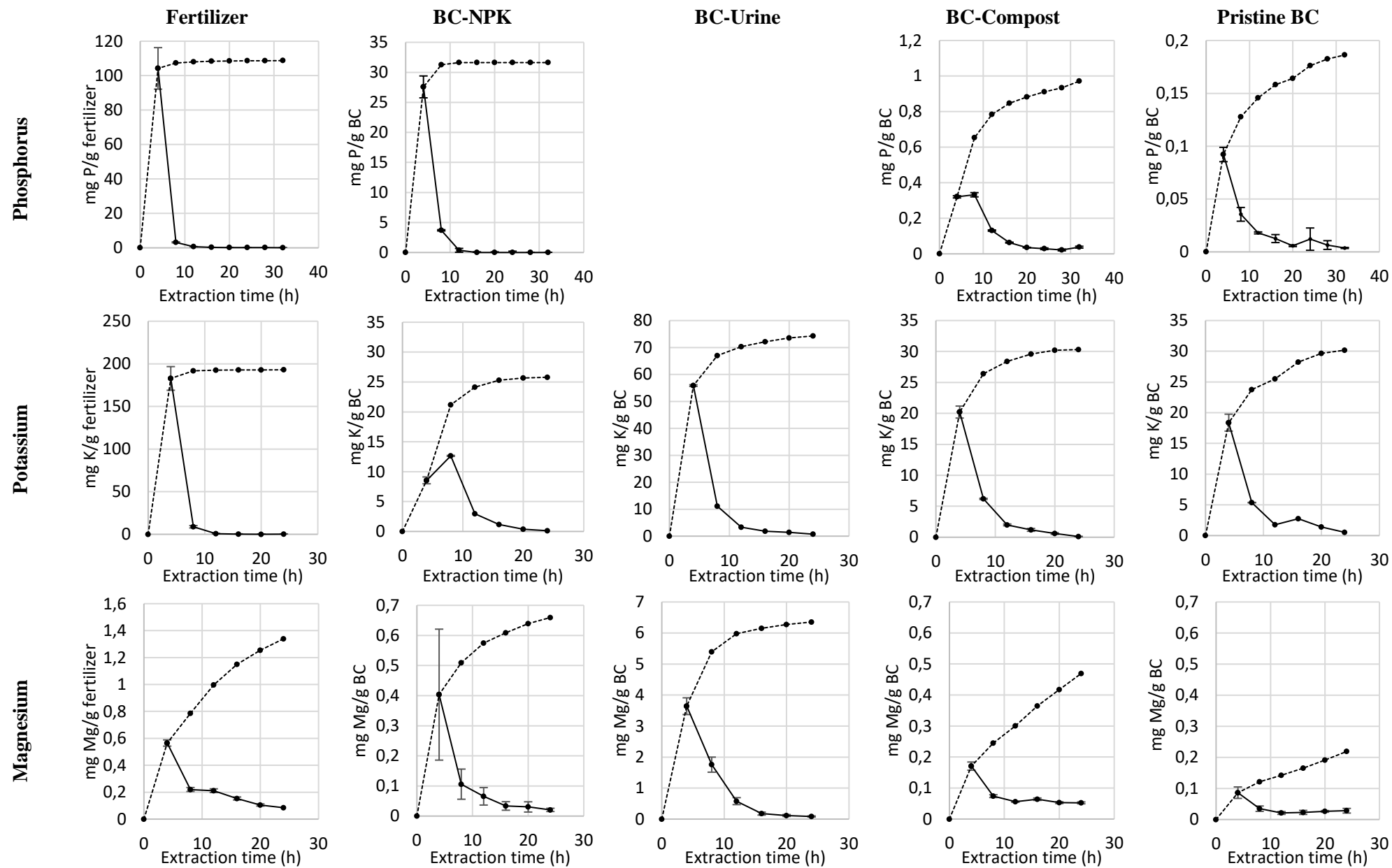


Figure 6. Phosphorus, potassium and magnesium release from fertilizer, BC-NPK, BC-Urine, BC-Compost and Pristine BC in (mg/g) as a function of time in hours. Continuous curve corresponds to the release rate of nutrient (P_{rel} , K_{rel} and Mg_{rel}) and discontinuous curve to the cumulated amount of nutrient released (P_{cum} , K_{cum} and Mg_{cum}).

Results of NO_3^- extraction are shown on Figure 5. Final values of $\text{NO}_3^-_{\text{cum}}$ are highly significantly different between chemical fertilizer, BC-NPK and BC-Compost ($p < 0.001$). $\text{NO}_3^-_{\text{tot}}$ of Pristine BC reaches a final value lower than the detection threshold of the method.

P_{rel} decreases continuously with time for all treatments (Figure 6). After 16 hours of extraction, P_{rel} stays constant for BC-NPK and pristine BC (values are not significantly different). The P_{cum} is higher for activated BC's and fertilizer than for pristine BC ($p < 0.001$).

K_{rel} (Figure 6) of BC-NPK shows an increase after 8 hours of extraction and stays constant after 20 hours. K_{rel} of BC-Urine shows a continuous decrease and remains stable after 16 hours of extraction. Values of K_{rel} are not significantly different after 12 hours for BC-Urine. K_{rel} increases between 12 and 16 hours for Pristine BC. Indeed K_{rel} after 16 hours is significantly different than K_{rel} after 12, 20 and 24 hours of extraction. K_{cum} of BC-Urine ($p < 0.001$) and fertilizer ($p < 0.001$) reach a higher value than pristine BC. The final value of K_{cum} is the same for pristine BC, BC-NPK ($p = 0.114$) and BC-Compost ($p = 0.955$).

Mg_{rel} decreases continuously with time for all treatments (Figure 6). Mg_{rel} reaches a stable value after 16 hours of extraction except for pristine BC where a small increase is observed. Mg_{rel} stays the same after 8 hours of extraction for BC-NPK and pristine BC. Mg_{cum} of fertilizer ($p < 0.001$), BC-Urine ($p < 0.001$) and BC-Compost ($p = 0.001$) are significantly higher than pristine BC. Pristine BC and BC-NPK have the same final value of Mg_{cum} ($p = 0.112$).

3.2.2.1. Releasing rate

Table 4 shows the growth rate (k) of exponential curves adjusted to releasing curves (P_{rel} , K_{rel} , Mg_{rel} , $\text{NO}_3^-_{\text{rel}}$) for chemical fertilizer, enhanced BC's and pristine BC for the three studied nutrients (Figure 5, Figure 6). As a reminder, this coefficient varies with the slope of the exponential curve. A high k corresponds to an important slope and thus a fast release.

Table 4. Growth rate of exponential curves adjusted to releasing curves obtained for the chemical fertilizer and for each BC.

		NPK Fertilizer	BC-NPK	BC-Urine	BC-Compost	Pristine BC
P_{rel}	k	0.869	0.518	-	0.110	0.196
	Standard error	0.200	0.025	-	0.126	0.019
K_{rel}	k	0.756	0.115	0.390	0.287	0.274
	Standard error	0.098	0.031	0.020	0.010	0.026
Mg_{rel}	k	0.120	0.277	0.209	0.081	0.101
	Standard error	0.013	0.092	0.013	0.013	0.022
$\text{NO}_3^-_{\text{rel}}$	k	3.260	1.025	-	0.570	-
	Standard error	0.858	0.090	-	0.056	-

The growth rate of the P_{rel} is higher for NPK fertilizer than for activated BC's and pristine BC. As far as K_{rel} is concerned, the growth rate of the fertilizer is the highest compared to enhanced and pristine BC's. BC-Urine has the highest coefficient among all enhanced BC's. Coefficient relative to Mg_{rel} is higher for BC-NPK and BC-Urine than for the fertilizer.

Moreover this coefficient is lower for BC-Compost than for pristine BC. In term of $\text{NO}_3^-_{\text{rel}}$, the growth rate of the fertilizer is three times more important than BC-NPK and six times higher than BC-Compost.

3.2.2.2. *Releasing capacity*

When normalized to the total content in nutrients (Table 3), differences between BC's and fertilizer are observed (Figure 7). BC-NPK releases respectively 80, 30 and 10% of its total P, K and Mg content. BC-Urine releases 90% of its total K content and 70% of its total Mg content. Pristine BC releases 10% of its total P and Mg content, and 90% of its total K content.

