

CRANFIELD UNIVERSITY

MARIA PIMENTA DA COSTA OCAMPO

**Evaluating phosphorus availability from sewage sludge derived
pyrochar and hydrochar on spring wheat**

School of Water, Energy and Environment

PhD

Academic Year: 2017 - 2021

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September 2021

This thesis is submitted in partial fulfilment of the requirements for
the degree Degree of Doctor of Philosophy

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ABSTRACT

The production of sewage sludge is expected to increase as the population continuously develops worldwide. Being a source of nutrients, the re-use of this material as soil amendment could address the current unstable situation. Sewage sludge could be an alternative source of available phosphorus to chemical fertilisers that could help to remediate the growing demand of mineral phosphorus reserves. In parallel, it also acts as a good source of organic matter for low fertile soils resulting from overexploitation and erosion events.

Even though recent studies have been focusing on the use of sewage sludge on land application, there is still a stigma attached to this practice as its use in agriculture has to be managed carefully due to its variability in physical-chemical properties. The perception of sewage sludge as a source of pollutants relies on current research and it's tampered by the huge diversity of feedstocks and the variability of it depending on the sampling.

Thermal treatments are assessed as route towards the production of alternative P fertilisers from sewage sludge. Two pyrochars were produced through pyrolysis at 400°C (P400-1) and 300°C (P300-1) for 1h using pre-oven dried (105°C-48h) sewage sludge from Spain (SS_{ES}). Two hydrochars were obtained through Hydrothermal Carbonization at 180°C (H180-4) and 240°C (H240-4) for 4h, using SS_{ES} adjusted to 20% dry matter.

P availability changes of SS_{ES} were evaluated after thermal treatments and its effect on soil available P content when added on their own (5, 10, 20 t ha⁻¹) and in combination with a commercialized sewage sludge from UK (SS_{UK}) as soil amendment (50% char 50% SS_{UK}, at 10, 20, 40 t ha⁻¹). Single and combined amendment were carried out at the same time, comprising a total of 136 pots (H:50 cm; D:10.5 cm). Thermal treatments reduced available-P in all derivatives H180-4 (45.9%), H240-4 (57.5%), P300-1 (76.2%), P400-1 (83.6%) from 150.4 mg kg⁻¹ SS_{ES}. Nonetheless, one single application over two cropping seasons of spring wheat in a glasshouse increased available-P to 23.7-26.7 mg kg⁻¹ from 1.5 mg kg⁻¹ in control soil when combined at 40 t ha⁻¹.

No significant improvement was observed in grain yield over two seasons among the treatments, but the nutrient balance and heavy metals assessment indicated an evolution of these materials in the soil over time. The use of pyrochars, produced a buffering effect that lasted two seasons preventing an acidification of the loamy sandy soil that couldn't be achieved through hydrothermal carbonisation.

This study shows the potential of thermal treatments as pre-treatment, and its limitations. Sewage sludge in agriculture must be managed carefully due to its variability in physical-chemical properties and their content of Al, Fe and heavy metals. Acidification of the soil should be avoided in order to obtain better results on P availability. Pyrolysis of sewage sludge may not replace mineral fertilisers, but it could be used to prevent acidification if used as a pre-treatment of sewage sludge, increasing carbon stability and organic matter in loamy sandy soil, immobilizing heavy metals, and providing a slow release of P.

KEYWORDS: Sewage sludge, Hydrothermal Characterisation, Pyrolysis, hydrochar, pyrochar, alternative fertilisers, soil analysis, heavy metal environmental risk, Phosphorus Use Efficiency, phytotoxicity on seed germination, grain yield.

ACKNOWLEDGEMENTS

Thank you all who have contributed to the development of this project. For those who transferred bits of knowledge and useful tips during lunch breaks and long shifts in the lab, I couldn't thank you enough. Special thanks to those who dedicated a word of encouragement and reminded me to appreciate each day and its circumstances.

Nuannat Simmons and Richard Andrews from the environmental analytical facility (EAF) at Cranfield University are acknowledged for the providing their training, performing CEC and analysing metal content in digested samples when during lockdown. Cristinel Putinica from the School of Water, Energy and Environment, Cranfield University is gratefully acknowledged for his technical assistance to set up the experiment in the glasshouse. Dr Ali Navabi, Cranfield's Centre for Climate and Environmental Protection, who kindly provided TG and BET data. To Nigel James who brought the samples of sludge for the combined amendments. Special thanks to Roberts, who stayed with us until late in b244 laboratory.

Many thanks to my supervisors Dr Ruben Sakrabani and Professor Wilfred Otten for their time, their infinite patience and their guidance through these four years at Cranfield University. Thanks to Professor Gabriel Gasco Guerrero and Professor Ana Maria Mendez Lazaro from the Technical University of Madrid, for opening the door to this experience and producing the materials.

Ever so grateful to Sir John and Lady O'Reilly who funded this project through the European Partnership Programme 2017 and gave me the opportunity to go on this adventure abroad and to Cranfield University for hardship fund that helped me greatly in the completion of this thesis.

This thesis is dedicated to the Ocampo Castano family, wherever you are, you inspire me daily.

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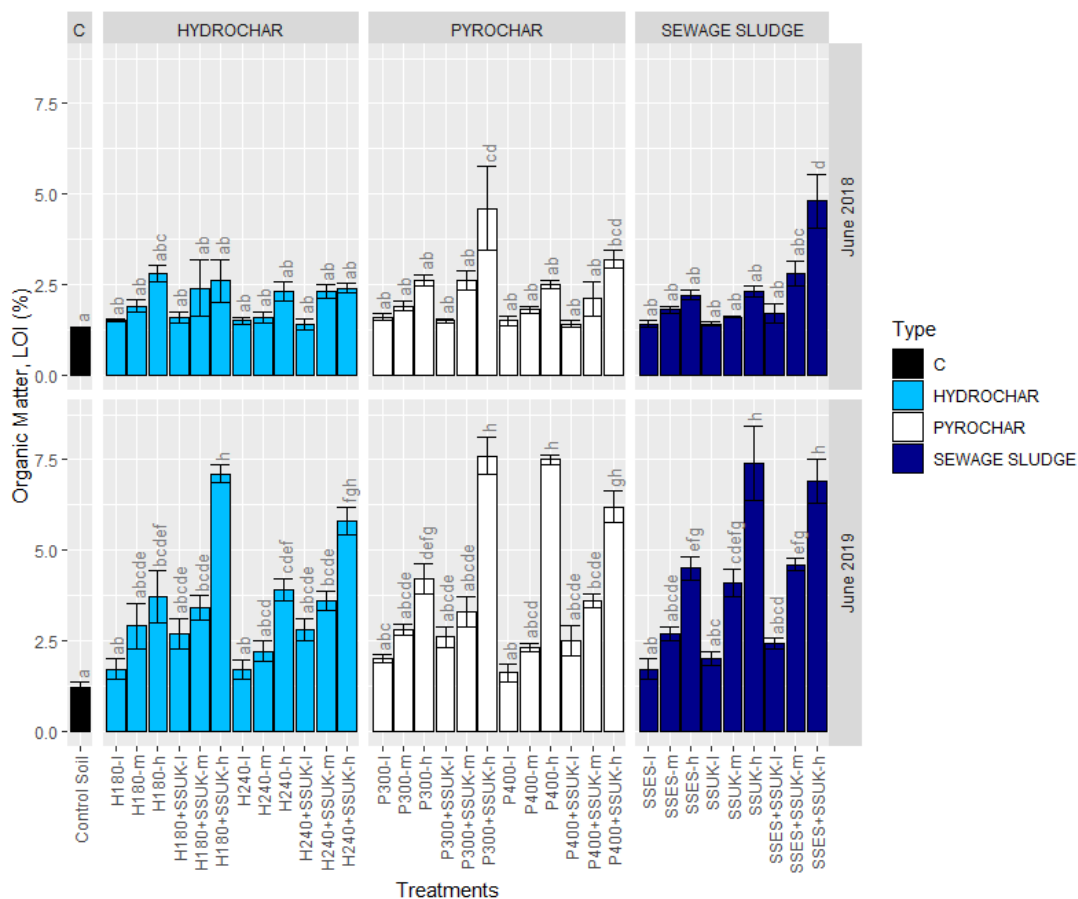


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LIST OF ABBREVIATIONS

AGB	Above Ground Biomass
AGW	Average grain weight
ANOVA	Analysis of Variance
ATP	Adenosine triphosphate
Av.P	Available Phosphorus
BET	Brunauer–Emmett–Teller
CEC	Cation Exchange Capacity
Corg	Carbon Organic
DEFRA	Department for Environment, Food & Rural Affairs
DMY	Dry Matter Yield
dTG	Derivative of Thermal Gravimetric Analysis
EC	Electro conductivity
EU	European Union
EUROSTAT	statistical office of the European Union
FAO	Food and Agriculture Organization of the United Nations
FTIR	Fourier-transform infrared spectroscopy
GDP	Gross domestic product
GI	Germination Index
HI	Harvest Index
HM	Heavy Metals
HTC	Hydrothermal Carbonisation
IBI	International Biochar Initiative
LOI	Loss on Ignition
LMMs	Linear Mixed Model
NG	Number of grains
NL30	Number of leaves day 30
NMR	Nuclear Magnetic Resonance
NPK	Nitrogen-Phosphorus-Potassium mineral fertiliser
NUE	Nitrogen Use Efficiency
OM	Organic Matter
OMF	Organo-Mineral Fertiliser
PAHs	Polycyclic Aromatic Hydrocarbons

PCA	Principal Component Analysis
pH	Potential of Hydrogen
PUE	Phosphorus Use Efficiency
REML	Restricted (or residual, or reduced) Maximum Likelihood
SEM	Scanning Electron Microscopy
TGA	Thermal Gravimetric Analysis
TOC	Total Organic Carbon
UK	United Kingdom
UNESCO	United Nations Educational Scientific and Cultural Organization
USDA	U.S. Department of Agriculture
WWTP	Wastewater Treatment Plant
XAS	X-ray Absorption Spectroscopy

LIST OF ELEMENTS ABBREVIATION

Al	Aluminium
As	Arsenic
B	Boron
C	Carbon
Ca	Calcium
Ca	Calcium
Cd	Cadmium
Cr	Chromium
Cu	Copper
Fe	Iron
H	Hydrogen
Hg	Mercury
K	Potassium
Mg	Magnesium
Mn	Manganese
Mo	Molybdenum
N	Nitrogen
Na	Sodium
Ni	Nickel

O	Oxygen
P	Phosphorus
Pb	Lead
Zn	Zinc
Al	Aluminium

SAMPLE ABBREVIATION

C	Control
H180/ H180-4	Hydrochar obtained at 180°C and 4h from SS _{ES}
H180- SS _{UK}	Hydrochar obtained at 180°C and 4h from SS _{ES} combined with SS _{UK}
H240/ H240-4	Hydrochar obtained at 240°C and 4h from SS _{ES}
H240- SS _{UK}	Hydrochar obtained at 240°C and 4h from SS _{ES} combined with SS _{UK}
P300/ P300-1	Pyrochar obtained at 300°C and 1h from SS _{ES}
P300- SS _{UK}	Pyrochar obtained at 300°C and 1h from SS _{ES} combined with SS _{UK}
P400/ P400-1	Pyrochar obtained at 400°C and 1h from SS _{ES}
P400- SS _{UK}	Pyrochar obtained at 400°C and 1h from SS _{ES} combined with SS _{UK}
SS	Sewage sludge
SS _{ES}	Sample of sewage sludge form Spain
SS _{UK}	Sample of sewage sludge form UK used for combined amendments

CHAPTER 1: THERMALLY TREATED SEWAGE SLUDGE AS A SOLUTION TO PHOSPHORUS (P) CRISIS

Summary: This chapter highlights the necessity to find an alternative source of P to ensure agronomic supply and presents the research objectives formulated to accomplish the research aim. It frames the gap of knowledge by presenting the available options of thermal treatments to produce a carbonaceous material from sewage sludge and includes a review of the studies conducted to date that have use them as means to test them as soil amendment with different purposes.

Highlights:

- Overview of current situation regarding P fertilisers and sewage sludge management;
- Review of previous research of sewage sludge thermally pre-treated as soil amendment, purpose, methodologies of analysis applied and results obtained;
- Statement of the research aim and objectives to accomplish it;
- Explanation of the thesis structure.

1.1 Overview of current situation

Phosphorus (P) is an essential element for all life forms as it is consumed in many metabolic processes (Bünemann, 2015; Miller & Arai, 2017a), and it plays an essential role in agronomic systems and thus in food production (Scholz *et al.*, 2013; Torri, Studart and Ea, 2017). Most P found in soil comes from the primary rock material, often apatite (Mullen, 2019). Once the P is released, it will be incorporated to organic matter, shifted to inorganic compounds or transferred between the systems as shown in Figure 0-1. Thus, pedogenesis and land use will determine the proportions of how P will be stored in the soil.

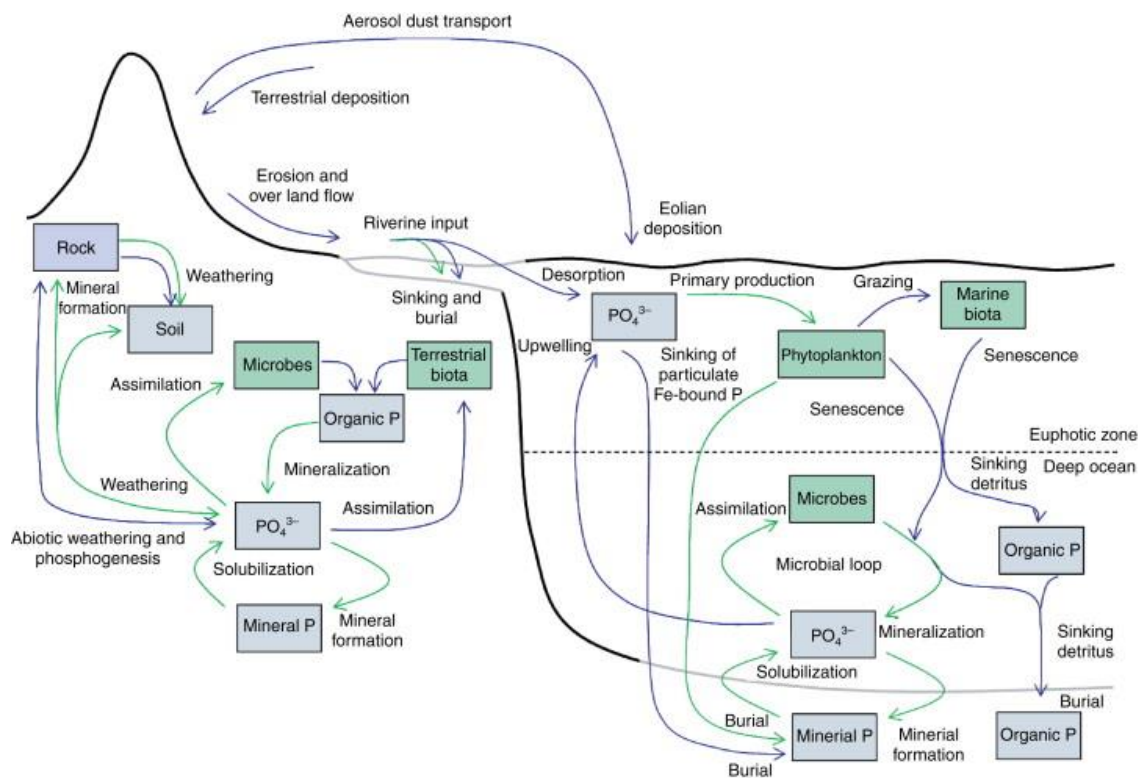


Figure 0-1 P cycle, P pools and flows. Microbiology (Mackey and Paytan, 2009).

Plants absorb P from the soil solution either directly through the root epidermis or with the assistance of mycorrhizas (Amalero *et al.*, 2003; Grace, 2007) (Figure 0-2). This element in the soil solution is predominantly found as a negatively charged ion and often combined with oxygen as orthophosphate anion. This is the form of P that is available for the plants. However, it is in a delicate equilibrium with calcium, aluminium and iron with which they can bind as an amorphous

mineral depending on their concentration in soil and pH changes (Sun *et al.*, 2015). On the other hand, P can also be presented as an organic form as orthophosphates di- and monoesters, like inositol phosphate, polyphosphates and phosphonates (Bünemann, 2015; Miller and Arai, 2017a). This would be accessible to the plant after its mineralization to orthophosphate anion as shown in the Figure 0-2.

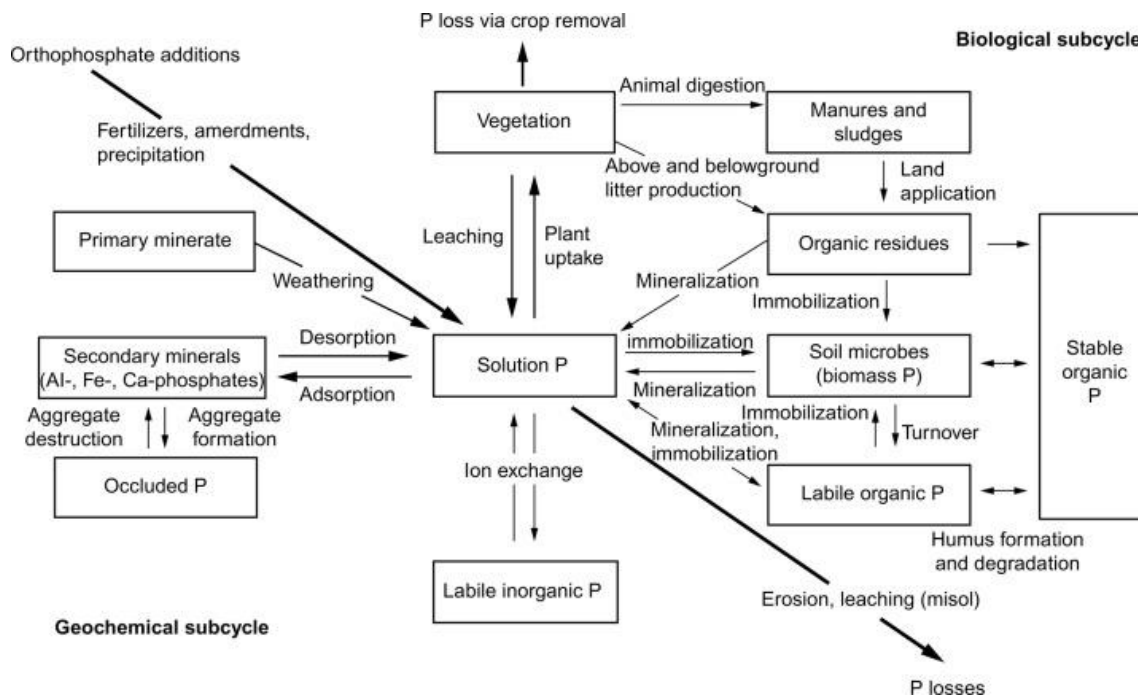


Figure 0-2 P dynamics in soil solution (Mullen, 2019).

Therefore, although most soils contain a considerable amount of P, it may not be in its soluble form, and the high to moderate soil P sorption capacity is a determinant factor that can reduce P use efficiency, making it less available for plants (Simpson *et al.*, 2011). On this account, P-deficiency is currently an important limitation for crop developing in different agricultural systems all over the world (Simpson *et al.*, 2011; Dai *et al.*, 2014; Zhu, Li and Whelan, 2018). To satisfy current food demands, modern agriculture systems have been relying on the use of P inputs (Torri, Studart and Ea, 2017) either as manures or as readily available orthophosphate obtained from P mineral rock (Hogan, McHugh and Morton, 2001)(Schneider and Haderlein, 2016a).

However, the production of P mineral fertilisers is monopolised by several countries shown in Figure 0-3, which political and socioeconomic instability compromises their distribution and market prize, making them an unreliable source of P for small food production (Schneider and Haderlein, 2016a). For example, late Russia's political decisions, not only has driven up gas and petrol costs but also phosphorus and potassium fertilisers which repercussion to global food production is yet to be quantified.

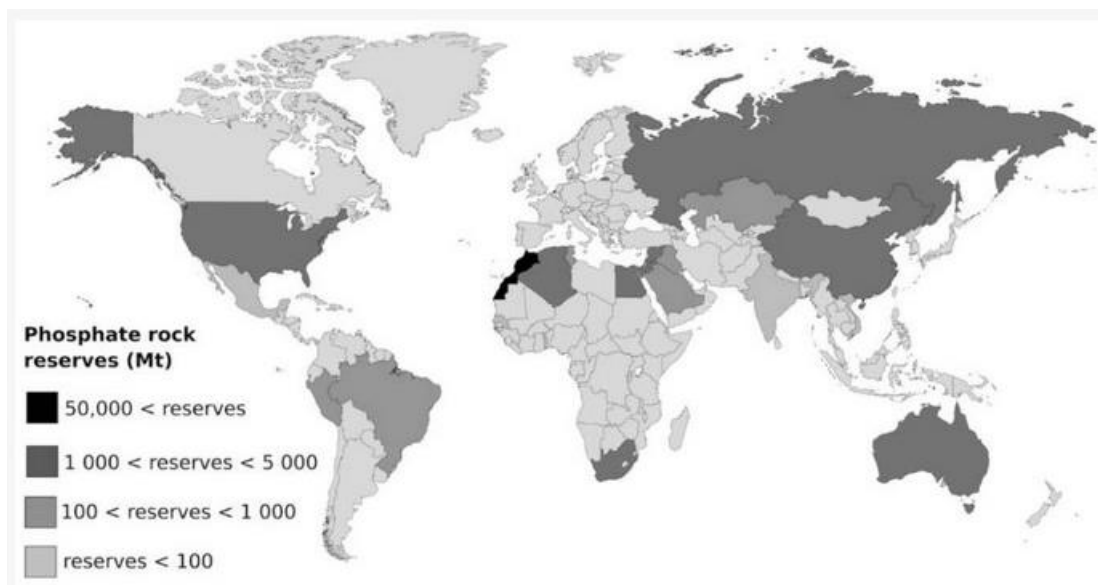


Figure 0-3 P mineral rock reserves (Daneshgar et al., 2018).

This represents a challenge, especially for developing countries with soils poor in P, and creates a vicious circle by compromising the economic growth as agricultural production has a significant role on it (Arif *et al.*, 2012). This disparity in soil P concentration from country to country is shown in Figure 0-4. During the first decade of 2000, P inputs were primarily destined to cropland (a) rather than grassland (b). Cropland received 87% of P in the form of P mineral fertiliser while grassland received 91% of P though manure (Fei Lin 2018). Despite this, cropland still experimented globally a deficit of P from 2002 to 2007 which positively shifted in 2008 and 2009 leading to an accumulation of available P. However, the economic crisis of 2009 caused an increment of the P mineral rock prices which limited its use then onwards. From 2009 P uptake in cropland mainly

relied on the already available P accumulated during the previous years and in fluctuating new inputs.

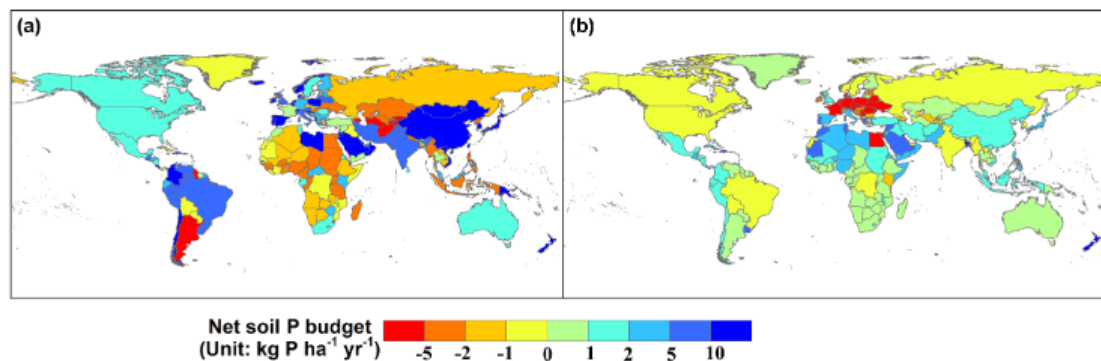


Figure 0-4 P pools and soil budgets (Lun et al., 2018).

As shown in in Figure 0-4., with a significant lower input of P compared to croplands, grassland had a P deficit during the same decade. Therefore, it's clear that the cropland's P budget would be extremely tight if the inputs from P mineral rock were hampered.

However, P fertilisers from P mineral rock are highly inefficient and its estimated that over 80% of mineral P is lost from the moment they are produced mainly in cropping systems (Cordell and White, 2011). Hence, in order to maintain an adequate level of plant available P (Simpson *et al.*, 2011) an excessively amount has been used (Kalkhajeh *et al.*, 2017; Miller and Arai, 2017b). However, due to a poor management and the lack of knowledge (A. Rashid, Awan and Ryan, 2005) and previous regulations, an excess of P has been added to farmlands causing downstream eutrophication (Horta and Torrent, 2007; Sun *et al.*, 2015) . This happens when an excessive quantity of nutrients enriches water systems, by either leachate, runoffs or erosion events as indicated by Kalkhajeh *et al.*, (2017), causing an undesirable proliferation of algae that reduces dissolved oxygen and thus, decreases water quality creating a threat for all aerobic organisms (Le Corre *et al.*, 2009a).

Additionally, P pools, both organic and mineral P phases, and soil organic C have been negatively affected by the increasing temperatures experimented during the climate change (Enqing Hou 2018). Soil particle size and high precipitation has

also been directly linked to available P losses (Enqing Hou 2018), being rich sandy-soils more prone to lose available P due to run offs and erosion (sim 1998)(Christine Alewell 2020).

These phosphate-rock fertilisers were first applied in the 1820s, but it took more than a century, around 1940s, for them to be highly in demand (Torri, Studart and Ea, 2017). Unfortunately, coming from a non-renewable material (Hogan, McHugh and Morton, 2001), its indiscriminate use has caused a depletion of phosphorus rock (Bünemann, 2015). Phosphorus Peak, determined by the point when the demand starts to surpass the supply (Cordell and White, 2011), has been estimated to take place by 2035 (Cordell *et al.*, 2011; Schröder *et al.*, 2011). For this reason, this element entered in the list of Critical Raw Materials of 2017 (European Commission, 2017). It is clear that, as argued Rockström *et al.*, (2009) not only boundaries have been crossed, for biodiversity loss and climate change, but also for nutrient cycle, first with nitrogen and now with phosphorus at a planetary scale (Rockström *et al.*, 2009).

This raises the concerns of how future societies would face this limitation (A Rashid, Awan and Ryan, 2005) that could even represent a threat for the next century economy (Cordell and White, 2011). According to UNESCO's World Population 2300 report (United Nations, 2017), a continuous growth of the world's population is expected in the coming years. Only in Europe, 38% of P mineral rock is used to grow cereals (Eurostat, 11-09-2021). While globally, compared to other crops, wheat critically determines global P fluxes as it receives the greatest P input, not only for domestic consumption but also for international trade (Figure 0-5) (Lun *et al.*, 2018). In fact, wheat contributes more than 10% to the value added in agriculture and almost 3% to GDP, making its production determinant not only for human nutrition but also for its economy (Wang *et al.*, 2018a). Consequently in the future, the unstable and hampered agricultural development may not be enough to meet the needs of the population which is in constant expansion (Wang *et al.*, 2013).

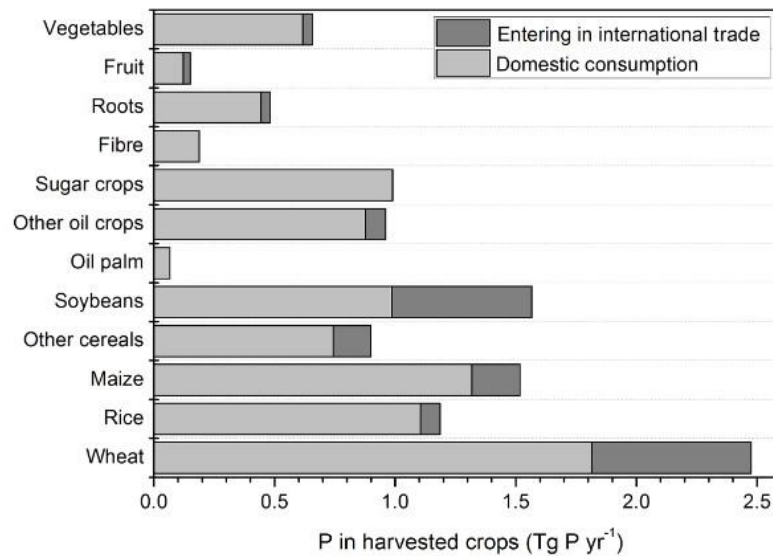


Figure 0-5 P demand in harvested crops data 2010 by Lun et al., (2018).

Therefore, to secure continuous food production to feed needs of a growing human population and preserve the environment, there must be a regulation of P fertilisers. The Environmental Agency among National institutions has created several codes of Good Agricultural Practice for farmers, growers and land managers (DARD, 2008) and Fertiliser Manuals (DEFRA, 2010) to give guidance lines of recommended P amounts for a certain types of crops, depending on the soil and its previous amount of P which are categorised by Index 0-9 (DEFRA, 2010).

Complementary, an effort has been made to recover P by exploring new sources of P and to make a more efficient use of P fertilisers to ensure a better management of P mineral deposits and reduce its demand (Le Corre *et al.*, 2009a). A possible solution to this problem could be found while providing an answer to mitigate another negative consequence of this continuous growth of the population, the increasing amount of sludge generated from wastewater treatment plants (WWTPs) (Huang and Tang, 2015; Faria *et al.*, 2018a). In fact, a significant amount of P needed in human societies ends up being collected in the WWTPS (Torri, Studart and Ea, 2017), as it is also present in detergents, and insecticides (Le Corre *et al.*, 2009a). The European Union established since 1991 that P must be removed from water in order to protect the environment (EEC

Council, 1991), making sewage sludge a suitable and promising source of recyclable P (Le Corre *et al.*, 2009a; Huang and Tang, 2015; Torri, Studart and Ea, 2017).

Disposal of sewage sludge is the last option in the hierarchical principle of the production and management of waste (European Parliament and Council, 2008). According to this, sewage sludge management must focus as well on prevention, preparation for re-use, recycling, or other forms of recovery, including energy recovery before a controlled discharge takes place. As a preventive measure, in the event of a recovery of sewage sludge from domestic, urban, or similar wastewater, Directive 2008/98/CE law establishes that sewage sludge use in agricultural land must be carried out only if the relevant treatments have been done previously to ensure the environmental protection.

Generally, the sewage sludge is stabilized in the treatment plant, a procedure by which its volume is reduced, and methane is obtained that can be used in the plant itself, and finally they are stored until collection by a waste manager.

1.2 Sewage sludge pre-treatments for agricultural use

1.2.1 Most used pre-treatments

Currently, composting followed by a soil application as fertiliser represents one of the main management routes of sewage sludge (Eurostat, 11-09-2021), since it allows the waste to be recycled, reducing its disposal (Fang and Wong, 1999). The composting process reduces the humidity of the sewage sludge and consequently its volume, which facilitates its later management (Wong and Selvam, 2006). During this process, the conditions of aeration, humidity and temperature must be rigorously controlled to carry out an optimum transformation of the organic matter by aerobic digestion. Three states can be distinguished as a function of temperature: mesophilic phase (35-40° C), thermophilic phase (55-65° C) and subsequent cooling (Chen *et al.*, 2017). Thermophilic conditions allow destroying a large part of the pathogenic organisms present in the waste, thus reducing the risk associated with them. Moreover, during the process of humification of organic matter, heavy metals bioavailability can be reduced by

affecting the form in which they are found in the waste (Wong and Selvam, 2006). Nonetheless, even after being subjected to an anaerobic digestion process and later to a composting, the concentration levels of heavy metals may still limit their application in agricultural soils depending on the sample (Zhu *et al.*, 2012).

Studies on sewage sludge application to grow crops run from 2 to 6 years, either in field and pot experiments with an overall improvement on soil properties and yield. These are presented in Table 0-1 and highlight that several factors may be taken into account to produce an optimal response. The risk of the accumulation of Polycyclic Aromatic Hydrocarbons (PAHs) was studied by Li and Ma, (2016) for example, who indicated a significant difference in the rate and timing of application of sewage sludge. The same rate 60t/ha showed a higher accumulation of PAHs if applied at once than over 6 years as 10t/ha. The sample of Li and Ma, (2016), reported a maximum concentration of 241 ng/g on the sum of 16 PAHs in soil after 6 years of application 10-60t/ha, while Oleszczuk and Baran, (2005) showed a higher accumulation of PHAs in agricultural soil, 374.7 ng/g of PAHs after 4.5 years at higher rates (Table 0-1). Nevertheless, no significant differences were found on the grains of spring wheat grown with sewage sludge of compared to control soil in Li and Ma, (2016) and the concentration of PAH's accumulated in Corn, Spring barley, winter rape, potatoes and cereal mixture in Oleszczuk and Baran, (2005) were also below the limits.

In turn, Diogenes L. Antille, Sakrabani and Godwin, (2014) reported significant increase of extractable-P and soil organic matter (7% to control soil) using organo-mineral fertilisers derived from sewage sludge and a linear improvement on dry matter yield (DMY) when growing rye grass. While Koutroubas *et al.*, (2014) reported in a field experiment growing two seasons of winter wheat with sewage sludge no issues of heavy metal accumulation in the soil or grains, obtaining taller plants compared to control and a yield improvement of 64.4-72.5% by applying 60 Mg/ha. Moreover, grain yield at 20 Mg sewage sludge was found in Koutroubas *et al.*, (2014) to be equivalent to the crop grown with inorganic fertiliser while improving protein grain content. Nonetheless, not every study shows positive outcomes depending on the feedstock, rate and time of the

experiment. Although Latare *et al.*, (2014) indicated a slow release of micronutrients from sewage sludge which increased accumulation in grains in the second season, they also reported an accumulation of Cd surpassing the legal limit at a rate of 20t/ha (Table 0-1).

In order to face this problem and reduce the risk, in recent years efforts have been focused on reducing the mobility of heavy metals in the composted sludge to allow its use as soil amendment. Some materials, such as calcium oxide (CaO) sawdust (Wong and Selvam, 2006) and even zeolites (clinoptilolite) (Zorpas *et al.*, 2000), can be added during the composting process. Consequently, the interest to improve the stabilization of the heavy metals in the sewage sludge has also opened a new way of using adsorbents. The resulting organic mixture can thus, be used as soil amendment and alternatively applied as immobilizer of heavy metals in areas contaminated by metals, pesticides and other substances (Wong and Selvam, 2006). Another way of reducing bioavailability of

Table 0-1 Studies on sewage sludge effect when applied to agricultural soil and effect on soil properties and yield.

Author	SS	Treatment	Length	Rates (dry weight)	Soil type	Purpose	Analysis list	Crop Study Outcome	Effect on soil properties	Effect on Yield
Helian Li et al (2016)	Composted SS	NA	6 years	Field Experiment (5x8 m plots) 5, 10, 20, and 40 t ha ⁻¹ year ⁻¹ over 6 years, and 60t/ha once	Fluvoaquic soil 64% sand, 18% silt 18% clay pH=8.9	Risk assessment of PHAs	Soil TOC K ₂ Cr ₂ O ₇ titration method, Soil pH (1:5 water). PAHS mass spectrometer	Wheat non-specified	Overall increase PAHs in soil, 16 types	No statistically significant differences between treatments and control soil, no significantly risk increase due to PAHs
A.M. Latare 2014 A	Dried SS to 2 mm	Dried non specified	2 years	10-20-30-40 t/ha 10 kg of soil, 2mm sieve, Comparison to 120, 60 and 60 kg N, P ₂ O ₅ and K ₂ O ha ⁻¹ , 0-15 cm	Alluvial Inceptisol, 2mm 10kg per pot (pH=7.95, 1:2.5)	Effect on yield and heavy metals risk assessment	pH (1:2.5 H ₂ O) organic carbon by Walkley and Black (1934); available Olsen P, acid digestion for Total metals (HNO ₃ :HClO ₄ ::3:1 v/v), grain yield.	Rice (<i>Oryza sativa</i> L.)Wheat Rice (<i>Triticum aestivum</i> L. cv. Malviya 234) rotation	Increase of available nutrients and heavy metals in soil, pH fluctuation after both harvest	Rice yield increased 45% at 40 t ha ⁻¹ . Cd concentration above the limit for Cd surpassed at 20 t/ha. Ni on the phytotoxicity limit Application of 40 t ha ⁻¹ . Increased N, P and K contents in straw and grains. Higher accumulation of nutrients in straw and grain of wheat than that of rice.
Koutroubas et al. (2014)	Anaerobic SS	NA	2 years	20, 40, and 60 Mg ha ⁻¹ year ⁻¹ , SS, one rate of inorganic fertiliser (IF, 120 kg N ha ⁻¹ year ⁻¹ plus 80 kg P ₂ O ₅ ha ⁻¹ year ⁻¹)	35,2% sand, 42,1% silt 22,7% clay pH=7.16. Field experiment	Effect on yield, Nitrogen Use Efficiency, and heavy metals risk assessment	pH (1:2.5 H ₂ O), EC (electrical conductivity, 1:5 H ₂ O), Kjeldahl N, NH ₄ -N and NO ₃ -N (extraction at 1:5 with 2 M KCl), Total P, Total K, CaCO ₃ content, particle size distribution, CEC,	Winter Wheat (500 seeds m ⁻²) 4 replicates	Increment of nutrients comparable to inorganic fertiliser. Levels of heavy metals remained under limits	Lower yield with higher rates but always higher than the control, 91 days
D. L. Antille et al. 2013, 2014	SS to produce Organo-mineral fertiliser (OMF10 & OMF15)	Granules, production of OMF	2 years	150 and 300 kg N/ha, sewage sludge, derived OMF10 OMF15, urea separately.	Two types: a sandy loam (67% sand, 13% clay, 20% silt), and a clay loam (46% sand, 25% clay, 29% silt). Pots	Testing two SS derived organo-mineral fertilisers effect on Nitrogen Use Efficiency, Soil organic matter, P availability, Dry matter yield (DMY) Comparison with feedstock and urea	Soil Total N, mineral N, extractable-P, pH, SOM, total above-the-ground biomass, total-N and total-P in harvested plant material	rye grass seeds (<i>Lolium perenne</i> L.)	Significant increment in soil mineral N, extractable phosphorus, . Soil organic matter.	Linear increment DMY with all amendments. Increment 2% to 27% of OMF compared to feedstock.
Oleszczuk and Baran (2005)	SS from mechanical-biological	NA	4.5 years	30, 75, 150, 300, and 600 Mg/h (33, 82.6, 165.3, 330.7, 661.4 t/ha) applied to first 20 cm	Sand 86%, silt 7% clay 7% 6 plots (15 m ² each), pH=4.3 soil	Risk assessment of PHAs	pH (KCl), CEC, TEB BS, Available P, K, Mg, TOC N and sum of 16 PAHs	Rotation: corn, spring barley, winter rape, potatoes, cereal mixture non-specified	Statistically increase of PAHs levels from 165 t/ha)	Accumulation of PAHs in grains directly affected by the rate. No threat to human health on levels detected.

heavy metals is through the stabilization of organic matter, and thus, thermal treatments could offer a solution and potentially reduce the environmental risk (A. Mendez 2012).

