Biochar-compost mixtures : interactions and impact on carbon sequestration and soil fertility

Marie-Liesse Aubertin

Sorbonne Université

Ecole doctorale « Science de l'Environnement d'Ile-de-France » (ED 129)

Laboratoire iEES Paris / Equipes FEST et PSG

Biochar-compost mixtures: interactions and impact on carbon sequestration and soil fertility.

Par **Marie-Liesse AUBERTIN**

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Dirigée par **Cornelia RUMPEL**

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Composition du jury :

Arnould SAVOURE, Professeur, SU (IEES), Paris	président du jury
Jens LEIFELD, Chargé de recherche, Agroscope, Zurich	rapporteur
Safya MENASSERI, Maître de conférences, AgroCampus Ouest (SAS), Rennes	rapportrice
Samuel ABIVEN, Professeur, ENS (Laboratoire de Géologie), Paris	examinateur
Katell QUENEA, Maître de conférences, SU (METIS), Paris	examinatrice
Cornelia RUMPEL, Directrice de recherche, CNRS (IEES), Paris	directrice de thèse

« Si un jour tu tombes, je serai là… »

Le sol

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Contents

List of abbreviations

ADEME	: agence de l'environnement et de la maîtrise de l'énergie
C	: carbon
CEC	: cationic exchangeable capacity
DOC	: dissolved organic carbon
$\delta^{13}C$	: C isotope signature
EC	: electrical conductivity
FID	: flame ionization detector
FTIR	: Fourier transformed infrared spectroscopy
GHG	: greenhouse gas emissions
HC	: hydrocarbons
IPCC	: intergovernemental panel on climate change
MINC	: mineral carbon
MIRS	: mid-infrared spectroscopy
N	: nitrogen
OC	: organic carbon
OM	: organic matter
PC	: pyrolysable organic carbon
PCA	: principal component analysis
PLSR	: partial least square regression
POM	: particulate organic matter
RC	: residual organic carbon
SOM	: soil organic matter
SOC	: soil organic carbon
TC	: total carbon
TGA	: thermogravimetric analysis
TOC	: total organic carbon
TN	: total nitrogen

General introduction

The Special Report on Global Warming of 1.5 °C from the Intergovernmental Panel on Climate Change in 2018 (Masson-Delmotte et al. 2018) states that limiting global warming up to 1.5 °C as compared to the preindustrial period, would require to reach 'net zero' human-caused emissions of carbon dioxide (CO_2) by 2050. This ambitious objective implies (i) to drastically reduce anthropogenic greenhouse gas (GHG) emissions and (ii) to balance any remaining emissions by removing CO_2 from the air. The latter involves the increase of CO_2 sinks, through the development of negative emission technologies (NET). Soil, and in particular cropland soil, represent a high potential for carbon (C) sequestration (Fuss et al. 2018; Amelung et al. 2020). When applied to soil, biochar, the solid residue from biomass pyrolysis (Lehmann and Joseph 2015), has useful negative emission potential that further increases C sequestration in soil (Smith, 2016).

The « 4 per 1000 » initiative was launched in 2015 at the COP 21 to set up actions to increase C sequestration in soils. This initiative highlights that soil (organic) C sequestration may contribute not only to climate mitigation, but also to food security by increasing soil sustainability (Rumpel et al. 2018). Indeed, maintaining the food security is a major issue in the context of an increasing world population, and it would require the increase of food production relying on soils. Application of organic amendments have widely been proven to increase soil quality due to the diversification of C sources, but also as a source of nutrients (Li et al. 2021). In spite of proven interest of biochar on soil quality, especially through its high C stability and water retention capacity, other organic amendments such as compost may additionally bring more labile and diversified organic matter to soil, thereby enhancing soil agronomic properties to a greater extent.

Both biochar and compost are produced from organic wastes, thus contributing to circular economy, another major issue in the context of increasing waste production. The two products do not necessarily compete for the same resources, as organic wastes can be separated into materials appropriate for pyrolysis and composting. Indeed, compost is ideally made from moist and nutrient-rich materials, whereas biochar is ideally made from dry porous materials with low nutrient contents (Steiner et al. 2015). Both materials are present at compost platforms, while moist nutrient materials are used for composting, non-compostable porous material is refused in the composting process. Production of biochar at the compost platform might be a way to add value to compost refuses. In the spirit of circular economy both materials may be used from soil amendment and joint application of biochar and compost on soil could enable the recycling of complementary organic wastes.

The combined soil application of biochar and another organic amendment such as compost, were found to presents benefits to soil quality and crop production (e.g. Agegnehu et al. 2017; Agegnehu et al. 2016a; Z. Zhou et al. 2022). In a financial point of view, applying biochar is the most expensive, with several thousand euros per hectare, while composts is made from waste products without energy-intensive production processes (Siedt et al. 2021). Therefore, mixing biochar with a low cost-production and compost, would reduce the costs of biochar application. The addition of biochar into compost by the composting platform may be a way to valorize vegetal biomass that is generally not highly valued by the composting process, such as compost refusal or organic wastes from local industries. It may also increase the competitivity of the final product by improving the ability of compost to increase soil fertility and by increasing the carbon in soil in a sustainable way. The Ph.D. project took part to a FUI (Fond Unique Interministériel) project, BIOCHAR 2021, animated by ETIA (Evaluation Technologique, Ingénierie et Applications) group, which aimed to test the interest of improving compost with biochar. Mechanisms driving biochar-compost interactions and their impacts on C sequestration are still far from being understood and therefore deserve further investigation. Aim of the thesis was to examine the mechanisms of biochar-compost interactions and their effect regarding (i) the C outputs through mineralization, leaching and transport, and (ii) the N retention and plant growth, through different time scales.

After a general state of the art, this work is divided into three parts. The state of the art describes current knowledges about the main processes driving the C dynamic in soil, makes a comparison of biochar and compost characteristics and describe the current knowledge about their interaction on the C dynamic. Then, the first part focuses on biochar-compost interactions that may occur during their blending, using thermal and spectroscopic analysis. The second part investigates the biotic biochar-compost interactions as mixed without soil on the biological stability of C during 1-year under controlled conditions and on biomass production. This chapter also examines the influence of artificial ageing. The third part investigates the biochar-compost interactions on the particle and N retentions during 26 months under field conditions, using isotope and the litterbag techniques. Finally, the work ends with a general discussion where all conclusions are compared to each other and to the literature, and proposing general perspectives of the work.

CHAPTER I

State of the art: Compost and biochar as complementary organic amendments and their interactions

Chapter I – State of the art: Compost and biochar as complementary organic amendments and their interactions

1 Organic amendments may improve carbon sequestration and soil fertility

1.1 Organic amendments are used to improve soil quality

1.1.1 Soil organic matter as a key-component for soil quality

Soil is a dynamic natural living system containing solids, water and air, and providing a wide diversity of ecosystem services (Hartemink 2016), that can be divided into four main categories: provisioning, regulating, supporting and cultural (Adhikari and Hartemink 2016). Up to now, focus in the literature has been mainly put on provisioning and regulating ecosystem services (Adhikari and Hartemink 2016). Among the regulating services, carbon (C) sequestration attracted considerable attention, as the ability of soils to store carbon may prevent or at least delaying its release in the atmosphere (Baveye et al. 2016) and may be associated with greater crop yields (Oldfield et al. 2019). Soil may store about 2000 Pg C, which is lower than C stocks from oceans and higher than in the atmosphere and plant biomass (Janzen 2004) (Fig. 1).

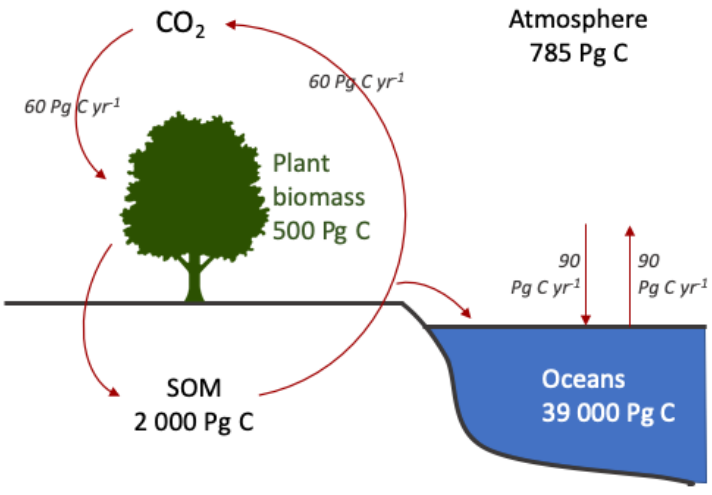

Figure 1 Carbon stocks and flows (adapted from Janzen 2004). 1 Pg = 1 * 1015 g.

Soil organic matter (SOM) constitutes 1-10 % of soil and is composed of 95 % of dead OM and 5 % of living organisms (Calvet et al. 2011) (Fig. 2). These proportions depend on soil type and may vary with soil depth. SOM originates from the decomposition of vegetal or animal biomass, which allows the

development of roots and soil microorganisms such as bacteria, fungi and micro-fauna. As organic carbon (OC) is a major component of SOM, OC analysis is commonly used to assess the quantity of SOM, using a conventional conversion factor of 1.724, although in some cases other factors such as 2 would allow for more accurate assumption (Pribyl 2010). Due to its strong enrichment in OC, SOM was found to thus play an key role in the soil C storage function, especially when stored in subsoils (Rumpel and Kögel-Knabner 2011). Furthermore, SOM also represents one of the most frequently used indicators for soil quality and agro-ecosystems fertility (Manlay et al. 2007; Bünemann et al. 2018). In data collected from 62 reviews on soil quality assessment approaches, total organic matter/carbon was the most frequently proposed soil quality indicator, as mentioned in 90 % of reviewed indicator sets (Bünemann et al. 2018). Soil quality can be defined as "the capacity of a soil to function within ecosystem boundaries to sustain biological productivity, maintain environmental quality, and promote plant and animal health" (Doran and Parkin 1994).

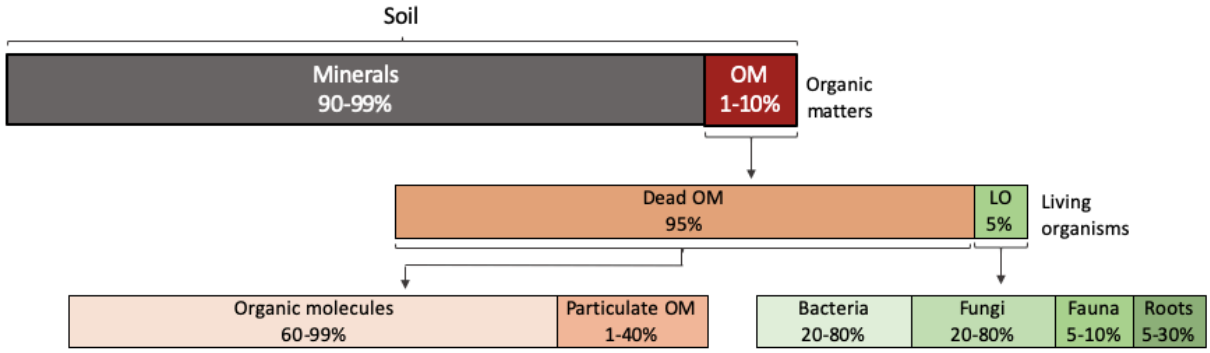

Figure 2 Soil organic matter: type and indicative mass proportions (adapted from Pellerin et al. 2020 and Calvet et al. 2011).

1.1.2 Organic amendments as soil organic matter sources

A wide diversity of organic amendments

Nowadays, the majority of the world's soil resources are in only fair, poor or very poor condition, and the most significant threats to soil function at the global scale are soil erosion, loss of soil organic carbon and nutrient imbalance (Montanarella et al. 2016). In a recent review, Chen et al. (2018) concluded that the use of organic amendments would increase the resilience of the agronomic systems, offering a greater buffering effect when conditions are less favorable. Furthermore, organic amendment has been evidenced as a good solution for rapidly accelerating soil regeneration processes and hence land reclamation, due to its positive effects on multiple soil properties (Larney and Angers 2012).

Organic amendment can be defined as any materials from plant and/or animals origins that are added/or incorporated in to the soil for the improvement and/or replacement of physical, chemical and biological properties of soil and in turn make the environment suitable for production and productivity (Aytenew

and Bore 2020). They can be subjected to specific treatment previously to their soil incorporation, resulting in a variety of organic materials, whose most common types include animal and green manure, compost, sewage sludge, municipal biosolids and biochar (Table 1) (Goss et al. 2013; Scotti et al. 2015; Sarkar et al. 2017).

Table 1 Organic amendments commonly used in agriculture (synthesized from Goss et al. 2013; Scotti et al. 2015; Sarkar et al. 2017).

Type	Feedstock	Treatment
Animal manure	Faeces, urine and animal bedding	Stacking and turning to promote partial aerobic and anoxic decomposition for surface and deeper layers, respectively
Green manure	Crop residues	-
Compost	Green wastes, municipal waste, animal manure	Aerobic decomposition
Sewage sludge	Residue from waste water treatment	-
Municipal biosolids	Residue from waste water treatment	Reduction of water content and further treatment to reduce pathogens and volatile organic matter
Biochar	Plant residues, animal manure	Thermal decomposition (pyrolysis)

Biochar and compost combination or comparison as a growing media

While the number of articles in academic journals on purposeful application of compost to soil increased slowly, the number of publications about biochar increased strongly, starting from 2010 (Fig. 3). Since 2014, the publication activity of biochar in the scientific literature exceeds that of compost, reaching now three times more publications than that of compost. Scientific publications with both term “biochar” and “compost” in their title started in 2009 and their number strongly increased since 2015 and recorded in 2021 6.6 % and 21 % of the publications on purposeful application of respectively biochar and compost to soil. These numbers evidence that biochar studies with comparison to or combined with compost is nowadays a growing topic.

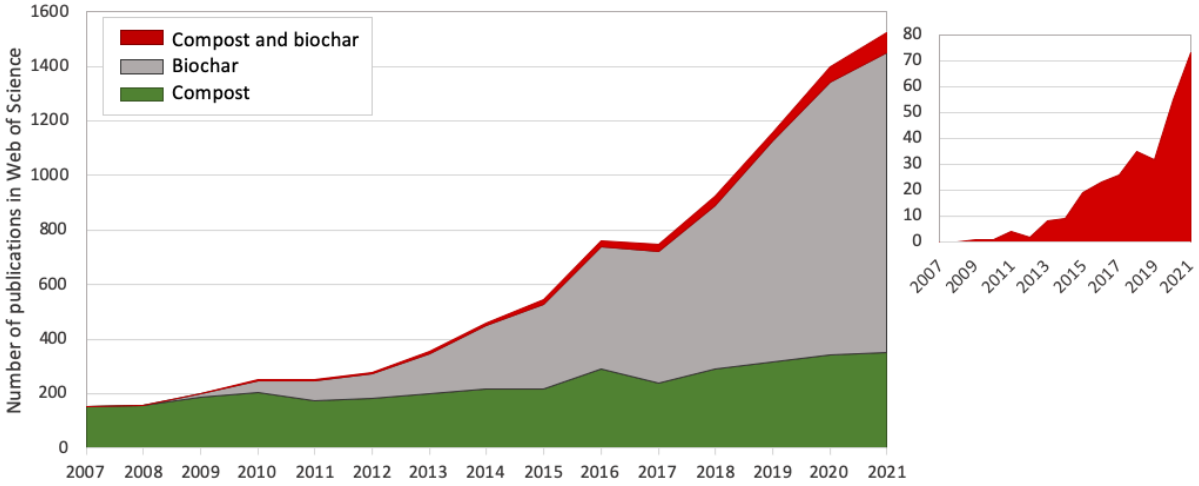

Figure 3 Number of publications in scientific journals listed in the ISI Web of Science (https://www.webofscience.com) edited from 2007 to 2021, with the term "biochar" or "compost" or "biochar" and "compost" in the title and with the term "soil" in all field of the research. Document types include Articles, Review articles, Proceedings papers, early access and book chapters. Web of science categories include "Environmental Sciences", "Soil Science", "Agronomy", "Engineering Environmental" and "Plant Sciences".

1.2 Organic amendments may increase carbon storage

1.2.1 Mechanisms of carbon storage in soil

Carbon storage corresponds to the difference between the outputs and the inputs of C in a soil. Hence, it depends on organic matter biotransformation, transfers and stabilization or destabilization when applied to soil (Pellerin et al. 2020) (Fig. 4). Carbon turnover or persistence in soil greatly vary depending on multitude of factors such as chemical recalcitrance, its association with aggregates of minerals and the environmental properties can remain very long time in soil (Basile-Doelsch et al. 2020; Schmidt et al. 2011; Sierra et al. 2018). Recently, Lehmann et al. (2020) suggested that carbon persistence is mainly controlled by three factors: molecular diversity, spatial heterogeneity and temporal variability of the soil ecosystem.

OM inputs may originate from both above- and belowground sources, from vegetal and animal sources and from endogenous and exogenous sources (Basile-Doelsch et al. 2020). There are different ways to increase OM outputs; for instance, by increasing animal grazing, by reducing the exportation of vegetal biomass from crop and intercrops or by increasing organic amendments. Once applied in soil, OM may be subjected to biotransformation, transport and/or stabilization processes (Fig. 4). The OM biotransformation is driven by soil fauna (e.g. earthworms), and microorganisms (e.g. bacteria, fungi).

Soil fauna exert both mechanical actions of fragmentation and OM incorporation into soil and biochemical actions through ingestion of OM and minerals, which favor organo-mineral associations (Bohlen et al. 2004). Microorganisms (fungi and bacteria) are the main drivers of OM chemical biotransformation, through the production of enzymes (Basile-Doelsch et al. 2020). The first biotransformation reactions are oxidative depolymerization, which result in the reduction of molecule size and to an increase of their chemical reactivity. Then, extracellular enzymes further decompose the molecules to low weight molecules, which can be absorbed by microorganisms. The latter mineralize them to CO_2 or reincorporate them into new organic matter compounds (Basile-Doelsch et al. 2020). OM transfer occurs mainly via pedoturbation, mainly through bioturbation from soil fauna, or water transport in the soil pore space (Basile-Doelsch et al. 2020).

It is now commonly admitted that soil microbial communities may decompose all types of substrates, even the most recalcitrant ones, but at different time scales (Lützow et al. 2006). Hence the recalcitrance of OM to decomposition may generally not only be attributed to its molecular recalcitrance, as previously thought, but may also result from processes which inhibit or stop their biodegradation and mineralization, mainly through (i) their physical protection within soil aggregates and (ii) their association with minerals (organo-mineral associations) or with other organic compounds (supramolecular associations) (Basile-Doelsch et al. 2020; Lützow et al. 2006; Pellerin et al. 2020; Kögel-Knabner et al. 2008; Kleber 2010). Indeed, physical OM protection may prevent from OM interaction with extracellular enzymes and microorganisms. In particular, OM adsorption on mineral surfaces inhibit enzymatic degradation, since the adsorption affinity on mineral surface is higher than the adsorption affinity on the active enzymatic site (Pellerin et al. 2020). Generally, molecular recalcitrance and inaccessibility through aggregation seem to determine the turnover dynamic in fast and intermediate cycling OM pools, while for the long-term persistence of OM, the relevance of special inaccessibility through organo-mineral interactions for SOM stabilization increases (Kögel-Knabner et al. 2008; Lützow et al. 2006). However, although generally not seen as a major SOM stabilization mechanism, intrinsic chemical recalcitrance of OM remains as an important factor for the long-term OM stabilization for the specific case of charred material derived from incomplete combustion (Marschner et al. 2008).

Soil C outputs occur through two main mechanisms: (1) OM (micro-)biological degradation leading to mineralization to the end products CO_2, H_2O, NH_4^+, etc. and (2) OM transportation through surface erosion and DOC losses to deeper soil horizon (Basile-Doelsch et al. 2020). Different agricultural practices allow to reduce C loss in soil; for instance, reducing soil tillage and covering soil with intercropping help to reduce the soil erosion. In this thesis, we focus on soil organic amendment, which is one of the way to increase soil organic carbon and soil fertility.

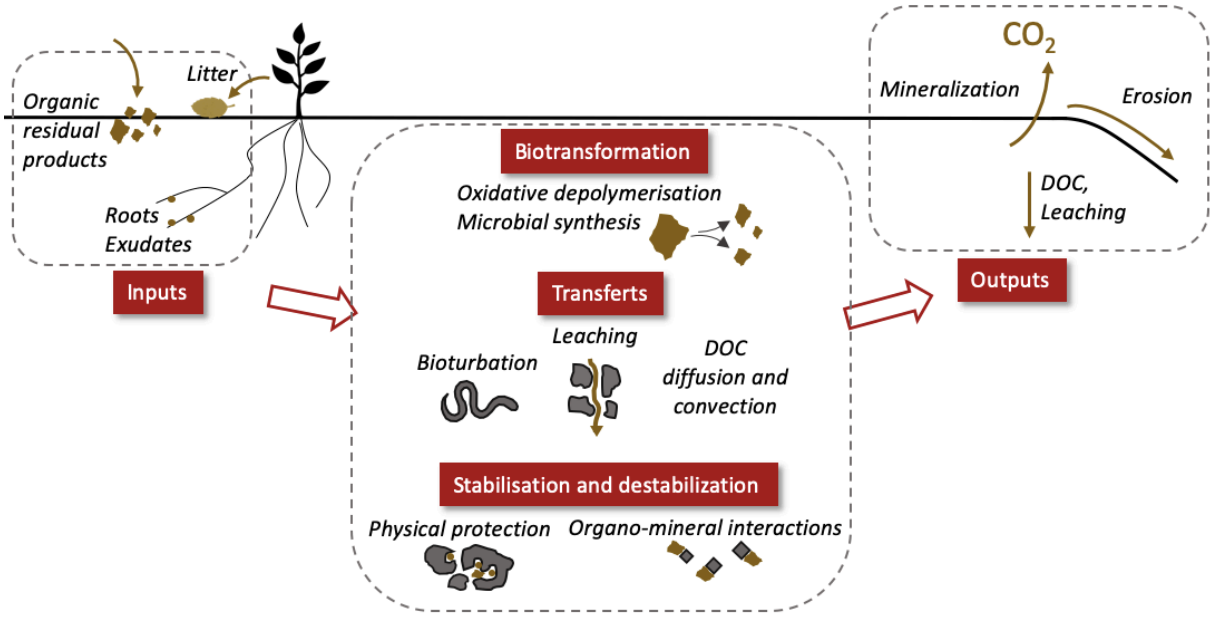

Figure 4 Processes controlling carbon storage in soils (adapted from Basile-Doelsch et al. 2020). DOC: dissolved organic carbon.

1.2.2 Estimation of molecular recalcitrance using thermal analysis

In the case of chemically stable material such as charred material, the chemical characteristics of OM remain as a potential driver of its long-term persistence in soil (Marschner et al. 2008) and it may result from specific bond energies at the molecular level (Barré et al. 2016). An energetic approach has been proposed to interpret and quantify OM turnover in soil, as the storage and flux of energy were found to be closely related to the carbon storage and fluxes (Currie 2003). Chemical bonds may store energy and the amount of energy may depend on the recalcitrance of the bonding to be broken. Indeed, the C-H bonds and saturated (single) bonds are relatively weak in comparison to aromatic bonds and therefore may store higher amount of energy compared to other molecular bonds and especially the unsaturated bonds (double or triple bonds) (Barré et al. 2016; Leinweber and Schulten 1992). The evolution of OM from high energy to less energetic molecular bonds along with time may result from biological degradation, transport and sorption process, that tend to increase the OM stability (Currie 2003). Soil microorganisms appear to preferentially mineralize high-energy OM, leaving behind material with low energy content (Barré et al. 2016). Furthermore, energetic evolution was also associated with the oxidative degradation of OM (LaRowe and Van Cappellen 2011). Subsequently, mineral-associated OM was shown to have a higher thermal stability than free OM for similar compound classes (Schulten and Leinweber 1999). Thermal analysis was proven as a useful technique for interpreting SOM stability and energy status, which may be correlated with its persistence in soils, as a function of both the OM degree of decomposition and the degree of mineral association (Plante et al. 2009; Peltre et al. 2013). Furthermore, correlations were evidenced between the thermal and biogeochemical stability of SOC

(Plante et al. 2011; Gregorich et al. 2015; Leifeld and von Lützow 2014). Hence, thermal stability has the potential to serve as an indicator of the distribution of SOM between biogeochemically labile and stable fractions, with the added value that data are obtained relatively rapidly and their measurement requires little sample preparation (Plante et al. 2009).

Thermal analysis result in the plotting of mass, heat or gas evolved from the samples, as a function of temperature. As the maximum peak temperatures recorded for a specific compound are characteristic parameters, the identification of typical patterns in the thermal curves together related to the degree of OM stability can be used for the characterization of SOM (Plante et al. 2009). Commonly, the combustion of chemical recalcitrant OM, such as lignin or other polyphenols, generally occur at higher temperature and provide less energy than combustion of more labile OM, such as carbohydrates (Ranalli et al. 2001; Strezov et al. 2004; Barré et al. 2016) (Fig. 5). Charring of woody biomass was found to separate thermally labile compounds, through the cleavage of weak covalent bonds occurring in the early stage of the pyrolysis below 400 °C, from thermally stable compound, through the cleavage of strong bonds, occurring at the later stage of pyrolysis between 484 °C and 523 °C (Leifeld 2007; M. Liu et al. 2015). However, secondary rearrangements of substances in the gas phase during char pyrolysis can culminate in the neoformation of low molecular weight heterocycles and polycyclic aromatic compounds, thereby inducing artefacts in the product yields and thermal pattern of the pyrolysis (Sharma et al. 2003; Yan et al. 2015; Zaror et al. 1985).

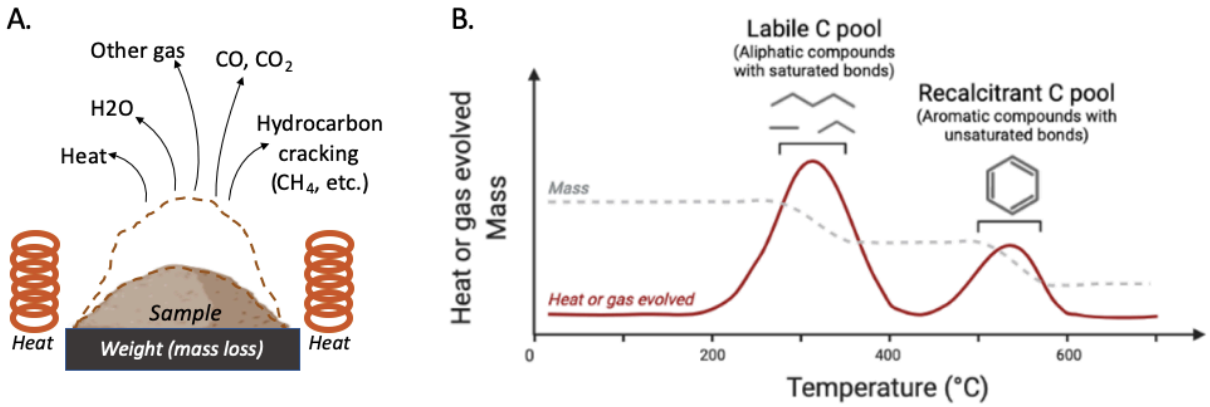

Figure 5 (A) Main mechanisms occurring during the heating of a sample composed of labile and recalcitrant C pools and (B) distinction of labile and recalcitrant C pool from thermal analysis results (adapted from Ranalli et al. 2001; Plante et al. 2009; Barré et al. 2016; Leifeld 2007; Mohan et al. 2006a).

Thermal degradation may allow for the estimation of labile and stable C of materials. Compost was found to emit large amount of hydrocarbons during the pyrolysis and therefore, the temperature at which the maximal amount of hydrocarbon was released may be a suitable indicator to assess the thermal energy required by microorganisms to decompose OM stage (Albrecht et al. 2015). Thermal method,

such as Rock-Eval® pyrolysis, was found as accurate enough to identify thresholds of compost maturity (Albrecht et al. 2015). Generally, the Rock-Eval® pyrolysis provides essential information on the amount and composition of SOM and uncharred material (Disnar et al. 2003). Although thermal degradation techniques are widely used to determine stable and labile biochar C and is considered as a promising technique, it however needs further development and optimization (Leng et al. 2019). Rock-Eval® analysis appears to be a powerful tool for black carbon quantification compared to other methods, as it may capture a major part of the black carbon continuum including its stable fractions (Poot et al. 2009). To our knowledge, no study analyzed biochar using the Rock-Eval® method. Hence, further studies should investigate the suitability of the Rock-Eval® technique for the characterization of biochar chemical properties.

1.3 Organic amendment as important drivers for soil fertility

According to the FAO, soil fertility is the ability of a soil to sustain plant growth by providing essential nutrients and favorable chemical, physical and biological characteristics as a habitat for plant growth (www.fao.org). Organic amendments represent a source of available macro- and micronutrients, although their release may be slower than inorganic fertilizers due to the progressive OM mineralization (Aytenew and Bore 2020; Abbott et al. 2018; Pang and Letey 2000). In particular, organic amendment release nitrogen, that may be up-taken by plant and microorganisms or be removed through N_2O emission and leaching (Fig. 6). However, while organic amendment was found to induce similar effect on crop yield than inorganic fertilized application over long-term period ($\geq$ 10 years), this effect became significantly greater when applied under specific soils conditions, such as low initial fertility, sandy texture, near-neutral pH values and tropical climate (Y. Chen et al. 2018). Indeed, organic amendment may provide an important source of carbon that may be slowly mineralized by microorganisms, or incorporated in the soil for longer-term storage or removed through CO_2 emission (Fig. 6). They additionally contribute to the improvement of soil physical, biological and chemical conditions for plant production (Fig. 6) (Larney and Angers 2012; Goss et al. 2013; Aytenew and Bore 2020). The main physical properties that can be affected my organic amendment are the soil structure, through increasing aggregate formation and aggregate stability, decreasing the bulk density, and increasing the water retention and infiltration; the chemical properties include the increase of soil pH increase, electrical conductivity (EC) and cation exchange capacity (CEC); and the biological include increases of microbial biomass and enzyme activity (Goss et al. 2013; Scotti et al. 2015). All these improvements on soil properties may benefit to crop yields. However, the effects on those parameters greatly vary depending on the type of organic matter, as well as soil characteristics and environmental conditions (Goss et al. 2013).

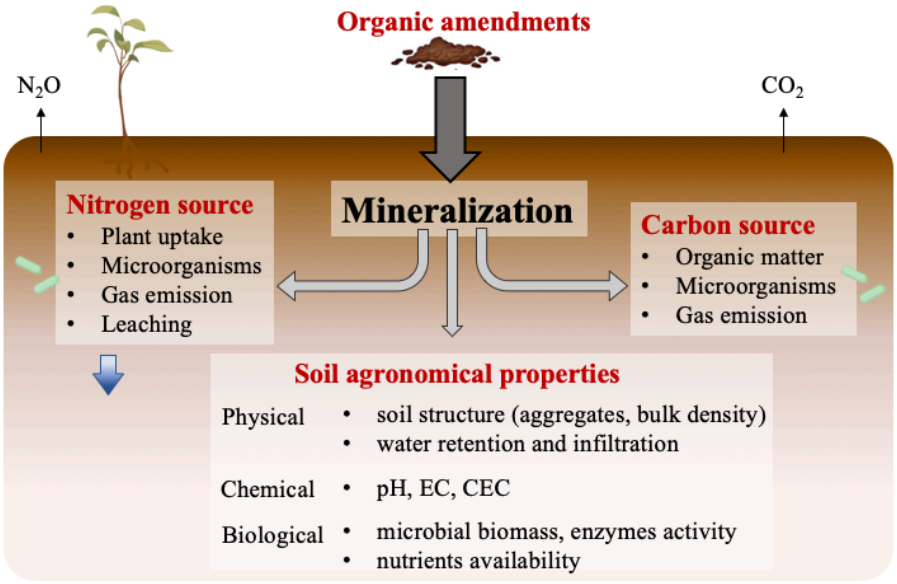

Figure 6 Main effects or organic amendments on soil properties by acting as a source of carbon and nitrogen (adapted from Scotti et al. 2015). EC: electrical conductivity.

2 Compost and biochar as complementary organic amendments

2.1 Different production processes and material characteristics

2.1.1 Composting

Compost is one of the most used soil organic amendment and it results from the aerobic decomposition of organic wastes. In this process, aerobic microorganisms break down organic matter and produce carbon dioxide (CO_2), ammonia, water, heat and a relatively stable organic end product. Green waste generally contains different compounds with contrasting chemical compositions, and thereby decompose heterogeneously. The composting process can be divided into four main stages (Fig. 7), characterized by the activity of different microbial groups (de Bertoldi et al. 1983; Smith and Collins 2007; Misra et al. 2003; Neklyudov et al. 2006; Nikoloudakis et al. 2018) : In the first mesophilic stage, easily biodegradable OM composed of simple carbon compounds (e.g. soluble sugars, organic acids) are mineralized by mesophilic organisms (optimum growth temperature range from 20 to 45 °C), leading to intensive bacterial activity and an increase in the compost temperature. As the temperature reaches 55-60 °C, the system turns from a mesophilic to a thermophilic stage, thereby favoring mainly thermophilic bacteria and actinomycetes (optimum growth temperature ranging from 50 to 70 °C) that contribute cleaving lignin-like organic components. Temperature continues to raise up to 65 °C or higher, which allows killing of pathogens and weed seeds, and thus sterilize compost. Mesophilic and thermophilic phases constitute the active decomposition stage, characterized by intense microbial

activity and rapid organic matter decomposition. Both the high temperature and the consumption of easily biodegradable OM result in a decrease in microbial activity and temperature during the cooling phase. As the temperature declines the mesophilic organisms reappear, especially fungi that have preference for the remaining plant cell-wall materials such as cellulose and hemi-cellulose. The last maturation stage is composed of a cooling phase where temperature declines progressively and a stabilization phase occurs, where the maturation continues at ambient temperature. The decomposition stage generally lasts 15 to 30 days and the maturation stage weeks or months. However, the duration of each composting stage depends on the initial composition of the organic matter, its quantity and the composition of the microbial population, as well as the efficiency of the process, with is controlled by wetting frequency, aeration and turning (Neklyudov et al. 2006; Smith and Collins 2007).

During the composting process, the heating peak sterilizes the material from pathogens. Compost contains between 130 and 300 g C kg^{-1}, between 6 - 30 g N kg^{-1}, 0.1 - 14 g P kg^{-1} and 4 - 11 g K kg^{-1} (Abbott et al. 2018). However, the nutrient content of the composts vary greatly between material origin of the compost, especially for immature composts, and these differences tend to decrease when the compost become more mature (Fuchs et al. 2008). At the end of the composting process, compost C:N ratio ranges between 10 and 25 (Abbott et al. 2018), which is favorable for microbial activity. Therefore, microorganisms such as fungi may colonize the compost during the maturation phase (Hoitink and Fahy 1986), thus increasing soil fungal biomass when applied to soil (Chander and Joergensen 2002; Bulluck et al. 2002). However, the quality of the mature compost differs depending on the feedstock material and the degree of decomposition.

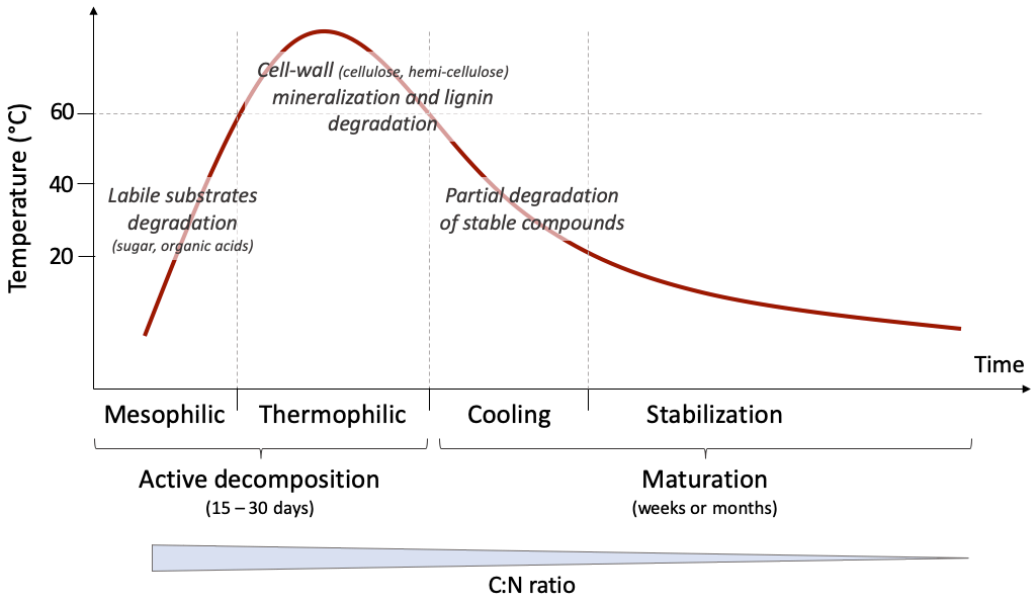

Figure 7 Temperature evolution and degradation of substrates during the composting process (adapted from: de Bertoldi et al. 1983; J. L. Smith and Collins 2007; Misra et al. 2003; Neklyudov et al. 2006; Nikoloudakis et al. 2018).

2.1.2 Pyrolysis

Biochar is the carbon-rich solid by-product of organic material pyrolysis, intended for use as a soil amendment or broader for environmental management (Lehmann 2007a; Lehmann and Joseph 2015). Biochar may be different from charcoal, as the latter, also resulting from biomass pyrolysis, may be used in the purpose of energy generation (Lehmann and Joseph 2015). Biochar may be generated from different biomass types, of animal as well as vegetal origin, that are thermally degraded under elevated temperature in the absence of oxygen (Kambo and Dutta 2015). Pyrolysis is a thermochemical decomposition, or thermal degradation, technique occurring in a oxygen-free environment, converting low-energy density biomass into medium calorific value gas called synthesis gas, high-density liquid product called bio-oil and high-density solid product called biochar (Bridgwater et al. 1999) (Fig. 8). Both oil and gas created during the thermal degradation can be captured to produce energy carriers such as electricity, bio-oil or hydrogen, that can then be re-use to further activate pyrolysis in a self-production process objective (Lehmann 2007a). High-temperature pyrolysis (typically above 700 °C), also called gasification, yields much lower amounts of solid by-products or non at all, and is therefore less appropriate to the creation of biochar (Lehmann 2007a).

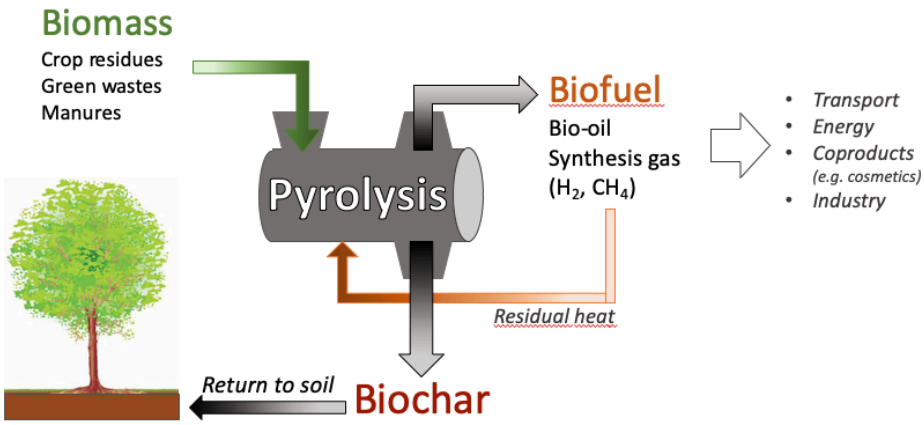

Figure 8 Pyrolysis products with biochar sequestration (adapted from: Lehmann 2007a).

During the pyrolysis process, both physical and chemical characteristics of the biomass are altered (Fig. 9). Temperature increase of the pyrolysis process induces increasing proportions of C and may induce variations of other elemental recoveries, such as nitrogen and phosphorous, as explained by the loss of volatile compounds and the dehydration of the initial biomass (Enders et al. 2012). Some elements, like P or K, are preserved during the pyrolysis and their concentration therefore is higher in the biochar than in the feedstock material (Siedt et al. 2021). Biochar chemical structure result from complex process occurring during the pyrolysis, in which many reactions such as dehydrogenation, hydrogen transfer and isomerization take place concurrently. Of particular importance for the final properties of biochar are the formation of rings of C atoms and their condensation and growth into larger sheet and stacks (Kleber

et al. 2015). Hence, the remaining chemical components from biochar are not necessarily available to plant or microorganisms, as they may be locked in the aromatic components. Pyrolysis also induces the increase of other physical parameters such as porosity, and thereby of the specific surface area, as well as other chemical parameters such as cation exchange capacity (CEC) and pH (Lehmann 2007a). During the pyrolysis, the composition of the biochar increases in aromatic molecules (aromatization) which condensation increases (condensation), resulting in the increase of fixed C content (Fig. 9). As for compost, both biochemical composition and physical characteristics (e.g. porosity) are highly dependent on the initial feedstock.

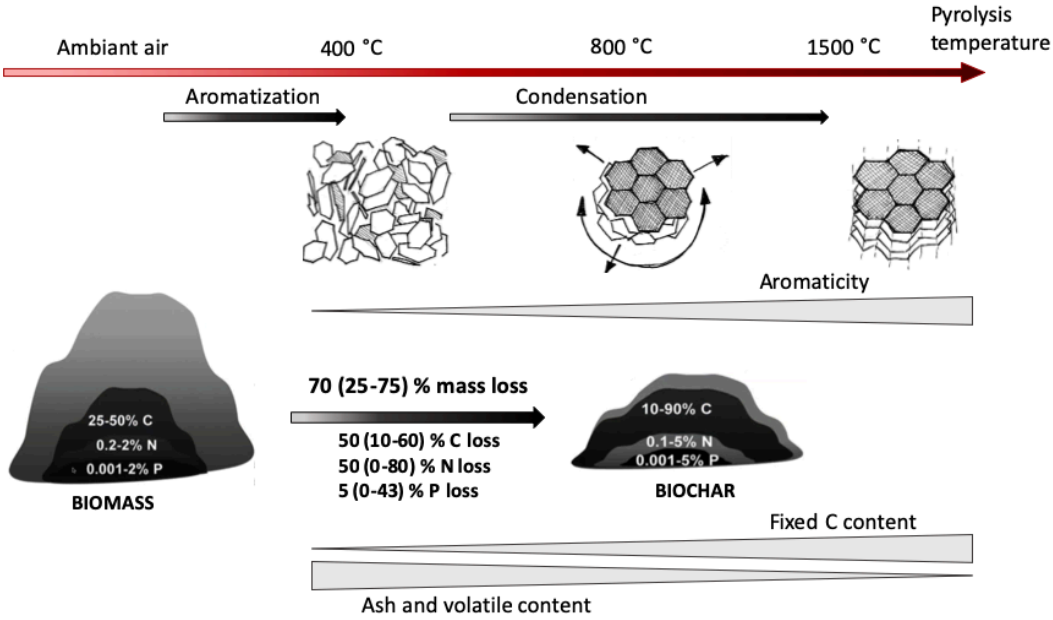

Figure 9 Impact of elevated temperature pyrolysis on physical structure and chemical characteristics of biochar (adapted from: Lehmann and Joseph 2015; Chia et al. 2015).

However, biochar yield, physical structure, chemical composition following its production may vary with a multitude of factors related to initial feedstock (chemical composition, particle size) and pyrolysis process (T, heating rate, pressure, residence time) (Abbott et al. 2018; Ahmad et al. 2014). In certain cases, biochar may be subjected to additional post-production treatments.

The physical structure of biochar is more friable compared to other amendments, with the porous structure conferring a low bulk density (< 0.5 g cm-3) and a high surface area (Abbott et al. 2018). The porous structure of biochar is heterogeneous, ranging from the micro- to the macro-scales, and often resemble to the original cell structure (Fig. 109). The high porosity of biochar confers it a large specific surface area. While micropores make the greatest contribution to the overall surface area, macropores exhibit very high volumes relative to micropores (Chia et al. 2015). Regarding chemical properties,

biochar is enriched in carbon aromatic rings (Kleber et al. 2015) (Fig. 11), relatively poor in nutrients, and with high CEC and pH above 7 (Lehmann 2007a).

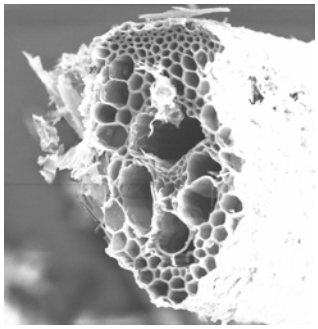

Figure 10 Porous structure from maize biochar (450 °C), scanning electron microscopy.