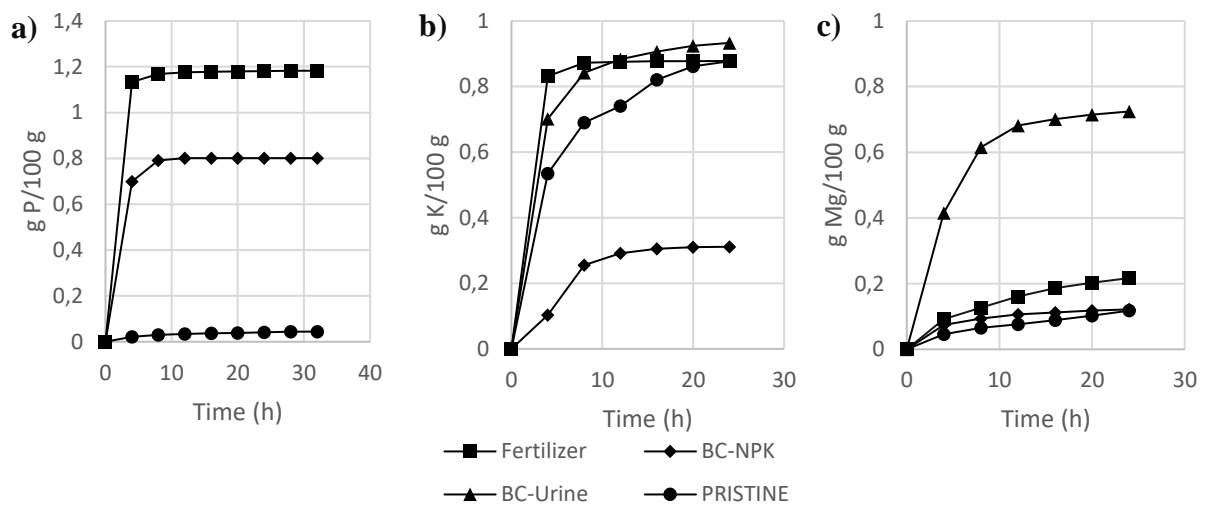


Figure 7. Fertilizer and BC's releasing capacity in terms of a) phosphorus, b) potassium and c) magnesium release. Square: Fertilizer, diamond: BC-NPK, circle: Pristine BC and triangle: BC-Urine

3.3. Microscopic analysis by SEM/EDX

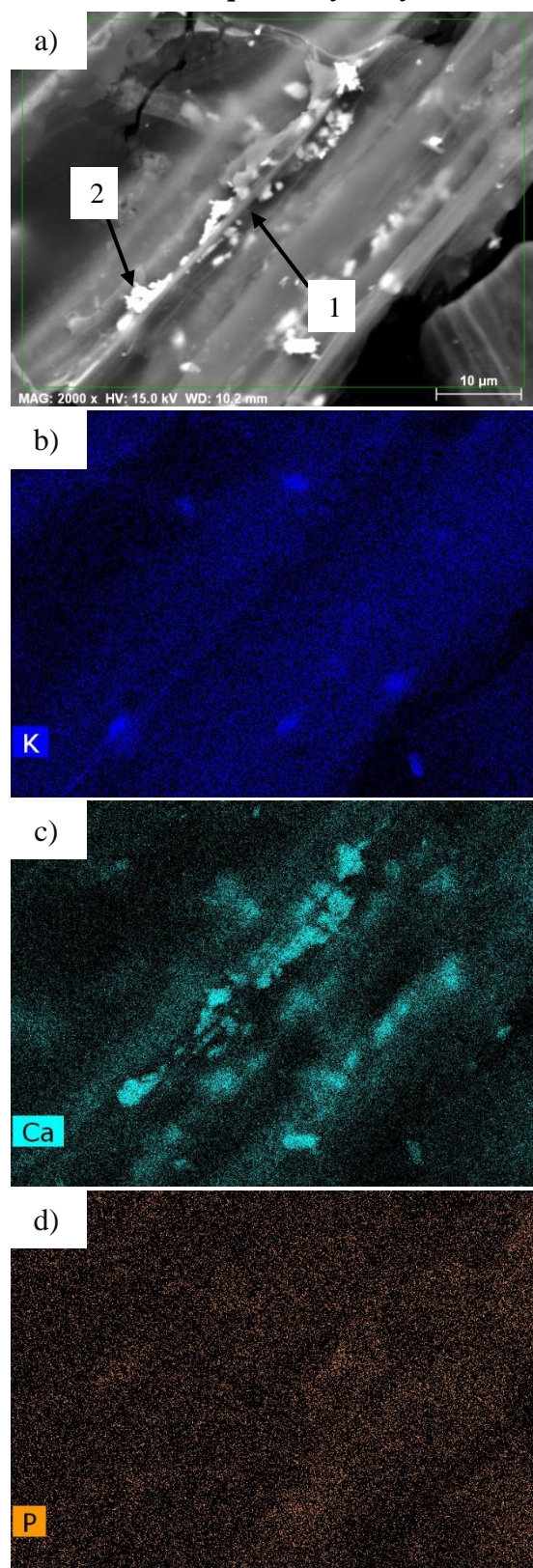


Figure 8. a) Scanning electron microscopy photographs of Pristine BC longitudinal pores (1) and precipitates (2), energy dispersive x-ray spectroscopy elemental maps for b) K, c) Ca and d) P

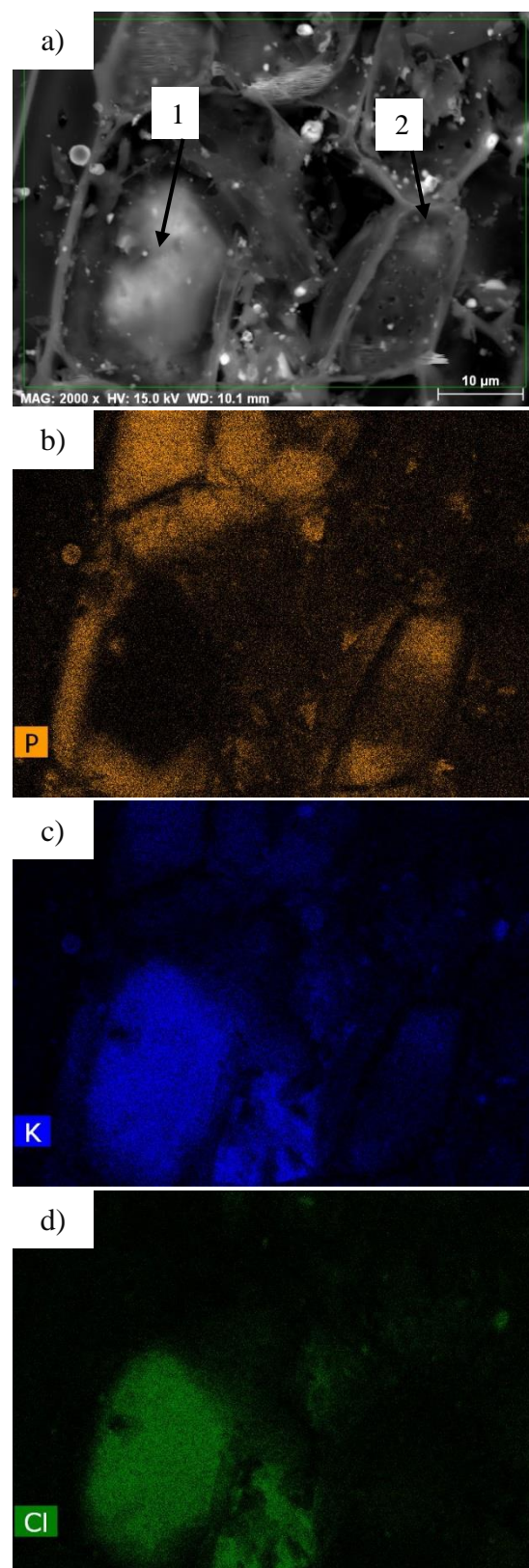


Figure 9. a) Scanning electron microscopy photographs of Massala BC pores (1) and precipitates (2), energy dispersive x-ray spectroscopy elemental maps for b) P, c) K and d) Cl.