1.2.2 Thermal treatments used for sewage sludge

The following thermal methods are the most common used to obtain valuable products from sewage sludge.

Studies have been reporting the great potential of the carbonaceous material from organic waste, obtained through thermal treatments (Table 0-2), not only as an alternative source of energy (Peng *et al.*, 2016) but also as an organic amendment (Gascó, Lobo and Guerrero, 2005; Gasco, Cueto and Méndez, 2007) and a new source of nutrients (Schneider and Haderlein, 2016a).

Table 0-2 Types of thermal treatments.

Process	Temperature (°C)	Retention time	Principal product	Subproduct
Combustion/ Incineration	800-1150	Short time (seconds)	Ash	-
Gasification	800	Long-time rates	Syngas	Bio-oil char
Fast Pyrolysis	>500	Short time (seconds)	Bio-oil	Syngas char
Slow Pyrolysis at high or moderate temperatures	300-700	Long-time rates	char	Bio-oil Syngas
Slow Pyrolysis at low temperatures (Torrefaction)	200- 300	Long-time rates	char	Bio-oil Syngas
Hydrothermal Gasification	>400	Long-time rates	Syngas	Bio-oil char
Hydrothermal Liquefaction	250-400	Long-time rates	Bio-oil	Syngas char
Hydrothermal Carbonization (HTC)	180-250	Long-time rates	char	Syngas Bio-oil

(Sohi *et al.*, 2009; Donatello and Cheeseman, 2013; Huang and Yuan, 2016; Mackay *et al.*, 2017)

To obtain chars as the main product, pyrolysis and hydrothermal characterisation are the preferred thermal treatments. This carbonaceous material obtained through thermal decomposition of organic matter in the absence of oxygen and used for amendment purposes, is often referred as biochar or low class biochar if $C_{org} > 50\%$ (Libra *et al.*, 2011; Kalderis *et al.*, 2014). Since sewage sludge is a more complex source of biomass than most common plant-based feedstocks, and the stigma attached to its use as soil amendment, “biochar” is a term that

creates some controversy when referred to a char obtained from sewage sludge. For this reason, some authors have used the term “sewchar” (Breulmann *et al.*, 2017), however and hereafter for simplicity those obtained from sludge will be referred generally as char.

1.2.2.1 Pyrolysis processes for char production

The pyrolysis process comprises of thermal decomposition of organic matter under anoxic conditions. As shown in Table 0-2, pyrolysis processes are diverse, being of greater interest those processes with larger retention times due to their higher yield of char production (Ngatia *et al.*, 2017). Even though authors often disagree on which is the minimum temperature for pyrolysis, slow pyrolysis is clearly the preferred option, performed from 30 min to several hours. Low temperature pyrolysis can be found as torrefaction ranging from 200 to 300°C, and pyrolysis at moderate-high temperatures (300-750°C). In both cases, the main reactions that occur in the waste during the thermal treatment are those of dehydration, decarboxylation, and aromatization (Huang and Tang, 2016a). As a result of the pyrolysis process, a carbonaceous residue, pyrochar hereafter, is obtained among a gaseous and a liquid phase. This last fraction consists mainly of aromatic hydrocarbons, oxygenated compounds, and water, the latter from the initial moisture content and from the one released from the indicated reactions. This liquid phase is favoured in processes at higher temperatures and when it condenses, it turns into a very viscous black liquid (tar) that can generate equipment-fouling problems, if a sealed condensation system is not available (Di Blasi, 2008). Regarding the gases produced, according to (Tekin, Karagöz and Bektaş, (2014) those with lower molecular weight, such as CO₂, CO, CH₄ and H₂, do not condense during the cooling process and can be recovered as a gaseous product with enough calorific value to be reused (Srinivasan *et al.*, 2015) or released directly. In addition, the produced syngas could be used in the chemical industry as a raw material.

Torrefaction treatment can be used just as a pre-treatment of the biomass that is later subjected to a pyrolysis at a higher temperature (Atienza-Martínez *et al.*, 2013) to improve the characteristics of the char (Zhang *et al.*, 2016) or as a main

treatment to produce a char with intermediate properties with respect to the original material. However, despite producing a higher percentage of tar, slow pyrolysis is mainly conducted under moderate temperatures to produce pyrochar. This way, as showed in Table 0-2, a greater degree of carbonization is achieved (Méndez, Terradillos and Gascó, 2013) and at the same time, a higher porosity is obtained because of a greater release of the tar (Das and Sarmah, 2015). Additionally, reaction time in these processes plays an important role in the degree of carbon stabilization, being possible to reach a higher extend even at low temperatures with longer retention times (Cely *et al.*, 2015).

1.2.2.2 Hydrothermal Carbonization (HTC) for hydrochar production

The hydrothermal treatment is a biomass conversion method invented in the 1910s to portray natural coalification (Zhai *et al.*, 2017a), and became better known a few decades later after it was introduced by the company Shell Oil in the 1980s (Tekin, Karagöz and Bektaş, 2014). In the recent years, there has been a great boost in research in the area of hydrothermal carbonization, since it allows the use of waste with a high moisture content often used with paper sludge, sewage sludge and slurry (Kalderis *et al.*, 2014). Therefore, in this case and contrary to pyrolysis, biomass can be treated directly or after adding water, depending on the percentage of dry mass, under subcritical conditions. Typical temperature values found in Hydrothermal carbonisation treatments are conditions in which the water remains in a liquid state due to the reactors pressure (100-250°C, up to 50 bar) (Kalderis *et al.*, 2014). Under these conditions, the water increases its density and its polarity changes, acquiring properties closer to those of hexane (Smith, Singh and Ross, 2016), being able to dissolve apolar substances, breaking organic compounds in their monomers and thus allowing a greater number of polymerization and acid-base reactions (Tekin, Karagöz and Bektaş, 2014).

Through hydrothermal carbonization, three different phases of the matter can also be distinguished. After the process, the solid carbonaceous product, hydrochar hereafter, is left remaining inside the reactor, while the gas phase is purged and connected to a condenser to separate the phases. This condensable

phase would be finally stored in a liquid form (oil) and the final gases emitted. The water contained in the reactor acts as a solvent for some gases that are released during the hydrothermal treatment (SO_x, NO_x, CO₂) (Parshetti *et al.*, 2013). This water content would be found trapped in the solid phase and partially liberated through the gas phase. The main emitted gases are commonly CO₂ (around 61.9%v) and traces of CH₄, N₂, O₂, H₂S, CO, and VOCs (Fakkaew, Koottatep and Polprasert, 2017). Then in principle, a treatment of the gaseous effluent would not be necessary (Kalderis *et al.*, 2014). Being a closed system, the resulting phases are better controlled, and these co-products can be repurposed in the chemical industry.

According to Tekin, Karagöz and Bektaş, (2014) and Smith, Singh and Ross, (2016), for HTC, the first stage that takes place is the dissolution in water, at 100 ° C the water-soluble portion disperses in it. Reaching a higher pressure and from 150 ° C hydrolysis and solubilization of polymers in subcritical conditions follows, destroying ethers and esters. Then hydrogen bonds break, and polymers begin to decompose into monomers. In this stage, there are intermediate products that contain aldehyde and hydroxyl groups, some of these combine forming glycolaldehyde, which in these moisture conditions form hydrates. From the fragmentation of the polymers, intermediate products such as furans and derivatives are also formed. Next, at around 200 ° C a re-polymerization takes place, regrouping of monomers to form chains whereby several functional groups are lost. Also, at this temperature decarboxylation is the main reaction, in which more functional groups such as carbonyl and carboxyl are lost. The final stage is the carbonization. The grade of carbonization will depend on the temperature and the residence time, and it is produced by means of condensation reactions between the previous polymers. These polymers join after losing hydrogen and breaking oxygen groups, and thus water molecules are released.

It is worth mentioning that this process does not require additives for its proper functioning in principle (Kalderis *et al.*, 2014). Nevertheless, some studies have tested to modify the final properties of the hydrochar, to add weak acids before to improve metals solubilization during the HTC process (Liu *et al.*, 2018). But

also some have tried doping the starting material with P, Mg, Al, Fe and lanthanide (LaCl_3), in order to obtain a hydrochar with a better capacity to contribute or either retain these substances (Dai *et al.*, 2014).

1.3 Effect of Pyrolysis and Hydrothermal Carbonisation on sewage sludge for soil amendments.

To date, studies that have conducted a comparison case of hydrochars and pyrochars that use sewage sludge as source of biomass have been scarce (Table 0-3). In fact, available studies of such processes often use different feedstocks and mixtures, whether is sewage sludge from different stages (Primary, secondary) as in Breulmann *et al.*, (2017) and Paneque *et al.*, (2017) or woodchips mixtures as in Schneider and Haderlein,(2016a). However, sometimes, the feedstock material is not analysed for contrast Schneider and Haderlein,(2016a). This diversity may provide valuable information but makes it difficult to predict results and compare process effects on sludge. Huang and Tang, (2016) produced a comparative analysis on the P contained in the chars after thermal treatments compared to the original sludge but the effect on soil is yet to be assessed. Only Paneque *et al.*, (2019) has compared the chars' effect to swine manure on an experiment to grow *Lolium perenne* focusing on N-efficiency Table 0-3.

Overall, a characterization to compare the physical-chemical properties of sludge derived pyrochar or hydrochar obtained under different conditions is most frequently done (Table 0-3). This characterization is a comprehensive study with the purpose of adjusting the conditions to improve efficiency or to determine which materials should be used for a posterior assessment. Properties such as pH, EC, Organic carbon (C_{org}), elemental analysis, porosity, surface area, ash content and Fourier-transform infrared spectroscopy (FTIR) are very common analysis for both pyrochar and hydrochar studies regardless of their use (Arai and Sparks, 2001; Gasco, Cueto and Méndez, 2007; Zhang, Lin and Zhao, 2014; Peng *et al.*, 2016; Yao *et al.*, 2017). FTIR analysis allows to understand the chemical composition on the surface and gain a better insight of the reactions occurred during the thermal processing. The use of pyrolysis and HTC is often

performed to produce a char for soil amendment and soil properties like pH, Electro conductivity (EC), Cation Exchange Capacity (CEC), water retention, organic matter and nutrient content are commonly studied. However, when it comes to assessing carbon stability and CO₂ sequestration, which normally includes an incubation experiment and a thermogravimetric analysis, pyrolysis is preferred to HTC given their higher carbon stabilization (Smith, Collins and Bailey, 2010; Calvelo Pereira *et al.*, 2011). On the other hand, when it comes to use wet residues such as sewage sludge for energy purposes, HTC it is more frequent featuring calculations of Higher Heating Value (HHV) after the elemental analysis results for comparing the chars with coal (He, Giannis and Wang, 2013; Peng *et al.*, 2016; Zhai *et al.*, 2017b). Combined treatments have also been considered for energy purposes as nitrogen compounds have been found to be better contained after a pre-treatment of HTC followed by a pyrolysis to mitigate the environmental impact of release of N-contaminants (Liu *et al.*, 2017).

As well as temperature, time is a key factor that also determines the degree of carbonization and stability, several studies have been conducted to determine the best combinations. vom Eyser *et al.*, (2015) indicated that for sewage sludge HTC require between 3 and 6 hours at temperatures around 200 °C, so that the hydrolysis reactions can take place long enough to improve the dehydration process of the sample. HTC at less than 1h of sewage sludge might be insufficient unless the temperature rises quickly enough to reach the limit of supercritical conditions (Parshetti *et al.*, 2013). Then, in order to treat the sewage sludge, a time of 4h at temperatures close to 200 °C should be appropriate (Hii *et al.*, 2014), hence generating a more stable hydrochar (Danso-Boateng *et al.*, 2015). Feedstock, residence time, temperature, types and number of thermal treatments are selected to obtain the optimal characteristics to cover the requirements to fit its purpose (Srinivasan *et al.*, 2015). More frequently, the sludge is anaerobic and is submitted to pyrolysis above 400 °C and HTC around 200 °C (Table 0-3). The

Table 0-3 Comparative studies on sewage sludge derived pyrochars and hydrochars.

Author	Feedstock	Treatment	Purpose	Crop	List of analysis
Suyun xu 2020	Secondary SS after thickening and swine manure	SS moisture content 96.6%, swine moisture content 81.57%. Pyrolysis mixture SS-swine 550°C 2h. HTC moisture adjusted to 85-80% 235°C, 5h. Pyrochars and hydrochars were soaked in 0.3 mmol/L of FeCl ₃ solution for 24 h. Inoculation 25% (v/v) from anaerobic sludge blanket and Co-digestion mixture swine-SS (1.74 ratio vs/vs)	Energy Characterisation: Methane generation. Comparison pyrochar and hydrochar bonded with and without Fe.	NA	Elemental, FTIR, pH (1:10 W/v), alkalinity, Dissolved Organic Matter, Total organic matter. Adsorption test to ammonium and VFAs by acetic acid, propionic acid, butyric acid and NH ₄ Cl.
M. Paneque (2019)	Secondary SS after thickening and swine manure	Pyrolysis 600°C, 1h. HTC 200°C, 260°C for 30 min and 3h, 3°C/min. Filtered and dried at 60°C, 48h	Amendment N fertilization evaluation with pot experiment, germination, and growth.	<i>Lolium perenne</i> in Calcic cambisol 5 and 25 t/ha	Germination, biomass production, root-to-shoot ratios. Inorganic N and organic N content, Total P, total K
Hongmei chen (2018)	Final SS, feedstock analysed	SS dried 105°C to constant weight, 1.67% humidity. HTC 180, 220, 260, 300°C then dried at 105°C to constant weight. Pyrolysis 50,650,750 and 850°C 2h 25°C/min	Energy / amendments / remediation Characterisation	NA	Proximal analysis, pH (1:100). Acid digestion by HNO ₃ for BCR sequential extraction of metals as soluble, reducible, oxidable and residual fraction.
T.Liu et al 2017	Final digested SS, feedstock analysed	SS moisture 81%, dried at 105°C for 24h. Crushed to 100-150 µm, then pyrolyzed. SS moisture 81% HTC at 200 °C for 30 min, centrifuged and dried 105°C, 24h. Pyrolysis of SS and hydrochar at 350-950°C, for 30 min 150 °C/min	Energy Characterisation N conversion pathways	NA	Product distribution (char, tar, gas); proximate analysis; Ultimate analysis; Total metals; FTIR, N speciation.
Breulmann (2017)	Primary sludge (PS), activated sludge, unsterilized (ASU) and activated sludge, stabilized (ASS), feedstock analysed	Activated sludge: Pyrolysis 400°C and 700°C (fast pyrolysis) for 1h. Primary sludge: HTC at (180°C for 4h and 8h, 200°C for 8 h). Activated sludge: HTC 200°C for 4h with addition of H ₂ SO ₄ .	Amendment Characterisation: Carbon sequestration potential	NA	pH (H ₂ O); pH (CaCl ₂), Proximal analysis, Total organic carbon, Ultimate analysis, CEC, BET, Porosity, Total Ca, Fe, K, Na, Mg, P, S, As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Zn, Pb; extractable carbon, nitrogen, ammonium, nitrate contents (cold and hot water extraction, Breulemann et al method (2012)), P (resin strip anion exchange membranes (BDH Prolabo, Tiessen and Moir 2008)).
M. Paneque (2017)	Primary sludge after anaerobic digestion and secondary nondigested but thickened.	Pyrolysis 600°C, 1h. HTC 200°C, 260°C for 30 min and 3h, 3°C/min. Filtered and dried at 60°C, 48h	Amendment Characterisation: N fertiliser	NA	pH distilled water (1:2.5, w/v). Yultimate analysis, available N ammonium and nitrate, 0.0125 CaCl ₂ . 13C and 15N nuclear magnetic resonance (NMR) spectroscopy. Organic carbon. FT-IR.
F.Schneider, SB. Herderlein (2016)	Various, includes SS. Feedstocks not analysed.	HTC at 200 °C (Biomass from pruning, non-digested sewage sludge), Pyrolysis at 700 °C, Woodchips (unspecified, <i>Prunus dulcis</i> & <i>Olea europea</i> , <i>Salix spp</i>), Lignite, grass (<i>Miscanthus giganteus</i>)	Amendment Characterization: Fertiliser, Availability of P	NA	pH (0.01 M CaCl ₂ , 1 to 2.5 wt/wt ratio); Dissolved organic matter (Elementar High TOC II); Total P (modified dry-ashing method after Enders and Ash contents were measured through weight loss after the combustion step (8 h; 500 °C) Lehmann (2013)); Sequential P extraction; P sorption to iron oxides; Total P, Fe, Mn, Mg, Ca, Al, and K by digestion and inductively-coupled plasma optical-emission spectrometry; Ash combustion (8 h; 500 °C)
R. Huang. Y. Tang (2016)	Activated secondary SS and anaerobic digested, feedstock analysed	SS moisture 74%, SS anaerobic moisture 79% Freeze dried SS, pyrolysis 250°C and 450°C for 4h, HTC 225°C at 4h and 6h	Amendment Characterization: P speciation	NA	P speciation (Hedley's method, 1982 -Xanes analysis); PNMNR; P (combustion 600 °C for 2 h and HCl extraction (1 M) for 16 h, UVevis spectrophotometer, Murphy and Riley, 1962)
R. Huang. Y. Tang (2015)	Activated secondary SS and anaerobic digested, feedstock analysed	SS moisture 74%, SS anaerobic moisture 79%, Activated SS: Pyrolysis (250, 350, 450, 600 °C. 4h) and HTC 225°C for 24h. Anaerobic SS: pyrolysis 450°C and HTC 225°C for 24h	Amendment Characterization: P speciation	NA	P sequential extraction NaHCO ₃ , NaOH and HCl; PNMNR; P (combustion 600 °C for 2 h and HCl extraction (1 M) for 16 h, UVevis spectrophotometer, Murphy and Riley, 1962)

time of the thermal treatment is no longer than a day, being frequently a few hours or even 30 min (Table 0-3). However, it is notable that despite it being a decisive variable for the thermal treatments (Kalderis *et al.*, 2014), the time and the ramping, how long it takes for the final temperature to reach and temperature steps ($^{\circ}\text{C min}^{-1}$) set for this matter, are sometimes not highlighted.

Additionally, for soil amendments it's frequent to find a report of the concentration of total elements from the original source after thermal treatments. The implications of this are still an area of concern as it may impact on soil nutrient balance and accumulation of heavy metals in the soil system. Several authors have indicated the reduction of the environmental risk compared to the original sewage sludge (Méndez *et al.*, 2012; Srinivasan *et al.*, 2015). However, to date, the results are inconsistent, and more research needs to be done to determine the best application of such materials, regarding process conditions, rates and soil- crop systems.

1.3.1 Potential recovery of P from sewage sludge and derivatives

1.3.1.1 Forms of P present in sewage sludge

There is little evidence for the direct uptake of organic P by plants and soil organic P polymers must be enzymatically broken down outside the cell prior to the uptake of inorganic P (Pi) (Lehmann and Joseph, 2015). Inorganic P is most commonly taken up by plants in the HPO_4^{2-} or $\text{H}_2\text{PO}_4^{-}$ form (Brunings *et al.*, 2012).

Thus, inorganic fertilisers from phosphate rock are used to increase these compounds used by plants to form ATP molecules, created during the respiration process, and consumed during polysaccharide, protein and nucleic acid biosynthesis (Hyland *et al.*, 2005). The phosphate group is transferred under the presence of specific enzymes, thus, without P inputs the plant won't be able to generate any of these processes nor survive.

In order to understand the forms of P present in sewage sludge, it's important to differentiate how P is removed from wastewater in the treatment plants. The common routes of P removal from wastewater are physical-chemical, such as dosing for precipitation, adsorption or ion exchange technologies, and biological removal under aerobic and anaerobic conditions (Bunce *et al.*, 2018). Sewage sludge concentrates the P from both physical-chemical and biological routes.

The most used method for P removal in wastewater is the chemical precipitation by addition of Al or Fe chloride (Hyland *et al.*, 2005; Petzet, Peplinski and Cornel, 2012; Shepherd, Sohi and Heal, 2016). Vivianite ($\text{Fe}^{2+}\text{Fe}_2^{2+}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) is considered the main product from the precipitation of P with Fe (Prot *et al.*, 2019). Efficiency of P recovery has been reported to increase up to 82.6% of TP by lowering pH and dosing FeCl_3 during anaerobic fermentation (Cao *et al.*, 2019). It is possible to extract P from vivianite in sewage sludge through centrifugation, magnetic separation and alkaline solution, with possibility of recycling Fe in the resulting hydroxide solution (Torri, Studart and Ea, 2017; Prot *et al.*, 2019). However, the studies involving this practice are still at small scale and only recover the magnetic forms of P (Prot *et al.*, 2019). P may also precipitate as struvite ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$), partially lost in adhesions to pipes and other structures of the WWTP and partially collected in the sewage sludge (Le Corre *et al.*, 2009a). This crystallization happens in the presence of Mg and ammonia and can occur spontaneously, and it can be induced from digested SS in fluidised bed reactors (Le Corre *et al.*, 2009a). Through these physical-chemical process P binds with elements that reduce its availability and would require to be transformed to an available form PO_4^{3-} by citric acid (Bunce *et al.*, 2018; Schütze, Gypser and Freese, 2020). A fraction of P is accumulated in microorganisms present in WWTP. Therefore, through the extraction of vivianite and struvite, the remaining organic fraction, the biologically accumulated phosphates as polyphosphates in microorganisms, would not be avail. The removal of P can be conducted at the WWTP through biological treatment, in which case it is incorporated into the sludge within the microbial biomass (Torri, Studart and Ea, 2017). Biological treatments are complex to maintain and it's efficiency for removing P is unreliable on its own, so it is good practice to pair it with a physical-chemical treatment to ensure the removal of P from the wastewater (Seviour, Mino and Onuki, 2003).

Complementary, P can be extracted directly from the wastewater through crystallisation of struvite, hydroxyapatite and calcium phosphate through ion exchange resins which on the contrary, reduce the volume of SS (Le Corre *et al.*, 2009a; Guida *et al.*, 2021). These techniques are often applied to the supernatant of anaerobic digester or anaerobic sludge liquors or secondary effluents because organic matter, nitrates and sulphates contained in the waste water in the early stages can hamper

the performance of the resins (Muhammad, Soares and Jefferson, 2019), thus sludge remains the principal source of P.

However, these processes constitute one of the greatest limitation for P availability in the raw sludges (Hogan, McHugh and Morton, 2001), as a portion of P remains stable in the complex formed (Shepherd, Sohi and Heal, 2016). Therefore, P contained in the sludge would be present in different forms, inorganic P as orthophosphates which are the readily available forms for the plants (Brunings *et al.*, 2012), as longer chains of polyphosphates, chemically bonded P to Al, Fe, Ca, Mg and Mn and as organic P, like phytic acid (Huang and Tang, 2015). Nonetheless, potentially the combination of inorganic P and organic P forms could benefit the amendments as the first would provide readily available P and the latter, the organic-P structures need enzymatic activity to break them into phyto-available forms of P, would work as slow fertilisers (Lehmann and Joseph, 2015).

1.3.1.2. Fate of P during thermal treatments

Organic matter changes after thermal treatments so it's logic to foresee a change in P speciation and thus, on phosphorus availability (Le Corre *et al.*, 2009a; Sadeghalvad, Azadmehr and Hezarkhani, 2017). For the assessment of P speciation, nuclear magnetic resonance (NMR) spectroscopy, sequential extraction, and P K-edge X-ray absorption spectroscopy (XAS) are currently the most common analysis (Uchimiya and Hiradate, 2014; Idowu *et al.*, 2017). Nevertheless, to provide a full characterization of P speciation these techniques should be contrasted (Bünemann, 2015).

Studies have shown that thermal treatments change the way P is presented in sewage sludge (Huang and Tang, 2015). Oven dried sludge was found to transform organic phosphorus forms to inorganic, indicating a shift in inorganic forms from 220°C generating apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{F,Cl,OH})$), a less labile form of P, from non-apatite inorganic phosphorus such as sodium aluminium phosphorus, magnesium silicon phosphorus, silicon phosphorus and aluminium silicon phosphorus (Li *et al.*, 2014). Ashes of sewage sludge obtained through incineration are currently the highest rate of recovery of P 60-90% relative to the wastewater in form of struvite and P_2O_5 (Egle *et al.*, 2016), which can be extracted through HCl (Xu *et al.*, 2012). However, the ashes of incinerated sludge are also rich in heavy metals along with SiO_2 , CaO , Al_2O_3 and Fe_2O_3 , oxides that could reduce P phytoavailability (Xu *et al.*, 2012). Moreover,

through incineration, the organic fraction is consumed, while it is preserved and stabilized through pyrolysis and HTC.

Thermal treatments are reported to reduce the amount of organic phosphate turning it into inorganic P forms (Huang and Tang, 2015). Contrary to incineration of sewage sludge where P_2O_5 is obtained in excess of oxygen (Smol, Kulczycka and Kowalski, 2016), after pyrolysis the polyphosphates in sewage sludge break into smaller chains of polyphosphates, pyrophosphates and orthophosphate (Huang and Tang, 2016a) and (Huang and Tang, 2016b). In pyrolysis, the higher the temperature up to 700°C where P may volatilize, the greater the orthophosphate found in the pyrochar and less abundance of phytic acid while increasing abundance of Fe, Al, Ca, Mn Mg, Al an Ca associated P, either by sorption or by formation of solid precipitation salts (Huang and Tang, 2015).

In contrast, after HTC it is not likely to find polyphosphates or pyrophosphates and only organic forms of P hydrolysed into only orthophosphates which can as well be associated with other mineral phases and metals. Compared to the feedstock, chars are therefore likely to have less available P due to the formation of stable Ca and Fe associated phosphorus species (Huang and Tang, 2016b). Chars are expected to work as slow P releasers with a fraction of available P, which is associated with their biomass stability (Huang and Tang, 2016a). C stability is said to be obtained best through high temperature of Pyrolysis (Lehmann and Joseph, 2015) so hydrochars are expected to have more readily available P than pyrochars but their effectiveness as fertilisers compared to pyrochars obtained from the same feedstock in actual crop production is an area of research that still needs to be filled.

1.3.2 Heavy metals from sewage sludge and the time bomb theory

Similarly to P, heavy metals are removed from the wastewater most commonly through physical-chemical precipitation (Zhao *et al.*, 2016). Iron salts are often used for removing divalent soluble forms of heavy metals by sulfuric precipitation with FeS or by forming insoluble chloride salts through $FeCl_3$, hence liberating more iron cations (Pohl, 2020). Other routes for heavy metal precipitation are obtained through lime, hydroxides, ferrous or aluminium sulphates and polymers such as polyacrylamide (Pohl, 2020). These heavy metals concentrate in the sludge and are one of the factors that limits their application in soil.

When the sewage sample is subjected to high temperatures to produce a char, a large part of the bioavailable heavy metals contained in it is lost, depending on the temperature settings and treatment. Heavy metals volatilisation was found to be conditioned to the temperature, moisture, and Cl content (Chanaka Udayanga *et al.*, 2018). Low temperatures of pyrolysis and hydrothermal carbonisation reduce volatilisation of most heavy metals concentrating them on the char (Liew *et al.*, 2021). The remaining heavy metals and nutrients are concentrated in the char in the form of hydroxides, oxides, and carbonates (Cely *et al.*, 2015; Huang and Yuan, 2016).

Studies have shown the reduction of bioavailability of heavy metals in chars, most frequently Cu, Zn, Ni and Pb (X. Wang *et al.*, 2016) (Cely *et al.*, 2015) (Méndez *et al.*, 2012). Pyrochars have shown higher stability and reduction of leaching compared to incinerated sewage sludge and original sewage sludge (Chanaka Udayanga *et al.*, 2018). Kaolin and phytic acid present in the char help to fixate heavy metal compounds, which would in turn reduce the availability of P. Later studies have shown that when it comes to improving the immobilization of heavy metals in a waste, hydrothermal carbonization treatments against hydrothermal liquefaction and hydrothermal gasification provide better results, generally detecting a greater effectiveness for temperatures in the treatment (Huang and Yuan, 2016) (Li *et al.*, 2012). Therefore, hydrothermal carbonization may be the most indicated option within the hydrothermal treatments indicated in Table 0-2, to obtain a higher value char from sewage sludge if intended for soil amelioration.

Nevertheless, there is concern that, following the cessation of application of organic wastes such as sewage sludges, bounded metals could be released to soluble forms by processes such as organic matter decomposition, S oxidation and soil acidification with a greater risk of accumulation in the tissues of plants (Gascó, Lobo and Guerrero, 2005) and of leaching in soils with little limestone content (Gascó *et al.*, 2005). This is often referred as the 'time bomb' theory (McBride, 2003).

For these reasons, mixtures of sewage sludge with different residues have been studied to optimize the properties of the substrate and reduce these risks, mixing for example the sludge with paper sludge in different proportions (Barriga *et al.*, 2010) to pinewood sawdust (Zhang, Zhang and Li, 2017). Long-term application of sewage sludge thermal derivatives containing metals and its mixture with organic matter or raw sewage sludge and its effect on soil productivity is yet to be assessed.

Thermal treatments effectiveness has recently been proven to reduce polycyclic aromatic hydrocarbons content from sewage sludge (Zielińska and Oleszczuk, 2016). Moreover, De la Rosa *et al.*, (2016), indicated that a pyrochar from sewage sludge at 500–620 °C, 20min had 2.7 times lower sum of 16 PAHs compared to wood pyrochar obtained in similar conditions. Furthermore, other traces dangerous organic substances, including organochlorine compounds and pharmaceutical load has been proved to be destroyed by increasing time and temperature (Hori *et al.*, 2008; vom Eyser *et al.*, 2015)

Therefore, through thermal treatments, a partial decontamination of the sewage sludge can be carried out, obtaining a better-quality material that could be later reused.

1.3.3 Effects on soil properties when applied as soil amendment.

The most notable difference between pyrochar and hydrochar effect on soil properties is pH variation. Both alkalinity and hydrophobic character are common characteristics in the char obtained by pyrolysis, both at high and low temperatures (Méndez, Terradillos and Gascó, 2013). According to (Méndez, Terradillos and Gascó, 2013), pH increment in the pyrochars is due to the result of polymerization reactions, condensation, and release of acid groups during pyrolysis. In regard of the higher hydrophobicity degree of the pyrochar, it appears to be affected by the exposure to moisture, and can be determined by the presence of aliphatic groups on the surface by infrared spectrometry, according to (Das and Sarmah, 2015). On the contrary, hydrochars seem to be formed by spherical particles with a large number of polar groups on the surface, which gives it a more hydrophilic character than raw sewage sludge (Kubo *et al.*, 2011; Zhang, Lin and Zhao, 2014). However, although hydrochars have a higher hydrophilic character than the starting residue, some studies have shown that hydrophobic zones can be produced due to the proliferation of fungi on the surface of the hydrochar (Steinbeiss, Gleixner and Antonietti, 2009; Abel *et al.*, 2013). This could be favoured by a higher content of organic matter in hydrochars, as well as in the lower degree of decomposition and lower stability compared to pyrochars. Due to the higher recalcitrant carbon content in pyrochars, these materials can persist for long periods of time in the soil after being applied. It has been previously reported that pyrochars can resist better microbiological degradation and mineralization (Srinivasan

et al., 2015) and that its hydrophobic character has not a negative effect in soil after its application, except in isolated cases (Jeffery *et al.*, 2015).

The porosity of the carbonaceous material constitutes another contrast. The distribution and size of the pores that give an irregular appearance to the surface of the hydrochar is due to the profuse release of intermediates products during hydrolysis reactions of the HTC treatment (Ju *et al.*, 2009). These pores in various sources of biomass tend to be smaller in the hydrochar than in the pyrochar, the latter formed with the release of tars with a higher proportion of macropores >50nm (Abel *et al.*, 2013). Little information could be found on porosity on same samples of sewage sludge thermally treated by pyrolysis to HTC, only (Breulmann *et al.*, 2017) indicated a higher pore volume on pyrochars and hydrochars from different sludge samples. According to (Abel *et al.*, 2013), the hydrochar could also have a greater deformation capacity than the char, so when applied to a soil and compacted, the pores could reduce its size even more, giving place to a mainly microporous material. This feature will have a different effect on the retention capacity and water availability for the plants. In general, the type of porosity of the pyrochar is more beneficial in order to improve the physical and structural characteristics of the soil (Abel *et al.*, 2013) (Rogovska *et al.*, 2014; Shi *et al.*, 2015).

The addition of pyrochar and hydrochar to soil has resulted in an overall reduction of the bulk density (Abel *et al.*, 2013; Rogovska *et al.*, 2014). The reduction in the degree of soil compaction, due to the increased porosity, resulted in an improvement in soil structure (Álvarez *et al.*, 2017a). This translated in better water retention, infiltration, root growth and soil respiration (Barriga *et al.*, 2010) (Denyes *et al.*, 2012; Álvarez *et al.*, 2017a)(Méndez *et al.*, 2012). Likewise, after the application of both materials, an increase in cation exchange capacity has been observed (Cely *et al.*, 2015; Smith, Singh and Ross, 2016). An increased CEC optimizes nutrient retention reducing by absorbing this nutrient on chars surface (Méndez, Terradillos and Gascó, 2013). This in turn could reduce leaching of nutrients and a potential eutrophication event, that is, if the amount of nutrients added through the amendment doesn't exceed the needs of the crop (Ngatia *et al.*, 2017).

Moreover, the increase of porosity and nutrients can also favour the proliferation of mycorrhizal fungi and alter microbial communities and their activity present in the soil

mixture (Lehmann *et al.*, 2011a) that participates in turn in P,S,N and C cycles, transforming complex organic forms into substances that can be absorbed by plants (Sohi *et al.*, 2009). (Steinbeiss, Gleixner and Antonietti, 2009) even suggested that the design of soil microbiota may be possible through the addition of char with specific compositions, which opens up another new area of study.

With regards to P availability in soil, however, it has been reported a variety of results with opposite outcomes. An increment in Total P on hydrochars was stated after Wang, Li and Chang, (2016) and (Zhang, Zhang and Li, 2017) experiments, while Zhang, Lin and Zhao, (2014) and Smith, Singh and Ross, (2016) obtained the opposite with a remaining Total P 200°C (92%) to 250°C (52%) at, 1h from the original SS. Nonetheless, a higher immobilization has been reported onto pyrochars, indicating an adsorption capacity of P depending on the pH (Dari *et al.*, 2016; Ngatia *et al.*, 2017). The effects on crop yield are addressed afterwards.

Sousa and Figueiredo, (2016) reported an increment of P from 0.39 to 100.31 mg/Kg after applying doses 0-50 g/kg of pyrochar from sewage sludge obtained at 300°C, sustained for 30 min. While (Álvarez *et al.*, 2017a) mixed hydrochar with a rich peat soil 50-50%, reduced available P from 1257 mg/kg to 402 mg/kg using a sample of sludge derived hydrochar containing 553 mg/kg available P. Results on hydrochar from sludge applied to agricultural soil with low P content and it's P use efficiency is unknown.

1.3.4 Results of soil amendments using thermal derivatives of sewage sludge on crop yield.

Among studies on sludge derived chars as soil amendment, winter wheat (*Triticum aestivum* L.) and rye grass (*L. perenne*) are the most common crops studied however, only a few reaches the maturity stage and analyse the grain. Other vegetable crops as radishes, bulbus like garlic, tomatoes and nut trees, which are not recommended by the Code of Practice of sludge use in soil amendment, have also been analysed (Department of the Environment, 1996). The most common practice when studying these amendments is to analyse the biomass to assess heavy metal and nutrient accumulation in the tissue (Wang, Camps-Arbestain and Hedley, 2014).

Jeffery *et al.*, (2011) meta-analysis on char crop productivity, featured in (Lehmann and Joseph, 2015), showed that sludge char was the only to produce a reduction of

50% on crop productivity on *L. Perenne* productivity compared to control soil. However, the data comes from one only study on sludge derived pyrochar (Wisnubroto, 2015). Since then, more studies on char derived from sewage sludge, collected in Table 0-4, whether in a glasshouse or in the field, have shown an overall improvement on soil fertility and crop productivity.

Rates have a determine effect and vary considerably, added in terms of t/ha, g/kg or a as a percentage of the container and are added frequently to the first 20 cm top layer. The amount added to a soil is commonly determined after measuring available P or the C organic content in the feedstock chosen in order to provide enough nutrients for the crops to develop at high yields, however, given the number of variables, it's common to compare different rates to determine for each case the best quantity. According to the studies gathered in Table 0-4, there the rate and yield don't follow a linear trend. A A T C Sousa and Figueiredo, (2016), for example indicated increasing productivity of plant in radish increased from 10-30 g/kg with an inflexion point at 30 g/kg onwards lowered productivity still over the control soil, using a char obtained from sewage sludge at low temperature (300°C, 11 °C/min sustained 30 min). From a rate range of 5% and 10% Khan *et al.*, 2013 also indicated a lower yield with higher rates, but always higher than the control, increasing shoot biomass (71.3–92.2%) and grain yield (148.8–175.1%). While You *et al.*, (2019) in a Peanut Field experiment, reported an optimal yield at 40 t/ha with 60.43% improvement, 52.29% at 60 t/ha and 35.72% at 20 t/ha.

The two studies that grow a crop using sludge derived hydrochars analyse phytotoxicity of the materials on a germination stage through a Zucconi test. According to Álvarez *et al.*, (2017) hydrochars stimulate the growth of the radicle significantly longer than peat and DMY increased 180% with hydrochar compared to peat. The germination of both sludge derived pyrochars and hydrochars also didn't reduce the germination of the seeds on *L perenne* in Paneque *et al.*, (2019), while other feedstock as wood did reduce the germination probably due to a lower N content. However, in the same study, pyrochars of sewage sludge didn't increase significantly DMY if N is not added as fertiliser, while when using hydrochars, despite their lower germination rate, DMY increase to almost double in the lower temperatures or remained as the control Table 0-4. Two feedstocks were compared, the secondary sewage sludge gave a lower survival of the seeds but a higher biomass production than primary sewage

sludge which was more humified, hence biochemically stabilized. Paneque *et al.*, (2019) suggested that N-organic compounds in hydrochars degrade faster than pyrochars from the same SS. Peptide-like structures in hydrochars are easier to degrade by microorganisms to more stable structures as N-heterocyclic aromatic compounds transformed through Pyrolysis and addition of N is recommended.