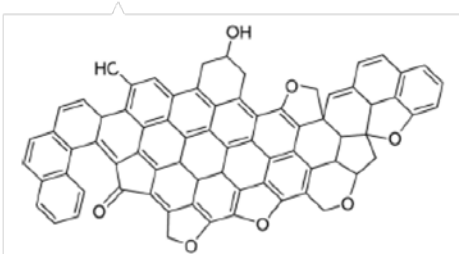

Figure 11 Biochar network (source: W.-J. Liu et al. 2015).

Thanks to its physical and chemical properties, biochar can be used for multiple purposes, including soil improvement, environmental purposes (mitigation of climate change, water pollution), waste management and energy production (Lehmann and Joseph 2015; Schmidt and Wilson 2012). Biochar can be used for a variety of purposes, including “mitigation for climate change”, “soil improvement”, “soil decontamination”, “waste management”, “animal farming”, “biogas production”, “water treatment”, “building sector”. (Fig. 12). Not every biochar is suitable for application to agricultural land and biochar can induce different effects on soils, depending on their feedstock diversity and pyrolysis process (Kavitha et al. 2018). Hence, multiple studies suggested that biochar production can be customized based on its final use (Aller 2016). Nowadays, the biochar market is in expansion and Asia Pacific dominated the global market in 2020, with China as the leading producer, followed by North America and by Europe. The main driving factors include the rising government policies for environmental protection and the growing use of biochar for livestock feed, while the restraining factors include the technological inefficiencies and absence of knowledge concerning advantages of the product (www.fortunebusinessinsights.com).

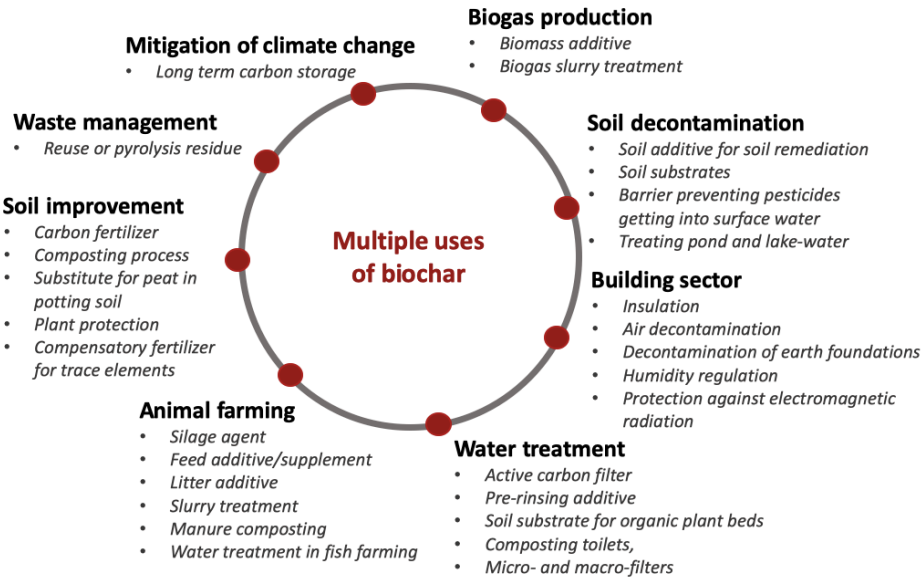

Figure 12 Multiple use of biochar (adapted from: Schmidt and Wilson 2012; Lehmann and Joseph 2015).

2.2 Contrasting effects on carbon storage

2.2.1 Mechanisms of carbon persistence in soil

Molecular recalcitrance

Due to their different production processes, compost and biochar have contrasting characteristics, regarding their physical structure as well as their chemical structure and composition. While green-waste compost is composed with a wide variety of molecules, including cellulose and lignin, biochar is mainly composed of C-enriched aromatic recalcitrant compounds (Siedt et al. 2021). In a meta-analysis of 128 observations from 24 studies, Wang et al. (2016) showed that only a small proportion of biochar is available for microbial decay, with a residence time of 108 days, and the remaining 97 % directly contribute to long-term C sequestration, with a mean residence time of 556 years. However, biochar decomposition rate may vary with experimental duration, biochar feedstock and production and soil clay content (Wang et al. 2016). Although pyrolysis induces a rapid loss of part of C, the remaining C is highly chemically recalcitrant and may therefore remain in soil at longer time scales than compost (Fig. 13).

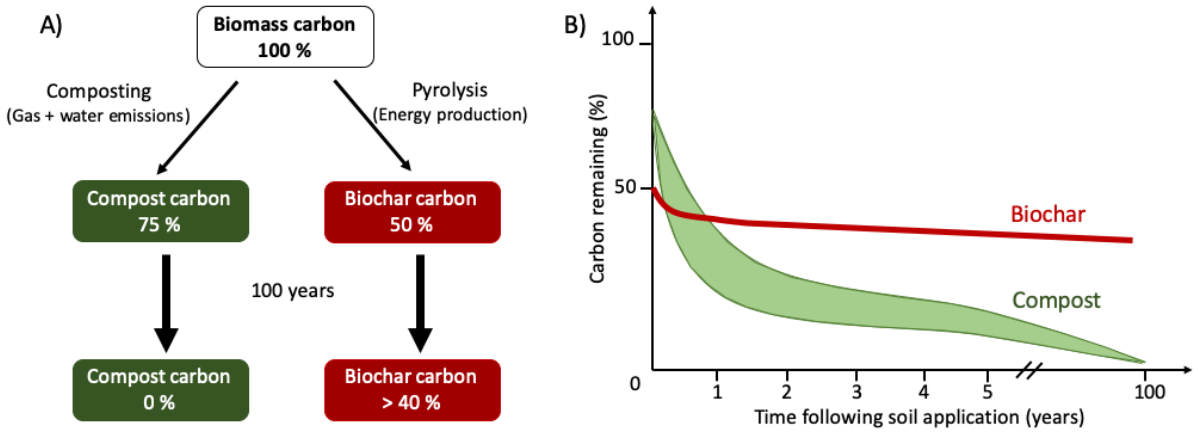

Figure 13 Schematics for green waste compost and biochar carbon remaining after decomposition in soil. (A) C remaining from biomass after composting and pyrolysis process and after 100 years decomposition in soil and (B) range of biomass C remaining after decomposition of crop residues (adapted from Lehmann et al. 2006; Kumar et al. 2010).

Stabilization into the soil matrix

Field experiments found that biochar and compost accumulated mainly in the physically unprotected free OM pool after 1-2 years on soil application (Herath et al. 2014; Fernández et al. 2014). Both biochar and compost application on soil may accumulate preferentially in the free SOM pool not protected by the soil matrix, mostly due to the presence of biochar (Plaza et al. 2016; Cooper et al. 2020). The organic particles from input accumulated preferentially in the free POM fraction in short-term, while the occlusion in the soil aggregates may occur at longer time scales. Furthermore, biochar and compost were found to incorporate with different intensities into the soil aggregates; biochar may accumulate in all aggregate fractions of 0-10 cm and 10-30 cm soil depth, while compost may accumulate preferentially in the 10-30 cm soil depth and in the larger aggregate fractions (> 0.053 mm) (Cooper et al. 2020).

2.2.2 Consequence on carbon cycle

Although subjected to friability and transport, biochar was found to have higher molecular recalcitrance than compost when exposed to soil. Therefore, biochar-derived C may affect the carbon cycle through the increase of net carbon withdrawal from the atmosphere (Lehmann 2007b; Smith 2016) (Fig. 14). In other words, when biochar is applied to soil, part of the biochar-derived C may remain in soil instead of being re-injected in the atmosphere. Soil C sequestration differs from soil C storage, as it consists in the C uptake from the atmosphere to its storage in soil (Pellerin et al. 2020). Briefly, atmospheric CO_2-C is captured by plant leaves through photosynthesis and may deposit in soil after plant death. When accumulated in soil, C may be mineralized by microorganisms, and thus be rejected to the atmosphere through their respiration. In the case of biochar, the dead plant is pyrolyzed and the organic carbon (OC) contained in plant concentrates in biochar, in a highly recalcitrant form. During pyrolysis, part of the C

is reused used as energy source and therefore is released into the atmosphere. As the biochar-derived C may persist a long time in soil, it remains in soil instead of being mineralized and released in the atmosphere.

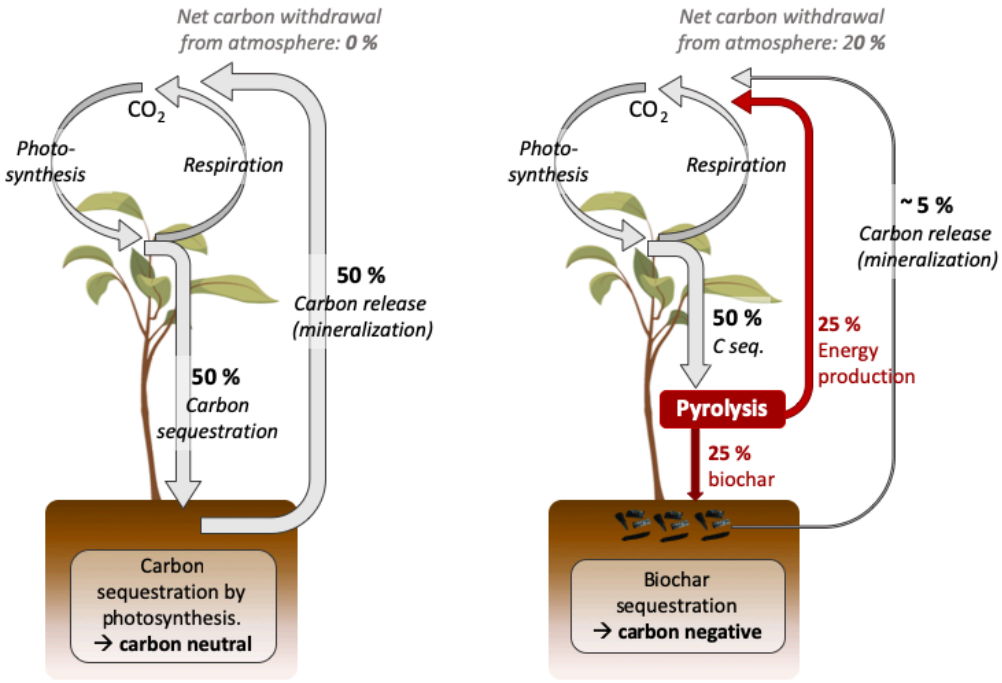

Figure 14 Change in carbon cycle due to pyrolysis (adapted from Lehmann 2007b).

2.2.3 Particle transport

Biochar may remain longer in soil than compost because of its higher chemical recalcitrance. However, as biochar may accumulate preferentially in the free POM fractions, its particles may easily be subjected to horizontal/lateral and vertical transports (Fig. 15). The major export flux of biochar from the site of amendment is via lateral/horizontal transport (Major et al. 2010; Foereid et al. 2011), with transport rates from less than 1 m yr^{-1} to more several km yr^{-1} (Rumpel et al. 2015). Immediately after deposition on soil, biochar may be exposed to forces exerted by wind and water. Raindrops impacting the soil surface detach biochar particles by rainsplash, and project them in all directions. Biochar horizontal transport may then be increased by runoff and by multiple erosion processes, as affected by tillage, wind and waterflow (Rumpel et al. 2015). Vertical transport in the soil profile is likely quantitatively less important and slower than horizontal transport, but may substantially change soil properties and biochar residence times. Illuviation in the soil column through larger pores and bioturbation by burrowing organisms or trees uprooting were hypothesized as important pathways of vertical transport of biochar particles (Rumpel et al. 2015), with a minimum time of a char particle to migrate vertically is 2 mm yr^{-1} (Carcaillet 2001). Consequences of particle transport is their deposition and accumulation in different

place than their initial application, for instance in groundwater (Fig. 15). Hence the C storage due to biochar application may not necessarily occur at the same place where it was deposited.

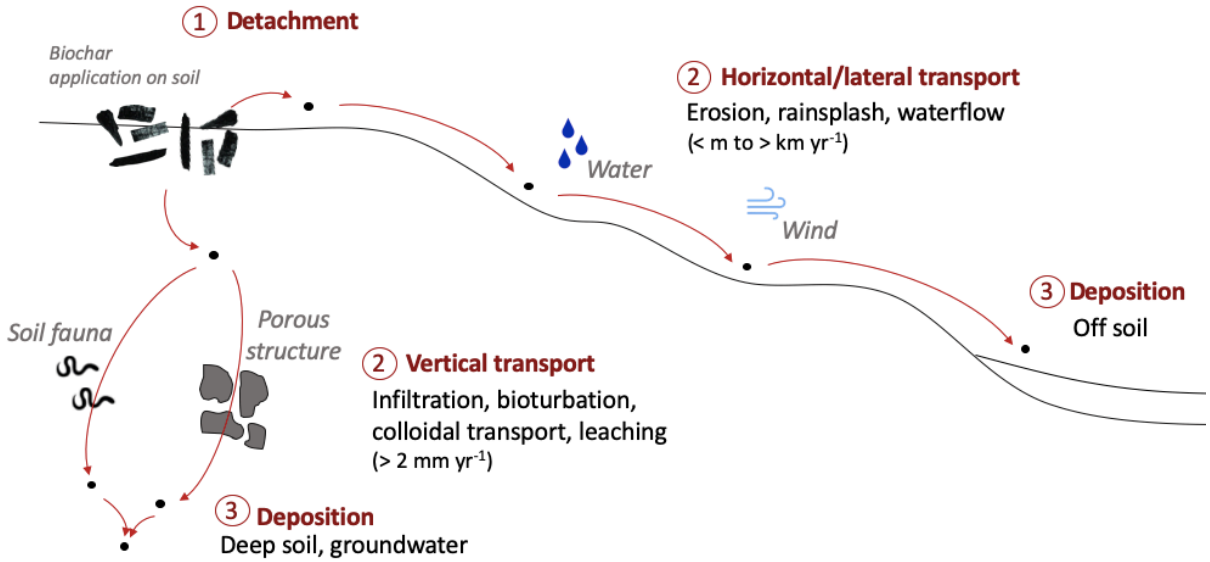

Figure 15 Main pathways and factors of biochar transport after application to soil (adapted from Rumpel et al. 2015).

2.3 Complementary effects on soil fertility

2.3.1 Main effects on soil fertility

Nutrient dynamics

Both compost and biochar may contain available nutrients (Tab. 2). Although abundant (Bulluck et al. 2002), micro- and macronutrients from compost are generally not immediately available after application to soil, as compost requires further decomposition for a slow release of available nutrients (Aytenew and Bore 2020) and in particular of nitrogen (N) (Diacono and Montemurro 2010). Biochar may also contain nutrients, but the amount is generally low and greatly depends on initial feedstock and production parameters (Hossain et al. 2020; El-Naggar et al. 2019). Contrary to compost, nutrients from biochar can be released from labile part, and may therefore be immediately available when applied on soil and hence are available at short term (Abbott et al. 2018).

Both biochar and compost may adsorb nutrients, although having different adsorption mechanisms; hydrophobic partitioning and pore filling have been suggested as the main adsorption mechanisms for compost and biochar, respectively (S. Tang et al. 2021). Additionally, biochar generally achieve higher adsorbing constant and lower desorption rates, when compared to compost (S. Tang et al. 2021). In

particular, N was shown to be temporary adsorbed and then slowly released with time after biochar application (Palanivell et al. 2020). The carboxylic and phenolic groups attached on biochar surface as a result of the aging process have negative charges and can therefore adsorb ammonium (NH_4^+) by electrostatic attraction (Nguyen et al. 2017). Although the pores of biochars induce larger surface for nutrient sorption, they can be blocked by soil particles or other matter when added to soil, thereby overwhelming weaken the sorption capacity of biochar-amended soil (S. Tang et al. 2021). Furthermore, organic coating on biochar surface may develop through time, thus allowing for higher sorption capacity of nutrients (Hagemann et al. 2017b). The C:N ration of plant biomass generally decrease during the composting process (Jiménez et al. 1991). Hence, soil amendment with immature compost, thus having high C:N ratio, may induce the immobilization of N already present in the soil, and therefore induce a negative effect on N availability (Goss et al. 2013).

Table 2 Comparison of the main characteristics of compost and biochar materials that may influence soil agronomic properties (minimal - maximal values) (adapted from Siedt et al. 2021). na: data not available in the publication.

Parameters	Green waste compost	Plant-derived biochar*
Elemental content		
C (%)	20.8-25.9	41.9-87.5
C:N ratio	11-21	29-133
N (%)	0.6-1.6	0.2-2.1
P (%)	0.15-1.4	0.01-2.33
K (%)	0.44-1.5	0.38-3.4
Chemical characteristics		
pH	7.2-8.4	6.9-11.0
CEC ($cmol^+ kg^{-1}$)	*na*.	7.6-304
Physical characteristics		
Porosity and surface area	Medium	Very high
Density	Low	Very low

*produced between 400 and 650 °C

Soil chemical, physical and biological properties

As a result of long-term use of N fertilizers, or when added in excessive amounts, N fertilizers may lead to soil acidification through time, which may become a yield-limiting factor (Schroder et al. 2011; Stamatiadis et al. 1999). Liming is therefore needed to sustain crop yield if N fertilizers are used routinely. Due to their elevated pH, both compost and biochar may induce a liming effect, that may

benefit to acid soils and biochar generally presents higher pH than compost, which confers a stronger liming effect (Siedt et al. 2021) (Tab. 2).

Subsequently to nutrient supply and adsorption, compost and biochar amendment may also affect soil other agronomic properties, thereby affecting the plant growth habitat. Compost and biochar may both reduce the soil bulk density (Bulluck et al. 2002; Zebarth et al. 1999; Razzaghi et al. 2020; Rabbi et al. 2021), thereby favoring water infiltration and roots development. Furthermore, biochar generally presents lower density than compost, due to its higher volume of pores (Siedt et al. 2021) (Tab. 2). Both materials were found to benefit for water-holding capacity, mostly in sandy soils for biochar application (Zebarth et al. 1999; Razzaghi et al. 2020; Rabbi et al. 2021). The ability of biochar on its hydraulic potential greatly depend on other factors including hydrophobicity, particle size, surface area, surface charges, etc., themselves depending on biochar initial feedstock and production parameters (Rabbi et al. 2021). Compost application on soil was found to generally improve aggregate stability in long-term experiments (> 3 years) (Diacono and Montemurro 2010), but this effect can be visible already 2 years after field exposure (Bipfubusa et al. 2008). Improvement of the soil structure following compost amendment may result from elevated OM and improved microbial activities (Bouajila and Sanaa 2011). Biochar was found to promote aggregate stability and the formation of macroaggregates in clayey soil for short term (< 3 months) incubations (Soinne et al. 2014; F. Sun and Lu 2014), as well as in longer-time field experiments (> 2 years) (Ma et al. 2016; Pituello et al. 2018). However, the effect of biochar on aggregate stability or formation highly depends on biochar type (Ma et al. 2016), soil type and biochar dose, as evidenced by the aggregate breakdown when high amount of biochar were added (Pituello et al. 2018).

Moreover, both compost and biochar may have positive effects on soil biota, as they may contain nutrients and labile C, although in different proportions (Siedt et al. 2021). Despite low C availability, biochar amendments may offer suitable physicochemical environment for microorganisms through the promotion of soil aeration, water holding capacity, liming effect, etc., that was demonstrated to result in the enhancing the soil microbial biomass (Palansooriya et al. 2019). However, the effect of biochar on microbial growth is not systematic and may greatly depend on biochar parameters, as other studies did not evidence significant effect of biochar application on soil microbial biomass (Quilliam et al. 2013). Furthermore, biochar may decrease the bioavailability, toxicity and mobility of organic and inorganic pollutants (Nartey and Zhao 2014). Well-mature compost is thought to contain highly active microbial communities (Chander and Joergensen 2002). In particular, microorganisms that colonize compost during the maturation phase may increase soil fungal biomass when applied to soil (Chander and Joergensen 2002; Bulluck et al. 2002). Additionally, other soil biota may be stimulated by compost application, thereby promoting microbial diversity and activity (Farrell et al. 2009). Depending on the

amended soil, compost effect on bacterial and/or fungal community structures could be followed or not by an increase in microbial densities and/or activities (Borken et al. 2002; Pérez-Piqueres et al. 2006).

Plant production

As a result of beneficial effects on soil fertility, mature compost amendment was shown to generally to favor seed germination and increase root and plant growth (Diacono and Montemurro 2010; Kranz et al. 2020). Ye et al. (2020) additionally suggested that the short-term (< 1 year) response of crop yield to biochar addition was mainly driven by its available N content. Generally, biochar amendment was found to increase crop yield in the tropical climatic conditions due to their low-nutrient, acidic soils, while on average, it induced no substantial effect on crop yield in temperate latitudes (Jeffery et al. 2017).

2.3.2 Contrasting responses to ageing processes

Once applied to the soil, organic amendments undergo an ageing process that may be affected by various natural factors including variation in temperature, rainfall events, microbial activity, sunlight irradiation, atmospheric oxygen and microorganisms (Fig. 16). Generally, the breakdown of physically uncomplexed OM that are not pyrolyzed OM is mainly mediated by soil microorganisms, thereby delivering available nutrients and diverse range of molecules in the SOM (Gregorich et al. 2006). While compost ageing may be mainly driven by microbial degradation, biochar ageing may be mainly driven by fragmentation and abiotic oxidation (Wang et al. 2020) (Fig. 16). After the rapidly mineralization of labile biochar compound, the remaining aromatic moieties may undergo physical, chemical and microbial degradations, leading to lower particle sizes, highly recalcitrant (Mia et al. 2017). Similarly, N removal from biochar and compost were attributed to different processes: biochar N removal may occur as N-rich colloidal particles, while compost N may be used by microorganisms and therefore better retained at early stage than biochar N after their application under tropical field conditions (Ngo et al. 2016).

From data collected from artificially and naturally weathered biochar, Spokas et al. (2014) highlighted the significant pathway of biochar disappearance is through physical breakdown of the biochar structure. Ageing may also substantially affect other biochar physical properties (surface area, porous structure) and chemical properties (ash content, surface functional groups, elemental content, CEC) (Wang et al. 2020). Oxidation of biochar particles generally result in the formation of carboxylic functional groups (Cheng et al. 2006), that may benefit to biochar adsorption behavior (Conte and Laudicina 2017).

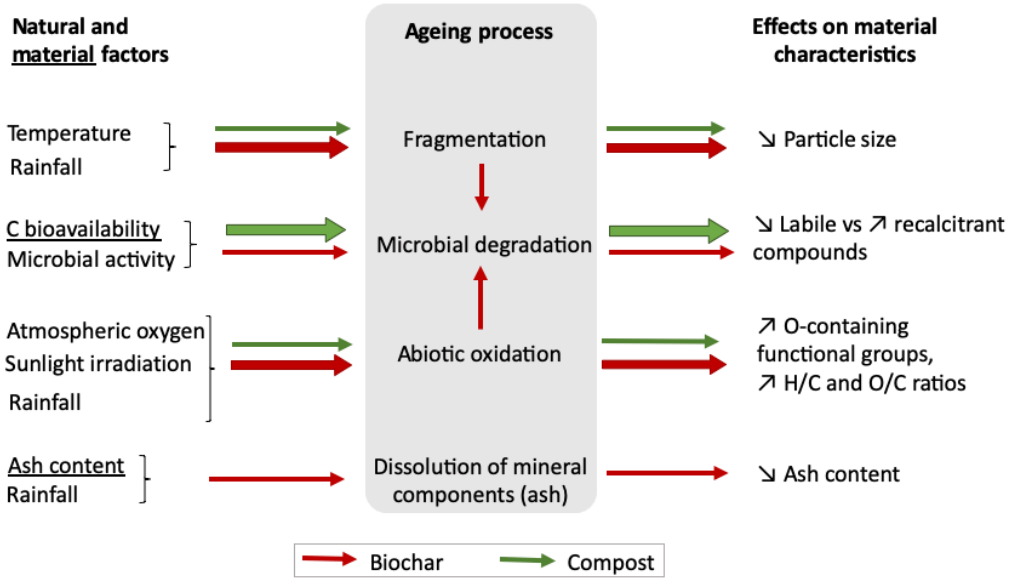

Figure 16 Mechanisms affecting biochar and compost stability from organic feedstocks (adapted from Wang et al. 2020; Mia et al. 2017; Pérez-Piqueres et al. 2006; Borken et al. 2002). Arrows show positive effects. Width of arrows represents importance of the mechanism.

3 Compost and biochar interactions

3.1 Interests of mixing biochar and compost

As a result of their different initial feedstock, organic wastes may be composed of a wide diversity of compounds with contrasting characteristics. In order to optimize their reuse, in the context of circular economy, the process or treatment of reuse should be adapted to their characteristics (Steiner et al. 2015). Hence, moist and nutrient-rich materials are better adapted to composting than to pyrolysis process, as they may allow for favorable environment of microbial degradation. Correspondingly, dry porous materials with low nutrient content are better adapted to pyrolysis than composting process, as they may facilitate heat transfer while avoiding nutrient loss at elevated temperatures (Steiner et al. 2015). The objective of the FUI project in which this work is embedded was firstly to valorize in-situ on compost platform, specific green waste compounds that were refused at the beginning of the composting process.

As we saw in the previous part of this state-of-the-art chapter, compost and biochar may have complementary effects as soil organic amendments, inducing favorable environment for plant growth and for carbon sequestration respectively. Multiple studies evidenced the beneficial effect of biochar-compost mixtures related to available nutrients and C sequestration (e.g. Oldfield et al. 2018; Agegnehu et al. 2017; Agegnehu et al. 2016a; Agegnehu et al. 2016b). Furthermore, their combination may allow for the diversification of carbon sources, which is thought to be beneficial for microbial diversity and

carbon persistence (Lehmann et al. 2020b). Soil amendment with biochar-compost mixture logically calls for the evaluation of potential interactions between both components, that could lead to synergies or antagonisms on their performance as organic amendments.

In order to create biochar-compost mixtures, biochar can be introduced before or after the composting process. Both types have advantages and drawbacks. Biochar addition before composting may improve composting performance and humification process, including enhancement of microbial activities and reduction of greenhouse gas and NH_4 emissions (Guo et al. 2020). However, from a practical point of view, it requires more logistical preparation than biochar mixture with mature compost. In our work, we focused on biochar addition after the composting process, i.e. with mature compost.

3.2 Nature of the interactions between biochar and uncharred organic matter

While the processes following uncharred OM application in soil and the OM stabilization are generally mainly attributed to biotic processes (Kuzyakov 2010; Angst et al. 2021), oxidation of biochar is believed to be dominated by abiotic processes (Wang et al. 2020; Cheng et al. 2006). Furthermore, Prévoteau et al. (2016) found that abiotic processes such as the redox properties of biochars were dramatically underestimated. Indeed, biochar may donate much more electrons to their environment than previously considered, and this may have bigger impact on soil biochemical processes than previously conjectured (Prévoteau et al. 2016). Biochar oxidation was shown to increase oxygen-containing functional groups on biochar surface, especially carboxyl groups, and to increase the specific surface area through the development of mesopores, thereby increasing the sorption capacity of biochar (Fan et al. 2018). Other biochar characteristics such as polarity may favor hydrogen bondings from O-containing functional groups of compost particles to biochar surface and non-polar compounds access hydrophobic sites on biochar surface (Sun et al. 2012; Ahmad et al. 2012) (Fig. I.16). Hence, oxidized biochar particles facilitate their interaction with organic molecules by interactions such as hydrogen bonding, charge transfer, van der Waals interactions, hydrophobic interactions, π-π bondings and pore filling mechanisms (Conte and Laudicina 2017; Ghaffar et al. 2015) (Fig. 17). Adsorption of non-black carbon compounds on black carbon surface may further increase the number of oxidized groups on the black carbon surface, thus favoring the formation of organic coating (Lehmann et al. 2005; Hagemann et al. 2017b; Conte and Laudicina 2017). Abiotic oxidation processes were shown to precede abiotic processes (Cheng et al. 2006). However, as far as we know, the temporality of abiotic oxidation process and its resulting interaction with uncharred material such as compost is not sufficiently understood. We could suggest that biochar and compost may interact through abiotic oxidation immediately during their blending.

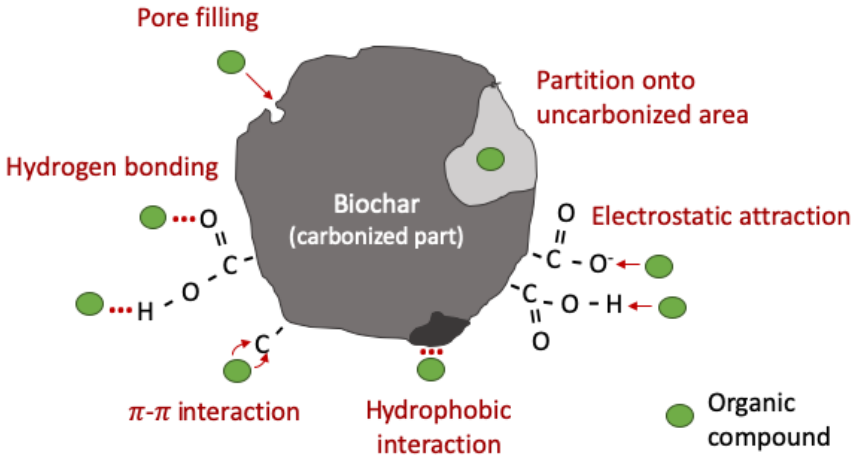

Figure 17 Interaction mechanisms of biochar with organic compounds (adapted from Ahmad et al. 2014; Ambaye et al. 2021; Fdez-Sanromán et al. 2020; Chen et al. 2008).

3.3 Mechanisms of biochar and compost interactions

3.3.1 Mechanisms of biochar and compost interaction as pure components

Carbon persistence

The sorption capacity of biochar with non-carbonized OM may increase with pyrolysis temperature and biochar properties such as surface area, pore volume, aromaticity and thermal stability (Kupryianchyk et al. 2016). Studies evidenced the physical protection of compost-derived particles by its occlusion and/or adsorption into the biochar porous structure, thereby protecting compost-derived labile C from microbial degradation (Jien et al. 2015; Jien et al. 2018) (Fig. 18). Other studies also suggested that biochar may have stabilized compost-derived labile C, thereby protecting it from biological degradation (Ngo et al. 2013; Tsai and Chang 2020; Schulz et al. 2013). Biochar may subsequently protect compost-derived from removal through transport processes after 1-year on tropical field conditions (Ngo et al. 2016). The authors suggested that lower C loss may be related to compost physical protection into biochar porous structure, thus preventing from particle loss through transport. Additionally and as previously introduced, the molecular diversity of carbon sources may increase C persistence (Lehmann et al. 2020). Indeed, high molecular diversity is believed to enhance microbial diversity, thereby reducing microbial specialization and investment strategies for soil biota, that could result in a slower decomposition (Kögel-Knabner 2017; Lehmann et al. 2020).

Nutrients cycling

The sorptive capacity of biochar has been suggested as some of the greatest potential that it may offer to develop slow release of nutrients from another OM (Abbott et al. 2018). It could thus be suggested

that when combined with mature compost, biochar may also adsorb nutrients released by compost, thereby significantly lowering nutrient losses and hence increase their availability for plant and microorganisms (Fig. 18). For now, and as far as we know, this suggestion has not been validated yet. Furthermore, Hagemann et al. (2017b) evidenced a nutrient-rich organic coating on the surface of co-composted biochar particles, that strengthens biochar-water interactions and enhanced nutrient retention. The authors suggested that the organic coating originated from the sorption of compost derived OC on biochar surface during composting and may allow for the retention and then slow release of nutrients from compost. Interestingly, they found that the chemistry of the coating was different from both biochar and compost, as the organic coating presented a higher electron exchange capacity than the one from both biochar and compost. They suggested that the reaction of compost organic matter with biochar created more reactive carbon moieties that then formed the organic coating. However, up to now, no studies evidenced that the co-application of biochar with a mature compost, that were not co-composted, may also lead to the formation of such organic coating on biochar surface.

Microbial biomass

Biochar large pore distribution and surface area (Chia et al. 2015) were found to provide potential habitats for soil micro-organisms (Jaafar et al. 2015). As mature compost is thought to contain highly active microbial communities (Chander and Joergensen 2002) and to promote soil microbial diversity and activity (Farrell et al. 2009), we could suggest that its combination with biochar may induce the colonization of biochar porous structure by microorganisms. Microbial processes were shown to actively participate to the OM stabilization through aggregate formation, since soil aggregate C are composed of nearly 50 % with microbial necromass derived C (Angst et al. 2021). However, as biochar was found to induce inhibitive effects on plant growth through the release of toxic compounds (Gale et al. 2016; Seehausen et al. 2017; Deenik et al. 2010), we could also suggest inhibitive effect of biochar-derived toxic compounds on microorganisms derived from compost. Further research would be needed to investigate the direct effects of biochar on microbial activity.

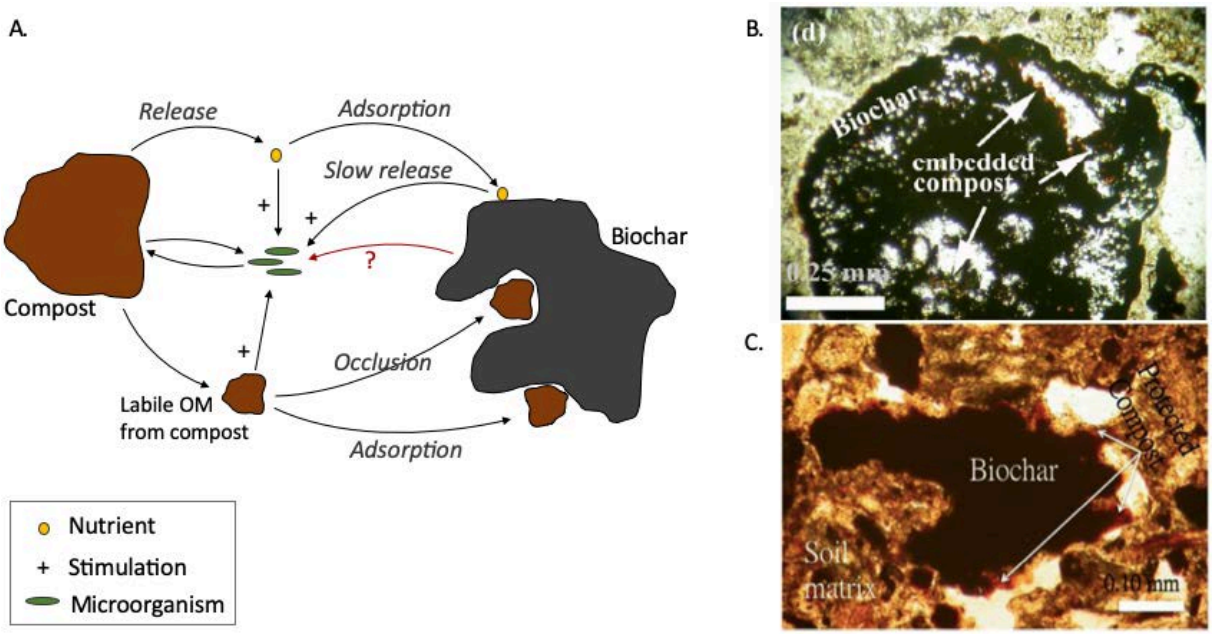

Figure 18 (A) Mechanisms underlying biochar-compost interactions on C mineralization (Jien et al. 2015; 2018; Chander and Joergensen 2002), (B) and pictures from plane polarized light microscope of compost embedded in biochar porous structure (Jien et al. 2015) and (C) compost adsorbed on biochar surface (Jien et al. 2018).

3.3.2 Mechanisms of biochar and compost interactions in relation to the soil matrix

Already after 70 days of incubation, biochar and compost co-application on soil was found to promote the formation of macroaggregates as a result of mutual interaction among the soil particles, biochar and compost, which resulted in the reduction of microbial degradation (Jien et al. 2015). Indeed, although mainly accumulating in the free POM fraction, not protected by the mineral matrix, biochar and compost co-application was also found to incorporate into soil aggregates (Plaza et al. 2016; Cooper et al. 2020). Hence, when applied to soil, biochar and compost particles may remain free or combine with mineral, thus being physically protected against microbial degradation and transport (Fig. 19). In a 8-months field trial, Plaza et al. (2016) suggested that biochar and compost could interact on the formation of organo-mineral associations.

As saw in the previous part (2.3.2), while compost disintegration is mainly promoted by microbial processes (Gregorich et al. 2006), biochar particles can be lost through transportation (Rumpel et al. 2015) and the highly friability potential of biochar could further enhance this transport process due to the high mobility of smaller biochar particles (Spokas et al. 2014). Carbon transport from biochar-compost co-application may thus preferentially concern free POM that may be enriched in biochar particles (Fig. 19). The possibility to decrease biochar friability potential through the use of another organic amendment would allow for a reduction of biochar-derived OC loss and thereby for enhanced

C storage. Moreover, the redistribution of biochar particle from coarse to small particle size may affect its aggregation potential, as the latter was found to increase with decreasing biochar particle size (Q. Zhang et al. 2015). Cooper et al. (2020) indicated that biochar ability to promote aggregate formation may increase with time. As microbial activity is one of the driver of aggregate formation and stabilization (J. Tang et al. 2011), we could suggest that the inclusion of biochar and/or compost particles into aggregates could be further enhanced by the microbial activity promoted by compost and biochar when co-applied on soil. Subsequently, the diversification microbial communities due to the co-application of multiple C sources (Kögel-Knabner 2017), may further benefit to soil structure.

Both organo-mineral interactions and soil aggregation are considered as the main mechanisms promoting the SOM stabilization (Basile-Doelsch et al. 2020) and hence the C persistence in soil. These protection mechanisms would directly impact the retention of particles from biochar and compost. Yet, only few studies focused on the biochar and compost interactions regarding OC distribution in soil and no studies focused on their interactions with regards to biochar friability. Equally unknown is the potential impact of biochar-compost interactions on their incorporation into soil aggregates.

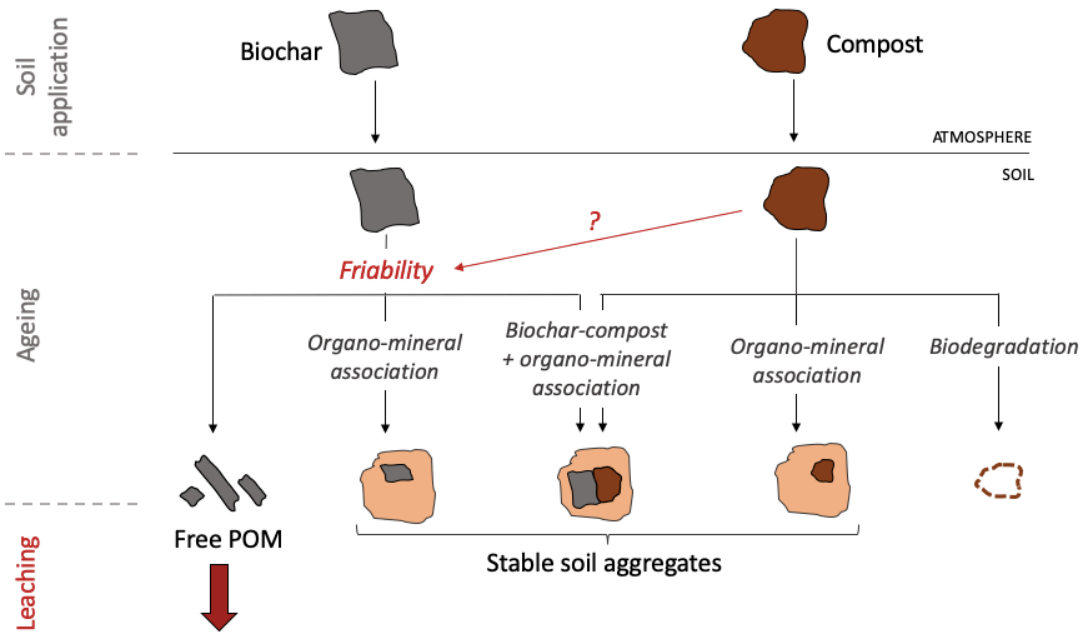

Figure 19 The fate of biochar and compost particles when co-applied in soil matrix (adapted from Cooper et al. 2020; Plaza et al. 2016).

3.4 Effects of biochar and compost interactions on C sequestration and soil fertility

3.4.1 Effect of biochar and compost co-application on C outputs

Effects on OM biological stability

The biological stability of OM is generally estimated through its potential of mineralization. Here, we reported different studies focusing on the effect of biochar-compost interactions on the mineralization of the mixture, as compared to the mineralization of individual components (Tab. 3). Several mechanisms may interfere during the mineralization of biochar-compost mixtures (part 3.3), leading to contrasting effects on the biological degradation, depending on parameters relative to materials and soil characteristics (Tab. 3). Lower C mineralization as a result of biochar-compost interactions was attributed to compost compounds rather than biochar compounds, since biochar was suggested to protect compost from biological degradation (Ngo et al. 2013; Tsai and Chang 2019). In the case of excessive compost application, biochar addition was found increase or decrease or have no effect on C mineralization, depending on the soil type (Tsai and Chang 2019; Tsai and Chang 2020). Higher of C mineralization as a result of biochar-compost interactions, was attributed to a stimulation of the mineralization of the most labile components from biochar over a short-term period (2 months) (Tsai and Chang 2020). Studies generally focused on the effect of soil amendment with biochar-compost mixtures on the C mineralization attributed larger changes on the C mineralization from compost rather than from biochar. The effects of compost on biochar mineralization remain rather scarce, although the presence of labile organic C sources has been shown to accelerate black carbon decomposition (Liang et al. 2010).

The studies we reviewed in this work (Tab. 3) last between 26 days and 14 months. However, ageing process may induce changes in the characteristics of biochar and compost (parts 2.2.3 and 2.3.2), which could influence their interactions on C mineralization. Hence, the effect of ageing on biochar-compost interactions as affecting biological stability would need further consideration.

Table 3 Co-application of biochar and mature compost on C mineralization. Exp.: experimental conditions. Lab: laboratory incubation. Field: fiels experiment. n.s.: not specified.

Exp.	Duration	Biochar feedstock	Compost feedstock	Soil texture	Application dose to soil	Interaction effect	Reference
Lab	60 days	Holm oak, 600 °C	pruning waste	sandy loam	to increase SOC to 1%. 50/50 C content	No evident interaction	Teutscherova et al. 2017
Lab	4 months	bamboo, 450 °C and jarrah, 600 °C	green and animal wastes	brown clay loam	Compost: 20 t ha−1 Biochar: 10 t ha−1	No evident interaction	Darby et al. 2016
Lab	56 days	rice husk, 700 °C	cow manure	sandy loam	Compost: 20 t/ha Biochar: 40 and 80 t/ha	Inhibition of C mineralization	Jien et al. 2018
Lab	70 days	rice husk, 700 °C and 400 °C	cow manure	sand, silty clay loam, silt loam	Compost: 20 t/ha Biochar: 40 and 80 t/ha	Inhibition of C mineralization	Jien et al. 2015
Field	5 months	willow wood, 550 °C	greenwaste, bagasse, chichen manure	acidic clay	Compost: 25 t/ha Biochar: 2.5 t/ha	No evident interaction	Agegnehu et al. 2016a
Lab	7 months	bamboo, 500-600 °C	buffalo manure	no soil	no soil	Inhibition of C mineralization	Ngo et al. 2013
Lab	3 months	garden peat, 450 °C	farm manure	n.s.	2 % w/w, different rates of biochar-compost mixtures	Inhibition of C mineralization	Qayyum et al. 2017
Lab	14 months	lead tree, 500-700 °C	swine manure	Clay and clay loam	Compost: 90 t/ha Biochar: 9 - 18 - 36 t/ha	Inhibition, stimulation and no evident interaction	Tsai and Chang 2019
Lab	13 months	ash, bamboo, lead tree, 500-700 °C	poultry-livestock manure	Clay and clay loam	Compost: 90 t/ha Biochar: 36 - 90 t/ha	Inhibition, stimulation and no evident interaction	Tsai and Chang 2020
Lab	26 days	wood, 410-510 and walnut shell, 900 °C	n.s.	silt loam	Compost: 100-120 kgN/ha Biochar: 1 % (ww)	Inhibition	Mukome et al. 2013

Effects of biochar-compost mixtures on particle removal through transport process

In an unsaturated flow leaching experiment, Iqbal et al. (2015) evidenced that adding biochar to mature compost did not affect the leaching of dissolved organic carbon. In a 1-year litterbag experiment conducted under tropical field conditions, Ngo et al. (2016) highlighted that in mixture, the presence of biochar decreased C removal of biochar-compost mixture through physical disintegration and/or leaching processes, probably due to the protection of compost in the biochar structure. In a three-years experiment under tropical field condition, Doan et al. (2015) showed that co-application of biochar and vermicompost significantly reduced the soil detachment, leaching and runoff water, even more than the single application of biochar or vermicompost. Hence, co-application of biochar with compost or another uncharred organic material may be a better way to stabilize SOM and sequestrate carbon in the soil than individual application through alleviation of particle removal (Jien 2019). However, studies investigating biochar-compost interactions on transport processes of the mixture are scarce and none of them was done under temperate conditions. How biochar and compost interaction may affect the retention of biochar and/or compost particles and the role of the soil matrix in this interaction still remains not sufficiently understood.