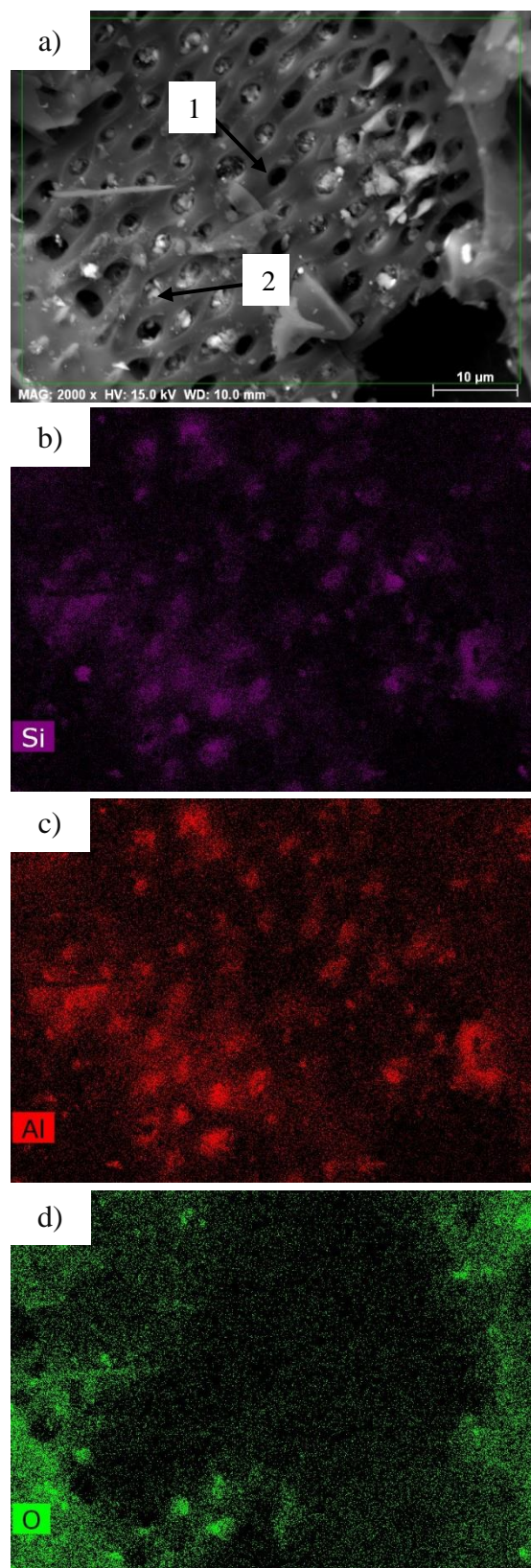


Figure 10. a) Scanning electron microscopy (SEM) photographs of BC-NPK pores (1) and precipitates (2), energy dispersive x-ray spectroscopy elemental maps (EDX) for b) Si, c) Al and d) O.

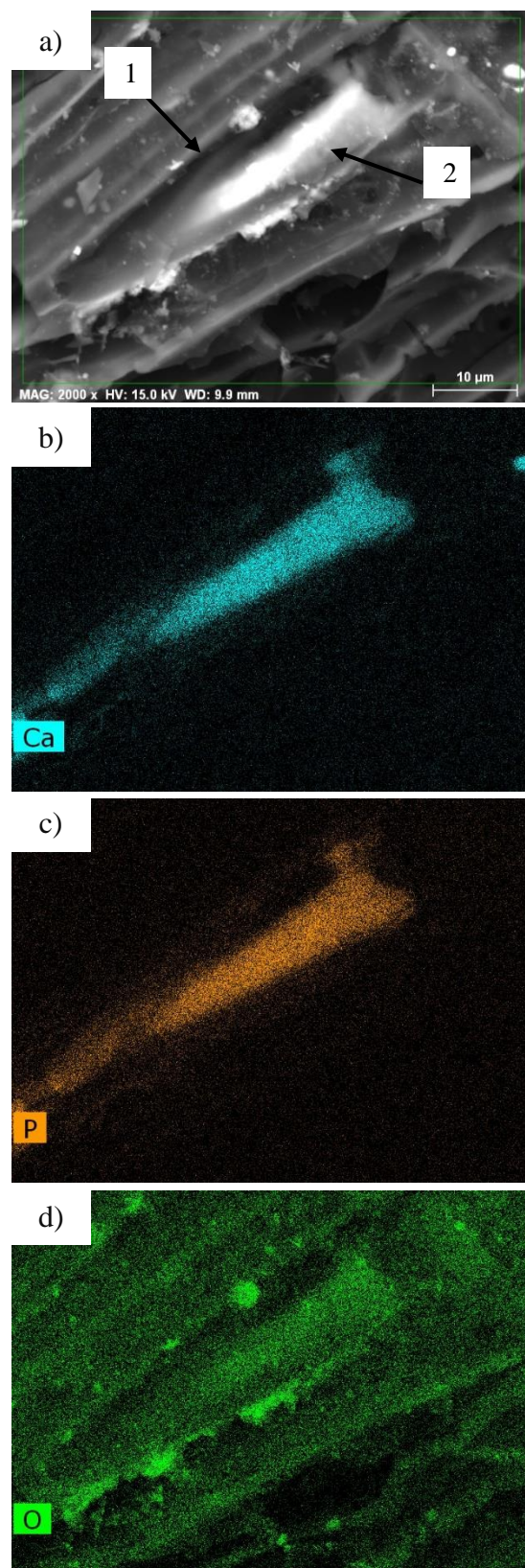


Figure 11. a) Scanning electron microscopy (SEM) photographs of BC-NPK longitudinal pores (1) and precipitates (2), energy dispersive x-ray spectroscopy elemental maps (EDX) for b) Ca, c) P and d) O.

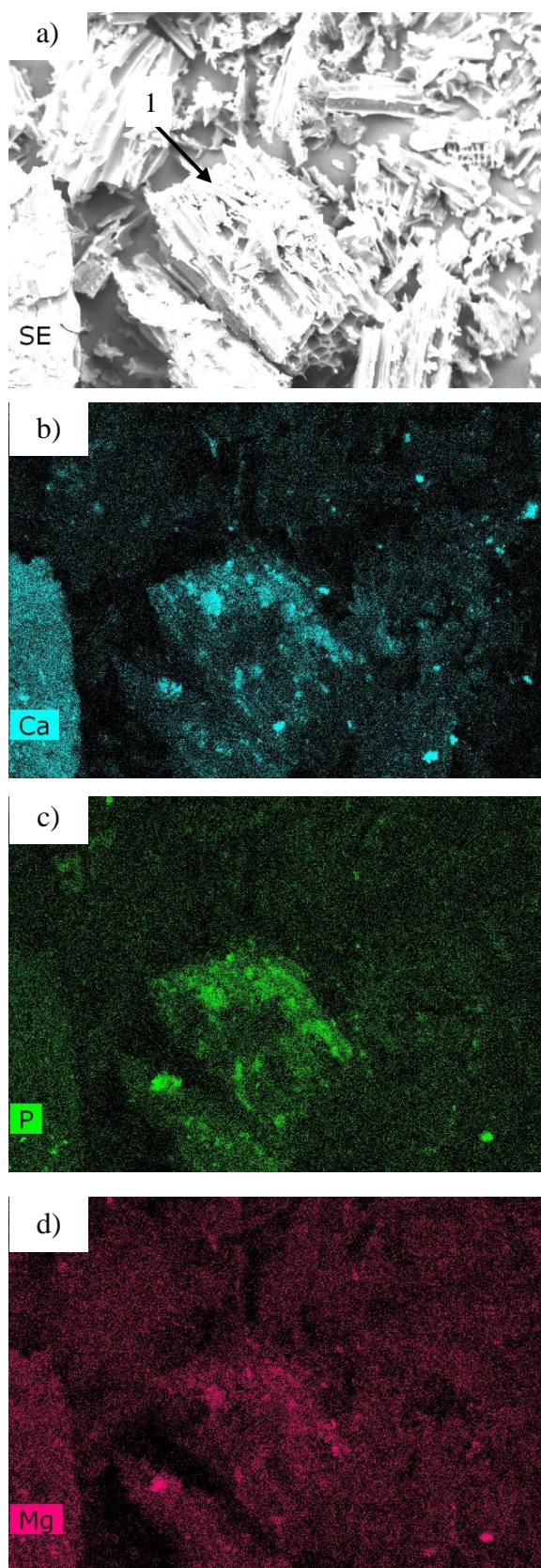


Figure 12. Energy dispersive x-ray spectroscopy elemental maps (EDX) of BC-Compost particles (1) for a) scattered electrons b) Ca, c) Mg and d) P.

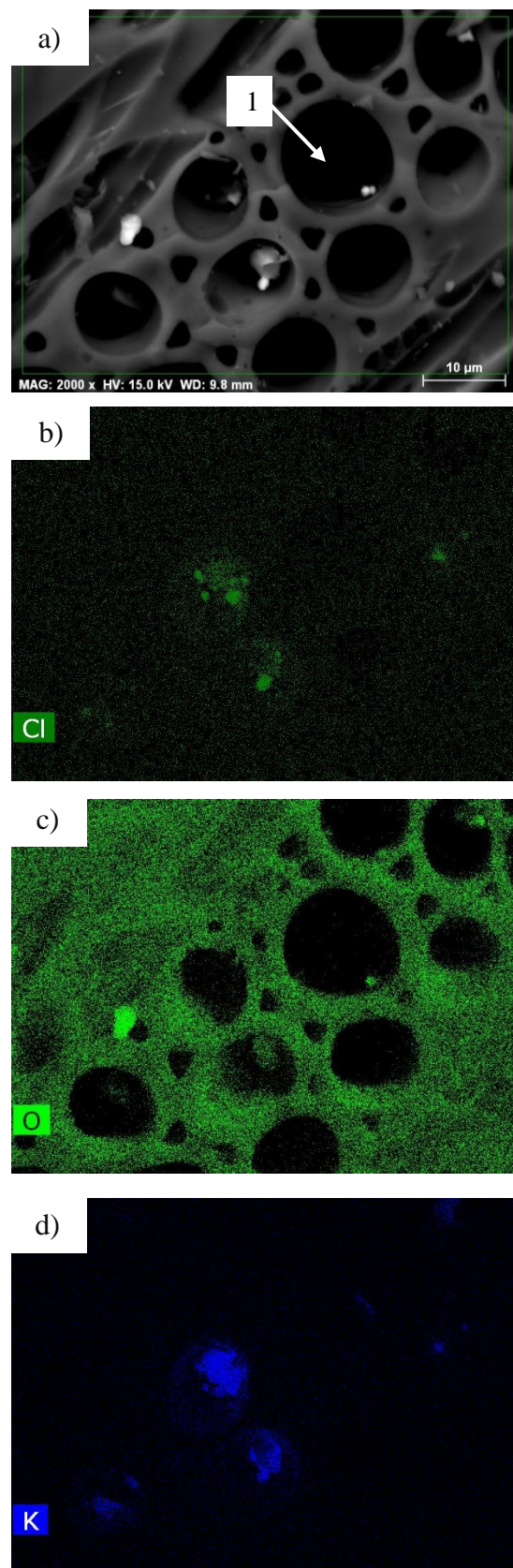


Figure 13. a) Scanning electron microscopy (SEM) photographs of Koumbia BC pores (1), energy dispersive x-ray spectroscopy elemental maps (EDX) for b) Cl, c) O and d) K.

