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Thermochemical valorisation of waste biomass through pyrolytic conversion: Horse stable residues derived biochar characterization

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List of Abbreviation

EBC: European Biochar Certificate

HHT: Highest heating temperature

SSA: Specific surface area

BET: Brunauer–Emmett–Teller theory

IBI: International Biochar Initiative

BCM: bio carbon minerals

GHG: Greenhouse gases

PSD: Pore size distribution

BD: Bulk density

WHC: Water holding capacity

PR: Penetration resistance

SOM: Soil organic matter

PAH: Polycyclic Aromatic Hydrocarbon

PCM: Pyrogenic Carbonaceous Material

CO_2 : Carbon Dioxide

LHV: Low Heating Value

ASTM: American Society for Testing and Materials International

DM: Dried Mass

OM: Organic Matter

SA: Surface Area

SEM: Scanning Electron Microscopy

CEC: Cation Exchange Capacity

EC: Electrical Conductivity

RT: Residence Time

PS: Pore Size

PV: Pore Volume

CH_4: Methane

N_2O: Nitrous Oxide

BQM: Biochar Quality Mandate

IBI-BS: International Biochar Initiative Biochar Standards

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Abstract

Different possible applications of biochar from pyrolyzed biomass are gaining greater and greater interest. This is mainly due to its effectiveness in waste management and to its usage as soil amendment that will ameliorate soil quality, reduce GHGs emission from the soil, the use of fertilizers and diminish the soil acidification phenomenon.

This research compares the chemical and physical characteristics of biochar obtained by different mixtures of horse stable residues (horse manure, peat and wood sawdust). To produce biochar, original feedstocks have been undergone slow pyrolysis treatment (HTT=600°C, RT= 2h, HR= 10°C/min). All measurements have followed an experimental design using mixture model.

Results of pH, PAH, BET and CHNSO analysis showed how all possible combinations of materials should be applied as soil amendment since: high pH level will prevent soil acidification, under-limit PAH concentration will not present a hazard for human health, and high SSA and PSD variation will provide habitats for microorganism, increase water retention capacity and detain soil GHG emissions.

Keywords: biochar, slow pyrolysis, agricultural residues, manure, biomass, waste disposal, soil amendment.

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1. Introduction

My thesis activity has been carried out at the Department of Bioproducts and Biosystem of Aalto University School of Chemical Engineering (Espoo, Finland) in the Clean Technologies research group. This group highlights the viewpoint of sustainable development, providing researches on responsible use of raw materials and development of cleantech-processes according to management and control of industrial environmental load.

This project is based on the "waste to energy" idea for which a better use of agricultural and industrial residues can be obtained by means of a thermochemical conversion process. In particularly, this essay focuses on the physical and chemical characterization of biochar products obtained by a slow pyrolysis treatment of horse stable residues (horse manure, peat and wood sawdust).

Nowadays in Finland there are more than 750 horse riding schools, riding stables and private stables, managing almost 75000 animals [1], and more than 800 000 m^3 of horse manure is estimated to be annually produced [2]. According to Finnish waste legislation, it is currently considered as a residue that must be incinerated, even if it contains important nutrients such as potassium, phosphorus and nitrogen. This kind of disposal involves several drawbacks such as huge CO_2 emissions, significant NO_x emission, high ash fusibility and loss of nutrients [3]. All these externalities imply design adjustment of power plants that will remarkably lead to higher management cost, resulting in a non-competitive energy source. The other main reuse of horse manure is its direct utilisation as a fertilizer with the main advantage of enhancing crops production. Even this application has some disadvantages like: soil acidification, negative impact on water quality, degradation-derived GHG production and N immobilization [4].

Concerning peat, this material is composed by mostly inorganic matter (65%) in which plants or animals' decomposition is inhibited by acidic and anaerobic conditions [5]. This substance, thanks to favourable climate conditions and geographical position, is widely spread in Nordic countries where is naturally accumulated in huge areas called "peatlands". As an example, in Finland it covers almost 94000 km^2 and it contributes to the 6,2% of annual energy production, being burnt as a fuel. In fact, Finland, differently from other countries and organizations, classifies peat as a "slow renewable biomass fuel", allowing its combustion for heat and electricity production [6]. Consequences of this procedure mainly concern the CO_2 emissions, since it generates 106 gCO_2/MJ (higher than coal) and peat extraction from bogs remove its natural carbon sink effect. In fact, peat naturally captures and stores the carbon dioxide produced during its forming process [7] . As a comparison, burning peat contribution is equal to the passenger-car-traffic one [8].

Lastly, wood represent one of the most important natural resources of Finland, having a high range of industrial application from sawmill to paper and pulp industry. More specifically, woody waste reutilised as fuels covered the 27% of total annual energy consumption of the country in 2017, being the biggest energy source (followed by oil 23% and nuclear 17%) [9]. Its relationship with manure and peat in combustion processes holds a greater interest. In fact, wood is commonly added to manure and peat fuels in order to improve LHV and reduce carbon dioxide emission [6].

In general, more valuable options for valorising these residues can be performed. Anaerobic digestion and gasification can represent one of them since they will produce biogas directly utilisable for heating and electricity generation. Another way could be the usage of these materials as original feedstock to produce biochar through a slow pyrolysis treatment. This innovative technology considerably promising due to its social, economic and environmental benefits: restrained operating cost in small and large scales (atmospheric pressure conditions and moderate temperatures), sustainable waste disposal and useful applications of the product.

As conclusion, the scope of this study is:

- Prove that the thermochemical conversion of waste through slow pyrolysis could represent a valuable and environomical alternative to their mere incineration.
- Perform a physical and chemical characterization of the produced biochar, resulting from an already optimized thermodynamic process.
- Construct a mixture model of the residues since they will always be inseparably mixed together and with other bending materials (i.e. straw), in order to predict the response for any combination of ingredients that can be empirically made and estimate the influence on the response of each single component and in combination with other.
- Evaluate biochar quality and its best application according to the measured properties, mostly focusing on the use as soil amendment, respecting the threshold imposed by the European legislation in term soil protection.

2. Literature review

2.1 Biochar

Concerning biochar field, the actual state of art has been deeply investigated in order to better understand all the features of its quality and characterization. In the next paragraphs a resume of biochar knowledge is presented mainly focusing on its definition, properties, applications and legislation.

2.1.1 Definition

Biochar is defined as a carbon-rich product obtained by pyrolysis of biomass under controlled condition (limited oxygen supply and low temperature). Mainly due to its inherent properties, it has been differentiated from other chars by its specific application to soil for sustainably sequestering carbon and concurrently improving soil functions. [10] [11] [12] The pyrolysis process consists in a thermo-chemical decomposition of organic material by heating it in a temperature range between 350-1000°C. Actually, pyrolysis is not the only available technology to produces biochar, but it represents the most common one since it has the highest values of biochar yields, in particular under 700°C (so-called slow pyrolysis). As examples, other techniques are gasification and hydrothermal conversion that focus respectively on syngas and bio-oil production. [13] Syngas and bio-oil, with biochar, represent the pyrolysis by-products (see 2.2.1).

Biochar is not a new concept, having its first application in the beginning of 19th century. What is more recent is its terminology: biochar nowadays refers to the particular application on soil amendment, feed additives, C sequestration and filtration of percolating soil´s water. This reference highlights the different meaning with respect to “char”,” charcoal”, “activated carbon” and “black-C”, that all concern the same field. The first term refers to the by-product derived from charring biomass with the intent of using it as a fuel or filter; the second, instead, means more a residue of burnt biomass. With “black-C” we can refer to all carbonaceous residues (char, charcoal, biochar, soot, graphite) of fire or heating processes, without any specific indication of the original feedstock. On the other hand, “activated carbon” refers to all the substances, biochars or coals, which have been activated by means of steam or chemicals in order to increase their specific surface area. [11]

As described above, the application of char for soil amendment has its root in the beginning of the 19th century, when covering the fields with char was a common procedure that reported significant improvements on farm revenues. Other reports tell about specific practices in China and Japan where agricultural fields were covered with biomass and manure and set on fire in order to produce “black earth”. The usage of that product revealed a good enhancement of future crops. [11] Despite these ancient procedures, global interest on biochar has only risen in the last few years; in particular when in the 2000s biochar substances gave a consistent explanation for the “Terra Petra” phenomenon and when its very long stability in soils has been proven. [14] These twofold discoveries made biochar an efficient and innovative tool for soil management. An example of biochars produced from different feedstock is given in Figure 1.

Figure 1 Selection of images of different biochars (right) and their original feedstock (left) [13]

2.1.2 Properties

Biochar abilities are rooted on its chemical and physical properties. All these properties must be deeply investigated in order to achieve a better understanding on their influence in the mechanism of soil amendment (or other uses) and their change in relation to the variation of the main parameters (original feedstock, pyrolysis highest treatment temperature, heating rate and residence time).

Before starting to rank all the specific properties, a clarification about the defining property of biochar is needed. Lehmann et al. states that "*the organic portion of biochar has a high Carbon content, which mainly comprises so-called aromatic compounds characterized by rings of six C-atoms linked together without Oxygen or Hydrogen*" [11]. In particular the irregular pattern of the aromatic rings is proper of biochar; differently from graphite, which has much more aligned and stacked sheets. In addition, biochar arrangement might contain O, H and minerals depending on the original raw material.

Chemical Properties

Proximate Analysis. This analysis expresses the mass percentage of moisture (water contained in the material at the site, time, and under the conditions it is sampled), ash (source of metals, silicates and important plant nutrients), volatile matter (includes the components which are liberated at high temperature in the absence of oxygen) and fixed carbon (the solid combustible residue) of both original biomass and biochar. Biomass usually follow ASTM standards or similar, on the other hand for biochar is common to use ASTM standards referred to coal. EBC (European Biochar Certificate) offers a better analytical method for the determination of biochar properties; improving the performance, reliability and comparability of biochar analysis [15].

Ultimate Analysis. These tests produce more comprehensive results than the proximate analyses by expressing mass percentage of C, H, N, O and S elements. The total C content and in particular the organic part of it are very common parameters to identify and classify biochar and useful to assess the carbon balance and sequestration in soils. As an example, they are used by EBC [10] both to distinguish biochar (C>50%) from Pyrogenic Carbonaceous Material (PCM, C<50%) and to rank the quality of the biochar yields (basic or premium). While organic feedstock is pyrolyzed, the majority of the organic matter is released as syngas and bio-oils, resulting in a consistent ash enrichment [16]. H content, or better the ratio of H/C contents, is used as an important parameter to determine the aromaticity, the carbonization degree and the biochemical recalcitrance of biochar. In fact, an increase in aromaticity, due to the dehydration and condensation, which occur during pyrolysis process, leads to a higher stability level of biochar. Common values for biomass-feedstock biochars produced above 400°C are less than 0,5 (0,7 for EBC). On the other hand, the N percentage value depends more on the original feedstock and in general constant N/C ratios are observed until 600°C of pyrolysis temperature. Finally, the O content is calculated indirectly from the other components due to its high cost of analysis. Exactly as H/C ratio, the O/C one is used as a parameter to evaluate biochar aromaticity and maturation; usually they are represented by means of Krevelen diagrams (either 2 or 3 dimensions plot) as a function of different biomass or treatment temperature. It must remain less than 0,4. In addition to CHNOS analysis, main elements and heavy metals tests are performed due the fact that main elements (P, K, Na, Mg, Mn, Ca, and Fe) play an important role in plant nutrition, and, even if biochar primary application is not agriculture, those elements have to be considered for regulatory requirements. [16] For example, some government agencies make this analysis compulsory in order to classify biochar as a soil amendment. Usually nutrient elements present a higher content in manure derived biochar. Instead, heavy metals and metalloids (defined as metallic elements presenting a higher density compared to water, at least 5 times, such as Cd, Cu, Pb, Cr, Ni, and Zn) percentages are determined in order not to exceed a threshold, over which these elements represent a potential toxic hazard. These elements are originally present in the raw material and during the pyrolysis process they may or may not volatize; as a result, the original feedstock is the most influencing parameter. Both kind of elements are normally found in the ash, which is concentrated in the biochar. Ash level is higher in straw or waste material, more than in woody feedstock. [4]

Polycyclic Aromatic Hydrocarbons (PAH). PAHs are defined as "*organic compounds, consisting only on C and H atoms, which are mostly colorless, white, or pale-yellow solids. They are a ubiquitous group of several hundred chemically related compounds, environmentally persistent with various structures and varied toxicity*". [17] PAHs are proved to be the cause of carcinogenic and mutagenic effects and very effective immunosuppressant by interference with both cellular membrane and its related enzymes. They are mostly produced by incomplete combustion of organic matter, both natural (forest or brush fires) and anthropogenic (coal, oil or wood burning). Presence of PAHs in soil is main due to natural deposition from close sources, but it can also occur if materials that contains PAHs are directly added to the soil. The last case has a relevant importance for biochar, in fact biochars can contain PAH of a few, up to a few hundred, milligrams per kilogram [16]. Their presence on soils is an indirect hazard for human health, also due to their significant sorbet capacity. PAHs are mostly due to HTT and original feedstock. Table 1 shows PAH thresholds in relevant counties. Also, in EBC [10] guidelines PAH thresholds are reported: "*the sum of the EPA's 16 priority pollutants, must be under 12 mg/kg DM for basic grade and under 4 mg/kg DM for premium grade biochar* "(see Table 4).

Table 1 Quality standards for PAH values in various countries expressed in mg/kg [4]

PAH	CANADA	UK	EU	USA
Naphthalene	8,8		5-60	29-100
Acenaphtylene	21,5			29-100
Fluorene	15,4			29-100
Phenanthrene	43			29-100
Antracene	61,5		5-100	29-100
Fluoranthene	15,4			29-100
Pyrene	7,7			1,1-1,8
Benz(a)antracene	6,2		0,5-12,5	1,1-1,8
Chrysene	6,2			1,1-1,8
Benzo(b)fluoranthene	6,2			1,1-1,8
Benzo(k)fluorantene	6,2			1,1-1,8
Benzo(a)pyrene	0,6	0,15	0,1-7,5	1,1-1,8
Indeno(123cd)pyrene				1,1-1,8
Dibenz(ah)antracene			0,1-30	1,1-1,8
Benzo(ghi)perylene			5-50	
ΣPAHS				

PH. PH value of produced biochar generally varies in a range from 4 (slightly acid) to 12 (strongly alkaline), even if only the alkaline ones are commonly used for soil amendments. It mostly depends on form and quality of mineral ashes, functional surface groups, soluble hydroxides and carbonates and pyrolytic condensates [4]. Typically, the main parameters that influence pH are feedstock and highest treatment temperature; showing higher values by increasing the temperature and by using manures as raw materials.

In order to compare the resulting value of the biochar chemical characterization obtained in this work some significant references values are reported in Table 2, focusing on same HHT but different kind of original raw materials. As we can see from the table, all biochar produced by different feedstock present a pH value around 10 (alkaline). All the manure derived products have a higher ash content value with respect to the vegetal wastes, the maximum value of 69,6% is found for pig manure and the minimum for wood (3,5%). As expected, all the biochars has a high C content value ranging from 41,5% of poultry manure to the almost 80% of wood.

Table 2 Reference values for chemical properties present in literature. Figures focused on different kind of feedstock with similar highest treatment temperature. (Abbreviations: FD feedstock, HTT highest treatment temperature, RT residence time, MS moisture content, VM volatile matter, FC fixed carbon, REF reference). All data are expressed on dry basis.

FD	**HTT**	**RT**	**ASH**	**VM**	**FC**	**C**	**H**	**S**	**N**	**O**	**PH**	**REF**
	[°C]	[h]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[#]	[#]
wheat-straw	600	150	12	-	-	73,4	2,1	-	1,4	14,9	9,2	[18]
corn straw	600	150	18	-	-	58,6	2	-	2	18,7	10,4	[18]
peanut shell	600	150	11	-	-	71,9	2	-	1,6	15	9,6	[18]
wood	550	120	3,5	-	-	80,2	-	-	0,17	-	9,49	[19]
poultry manure	550	120	44,4	-	-	41,5	-	-	3,7	-	10,26	[19]
cow manure	500	240	67,5	17,2	14,7	-	-	-	-	-	10,2	[20]
pig manure	550	240	69,6	10,7	19,2	-	-	-	-	-	10,8	[20]
sawdust	500	240	9,94	17,5	72	-	-	-	-	-	10,5	[20]
diary manure	700	120	39,5	27,7	34,7	56,67	0,94	0,15	1,51	4,13	9,9	[21]
poultry litter	700	120	46,2	18,3	35,5	45,91	1,98	0,63	2,07	10,53	10,3	[21]
swine manure	700	120	52,9	13,4	33,8	44,06	0,74	0,85	2,61	4,03	9,5	[21]

Physical Properties

Specific Surface Area (SSA). Surface area is a very important characteristic as it influences all the essential soil functions for fertility such as water retention, air nutrient cycling and microbial activity. [11] The particles that compose the soil has usually a low specific surface area that makes the biochar a really effective tool on soil amendment having a much higher value. This property largely depends on the carbon mass, composing fundamental molecular structure, removed during pyrolysis process thanks in particular to HTT. In order to increase this parameter, several post-treatments and procedures can be performed. For example, the most spread treatment is to pre-wash with a diluted acid solution the feedstock before starting the carbonization. This will remove the inorganic matter resulting in a less amount of ashes, therefore loss of structure. Concerning the post-treatments activations, commonly adopted in industrial scale, two main categories are considered: the physical and chemical activations. Physical activation consists in partial gasification at high temperature (more than 900°C) by means of steam, carbon dioxide, air or a mixture of these oxidizing gases. On the other hand, chemical activation entails the use of zinc salts and phosphoric acid to the C precursors. It produces the so-called "super active" carbons but, in the meantime, it generates secondary pollutants that needed to be disposal [11]. Both methods increase the SA exploiting smaller pores that were unutilized. The SSA has been found to be strictly dependent on particle size distribution, in particular micro-pores contribution on total surface area is about the 70% while the rest is shared among meso- and macro-pores. [22] The evaluation of these property is usually carried out by Brunauer-Emett-Teller (BET) single or multipoint models. Usually the single one is recommended for biochar with a low variation on pore size distribution, differently, the multipoint model is more indicated for complex micro-meso and macro pores distributions, where the single one will bring to an overestimation or underestimation of the SSA value.

Particle Size Distribution (PSD). As mentioned above, the particle size distribution of biochars has a significant correlation with the specific surface area. However, it plays different roles depending on the size category. Pores are subdivided into three main categories: micro-pores ($d_{int} \leq 2\ nm$), mesopores ($2 < d_{int} < 50\ nm$) and macropores ($d_{int} > 50\ nm$). Micropores are mostly responsible for the surface area value and for the high adsorptive capacity of small molecules such as gasses or solvents, on the contrary, mesopores are more related to liquid-solid adsorption processes. Finally, macropores focus more on soil functions such as aeration, hydrology and habitat for soil microbes. PSD mostly depends on original feedstock, highest treatment temperature, heating rate and residence time too; it can be measured by nitrogen adsorption or scanning electron microscopy (SEM). Because off this, it is very important to manage all the different parameters in order to achieve the required average pore size for the desired application.

Density. A differentiation between two kinds of density is adopted: we can refer to a molecular level, highlighting the C-structure degree of packaging, called solid density; bulk density, for material consisting of multiple particles, their porosity and voids. Usually an inverse relationship exists between these two kinds of densities, an increase in solid density is accompanied by a decrease in bulk one, as porosity develops during pyrolysis. In fact, during this process the loss of volatile and condensable compounds from the initial phase of the biochars and the concomitant relative increase in graphite-like crystallites structure lead to the increase of solid density. [11]

Porosity. Biochar porosity has been widely investigated by Brewer et al [23]. They define porosity (ε) as: $\varepsilon = 1 - \frac{\rho_e}{\rho_s}$. Where ρ_e represents the envelope density, which is the sample mass divided by the total sample volume that would be measured if an "envelope" were placed around each individual sample particle; and ρ_s represents the skeletal density that is the sample mass divided by the sample skeletal volume, where skeletal volume is the volume occupied by the solid sample (and any pores not accessible to the analysis gas). This property, as can be easily assumed, has a direct relation with densities and pore size distribution, and it can be used as an effective parameter to characterize different kinds of biochars.

Cation Exchange Capacity (CEC). Cation exchange capacity is defined as the total amount of positive charge that can be exchanged per unit mass of soil. It influences the soil structure stability, nutrient availability (low CEC are more likely to develop deficiencies of potassium and magnesium), soil pH (the lower is the CEC of a soil, the faster the pH will decrease with time) and the soil's reaction to fertilisers and other ameliorants. [24]

Water Holding Capacity (WHC). This property, as CEC, is directly referred to soil and is defined as the amount of water that a given soil can hold for crop use. So, hand in hand with particle size distribution, it provides a large number of microenvironments for microbes to grow in and root hairs to penetrate.

Electrical conductivity (EC). It is the ability of a material to transmit (conduct) an electrical current; the electrical conductivity of soils varies depending on the amount of moisture held by soil particles. Sands have a low conductivity, silts have a medium conductivity, and clays have a high conductivity. Consequently, EC correlates strongly to soil particle size and texture. [25]

***Yield*.** Biochar yield is usually expressed as the ration between obtained biochar weight and original biomass weight ($Y = {}^{M_{biochar}}/_{M_{biomass}}$). This value, for all kind of original feedstock, is around the 30%. However, it can be expressed also on dry, ash free, carbon and energy basis highlighting the desired property.

In order to compare the resulting value of the biochar chemical characterization obtained in this work some significant references values are reported in Table 3, focusing on same HHT but different kind of original raw materials. As the figures in the tables highlight, the specific surface area of the different biochars strongly depends on the single original feedstock, having as maximum values of 203 and 186,5 m^2/g for sawdust and dairy manure respectively; on the other hand, swine manure and corn-straw biochars present the lowest values (4,11 and 7). Concerning yield production, as expected, almost all kind of raw material result in 30% of final byproduct; on average, manure derived biochars show a higher value than the agricultural waste ones. In the same way, CEC figures of manures are 5 times higher than the others.

Table 3 Reference values for physical properties present in literature. Figures focused on different kind of feedstock with similar highest treatment temperature. (Abbreviations: FD feedstock, HTT highest treatment temperature, RT residence time, SSA specific surface area, CEC cation exchange capacity, EC electrical conductivity, PS particle size, REF reference). All data are expressed on dry basis.