Biochar-compost interactions on C recalcitrance, using the thermal stability approach

As previously seen, thermal analysis could allow for the estimation of OM chemical recalcitrance (part 1.2.2). However, mechanisms driving thermal interactions are complexes and there are still unresolved issues related to differences in the thermal stability of single components compared to their mixtures (Plante et al. 2009). Therefore, when different C sources are mixed before thermal analysis, the thermal stability of the mixture could be slightly biased as compared to the additional effects of the components when analyzed separately. For instance, the co-pyrolysis of biomass-coal mixtures evidenced interactions on the yield and composition of the pyrolysis products, as a result of interactions occurring during the analysis (Tab..4). Various factors were shown to affect the biomass-coal interactions, such as the pyrolysis parameters (e.g. temperature) and material characteristics and amount (Tab. 4). The interaction processes may include adsorption on surfaces, such as electrostatic interaction, surface complexation and precipitation, ion exchange, functional groups and π-π interactions, and hydrophobic sorption (Ahmed and Hameed 2020).

Table 4 Interactions following the co-pyrolysis of vegetal biomass and coal material with high thermal stability.

Biomass feedstock	Pyrolysis technique	Effect of interaction	Factors affecting the interaction	Reference
walnut shell and pine	TG, Fixed-bed reactor	Higher tar, char and gas. Change the tar composition.		He et al. 2021
poplar sawdust	TGA	Higher the decomposition of lignite and the pyrolysis oil yield.	Biomass type and amount volatile matter	Guo et al. 2015
pinewood	TGA, low and moderate heating rate with pyrolysis GC-MS	Change the composition of the pyrolysis oil	Pyrolysis technique	Jones et al. 2005
rice straw and wood	drop tube fixed-bed reactor	Higher gas yield and lower tar and char yields	Biomass type	Krerkkaiwan et al. 2013
sawdust	TGA	Lower char yields due a higher rate of degradation		Park et al. 2010
pine wood	semi-batch type drop tube reactor	Higher tar, and lower char, CH_4, and C_2H_4		Soncini et al. 2013
pine sawdust	TGA	Higher volatile yield values.		Ulloa et al. 2009
cedar sawdust	infrared heating furnace	Higher tar yield	Void space between biomass and coal articles	Zhu et al. 2021
corn cob	TG and Py-GC-MS	Higher decomposition and cracking of tar macromolecules to form semi-coke		R. Zhou et al. 2022
legume straw	free fall reactor	Higher liquid and tar yield and lower char yields. Change in the gaseous composition (higher CH_4 / lower CO, CO_2 and H_2).	Quantity of biomass, pyrolysis temperature	Zhang et al. 2007

3.4.2 Effects of biochar and compost on soil fertility and plant growth

As previously reported (part 3.3.1), one of the most dominant biochar-compost may be related to the nutrient and especially compost-derived nitrogen retention on biochar porous structure (Abbott et al. 2018). Biochar was evidenced to retain available nutrients, making it effective in reducing N losses, and benefit to composting performance when co-composted (Mujtaba et al. 2021; Guo et al. 2020). However, after the composting process, co-composting process induced no significant effect on nutrient leaching from biochar, and biochar did not significantly reduce the leaching of nutrients released from compost, as compared to compost only treatment (Iqbal et al. 2015). Further, Ngo et al. (2016) did not evidence a significant biochar-compost interaction effect on N removal, from a 1-year field experiment under tropical field conditions. Such absence of significant biochar-compost interaction on nutrient retention is surprising, as they are not consistent with mechanisms of biochar-compost that may favor the nutrient retention and N slow release (part 3.3.1). Hagemann et al. (2017a) highlighted biochar nitrate capture as a relevant process controlling total nitrate budgets of co-composted biochar, resulting in slow nitrate release. The potential effects of biochar and mature compost interactions on nutrient retention still need further investigation.

The liming effect due to biochar addition may reduce exchangeable soil aluminium (Al), which is believed to be very toxic to plants (Zheng 2010). Steiner et al. (2007) reported that Al toxicity reduction following hardwood-derived biochar application. Therefore liming effect of biochar is often reported as one of the main mechanisms behind the increased crop yields (Wang et al. 2019). On the other hand, several studies reported inhibitive effects of biochar on plant growth through the release of toxic compounds (Gale et al. 2016; Seehausen et al. 2017; Deenik et al. 2010). Further research would be needed to investigate the effect of compost on the inhibitive effect on plant growth from biochar.

Agegnehu et al. (2017) evidenced that biochar-compost application were more generally effective in improving soil properties and crop yield than biochar alone. A recent meta-analysis reported beneficial effects of co-composted biochar to further improve compost performance on soil fertility and crop yield only in sandy soils or during a drought event (Wang et al. 2019). Most studies focus on co-composted biochar application and not biochar mixture with mature compost.

4 Objectives of the study

Due to their different production process, biochar and compost present contrasting characteristics, which then induce complementary effects on C sequestration and soil fertility when co-amended in soil (e.g. Oldfield et al. 2018). In particular, biochar and compost were shown to benefit to plant production preferentially when co-amended in sandy and poor-nutrient soils and/under drought conditions rather than under temperate climate (e.g. Wang et al. 2019). Biochar and compost were shown to interact through several mechanisms, including physical protection of compost-derived labile C, particles and nutrients into biochar porous structure. However, their effects on biological mineralization may depend on materials and soil characteristics, thereby favoring certain biochar-compost mechanisms over others. Equally uncertain are the effects of biochar-compost interactions on biochar and compost particles retention, as well as on biochar potential for physical degradation. The main soil parameters characteristics that may contribute to plant growth following biochar and compost amendment have been attributed to nutrient availability, water holding capacity, liming effect (pH) and soil biological processes (Wang et al. 2019). Biochar and compost were found to interact on soil fertility through changes in nutrients dynamic (Hagemann et al. 2017a). However, such effect has not been validated using biochar combined with mature compost and under crop field conditions. Although biochar and compost were evidenced to interact on C removal and soil fertility in the first months or years after their blending, the temporality of their effect still remains in question. Indeed, abiotic processes were shown to affect biochar oxidation previously to biological degradation processes (Cheng et al. 2006) and ageing processes may induce changes in biochar and compost characteristics (Abbott et al. 2018) which, among other, may increase the sorption potential of biochar (Nguyen et al. 2017).

Although several studies investigated the interactions mechanisms between biochar and compost and their effects as organic amendment, research gaps still remain concerning the temporality and mechanisms of their interaction as well as their effects on C persistence and soil fertility. **The aim of the thesis was to investigate the mechanisms controlling the biochar-compost interactions and their effects on carbon sequestration and soil fertility.** The main research questions addressed in the thesis were mostly focused on soil carbon sequestration, as compared to the soil fertility.

Our work was divided into three individual experiments aiming to answer the following questions (Q.) and to validate their corresponding hypothesis (Hyp.). The following figure (Fig. 20) summarizes the global approach of our work, with corresponding experimental design and analytical methods.

Q.1: Does the blending of biochar and compost affect their chemical characteristics? (Chapter II)

Hyp.1: Compost may promote biochar abiotic oxidation during their blending and such interactions may affect the chemical signature and thermal stability of the mixture.

Q.2: Does weathering changes the effect of biochar-compost interactions on the biological stability of the mixture and on plant growth? (Chapter III)

Hyp.2.1: Weathering may promote biochar and compost interactions on their biological stability through lower compost-derived C and higher biochar-derived C mineralization.

Hyp.2.2: Weathering may increase the positive effects of biochar- compost interactions on plant growth.

Q.3: Do biochar and compost interactions benefit to C and N retention under temperate field conditions? (Chapter IV)

Hyp.3.1: Compost may reduce biochar-derived C removal through alleviating its physical disintegration.

Hyp.3.2: Biochar and compost may induce synergistic effects on the incorporation of particles into soil aggregates.

The effects of weathering on chemical and biological properties of the mixture was allowed by an artificial physical weathering, as it has been reported as an efficient way to simulate long-term ageing (Wang et al. 2020). We investigated the effect of biochar-compost interaction on the particle removal under field conditions using the litterbag technic. In order to localize particle accumulation in C pools of soil amended with the mixture, we combined aggregate and density fractionation. Analytical methods to investigate changes of chemical characteristics due to biochar-compost blending included both Rock-Eval® thermal and FTIR spectroscopic analysis (MIRS). We used stable isotope signature to distinguish mechanisms affecting biochar and compost separately within the mixture. Based on the isotope signature evolution from each component when individually applied, we could calculate the expected result from a mixture where additive effects, i.e. no interaction, would occur. The comparison of the expected and the measured mixture allowed for the estimation of biochar-compost interactions.

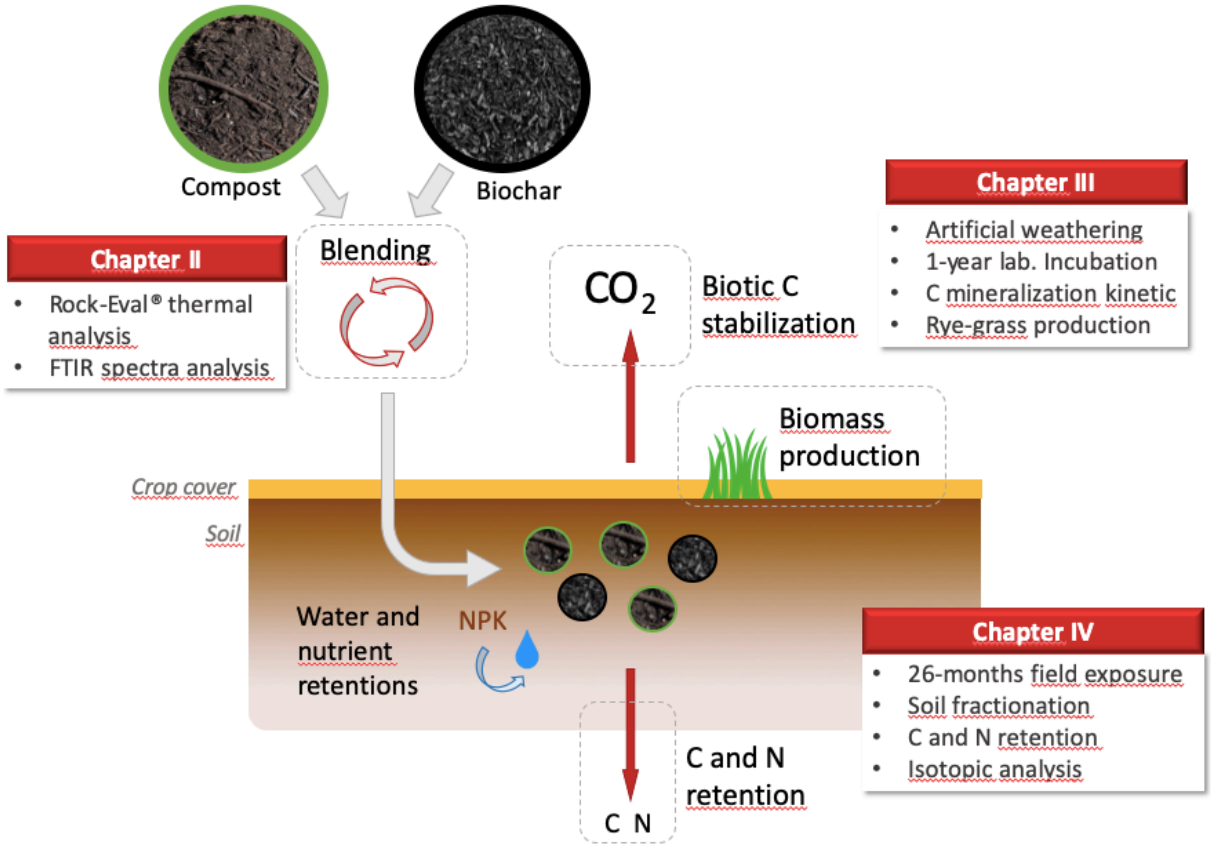

Figure 20 General approach, experimental design and analytical methods of the thesis.

CHAPTER II

Abiotic interactions of biochar and compost during their blending may reduce the biochar thermal stability.

This chapter is based on the article in preparation.

Marie-Liesse AUBERTIN[(1,2)*], David SEBAG[(3)], Pascal JOUQUET[(4)], Daniel PILLOT[(3)], Violaine LAMOUREUX-VAR[(3)], Isabelle KOWALEWSKI[(3)], Cyril GIRARDIN[(2)], Sabine HOUOT[(2)], Cornelia RUMPEL[(1)]

[(1)] *Sorbonne University, Institute of Ecology and Environmental Sciences, UMR 7618, CNRS-UPMC-UPEC-INRA-IRD, Paris, France*

[(2)] *Paris-Saclay University, INRAE, AgroParisTech, UMR EcoSys, 78850 Thiverval-Grignon, France*

[(3)] *IFPEN, Earth Sciences and Environmental Technologies Division, Rueil-Malmaison, France*

[(4)] *IRD, iEES Paris UMR 242, Centre IRD Ile de France, Bondy, France*

*Corresponding author: marieliesse.aubertin@gmail.com

Chapter II - Abiotic interactions of biochar and compost during their blending may reduce the biochar thermal stability.

1 Abstract

Upon environmental exposure, interactions among organic materials are mostly thought to occur via biotic mechanisms. In this study, we tested if this interaction also occurs instantaneously through physical mixing of two substrates. To this end, we analyzed five biochar-compost mixtures differentiated by biochar type using Rock-Eval® thermal analysis and Fourier transformed infrared (FTIR) spectroscopy. Unexpected lower CO_2 emission temperature of the mixture at the oxidation stage were correlated with unexpected decrease of aromatic carbon from the mixtures immediately after mixing. In contrast to other studies which show that the interactions of organic matter types following thermal analysis may occur mainly due to methodological bias, our results open a new perspective of abiotic interactions occurring during the blending.

2 Introduction

Co-application of organic amendments with contrasting properties such as biochar and compost has been suggested as a promising avenue to improve C sequestration in soils (Ngo et al. 2016; Teutscherova et al. 2017; Jien et al. 2015). While biochar is a stable organic matter (OM) compound originating from pyrolysis at high temperature and enhanced with aromatic structures, compost originates from microbial decomposition and contains more labile compounds (de Bertoldi, Vallini, and Pera 1983). Upon environmental exposure, interactions between both materials may prevent biochar and compost from physical disintegration and microbial decomposition (Ngo et al. 2016; Jien et al. 2015). Laboratory incubation studies evidenced biotic processes such as the stimulation of biochar decomposition by addition of labile compounds such as glucose (Nocentini et al. 2010) or compost (Aubertin et al. 2021) as an underlying explanation. In the current state of knowledge, biochar-compost interactions are thought to be induced through microbial processes driving decomposition and turnover of organic compounds (Kuzyakov 2010; Paul 2016).

However, abiotic processes, in particular oxidation has been found to precede biotic processes and enhance the creation of negative surface charge and CEC of biochar (Cheng et al. 2006). In particular,

it was shown to increase oxygen-containing functional groups on biochar surface, especially carboxyl groups, and to increase the specific surface area through the development of mesopores, thereby increasing the sorption capacity of biochar (Fan et al. 2018). The increase of oxygen-containing functional groups may favor the adsorption of organic coating, which may further increase the number of oxidized groups on biochar surfaces (Conte and Laudicina 2017). Subsequently, the adsorbing capacity of biochar may promote physical protection of labile OM by sorption or incorporation into microaggregates (Maestrini, Nannipieri, and Abiven 2015) and improve nutrient retention (Cheng et al. 2006). Recently, Prévoteau et al. (2016) highlighted the dramatically underestimation of the electron donating capacity of biochar, although it confers a high potential for redox processes on biochar surface.

Similarly, the reaction of compost OM with biochar was found to create more reactive carbon moieties, thereby favoring the formation of organic coating on biochar surface (Hagemann et al. 2017b). Indeed, the chemistry of a coating from co-composted biochar with uncharred material was found to be different from both biochar and compost compounds (Hagemann 2017b). However, the formation of organic coating on biochar surface, when combined with mature compost still remains unexplored. Infrared spectroscopy has been proven as a powerful tool to chemically characterize and to estimate changes in the type of functional groups of biochar or black carbon (Cao et al. 2017; Lago et al. 2021; Cheng et al. 2006) and compost compounds (Ait Baddi et al. 2004). Biochar resistance to oxidation is commonly considered as a proxy to assess its stability (Leng et al. 2019). However, although generally not seen as a major SOM stabilization mechanism, the intrinsic chemical recalcitrance of OM remains an important factor for the long-term OM stabilization of charred material (Marschner et al. 2008). Hence the oxidation potential of biochar may be related to its chemical recalcitrance. Thermal analysis was suggested as good tool to evaluate the recalcitrance of OM (Barré et al. 2016) and to allow sensitive detection of organic amendments in soils under arable land use (Tokarski et al. 2018). In particular, the Rock-Eval® analysis appears to be a powerful tool in black carbon analysis and quantification, as it may capture a major part of the black carbon continuum including its stable fractions (Poot et al. 2009). As far as we know, no studies have ever investigated the thermal behavior of biochar-compost mixtures, using the Rock-Eval® analysis.

The aim of this study was to investigate abiotic interactions between biochar and compost during their mixture. Therefore, we analyzed the thermal behavior and the spectroscopic signatures of biochar-compost blends immediately after their mixing. We used five biochar-compost mixtures prepared with contrasting types and hypothesized that biochar and compost abiotic interactions may occur during their mixture. We investigated the interactions by comparing the mixture results to the expected results, calculated from the analysis of the components treated separately.

3 Materials and methods

3.1 Materials

Commercial grade biochars were obtained from VT-Green (Allier, France), using an industrial pyrolysis reactor (Biogreen® Technology, ETIA, Oise, France). Five feedstocks were selected for biochar production: maize cobs (*Zea mays* L.), miscanthus straws (*Miscanthus x giganteus*, Greef and Deuter), wood granules (< 8 mm) from resinous trees (granula), and coffee residues resulting from coffee liqueur extraction. Detailed information on the feedstock origin from biochars are provided in the study of (Nobile, Denier, and Houben 2020). Feedstocks were pyrolyzed with a temperature ranging from 450 to 650 °C (Tab. 5) without oxygen and with a residence time of 10 min. The compost was made from green wastes at the platform Fertivert (Normandy, France) with a process including 4 months fermentation and 2 months maturation. The components were dried at 40 °C and ball-milled (< 200 µm) previously to their mixing. The drying process enabled to reduce the biotic processes and the grinding allowed for higher abiotic interactions due to higher surface area and for a better homogenization of the mixture. Each biochar was mixed with the compost, with a massic biochar-compost ratio of 20/80 %. This ratio allowed similar volume of the components, since the volumic mass of the biochar was lower than the one of compost.

The total carbon content (TC) and nitrogen (TN) of the mixtures and single components were analyzed with an elemental analyzer (Vario Isotope Select, Elementar France, Lyon) and TC corresponded to organic carbon (OC), since all component were considered as pure OM. Moisture, ash content, volatile matter and fixed carbon were determined by thermogravimetric analyses (TGA/DSC1 STAR System, Mettler-Toledo, Viroflay, France) (Aubertin et al. 2021). The pyrolysis temperature of biochar productions and the elemental content and proximate analysis of the compost and biochars are presented in Table 5.

Table 5 Pyrolysis temperature (Tpyr) of biochar production, total carbon (TC) and total nitrogen (TN) from elemental analyzer and proximate analysis of compost and biochars.

Feedstock	Tpyr (°C)	TC (wt %)	TN (wt %)	Moisture (%)	Volatile matter (%)	Fixed C (%)	Ash (%)
Compost							
Compost	-	21.0	2.3	4.2	38.8	1.9	59.3
Biochar							
Coffee	650	74.1	3.6	3.3	37.1	56.8	6.1
Granula	550	77.2	0.4	1.6	29.9	66.6	3.5
Maize	450	63.9	1.1	2.5	25.9	45.6	28.5
Miscanthus	550	74.0	0.5	2.5	22.8	63.6	13.6
Refusal	450	55.5	0.9	3.2	32.0	49.4	18.6

3.2 Choice of the Rock-Eval® thermal technique

During the temperature evolution, thermal reaction may be exothermic or endothermic, depending on the heat they may emit or absorb, and it may induce mass loss of the sample through the emission of gaseous compounds such as CO, CO_2, CH_4, H_2 and H_2O (Mohan et al. 2006). Hence, thermal techniques are generally based on the evolution of the sample weight, as recorded by thermogravimetry (TG) analysis, or of the temperature difference between the sample and a standard, as recorded by both differential thermal analysis (DTA) and differential scanning calorimetry (DSC) methods, or of gas evolved, as recorded by both evolved gas analysis (EGA) and Rock-Eval®, as a function of temperature (Plante et al. 2009). Both EGA and Rock-Eval® pyrolysis correspond to coupling techniques where the thermal reaction products are subsequently measured by other detectors and are thus interesting to have a better distinction of the underlying processes and reactions observed during the temperature program (Plante et al. 2009; Behar et al. 2001). Additionally, the most commonly used pyrolysis device for analytical purposes is followed by a gas chromatographic (GC) separation step prior to identification by mass spectrometry (MS) (Derenne and Quénéa 2015). As this analytical pyrolysis device may not allow for the detection of the most polar products or the heaviest ones, it can be optimized for instance by coupling with other devices, but it may be more difficult to interpret (Derenne and Quénéa 2015). While all analytical pyrolysis GC-MS, EGA and Rock-Eval® determines the CO and CO_2 gas the nature and amount of volatile products formed during thermal degradation of material, the Rock-Eval® additionally determines amount and nature of hydrocarbons cracking and thus the H- bondings, using a flame ionization detection during the thermal degradation of the material (Behar et al. 2001; Lafargue et al. 1998). Hence, the Rock-Eval® analysis appears to determine a more complete range of thermal characteristics as compared to the other thermal analysis techniques.

3.3 Rock-Eval® thermal analysis and use of the data

Presentation of the Rock-Eval® technique

The Rock-Eval® technic was initially designed for petroleum source rocks analysis, in order to estimate the maturity degree of rocks. This technic consists of progressive temperature increase in anoxic conditions (pyrolysis stage), followed by a second heating under oxygen (oxidation stage) (Lafargue et al. 1998; Behar et al. 2001). During the pyrolysis stage, the released hydrocarbons are monitored by a flame ionization detector (FID) and during both pyrolysis and oxidation stage, released CO and CO_2 are monitored on line by means of an infra-red cell (Fig. 21).

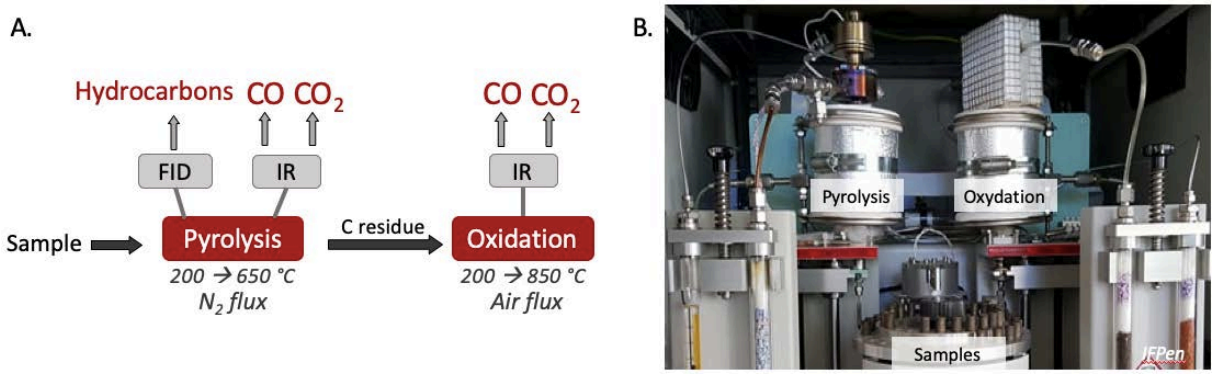

Figure 21 Rock-Eval® (A) functioning principle (adapted from Disnar et al. 2003) and (B) engine. FID: flame ionization detector; IR: infra-red cell.

Rock-Eval® Analysis

The analyses were gathered on a Rock-Eval® 6 (Vinci Technologies), following an analytical method dedicated to soil analysis as described in Disnar et al. (2003) and after prior calibration using the standard rock # IFPEN_160 000. The pyrolysis stage was performed under N_2 and the temperature raised from 200 up to 800 °C at 25 °C/min. The studied biochars had underwent different temperatures of pyrolysis during their production, ranging from 450 to 650 °C. Since the interactions of free radicals during pyrolysis process may be affected by the temperature (He et al. 2021), we allowed a better comparison of the pyrolysis results among the biochars by raising up to 800 °C the pyrolysis stage from Rock-Eval®, instead of the conventional temperature of 650°C of the soil dedicated analytical method. At the end of the pyrolysis stage, temperature cooled down and the oxidation step followed with a temperature rise from 200 up to 850 °C at 25 °C/min. During the analytic process, hydrocarbon rate from the outgoing flow was measured using a flame ionization detector, while the CO_2 and CO evolved were measured with infra-red detector. Peak temperature Tpeak $S4CO_2$ was determined as the temperature at which the higher CO_2 emission was observed during the oxidation stage and Max $S4CO_2$ was determined as the maximal CO_2 emission during the oxidation stage. As Tpeak $S4CO_2$ may be influenced by the amount

of sample being used for analysis (Hazra et al. 2020), we chose the same weight for all samples: 6 mg of compost, biochars and their mixtures.

Use of the data

For the thermograms analysis, we chose to work with values in mV rather than converted into mg C, in order to avoid considering the uncertainty related to the conversion of the machine. We defined biochar-compost interaction from thermal results on biochar-compost mixtures as any deviation in the experimental results when compared to the expected results based on individual components contributions. In order to investigate the biochar-compost interactions of temperature parameters, we calculated the expected values based on signal reconstructed using Rock-Eval® thermograms measured on their composing endmembers for temperature parameters (Kanari et al. 2021). Therefore, we calculated the expected CO_2 thermograms at the oxidation stage from the biochar-compost mixtures by summing the contribution of the single components, as shown in Eq. 1. The expected mixtures, correspond to the simple additional effect of the components of the mixtures, without any synergetic interaction.

$$CO_{2\ \text{Mixture (expected)}} = 0.2 * CO_{2\ \text{Biochar}} + 0.8 * CO_{2\ \text{Compost}} \quad \textbf{(1)}$$

We calculated the differential CO_2 thermogram at the oxidation stage for the mixtures, by subtracting the expected values from the measured values (Eq. 2).

$$\text{Differential } CO_{2\ \text{Mixture}} = CO_{2\ \text{Mixture (measured)}} - CO_{2\ \text{Mixture (expected)}} \quad \textbf{(2)}$$

With these data, we calculated the interaction ratio of the mixtures, corresponding to the part of the $S4CO_2$ that was emitted at a different temperature than expected (Eq. 3). These values were then used as Rock-Eval® parameters for the PLSR model.

$$\text{Interaction ratio } (\%CO_2) = \frac{\text{positive area under differential } CO_{2\ \text{Mixture}}}{\text{total area under } CO_{2\ \text{Mixture (measured)}}} \quad \textbf{(3)}$$

3.4 FTIR spectra acquisition and pre-processing

The mixtures and their single biochar and compost components were ground to a fine powder (< 200 µm) and scanned with a spectrometer (FTIR 660, Agilent, Les Ulis, France) in the mid-infrared (MIR) spectral range from 4000 to 400 cm^{-1} with a KBr separator and a DTGS detector. The diffuse reflectance (DR) measurements were made at 1 cm^{-1} intervals but a 2 cm^{-1} interval was considered in the analysis. The DR was converted to absorbance (A) using the equation: A = log(1/DR). The spectra were smoothed using the Savitzky-Golay smoothing method (a window size of 31 cm^{-1} and a polynomial order of one) to further eliminate noise. The wavenumbers corresponding to CO_2 (2500-2300 cm^{-1}) were removed. We made 8 to 10 replicate analysis for each biochar-compost mixture. The band assignments to wavenumbers are reported in Table 6.

Table 6 Chemical bond assignment to wavenumbers.

Wavenumber (cm^{-1})	Band assignment	Reference
3400	-OH stretching vibration of bonded hydroxyl groups and water	Cheng et al. 2006 Bekiaris_2016
3600–3100	-OH stretching vibration	Okolo et al. 2015
1690, 1720	Carboxilic and ketones C=O	Ascough et al. 2011, Kamegawa et al. 2002, Singh et al. 2016
1650	Aromatic C=O stretching vibration	Okolo et al. 2015
1600, 1510	C=C vibration of the aromatic skeleton of lignin	Weiland and Guyonnet 2003 Toscano et al. 2015
1600	Aromatic C=C and C=O of quinone	Ascough et al. 2011
1460	Aromatic C=C stretching vibration	Okolo et al. 2015
1435	Aliphatic CH2 and CH3 bending vibration	Okolo et al. 2015
1280–1000	Aliphatic skeletal C-C; C-O stretching; and -OH bending vibrations	Okolo et al. 2015
1019, 960	C-OH, C-O-C, C-C, ring from PECTIN	Toscano et al. 2015

3.5 The PLSR model

We evaluated the relationships between the CO_2 difference from Rock-Eval® oxidation stage between measured and expected mixtures, and the chemical bonds of the biochar-compost mixtures. Therefore, partial-least square regression model (PLSR) was performed on the full FTIR spectra of the mixtures using the R 'pls' package (Mevik and Wehrens 2007). Leave-one-out cross-validation was used to select the optimal number of components to be used in the calibration model. Five components were used as the optimal number of PLSR components. The list of PLSR components associated with % variance and

predicted minimum residual sum of squares during validation, as well as the train and cross-validated R^2 are reported in Fig. 22 and in Tab. 7. The model with 5 components showed a % variance of 99.2 %, a RMSE of 3.5 and a train data R^2 of 0.76. The loading values of each component provided an indication of the importance of wavenumbers in the prediction of the PLSR model. All the transformations of the spectra and the PLSR model were implemented using R version 2020 software 3.6.3.

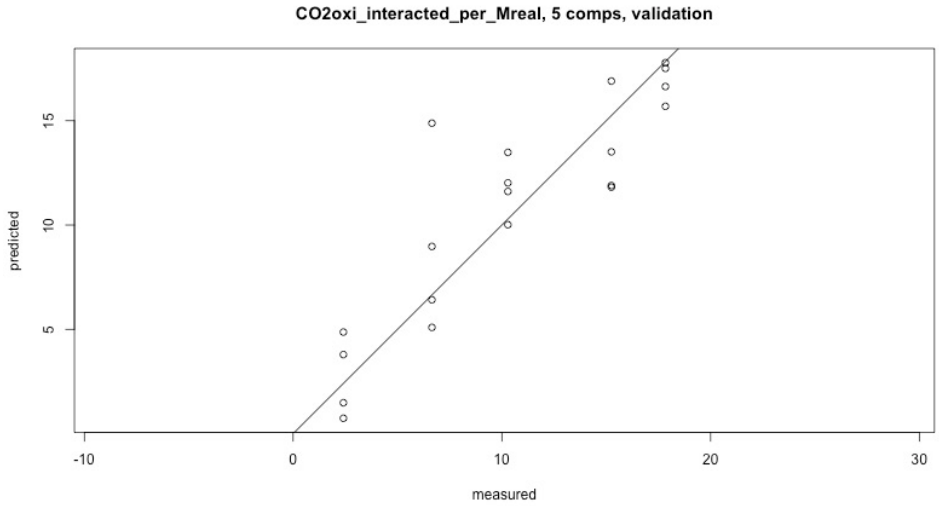

Figure 22 Validation of the PLSR model.

Table 7 Partial least square regression (PLSR) components associated with % variance and predicted minimum residual sum of squares (RMSE) during validation.

	Comp 1	Comp 2	Comp 3	Comp 4	Comp 5
% variance	84.9	96.8	98.0	98.8	99.2
RMSE	5.4	5.6	4.8	3.9	3.5
R2 – train	0.12	0.17	0.51	0.73	0.76
R2 - CV	0.00	-0.02	0.20	0.46	0.58

4 Results

4.1 Emissions during the Rock-Eval® thermal analysis

The main Rock-Eval® parameters are reported in Tab. 8. As we worked based on data from the thermograms, we calculated the contribution in carbon of each emission from the Rock-Eval® thermal is reported in Tab. 9. The CO_2 emission at the oxidation stage was the highest emission, as it represented respectively 65 ± 0 %, 87 ± 3 % and 79 ± 2 % of the total emissions from compost, biochar and the mixtures (Table 9). When regarding the thermogram of the CO_2 emission at the oxidation stage of the biochar-compost measured mixtures, the highest values ranged between 2206 and 3024 mV mg^{-1}, with corresponding temperatures ranging between 429 and 488 °C (Fig. 23). The two peaks corresponding to compost and biochar compounds were distinguishable for the measured and the expected mixtures, with the compost emission starting at lower temperature and recorded lower values than the biochar. For the mixtures containing biochars produced at temperatures > 450 °C, the peak attributed to the biochar compound was shifted to lower temperatures and to higher values, as compared to the expected mixtures, based on results from single components. The expected mixture corresponded to a simulated additive effect of the pure components and therefore, differences between measured and expected mixtures evidenced interactions between biochar and compost on the CO_2 emission from biochar at the oxidation stage.

The hydrocarbon cracking (FID signal) was null for the biochar and it recorded 5 ± 0 % for the compost 3 ± 0 % for the mixtures emissions (Tab. 9). During the pyrolysis stage, biochar-compost mixtures resulted mainly on hydrocarbon cracking, as revealed by the two peaks at 375 °C and 470 °C, with the second peak recording the highest values, between 371 and 403 mV mg^{-1} (Fig. 24). The first peak of the measured mixtures recorded lower values than the expected mixtures, while no differences between measured and expected mixtures were observed at this temperature for the CO and CO_2 emissions during the pyrolysis stage. Hence, our results evidenced biochar-compost interaction to decrease the thermal breakdown of hydrocarbons from compost within the mixture. The CO_2 emission from pyrolysis was the second highest emissions from compost and the mixtures, as it represented respectively 20 ± 0 % and 11 ± 1 % of the compost and the mixture emissions, and only 2 ± 1 % for the biochars. The CO emission at the pyrolysis stage represented respectively 8 ± 0 %, 1 ± 1 % and 5 ± 0 % of the compost, biochar and mixtures emissions. The highest values of the thermograms of both CO and CO_2 emissions at the pyrolysis stage of the measured mixtures did not exceed 175 mV mg^{-1} (Fig. 24). CO emission at the oxidation stage represented the second highest emissions for biochars, with 9 ± 3 % of the total emissions, while it recorded respectively 2 ± 0 % and 3 ± 1 % of the compost and mixtures (Fig. 24). Thermogram of CO emissions at the oxidation stage from the measured mixture recorded

lower emissions than expected, which showed biochar-compost interactions on the reduction of this emission from the biochar compound.

Table 8 Rock-Eval® parameters of the compost, biochars and mixtures. PC: pyrolysable organic carbon; RC: residual organic carbon; TOC: total organic carbon, MINC: mineral carbon; TC: total carbon (Behar, Beaumont, and Penteado 2001).

Biom	PC (%)	RC (%)	TOC (%)	MINC (%)	TC (%)
Compost					
Compost	31 *3*	69 *3*	17 *1*	7 *1*	24 *1*
Biochar					
Maize	3 *0*	97 *0*	73 *6*	5 *0*	78 *6*
Refusal	3	97	71	6	76
Miscanthus	1 *0*	99 *0*	87 *5*	3 *0*	90 *5*
Granula	4 *0*	96 *0*	86 *2*	6 *1*	92 *2*
Coffee	2 *0*	98 *0*	85 *1*	3 *0*	89 *1*
Mixture					
Coffee	15 *0*	85 *0*	29 *1*	7 *1*	36 *1*
Granula	17 *1*	83 *1*	28 *0*	7 *0*	35 *1*
Maize	17 *1*	83 *1*	26 *1*	7 *0*	34 *2*
Miscanthus	15 *0*	85 *0*	29 *0*	6 *0*	35 *0*
Refusal	18 *2*	82 *2*	25 *2*	7 *0*	32 *2*

Table 9 Contribution in carbon of each emission from the Rock-Eval® thermal (mean ±*sd*). HC: hydrocarbon cracking.

Type	---------- Pyrolysis emissions (%) ----------			----- Oxidation emissions (%) -----	
	HC	CO	CO_2	CO	CO_2
Compost	5 *0*	8 *0*	20 *0*	2 *0*	65 *0*
Biochar	0 *0*	1 *1*	2 *1*	9 *3*	87 *3*
Mixture	3 *0*	5 *0*	11 *1*	3 *1*	79 *2*

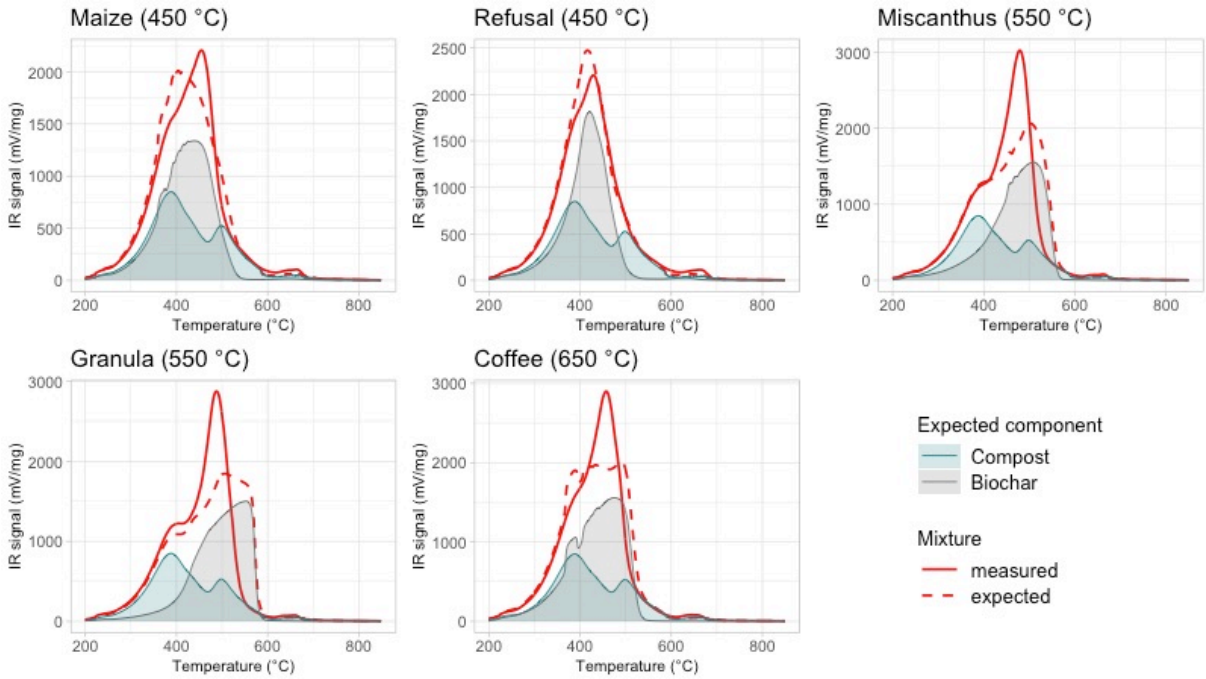

Figure 23 Rock-Eval® thermograms from the CO_2 emitted at the oxidation stage of the measured and expected mixtures, as well as the expected biochars and compost. IR: Infra-red.

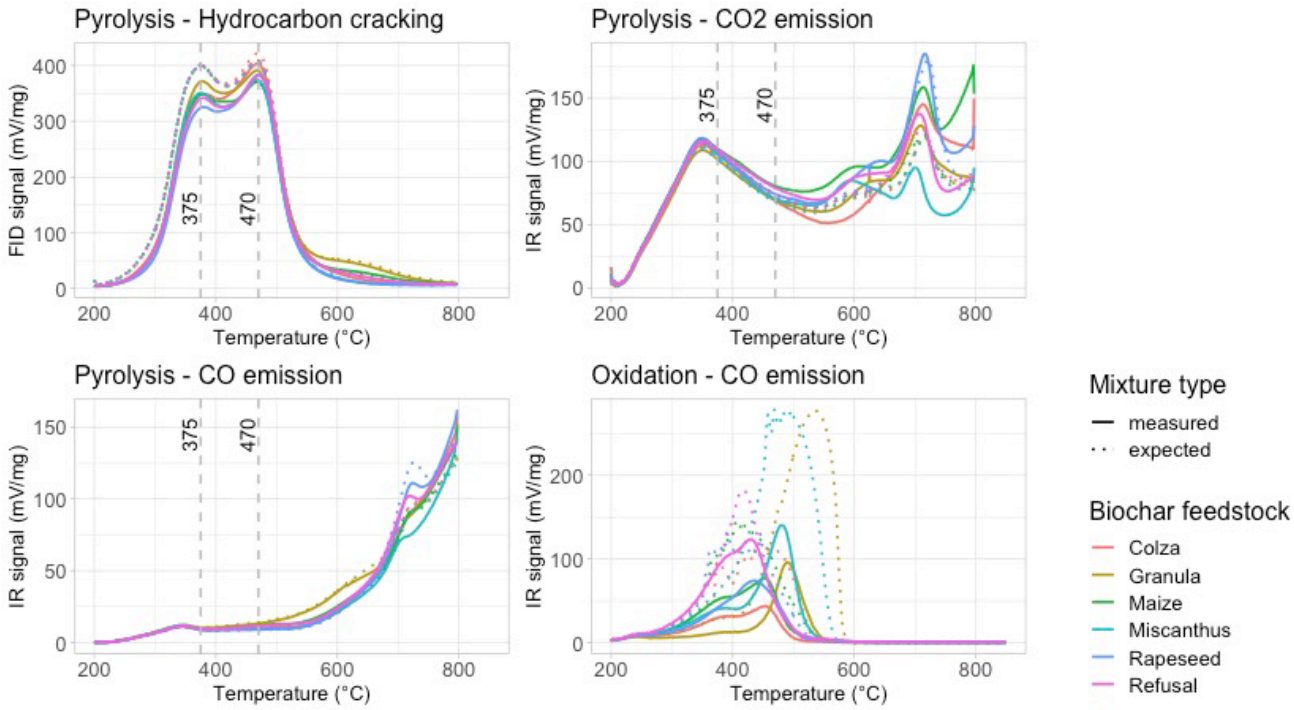

Figure 24 Thermograms of the emissions during the pyrolysis and oxidation stages of the Rock-Eval® analysis, from the measured and expected mixtures. IR: infra-red; FID: flame ionization detector.

4.2 Differential thermogram of Rock-Eval® CO_2 at the oxidation stage

When focusing on the CO_2 emissions at the oxidation stage, two main peaks stood out from the subtraction of the measured and expected mixtures thermograms; one positive and one negative (Fig. 25). The differential thermograms from mixtures containing biochars produced at temperature > 450 °C exhibited similar positive and negative areas (Table 10), with both peaks reaching about 1000 and -1000 mV mg^{-1}. This indicated that biochar and compost may have interacted to lower the CO_2 emissions temperature from the biochar compound, at the oxidation stage. The differential thermograms from mixtures containing biochar produced at 450 °C stood out lower maximal values of the peaks than the other mixtures, around 500 mV mg^{-1}. We defined the "interaction ratio" as the part of CO_2 at the oxidation stage that was emitted at lower temperature than expected. It estimated quantitative values of the change in thermal behavior of the mixture that was induced by biochar-compost interactions. The interaction ratio represented up to 14 % of the total C emissions and was higher for the mixtures containing biochars produced at temperatures > 450 °C, ranging from 10.3 % to 17.8 % of the total CO_2 emission at the oxidation stage, than for the mixtures containing biochars produced at 450 °C, ranging from 2.4 to 6.6 % of the total CO_2 emission at the oxidation stage (Table 10).