SEM/EDX was made on pores of BC-NPK (Figure 10a). Si and Al are often found together inside pores of BC (Figure 10b and 10c). However Si is sometimes found with only oxygen but no Al (Figure 10d).

Elemental maps applied on M-6 BC pores highlight phosphorus found on pore walls (Figure 9a) whilst K and Cl are located inside the pore. These two elements are often found together (Figure 9c and 9d). The same precipitates of K and Cl are found in K-18 pores (Figure 13b and d). K precipitates appear on pristine BC (Figure 8b). Ca is abundant on all types of BC. Precipitates of P and Mg are found together on BC-COMPOST (Figure 12b and 12c). BC-NPK elemental mapping highlights the presence of P and Ca together (Figure 11b and 11c), while no P was found on pristine BC (Figure 8d). This kind of association is found in BC microporosity or along larger pores.

4. DISCUSSION

The main focus of this study is to understand how BC can increase availability of nutrients over time (1 versus 2 cultivation season) in tropical soils in Burkina Faso. Papers published in the last decades allow us to make hypotheses based on current scientific knowledge. This study tried to answer this question by testing different possibilities.

4.1. Effect of duration of BC amendment in soil on nutrients dynamics

BC oxidation increases over time when BC remains in soil. This induces the presence of new functional groups at BC surface that can increase the cation exchange capacity (CEC) of this product (Lehmann et al., 2005). This chemical oxidation and weathering could improve the BC nutrient retention over time. Moreover, the high BC porosity could be the host of nutrients applied on soils through NPK fertilizers and could increase the fertilizer use efficiency. Finally, BC contains intrinsic nutrients that can be released or be available for plants (Angst et al., 2013). Three types of BC have been compared: pristine BC, BC remained in soil for 6 months (M-6 BC) and BC remained in soil for 18 months (K-18 BC).

Dynamics curves of BC coming from M-6 and K-18 are compared to pristine BC to better understand nutrients dynamics over time (Figure 1, Figure 2, Figure 3). However it is important to take into account the physico-chemical properties of the soil (initial properties before the amendment, Table 1). K-18 and M-6 BC release significantly different amount of P (respectively 0.25 and 0.075 mg/g BC) (Figure 1). This difference could be the result of a fast release of P and followed by an accumulation of P at BC surface. However, in the first twenty centimeters, the soil P content in K-18 is three times higher than in M-6. Nevertheless Mg and K contents in BC do not seem to be influenced by the soil composition: the total Mg and K soil contents are two times higher in M-6 than in K-18 and no such trend is observed in their respective BC's.

Finally adding BC in soil does not seem to improve the nutrients availability over two seasons of culture. The major part of the BC nutrient content is released during the first months of cultivation.

It is interesting to compare BC and soil bioavailable nutrients concentrations. The quantity of nutrients in BC is negligible compared to the nutrient concentrations in soil. Analyzes of K-18 BC show a release of around 0.25 mg P/g of BC (Figure 1) and a content of 5.3 mg/g of soil (Table 1). Taking into account that BC has a low density, for a same volume unit, K-18 BC contains far less P than soil. This study suggests that BC has an impact on nutrients cycling in the water-soil-plant system during the first months of cultivation. After 18 months, the BC contains only small quantities of nutrients. However, biochar without nutrients still affects the soil properties (water retention and pH for instance) despite the fact that BC is depleted of nutrients. Through this experiment, our study proves that pure BC alone cannot replace chemical fertilizers and deliver nutrients during a longer period of time.

4.2. Effect of BC loading and activation

Since pristine BC do not have the appropriate behavior to replace chemical fertilizer, another possibility has been explored. Several studies show that BC can be loaded with nutrients

through different ways: maceration with dissolved fertilizer (BC-NPK and BC-Urea), maceration in cow urine (BC-Urine) and activation by a co-composting process (BC-Compost). Those different ways and their consequences on nutrients dynamics were tested in this study.

4.2.1. Nutrient adsorption on BC

4.2.1.1. Adsorption capacity

During the enhancement process, BC adsorbs nutrients. However BC has a limited adsorption capacity. Langmuir isotherm coefficient (Q_0) indicates that the maximum amount of NO_3^- that BC can adsorb was around 68.9 mg/g of BC (Table 2). In the literature, the ratio between the equilibrium concentration in liquid phase and on BC is often below 1 and increases with the initial concentration (Wen et al., 2017; Aghoghovwia, 2018). In our study this ratio reaches 400. This ratio difference could be the consequence of the preparation of the NO_3^- solution. Indeed in most studies this solution is prepared with pure NO_3^- or NH_4^+ solutions. In this study a chemical fertilizer has been used to load BC. This allows us to be representative of the loading processes used in Burkina Faso. The BC surface was thus covered by NO_3^- but also by other nutrients from the fertilizer. It is important to notice that our experiment were carried out using higher NO_3^- concentration than in the literature. This could also induce a ratio difference.

This experiment demonstrates that a maximum loading of BC requires a huge amount of fertilizer, some of which remains in the solution and is not adsorbed on BC surface. We could thus recommend not to saturate BC in order to limit losses in solution.

4.2.1.2. Nutrients adsorbed on BC after loading

A BC:fertilizer ratio of 1 (v:v) has been chosen for the enhancement experiments. A comparison between the different total nutrients contents gives information about the efficiency of the enhancement process.

Maceration of BC with fertilizer or in urine induces a transfer of nutrients from the liquid phase to the solid phase (biochar surface and porosity). This is proved by the total nutrients contents of the different products (Table 3). The N, P, K and Mg contents are higher in BC-NPK than in pristine BC. This difference could be explained by the relocation of those nutrients from fertilizer to BC surface. BC-UREA also shows the same behavior with a high increase in N content in comparison to pristine BC.

P contained in URINE was not adsorbed by BC during the loading process: BC-Urine and pristine BC have the same P content (Table 3). BC-Urine contains less N than pristine BC, suggesting a release of N from BC during the loading process.

Globally P and Mg are easily transferred from the liquid part to the BC structure. Indeed almost 40% of P and almost 60% of Mg from NPK fertilizer in solution and 50% of Mg from URINE were adsorbed by BC during the loading process. However N and K are adsorbed at a lower rate. Only 16% of N and 22% of K coming from NPK fertilizer, 36% of N coming from urea and 23% of K coming from urine were adsorbed by BC during the process. This can be partially explained by the higher amounts of N and K in the fertilizer (respectively 135.61 mg/g

and 219.80 mg/g) compared to the other nutrients (Table 3). Moreover the initial concentrations of BC in N and K were already higher than those in P and Mg.

4.2.2. Impact of the enhancement on nutrients release

Enhancement processes allow BC to adsorb nutrients. Enhanced BC can thus become a new source of nutrients in soil (Schmidt et al., 2017). The BC's ability to release nutrients is determined by dividing the cumulated amount of nutrient released by the total initial content. The rate of growth gives information about the releasing rate of each component: the higher the coefficient, the faster the release.

Pristine BC releases almost 90% of its K content, 10% of its Mg content and less than 5% of its total P content (Figure 7). These results indicate the release dynamics of BC before being enhanced, with highly mobile K, and strongly retained Mg and P.

4.2.2.1. Releasing rate

BC's seem to release P and K at a lower rate than chemical fertilizer. As far as P is concerned, the major trend is that the releasing rate increases with the amount of P released. However, BC-Compost is an exception since it releases more P than pristine BC but at a lower releasing rate (Table 4).

BC-NPK and BC-Compost release approximately the same amount of Mg. However the releasing rate is higher for BC-NPK than for BC-Compost.

In terms of K release, BC-NPK has a different behavior than for the two other nutrients. Indeed its releasing rate is lower than in any other component, even BC-Compost. However no K seems to be adsorbed on BC during co-composting.

NO_3^- release shows a lower rate of growth for BC-Compost than for chemical fertilizer and BC-NPK.