FEEDSTOCK	**HTT**	**RT**	**SSA**	**CEC**	**EC**	**YIELD**	**PS**	**REF**
	[°C]	[min]	[m^2/g]	[cmol/kg]	[dS/m]	[%]	[nm]	[#]
wheat-straw	600	150	177	1,3	-	24,6	2,5	[18]
corn-straw	600	150	7	20,1	-	26,7	6,3	[18]
peanut-shell	600	150	185	1,2	-	28,5	2,4	[18]
wood	550	120	-	15,8	0,17	-	-	[19]
poultry manure	550	120	-	28,3	7,64	-	-	[19]
cow manure	500	240	21,9	149	-	57,2	5,04	[20]
pig manure	550	240	42,4	132	-	28,3	5,8	[20]
sawdust	500	240	203	41,7	-	35,8	2,23	[20]
dairy manure	700	120	186,5	-	0,702	35	-	[21]
poultry litter	700	120	50,9	-	2,22	36,7	-	[21]
swine manure	700	120	4,11	-	0,194	36,4	-	[21]

2.1.3 Biochar quality depending on feedstock composition

As Table 2, Table 3 and Qambrani et al.´s work [26] show, original feedstock selection has a significant influence on biochar properties and its elemental composition, especially in the proportion of organic and inorganic compounds. Raw materials that contain high nutrients (i.e. manures) result in biochar with high nutrient content compared with plant ones that have bigger amounts of cellulose, hemicellulose and lignin. Concerning final structure, O-rich and H-poor feedstock materials develop a stronger system of cross-linkages, resulting in more compact mass. Pyrolyzed manure shows a higher level of P and C, while the N content usually decreases due to loss of volatiles components (higher than in plant-based ones). On the other hand, in vegetal waste biochars C and N values increased, as well as P but with a lower trend.

Most of the properties listed above are mainly affected by HTT, but their order of magnitude is given by the selection of the original material. This is especially true for functional group composition, which, as Fourier-transform-infrared (FTIR) analyses demonstrate, are primarily determined by the type of feedstock and after by temperature range used during its formation. [26]

2.1.4 Applications

As described above (2.1.1), global interest in biochar application for environmental management raised only in the recent years after its social and financial benefits have been recognized. This application covers four main areas, linked one to the other: soil improvement, waste management, climate change mitigation and energy production (Figure 2). [11]

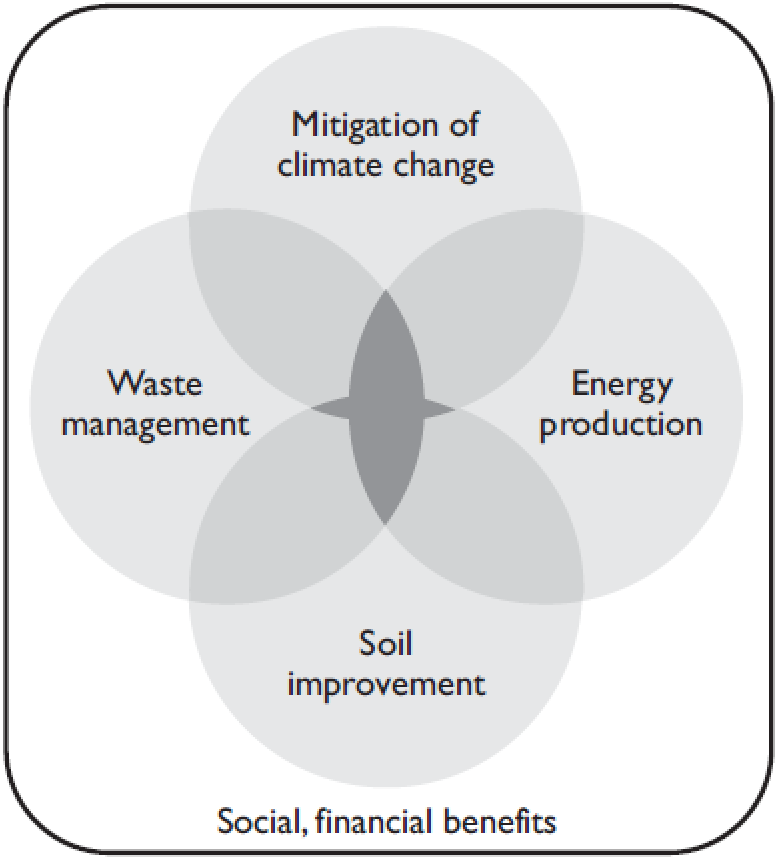


Figure 2 Motivation for applying biochar technology [11]

Biochar as a soil amendment

In developed and even more in developing countries, where soil fertility is a necessity and not an improvement, loss and degradation of agricultural field, resulting in low nutrient content and mineralization of soil organic matter, is nowadays a challenge that needs to be counteracted. For the firsts is mainly due to the massive and intensive use of agrochemicals that compromise the soil and water resources properties such as soil acidification, soil organic matter (SOM) depletion and severe soil erosion. [4] A common practice to decrease the use of chemical fertilizers is the addition of organic matter as manure and/or compost, but with a lower efficiency and a much bigger amount of material added in the field. On the other hand, in developing countries, both lack of technologies and harsh environment make sustainable agriculture and food security a very hard goal to be achieved. Here, a common technique to fertilize soils, comparable to biochar adoption, is the so called “slash-and-burn” fertilization method, which consists in burning vegetation wastes directly above the field, with a negative impact on deforestation and air pollution. [13] Considering all these factors, biochar provides a significant opportunity to improve soil quality in both areas since it uses locally available and renewable materials without a drastic impact on the ecosystem and with a rapid return on investment for farmers. In fact, this adoption does not require new resources, but makes more efficient and more environmentally conscious the use of existing ones. [11] Biochar must be seen as an addition to already existing fertilizing approaches and not as an alternative one.

Concerning biochar impact on soil quality, several studies has investigated its main effects. For example, Mukherjee et al [27] demonstrate that the response of soils to biochar amendment varies depending on rate of biochar application, biochar type and time of application. In their work, they report how incorporation of biochar enhance specific surface area up to 4,8 times that of adjacent soils and increase the water holding capacity in different kind of soil (major in sandy loam ones). More specific, Zheng et al [13] report the influence of two kind of biochar (corn cobs and wood chips), produced at 450°C for 60 min, on corn yields by adding them into the standard corn growing practices (cultivation, fertilization and control). They conclude that the application of biochar significantly increases crop yields even in the absence of nitrogen fertilizer (18% and 23%); a more significant increase has been found with N-fertilizers about 72% and 44% for corn and wood respectively. In addition, their work also shows that, after harvesting, the soil organic matter, soil pH, available phosphorus, and CEC generally increased in the field plots treated with biochar.

The majority of laboratory studies focus the attention on the short-term effects of biochar addition to soil. However, Jones et al [28] investigated the impact of biochar on crop performance and soil quality on longer period (3 years). They applied a commercial available biochar into maize standard farming practices, investigating the vegetation and soil responses (microbial growth, C cycling and N cycling). Results show a no significant difference in growth of maize crop, germination efficiency, seedling emergence rates and leaf chlorophyll content in the first year, a relevant effect on the nutritional quality of subsequent grass crop and an increase in foliar N content in year two; and only an increase in grass biomass production in the last year. Concerning soil, biochar had a small but positive effect on pH (best result in the second year), while others physical properties were not significantly affected. Others little effects were on soil organic matter, C turnover and N cycle (mineralization and nitrification). However, soil respiration has increased and higher growth rates of fungal and bacteria communities have been noticed over the whole period.

In conclusion, biochar application as a soil amendment present an overall good impact both in short and long terms; the main drawbacks are related with availability, economic cost and practical aspects such as wind erosion and human inhalation.

Biochar to manage wastes

All different kinds of waste, such as forest residues (logs, dead wood, branches), mill residues (lumber, pulp, veneers), field crop residues, urban wastes and animal ones, pose a significant environmental burden that leads to ground and surface water pollution [11] [26] [29]. Such materials can be considered economically and ecologically attractive since they can be used in a pyrolysis process as feedstock for an indirect energy production. The main advantage of pyrolysis is that the volume and the weight of waste material is considerably decreased, both reducing waste-disposal costs associated with traditional methods of waste management and offering energy services to agriculture and industry. As a matter of fact, traditional disposal strategies result less effective than biochar solution, for example the land filling of organic waste and the anaerobic digestions of animal ones result in the release of methane and nitrous oxide, and these gases are 25 and 300 times, respectively, more potent as GHGs than CO_2. [26] Moreover, the production of biochar rather than composting could better immobilize carbon. The produced biochar can be adopted as a soil amendment, as deeply discussed above, or as a tool for the removal of organic and heavy metal contaminants from aqueous media in water and wastewater treatment technology. This particular application, mostly depend on surface functional groups (OH, COOH, ketones, etc.) and its net negative surface charge. These properties make the biochar a super-sorbent for the removal of both organic and inorganic contaminants (Al, Mn, As, Cd, Cu, Ni and Pb). In particular, concerning lead adsorption, biochar has been found considerably more effective with respect to activated carbons. [30] [31]

In conclusion biochar production from wastes material represents a better alternative to traditional residual disposal technique since it significantly decreases the final greenhouse gasses (GHG) emission independently on its kind of application.

Biochar to mitigate the climate change

Biochar applied to soil not only brings to an improvement of soil quality, but it even has a secondary effect on mitigate the climate change by sequestering carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O). In particular, due to its stability and recalcitrant nature, it makes these gases staying for a much longer period in the soil, slowing down the N and C cycles (Figure 3). This basically consists in the so called "Carbon sequestration process" in which carbon is captured and stored, preventing to be emitted into the atmosphere, in a passive carbon pool that is stable or inert. [26] Even if the annual CO_2 uptake by plants through photosynthesis is 8 times bigger than anthropogenic one, it is estimated that only redirecting a small amount of carbon into biochar will hugely diminish its concentration in atmosphere.

As a matter of fact, agriculture consists in one of the primary contributors of GHGs emission: it contributed 42% of the total of the 8% GHG emissions attributable NO_2 in 2004 and methane, mainly due to livestock originated from manure (indirectly related to agriculture), made up almost the 14%. [14]

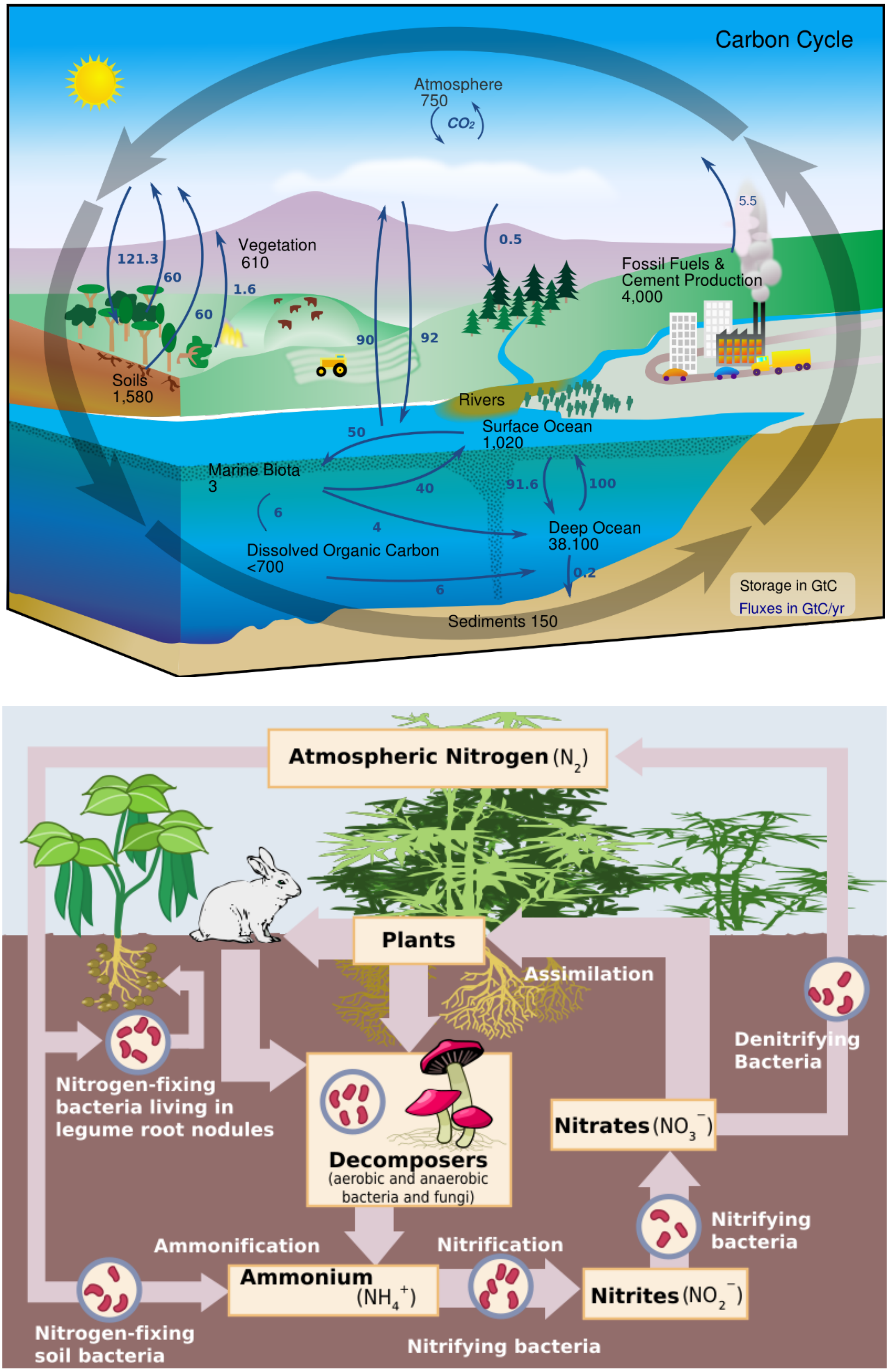


Figure 3 Schematic representation of the flows of carbon, storage and exchange, (above) [32]and nitrogen (below) through the land environment [33]

Briefly, atmospheric CO_2, in the carbon cycle, is fixed by photosynthetic organisms and then it is converted into biomass that is mixed with soil when these organisms die. The biomass in soil is mineralized and microbial respiration causes the evolution of CO_2 to the atmosphere. [26] Switch even a small amount of the carbon cycling between the atmosphere and plants into a much slower biochar cycle would greatly affect the total CO_2 emission: Gai et al. estimates, for example, that "*the diversion of 1% of net annual plant uptake into biochar would mitigate almost 10% of current anthropogenic carbon emissions; moreover, converting biomass carbon to biochar carbon enables up to 50% of the initial carbon to be sequestered in a relatively stable form*", depending mostly on the original feedstock. [26] [14] So, the biochar acts as a passive carbon sink remaining in the soil for long periods (see Figure 4), thanks to high levels of resistance to chemical and biological degradation; despite this, some indirect sources of carbon dioxide due to pyrolysis product burning and C-cycle must be taken into account.

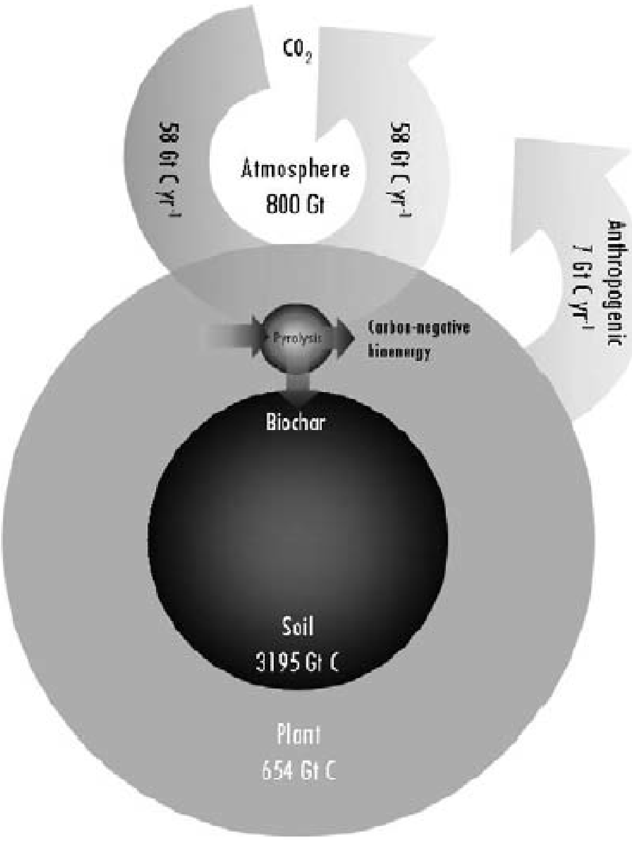


Figure 4 "*The global carbon cycle of net primary productivity (total net photosynthesis flux from atmosphere into plants) and release to the atmosphere from soil (by microorganisms decomposing organic matter) in comparison to total amounts of carbon in soil, plant and atmosphere, and anthropogenic carbon emissions (sum of fossil fuel emissions and land-use change)*" [11]

Methane emissions from soil are connected with anaerobic conditions, typical of wetlands, paddy fields, and landfills, where methanogenesis process by microorganism is promoted. CH_4, as greenhouse gas, is almost 25 times more powerful than CO_2 in absorbing thermal radiation, which makes it a serious hazard for global warming. Nevertheless, applying biochar to soils shows a huge decrease of methane emission. Rondon et al. found that methane emissions were close to zero when biochar was applied at a rate of 2% (w/w) to soil. [34] These values, however, significantly depends on biochar properties, type of soil, soil microorganism and management of water and fertilizer; in any case, the increasing of soil aeration is the wisest explanation for this phenomenon because it may lead to further reductions in the frequency and extent of the anaerobic conditions.

Nitrous oxide is produced by soil microorganisms through nitrification and denitrification (see Figure 3) and is 300 times more effective than CO_2 concerning global warming. Its production from agricultural sources is greatly affected by the presence of moisture in soil and nitrogen fertilizers. Biochar application to soils show a huge reduction of N_2O, ranging from 50% to 80%, depending on soil type and application rates (no reduction has been seen for rates lower than 10%). [26] [14] In addition, biochar improves the biological immobilization of inorganic N decreasing ammonia volatilization, as it contains low N concentrations and high C/N ratios.

As examples sustaining the positive effect of biochar to mitigate climate change, by efficiently adsorbing NH_3, CO_2, N_2O from soil have been reported by Xiapu et al. [18] and Singh et al. [19]. In particular, the latter applied four different kind of biochar in two different kind of soils, investigating their effects over three wet and dry cycles. Results shows that both N_2O and CO_2 emissions were affected by biochar, soil, time and biochar x soil x time during all the W-D cycles; the greatest emissions were during the firsts days of application but on a longer time all of them showed a decreasing trend with respect to the control soils.

Biochar for energy production

Energy production in biochar field has a double nature, both direct and indirect; in fact, as mentioned above, pyrolysis byproduct: syngas and bio-oil (35% and 30% on the total) can be burnt to generate heat (indirect), and biochar itself can be used as a fuel (direct). Even if the direct usage is not a common practice nowadays, the biochars present a high heating values not so different from the original biomass. In particular, in Cantrell et al.´s work [21], it shows a slight increase using low HHT (i.e. 300-400°C) and almost the same value of original feedstock with higher temperatures.

Much more attractive is the production of syngas and bio-oil as a source of green energy for a future supply. Most likely, they will never be able to satisfy the future energy demand or solve energy crises on its own, but, in any case, even a small fraction of the global potential of these sources will be an important help, better than the direct burning of biomass. This will be addressed particularly in the regions with low energy distribution availability (Asia and Latin America). [11]

2.1.5 Legislation

Since the concept of biochar as a soil amendment and a climate change mitigator is relatively new, national and international legislators are not yet adequately prepared about its production and application. Presently, governmental agencies involved in agricultural and environmental fields are preparing new regulatory plans specifically for the biochar; in the meanwhile, they have modified existing national legislations for fertilizers, soil improvers and composts to guarantee its application on soils. As a result, voluntary biochar product standards have been developed by non-governmental associations such as European Biochar Certificate (EBC, 2012) by European Biochar Foundation and Biochar Quality Mandate (BQM, 2014) by British Biochar Foundation in Europe, and International Biochar Initiative Biochar Standards (IBI-BS, 2015) by International Biochar Initiative in United States.

In order to understand the general picture of biochar standardization, current and future legislation in the main countries, Meyer et al. [35] and Van Laer et al. [12] deeply investigate this topic in their reviews. They found that all voluntary product standards have the aim to guarantee the sustainability and/or the quality of the biochar, enabling the consumer to better understand and select the right product among a different variety.

For IBI-BS biochar products must have a carbon content of at least 10% and an H/C ratio of less than 0,7. As a common feature for all the standards, it makes compulsory to declare biochar main properties (moisture content, total ash content, total nitrogen content, pH-value, electrical conductivity, $CaCO_3$ content and particle size distribution) and to respect thresholds for heavy metals and organic pollutants including polycyclic aromatic hydrocarbons (PAH); polychlorinated biphenyls (PCBs); polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). [35] In addition, biochar producers must keep records of feedstock (chain of custody and test result), any kind of raw material can be utilized, except for hazardous municipal solid waste. Besides, a GHG balance for the obtained product is not mandatorily required.

Similarly, BQM defines the biochar and requires the key properties of the product, with an additional concerning on Maximum Permissible Limits (MPL) for toxicants and a proposal in which the maximum net life-cycle GHG emissions (plus particular matter, volatile organic compounds and carbon monoxide) per unit of feedstock consumed should be lower than the respective one of directly burnt biomass. BQM identifies two quality grades, standard and high, mainly due to MPL and heavy metals threshold and more generally evaluates its sustainability, by monitoring the source of the biomass (including chain of custody), both evidencing that the biomass source has to be legally and sustainably managed, and both by means of Life Cycle Assessment (LCA) methodology to ensure that a minimum greenhouse gas saving is met compared to alternative uses of the biomass. [35]

On the other hand, stricter guidelines and more detailed requirements are present in the EBC. In fact, it introduces annual inspections of production plants (only for above 50 ton/year size) and precise analytical methods for all the analysis, that must be conducted by accredited laboratories. This certificate aims to introduce a control mechanism based on the latest research and practices. They provide customers with a reliable quality control assessment, to give producers the opportunity of demonstrating that their product meets well-defined quality standards, providing a firm state-of-the-art knowledge transfer as a sound basis for future legislation; and to prevent and hinder misuse or dangerous actions from the start. [10] BQM identifies two categories of biochar (basic and premium quality) with its own threshold values and ecological requirements; on the contrary, the EBC sets also limits on the usable raw materials, listing all the allowed biomass feedstock in an annex. Moreover, others environmental aspects of the production process including emissions, energy efficiency, heat recovery, feedstock procurement (e.g. the feedstock should in general not transported more than 80 km to the pyrolysis plant), biochar storage, fire and dust protection, handling, and labelling are controlled. [35]

In order to better visualize analogies and differences among the different voluntary standards and the regulations existing in some countries, the main features and their thresholds are reported in Table 4 -Table 5 -Table 6.