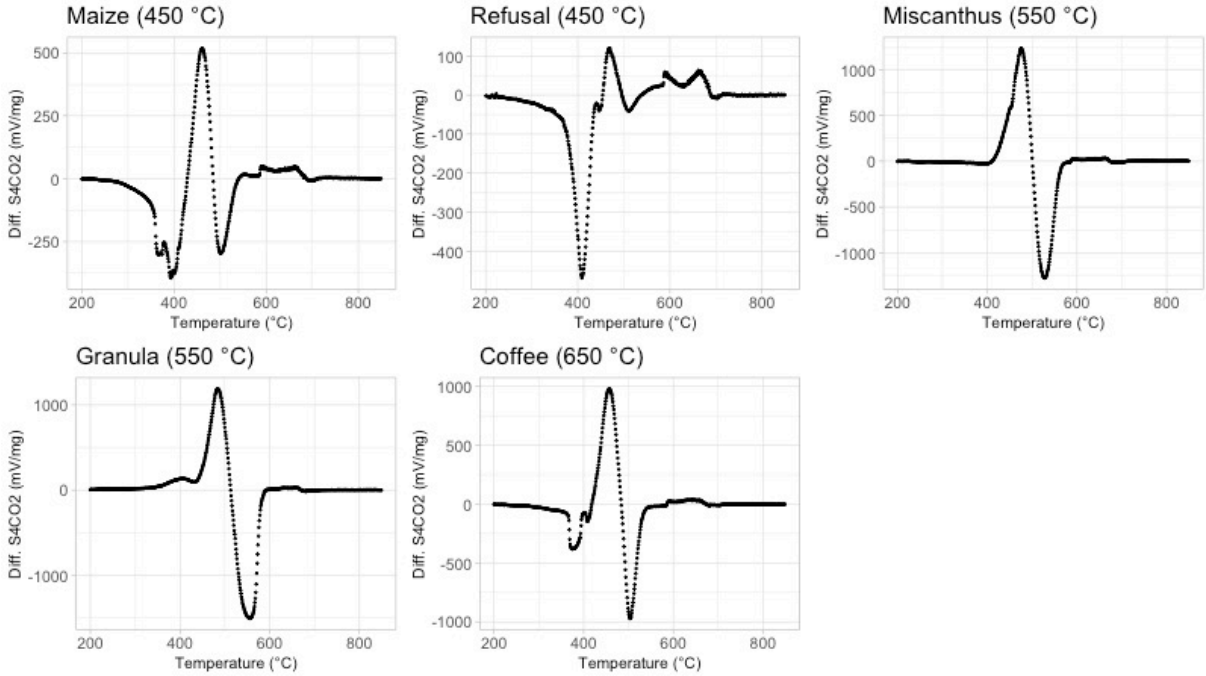

Figure 25 Differential thermograms from the CO_2 emission at the oxidation stage of the measured and expected mixtures. Positive area corresponds to higher CO_2 emissions from the measured mixture than the expected mixture and negative area correspond to higher CO_2 emissions from the expected mixture than the measured mixture.

Table 10 Area under curve from the differential thermograms and interaction ratios of the CO_2 emission at the oxidation stage. Area under curve are presented in % from the total area. The interaction ratios are presented in % of the total CO_2 emission at the oxidation stage of the measured mixture and in % of the total carbon emissions (TC).

Biochar feedstock of the mixtures	Area under curves (%)		Interaction ratios (%)	
	> 0	< 0	(oxidation CO_2)	(TC)
Maize (450°C)	39.4	60.6	6.6	5.0
Refusal (450°C)	25.9	74.1	2.4	1.8
Miscanthus (550°C)	50.9	49.1	15.2	12.0
Granula (550°C)	46.8	53.2	17.8	14.0
Coffee (650°C)	46.2	53.8	10.3	8.2

4.3 Correlation between interaction ratios and FTIR spectra from the mixtures

We investigated if the combustion performance of biochar-compost mixtures during the Rock-Eval® analysis could be predicted by specific chemical bonds. Therefore, we correlated the quantitative values from the interaction ratios from Rock-Eval® analysis, with qualitative values from the full FTIR spectra from the mixtures, using a PLSR model (Fig. 26). Water and aromatic compounds were the main contributor to the prediction model, as evidenced by wavenumbers attributed to stretching -OH vibration (3400 cm^{-1}), aromatic C=C stretching vibrations of aromatic rings (1600 cm^{-1}) and aromatic C=O stretching vibration (1650 cm^{-1}) from the first component of the PLSR model. To a lesser extent, aliphatic compounds and O- and H- functional groups also contributed to the model, as evidenced by wavenumbers attributed to -OH stretching vibration (3600 cm^{-1}), aliphatic C=O and -COOH stretching vibrations (1700 cm^{-1}), aromatic C=O stretching modes (1555 cm^{-1}), aliphatic CH_2 and CH_3 bending vibration (1435 cm^{-1}), aliphatic skeletal C-C; C-O stretching; and -OH bending vibrations (1220 cm^{-1}) and out-of-plane aromatic C-H bending vibrations (970 cm^{-1}) from the second component.

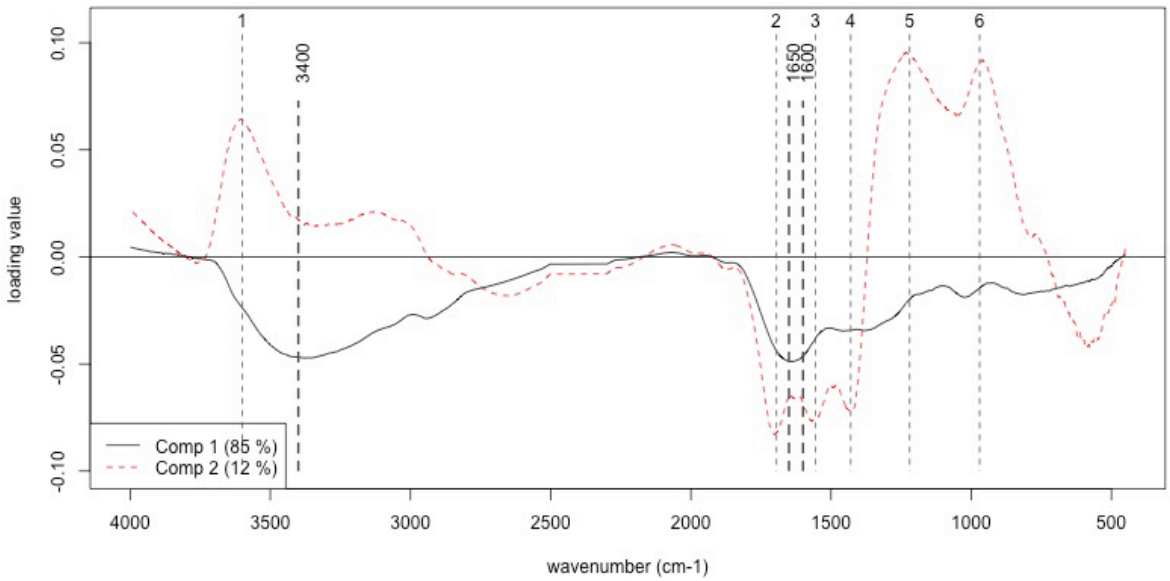

Figure 26 Loading values, corresponding to the contribution of the spectra regions used to construct the predictive models for the two main components of the PLSR model. The wavenumbers from 1 to 6 correspond respectively to 3600, 1700, 1555, 1435, 1220 and 970 cm^{-1}.

4.4 FTIR spectroscopic signature

FTIR spectra of the mixtures recorded three main peaks attributed to O-H bonds (3400 cm^{-1}), aromatic C=C and C=O bonds (1600 cm^{-1} and 1650 cm^{-1}) and aliphatic C-H bonds (1312 cm^{-1}), with the first two prominent absorptions corresponding to the chemical bonds that mainly contributed to the prediction model (Fig. 27). For those chemical bonds, FTIR spectra from the measured mixtures recorded lower or similar absorbance than the expected mixtures. This evidenced biochar-compost interactions to lower content in water and aromatic compounds already before the thermal analysis, and thereby during the blending. The aliphatic compounds and O- and H- functional groups that contributed to a lesser extent to the prediction model did not correspond to specific peak on the FTIR spectra of the mixtures, thus showing that they constituted rather minority amounts in the mixtures. The aliphatic skeletal C-C; C-O stretching; and -OH bending vibrations (1220 cm^{-1}) recorded higher values for the measured than for the expected mixture, while the opposite effect was recorded for the other aliphatic compounds and O- and H- functional groups that were involved in the model.

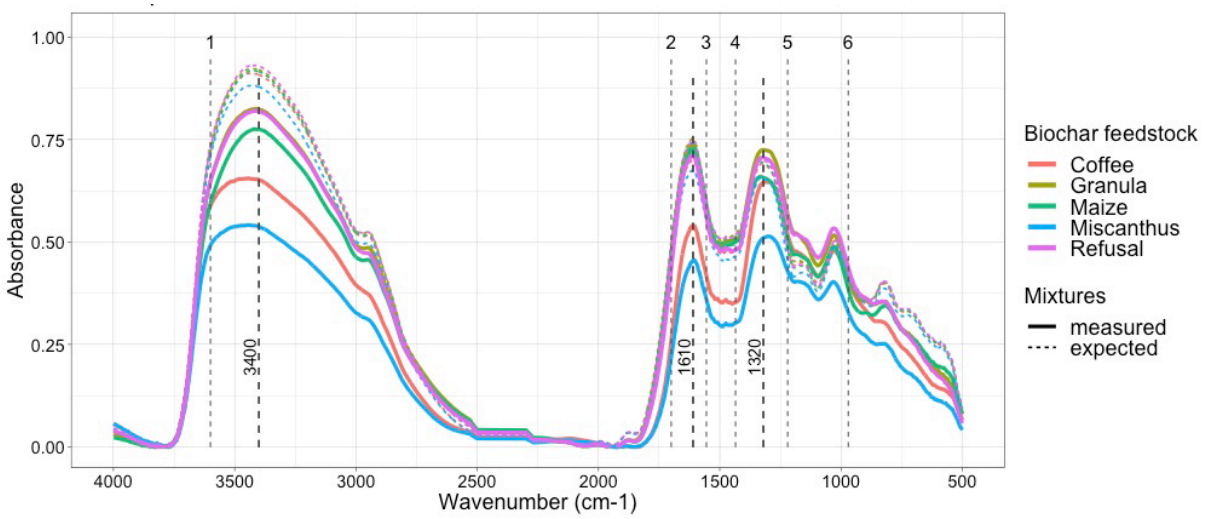

Figure 27 FTIR spectra of the biochar-compost mixtures. The wavenumbers from 1 to 6 correspond respectively to 3600, 1700, 1555, 1435, 1220 and 970 cm^{-1}.

5 Discussion

The Rock-Eval® thermal analysis revealed biochar-compost interactions through lower hydrocarbon cracking and lower CO emissions and temperature of CO_2 emission at the oxidation stage. The hydrocarbon cracking from compost between 320 and 390 °C during the pyrolysis stage may involve biological constituent such as polysaccharides and lignin (Disnar et al. 2003). The decrease of hydrocarbon cracking from the compost compound during the Rock-Eval® pyrolysis stage may indicate an increase of thermal stability, that can be attributed to changes in the chemical structure of the OM, or to the retention of hydrocarbons from compost within the porous structure of biochar, as adsorption processes were already observed in soils containing high amount of clay content (Kanari et al. 2021). Mechanisms of this interaction may involve the promotion of volatile compounds during the pyrolysis stage (Park et al. 2010; Krerkkaiwan et al. 2013; L. Zhang et al. 2007; Yuan et al. 2012), that may remained adsorbed onto the porous biochar surface. The CO_2 emission at the oxidation stage recorded as the main emission occurring during the Rock-Eval® thermal analysis, and was attributed to the presence of biochar compound (Hazra et al. 2020; İnan et al. 2017). When biochars produced at temperatures > 450 °C were combined with compost, the combustion of the mixture started at lower temperature and exhibited higher reaction rates as compared to pure biochar. These results are consistent with coal-biomass mixture (Kastanaki and Vamvuka 2006). As the biochars produced at temperatures > 450 °C recorded higher fixed carbon content than the biochars produced at 450 °C (Tab. 5), we suggested that the thermal cracking may have affected preferentially the fixed carbon than the volatile compounds. The fixed carbon combustion was found as the main combustion process of the biochar,

while volatilization and gas-phase combustion was the main process for biomass (Yi et al. 2013). Volatile content and H- and OH- radicals from biomass may promote a faster heat release from coal and increase thermal reactivity of the mixtures during the oxidation stage, as compared to single component (Lu et al. 2008; Haykiri-Acma and Yaman 2008). Furthermore, it has been reported that C-H and C-O bonds of biomass may react with and promote the cracking of the C=C bonds from coal during combustion, thus accelerating char oxidation and reducing activation energy (Oladejo et al. 2018).

The FTIR spectra evidenced unexpected decreases of aromatic compounds and water content. The surface of aromatic carbon has been shown to react with its near-environment, as it can be oxidized and adsorb particles (Lehmann et al. 2005). According to our results, biochar-compost may have interacted in a very short time (a few hours) and with a very low humidity (2-3 % for biochars and 4 % for compost, Tab. 5). It is very unlikely that biotic processes have occurred in such conditions, thus the interactions may result from abiotic mechanisms only. A recent study pointed out that the electron transfer rates of chars were the highest in the first three hours of the reaction with reactive solutions, and then decrease sharply over time (Prévoteau et al. 2016). Our results seem to agree with the high capacity of biochars to be oxidized in a very short time after it is put in presence of electron acceptor material. Furthermore, the oxidation reactions in our study may have been facilitated by the fine grinding of the pure components. Among the abiotic processes that may be induced by aromatic OM, the sorptive protection was evidenced as a dominant negative priming mechanism (DeCiucies et al. 2018). Abiotic oxidation may lead to the formation of carboxylic and oxidized groups on biochar surface that can create CEC and negative surface charge (Cheng et al. 2006; Lehmann et al. 2005) that can react with other OM particles. Abiotic oxidation processes appear as the first cause oxidation of biochar surfaces and may happen on the biochar particles themselves by chemisorption of O at unsaturated ring sites (Cheng et al. 2006) or may result from the adsorption of non-biochar compounds (Lehmann et al. 2005).

The FTIR wavenumbers assigned to aromatic compounds and water content were correlated to the changes of thermal behavior from biochar-compost mixtures. Indeed, the PLSR model evidenced the implication of water and aromatic compounds and, to a lesser extent, aliphatic compounds and O- and H- functional groups, in the prediction of biochar-compost on lower CO_2 temperature emissions at the oxidation stage. Aromatic rings are more recalcitrant than aliphatic bonds, and thus may have lower reactivity for thermal analysis (Barré et al. 2016). The unexpected dehydration of the biochar-compost mixture could result from the obstruction of biochar porous structure with fine compost particles during the blending, thus lowering the biochar porosity and thereby the water retention of the mixture. Water content may be involved in biochar-compost interactions during the thermal analysis, as water may promote further cracking of tar and produce more volatile compounds, thereby increasing the pyrolysis oil yields (Abnisa and Wan Daud 2014). Hence, the unexpected lower water content of the mixtures should have benefit for lower biochar-compost interactions during the oxidation stage. We thus assumed

that the unexpected lower aromatic compounds in the mixtures contributed to a greater extent than the unexpected lower water content, to the biochar-compost interactions during the thermal analysis.

We conclude that biochar-compost interactions may have occurred during their blending, thereby at least partially affecting their thermal stability. While most studies indicated that the interactions of pure organic matter observed following thermal analysis may occur mainly due to a bias of the method, our results open a new perspective of abiotic interactions occurring during the blending, thus already before the thermal analysis. As thermal stability has been suggested as a good proxy to estimate SOM biological stability and soil persistence (Leifeld and von Lützow 2014; Gregorich et al. 2015; Barré et al. 2016), further research would be needed to explore the consequences of abiotic interactions occurring during biochar-compost blending on their microbial degradation.

CHAPTER III -

Biochar-Compost Interactions as Affected by Weathering: Effects on Biological Stability and Plant Growth

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Marie-Liesse Aubertin [1,2], Cyril Girardin [2], Sabine Houot [2], Cécile Nobile [3], David Houben [3], Sarah Bena [4], Yann Le Brech [4] and Cornelia Rumpel [1]

[1] *Institute of Ecology and Environmental Sciences, UMR 7618, CNRS-UPMC-UPEC-INRA-IRD, Sorbonne University, 75005 Paris, France*

[2] *National Institute for Agricultural Research, Ecosys Soil, UMR INRA-AgroParisTech, 78820 Thiverval-Grignon, France*

[3] *UniLaSalle, AGHYLE, 60026 Beauvais, France*

[4] *LRGP–CNRS, Lorraine University, 54000 Nancy, France*

Chapter III - Biochar-Compost Interactions as Affected by Weathering: Effects on Biological Stability and Plant Growth

1 Abstract

Biochar addition to compost is of growing interest as soil amendment. However, little is known about the evolution of material properties of biochar-compost mixtures and their effect on plants after exposure to physical weathering. This study aimed to investigate the physico-chemical characteristics of fresh and weathered biochar-compost mixtures, their biological stability and their effect on ryegrass growth. To this end, we used the contrasting stable isotope signatures of biochar and compost to follow their behavior in biochar-compost mixtures subjected to artificial weathering during 1-year of incubation. We assessed their impact on ryegrass growth during a 4-week greenhouse pot experiment. Weathering treatment resulted in strong leaching of labile compounds. However, biochar-compost interactions led to reduced mass loss and fixed carbon retention during weathering of mixtures. Moreover, weathering increased carbon mineralization of biochar-compost mixtures, probably due to the protection of labile compounds from compost within biochar structure, as well as leaching of labile biochar compounds inhibiting microbial activity. After soil application, weathered mixtures could have positive effects on biomass production. We conclude that biochar-compost interactions on soil microbial activity and plant growth are evolving after physical weathering depending on biochar production conditions.

2 Introduction

According to the last report of the Intergovernmental Panel of Climate Change (IPCC), global temperatures have increased by 1 °C above pre-industrial levels due to human activity (Field et al. 2014). Further increase should be limited to 1.5 °C in order to prevent dangerous climate change. To achieve this goal, active carbon dioxide removal from the atmosphere and its storage is needed (Field et al. 2014). Soil carbon sequestration and biochar application to soils may be used for this purpose. As negative emission technologies (NETs), their implementation may be able to achieve long-term carbon sequestration and may have advantages over the other NETs related to their effect on land use, water use and energy requirement (P. Smith 2016).

Soil carbon (C) sequestration may be enhanced by the addition of organic amendments. While organic residues such as plant material or manure are usually transformed into amendments through composting, they may also be the feedstock for biochar production (Abbott et al. 2018). Biochar is a solid pyrolysis product intended to be used as soil amendment (Lehmann and Joseph 2015a). It is mainly composed of aromatic C and has favourable properties such as large porosity and surface area in addition to high cation exchange capacity, depending on feedstock, pyrolysis conditions and particle size (W.-J. Liu, Jiang, and Yu 2015; Glaser et al. 2002; Alghamdi 2018). Biochar is known to improve soil properties such as water retention under drought conditions (Paetsch et al. 2018), and soil aggregate stability and porosity (Obia et al. 2016; F. Sun and Lu 2014). Due to its low nutrient content, biochar should be combined with nutrient additions through mineral fertilizers, compost and/or growth promoting micro-organisms to further increase its beneficial effects on plant growth when applied to soil (Abbott et al. 2018). On the other hand, compost is rapidly mineralized after soil application and its carbon sequestration potential may be enhanced by combination with organic and inorganic additives (Barthod et al. 2018). Mixtures of both materials may therefore be an innovative practice, leading to more efficient soil amendment as compared to their single use.

Biochar combination with other organic amendments may have synergistic effects on organic C retention, which were attributed to physical protection of compost by its occlusion into aggregates or adsorption on biochar surface (Jien et al. 2018; 2015; Ngo et al. 2013). Other studies found that biochar and mature compost mixtures induced a negative priming effect (Qayyum et al. 2017) or a neutral effect (Teutscherova et al. 2017) on C mineralization when compared to application of compost. Soil addition of biochar-compost mixtures was shown to promote plant growth, biomass accumulation, yield and to improve soil properties such as water holding capacity (Agegnehu et al. 2017; Trupiano et al. 2017; Naeem et al. 2018; Manolikaki and Diamadopoulos 2019; Zulfiqar et al. 2019; Tsai and Chang 2019). Yet the synergistic effects of freshly applied biochar-compost mixtures on plant growth and performance are still under debate (Seehausen et al. 2017). Indeed, application of fresh biochar-compost mixture has been found to have neutral (Trupiano et al. 2017) or even antagonisms effects (Seehausen et al. 2017). This may be due to release of toxic compounds contained in the biochars' labile fraction (Gale et al. 2016; Kołtowski and Oleszczuk 2015; Buss and Mašek 2014; Deenik et al. 2010) or to low availability of nutrients due to the biochars' high sorption capacity (Seehausen et al. 2017).

When applied to the field and exposed to weathering, the mixture effects may prevent carbon and nitrogen losses as compared to the single use of compost and biochar (Ngo et al. 2016). Physical weathering may increase the biological stability of biochars and reduce their priming effect on native SOM mineralization (Naisse et al. 2015). Moreover, weathering may change the biochar structure (Spokas et al. 2014) and its effects on soil properties (Paetsch et al. 2018). These effects may also change the compost-biochar interactions in mixtures and their amendment effects. Indeed, several studies

observed an alleviation of beneficial effects of biochar-compost addition on biomass production over time (Prodana et al. 2019; Doan et al. 2015; H.-P. Schmidt et al. 2014). However, to the best of our knowledge, no studies have focused on the effect of weathering on biochar-compost mixture properties and their biological stability.

Therefore, the aim of the present study was to investigate the effect of artificial weathering on chemical characteristics and biological stability of biochar-compost mixtures and the consequences for plant biomass production after soil amendment. We used two industrially produced biochars from maize and *Miscanthus*, a green-waste compost and the corresponding biochar-compost mixtures. The mixtures and pure media were subjected to a physical weathering to mimic natural aging mechanisms. Thanks to contrasting stable carbon isotope ratios of biochars derived from C4 plants and compost derived from C3 plants, we were able to monitor the mineralization of the two components of the mixtures during a 1-year of laboratory incubation with a soil inoculum. In addition, we investigated in a 4-weeks pot experiment the effect of fresh and weathered biochar-compost mixtures on ryegrass growth growing on two different soils. We hypothesized that (i) biochar addition to compost would induce synergetic effects on biological stability and plant growth and that (ii) physical weathering would weaken these interactions. The chosen biochars differed by their initial feedstocks and temperature of production, but we wanted to compare two biochars independently from their characteristics. The two biochars were chosen because of their different stable isotopic signatures that were significantly different from the one of the compost.

3 Materials and methods

3.1 Biochar and compost

Biochars were produced from maize cobs (*Zea mays* L.) and elephant grass (*Miscanthus* × *giganteus*, Greef and Deuter), through pyrolysis without oxygen during 10 min at respectively 450 and 550 °C. Pyrolysis was performed by VTGreen (Allier, France), using an industrial pyrolysis reactor (Biogreen®Pyrolysis Technology, ETIA, Oise, France). The compost was made from green wastes at the platform of Fertivert (Normandy, France). The composting process consisted of 4 months fermentation and 2 months maturation. Three compost turnings were applied. The biochar from maize cobs and the compost are the same than the ones used in Nobile et al. (2020). General parameters of the biochars and the compost are listed in Tables 12 and 13. Biochar-compost mixtures were prepared by mixing 20 % (*w*/*w*) of each biochar with 80 % (*w*/*w*) of compost, thus allowing for a similar C content

for both biochar and compost in the mixture. The biochars and mixtures were air-dried at ambient temperature and the compost was stored at 4 °C.

3.2 Physical Weathering

The mixtures and pure media were subjected to a physical weathering through wet-drying and freeze-thawing cycles to mimic natural aging mechanisms. The weathering procedure was inspired by Naisse et al. (2015). Briefly, we placed 100 g (d.w.) of compost or biochar-compost mixtures in PVC cylinders (ø 9.5 cm). Two PVC cylinder (ø 5 cm) were used for the weathering of 30 g of maize and *Miscanthus* biochars. We covered the bottom of all tubes with a polyamide canvas with 20 µm mesh size (SEFAR-Nitex, Sefar AG, Haiden, Switzerland) and placed them on smaller tubes of 10 cm height to elevate the device. All was then put in a 10 cm ø beaker, in order to recover the lixiviates (Fig. 28). We mimicked weathering processes through three successive cycles including three cycles of wetting/drying and three cycles of freezing/thawing. Wetting/drying steps consisted of saturating the samples with distilled water, leaving them at room temperature during 3 h followed by drying of the sample at 60 °C overnight. Freezing/thawing steps consisted of saturating samples with distilled water with the same amount as for the previous cycles, freezing at −20 °C overnight and thawing during 6–7 h at 28 °C. We replicated these experiments 2 times. At the end of the weathering procedure, we dried the solid samples at 60 °C during 2 days and lixiviates until complete evaporation. Mass and carbon loss after artificial weathering were assessed by mass balance.

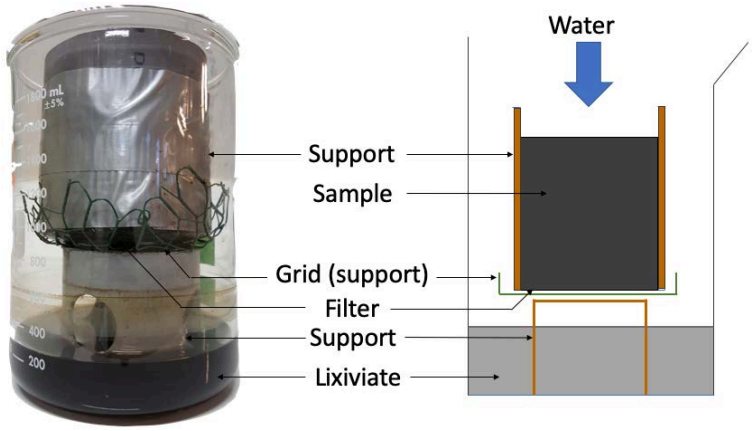


Figure 28 Experimental set-up for the artificial weathering of samples.

3.3 Material Properties: Physico-chemical, Elemental and Thermogravimetric Analysis

To measure pH and electrical conductivity (EC), 2 g of sample were mixed with 40 mL of distilled water and centrifugated for 1 h. The pH (780 pH meter, Metrohm, Herisau, Switzerland) was measured in the supernatant and the mixtures were filtered (glass microfibres paper, Fisherbrand) before EC (InLab® 738-ISM, Mettler Toledo, Columbus, Ohio, USA) measurement. We evaluated the effect of weathering on dissolved organic carbon content (DOC) and elemental content. For DOC determination, 2 g of dried samples were sieved at 2 mm and mixed with 40 mL of distilled water, (1:20 w/v) ratio. The samples were shaken during 1 h, centrifugated at 4750 t/min during 20 min and the supernatant recovered by filtration (glass microfibres paper, Fisherbrand). DOC was analysed using a Total organic carbon analyzer (TOC-5050A, Shimadzu, Marne-la-Vallée, France). The determination of C, H, N and O of solid samples was performed using a CHN-O analyzer (FlashEA 1112 Series, Thermo-Fisher Scientific, Illkirch, France).

Ash content, volatile matter and fixed carbon of dry matter were determined by thermogravimetric analyses (TGA/DSC1 STAR System, Mettler-Toledo, Viroflay, France). The samples (in 70 µL crucibles, 77approx. 6–7 mg) were first heated at 105 °C during 30 min to determine the moisture content. Thereafter, the temperature was increased by 15 °C min^{-1} to 900 °C during 40 min under N_2 atmosphere to determine volatile content. Temperature was then kept at 900 °C under air flux (50 mL min^{-1}) for 6 min to determine ash content.

3.4 Biological stability: Incubation

Laboratory incubation was carried out under optimum conditions after the addition of a microbial inoculum (4 mL soil inoculum per 100 g of sample). The inoculum was prepared with 50 g of soil from a cropland field (Haplic Luvisol, FAO and IUSS 2015), Beauvais, Northern France), by preparing a water extract with 200 mL of distilled water. The soil was not carbonated, contained 154 mg g^{-1} organic C, 18 mg g^{-1} total N and had a pH (water) of 7.7 (Table 11). After inoculum addition, 20 g of sample were placed in 100 mL glass vials and covered with rubber septa. We carried out the incubation in triplicate for 8 treatments (2 biochar/compost mixtures, a compost and one biochar (all fresh and weathered) at 20 °C during 12 months. As we hypothesized that pure biochars will behave similarly, we used only *Miscanthus* biochar as control sample. We adjusted the water content to 60 % at the beginning of the incubation, when the flask's atmosphere was free of CO_2. We monitored the decomposition of the materials by measuring release of CO_2-C using a micro-GC (490 Micro-GC, Agilent Technologies, Les Ulis, France) (Fig. 29) and the stable carbon isotope ratio of CO_2-C with an isotopic ratio mass

spectrometer (Vario isotope select, Elementar, UK-Ltd, Cheadle, UK) at day 1, 3, 7, 16, 24, and then once a month until the end of the incubation. At each CO_2-C measurement date, we also determined the isotopic signature of the CO_2 emitted by compost, biochar and compost-biochar mixtures. Thanks to the isotopic ^{13}C signature of the C4-biochar, which is distinctly different from C3 compost, we were able to determine the contribution of carbon mineralized from biochar or compost in CO_2 emitted from the biochar-compost mixtures. After each measurement, we flushed the bottles with synthetic CO_2 free-air. The results are expressed as cumulated CO_2-C emitted form fresh and aged samples in terms of initial total C content of the compost or biochar within the fresh samples.

Table 11 Characteristics of the Calcaric Cambisol and Haplic Luvisol used for the pot experiment.

	Unit (Dry Matter)	Calcaric Cambisol	Haplic Luvisol
Clay	%	33.3	17.6
Silt	%	46.1	66.9
Sand	%	20.6	15.6
$CaCO_3$	g kg^{-1}	563.3	0.0
organic C	g kg^{-1}	9.5	15.4
total N	g kg^{-1}	2.6	1.8
C/N		3.6	8.6
pH KCl		7.8	7.4
pH water		8.0	7.8
CEC	cmolc kg^{-1}	14.0	12.5
P water	mg kg^{-1}	1.2	3.9
Available P	mg kg^{-1}	19.7	71.2
Available K	mg kg^{-1}	326.8	291.9
Available Mg	mg kg^{-1}	271.1	100.7
Available Ca	mg kg^{-1}	46727.4	3868.6

Figure 29 Measure of the CO2-C released by the samples during the incubation, using a micro-GC.

3.5 Effect on Biomass Production: Pot Experiment

A pot experiment was carried out with fresh and weathered compost and mixtures added to two different agricultural soils sampled in Beauvais (Northern France) and classified as a silt loam Haplic Luvisol and a clay loam Calcaric Cambisol (FAO and IUSS 2015). Soil characteristics are shown in Table 12.

After sieving the soil (4 mm), the composts and mixtures were applied at respectively 16t ha^{-1} and 20 t ha^{-1} to 0.4 kg of soil. Both fresh and weathered amendments were applied to soil at a similar rate, considering the mass loss during the weathering treatment. The pots were sown with 0.15 g pot^{-1} of Italian ryegrass (*Festuca perennis* Lam. ex *Lolium multiflorum*) seeds. Thereafter, they were kept in a growth chamber under controlled conditions: 16 h day^{-1} of light, a temperature of 24 °C (day) and 20 °C (night) and addition of distilled water every two days (Fig. 30). We harvested the plants 4 weeks after sowing by cutting at 2 cm from soil surface. Biomass production was determined gravimetrically after 72 h drying at 60 °C.

Figure 30 Pot experiment with ryegrass.

3.6 Calculations and statistics

Presentation of the isotopic technique

C isotopes can be used to trace C in the environment with the use of either natural abundance or labelling methodologies. Natural abundance techniques is based on the fact that different carbon pools in the environment can have different ratios of C isotopes (Staddon 2004), while labelling methodologies

consist on the introduction of C compounds either enriched or depleted in stable or radioactive carbon isotopes (^{13}C or ^{14}C), allowing for the tracing of the fate of C originating from the introduced compound.

The C isotopic signature ($\delta^{13}C$) of a material, expressed in ‰, estimates its fractionation of ^{12}C and ^{13}C and is measured based on the ^{13}C / ^{12}C ratio, relative to the Pee Dee Belemnite (PDB) standard (Eq. 4).

$$\delta^{13}C_{material} = \left(\frac{\left(^{13}C/_{12}C\right)_{material} - \left(^{13}C/_{12}C\right)_{PDB}}{\left(^{13}C/_{12}C\right)_{PDB}}\right) * 1000 \quad \textbf{(4)}$$

Hence, the determination of the carbon origin in a mixture containing two components with distinct C isotopic signatures ($C_{component\ 1\ in\ the\ mixture}$, expressed in % total C in the mixture) is possible if the C isotopic signatures from each component is known (Eq. 5).

$$C_{component\ 1\ in\ the\ mixture} = \frac{\delta^{13}C_{component\ 1\ in\ the\ mixture} - \delta^{13}C_{component\ 2}}{\delta^{13}C_{component\ 1} - \delta^{13}C_{component\ 2}} \quad \textbf{(5)}$$

In our study, we used biochar from C_4 plants feedstock and compost from C_3 plants feedstock. Therefore, it was possible to distinguish the part of organic C originating from biochar and compost within a biochar-compost mixture.

Isotopic analysis

Stable C isotope signatures ($\delta^{13}C$) were used to estimate the contribution of biochar and compost to the mixtures and the CO_2 emissions from the mixtures. The partitioning was done with Equation 6:

$$C_{biochar,mix} = (\delta^{13}C_{mixture} - \delta^{13}C_{compost})/(\delta^{13}C_{biochar} - \delta^{13}C_{compost}) \quad \textbf{(6)}$$

where $C_{biochar,mix}$ is biochar carbon in the mixture or in CO_2-C emitted from the mixture (%); $\delta^{13}C_{mixture}$ is the stable C isotope signature of the mixture, $\delta^{13}C_{biochar}$ is the stable C isotope signature of biochar and $\delta^{13}C_{compost}$ is the stable isotope signature of compost.

To evaluate interactions between biochar and compost in mixtures, we calculated expected values for the mixtures according to Equation 7. The comparison between the expected and the measured values of the mixtures were used to assess interactions between biochar and compost.

$$m_{biochar,mix}/m_{mixture} = C_{mixture} \times C_{biochar,mix}/C_{biochar} \quad \textbf{(7)}$$

where $m_{biochar,mix}$ is the mass of biochar within the mixture (g); $m_{mixture}$ is the mass of the mixture (g); $C_{mixture}$ is the C content of the mixture; and $C_{biochar}$ is the C content of biochar.

Statistics

To calculate differences between fresh and weathered materials, we tested for normality using the Shapiro-Wilk test. For the normally distributed data, we performed analysis of variances (ANOVA) and Tukey multiple comparison. When data did not follow a normal distribution, we used Kruskal-Wallis tests with Bonferroni corrections. The level of significance was set at $p = 0.05$. We performed all statistical analyses using the R software (version 3.5.2).

4 Results

4.1 Leaching due to physical weathering

Material losses ranged from about 20 mg g^{-1} for maize biochar to about 150 mg g^{-1} for compost (Fig. 31). Artificial physical weathering thus resulted in twice as much material loss from compost as compared to biochars. Mass losses for both mixtures were around 75 mg g^{-1}. They were about two times lower than expected from the losses of individual materials (Fig. 31).

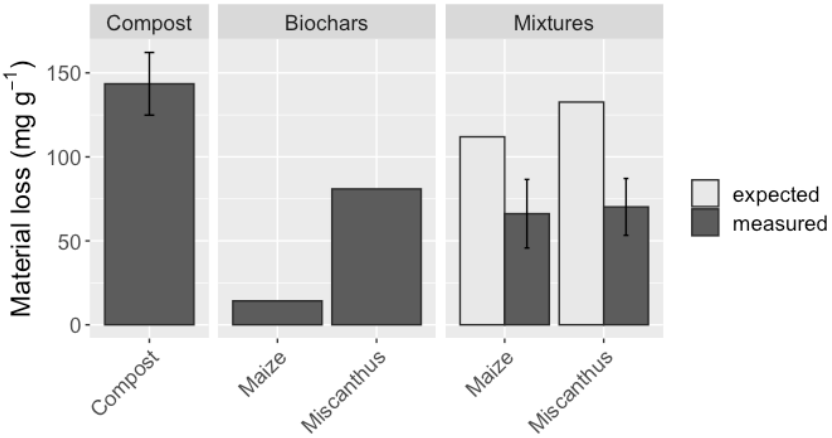


Figure 31 Total mass loss during physical weathering of compost, biochars and their mixtures. Data are presented as mean ± sd ($n = 2$ for the compost and the mixture and $n = 1$ for the biochars). Expected values for mixtures were calculated based on mass losses measured for individual components.

4.2 Properties of the fresh and weathered materials

4.2.1 Elemental composition

Fresh compost was composed of 226 mg g^{-1} C, 20 mg g^{-1} H, 112 mg g^{-1} O and 23 mg g^{-1} N (Tab. 12). Fresh biochars contained at least twice more C than the fresh compost, with biochar from maize and *Miscanthus* containing respectively 591 and 778 mg g^{-1} C (Tab. 12). Hydrogen content of biochars were similar to compost, whereas O and N content of biochars were at least twice lower than for compost. Following the mixing ratio, carbon content of the mixtures ranged between 298 mg g^{-1} and 332 mg g^{-1} and all other elemental components had similar values for both mixtures. The mixtures showed similar C/N ratios independently from biochar feedstocks.

Table 12 Elemental composition of fresh (F) and weathered (W) compost, biochars and biochar-compost mixtures. Expected (exp) values were calculated for the weathered mixtures. Data are presented as means ± sd (n = 3). The letters represent differences among treatments.

			C (mg g^{-1})	H (mg g^{-1})	O (mg g^{-1})	N (mg g^{-1})	C/N
Compost							
Compost	F		226 ± 1 ^{i}	20 ± 1 ^{ab}	112 ± 4 ^{a}	23 ± 0 ^{a}	10 ± 0 ^{g}
	W		209 ± 5 ^{j}	17 ± 5 ^{abc}	99 ± 4 ^{b}	21 ± 1 ^{ab}	10 ± 0 ^{g}
Biochars							
Maize	F		591 ± 1 ^{d}	21 ± 1 ^{ab}	48 ± 3 ^{d}	8 ± 0 ^{gh}	72 ± 0 ^{c}
	W		618 ± 0 ^{c}	21 ± 0 ^{ab}	76 ± 5 ^{c}	9 ± 0 ^{fg}	65 ± 0 ^{d}
Miscanthus	F		778 ± 1 ^{a}	13 ± 1 ^{c}	18 ± 3 ^{e}	4 ± 0 ^{hi}	186 ± 0 ^{b}
	W		742 ± 1 ^{b}	16 ± 2 ^{bc}	58 ± 6 ^{d}	4 ± 0 ^{i}	189 ± 0.3 ^{a}
Mixtures							
Maize	F		298 ± 3 ^{h}	19 ± 1 ^{ab}	103 ± 0 ^{ab}	17 ± 0 ^{ef}	17 ± 0 ^{f}
	W		350 ± 3 ^{f}	22 ± 1 ^{a}	78 ± 1 ^{c}	18 ± 0 ^{cd}	20 ± 0 ^{ef}
		exp	321	18	92	18	18
Miscanthus	F		332 ± 1 ^{g}	19 ± 2 ^{ab}	107 ± 3 ^{ab}	19 ± 0 ^{bc}	17 ± 0 ^{f}
	W		374 ± 3 ^{e}	20 ± 1 ^{ab}	83 ± 1 ^{c}	17 ± 0 ^{de}	22 ± 0 ^{e}
		exp	355	16	87	16	22

Compost weathering induced decreasing contents of all elements, while mostly C and O were affected for biochars. As a result of weathering, C content respectively increased and decreased for the maize and *Miscanthus* biochars, while O content more than doubled for both biochars. The expected C content of the weathered mixtures were slightly lower than the measured ones ranging between 321 and 355 mg g^{-1}. As for biochars, weathering affected mainly the C and O contents of the mixtures; O contents of the weathered mixtures were slightly lower than the expected values. For both mixtures, weathering increased the C/N ratio (Table 12).

4.2.2 Physico-chemical properties, dissolved organic carbon and stable $\delta^{13}C$ ratio

Table 13 shows physico-chemical properties and the dissolved organic carbon content (DOC) of the materials. pH and electrical conductivity (EC) ranged from 8.1 to 10.5 and from 109 to 1598 µS cm^{-1}, respectively. Compost had lower pH (8.4), and EC (944 µS cm^{-1}) than both biochars. Both biochars showed similar pH (around 10.5), but maize biochar had higher EC than *Miscanthus* biochar. The pH and EC of fresh mixtures were in between the values from compost and biochars.

Fixed C content ranged between 0.6 and 67.8 %, DOC varied between 2.2 and 277.2 mg g^{-1} C, whereas ash content ranged between 13.6 and 59.3 % and volatile matter content between 17.8 and 38.8 %. Compost showed lower fixed C and higher DOC, ash content and volatile matter than biochars. Both biochars had similar volatile C but varied in ash content and fixed C; maize biochar presented a twice-higher ash content and a lower fixed C content (45.6 vs. 63.6%) than *Miscanthus* biochar. We assumed that differences between the two biochars were mainly driven by production temperature rather than initial feedstock, as it has been found to be the main driver of biochar chemical composition (Uchimiya et al. 2011; Enders et al. 2012; Wiedner et al. 2013). Maize mixtures showed higher pH (9.1 vs. 8.9) and ash contents (54.0 vs. 51.2%) and lower volatile matter contents (35.1 vs. 38.2%) compared to *Miscanthus* mixture.

Table 13 Chemical characteristics of fresh (F) and weathered (W) compost, biochars and biochar-compost mixtures. Expected (exp.) values were calculated for the weathered mixtures. EC: electric conductivity; DOC: dissolved organic carbon. Data are presented as means ± sd (n = 3) for pH, EC, DOC and $\delta^{13}C$. Proximate analysis was carried out for 1 sample. The letters represent differences among treatments.

			pH *	EC (µS cm^{-1})	DOC (mg g^{-1} C)	$\delta^{13}C$ (‰)	Ash (%)	Volatile (%)	Fixed C (%)
Compost									
Compost	F		8.4 ^{g}	944 ± 18 ^{cd}	277.2 ± 49.0 ^{a}	−28.9 ± 0.1 ^{gh}	59.3	38.8	1.9
	W		7.9 ^{h}	215 ± 4 ^{fg}	73.5 ± 2.4 ^{cd}	−29.2 ± 0.0 ^{h}	63.0	36.4	0.6
Biochars									
Maize	F		10.5 ^{a}	1640 ± 62 ^{a}	36.7 ± 1.6 ^{f}	−15.3 ± 0.1 ^{bc}	28.5	25.9	45.6
	W		8.7 ^{e}	109 ± 3 ^{g}	15.5 ± 0.1 ^{fg}	−15.3 ± 0.0 ^{c}	23.5	35.7	40.8
Miscanthus	F		10.4 ^{a}	1516 ± 14 ^{bc}	3.6 ± 0.7 ^{g}	−14.9 ± 0.1 ^{ab}	13.6	22.8	63.6
	W		9.4 ^{b}	129 ± 3 ^{g}	2.2 ± 0.1 ^{g}	−14.5 ± 0.1 ^{a}	14.4	17.8	67.8
Mixtures									
Maize	F		9.1 ^{c}	1588 ± 12 ^{ab}	203.2 ± 7.9 ^{bc}	−22.3 ± 0.3 ^{ef}	54.0	35.1	10.9
	W	real	8.6 ^{e}	224 ± 3 ^{ef}	50.1 ± 1.1 ^{ef}	−21.9 ± 0.0 ^{de}	48.9	34.0	17.1
		exp	8.1	186	57.6	−25.4	52.2	36.2	11.6
Miscanthus	F		8.9 ^{d}	1598 ± 20 ^{a}	210.3 ± 9.3 ^{ab}	−23.2 ± 0.1 ^{fg}	51.2	38.2	10.6
	W	real	8.5 ^{f}	238 ± 15 ^{de}	54.3 ± 1.5 ^{de}	−21.9 ± 0.1 ^{d}	46.3	37.1	16.6
		exp	8.3	192	54.0	−25.2	49.7	31.3	19.0

* the standard deviations of pH were <0.05.

Weathering induced an increase of fixed C from around 10 % to 17.1 % and 16.6 % for maize and *Miscanthus* mixtures. In contrast, EC and DOC showed 4 times lower values after weathering. When compared to the expected values, slightly higher EC values than expected were recorded for both mixtures after weathering. In addition, the weathered mixture with maize biochar showed lower DOC (50.1 vs. 57.6 mg g C^{-1}) and higher fixed C (17.1 vs. 11.6 %) than expected. The weathered *Miscanthus* mixture showed higher volatile matter than expected (37.1 vs. 31.3 %) (Table 13). During weathering, the isotopic signatures remained unchanged for compost, biochars and the mixture containing maize biochar, but decreased for the mixture containing *Miscanthus* biochar. The $\delta^{13}C$ ratios of the weathered mixtures (21.9 ‰) were lower than expected (25.4 and 25.2 ‰).

4.3 Biological stability

Cumulative CO_2-C released during 1-year of incubation from fresh and weathered compost, *Miscanthus* biochar and both mixtures are presented in Figure 32. After 1 year of incubation, the fresh compost showed the highest cumulative C mineralization with values up to 30 mg g^{-1} of initial carbon. In contrast, very few C was mineralized from *Miscanthus* biochar. The isotopic signatures of carbon were used to assess the origin of C mineralized from biochar-compost mixtures. The data indicated that compost released between 15 and 20 mg g^{-1} C when incubated in mixtures, while biochar released between 10 and 15 mg g^{-1} C when incubated in mixtures. Compost showed lower C-mineralization in mixture compared to individual incubation. Conversely, biochar showed higher C-mineralization when combined with compost compared to individual incubation.