Overall, the amended soil is frequently a neutral sandy loam soil with low nutrient content, this is used to tailor the conditions to the particularity of the experiment. Some studies include a dose of inorganic fertilisers to complement the amendment and to reduce any possible nutrient limitations. It ranges from a single application along the amendment Hossain *et al.*, (2010), to several during the same crop season Khan *et al.*, (2013), and as extensive as in Shepherd *et al.*, (2017) (Table 0-4). Faria *et al.*, (2018) also highlighted the benefit from mixing NP fertilisers, indicating that K could be a limiting factor too when growing corn with pyrochar derived from SS. They interestingly obtained best results the second season with low temperatures 300°C confirming the theory of the slow fertiliser effect through thermal treatments of Sewage sludge. Mackay *et al.*, (2017) thermal products of sewage sludge, from gasification, incineration, and pyrolysis at 600°C showed a significantly lower available P to spring wheat, and P uptake on the plant tissue was only significantly higher to control soil with dried sewage sludge and the ashes from incineration. However, no data is available regarding the P accumulated in grains as the crop was harvested before flowering on the 55th day after sowing. This may indicate that when using a stabilized form of sewage sludge such as pyrochar, an additional source of nutrients should be incorporated in early stages to produce optimal yields (Mackay *et al.*, 2017). Furthermore, Hossain *et al.*, (2010), obtained a yield 97% greater from NPK inorganic fertiliser mixed with char than char alone. In fact, Hossain *et al.*, (2010) only obtained a significantly different DMY when char was combined with NPK fertiliser, 48,6 % higher compared to control. However, no significant heavy metal uptake in tomatoes was detected by using pyrochar or pyrochars combined with NPK fertiliser in Hossain *et al.*, (2010), while by applying NPK fertiliser alone, Cd levels were detected right on the limit for Australian soils. Moreover, (Khan *et al.*, 2013) reported a decreased bioaccumulation of As, Cr, Co, Cu, Ni, Pb and an increased accumulation of Cd and Zn in rice grains, although these still were below the legal limits.

Table 0-4 Sewage sludge derived pyrochar and hydrochars effect when applied to agricultural soil and effect on soil properties and yield.

Author	SS	Thermal Treatment	Length of experiment	Rates (dry weight)	Soil type	Purpose	Analysis list	Crop	Effect on soil properties	Effect on Yield
M.Paneque 2019	Primary SS, Secondary sewage sludge after thickened from aeration treatment and wood chips	Pyrolysis 600°C, 1h. HTC 200°C, 260°C 30 min 3h. Chars dried at 40°C grounded and sieved <2mm	80 days	5 and 25 t/ha	Calcic Cambisol, pH= 8.5 pot experiment	Effect on germination and DMY. N fertilization potential	pH (1:10 w/w), C organic, N organic, acid digestion HNO3/HCl for Total N, P, K Cd, Cu and Zn. Water Holding Capacity, phytotoxicity, DMY.	<i>Lolium perenne</i>	Benefit from N fertilization potential from hydrochars	No negative effect on <i>L.perenne</i> germination by using sewage sludge derived pyrochars but hydrochars of sewage sludge and pyrochar from wood lowered it. Best yield obtained through hydrochars at lower temperature of SS, close to double control yield.
M. L. Álvarez et al (2017)	Anaerobic SS, urban waste, commercial brown peat	HTC 205–215 °C 6h, 17-19 bar 190–200 °C during 6 h, 16-17 bar	Incubation experiment 42 days, phytotoxicity (Zucconi) 2 days, DMY 42 days	Hydrochars to peat 50%, peat 100% and hydrochars 100%	Peat	Test hydrochars and mixture with peat as growing media.	pH & EC (1:10, H2O) CEC, Olsen-P, WHC, proximate analysis, thermogravimetry, exchangeable K, Ca, organic carbon Wakley-Black, soluble carbon, N-Kjedahl, porosity, bulk density, air space, coarseness index, phytotoxicity (Zucconi test, 1:10 water), microbial biomass chloroform fumigation-extraction method & potassium dichromate, enzymatic activity with nitrophenol by spectrophotometry, DMY	<i>Lolium perenne</i>	Hydrochar increased air space, WHC, and total porosity. Hydrochar promotes enzymatic activity.	DMY increased 180% with hydrochar compared to peat. Hydrochars stimulate the growth of the radicle significantly longer than peat.
Y. Yue 2017 E	Municipal SS	Pyrolysis 500 °C for 2 h with a heating rate of 10 °C min ⁻¹ .	Unspecified, until crop grew 15-20 cm	0%, 1%, 5%, 10%, 20% and 50%, in mass ratio, pots	Urban soil loamy soil, pH= 8.4	Amendment for urban soil to grow grass. DMY, heavy metals risk assessment.	pH, EC, texture, Soil organic carbon, black carbon, available P and K; DMY, Total N (Kjeldahl) , P, K, Zn, Cr, Cu, Pb, Cd, As; bioconcentration factor Zn, Cr, Cu, Pb, Cd, As digestion H2SO4- H2O2 by plasma spectrometry (ICP), Colwell P and DGT P, and Total P in plant biomass, DMY.	Turf grass (<i>Poa pratensis</i> L)	Increment of nutrients and heavy metals in soil with amendments, Total N, P and K increased 8-16%, 51-91% and 10-28% respectively.	DMY increased with increasing rates of pyrochar, average 74%, 50% rate recommended. Lower plant heavy metal uptake with lower rates. Metals in biomass did not match bioavailable metals.
Jessica E. Mackay et al (2017)	SS, dry granules dried at 104°C and dewatered SS, and monopotassium phosphate (KH2PO4)	Pyrolysis 600°C, two gasification and one incineration (800°C)	55 days per season	520 - 1310 mg of material per kg soil, to obtain 20 and 50 mg P/kg. Nutrients added: K2SO4, CaCl2.2H2O, MnSO4.H2O, ZnSO4.7H2O, CuSO4.5H2O, Na2MoO4.2H2O, NH4NO3 and MgSO4.7H2O.	Sandy loam (16.5% clay) mixed with sand 1:1 w pH=5.3 (1:5 H2O), pots (2.5 kg soil/pot)	P availability to wheat	pH, EC (1:2.5 0.01 CaCl2 and 1:5 H2O), WHC, ; Elemental analysis, Total P, C, N, K, Ca, digestion ICP-OES; Sequential extraction P	Pre-germinated seeds of spring wheat (<i>Triticum aestivum</i> L. var. Axe) were	Highest available P on inorganic phosphate and dried sewage sludge amendment	DMY and P uptake highest with inorganic P-fertiliser. Greater biomass with P20 26-40 days but after 55 days DMY P20 and dried sewage sludges not significantly different. Third growing period increased 10 times P uptake in incinerated and dried SS. Gasifier and pyrolyzed sewage sludge were not different to control soil related to P uptake on the third period.

Table 0-4 Sewage sludge derived pyrochar and hydrochars effect when applied to agricultural soil and effect on soil properties and yield (continuation)

Author	SS	Thermal Treatment	Length of experiment	Rates (dry weight)	Soil type	Purpose	Analysis list	Crop	Effect on soil properties	Effect on Yield
W. M. Faria et al. (2017)	SS, NPK fertiliser	Pyrolysis 300°C-500°C and 300°C-500°C + NPK	2 years	15 Mg/ha	Red-Yellow Latosol (Typic Haplustox) Clay texture, 24 plots, 6 treatments 4 repetitions	Comparison to inorganic fertiliser	TC, TN, NO ₃ ⁻ , NH ₄ ⁺ , pH(CaCl ₂), P, K ⁺ , Ca ²⁺ , Mg ²⁺ , S Al ³⁺ , H ⁺ Al ³⁺ , Sb ECEC, CEC, BS, B, Cu, Fe, Mn, Zn, FA,HA,Humin, PV, SSA Thermotolerant coliforms	Corn (<i>Zeamays L.</i>), Field Experiment	Increased soil CEC and P, Mg, Cu and Zn. No effects on soil K.	Higher grain yield, nutrients on the second season. Significantly higher micronutrients with both pyrochars in both seasons. Could replace fertilisers combined with K fertiliser. No significant differences in grain yield second season among amendments. Significantly improved in the first season with pyrochar at 300°C and NPK combination
A.A. T.C. Sousa & C. c. Figueredo 2015	The sludge air dried, sieved at 8 mm	Pyrolysis (torrefaction) 300°C, 11 °C min ⁻¹ 30 min residence time, sieved 2 mm	35 days	0-10-20-30-40-50 g/ kg or 0, 1, 2, 3, 4 and 5% in a 2kg soil mix, 2L pot	Oxisol clayey texture	Effects on soil fertility and radish growth	Available P Mehlich CEC KCL 1 mol, pH CaCl ₂ 1:2.5 (v:v), germination, number of leaves, DMY of the plant	Radish <i>Raphanus sativus L. (Cv,Crimson Giant)</i>	Enrichment of P 275 times to control soil, N and increased Ca, Mg and CEC	Increased productivity at 10-30 g/kg, lower yield from 30 g/kg
X. D. Song 2014	Sewage sludge 8 wt.% and a LHV of around 15 MJ kg ⁻¹	Pyrolysis range of 400, 450, 500, 550°C, time not specified	NA	270t/ha, 216 t/ha, 200 t/ha 8cm depth sieved 10 mm	silt (sandy) loam soil (sand 8%, sile 70.5% and clay 21.5%) sieved 4 mm sterilized at 105°C then sieved at 2 mm,	Yield and heavy metal assessment	pH solid:water 1:5 (mL/mL), Elemental analysis P, proximal analysis, heavy metals ICP, Surface area, porosity, BET, TN, TP, TK, FTIR and SEM	Garlic (<i>Allium sativumL.</i>)	Not included	Yield improved 256% higher than reference at 216 t/ha. Pyrochar at 450°C gave lowest level of heavy metals in garlic.
Khan et al 2013	De-watered and air-dried	Pyrolysis 500 °C for 6h	91 days	Rates 5 and 10 % w/w. Applied with fertiliser: NH ₄ NO ₃ and K ₂ HPO ₄ . Pot experiment	Acidic Paddy soil Clay 0.63% Silt 22.1%, Sand 77.3%, 2 mm, pH= 4.02	Yield and heavy metal assessment and greenhouse emissions	EC, LOI, Porosity BET, TN, TC,TS a macro analyser, DOM, DMY, grain yield, number of tillers and height of tillers	Rice (<i>Oryza sativa L.</i>)	Increment of soil pH, TN, soil organic carbon, available nutrients. N ₂ O emissions potential CH ₄ sink	Lower yield with higher rates but always higher than the control. increased shoot biomass (71.3–92.2%), grain yield (148.8–175.1%. Overall increased bioaccumulation Cd and Zn below limits. Decreased the bioaccumulation of As, Cr, Co, Cu, Ni, Pb
M. Hossain 2010	Sewage sludge air dried	Pyrolysis 10 °C min ⁻¹ rate to 550 °C. N flow of 100 mL min ⁻¹	112 days	10 t/ha, Soil + char soil + fertiliser (N-P-K) soil + char + fertiliser	Chromosol 4 mm, air dried 36°C. pH= 4.5	Growth, yield and heavy metal assessment	CEC, EC, pH in 0.01 M CaCl ₂ (1:5), Total N, Available P (Colwell), Ammonium N and Nitrate N (KCl extract), Al, Ca, Mg, K, Na, 15 heavy metals ICP, Yield, number of fruits, DMY	Cherry tomato (<i>Lycopersicon esculentum</i>)	Char increased EC, pH, TN, available P and CEC	Highest plant growth for sewage sludge char from the 8th to 15th week. 4.5 cm longer that combined with NPK and only NPK. Only significantly different DMY when char is combined with NPK fertiliser 48,6 % higher compared to control. Yield was 97% greater from NPK + char than char alone. Pyrochar of sewage sludge alone produced 64,45% increase in yield compared to control soil. No significant heavy metal uptake by the plant, but Cd levels of NPK alone was on the limit.

1.4 Knowledge gaps

The motivation for this project lays in the current need to procure an alternative to the phosphate rock traditional fertiliser. Previous studies indicate the potential use of the carbonaceous material obtained from thermal treatments as soil amendment.

In view of the scarcity of comparative studies of hydrochars and pyrochars derived from sewage sludge on crop production, the effect of temperature and time in pyrolysis and in hydrothermal carbonization processes on P availability remains a subject to be exploited. These thermal treatments would enlighten the reasons why a significant proportion of the phosphorus added through sewage sludge is untapped and sometimes even lost after its application, which is still an opportunity of research (Cordell *et al.*, 2011). In addition, there is an imperative need to determine the best rates for P inputs in pyrochars and hydrochars amendments for different types of soils and cultivars, as well as the frequency, so a guidance prior to application could be established (Hogan, McHugh and Morton, 2001; Wang, Camps-Arbestain and Hedley, 2014). Likewise, the liming effect of pyrochars compared to the acidity of hydrochars could affect the concentration of Fe and Al in the soil solution, which could modify differently soil pH, the P available to plants and thus a difference in P efficiency, phytoavailable heavy metals, and crop yield (Cui *et al.*, 2011; Hansen *et al.*, 2016). As stated, most soils studied on sludge derived chars are low in organic matter and often require a dose of readily available nutrients, hence a comparative study on a mixture of these chars with a source of labile carbon could also provide valuable information.

For an assessment of nutrient imbalance and heavy metal of both thermal treatments a study of an edible crop is imperative. A study on spring wheat grown until its maturity could help to fill the knowledge gap that is needed to determine the relation between the addition of sludge derived chars and crop food quality. Wheat (*Triticum aestivum* L.), one of the major crops all over the world for being a main staple food, has received a major P fertiliser inputs during the last decades (A Rashid, Awan and Ryan, 2005) obtaining significant increases in grain yield

(Ali *et al.*, 2015). However, plant analysis criteria for wheat nutrient concentration still need to be standardized (A Rashid, Awan and Ryan, 2005). For this reason, recent studies have indicated the need of finding an adequate methodology in identifying P deficiency in growing crops. Total P contained in grains could be the first approach to P use efficiency. Furthermore, as phytate concentration as it represents the largest stock of phosphorus in cereal grains and it forms complex with nutritionally essential metals as Fe, Ca and Zn, the assessment of the accumulation of these elements could prove to be useful (Madsen *et al.*, 2017).

For this reason, it is necessary to carry out a more exhaustive study, contributing towards the understanding of phosphorus sorption mechanisms during thermal treatments and nutrient dynamics in agricultural systems.

1.5 Research aim and objectives

1.5.1 Aim

To evaluate interactions in phosphorus availability from sewage sludge and its thermally treated derivatives such as pyrochar and hydrochar on spring wheat when added on its own and in combination with sewage sludge cake as soil amendment.

1.5.2 Objectives

1.5.2.1 To evaluate the effects of temperature after thermal processing on the physical-chemical properties of sewage sludge.

Hypothesis-1

Increasing temperature results in more stable carbon, which reduces phytotoxicity to spring wheat. Chars produced with a higher carbonization degree have a lower presence of ammonia, fatty acids, PAHs, and most importantly, volatile and soluble compounds and salts, which can reduce seed germination rates (Rombolà *et al.*, 2015).

1.5.2.2 To assess the efficacy of the pyrochar and hydrochar as fertiliser for the production of spring wheat on its own and in combination with sludge cake in a low phosphorus index soil.

Hypothesis-2a

Crop yield will be enhanced in comparison with the control soil using combined soil amendments with thermal derivatives.

Hypothesis-2b

Higher carbon stability associated with increased temperature processing, HTC (180-240°C) pyrolysis (300-400°C), directly enhance crop yield.

Hypothesis-2c

Accumulation of phosphorus in the soil and in the crop will increase directly with the application rates.

1.5.2.3 To evaluate the changes in soil conditions after different types of amendments, in order to provide useful recommendations.

Hypothesis-3

Soil properties (pH, EC and organic matter content) will be significantly enhanced compared to control soil after combined treatments at highest rates, proving benefits of using sludge derived char as organic amendment.

1.5.2.4 To evaluate the potential environmental risks associated with nutrients balance and heavy metals.

Hypothesis-4a

Accumulation of nutrients on the base of soil profile will be significantly lower for treatments with higher carbon stability, namely those less prompt to degrade in the soil and thus to release an excess of nutrients with possibility of contamination to water systems.

Hypothesis-4b

The risk of accumulated heavy metals in the plant will be less due to its immobilization after the carbonization of sludge.

1.6 Overview of thesis structure

This thesis is presented in the same order as the research aim and objectives. The literature review that identified the gap of knowledge and the best options available for thermal treatments guided the conditions for the production of the chars.

The characterisation of the material's structural and physical-chemical properties were then assessed to determine significant changes to the original feedstock. The effect of the type of thermal treatment and the temperature constituted the base line for the study of phosphorus use efficiency and environmental risk of these materials.

This project has evaluated interactions in phosphorus availability from sewage sludge and its thermally treated derivatives obtained through pyrolysis and hydrothermal carbonisation at two different temperatures to fill the gap of knowledge (Chapter 1). These materials were analysed for their physical chemical and structural changes (Chapter 2), and then added to a loamy sandy soil on a single application using 3 different rates to grow two seasons of spring wheat (Chapter 3-4). The materials were applied on its own and in combination with a non-thermally treated sewage sludge to assess changes on the soil properties and changes of available P from raw materials (Chapter 3) and their effectiveness as P-fertiliser to produce wheat grain (Chapter 4).

Finally, the germination test followed by two seasons spring wheat grown with the amendments provided data on phytotoxicity, nutrient balance and heavy metal accumulation in the soil and in the grains (Chapter 4) to test all the hypotheses above listed. The links between the thesis chapters are schematically presented in Figure 0-6.

Chapters 2,3 & 4 are written as independent journal articles ready to be submitted to the following journals:

- Chapter 2: Waste Management (to be submitted)
- Chapter 3: Agronomy (to be submitted)

- Chapter 4: Plant and Soil (to be submitted)

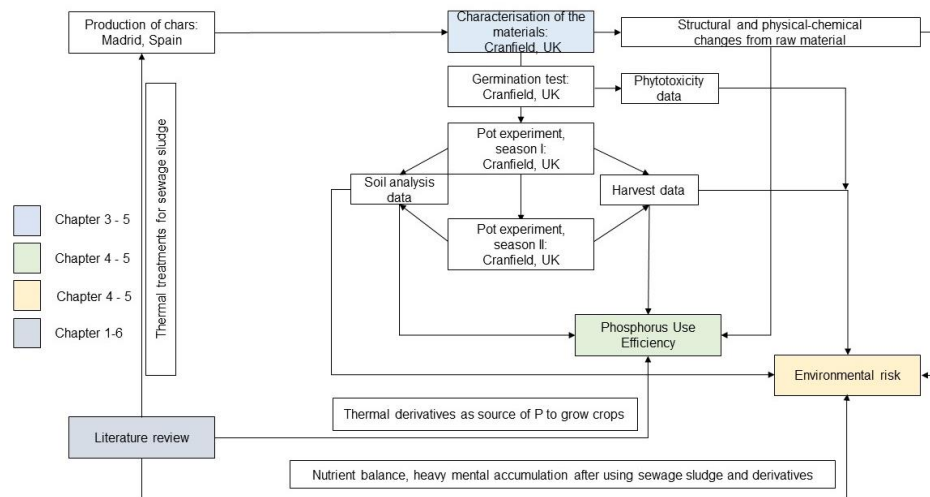


Figure 0-6 Thesis structure

CHAPTER 2: CHARACTERISATION OF PYROCHARS AND HYDROCHARS DERIVED FROM SEWAGE SLUDGE: STABILITY AND AGRONOMIC PROPERTIES

Summary: This chapter comprises data collected from the characterisation of thermal derivatives. The structural and physical-chemical properties variations to the original feedstock are addressed to find statistical differences between samples to ensure a diversity of options of P-fertilisers from the same feedstock (Objective 1). It also emphasizes the effect of temperature selected on the processing to obtaining a carbonaceous material with different degrees of organic matter stabilisation.

Highlights:

- Four types of carbonaceous materials were obtained from the same sample of sewage sludge. Chars showed significantly different physical chemical and structural results.
- Differences of porosity and surface area were linked to adsorption capacity of the carbonaceous materials.
- Based on characterization results, pyrolysis would provide a higher carbon stability compared to hydrothermal carbonisation.
- Hydrothermal carbonisation produces a material with more functional groups, a higher adsorption capacity, mainly labile organic matter and a lower reduction of the CEC from the same feedstock.

Chapter 2 was written as independent journal article and is ready to be submitted to: Waste Management.

2.1 Introduction

The increasing amounts of sewage sludge produced is a current cause of concern (Zhai *et al.*, 2017b) as it contains the pollutants removed from the waste water (Singh and Agrawal, 2008; Jin *et al.*, 2016; Stefaniuk and Oleszczuk, 2016). Renewed efforts are being made to reduce its disposal and promote new valorisation routes (Sharma *et al.*, 2017). Thermal processes are the most promising pathways to obtain valuable by-products from sewage sludge (Manara and Zabaniotou, 2012a; Huang and Tang, 2015). Thermal treatments unlike composting, subject the material from moderate to high temperatures, most commonly between 200-700°C. These treatments can significantly decompose organic pollutants, including pharmaceuticals such as diclofenac, carbamazepine, metoprolol and propranolol, reduce their concentrations by 39% to 97% (vom Eyser *et al.*, 2015). It also reduces its volume, which makes it easier to manage (Huang and Tang, 2015). Significant attention has been given to the treatments that produce mainly syngas and bio-oil for energy recovery (Manara and Zabaniotou, 2012a). More recently, the potential applications of the solid by product, here after referred to as char, are being investigated more frequently, focusing on those treatments that obtain it as a main product (Fakkaew, Koottatep and Polprasert, 2017). The carbonaceous end product is normally referred to as biochar when it is obtained from biomass and contains more than 50% organic carbon (C_{org}) (Lehmann *et al.*, 2011a). Diverse processes have been reported to enhance suitability of sewage sludge for soil amendments (Abel *et al.*, 2013; Zhang, Lin and Zhao, 2014). Sludge derived chars are also of interest as an organic amendment (Gascó, Lobo and Guerrero, 2005; Gasco, Cueto and Méndez, 2007) as they increase carbon stability in soil (Álvarez *et al.*, 2017a) and reduce the mobility of heavy metals from the original feedstock (Shi *et al.*, 2013; Zhai *et al.*, 2017b). Soil remediation has been also considered as a possible application of this residue, as it has been proven to adsorb heavy metals in contaminated soils (Grobela *et al.*, 2017).

Common temperature ranges for char obtained through slow pyrolysis are 300-500°C, or as low as 200-300°C (torrefaction), in both cases sustained from several minutes to hours. On the other hand, the hydrothermal carbonization (HTC) process produces another type of material now mostly known as hydrochar, a solid material like char but obtained with water content as high as 80% which reaches subcritical conditions and

that needs to be filtered afterwards from the liquid phase after production. On the contrary to pyrolysis, HTC occurs in an aqueous medium normally at lower temperatures (<300 °C) and longer retention times (2-6 h) than the production of pyrochars. Because sewage sludge contains a high percentage of moisture, an important part of the energy during char production is consumed in the drying process. However, HTC reduces the need of pre-drying sludge which is required for an optimal pyrolysis performance (Manara and Zabaniotou, 2012a; Huang and Tang, 2015). Thus, HTC opens a range of options for potential biomass sources with high moisture contents (Libra *et al.*, 2011; Méndez *et al.*, 2012 ; Huang and Tang, 2016). The choice of thermal treatment results in specific structural and physicochemical properties of the carbonaceous materials (Srinivasan *et al.*, 2015), which are closely related to the type of feedstock (Li *et al.*, 2019) and potentially could bring different outcomes when added to a soil (Schneider and Haderlein, 2016b; Paneque *et al.*, 2019). However, few studies have been compared using the same source to make different types of chars making it difficult to generalise and compare results.

Hence, if the effects of the thermal treatment could be better understood, the production of char could be tailored by modifying the conditions according to their use. To obtain different products, temperature and time of processing (Huang and Yuan, 2016), from ramping to retention times, pH adjustments, chemical doping (Dai *et al.*, 2014) or even sequential thermal treatments, are the factors that can be considered that will determine the physical and chemical characteristics of the char or hydrochar, and its carbon stability, and thus the best method to use it (Srinivasan *et al.*, 2015).

This paper seeks to provide new information on physical and chemical attributes of hydrochar and pyrochar and their stability that could affect their behaviour as soil amendment. For the first time, in the same physical and time frame, two types of char obtained from pyrolysis (pyrochars) and two others obtained from HTC (hydrochars) using the same feedstock of anaerobic digested sewage sludge were compared. These chars were produced by only varying temperature during the process.

We expect that (i) pyrolysis and HTC to have a significant effect on sludge properties producing different chars using the same feedstock, (ii) thermal treatments will increase carbon stabilization and porosity of sludge, best using higher temperatures of pyrolysis.

2.2 Materials and Methods

A sample of dewatered anaerobic digested sewage sludge, SS_{ES}, was obtained from a municipal sewage treatment plant in Avila (Spain) and used as feedstock for the thermal treatments. A second sample of dewatered anaerobic digested sewage sludge, hereafter referred to as SS_{UK}, was obtained from a municipal sewage treatment plant in UK. SS_{ES} and SS_{UK} were oven dried at 105°C for 48h.

2.2.1 Thermal treatments to produce pyrochars and hydrochars

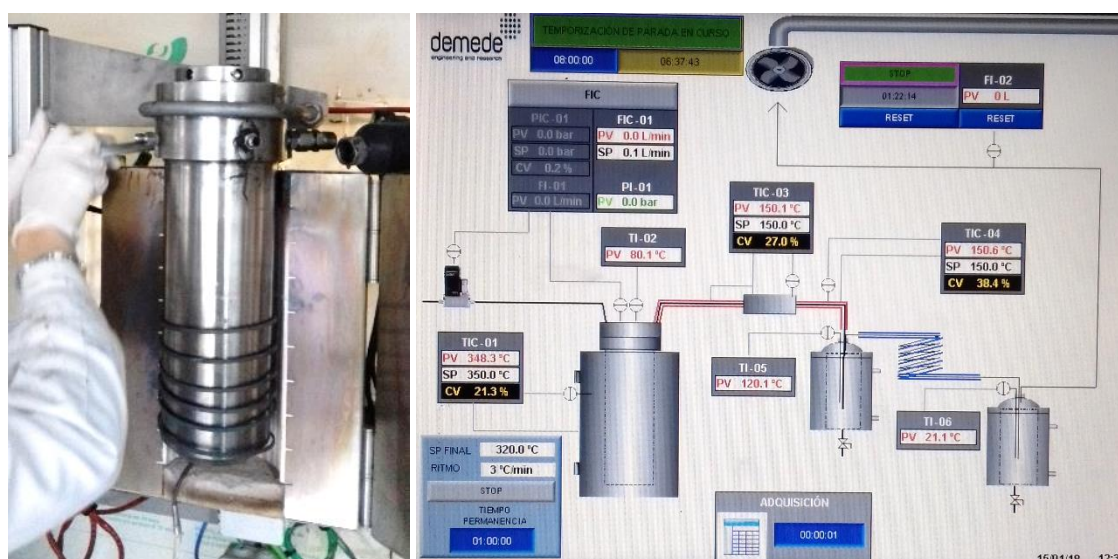


Figure 0-1 Reactor and thermal processing diagram.

Two types of pyrochars and two types of hydrochars were produced from a sample of sewage sludge (SS_{ES}), at the Polytechnic University of Madrid (UPM) (Figure 0-1). Pyrochar samples were prepared as follows: 500 g of SS_{ES} was oven-dried at 105°C for 48h and then placed in a metallic crucible and pyrolyzed in a Heron electric furnace (model 12-PR/300 series 8B) (Gascó, Paz-Ferreiro and Méndez, 2012; Cely *et al.*, 2015). The experiments were performed by increasing the temperature at a rate of 3°C min⁻¹. The samples were pyrolyzed at 300°C for 1h (P300-1) or 400°C for 1h (P400-1). Temperature settings were selected to obtain a physicochemical contrast without compromising production efficiency.

Hydrochar samples were prepared as follows: SS_{ES} was mixed with deionised water to obtain a water content of 0.2 (g/g) (Figure 0-2). Then, the mixture was placed inside the hydrothermal reactor (Demede S.L, Spain) (Kalderis *et al.*, 2014). The experiments were performed at 180°C and 240°C by increasing the temperature at a rate of 3°C

min⁻¹ and then maintained for 4 h once the target temperature was achieved (hereafter referred to as H180-4 and H240-4, respectively). When the process was completed the hydrochar was filtered and oven-dried at 80°C for 24h.

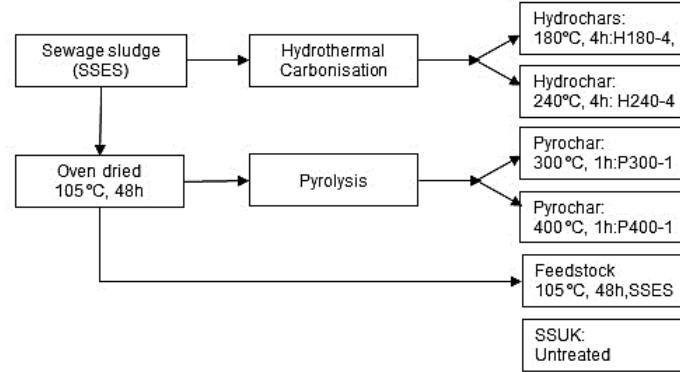


Figure 0-2 Samples produced through pyrolysis and hydrothermal carbonisation of SS_{ES}.

2.2.2 Analytical Methods

All char samples were weighted, crushed, sieved through a 2 mm mesh. To assess the effect of the type of thermal treatment and the temperature selected on the feedstock, after thermal treatments moisture content and organic matter were determined through loss on ignition (LOI) (BS EN 13039:2000) using 1g of sample at 550°C (Bachmann *et al.*, 2016). This technique was selected for its practicality when analysing numerous samples at once and for the low amount of sample required. To determine the content of carbonate, a further ashing was performed at temperatures >950°C to degrade the mineral phase, using the same samples after measuring their weight loss at 550°C. Contents were calculated as follows:

$$\text{Moisture (\%)} = \frac{(m1 - m2) \times 100}{m2 - m0} \quad (3-1)$$

$$\text{LOI(\%)} = \frac{(m2 - m3) \times 100}{m2 - m0} \quad (3-2)$$

$$\text{CaCO}_3(\%) = \frac{(m3 - m4) \times 100}{m2 - m0} \quad (3-3)$$

$$\text{Ash (\%)} = \frac{(m4 - m0) \times 100}{m2 - m0} \quad (3-4)$$

where m_0 = cup weight (T); m_1 = sample plus cup measured in balance; m_2 = total weight after drying a minimum of 17h, in our case we did 24h; m_3 = sample after first ignition at 550°C plus cup (ashes + inorganic C); m_4 = samples plus cup after second ashing at 950°C (only ashes).

To compare the carbonization degree the sludge sample, pyrochars and hydrochars were analysed using four replicates per sample, for total C, H, N (expressed in %) through elemental analysis. For this, each sample was oven dried at 150°C, 24h prior to the analysis and 20 mg $\pm$ 0,001 mg of fine char sample (crushed to <2 mm particle size) were weighed (Oakleyweight Sartorius balance Pro 11) and placed in the Elemental Analyser (Isoprime Elementar EL III CHN).

High Heating Value (HHV) to compare SS_{ES}, pyrochars and hydrochars to fossil carbon was estimated by using Dulong's approximation in (Smith, Singh and Ross, 2016):

$$HHV (MJ/kg) = 0,3383 \cdot C\% + 1,422 \cdot H\% - (O\%/8) \quad (3-5),$$

where O% is obtained as: $O\% = Ash\% - C\% - N\% - H\%$ using Ash (%) obtained after LOI at 950°C.

Following, to assess the stability degree of the organic matter a thermogravimetric (TG) and derivative thermogravimetric (dTG) thermal analyses of the samples were conducted in a Pyris 1, Perkin Elmer as for these analyses, 80 mg of sample was heated at 15 °C min⁻¹ until 850 °C under air atmosphere using a flow of 40ml min⁻¹ (Méndez *et al.*, 2012; Cely *et al.*, 2015).

To quantify the effect of the different thermal treatments on the surface functional groups, the Fourier-transform infrared spectroscopy (FTIR) contrast was performed with a Vertex 70 FT-IR spectrometer, which uses Attenuated Total Reflection (ATR) to give an insight of the process efficiency, and scan functional groups changes after thermal processing. Each sample was ground to fine dust using a mortar. Approximately 1g was placed on top of the crystal and analysed 10 times to assess if the sample was homogeneous when it comes to functional groups. For each reading the data was transformed from ATR to absorbance (ABS) to transmittance (T) and then balanced using software OPUS_7.5.18 (Bruker, 2021). This methodology removes noise from the spectrum and places all results in the original position in the

axes, making all samples comparable to one another. After correcting all curves, the means were calculated for each sample using Excel 2016.

Following, specific surface area, meso (10-50 nm) and micro (<10 nm) porosity were determined with a Brunauer–Emmett–Teller Surface Area (BET) analyser 3P Meso 222 sorption analyser (3P instruments) using nitrogen as the adsorbate to assess structural changes.

Finally, the impact of the thermal process on the sewage sludge Cation Exchange Capacity (CEC) was analysed following the ammonium acetate method (Jackson, Farrington and Henderson, 1986). This method was selected to avoid a centrifuge step needed with CEC determination with barium chloride as chars would float hampering the supernatant analysis.

2.2.3 Statistical analyses

The statistical analysis of experimental data was undertaken for multivariate and Principal Components Analysis (PCA) followed by clustering analysis using (K-means) using JMP-16. Variables studied were expected to be constant among individuals, fixed effects, as samples of each material were considered to be homogeneous. Thus, the analysis of variance was performed through one-way ANOVA followed by a post-hoc analysis. The least significant differences to compare the means were obtained with the Tukey test with a probability level of 5% ($p < 0.05$) using STATISTICA 13.3.704.19.

2.3 Results and discussion

2.3.1 Carbonization degree of pyrochars and hydrochar

All treatments reduced the organic matter content and are considered to be lower-class biochar (IBI, 2015). As shown in Table 0-1, both sewage sludge samples, SS_{ES} and SS_{UK}, had a high content in OM of 68.4% and 63.3%, respectively. The lowest OM content was for the pyrochar obtained at 400°C (46.7%). After thermal treatments OM was reduced as follows: H180 (16.4%) H240 (21.5%); P300 (3.5%), P400 (31.7%) from SS_{ES} (Table 0-1). Compared to other chars, the pyrochar P300-1 reduced the least concentration of labile organic matter.

Table 0-1 Main properties of sewage sludges (SSES), pyrochar from pyrolysis and hydrochar from hydrothermal carbonization of SSES.

Sample	C/N	Moisture content (%)	LOI (%)	CaCO ₃ (%)	Ash (%)
SS _{ES}	6.38	3.5ab	68.4e	5.7f	28.7b
H180-4	8.85	2.8ab	57.2c	4.5c	39.8d
H240-4	9.50	2.8b	53.7b	4.1b	42.2e
P300-1	6.71	1.7ab	59.2d	6.1d	37.7c
P400-1	7.28	0.3a	46.7a	4.6a	50.7f
SS _{UK}	7.67	71.7c	63.3f	10.8e	9.2a

Values in column followed by the same letter are not significantly different ($p = 0.05$) using the Tukey STATGraphics Centurion for Homogeneous Groups.

Moisture content (%), LOI (%), CaCO₃ (%), Ash (%) values obtained from dried samples:

SS_{ES} = Sewage sludge (Spain) dried 105°C, 48h; H180-4 = hydrochar from SS_{ES} at 180°C for 4h; H240-4 = hydrochar from SS_{ES} at 240°C for 4h; P300-1 = pyrochar from SS_{ES} at 300°C for 1h; P400-1= pyrochar from SS_{ES} at 400°C for 1h. SS_{UK}= commercialized sewage sludge (UK) used for combined treatments, untreated and added at 72% moisture content.

As opposed to the other pyrochar P400-1 and hydrochars, P300-1 had a higher total C and N content (Table 0-1) than the original sludge (SS_{ES}). These results was similar to other show previously by Figueiredo et al., (2018). For all thermal treatments, total N was partially lost, perhaps volatilized or solubilize. In a comparison study of N compounds during pyrolysis and HTC, Liu *et al.*, (2018) indicated a loss of N through deamination, formation of HCN and oxidation of NH₃ to N₂ through heat. Hydrochars from sewage sludge tend to have a lower N content but a higher stability due to N transformation from ammonium inorganic salts and labile proteins to heterocyclic-N compounds. Thus the C/N ratio increased in all cases with increasing temperature (Table 0-1) which agrees with results findings by Barriga et al., (2010) and (Paneque *et al.*, 2019). Soil fertility and crop productivity is expected to be greater in soils amended with char with C/N < 9 ratios (Liu *et al.*, 2013) which would favour pyrochars over hydrochars (Table 0-1) as the highest C/N ratio was for H240-4 (C/N=9.5). Nevertheless, according to Sousa and Figueiredo, (2016) a C/N lower than 30, is likely

that the nitrate content would be available due to a balance of net N mineralization and immobilization. This is the case for all our chars which would favour crop production if used as soil amendment.

As expected, the temperature of both treatments significantly affected the physicochemical structures as shown in the Van Krevelen graph (Figure 0-3). After thermal treatments H/C and O/C ratios of SS_{ES} were considerably lower in both hydrochars and pyrochars. Previously, it was shown that these ratios are being favoured by higher temperatures and pyrolysis (Song and Guo, 2012; Méndez, Terradillos and Gascó, 2013). Thus, the characteristics of both hydrochars and pyrochars changed towards sub-bituminous coals as reported previously by (Manara and Zabaniotou, 2012b), hence why chars derived from sewage sludge are also studied for energy purposes (Peng *et al.*, 2016). Nonetheless, HHV didn't increase but was significantly lower in H180-4 (16.44 MJ kg⁻¹ and P400-1 (14.93 MJ kg⁻¹) from 17.94 MJ kg⁻¹ in SS_{ES} (Table 0-2). The reduction of H/C ratio could indicate a further condensation and possible formation of aromatic compounds while a lower O/C could be related to hydrolysis and the loss of functional groups. The difference between sewage sludge samples is mainly on the H/C ratio giving the standard deviation of SS_{UK}. SS_{UK} had less C, H and O than SS_{ES} could be explained by the lower organic matter content of 63.3% for SS_{UK} against 68.4% for SS_{ES} (Table 0-1).