Table 4 Overview of voluntary biochar standards, existing biochar legislation and biochar legislation proposals [35]

		Voluntary product standards					National legislation					
		IBI–BS	EBC		BQM		Germany	Austria	Switzerland	Italy	EC regulation 2003/2003	EC regulation 2003/2003
			Basic	Pre-mium	Standard Gr.	High Gr.	Fertilizer Ordinance	Fertilizer Ordinance Soil Improvers etc.	Fertilizer Ordinance[4]	Fertilizer Decree #75	REFERTIL recommendations	ESPP Suggestion
Summary of the standard	Subchapter	1.1	1.2		1.3		2.1	2.2	2.3	2.4	3.1	3.3
Quality requirements for biochar	Unit											
Organic Carbon content	(%)	≥10	≥50 for biochars		≥10[2]		>80	–	≥50	≥20	≥50 for PBC, declaration for ABC	>30
Hydrogen/Organic Carbon – Ratio		≤0.7	<0.7		≤0.7		–	–	<0.7	≤0.7	Optional declaration	<0.7
Oxygen/Organic Carbon – Ratio		–	<0.4		–	–	–	–	–	–	–	–
Total ash content	%	–	–	–	–	–	–	–	–	≤ 60%	Optional declaration	–
pH–Value		–	–	–	–	–	–	–	–	4–12	6–10	–
Salinity (electrical conductivity)	mS/m	–	–	–	–	–	–	–	–	≤1000	Optional declaration	–
Moisture content (of powdery biochar)	%	–	≥30		≥20		–	–	≥30	≥20	≥40% for PBC, ≥20% for ABC	30–40%[9]
Germination Test		Pass	–	–	–	–	–	–	–	Reporting Obligation	Mandatory	–
Worm Avoidence Test		–	–	–	–	–	–	–	–	Reporting Obligation	–	–
Organic Pollutants												
PAH content (US EPA 16)	mg/kg dm	≤300	<12	<4	<20	<20	–	<6	≤4	<6	≤6[5]	<6
B(a)P toxic equivalency	mg/kg dm	≤3	–	–	–	–	–	–	–	–	–	–
PCBs	mg/kg dm	≤1[1]	<0.2		<0.5		–	<0.2	–	<0.5	≤0.2	<0.2
PFTs (PFOA and PFOS)	mg/kg dm	–	–	–	–	–	≤0.1	<0.1	–	–	–	–
PCDDs/Fs toxic equiv. (I–TEQ$_{DF}$)	ng/kg dm	≤17	<20		<20		≤30[3]	≤20	≤20	<9	≤20[6]	<20
Campylobacter species pluralis		–	–	–	–	–	–	not detectable in 50 g.	–	–	–	–
Escherichia Coli		–	–	–	–	–	–	not detectable in 50 g.	–	–	1000 CFU/g for E. Coli[7]	–
Listeria moncytogenes		–	–	–	–	–	–	not detectable in 50 g.	–	–	–	–
Salmonella species pluralis		–	–	–	–	–	–	not detectable in 50 g.	–	–	No salmonella sp. in 25 g[7]	–

Table 5 Continue of Table 4

		Voluntary product standards					National legislation					
		IBI–BS	EBC		BQM		Germany	Austria	Switzerland	Italy	EC regulation 2003/2003	EC regulation 2003/2003
			Basic	Pre-mium	Standard Gr.	High Gr.	Fertilizer Ordinance	Fertilizer Ordinance Soil Improvers etc.	Fertilizer Ordinance [4]	Fertilizer Decree #75	REFERTIL recommendations	ESPP Suggestion
Heavy Metals												Draft limits for organic soil improvers
Arsenic (As)	mg/kg dm	≤100	<13	<13	≤100	≤10	≤40	≤40	–	–	≤10	–
Cadmium (Cd)	mg/kg dm	≤39	<1.5	<1	≤39	≤3	≤1,5	≤3	≤1	≤1.5	≤1.5	≤3
Chromium (Cr)	mg/kg dm	≤1200	<90	<80	≤100	≤15	–	–	–	–	≤100	–
Chromium VI (Cr VI)	mg/kg dm	–	–	–	–	–	≤2	≤2	–	≤0.5	≤0.5	≤2
Cobalt (Co)	mg/kg dm	≤100	–	–	–	–	–	–	–	–	–	–
Copper (Cu)	mg/kg dm	≤6000	<100	<100	≤1500	≤40	–	–	≤100	≤230	≤200	–
Lead (Pb)	mg/kg dm	≤300	<150	<120	≤500	≤60	≤150	≤100	≤120	≤140	≤120	≤150
Mercury (Hg)	mg/kg dm	≤17	<1	<1	≤17	≤1	≤1	≤1	≤1	≤1.5	≤1	≤1 – 1.3
Manganese (Mn)	mg/kg dm	–	–	–	–	≤3500	–	–	–	–		–
Molybdenum	mg/kg dm	≤75	–	–	≤75	≤10	–	–	–	–	–	–
Nickel (Ni)	mg/kg dm	≤420	<50	<30	≤600	≤10	≤80	≤100	≤30	≤100	≤50	≤90
Selenium (Se)	mg/kg dm	≤200	–	–	≤100	≤5	–	–	–	–	–	–
Thalium (TI)	mg/kg dm	–	–	–	–	–	≤1	–	–	–	–	–
Zinc (Zn)	mg/kg dm	≤7400	<400	<400	≤2800	≤150	–	–	≤400	≤500	≤600	–
Additional requirements												
Feedstock limitations		No hazar-dous muni-cipal solid waste	Detailed positive list of permitted feedstocks		Only biomass feedstocks		Only chemically untreated wood	–	Only chemically untreated wood	Biomass of vegetable origin from agriculture and forestry,olive pomace, grape marcs, cereal bran, fruit stones and woodshells, non–treated residues of wood processing	Biomass by–products only. Biomass feedstocks that do not compete with human food–, animal feed–, plant nutrition production and supply. For other alternative feedstocks alternative criteria have still to be developed.	No hazardous chemical wastes, hospital wastes, radioactive materials and (mixied) MSW (waste streams with more than 5% mixed, unsorted or residual municipal solid refuse
Feedstock sustainability requirements		–	Yes		Detailed requirements		–	–	–	–	Yes	–

Table 6 End of Table 4

		Voluntary product standards					National legislation					
		IBI-BS	EBC		BQM		Germany	Austria	Switzerland	Italy	EC regulation 2003/2003	EC regulation 2003/2003
			Basic	Pre-mium	Standard Gr.	High Gr.	Fertilizer Ordinance	Fertilizer Ordinance Soil Improvers etc.	Fertilizer Ordinance [4]	Fertilizer Decree #75	REFERTIL recommendations	ESPP Suggestion
Admitted production technologies		Not speci-fied	Pyrolysis and Gasification		Not specified		Not specified	Not specified	Pyrolysis and Gasification	Pyrolysis and Gasification	Pyrolysis (reductive thermal processing)	Pyrolysis / Gasification
Minimum/Maximum process temperature		–	Min: 350 °C Max: 1000 °C		–		–	–	–	–	Min. 450 °C, Max. 850 °C (material core temperature)	–
Admitted PAH analysis methods		Soxhlet with toluene (EPA 8270 EPA 3540)	DIN EN 15527:2008–09 with toluene / DIN ISO 13887:1995–06: Principle B		DIN EN 15527:2008–09 DIN ISO 13887:1995–06: Principle B		n.a.	Methods according to the state-of-the-art of science and technology	Extraction solvent toluene mandatory	Not defined	CEN/TS 16181:2013 (PAH16, PAH19) [8]	DIN ISO 13877:1995–06 Principle B (Soxhlet Extraction with toluene) or DIN EN 15527:2009–09 (ultrasonic extraction/ shacking or soxhlet extraction with toluene)
GHG balance standard for biochar product		–	Standards to avoid GHG emissions		Positive GHG balance obligatory		–	–	Standards to avoid GHG emissions	–	Standards to avoid GHG emissions	–
On-site verification		–	Yes		–		–	–	Yes	–	Yes	Not decided yet

Abbreviations used in the table:

ABC –	Animal Bone Biochar;
B(a)P –	benzo(a)pyrene;
C org –	Organic carbon;
Dm –	dry matter;
Gr –	Grade;
H –	hydrogen;
mS/m –	MiliSiemens per meter;
PBC –	Plant derived Biochar;
PFOA –	Perfluorooctanoic acid;
PFOS –	Perfluorooctane sulfonate;
PFTS –	Perfluorinated tensides.

Notes:

1. US EPA 7.
2. 10% stable organic carbon which is estimated to remain in the soil after 100 years.
3. ≤8 if the product is used on pastures for fodder production or on arable land without tillage.
4. in combination with the ChemRRV-ordinance and the approval of the Swiss WBF.
5. PAH19s are recommended pre-normative for future EU legislation.
6. Mandatory measurement only if PCB > 0.07 mg/kg.
7. Sampling frequency proposed for <1000, <5000 and >10,000 t/y throughput material processing capacities.
8. Wessling Group recommends a modification of draft prEN 16181:2010.
9. For biochars with >10% of particles diameter < 100 µ.

2.2 Pyrolysis

Concerning pyrolysis process field, a brief analysis of the actual state of art has been reported in the next paragraphs. The focus has been posed on its definition and subcategorization, reflecting on pyrolysis by-product yields, and on the influence of process parameters (temperature, heating rate and residence time) on obtained biochar properties.

2.2.1 Definition

Pyrolysis is one of the main thermochemical processes commonly used to convert biomass into more energy valuable byproducts as bio-oil (condensable liquid), biochar (solid) and synthesis gas (non-condensable gases). Unlike previous methods of producing fuel by waste residues, pyrolysis has the main benefit to exploit emissions of the thermochemical degradation condensing them into bio-oil. This process, under anaerobic conditions, high temperatures and pressures, makes the main structures of biomass (cellulose, hemicellulose and lignin) to cross-link, depolymerize and fragment at different specific temperatures. [14] [26] [29] The required heat is usually insured by external sources such as heaters, but in some cases, it can be provided by burning part of original biomass and byproducts or, in more efficient plants, by recirculation of final hot-gases.

Pyrolysis process, depending on temperature, heating rate and residence time, leads to different values of biochar, bio-oil and syngas yields. A subdivision of different kinds of pyrolysis, with its specific range values of process parameters, has been made focusing on the main desired yield. As can be easily deduct, maximizing one single yield relative to original feedstock is always at the expense of the others two. Pyrolysis subclasses are generally known as slow pyrolysis, fast pyrolysis and gasification.

Slow pyrolysis focuses on the production of biochar, having an almost equal percentage with syngas content (see Table 7). Long residence times (several hours), low heating rates (0,01-2 C°/s) and a temperature range between 300-700 C° are common values of this category. These values result in a decreasing of liquid production, benefiting biochar, by improving cracking reactions. [26] [29] Its main attraction is the easily possible application on small scales, due to atmospheric pressure conditions and moderate temperatures.

Fast pyrolysis, instead, has the highest result in bio-oil production and the lowest in biochar (75% and 12% respectively, see Table 7). This is due to the fact that it has been developed and optimized before the understanding of biochar as a valuable product and not as a waste. At that time, bio-oil represented the highest valued product with different applications (i.e. direct use in non-modified engines). Improving the depolymerization phenomena during pyrolysis is the main responsible of such a high bio-oil yield. This is obtained by short residence times (few seconds), rapid heating rate (HR>2 C°/s) and temperature range between 500-1000 C°. The biochar obtained by this pyrolysis category is mainly composed by recalcitrant conjugated aromatic structure. [26]

Gasification is a process that converts carbonaceous materials into carbon monoxide (CO), hydrogen (H_2) and carbon dioxide (CO_2). So, the syngas content is almost the 85% of the total products with small amounts of biochar and bio-oil, 10% and 5% respectively (see Table 7). This value is achieved by means of high temperature (750-900 C°) and short residence time (dozens of seconds). Differently from the other kinds of pyrolysis, in gasification, the limited oxygen environment can also be achieved by means of steam. Global interest on producing syngas is nowadays well confirmed since it can be used as a fuel both in existing gas turbines and fuel cells, showing higher calorific values and efficiencies with respect to the original biomass.

In order to summarize, in Table 7 average yields from different biochar production technologies are reported. Concerning maximization of biochar yield, the main factors are: high lignin, ash and N contents in original feedstock, low highest treatment temperature and heating rate; and long residence time. [29]

Table 7 Averaged percentage of yields from different kind of biochar production technologies [26]

PROCESS	**TEMPERATURE**	**RESIDENCE TIME**	**YIELDS**		
			BIOCHAR	**BIO-OIL**	**SYNGAS**
Slow Pyrolysis	300-700°C	hours-days	35%	30%	35%
Fast Pyrolysis	500-1000°C	< 2s	12%	75%	13%
Gasification	750-900°C	10-20 s	10%	5%	85%
Hydrothermal Carbonisation (HTC)	180-300°C	1-16 h	50-80%	5-20%	2-5%
Torrefaction	300°C	10-60 min	80%	0%	20%

2.2.2 Parameters and their effect on biochar production

In order to produce a tailor-made biochar for the desired application, a knowledge about how original feedstock and pyrolysis parameters influence biochar properties must be known. As previously mentioned (see 2.1.3), almost all biochar properties values are affected by main process parameters as highest treatment temperature (HTT), residence time (RT) and heating rate (HR). Approximately all works present in literature show a good agreement concerning these relationships [26] [36], independently on the selected biomass (manure [20] [21], crop-straw [20] [22] [37] [38] or wood [20] [37] [38] [39] [40]).

In particular, it is reported that increasing HTT results in a growth of specific surface area, CEC, pH, recalcitrance and ash content values; while yield, H and O contents, and volatile matter decrease. Temperature has also been found to influence biochar final structure, since low temperature biochars show a more aliphatic and cellulose one, resulting in a variation of sorbent capacity. [26]

On the other hand, heating rate is not reported to have a significant influence on properties except for yields. In fact, higher HRs increase bio-oil production, while lower values, enhancing devolatilization, result in a major biochar yield. [26] As an example, Gheorghe et al. [40] report that doubling the HR the biochar yield decreases by 10% changing the heating rate from 5 to 10°C/min (using cherry sawdust as feedstock).

Also, residence time has been found to have a less significant influence on final biochar properties than HTT, particularly in slow pyrolysis. Nevertheless, rising residence time leads to a decrease of biochar yield, H, O and volatile matter contents; while, heating value, SSA and C content increase. [36] As reference, Ronsse et al. [39] investigated the influence of two different residence times (10 and 60 min) on biochar properties obtained by pyrolyzing pine wood, wheat straw, green waste and algae at 300, 450, 600 and 750°C. They conclude that all the properties were mainly influenced by HTT and slightly by residence time, which only affects biochar yield at low temperatures (from almost 90% to 50% at 10 and 60 min respectively at HTT<450°C) and higher heating value that marginally increase by increasing RT.

3. Experimental

3.1 Biochar Production

3.1.1 Materials

Horse stable residues, consisting of horse manure, peat and wood sawdust, have been used in this research to produce biochar. All these wastes have been taken directly from a horse riding school close to the city of Helsinki. Specifically, the used peat is a commercial one named "BALTIC PEAT" produced in Estonia with an organic matter content of minimum 90%, pH value of 3,5-4,5 and a humidification grade of H2-H6 (all data are taken from product label). Also, the wood sawdust is a commercial available one, named "POLKKYpets" and produced by the company "Pölkky Oy" (Finland) from Finnish pine and spruce sawn timber.

3.1.2 Sample preparation

The "as received" moisture content of manure and peat was found to be enormously bigger in respect to the sawdust one, almost 53% for peat and even bigger for manure (68% [4]). Since this work aims to characterize a mixture of these three elements, it can be assumed that, in industrial scale, this mixture will undergo to a drying process before being pyrolyzed. So, in order to make the all values more comparable, peat and manure initial moisture content have been reduced by drying. In particular, horse manure has been left for seven days at ambient temperature and forced ventilation, while peat has been dried in a ventilated oven at 40°C for almost 18 hours. All elements obtained moisture content values are shown in 4.2.

All the original biomasses have been grinded in order to achieve an average size about 2-5 mm. This process helped the homogenization of both pure materials, as peat is composed by different kinds of elements, and mixed materials. Seven different kinds of samples have been produced and characterized, each mixture composition is shown in Table 8, and all production have been made in triplicate for statistical reasons.

Table 8 List of all the samples used to produce biochar, with each specific original biomass composition

SAMPLE	HORSE MANURE	PEAT	WOOD
[name]	[%]	[%]	[%]
Manure	100	0	0
Peat	0	100	0
Wood	0	0	100
MPW	33,33	33,33	33,33
MP	50	50	0
MW	50	0	50
PW	0	50	50

3.1.3 Experimental setup

Pyrolysis of all the samples has been carried out in a quartz tube furnace (NBD-O1200, Nobody Material Science and Technology CO., LTD, China). Experimental setup scheme and photos are shown in Figure 5. Anaerobic conditions have been obtained by means of a 10 ml/min nitrogen flow, controlled by a flowmeter, and almost 2g of sample per crucible have been processed. In their previous work [4], Caro et al. have found optimal values of process parameters, specifically a heating rate of 10°C/min, an HTT of 600°C and a residence time of 2 hours. Synthesis gasses produced during pyrolysis have been condensed by means of a cooling system and all the treatments took place in a laminar flow suction hood with maximum aspiration level. The operating scheme of the furnace is shown in Figure 5C.

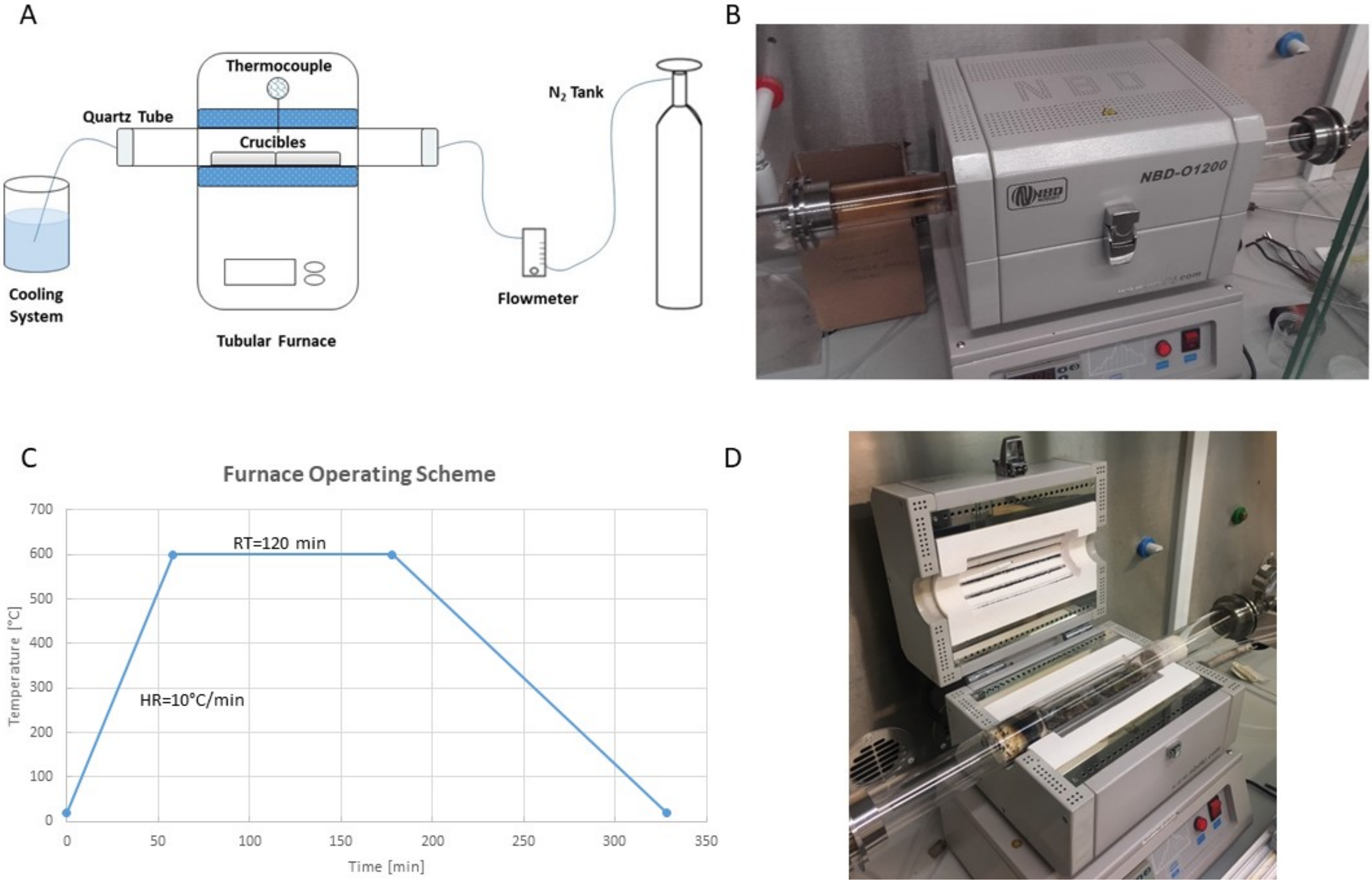


Figure 5 Experimental setup scheme (A), furnace operating scheme (C), closed furnace picture (B) and open furnace picture (D)

3.2 Biochar Characterization

3.2.1 TGA analysis

Thermo-gravimetric analysis (TGA) has been carried out for both original biomass and obtained biochar samples. It evaluates the mass change as a function of temperature or time. [4] [41] Thanks to this test, it is possible to understand the behavior of the material in function of increasing temperature. For this reason, it is used to assess thermal decomposition/stability and its kinetics, giving primary information about biochar yield and moisture, volatile matter, fixed carbon and ash contents. For this analysis a TA instrument named TGA Q500 (USA) has been adopted and its picture is shown in Figure 6. The used test method pathway was: heating the sample in inert environment (guaranteed by a 60 Nml/min flow of nitrogen) from 20°C up to 900°C with a heating rate of 10°C/min and a final 5 minutes-long isothermal combustion at 900°C with pure oxygen.

Figure 6 Picture of TA instrument (TGA Q500) with open furnace and unloaded pan

3.2.2 Proximate analysis

Proximate analysis, including moisture, volatile matter, fixed carbon and ash contents, has been conducted both for original biomass and obtained biochar. Concerning biomass all the analysis has been carried out following the reference ASTM standard. Precisely ASTM E1756-08 has been followed for moisture content (MC) [42], for which the content is obtained by a sample mass difference before and after a drying treatment of 24 hours at 105 ± 3°C in a ventilated oven (see Table 9). Ash content (ASH), instead, has been assessed following ASTM E1755-01 [43], by a sample mass difference in an open crucible before and after being left for 3 hours at 550 ± 25°C in a muffle furnace (see Table 9). Similarly, volatile matter content (VM) has been evaluated by a sample mass difference, this time using a closed crucible with a closely fitting lid, before and after a 7 minutes treatment at 950 ± 20°C, as indicated in ASTM E872-82 [44] (see Table 9). Lastly, fixed carbon content (FC) has been obtained as the difference between 100 and the sum of the other contents, as shown in Table 9.

On the other hand, proximate analysis for biochar samples has been carried out following EBC analytical methods [10]. These procedures are very similar to previous one, with only slight difference on set point temperatures.

A resume of equations and a picture of the muffle furnace used for proximate analysis is shown in Table 9 and Figure 7 respectively.