After weathering, cumulative compost C mineralization amounted to 10 mg g^{-1} C, which was significantly lower than C mineralization of fresh compost (Fig. 32). Biochar C-mineralization was not significantly affected by weathering when individually incubated. When combined with compost it mineralized significantly less than in fresh mixtures. In contrast, compost mineralized significantly more in weathered mixtures as compared to fresh mixtures and reached values between 20 and 25 mg g^{-1} C after 1-year incubation.

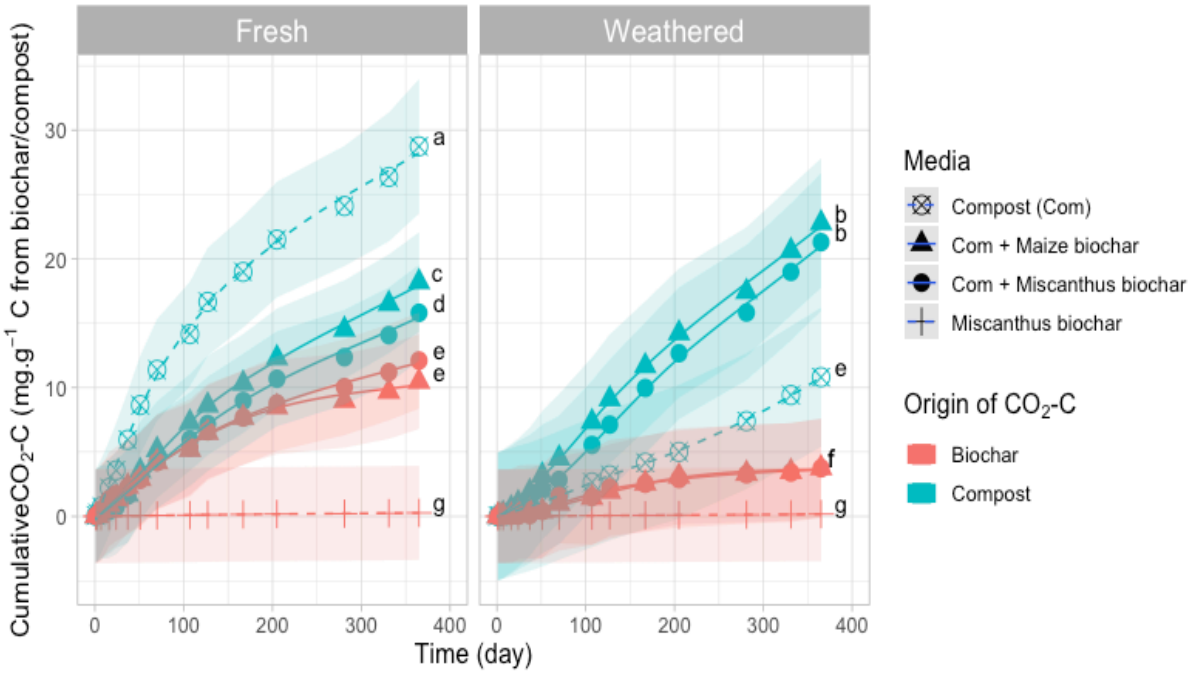


Figure 32 Cumulative CO_2-C mineralized from biochar and compost when incubated alone or in mixture. Turquoise and red colors represent C mineralized from compost and biochar respectively. The colored ribbon represents the standard deviations. The letters represent the significant differences from a two-ways ANOVA analysis (n = 3).

4.4 Ryegrass growth

Biomass of Italian ryegrass was higher when grown on Haplic Luvisol as compared to Calcaric Cambisol, as shown for the unamended controls (Fig. 33). All organic amendments stimulated ryegrass growth, when applied to Calcaric Cambisol. However, when applied to Haplic Luvisol, organic amendments induced neutral or negative effects on biomass. For both soils, application of fresh biochar-compost mixtures did not lead to significant differences in ryegrass biomass as compared to fresh compost alone. Physical weathering decreased the effect of compost addition to Calcaric Cambisol on biomass, but the effect was still positive as compared to the control. Concerning the Haplic Luvisol, compost addition tended to decrease biomass. For both soils and after weathering, the mixture containing *Miscanthus* biochar induced significantly higher biomass than the compost alone, while the mixture containing maize biochar showed similar effects as compost alone.

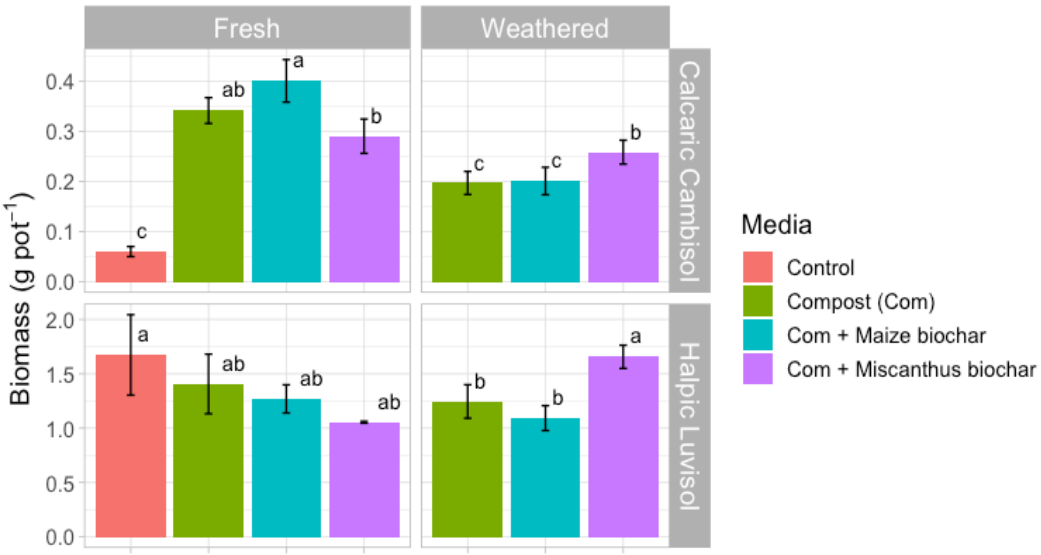


Figure 33 Biomass of ryegrass after addition of compost or its mixture with maize and *Miscanthus* biochars, grown on two soil types. Data are presented as means ± sd (n = 3). The letters represent the significant differences from a one-way ANOVA analysis (n = 4) within each treatment and soil type.

5 Discussion

5.1 Weathering effects on material properties

Physical weathering induced much higher mass loss from compost as compared to biochar and mixtures. This may probably be explained by the high leaching losses. Biochar mass loss amounted to 75 mg g^{-1}, which is much lower than observed for gasification biochar (Naisse et al. 2015). This may be due to the lower friability of biochar produced by pyrolysis making it less prone to particle losses (Spokas et al. 2014). Lower mass loss for the mixtures than expected, may be explained by protection of compost from leaching losses by its association with the biochar structure (Jien et al. 2015; Cooper et al. 2020). Both weathering cycles may affect release of dissolved organic matter and cause cracking on biochar-surfaces, thus leading to changes in pore structure (Wang et al. 2020). While DOC was lower than expected in weathered mixtures, EC values were higher than expected (see below). We therefore suggest that there may be interactions between biochar and compost leading to solid particles retention during weathering treatment.

Compost weathering induced a decrease of the content of all main elements, following strong leaching due to weathering treatment (Tab. 12). However, weathering of biochars affected only C and O contents

and led to decreasing C content and increasing O content. Our results are consistent with data of Naisse et al. (2015), who suggested that these observations may indicate oxidation processes induced by weathering (Baldock and Smernik 2002) . In contrast, weathering of the mixtures increased their C contents, while it decreased their O contents. This might be related to a preferential elimination of O relative to C in the labile fraction of the mixtures. This hypothesis may be supported by the visual observation of high loss of soluble compounds during weathering. Indeed, strong decreases of DOC and EC of the remaining substrates indicated that soluble compounds were removed by leaching during artificial weathering (Tab. 13). In contrast to the mixture containing *Miscanthus* biochar, the DOC content of the mixture containing maize biochar decreased slightly stronger than expected. The strong decrease of EC as a result of weathering is consistent with the results of Yao et al. (2010), who evidenced a rapid decline of EC from 0.7 to 0.2 mS cm^{-1} following leaching losses from biochar. EC reduction after weathering may be due to the leaching of mineral biochar compounds. This is supported by the lower ash content of the material remaining after weathering. Ashes and volatile compounds were both partly removed during weathering, except for volatile compounds of maize biochar. Both ashes and volatile compounds compose the labile fraction of all materials and are more likely to be leached than the more stable compounds. In particular, ash represents the mineral material contribution, which may be an indicator of nutrient content (Aller 2016).

Fixed C slightly decreased for compost and biochars following weathering treatment, while it increased for the mixtures (Tab. 13). Fixed C is mainly composed by fused aromatic C structures and may be used as an indicator of the C sequestration potential of biochars (Enders and Lehmann 2017). Higher fixed C of the mixtures than the expected values after weathering might result from the increasing chemical recalcitrance of the materials due to labile compounds leaching. These observations are in agreement with the lower than expected $\delta^{13}C$ ratios of the mixtures, might indicate preferential leaching of ^{12}C enriched compounds, e.g., C3-compost or labile polysaccharides, which are ^{13}C enriched compared to recalcitrant compounds (Amelung et al. 2008).

5.2 Biological Stability

5.2.1 Biological Stability of the Fresh Materials

During the incubation, compost showed the highest cumulative C-mineralization, while biochar C hardly mineralized. The stable OC of biochar in soil, estimated to compost about 97 % of total biochar (Wang et al. 2016), is mainly composed of both aromatic OC and the OC fractions stabilized by soil minerals (Han et al. 2020). As we worked in an incubation with soil inoculum, the stable OC of biochar was mainly due to a high content of aromatic OC. The C-mineralization of the mixtures ranged between

those of its individual components. These results are in agreement with other studies (Ngo et al. 2013; Jien et al. 2018; Teutscherova et al. 2017) and may be explained by a higher content of labile C in compost than in biochar (W.-J. Liu, Jiang, and Yu 2015). It was interesting to note that compost showed a lower C-mineralization when combined with biochar than when incubated individually. Two mechanisms could explain observation: the adsorption of labile fraction on the biochar surface (Ngo et al. 2013), and the presence of phenolic compounds or salts originating from biochar (Gale et al. 2016; Kołtowski and Oleszczuk 2015; Deenik et al. 2010), which might inhibit microbial activity in compost-biochar mixtures. The opposite effect was observed for biochar, since biochar C mineralized more when combined with compost than when individually applied. Indeed, several studies showed positive priming effect when labile substrates were added to biochar (Zimmerman et al. 2011; Wang et al. 2016; Setia et al. 2011).

5.2.2 Effect of Weathering on the Biological Stability

The cumulative C-mineralization from compost after 1 year of incubation was significantly lower for weathered compost compared to fresh compost when individually incubated (10 vs. 30 mg g^{-1}). This negative effect of weathering on C-mineralization from compost was attributed to the strong leaching of easily mineralizable labile components. On the other hand, the absence of weathering effects on biochar C mineralisation may be explained by the high stability of biochar with only few labile compounds (Wang et al. 2016).

C-mineralization from compost in the mixture increased significantly after weathering, when compared to the fresh mixtures (Fig. 32). This may be due to the protection of labile compounds by biochar and/or the removal of biochar compounds, which inhibited microbial activity and thus C-mineralization from compost (see above). Indeed, fresh biochar may contain large amounts of salts, which may inhibit microbial activity when applied to soil (Setia et al. 2011; Wen et al. 2019; Luo et al. 2019). This could lead to the negative priming effect of biochar on native C often observed immediately after soil addition (Ventura et al. 2015).

Weathering also reduced biochar C-mineralization, within the mixtures (Fig. 32), most probably due to the leaching of easily mineralizable C and nutrients from compost, which stimulated biochar C-mineralization before weathering (see above). Our results thus indicate that weathering affects biochar-compost interaction in mixtures, which might also impact their effects on plant growth.

5.3 Ryegrass Growth

5.3.1 Effect of the Fresh Media on Ryegrass Growth

Higher ryegrass biomass was recorded when grown on Haplic Luvisol as compared to Calcaric Cambisol, regardless the organic amendment (Figure 3). Moreover, the addition of organic amendments containing compost had positive effects on biomass when applied on Calcaric Cambisol, but the effects were neutral or negative when applied to Haplic Luvisol (Fig. 33). Our results were consistent with the results of Von Glisczynski et al. (von Glisczynski et al. 2016b), who also did not find any plant growth promoting effect of biochar-compost mixtures application on Haplic Luvisol. As reviewed by Faucon et al. (Faucon et al. 2015), organic amendments such as compost may promote plant growth by providing readily available nutrients or releasing them through mineralization. The available P concentration of the Calcaric Cambisol was much lower than that of the Haplic Luvisol (19.66 vs. 71.18 mg kg^{-1}) (Tab. 11), suggesting a possible P-limitation for plant growth in this soil, which might have been alleviated by compost application.

Addition of biochar compost mixtures led to similar ryegrass biomass than compost along (Fig. 33). As reported in the literature, the combination of biochar with compost can have synergic (Doan et al. 2015; Schulz and Glaser 2012), antagonistic (Seehausen et al. 2017; Sanchez-Monedero et al. 2018) or neutral effects (Trupiano et al. 2017; Seehausen et al. 2017; Teutscherova et al. 2017; Libutti and Rivelli 2020; Kammann et al. 2015) on plant growth. Several factors may impact plant growth after biochar-compost mixtures addition and the mechanisms are still poorly understood (Agegnehu et al. 2017). It was suggested that pre-treatment of biochar may be beneficial for plant growth before its soil application (Kammann et al. 2015). Moreover, it was shown that weathering may alter biochar properties (Naisse et al. 2015). Therefore, we tested in the following, if weathering of biochar/compost mixtures influenced plant growth.

5.3.2 Effect of Weathered Amendments on Ryegrass Growth

Irrespective of the soil type, weathered compost had negative or neutral effects on biomass when individually applied (Fig. 33). This is most likely due to the weathering-induced loss of readily-available nutrients and easily-mineralizable C compounds (Tab. 13 and Fig. 32).

The addition of weathered biochar-compost mixtures to both soils had neutral or positive effects on biomass compared to the effect of compost applied individually depending on the biochar feedstock (Figure 3). The positive effect of the weathered *Miscantus* mixture on biomass may result from better compost mineralisation through the removal of compounds, which inhibit microbial activity as

discussed above (Section 5.3.1). However, the weathered maize mixture showed neutral effect on biomass when compared to the effects of weathered compost alone. Our results showed that weathering of biochar-compost mixtures could lead to positive growth effect. These results are in agreement with a recent field study, showing positive growth effects on the second crop after soil application (Doan et al. 2021). In addition, our results also showed that neutral effects of weathering depending on biochar feedstocks and/or soil type may occur (Doan et al. 2021; Glisczynski et al. 2016a). Further studies would be needed to investigate the mechanisms controlling the variation of biochar-compost interactions on plant growth over time.

6 Conclusions

We investigated the effect of two biochar-compost mixtures and weathering on their material properties, biological stability and on plant growth after addition to two contrasting soils. Our results showed that the physical weathering led to the alteration of material properties of the mixtures, in particular through leaching of labile compounds. These effects could impact the mineralisation of the mixture and also plant growth after soil addition. We suggest that the mixtures contained inhibitive compounds for microbial activity in their labile fraction, as shown by the negative effect on compost mineralisation when combined with biochar. The increase of compost mineralisation within the mixtures after weathering may have provided more plant available nutrients, which could promote plant biomass production when compared to individual compost application. On the other hand, biochar mineralisation was also affected by weathering, indicating that weathering may influence its C sequestration potential.

We conclude that biochar-compost interactions are evolving after physical weathering most probably due to its effect on leaching of soluble compounds. The effect of fresh and weathered biochar-compost mixtures on plant growth depend on biochar production conditions. Further studies should focus on mechanisms influencing the nutrient supply of biochar-compost mixtures.

CHAPTER IV

Mechanisms affecting the fate of biochar and compost mixtures and N adsorption in agricultural soil

This chapter is based on the article in preparation.

Marie-Liesse AUBERTIN[(1,2)*], Cyril GIRARDIN[(2)], Sabine HOUOT[(2)], Vincent MICONNET[(2)], David HOUBEN[(3)], Cornelia RUMPEL[(1)]

[(1)] *Institute of Ecology and Environmental Sciences, UMR 7618, CNRS-UPMC-UPEC-INRA-IRD, Sorbonne University, 75005 Paris, France*

[(2)] *Université Paris-Saclay, INRAE, AgroParisTech, UMR EcoSys, 78850 Thiverval-Grignon*

[(3)] *UniLaSalle, AGHYLE UP 2018.C101, 60000 Beauvais, France*

*corresponding author : marieliesse.aubertin@gmail.com

Chapter IV - Mechanisms affecting the fate of biochar and compost mixtures and N adsorption in agricultural soil

1 Abstract

Joint field application of biochar and compost has been suggested as a promising strategy to improve soil organic carbon (SOC) storage, soil quality and crop production. However, little attention has been paid to the mechanisms controlling the residence time of these materials after joint application to temperate agricultural soils. Aim of the study was to examine if there are biochar-compost interactions affecting the fate of both materials during 2 years of field exposure under temperate climate. Moreover, we aimed to investigate the effect of the soil substrate on this interaction. To this end, *Miscanthus* biochar and green-waste compost were placed mixed or separately in two types of litterbags; one treatment with pure organic matter (OM) and another treatment with addition of soil substrate. We used stable isotope labelling at natural abundance to follow the fate of compost and biochar in the mixtures from pure components and from the free POM fractions in the treatments with soil addition. Subsequently, we studied the chemical composition of the mixtures with Fourier transformed infrared spectroscopy (FTIR). When added to soil substrate, biochar and compost mainly accumulated in the free POM fraction and their fate was not significantly affected by the soil substrate. The fate of compost OC was mainly controlled by occlusion in soil aggregates and mineralization mechanisms, while biochar OC underwent free particle redistribution from coarse to finer grain size fractions. Our results showed that there are biochar-compost interactions affecting OC oxidation, biochar physical disintegration, compost mineralization and N adsorption potential. However, these effects induced by the biochar-compost interaction were not strong enough to significantly affect the particle release, as no effect were observed on OC release. We conclude that although not significantly affecting the OC and N release, biochar and compost may interact on ageing mechanisms and biochar adsorption behavior.

2 Introduction

Composing and pyrolysis are widely used technologies for waste management, conducting to the formation of end-products with contrasting properties. Biochar, the solid residue from biomass pyrolysis, is enriched in recalcitrant organic carbon (OC), thereby promoting soil organic C (SOC) sequestration (Lehmann and Joseph 2015), while compost is composed of comparably labile organic compounds (Mujtaba et al. 2021). Both materials were shown to benefit for agronomic properties and

plant growth after soil application (Abbott et al. 2018; Agegnehu et al. 2016a). Their co-application as soil organic amendment has been suggested as a promising avenue to promote agronomic properties and plant production while enhancing soil C sequestration, through diversified organic matter (OM) inputs (Agegnehu et al. 2017; Abideen et al. 2020).

Once applied on soil, organic matter may undergo aging processes leading to C removal through biological degradation or physical transportation. Although highly recalcitrant to microbial degradation, aromatic substrates like biochar and charcoal may undergo fragmentation processes (Wang et al. 2020; Spokas et al. 2014), that may favor its loss through transportation (Rumpel et al. 2015). Field experiments conducted under tropical conditions showed that biochar in mixture with compost may protect compost particles from biological disintegration and removal from its site of deposition (Ngo et al. 2016; Ngo et al. 2013), probably as a result of the adsorption and/or occlusion of compost particles into its porous structure, (Jien et al. 2015; Jien et al. 2018). Another study investigating the fate of charcoal mixtures with decomposing plant litter during 10 years of field exposure under boreal climate, recorded greater C and mass losses than expected, as a result of labile OM loss promoted by charcoal through stimulation of microbial activity (Wardle et al. 2008). Hence, the climatic conditions seem to be of major importance for interactions through the combination of labile and stable OM types with contrasting effects on the fate of their constituting C. A research gap concerns field studies conducted under temperate conditions and focusing on interactions between different OM types on C loss and the role played by the soil matrix during this process.

When added to soil, biochar alone or combined with compost accumulates mostly in the free particulate organic matter (POM) fraction (Greenberg et al. 2019; Grunwald et al. 2017; Herath et al. 2014; Plaza et al. 2016; Paetsch et al. 2017), and consequently may be subject to rapid removal from the site through physical transport processes (Rumpel et al., 2015). Physical biochar removal may be favored by its high friability, leading to the reduction of the particle size (Spokas et al. 2014; Wang et al. 2013). To a lesser extent, joint application of biochar and compost may lead to the protection of biochar in aggregates and/or mineral associations (Grunwald, Kaiser, and Ludwig 2016; Plaza et al. 2016; Greenberg et al. 2019). The mechanisms determining the fate of biochar-compost mixtures in the field may be influenced by their mode of occurrence in soil: as organic matter patches or intimately mixed within the soil matrix. Up to now, no studies were carried out to address the mechanisms affecting their fate when occurring alone or closely mixed within the soil matrix.

The aim of this study was to elucidate the mechanisms affecting carbon removal of biochar-compost mixtures during two years after their field exposure under temperate climate conditions and the role of the soil matrix in controlling these interactions. To this end, we investigated two modes of occurrence: (1) as pure mixtures and (2) within the soil matrix. We focused on the free POM fraction > 50 µm, which

may be used as an indicator for processes occurring at an annual timescale (van Wesemael et al. 2019) and could thus be adapted for mid-term experiments (< 2 years). We used the litterbag approach to allow investigation of biochar and compost dynamics under field conditions by using a mass balance approach (Ngo et al. 2016). This quantitative approach allowed for investigating interactions of the two components of the mixture based on expected values for each component (Wardle et al. 2008). Moreover, we used natural ^{13}C isotope labeling to allow for differentiation of carbon originating from compost and biochar. All samples were subjected to elemental and stable carbon isotope analyses. In addition, we investigated their chemical composition by Fourier Transformed Infra Red Spectroscopy (FTIR). We hypothesized that (i) biochar and compost interaction induce the protection of both materials, thereby reducing their particle removal and that (ii) when biochar and compost are added to a soil matrix, the protection through their interaction increase this retention because of particle incorporation into soil aggregates.

3 Material and method

3.1 Material and field experiment

Biochar was produced from *Miscanthus* (Miscanthus x giganteus, Greef and Deuter) feedstock, which was pyrolyzed at 550°C for 10 min, using an industrial pyrolysis reactor (Biogreen® Pyrolysis Technology, ETIA, Oise, France). Compost was made from green wastes at the platform of Fertivert (Normandy, France). Biochar and compost were mixed at rates of 1/3 % (dw.) of biochar and 2/3 % (dw.) of compost. The field experiment was carried out on a Haplic Luvisol (World Reference Base for Soil Resources) soil situated at Beauvais in Northern France (49,45°N | 2,13°E). The climate at the site is temperate with 11 °C mean annual temperature and 644.8 mm mean annual precipitation. The soil was alkaline with a pH of 8.1, a silt loam texture, and organic carbon content of 13.3 mg g^{-1}, and a carbonate content of 4.3 mg g^{-1}. Chemical characteristics of initial soil, biochar and compost are reported in Table 14.

Table 14 Chemical characteristics of initial compounds (n=4).

Type	Unit	Soil	Biochar	Compost
pH	-	8.1	8.3	10.0
Total organic C	mg g^{-1}	13.3	754.5	243.3
Total N	mg g^{-1}	1.2	5.5	22.1
δ ^{13}C	‰	-24.7	-14.5	-29.5
C:N	-	11.3	137.5	11.0
CaCO3	mg g^{-1}	4.3	-	-
Clay	g 100 g^{-1}	21.2	-	-

Silt	g 100 g^{-1}	73.6	-	-
Sand	g 100g^{-1}	5.2	-	-

The field experiment was set up as a randomized block design with 7 treatments and 4 replicates with 3.2 x 10 m plot size. The 7 treatments consisted of: (1) control soil (soil), (2) soil with biochar (soil+biochar), (3) soil with compost (soil+compost), (4) soil with biochar-compost mixture (soil+mixture), (5) biochar, (6) compost and (7) biochar-compost mixture. For the treatments containing soil matrix, 375 g (dw.) of soil were placed in a nylon litterbag (20 cm x 20 cm) with 500 µm mesh size, in order to prevent soil macrofaunal activity. Then, 30 g (dw.) of compost and/or 15 g (dw.) of biochar were added, corresponding to 10 % (dw.) of added mixture (6.66 % compost + 3.33 % biochar). All litterbags were deposited in the field in April 2019 at 10 cm depth (Fig. 34), just before the seeding of maize. Maize crop was cultivated from April to September 2019, followed by wheat from October 2019 to July 2020 and by barley from September 2020 to July 2021. A surface tillage was carried out before the seeding of each crop, but not deep enough to affect the position of the litterbags, which thus remained unchanged during all the experiment. Nitrogen fertilization was added in March 2019 (60 kg N ha^{-1}), March 2020 (102 kg N ha^{-1}), April 2020 (62 kg N ha^{-1}), March 2021 (100 kg N ha^{-1}) and April 2021 (80 kg N ha^{-1}). Mean monthly temperature from April 2019 to July 2021 was 5.0 – 18.7 °C (annual mean 11.7 °C) and annual rainfall was 580.5 mm.

The 4 treatments containing soil were collected in July 2020, after 14 months of field exposure, and the 3 treatments with pure organic matter were collected after 4, 10, 14 and 26 months of field exposure. After collection, samples were air-dried at ambient temperature during 2 months, weighed and then stored in dry conditions at ambient temperature for 6 months before analysis.

Figure 34 Litterbag deposition on field, at about 10 cm depth.

3.2 Separation of free POM fractions in treatments with soil

The treatments containing soil at the initial time and sampled after 14 months were fractionated in order to (i) separate the free particulate organic matter (POM) from the aggregates and to (ii) distinguish the sizes of particle or aggregates along the gradient 2 mm > 0.2 mm > 0.05 mm. The fractionation protocol consisted into two steps. In the first step, the sample underwent a particle-size fractionation by wet-sieving, according to a protocol adapted from the method described by John et al. (2005). Briefly, 10 g of each air-dried litterbag were placed in a 2 mm sieve, moistened by capillarity during 5 min and then submerged in distilled water for 5 min to minimize aggregate dispersion by slaking. Thereafter, the sieve was moved up and down immersing the sample completely, in 1 sec by 2.5 cm with 50 repetitions, using the machine of Hénin (Hénin 1958). The fraction still remaining on the sieve was then carefully recovered using a squeeze bottle of distilled water. The wet-sieving procedure was repeated with 200 µm and 50 µm sieves and thus resulted in the separation of four size-class fractions per sample: 4 – 2 mm, 2 mm – 200 µm, 200 – 50 µm and < 50 µm. The < 50 µm fraction was mixed with 0.5 g L^{-1} $CaCl_2$ and put at 4 °C for 12 h to allow flocculation. The flocculate was then recovered by siphoning and considered as organo-mineral fraction < 50 µm, while the total dissolved carbon from the supernatant was analyzed (TOC-5050A, Shimadzu, Marne-la-Vallée, France). In the second step, the free POM fractions were separated from the soil aggregate fractions through a water-densimetric separation (Feller, n.d.; Balesdent 1996). Each of the size-class fraction was put in distilled water, where light-density organic particles (< 1g cm-3) corresponding to POM were separated from heavy soil aggregate fractions (> 1g cm^{-3}) by repeated flotation-panning. The light fraction corresponding to free POM, contained both amendment inputs particles and other organic debris, while the heavy fractions may contain soil aggregates and both adsorbed OM and occluded POMs.

At the end of the fractionation, we obtained three free POM fractions per sample differing by their size (Fig. 35):

- large coarse free POM (4-2 mm),
- small coarse free POM (2 mm – 200 µm),
- fine free POM (200-50 µm)

Mass, OC and N recoveries from the fractionation were respectively 98.6 ± 0.3 %, 98.1 ± 6.7 % and 105.1 ± 5.3 %.

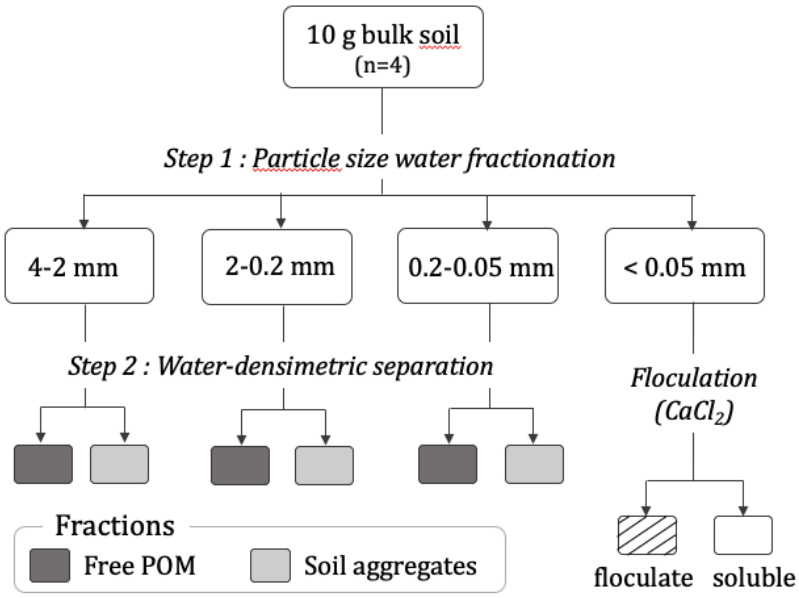


Figure 35 Particle-size and water-densimetric fractionation of the treatments with soil.

3.3 Elemental and isotopic composition and data analysis

All fractions were grounded prior to analysis. The bulk soil and aggregate fractions from treatments with soil were decarbonated using the acid fumigation prior to analysis of organic carbon (OC) and nitrogen concentrations, as well as the stable carbon isotope signatures (Harris et al. 2001). Biochar and compost had distinct natural isotopic signature (Table 14), which allowed for their distinction by using stable C isotope analysis. A presentation of the stable isotopic analysis has been written in Chapter III, part 3.6). Elemental and isotopic analyses were performed using an elemental analyzer (EA Vario Isotope Select, Elementar, Lyon, France) coupled to an isotope ratio mass spectrometer (IRMS Precision, Elementar, Lyon, France). The stable carbon isotope ratios were expressed in $\delta^{13}C$ (‰) relative to the V-PDB (Vienna-Pee Dee Belemnite) standard. Hydrogen content (Thermo Scientific Flash2000) and oxygen content (CE, Instruments NA 2100 Protein) of POM fractions of treatments without soil were also analyzed.

In order to determine biochar-compost interactions, OC and N releases determined for biochar-compost mixtures were compared with “expected mixtures”, calculated from the analysis of each component measured separately. Difference between measured and expected mixtures revealed synergistic biochar and compost interactions, if positive, and antagonistic interactions, if negative.

We calculated of the OC and N releases (OC,N release$_{(t)}$), based on the amount of OC or N ($Q_{OC,N}$, in $g_{OC,N}$) from the treatments without soil (Eq. 9) and with soil (Eq. 10). The $Q_{OC,N}$ was calculated from elemental composition (% OC,N, in %) and the mass of the litterbags ($m_{litterbags}$, in g) (Eq. 8).

$$Q_{OC,N\,(t)} = \%OC,N_{(t)} * m_{litterbag\,(t)} \quad \textbf{(8)}$$

$$OC,N\ release_{\,(t)}\ (\%\ initial) = 100 * \frac{Q_{OC,N\,(t=0)} - Q_{OC,N\,(t)}}{Q_{OC,N\,(t=0)}} \quad \textbf{(9)}$$

$$OC,N\ release_{\,(t)}\ (g\ OC,N\ kg^{-1}) = 10^3 * \frac{Q_{OC,N\,(t=0)} - Q_{OC,N\,(t)}}{m_{litterbag(t=0)}} \quad \textbf{(10)}$$

With mOC,N_{fract}: mass of OC or N in the fraction: $mOC,N_{fract\,(t)} = \%C_{fract\,(t)} * \%m_{fract\,(t)} * m_{litterbag\,(t)}$

Based on the Eq. 11, we distinguished the carbon originated from biochar within the mixtures ($\%C_{biochar\ in\ mixture}$) from the treatments without soil and the free POM fractions from treatment with soil, by using stable C isotopic signatures ($\delta^{13}C$) (Eq. 12). Changes of the $\delta^{13}C$ ratios allowed for direct assessment of the fate of components of the mixtures.

$$\delta^{13}C_{Mixture} * Q_{OC,N\ Mixture} = \delta^{13}C_{Biochar} * Q_{OC,N\ Biochar} + \delta^{13}C_{Compost} * Q_{OC,N\ Compost} \quad \textbf{(11)}$$

$$\%C_{biochar\ in\ mixture\,(t)} = \frac{\delta^{13}C_{Mixture\,(t)} - \delta^{13}C_{Compost\,(t)}}{\delta^{13}C_{Biochar\,(t)} - \delta^{13}C_{Compost\,(t)}} * 100 \quad \textbf{(12)}$$

With $\delta^{13}C$ in ‰ and $\%C_{biochar\ in\ mixture}$ in %.

The OC and N releases from the expected mixture was calculated for the treatments without soil (OC,N $release_{Mix,exp}$) (Eq. 13) and for the free POM fractions from the treatments with soil (OC,N $release_{Soil+Mix,exp}$) (Eq. 14). For the treatment without soil, we used the part of OC and N originating from biochar biochar:compost ratio from the mixture (OC,N $ratio_{BC/Comp}$) to calculate the variation of each component separately in good proportions.

$$OC,N\ release_{Mix,exp\,(t)}\ (\%\ initial) = \%C_{biochar\ in\ mixture\ \,(t)} * OC,N\ release_{Biochar\,(t)} \quad \textbf{(13)}$$
$$+ (1- (\%C_{biochar\ in\ mixture\ \,(t)}) * OC,N\ release_{Compost\,(t)}$$

$$OC,N\ release_{Soil+Mix,exp\,(t)}\ (gOC,N\ kg^{-1}) = \quad \textbf{(14)}$$

$$\text{OC, N release}_{\text{Soil+Biochar (t)}} + \text{OC,N release}_{\text{Soil+Compost (t)}} - \text{OC,N release}_{\text{Soil (t)}}$$

3.4 FTIR spectra acquisition and pre-processing

All treatments without soil were ground to a fine powder (< 200 µm) and scanned with a spectrometer (FTIR 660, Agilent, Les Ulis, France) in the mid-infrared (MIR) spectral range from 400 to 4000 cm^{-1} with a KBr separator and a DTGS detector. The diffuse reflectance (DR) measurements were made at 1 cm^{-1} intervals but a 2 cm^{-1} interval was considered in the analysis. The DR was converted to absorbance (A) using the equation: A = log(1/DR). The spectra were smoothed using the Savitzky-Golay smoothing method (a window size of 31 cm^{-1} and a polynomial order of one to further eliminate noise). The wavenumbers corresponding to CO_2 (2500-2300 cm^{-1}) were removed. We calculated the mean values from five replicate analyses for each sample. We focused on the 2300-400 cm^{-1} region of the spectra, as this contained most of the information related to the organic functionalities. Assignments of the infrared absorption bands were based on a literature compilation (Okolo et al. 2015; Toscano et al. 2015; Chia et al. 2012; Jackson et al. 1995; Bekiaris et al. 2016; Weiland and Guyonnet 2003).

3.5 Statistics

The normal distribution and homoscedasticity of variances of data were assessed using Shapiro test and Levene test, respectively. The non-normally distributed data were transformed with logarithmic transformation. If the transformed data were still not normally distributed, we used non-parametric analysis. Comparison between treatment and time sampling were undertaken by analysis of variances (ANOVA) or by paired t-tests for normally distributed data, and by Kruskal-Wallis tests or paired Wilcoxon tests for non-normally distributed data. Statistical analysis was performed using R software (version 3.6.3).

4 Results

4.1 Treatments without soil

4.1.1 Mass loss and elemental composition

Mass loss and elemental content of litterbags without soil are reported in Table 15. When exposed alone, compost mass decreased by 12 % after 26 months of field exposure, while it increased by 22 % for

biochar when exposed alone and remained stable for the mixture. The organic carbon (OC) content from the biochar treatment decreased significantly during field exposure, from 755 to 593 g kg^{-1} (Tab. 15). Although the compost and the mixtures' OC contents did not significantly differ, they tended to decrease, from 243 to 215 g kg^{-1} for the compost and from 379 to 346 g kg^{-1} for the mixture. N contents ranged between 3.3 and 7.2 g kg^{-1} for biochar, 19.8 and 22.1 g kg^{-1} for compost and 13.9 and 18.9 g kg^{-1} for the mixture treatments. While N content of the pure compost treatment did not significantly differ through time, it significantly decreased for pure biochar treatments from 7.2 g kg^{-1} at 14 months to 3.3 g kg^{-1} at 26 months (Tab. 15). For the mixture treatment, the N content increased up to 18.9 g kg^{-1} after 10 months, and thereafter decreased to initial values. The stable C isotope signature ($\delta^{13}C$) remained unchanged through time with 14.6 ‰ for biochar, 29.5 ‰ for compost and 20.1 ‰ for the mixture treatment (Tab. 15). The H:C ratios ranged from 0.028 (biochar) to 0.111 (compost) and O:C ratios from 0.108 (biochar) to 0.800 (compost). While these ratios showed no changes with time for compost and mixtures, they increased after 26 months for biochar.

Table 15 Mass loss in the litterbags (% initial) and elemental composition of treatments without soil (mean ± SD, n=4). Letters represent significant differences between time samplings, for each type.

Type	Time (month)	Mass loss (% initial)		C (g kg^{-1})		N (g kg^{-1})		$\delta^{13}C$ (‰)		H:C		O:C	
Compost	0	0.0 *0.0*	b	243.3 *0.0*	a	22.1 *0.0*	a	-29.5 *0.0*	b	0.108 *0.002*	a	0.788 *0.035*	a
	4	9.5 *1.8*	ac	237.6 *11.9*	a	21.0 *1.0*	a	-29.5 *0.0*	ab	0.111 *0.001*	a	0.776 *0.060*	a
	10	8.9 *3.6*	ac	231.8 *13.1*	a	21.5 *1.1*	a	-29.4 *0.1*	a				
	14	4.0 *2.5*	ab	215.5 *8.5*	a	19.8 *0.9*	a	-29.4 *0.0*	ab				
	26	12.1 *4.3*	c	215.3 *7.5*	a	19.9 *0.9*	a	-29.5 *0.0*	b	0.111 *0.001*	a	0.800 *0.038*	a
Biochar	0	0.0 *0.0*	b	754.5 *0.0*	a	5.5 *0.0*	ab	-14.5 *0.0*	ab	0.028 *0.001*	b	0.114 *0.003*	ab
	4	0.1 *2.0*	b	691.2 *41.2*	a	5.4 *0.1*	ab	-14.6 *0.1*	ab	0.028 *0.001*	ab	0.108 *0.006*	b
	10	-17.0 *6.8*	a	622.3 *39.8*	ab	5.6 *1.1*	a	-14.5 *0.0*	a				
	14	-8.7 *5.7*	ab	624.8 *47.8*	ab	7.2 *0.9*	a	-14.7 *0.1*	b				
	26	-21.7 *11.7*	a	593.1 *37.9*	b	3.3 *0.4*	b	-14.6 *0.0*	ab	0.031 *0.001*	a	0.158 *0.013*	a
Mixture	0	0.0 *0.0*	ab	379.2 *0.0*	a	17.2 *0.0*	ab	-20.1 *0.0*	ab	0.062 *0.001*	a	0.420 *0.007*	a
	4	3.5 *1.0*	b	382.3 *26.7*	a	14.0 *0.7*	a	-20.2 *0.3*	ab	0.061 *0.001*	a	0.401 *0.023*	a
	10	2.2 *3.4*	ab	376.3 *5.1*	a	18.9 *0.8*	b	-20.1 *0.2*	ab				
	14	-2.6 *6.0*	ab	353.2 *13.3*	a	13.9 *0.3*	a	-20.4 *0.1*	b				
	26	-2.3 *5.2*	a	346.1 *10.8*	a	15.8 *3.7*	ab	-20.0 *0.2*	a	0.060 *0.003*	a	0.419 *0.022*	a

4.1.2 OC and N released in treatments without soil

The OC and N released from all treatments without soil are represented in Figure 36. Organic C loss from compost and mixture treatments increased with time, up to respectively 22.3 ± 1.4 % and 14.0 ± 1.7 %, after 26 of field exposure. After 26 months of exposure, OC loss from biochar treatment was 4.7 ± 2.9 % (Fig. 36). After 10 and 26 months of exposure, OC loss from the measured mixture treatment tended to be higher than expected, based on the results of individual biochar and compost treatments. When considering the changes of OC derived from biochar or compost within the mixture using the isotopic signature (Fig. 37), we observed no significant differences compared to the results for its two components. After 26 months of field exposure, compost-derived OC loss when added with biochar and as pure component were respectively 22.1 ± 4.0 % and 22.3 ± 1.4 %, while biochar-derived OC loss when added with compost and as pure component were respectively 8.6 ± 0.9 % and 4.7 ± 2.9 % (Fig. 37). After 4 months of exposure, the biochar-derived OC loss tended to be higher in the mixture treatment than when exposed alone.

Nitrogen loss from compost treatment increased progressively, up to 21.0 ± 2.6 % after 26 months (Fig. 36). N from the biochar treatment was increasingly retained during the first 14 months, up to -42.6 ± 18.7 %, and then was lost at month 26, up to 26.7 ± 13.4 %. N from the mixture treatment was lost at months 4 and 14, with a maximum of 18.7 ± 3.6 % loss at month 4, and remained constant for the rest of the incubation period. After 26 months of exposure, the N loss from the mixture treatment was 2.4 ± 27.2 % (Fig. 36). No statistical differences were found between the measured and the calculated mixtures, except for N release at months 10 and 14. At month 10, the N of the mixture was retained while the N release was expected and at month 14, higher amounts of N than expected were released.

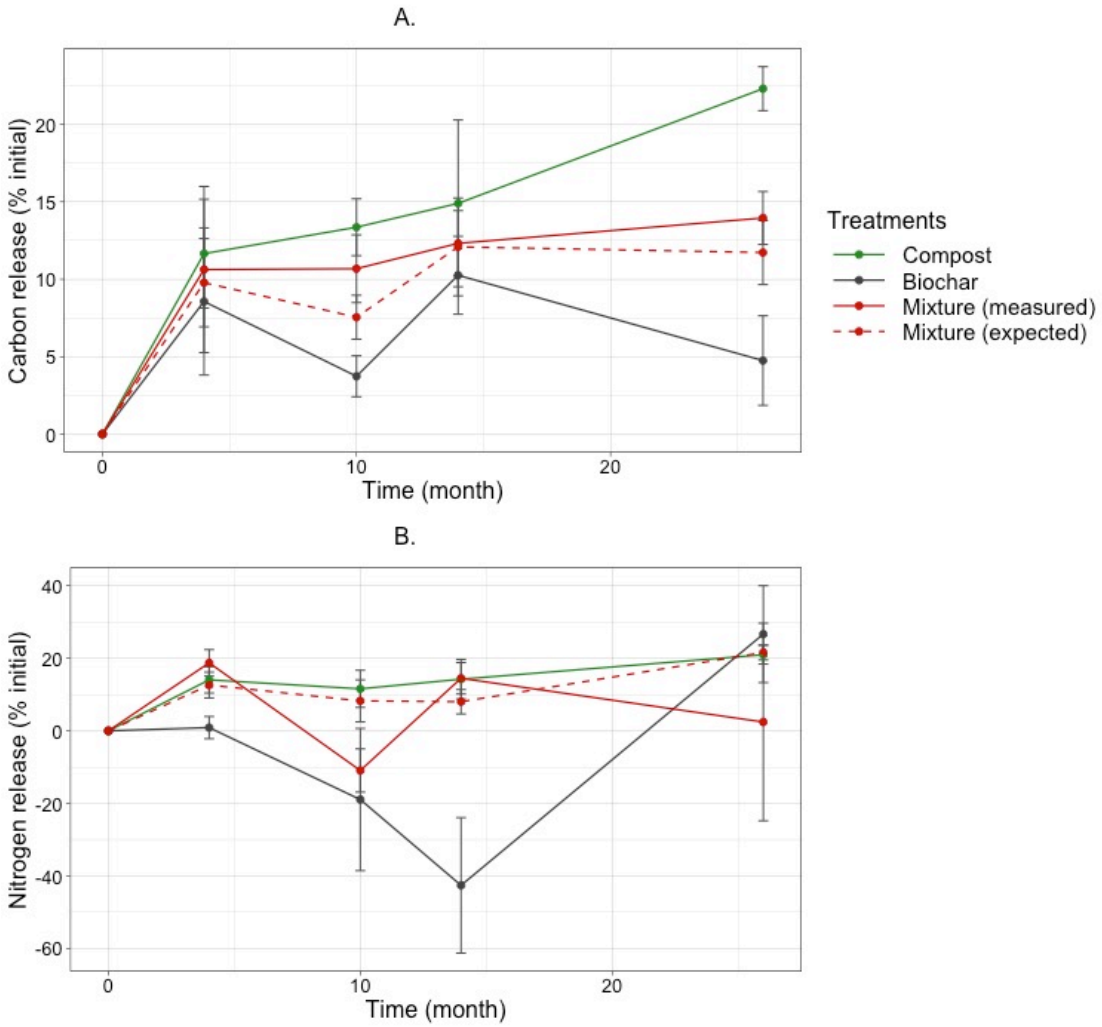


Figure 36 OC and N releases from treatments without soil (mean ± SD, n=4). No statistical differences were found between the measured and the calculated mixtures ($p > 0.05$), except for N loss at months 10 and 14.