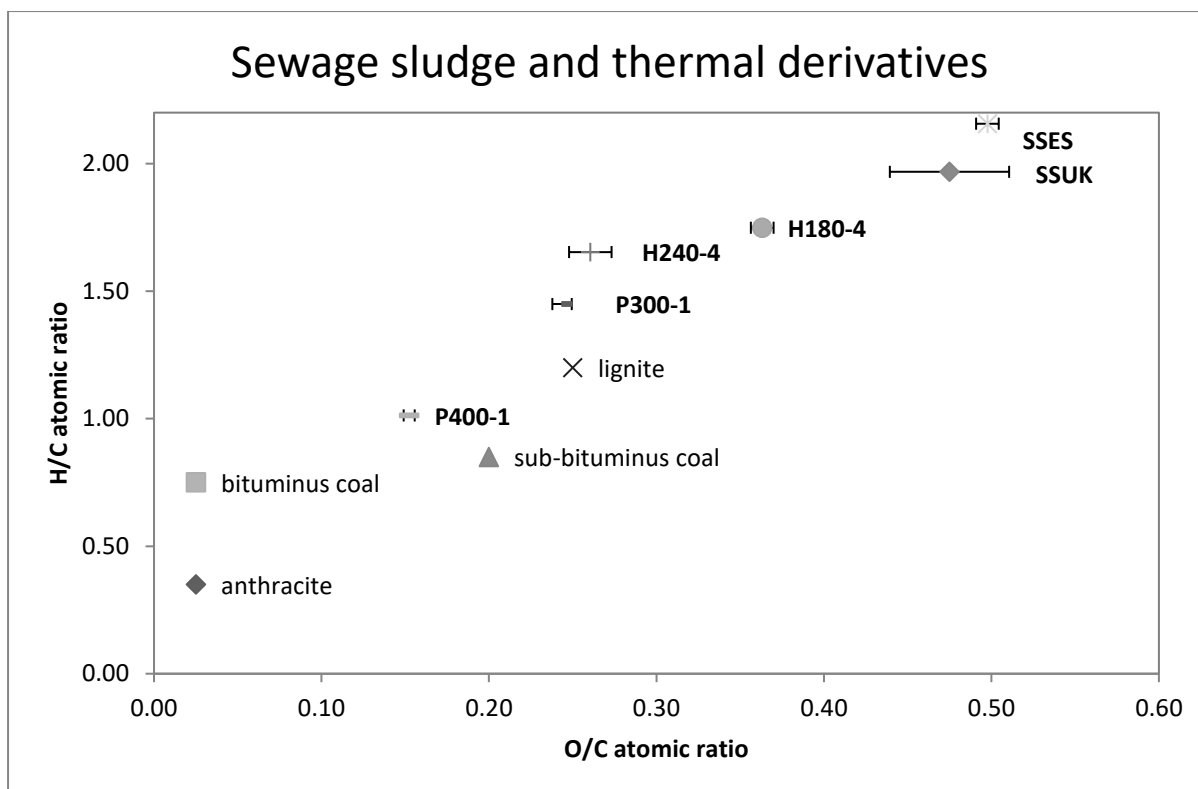


Figure 0-3 Van Krevelen Graph.

SS_{ES} = Sewage sludge (Spain) dried 105°C, 48h; H180-4 = hydrochar from SS_{ES} at 180°C for 4h; H240-4 = hydrochar from SS_{ES} at 240°C for 4h; P300-1 = pyrochar from SS_{ES} at 300°C for 1h; P400-1= pyrochar from SS_{ES} at 400°C for 1h. SS_{UK}= commercialized sewage sludge (UK) used for combined treatments, untreated and added at 72% moisture content.

Table 0-2 Elemental analysis and HHV predicted of sewage sludge and corresponding hydrochar and pyrochar samples

¹ Calculated by difference with ash content from Table 0-1

² HHV estimated by Dulong approximation in A.M. Smith et al. (2016)

Values in column followed by the same letter are not significantly different ($p = 0.05$) using the Tukey test.

SS_{ES} = Sewage sludge (Spain) dried 105°C, 48h; H180-4 = hydrochar from SS_{ES} at 180°C for

Samples	Elemental analysis (%)					HHV predicted ² (MJ kg ⁻¹)
	C	H	N	S	O ¹	
SS _{ES}	35.11a	6.31e	5.50d	-	23.30d	17.94cd
H180-4	33.90a	4.94b	3.83a	-	16.41c	16.44b
H240-4	34.98a	4.82ab	3.68a	-	12.15a	17.17bc
P300-1	38.66b	4.67a	5.76e	-	12.56a	18.15d
P400-1	34.48a	2.91c	4.73c	-	7.00b	14.93a
SS _{UK}	34.88a	5.72d	4.55b	-	22.09d	17.17bc

4h; H240-4 = hydrochar from SS_{ES} at 240°C for 4h; P300-1 = pyrochar from SS_{ES} at 300°C for 1h; P400-1= pyrochar from SS_{ES} at 400°C for 1h. SS_{UK}= commercialized sewage sludge (UK) used for combined treatments, untreated and added at 72% moisture content.

2.3.2 Functional groups characterization through Fourier-transform infrared spectroscopy (FTIR)

The peaks of the FTIR graph showed that no different functional groups were created after thermal treatments. This is commonly referred as fingerprints and agrees with previous reports for char derived from sludge through pyrolysis (Hossain *et al.*, 2011a), and HTC (Zhang *et al.*, 2014; Peng *et al.*, 2016). However, although the peaks appeared in the same areas of the spectrum, indicating similar functional groups, the intensity of these peaks varied greatly depending on the area of the sample studied. Contrary to chemical analysis, this method only analyses a fraction of the surface area just like other high precision methods, like SEM. For this reason, the average of 10 was obtained for each sample in order to compare them (Figure 0-4). Thus, we suggest that FTIR analysis on similar samples should therefore be tested for homogeneity first to provide a more representative FTIR results of each material is available in the Appendix, (Figure A 1).

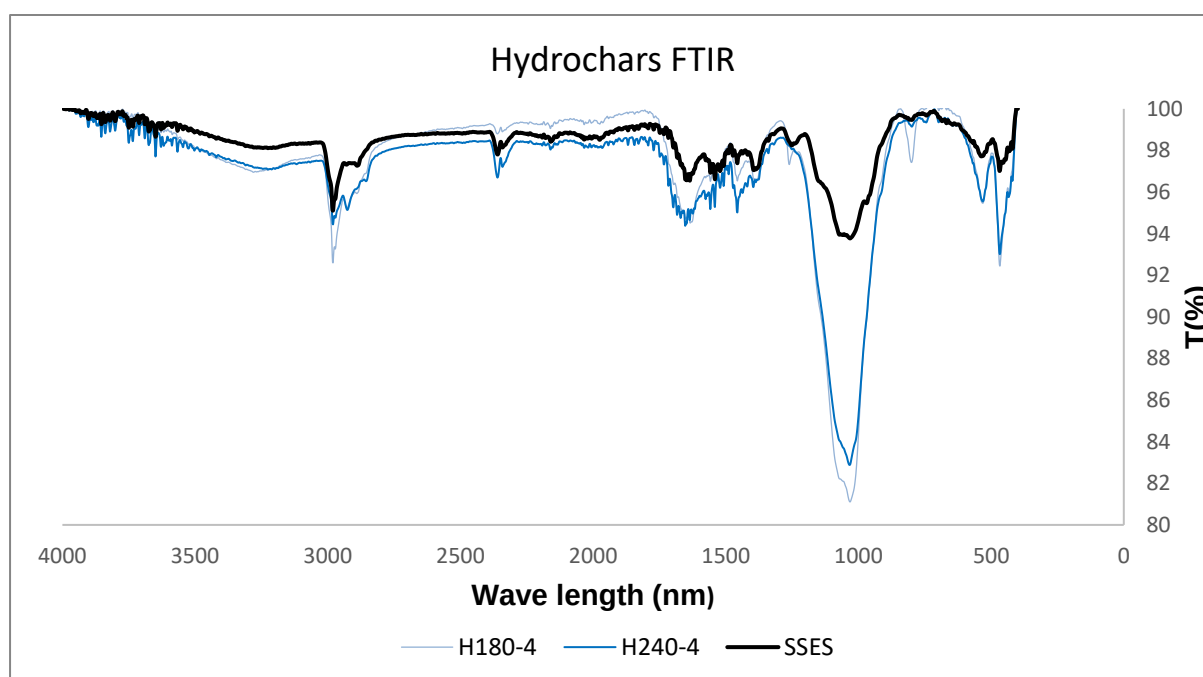
FTIR results show a difference in how these elements were organized on the surface area (Figure 0-4). Despite being from different sources, SS_{UK} and SS_{ES} had the same

peaks for functional groups -OH (3500 cm^{-1}), -COOH ($1558\text{--}1457\text{ cm}^{-1}$), C-O (1089 and 1054 cm^{-1}) and higher aromaticity C=C (1654 cm^{-1}) confirmed by less aliphatic carbons C-H (2900 cm^{-1}). According to the FTIR (Figure 0-4), pyrochars showed the highest loss of functional groups and bonds from 1500 cm^{-1} to 3445 cm^{-1} whereas hydrochars increased the peaks intensity in this range. The peak from 2300 to 2400 cm^{-1} is a distinctive peak related to the CO_2 present in the air and in the sample as the reading was taken in an open surface (Peng *et al.*, 2016).

Pyrolysis results in de-hydration, followed by a decarboxylation and, at highest temperatures, aromatization during the carbonization (Di Blasi, 2008). Small molecular carbohydrates are the first to decompose at $200\text{--}300^\circ\text{C}$, while most cellulose and lignin are pyrolyzed in the temperature range of $300\text{--}350^\circ\text{C}$ and protein and lipid in the temperature range of $200\text{--}600^\circ\text{C}$. Because of the overlapping pyrolysis temperature ranges, cross-linking reactions between different compounds could occur, which makes the pyrolysis mechanism more complex (Hu *et al.*, 2019). Therefore, a reduction of the signal for NH and OH bonds between $3000\text{--}3300\text{ cm}^{-1}$, CH_3 at $2800\text{--}3000\text{ cm}^{-1}$ and CH_2 at 1431 cm^{-1} was expected with higher temperatures of pyrolysis in our experiments (Hossain *et al.*, 2011a) (Figure 0-4). On the other hand, the solution of polymers occurs under sub-critical conditions around 200°C followed by a reaggregation of the monomers to form longer chains finalized by a carbonization, where the formed polymers condense (Tekin, Karagöz and Bektaş, 2014; Smith, Singh and Ross, 2016). Thus, having selected a hydrochar under and one above 200°C , differences of the physical chemical characteristics between the two samples are expected. Moreover, temperature effect on hydrochars in regards of bonds proved to be greater than those between pyrochars. HTC increased asymmetric and symmetric aliphatic groups, 2964 cm^{-1} and 2848 cm^{-1} present in SS_{ES} (Figure 0-4), which is in agreement with results reported previously by Hossain *et al.*, (2011) and Peng *et al.*, (2016). Both hydrochars promoted another signal assigned to aromatic C-H vibration at 2922 cm^{-1} and C=C at 1652 cm^{-1} ($1730\text{--}1650\text{ cm}^{-1}$). The signal C=C bonds was similar for both hydrochars but lower in aliphatic 2964 cm^{-1} for H180-4. This may suggest that aromatic compounds were partially re-created by HTC but partially destroyed at higher temperatures, which was corroborated by rocking signal of aromatic C-H at 798 cm^{-1} only for H180-4. Similarly, higher temperatures of pyrolysis showed a reduction of the aromatic structures as reported by Hossain *et al.*, (2011).

P300-1 increased the signal at 1652 cm^{-1} associated to C=C but reduced it for P400-1. This aromatization trend on sludge is in accordance with previous research.

It is important to note that all thermal treatments showed a stronger signal at $979\text{--}1163\text{ cm}^{-1}$ than SSES , where H180-4 showed a higher intensity. This area is associated to SiO_2 content (1000 cm^{-1}) and C-O bonds ($950\text{--}1400\text{ cm}^{-1}$). Since the materials were obtained from the same feedstock, it is likely that the C-O bonds are responsible for the differences in the peak of intensity and could suggest that these bonds were not lost but re-created through thermal treatments as suggested by J. hong Zhang et al., (2014). In the case of HTC this could be due to new formed acidic groups and its derivatives which is in accordance with an increase in signal at 3200 cm^{-1} (-OH) and 1456 cm^{-1} (-COOH) for both hydrochars (Figure 0-4), which is opposite to the decrease on -OH groups reported by Peng et al., (2016). Pyrochar of sewage sludge had lower presence of -OH at higher temperature as previously reported by Hossain et al., (2011). This could indicate that that -CO bonds are mainly related to new aliphatic ethers as suggested by Peng et al., (2016) and remaining acid groups from SSES . In the case of HTC this would indicate that these groups are promoted at lower temperatures of HTC and later destroyed at higher temperatures as the signal is lower for H240-4 than H180-4 ($950\text{--}1400\text{ cm}^{-1}$) (Figure 0-4).



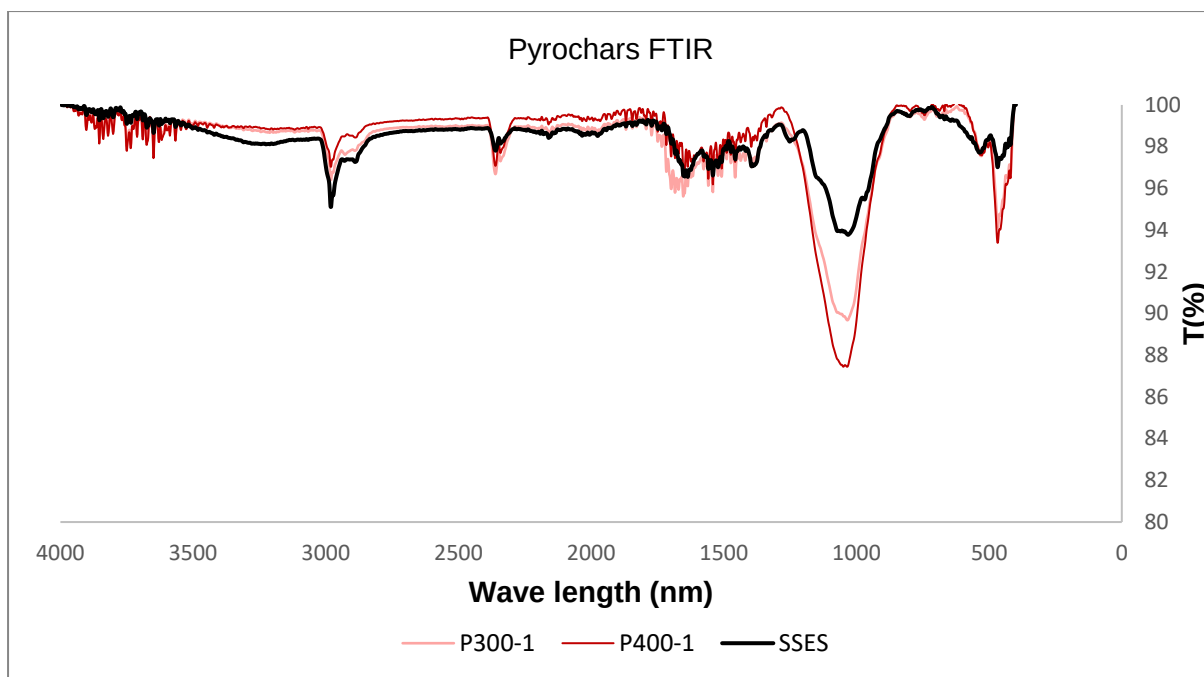
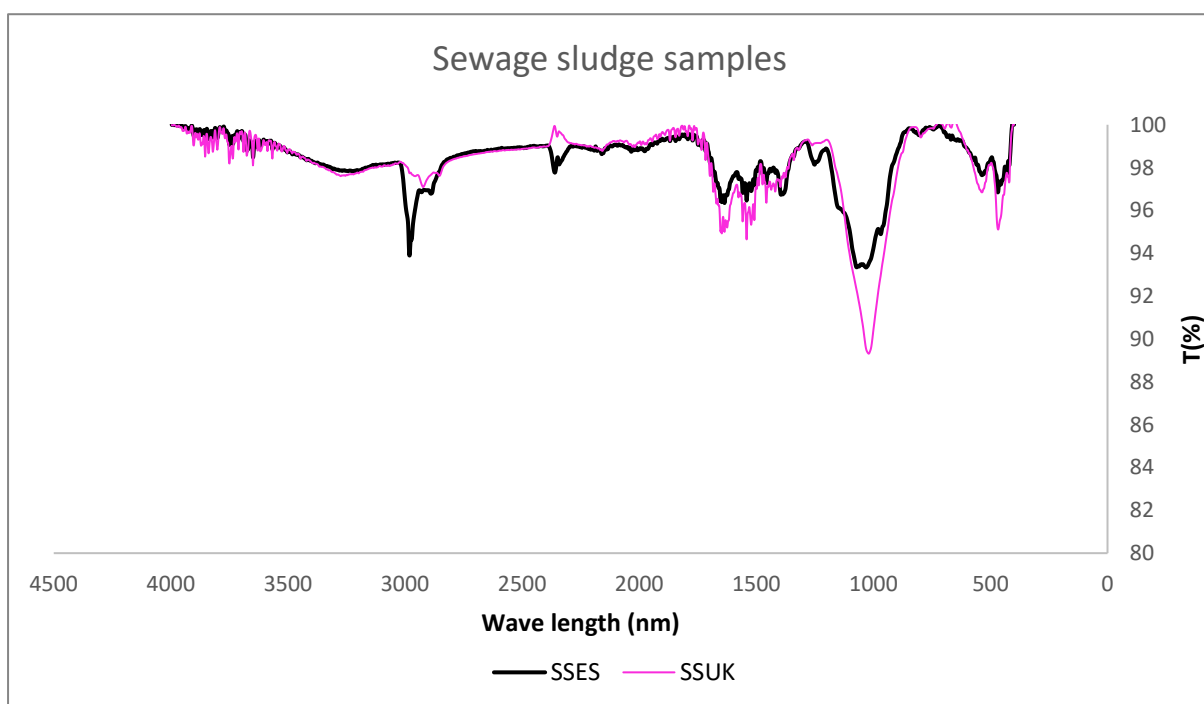
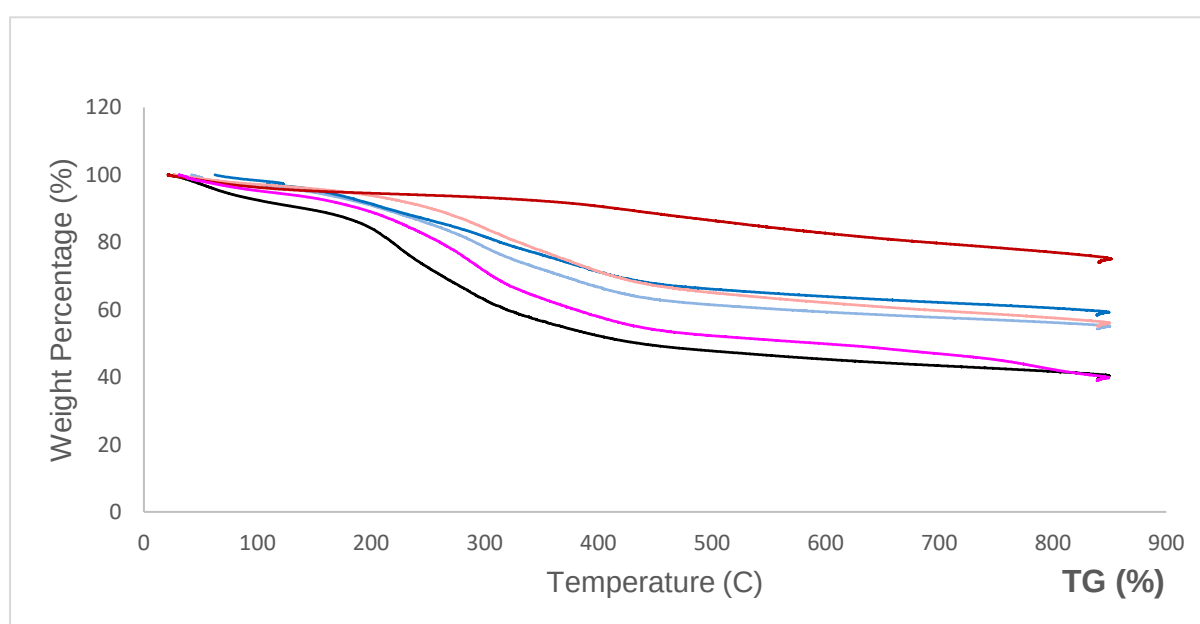


Figure 0-4 FTIR

SS_{ES} = Sewage sludge (Spain) dried 105°C, 48h; H180-4 = hydrochar from SS_{ES} at 180°C for 4h; H240-4 = hydrochar from SS_{ES} at 240°C for 4h; P300-1 = pyrochar from SS_{ES} at 300°C for 1h; P400-1= pyrochar from SS_{ES} at 400°C for 1h. SS_{UK}= commercialized sewage sludge (UK) used for combined treatments, untreated and added at 72% moisture content.

2.3.3 Carbon stability

Thermogravimetric analysis in air atmosphere of SS_{UK}, SS_{ES} and the thermal derivatives is used for assessing organic matter stability after using thermal treatments. The more resistant and structurally ordered the organic fraction contained in the samples, the higher the temperature at which loss occurs (Cely et al., 2015). After thermal treatments and in particular at higher temperatures, SS_{ES} became more stable after the treatments as the weight percentage curve stands above SS_{ES} curve (Figure 0-5). Using the derivate of TG, a deeper insight can be obtained as this graph will display 4 main regions that cannot be easily spotted otherwise. (Figure 0-5). The weight loss from room temperature to 105°C relates to the higher water content for the raw material (SS_{ES}) than the other samples, consistent with our findings reported in Table 0-1. From 200°C to 550°C, when the oxidation of the labile organic matter takes place, the sample weight was reduced further for samples produced at higher temperatures of pyrolysis and HTC. P300-1 showed a lower reduction than H180-4 despite having a higher content of organic matter (Table 0-1), proving that HTC at temperatures below 200°C in our case didn't stabilize organic carbon as well as the others. Refractory carbon and clay decomposed at temperatures higher than 550°C seemed to occur mostly for samples that had undergone pyrolysis at higher temperatures. Finally, SS_{UK} used for combined amendments contained more carbonates giving a grater sign at (700-800°C) than the other materials, which is in accordance with the CaCO₃ reported in Table 0-1.



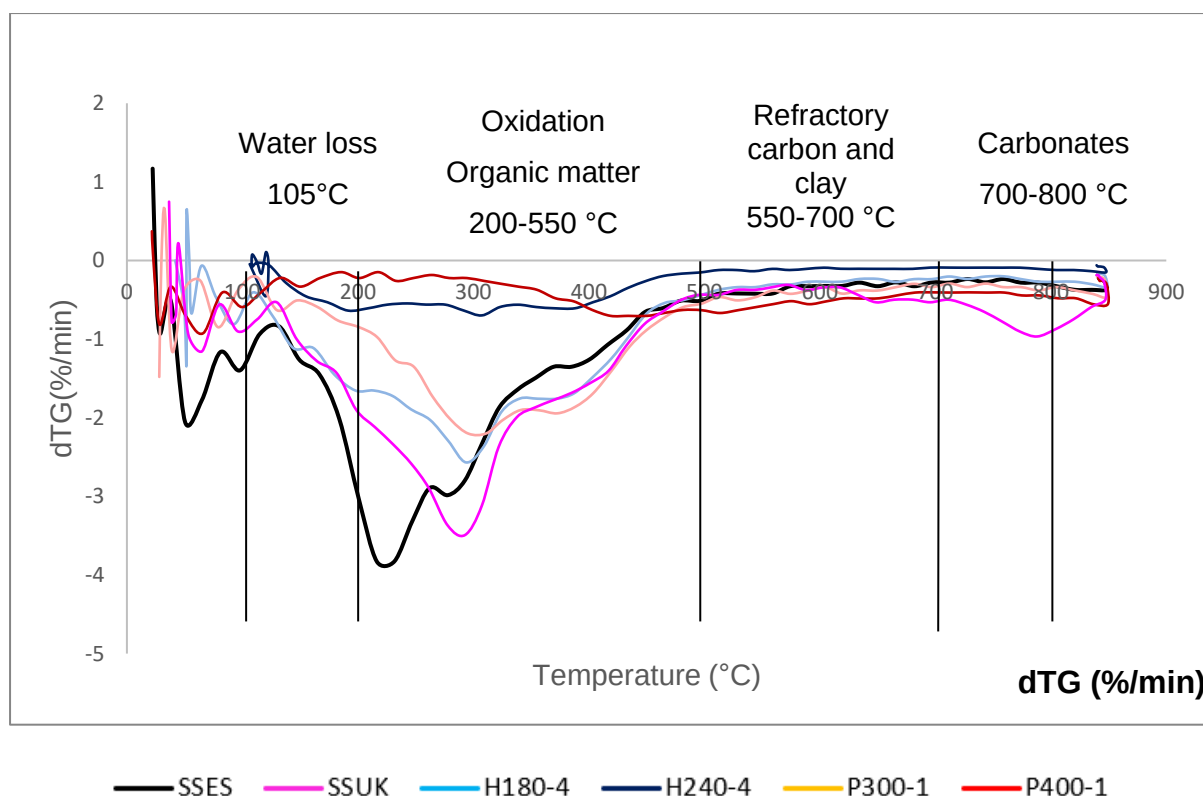


Figure 0-5 Derivate Analysis (DTA and derivative, dTG).

The accuracy of the TGA is ± 0.001 mg. TG's data kindly provided by Dr Ali Navabi, Cranfield's Centre for Climate and Environmental Protection, Whittle Building, Cranfield University, Cranfield, Bedfordshire MK43 0AL, UK

dTG (%/ min), derivate of TG(%). $m/t = \{m_i - m(i-1)\}/\{t_i - t(i-1)\}$ where m is mass lost(%) and t is the time (min)

SS_{ES} = Sewage sludge (Spain) dried 105°C, 48h; H180-4 = hydrochar from SS_{ES} at 180°C for 4h; H240-4 = hydrochar from SS_{ES} at 240°C for 4h; P300-1 = pyrochar from SS_{ES} at 300°C for 1h; P400-1= pyrochar from SS_{ES} at 400°C for 1h. SS_{UK}= commercialized sewage sludge (UK) used for combined treatments, untreated and added at 72% moisture content.

2.3.4 Physical structural differences

While little differences could be appreciated from a SEM analysis (Appendix, Figure A 2), there are quantitative differences of adsorption and structure between pyrochars and hydrochars from SS_{ES}.

2.3.4.1 The Brunauer, Emmett and Teller (BET) technique for porosity and surface area

Thermal derivatives used in the amendments were physically different as a result of the type of processes and temperature selected (BET, Table-3). After treating SSES, larger pores were generated, and the surface area expanded. Both samples of sewage sludge had similar low surface area 2.043 m²/g (SS_{ES}) and 1.726 m²/g (SS_{UK}) with a microporosity (<10nm) 29% (SS_{ES}) and 36 % (SS_{UK}). Higher temperatures generated larger pores in both processes, being P300-1 and H180-4 mainly mesoporous (10-50 nm), while H240-4 and P400-1 were mainly macroporous (>50 nm) (Table 0-3). This could be due to the gases released during the thermal processes (Méndez, Terradillos and Gascó, 2013; Smith, Singh and Ross, 2016).

Nonetheless, the surface area of pyrochars increased from 2m²/g SS_{ES} to 4.9 m²/g for temperatures of 300°C to 17 m²/g for temperatures of 400°C, similarly to increases previously reported by Méndez et al., (2013), while for HCT it increased ten times from 2.0 m²/g (SS_{ES}) to 19.9 m²/g for temperatures of 240°C and 20.1 m²/g for temperatures of 180°C. Given that the materials were not subjected to an activation process, these values of surface area are considerably lower than powder activated charcoal over 900 m²/g (Danso-Boateng et al., 2020) or other activated carbons produced from sewage sludge, which have been reported to be over 500 m²/g when treated with ZnCl₂ (Dos Reis et al., 2016).

Table 0-3 BET and Mesoporous Analysis (BJH) of SSES, thermal derivatives (H180-4, H240-4, P300-1 and P400-1).

Sample	BET surface area (m ² /g)	Adsorption average pore width (A) (nm)	MicroPore 2-10 nm (%)	MesoPore 10-20 nm (%)	MesoPore 20-50 nm (%)	MesoPore 10-50 nm (%)	MacroPore >50 nm (%)
SS _{ES}	2.043	24.907	35.8	11.47	6.26	17.73	46.47
H180-4	20.131	33.571	9.09	10.47	36.54	47.01	43.9
H240-4	19.998	30.896	10.41	6.95	33.86	40.81	48.78
P300-1	4.964	36.745	18.96	17.57	28.02	45.59	35.45
P400-1	16.941	25.316	11.37	11.05	30.27	41.32	47.3
SS _{UK}	1.726	33.752	28.52	13.72	21.9	35.62	35.86

*Total pore volume filled at a relative pressure p/p₀ equal to 0.99 A.Bsgreev 2001. BET data kindly provided by Dr Ali Navabi, Cranfield's Centre for Climate and

Environmental Protection, Whittle Building, Cranfield University, Cranfield, Bedfordshire MK43 0AL, UK

SS_{ES} = Sewage sludge (Spain) dried 105°C, 48h; H180-4 = hydrochar from SS_{ES} at 180°C for 4h; H240-4 = hydrochar from SS_{ES} at 240°C for 4h; P300-1 = pyrochar from SS_{ES} at 300°C for 1h; P400-1 = pyrochar from SS_{ES} at 400°C for 1h. SS_{UK} = commercialized sewage sludge (UK) used for combined treatments, untreated and added at 72% moisture content.

2.3.4.2 Adsorption Isotherms of N₂ derived from the BET analysis

Given the change of porosity and surface area described above, after treating SS_{ES}, the adsorption capacity towards N₂ was larger for thermal derivatives. When comparing the chars, different responses were obtained after pyrolysis and HTC, and a greater difference was obtained between pyrochars. The maximum adsorbance in pyrochars 29.7 cm³/g in (P300-1) to 76.9 cm³/g (P400-1), while for hydrochars was 108.1 cm³/g (H240-4) and 118.5 cm³/g (H180-4), indicated that hydrochars have a higher adsorption potential. This is shown in Figure 0-6, through the isotherms of adsorption, which describes the equilibrium of adsorption to a surface under a constant temperature. Isotherms are considered to be of type III or IV (Khalfaoui *et al.*, 2003; Méndez, Terradillos and Gascó, 2013). These results combined with the BET suggest that adsorption was improved with the increment of surface area and the generation of mesopores in all the samples, confirmed by the adsorption average pore with (Table 0-3). The isotherms indicated that there was an unrestricted multilayer formation process even at higher relative pressure, as the adsorption significantly increases after relative pressure 0.75 (P/P₀) in all cases. The N₂ desorption of the samples does not behave exactly as the adsorption phase (Figure 0-6). This hysteresis indicate most likely that the isotherms are of type IV, meaning that the adsorption occurs mainly on the mesoporous material, followed by a capillary condensation that takes place in these types of pores (Méndez, Terradillos and Gascó, 2013).

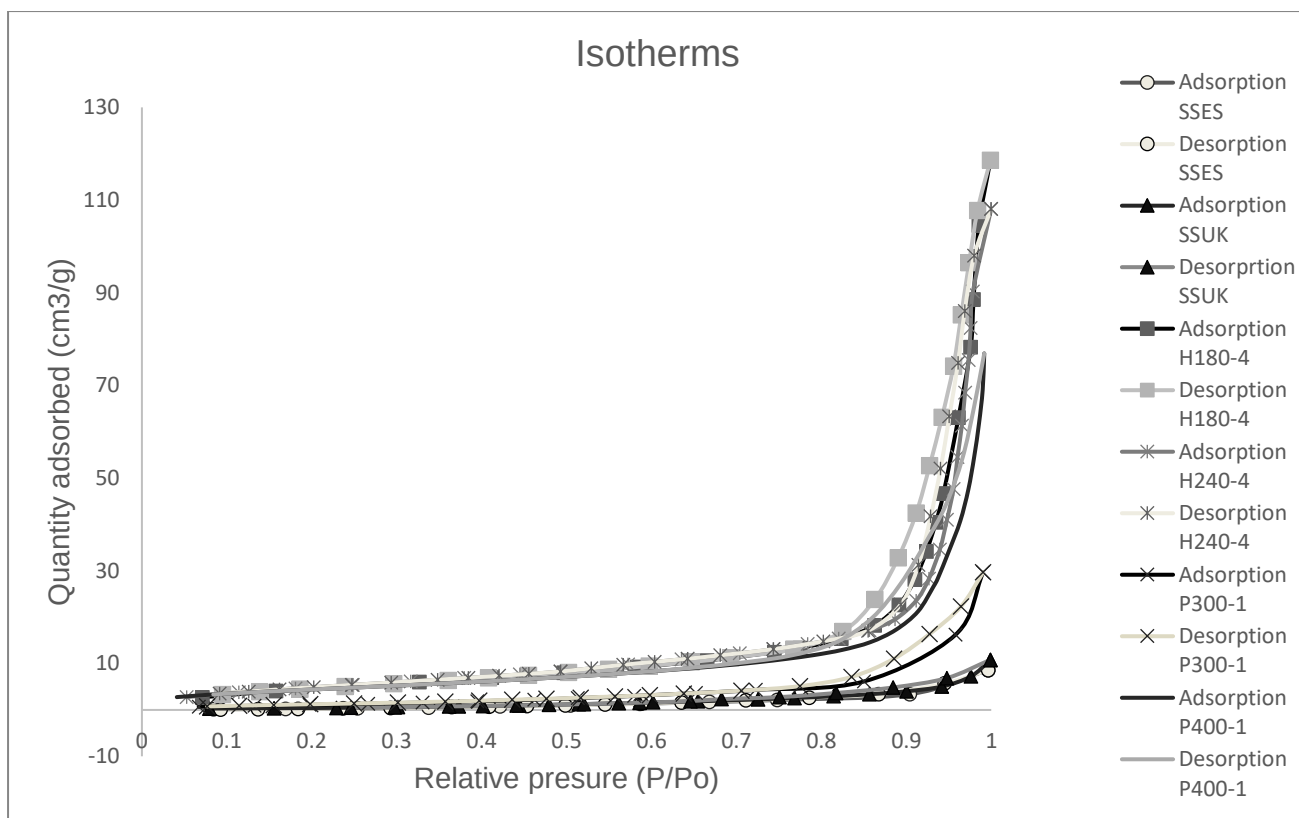


Figure 0-6 Isotherms BET and mesoporous analysis.

SS_{ES} = Sewage sludge (Spain) dried 105°C, 48h; H180-4 = hydrochar from SS_{ES} at 180°C for 4h; H240-4 = hydrochar from SS_{ES} at 240°C for 4h; P300-1 = pyrochar from SS_{ES} at 300°C for 1h; P400-1= pyrochar from SS_{ES} at 400°C for 1h. SS_{UK}= commercialized sewage sludge (UK) used for combined treatments, untreated and added at 72% moisture content.

2.3.5 Cation Exchange Capacity (CEC)

After thermal treatments, every sample showed a significant reduction in CEC from the original SS_{ES} (Table 0-4), from 193.7 cmol⁺/kg (SS_{ES}) to 131 cmol⁺/kg (H180-4), 93.5 cmol⁺/kg (H240-4), 47.7 cmol⁺/kg (P300-1) and 41.3 cmol⁺/kg (P400-1), which is in agreement with previous studies (Cheng *et al.*, 2006; Méndez *et al.*, 2012; Song and Guo, 2012). No significant differences were found between pyrochars obtained at 300°C and 400°C, while CEC of H180-4 was significantly higher than H240-4. SS_{UK} had a similar CEC to H180-4 (137.2 cmol⁺/kg) but lower than SS_{ES}. The results on the sample of soil used later for the pot experiment indicated that the base line was considerably low and that both bags of soil were statistically similar (10 cmol⁺/kg).

CEC was found to be correlated with the data from LOI and O/C and H/C but not with C/N ratio, ash content nor CaCO₃ and the other variables. Given the negative loadings

when comparing all the variables, only those with correlation greater than 0.3 were used. The first principal components explained the 96.5% of the total values for PC1 (75.5%) and PC2 (21%), the factor matrix is listed in the Appendix (Figure A 3), this made it possible to distinguish three different clusters in a plot PC1/PC2. The principal component plot (Figure 0-7) shows three different clusters according to treatments, the sludge regardless of the source, another for pyrochars and other for hydrochars. The hierarchy analysis showed that hydrochars had more similarities than pyrochars (Figure A 5).

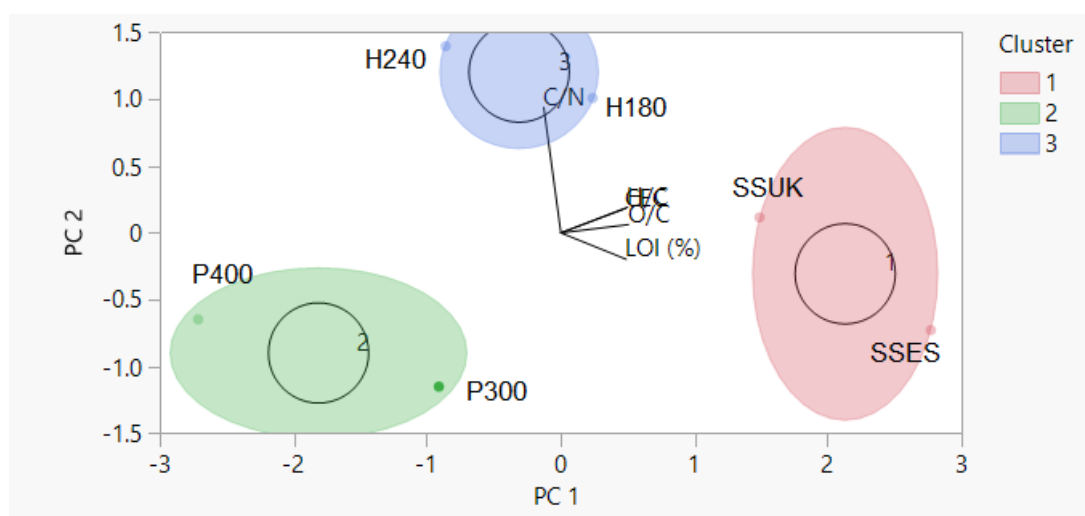


Figure 0-7 Principal component analysis of raw materials obtained using JPM-16.

According to Smith et al., (2016), a lower CEC could be linked to a lower number of carboxylic groups (-COOH) which could retain cations in surface (Faria *et al.*, 2018b). These groups were generated during HTC, as confirmed previously (Figure 0-4). The FTIR showed a lower signal for carboxylic acids groups on the surface of pyrochars than SS_{ES} (1380 cm⁻¹) (Figure 0-4). The change in surface area (Table 0-3), also could have facilitated a lower reduction of the original value of CEC in hydrochars where H180-4 had a greater potential of absorbance than H240-4 which agrees with CEC significant differences (Table 0-4). However, CEC is expected to shift in soil over time (Faria *et al.*, 2018b) and differently from feedstock to feedstock (Cely *et al.*, 2015).

Table 0-4 Cation Exchange Capacity of SSES, H190-4, H210-4, P300, P400, and soil (cmol+/kg).