Table 9 List of equation used for proximate analysis (Abbreviations: MC moisture content, ASH ash content, VM volatile matter, FC fixed carbon)

CONTENT	EQUATION	EQUATION TERMS
MC	$MC = \frac{W_0 - W}{W_{S0}}$	W_0= sample+crucible initial weight; W= sample+crucible dry weight; W_{S0}= sample initial weight.
ASH	$ASH = 100 - \frac{W_0 - W}{W_{dS0}}$	W_0= dried sample+crucible initial weight; W= sample+crucible resulting weight; W_{dS0}=dried sample initial weight.
VM	$VM = \frac{W_i - W_f}{W_i - W_c}$	W_i= dried sample+crucible+lid initial weight; W_f= sample+crucible+lid resulting weight; W_c= lid+crucible weight;
FC	$FC = 100 - ASH - VM$	

Figure 7 Picture of muffle furnace used for proximate analysis

3.2.3 CHNSO analysis

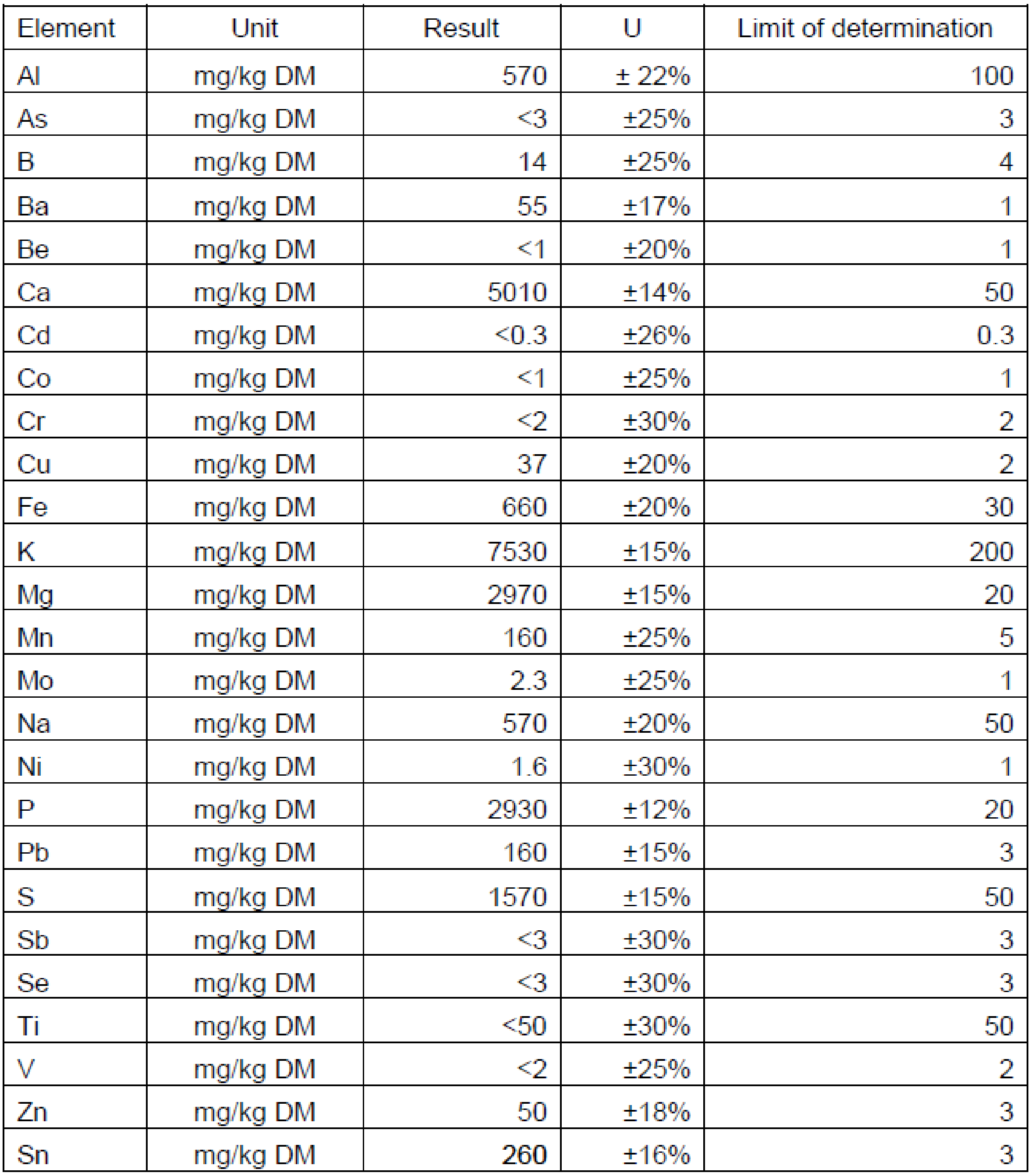
Carbon, hydrogen, nitrogen, Sulphur and oxygen contents of biochars have been determined by means of a Perkin Elmer CHNS/O 2400 series II analyzer (dry combustion method). In particular, C, H, N and S contents were directly measured by the device, while O is calculated as the difference between 100 and the sum of the other contents and ash, following EBC guideline [10]. This is due to the assumption that the sample is essentially consisted by these elements. This analysis, for mixing model design statistical reason, has been performed in triplicate for the MPW mix, in duplicate for the pure materials (M, P, W) and in single for MP, MW and PW mixtures (see 5).

Concerning original biomass CHNS/O one, reference data are shown in Table 10, in order to make a comparison with biochar measured values.

Table 10 Reference values of carbon, hydrogen, nitrogen, sulphur and oxygen contents of original biomass. (* S content for peat and wood contains also other elements)

SAMPLE	C	H	N	S	O	H/C	O/C	REF
MANURE	47,30 %	6,14 %	1,68 %	0,82 %	36,12 %	0,13	0,76	[4]
PEAT	56,00 %	5,00 %	1,00 %	1,00 %	37,00 %	0,09	0,66	[45]
WOOD	50,00 %	6,00 %	1,00 %	1,00 %	42,00 %	0,12	0,84	[46]

Usually this analysis is coupled with main elements and heavy metals analysis. In this work these kinds of analysis have not been performed since the high availability of these data in literature. As an example, Figure 8 shows elemental composition of manure biomass [4], where it can be easily noticed the high amount of nutrients (Ca, K, Mg, P, S). During pyrolysis, almost all of these elements remains in the obtained biochar having a higher concentration due to the loss of mass thought the process [21].



Element	Unit	Result	U	Limit of determination
Al	mg/kg DM	570	± 22%	100
As	mg/kg DM	<3	±25%	3
B	mg/kg DM	14	±25%	4
Ba	mg/kg DM	55	±17%	1
Be	mg/kg DM	<1	±20%	1
Ca	mg/kg DM	5010	±14%	50
Cd	mg/kg DM	<0.3	±26%	0.3
Co	mg/kg DM	<1	±25%	1
Cr	mg/kg DM	<2	±30%	2
Cu	mg/kg DM	37	±20%	2
Fe	mg/kg DM	660	±20%	30
K	mg/kg DM	7530	±15%	200
Mg	mg/kg DM	2970	±15%	20
Mn	mg/kg DM	160	±25%	5
Mo	mg/kg DM	2.3	±25%	1
Na	mg/kg DM	570	±20%	50
Ni	mg/kg DM	1.6	±30%	1
P	mg/kg DM	2930	±12%	20
Pb	mg/kg DM	160	±15%	3
S	mg/kg DM	1570	±15%	50
Sb	mg/kg DM	<3	±30%	3
Se	mg/kg DM	<3	±30%	3
Ti	mg/kg DM	<50	±30%	50
V	mg/kg DM	<2	±25%	2
Zn	mg/kg DM	50	±18%	3
Sn	mg/kg DM	260	±16%	3

Figure 8 Manure biomass elemental analysis [4]

3.2.4 SEM analysis

Scanning Electron Microscopy (SEM) analysis has been conducted on pure-mixture biochars to study their microstructure and, by means of the software ImageJ, to visualize pore size. The employed device was Zeiss Sigma VP (Germany), with different magnifications using an electron beam at 20keV and a previous sputtering with Platinum-Palladium at 35mA.

3.2.5 BET analysis

Specific surface area, pore volume and pore size of all the produced biochar have been determined by means of Bruner-Emmett-Teller analysis (using Tristar II-Micrometrics, USA device, see Figure 9 Picture of the used BET analyser, with covered liquid nitrogen tank.). This technique is based on the physical adsorption of N_2 gas on the surface of the processed material. All the adsorption isotherm measurements were carried out at liquid-N temperature (77 K) by increasing nitrogen relative pressure from 0 to 0,99. Tested material have been dried for 30 min at 105°C under constant nitrogen flow. Test sample mass (M_s [g]) has been calculated as:

$M_s = \frac{10}{SSA_{exp}}$ where SSA_{exp} is the expected specific surface value, expressed in m^2/g.

All the obtained data were processed by means of the BET equation in order to determine pores total volume and SSA:

$$\frac{1}{[V_A(\frac{P_0}{P}-1)]} = \frac{C-1}{V_M C} * \frac{P}{P_0} + \frac{1}{V_M C} \quad [4]\ [47]$$

where:

P = partial vapour pressure of adsorbate gas in equilibrium with the surface at 77.4 K (b.p. of liquid nitrogen), [Pa].

P_0 = saturated pressure of adsorbate gas [Pa].

V_A = volume of gas adsorbed at standard temperature and pressure (STP) [273.15 K and atmospheric pressure (1.013 × 105 Pa)], [ml].

V_M = volume of gas adsorbed at STP to produce an apparent monolayer on the sample surface, [ml].

C = dimensionless constant that is related to the enthalpy of adsorption of the adsorbate gas on the powder sample.

The Barrett-Joyner-Halenda (BJH) method have been adopted for pore size distribution estimation on pore volume basis. The method utilizes the Kelvin equation for pore size distribution using the adsorption branch.

Average pore size was determined as $d_{avg} = 4 \times V/SSA$ for cylindrical pores, where V is the total volume and SSA specific surface area of the measured pores, this choice is in according with SEM results (see 4.8) and resulted SSA_{BET}>SSA_{BJH}.

Micropores volume and surface has been determined according to the t-plot method. These results have been compared with total pore volume and SSA obtained by BET equation. Contribution of micropores and meso-macropores have been expressed in percentage.

All adopted methods are in agreement with common procedures on porous materials. [22] [48]

Figure 9 Picture of the used BET analyser, with covered liquid nitrogen tank.

3.2.6 PAH analysis

PAH analysis has been conducted on the same number of samples of the CHNSO one. The sample (ca. 0.5 g of dry weight) was weighed into an extraction thimble and extracted (reflux method) with 50 ml of analytical grade toluene for two hours. Finally, the extract was concentrated to 10 ml under gentle nitrogen evaporation. PAHs in the extract were analysed by gas chromatograph – mass spectrometer (Agilent GC 7890A and 5975C Inert MSD). Internal standard was applied in quantification of PAH concentrations. The column was an HP 5MS (30 m x 0.25 mm x 0.25 µm). Temperature program was as follows: 90°C (0.5 min), 20°C /min to 250°C; 5°C /min to 275°C; 20°C /min to 320°C (5 min). The following temperatures were applied: transfer line: 280°C; MSD 150°C; injector 250°C. Injection volume was 1,0 µl, and carrier gas (helium) flow 1.5 ml/min.. [4]

3.2.7 PH analysis

The pH level for all samples, both original biomass and produced biochar, has been determined following the same procedure, suggested by EBC analytical methods [15]. So, a 25 ml volume of 0,01 M $CaCl_2$ solution has been prepared and added to a 5 ml volume of sample in a glass vessel. In order to obtain a homogeneous suspension, the solution has been stirred for 1 h. After this treatment, the pH level has been measured by means of the Orion 2 Star (Thermofisher scientific, USA) pH-meter, (see Figure 10).

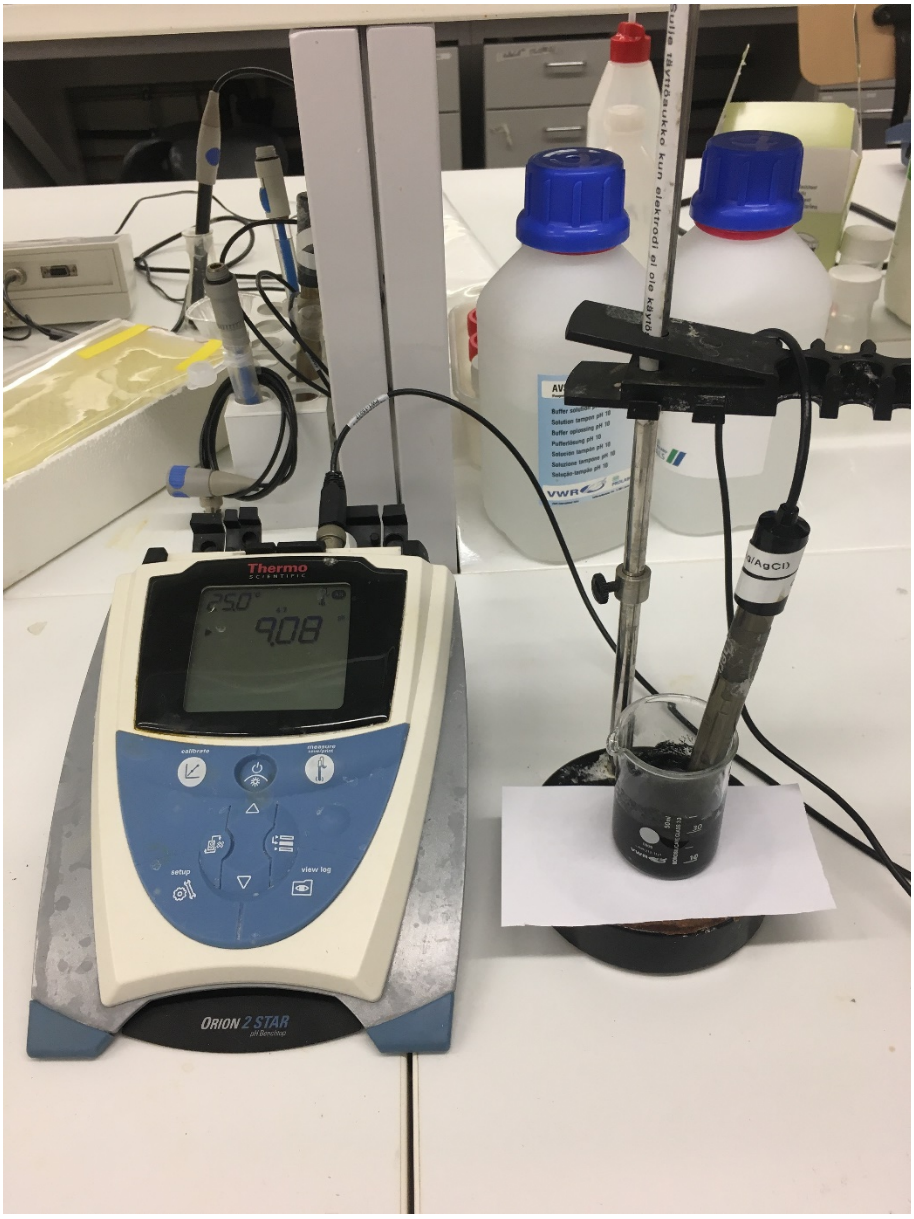


Figure 10 Orion 2 Star pH-meter measuring pH level of a biochar solution

4. Results and Discussion

4.1 TGA analysis results

TGA and DTGA (Differential-TGA) curves for all the biomasses are shown in Figure 11. From these curves we can deduce information about biomass composition both in terms of moisture, ash, volatile matter and fixed carbon contents and cellulose, hemicellulose and lignin ones (biomass main polymers).

According to literature [11] [49] [50] cellulose, hemicellulose and lignin behave in a completely different way under thermal decomposition. In particular, their degradation temperature ranges are 240-350°C, 200-260°C and 280-500°C respectively.

TGA curves for all material show the highest mass loss up to 350°C, about 55% for manure and peat and even bigger for wood. These results are in good agreement with structural composition of these materials, where, for example sum of cellulose and hemicellulose for manure was almost 58% [4] and 61-82% on average for wood [51]. In addition, the plot shows how constant mass is only reached after a temperature of 550°C, which represents the complete degradation of lignin. Since a higher level of lignin brings to higher biochar yields [11], we could expect that peat will result in the major yield followed by manure and wood.

DTGA curves, on the other hand, give information about the cellulose degradation. In particular, the maximum peak of the curve is attributed to the complete degradation of the polymer. Another time, it is demonstrated how cellulose content in wood and manure is significantly bigger than peat one, having their DTGA peaks respectively at almost 380-350°C and 320°C.

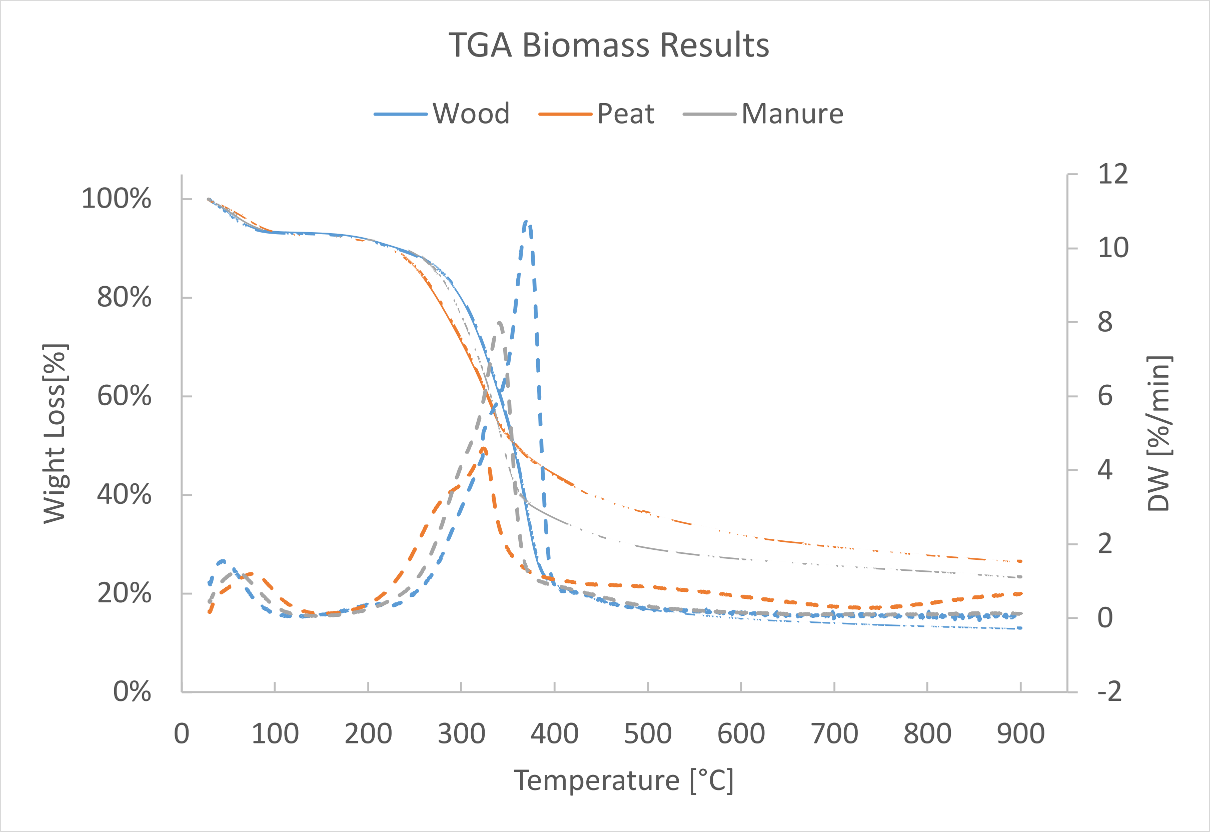


Figure 11 TGA (solid line) and DTG (dash line) curves of the three different biomasses

Concerning proximate analysis data from TGA curves, a first mass loss in a temperature range between 30-150°C is due to the water evaporation [11] [49] [50]. The second and biggest one, which occurs in the range 200-550°C, is mainly related with the release of volatile matter (CO_2 and CH_4) [41]. Finally, from 600 to 900°C the last mass loss reflects fixed carbon and ash contents. As can be easily noticed, the amount of VM produced from biomass is directly related with cellulose and hemicellulose (in part also with lignin) contents, while fixed carbon is mainly due to lignin.

So, from Figure 11, we can see how almost all the three curves behave in the same way in the range of 30-150°C. This trend denotes that the desired equal moisture content level, obtaining by drying procedures (see 3.1.2), has been achieved. After this point, we can notice how the curves continue differently. Wood TGA shows the most inclined slope, followed by manure and peat, as a consequence a higher value of volatile matter in this material is expected. On the other hand, peat and manure weight losses at 900°C present higher values (around 30%), that will reflect in a major content of ash. Wood plot at 600°C presents a mass loss of almost 20%, which increases by 10 and 15% in manure and peat respectively. As a result, biochar yield is expected to be higher in peat derived one, followed by manure and wood.

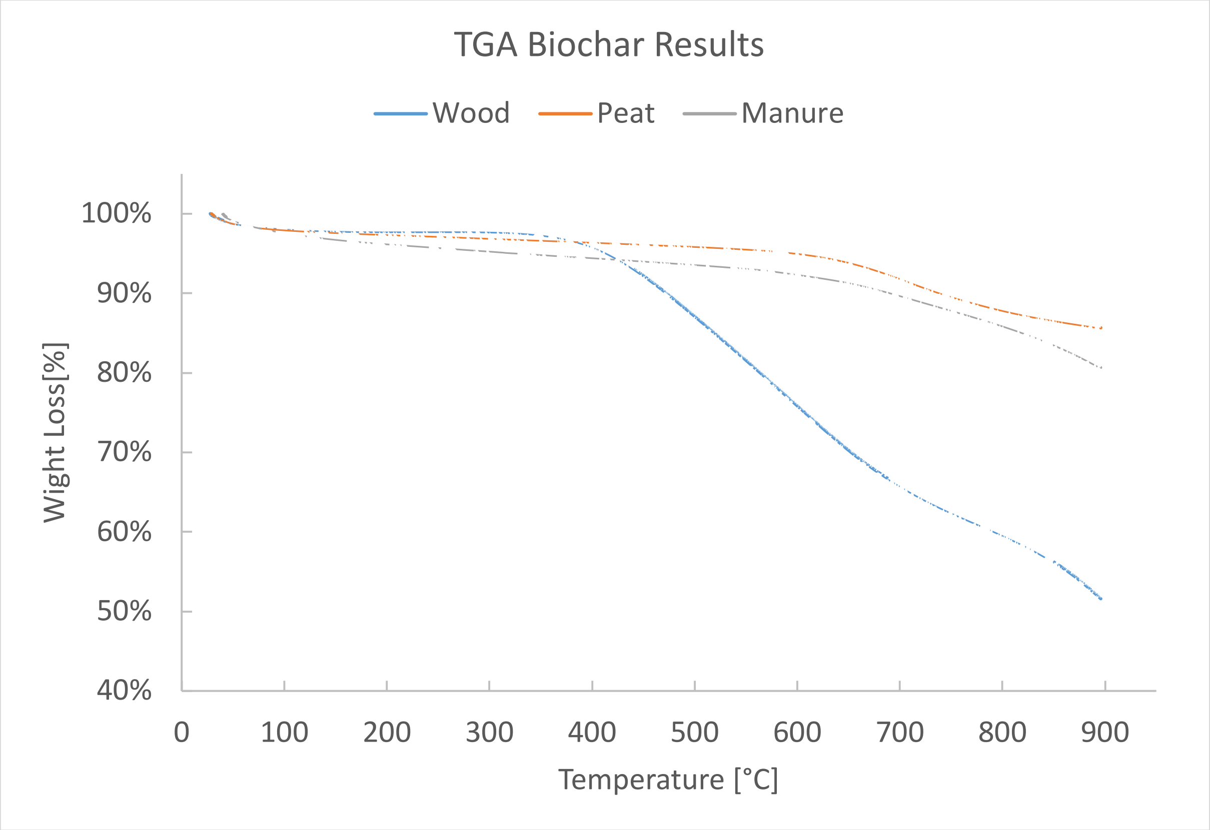


Figure 12 TGA of wood, peat and manure biochar

In this work, TGA has been performed also on biochar obtained by pure mixture materials and their profiles are shown in Figure 12. As we can see from the graph, all curves follow a similar thermal-degradation trend up to 500°C. These means that, moisture and volatile matter of peat and manure will be very close one to each other, while wood one would be higher but not as relevant as original biomass one. In light of this, the VM content of the biochar can be deduced by this analysis without performing the specific procedure (more dangerous and demanding). After that point, a clear difference among the curves can be noticed resulting in a higher mass loss for wood biochar (almost 25% in the range 500-900°C) with respect to peat and manure. Particularly, peat biochar shows the lowest total weight loss, only less than 10%. This is manly related with the original mineral content of the feedstock.