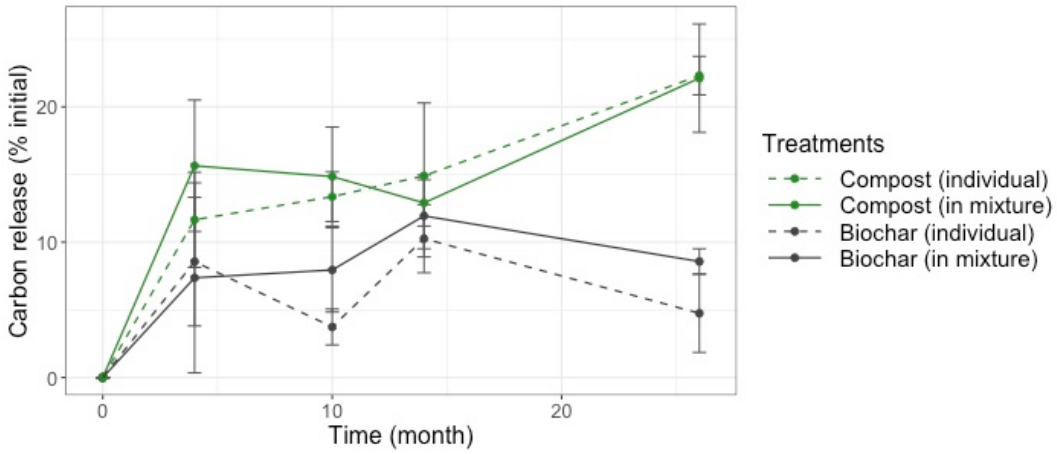


Figure 37 Losses from compost- and biochar- derived OC when considered in the mixture (continued line) or measured as single component (dash line). No statistical differences were found between treatments for each component ($p > 0.05$) (mean ± SD, n=4).

4.1.3 FTIR spectroscopic analysis

MIRS spectra of all treatments without soil are presented in Figure 38. Field exposure induced a decrease of aromatic C=C features (1525-1425 cm^{-1}) in all treatments without soil and a corresponding strong increase of aliphatic C-O and C-C features (1060-900 cm^{-1}) for biochar treatment, leading to the appearance of C-O bonds (1035 cm^{-1}).

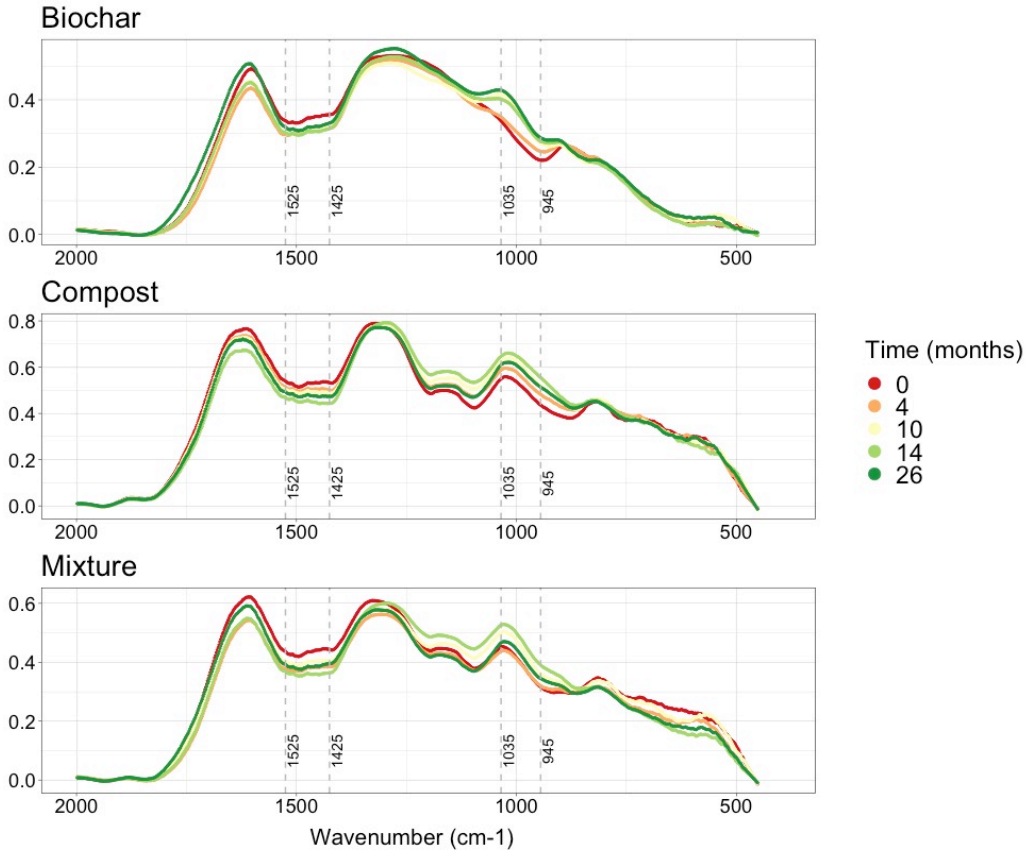


Figure 38 FTIR spectra of the treatments without soil (mean, n=4).

4.2 Free POM fractions from treatments with soil

4.2.1 Fraction recovery

While no free POM fraction was recovered from the unamended treatment (control), most of the OC and N from the OM inputs in the other treatments accumulated in the free POM fractions (Fig. 39). OC in aggregate and free POM fractions ranged respectively from 10.6 ± 0.3 g OC kg^{-1} to 17.2 ± 0.3 g OC kg^{-1} and from 0.0 g OC kg^{-1} to 38.2 ± 5.3 g OC kg^{-1}. Nitrogen in aggregate and free POM fractions ranged respectively from 1.1 ± 0.1g N kg^{-1} to 1.67 ± 0.1 g N kg^{-1} and from 0.2 ± 0.0 g N kg^{-1} to 1.4 +

0.2 g N kg^{-1}. All cumulated aggregate fractions and free POM fractions were significantly affected by time and treatment effect (Tab. 16), with the OC and N contents decreasing in the cumulated free POM fractions and increasing in the cumulated aggregate fractions (Fig. 39). In the free POM fractions, higher OC accumulation was recorded when soil was amendment with pure biochar than with pure compost, while the contrary was observed for N accumulation. The soil+mixture treatment resulted in the cumulation of the OC from free POM fractions from biochar and compost amendment. The soluble fractions were very heterogeneous among the replicates and did not show any significant difference from zero (Fig. 40).

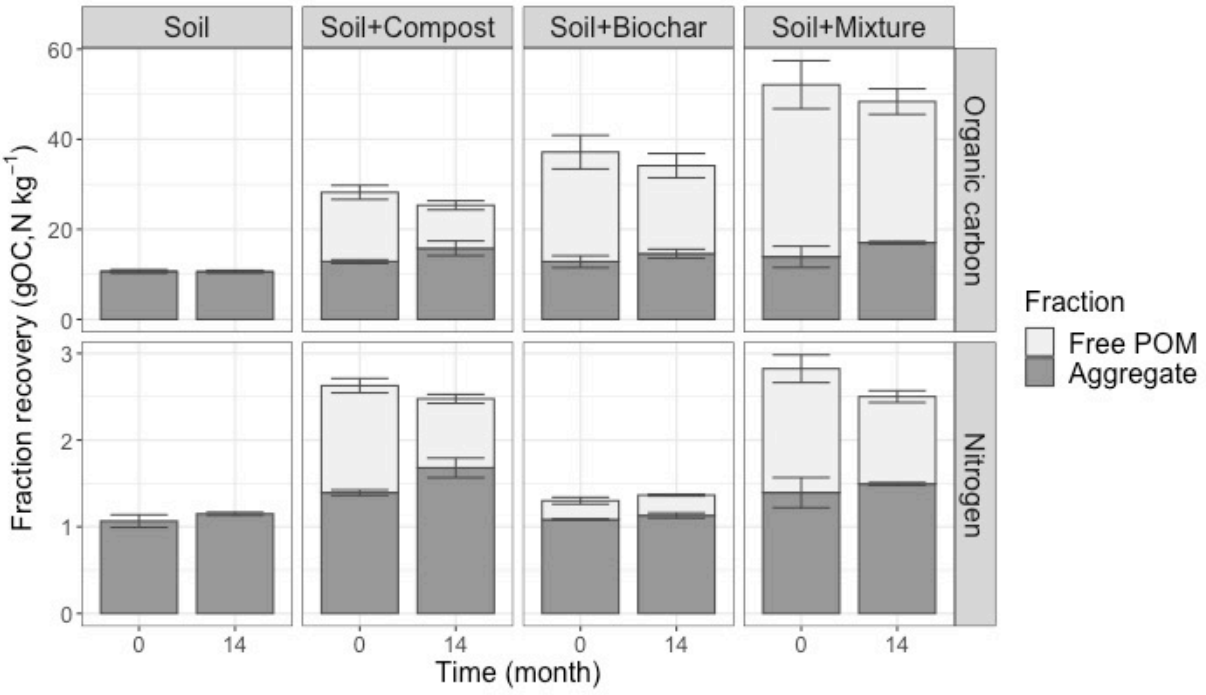


Figure 39 OC and N recoveries of the aggregates and free POM fractionation (mean ± SD, n=4) from the treatments containing soil, at the initial time and after 14 months of field exposure.

Table 16 Variance analysis for the effect of time and treatment type and their interaction on the organic carbon content and the nitrogen content, of the cumulated aggregates fractions and of the cumulated free POM fractions, from all treatments containing soils at both initial time and after 14 months of field exposure.

Analysis	Fraction	Effect	Df	F ratio	P value	
Organic C	free POM	Time	1	19.94	2.99e-4	*
		Treatment	2	98.35	2.05e-10	*
		Time: Treatment	2	0.21	0.81	
	aggregate	Time	1	21.11	1.16e-4	*
		Treatment	3	23.94	2.16e-07	*
		Time: Treatment	3	2.97	0.052	
Nitrogen	free POM	Time	1	51.28	1.15e-05	*
		Treatment	2	239.11	2.15e-10	*
		Time: Treatment	2	14.60	6.10e-4	*
	aggregate (log transformation)	Time	1	15.58	0.001	*
		Treatment	3	51.03	2.05e-08	*
		Time: Treatment	3	1.72	0.20	

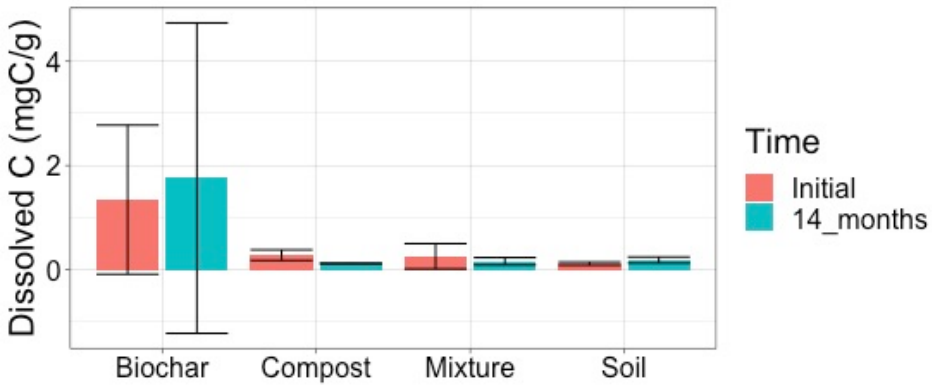


Figure 40 Dissolved carbon in the supernatant < 50 µm after fractionation of the treatments containing soil.

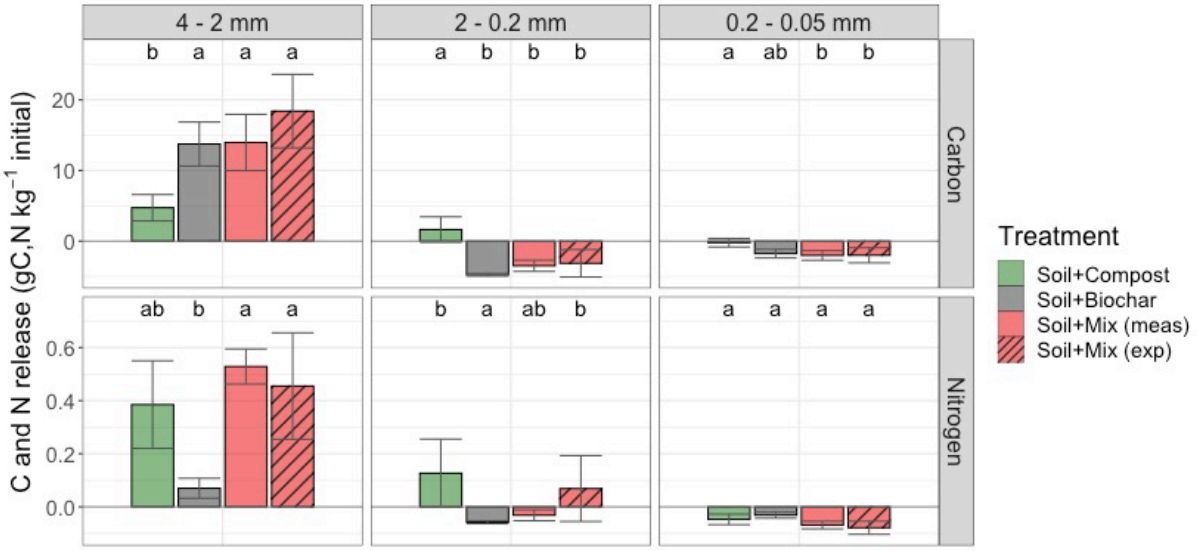
4.2.2 OC and N released in the free POM and aggregate fractions

The OC released from the cumulated free POM fractions after 14 months of field exposure was the highest in the 4-2 mm fraction, ranging from 4.7 ± 1.9 g OC kg^{-1} to 14.0 ± 4.0 g OC kg^{-1}, with higher values recorded for the soil+biochar and soil+mixture treatments (Fig. 41.A). Similarly, the highest N release from the free POM fractions was recorded for the 4-2 mm fraction, ranging from 0.06 ± 0.04 g N kg^{-1} to 0.52 ± 0.07 g N kg^{-1}, with the highest values recorded for both soil+compost and soil+mixture treatments. The free POM < 2 mm, showed OC and N gains for the soil+biochar and soil+mixture treatments, of up to 4.78 ± 0.19 g OC kg^{-1} and to 0.07 ± 0.01 g N kg^{-1}. Except for the N gain in the 0.2-0.05 mm fraction, no changes in OC and N were recorded for the soil+compost treatment in the < 2 mm free POM fractions. OC and N releases of soil+mixture treatment were similar to the expected ones. However, in the 4-2 mm fraction, the OC release from the free POM fraction of the measured soil+mixture tended to be lower than the expected value.

The unamended soil treatment (control) did not show any significant changes through time in the aggregate fractions > 0.05 mm, while it gained significant amounts of OC and N in the 0-0.05 mm aggregate fraction, corresponding to 0.93 ± 0.39 g OC kg^{-1} and 0.04 g N kg^{-1} (Fig. 41.B). The biochar and compost amendments led to changes of OC and N concentrations in the 4-2 mm and 0-0.05 mm aggregate fractions. In particular, soil amendment with compost led to accrual, up to 3.23 ± 1.20 g OC kg-1 and 0.20 ± 0.08 g N kg-1 in the 4-2 mm fraction, while biochar induced led to OC and N gains of up to 3.41 ± 1.68 g OC kg^{-1} and 0.08 ± 0.07 g N kg^{-1} in the 0-0.05 mm aggregate fraction,. The soil+mixture treatment gained OC and N in the same range than compost and biochar for the same fractions, except for the OC gain in 0-0.05 mm fraction, which was in the same range than those of the soil+biochar treatment. The OC and N gains of the soil+mixture treatment were similar to expected values. For both 2-0.2 mm and 0.2-0.05 mm fractions, no significant changes of OC and N were recorded for all treatments, except for the OC of the 2-0.2 mm aggregate fraction, where the soil+compost treatment showed an OC release of 1.75 g OC kg^{-1}. The OC and N release of the the 2-0.2 mm and 0.2-0.05 mm fractions of soil+mixture treatments were similar to expected values, except for the OC release in the 2-0.2 mm fraction were release was significantly lower than expected.

Results of the mass recovery, OC, N, C:N ratio and $\delta^{13}C$ are reported in supplementary material, tables SIV.1 and SIV.2. The $\delta^{13}C$ ranged between 14.9 ± 0.1 ‰ for the free POM fractions isolated from soil+biochar treatment and 29.6 ± 0.1 ‰ for the free POM fractions isolated from soil+compost treatment. These values remained significantly stable through time.

A) Free POM fractions



B) Aggregate fractions

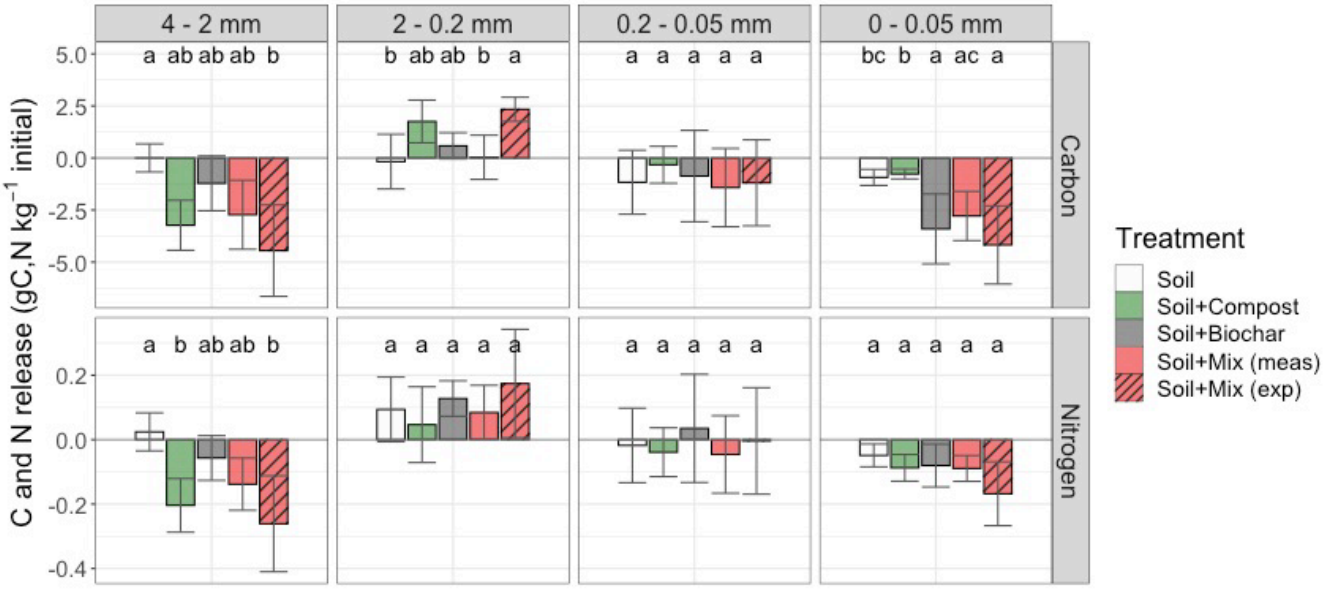


Figure 41 Variation of OC and N from free POM fractions (A) and aggregate fractions (B) after 14 months of field exposure, as compared with the initial time (mean ± SD, n=4). Positive values represent losses and negative values represent gains. Letters represent significant treatment effect, for each grain size fraction.

Using stable isotopic measurements, we were able to distinguish the fate of biochar- and compost-derived OC in the free POM fractions extracted from the soil+mixture treatment (Fig. 42). Biochar-compost interactions were assessed by comparing OC derived from biochar and compost calculated from the soil+mixture treatment with OC derived from both soil+biochar and soil+compost treatments. Independently from their individual amendment or combined amendment, biochar and compost

amendments induced OC releases when extracted from the 4-2 mm fraction, while in the finer fractions, they induced OC gain for the biochar-derived OC and no significant changes for the compost-derived OC. For the 4-2 mm free POM fraction, biochar- and compost-derived OC losses ranged respectively from 8.3 ± 4.6 g OC kg^{-1} to 13.7 ± 3.1 g OC kg^{-1} and from 4.7 ± 1.9 g OC kg^{-1} to 5.6 ± 1.6 g OC kg^{-1} (Fig. 42). For this grainsize, although no significant effect of interaction were recorded between biochar and compost on OC retention, biochar tended to release lower OC content when combined with compost than when amended as pure component to soil substrate. In the 2-0.2 mm and 0.2-0.05 mm grainsizes free POM fractions, biochar amendment induced OC gain, ranging respectively from 3.5 ± 0.4 g OC kg^{-1} to 4.8 ± 0.2 g OC kg^{-1} and from 1.6 ± 0.5 g OC kg^{-1} to 1.8 ± 0.6 g OC kg^{-1}. In the 2-0.2 mm fraction, the biochar-derived OC gain was significantly lower when co-applied with compost than when amended as pure component. No significant OC release or gain was recorded for the soil amended with compost for the 2-0.2 mm and 0.2-0.05 mm grain sizes free POM fractions.

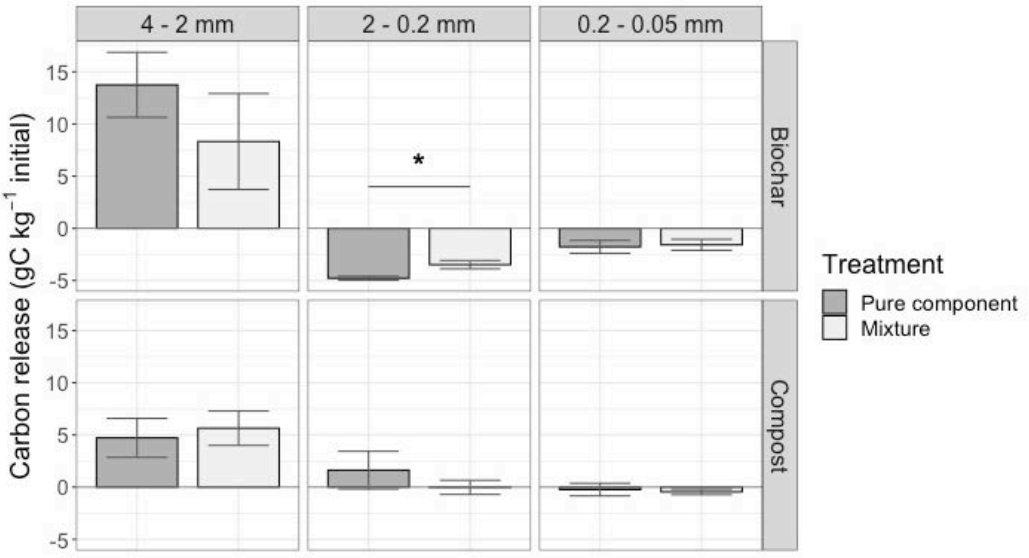


Figure 42 Variation of biochar- and compost-derived OC, when added as pure component or when mixed with each other, after 14 months of field exposure (mean ± SD, n=4), using differences of biochar and compost stable isotopic signatures. Positive values represent losses and negative values represent gains. Stars represent significant treatment effect, for each of the free POM fractions.

5 Discussion

5.1 Chemical composition in treatments without soil

While compost and mixture treatments did not show any significant differences in their chemical composition, the OC content of the biochar treatment decreased through time, with corresponding increases of both H:C and O:C ratios. These results agree with a previous laboratory study showing that organic C content from *Miscanthus* biochar decreased after artificial weathering with corresponding increase of O:C ratio (Aubertin et al. 2021). The H:C and O:C atomic ratios are commonly used as indicators for biochar stability, with higher ratios indicating lower aromaticity and higher oxidation state of biochar, respectively (Mia et al. 2017a; Xiao et al. 2016; Leng et al. 2019). Higher ratios were consistent with the higher content of aliphatic features and lower aromatic features recorded by FTIR spectroscopy of the biochar treatment, with increasing time of exposure. Similarly, other field studies found that the environmental exposure significantly reduced biochar C and aromatic structures, along with increasing O content and functional groups such as carboxylic, lactonic, phenolic, carbonyl and carboxylate groups (Liu et al. 2021; Sorrenti et al. 2016). While Aubertin et al. (2021) found significant decrease of organic C for the biochar-compost mixture after artificial weathering, our results only found tendency of organic C decrease through time for the mixture treatment. This may be due to the fact that the artificial weathering may consist of higher water rainfall simulation than natural ageing under temperate conditions (Wang et al. 2020).

Both OC and N losses from compost and mixture treatments were mainly driven by mass losses, as their chemical composition remained stable through time (Table 15). For all treatments, the highest OC loss occurred in the first 4 months, during the summer, which corresponds to the hottest period with the highest rain intensities of the year. This result is consistent with results from Ngo et al. (2016), who attributed the highest OC removal occurring in the first 16 weeks of incubation, to the tropical climatic conditions, corresponding to the hottest period and rainy season in their field. The compost treatment showed the highest OC loss during the 26 months of field exposure, due to the degradation of its initial higher amounts of labile OC, when compared to biochar treatment. As biochar treatment induced a decrease of OC content and no significant change of $\delta^{13}C$, the mass gain may have been related to additional carbon from the soil above the litterbag. Indeed, the litterbags was permeable to < 0.05 mm particles, and it has been shown that biochar porous structure can physically protect OM particle from leaching (Jien et al. 2015). Biochar and compost did not show significant interactions preventing or stimulating OC losses, as shown by the absence of significant differences between measured and expected losses from the mixture. However, a tendency of higher OC losses than expected in the mixture treatment, might be related to priming effects evidenced in laboratory experiments (Aubertin et al.

2021). The authors found that these effects were reduced after the leaching of fine particles, which could explain the absence of significant results after prolonged field exposure. Our results were consistent with a 10 years field study using litterbag method in a boreal forest soil, where charcoal combination with decomposing plant material was found to release higher OC than the expected values (Wardle et al. 2008). However, when exposed in tropical climate conditions, biochar combination with compost in litterbags was found to induce lower OC loss than components considered separately, after 52 weeks of field exposure (Ngo et al. 2016). The tendentially lower than expected OC release in our study, may result from the biochar-compost mixture promotion in the formation of organic aggregates (Ngo et al. 2016; Jien et al. 2015).

The biochar treatment induced a strong N gain at months 10 and 14, which could be a result of adsorption of fertilizer N to the oxygen functional groups, occurring during field exposure (Cai et al. 2016). Our results were coherent with the ones of Palanivell et al. (2020), who found that N can be temporary retained by biochar and then be slowly released with time. Consequently, as compared to the expected results, the measured mixture treatment recorded higher N gain at month 10 and higher N loss at month 14. These results may evidence that biochar and compost interactions may affect the biochar sorption behavior toward nitrogen.

5.2 Effect of the soil matrix on the OC and N accumulation

In the free POM fractions, the higher OC accumulation after biochar amendment and the higher N accumulation after compost amendment in soil is consistent with the higher OC content in biochar and higher N content in compost materials. The OC and N released and gain of free POM fractions and aggregate fractions of soil+mixture treatment were expected, indicating an additive effect of biochar and compost on the retention of OC and N. The additive effect on OC retention was consistent with the results from treatments without soil after 14 months of field exposure, where additive effects were also recorded. Hence, the soil matrix did not promote any significant interactions between biochar and compost with regards to the OC retention. However, the N release was from soil+mixture treatment with soil matrix was expected, while the mixture treatment without soil showed higher N release than expected after 14 months of exposure. Furthermore, the N of the free POM fractions from the soil+biochar treatment, when exposed in soil matrix, did not show any significant changes, while in the biochar treatment without soil, significant N accrual occurred after 14 months of exposure. These results suggested that the soil matrix may have alleviated the adsorption of N onto biochar surfaces. Fine soil particles could have blocked micro- and mesopores of biochar, thereby weakening its pore-filling effect

on sorption behavior, since pore-filling is considered as one of the main adsorption mechanisms of biochar (S. Tang et al. 2021).

5.3 OC and N released from the treatments containing soil

When biochar and compost were added to the soil matrix, the OC and N from the organic inputs accumulated mainly in the free POM fractions, while a small amount accumulated in the aggregate fractions, as indicated by the OC and N gains in the 4-2 mm and 0-0.05 mm aggregate fractions. These results are in agreement with many other studies, where biochar and compost accumulated both in aggregates and free POM, but in much higher amounts in the free POM fraction (Plaza et al. 2016; Herath et al. 2014; Grunwald et al. 2017; Greenberg et al. 2019; Paetsch et al. 2017; Fernández et al. 2014). The general higher OC and N gains in the 4-2 mm aggregate fraction and loss or no effect for the 2-0.2 mm and 0.2-0.05 mm fractions could have resulted from the vertical transport of aggregates < 0.5 mm, which could have been lost from the litterbags. The 0-0.05 mm fraction contained both aggregates and free POM particles. Hence, OC and N gain in this fraction could be attributed to higher free POM particles, as suggested by the higher OC recovery in this fraction after 14 months of exposure (supplementary material, Tab. S2).

All treatments with soil recorded OC release from the 4-2 mm free POM fractions after 14 months of field exposure, while both soil+biochar and soil+mixture treatments additionally led to OC gain in the < 2 mm free POM fractions. Organic C and N release from the litterbags could be attributed to several factors, including biological degradation (Sun et al. 2016; Chami et al. 2016), physical degradation and transport (Ngo et al. 2016), and occlusion into soil aggregates (Cooper et al. 2020). The soil+compost derived OC that was gained in the 4-2 mm aggregate fraction corresponded to about half of the OC lost in the 4-2 mm free POM fraction, thereby evidencing that only part of the OC removal of the free POM fractions could have been occluded into the soil matrix. The compost-derived free POM may thus have been subjected to strong mineralization. In contrast, biochar may contain very small amount of labile C and therefore may be quite stable toward microbial decomposition (Wang et al. 2016). Except for the 0-0.05 mm aggregate fraction, soil+biochar induced only low OC and N gains, suggesting the preferential mechanism of biochar free particle redistribution. Indeed, as biochar potential for friability is generally high (Spokas et al. 2014), the redistribution of biochar free POM fractions from coarse to finer particles may be the main mechanism driving the OC and N release in the 4-2 mm free POM fraction. During field exposure, rainfall and freeze-thaw cycles have been shown as dominant causes of biochar physical fragmentation and breakdown (Wang et al. 2020). Water adsorbed on biochar during rainfall events can thus cause graphite sheets to swell, resulting in structural expansion (Spokas et al. 2014). Our results

are consistent with results from de la Rosa et al. (2018), who evidenced the increase of biochar physical fragmentation over 24 months under field conditions.

No significant effects of biochar-compost interactions were recorded for the OC and N release or gain for both free POM and aggregate fractions, as revealed by the absence of significant differences between values for measured and expected soil+mixtures, except for OC release in the 2-0.2 mm aggregate fraction. In the latter, the soil+mixture treatment released less OC than expected, probably as a consequence of compost protection from biological degradation in the biochar porous structure (Jien et al. 2018).

When distinguishing the compost- and biochar-derived OC in the free POM fractions of the soil+mixture treatments, our results indicated no significant differences of compost-derived OC release when combined with biochar and when individually applied to the soil matrix. This result is consistent with the absence of significant difference for the mixture treatment without soil. However, previous laboratory studies evidenced that compost mineralization was affected when combined with biochar (Aubertin et al. 2021). The absence of significant effects of biochar on compost-derived OC retention may be attributed to other mechanisms than biological degradation, such as compost inclusion in soil aggregates, which may have a stronger effect than the C mineralization on the OC release of compost particles. Indeed, compost amendment induced strong OC and N gains in the 4-2 mm aggregate fraction, thus evidencing the occlusion in soil aggregates of part of the compost released from the free POM fraction. However, as the occlusion of the compost particles could explain only part of the OC and N release from the free POM fraction, our results suggested that the inhibitive effect of biochar on part of the compost-derived OC mineralization was alleviated due to the 14 months of weathering (Gale et al. 2016). Our values indicated a tendency for lower biochar-derived OC release from the 4-2 mm free POM fraction and a significant lower biochar-derived OC gain in the 2-0.2 mm free POM fraction, as compared to the soil+biochar treatment. Additionally, ageing may also induce biochar particle fragmentation (Spokas et al. 2014), and adsorption of clay particles from above soil on biochar surface, thus providing additional adsorption sites (Liu et al. 2021). The lower biochar-derived OC gain due to the presence of compost could be explained by the protection of biochar from physical degradation by compost adsorption on biochar surface, thus forming a protecting coating (Jien et al. 2015; Hagemann et al. 2017b). Indeed, ageing may impact the biochar porous structure, leading to its surface area increase and thus to its sorption capacity and to the creation of more available sites for chemical binding (Sorrenti et al. 2016; Tan et al. 2020; Liu et al. 2021; Ahmad et al. 2014). Chemical bonding of biochar coarse particles with compost POM may have occurred and been promoted by biochar aging, thereby inhibiting friability of biochar coarse free POM.

6 Conclusions

Our approach did not evidence significant effects of biochar-compost interaction on the retention of particles, when exposed for 26 months under temperate crop field conditions. When mixed with the soil matrix, biochar and compost particles mainly accumulated in the free POM fraction and therefore, the soil matrix did not have a major effect on the fate of biochar and compost particles. Compost OC release was mainly controlled by occlusion in soil aggregates and mineralization, while biochar OC was redistributed as free POM from coarse to fin particle size fractions. Our results indicated that biochar and compost protected each other from oxidation, probably as a result of compost adsorption into biochar porous structure. Compost was shown to protect biochar from physical disintegration, thereby reducing biochar particle size, while biochar was shown to reduce the compost OC release in the 2-0.2 mm aggregate fraction, probably as a result of compost protection against microbial degradation. However, there were no biochar-compost interactions with effects on OC dynamics during (14 months). In contrast, the interaction of both materials may affect N dynamics. We conclude that although not significantly affecting OC release, biochar and compost may interact on ageing mechanisms and biochar adsorption behavior. To our knowledge, our results thus constitute one of the very few evidences of an effect of compost on biochar physical disintegration and N retention. These results call for further investigation on the biochar-compost interactions on longer term studies and on their impact on the fate of particles.

CHAPTER V

General discussion, conclusion and perspectives

Chapter V – General discussion, conclusion and perspectives

In the context of climate change and growing population, there is an urgent need to find solutions to decrease atmospheric greenhouse gas and to increase food production (Masson-Delmotte et al. 2018). Biochar appears as a solution to sequester atmospheric C in soil through the enrichment of recalcitrant organic C from organic waste origin, while it may also benefit for soil agronomic properties such as water content, pH and soil density (Lehmann and Joseph 2015; Agegnehu et al. 2017). Since biochar does not contain large amounts of labile compounds that may be easily assimilated by microorganisms, its combination with mature compost would constitute more diversified sources of OM, thereby providing labile OM for microbial activity. Compost is commonly used as an organic amendment for soil and benefits for crop production, because it provides labile C, has positive effects on water retention and may provide available nutrients (Abbott et al. 2018). Although biochar and compost co-application is of growing interest due to its double interest on C sequestration and soil agronomic properties (Agegnehu et al. 2017; Sánchez-Monedero et al. 2019), research gaps remain concerning the mechanisms and effects of biochar-compost interactions as soil amendments. The present work investigated mechanisms controlling biochar-compost interactions and their implication for carbon sequestration and soil processes, considering three different time scales.

1 General discussion

1.1 Biochar-compost interactions during their blending may affect biochar biological stability

Our work evidenced that, right after its blending with compost, *Miscanthus* biochar contribution of aromatic compounds decreased with corresponding increased contribution of aliphatic compounds and oxygen-containing functional groups. We attributed these chemical changes to biochar abiotic oxidation (Chapter II). Abiotic processes were shown to precede biotic processes for biochar oxidation (Zimmerman 2010; Cheng et al. 2006). Furthermore, the chemical changes on biochar surface after blending with compost induced the decrease of biochar thermal stability (Chapter II). Thermal stability of SOC was found to be a suitable indicator to estimate of its biological stability (Leifeld and von Lützow 2014; Gregorich et al. 2015; Barré et al. 2016). Hence, we suggested that initial abiotic oxidation when combined with compost may decrease its biological stability through the decrease of its chemical recalcitrance.

Abiotic oxidation of biochar surface was shown to induce the formation of oxygen-containing functional groups (Cheng et al. 2006), which may significantly enhance the adsorption performance of biochar toward nutrients, due to hydrogen bonding and electrostatic interaction (Cai et al. 2016). Hence, the initial abiotic oxidation of biochar may have increased the sorption capacity of biochar toward nutrients from compost, thereby further stimulating the microbial activity and in turn, enhancing the mineralization of biochar-derived labile C.

In our laboratory incubation (Chapter III), we mixed biochar and compost as pure organic matter, in order to follow the CO_2-C released by each component and compare it with C release when individually incubated. Compost was shown to increase biochar-derived C mineralization (Chapter III). We attributed the higher biochar mineralization of biochar when combined with compost, to the promoting effect of compost-derived nutrients on microbial activity. As biochar abiotic oxidation previously to the incubation may decrease its chemical recalcitrance and increase its nutrient sorption capacity thereby favouring microbial degradation, we suggest that initial biochar abiotic oxidation may have contributed to lower the biological stability of biochar. As we did not analyze the degree of aromaticity of the biochar-derived C that was degraded during the incubation (Chapter III), we could not determine if this C was composed with chemically recalcitrant molecules, which, in such case, would indicate a priming effect of compost on biochar biological degradation.

1.2 When applied on soil, the effects of biochar-compost interaction on carbon storage and nitrogen retention may be time-dependent

Once applied on soil, biochar and compost may undergo biotic and abiotic ageing processes. In the short-term (< 1 year), compost generally undergoes higher biological degradation than biochar when individually applied (Teutscherova et al. 2017; Ngo et al. 2013; Agegnehu et al. 2016a; Qayyum et al. 2017), as it generally contains a larger part of labile C. In our laboratory incubation (Chapter III), biochar was shown to substantially reduce compost-derived C mineralization, while compost increased biochar-derived C mineralization. Then, the effects of biochar-compost interactions on biological degradation were alleviated after (artificial) weathering, probably as a result of biochar-derived labile compounds (ash) and toxic components and compost-derived nutrients removal (Chapter III). Hence, although it could be affected by compost protection onto biochar porous structure (Ngo et al. 2013), we preferentially attributed the inhibitive effect of biochar on compost-derived C mineralization to the presence of toxic compounds from biochar (Gale et al. 2016; Kołtowski and Oleszczuk 2015), thereby highlighting the importance of biochar-derived toxic compounds on biochar-compost interactions.

Artificial weathering generally led to stronger biochar-compost interactions on elemental composition and particle retention than natural ageing, as shown by the stronger reduction of O:C ratio for biochar after artificial weathering while it remained constant under natural ageing (Chapters III & IV). In our experiment, artificial aging may have induced stronger water inputs as compared to natural ageing, corresponding to stronger rainfall events. However, intense rainfall event was demonstrated to induce strong C and N removal from both compost and biochar (Chapter IV, Ngo et al. 2016). In general, artificial ageing are reported to release higher quantities of DOC, ash and small particles and to induce more pronounced changes on biochar surface morphology, as compared to natural processes (Wang et al. 2020). As we could not distinguish the C removal from biological degradation or from transport in the litterbags experiment (Chapter IV), it was not possible to estimate for how long the natural ageing induced the removal of biochar-derived toxic components on microbial activity.

While biochar-derived C compounds are generally more recalcitrant than compost-derived C, they may preferentially be removed through leaching or transport processes (Rumpel et al. 2015). Our field experiment (Chapter IV) was conducted with the litterbag technic, in order to estimate the C removal through particle transport in addition to biological degradation. Our work did not evidence biochar-compost interactions effects on their particle integration into soil aggregates, probably due to the short-term of the experiment (14 months) or to the soil type. Additionally, our work was the first to evidence that compost significantly reduced biochar physical disintegration, as shown by the positive effect of compost on biochar physical stability. As biochar fragmentation plays an important role in the ageing process of biochar (Mia et al. 2017; Wang et al. 2020), this could lead to the slowdown of biochar ageing and biochar-derived particles removal through transport processes. However, in our experiment, the reduction of biochar friability was not strong enough to induce significant C retention from the mixture (Chapter IV).

Although not evidenced under artificial weathering (Chapter III), the N content from *Miscanthus* biochar particles decreased during natural weathering (Chapter IV). Rainfall events may induce abiotic biochar oxidation, which could benefit to N retention on biochar surface (Wang et al. 2020). Hence, the absence of N retention under artificial weathering could result from the leaching of N-enriched small biochar particles, as biochar particles may be more enriched in N than coarse particles (Rumpel et al. 2007). Under field conditions, biochar may be subjected to other abiotic processes, such as photochemical transformation, and biotic processes, which could further enhance their surface oxidation (Wang et al. 2020).

In the field experiment, biochar-compost interactions was shown to significantly affect the sorption behavior of the particles, as it increased higher N retention after N fertilization then lowered the N release, as compared to the expected mixture (Chapter IV). However, this effect was not visible anymore

when biochar-compost were mixed with the soil matrix (Chapter IV) and did not significantly improved compost benefits to plant yield (Nobile et al. *in prep*).

In the pot trial, the improvement of biochar-compost amendment in comparison to amendment of compost alone after weathering was attributed to the removal of toxic compounds from biochar during artificial weathering (Chapter III). As this effect was not observed under natural conditions (Nobile et al. *in prep*), we suggested that the natural ageing did not removed the toxic compounds as much as under artificial conditions. Figure 43 summarizes the interaction mechanisms affecting C removal and soil fertility through time.

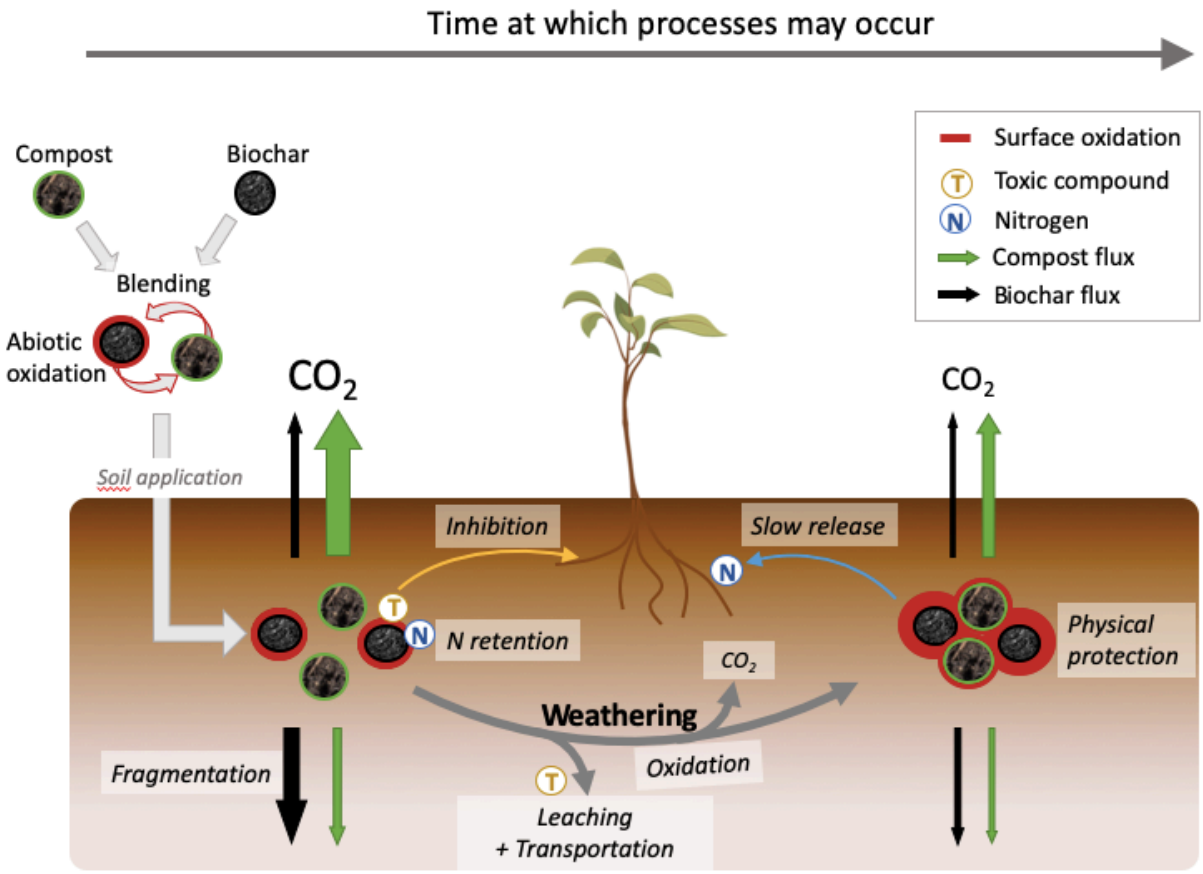


Figure 43 Biochar-compost interaction mechanisms affecting C removal and soil fertility through time.