Sample	Average of Na	±	Average of Mg	±	Average of Ca	±	Average of K	±	Average of Mn	±	Average of CEC	±
SS _{ES}	8.6 c	0.5	53.5 c	4.0	58.6 ab	5.7	10.4 d	0.5	0.34 ab	0.0	193.7 e	9.5
H180-4	3.6 ab	1.3	30.7 bc	10.9	51.6 ab	19.5	6.1 cd	2.1	0.34 ab	0.1	131.0 c	2.5
H240-4	3.8 b	0.8	20.8 ab	4.1	46.7 ab	10.0	5.7 cd	1.2	0.19 ab	0.0	93.5 d	1.8
P300-1	3.6 ab	0.1	20.6 ab	0.3	40.1 ab	0.4	4.8 abc	0.2	0.30 ab	0.0	47.7 b	0.3
P400-1	3.4 ab	1.1	18.3 ab	5.3	47.9 ab	14.7	5.6 bcd	1.9	0.46 b	0.1	41.3 b	0.6
SS _{UK}	2.4 ab	0.8	20.0 ab	6.3	115.9 b	37.6	2.2 abc	0.7	0.1 a	0.0	137.2 c	2.9
Soil I	0.0 a	0.0	0.6 a	0.2	9.0 a	3.9	0.2 ab	0.2	0.1 a	0.1	10.0 a	0.1
Soil II	0.0 a	0.0	0.3 a	0.1	9.9 a	2.4	0.0 a	0.0	0.1 a	0.0	10.6 a	0.6

Values in column followed by the same letter are not significantly different ($p = 0.05$) using the Tukey test.

SS_{ES} = Sewage sludge (Spain) dried 105°C, 48h; H180-4 = hydrochar from SS_{ES} at 180°C for 4h; H240-4 = hydrochar from SS_{ES} at 240°C for 4h; P300-1 = pyrochar from SS_{ES} at 300°C for 1h; P400-1= pyrochar from SS_{ES} at 400°C for 1h. SS_{UK}= commercialized sewage sludge (UK) used for combined treatments, untreated and added at 72% moisture content.

2.4 Conclusions

Temperature and the type of treatment had a significant effect resulting in char with different physicochemical characteristics and organic matter stability despite being produced from the same sample of sewage sludge.

On average, pyrochars lost more functional groups from the original sample and gained a higher carbonization state than hydrochars with higher temperatures being P400-1 the most stable material. On the contrary, the stronger signal for -C-O, -OH and -COOH in hydrochars indicated that these bonds were not lost but re-created through HTC.

Organic matter reduced in all samples significantly, from 68.4% in SS_{ES}. Pyrolysis at 300°C-1h produced a material with higher organic matter content (59.2%) than the hydrochars obtained at lower temperatures (H180-4: 57.2%, H240-4: 53.7%). Nonetheless, P300-1 had a higher organic matter stability than H180-4 in the dTG range 200-300°C, thus it could be a good alternative for an organic amendment.

In turn, hydrochars could provide readily available organic matter providing a higher CEC than pyrochars, and greater adsorption capacity. CEC was reduced further after pyrolysis from 193.7 cmol+/kg (SS_{ES}), 131 cmol+/kg (H180-4), 93.5 cmol+/kg (H240-4) compared to 47.7 cmol+/kg (P300-1) and 41.3 cmol+/kg (P400-1). All thermal treatments improved surface area from 2 m²/g(SS_{ES}) to 5-17 m²/g (pyrochars) and to 20 m²/g (hydrochars) and generated mesopores in the chars. Due to this, adsorption increased most greatly in hydrochars, reaching a maximum absorbance over 100 cm³/g for H180-4, which could be of interest for agronomic purposes.

This study highlights the possibility of using different thermal treatments to tailor the physical chemical characteristics of sludge towards its use as soil amendment. These thermal treatments could promote the recovery of organic matter to ease the pressure of agricultural land and landfill while providing a solution to sewage sludge management (Le Corre *et al.*, 2009b; Rockström *et al.*, 2009). In the following Chapter, Chapter 3, the effect of the thermal processes studied on available P are further tested in a pot experiment to grow spring wheat. Changes in soil P concentration, pH and soil organic matter variations over two seasons are quantified to assess the potential use of these chars as P-fertiliser and organic amendments.

CHAPTER 3: EVALUATING PHOSPHORUS AVAILABILITY FROM SEWAGE SLUDGE DERIVED PYROCHAR AND HYDROCHAR TO SPRING WHEAT

Summary: In this chapter thermal treatments were assessed as alternative source of P for crops. Variations in P availability of thermal derivatives obtained from the same sample were evaluated over two seasons of growing spring wheat when added on its own (5, 10, 20 t ha⁻¹) and in combination with a commercialized sewage sludge (SS_{UK}) as soil amendment (50% char 50% SS_{UK} at 10, 20, 40 t ha⁻¹) (Objective 2). Aluminium (Al) and iron (Fe) total content were analysed as well as changes in pH, EC and organic matter after thermal treatments (Objective 1) to evaluate their effects on soil properties and their involvement on P availability fluctuations (Objective 3).

Highlights:

- Thermal treatments reduced available-P in all derivatives H180-4 (45.9%), H240-4 (57.5%), P300-1 (76.2%), P400-1 (83.6%) from 150.4 mg kg⁻¹ SS_{ES}.
- One single application to grow two seasons of spring wheat resulted in an increase in available-P over both seasons when treatments were applied on their own, proving that sewage sludge and derivatives act as slow P-fertiliser.
- The use of pyrochars, produced a buffer effect that lasted two seasons preventing an acidification of the loamy sandy soil.
- Organic matter increased directly with rate favoured by combined amendments; this effect was intensified after two seasons of growing spring wheat.
- Combined amendments boosted the availability of P in the first season and hampered it in the second for the highest rates.
- Al content in sewage sludge and char aging proposed as a limitation to ensure available-P for both seasons.

Chapter 3 was written as independent journal article and is ready to be submitted to: Agronomy.

3.1 Introduction

Sewage sludge concentrates all pollutants removed from the wastewater (Gascó, Lobo and Guerrero, 2005; Manara and Zabaniotou, 2012a; Peng *et al.*, 2016), which includes a mixture of pathogenic microorganisms, inorganic particles and heavy metals (Hillman *et al.*, 2003; Huang and Tang, 2015; Shepherd, Joseph, *et al.*, 2017). However, it also contains a high percentage of organic matter (OM), macronutrients (nitrogen, phosphorus, potassium, calcium and magnesium) and micronutrients, which are of agricultural interest (Gasco, Cueto and Méndez, 2007; D.L. Antille, Sakrabani and Godwin, 2014; Torri, Studart and Ea, 2017). The production of sewage sludge has been reported to be from tens to thousands of tons in dry matter per year in Europe (*Sewage Sludge Production EU 2017*, visited on 16-6-2020) and is expected to increase further with growth of the world population (United Nations, 2017; Zhai *et al.*, 2017b) and industrial production (Sharma *et al.*, 2017).

Modern agricultural systems currently rely on the use of phosphorus fertilisers as a mined source from phosphate rock (Schneider and Haderlein, 2016c). This use is causing a depletion of this non-renewable material (Bünemann, 2015) entering it in the list of Critical Raw Materials (European commission, 2020). Increased use of detergents and insecticides (Le Corre *et al.*, 2009a) and food waste (Hannah *et al.*, 2018), causes a significant amount of P to end up being collected at wastewater treatment plants. Consequently, sewage sludge could be a potential renewable source for phosphorus fertiliser (Torri, Studart and Ea, 2017; Faria *et al.*, 2018a), reducing its disposal and the demand of mineral fertilisers if used as a soil amendment (Sharma *et al.*, 2017).

The use of sewage sludge in agricultural land, following the Directive 2008/98 / EC, has been the main form of management of this waste in most countries of the European Union (EUROSTAT, 2015). However, a correct management of sewage sludge is necessary in order to protect the environment and reduce the health hazard (Singh and Agrawal, 2008; Jin *et al.*, 2016; Stefaniuk and Oleszczuk, 2016). Currently, efforts are focused on reducing the amount going to landfill and incineration (Sharma *et al.*, 2017).

Currently, composting followed by a soil application as fertiliser represents one of the main management routes of sewage sludge in Europe (EUROSTAT, 2017). However, the direct use of sewage sludge in agricultural land is limited by the metal content and presence of some pathogenic compounds (Instruments, 1989; DEFRA, 2009). Thus, more recently, thermal treatments have been considered as an alternative route to convert sewage sludge into a more adequate resource (Srinivasan *et al.*, 2015; Álvarez *et al.*, 2017a; Bhatt *et al.*, 2018; Paz-Ferreiro *et al.*, 2018). Through pyrolysis and hydrothermal carbonization, a carbonaceous material is obtained as the main product, reducing the bioavailability of pollutants concentrated in it (Shi *et al.*, 2013) and enhancing soil properties when used as soil amendments (Faria *et al.*, 2018a; Paz-Ferreiro *et al.*, 2018). For agronomic purposes, slow pyrolysis can be performed at two ranges of temperatures 200-300°C, also known as torrefaction (Ngatia *et al.*, 2017), or proper pyrolysis at 300-750°C using pre-dried feedstock. Hydrothermal carbonization (HTC) takes place in an aqueous medium under moderate temperature 180-260°C (Kalderis *et al.*, 2014; Kambo and Dutta, 2015), using longer retention times than most pyrolysis processes (2-6h) (Kim, Lee and Park, 2014; Tekin, Karagöz and Bektaş, 2014) and autogenous pressures (2-6 MPa) determined by the reactions under subcritical-water conditions (Kambo and Dutta, 2015).

The term biochar is commonly associated with a wide variety of carbonaceous materials from different sources (Li *et al.*, 2019) but mostly obtained from plant based biomass through pyrolysis at high temperatures (El-Naggar *et al.*, 2019). For land applications the term biochar is used for materials with an organic carbon content >50% (Lehmann *et al.*, 2011b; Bachmann *et al.*, 2016). A material with lower organic carbon is referred to as a lower classed biochar (IBI, 2015). In this paper, (IBI, 2015). In this paper, we are comparing pyrolysis and HTC, in order to do so we will refer to our thermal derivatives (chars) as pyrochar and hydrochar, respectively as more recently, several authors used this terminology (Schneider and Haderlein, 2016c; Álvarez *et al.*, 2017b)

Few research has been found to assess and compare P availability of hydrochars derived from sewage sludge applied as soil amendments and none have been tested mixed with raw sewage sludge. Other sources of biochar have been mixed with sewage sludge (Gartler *et al.*, 2013; Bair *et al.*, 2016; Paramashivam *et al.*, 2016) but neither considered P efficiency nor compared HTC and pyrolysis. For example,

Wagner and Kaupenjohann (2014) used hydrochar and pyrochar to assess metal immobilization in a land amended with sewage sludge, and quantified P uptake by *Avena sativa L.* Such combinations with sludge and manures have been proven to benefit nutrient cycling (Zafar, Abbasi and Khaliq, 2013; Zafar, Rizwan and Shahid, 2017). There is also less information available on hydrochars than for pyrochars on land application (Breulmann *et al.*, 2017) and yet no regulations regarding the use of sludge mixtures with other sources of nutrients such as chars (Paramashivam *et al.*, 2017). Therefore, comparative studies of chars using the same feedstock prepared by pyrolysis or HTC using different temperatures and rates of application combined or not with sewage sludge will ease the gap of knowledge. The objective of this paper is to assess the potential of pyrochar and hydrochar as phosphorus fertilisers to establish spring wheat and its effect on soil properties, plant uptake is described in Chapter 5 that covers crop response to amendments. We hypothesize that combining sewage sludge soil amendments with thermal derivatives will: (i) enhance P availability in soil for spring wheat; and (ii): improve soil physicochemical properties.

3.2 Materials and Methods

3.2.1 Experimental site and soil description



Figure 0-1 Glasshouse pot experiment.

A pot experiment of 100 days duration was conducted over two seasons from June-August (2018) and April-June (2019) at the glasshouse facility at Cranfield University,

UK (Figure 0-1). Temperature ranged from 13°C to 35°C on average, measured with TermoPro TP50; the glasshouse was vented when temperatures reached 21°C with additional cooling from fans and through wetting the floors to maintain a temperature below 35°C, (average temperature for season 1 was 24.4°C and 23.8°C for season 2).

The topsoil (Baileys of Norfolk Ltd) was as a loamy sand with low P content (Index 1 P-K-Mg: 15-69-33 mg l⁻¹). Soil was manually crushed and dried for a week in the glasshouse compartment over tarpaulins and then sieved to 2 mm. Particle size was quantified according to ISO 11277:1998, pH according to ISO 10390:2005, using a ratio (1:10) with deionized water (Arif *et al.*, 2017), EC using the same extract (filtered through Whatman No2), Olsen-P for available P (ISO 11263:1994) and Loss on Ignition (LOI, BS EN 13039:2000) at 550°C sustained for 2h. Total P, K, Fe and Al were analysed following ISO 11047:1998. No pressure was used to pack the soil into the columns, achieving a density of 1.3 kg m⁻³. All columns had the same amount of soil (5.18 kg per column) leaving approximately 5 cm of space to the top of the column.

3.2.2 Preparation of sewage sludge and chars



Figure 0-2 Experiment set up.

The experiment was divided in three main phases: (1) production of the chars, (2) characterization and (3) glasshouse experiment (Figure 0-2). Two pyrochars were produced using a Heron electric furnace model 12-PR/300 series 8B at the Polytechnic University of Madrid (Spain) through pyrolysis in a metallic crucible for 1 hour at 300°C (P300) and 400°C (P400) using pre-oven dried (105°C-48h) sewage sludge (SS_{ES}) from the Avila Wastewater Treatment Plant, Spain. Two hydrochars were obtained in another reactor supplied by Demede S.L (Spain) through hydrothermal carbonization of SS_{ES} mixed with distilled water (20% of dry matter) for 4 hours at 180°C (H180) and 240°C (H240) under autogenous pressure. All samples were oven dried (105°C-48h) and transported to Cranfield University. Once received, the materials were weighed, crushed, sieved through a 2 mm mesh and stored in sealed bags at room temperature.

3.2.3 Experimental design

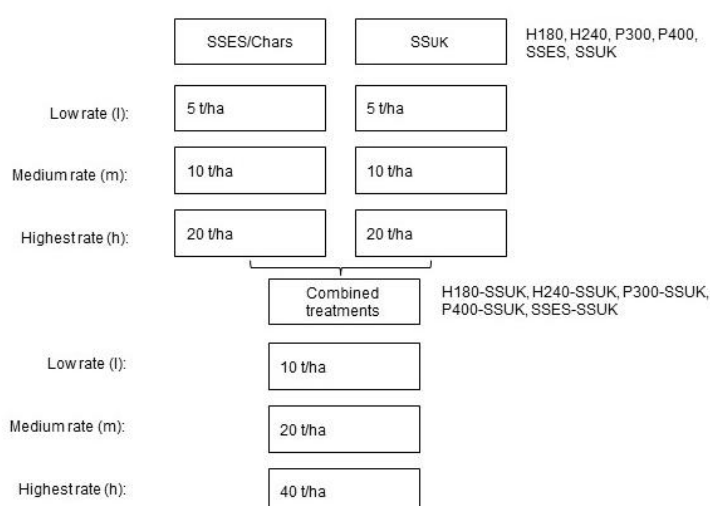


Figure 0-3 Rates diagram.

A column experiment (H:50 cm, D:10.5 cm) was setup in the glasshouse facility following a randomized design with three application doses and a control; all treatments were replicated four times. The char application rates were 5, 10, 20 t ha⁻¹ (equivalent to 4.33, 8.66 and 17.32 g per column in dry matter respectively) added as a single application for the two seasons. To study the effect of the addition of OM with the chars, a commercialized local sewage sludge (SS_{UK}) was combined using the same amount to double the rates (50-50%, 10, 20, 40 t ha⁻¹) as soil amendment also applied once during the two seasons as explained on Figure 0-3.

The amendment was incorporated in the first 5 cm of the soil in each column by placing it at the top and mixing manually with a spatula. In order to ensure there was enough soil moisture for the seeds to germinate in the first season, 40% of field capacity was used with 50 mL water added the next day, while in the second season 70 mL was added to re-moisture the column. This design led to a total of 136 columns, placed vertically and with 5 cm between them. Each column was cut from a pipe with diameter of 10 cm and prepared with voile and a bottom layer of gravel to prevent soil loss whilst allowing for free drainage. At regular intervals, 30-100 mL deionized water was added to the column to replace the amount lost through evapotranspiration.

The crop selected was, spring wheat (KWS Willow), for being a dominant staple food, demanding globally major P fertiliser inputs for the last decades Figure 0-5. Spring wheat was sowed at 2 seeds per pot, equivalent to the maximum recommended density (Nan *et al.*, 2000; Salantur, Ozturk and Akten, 2006). The seeds were sown 2 cm deep and after the application of the amendment. Wheat and rye grass as shown in Table 0-4, have been used previously used in other studies of sewage sludge derived pyrochars and hydrochars which makes them an interesting choice for comparison. Compared to rye grass, wheat provided the opportunity to evaluate the risk of accumulation on heavy metals in the grains, and thus its potential effect in the food chain not only for cattle but also for humans. Spring wheat was chosen against winter wheat to conveniently reduce costs derived from glasshouse temperature regulation during winter and because the department had already experience dealing with spring wheat pests and the required pesticides were at hand, making it an easy crop to grow without much experience.

Nitrogen was applied manually in the form of a ammonium nitrate, NH_4NO_3 salt, following the nutrient management guide for arable crops for Soil Nitrogen Supply (SNS Index) 1-2 (AHDB, 2020) at every season. Therefore, after the sludge amendments, the first application of N was applied 45 days in the first 2 cm after the sowing during the tillering stage at 30 kg ha^{-1} (equivalent 0.07g per column) and the same amount again after 20 days during the flowering stage. No other nutrients were added to this soil.

3.2.4 Sampling and measurement of soil changes

To quantify the effect of the amendments on soil properties changes in pH, electric conductivity (EC) and available Phosphorus (P), were analysed in the top layer of soil <5 cm at the start and after harvest in September 2018 and October 2019. Then OM and Total P, Fe, Al, and K were measured at the start and at harvest in October 2019, but not in September 2018 to avoid removing too much char between seasons. For starting conditions, a surrogate was re-created at the lab using dried materials (105°C, 48h). Between seasons a voile was placed on top to prevent any modification, to be removed just before the second season.

3.2.5 Statistical analyses

The statistical analysis of experimental data was undertaken using JMP-16. First, a Multivariant analysis and a PCA was conducted to find correlations among variables. Then, given the block design, a Linear Mixed Model was used to assess if the type of treatment and season had a significant effect on the results of available-P. The model was constructed using treatment and season of sampling as full factorial, and the replicates (A, B, C and D) were nested under treatment and considered a random effect. Therefore, the method used was a restricted (or residual, or reduced) maximum likelihood (REML) with Standard Least squares. Finally, the least significant differences were obtained to compare the means using Tukey test and a probability level of 5% ($p < 0.05$). The results were plotted using R to show the observations from initial conditions and through two seasons and JMP-16 derived from the REML analysis. Additional statistical outputs can be found in the APPENDIX (5.7A.1.2).

3.3 Results

3.3.1 Effect of the thermal treatments on char characteristics

The pH and EC altered during thermal treatment. The pH of hydrochars was acidic while pyrochar at higher temperatures was more alkaline than the original material (Table 0-1). The EC decreased after all thermal treatments, but mostly during pyrolysis which reduced the EC by 79.3% and 92.1% for P300 and P400, respectively, compared to an EC of $581.3 \mu\text{S cm}^{-1}$ for the untreated SS_{ES} material. Hydrochars and pyrochars were significantly different in total P content. Compared to the original sewage sludge the total P increased as follows: H180 (39.5%), H240 (55.9%), P300

(35.8%) and P400 (77.7%). Total Al and Fe increased for all thermal treatments with the highest increases for the highest temperatures (Table 0-1). Nutrient and metal content differed between SS_{ES} and SS_{UK}. Total Al was 6-7 times the amount of total Fe incorporated through SS_{ES} and its derivatives, while in SS_{UK} inputs of Total Fe were at least one order greater than SS_{ES}. Although, plant available-P (Olsen P) decreased for all thermal treatments, hydrochars lost much less than pyrochars. Thermal treatments reduced the amount of Available P contained in the feedstock H180 (45.9%), H240 (57.5%), P300 (76.2 %), P400 (83.6%) from 150.4 mg kg⁻¹ SS_{ES}). The sludge used in the combined amendments had also a low available P (21.3 mg kg⁻¹).

3.3.2 Effect of the amendments on soil pH

The soil was characterized as a loamy sand (86.6% sand, 11.2% silt, 2.2% clay), with a pH of 7.9 (Table 0-1). At the start of the first season in June 2018, soil pH reduced significantly when sewage sludge SS_{UK} was added in combination with the pyrochar or hydrochar (Figure 0-4) with the lowest pH when H180+SS_{UK} was applied at 40 t ha⁻¹. At the end of the first season (September 2018), application of sewage sludge SS_{UK} alone resulted in the lowest value, pH₁=5.7, followed by the application of SS with both hydrochars at the highest application rate (pH=6.0). The use of thermal treatments on their own or a combination of pyrochar with sewage sludge did not affect the pH significantly compared to the control soil.

After the second season (October 2019), the treatment with SS_{UK} sewage sludge alone and the treatment that combined sludge with hydrochars at the highest application rate caused the largest reduction in pH compared to control soil (from pH=6.2 for the control to 5.8 and 5.7 for H240+SS_{UK} and H180+SS_{UK}, respectively). Addition of pyrochar at 20t ha⁻¹ increased the pH (Figure 0-4). Immediately after application of the amendments, the EC increased (See supplementary material), and although it continued to rise during the first and in particularly so during the second season, it stayed below 300 µS cm⁻¹ at all times and was therefore not expected to significantly affect crop growth.

Table 0-1 Main properties of sewage sludge and derive pyrochars from pyrolysis and hydrochars from hydrothermal carbonization

	Aqua Regia Total elements (g kg ⁻¹)					
	pH (1:10) H ₂ O	EC (μS cm ⁻¹)	P	Al	Fe	Olsen P (mg kg ⁻¹)
SS _{ES}	7.19 f	581 e	45.6 a	30.7 f	3.7 c	150.4 e
H180	5.24 a	305 d	63.6 b	42.9 d	5.7 b	81.4 d
H240	5.55 b	295 c	71.2 d	47.0 g	6.8 bd	63.9 b
P300	6.36 d	120 b	62.0b	40.3 a	5.3 bc	24.6 a
P400	7.50 g	46 a	81.1 e	52.9 c	8.2d	35.8 ab
SS _{UK}	6.13 c	322 f	43.7a	9.6 e	50.2 e	21.3 c
Loamy sand soil*	7.9	17	0.3 c	2.8 b	5.6 b	0.5

*Perticle size : 93.8% Sand (0.063-0.212 mm), 5.6% Lime (0.02 mm-0.63mm), 0.6% clay(<0.002 mm)

Letters show significant differences (p < 0.05) according to a one-way analysis of variance followed by a Tuke's honestly significant difference (HSD) multiple-means comparison of data from the same year Statistica program.

SS_{ES} = Sewage Sludge (Spain) dried 105°C, 48h; H180 = Hydrochar from SS_{ES} at 180°C for 4h; H240= Hydrochar from SS_{ES} at 240°C for 4h; P300= Pyrochar from SS_{ES} at 300°C for 1h; P400= Pyrochar from SS_{ES} at 400°C for 1h; SS_{UK}= Commercialized Sewage Sludge (UK) used for combined treatments 72% moisture.

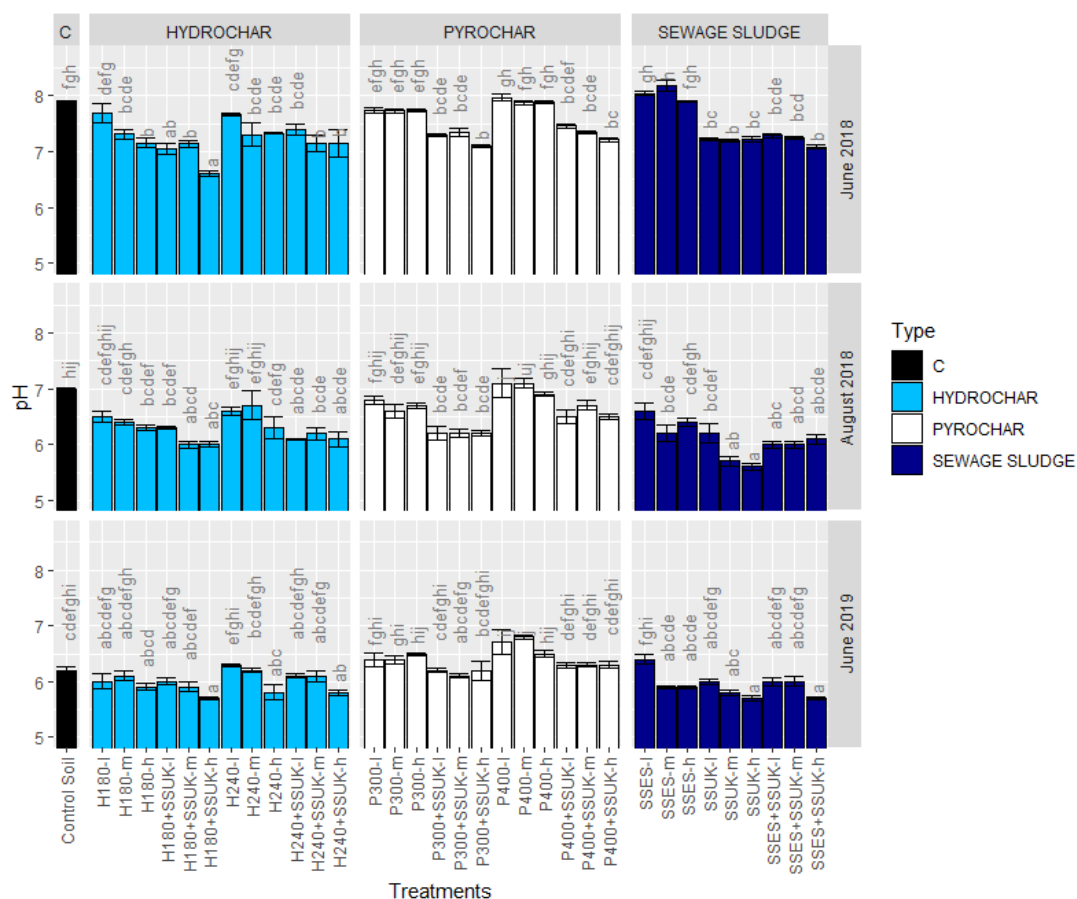


Figure 0-4 Changes in soil pH after amendments with SS_{ES} derivatives (hydrochars (H) and pyrochars (P)) SS_{UK} mixed in the combined treatments.

Letters show significant differences ($p < 0.05$) according to a one-way analysis of variance followed by a Tukey's honestly significant difference (HSD) multiple-means comparison of data from the same year Statistica program. SS_{ES} stands for Sewage Sludge (Spain) dried $105^{\circ}C$. 48h; H180 Hydrochar from SS_{ES} at $180^{\circ}C$ for 4h; H240 Hydrochar from SS_{ES} at $240^{\circ}C$ for 4h; P300 Pyrochar from SS_{ES} at $300^{\circ}C$ for 1h; P400 Pyrochar from SS_{ES} at $400^{\circ}C$ for 1h; SS_{UK} Commercialized Sewage Sludge (UK) used for combined treatments 72% moisture. Example: H180+ SS_{UK} l indicates a combined treatment (50:50) at the lowest rate of H180 ($5t\ ha^{-1}$) mixed with wet SS_{UK} ($5t\ ha^{-1}$), giving a total of $10\ t\ ha^{-1}$ applied.

L:low($5\ t\ ha^{-1}$) m:medium ($10t\ ha^{-1}$), h:high ($20\ t\ ha^{-1}$) for treatments on their own.
L:low ($10\ t\ ha^{-1}$) m:medium ($20t\ ha^{-1}$), h:high ($40\ t\ ha^{-1}$) for combined amendments.

3.3.3 Effect of the amendments on OM

Given the OM levels in raw materials (Chapter 2, Table 0-1) on initial conditions (Figure 0-5, June 2018) at all application rates, the thermal derivatives of SS_{ES} were less effective at increasing OM than the dried sewage sludge (SS_{ES}) they were derived from. Nonetheless, the soil selected had low content (1.3%), and once applied, the amendments significantly provided an increment over 2.5% of OM for combined amendments P300+SS_{UK}, P400+SS_{UK} and SS_{ES}+SS_{UK}. This effect improved over time: after 2 seasons OM increased significantly for higher rates of combined SS_{ES}+SS_{UK}, H180+SS_{UK} and P300+SS_{UK} but also for P400 and SS_{UK} on their own, 6.24-7.64% OM against 1.21% in control loamy sandy soil (Figure 0-5). In this case, the concentration of OM was directly dependent to the rate added.

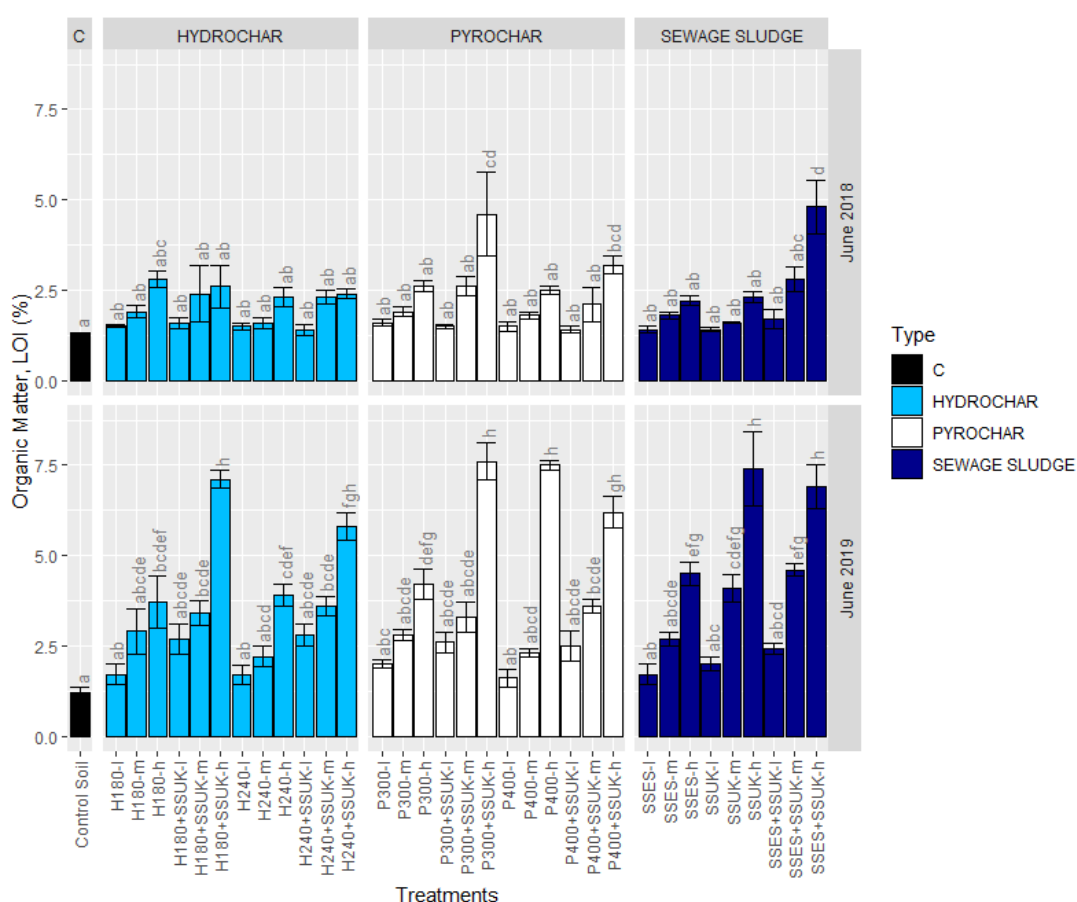


Figure 0-5 Changes in soil organic matter (LOI)* after amendments with SS_{ES} derivatives and SS_{UK} mixed in the combined treatments.

* LOI(1%) = 10g kg⁻¹ = 10,000 mg kg⁻¹ Organic Matter

Letters show significant differences (p < 0.05) according to a one-way analysis of variance followed by a Tukey's honestly significant difference (HSD) multiple-means comparison of data

from the same year Statistica program. SS_{ES} stands for Sewage Sludge (Spain) dried 105°C. 48h; H180 Hydrochar from SS_{ES} at 180°C for 4h; H240 Hydrochar from SS_{ES} at 240°C for 4h; P300 Pyrochar from SS_{ES} at 300°C for 1h; P400 Pyrochar from SS_{ES} at 400°C for 1h; SS_{UK} Commercialized Sewage Sludge (UK) used for combined treatments 72% moisture. Example: H180+SS_{UK} I indicates a combined treatment (50:50) at the lowest rate of H180 (5t ha⁻¹) mixed with wet SS_{UK} (5t ha⁻¹), giving a total of 10 t ha⁻¹ applied. L:low(5 t ha⁻¹) m:medium (10t ha⁻¹), h:high (20 t ha⁻¹) for treatments on their own. L:low (10 t ha⁻¹) m:medium (20t ha⁻¹), h:high (40 t ha⁻¹) for combined amendments.

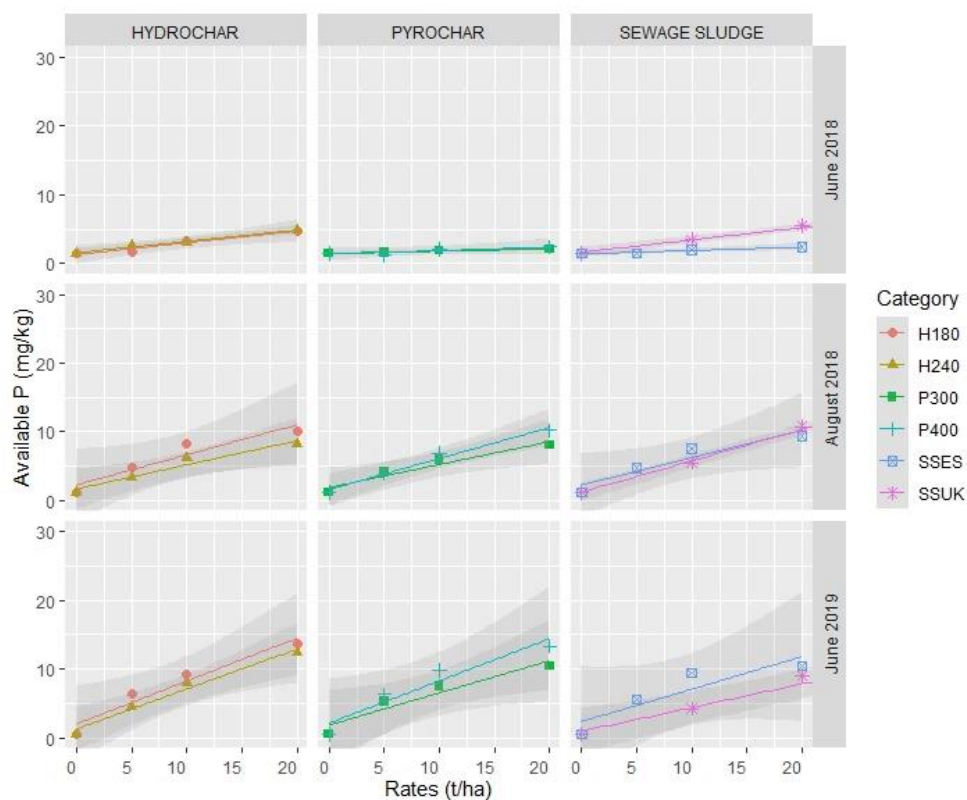
3.3.4 Effect of the amendments on Total P, Fe, Al.

For all amendments total P significantly increased immediately after application to a maximum 3 g kg⁻¹ SS_{ES}+SS_{UK} and P300+SS_{UK} (Total P_i, Table 0-2). Surprisingly, after two seasons (June 2019), total P showed the greatest increment at the highest rates especially for combined amendments of hydrochars, with increases ranging from 120.5-550.0% (total P_f, Table 0-2). In the control soil without any amendments, available P decreased from 240 mg kg⁻¹ to 234.9 mg kg⁻¹. Both applications of pyrochar and hydrochar increased total P more than the application of the sewage sludge that they were derived from. In both cases (Table 0-1), the higher the temperatures of the thermal treatment the larger the increase in total P in particular through pyrolysis. However, when the thermal derivatives were applied to soil in combination with the sewage sludge, the highest increase in total P was found for hydrochars (over 17 g total P_f kg⁻¹ (Table 0-2)). Fe increased immediately after application for H180-SS_{UK}, SSES-SS_{UK} but not Al (Table 0-2). Total Fe increased only in combined amendments (18.7-87.4%) while Al did it in P400 and all combined amendments except SS_{ES}+SS_{UK} (43.7-217.9%). Control soil on the other hand reduced Total P 4.2%, Total Fe 0.5%, 11.5% Total Al after the second season. Like with P, total Fe content increased during the two growing seasons for all thermal treatments when combined with sewage sludge but decreased when hydrochars or P300 were applied on their own. Total Al_i concentration after application was almost a third of the concentration of total Fe_i and almost half after the second season. Al also increased over the two seasons, but was only significantly different for H180+SS_{UK} 11.79 g kg⁻¹. These concentrations along with changes in pH and EC may contribute to change the availability of P.

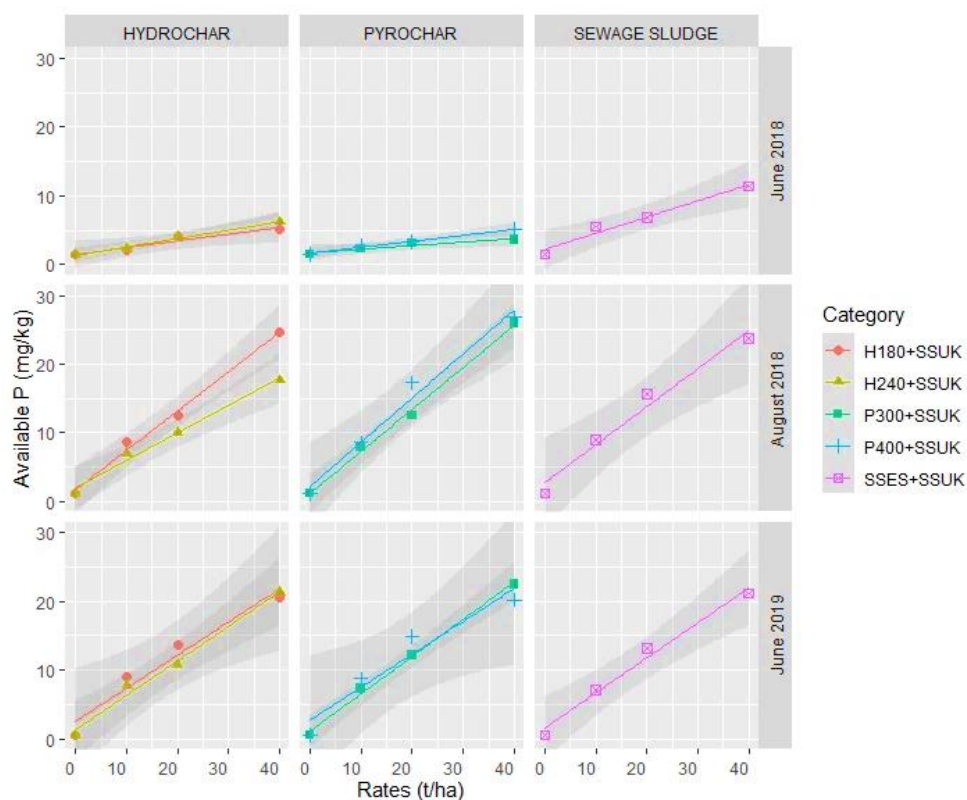
Total P, Fe and Al were also analysed in the bottom of the column after the second harvest and none of the amendments showed significant differences to the control soil (Appendix, Table A 4).