4.2.2.2. Mineral enhancement

BC-NPK releases only 30 mg K/g of BC-NPK (30% of its total K content), which corresponds to the same amount of K released by pristine BC. That means that adsorbed K has not been released during the experiment. Mg release curves bring out that 90% of the BC-NPK Mg content are not released. Finally BC-NPK has a higher release potential for P than for any other nutrient. Indeed BC-NPK releases 80% of its total P content (Figure 7). That means that P has not been strongly adsorbed on BC during loading process.

Moreover a chemical fertilizer containing NO_3^- has been used to load pristine BC. This loading allowed BC-NPK to release around 14 mg NO_3^- /g of BC which is still more than pristine BC (Figure 5).

The differences observed between the dynamics of these nutrients could be caused by the way they are adsorbed on BC surface. Indeed, SEM/EDX elemental mapping shows that P and K are not always found together (Figure 9). The energy for the release could be higher for elements located in pores and thus enclaved in the BC porosity than elements located on BC

surface within pores. Their ionic radius could explain this phenomenon. Ionic radius of Mg^{2+} and K^+ are respectively 65 and 138 pm and ionic radius of P^{3-} is 212 pm (Hill et al., 2008). Thanks to their smaller ionic radius, Mg^{2+} and K^+ can be located in small pores and thus more retained.

Ionic charges of these ions may also justify varying behaviors. Mg^{2+} and K^+ are cations and P (whose form under alkaline conditions is HPO_4^{2-} (Weil et al., 2016)) is an anion. BC is known as being negatively charged because of functional groups formed at its surface (Lehmann et al., 2005). Covalent bonds are probably dominant between Mg or K and BC surface. PO_4^{3-} could be physically retained in BC porosity or chemically adsorbed thanks to calcic bonds since BC contains a lot of Ca.

4.2.2.3. Organic enhancement

BC-Urine releases more than 90% of its K content and almost 75% of its Mg content. The more important amount of Mg contained in urine could be one reason for this behavior.

Compared to pristine BC, BC-Compost releases 5 times more P and 2 times more Mg (Figure 6). That means that the co-composting process allows BC to be loaded with nutrients. However, no K seems to be adsorbed by BC during this process. NO_3^- is known as being part of the cortege of nutrients in compost (Kammann et al., 2015; Hagemann, Joseph, et al., 2017; Hagemann, Kammann, et al., 2017). That is why NO_3^- dynamics has also been studied for this enhanced BC. Experiment demonstrated the potential of a co-composting process to load BC with NO_3^- . Indeed the amount of NO_3^- released by BC-Compost is around 0.17 mg NO_3^-/g of BC since pristine BC released almost no NO_3^- (below the detection threshold).

The differences observed for BC-Compost could be explained by the formation of organo-mineral complexes on BC during co-composting (Joseph et al., 2013; Prost et al., 2013). An increase in BC organic carbon (C) content after co-composting has been observed in other studies (Prost et al., 2013; Kammann et al., 2015). Hence, the amount of nutrients adsorbed and the releasing rate could be impacted by the development of such complexes. Since cow urine is also an organic component, this mechanism could also have occurred during maceration with BC (it has not been investigated in this study). This could explain the more important amount of Mg adsorbed and released by BC-Urine.

4.3. Enhanced BC as a slow-release fertilizer

Enhanced BC's have obviously a lower releasing rate than chemical fertilizers. Indeed the computation of the rate of growth highlights the ability of BC's to release P and K more slowly than chemical compounds. A low releasing rate is something that slow-release fertilizers must fulfill: a too fast release induces significant losses in water and in atmosphere.

The cumulative amount of nutrients released is also an indicator for a good slow-release fertilizer. The goal of such a compound is to substitute chemical fertilizers. It would not be the case if it releases a too small amount of nutrients. BC-Urine seems to be the best component in terms of cumulative nutrients released. This enhanced BC releases far more Mg than the chemical fertilizer and almost 40% of the cumulative K released by the chemical fertilizer.

However, BC-NPK is the compound that releases the highest amount of P (around 30% of the cumulative amount of P released by the chemical fertilizer). BC-Compost do not release important amount of nutrients. However its application on field is often coupled with the application of compost which also contains a large cortège of nutrients.

5. CONCLUSION

The aims of the present work were to study (1) the dynamic of nutrient retention and release from enhanced biochar in order to highlight the ability of biochar to substitute chemical fertilizers; (2) the microscopic distribution of elements on biochar surface as a function of the duration of BC amendment in soil and after enhancement processes.

Two assumptions were made:

- Biochar remained in soil is partly oxidized and an accumulation of negative charges appears on its surface, increasing its ability to retain nutrients.
- Biochar enhanced by maceration in nutrient solution or activated by co-composting is loaded with nutrients that are progressively released.

Our results show that pure biochar cannot retain nutrients and make them available for plants over two seasons of culture. The nutrient content of biochar is rapidly released (during the first months of cultivation). The consequence of this fast release is that biochar becomes depleted of nutrients. Biochar oxidation does not seem to have an effect on nutrients retention: biochar cannot retain nutrients from further amendments (measured on two seasons of cultivation).

Enhancement processes were tested to find a way to load biochar with nutrients. Biochar was enhanced by chemical fertilizer, by cow urine and through activation by a co-composting process. Among all types of enhanced biochar, results suggest that BC-Urine is the best one in terms of Mg and K release. BC-NPK has the best release capacity in terms of P release. Moreover, our work demonstrates that biochar has a high capacity to adsorb N: BC-Urea and BC-NPK both adsorbed important amounts of N. The release of N still needs to be explored.

We can then conclude that biochar is a good support for a slow-release fertilizer when it is enhanced by cow urine or P fertilizers. Other ways of enhancement could be explored such as maceration in human urine. This study used maceration of biochar during 48 hours with a nutrient solution to load biochar. However bentonite could be added to the process (Joseph et al., 2013). This could potentially increase the amount of nutrients adsorbed by biochar. Furthermore nutrients release could be different.

It is necessary to keep in mind that this lab experiment studied the nutrients release after 24 to 32 hours of extraction with a permanent contact with water. Soil columns experiments should be carried out to study the behavior of enhanced biochar in more field-like conditions.

APPENDIX

1. APPENDIX 1: STATE OF ART

1.1. Environmental and economic issues of fertilizers

Agriculture is facing a major challenge in term of efficient fertilizer use. The fertilizer use efficiency is currently not higher than 40 % (González et al., 2015). Those compounds being very expensive, it is primary to enhance it. Losses of nitrogen (N) are mainly caused by volatilization, biological activity (denitrification) and water activity (erosion, lixiviation and runoff). It seems that retention of ammonium (NH_4^+) and nitrate (NO_3^-) (which are the two forms of N involved in the leaching process) is correlated to soil texture. Clay particles have a better retention capacity of NH_4^+ than sandy ones (Saraswathy et al., 2007).

1.2. Concepts of biochar and slow-release

1.2.1. Definitions and properties of biochar and slow-release

Biochar is a carbon-rich product made by pyrolysis at high temperature of organic matter as for instance culture residues. It is composed of condensed aromatic groups that are partially responsible for its high recalcitrance in soil. Biochar protection through silicon accumulation on its surface, which depends on pyrolysis temperature, also seems to play a role in biochar recalcitrance (Guo et al., 2014). Functional groups are fixed along those aromatic groups and interact with nutrients (Glaser, 2007). This compound has been studied for many of its aspects. Indeed, biochar was recognized as being an efficient tool for extracting antibiotics from animal residues thanks to high specific surface and hydrophobic surfaces (Mitchell et al., 2015). Its ability to sorb metals was explained through different mechanisms such as complexation, reduction or cation exchanges at the biochar surface (Li et al., 2017).

Pre-Columbian populations had areas with rich soils called Terra Preta or Dark Earth. Scientists identified a lot of charred organic materials in these soils that were initially poor and highly acidic. Charcoal was put into the soil and its characteristics allowed them to produce enough to feed themselves (Glaser, 2007). The use of unsuitable methods for increase the productivity of soils causes the depletion of the soils at long term. Soil scientists are looking for a way to increase the productivity of poor soils without depleting it. The production of biochar from green residues could be a way to create soils similar to the ones of Terra Preta. Thanks to previous studies it is now well known that biochar brings positive aspects to highly weathered agricultural soils (Glaser, 2007; Jeffery et al., 2011; Crane-Droesch et al., 2013).