4.2 Proximate analysis results

Proximate analysis results of original biomass are shown in Table 11.Figures highlight a moisture content for the species ranging between 7,1% to 8,8. Biomass moisture content under 10% before a pyrolysis process can be assessed as optimum values (similarly to combustion process requirements [52]), since it will result in an acceptable biochar yields even on wet basis (see 4.3). Concerning volatile matter content, the maximum value is attributed to wood 87,4% followed by manure and peat (77,2 and 74,8 respectively). As both Table 11 and Figure 13 show, the ash content of biomasses significantly varies depending on their nature. As expected, wood content is the lowest, almost close to zero, and manure one is the highest (7,4%), due to the presence of a highest amount of inorganic matter such as minerals. Finally, fixed carbon contents range between 12,3% to 23,8%. All obtained data are in good agreement with TGA results (see 4.1 and Figure 15).

Table 11 Proximate analysis and composition data of manure, peat and wood original biomass

SAMPLE	**PROXIMATE ANALYSIS**			**COMPOSITION**			
	VM	**ASH**	**FC**	**MC**	**VM**	**ASH**	**FC**
	[$\%_{db}$]	[$\%_{db}$]	[$\%_{db}$]	[%]	[%]	[%]	[%]
Manure	77,2	7,4	15,4	7,1	72,1	6,9	13,9
Wood	87,4	0,24	12,3	7,6	81,2	0,3	10,9
Peat	74,8	1,4	23,8	8,8	68,7	1,3	21,2

Table 12 Biochar composition of all pure mixtures obtained by proximate analysis data (*= derived by TGA curves)

BIOCHAR COMPOSITION

SAMPLE	**MC**	**ASH**	**VM***	**FC**
	[%]	[$\%_{db}$]	[$\%_{db}$]	[$\%_{db}$]
Wood	0,3 %	1,4 %	22,3 %	76,3 %
Peat	1,4 %	3,1 %	4,1 %	92,8 %
Manure	1,9 %	21,8 %	6,1 %	72,1 %

Biochar compositions of pure mixtures are shown in Table 12. As we can see, the moisture content of all biochars is very low (less than 2%) due to their storage in a desiccator after the pyrolysis process. As expected, volatile matter content significantly decreases while both ash and fixed carbon contents show an opposite trend. Alike as original biomass, manure derived biochar result in the highest ash content, almost 22%, and wood has the highest VM value.

According to Antal and Gronli [53], most valuables charcoals for fuel usage (i.e. domestic cooking) typically contain 20-30% of VM and 0,5-5% of ash. Therefore, obtained results discourage the use of studied biochars as fuels, with the exception of wood biochar that observes suggested range.

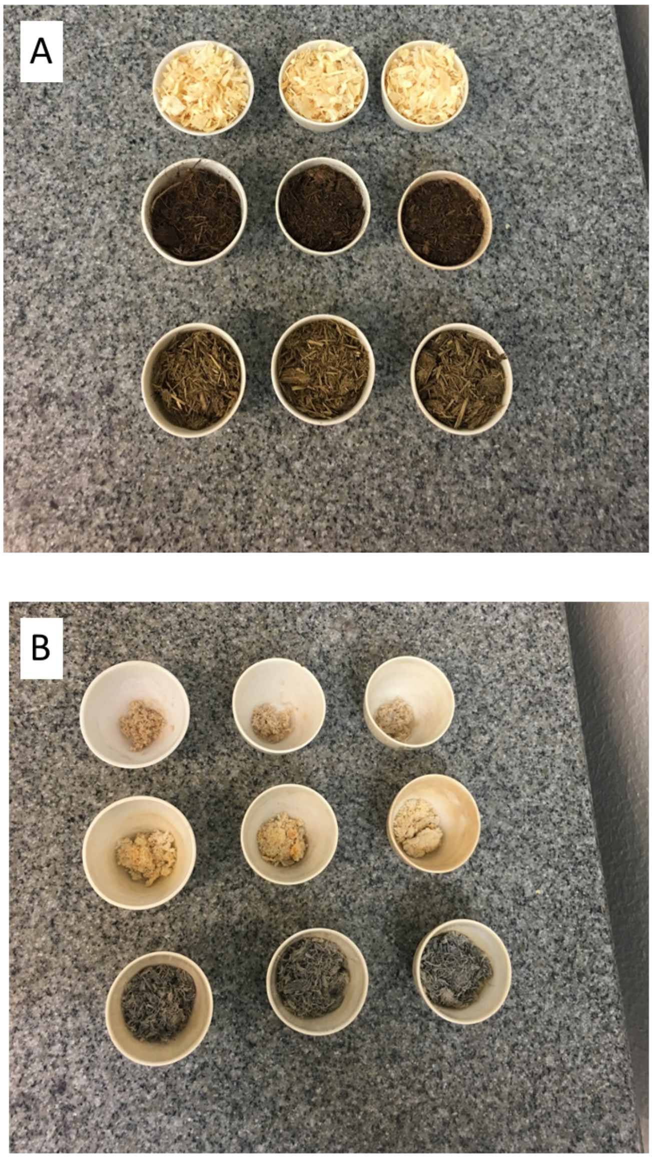


Figure 13 Ash content measurement procedure: open crucible with 1g of biomass (A) and same crucibles with ash residues after determination process (B)

4.3 Biochar yields results

As we can see from Figure 14, the shape of original feedstock is preserved after the pyrolysis process. This does not happen for volume, which is significantly reduced. This diminution is very clearly in woody materials where biochar volume is halved from biomass one. This phenomenon has a positive implication for waste disposal management (see 2.1.4).

Figure 14 Original biomass (A=wood, B= peat, C=horse manure) and their respective obtained biochar (D, E, F)

Biochar yield results from all different kind of tested mixtures are shown in Table 13. All the figures ranged from almost 20% to 30% on wet basis and 21-31% on dry basis. These results are in good agreement with literature where the mean value for biochar yield is usually 1/3. In addition, the slightly difference between wet and dry basis highlights how is important to pre-treat the original feedstock diminishing its moisture content.

As expected, yields vary depending on original feedstock, in particular it is another time demonstrated how manure derived biochars presents higher values with respect to agricultural residues ones. In fact, wood yield is 21% while horse manure is 10% bigger.

Concerning material mixtures yields, the figures highlight how mix yield is almost the averaged value weighted on the components percentages. This result is in good agreement with the assumption of physically bounded mixtures without chemical interactions.

Comparing measured yield results with TGA curves (see 4.1 and Figure 15), we can notice how wood and manure predicted values reflect the measured one, according also with their lignin content. Only peat present a small disagreement, measured value lower than predicted, possibly due to its heterogeneity.

Table 13 Biochar yields according to original feedstock mixtures expressed both in wet basis (wb), dry basis (db) and dry ash-free basis (daf).

AVERAGE YIELD RESULTS

SAMPLE	**YIELD**		
[Name]	**[$\%_{wb}$]**	**[$\%_{db}$]**	**[$\%_{daf}$]**
Manure	29	31	34
Wood	19	21	21
Peat	28	30	31
MPW	27	29	30
MP	29	31	33
MW	26	28	29
PW	26	29	29

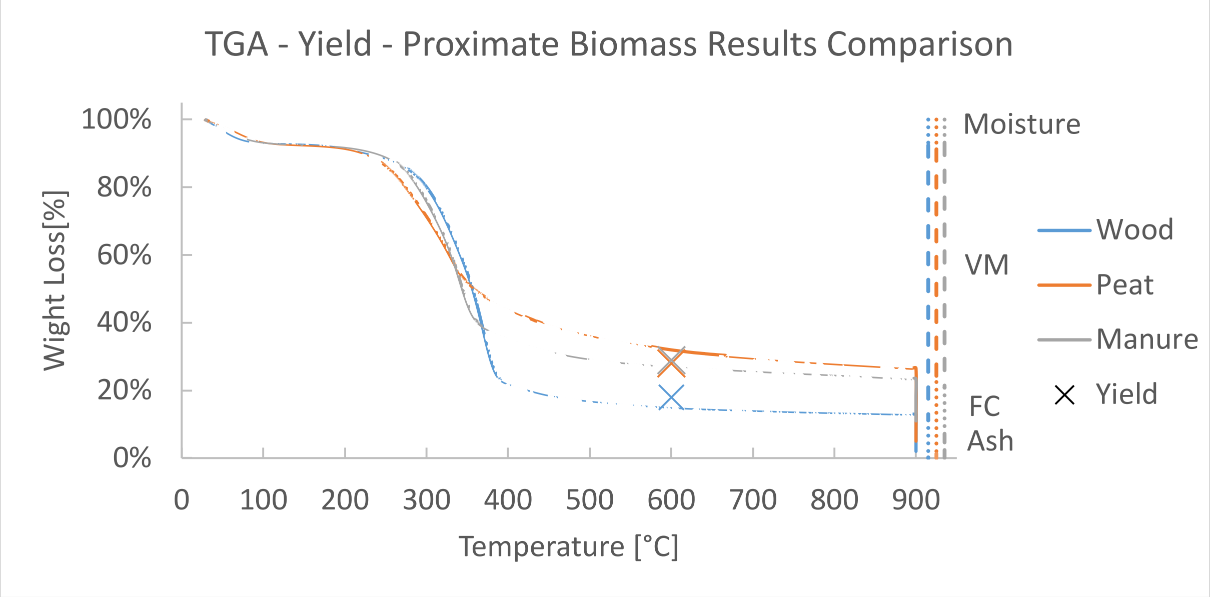


Figure 15 Comparison among TGA curves, yield and proximate analysis measured results for pure original biomasses

4.4 CHNSO analysis results

Ultimate analysis contents are shown in Table 14. Carbon content varies from 68% to 90% (manure and wood respectively), also peat show a high carbon content close to the maximum. All the produced chars exceed by at least 18% the carbon content limit imposed by all voluntary biochar product standards to be classified as a biochar. Comparing figures of Table 14 and Table 10, we can notice how C content significantly increases, close to 30% more, when biomasses are pyrolyzed. This growth is associated with a decrease of H and O contents, phenomena well confirmed in literature [54] [55] [56]. On the other hand, N relationship and its related behavior with temperature is not well understood [21], in this case shows different trend depending on the feedstock. Concerning Sulphur content, its percentage in horse manure decreases after pyrolysis, this is common for manure-based biochars, where it shows higher sensitive behavior to vapor phase mass loss. In which is supposed that some S contained in volatile organic compounds is lost at 350°C and other S is more resistant to bond breakages. [21] Another time mixture of pure elements shows an average value weighted on mass composition.

Table 14 CHNSO contents and atomic ratios of all the obtained biochars

BIOCHAR AVERAGE CHNSO

SAMPLE	C	H	N	S	O	H/C	O/C
Wood	89,84 %	2,11 %	0,64 %	0,23 %	6,94 %	0,02	0,08
Peat	87,28 %	2,48 %	1,68 %	0,36 %	6,70 %	0,03	0,08
Manure	68,23 %	1,66 %	2,00 %	0,23 %	20,90 %	0,02	0,31
PW	78,55 %	2,17%	1,20 %	0,17 %	16,88 %	0,03	0,21
MP	74,44 %	2,13 %	1,47 %	0,17 %	17,33 %	0,03	0,23
MW	78,34 %	2,18 %	1,44 %	0,20 %	14,17 %	0,03	0,18
MPW	80,12 %	2,11 %	1,71 %	0,18 %	12,87 %	0,03	0,16

In contrast to the large variation between the raw biomass samples, the biochars, as previously described, became similar in terms of the elemental composition. This is also highlighted by H/C and O/C atomic ratios, plotted in Figure 16, where biomass values are situated in opposite part of biochar one. As we can see from the graph, all the produced biochars show an O/C level lower than the 0,4 limit of standards. The reduction of these two ratios after pyrolysis is a result of dehydration and decarboxylation reactions [54], generally a low level of O/C corresponds to a low polarity and hydrophilic surface, while the lower is the H/C ratio the highest is the degree of aromaticity and carbonization, resulting in a most stable forming structure [18]. So, peat and wood biochar (0,08) show a better stability than manure one (0,31), in particular its location in the area of low H/C - higher O/C may be attributed to the fact that ash minerals alter their composition through fusion and sintering during pyrolysis. [57]

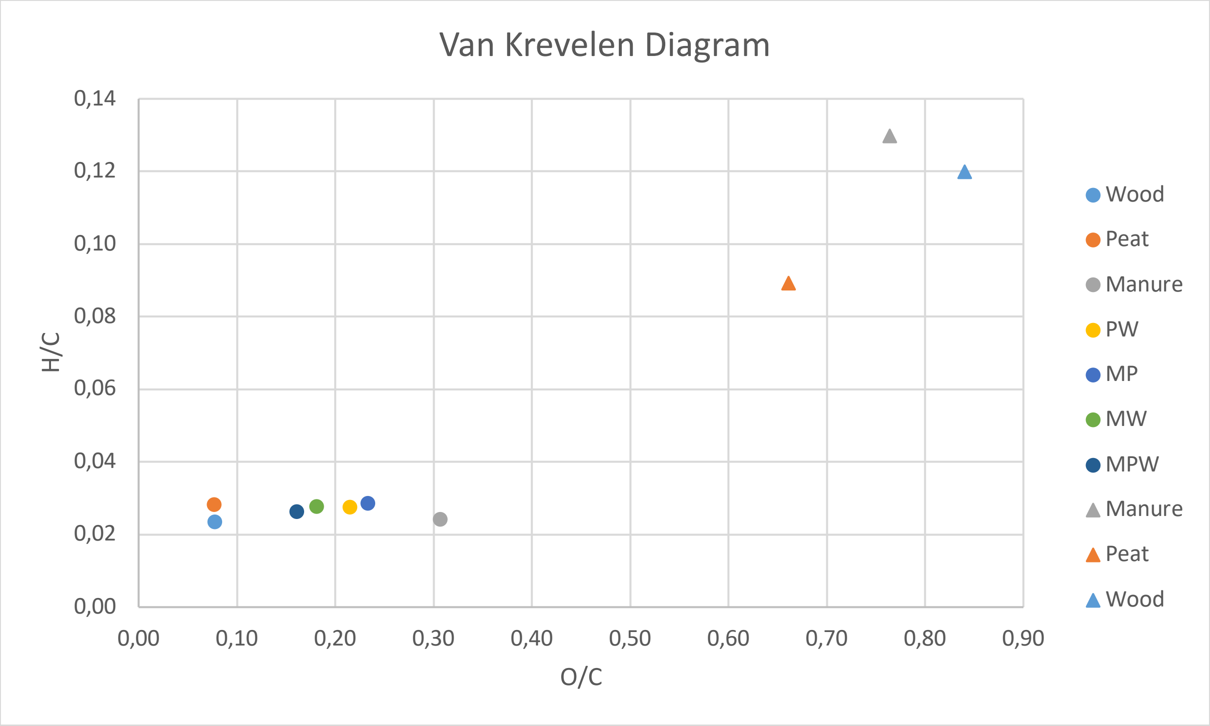


Figure 16 Van Krevelen diagram of original biomass (triangles) and produced biochars (circles)

4.5 PAH analysis results

Total and single compound amounts of PAH are shown in Table 15. As we can see from the figures, total PAH concentrations range between 4 and 9,1 mg/kg. All obtained values are well below the EBC limit of 12 mg/kg, so that all biochars can be applied to soil. On the other hand, any of these can be classified as EBC premium quality product since no one present a value under the threshold of 4. Unexpectedly, biochar mixtures do not behave as a mass weighted value, in fact in all the studied mixtures values of PAH levels are bigger than the expected ones, in particular where peat is present. The explanation of this phenomena is not completely understood and need to be better investigated. A possible correlation between biochar SSA and pore size distribution or/and functional surface group with PAH concentrations may give an explanation. Relationship with SSA, PSD and pore volume will be investigated in chapter 5. Generally, all these values are assumed to be higher than the ones obtained by analyzing the same biochar produced at industrial scale. This is due to the fact that the small dimension of the quartz tube does not permit the perfect leak of gaseous PAH, that, once condensed, will deposit on the biochar.

In addition, Table 15 shows how naphthalene compound is the most abundant one; this result is in good agreement with literature [16].

Table 15 List of both single PAH compound concentrations expressed in ng/g and both total PAH concentration expressed in mg/kg according to EBC standards. (1: LOD= 10-50 ng/g and 2: LOD= 50-100 ng/g.)

PAH BIOCHAR AVERAGE VALUES

SAMPLE	Wood	Peat	Manure	MPW	MW	MP	PW
PAH COMPOUND	[ng/g]	[ng/g]	[ng/g]	[ng/g]	[ng/g]	[ng/g]	[ng/g]
Naphthalene[1]	3371	5464	5625	6772	5383	5069	5989
Asenaphtylene[1]	62	60	48	40	40	100	LOD
Asenaphtene[1]	94	96	LOD	78	LOD	86	LOD
Fluorene[1]	49	LOD	LOD	LOD	LOD	70	LOD
Phenanthrene[1]	161	115	808	419	102	462	303
Anthracene[1]	110	96	174	197	76	222	61
Fluoranthene[1]	34	50	66	172	72	158	42
Pyrene[1]	19	49	35	124	44	120	LOD
Benz(a)antracene[1]	73	88	74	214	98	194	842
Chrysene[1]	40	40	61	194	68	170	LOD
Benzo(b)fluoranthene[2]	LOD	LOD	92	261	48	239	LOD
Benzo(k)fluorantene[2]	LOD	LOD	62	141	LOD	157	LOD
Benzo(a)pyrene[2]	LOD	LOD	79	174	75	172	LOD
Benzo(ghi)perylene[2]	LOD	LOD	LOD	94	LOD	116	LOD
Dibenz(ah)antracene[2]	LOD	LOD	LOD	58	LOD	LOD	LOD
Indeno(1,2,3-cd)pyrene[2]	LOD	LOD	LOD	89	LOD	110	LOD
ΣPAHS [mg/kg]	4,0	6,1	7,1	9,1	6,0	7,4	7,2

4.6 PH results

Values of pH for both original feedstock and produced biochars are shown in Figure 17. As it can be immediately noticed from the plot, all produced biochars are alkaline. This result supports their application to soil, contrasting the acidification phenomenon (see 2.1.4). Biochar pH levels vary from slightly alkaline (7,41 for peat) to very strongly alkaline (10,1 for manure), in this case mixtures show values averaged on mass composition. Concerning original biomass, almost all materials are acidic: peat is ranked as ultra-acidic while wood extremely acid, having levels of 3 and 4,3 respectively. The only exception is made by manure that with a pH of almost 7 is classified as neutral. Comparing obtained values with literature [19], we can notice that they are lower, particularly for wood biochar, this is mainly due to the adoption of $CaCl_2$ solution instead of simple distilled water. This is consistent with Bachmann et al. (2016), which affirm that "*the use of $CaCl_2$ solutions delivered lower pH values at lower ash contents*" [16].

The significant increase of pH level and its less variation depending on feedstock after pyrolysis treatment are a well confirmed phenomena. This is mainly a consequence of organic functional groups (-COOH and –OH), that decreases with the increase of HTT, carbonates and inorganic alkalis, whose effect gets importance above 500°C [56].

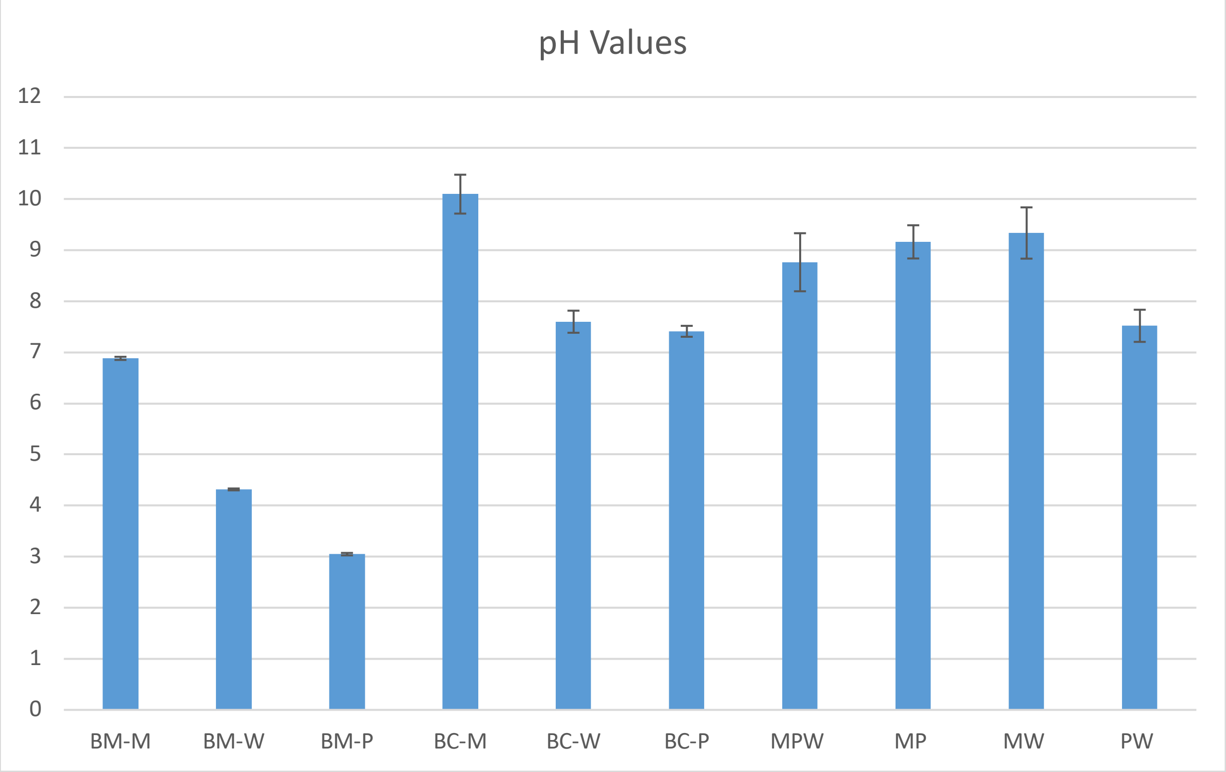


Figure 17 pH values of original biomasses (BM) and produced biochars (BC) for all mixtures, data are reported with its standard deviation

4.7 BET analysis results

BET results are shown in Table 16, where we can see that averaged SSA for all studied biochars varies between 45-350 m^2/g. This value has been measured according to multipoint surface area model for materials with high variation in pore size. Considering that biochars have complex structures where all kinds of pores coexist, this measure is supposed to be representative since the single point measure at p/p_s=0,299, showing higher values for all conducted analysis, will overestimate this value (see 2.1.2) [16].