3.3.5 Effect of the amendments on soil concentrations available P.

Despite the reduction from original conditions, the application of thermal derivatives in soil resulted in a significant increase available-P immediately after application (June 2018) for the highest rates treatments on their own except pyrochars (Figure 0-6a), and highest rates of combined amendments (Figure 0-6b). The treatment resulting in the highest initial available P was $SS_{ES}+SS_{UK}$; 11.4 mg kg^{-1} (Figure 0-6b). Available P increased with time during the first growing season. After the first harvest (August 2018) available P was found in soil samples 2-5 times larger (Figure 0-6) with no significant differences between applications at the same rate for single amendments between chars. The treatments resulting in the highest of available P were $SS_{ES}+SS_{UK}$, $P300+SS_{UK}$, $P400+SS_{UK}$ and $H180+SS_{UK}$ ($23.7\text{-}26.7 \text{ mg kg}^{-1}$ Figure 0-6b) which was considerably lower than what is recommended for growing spring wheat on this type of soil ($69\text{-}115 \text{ mg P}_2\text{O}_5 \text{ kg}^{-1}$, AHDB 2020). After the second harvest (June 2019) however, available P was reduced in those combined treatments at 40 t ha^{-1} and all rates of SS_{ES} on its own. All combined amendments at the highest rates obtained again the best result with values ranging between $20.2\text{-}22.45 \text{ mg kg}^{-1}$ (Figure 0-6b). Nonetheless, for treatments of chars on their own, SS_{UK} and for other rates with combined amendments available P continued to increase, with increases ranging from 4% (for $H180+SS_{UK}$ 10 t ha^{-1}) to 60% (for $P400$ 5 t ha^{-1}). In contrast, available P in the control soil decreased from 1.5 to 0.5 mg kg^{-1} (57.3%) after 2 seasons. To compliment Figure 0-6, the raw data with statistical analysis and increments can be found on the (Appendix, Table A 2).



a)



b)

Figure 0-6 Available P (Olsen-P) in soil changes after initial conditions (June 2018), after first harvest (August 2018) and final conditions after second harvest (August 2019) of spring wheat with single (a) and combined amendments with SSUK(b). Tukey test in Appendix (Table A 2).

Letters show significant differences ($p < 0.05$) according to a one-way analysis of variance followed by a Tukey's honestly significant difference (HSD) multiple-means comparison of data from the same year Statistica program. SS_{ES} stands for Sewage Sludge (Spain) dried 105°C. 48h; H180 Hydrochar from SS_{ES} at 180°C for 4h; H240 Hydrochar from SS_{ES} at 240°C for 4h; P300 Pyrochar from SS_{ES} at 300°C for 1h; P400 Pyrochar from SS_{ES} at 400°C for 1h; SS_{UK} Commercialized Sewage Sludge (UK) used for combined treatments 72% moisture. Example: H180+SS_{UK} I indicates a combined treatment (50:50) at the lowest rate of H180 (5t ha⁻¹) mixed with wet SS_{UK} (5t ha⁻¹), giving a total of 10 t ha⁻¹ applied.

3.4 Discussion

The use of sewage sludge as an alternative source of P is still an object of debate when suggested as a possible solution for agriculture. We showed various results when of a sewage sludge applied after thermal transformation into pyrochar or hydrochar, or in combination with other sewage sludge and thermal derivatives. For the first time we compared all treatment combinations, including the effect of temperature during the preparation of thermal derivatives, in one single experiment under controlled conditions and with material derived from the same feedstock. Available P, pH, EC, metal concentration after the seasons, indicated how the type of application affects soil characteristics and how they developed into a second growing season without additional applications. In the majority of treatments, the available P, EC and metal content increased, while soil became more acidic. We showed that despite the fact that available P was reduced through pyrolysis and HTC the chars increased available P in a poor loamy sandy soil acting as a slow-releasing fertiliser (Gronwald *et al.*, 2016). The greatest gain in P availability was obtained when applications of hydrochar or pyrochar were combined with sewage sludge Figure 0-6. However, the effectiveness was affected by the conditions used to produce the thermal derivatives and the metals contained in the chars and the sludge used for combined amendments.

3.4.1 Effect of amendments on soil properties

3.4.1.1 Effect of soil pH variations

Given the importance of soil pH for many processes in soil and the way it influences the bioavailability of nutrients it is essential to consider the way amendments of soil with hydrochars and pyrochars affects the pH (Xu *et al.*, 2014). We found that the pH

progressively declined for all amendments and for the control soil. Acidification after using sewage sludge as soil amendment has been reported previously to reduce to a greater extent pH compared to treated sewage sludge (Antoniadis and Alloway, 2002; McBride, Richards and Steenhuis, 2004) and it has been related to the mobilization of metal content (Dede, Ozdemir and Hulusi Dede, 2012) and mineralization of organic N and S from sludge (McBride, Richards and Steenhuis, 2004). For instance, the oxidation of NH_4^+ to NO_3^- releases protons, but some components added to the soil can prevent them from reaching the soil solution. Additionally, the deionized water used for irrigation with pH below 6 and the choice of N fertilization through ammonium nitrate could have significantly contributed to the acidification of the soil after two seasons. Nonetheless, both types of thermal derivatives when mixed with sewage sludge proved to have a buffering effect during the first season, preventing the more significant acidification of 2 units of pH when sewage sludge was used on its own. This continued for pyrochars, but hydrochars' buffering effect was not maintained into the second season where hydrochar and their combinations with SS_{UK} gave a lower pH than control soil. This result could be explained by the results in Table 0-1. As expected, after submitting sewage sludge to higher temperatures of pyrolysis a more alkaline char was obtained, while HTC and lower temperatures of pyrolysis generated a more acidic pyrochar, which is in accordance with previous research (van Zwieten *et al.*, 2010; Kalderis *et al.*, 2014; Cely *et al.*, 2015; Danso-Boateng *et al.*, 2015; Ok *et al.*, 2015; Dai *et al.*, 2017; Chen *et al.*, 2018). The ability of chars to raise the pH is a result of a series of polymerization and condensation reactions, the release of acid groups and the presence of oxygen based functional groups, carbonates, Ca and K chloride salts (Ok *et al.*, 2015; Zielińska and Oleszczuk, 2015). Thus, pyrochars were most successful in preventing acidification in particular when applied on their own and obtained at higher temperatures (P400, Figure 0-4).

3.4.1.1 Effect of amendments in soil Total P, Al, and Fe

As indicated, total P and metals were concentrated in the thermal derivatives, and in particular when these were prepared at higher temperatures (Méndez *et al.*, 2012; Jin *et al.*, 2016; Liu *et al.*, 2018). In agreement with a previous study by Hossain *et al.* (2011) the pyrochar obtained at higher temperature (P400) had a higher amount of total and available P than P300 (Table 0-1) due to a higher carbonization and higher inorganic fraction in the char Chapter 2, Table 0-1. Upon application to soil, the

increment presence of Total P (in our case 120.5-550.0% after the second season) has been reported before (Zafar, Abbasi and Khaliq, 2013). The reason for the increase in total P, Fe and Al, probably is caused by the effectiveness of the metal analysis through acid digestion of char samples, which is conditioned by the capability of the acidic solution to reach the surface of the material. These thermal derivatives are porous (Abel *et al.*, 2013) and aqua regia contact is limited to the external and internal pores that are connected to the exterior. A change in porosity and exposed surface area could explain why more total P, Al and Fe is recovered in the digested extract after the second season (Table 0-2) as also recently reported by (Chen *et al.*, 2021). Surface area has been found to change over time as the char ages (Lehmann and Joseph, 2015) as it breaks in smaller particles (Spokas *et al.*, 2014) and creates micropores whilst labile C is consumed (Dong *et al.*, 2017). In fact, total P results have been found to vary greatly (up to 30g kg⁻¹) with the particle size from the same sample of char (Ma and Matsunaka, 2013). This may also explain the large variability in the results in particular after the second season (Table 0-2). This variability was probably enhanced by a different degree of aging of the chars (Gronwald *et al.*, 2016) and plant interaction (McBride, Richards and Steenhuis, 2004).

Table 0-2 Total P, K, Fe, and Al (g kg⁻¹)

Treatments highest rate (h)	Total P _i		Total P _f		Total Fe _i		Total Fe _f		Total Al _i		Total Al _f	
Control soil	0.24	a	0.23	a	10.19	a	10.14	ab	3.75	ab	3.32	a
H180+SSUK	3.27	e	17.37	e	14.48	b	17.19	c	3.72	ab	11.79	d
H180	1.56	bc	5.44	abc	10.85	ab	9.39	ab	3.89	ab	6.71	abc
H240+SSUK	2.74	de	17.81	e	13.64	ab	18.31	cd	3.69	ab	10.70	cd
H240	1.64	bc	5.67	abc	10.89	ab	8.41	a	3.82	ab	7.25	abc
P300+SSUK	3.06	e	12.19	de	12.31	ab	23.07	d	3.48	ab	10.83	cd
P300	1.53	bc	6.10	bc	10.84	ab	9.08	a	4.19	ab	7.22	abc
P400+SSUK	2.77	de	10.06	cd	13.15	ab	18.49	cd	3.53	ab	9.38	bcd
P400	2.56	de	6.73	bcd	9.43	a	11.26	ab	4.48	b	8.82	bcd
SSES+SSUK	3.06	e	7.54	bcd	14.72	b	14.70	bc	3.94	ab	6.01	ab
SSES	1.11	b	3.56	ab	10.80	ab	10.05	ab	3.54	ab	6.89	abc
SSUK	2.05	cd	4.52	abc	13.37	ab	18.56	cd	3.13	a	4.50	a

Letters show significant differences ($p < 0.05$) according to a one-way analysis of variance followed by a Tukey's honestly significant difference (HSD) multiple-means comparison of data from the same year Statistica program. SS_{ES} stands for Sewage Sludge (Spain) dried 105°C. 48h; H180 Hydrochar from SS_{ES} at 180°C for 4h; H240 Hydrochar from SS_{ES} at 240°C for 4h; P300 Pyrochar from SS_{ES} at 300°C for 1h; P400 Pyrochar from SS_{ES} at 400°C for 1h; SS_{UK} Commercialized Sewage Sludge (UK) used for combined treatments 72% moisture. Example: H180+SS_{UK} l indicates a combined treatment (50:50) at the highest rate of H180 (20 t ha⁻¹) mixed with wet SS_{UK} (20 t ha⁻¹), giving a total of 40 t ha⁻¹ applied. h:high (20 t ha⁻¹) for treatments on their own and (40 t ha⁻¹) for combined amendments. i: June 2018, f: June 2019

3.4.1.2 Effect of amendments in soil OM

Soil amendments with sewage sludge and derivatives increased OM directly proportional to the rate of amendment (Figure 0-5). No reason has been found to why the combination of hydrochars at the highest rate didn't increase significantly OM like the other combinations on initial conditions, nor for the differences between treatments in the second season where the highest rate gave the best results. However, the significant increment of OM after growing a crop using sludge has also been reported before (Antolín *et al.*, 2005). A possible explanation for the increase in of soil OM could be due to the mineralization of the roots that remain in the soil after the two seasons (Ayaga, Todd and Brookes, 2006).

By adding an organic amendment rich in labile C and nutrients to the soil, an increase of the microbiota is expected (Lehmann *et al.*, 2011b) which normally is followed by a higher mineralization of soil OM (Zimmerman, Gao and Ahn, 2011), also known as priming effect (Wang, Xiong and Kuzyakov, 2016). However, other studies have reported a lower mineralization rate of soil OM for char (Zimmerman, Gao and Ahn, 2011). This, according to Lehmann *et al.* (2011), could be due to the changes in the community biodiversity, and changes in invertebrates (Marks *et al.*, 2014) or through promoting fungi (Steinbeiss, Gleixner and Antonietti, 2009; Zhang *et al.*, 2018), thus changing the enzymes released (Bailey *et al.*, 2011; Álvarez *et al.*, 2017a). Moreover, thermal treatments are known to stabilize organic carbon (Gronwald *et al.*, 2016) (Yao *et al.*, 2017), meaning that less labile C can be consumed at the beginning leaving the recalcitrant one to be transformed and consumed over time (Wang, Xiong and Kuzyakov, 2016). This could explain changes in mineralization after two seasons but wouldn't explain the result of OM in P400 on its own as chars obtained at lower temperatures combined with SS_{UK} gave also a higher content in OM (Zimmerman, Gao and Ahn, 2011).

Despite the lack of information on microbiology, the greater dissolution of chars after being mixed with sewage sludge is indirectly verified by the increase in EC (See supplementary information) as was also found by Lehmann *et al.* (2011). The continuous release of available P of amendments on its own (Figure 0-6)

suggests that mineralization of OM continued to for two seasons while the crops generated OM in soil amended with the highest rates. Without any amendment OM in control soil remained the same after two seasons proving that sewage sludge and derivatives could be a potential solution for an organic amendment.

3.4.2 Impact of soil properties and combined amendments on available-P

Despite the use of thermal treatments, no significant differences were found between hydrochars, pyrochars and the feedstock regarding available P in the same seasons at the rates studied. Overall, the rates and the way of application, on their own or combined with SS_{UK}, had a greater impact.

According to Zafar et al., (2017), inorganic P fertilisers like triple super phosphate when applied alone do not produce the same outcome than when added with a source of OM, because -COOH functional groups prevent the Fe and Al in the soil from binding with P. Char from SS_{ES} contained a portion of OM (Table 0-1) which would have labile organic carbon (Marks *et al.*, 2014) and such compounds on the surface Figure 0-4 as in (Zhang, Lin and Zhao, 2014; Figueiredo *et al.*, 2018b). Thus, in the present research the char by itself also improved available P on its own significantly (Figure 0-6a). This proved that pyrochars and hydrochars are slow P releasers which hampers available-P efficiency in the first season if no additional source is provided (Figure 0-6a). The potential of the chars was then further enhanced in the first season by the additional input of OM added through SS_{UK} in the combined amendments. Combined amendments with SS_{UK} promoted P desorption (Moradi *et al.*, 2012). The already available-P in derivatives along with the desorbed one, lead to the highest P availability through all combined amendments after two seasons (Figure 0-6b). The general increment of total P may have also contributed to the increment in available P through the aging of the char (Ma and Matsunaka, 2013; Spokas *et al.*, 2014; Lehmann and Joseph, 2015; Dong *et al.*, 2017).

Although Arif et al. (2017) found a correlation with OM and available P efficiency for a mixture of manure with char, this is not the case for the present study. The increase in metals in the soil after two seasons (Table 0-2) and the significant change of pH is perhaps the main reason for the shifts and the last reduction of

available P in most combined amendments after the second season compared to the previous one (Figure 0-6b), stressed by the addition of SS_{UK} (Wagner and Kaupenjohann, 2014).

According to the data presented in Figure 0-4, pH shifted from the range of calcium and aluminium phosphates formation to the main area of aluminium phosphates (Figure 0-7), crossing the area of highest P availability in the first season which is in accordance with first season available-P results (Figure 0-6). Iron present in the sludge may have not produced a significant interference in the soil studied as its fixation would occur at pH below 5.

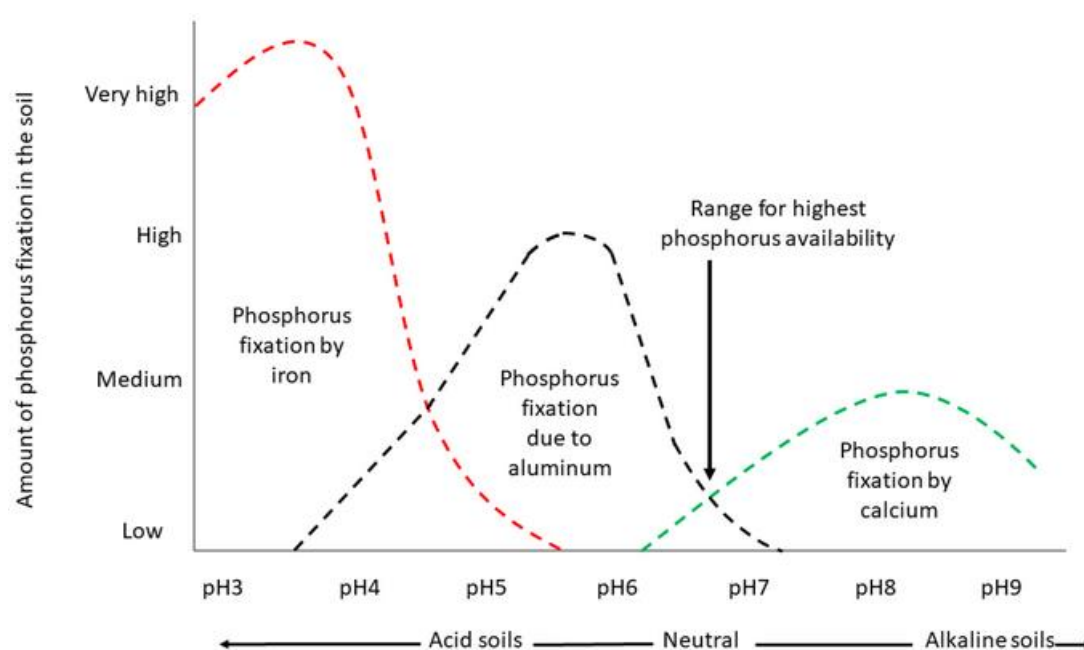


Figure 0-7 Availability changes in P soil conditioned by pH. Figure taken from (Penn and Camberato, 2019) as in (Price, 2006).

This metal fixation did not have the same effect in amendments on their own which provided a stable yet low content of available-P (Figure 0-6a), as in (Glaser and Birk, 2012; Faria *et al.*, 2018a). Thus, available P results showed the ability of thermal derivatives to release P slowly, potentially offering a longer lasting release than the original feedstock of sewage sludge dried at 105°C, 48h and a commercialized SS_{UK} alone.

Acidification of the studied loamy sandy soil to these levels, can cause the loss of base cations, promoting the clay mineral dissolution, incrementing Al saturation already enhanced by the additional input, reducing soil mixture CEC,

losing soil fertility, and consequently producing lower yields (Goulding, 2016). Liming for controlling pH variation could be taken into consideration in future research when applying sewage sludge and derived chars with similar characteristics to obtain optimum yields (Yao *et al.*, 2019), or perhaps combinations of with pyrochars which is an area yet to study. Nevertheless, sewage sludge feedstock selection remains the most determinant factor and its composition should be carefully considered prior to production of any material. Sewage sludge produced through AlCl_3 dosage, or which contain a significant concentration of Al should be ultimately avoided for P fertilization purposes.

3.5 Conclusions

From our research we draw the following conclusions:

- Thermal treatments processing conditions such as temperature and duration, did have a significant effect in the properties of pyrochars and hydrochars from the same feedstock of sewage sludge (SS_{ES}).
- Despite the loss of OM through thermal treatments: H180(16.4%) H240 (21.5%); P300 (3.5%), P400 (31.7%) from 68.4% OM in SS_{ES} , when applied as soil amendments, OM increased significantly after two seasons. The higher rates of combined amendments $\text{SS}_{\text{ES}}+\text{SS}_{\text{UK}}$, H180+ SS_{UK} and P300+ SS_{UK} and P400 and SS_{UK} on their own, gave a concentration 6.24-7.64% OM against 1.21% in control loamy sandy soil.
- Available-P was also reduced after thermal treatments H180 (45.9%), H240 (57.5%), P300 (76.2 %), P400 (83.6%) from 150.4 mg kg^{-1} SS_{ES} . Nonetheless, after two seasons little differences were found between the soil amended with chars and the feedstock regarding P availability. Availability of P changed over two seasons, increasing in most amendments from 4-60%, while available P in the control soil decreased from 1.5 to 0.5 mg kg^{-1} . The greatest amount of available-P was obtained through combined amendments of sludge thermal derivatives with a commercialized sludge (SS_{UK}) at the highest rate 40 t ha^{-1} . The best result was obtained in the first season 26,7 mg kg^{-1} . which was considerably lower than what is recommended for growing spring wheat on this type of

soil (69-115 mg P₂O₅ kg⁻¹, AHDB 2020). Data suggests that Al added through SS_{UK} had a negative impact in P availability after two seasons and that the extra input of C labile accelerated the aging of the chars.

- The most important difference between conditions and process was observed in soil pH changes. When applied to the soil, pyrochars, best if obtained at higher temperature, produced a buffer effect that lasted two seasons preventing an acidification as the one obtained with untreated sewage sludge and hydrochar with pH below 6.

Therefore, we conclude that one single application of pyrochars from dried anaerobic digested sludge improved OM and available-P over two cropping seasons, preventing acidification of a poor loamy sandy soil. This shows the potential of pyrolysis as pre-treatment, the changes over time in soil properties, and the limitations of using sewage sludge containing Al to produce alternative P-fertilisers.

Sewage sludge phytotoxicity and the risk of heavy metal accumulation in soil and in grains is covered in the following chapter, Chapter 4. Phosphorus use efficiency and the effect of the soil properties alterations previously discussed would be linked to spring wheat development and yield productivity, to finally assess if these materials could be considered a feasible alternative source of P-fertilisers.

CHAPTER 4: ENVIRONMENTAL HAZARD AND ASSESMENT OF HYDROCHARS AND PYROCHARS FROM SEWAGE SLUDGE USED AS ALTERNATIVE P FERTILISERS TO GROW SPRING WHEAT

Summary: This chapter contains a comprehensive study on sewage sludge, pyrochars and hydrochars environmental risks when applied as soil amendments and crop response to them. This study was conducted in parallel to complement the study presented in Chapter 4. It comprises a germination test, an assessment of heavy metal accumulation on the system and the risk of mobility of nutrients and heavy metals though the profile derived from the thermal treatments performed (Objective 1 and 4). The analysis of the grains provided information on phosphorus use efficiency (PUE) by contrasting P uptake in comparison with control soil (Objective 2). Finally, the amendment was evaluated as means to increase grain quality by enrichment of Fe and Zn, and crop yield. The conditions of the use of sewage sludge and thermal derivatives as P-fertilisers are discussed.

Highlights:

- The limitations of Zucconi test to predict the germination of the seeds in a pot experiment.
- PUE couldn't be linked to spring wheat productivity. None of the sewage sludge amendments produced a significant improvement of grain yield during the 2-year experiment.
- The variability between replicates became greater over time, especially when SS_{UK} is added in combined amendments.
- Sewage sludge and derived amendments didn't increase Zn in grains but proved to enrich them with Fe, providing a potential solution to malnutrition.
- The variability of heavy metal concentration in soil after amendments over time suggests that for the highest rates, only SS_{UK} could be applied in Europe, while in the UK, the pyrochar obtained with higher temperatures would too be compliant to Zn soil concentration limits.

Chapter 4 was written as independent journal article and is ready to be submitted to: Plant and Soil.

4.1 Introduction

Nutrient deficiency constitutes a major issue in developing countries where Iodine, Vitamin A and Iron are the greatest cause of concern (Ameringen, 2009). However, Iron deficiency can also be seen in developed countries, causing anaemia especially in women whose recommended intake is higher than men (Alwan, Hamady and Cade, 2011; WHO, 2011). The lower intake of Fe, Folate, Se, Vitamin B12 and Vitamin D in the last decade has been reported in the UK (England and Agency, 2017; Advisory and Sacn, 2021). Intake of Fe in females for example, has dropped most significantly in various groups of ages, falling below the lower reference nutrient intake (4.7 mg/day) (Advisory and Sacn, 2021, p107). For this reason, incrementing the concentration of micronutrients in staple foods such as wheat, has been proposed as a solution to malnutrition, especially for those with limited access to diverse food crops to obtain all necessary nutrients (Murphy, Reeves and Jones, 2008). Wheat also contributes on average more than 10% to the value added in agriculture and almost 3% to GDP, making its production important not only for human nutrition but also for its economy (Wang *et al.*, 2018b). However, it has been observed a reduction of 3.4 mg Fe/kg in grains of spring wheat cultivars from historical data compared to modern cultivars introduced in 2003 (Murphy, Reeves and Jones, 2008). For the period between 2019 and 2020, in the UK the consumption of wheat had been 14.7 Mt, thus enriching wheat grains nutrients could proof to be useful (Cox, 2011).

Selecting of the right variety of wheat and modify it genetically has been studied before as a way to increase Fe and other micronutrients such as Zn in grains up to 10 mg/kg and 5 mg/kg, respectively (Uauy *et al.*, 2006). However, concentration of Fe and Zn in grains can be influenced by soil nutrient balance (Handel *et al.*, 2010) and thus it could be possible to enrich grains by modifying soil properties. Sewage sludge commonly used for soil amendments already contains a great variety of macronutrients, such as N, P, Mg and K, and micronutrients such as Fe and Zn, that could enrich wheat grains and hence provide a solution to tackle quality of wheat (Eid *et al.*, 2019).

The use of sewage sludge in agricultural land is an on-going source of debate (Bengtsson and Tillman, 2004; Harder *et al.*, 2017). It is worth to highlight that a better understanding on hazardous chemicals and heavy metals sources and its impact on human health and environmental systems, has had a great impact on the last decades

(Jones, Gardner and Ellor, 2014). Societal consumption, the industry and infrastructures have evolved and as a result, heavy metals concentrated in sewage sludge have been reduced greatly compared to the sludge produced and used in land previously (*Municipal Sewage Sludge*, 1995) (Kirchmann *et al.*, 2017). For example, from 1970 to 2012 concentrations of Pb changed from over 200 to 22 mg/kg, for Cd from over 10 to 1 mg/kg and for Hg from over 4 to 0.1 mg/kg in Swedish sewage sludge (Kirchmann *et al.*, 2017). Moreover, since 1991 the European Union established that nutrients such as P, N and K had to be removed from waste water in order to protect the environment (EEC Council, 1991), making sludge a promising source of recyclable nutrients (Le Corre *et al.*, 2009a; Feng, Luo and Chen, 2015; Huang and Yuan, 2016), and organic matter (TORRI, CORRÊA and RENELLA, 2017). Therefore, the quality of sewage sludge has been enhanced over the last century (Jones, Gardner and Ellor, 2014), while regulations regarding the use of it in agricultural land and heavy metals maximum levels in certain foods (European Commission, 2006) have become more restrictive (Mininni *et al.*, 2015). Ensuring that heavy metal concentration meets legal limits is a minimal requirement to the application of sewage sludge but it doesn't consider a potential nutrient imbalance (Yoshida *et al.*, 2018) (Vymazal, 2019). Moreover, the accumulation in plant tissues (Gascó, Lobo and Guerrero, 2005) and leaching of heavy metals and excess of nutrients, could still be a possible risk if regulations are disregarded (Gascó *et al.*, 2005), especially in cases of continuous applications of sewage sludge (Bhogal *et al.*, 2003). Nonetheless, while it has been reported an accumulation of heavy metals in spring wheat using domestic sewage sludge the concentration often remained below legal limits (Lakhdar *et al.*, 2010; Antonkiewicz *et al.*, 2019; Eid *et al.*, 2019). To maintain legal limits, the use of untreated sludge for agricultural soil is forbidden in Europe while on the contrary, the use of treated sludge is encouraged by the Directive 86/278/CEE as main route of management. Hence, to date in the EU the most common commercialized product is a dewatered and anaerobically digested sewage sludge for agricultural purposes (Eurostat, 2021), which can be an affordable solution for farmers (Bengtsson and Tillman, 2004). To further pursue the minimal environmental risk in the commercialization of this product, new procedures and technologies are being studied (Kelessidis and Stasinakis, 2012) followed by an environmental risk assessment previous to the application of sludge as soil amendment (Yoshida *et al.*, 2018).

For this reason, the use of biological, chemical, composting, and other alternative pre-treatments to the application of sewage sludge are recommended by the Directive 86/278/CEE. Recently, thermal treatments have been considered one of the most promising routes to reduce the bioavailability of pollutants concentrated in sewage sludge (Shi *et al.*, 2013) (Zielińska and Oleszczuk, 2015). Through pyrolysis and hydrothermal carbonization of SS, a char is obtained as the main product that concentrates nutrients that could be recycled if applied soil amendment (Álvarez *et al.*, 2017a)(Bhatt *et al.*, 2018)(Paz-Ferreiro *et al.*, 2018)(Srinivasan *et al.*, 2015), providing an alternative to mineral P-fertilisers (Liu, Liu and Zhang, 2014). It has been proposed by (Madsen *et al.*, 2017) that phytate concentration could be the most relevant storage for phosphorus in cereal grains forming complex with trace nutrients like Fe, Ca and Zn. It has also been observed that the bioavailability of elements is reduced with higher temperatures of thermal treatments for Cu, Ni and Zn (Méndez *et al.*, 2012) but if this effect is continued overtime, it is still an area for further exploration. Similarly, the obtention of chars using the same feedstock of sewage sludge under several process variations, application rates and combinations for the same location, soil, crop and time frame, would fill a gap of research.

Therefore, more research needs to be done on alternative treatments to pre-condition sewage sludge, to be used as reference and avoid more causes of confusion, mismanagement, and disagreements (McBride, 2003; Bengtsson and Tillman, 2004). The objective of this paper is to evaluate the potential environmental risk derived from heavy metal accumulation and nutrient balance changes of pyrochar and hydrochar from the same sewage sludge sample used as alternative P- fertilisers to grow spring wheat. We expect that thermal treatments will (i) reduce phytotoxicity of original sewage sludge (ii) increase nutrients in grains-, (iii) reduce the heavy metals accumulated in grains compared to the anaerobic digested sludge, best at higher temperature of pyrolysis. Furthermore, combinations of such materials with another source of organic matter and its effects on the chars' properties, soil and crop response over time are also an area to be further explored. For this reason, we recreated the same experiment adding a commercialized sewage sludge as source of organic matter and readily available nutrients. By combining sewage sludge soil amendments with thermal derivatives, we hypothesize that: (iv) there will be a greater increase of nutrients in grains than in single amendments (v) chars will reduce the accumulation

of heavy metals in the grains compared to combined anaerobic digested sewage sludge samples.

4.2 Materials and Methods

The experiment was divided in three main phases: (1) production of the chars, (2) characterization of materials and (3) glasshouse experiment.

4.2.1 Materials for amendment preparation

Two pyrochars were produced using a Heron electric furnace model 12-PR/300 series 8B at the Polytechnic University of Madrid (Spain) through pyrolysis in a metallic crucible for 1 hour at 300°C (P300) and 400°C (P400) using pre-oven dried (105°C-48h) sewage sludge (SS_{ES}) from the Avila Wastewater Treatment Plant, Spain. Two hydrochars were obtained in another reactor supplied by Demede S.L (Spain) through hydrothermal carbonization of SS_{ES} mixed with distilled water (20% of dry matter) for 4 hours at 180°C (H180) and 240°C (H240) under autogenous pressure. All samples were oven dried (105°C-48h) and transported to Cranfield University. Once received, the materials were weighted, crushed, and sieved through a 2 mm mesh and stored in sealed bags at room temperature.

Two types of sewage sludge were studied for their effectiveness as alternative P fertiliser for growing spring wheat, in regard to nutrient use efficiency and potential risk on nutrient balance and heavy metals accumulation in both the soil and the plant material. For this matter, the first sludge was treated thermally using pyrolysis and hydrothermal carbonization, while the other was applied as it was received from the supplier to mimic a typical situation in which a farmer applies a commercialized product. In parallel, the same experiment was conducted mixing both sludge and sludge derivatives from SS_{ES} with SS_{UK} (obtained from a water utility in the UK) to assess the effect of the organic matter on soil properties and its performance as P fertiliser.

4.2.2 Crop selection

The crop selected for the present experiment was spring wheat *Triticum aestivum* (KWS Willow). Wheat is one of the most relevant crops all over the world for being one of the main staple cereals (FAO, 2012). Wheat also contributes more than 10% to the value added in agriculture and almost 3% to GDP, making its production determinant

not only for human nutrition but also for its economy (Wang *et al.*, 2018a). To sustain the intensive growth of wheat it is recommended the use of P fertiliser which can be a cause of a depletion of P in soil, thus the use of wheat could be a good reference for the potential of these materials as P-fertilisers (A Rashid, Awan and Ryan, 2005).

To calculate P nutrient use efficiency (PUE) available P applied is related to the one extracted through acid digestion of the grains and compared to control soil (Zafar, Rizwan and Shahid, 2017).

$$\text{Grain P uptake (kg ha}^{-1}\text{)} = [\text{Total P in grain (\%)} \times \text{grain yield kg ha}^{-1}]/100 \quad (4-1)$$

$$PUE(\%) = \frac{(\text{P uptake fertilized treatment} - \text{P uptake control})(\text{kg ha}^{-1})}{\text{Available P applied through fertiliser (kg ha}^{-1})} \times 100 \quad (4-2)$$

$$\text{Rate (g pot}^{-1}\text{)} = t \text{ ha}^{-1} \times 10^{-4} \text{ ha m}^{-2} \times 0.0087 \text{ m}^2 \text{ pot}^{-1} \times 10^6 \text{ g t}^{-1} \quad (4-3)$$

$$\text{Yield calculation (t ha}^{-1}\text{)} = \text{Yield } \frac{\text{g}}{\text{pot}} \times \frac{1}{0.0087 \text{ m}^2} \times \frac{10^4 \text{ m}^2}{\text{pot}} \times \frac{10^{-6} \text{ t}}{\text{g}} \quad (4-4)$$

$$\text{Available P (kg ha}^{-1}\text{)} = \text{Available P mg kg}^{-1} \times \frac{1 \text{ kg soil mix in 5 cm}}{\text{m}^3 \text{ soil mix in 5 cm}} \times 10^4 \text{ m}^2 \text{ ha}^{-1} \times 0.05 \text{ m } 10^{-6} \text{ kg mg}^{-1} \quad (4-5)$$

4.2.3 Phytotoxicity test

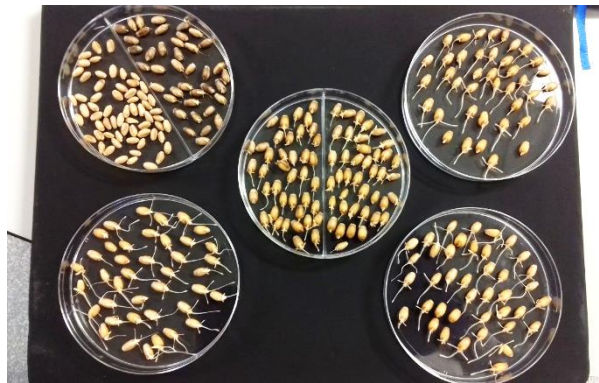


Figure 0-1 Zucconi test, seeds germinated for 2 days.

The Zucconi Test was used to assess phytotoxicity of the materials described above through the germination of the spring wheat seeds using a water extract. The extract was obtained adding 2g of char or sludge previously dried at 105°C for 48h to 20 ml of deionized water (1:10), shaking it in plastic bottles for 1h at 300rpm and leaving it to stand for another hour. After that 5ml of the extract was pipetted over a petri dishes

(9.5 cm D), where 10 seeds of spring wheat were lined on a filter paper Whatman #2. The petri dishes were sealed with paraffin tape and placed under constant conditions of temperature (20°C) in the dark for 2 days (Figure 0-1). Four replicates were used for this experiment. Germinated seeds (the ones with a root > or equal 0.2 cm (Meunchang, Panichsakpatana and Weaver, 2005)) , were counted at the end after 48h. The risk of phytotoxicity was considered minimal if the germination index was >60%. To calculate the germination index, the following equations were used:

$$\text{Germinated seeds}(\%) = \frac{N^{\circ} \text{ of germinated seeds(extract)}}{N^{\circ} \text{ of germinated seeds control}} \times 100 \quad (4-6)$$

$$\text{Root lenght 2nd day}(\%) = \frac{\text{Average root lenght (exctract)}}{\text{Average root lenght control}} \times 100 \quad (4-7)$$

$$\text{Germination index} = \text{Germinated seeds}(\%) \times \text{root lenght 2nd day}(\%)/100 \quad (4-8)$$

The seeds from the same Zucconi test were left to grow and the process was stopped after 7 days from the addition of the extract, by pipetting 1-2ml of denatured ethanol (50%). Pure ethanol 95.9% was diluted by half to obtain this solution. After this, each petri dish was opened, and the main radicle was measured to compare the elongation of the roots between treatments.

4.2.4 Experimental site and soil description

After the phytotoxicity test, two seasons of spring wheat were grown in a glasshouse experiment of 100 days duration each, from June to August (2018) and from April to June (2019) at Cranfield University, UK. Temperature ranged from 13°C to 35°C on average, measured with TermoPro TP50; the glasshouse was vented when temperatures reached 21°C with additional cooling from fans and through wetting the floors to maintain a temperature below 35°C.

The topsoil (Baileys of Norfolk Ltd) was as a sandy loam soil with low P content (Index 1 P-K-Mg: 15-69-33 mg l⁻¹. Soil was air dried for a week in the glasshouse compartment over tarpaulins and then crushed and sieved (2mm). There after 5.18 kg of soil was packed in columns (H:50 cm, D:10.5 cm) achieving a density of 1.3 kg m⁻³ without adding any pressure.

4.2.5 Experimental design

The column experiment was setup in a randomized design using four replicates to test three application rates and a control. The application rates were 5, 10, 20 t ha⁻¹ (equivalent to 4.33, 8.66 and 17.32 g per column in dry matter respectively) for treatments on their own. To study the effect of the addition of organic matter with the chars, a commercialized local sewage sludge (SS_{UK}) was mixed with the materials produced using the same amount to double the rates (50-50%, 10, 20, 40 t ha⁻¹) as soil amendment, for the combined amendments. Every amendment was done just once at the beginning of the experiment in the first 5 cm of the soil in each column by pouring the content on top and mixing manually with a spatula.

A total of 136 columns were placed vertically leaving 5 cm between them. Each column was cut from a pipe and prepared with voile and a bottom layer of gravel to prevent soil loss and allow free drainage. A moderate drought was set to prevent any leachate (Liu *et al.*, 2012). Thus, starting from 40% FC, 30-100ml deionized water were poured daily to the column to replace the amount lost depending on the conditions.

Spring wheat was sowed at 2 seeds per pot, equivalent to the maximum recommended density (Nan *et al.*, 2000) (Salantur, Ozturk and Akten, 2006). The seeding was done by placing the seed in a 2 cm deep hole and after application of the amendment. The following days while the seeds developed the radicle some had to be repositioned as the daily watering made them float to the surface. In the columns with combined treatments, the crust formed at the top was broken before seeding. The seeding was done in 34 columns/day so that the experiment and thus the sampling was carried out in four blocks.