Biochar can be made from different types of biomass such as rice or bamboo straws (Archanjo et al., 2017), hardwood or coniferous wood chips (Schmidt, Kammann, et al., 2014) or from cotton straws (Burgeon, 2017). The use of waste feedstock is an ideal way to produce biochar while keeping a sustainable organic matter cycle. After harvesting, biomass is introduced in an oven where pyrolysis takes place. Many ways of pyrolysis exist and will have specific impacts on the produced biochar. Chemical structure of biochar is composed of condensed aromatics and functional groups resulting from a partial oxidation (Glaser, 2007). The type of functional groups depends on the pyrolysis temperature. Yuan (2011) demonstrated that the amount of COOH and OH groups decreases while the pyrolysis temperature increases (Yuan et al., 2011). This temperature depends on the oven type used for the pyrolysis. Kon-Tiki oven will heat biomass at a temperature around 700 °C (Archanjo et al., 2017; Schmidt et al.,

2017) while a top lift updraft gasifier drum oven (TLUD) will have a mean temperature of 450 °C. Pireg reactor (Hagemann, Joseph, et al., 2017) and Schottdorf-type reactor (Schmidt, Kammann, et al., 2014) also have a heating temperature around 700-750 °C.

The first property of biochar that can be helpful for agricultural lands is its role in increasing the soil cation exchange capacity (CEC). Biochar is initially barely charged and by adding this compound into the soil, the amount of negative charges increases, allowing cations like calcium (Ca^{2+}) and magnesium (Mg^{2+}) to get fixed and become available for plants (Lehmann et al., 2005).

Secondly biochar has a buffer effect concerning soil pH. Indeed, the application of biochar on acidic soils increases their pH through a liming effect (Jeffery et al., 2011). Nutrients availability is strongly influenced by the acid-base character of soils. At some pH values, nutrients can be less available. On the other hand, other cations, which can be toxic at high concentrations, become more available.

Finally, thanks to its high porosity, biochar can enhance soil water retention capacity. This aspect is closely related to the decrease of NO_3^- leaching while using biochar in soils. This can be explained by the fact that NO_3^- ions can be kept in biochar thanks to hydrogen bonds with hygroscopic water close to the biochar surface (Kammann et al., 2015).

A slow-release fertilizer is defined as a fertilizer containing a plant nutrient in a form which delays its availability for plant uptake and use after application, or which extends its availability to the plant significantly longer than a reference 'rapidly available nutrient fertilizer' such as ammonium nitrate or urea, ammonium phosphate or potassium chloride (Trenkel, 2010). This avoids important lixiviation of NO_3^- fertilizer and thus enhance their efficiency (Richards et al., 1993). Indeed current efficiency of N fertilizers is about 30-40 % (González et al., 2015). Moreover slow-release fertilizers diminish environmental issues about presence of NO_3^- in water (Li et al., 2016). Biochar seems to be a good support in the fabrication of slow-release fertilizers because of its important specific surface.

1.3. Effect of biochar on nutrients cycling

Application of biochar into soils has an impact on nutrients cycling. First of all, biochar contains nutrients which will be released in the soil solution. Furthermore, biochar has an intrinsic ability to retain nutrients.

Biochar composition depends on the plant from which it comes but also on the mean of production. The temperature during the pyrolysis process has an influence on the nutrient composition of biochar. Volatilization of nutrient during the heating is one of the causes for the loss of nutrients. Nutrients volatilization temperature vary from one to another. While N will be volatilized at a temperature around 400 °C, phosphorus is volatilized at approximately 770 °C and calcium at 1400 °C (Neary et al., 2005). When biomass is pyrolyzed at high temperature, N in biochar is mainly represented by NO_3^- because of the volatilization of ammonia (NH_3). If the pyrolysis temperature is low the main form of N will be NH_4^+ (DeLuca et al., 2009). At

high temperature of production phosphorus crystallizes with magnesian, ferric and calcic-phosphate (Zornoza et al., 2016).

In addition to its intrinsic nutrients, biochar has an influence on nutrients dynamics in soil (Figure 14).

Firstly biochar seems to increase the biological fixation of dinitrogen (N_2) (Mia et al., 2014). This kind of fixation is due to a symbiosis between legumes and bacteria which possess the nitrogenase enzyme and are located in nodules on plant roots (Herridge et al., 2008). Mia et al (2014) reviewed some mechanisms, which can possibly explain this positive impact of biochar on N_2 fixation, such as the increase of pH or the increasing nodulation. The presence of biochar in soil allows the limitation of NH_3 emissions, knowing that NH_3 emissions are the main factor of N-based fertilizers losses in agricultural soils (Macnack et al., 2013). The mechanisms driving these effects are the adsorption of NH_3 (Clough et al., 2013) and NH_4^+ (Chen et al., 2013) on biochar. NH_4^+ adsorption on biochar has another consequence: the decreasing amount of NH_4^+ available for nitrifying bacteria, which in turn results in a lower rate of nitrification in soils amended with biochar (Taghizadeh-Toosi et al., 2012). However, the activity of such microorganisms could be altered by the physico-chemical properties of the soil, which could have been modified by the addition of biochar, such as the pH (Gul et al., 2016). A decrease in nitrous oxide (N_2O) emissions is also noticed in soils amended with biochar. N_2O is a greenhouse gas, emitted when the denitrification process is not completed. This process results from the activity of the *nosZ* gene, which transforms N_2O into N_2 . That phenomenon mostly occurs when there is a lack of aeration in the soil. The decrease in N_2O emissions is caused by two mechanisms. The first one is the immobilization of NO_3^- by biochar, making NO_3^- not available for denitrifying bacteria (Zheng et al., 2012). The second one is the increasing bulk porosity of soils, because of the high porosity of biochar (Gul et al., 2015). One other reason for the decreasing amount of N_2O emitted in amended soils is the enhancing of the expression of the *nosZ* gene by the biochar (Harter et al., 2014). Since N_2O can be retained in micropores in soil (Maag et al., 1996) biochar porosity could also play a role in the longer sequestration of N_2O in soil, making microorganisms activity possible during a longer period.

The biochar has an impact on the phosphorus cycle as well. Phosphorus becomes available for plants when its organic form is hydrolyzed into orthophosphate. This hydrolysis is performed by microorganisms using an enzyme (alkaline phosphatase). Studies show that the application of biochar increases the amount of microbial biomass carbon (Lehmann et al., 2011), which is correlated with the increase of the P hydrolysis rate (Masto et al., 2013). The phosphorus use efficiency seems to be improved by the addition of biochar in soils, regardless of the source of P.

Biochar application on a Dutch field induces an increase in phosphate (PO_4^{3-}) and potassium (K) content in the soil (van de Voorde et al., 2014).

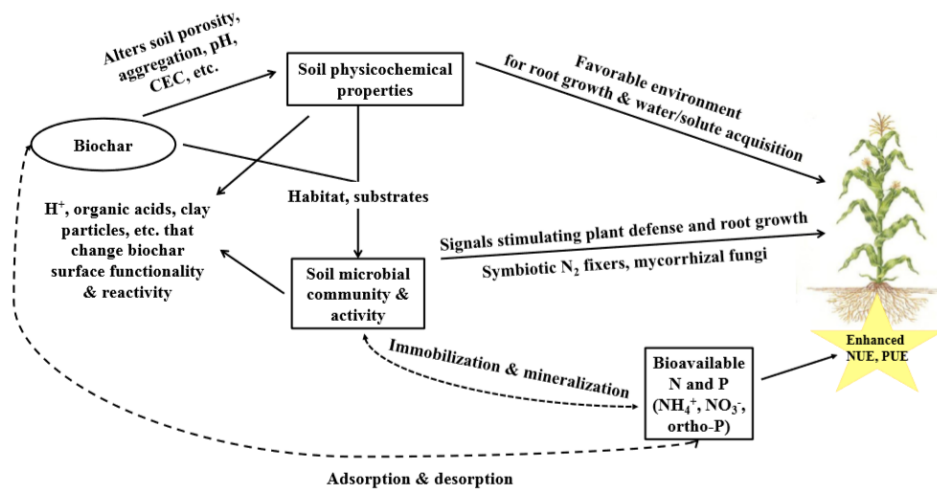


Figure 14. Conceptual model of the relation between biochar, soil and microorganisms in biogeochemical terms (Gul et al., 2016)

Biochar size influences nutrients release dynamics. Smaller biochar particles tend to release a higher amount of nutrients such as potassium (K), phosphorus (P) and magnesium (Mg) (Angst et al., 2013). That can be explained by the larger surface in contact with the extraction solution during the experiments. Important differences have been noticed between the amount of nutrient extracted from smaller particles, and from larger particles (Figure 15).