As expected, wood biochar presents the highest value and manure one the lowest, these results are in good agreement with literature [4] [19] [21]. Also, mixtures show high values of SSA, all above 150 m^2/g according with pure material composition.

Table 16 BET results for all produced biochars. (mv= mean value, err= error given by the machine)

AVERAGE BET RESULTS

SAMPLE	SSA		PORE VOLUME	PORE SIZE
	mv	err	mv	mv
	[m^2/g]	[m^2/g]	[cm^3/g]	[nm]
Manure	44,96	±1,29	0,03	2,92
Wood	351,37	±10,19	0,19	2,16
Peat	307,14	±9,22	0,18	2,32
MPW	227,79	±6,54	0,13	2,20
MP	197,23	±5,63	0,11	2,25
MW	180,79	±5,13	0,10	2,22
PW	313,53	±8,95	0,17	2,19

Figure 18 presents adsorption isotherms of all studied biochars. Trends are found to be very similar among all curves, in particular the rapid increase until p/p_s = 0,1 resemble type I IUPAC isotherm while the slight increase between 0,1 and 0,9 is found to represent type IV [58]. According to IUPAC classification, type I isotherm is characteristic of microporous materials while type IV of mesopores, indicating the well-developed structures of these two kinds of structures.

The increasing N_2 adsorbed quantity trend from manure to wood confirm previous behaviour of SSA and pore volume.

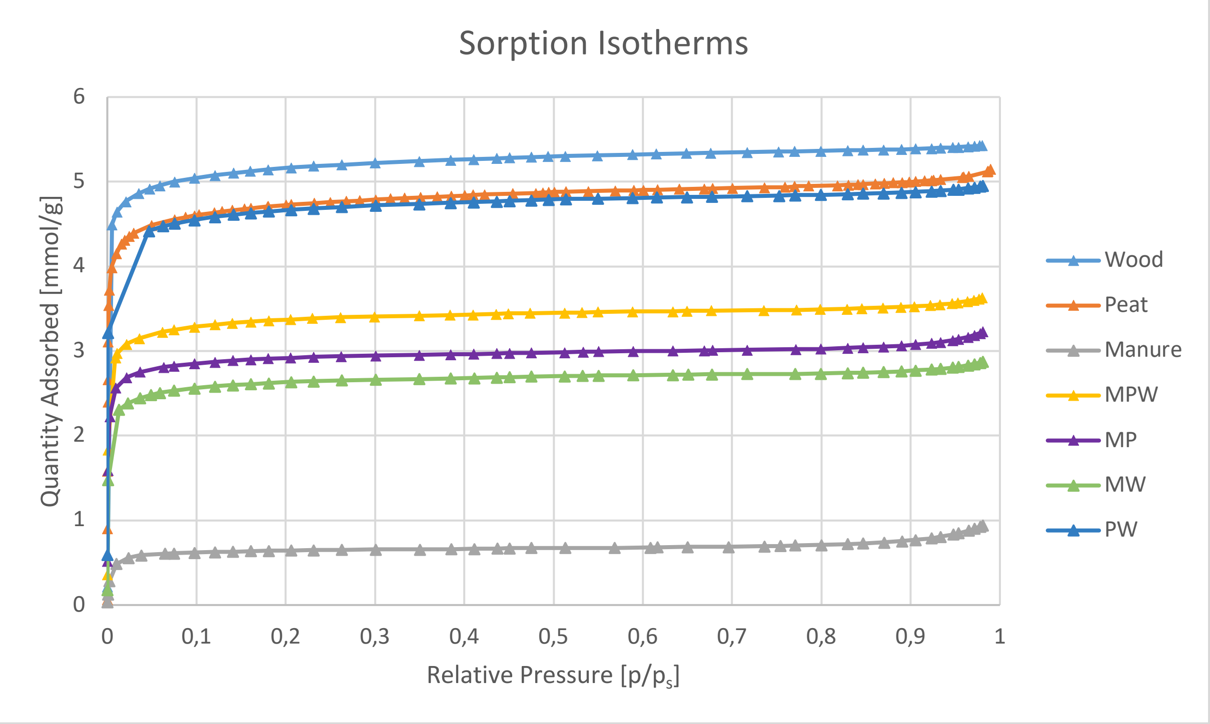


Figure 18 Adsorption isotherms of N_2 for all produced biochars

Results of particle size distribution by volume are presented in Figure 19. The diagram highlights how PSD varies depending on original feedstock. In particular manure derived biochar shows the highest amount of macropores, almost 20%, while peat and wood present higher percentages in micropores. The high content of micropores is also demonstrated by its contribution on total area and volume (Figure 20). Figures of PSD and area contribution are found to be in good agreement with previous studies, while volumes ones show a higher percentage of micropores contribution [22]. In addition, Ioannidou et al. [59] found that lignin develops macropores while cellulose is favours the formation of micropores, which perfectly matches with obtained results.

This discordance can be mainly explained by the different nature of original feedstock structure and the not so harsh HTT adopted. In fact, biochar produced at temperatures above 600°C have a higher percentage of meso- and macropores because, in this condition, micropores collapses increasing their size [11].

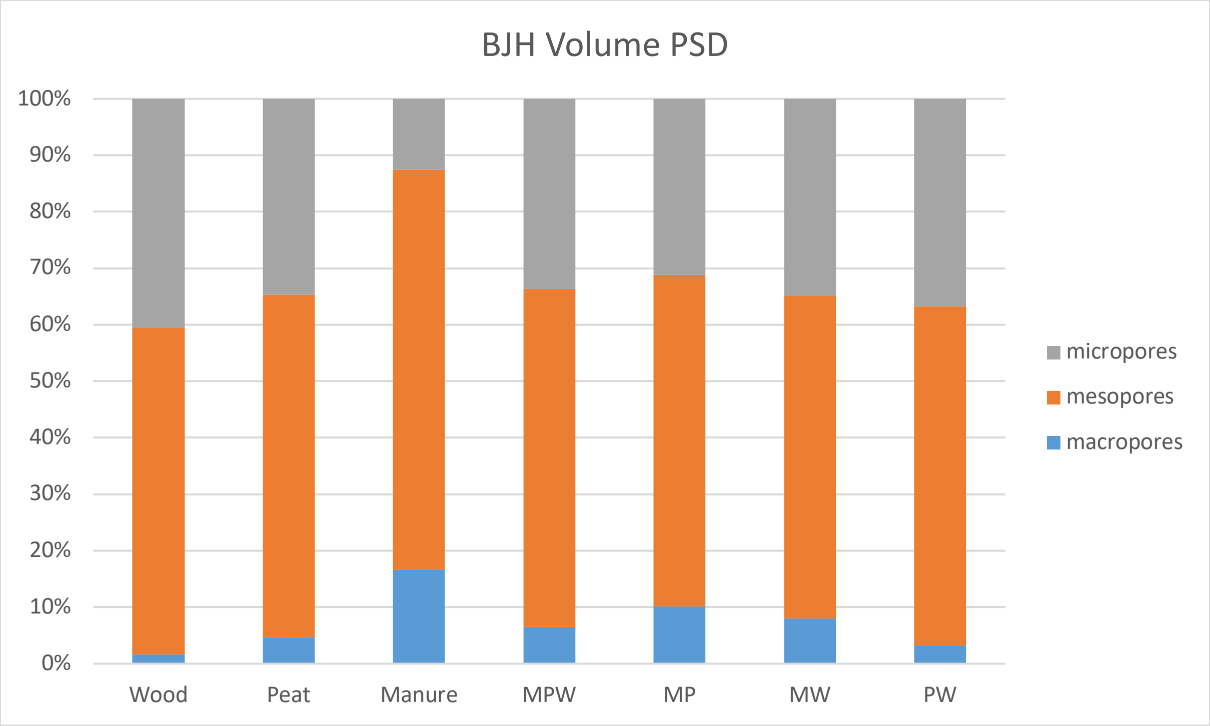
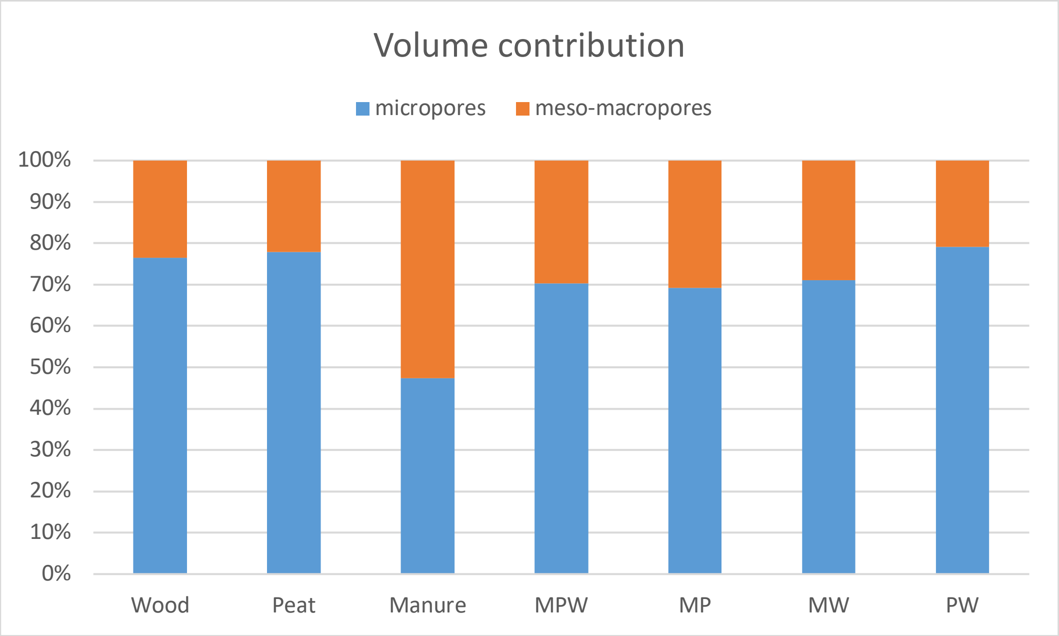


Figure 19 Particle size distribution of all studied biochars derived using BJH model for pore volume

Bringing them all together, BET values suggest that the most valuable application of these biochars and in particular its mixtures would be soil amending since high percentage of micropores will provide a habitat for microbes and their activity. Additionally, the significant presence of other pores will provide various adsorption responses of contaminants from soils [21].



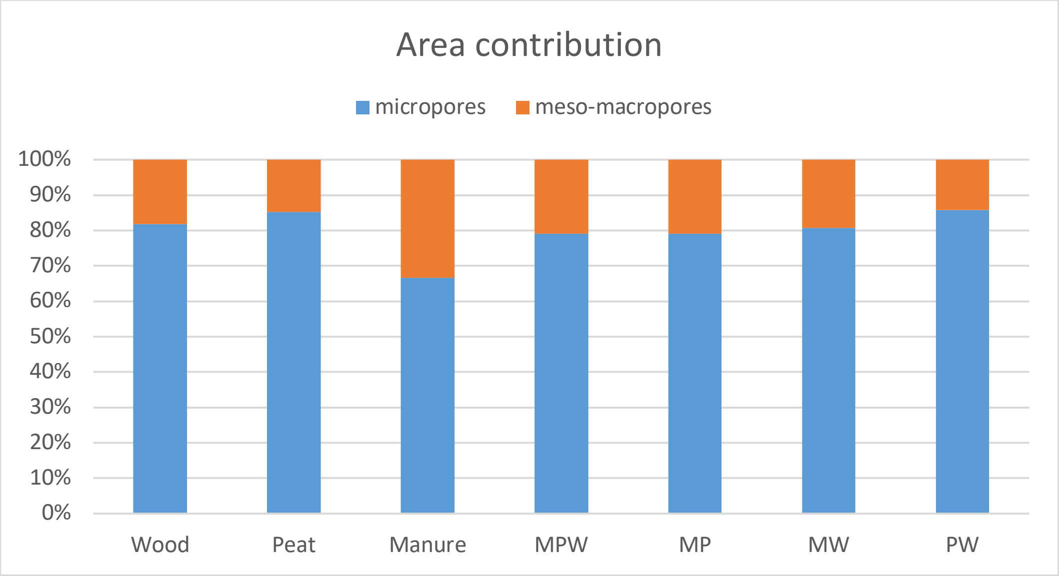


Figure 20 Contribution of micro-, meso- and macrospores volume in the total pore volume (above) and area in total SSA (below) for all studied biochars according to BET and t-plot data

4.8 SEM imagines

SEM images of biochars derived from pure mixtures are shown in Figure 21-Figure 22-Figure 23. These images illustrate the pore formation, especially of macropores, that are more easily displayable at different scales. Manure and wood biochars demonstrate a much more homogenous pore arrangement in an array of cylinder-like structures. These cylinders can be remarkably visualized in cross-sectional surface images at 10 μm (Figure 21- Figure 23). A much more heterogeneous arrangement can be found in peat biochar, where no cylinder-like structures can be easily identified. This difference is due to original biomass structure.