Additional nitrogen was applied manually in the form of a NH₄NO₃ salt and the same quantity was measured for all treatments, as the one following The Nutrient Management guide for arable crops for Soil Nitrogen Supply (SNS Index) 1-2 (AHDB, 2020). The addition of N is especially important when working with char amendments as this nutrient may be immobilized partially due to labile C content (Abalos *et al.*, 2013)(Lehmann and Joseph, 2015) and generally in sewage sludge available N for the plants is expected to be a small fraction of total N (Kirchmann *et al.*, 2017). Therefore, after the sludge amendments, the first application of N was applied 45 days after the sowing during the tillering stage at 30 kg/ha (equivalent 0.07g/column) and

same amount again 20 days after during the flowering stage, so that 60 kg N/ha were added as salt. The ammonium nitrate (NH_4NO_3) was applied in the first 2 cm to avoid root breaking, mixing it in the topsoil by adding the daily dose of deionized water. During the second season, the same procedure was followed except for the addition of the first dose after sowing as the sludge and derivatives amendment was added only at the start of the first season. No other nutrients were added to this soil.

4.2.6 Sampling and measurement of soil changes

In order not to remove any char from the soil, for starting soil conditions, a surrogate was recreated in at the laboratory in parallel and using the same proportions as at the glasshouse but using dried materials at (105°C, 48h) and storing them in plastic bags in room temperature. To determine plant nutrient balance soil total P, K, Ca, Mg, Na and B were calculated, and to assess possible interferences to it Total Fe, Cu, Mn, Zn, Cr and Al were analysed on starting conditions and final conditions after the second harvest from the columns in the glasshouse. To quantify the biohazard risk related to heavy metal accumulation Total As, Cd, Pb and Hg were analysed as well. Samples taken were oven-dried at (60°C for 48h) and ground to fine dust and analysed 0.5 g $\pm$ 0.0001g using acid digestion with aqua regia, following ISO 11047:1998.

4.2.1 Measurement of crop response to soil amendments



Figure 0-2 Spring wheat pot experiment season 1.

The production of grains and the total biomass per treatment was calculated to assess crop response (



Figure 0-2). The wheat was cut just above the roots and dried at 60°C for 48h to determine yield. Next, the ear was separated using a plastic rubber tube to allow easier separation of the grains. To compare the results with the control soil during the two seasons, the same elements studied in the soil were analysed in the grains following the same method. The grains obtained from the highest rates (20 t/ha for amendments on their own, 40 t/ha for combined ones) were ground to fine dust with a conventional coffee grinder with stainless steel blades cleaned in between samples to avoid cross-contamination (Murphy, Reeves and Jones, 2008). The number of grains and the average weight were also registered. The number of seeds was counted with a device (Seed counter Elmor 1).

$$\text{Harvest Index (HI)} = \frac{\text{Total grain weight treatment (kg/ha)}}{\text{Total overground weight (kg/ha)}} \quad (4-9)$$

4.2.1 Statistical analyses

Firstly, the statistical analysis of the raw materials was undertaken using STATISTICA 13.3.704.19 and involved the analysis of variance one-way (ANOVA), the least significant differences to compare the means using Tukey stand a probability level of 5% ($p < 0.05$) and were plotted using R.

Then the statistical analysis of experimental data extracted from the glasshouse experiment was undertaken using JMP-16. First, a Multivariate analysis and a PCA was conducted to find correlations among observations in soil and grain analysis. Given the little variability between replicates for the soil samples and grain analysis, the replicates were treated as fixed factors and analysed through one-way ANOVA using STATISTICA 13.3.704.19 using box-cox before performing the analysis of variance one-way (ANOVA), the least significant differences to compare the means using Tukey stand a probability level of 5% ($p < 0.05$) and were plotted using R.

However, yield results showed a great variability among replicates and these could no longer be considered fixed effects but random effect. To assess this, two cluster analysis were conducted and the data was normalized using STATISTICA 13.3.704.19 using box-cox before performing the analysis of variance one-way (ANOVA). The first cluster analysis was conducted using the position of the columns, from 1 to 136, as categorical factor using K-Means to determine if the random position of the columns in the glasshouse had a significant effect on the variability of the yield results. The second cluster analysis was performed to obtain the hierarchy using treatments as categorical factor for the same observations in order to determine if the variability on the yield results could be linked to the type of treatment. The multivariate and cluster analysis were conducted separately for each season and plotted with JMP-16. Additional statistical outputs can be found in the APPENDIX (5.7A.1.3).

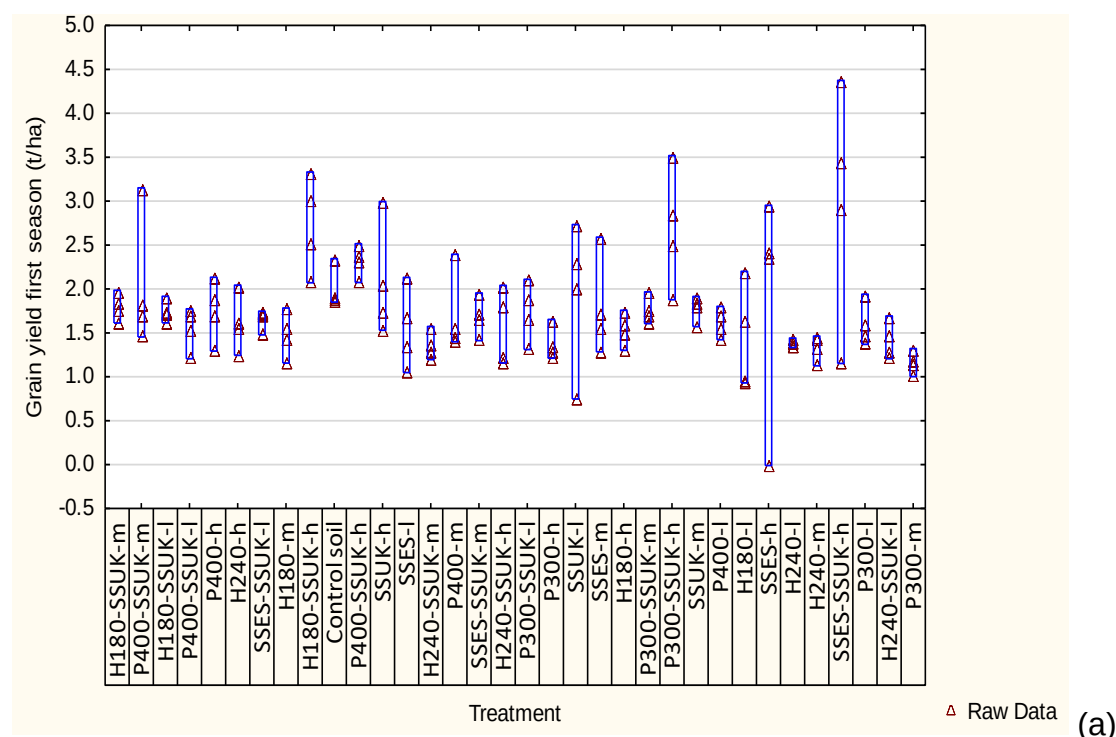
4.3 Results

4.3.1 Effect of the amendments on the yield

We found large variability between replicates, in particular when greater quantities of SS_{UK} were combined with other amendments (Figure 0-3a). This variability further increased in the second season in combined treatments (Figure 0-3b), giving a single homogeneous group (**Error! Reference source not found.**). The Box-cox normalization confirmed that none of the treatments significantly affected spring wheat grain yield in both seasons.

To understand if the random position in the glasshouse had a significant effect on the variability of the results (Figure 0-3), a multivariate analysis was conducted separately for each season using grain yield, number of grains and total above biomass. N30 and

average grain weight didn't have a correlation over 0.3 and were left out for the analysis. The distribution of the columns is shown in Figure A 8 (Appendix). Columns were attached to the bench's legs forming three lines across the glasshouse compartment, with 44-45 columns each. To simplify the analysis, 12 clusters were studied to determine 4 possible zones of influence per line. The first cluster analysis was therefore conducted using the position of the columns from 1 to 136 as categorical factor. As shown in Figure A 8 (Appendix) for season 1, it is possible that the columns at the end of the third row were somewhat influenced by that position as columns 127 to 136 are grouped in the same cluster number 10. However, that effect was not detected in the following year and no other effect could be determined. Following, another hierarchy cluster analysis was performed using treatments as categorical factor for the same observations, but no clusters could be related to a same type of treatment or rate for both seasons, (Figure A 9, Figure A 10, Figure A 11 & Figure A 12, Appendix). The variability of the yield results might have been a result of the combination of the effect of the physical-chemical changes, the position of the glasshouse or pest, but it could not be attributed to one only cause.



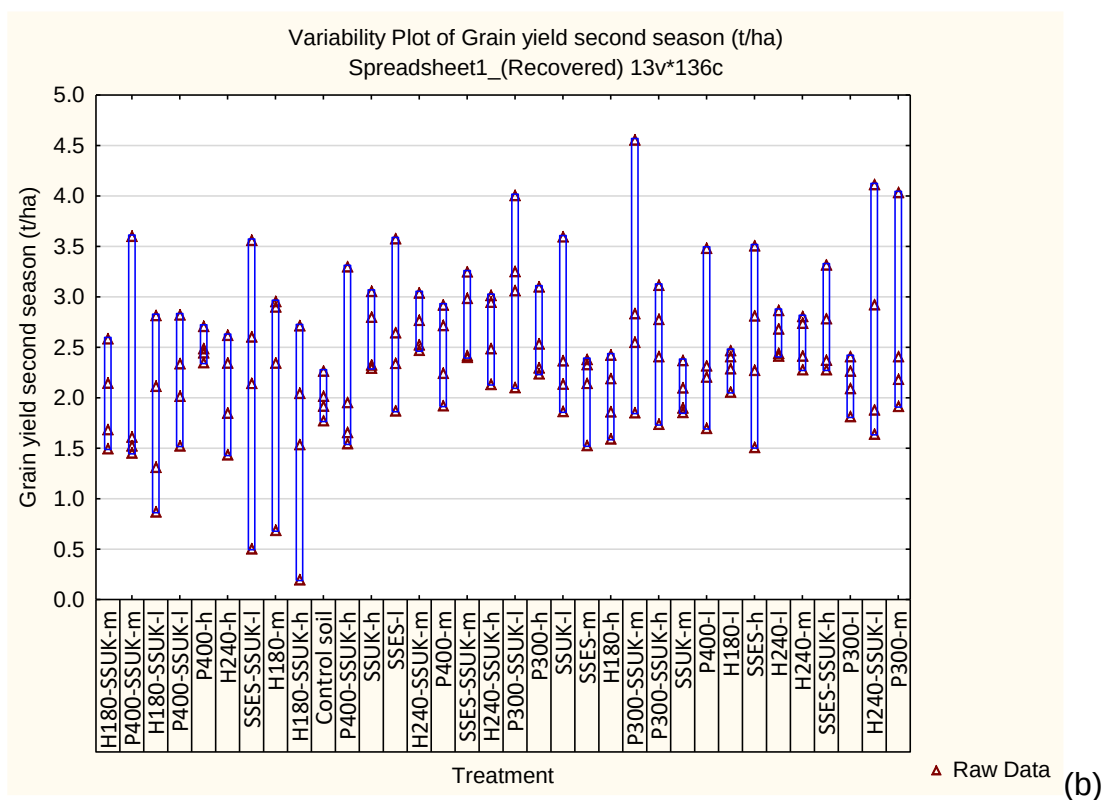


Figure 0-3 Grain yield (t/ha) variability for the first season (a) and second season (b) plotted with STATISTICA 13.3.704.19.

Table 0-1. Grain yield and agricultural index

	Rate (t/ha)	Grain Yield ₁ t/ha		Grain Yield ₂ t/ha		HI ₁	HI ₂
Control-soil	0	2.0	abcd	2.0	a	42.55	49.46
H180+SSUK-l	10	1.7	abcd	1.8	a	31.10	44.85
H180+SSUKm	20	1.8	abcd	2.0	a	31.60	47.82
H180+SSUK-h	40	2.7	cd	1.6	a	37.61	48.58
H180-l	5	1.4	abc	2.3	a	32.64	50.60
H180-m	10	1.5	abc	2.2	a	29.93	50.71
H180-h	20	1.5	abc	2.0	a	29.85	46.43
H240+SSUK-l	10	1.4	abc	2.6	a	30.73	51.71
H240+SSUK-m	20	1.4	ab	2.7	a	27.34	54.07
H240+SSUK-h	40	1.6	abc	2.6	a	23.42	46.92
H240-l	5	1.4	abc	2.6	a	32.39	53.65
H240-m	10	1.3	ab	2.6	a	32.23	50.64
H240-h	20	1.6	abcd	2.1	a	33.08	45.36
P300+SSUK-l	10	1.7	abcd	3.1	a	30.55	53.23
P300+SSUK-m	20	1.8	abcd	3.0	a	32.04	49.92
P300+SSUK-h	40	2.7	bcd	2.5	a	38.93	43.41

P300-l	5	1.6	abc	2.1	a	33.75	48.38
P300-m	10	1.2	a	2.6	a	29.70	48.89
P300-h	20	1.4	abc	2.5	a	32.75	49.67
P400+SSUK-l	10	1.6	abc	2.2	a	32.90	49.38
P400+SSUK-m	20	2.0	abcd	2.1	a	35.41	45.24
P400+SSUK-h	40	2.3	abcd	2.1	a	34.09	44.03
P400-l	5	1.6	abcd	2.4	a	37.23	48.66
P400-m	10	1.7	abcd	2.5	a	35.99	50.45
P400-h	20	1.8	abcd	2.5	a	37.18	49.72
SSES+SSUK-l	10	1.7	abcd	2.2	a	29.78	50.06
SSES+SSUK-m	20	1.7	abcd	2.8	a	25.39	48.16
SSES+SSUK-h	40	3.0	c	2.7	a	37.56	47.62
SSES-l	5	1.6	abc	2.6	a	39.23	53.57
SSES-m	10	1.8	abcd	2.1	a	35.73	52.64
SSES-h	20	1.9	abcd	2.5	a	32.06	50.97
SSUK-l	5	1.9	abcd	2.5	a	33.10	52.06
SSUK-m	10	1.8	abcd	2.1	a	37.84	44.74
SSUK-h	20	2.1	abcd	2.6	a	41.54	46.60

1: First season, 2: Second Season, AE (kg grain/kg Olsen P)

4.3.2 Effect of the amendments on spring wheat development

4.3.2.1 Germination rates

In the Zucconi test, dried sewage sludge samples extracts were the most phytotoxic, evidenced by low germination rates of 11.4% (SS_{ES}) and 6.3% (SS_{UK}). Only pyrolysis reduced the phytotoxicity of the sewage sludge, whereas hydrochars gave also a low germination index of 38.4% (H240-4), 27.4% (H180-4). As expected, in the pot experiment, when mixed with soil the effect was not as phytotoxic, showing a greater germination of spring wheat (Table 0-2). However, some treatments at the highest application rates of pyrochar or hydrochar did not grow all the seeds. SS_{ES} + SS_{UK} gave the lowest germination rate (62.5%) which was consistent in the second year. The only treatments that germinated all the seeds were the derived chars at lowest temperatures of pyrolysis (P300-1) and (H180-4), and H240-4 whether applied on their own or when mixed with SS_{UK}.

4.3.2.1 Plant growth

Most amendments had a positive effect during the tillering stage on the number of leaves (after 30 days, NL30) compared to control soil (Table 0-3). All mixtures with the raw sewage sludge (SS_{UK}) developed more leaves, in particular when SS_{ES}+SS_{UK} was

applied at the medium rate, which resulted in 16 leaves against 7 for the control. However, there was a noticeable reduction of the number of leaves in the second season compared to the first one, shifting from an average of 10 leaves to 4 per plant. The above-ground biomass (AGB) was significantly higher after the first season for H180-SS_{UK} (7.6 t/ha) and SS_{ES}-SS_{UK} (7.9 t/ha) when applied at the highest rates. Despite the lack of difference among the treatments, the lower values for AGB the second year gave a higher Harvest Index (**Error! Reference source not found.**). The number of grains was significantly higher for SS_{ES}+SS_{UK} (139 compared to 63 in control soil) in the first season, and for P300-SS_{UK} at 40 t/ha in the second season (106 compared to 64 in the control soil), but no other effects were found for any of the treatments (Table 0-3).

Table 0-2 Zucconi test results dilution (1:10) after 2 days under 20°C, ethanol added 50% and kept under 3°C for three days.

Sample	Water extract, Zucconi germination test (2nd day)					Ungerminated seed mixed with soil			
	Seed radicle length (cm)	Mean germinated seeds	Root length (%)	Germinated seeds (%) Zucconi Test	Germination Index (%)	Seeds that make it to the flowering stage (%)			
						Pot experiment (lowest)*			
						On their own		Mixed with SS _{UK}	
						y1	y2	y1	y2
SS _{ES}	0.2a	5.5b	19.2	59.5	11.4	87.5(m) (h)	87.5 87.5(m)	87.5(m) 62.5(h)	62.5 (h)
H180-4	0.4a	8.3a	30.8	89.2	27.4	100 all	100 all	100 all	100 all
H240-4	0.5a	8.8a	40.6	94.6	38.4	87.5(m)	87.5(m)	100 all	100 all
P300-1	0.9b	9.0a	78.0	97.3	75.9	100 all	100 all	100 all	100 all
P400-1	1.0b	9.0a	89.5	97.3	87.1	87.5(l)	95.8 (h)	100 all	87.5(m)
SS _{UK}	0.1	14.7	14.7	42.5	6.3	87.5(h)	87.5(h)	-	-
Soil	0.7	9.3	68.3	92.5	63.2	100 all	100 all	-	-
D.W.	1.2b	9.3a	100	100	100				

SS_{ES} = Sewage Sludge (Spain) dried 105°C, 48h; H180-4 = Hydrochar from SS1 at 180°C for 4h; H240-4 = Hydrochar from SS1 at 240°C for 4h; P300-1 = pyrochar from SS1 at 300°C for 1h; P400-1= pyrochar from SS1 at 400°C for 1h; SS_{UK}= Commercialized Sewage Sludge (UK) used for combined treatments 72% moisture. D.W.= deionised water used for irrigation

l: lowest rate (5 t/ha for treatments on their own, 10 t/ha for combined treatments), m: medium rate (10 t/ha for treatments on their own, 20 t/ha for combined treatments), h: highest rate (20 t/ha for treatments on their own, 40 t/ha for combined treatments)

Phytotoxicity is said to be minimal if the Germination Index is > 60% (Alisa Jane Savage), Germination considered if > or = 0.2 cm

*if not indicated, the rest doses flowered all the seeds (100% in comparison with control). All seeds made it to the flowering stage in control soil for both seasons, this is a total of 8 seeds (2 seeds per pot, 4 replicates A, B, C and D).

Table 0-3. Plant development

		AGB (t/ha)				GN				AGW (mg/seed)				NL ₃₀					
		1st season		2nd season		1st season		2nd season		1st season		2nd season		1st season		2nd season			
Treatments	Rate (t/ha)	Control Soil	0	4.7	ab	4.0	a	63	abcd	64	a	27.6	a	27.0	a	7	ab	3	ab
H180+SSUK-l	10	5.6	abcd	4.0	a	63	abcd	88	ab	24.5	a	18.5	a	10	abc	3	ab		
H180+SSUK-m	40	5.7	abcd	4.1	a	68	abcd	74	ab	23.5	a	23.9	a	11	abc	3	a		
H180+SSUK-h	20	7.6	cd	3.8	a	106	de	67	ab	23.2	a	19.3	a	12	abc	3	ab		
H180-l	5	4.4	ab	4.6	a	57	abc	77	ab	21.1	a	26.1	a	9	abc	3	ab		
H180-m	10	4.9	abc	4.5	a	52	ab	95	ab	25.9	a	21.4	a	12	bc	4	ab		
H180-h	20	5.1	abcd	4.4	a	61	abc	73	ab	22.1	a	23.9	a	11	abc	4	ab		
H240+SSUK-l	10	4.6	ab	5.1	a	45	a	79	ab	29.1	a	28.1	a	10	abc	4	ab		
H240+SSUK-m	40	5.0	abc	5.0	a	59	abc	80	ab	20.4	a	29.8	a	9	abc	4	ab		
H240+SSUK-h	20	6.6	abcd	5.6	a	67	abcd	96	ab	20.4	a	23.9	a	9	abc	4	ab		
H240-l	5	4.3	ab	4.9	a	55	abc	76	ab	21.8	a	29.8	a	8	abc	3	ab		
H240-m	10	4.2	ab	5.1	a	53	ab	83	ab	22.1	a	26.8	a	9	abc	5	ab		
H240-h	20	4.9	abc	4.6	a	56	abc	79	ab	25.0	a	22.5	a	11	abc	4	ab		
P300+SSUK-l	10	5.7	abcd	5.8	a	57	abc	95	ab	26.6	a	28.6	a	10	abc	3	a		
P300+SSUK-m	20	5.5	abcd	5.9	a	64	abcd	93	ab	24.8	a	27.0	a	11	abc	4	ab		
P300+SSUK-h	40	6.9	bcd	5.8	a	98	cde	106	b	23.7	a	20.5	a	10	abc	5	ab		
P300-l	5	4.7	ab	4.4	a	62	abcd	74	ab	22.3	a	25.1	a	9	abc	4	ab		
P300-m	10	3.9	a	5.4	a	47	a	87	ab	21.6	a	25.8	a	10	abc	5	ab		
P300-h	20	4.2	ab	5.1	a	56	abc	86	ab	21.3	a	25.6	a	8	abc	4	ab		
P400+SSUK-l	10	4.7	ab	4.4	a	63	abcd	73	ab	22.2	a	25.5	a	10	abc	4	ab		
P400+SSUK-m	20	5.7	abcd	4.5	a	69	abcd	70	ab	25.3	a	24.5	a	12	abc	4	ab		
P400+SSUK-h	40	6.8	bcd	4.8	a	92	abcd	84	ab	21.9	a	21.2	a	13	bc	5	ab		
P400-l	5	4.3	ab	5.0	a	64	abcd	81	ab	22.4	a	25.7	a	10	abc	4	ab		
P400-m	10	4.7	ab	4.9	a	53	ab	81	ab	28.5	a	26.4	a	12	abc	4	ab		
P400-h	20	4.7	ab	5.0	a	65	abcd	81	ab	23.2	a	26.9	a	11	abc	4	ab		
SSES+SSUK-l	10	5.6	abcd	4.4	a	60	abc	68	ab	24.4	a	26.1	a	9	abc	3	ab		
SSES+SSUK-m	20	6.6	abcd	5.7	a	57	abc	95	ab	27.4	a	25.1	a	16	c	7	b		
SSES+SSUK-h	40	7.9	d	5.6	a	139	e	99	ab	18.0	a	23.6	a	7	ab	6	ab		
SSES-l	5	4.7	ab	5.0	a	50	ab	77	ab	28.1	a	29.1	a	11	abc	4	ab		
SSES-m	10	5.0	abc	4.6	a	70	abcd	84	ab	22.1	a	21.5	a	11	abc	4	ab		
SSES-h	20	4.6	ab	5.4	a	52	ab	101	ab	26.7	a	21.5	a	3	a	4	ab		
SSUK-l	5	5.0	abc	4.7	a	65	abcd	73	ab	27.3	a	29.3	a	9	abc	4	ab		
SSUK-m	10	5.0	abc	3.9	a	62	abc	70	ab	25.4	a	25.8	a	9	abc	3	ab		
SSUK-h	20	6.5	abcd	5.1	a	75	abcd	89	ab	24.6	a	25.6	a	11	abc	4	ab		

AGB: Above-ground biomass, GN: Grain number, AGW: Average grain weight, NL30: Number of leaves day 30.

Values in column followed by the same letter are not significantly different ($p = 0.05$) using Tukey HSD test with Statistica program.

l:low (5 t/ha) m:medium (10t/ha), h:high (20 t/ha) for treatments on their own. l:low (10 t/ha) m:medium (20t/ha), h:high (40 t/ha) for combined amendments. Values in column followed by the same letter are not significantly different ($p = 0.05$) using Tukey HSD test with Statistica program.

4.3.3 Effect of the amendments on soil and grain quality

4.3.3.1 Concentration of elements in raw materials

As shown in Table 0-4, the sample soil was confirmed to be low in all elements which was what we were looking for in order to have the lowest interference for the amendment study. The acid digestion of the chars derived from SS_{ES} showed an increase of concentration of elements after the thermal treatments, which confirmed our hypothesis-2c. There were significant differences between pyrolysis and hydrothermal carbonization, but also related to temperature adjustments. Temperature adjustments gave more significant differences between pyrochars than hydrochars (Table 0-4). In all cases for pyrochars and hydrochars, those obtained at higher temperature had a higher concentration, the only exception being mercury for P400-1 which was below detection limits, as was the case for the sample soil. The main difference between the two sludge samples was that Ca and Fe were more concentrated in SS_{UK}, and Al and K were higher in SS_{ES}.

Table 0-4 Total elements of SS_{ES}, thermal derivatives and SS_{UK} used for the combination treatments.

		Total (mg/kg)																	
Sample	Mo	Hg		Cr		Pb		Ni		Co		Cd		Zn		Cu			
SS _{UK}	9.1	a	0.1	a	9.1	a	17.4	d	30.3	ab	3.9	a	1.0	a	1189.7	a	346.9	d	
SS _{ES}	5.6	d	0.7	a	5.6	c	38.3	e	26.0	a	3.4	b	0.9	a	1117.0	a	293.8	c	
H180-4	8.7	a	0.6	a	8.7	a	51.0	a	30.6	ab	3.9	a	1.1	a	1591.4	b	451.1	a	
H240-4	9.4	b	0.6	a	9.4	ab	54.4	b	31.5	ab	4.1	a	1.1	a	1760.3	d	506.1	e	
P300-1	8.3	a	0.5	a	8.3	ad	50.2	ae	33.7	c	3.9	a	0.9	a	1611.5	b	446.9	a	
P400-1	10.7	b	-	b	10.7	b	56.5	b	40.9	c	4.9	c	1.2	a	2051.9	e	556.4	f	
Loamy sand soil	0.2	c	-	b	0.2	e	11.8	c	5.3	d	3.1	b	0.1	b	20.7	c	5.1	b	
Sample	Na	Mg		K		Ca		P		Al		Fe		B		Mn			
SS _{UK}	432.3	c	4072.1	b	1194.2	c	44073.5	b	43716.2	a	9627.8	e	50236.2	e	23.1	c	197.6	b	
SS _{ES}	1164.9	d	7022.2	c	3985.2	d	26047.6	d	45636.1	a	30705.3	f	3697.4	c	29.2	d	738.0	c	
H180-4	762.8	a	8025.3	d	3450.5	a	35533.1	a	63659.2	b	42887.1	d	5659.8	b	15.7	a	1062.0	e	
H240-4	832.8	a	9684.2	f	3530.8	a	37984.1	a	71157.0	d	47036.7	g	6814.1	bd	18.6	a	1168.5	f	
P300-1	1589.0	e	8885.9	e	5017.3	e	34260.5	a	61957.8	b	40320.5	a	5304.2	bc	35.0	e	1009.3	d	
P400-1	2024.9	f	11805.1	g	6606.9	f	45307.3	b	81103.0	e	52867.3	c	8213.1	d	42.2	f	1299.8	g	
Loamy Sand soil	20.6	b	341.7	a	327.7	b	646.8	c	259.7	c	2759.7	b	5594.7	b	1.7	b	159.9	a	

4.3.3.2 Accumulation of elements in soil

On initial conditions after applying the amendments, there was a general enrichment in nutrients, trace elements and heavy metals through all amendments. The only non-significant changes to control soil on initial conditions were for K, B, As, Hg, Al, Co and Ni, and among these, B, Co and Ni remained statistically the same after the second season in all treatments. Combined amendments and the pyrochar obtained at the highest temperature resulted on the highest increment of most elements, P, Ca, Mg, Na, Mn and Zn, in the first season (Table 0-5). Even though SS_{UK} was applied in the same quantity as the chars for combined amendments, it did not increase proportionally the concentration of elements in the soil. Zn increased from 98% to 148% in combined amendments and P400 and Fe was only significantly different in the soil with P400 (13% less Fe). After 2 years, most elements were detected in greater quantities in the top layer of the amended soil compared to initial conditions which was opposite to what we were expecting. However, no sample was taken in between seasons for acid digestion and no additional sludge or derivatives were applied. SS_{ES} derived pyrochars and hydrochars released more nutrients and heavy metals (Table 0-6). Overall, in the second season temperature didn't make a significant difference but the type of thermal treatments and whether they were applied on their own or combined. Combined amendments produced a higher increment in all elements which we reported previously for total P, Fe and Al in previous paper. Significant ($p < 0.05$) increments relative to the sewage sludge they were derived from were found especially when combined (Table 0-6). In numbers, this increments are: for P (182-400% all combined), K (77% P300-SS_{UK}), Ca(280-428% P300-SS_{UK}, H180-SS_{UK} and H240-SS_{UK}), Mg (120-154% all combined and P400), Na (132-242% all combined and P400), B (100% P300-SS_{UK}), Fe (82-130% all combined), Cu (217-346% all combined), Mn (57-59% H180-SS_{UK}, P300-SS_{UK}), Zn (99-103% H180-SS_{UK} and H240-SS_{UK}), Cd (108-134% P300-SS_{UK}, H180-SS_{UK} and H240-SS_{UK}), Cr (77-123% all combined) and Mo (243-378% all combined).

Table 0-5 Average elements in soil mg/kg (Initial conditions only highest rates, before first season)

Sample	P		K		Ca		Mg		Na		B		Fe		Cu		Mn		Zn		As		Cd		Pb		Hg		Cr		Mo		Al		Co		Ni	
Control soil	241	e	450	ab	847	d	478	d	24	d	7	ab	10189	a	6	d	148	ab	20	e	10	a	0.090	a	12	b	0.004	a	11	a	0.365	e	3753	ab	3.960	a	16	a
H180	1564	bc	431	ab	1884	ace	556	cde	41	ad	7	ab	10854	ab	19	b	161	ab	52	bc	12	a	0.108	a	11	ab	0.100	a	13	a	0.660	abc	3886	ab	4.113	a	14	a
H180-SSUK	3268	a	379	ab	2979	b	701	ab	54	abc	8	ab	14477	b	41	a	168	ab	99	a	12	a	0.226	b	11	ab	0.024	a	14	ab	1.021	d	3715	ab	3.972	a	12	a
H240	1644	bc	349	a	1634	ade	612	ace	39	ad	6	b	10893	ab	21	be	181	ac	55	bc	11	a	0.126	a	15	c	0.106	a	11	a	0.612	abe	3819	ab	4.256	a	16	a
H240-SSUK	2744	ad	395	ab	2480	abc	676	abc	60	bc	8	ab	13643	ab	35	ac	179	ac	89	a	12	a	0.133	a	10	ab	0.162	a	14	ab	0.864	bcd	3686	ab	4.172	a	11	a
P300	1535	bc	445	ab	1675	ade	676	ac	68	cg	8	ab	10845	ab	19	b	182	ac	56	bc	10	a	0.160	ab	16	c	0.006	a	12	a	0.549	ae	4191	ab	4.403	a	10	a
P300-SSUK	3059	a	404	ab	2675	bc	708	ab	95	ef	8	ab	12314	ab	39	a	165	ab	98	a	11	a	0.160	ab	10	ab	0.063	a	13	a	0.916	cd	3482	ab	3.904	a	11	a
P400	2560	ad	463	ab	2276	abc	809	b	102	f	7	ab	9432	a	30	c	206	c	79	ad	9	a	0.126	a	16	c	0.067	a	11	a	0.730	abc	4476	b	4.059	a	10	a
P400-SSUK	2774	ad	448	ab	2510	abc	677	abc	88	ef	9	a	13154	ab	36	ac	174	ac	87	ad	11	a	0.155	ab	10	ab	0.002	a	14	ab	0.923	cd	3531	ab	4.447	a	13	a
SSES	1110	b	439	ab	1123	de	517	de	53	abc	8	ab	10797	ab	14	bd	152	ab	40	be	11	a	0.114	a	10	ab	0.022	a	12	a	0.596	abe	3536	ab	4.112	a	14	a
SSES-SSUK	3059	a	504	b	2840	b	719	ab	82	eg	9	a	14719	b	40	a	182	ac	94	a	13	a	0.149	a	10	ab	0.067	a	18	b	1.034	d	3936	ab	4.837	a	18	a
SSUK	2053	cd	410	ab	2481	abc	541	de	44	ab	8	ab	13368	ab	29	ce	132	b	68	cd	11	a	0.120	a	9	a	0.036	a	14	ab	0.836	abcd	3132	a	4.149	a	22	a

Table 0-6 Average elements in soil mg/kg (Final conditions only highest rates, after the second season)

Sample	P		K		Ca		Mg		Na		B		Fe		Cu		Mn		Zn		As		Cd		Pb		Hg		Cr		Mo		Al		Co		Ni	
Control Soil	235	c	421	a	471	b	400	a	24	a	6	abc	10140	ab	5	b	151	b	22	c	10.24	b	0.111	b	10	d	0.095	a	12	a	0.360	b	3317	b	4.13	abcd	19	a
H180	5436	abc	415	a	3571	ab	687	a	34	a	4	ab	9395	ab	42	ab	222	ab	298	ab			0.194	ab	17	abcd	0.082	a	11	a	0.678	ab	6714	abc	3.32	c	41	a
H180-SSUK	17368	e	700	abc	13140	d	1333	b	72	bcd	6	ab	17186	c	152	d	363	c	627	e			0.462	c	23	bc	0.379	bc	23	bcd	2.352	d	11795	d	4.77	bd	50	a
H240	5673	abc	492	ab	3752	ab	825	ac	41	abc	3	a	8408	a	49	ab	256	abcd	313	ab			0.201	ab	17	abcd	0.259	abc	10	a	0.914	ab	7246	abc	3.72	abc	23	a
H240-SSUK	17806	e	692	abc	13768	d	1445	b	74	cd	6	ab	18309	cd	156	d	353	cd	638	e			0.465	c	22	abc	0.385	c	24	cd	2.554	d	10700	ad	4.25	abcd	26	a
P300	6098	ab	490	ab	3786	ab	689	a	48	abc	6	abc	9083	a	51	ab	222	ab	285	ab			0.207	ab	15	abd	0.168	abc	11	a	0.910	ab	7216	abc	3.67	abc	34	a
P300-SSUK	12194	de	1057	d	9916	cd	1539	b	106	d	14	e	23065	d	144	d	359	c	341	a	11.40	b	0.414	cd	24	c	0.242	abc	29	d	2.730	d	10826	ad	5.25	d	26	a
P400	6732	abd	796	bcd	4334	ab	1236	bc	97	d	11	de	11256	ab	75	ac	282	acd	195	bd	11.23	b	0.216	ab	19	abc	0.057	a	15	a	1.119	abc	8820	acd	4.44	abcd	35	a
P400-SSUK	10056	bd	888	cd	7240	ac	1374	b	92	d	13	e	18486	cd	111	cd	296	acd	281	ab	11.43	b	0.297	ad	20	abc	0.058	a	23	bcd	1.961	cd	9378	acd	4.61	abd	33	a
SSES	3564	ac	597	abc	2609	ab	607	a	31	a	7	bcd	10050	ab	35	ab	228	abd	315	ab	2.83	a	0.199	ab	16	abcd	0.152	ab	13	a	0.571	ab	6890	abc	4.01	abcd	19	a
SSES-SSUK	7541	abd	438	a	5422	ac	686	a	37	ab	5	ab	14703	bc	65	ac	208	ab	361	a			0.281	a	15	abcd	0.151	ab	16	ab	1.347	ac	6008	bc	3.50	ac	30	a
SSUK	4515	abc	471	ab	4081	ab	674	a	45	abc	9	cd	18563	cd	56	abc	183	ab	141	cd	10.04	b	0.210	ab	14	ad	0.062	a	22	bc	1.315	ac	4502	b	4.60	abd	23	a

4.3.3.3 Accumulated elements in the grains

Few significant differences could be seen in macronutrients in grains grown with the treatments compared to the control soil (Table 0-7 and Table 0-8). Some nutrients like K were significantly accumulated in the grains but after the second season no benefit was shown for amendments with chars.

Contrarily to what we expected, P not only did not increase in grains, but it didn't show any significant differences for any of the seasons and thus neither for Phosphorus (P) uptake (Table 0-9). However, when contrasting P uptake with the amount of available-P applied at the beginning of the experiments through the amendment, PUE results were changing from season to season. Some amendments showed a negative PUE when contrasted to control soil which had lower available P (Table 0-1, Chapter 3) whilst others did increase it. From all the amendments, P400 gave the highest improvement of PUE, 192.2% first season and 271.2% the second. However, this is based on the available P analysed when applied and doesn't take into account the increment over time. For this reason, another PUE has been calculated for comparison, referring the P uptake in season 2 to the available P present after first harvest, in this case PUE for P400 season 2 is 28.4% as there is 10 times more available P in soil. The following treatments improved PUE in both seasons: H180, P400, SS_{ES}, P300-SS_{UK} and SS_{ES}-SS_{UK}, although the effect decreased in the second season for all of them Table 0-9. The positive PUE are considerably higher than those obtained for mineral fertilisers, supporting the idea that some organic amendments could provide more P-effective (Schröder *et al.*, 2011). However, there were also negative results for PUE possibly linked to the available-P shift in soil explained above related to acidification of the soil as P400 is the one that obtained the best result. (Zafar, Rizwan and Shahid, 2017) used single super phosphate, rock phosphate, composted rock phosphate and poultry manure, which maximum PUE was 18% for the latter applied at 90 kg P ha⁻¹ to grow spring wheat. This rate was considerably higher than ours, being 17.7 kg available-P ha⁻¹ the highest amount in soil after first harvest, while P uptake values are similar in order of magnitude (1.8-21.3%). Nonetheless, their grain productive reached a maximum of 2226 kg ha⁻¹ indicating that P-mineral fertilisers despite having a lower PUE still obtain better results.

As shown in Table 0-10 and Table 0-11, there are no significant differences of Cu and Zn between treatments. However, Fe increased significantly compared to control soil in the first season for H240-SS_{UK}, and in the second for H180-SS_{UK}, H240, H240-SS_{UK}, P300-SS_{UK}, P400 and P400-SS_{UK}. Mn increased significantly in the first season for H240-SS_{UK}, SS_{ES}-SS_{UK}. Overall, the concentration of Fe in grains reduced after the second season compared to the first but it was still being significantly higher than with the control soil.

Cd did not differ from the control after the first season (Table 0-12), but after the second season it significantly increased for SS_{ES} and SS_{ES}+SS_{UK} (Table 0-13). Pb content in the grains was higher for P400 and P400-SS_{UK} in the first seasons being the combined one higher. For Hg, no significant differences were found on the first season to control soil, but in the second pyrochars P300 and P400-SS_{UK} significantly increased its concentration in the grains.

Table 0-7 Concentration of nutrients in grains extracted through acid digestion, mg/kg (First season, only highest rates).