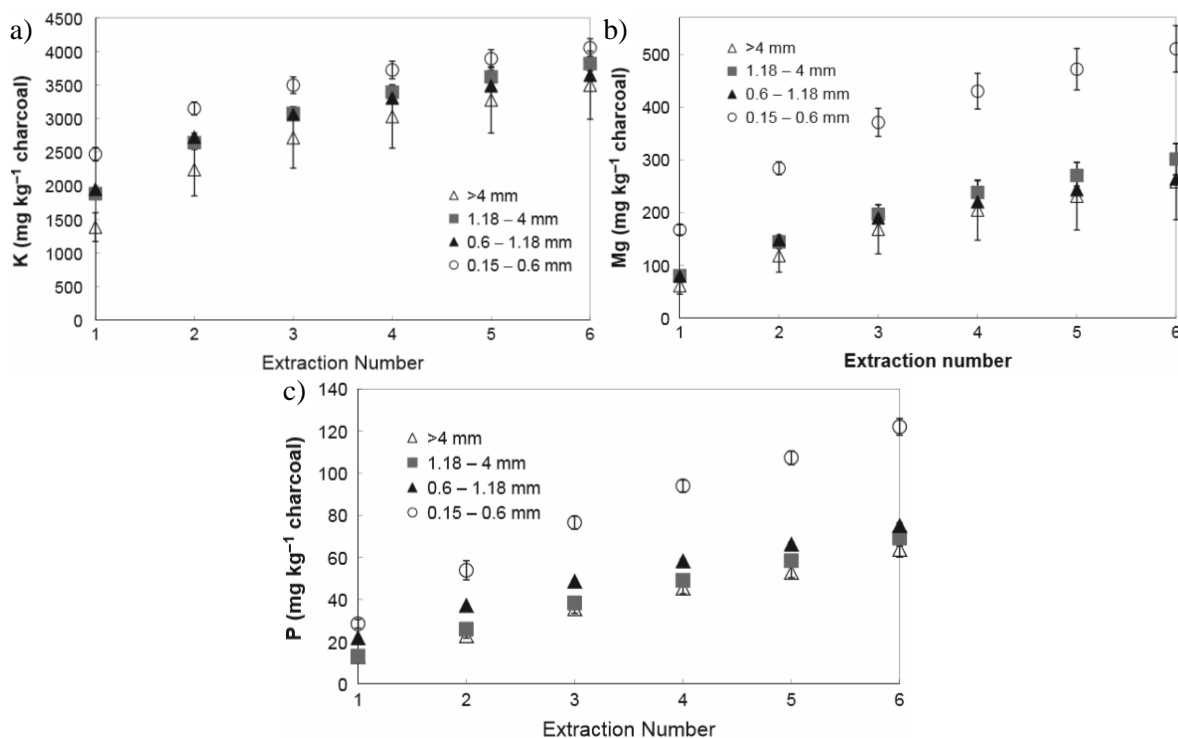


Figure 15. Serial extractions of a) potassium, b) magnesium and c) phosphorus from biochar as a function of the biochar particles size (Angst et al., 2013)

1.4. Organic coating on longtime charcoal

Biochar added in soils is oxidized, resulting in the formation of functional groups, at the biochar surface at the beginning of the process, and then near the core of the particle (Lehmann

et al., 2005). Those functional groups allow biochar to enhance its cationic exchange capacity. Nutrients can then be fixed at biochar surface and on pores walls.

Hardy (2017) analyzed organic coating on longtime charcoal, which remained in soils for different periods of time (Hardy et al., 2017). An increase in silicon (Si), aluminum (Al) and iron (Fe) content with cultivated time was noticed as well as an increase in oxygen (O), suggesting that oxygen is the element on which those three inorganic elements can be fixed. Indeed carboxyl groups get formed at the biochar surface with time, and are highly involved in the stabilization of organic matter process (Kramer et al., 2012; Kleber et al., 2015). However, N content does not seem to vary with the cultivation time. This precipitation of organo-mineral associations (Figure 16) can happen at the biochar surface but also in pores (Hardy et al., 2017) which offer an important specific surface. Organic coating seems to be formed by organo-mineral associations whose size varies between few nanometers and more than 50 nm (Archanjo et al., 2017).

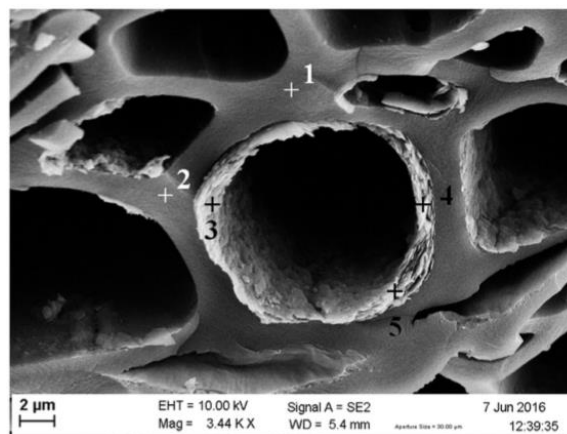


Figure 16. SEM photograph of inorganic precipitates on biochar remained in soil during 200 years. (Hardy, 2017)

1.5. Biochar enhancement

Biochar can be enhanced by several methods of activation and loading. Activation consists in modifying biochar surface structure to obtain new functional groups that can in turn capture nutrients and make them available for plants with a low need of uptake energy (Joseph et al., 2013). Cha (2016), Jibril (2008) and Gu (2013) activated biochar by chemical reactions with KOH or acids (Jibril et al., 2008; Gu et al., 2013; Cha et al., 2016). Loading processes consist in the adsorption of nutrients at biochar.

In a context of cooperation and help to producers in emerging countries, another way of thinking must be developed. Schmidt (2017) tried to use different affordable and handy sources of loading (Schmidt et al., 2017). He proved that those sources of enhancement were efficient to increase yields. In enhancement processes, the involved nutrients can be fixed at the biochar surface. Indeed, biochar alone cannot meet plant nutrients requirements. During plant growth, C and N are the only elements produced by the plant. Those elements can be used by plants but they need other nutrients that must be added to the soil (Glaser et al., 2012). Enhancement is a way of adding nutrients on biochar which will then be released for plants.

1.5.1. Organic enhancement

1.5.1.1. Co-composting

A first option is the co-composting process during which biochar is mixed with compost during the entire composting time. A symbiosis occurs between compost and biochar: bacteria and micro-organisms that are involved in composting process alter biochar which acts like a residence place for those micro-organisms. Compost becomes then more broken down and biochar holds up nutrients like N that can be available for plants when added into soil (Hagemann, Joseph, et al., 2017). From a chemical point of view, high temperature in compost can enhance the oxidation of biochar and thus its capacity to retain nutrients (Thies et al., 2009).

Biochar:compost ratios are fluctuant in the literature. While Hagemann (2017) used a volume ratio of 4 %, Khan (2014) tried different ratios between 5 and 10 % and co-composting process of Schmidt reaches a ratio of 30 % (Schmidt, Kammann, et al., 2014; Schmidt et al., 2017). Biochar is incorporated in compost at the beginning of the process (Hagemann, Joseph, et al., 2017; Schmidt et al., 2017). The duration of the process is variable and depends on the environment, on the protocol but also on the nature of the compost. In greenhouses, with 20-50 °C and with a rolling two or one times a week, twelve weeks are needed (Khan et al., 2014). Archanjo (2017) incorporated biochar to compost and manure during only 45 and 63 days (Archanjo et al., 2017).

Schmidt (2014) demonstrated the absence of relevant effects of co-composted biochar on calcareous soils under temperate climate (Schmidt, Kammann, et al., 2014). However it seems that this use of biochar induces decreasing emissions of NH₃ in atmosphere and increases nitrification (Khan et al., 2014). The decrease in NH₃ emissions is probably caused by the high specific surface of biochar and its high capacity to adsorb NH₄⁺ and absorb NH₃ (Agyarko-Mintah et al., 2017).

Using FT-IR analyzes, Hagemann (2017) showed that peaks of co-composted biochar are a combination of those of pristine biochar and of compost alone (Hagemann, Joseph, et al., 2017). He made then the hypothesis that biochar nanoparticles interact with organic matter of the compost by hydrogen bonds. Those interactions form an organic coating at the surface of biochar. Oxidation of biochar surface induces the formation of functional groups, which facilitate the formation of an organic coating. This coating seems to protect biochar from degradation. It could be the reason for the high recalcitrance of biochar in soil with years. Hagemann (2017) designated organic coating as being the main way of alteration of biochar in soils (Hagemann, Joseph, et al., 2017).

However Archanjo (2017) did not find a lot of C/O functional groups on biochar surface (Archanjo et al., 2017). He observed Fe oxides (hematite and magnetite) and organo-mineral associations on few particles of biochar. A higher aromaticity has been observed next to those Fe oxides.

1.5.1.2. Use of cow urine

Organic and mineral fertilizers can be used to load biochar. Cow urine was used by Schmidt and they demonstrated that this kind of amendment enhances the crop productivity, so that yields were consequently higher after this treatment (Schmidt et al., 2017).

Schmidt used biochar enhanced with urine and proved that yields were higher after this treatment, even with a low dosage application of less than 1 t.ha⁻¹ and were higher than an optimal level obtained in conventional farming. He compared that treatment with biochar alone and urine alone treatments that did not give better results (Schmidt et al., 2015).

1.5.2. Mineral enhancement

Other studies showed the adsorption capacity of biochar through the addition of NH₄⁺ (Wen et al., 2017), diammonium phosphate and potassium chloride (Qian et al., 2014), or urea (Joseph et al., 2013; Manikandan et al., 2013) and Manikandan demonstrated that new chemical functions appeared at biochar surface after activation (Manikandan et al., 2013). It appears that N from mineral sources interacts mainly with carboxyl groups at the charcoal surface to form stable components such as amides or nitriles (Bimer et al., 1998). Such enhanced charcoal can then be able to remove sulfur components from soil by oxidation (Bimer et al., 1998).