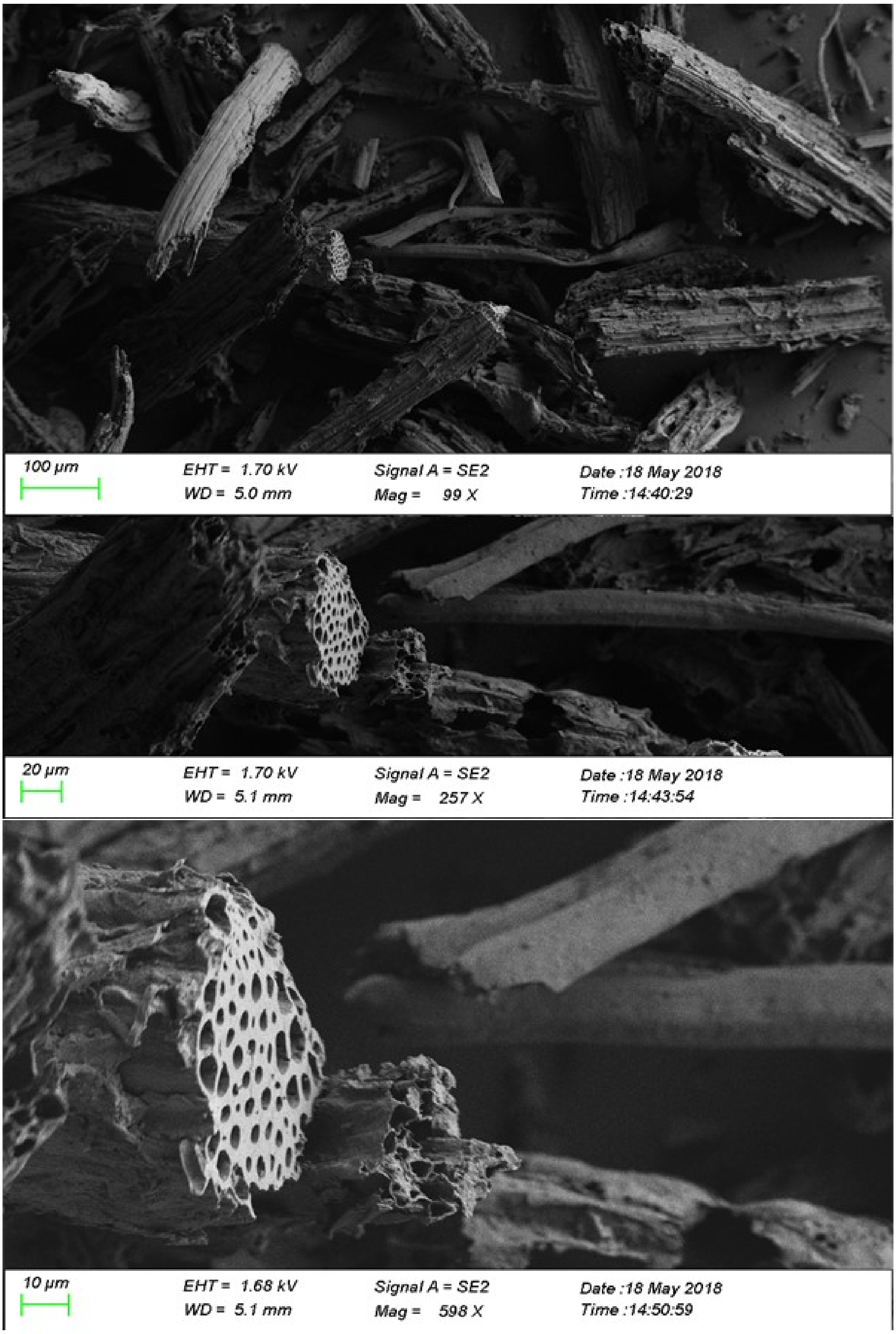


Figure 21 SEM images at different scales of wood biochar

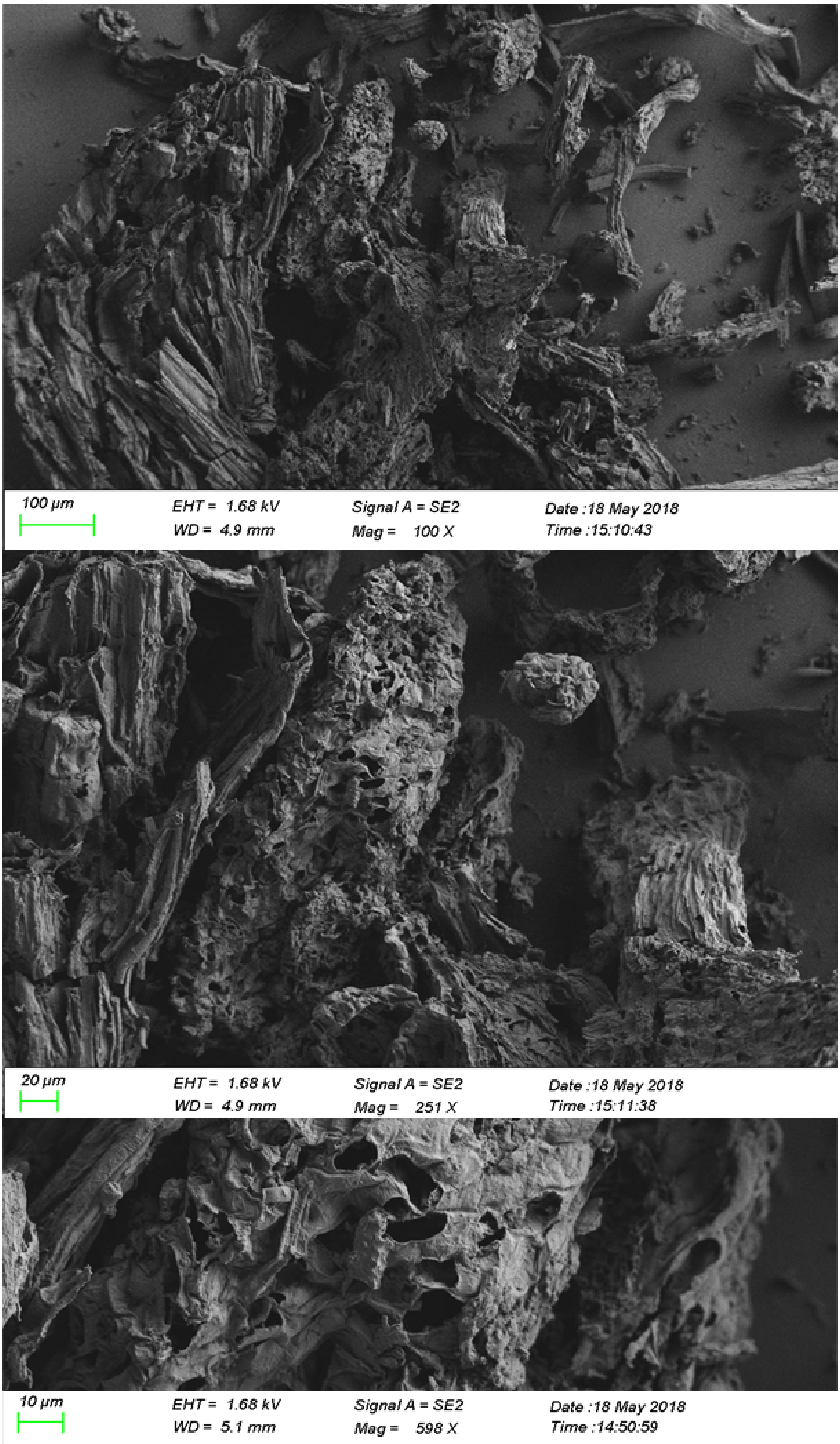


Figure 22 SEM images at different scales of peat biochar

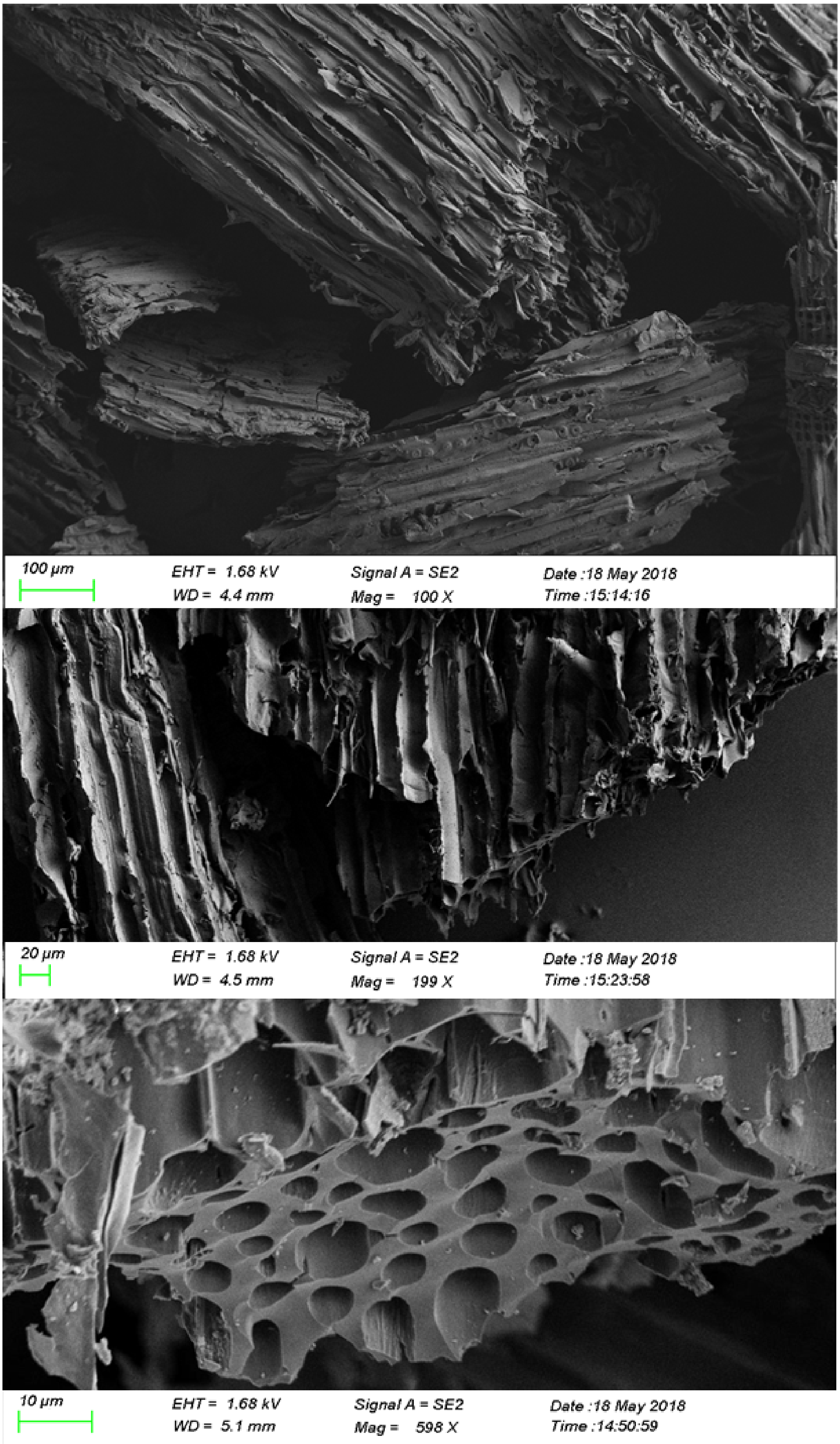


Figure 23 SEM images at different scales of manure biochar

4.9 Biochar physical and chemical properties resume

Table 17 Resume of all studied biochars' properties

Material	Samples	Ash	VM	FC	C	H	N	S	O	H/C	O/C	Yield	SSA	PV	PS	PH	PAH
		[%$_{db}$]	[%$_{db}$]	[%$_{db}$]	[%]	[%]	[%]	[%]	[%]	[#]	[#]	[%]	[m^2/g]	[cm^3/g]	[nm]	[#]	[mg/kg]
Biomass	Manure	7,4 %	77,2 %	15,4 %	47,3 %	6,1 %	1,7 %	0,8 %	36,1 %	0,13	0,76	-	-	-	-	6,88	-
	Wood	0,2 %	87,4 %	12,3 %	50,0 %	6,0 %	1,0 %	1,0 %	42,0 %	0,12	0,84	-	-	-	-	4,32	-
	Peat	1,4 %	74,8 %	23,8 %	56,0 %	5,0 %	1,0 %	1,0 %	37,0 %	0,09	0,66	-	-	-	-	3,05	-
Biochar	Manure	21,8 %	6,1 %	72,1 %	68,2 %	1,7 %	2,0 %	0,2 %	20,9 %	0,02	0,31	29 %	45	0,03	2,92	10,10	7,1
	Wood	1,4 %	22,3 %	76,3 %	89,8 %	2,1 %	0,6 %	0,2 %	6,9 %	0,02	0,08	19 %	351	0,19	2,16	7,60	4
	Peat	3,1 %	4,1 %	92,8 %	87,3 %	2,5 %	1,7 %	0,4 %	6,7 %	0,03	0,08	28 %	307	0,18	2,32	7,41	6,1
	MPW	16,3 %	-	-	80,1 %	2,1 %	1,7 %	0,2 %	12,9 %	0,03	0,16	27 %	228	0,13	2,20	8,76	9,1
	MP	13,1 %	-	-	74,4 %	2,1 %	1,5 %	0,2 %	17,3 %	0,03	0,23	31 %	197	0,11	2,25	9,16	7,4
	MW	13,6 %	-	-	78,3 %	2,2 %	1,4 %	0,2 %	14,2 %	0,03	0,18	26 %	181	0,10	2,22	9,34	6
	PW	2,9 %	-	-	78,6 %	2,2 %	1,2 %	0,2 %	16,9 %	0,03	0,21	26 %	314	0,17	2,19	7,52	7,2

5. Experimental Design using Mixture Model

5.1 Simplex-Centroid Design

Experiments that can be modelled by means of mixture models are the ones where measured response is assumed to depend only on the relative proportions of the components present in the mixture and not on the total amount of the mixture. [60] So, calling q the number of components and x_i the fraction of the i-th component in the mixture, we have that mixture components are subject to the constraint that they must sum to one (see Equation 1):

Equation 1 Mixture model constrain

$$x_i \geq 0 \ (i = 1,2, \dots, q); \quad x_1 + x_2 + \cdots + x_q = 1$$

In these mixture problems, the purpose of the model is to predict the response for any combination of ingredients that can be empirically made and estimate the influence on the response of each single component and in combination with other.

Several different types of mixture designs can be adopted depending on their purpose. The most common ones are simplex lattice, simplex centroid, simplex axial and extreme vertex designs. In cases where the number of components is not elevated, there are no additional constrains on components and the response is expected to fit with low order polynomial equation; the simplex centroid or lattice models are recommended.

The design of these two models is very similar, but the simplex centroid, unlike the lattice, does not requires specifications in the selection of design points, resulting in a smaller amount of total observations and an easier experimental implementation [60] [61]. So, a total run of $2^q - 1$ are taken, corresponding to the sum of q pure components, $\binom{q}{2}$ binary mixtures with equal portion, the $\binom{q}{3}$ ternary mixtures with equal portion and so on.

Different kind of regression functions (linear, quadratic, full cubic…) can be applied to model experimental design data. However original equations (i.e. linear $y = \beta_0 + \sum \beta_i x_i$) must be manipulate in order to uniquely determine the β_i due to mixture constrain (Equation 1). A good approach has been proposed by Scheffé where all β_i are relabeled since $\beta_0 = \beta_0 \times 1 = \beta_0 \times \sum x_i$, resulting in the following canonical form of regression functions:

Linear:

$$y = \sum \beta_i x_i$$

Quadratic:

$$y = \sum \beta_i x_i + \sum \sum\nolimits_{i<j} x_i x_j$$

Full Cubic:

$$y = \sum \beta_i x_i + \sum \sum\nolimits_{i<j} x_i x_j + \sum \sum\nolimits_{i<j} \delta_{ij} x_i x_j (x_i - x_j) \ + \sum \sum \sum\nolimits_{i<j<k} x_i x_j x_k$$

Usually, a special cubic regression function, where the $\delta_{ij} x_i x_j (x_i - x_j)$ terms are removed, is applied to the simplex centroid mixture models defining them as Scheffé type.

5.2 Model Implementation

According to Scheffé type model and being the number of components q=3 (wood, peat and horse manure), a total run of 7 design points has been taken, shown in Figure 24. As we can see, in this experimental region there are no upper or lower limits on the proportions of the three ingredients, except the only external constrain that they must sum to one [62]. In fact, points P1-3-5 represent the pure mixture elements while 2-4 and 6 are the binary mixture (2nd degree centroids), having two non-zero components with equal values. Point P7 represent ternary mixtures including all components in same percentage.

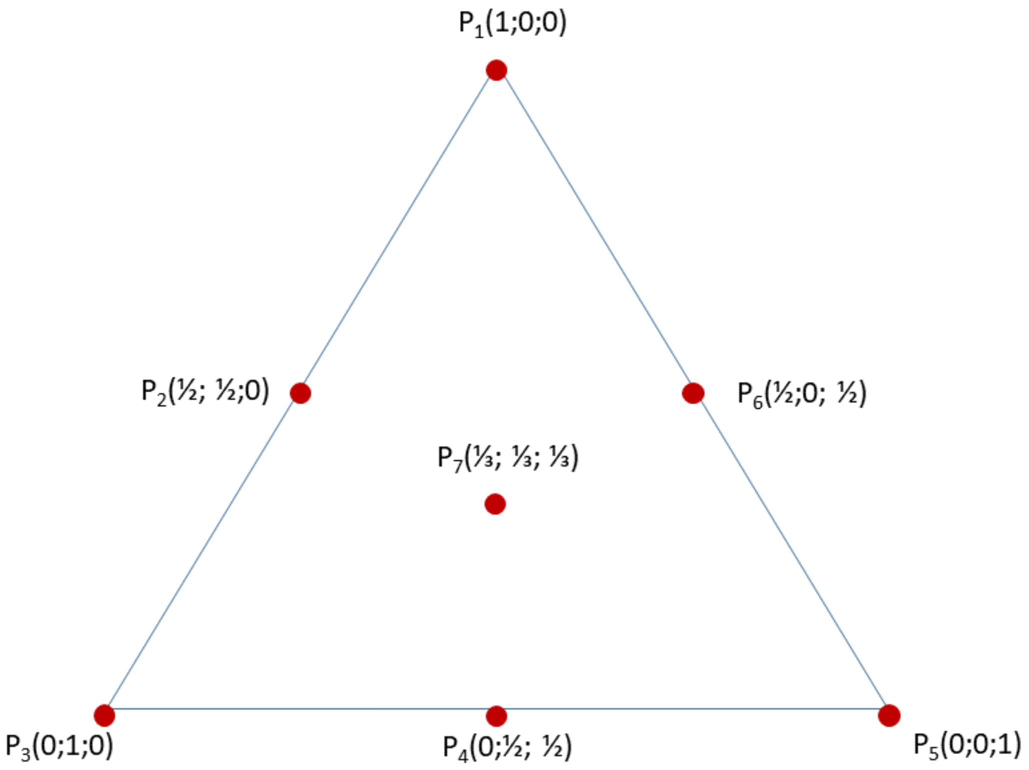


Figure 24 Representation of the selected design points for the mixture model

For yield, pH and BET analysis all the runs have been performed in triplicate. For the remains experiments, only P7 has been run in triplicate, while the second-degree centroids in single and the pure in duplicate. This choice is in agreement with making the minimum amount of measurements, still having a correct statistical result in the model.

All obtained results have been analysed by means of the software MODDE. So that, an analysis of the impact of each term of the special cubic equation (shown in Equation 2) have been performed in order to neglect the irrelevant ones.

Equation 2 Special cubic equation used for Scheffé type simplex centroid mixture model

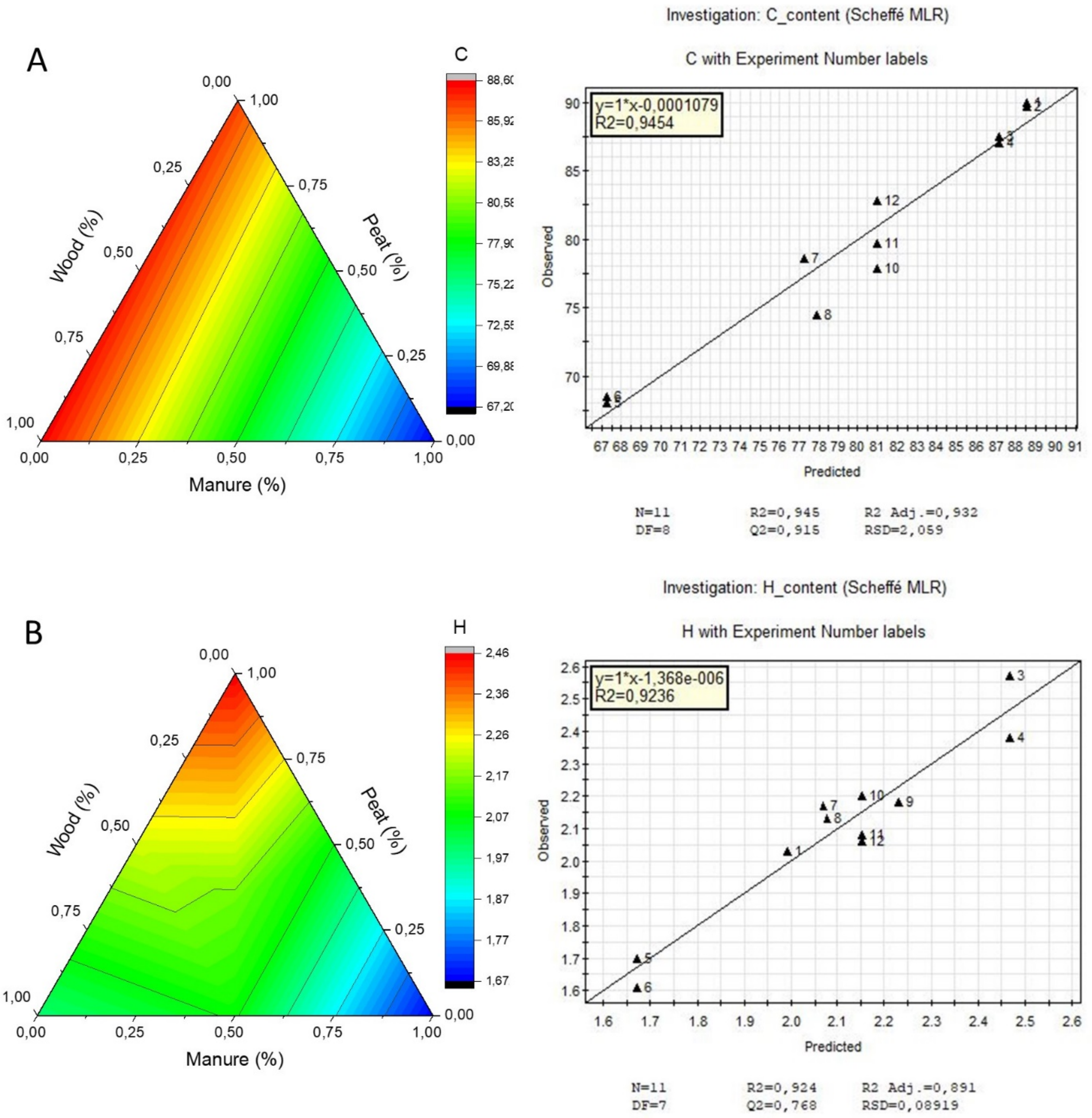
$$y = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \beta_{123} x_1 x_2 x_3$$

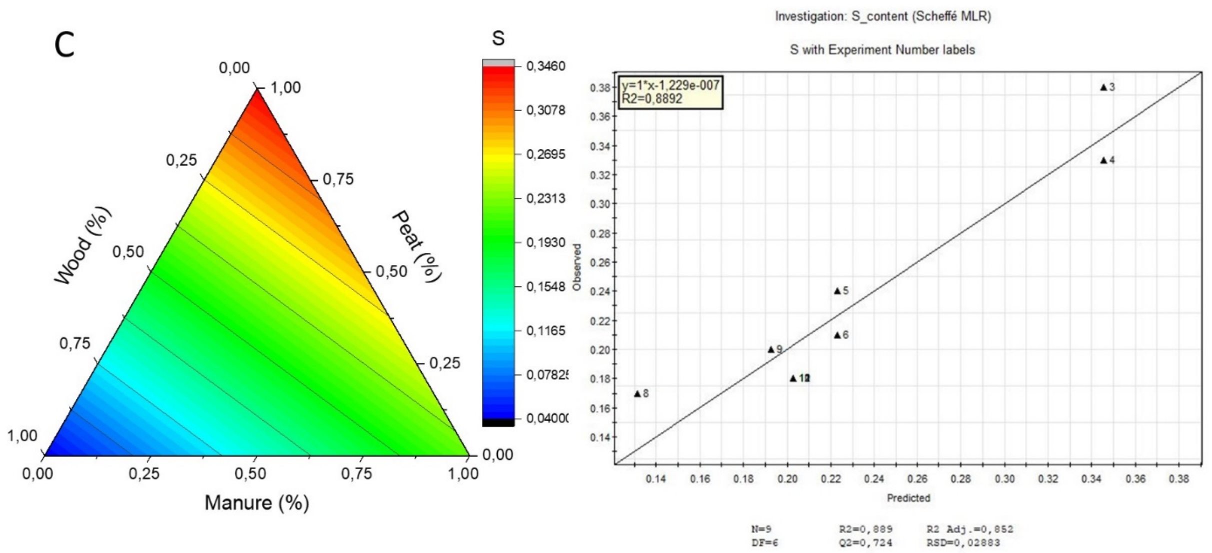
Always by means of MODDE, an ANOVA analysis has been conducted in order to estimate the model probability of regression and lack of fit.

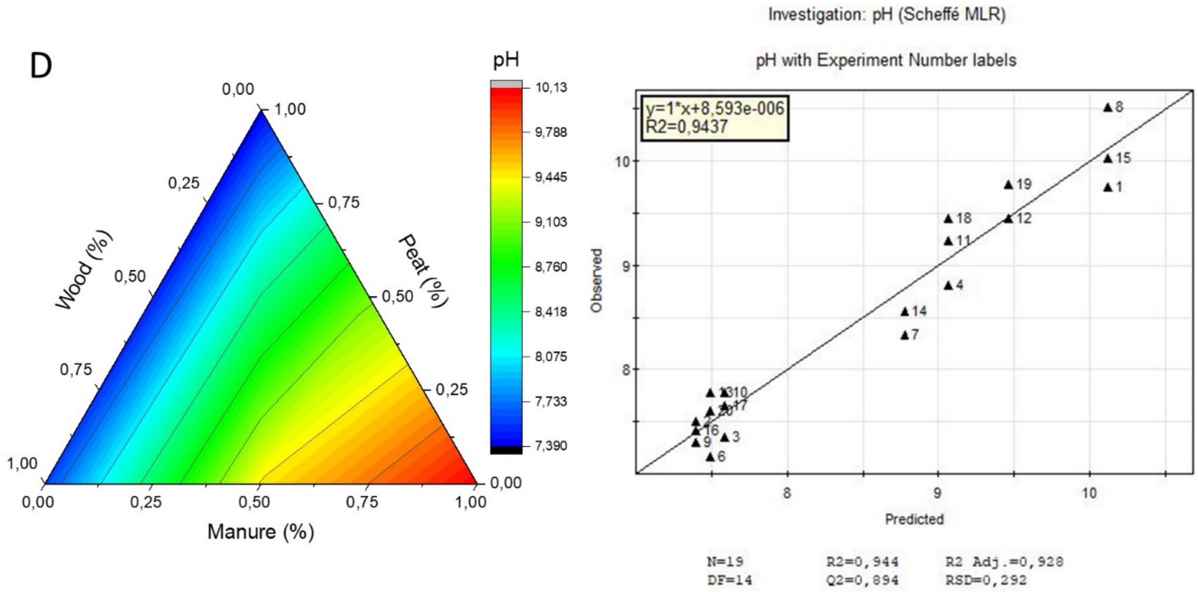
Finally, the β coefficients have been obtained and predicted values of each properties have been plotted.

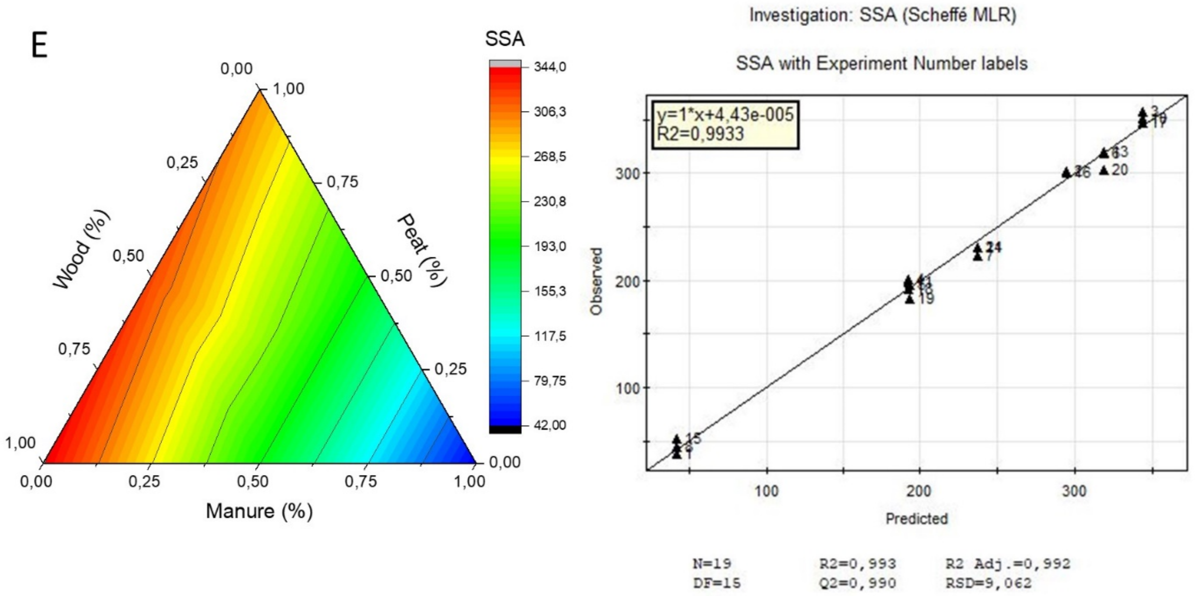
5.3 Model Results and Discussion

Predicted values of main biochar properties resulted by Scheffé type mixture model design are shown in Figure 25. As we can see from the plots (A-B-C-D-E-F), almost all the properties showed a linear dependence with pure mixtures (β_i>> β_{ij}), only one quadratic term over three has been found to be not negligible respect to the others for each property. The only exception is PAH, where β_{ij} coefficients present a higher value, which show that interactions among all the components is relevant and should not be neglected.