2 General conclusion

Our results evidenced that biochar and compost interactions affected their chemical characteristics and sorption capacity through contrasting processes, leading to changes of biological and physical stability at different time scales. Interactions between both materials may occur already during their blending through biochar abiotic oxidation. This process may lead to altered biological stability and sorption behavior of biochar. After field exposure, biochar and compost may interact with influences on their biological stability, probably due to the presence of labile compounds, nutrients from compost and toxic compounds. Weathering affected biochar-compost interactions, as it induced the alleviation of their interactions concerning their biological stability and the reduction of biochar physical disintegration. However, although biochar-compost interactions were evidenced in our work, they may not have influenced significantly the soil C storage after 26 months under temperate climate conditions. Our field experiment also did not evidence significant effect of biochar-compost interaction regarding their occlusion into soil aggregate, probably rather occurring at longer time-scales. Regarding soil fertility, biochar and compost induced synergistic effects for a better N retention after N fertilization, followed by a significant slower N release. However, his effect was not strong enough to induce synergies on plant growth at the field scale. In the pot trial, artificial weathering removed biochar-derived toxic compounds, which increased or had neutral effect on the benefit of biochar to improve compost performance for plant production. To conclude, our work showed the benefit of combining biochar and compost as soil organic amendments on C sequestration, N retention and plant production, without the risk of side effects due to their interactions.

3 Research perspectives

Microbial colonization

The effects of organic amendment on soil biota is of major importance, since microbial activity is known to play a key-role in the dynamic of SOM (Paul 2016). Contrasting results evidenced or rejected the ability of biochar to act as a habitat for microorganisms in a short-term (< 3 years) (Jaafar et al. 2015; Quilliam et al. 2013). Negative effects can result from the inhibitive effects of biochar-derived toxic compounds for living organisms (Chapter III, Gale et al. 2016). We discussed above that abiotic oxidation on biochar surface during its blending with compost could increase the biochar mineralization when combined with compost through higher nutrients sorption capacity (Cai et al. 2016) and lower biological stability (Gregorich et al. 2015). Additionally, a wider diversity of C inputs may be favorable to microbial diversity (Kögel-Knabner 2017). Recent studies showed that biochar behavior toward

microorganisms was affected by its electrochemical properties, as biochar may act as an electron shuttle for microorganisms which participate in redox reactions, such as nitrification and denitrification (Dai et al. 2021). The effects of compost on such interactions would be interesting to elucidate. Hence, the mechanisms affecting microbial colonization, growth and diversity when amended with biochar-compost mixture in soils amended with biochar and compost are complex and would need to be clarified.

Physical protection and organic coating

The physical protection of biochar and compost could protect them from biological and physical disintegration. Such mechanisms could as well have promoted the lower compost-C derived mineralization and particles losses, as well as the alleviative effect on biochar friability, observed in our work (Chapters IV & V). Therefore, mechanisms driving biochar and compost physical protection through occlusion and adsorption, and its evolution through time would be highly interesting to explore. In particular, as biochar was shown to physically protect compost from biological and physical disintegration (Jien et al. 2018; Ngo et al. 2016; Jien et al. 2015), further studies should explore the effect of compost on biochar physical stability. Moreover, recent studies demonstrated the role of biochar oxidation to increase its sorption capacity toward organic material (Fan et al. 2018), thereby inducing the formation of organic coating (Hagemann 2017b; Conte and Laudicina 2017). The organic coating may then promote for a better nutrient retention capacity of biochar particles (Hagemann et al. 2017b). Further research could investigate the formation of organic compounds through time, as a result of biochar-compost interactions.

Water retention

In the context of global warming, the issue of soil water retention becomes more and more important, as it affects both microbial activity and plant growth. Biochar and compost were shown to induce synergistic positive effect on water-storage capacity of a sandy soil under temperate field conditions (Liu_2012). More recently, biochar addition during the composting process was shown to increase the available water content of a loamy sand when compared of compost without biochar addition (Galb_2020). Another study found that mixing biochar and compost reduced the equivalent pore diameter in a sandy soil, thereby improving the water holding capacity (Al-Omran_2021). Most studies were done on sandy soil. Further research would be needed to explore the potential interaction of biochar and compost on loam and clay soils under drought conditions.

Generalization of biochar-compost interactions

Our work was focused on a limited number of biochar-compost mixtures, using the same compost and differing from their biochar feedstocks and production temperature. However, biochar properties may greatly vary upon their initial feedstocks and production process (temperature, residence time during the pyrolysis) (Chia et al. 2015). Similarly, the nature of compost may affect its impacts on soil

characteristics (Pérez-Piqueres et al. 2006). Our results showed that the soil type could change the effect of biochar-compost amendment on the plant production (Chapter III). Hence, our conclusions need to be validated over a larger variety of biochar-compost mixtures, using different feedstocks and production temperature biochars, different compost feedstocks, different ratios and on different soil application, in order to be generalized.

Our work was based on the mixture of biochar with mature compost. As co-composting of biochar and green waste was shown to induce positive effects during composting process (Guo et al. 2020), it would be interesting to investigate the effect of co-composting on biochar and compost interactions as organic amendments.

A wide dataset of biochar interactions with other organic wastes could benefit for the implementation of models evaluating their co-application effects as soil amendment. Indeed, models integrating the interaction effects of biochar with another organic matter could be used to refine estimation of their benefits on C sequestration, agronomic properties and waste management. For instance, such models would be useful for local circular economy planification at territorial scale, to optimize the reuse of organic wastes for the co-benefits of agronomic and environmental issues.

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ANNEXES

ANNEX 1 - Chapter IV - Supplementary material

Table SIV.1 Mass recovery and elemental content of free POM factions from treatments with soil. The soil treatment (control) did not contain any free POM fraction. Letters represent significant differences between treatment and time for each grain size (mean ± SD, n=4).

Grain Size	Treatment	Time (month)	Mass recovery (%)			OC (g C kg^{-1})			N (g N kg^{-1})			C:N			$\delta^{13}C$ (‰)		
4 – 2 mm	Soil + Compost	0	2.4	*0.6*	b	303.3	*6.1*	cd	23.3	*0.5*	a	13.1	*0.2*	d	-29.2	*0.2*	d
		14	1.1	*0.4*	c	252.0	*8.9*	c	16.7	*0.8*	b	15.3	*1.1*	d	-28.5	*0.6*	cd
	Soil + Biochar	0	2.7	*0.5*	b	739.0	*23.3*	b	5.5	*0.7*	d	137.5	*20.1*	a	-15.0	*0.4*	a
		14	1.3	*0.3*	c	662.6	*31.0*	ab	7.8	*1.5*	cd	87.0	*15.1*	b	-14.9	*0.3*	ab
	Soil + Mixture	0	5.0	*0.5*	a	553.7	*61.7*	abd	17.4	*3.3*	b	32.5	*9.9*	cd	-20.1	*1.7*	bcd
		14	2.7	*0.4*	b	556.7	*17.1*	acd	12.0	*0.9*	c	47.2	*4.1*	c	-17.9	*0.3*	abc
2 – 0.2 mm	Soil + Compost	0	2.5	*0.6*	ab	285.6	*19.5*	c	25.6	*1.4*	a	11.0	*0.3*	c	-29.6	*0.1*	c
		14	2.4	*0.1*	bc	240.9	*27.6*	c	20.1	*1.6*	b	12.1	*0.7*	bc	-29.1	*0.2*	bc
	Soil + Biochar	0	0.6	*0.1*	d	577.6	*25.3*	a	7.7	*0.3*	c	74.4	*4.6*	a	-15.7	*0.5*	ad
		14	1.5	*0.2*	c	540.2	*21.9*	a	6.9	*0.4*	c	79.9	*7.1*	a	-14.9	*0.1*	a
	Soil + Mixture	0	2.4	*0.6*	abc	382.7	*10.4*	b	23.7	*0.8*	a	16.2	*0.8*	abc	-24.4	*0.8*	bcd
		14	3.3	*0.5*	a	391.0	*19.0*	b	17.7	*0.4*	b	22.6	*0.3*	ab	-21.3	*0.3*	abd
0.2 – 0.05 mm	Soil + Compost	0	0.3	*0.1*	bc	242.7	*39.7*	c	25.0	*3.0*	c	9.5	*0.8*	b	-29.6	*0.1*	c
		14	0.5	*0.2*	b	207.2	*32.3*	c	20.4	*3.5*	bc	10.1	*0.2*	b	-29.4	*0.2*	bc
	Soil + Biochar	0	0.2	*0.1*	c	613.8	*48.9*	a	8.0	*0.7*	ab	75.1	*6.4*	a	-15.8	*0.6*	ad
		14	0.6	*0.1*	ab	477.8	*92.8*	b	7.3	*1.1*	a	64.7	*21.9*	a	-15.2	*0.4*	a
	Soil + Mixture	0	0.3	*0.2*	bc	416.1	*73.1*	b	31.1	*16.5*	c	14.4	*4.5*	b	-23.7	*2.0*	bcd
		14	0.9	*0.2*	a	384.4	*19.6*	b	16.6	*1.2*	abc	23.6	*1.3*	ab	-20.1	*0.4*	abd

Table SIV.2 Elemental content of the aggregate factions of treatments with soil. Letters represent significant differences between type and time samplings, for each grain size (n=4).

	Type	Time (month)	OC (gC kg^{-1})		N (gN kg^{-1})		C:N		δ^{13}C (‰)	
4-2mm	Soil	0	15,1 *1,9*	c	1,3 *0,2*	ab	11,6 *0,6*	c	-30,0 *0,7*	d
		14	16,4 *0,5*	c	1,1 *0,0*	a	14,4 *0,5*	ab	-32,9 *0,6*	abc
	Compost	0	21,6 *4,8*	ab	1,6 *0,1*	b	13,6 *2,3*	bc	-31,3 *1,3*	cd
		14	28,5 *18,9*	ab	1,7 *0,5*	b	15,7 *4,9*	ab	-31,5 *2,9*	abcd
	Biochar	0	17,8 *1,4*	bc	1,2 *0,1*	a	15,1 *0,5*	ab	-32,9 *0,6*	abc
		14	20,5 *1,3*	ab	1,1 *0,1*	a	18,2 *1,4*	a	-35,0 *2,2*	ab
	Mixture	0	22,4 *6,3*	ab	1,7 *0,5*	b	12,9 *0,6*	bc	-32,0 *0,9*	bcd
		14	22,5 *2,2*	a	1,3 *0,0*	ab	16,7 *1,8*	a	-35,0 *1,1*	a
2mm-200µm	Soil	0	13,7 *0,4*	e	1,2 *0,0*	c	11,7 *0,4*	c	-30,4 *0,1*	c
		14	16,6 *0,7*	de	1,2 *0,0*	c	14,2 *0,3*	abd	-33,0 *0,4*	bd
	Compost	0	20,5 *4,0*	abcd	1,4 *0,1*	b	14,3 *2,9*	bcd	-31,7 *1,8*	bc
		14	23,5 *1,2*	ab	1,9 *0,1*	a	12,4 *0,2*	bc	-31,9 *0,1*	bc
	Biochar	0	17,1 *0,4*	cde	1,1 *0,0*	c	15,5 *0,2*	ad	-33,5 *0,3*	ad
		14	21,6 *1,6*	abc	1,2 *0,1*	c	18,6 *1,2*	a	-35,0 *0,7*	a
	Mixture	0	19,0 *1,3*	bcd	1,4 *0,1*	b	13,6 *0,2*	bcd	-32,8 *0,4*	bcd
		14	28,7 *1,5*	a	1,8 *0,1*	a	15,5 *0,2*	ad	-33,7 *0,5*	ad
200-50µm	Soil	0	11,5 *0,4*	d	1,0 *0,0*	ab	11,5 *0,3*	f	-30,8 *0,1*	d
		14	14,3 *0,3*	cd	1,0 *0,0*	a	14,7 *0,5*	cd	-33,8 *0,0*	abc
	Compost	0	16,6 *1,8*	bcd	1,2 *0,1*	bc	13,4 *1,3*	de	-32,7 *1,1*	acd
		14	19,2 *1,5*	ab	1,5 *0,2*	c	12,9 *0,6*	ef	-32,8 *0,3*	ad
	Biochar	0	19,8 *10,3*	bc	1,3 *0,7*	ab	15,6 *0,1*	bc	-33,9 *0,2*	bc
		14	20,6 *1,1*	ab	1,0 *0,0*	ab	20,3 *0,7*	a	-33,7 *1,1*	abc
	Mixture	0	16,1 *0,9*	bcd	1,1 *0,1*	abc	14,3 *0,3*	cde	-33,2 *0,2*	acd
		14	22,9 *1,1*	a	1,4 *0,1*	c	16,8 *0,5*	b	-34,5 *0,5*	b
0-50µm	Soil	0	12,9 *0,8*	d	1,2 *0,2*	b	10,6 *0,7*	f	-30,9 *0,1*	bcd
		14	16,8 *0,9*	cd	1,3 *0,1*	b	12,9 *0,3*	ef	-33,8 *0,2*	d
	Compost	0	21,3 *2,3*	cde	1,5 *0,2*	ab	14,6 *1,8*	e	-33,8 *1,0*	d
		14	24,3 *0,6*	bcde	1,9 *0,1*	c	12,9 *0,4*	ef	-33,8 *0,2*	cd
	Biochar	0	28,1 *9,8*	bce	1,0 *0,4*	b	27,0 *1,6*	b	-26,3 *0,4*	a
		14	42,3 *2,9*	a	1,3 *0,0*	ab	32,7 *1,8*	a	-26,5 *0,9*	ab
	Mixture	0	34,5 *3,7*	abe	1,7 *0,1*	ac	19,9 *1,2*	d	-27,6 *1,3*	ab
		14	40,2 *1,7*	ab	1,8 *0,0*	ac	23,0 *0,6*	c	-29,1 *0,2*	abc

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Published

Aubertin, M.-L., C. Girardin, S. Houot, C. Nobile, D. Houben, S. Bena, Y. Le Brech, C. Rumpel. 2021. "Biochar-Compost Interactions as Affected by Weathering: Effects on Biological Stability and Plant Growth." Agronomy 11 (2): 336. https://doi.org/10.3390/agronomy11020336.

Submitted in Earth Science Reviews

Védère C., M. Lebrun, N. Honvault., **M.-L. Aubertin**, C. Girardin, P. Garnier, M.-F. Dignac, D. Houben, C. Rumpel. How does soil water status influence the fate of soil organic matter? A review of processes across scales.

In preparation

Aubertin M.-L.; D. Sebag; P. Jouquet; D. Pillot; I. Kowalewski; V. Lamoureux-Var; C. Girardin; S. Houot; C. Rumpel. Abiotic interactions of biochar and compost during their blending may reduce the biochar thermal stability.

Aubertin M.-L.; C. Girardin; D. Houben; S. Houot; C. Rumpel. Mechanisms affecting the fate of biochar and compost mixtures and N adsorption in agricultural soil.

Nobile, C.; M. Lebrun; C. Vedere; N. Honvault; **M.-L. Aubertin**; M.-P. Faucon; C. Girardin; S. Houot; L. Kervroedan; A.-M. Dulaurent; C. Rumpel; D. Houben. Biochar and compost addition improved soil organic carbon content without affecting crop yields in three French cropping systems.

Honvault, N.; D. Houben; M. Lebrun; C. Vedere; C. Nobile, J. Guidet, L. Kervroëdan, **M.-L. Aubertin,** C. Rumpel, M.-P. Faucon, A.-M. Dulaurent. Effects of contrasted biochar-compost mixtures on earthworm communities in a temperate agricultural soil

List of communications

Oral

2019, 6-11 October Adelaide (Australia)	**7th International Symposium on Soil Organic Matter : Soil organic matter in a stressed world** "Characterization of biochar-compost mixtures and the effect of a physical alteration of one of those mixtures."
2020, 4-8 May Online	**EGU General Assembly** "Does compost and biochar interact on the stability of the mixture and does these interactions change after weathering ?"
2021, 21-25 June Online	**Journée d'étude des sols – French Association of Soil Studies** "Effet des mélanges biochar-compost sur les propriétés agronomiques du sol."
2021, 23-27 August Online	**Eurosoil Congress** "Differenciation of biochar and compost in mixtures, using Rock-Eval oxidation and mid-infrared spectroscopy - Surprising abiotic interactions."

Poster

17-20 June 2019 Poitiers (France)	**Food security and climate change: 4 per 1000 initiative new tangible global challenges for the soil.** "Effect of miscanthus biochar addition to compost on the carbon stability of compost-biochar mixtures"
2-3 December 2019 Paris (France)	**CarboSMS : Carbone des sols, Mécanismes de Stabilisation** "Characterization of biochar-compost mixtures and effect of aging"

RESUME LONG DE LA THESE EN FRANCAIS

Introduction générale

Selon le dernier rapport spécial du GIEC, la limitation d'un réchauffement global à 1.5 °C nécessiterait d'atteindre la neutralité carbone (C) d'ici 2050 (Masson-Delmotte et al. 2018). Cet objectif ambitieux implique (i) de réduire drastiquement les émissions de gaz à effet de serre d'origine anthropique et (ii) de compenser les émissions de CO2 par le re-captage du C. Ce dernier implique l'augmentation des stocks de carbone par les techniques dites d' « émissions négatives ». Le sol représente un haut potentiel pour stockage de C (Fuss et al. 2018; Amelung et al. 2020). et l'amendement de biochar, produit solide issu de la pyrolyse, permettrait une séquestration durable de C dans le sol (Smith, 2016). L'initiative 4 pour 1000, lancée lors de la COP 21 en 2015, souligne que au-delà d'un effet bénéfique pour l'atténuation du réchauffement climatique, la séquestration du C contribue également à améliorer la qualité du sol et ainsi, à la sécurité alimentaire (Rumpel et al. 2018). Malgré ses effets bénéfiques pour la qualité du sol, notamment au travers notamment de sa capacité de rétention en eau, l'effet du biochar sur la fertilité du sol reste limitée. Ainsi, l'apport de biochar nécessite d'être combiné à un autre amendement organique, tel que le compost, pour augmenter encore davantage ses effets bénéfiques sur la fertilité du sol. Par ailleurs, l'utilisation de biochar et de compost s'inscrit donc dans une démarche d'économie circulaire, puisqu'ils sont tous deux issus de déchets organiques.

L'apport combiné de biochar et de compost présente des bénéfices évidents pour la qualité du sol et la production des plantes, en particulier dans les sols sableux, pauvres en nutriments et/ou en condition de sécheresse (e.g. Agegnehu et al. 2017; Agegnehu et al. 2016a; Z. Zhou et al. 2022). Cependant, les mécanismes d'interaction biochar-compost concernant la rétention en C et en azote (N) soulève encore de nombreuses questions. L'objectif principal de la thèse est d'étudier les mécanismes d'interaction entre biochar et compost, ainsi que leurs effets, sur (i) les sorties de C du sol (minéralisation, solubilisation, transport) et (ii) la fertilité du sol (rétention en N et production végétale). Après un état de l'art sur les connaissances actuelles concernant les mélanges biochar-compost et leurs interactions sur le stockage de C et la fertilité du sol, nous présenterons successivement les différentes études, s'articulant en trois grandes parties. La première étude concernera les interactions potentielles entre biochar et compost lors de leur mélange. La seconde étude s'intéressera aux interactions abiotiques entre biochar et compost pendant un an en conditions contrôlées. La troisième étude concernera les effets des interactions biochar-compost sur la rétention des particules et de l'azote en conditions au champ, ainsi que de l'influence de la matrice sol, en utilisant la technique des litterbags. Enfin, la dernière partie de la thèse proposera une discussion générale en s'appuyant sur les conclusions principales des études, ainsi que des pistes de perspectives à explorer pour approfondir la problématique principale de la thèse.

Chapitre I – Etat des connaissances sur les composts et biochars : des amendements organiques complémentaires, pouvant interagir.

1. Les amendements organiques peuvent améliorer la séquestration du carbone et la fertilité du sol

Le sol peut être défini come un système vivant contenant des solides, de l'eau et de l'air, fournissant une grande diversité de services écosystémiques (Hartemink 2016), pouvant être divisés en quatre catégories principales : provision, régulation, support et culturel (Adhikari and Hartemink 2016). Parmi ces services écosystémiques, la séquestration du carbone (C) et la production de matières consommables sont ceux sur lesquels nous nous intéresserons pour ce travail de thèse. Ces deux services rendus par le sol sont en grande partie possible grâce à la présence de matière organique (MO), composant issu des matières organiques vivantes ou mortes et présent entre 1 et 10 % du sol (Calvet et al. 2011). La MO représente un des indicateurs les plus utilisés pour estimer la qualité du sol et sa fertilité (Manlay et al. 2007; Bünemann et al. 2018). Aujourd'hui, une grande partie des sols dans le monde sont appauvris en MO à cause de facteurs comme l'érosion et l'épuisement des nutriments (Montanarella et al. 2016). Les amendements organiques sont fréquemment utilisés pour pallier aux problèmes de baisse de fertilité du sol et/ou pour régénérer des sols appauvris (Chen et al. 2018, Larney and Angers 2012). Les amendements organiques peuvent augmenter le stockage de carbone au moyen de différents mécanismes d'entrée, de sortie et de stabilisation dans le sol. Une fois incorporé au sol, les amendements organiques peuvent être biotransformés, transférés et/ou stabilisés grâce à des protections physiques ou d'association organo-minérales (Basile-Doelsch et al. 2020). Les mécanismes de sortie de la MO du système sol comprennent le lessivage, l'érosion et la minéralisation. Les amendements organiques peuvent également améliorer la fertilité du sol en jouant sur différents facteurs, tels que les ressources en carbone organique et en nutriments, mais aussi sur des propriétés physiques (structure du sol, rétention en eau), chimiques (pH, CEC) et biologiques (activité microbienne) (Goss et al. 2013; Scotti et al. 2015). Les amendements organiques sont issus de matière organique végétale ou animale, qui ont subi ou non un traitement et dont l'incorporaion au sol améliore la fertilité du sol (Aytenew and Bore 2020). Parmi les amendements organiques, un nombre d'étude croissant s'intéresse à l'utilisation combinée de biochar et de compost ou à leur comparaison.

2. L'utilisation de compost et biochar comme amendement organique

Compost et biochar sont issus de traitements différents : respectivement compostage et pyrolyse. Le compostage consiste en la dégradation des matières organiques par la succession de quatre grandes étapes. Les deux premières étapes correspondent à des processus actifs de décomposition, avec la dégradation des substrats labiles conduisant à une montée en température (phase mésophylique), suivi de la dégradation de molécules plus complexes où le paroxysme de la température est atteint et commence à redescendre (phase thermophylique). Viennent ensuite les processus de maturation, avec la décomposition plus lente des molécules

stables où la température continue de décroître (phase de refroidissement), puis une dernière étape où la température se stabilise (phase de stabilisation). La pyrolyse quant à elle correspond à une montée en température de la biomasse généralement entre 400 °C – 650 °C, en l'absence d'oxygène (Lehmann 2007a). Les produits issus de la pyrolyse sont gazeux (bio-gaz), liquides (bio-huile) et solide (biochar). Les produits gazeux et liquides peuvent être réutilisés pour produire de l'énergie, permettant ainsi l'autonomie énergétique du processus de pyrolyse.

Les différences de traitement permettant la formation de compost et biochar induisent des différences de propriétés des matériaux. Ainsi, le compost mature contient une quantité moins importante de C que le biochar, sous des formes moins aromatiques et donc moins récalcitrantes biologiquement que ce dernier (Siedt et al. 2021). Du fait de sa plus grande récalcitrance, le C issu du biochar tend à rester plus longtemps dans le sol que le compost (Fig. 13). Ainsi, l'amendement de biochar ou de compost aura un effet différent sur le cycle du carbone, puisque suite à un apport de biochar, le carbone reste en partie stocké dans le sol, au lieu d'être minéralisé, comme c'est le car pour un apport de compost. Cependant, les particules de biochar sont davantage sujettes à la dégradation physique and les particules de compost, ce qui peut entraîner leur transport par lessivage.

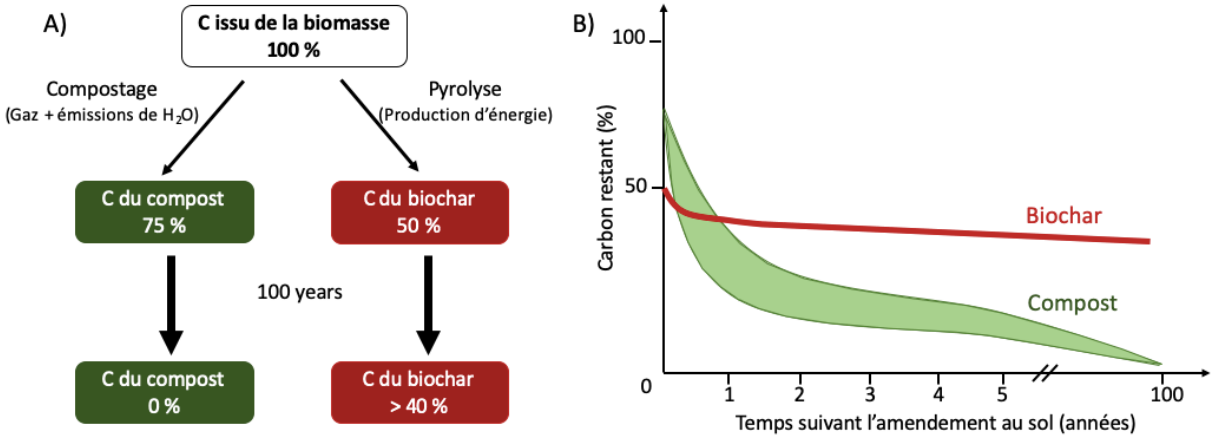

Figure 44 Carbone issue du compost et du biochar, restant dans le sol au cours du temps (A) et cinétique de dégradation du C 100 ans après son application au sol (B) (adapté de Lehmann et al. 2006; Kumar et al. 2010).

Compost et biochar ont tous deux des effets bénéfiques sur la fertilité du sol, ces effets étant d'autant plus prononcés que le sol amendé est pauvre en nutriments, sableux et/ou en conditions sèches (Zebarth et al. 1999; Razzaghi et al. 2020; Rabbi et al. 2021). En effet, compost et biochar comportent tous deux des nutriments directement disponibles pour les plantes et microorganismes, mais dans des proportions différentes. Le compost contient très peu de nutriments lorsqu'il est appliqué au sol, mais sa décomposition délivre progressivement des nutriments disponibles (Aytenew and Bore 2020). Le biochar comporte dans certains cas des nutriments disponibles lorsqu'il est amendé au sol, mais une fois ces nutriments utilisés ou lessivés, il n'en délivre plus de manière significative (Abbott et al. 2018). L'une des spécificités du biochar est son haut potentiel d'adsorption,

permettant la rétention puis le relargage progressif des nutriments au cours du temps (Palanivell et al. 2020). Bien que les amendements en biochar et compost aient tous deux un effet de chaulage sur le sol, du à leur pH basique, de rétention en eau et de diminution de la densité du sol, les effets du biochar sont généralement plus fort que ceux du compost (Siedt et al. 2021). De même, compost et biochar ont tous deux montré des habilités à améliorer la stabilité et à promouvoir la formation des agrégats (Diacono and Montemurro 2010, Ma et al. 2016). Cependant, une étude a démontré que l'amendement d'une large dose de biochar dans un sol argileux pouvait aussi induire la rupture des agrégats, suite au renforcement des forces de répulsion entre les particules de même charge (Pituello et al. 2018). Compost et biochar induisent tous deux des effets positifs sur les microorganismes du sol (Siedt et al. 2021, Farrell et al. 2009). Le compost peut en outre être source de microorganismes qui se sont développés lors de la phase de maturation (Chander and Joergensen 2002; Bulluck et al. 2002). Les effets des compost et biochar sur les plantes sont généralement positifs, puisqu'ils a été démontré qu'ils pouvaient favoriser la germination, ainsi que la croissance racinaire et végétative (Diacono and Montemurro 2010; Kranz et al. 2020, Ye et al. 2020). Dans tous les cas, les effets du compost ou biochar sur les propriétés agronomiques du sol et sur la production végétale sont largement dépendant des caractéristiques de ces derniers, eux-mêmes dépendant des paramètres de leur formation.

Enfin, les particules de compost et biochar tendent à répondre de manière différente aux facteurs naturels d'altération, tels que les variations d'humidité, de température, de luminosité, etc. Le biochar se dégrade en majorité suite à des processus physique de rupture des particules et d'oxydation abiotique (Spokas et al. 2014, Wang et al. 2020), tandis que le compost se dégrade majoritairement suite à des processus biotiques.

3. Les interactions biochar-compost

Compost et biochars permettent de valoriser des déchets organiques de nature différente, le compostage étant plus adapté à des résidus humides et riche en nutriments et la pyrolyse à des résidus pauvres en nutriments, poreux et récalcitrants à la biodégradation (Steiner et al. 2015). De ce fait, la combinaison de compost et de biochar permet de valoriser un plus large panel de résidus que l'utilisation de chaque composants pris séparément. Le mélange de ces composants peut se faire en amont ou en aval du processus de compostage. Lorsqu'il se fait en amont, l'ajout de biochar améliore significativement certains paramètres du compostage, tels que le temps de compostage, la montée en température et la réduction des émissions de NH_4 (Guo et al. 2020). Cependant, d'un point de vue purement technique, le mélange en amont du compostage demande davantage d'anticipation que le mélange en aval. Le projet FUI Biochar 20210 dans lequel s'inscrit ce travail de thèse sera focalisé sur un mélange réalisé en aval du processus de compostage.

Il a été prouvé que le compost et le biochar pouvaient interagir sur la stabilité biologique du carbone, ainsi que sur la rétention des nutriments en l'activité microbienne. En effet, le biochar peut protéger les particules de compost de la dégradation microbienne et de la perte par transport en les adsorbant ou en les intégrant dans sa structure poreuse (Jien et al. 2015, Jien et al. 2018, Ngo et al. 2013, Ngo et al. 2016). Par ailleurs, la

diversification des sources de carbone peut favoriser la persistance de ce dernier (Lehmann et al. 2020). Par ailleurs, Le biochar peut adsorber et ainsi retenir les nutriments fournis par le compost (Jien et al. 2019, Abbott et al. 2018). Pour le moment, les études ont surtout porté sur l'effet d'un ajout de biochar sur la dégradation microbienne du compost. La question de l'effet du compost sur le potentiel de dégradations microbiennes et physiques particules de biochar demeure encore en suspens (Fig. 18).

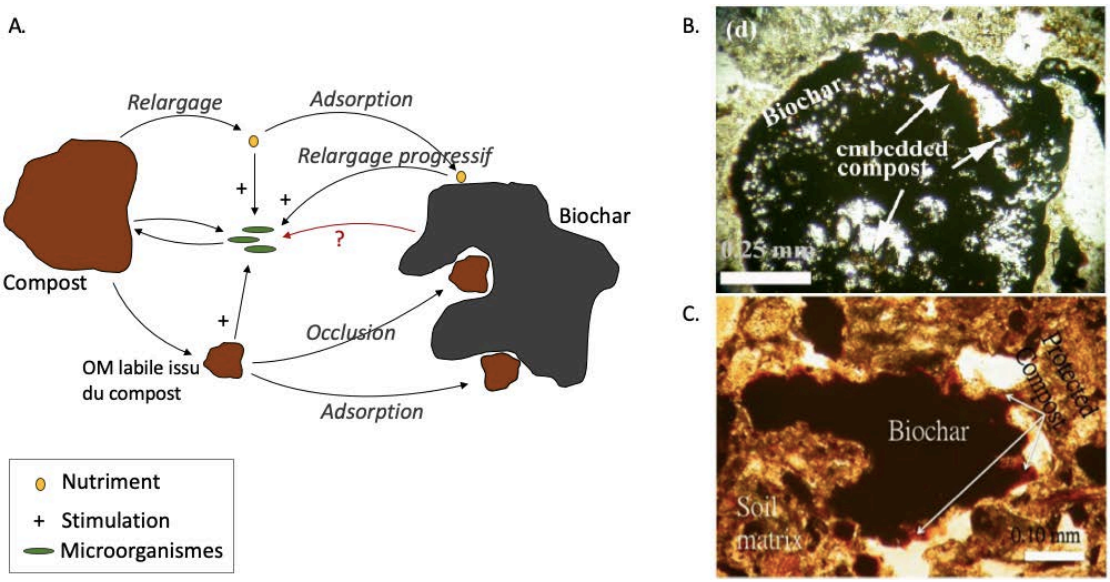

Figure 45 Mécanismes sous-jacent aux interactions biochar-compost sur la minéralisation du C (A) et photos au microscope polarisé de particules de compost intégrés ou adsorbé au biochar (B) et (C) (Jien et al. 2015; 2018; Chander and Joergensen 2002).

Après ajout au sol, la co-application de biochar et compost peut promouvoir la formation d'agrégats, diminuant ainsi la dégradation microbienne (Jien et al. 2015). Bien que la plupart des particules de compost et de biochar s'accumulent généralement dans les fractions libres de matières organiques particulaires, une partie peut également s'acumuler dans les agrégats du sol (Cooper et al. 2020, Plaza et al. 2016). Par ailleurs, il a été démontré que le mélange biochar-compost pouvait promouvoir leur association aux minéraux (Plaza et al. 2016). Comme décrit précédemment, le biochar est hautement friable (Spokas et al. 2014) et sa dégradation physique renforce son potentiel de transport. Aujourd'hui, l'effet du compost sur la friabilité du biochar est encore peu compris et nécessiterait des études plus approfondies (Fig. 19).

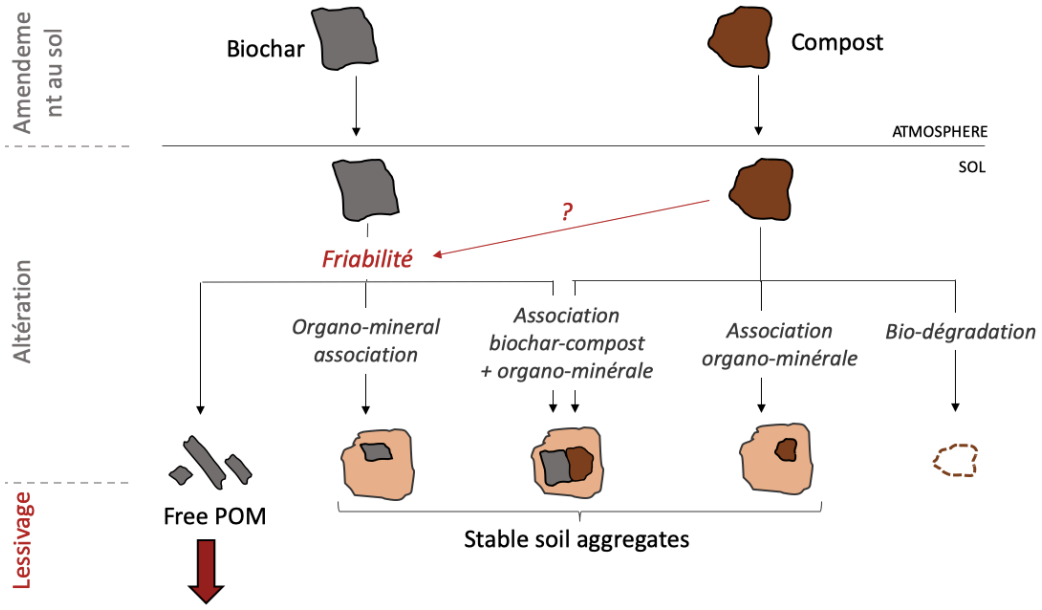

Figure 46 Le devenir du mélange biochar-compost après amendement au sol (adapté de Cooper et al. 2020; Plaza et al. 2016).

L'étude de la stabilité thermique d'un composant organique permet d'estimer son état énergétique. Ce dernier est relié à son degré de récalcitrance (Barré et al. 2016). Généralement, les composés récalcitrants ont une stabilité thermique plus élevée que les composés labiles (Ranalli et al. 2001, Strezov et al. 2004). Aujourd'hui, peu d'études s'intéressent à la stabilité thermique du biochar et aucune étude, à notre connaissance, n'a étudié la stabilité thermique d'un mélange entre biochar et un autre composant organique. Or, on sait que le mélange d'un composant organique stable, tel que le charbon de terre, avec de la biomasse végétale induit un effet d'interaction lors de l'analyse, biaisant ainsi les rendements en produits de pyrolyse et les compositions chimiques de ces derniers (eg. He et al . 2021).

4. Les objectifs de la thèse

L'objectif principal de la thèse était d'étudier les mécanismes contrôlant les interactions biochar-compost, ainsi que leurs effets sur la séquestration du carbone et la fertilité du sol. Pour ce faire, ce travail de thèse s'articule en trois études, chacune répondant à une question scientifique :

Q1 :Le mélange entre biochar et compost affecte-t-il leur caractéristiques chimiques ?

Q2 : L'altération du mélange biochar-compost affecte-t-elle leurs interactions sur la stabilité biologique du mélange ainsi que sur la croissance des plantes ?

Q3 : Les interactions biochar et compost bénéficient-elles à la rétention du carbone et de l'azote en conditions au champ et en climat tempéré ?

La figure 20 récapitule les différentes parties de ce travail de thèse.

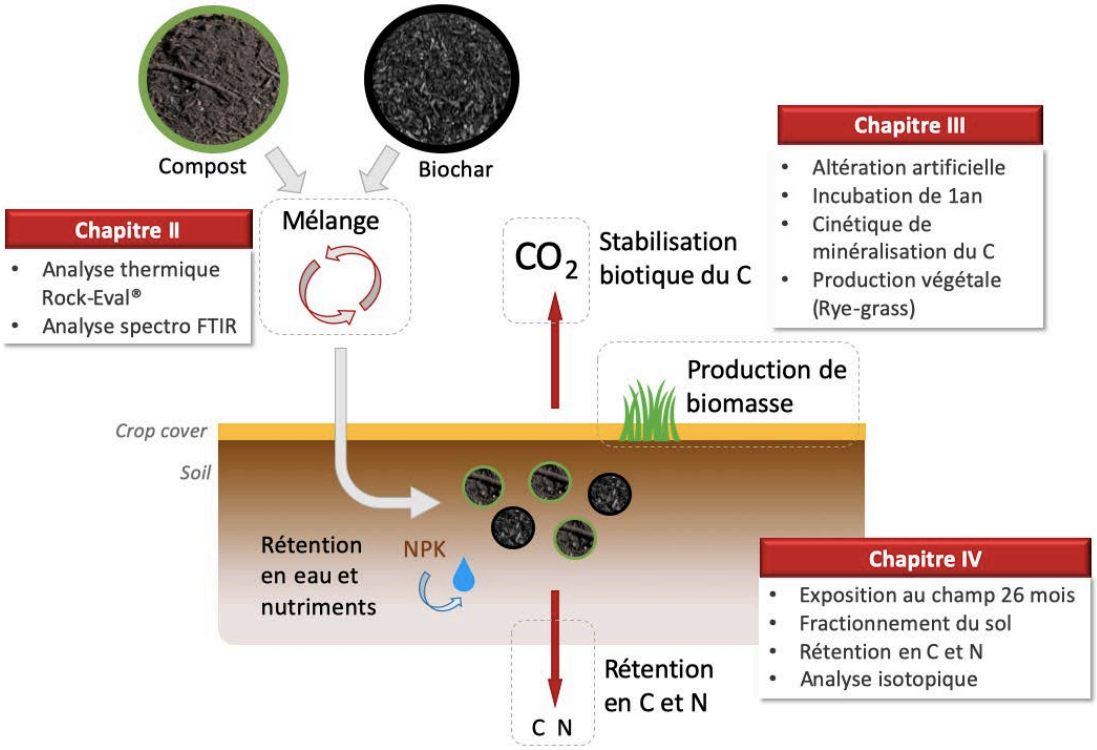

Figure 47 Approche générale de la thèse, design expérimental et méthodes analytiques.

Chapitre II – Les interactions abiotiques du biochar et du compost lors de leur mélange pourraient réduire la stabilité thermique du biochar.

Aujourd'hui, les interactions biochar-compost peuvent être induites par des processus biotiques (Kuzyakov 2010, Paul 2016). Or, les processus d'interaction abiotiques entre biochar et un autre composant organique tendent à être sous-estimés (Prévoteau et al. 2016). Les processus abiotiques d'oxydation précèdent généralement les processus biotiques d'oxydation et sont donc dominant dans les premiers temps après le mélange du biochar avec un autre composant (Cheng et al. 2006). L'oxydation de surface du biochar conduit généralement à la formation de groupes fonctionnels de surface, favorisant l'adsorption de composants organiques sur les particules de biochar (Conte and Laudicina 2017). La stabilité thermique a été démontrée comme une approche efficace pour estimer rapidement les variations de stabilité biologique (Barré et al. 2016). L'objectif de cette première étude de la thèse visait à explorer les potentielles interactions abiotiques entre biochar et compost lors de leur mélange, en amont de leur apport au sol. L'étude a été basée sur cinq mélanges biochar-compost, différant par la nature du biochar et sa température de pyrolyse, analysés avec des méthodes d'analyses thermiques (Rock-Eval®) et spectroscopiques (FTIR). Ces méthodes ont pu être corrélées grâce à un modèle de régression partielle des moindres carrés (PLSR), permettant la mise en relation des variations de groupements chimiques du mélange avec ses variations de stabilité thermique, et ainsi, de stabilité biologique. Afin de mettre en évidence les effets d'interaction entre biochar et compost, les résultats des analyses des

mélanges ont été comparés avec des résultats de mélange calculés, à partir des analyses des composants seuls. La différence entre résultats d'analyses de mélanges mesurés et calculés permet la mise en évidence d'interaction entre ces deux composants.

Le Rock-Eval® est une technique issue des recherches sur l'exploration pétrolière et se développe depuis quelques années pour l'analyse énergétique des matières organiques du sol. Cette méthode consiste en une première phase de pyrolyse, pendant lesquelles sont émis des hydrocarbures, du CO et du CO_2, puis une phase d'oxydation, pendant lesquelles sont émis du CO et du CO_2 (Fig. 21).

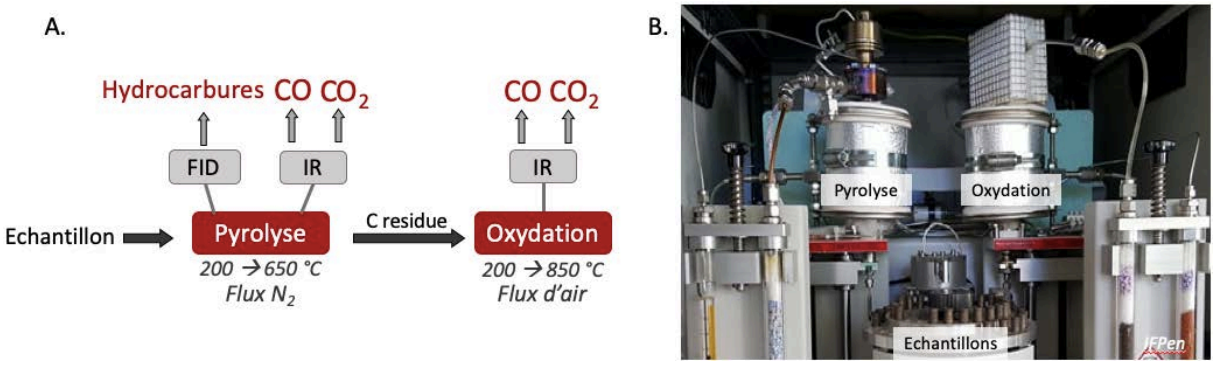

Figure 48 Principe de fonctionnement du Rock-Eval® (A) (adapté de Disnar et al. 2003) et machine (B) FID: détecteur de flamme ionique; IR: cellule infra-rouge.

Les résultats ont mis en évidence que la majeure partie des émissions de carbone avait lieu lors de la phase oxydative, pour les émissions de CO_2. De ce fait, l'étude se concentrera sur ces émissions (Fig. 23). Dans la plupart des cas, les résultats ont montré que les émissions de CO_2 lors de la phase d'oxydation étaient différentes entre les mélanges mesurés et ceux attendus, mettant ainsi en évidence la présence d'interactions biochar-compost sur la stabilité thermique du mélange. En particulier, les différences entre mélanges mesurés et attendus concernent le deuxième pic d'émission de CO_2 du mélange, en phase oxydative. Ce deuxième pic correspond à celui du biochar au sein du mélange, puisque les températures d'émission et les teneurs émises par le biochar sont supérieures à celles issu du compost, lorsqu'ils sont analysés séparément. Ainsi, les résultats de l'analyse Rock-Eval® concluent sur un effet d'interaction entre biochar et compost, induisant la réduction de la stabilité thermique du biochar. L'analyse sous les courbes des thermogrammes de CO_2 lors de la phase d'oxydation a permis de déterminer des ratios d'interaction correspondant à la part des émissions de CO_2 résultant de l'interaction entre biochar et compost. Ce ratio permet de comparer le degré d'effet d'interaction biochar-compost sur la baisse de stabilité thermique du biochar. En effet, plus ce ratio est élevé, plus l'effet d'interaction est fort.