Schmidt (2017) applied biochar enhanced with mineral fertilizer with a low-dosage application at the root zone of the plant. This treatment gives higher yields in comparison with application of mineral fertilizers without biochar support (Schmidt et al., 2017).

1.5.2.1. NPK fertilizer

Enhancement of biochar with NO₃⁻ fertilizers has been used in several studies. However, enhancement conditions and biochar:N ratio were highly variable.

Schmidt and Hagemann macerated biochar with NO₃⁻ fertilizer solution (Hagemann, Kammann, et al., 2017; Schmidt et al., 2017). However, their techniques were different in terms of duration of maceration since Schmidt let exchanges occur between biochar and NO₃⁻ solution during one hour and Hagemann during one night. The amount of N in contact with biochar also differs from one to another. Hagemann (2017) used a concentration of 1.25 g of N per kg of biochar and Schmidt (2017) does not precise the concentration. Wen (2017) studied the adsorption of NH₄⁺ on biochar, using a concentration of 1.25 g of NH₄⁺ per 0.25 g of biochar (Wen et al., 2017). However, after this maceration, Wen (2017) added a microwave irradiation step. It seems that the enhancement of biochar with NPK through the formation of granules can also give results (Qian et al., 2014). In this study bentonite is added to the solution and the reaction between components lasted four weeks.

While Hagemann (2017) and Schmidt (2017) do not rinse or dry their products of activation, Wen (2017) rinsed biochar with distilled water and dry it at 40 °C.

Conclusions have already been drawn by previous studies about the use of biochar loaded with NPK. According to them, when applying enhanced biochar treatments, the crop yields are only equal or higher (depending on other adjuvants to the amendment system) than

these obtained with conventional chemical fertilizers. This kind of amendment has an impact on greenhouse gases emissions as well, as an important reduction of N₂O and methane (CH₄) emissions were detected (Qian et al., 2014). In terms of soil properties, enhanced biochar seems to increase water content and water retention of soils. N adsorbed on biochar during activation process acts like a source of available nutrients for plants during 20 days, proving the slow release capacity of enhanced biochar (Figure 17). However this duration of release can be enhanced by microwave irradiation (Wen et al., 2017).

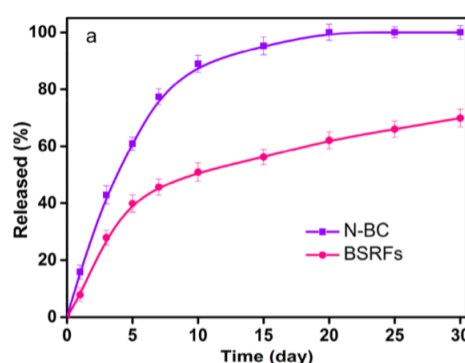


Figure 17. Releasing curves of biochar loaded with N (N-BC) and biochar loaded with N and then irradiated by microwave (BSRFs) over time (hours). (Wen, 2017)

1.5.2.2. Urea

Loading by addition of urea is also a spread method of biochar enhancement. Maceration is the major technique to create an enhanced biochar with urea. It is important to notice that urea is a component that can be transformed into several N-reagents during a maceration process under high temperature (Bimer et al., 1998) (Figure 18). It is thus difficult to identify the exact reactions that happen during an activation with urea.

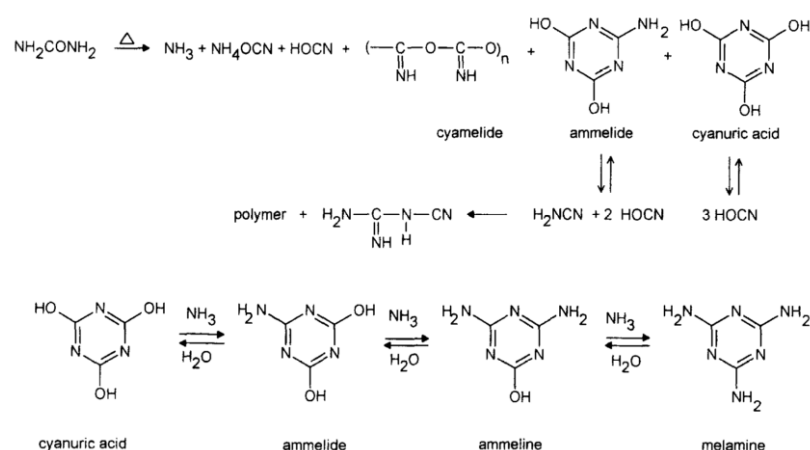


Figure 18. Derived forms of urea produced during an activation under 300 °C (Bimer et al. 1998)

When the urea is hydrolyzed by the urease enzyme, it becomes NH₄⁺. NH₄⁺ can then be nitrified, resulting in the production of NO₃⁻, which can in turn be lixiviated. Biochar can play a role in this process by protecting urea from this enzyme (González et al., 2015). This could

possibly be the reason of a slower release of NO_3^- when urea is absorbed on biochar during an activation process.

Different concentrations can be found in the literature. Manikandan (2013) used 10 g of urea with 10 g of biochar while Gonzalez (2015) put two times more biochar than urea. Dissolution of urea can be done before adding biochar to the solution (Manikandan et al., 2013; Schmidt et al., 2017) or at the same time (González et al., 2015).

Maceration can be done on a hot plate (González et al., 2015) but also during a longer duration without any source of heating (Manikandan et al., 2013; Schmidt et al., 2017). In some studies, the biochar resulting from the maceration is dried in an oven at 65 °C to remove humidity (Manikandan et al., 2013). Gonzales (2015) studied the encapsulation of urea-impregnated biochar with polymers in comparison with biochar impregnated with urea without encapsulation (González et al., 2015). He found out that N-NO_3^- leaching was more important for the non-encapsulated biochar than for the encapsulated one. However, the amount of N-NO_3^- leaching was still lower than the one obtained with urea alone without any support.

2. APPENDIX 2: Laboratory analyzes

<i>Paramètre</i>	<i>Méthode d'analyse utilisée</i>
<i>Granulométrie</i>	Méthode par sédimentation - Méthode de la pipette dérivée de la norme NF-X 31-107 Les différentes fractions sont les suivantes : les sables grossiers ($> 200 \mu\text{m}$), les sables fins ($> 50 \mu\text{m}$ et $\leq 200 \mu\text{m}$), les limons grossiers ($> 20 \mu\text{m}$ et $\leq 50 \mu\text{m}$), les limons fins ($> 2 \mu\text{m}$ et $\leq 20 \mu\text{m}$) et les argiles ($< 2 \mu\text{m}$). Elles sont exprimées en % par rapport à la terre sèche décarbonatée.
<i>pH_KCl</i>	Rapport volume/volume : 1/5 (mise en solution avec KCl 1N) – Détermination au pHmètre Norme NF ISO 10390
<i>pH_H₂O</i>	Rapport volume/volume : 1/5 (mise en solution avec H ₂ O déminéralisée) – Détermination au pHmètre Norme NF ISO 10390
<i>Carbone organique</i>	Dosage du Carbone organique par combustion sèche (analyse élémentaire) après décarbonatation avec HCl des échantillons carbonatés Méthode dérivée de la norme ISO 10694
<i>Taux d'humus</i>	Teneur en Carbone organique (%) * 2 (Prybil, 2010 – Delcour & el Attar, 1964)
<i>Eléments échangeables : Mg, K</i>	Extraction à l'acétate d'ammonium 0,5N-EDTA 0,02M, pH 4,65 (rapport masse/volume : 1/5) Dosage des éléments par spectrophotométrie d'absorption atomique dans la flamme air/acétylène Méthode dérivée de la norme NF X 31-108
<i>Phosphore échangeable</i>	Extraction à l'acétate d'ammonium 0,5N-EDTA 0,02M, pH 4,65 (rapport masse/volume : 1/5) Dosage du P au spectrophotomètre UV visible - Méthode colorimétrique au bleu de molybdène à la longueur d'onde de 880 nm
<i>Azote total Kjeldahl</i>	Méthode dérivée de la norme NF ISO 11261 – Méthode de Kjeldahl modifiée

Source :

Le Brabant Wallon : Pôle Laboratoire d'Analyses Agricole.

<http://www.brabantwallon.be/bw/entreprendre-travailler/agriculture-1/pole-laboratoires-d-analyses-agricoles/> [viewed on July 28, 2018]

3. APPENDIX 3: Cow urine harvesting



4. APPENDIX 4: Biochar aggregation with soil in Koumbia experimental parcels



5. APPENDIX 5: Filtration setup for the serial extractions



6. APPENDIX 6: Mineralization and perchloric acid attack

Mineralization (Kjeldahl method) of biochar and fertilizer for the dosage of total N (a) and heating with perchloric acid for the dosage of total P (b).

a)



b)



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