C
S
0,3460
0,3078
0,2695
0,2313
0,1930
0,1548
0,1165
0,0782
0,0400
Wood (%)
Peat (%)
Manure (%)
0,00
0,25
0,50
0,75
1,00
Investigation: S_content (Scheffé MLR)
S with Experiment Number labels
y=1*x-1,229e-007
R2=0,8892
Observed
Predicted
0.14
0.16
0.18
0.20
0.22
0.24
0.26
0.28
0.30
0.32
0.34
0.36
0.38
3
4
5
6
9
12
8
N=9
DF=6
R2=0,889
Q2=0,724
R2 Adj.=0,852
RSD=0,02883


D
pH
10,13
9,788
9,445
9,103
8,760
8,418
8,075
7,733
7,390
Wood (%)
Peat (%)
Manure (%)
0,00
0,25
0,50
0,75
1,00
Investigation: pH (Scheffé MLR)
pH with Experiment Number labels
y=1*x+8,593e-006
R2=0,9437
Observed
Predicted
8
9
10
8
15
19
1
18
12
11
4
14
7
10
17
16
3
9
6
N=19
DF=14
R2=0,944
Q2=0,894
R2 Adj.=0,928
RSD=0,292


E
SSA
344,0
306,3
268,5
230,8
193,0
155,3
117,5
79,75
42,00
Wood (%)
Peat (%)
Manure (%)
0,00
0,25
0,50
0,75
1,00
Investigation: SSA (Scheffé MLR)
SSA with Experiment Number labels
y=1*x+4,43e-005
R2=0,9933
Observed
Predicted
100
200
300
3
13
20
24
7
19
15
N=19
DF=15
R2=0,993
Q2=0,990
R2 Adj.=0,992
RSD=9,062

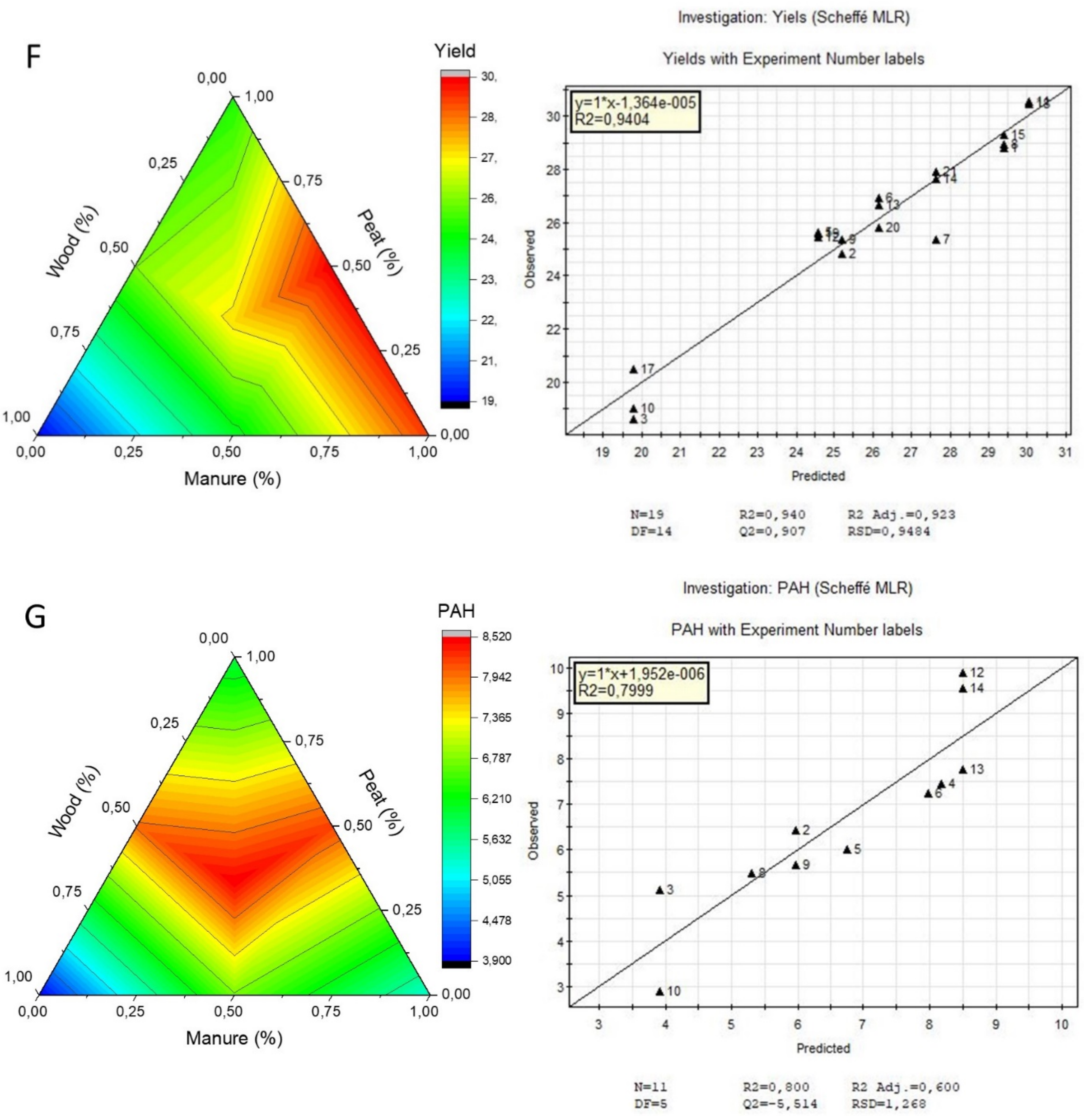


Figure 25 Property predicted values contour plot (left) and measured values vs predicted values plot (right) (Values of C, H, S and Yield are expressed in [%], while SSA [m^2/g], PAH [mg/kg] and pH is pure number)

Main variables of ANOVA statistical analysis are shown in

Table 18. In the table:

- n represent the number of observation considered for the model
- $R^2 = {SS_{reg}}/{SS_{tot}}$ represent the goodness of fit
- $SS_{reg} = \sum(\hat{y}_i - \bar{y})^2$, regression sum of squares explained by the model
- $SS_{tot} = \sum(y_i - \bar{y})^2$, total sum of squares

- $R^2_{adj} = 1 - \frac{SS_{reg}/_{(n-p)}}{SS_{tot}/_{(n-1)}}$ represent the adjusted goodness of fit

Quality of produced models can be deducted from both

Table 18 and Figure 25, where a good agreement between predicted and observed value (R^2 close to one) can be found for almost all the properties. Moreover, almost all the models are statistically good, having probability of regression close to zero ($p_{regression}$ <0,005) and only SSA and Yields properties present lack of fit since its p-value is close to zero. This SSA value is mainly due to BET machine intrinsic characteristics.

Table 18 Relevant ANOVA statistic values for each modelled property.

ANOVA TABLE

PROPERTY	n	R^2	R^2_{adj}	$p_{regression}$	$p_{lack\text{-}of\text{-}fit}$
C	11	0,945	0,932	<0,005	0,147
H	11	0,924	0,891	<0,005	0,523
S	10	0,889	0,852	<0,005	0,116
pH	19	0,944	0,928	<0,005	0,182
SSA	19	0,993	0,992	<0,005	0,008
Yield	19	0,94	0,856	<0,005	0,026
PAH	11	0,8	0,6	0,077	0,23

The only property found not to follow a mixture model is PAH as it is characterized by the lowest coefficient of determination (0,8) and being statistically poor ($p_{regression}$ =0,077).

Actually, the behaviour of PAH is not completely understood. In order to find some possible correlations among PAH and all the others investigated properties, a correlation matrix have been performed by means of MODDE. Results of this analysis are shown in Figure 26, where PAH presents a weak negative correlation with SSA (-0,37) and PV (-0,40) and a weak positive correlation with manure (0,32). SSA and PV, or surface functional groups, were supposed to be the most likely properties to give an explanation on PAH behaviour.

However, even PCA does not explain very well PAH trend, but it can be an indication that variables having a strong effect on PAH are not present in the studied dataset. These results suggest the need of deeper studies on PAH mechanism of formation and interaction with porous materials.

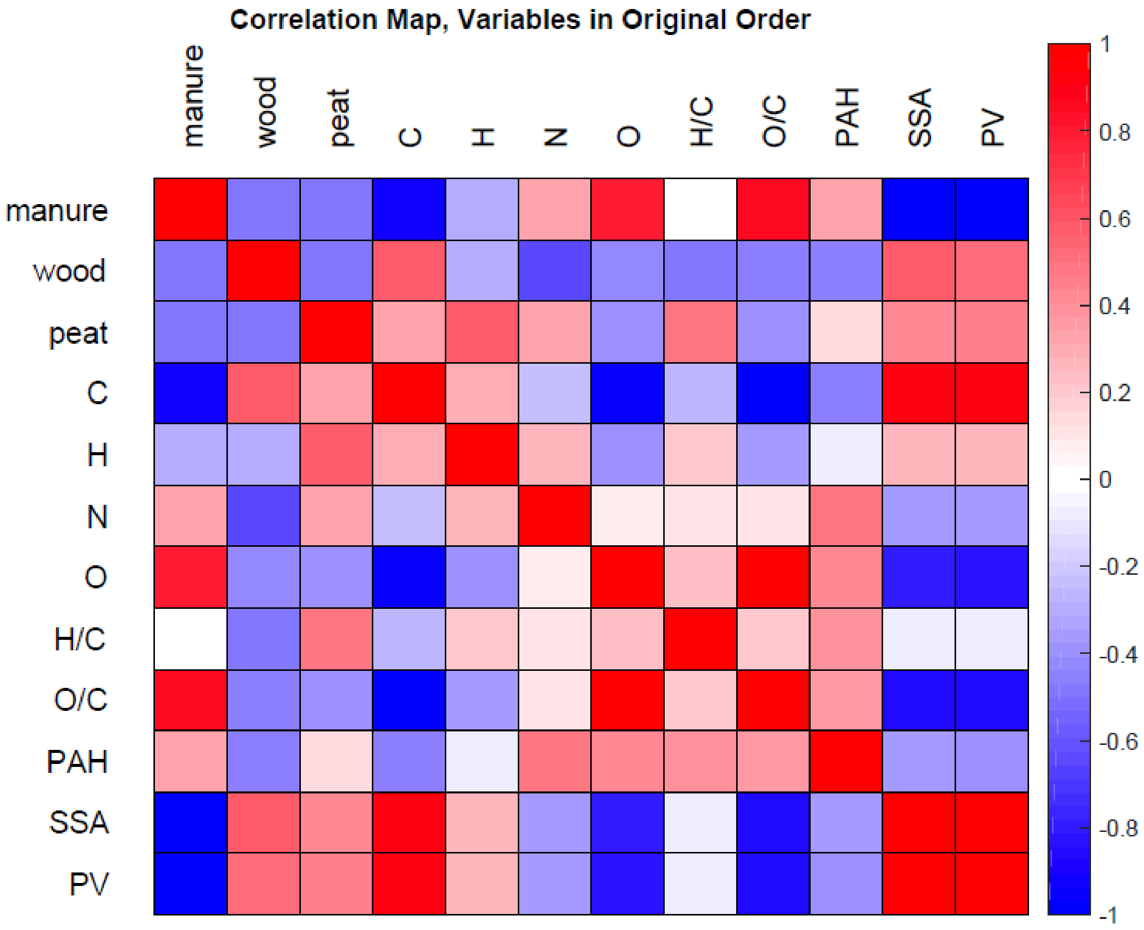


Figure 26 Correlation matrix among all investigated biochar properties.

6. Conclusion

In this essay results about the thermo-chemical characterization of biochars produced by slow pyrolysis conversion of horse stable residues have been reported. These wastes have been processed in a quartz tube furnace at 600°C for 2 hours with an initial heating rate of 10°C/min, treating different kind of material combinations: pure mixtures of each element, binary mixtures of each pair of elements and a ternary mixture including all components in same percentage value. As a result, a detailed set of information has been provided to prove the quality of produced biochars and their applicability.

Proximate and CHNSO analysis results show how the produced biochars present less elemental composition variation respect to original biomass. In particular, the carbon content of all products is bigger than 50%, allowing the classification of obtained chars as "biochar" in agreement with major voluntary biochar product standards (EBC, BQM and IBI-BS).

A larger variation of specific values depending on the choice of original feedstock has been found in pH, PAH and BET analysis. Specifically, BET results demonstrate how woody and peat biochar present higher SSA values, more than 181 m^2/g in every sample where at least one of the two substances is present. In addition, it shows how a higher percentage of macropores is present in manure biochar, resulting in a less SSA (only 45 m^2/g). PH results demonstrate how pyrolytic conversion hugely increases this value, since all produced biochar are classified as alkaline. Lastly, PAH analysis demonstrate that all biochar can be applied to soil having a value less than the threshold of 12 mg/kg.

Besides, the application of the mixture model to the experimental data has demonstrated how mixtures subjected to pyrolysis behave as physically bounded materials. This approach allowed to predict the response of the main properties for any combination of ingredients and to estimate the influence of each component on the final value, with very good agreement between predicted and observed values. This result suggests the possible application of this kind of approach also to other kinds of materials. The only exception was made by PAH, in fact, this property has been found not to behave as a function of mixtures components, having higher concentrations in mixtures than pure materials. Further analysis and studies must be performed in order to acquire a better understanding of PAH behaviour and mechanisms of formation.

Concluding, all the results prove how generally the pyrolytic conversion of the residues ends in value added by-products, confirming this treatment as a better waste manage alternative with respect to incineration. Moreover, yield results highlight how volume of original biomass has been diminished, still having acceptable mass ratios. Concerning specific produced biochars, their quality has been investigated following EBC criteria. So that, pH, PAH and BET results suggest its most valuable application as a soil amendment since: high pH level can prevent soil acidification issue, under-limit PAH concentration will not present a hazard for human health, and high SSA and PSD variation will provide habitats for microorganism and detain soil GHG emissions.

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8. Appendix

8.1 Moisture Content

Table 19 Moisture content measurements for all different biomasses

Sample	Tare	WS0	W0	W	MC
[#]	[g]	[g]	[g]	[g]	[%]
W1	1,8075	1,8511	3,6586	3,5192	7,5%
W2	1,8182	1,5826	3,4008	3,2775	7,8%
W3	1,8406	1,8	3,6406	3,5049	7,5%
M1	1,8335	1,4837	3,3172	3,2138	7,0%
M2	1,8369	1,7694	3,6063	3,4792	7,2%
M3	1,8219	1,6195	3,4414	3,3253	7,2%
P1	1,8353	2,0573	3,8926	3,7218	8,3%
P2	1,8211	2,166	3,9871	3,7987	8,7%
P3	1,8249	3,3783	5,2032	4,8890	9,3%

8.2 Ash Content

Table 20 Ash content measurements for all different biomasses

Sample	Tare	W0ds	W0	W	Ash
[#]	[g]	[g]	[g]	[g]	[%]
W1	20,1922	1,3431	21,5359	20,1961	0,25%
W2	17,3122	1,4522	18,765	17,3164	0,25%
W3	17,5287	1,4962	19,0256	17,5326	0,21%
M1	20,9196	2,1077	23,0278	21,0698	7,1 %
M2	19,8003	1,6627	21,4636	19,9157	6,9 %
M3	18,8127	1,9401	20,7335	18,9515	8,1 %
P1	21,5776	2,2966	23,8747	21,6197	1,81%
P2	21,1512	1,8342	22,9863	21,1747	1,23%
P3	13,0081	1,891	14,9	13,0304	1,13%

8.3 Volatile Matter

Table 21 Volatile matter content measurements for all different biomasses

Sample	Wc	IB	Wi	Wf	VM
[#]	[g]	[g]	[g]	[g]	[%]
W1	25,0006	1,4691	26,4697	25,17861	87,88%
W2	20,4147	1,0813	21,4961	20,5584	86,71%
W3	35,5728	1,208	36,7803	35,7214	87,69%
P1	32,6386	1,1626	33,8014	32,9296	74,97%
P2	37,4888	1,7504	39,2392	37,9321	74,67%
P3	21,8193	1,2273	23,0466	22,1287	74,79%
M1	25,1406	1,344	26,4842	25,4495	77,01%
M2	25,7589	1,1808	26,9401	26,0196	77,93%
M3	26,0131	1,3868	27,4003	26,3378	76,59%

8.4 CHNSO

Table 22 CHSNO measurements for selected samples of biochar

Sample	C	H	N	S	O	H/C	O/C
W1	89,98%	2,03%	0,55%	0,20%	6,99%	0,02	0,08
W2	89,70%	2,19%	0,73%	0,25%	6,88%	0,02	0,08
P1	87,47%	2,57%	1,61%	0,38%	6,16%	0,03	0,07
P2	87,08%	2,38%	1,74%	0,33%	7,24%	0,03	0,08
M1	67,99%	1,70%	2,06%	0,24%	20,91%	0,03	0,31
M2	68,46%	1,61%	1,93%	0,21%	20,89%	0,02	0,31
PW3	78,55%	2,17%	1,20%	0,17%	16,88%	0,03	0,21
MP1	74,44%	2,13%	1,47%	0,17%	17,33%	0,03	0,23
MW1	78,34%	2,18%	1,44%	0,20%	14,17%	0,03	0,18
MPW1	77,88%	2,20%	1,68%	0,18%	15,01%	0,03	0,19
MPW2	79,68%	2,08%	1,75%	0,18%	13,52%	0,03	0,17
MPW3	82,80%	2,06%	1,70%	0,18%	10,10%	0,02	0,12

8.5 Yield

Table 23 Yield measurements for all different biomasses

Material [name]	Tare [g]	IBM Weight [g]	AT Weight [g]	BC Weight [g]	BC Yied [%]
Manure 1	39,9545	4,015	41,1103	1,1558	28,79%
Manure 2	39,9443	4,8595	41,3508	1,4065	28,94%
Manure 3	82,1229	8,3493	84,5682	2,4453	29,29%
Wood 1	39,9458	3,0607	40,516	0,5702	18,63%
Wood 2	82,2556	8,2745	83,83	1,5744	19,03%
Wood 3	82,1146	8,5644	83,8695	1,7549	20,49%
Peat 1	82,1745	11,1618	84,9466	2,7721	24,84%
Peat 2	82,1707	13,9554	85,7105	3,5398	25,37%
Peat 3	82,1195	14,3694	86,7883	4,6688	32,49%
MPW 1	82,1535	7,7095	84,1091	1,9556	25,37%
MPW 2	82,1407	9,0719	84,649	2,5083	27,65%
MPW 3	82,1361	9,1797	84,6989	2,5628	27,92%
MP 1	82,1256	8,2544	84,6766	2,551	30,90%
MP 2	82,1109	8,2957	84,6437	2,5328	30,53%
MP 3	82,1028	8,47	84,6826	2,5798	30,46%
MW 1	82,1294	8,0447	84,1916	2,0622	25,63%
MW 2	82,1141	8,3956	84,2626	2,1485	25,59%
MW 3	82,1048	8,2461	84,2029	2,0981	25,44%
PW 1	82,1256	8,255	84,3487	2,2231	26,93%
PW 2	82,1091	8,1692	84,2877	2,1786	26,67%
PW 3	81,7819	8,8519	84,0645	2,2826	25,79%

8.6 PAH

Table 24 PAH measurements for selected samples of biochar (1: LOD= 10-50 ng/g and 2: LOD= 50-100 ng/g.)

PAH compound	W2	W3	P2	P3	M2	M3	MPW1	MPW2	MPW3	MW2	MP2	PW2
	[ng/g]	[ng/g]	[ng/g]	[ng/g]	[ng/g]	[ng/g]	[ng/g]	[ng/g]	[ng/g]	[ng/g]	[ng/g]	[ng/g]
Naphthalene^1	4991	1750	5988	4940	5944	5306	8744	6010	5563	5383	5069	5989
Asenaphtylene^1	LOD	123	39	80	75	21	53	46	20	40	100	LOD
Asenaphtene^1	LOD	187	72	120	LOD	LOD	141	92	LOD	LOD	86	LOD
Fluorene^1	LOD	97	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	70	LOD
Phenanthrene^1	67	254	85	145	1550	65	536	493	227	102	462	303
Anthracene^1	63	156	91	100	281	67	149	242	200	76	222	61
Fluoranthene^1	LOD	68	44	56	105	26	82	161	272	72	158	42
Pyrene^1	LOD	38	54	43	70	LOD	65	104	204	44	120	LOD
Benz(a)antracene^1	LOD	146	68	108	148	LOD	LOD	163	480	98	194	842
Chrysene^1	LOD	80	LOD	79	121	LOD	LOD	132	449	68	170	LOD
Benzo(b)fluoranthene^2	LOD	LOD	LOD	LOD	183	LOD	34	208	541	48	239	LOD
Benzo(k)fluorantene^2	LOD	LOD	LOD	LOD	123	LOD	LOD	LOD	424	LOD	157	LOD
Benzo(a)pyrene^2	LOD	LOD	LOD	LOD	158	LOD	76	LOD	446	75	172	LOD
Benzo(ghi)perylene^2	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	283	LOD	116	LOD
Dibenz(ah)antracene^2	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	175	LOD	LOD	LOD
Indeno(1,2,3-cd)pyrene^2	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	267	LOD	110	LOD
ΣPAHS	5120	2900	6440	5670	8760	5490	9880	7760	9550	6010	7440	7240

8.7 BET

Table 25 BET measurements for all different biochars

Sample	SSA	PV	PS
[#]	[m²/g]	[cm³/g]	[nm]
M1	38,3702	0,029188	3,04283
M2	44,2764	0,032712	2,95522
M3	52,2377	0,036081	2,76281
W1	356,7015	0,188271	2,11124
W2	351,0442	0,183297	2,08859
W3	346,3744	0,196576	2,27009
P1	301,7686	0,179269	2,37625
P2	319,6375	0,177339	2,21925
P3	300,0267	0,177566	2,36734
MPW1	223,003	0,121634	2,18176
MPW2	230,411	0,127953	2,2213
MPW3	229,9527	0,125881	2,18969
MP1	200,979	0,112285	2,23475
MP2	198,3723	0,111918	2,25673
MP3	192,3417	0,108905	2,26482
MW1	195,4671	0,108651	2,22342
MW2	164,8023	0,092368	2,24191
MW3	182,099	0,099651	2,18895
PW1	317,7354	0,171761	2,16231
PW2	319,4938	0,172338	2,15764
PW3	303,3559	0,170105	2,24297

8.8 pH

Table 26 pH measurements for all different biochars

Material	Maesure 1	Maesure 2	Maesure 3	AVGmes
Manure 1	9,72	9,76	9,78	9,75
Manure 2	10,53	10,51	10,48	10,51
Manure 3	10,05	10,02	10,03	10,03
Wood 1	7,37	7,34	7,37	7,36
Wood 2	7,78	7,78	7,78	7,78
Wood 3	7,56	7,77	7,65	7,66
Peat 1	7,56	7,5	7,48	7,51
Peat 2	7,35	7,28	7,27	7,30
Peat 3	7,45	7,42	7,4	7,42
MPW 1	8,34	8,32	8,32	8,33
MPW 2	8,53	8,57	8,58	8,56
MPW 3	9,39	9,41	9,42	9,41
MP 1	8,81	8,79	8,83	8,81
MP 2	9,19	9,24	9,26	9,23
MP 3	9,4	9,46	9,49	9,45
MW 1	8,8	8,82	8,74	8,79
MW 2	9,46	9,43	9,47	9,45
MW 3	9,79	9,77	9,75	9,77
PW 1	7,16	7,18	7,17	7,17
PW 2	7,81	7,75	7,78	7,78
PW 3	7,46	7,77	7,6	7,61

Table 27 pH measurements for all different biomasses

Manure 1	6,87	6,91	6,92	6,90
Manure 2	6,83	6,85	6,86	6,85
Manure 3	6,88	6,9	6,92	6,90
Wood 1	4,34	4,31	4,31	4,32
Wood 2	4,34	4,33	4,33	4,33
Wood 3	4,3	4,29	4,3	4,30
Peat 1	3,07	3,08	3,08	3,08
Peat 2	3,04	3,03	3,04	3,04
Peat 3	3	3,04	3,06	3,03