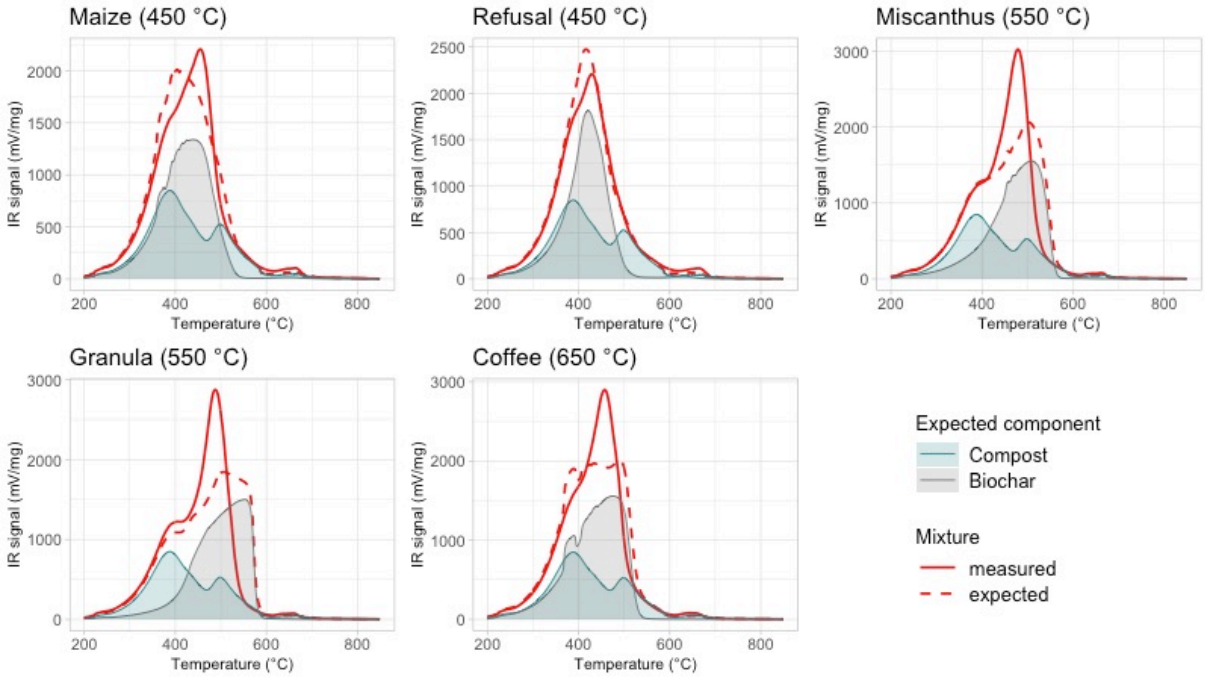

Figure 49 Thermogrammes Rock-Eval® pour le CO_2 émis lors de la phase d'oxydation pour les mélanges mesurés et calculés à partir des résultats des composants seuls.

Les résultats du spectre infrarouge montrent une différence entre mélanges mesurés et calculés pour les pics observés à 3400 et 1610 cm^{-1}, indiquant de possibles effets d'interaction entre biochar et compost pour les liaisons chimiques (Fig. 27). En particulier, les interactions entraînent une diminution des groupements -OH (3400 cm^{-1}) et des liaisons aromatiques C=O et C=C (1610 cm^{-1}). Étant donné que les analyses infra-rouge ont été réalisées après le mélange et avant l'analyse thermique, on en conclut que les effets d'interaction sur les groupements chimiques ont eu lieu lors du mélange entre biochar et compost.

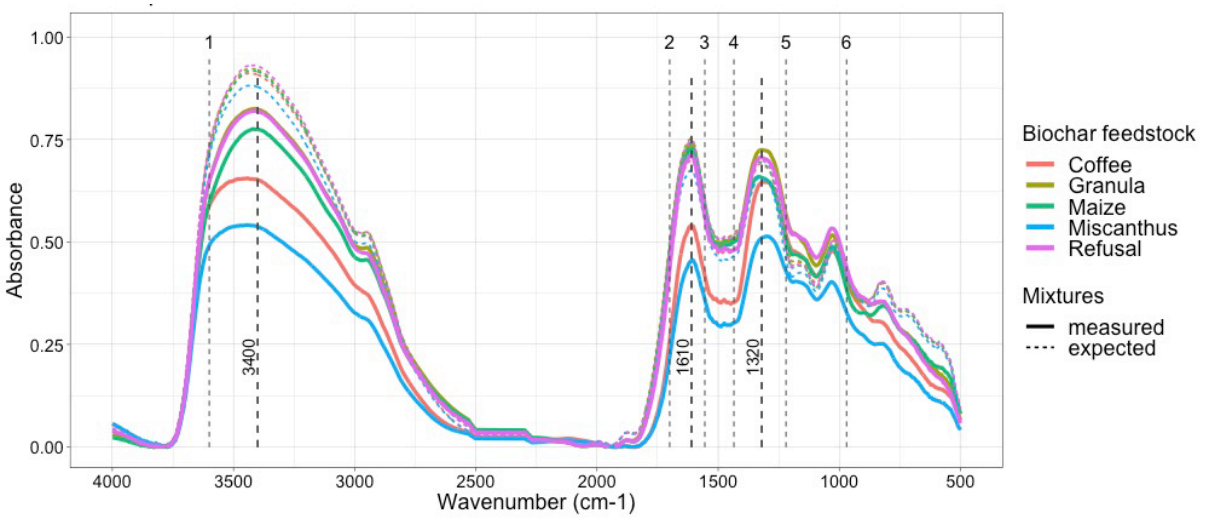

Figure 50 FTIR spectra of the biochar-compost mixtures. The wavenumbers from 1 to 6 correspond respectively to 3600, 1700, 1555, 1435, 1220 and 970 cm^{-1}.

Les ratios d'interaction, calculés à partir des résultats de l'analyse thermique, ont pu être corrélés avec les longueurs d'onde issu des spectres infrarouges, grâce au modèle PLSR. Ce dernier a mis en évidence la corrélation entre les ratios d'interaction et certaines longueurs d'ondes du spectre infra-rouge (Fig. 27, longueurs d'onde 1 à 6). Les longueurs d'onde les mieux corrélées aux ratios d'interaction sont donc les liaisons chimiques participant au changement de stabilité thermique. Sur le spectre infrarouge, ces longueurs d'onde correspondent à des « creux de pics », ce qui montre qu'il ne s'agit pas d'éléments présents en grandes quantités. Cependant, ces longueurs d'onde correspondent également à des endroits du spectre où les mélanges mesurés et attendus diffèrent. Ainsi, les interactions ayant affecté les liaisons chimiques ont également affecté la stabilité thermique des biochars au sein des mélanges.

L'analyse thermique d'un mélange de deux composants peut induire des biais d'analyse et ainsi modifier les résultats par rapport à ce qui est attendu. Or, le fait qu'il a été possible de relier ces interactions à des interactions observées sur les spectres infrarouges montre que ces interactions thermiques ont pu se produire lors du mélange, avant l'analyse thermique. Ainsi, biochar et compost pourraient interagir grâce à des processus abiotiques dès lors de leur mélange. Le mélange biochar-compost ayant été réalisé sur des poudres sèches et les analyses ayant été réalisées juste après le mélange, les interactions observées ne peuvent être dû qu'à des processus abiotiques. Par ailleurs, il a récemment été démontré que le biochar possédait une forte capacité de donner des élections (Prévoteau et al. 2016), privilégiant ainsi la piste des oxydations abiotiques pour expliquer les interactions entre biochar et compost lors de leur mélange.

Cette étude montre la possibilité d'interaction entre biochar et compost lors de leur mélange, sur leur caractérisation chimique. Or, ces interactions étant probablement dû à des effets de surface, elles ont pu être amplifiées grâce au fait que les composants aient été broyés avant leur mélange, augmentant ainsi leur surface de réaction. Il est très probable que l'intensité des interactions observées dans cette étude soit directement corrélée avec la granulométrie des composants avant leur mélange. Dans des cas concrets de mélange entre biochar et compost pour apport au champ, où les composants ne sont en général pas broyés avant leur utilisation, on pourrait donc s'attendre à un effet très faible, voire négligeable des interactions entre biochar et compost lors de leur mélange. Des études complémentaires seraient intéressantes à réaliser pour étudier l'effet de la granulométrie des composants avant mélange sur leur interaction durant le mélange. Plus globalement, notre étude entraîne des réflexions sur les interactions possibles entre biochar et compost lors de leur stockage, dans le cas où le mélange est réalisé avant apport au sol. Nous avons montré un effet possible d'oxydation abiotique lors de leur mélange. Or, nous savons que d'autres paramètres peuvent également affecter les composants avant leur application au sol, comme la lumière ou l'humidité (Wang et al. 2020). Ainsi serait-il intéressant de voir si l'effet de ces paramètres sur la caractérisation chimique des mélanges peut être affecté par des interactions entre biochar et compost.

Chapitre III – L'effet de l'altération sur les interactions entre biochar et compost sur la stabilité biologique du mélange et la croissance des plantes.

La littérature scientifique montre des effets contrastés d'interaction entre biochar et compost sur leur stabilité biologique, révélant ainsi le besoin de mieux comprendre les mécanismes sous-jacents à ces interactions. En effet, certaines études ont mis en évidence que la protection physique du compost dans la structure poreuse du biochar pouvait induire une diminution de la stabilité biologique du compost (Jien et al. 2018, Ngo et al. 2013), tandis que d'autres études n'ont trouvé aucun effet significatif d'interaction entre biochar et compost sur leur stabilité biologique (Teutscherova et al. 2017, Darby et al. 2016). En outre, les effets du compost sur la stabilité biologique du biochar n'ont pas encore été explorés. La littérature scientifique montre également des effets contrastés d'interaction entre biochar et compost sur la croissance des plantes, par rapport à l'application de compost seul (e.g. Seehausen et al. 2017, Gale et al. 2016, Naeem et al. 2018, Zulfiqar et al. 2019). De ce fait, les effets d'un ajout de biochar à du compost sur la croissance des plantes nécessitent davantage d'approfondissement. L'objectif de cette deuxième étude de la thèse a été d'explorer les effets d'interaction dans le temps entre biochar et compost sur la stabilité biologique de chacun des composants, ainsi que leur effet sur la croissance des plantes.

Nous avons réalisé deux mélanges biochar-compost, dont la nature des biochars différait et dont la signature isotopique stable était significativement différente de celle du compost. Puis nous avons altéré artificiellement les mélanges ainsi que leurs composants séparément, suivant des cycles de humidification/séchage et chaud/froid. Une grande quantité d'eau a été mise à chaque étape de l'altération, pour simuler les pluies et le lessivage. Les mélanges frais et altérés, ainsi que les composants pris individuellement, ont été incubés pendant un an à une température et humidité constantes de 20 °C et 60 % d'humidité (% poids sec), respectivement . Nous avons évalué l'évolution des émissions de CO_2, ainsi que de la signature isotopique stable du C-CO_2. La méthode d'isotopie stable permet de distinguer les effets des deux composants de signature isotopique différente, au sein d'un mélange. Par ailleurs, nous avons amendé les mélanges frais et altérés ainsi que le compost seul à deux types de sol, calcaric cambisol et haplic luvisol, sur lesquels nous avons fait pousser du rye-grass.

Les résultats ont montré que, lors de l'altération, les mélanges mesurés perdaient moins de matière que ceux calculés, mettant ainsi en évidence que le biochar et le compost pouvaient interagir pour une meilleure rétention de matière (Fig. 31). Par ailleurs, la quantité de C est plus élevée dans les mélanges mesurés que dans les mélanges calculés et inversement, la quantité d'O est plus élevés dans les mélanges mesurés que dans les mélanges calculés. Cela montre que biochar et compost interagissent pour une meilleure rétention en C et un lessivage plus important d'éléments labiles enrichis en oxygène.

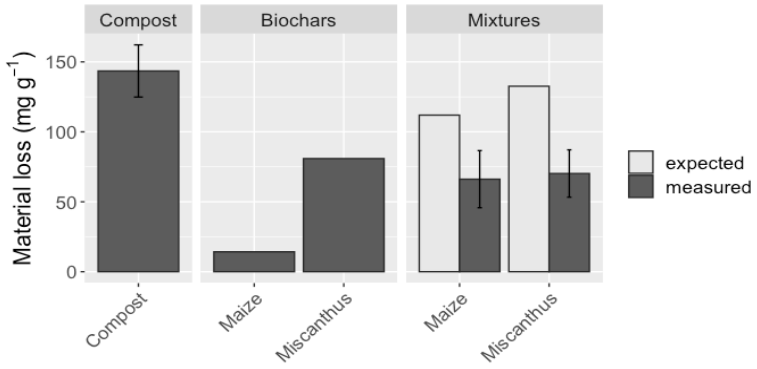

Figure 51 Perte de masse lors de l'altération du compost, des deux biochars ainsi que de leur mélange mesuré et calculé (moyenne ±sd).

La stabilité biologique des biochars et du compost se comporte différemment en fonction de s'ils sont incubés mélangés ou individuellement (Fig. 32). La minéralisation du compost frais diminue significativement lorsqu'il est mélangé au biochar, tandis que la minéralisation du biochar augmente significativement lorsqu'il est mélangé au compost. Après altération, ces effets d'interaction sont atténués et la minéralisation du compost mélangé au biochar dépasse celle du compost lorsqu'il est appliqué individuellement.

Plusieurs hypothèses peuvent expliquer les effets, tantôt négatifs, tantôt positifs, du biochar sur la minéralisation du compost. Du fait de ses fortes propriétés de sorption, le biochar peut aisément immobiliser des éléments solubles, dont le carbone organique dissous, et/ou des particules mobiles issues du compost et ainsi les protéger contre la dégradation microbienne et le lessivage (e.g. Jien et al. 2015, Ngo et al. 2013). Dans le cas de notre incubation avec des matières fraîches, le biochar peut avoir protégé de la dégradation microbienne le carbone issu du compost frais, ce qui est bénéfique pour le stockage de carbone. Dans le cas de l'incubation après altération, le biochar peut avoir protégé du lessivage des composés labiles issus du compost. Ces composés sont alors minéralisables après l'altération artificielle, ce qui peut expliquer la plus grande minéralisation observée du compost en présence du biochar. Par ailleurs, des études ont montré que certains biochars pouvaient contenir des éléments toxiques pour la croissance des plantes parmi les éléments mobiles et/ou solubles (e.g. Gale et al. 2016). En supposant que ces éléments puissent également être toxiques pour les microorganismes, la présence de biochar frais pourrait avoir restreint la minéralisation du carbone issu du compost frais. Le lessivage lors de l'altération artificielle a pu éliminer une partie de ces éléments toxiques du biochar, ce qui a eu pour conséquence un regain de la minéralisation du compost en présence de biochar.

Dans les deux cas d'incubation de matériaux frais et altérés, le compost a eu un effet stimulant sur la minéralisation du biochar, probablement à cause d'un « priming effect » dû à son apport en MO labile et en nutriments, en quantités plus importantes que ceux du biochar. On en conclut que suite à leur mélange, biochar et compost interagissent significativement, probablement à cause d'éléments labiles ou facilement solubles ou transportables avec le lessivage.

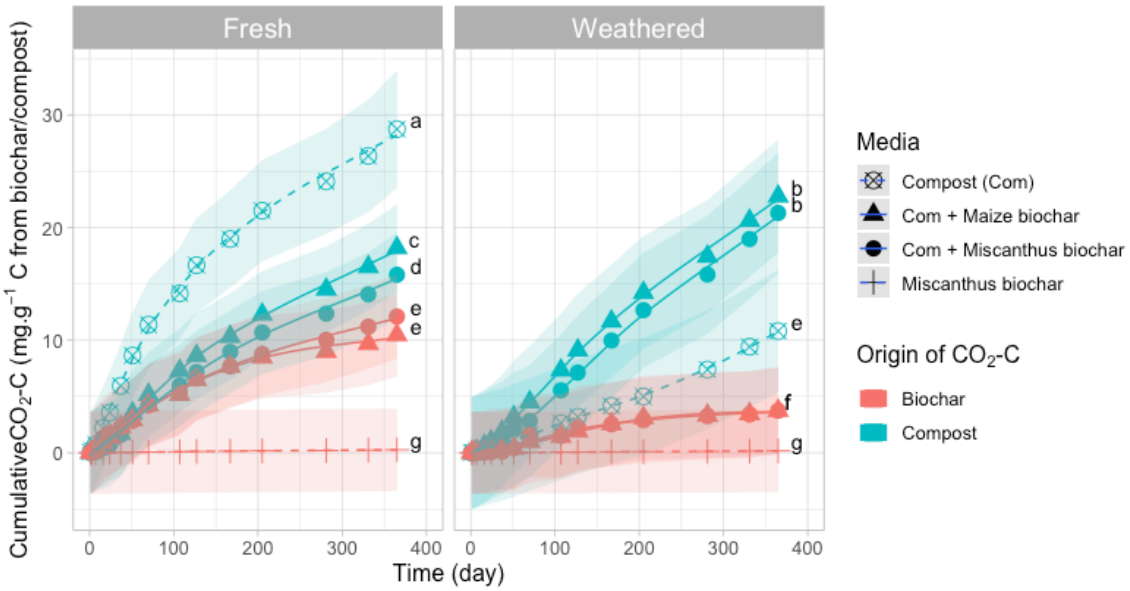

Figure 52 C-CO_2 cumulé issu de la minéralisation du biochar et du compost lorsqu'incubés individuellement ou mélangés. Les couleurs turquoises et rouge représentent le C mineralisé issu du compost et du biochar respectivement. Les lettres représentent les différences significatives d'une analyse ANOVA 2 facteurs (n = 3).

L'amendement au sol de compost ou mélanges frais diffère selon les sols. Pour le calcaric cambisol, les amendements ont eu un effet positif sur la production végétale, tandis qu'ils n'ont pas eu d'effet significatif sur le haplic luvisol. Après altération, les effets bénéfiques du compost seul sur le calcaric cambisol diminuent, alors que lorsqu'il est mélangé avec le biochar de miscanthus, cet effet reste constant. Par ailleurs, après altération, l'apport de mélange compost et biochar de miscanthus a un effet significativement plus important que l'apport de compost seul sur la production végétale, pour les deux sols. Il est possible que l'effet bénéfique de l'apport de biochar de miscanthus lorsqu'il est mélangé avec le compost, visible seulement après altération, soit dû au lessivage d'éléments toxiques (Gale et al. 2016). Dans le cas d'un apport de mélange compost et biochar de miscanthus, le biochar peut améliorer l'effet bénéfique du compost sur la production végétale, après lessivage des éléments toxiques. Cependant, cet effet bénéfique du mélange biochar-compost sur la production de biomasse n'est pas systématique car il dépend de plusieurs paramètres incluant le type de sol, le type de biomasse utilisée pour la production de biochar ainsi que les paramètres de production du biochar tels que la température de pyrolyse. Notre étude met également en avant la question du traitement de la toxicité potentielle de certains biochars avant leur apport au sol.

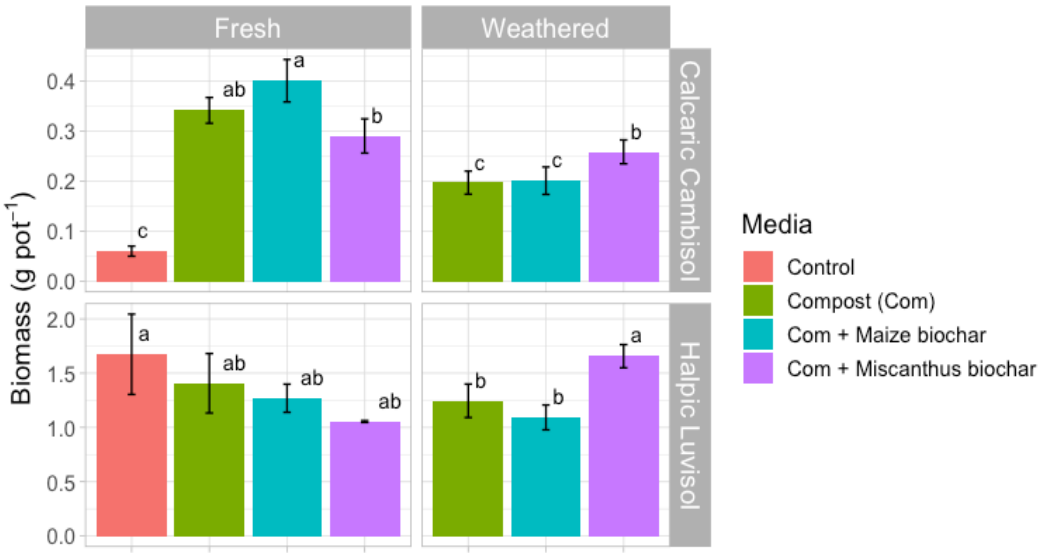

Figure 53 Production végétative de ryegrass après ajout de compost ou de mélange biochar-compost, sur deux types de sol (moyenne ± sd, *n* = 3). Les lettres représentent les différences significatives issues d'analyse ANOVA 1 facteur pour chaque traitement et type de sol.

Chapitre IV – Les mécanismes affectant le devenir du mélange biochar-compost et l'adsorption d'azote dans le sol agricole.

Le biochar pourrait réduire le lessivage de particules de compost dans le sol en conditions terrain et climat tropical (Ngo et al. 2016), probablement grâce à la protection de ces particules dans la structure poreuse du biochar (Jien et al. 2018). Cependant, les effets en climat tempéré sont encore mal connus. Par ailleurs, le biochar étant hautement friable (Spokas et al. 2014), il peut facilement être sujet au transport (Rumpel et al. 2015). Les effets du compost sur le lessivage des particules de biochar n'ont à ce jour pas encore été explorées. Une fois amendé au sol, les particules de biochar et compost s'accumulent en grande partie dans la fraction particulaire du sol, tandis qu'une petite partie peut s'introduire dans les agrégats du sol (Cooper et al. 2020) et/ou s'associer avec les minéraux du sol (Plaza et al. 2016). L'objectif de ce chapitre est d'étudier les interactions entre biochar et compost sur la rétention des particules au cours du temps, ainsi que l'effet de la matrice sol sur ces interactions. Nous posons l'hypothèse que la matrice sol affecte les interactions entre biochar et compost sur la rétention des particules.

Pour ce faire, nous avons travaillé sur des mésocosmes mis en conditions au champ ; des mélanges biochar-compost (20/80 % massique), composés avec du biochar de miscanthus, ont été mélangés ou non à du sol à hauteur de 10% (masse sèche) puis mis dans des litterbags. Ces derniers ont été enfouis à environ 5 cm de la

surface dans un champ agricole, juste avant le semis du maïs. L'expérience a duré 24 mois au total et des prélèvements des litterbags ont été réalisés aux mois 4, 10, 14 et 24, afin de suivre l'évolution des teneurs en carbone (C) et azote (N) au cours du temps. L'origine du C restant a également pu être estimée grâce aux techniques d'isotopie stable ($\delta^{13}C$). Les litterbags contenant mélange + sol, prélevés aux temps 0 (initial) et 14 mois ont été fractionnés afin de déterminer les fractions accumulatrices des particules de biochar et/ou de compost, et de voir si ces particules ont été intégrées dans les agrégats. Dans un deuxième temps, une étude approfondie des fractions de particules libres (free POM), i.e. non incluses dans les agrégats, a permis de suivre l'évolution de leur composition en biochar et compost.

Les résultats des litterbags contenant les mélanges biochar-compost sans sol ajouté, montrent que le compost relargue plus de C que le biochar, probablement suite à un plus grand potentiel de minéralisation. De plus, biochar et compost n'ont pas induit d'interactions significatives sur le relargage de C au cours du temps, comme l'attestent les résultats similaires de C issu du mélange mesuré (measured mixture) et du mélange calculé (expected mixture) à partir des résultats des composants seuls (Fig. 36 A). Les analyses isotopiques de ces litterbags sans sol nous ont permis de distinguer les pertes de C issues du compost et du biochar et confirment que biochar et compost n'interagissent pas significativement sur la rétention des particules dans le mélange lorsque ce mélange n'est pas amendé au sol (Fig. 37).

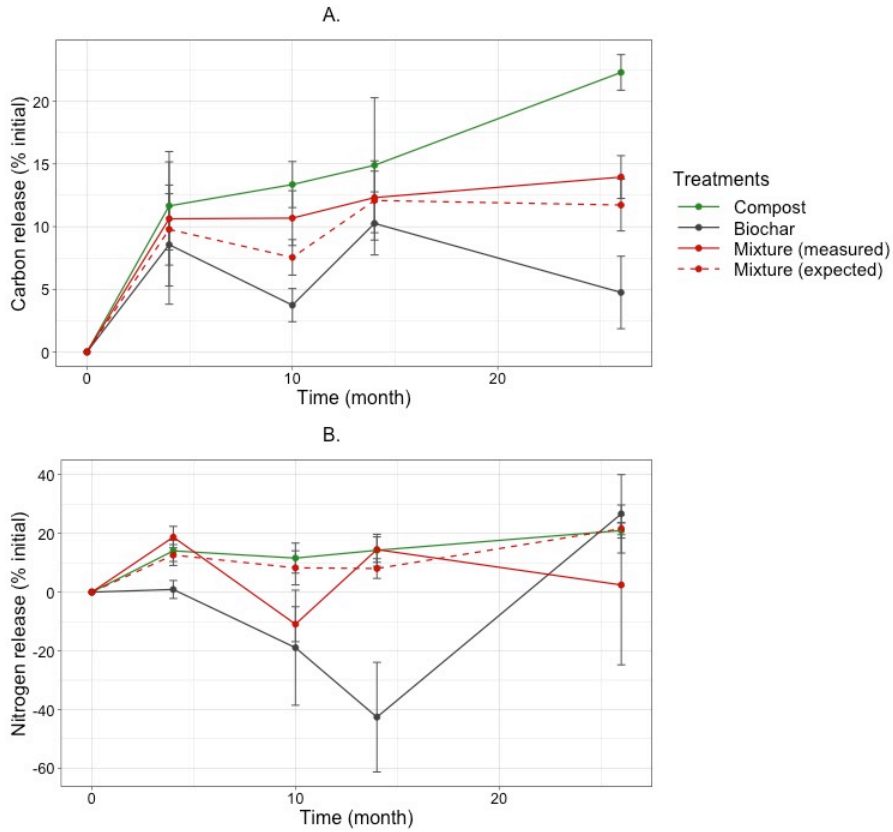

Figure 54 Perte en carbone organique et en azote pour les litterbags sans ajout de sol (moyenne ± écart type, n=4). Aucune différence significative n'a été trouvée entre le mélange mesuré (measured mixture) et le mélange calculé (expected mixture) ($p > 0.05$), excepté pour la perte d'azote aux mois 10 and 14.

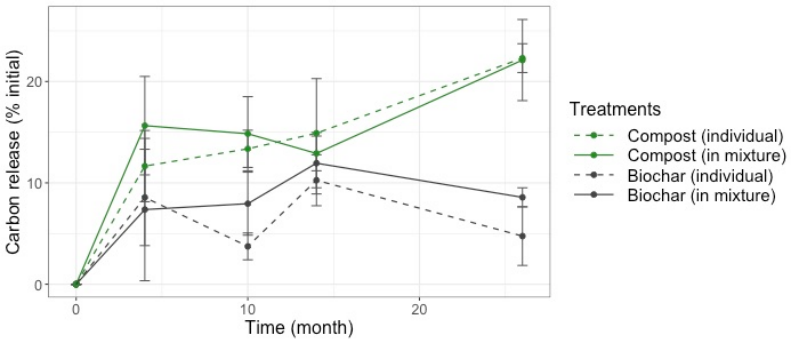

Figure 55 Perte de carbone organique dérivé du compost (en vert) ou du biochar (en gris), pour les litterbags avec mélange biochar-compost (trait plein) ou pour ceux avec les composants individuels (traits pointillés). Aucune différence statistique n'a été trouvée entre les mélanges et les composants individuels, pour chaque composant ($p > 0.05$) (moyenne ± écart type, n=4).

En revanche, les résultats concernant l'azote ont permis de détecter une interaction entre biochar et compost sur la rétention en azote au mois 10, suivi de son relargage progressif. (Fig. 36 B). Cet effet est probablement dû au potentiel absorbant du biochar (Cai et al. 2016). Ces résultats sont cohérents avec une étude récente montrant le potentiel du biochar à retenir l'azote puis à le relarguer plus lentement (Palanivell et al. 2020).

Après amendement au sol, la majorité des particules de biochar et de compost se sont accumulées dans les fractions de matières organiques particulaires libres (fraction free POM). De ce fait, nous nous intéressons dans cette étude principalement au devenir des fractions free POM. Les résultats ne montrent pas d'effet d'interaction significative entre biochar et compost concernant la teneur en carbone totale des litterbags (Fig. 41A). En revanche, les résultats d'isotopie stable du carbone montrent qu'une partie des particules libres du biochar > 2 mm a été redistribué dans la fraction POM 2-0.2 mm pour les composants purs, de manière significativement plus importante que lorsque le biochar a été mélangé au compost (Fig. 42). Cela met en évidence que lorsque le biochar est mélangé au compost, les particules de biochar sont protégées de la désintégration physique par le compost. Ainsi, en présence de compost, la friabilité du biochar est amoindrie. Une explication peut être la liaison de particules de compost avec les liaisons oxygénées du biochar, faisant suite à sa désintégration physique (Wang et al. 2020). L'effet du compost sur la friabilité du biochar affecte la rétention des particules de biochar, si l'on considère que les particules fines de biochar sont plus mobiles que les particules grossières. Cependant, les effets du compost sur la friabilité du biochar ne sont pas visibles dans les échantillons globaux, probablement dû au fait que leur effet sur les teneurs en carbone globales ne sont pas suffisamment forts.

Concernant l'azote, aucun effet d'interaction d'a été constaté sur sa rétention lorsque le mélange a été amendé au sol (Fig. 41). Cet effet est différent de ce qui a été observé pour les interactions sans sol, probablement dû au fait que lorsqu'il est amendé au sol, l'effet d'interaction biochar-compost sur la rétention en azote par le biochar

est réduit à cause d'un effet de concurrence avec d'autres éléments du sol. Il est également possible que lorsqu'il est mélangé au sol, l'effet d'interaction biochar-compost sur la rétention de l'azote ne soit pas assez fort pour être détecté avec les analyses azote que nous avons réalisées au GC-MS.

Biochar et compost interagissent sur la rétention des particules de biochar, puisque le compost protège le biochar contre la friabilité. Or, cet effet est trop faible pour être visible sur le C organique total de l'échantillon. De même, biochar et compost interagissent pour une meilleure rétention de l'azote. Or, cet effet est sûrement trop faible pour être visible lorsque le mélange est ajouté au sol.

A) Free POM fractions

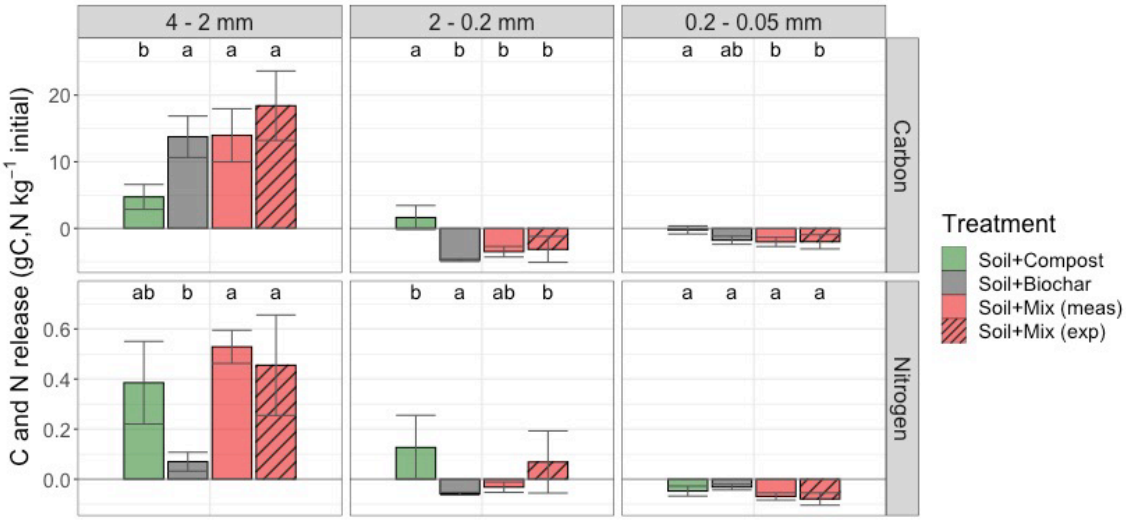

Figure 56 Variation of OC and N from free POM fractions (A) after 14 months of field exposure, as compared with the initial time (mean ± SD, n=4). Positive values represent losses and negative values represent gains. Letters represent significant treatment effect, for each grain size fraction.

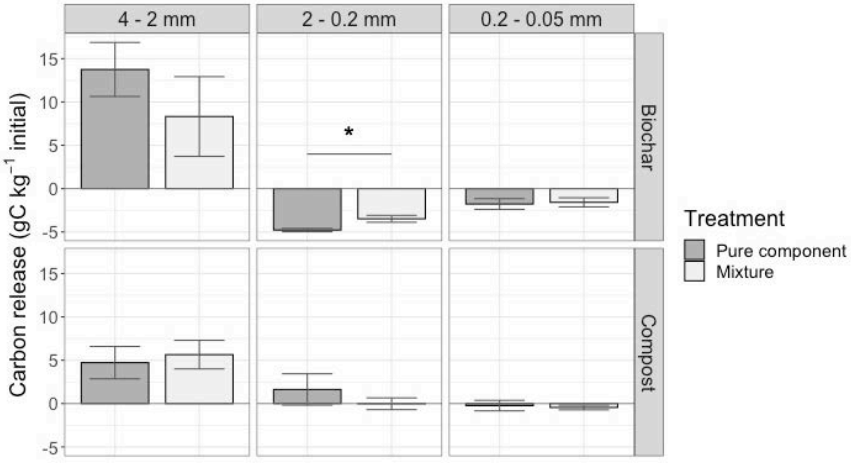

Figure 57 Variation of biochar- and compost-derived OC, when added as pure component or when mixed with each other, after 14 months of field exposure (mean ± SD, n=4), using differences of biochar and compost stable isotopic signatures. Positive values represent losses and negative values represent gains. Stars represent significant treatment effect, for each of the free POM fractions.

Chapitre V – Discussion générale et conclusion

Les résultats des différentes études de cette thèse ont montré que biochar et compost pouvaient interagir à différentes échelles de temps, et ce dès leur mélange. Les effets impliquent aussi bien des processus d'ordre abiotique (oxydation) que biotique (minéralisation) et influencent notamment la rétention en carbone et en azote. Un récapitulatif schématisé des différents mécanismes mis en évidence dans la thèse est présenté dans la figure 43.

Lors de leur mélange, biochar et compost augmentent de manière immédiate l'oxydation abiotique en surface du biochar, ce qui a pour effet de réduire sa stabilité thermique (chapitre II). D'un point de vue pratique, cela signifie que le biochar et le compost pourraient interagir sur les propriétés de surface du biochar lorsqu'ils sont mélangés avant leur apport au sol. Il serait intéressant d'étudier si cette interaction affecte significativement les propriétés de sorption du biochar pour les nutriments issus du compost et/ou du sol. Ce résultat pose également la question de l'effet du stockage des mélanges avant leur amendement au sol, puisqu'il a été démontré que des facteurs environnementaux tels que la lumière ou l'humidité, pouvaient induire des processus de dégradation abiotiques (Wang et al. 2020).

A moyen terme, biochar et compost interagissent sur les processus biologiques de décomposition, en réduisant la décomposition du compost et en augmentant la décomposition du biochar (priming effects). Après altération et lessivage des particules les plus mobiles et nutriments, tandis que le biochar stimule progressivement la décomposition du compost. Reste à savoir si cet effet des biochar sur la décomposition du compost est durable, ou si elle résulte elle aussi d'un priming effect suivant l'altération physique. Pour répondre à cette question, il serait judicieux de réaliser une altération artificielle des mélanges, en étudiant les variations de composition du lixiviat ainsi que les variations de teneur en azote. Cela donnerait des informations concernant les éléments mobiles, responsables de la variation d'interaction entre biochar et compost sur la dégradation microbienne, et également de répondre à la question des éléments toxiques présentes initialement dans le biochar.

Après amendement au sol, les interactions biochar-compost varient au cours du temps et diminuent le relargage de C dû à la minéralisation du compost et au transport des particules de biochar. La présenc de compost permet de réduire le potentiel de friabilité du biochar, probablement grâce aux liaisons compost-biochar sui se sont

formées suite à la désintégration physique du biochar. Cependant, bien que ces effets d'interaction sur la rétention du carbone soient observables avec les techniques d'isotopie stable du carbone, ils demeurent trop faibles pour induire un changement significatif de rétention de particules à une échelle plus globale du mélange. En outre, la capacité d'adsorption du biochar est modifiée, ce qui influence son comportement d'adsorption de l'azote. Les litterbags sans sol ont montré que le biochar pouvait adsorber l'azote issue du compost. Mais cet effet n'était plus visible lorsque le mélange biochar-compost était amendé au sol. Enfin, les résultats sur les plantes ont montré que le biochar pouvait, dans certains sols et pour certains biochars, améliorer significativement les effets du compost sur la production végétale.

L'ensemble des résultats de la thèse appellent à des questions plus larges, telles que les effets du compost sur les éléments toxiques du biochar, ou quels sont les effets d'interaction biochar-compost sur la colonisation microbienne du biochar, ce dernier étant un potentiel substrat propice au développement microbien. La colonisation microbienne participe également au développement d'un manteau de matière organique en surface du biochar (organic coating), qui affecte le potentiel d'adsorption du biochar ainsi que sa biodégradabilité. Les études concernant le développement de ce manteau organique sont très récentes (Hagemann et al. 2017, Conte and Laudicina 2017) et nécessitent davantage de recherche. Finalement, ce travail de thèse a abordé dans une moindre mesure les questions concernant les propriétés agronomiques du sol. Des études pourraient permettre d'approfondir la compréhension sur les effets d'interaction entre biochar et compost sur les propriétés du sol tels que la rétention en eau et en nutriments tels que le phosphore ou le potassium. Les résultats dépendent de nombreux paramètres tels que le type de biochar, le type de compost, le type de sol et le ratio biochar/compost. Afin de pouvoir généraliser les effets d'interaction entre biochar et compost, il est nécessaire de réaliser un plus grand nombre d'études avec biochar et compost. La généralisation des connaissances des effets d'interaction entre biochar et compost permettrait d'améliorer la valorisation des déchets destinés à la pyrolyse ou au compostage. Cela pourrait être utile pour une valorisation plus appropriée des déchets de la part des émetteurs, tels que les communes, et les utilisateurs que sont les agriculteurs notamment.

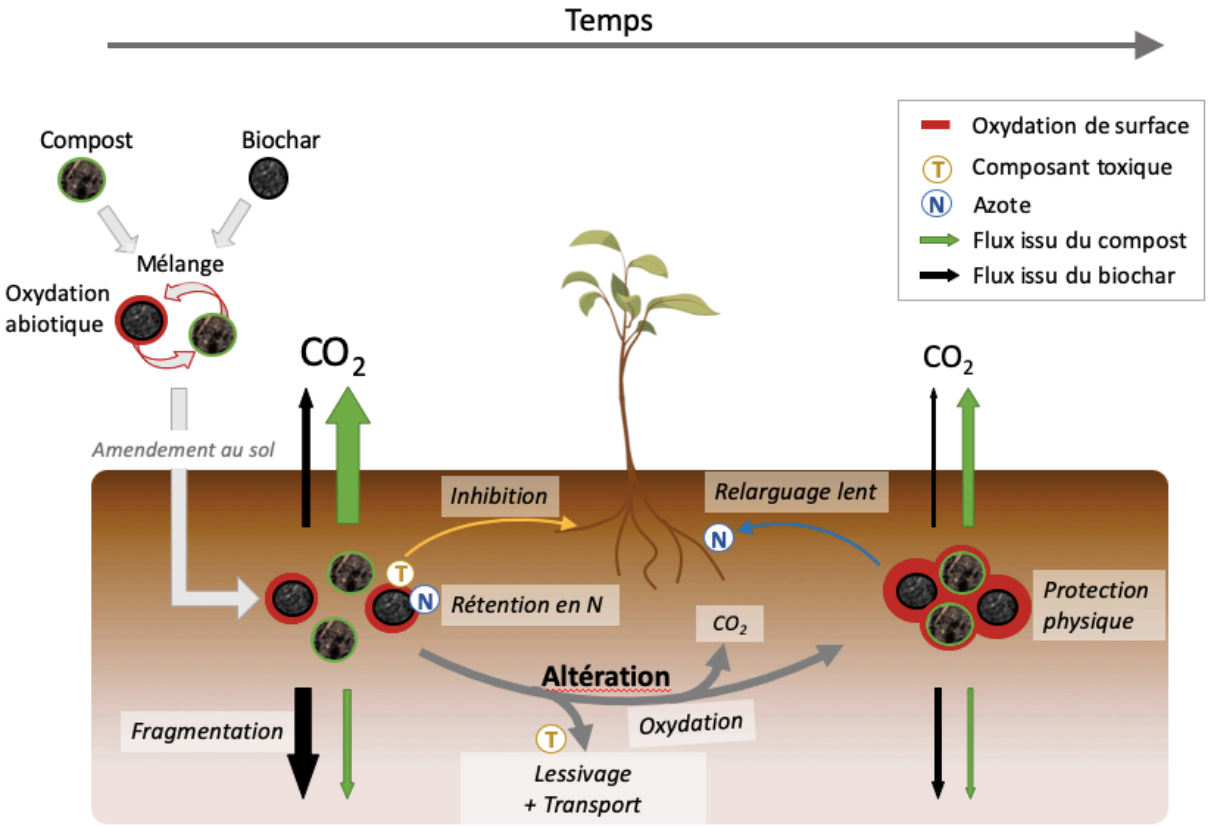

Figure 58 Mécanismes d'interaction biochar-compost affectant la perte de C et la fertility du sol au cours du temps.

Biochar-compost mixtures: interactions and impact on carbon sequestration and soil fertility.

In the context of global challenge, innovative organic amendment strategies could be used to improve soil agronomic properties in addition to increasing carbon (C) sequestration in soil. The combination of highly stable biochar with compost, a nutrient-rich material containing labile C, may be a solution to improve C sequestration while enhancing soil fertility in the context of a circular economy. Aim of the thesis was to examine if there are biochar-compost interactions and if yes, what are the mechanisms determining their effect on C and nitrogen (N) dynamics and plant growth, at different time scales. To this end we used laboratory and field experiments and analyzed for biological and thermal stability. The thermal stability of biochar was affected by biochar-compost interactions, which may already occur during their blending. Artificial weathering influenced the biological stability of both materials. Under field conditions, these processes did not significantly influence the carbon dynamics of the mixture, while biochar friability and N dynamics were affected by biochar-compost interactions. We conclude that biochar and compost interactions may occur at different time scales and affect their material properties and performance as soil amendment.

Key-words: Biochar, compost, carbon sequestration, N retention, amendment, soil aggregates

Mélanges biochar-compost : interactions et effets sur la séquestration du carbone et la fertilité du sol.

Dans le contexte actuel des enjeux environnementaux, des stratégies innovantes d'amendement organique peuvent être utilisées afin d'améliorer les propriétés agronomiques du sol, tout en augmentant la séquestration du carbone (C) dans le sol. La combinaison de biochar hautement stable avec du compost, matériau riche en nutriments et contenant du C labile, pourrait être une de ces stratégies, dans un contexte d'économie circulaire. L'objectif de la thèse était d'étudier l'existence d'interactions entre biochar et compost et le cas échéant, de déterminer les mécanismes responsables de leurs effets sur la dynamique du C et de l'azote, ainsi que sur les plantes, à différentes échelles de temps. Pour ce faire, nous avons réalisé des expériences au laboratoire et au champ et analysé les stabilités thermiques et biologiques. La stabilité thermique du biochar a été affectée par les interactions biochar-compost, survenant dès leur mélange. L'altération artificielle a induit des changements sur la stabilité biologique des deux composant. Dans les conditions au champ, les processus induits pas les interactions biochar-compost n'ont pas impacté significativement la dynamique du C des mélanges, contrairement à leurs effets sur la friabilité du biochar et la dynamique de l'azote. En conclusion, les interactions entre biochar et compost peuvent se produire à différentes échelles de temps et affecter significativement les propriétés des matériaux ainsi que leur performance en tant qu'amendement organique.

Mots-clés: Biochar, compost, séquestration du carbone, rétention en azote, amendement, agrégat du sol