	P		K		Ca		Mg		Na		B	
Control grain	3329.32	a	4278.37	a	531.84	a	1268.39	a	15.61	a	1.16	a
Control soil	3783.80	a	5538.84	ab	589.00	a	1285.15	a	26.26	ab	1.89	ab
H180	6033.80	a	7328.84	c	800.34	ab	1830.65	a	29.36	ab	2.46	b
H180-SSUK	4683.80	a	6868.84	bc	872.34	ab	1508.65	a	40.56	ab	2.46	b
H240	4293.80	a	6708.84	bc	707.34	ab	1351.15	a	30.76	ab	2.13	ab
H240-SSUK	4808.80	a	7043.84	bc	864.84	ab	1558.65	a	42.11	ab	2.97	b
P300	4928.80	a	6808.84	bc	888.84	ab	1513.65	a	42.41	ab	2.13	ab
P300-SSUK	3528.80	a	6708.84	bc	725.84	ab	1341.15	a	37.21	ab	2.25	ab
P400	5008.80	a	7368.84	c	634.84	a	1767.15	a	25.81	ab	2.29	ab
P400-SSUK	4338.80	a	6898.84	bc	838.84	ab	1490.15	a	51.11	b	2.86	b
SSES	5903.80	a	7908.84	c	879.34	ab	1846.65	a	59.36	b	2.91	b
SSES-SSUK	5418.80	a	8158.84	c	1038.84	b	1823.15	a	38.71	ab	3.02	b
SSUK	3533.80	a	6698.84	bc	691.84	ab	1308.15	a	28.31	ab	2.09	ab

Table 0-8 Concentration of nutrients in grains extracted through acid digestion, mg/kg (Second season, only highest rates).

	P		K		Ca		Mg		Na		B	
Control grain	3329.32	a	4278.37	a	589.00	a	1268.39	a	15.61	a	1.16	a
Control soil	4839.32	abc	6153.37	b	579.00	a	1472.39	ab	7.53	a	2.16	abc
H180	5889.32	bc	7398.37	bc	848.50	a	1765.89	abc	37.66	bc	2.26	abc
H180-SSUK	4574.32	abc	6493.37	b	752.50	a	1621.89	abc	47.31	c	2.38	bc
H240	4379.32	ab	6268.37	b	653.00	a	1445.39	ab	19.91	ab	1.96	abc
H240-SSUK	4609.32	abc	6363.37	b	633.00	a	1603.89	abc	22.26	ab	2.16	abc
P300	4204.32	ab	6238.37	b	594.50	a	1469.39	ab	24.51	ab	1.62	ab
P300-SSUK	3989.32	a	6258.37	b	738.00	a	1455.39	ab	24.46	ab	1.99	abc
P400	4549.32	abc	6563.37	bc	520.00	a	1637.39	abc	18.91	ab	1.87	abc
P400-SSUK	4104.32	ab	6293.37	b	728.00	a	1457.39	ab	23.91	ab	1.87	abc
SSES	6274.32	c	8083.37	c	799.50	a	2004.89	c	21.11	ab	2.96	c
SSES-SSUK	4929.32	abc	6873.37	bc	812.00	a	1786.89	bc	18.71	ab	2.53	bc
SSUK	4324.32	ab	6468.37	b	722.00	a	1595.89	abc	16.51	ab	2.96	c

Table 0-9 Grain P uptake (kg/ha) and PUE for both seasons.

Sample	Grain P uptake season 1 (kg/ha)		Grain P uptake season 2 (kg/ha)		Available P applied through fertiliser (kg/ ha)	PUE 1 st season (%)	PUE 2 nd season (%)	Available P in soil after first harvest (kg/ ha)	PUE 2 nd season % Corrected *
Control soil	7.6	a	9.7	abc	0				
H180	9.3	a	11.9	bc	2.2	77.9	102.3	6.0	37.4
H180-SS _{UK}	12.8	a	7.4	abc	2.6	171.6	-15.9	16.2	-2.6
H240	6.9	a	9.0	ab	2.3	-27.5	-26.7	4.7	-13.1
H240-SS _{UK}	7.5	a	12.2	abc	3.3	-2.4	77.6	11.3	22.5
P300	6.8	a	10.7	ab	0.4	-178.4	237.8	4.6	22.7
P300-SS _{UK}	9.5	a	10.0	a	1.5	124.5	23.7	17.1	2.1
P400	8.8	a	11.4	abc	0.6	192.2	271.2	6.0	28.4
P400-SS _{UK}	10.1	a	8.7	ab	2.5	98.7	-38.1	17.7	-5.5
SS _{ES}	11.4	a	15.9	c	4.9	78.7	127.7	12.1	51.1
SS _{ES} -SS _{UK}	16.1	a	13.3	abc	6.9	123.7	52.2	15.6	23.1
SS _{UK}	7.4	a	11.3	ab	0.7	-31.3	252.2	5.5	30.5

Available-P analysed through Olsen Method, discounting available-P in control soil.

*corrected based on available P after first harvest just from the amendment discounting available P in control soil

Values in column followed by the same letter are not significantly different (p = 0.05) using Tukey HSD test with Statistica program.

Table 0-10. Concentration of elements in grains extracted through acid digestion, mg/kg (First Season, only highest rates).

First season	Fe		Cu		Mn		Zn		Cr		Al	
Control grain	41.55	ab	5.48	a	25.86	ab	23.32	a	1.73	b	0.75	ab
Control soil	28.18	a	5.38	a	15.74	a	18.77	a	-1.05	a	-0.62	ab
H180	49.93	ab	6.88	a	41.39	abc	36.60	a	-0.78	ab	-0.17	ab
H180-SSUK	43.58	ab	6.80	a	40.69	abc	32.35	a	-1.02	a	-0.93	ab
H240	38.08	ab	5.98	a	25.99	ab	31.85	a	-1.35	a	0.37	ab
H240-SSUK	60.08	b	6.69	a	45.74	bc	49.25	a	-0.48	ab	-1.04	ab
P300	51.88	ab	6.30	a	23.17	ab	23.70	a	-0.09	ab	0.64	ab
P300-SSUK	43.13	ab	5.19	a	27.87	ab	24.30	a	0.22	ab	0.95	ab
P400	42.83	ab	4.86	a	20.26	ab	19.31	a	-0.13	ab	1.26	b
P400-SSUK	52.73	ab	6.18	a	26.89	ab	24.80	a	-0.34	ab	1.10	ab
SSES	41.88	ab	6.89	a	38.49	ab	30.80	a	-1.38	a	-0.65	ab
SSES-SSUK	35.08	ab	7.60	a	67.14	c	35.95	a	-1.43	a	-2.50	a
SSUK	41.88	ab	5.22	a	32.86	ab	38.10	A	-1.23	a	-1.53	ab

Table 0-11. Concentration of elements in grains extracted through acid digestion, mg/kg (Second Season, only highest rates).

Second season	Fe		Cu		Mn		Zn		Cr		Al	
Control grain	41.55	c	5.48	a	25.86	abc	23.32	a	1.73	a	0.75	ab
Control soil	19.05	a	5.50	a	23.46	abc	19.82	a	0.17	a	-2.07	a
H180	26.55	ab	5.81	a	27.81	abc	20.92	a	-0.50	a	-3.56	a
H180-SSUK	39.50	c	6.65	a	22.39	ab	22.27	a	-0.24	a	-2.81	a
H240	34.10	bc	6.14	a	24.17	abc	25.90	a	-0.30	a	-0.62	ab
H240-SSUK	29.90	abc	6.25	a	35.16	bc	28.82	a	-0.42	a	-1.85	a
P300	31.50	abc	4.93	a	17.39	a	14.82	a	-0.15	a	-2.36	a
P300-SSUK	39.90	c	5.08	a	24.21	abc	19.99	a	1.70	a	-3.15	a
P400	32.45	bc	5.41	a	18.97	ab	18.74	a	-0.22	a	-2.66	a
P400-SSUK	35.35	bc	4.76	a	21.43	ab	18.88	a	0.10	a	-1.90	a
SSES	23.05	ab	5.11	a	39.13	c	28.25	a	-0.36	a	-1.83	a
SSES-SSUK	25.90	ab	5.16	a	34.16	bc	22.67	a	-0.20	a	-0.15	ab
SSUK	25.25	ab	5.62	a	28.01	abc	27.87	a	0.08	a	5.99	b

Table 0-12. Concentration of heavy metals in grains extracted through acid digestion mg/kg (First Season, only highest rates).

First season	As		Cd		Pb		Hg		error	Co	
Control grain	0.00	a	0.03	ab	0.00	ab	-0.01	0.00	a	0.03	a
Control soil	0.02	ab	0.03	a	0.00	ab	0.48	0.18	bc	0.02	a
H180	0.17	c	0.05	ab	0.02	ab	0.19	0.05	abc	0.02	a
H180-SSUK	0.09	abc	0.04	ab	0.01	ab	0.07	0.01	ab	0.05	a
H240	0.09	abc	0.04	ab	0.02	ab	0.03	0.00	ab	-0.01	a
H240-SSUK	0.07	abc	0.05	b	0.02	ab	0.01	0.00	ab	0.02	a
P300	0.06	abc	0.04	ab	0.00	ab	0.14	0.01	abc	0.00	a
P300-SSUK	0.03	ab	0.05	ab	0.00	ab	0.58	0.25	c	0.01	a
P400	0.06	abc	0.03	ab	-0.01	a	0.15	0.07	abc	-0.01	a
P400-SSUK	0.05	abc	0.04	ab	0.04	b	0.02	0.02	ab	0.03	a
SSES	0.13	bc	0.04	ab	0.02	ab	-0.05	0.03	a	0.03	a
SSES-SSUK	0.07	abc	0.04	ab	0.01	ab	0.21	0.14	abc	0.17	b
SSUK	0.03	ab	0.04	ab	0.02	ab	0.05	0.02	ab	0.03	a

Table 0-13 Concentration of heavy metals in grains extracted through acid digestion mg/kg (Second Season, only highest rates).

Second season	As		Cd		Pb		Hg		error	Co	
Control grain	0.02	a	0.03	abc	0.00	a	-0.01	0.00	a	0.03	a
Control soil	0.01	a	0.02	a	-0.01	a	-0.01	0.03	a	0.00	a
H180	0.09	a	0.03	abc	0.00	a	0.19	0.06	abc	0.01	a
H180-SSUK	0.06	a	0.03	abc	0.00	a	0.01	0.02	ab	0.02	a
H240	0.10	a	0.03	abc	0.00	a	0.14	0.07	abc	0.01	a
H240-SSUK	0.07	a	0.03	abc	-0.01	a	0.04	0.02	ab	0.03	a
P300	0.08	a	0.03	abc	-0.02	a	0.39	0.13	c	0.00	a
P300-SSUK	0.06	a	0.03	abc	-0.01	a	0.16	0.02	abc	0.02	a
P400	0.07	a	0.02	a	-0.01	a	0.05	0.01	ab	0.00	a
P400-SSUK	0.05	a	0.03	abc	-0.01	a	0.27	0.09	bc	0.01	a
SSES	0.10	a	0.04	bc	-0.02	a	0.06	0.04	ab	0.03	a
SSES-SSUK	0.05	a	0.05	c	-0.03	a	0.01	0.02	ab	0.04	a
SSUK	0.04	a	0.03	ab	0.00	a	-0.02	0.02	a	0.02	a

4.4 Discussion

The Zucconi test conducted at the start of the pot experiment provided an insight on the phytotoxicity of the materials (Benavente *et al.*, 2018). Higher temperatures of pyrolysis reduced the phytotoxicity of SS significantly, which confirmed our hypothesis. However, the results of the pot experiment on the germination of the seeds proved that the Zucconi test didn't emulate the conditions when the amendments were mixed with the soil. This test creates an artificial scenario in which the seeds are permanently immersed in the water solution with no interactions with soil. Nonetheless, the Zucconi test indicated that with exception of pyrolyzed sludge, these materials including hydrochars should therefore not be used as direct growing media and that the amount added to the soil must be well studied previously to their application.

Regarding the yield, the lack of clear differences across treatments may have been obscured by the high variability in the data and the relative low number of samples, as was also reported by (Poorter, Fiorani, *et al.*, 2012). We also noted that the yield of spring wheat grown was low and did not surpass 3.1 t/ha recorded in the second season (**Error! Reference source not found.**). The crop had to be sprayed on multiple occasions, to overcome *Septoria tritici* and powdery mildew diseases, the latter being particularly difficult to remove in the first season. The limited space available for the roots to grow (Poorter, Bühler, *et al.*, 2012), the conditions in a greenhouse compared to field experiments (Zabihi *et al.*, 2011) and pest issues (Conner, Kuzyk and Su, 2003) can cause a reduction of yield in spring wheat, so we partially attribute this to the low productivity and great variability between samples. The reduction of number of leaves developed on day 30th after sowing compared to the first season could serve as an indicator of this stress.

Despite the little differences among the yield results, the acid digestion showed the effect of the treatments and temperature selected. Nonetheless, to obtain a better evaluation of how the plant reacted to the different treatments it is important to understand first what happened through the thermal treatments and the subsequent changes of the amendments in the soil.

As indicated previously in Table 0-4, increasing temperatures of pyrolysis between 300-500°C and hydrothermal carbonisation concentrated nutrients, except N, trace metals and heavy metals in the raw materials (Hossain *et al.*, 2011a; Méndez *et al.*, 2012). The possible reason for mercury to be below the detection level in the pyrochar obtained at 400°C may be that mercury's boiling point is 356.7°C (Sedlar *et al.*, 2015). Therefore, when applying these chars at the same rates as their feedstock (SS_{ES}), comparatively, more elements to the soil mixture were added which was reflected in our soil analysis for the initial conditions (Table 0-5). However, the results from the second season (Table 0-6) were not as we expected. At first our hypothesis was that total elements would remain the same in soil or reduced due to their absorption by the plant or leaching through the column, but our data showed a general increment in soil (Table 0-6). In Chapter 3, we covered the increments in total P, Al and Fe after the second season (Table 0-2). We suspect the same reason can be applied to the rest of the elements presented in this study. We suggest that a change in exposed surface area could explain why more total elements are detected in the acid digestate of the soil sample of the second season.

The increment of Total P has been proved by Chen *et al.*, (2021) through comparison of an artificially chemical aged char doped with P. Surface area has been found previously to change over time as the char stays in the soil (Lehmann and Joseph, 2015), increasing through the reduction of particle size. Char applied as dust <0.42 mm to pellet, >2 mm, has been reported to increase 2 to 3 orders mm²/g (Spokas *et al.*, 2014) and the appearance of new micropores as labile C is consumed (Dong *et al.*, 2017). Nonetheless Chen *et al.*, (2021) suggests that eventually the char may develop a smooth surface after years of aging, reducing surface area and producing changes in P availability. Therefore, it is reasonable to suspect that changes in structure limit the effectiveness of acid digestion analysis (Ma and Matsunaka, 2013). The higher variability in the second season between samples and replicates could be also related to the different degree of aging of the chars (Gronwald *et al.*, 2016) and thus plant and soil interactions (McBride, Richards and Steenhuis, 2004).

Despite the ambiguous yield productivity results (**Error! Reference source not found.**), there were some differences regarding the elements accumulated in the grains among treatments from season to season (Table 0-7 to Table 0-13). Despite the high concentration of mineral nutrients in soil after the amendments reported in Table 0-5 and Table 0-6, the analysis indicated that the grains didn't accumulate all elements significantly (Table 0-7 and Table 0-8). When comparing Marles, (2017) expected values of nutrients in wheat grains to ours, SS_{ES}+SS_{UK} gave a 30% higher concentration in the first season for Ca (800 mg /kg) and 12-10% more K (7300 mg/kg) during first sand second season of SS_{ES} for. Mg and P remained in the ranges: 2000-2200 mg/kg and 2500-9100 mg/kg respectively. Sewage sludge amendments proved to enrich wheat grains with Fe specially after the second season (Table 0-10 and Table 0-11) in soil amended with hydrochars and pyrochars, which confirmed our Hypothesis. Nonetheless, despite the increase in soil total Fe the second season (Table 0-6), the concentration in grains did not increase and was generally lower than the previous season (Table 0-11). It is possible that the soil pH changes (previously reported in Chapter 3, Figure 0-4) and plant response could explain these results. In our study soil Fe was significantly concentrated in the soil in the second season along with Al and Mn. When Al is added to soil, it has been reported that crops prevent it from entering in the plant system via the exudation of organic anions through the roots (Austruy *et al.*, 2014) while Fe and Mn are absorbed (Mariano and Keltjen, 2003). In the case of spring wheat this effect has been reported by (Papernik *et al.*, 2001) to occur through malate possibly applicable to our case. In our present study Fe and Mn were accumulated significantly in the wheat grain while Al was below the detection limits in the grain (Table 0-10 and Table 0-11).

Fe-P and Ca-P bonds have been found to increase in the chars during pyrolysis and Hydrothermal Carbonisation of sewage sludge (Huang and Tang, 2016a). P liberated from Ca-P through organic acids could explain the greater P availability after season 1 reported for spring wheat in our experiment (Chapter 3, Figure 0-6). Given the reduction of pH after the first season (Chapter 3, Figure 0-4), Fe would have not started forming Fe-P compounds but Al probably did given the pH range Figure 0-7 (Havlin *et al.*, 2016). Thus, it is possible that the lower pH in

combined amendments could have reduced the phytoavailability of P, reducing thus their appearance in grain in season 2 (Table 0-11). Furthermore, not only organic acids have been reported to be released to limit the intake of Al but also phosphates (Mariano and Keltjen, 2003). Despite P is absorbed by the plant its concentration is not constant in the plant tissue (Shane, Lambers and Cawthray, 2008). This would partially agree with the higher concentration of Total P reported in soil in the second season (Chapter 3, Table 0-2). No explanation can be given to the reduction of Fe accumulation in the second season grains compared to the first season as pH remained over the area of Fe-P fixation in soil Figure 0-7. (Table 0-11). Phosphates are also known to immobilize Zn and Pb in soil which has been reported to occur only in cultivated soil (Austruy *et al.*, 2014). This could provide an explanation to the non-significant values of Zn, Pb and P, compared to control soil for both seasons. These are suggestions based purely on literature and thus further research into this is required to elucidate the mechanisms behind these unexpected results.

Finally, despite none of the materials surpassed the concentration of metals limits in the sewage sludge for in agriculture soil use on initial conditions (Table 0-4)(Annex IB, EU Directive 86/278/EEC), it is worth to acknowledge that in the case of this study, the use of chars would be legally restricted given the values of heavy metals obtained in soil after two seasons (Annex IA,EU Directive 86/278/EEC). The high level of Zn in soil (limit 150 mg/kg in pH_{soil}<7, 300 mg/kg in pH_{soil}>7 Annex IA,EU Directive 86/278/EEC), indicated that at the highest rates only SS_{UK} on its own could be applied and none of SS_{ES}, their derivatives and combinations (Table 0-6, SS_{UK} Zn=141 mg/kg) in Europe, in the UK DEFRA's limit for Zn is 200 (mg/kg) which would include P400 on its own (Table 0-6, P400 Zn=195 mg/kg)(Department of the Environment, 1996). Cu, Fe, Mn and Zn, in grains were found in accordance with the expected ranges (Marles, 2017). Moreover, heavy metals in none of the grains exceeded the maximum permissible food safety levels (European Commission, 2006). Levels remained below >0.1 mg/kg for Cd, 0.2 mg/kg for Pb and 0.5 mg/kg for Hg. Only Hg in the first season grown with P300+SS_{UK} at the highest rate showed a value above the limit 0.58 mg/kg with the greatest error in the table for mercury, 0.25 (Table 0-12).

Wang et al., (2016) reported that Hg concentration increased with increasing soil Fe and Mn and decreasing soil pH, probably due in part to Hg sorption of solid phase Fe and Mn oxides or hydroxides (Thanabalasingam and Pickering, 1985; Nguyen *et al.*, 2013; Kim, Lee and Park, 2014). However, in this case it might not be related as other treatments indicated a greater drop of pH in the second season and mercury levels are there under the limit Table 0-13.

Hydrochars and pyrochars are known to influence soil microbiota (Lehmann and Joseph, 2015). In the present research, no analysis was performed to evaluate changes in root morphology or P scavenge mechanisms, to quantify the effects that pyrochars and hydrochars might have had on the rhizosphere. This could be initially addressed through a comparison of the fine root diameter, specific root area, root tissue density and root phosphatase activity, determined through a photometric microplate assay (Lugli *et al.*, 2020). To study the arbuscular mycorrhizal (AM) or other fungi colonisation, a PCR and analysis could be useful, possibly comparing the expression of P transporter genes, hyphal length density and the mycorrhizal response, contrasting P uptake with the dry matter weight of AM (Grace, 2007). Total P variations in the soil solution and Total P up-taken by the plant could also be studied using the methods described in (Kirk, Santos and Santos, 1999) and (HEDLEY, WHITE and NYE, 1982) by artificially isolating the roots from the soil mixture using a mesh or a compartment and digesting separately the samples using ICP-MS. This could be an interesting area of research to gain a better understanding on P uptake by the roots affected by char amendments. However, most of these methods are destructive and difficult the continuity of the experiment for several seasons.

4.5 Conclusions

From our research we draw the following conclusions:

- Temperature had a decisive role on the concentration of the elements present in SS_{ES} feedstock.
- The Zucconi test indicated that all thermal treatments reduced the phytotoxicity of an anaerobic digested sewage sludge sample, best through pyrolysis at higher temperatures. However, it also indicated that

the sludge and derived hydrochars should not be used as direct growing media but mixed in the soil.

- Sewage sludge amendments didn't have a significant effect on grain yield during the 2 year experiment which rejects the hypothesis.
- The variability between replicates becomes greater over time, especially when SS_{UK} is added in combined amendments.
- Sewage sludge and derived amendments didn't increase Zn in grains but proved to enrich them with Fe, providing a potential solution to malnutrition.
- The greater concentration of heavy metals after thermal treatments could limit the use of all of the chars due to the Zn accumulation in soil above legal limits. At the highest rates only SS_{UK} on its own could be applied and none of SS_{ES}, their derivatives and combinations in Europe while in the UK P400 would be also acceptable.

CHAPTER 5: INTEGRATED DISCUSSION

Summary: This chapter contains a synthesis of the research on thermal treatments used to produce alternative P-fertilisers from sewage sludge and their performance when applied to grow two seasons of spring wheat, presented in the previous chapters. This thesis findings are presented according to the objectives in order to answer all the hypothesis. The effect of the thermal treatment types and the temperatures selected, the efficacy of the derivatives as fertilisers, their impact on soil conditions and the environmental risk regarding nutrient balance and heavy metal accumulation in the soil and the wheat grains for both seasons. The study limitations are addressed and complemented with a list of suggestions for future work. Finally, contributions to knowledge are highlighted.

Highlights:

- Summary of impact of thermal treatments type of process and temperature selected on structural and physical-chemical properties on sewage sludge;
- Statement of efficacy of thermal treatments of sewage sludge to improve spring wheat production;
- Discussion of amendments effect on soil properties when added on their own and in combination with untreated sewage sludge;
- Discussion of sewage sludge limitations as alternative P-fertiliser based on the environmental risk and P use efficiency results;
- Summary of the intellectual contributions to knowledge of this research.

5.1 Discussion of research finding

As agricultural production and usage of fertilisers are expected to increase, alternative fertilisers to P mineral rock are required to sustain and ensure future food demand. Being a source of nutrients, sewage sludge has been assessed as a possible source of available P for farmland. This PhD has evaluated the effectiveness of two sludge samples, one oven dried and thermally transformed onto pyrochars through pyrolysis and onto hydrochars through hydrothermal carbonisation, and the other applied as purchased from a local supplier, which represents an example of what is currently an available option for farmers. The analysis of the soil changes, grain yield and grain quality on different combinations of amendments and rates has proven the potential use of these thermal treatments and their limitations which provide useful information for future work.

5.2 Thermal treatments pyrolysis and hydrothermal carbonisation differences.

The first objective of this project was to evaluate the effects of temperature after thermal processing on the physical-chemical properties of sewage sludge.

Through the characterisation it is clear that the temperatures selected had a significant effect on the porosity, carbon stability, the labile organic matter content (Chapter 3) and the nutrient content (Chapter 4 & 5). While the type of process had a significant greater effect than temperature to produce a material from the same feedstock, with differences in functional groups, adsorption capacity and Cation Exchange Capacity (Chapter 3). These factors were bound to affect the availability of nutrients and other elements concentrated in the chars after thermal treatments (Hossain *et al.*, 2011a; Huang and Tang, 2015, 2016a).

The changes in CEC, surface area and adsorption capacity that favoured hydrochars to pyrochars (Chapter 2) may have been the reason for a greater P availability on initial conditions of hydrochars (Table 0-1). The greater reduction of CEC after pyrolysis compared to hydrochars has also been reported by Breulmann *et al.*, (2017) and has been related to a reduction of functional groups, specifically carboxylic groups (Faria *et al.*, 2018b) which was reported in Chapter 2 for pyrochars but not hydrochars (Figure

0-4). In the characterisation, hydrochars gained surface area, increased carboxylic groups and reduced significantly less CEC after thermal treatments H180-4 (-32%), H240-4 (-52%), P300-1 (-75%), P400-1 (-79%) from 193.7 cmol⁺/kg.

As a result, data showed that hydrochars contained greater amount of available P compared to pyrochars (Chapter 3, Table 0-1). This has not been studied before for the same feedstock on both types of thermal treatments, for sewage sludge or the type of biomass (Chapter 1, Table 0-3). Breulmann *et al.*, (2017) extracted P using resin strip anion exchange membranes from different samples of sludge thermally treated and concluded that both pyrolysis and HTC reduced availability of P. This has been confirmed in Chapter 3.

Huang and Tang, (2015) suggested that the carbon stabilization would have a direct effect in availability of P after both processes. In Chapter 2 (Figure 0-5) it was estimated also for the first time for the same feedstock that pyrochars had higher C stability than hydrochars. Studies have shown this on hydrochars (Kalderis *et al.*, 2014; Peng *et al.*, 2016) and pyrochars (Méndez, Terradillos and Gascó, 2013) separately. However, the present study confirms this when comparing chars with the feedstock but proves that C stability is enough for chars to provide significantly different outcomes on available-P once aged in the soil. Moreover, as reported in Chapter 3 (Table 0-1) the most stable char (P400) contained a higher amount of available-P than P300, as previously seen in (Hossain *et al.*, 2011a) where the reduction of available-P would occur in pyrolysis after 400°C, while in HTC is gradual.

It was evident nonetheless, that the stabilization of sludge would be linked to the capability of the chars to act as slow fertilisers (Huang and Tang, 2015). On initial conditions all the chars provided a significantly lower amount of available P compared to the feedstock for treatments on their own (Appendix, Table A 2). According to our results, the mixture with SS_{UK} may have speeded the degradation of the chars from the application until season 1, increasing P availability for combined amendments 185%-611% compared to treatments on their own for the highest rates 69%-327%. As stated in Chapter 3 available P continued to increase until season 2, for treatments on their own it was 10-60% second season, compared to a maximum increase of 21% and a maximum reduction of 27% in combined from season 1 to season 2 (Figure 0-6). The statistical analysis indicated that despite the significant differences between

samples of hydrochars and pyrochars (Table 0-1), no differences could be found once aged in the soil between chars (Table A 2). Thus, this project quantifies for the first time the importance of testing P availability changes of the chars of both processes in a crop experiment and highlights that a characterisation study can't be used to predict available P levels alone. The concentration of available-P in the feedstock P proved to set the roof limit to the quantity of available P that could be reached in two seasons by the amendments, and thus the quantity of application to directly affected its result.

One of the advantages to thermally treating sewage sludge was the reduction of the phytotoxicity as shown in Chapter 4. This was only achieved by pyrolysis and in particular at higher temperatures, thus the first hypothesis would be confirmed for the germination phase. This contradicts previous research, Álvarez *et al.*, (2017a) found hydrochars from sewage sludge obtained around 200°C to be phyto-estimulant (GI over 100%) to the growth of *L. Perenne* while pyrochar from sewage sludge at 600 °C were moderate phytotoxic 50-80%. Thus, the results depend on the seed and feedstock used (Gascó *et al.*, 2016). Nonetheless, during the pot experiment a different outcome was obtained. For each process the treatments with lower temperatures established all the seeds on both seasons, while P400-1 and H240-4 reduced it to 87.5% like the feedstock. Therefore, pyrolysis of the feedstock studied may benefit the germination stage (first 2 days) but won't ensure the emergence of all of the seeds (Chapter 4, Table 0-2). With the data gathered, it is unclear why these results at the glasshouse were obtained, nor how generic these results would be as only one soil type was tested. It is unlikely that the changes in surface area, porosity and adsorption capacity, that were expected to improve water retention in soil improving soil conditions (Méndez, Terradillos and Gascó, 2013), had an effect on this outcome, as this would favour hydrochars over pyrochars. Nor can be linked the differences on organic matter content, available-P or low carbon stability as both chars produced at lower temperature grew all the seeds for 2 seasons compared to feedstock. Neither can be related to the content of Zn in the chars (Chapter 4, Table 0-4) or in the soil mixture (Table 0-5), suggested by (McBride, Richards and Steenhuis, 2004) to be the cause of phytotoxicity in sewage sludge to grow red clover (*Trifolium pratense* L.).

Ultimately, despite these differences in the emergence stage among amendments (Table 0-2), the plants that did reach the maturity compensated the productivity as no

significant changes in yield per pot were observed. Therefore, the Zucchini test had some limitations but served as a screening test for initial reference.

5.3 Efficacy of the pyrochar and hydrochar as fertiliser.

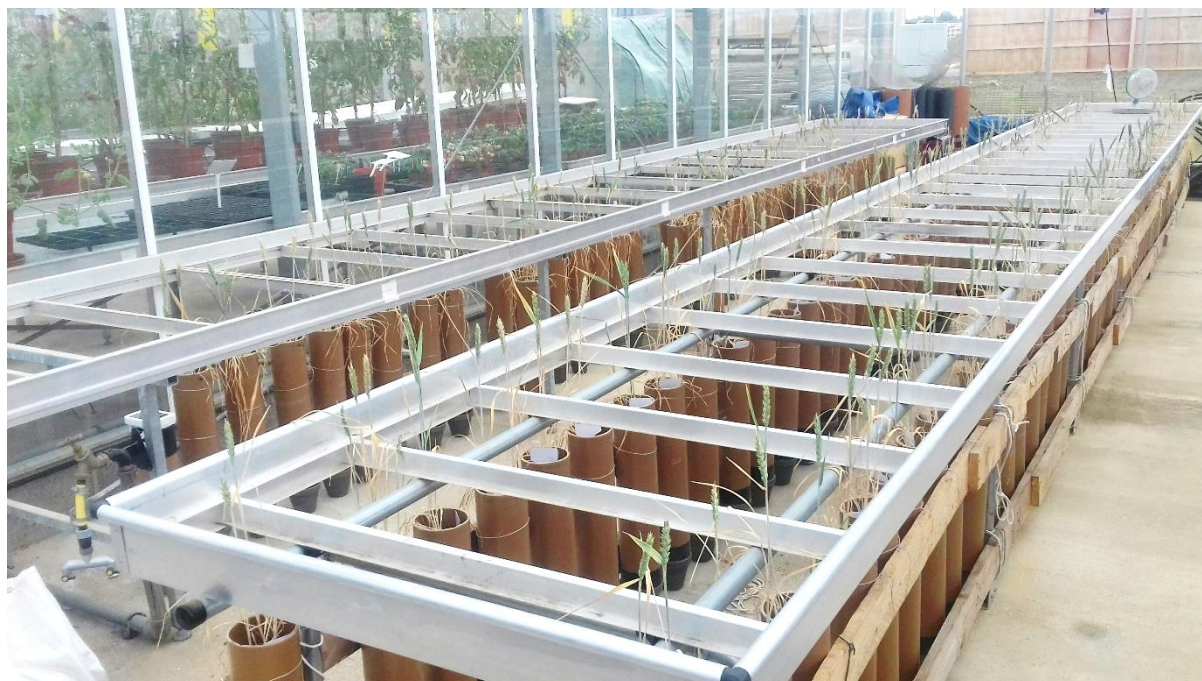


Figure 0-1 Pot experiment, second season.

Data on grain yield as shown in Chapter 4, **Error! Reference source not found.** indicated no significant differences given the large variability of the results from one replicate to the other (Figure 0-3). Thus, the two following hypothesis (2-a, 2-b) that stated that carbon stability and combined amendments would enhance spring wheat yield compared to control soil were rejected. The accumulation of nutrients in the soil did increase directly with the application rates (Chapter 3, Table 0-2) and although the grains on the lower rates couldn't be tested, a significant increase was quantified for the highest rates compared to the control soil (Chapter 4, Table 0-5, and Table 0-6). Therefore, this only partially confirms our hypothesis 2-c. for the highest rates.

Only one application was carried out without additional amendments so to see the effect over time of a specific dose, similarly to other studies on sewage sludge derivatives. It was yet unknown the effect of such materials applied yearly to P availability and crop productivity as efforts are put in determining first the best rate for each case and after, the durability of the effects (Table 0-4).

No grain yield differences from season 1 to season 2 it could be seen, but lower number of tillers and leaves as shown in Chapter 4, Table 0-3, which could be an indicator of stress. (Racioppi et al., 2020).

Through the characterisation of the raw materials, it was confirmed that P availability was reduced after thermal treatments (Chapter 3, Table 0-1) and that in turn Total P was concentrated in the chars as shown in (Chapter 3, Table 0-2). Despite that the rates chosen didn't provide enough P to increase the P soil index, during the length of the experiment, an overall increase of available P directly related to the amount added to the soil was expected for the second season as seen in Faria *et al.*, (2018) (Table 0-4). The hydrochars on their own managed to significantly increase the available P at the highest rates from initial conditions compared to pyrochars which on their own didn't show any improvement compared to control soil. This initial difference between pyrochars and hydrochar might be related to the higher loss of available P after pyrolysis as described in Chapter 3, Table 0-1. However, available P didn't show a consistent increment for combined amendments. A possible explanation to second season results on P availability has been suggested through the effect of the aging and the interactions of P, Fe and Al concentration in soil with the plant. The increase of EC (Chapter 3, Table 0-1) and increment of Total P, Fe Al (Chapter 3, Table 0-2), heavy metals and other elements (Chapter 4, Table 0-4) indirectly proves changes in the amendments from initial conditions as they are the preliminary source of these variables.

In acidic soils, phosphates are bound to be weakly bonded to Al and Fe oxides making them available to crops. However, progressively the P that is not taken up by the plant is likely bound to Al and Fe re-precipitating and producing highly crystalline Al-P and Fe-P (Ch'Ng, Ahmed and Majid, 2014). Al and Fe have been reported before to be adsorbed by pyrochars and compost that help to raise the pH of the soil, so that the phosphate remains unfixed to these elements (Ch'Ng, Ahmed and Majid, 2014). In this thesis, as the chars are produced from sewage sludge, the pH of the pyrochars didn't raise the soil pH to a basic level, thus the amendment didn't keep Al and Fe from forming these bonds. The two samples of sludge SS_{ES} and SS_{UK} had also a relatively low pH compared to other authors as Latare *et al.*, (2014), who used a sewage sludge that obtained a high pH above 8 and reported the need of adding low rates of sewage

sludge (below 30 t/ha) combined with readily available forms of NPK to ensure a good productivity in the first seasons.

Fe-P and Al-P interactions are reinforced by the analysis of the grains (Chapter 5, Table 0-7 & Table 0-8) which indicated that despite Fe and P being present in the soil in higher quantities than in the previous season, the uptake was lower PUE (Chapter 4, Table 0-9) indicated clearly that the P in soil in some cases was not taken up by the plant. P uptake in hydrochar treatments and those combined with SS_{UK} were likely to be hampered and compared to control soil these accumulated less P in the grains giving a negative PUE or lower PUE during the second season. These treatments are those with a lower soil pH and those that reduced their grain yield from season 1.

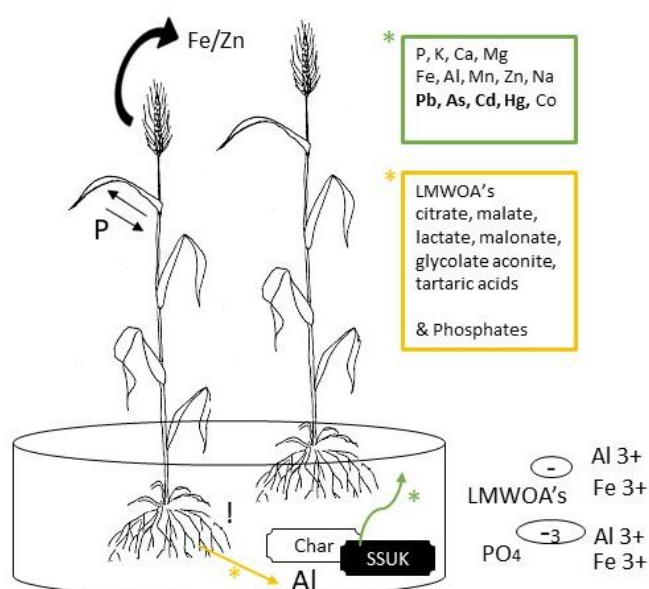


Figure 0-2 Wheat response to Al and Fe in soil based on (Austruy *et al.*, 2014).

In Chapter 3 it was suggested that the addition of Al though the amendments, greatly contained in SS_{ES} and derivatives (Table 0-1), could have provoked an undesirable reaction from the crop. In the presence of Al the crop may prevent it's uptake by exudating phosphates (Mariano and Keltjen, 2003) and low molecular weight organic acid (LMWOA's) (Austruy *et al.*, 2014) such as malate in the case of wheat (Papernik *et al.*, 2001) stressing the plant and reducing PUE (Chapter 4, Table 0-9), as illustrated in Figure 0-2. This was quantified in our data by the significant presence of Fe and Mn in the wheat grain while Al was below the detection limits in the grain (Table 0-10 and Table 0-11) and moreover, by the reduction of Fe accumulated in the grains in season

2. This could be due to a precipitation of Fe with P from the possible exudated one from the stressed plant and the newly released phosphorus that was quantified in Chapter 3 (Table 0-2). Therefore, it is likely that the lower pH in combined amendments could have reduced the phytoavailability of Fe and P (Havlin *et al.*, 2016), reducing thus their appearance in grain in season 2 (Table 0-11). In order to confirm this theory, a study of root exudation and P speciation changes should be conducted in future work. Heavy metal content added through the amendments was suggested as a possible interference to P efficiency through phosphate immobilization and proposed as an explanation to the non-significant concentration of Zn, Pb and P in grains for both seasons (Austruy *et al.*, 2014).

The slow availability of P proved to have certain impact on the yield from season to season. Available-P remaining in soil after the second harvest was reduced from the first harvest in control soil (57.3%), all combined treatments of pyrochars (3-25%), H180-SS_{UK} 40t/ha (16%) and all amendments containing SS_{ES} (11-27%) whereas the rest had a range of enhancement of 4-60% including single amendments (Chapter 3, Figure 0-6). Finally, as shown in Table 0-9 PUE technically improved greatly if compared to the available-P on initial conditions, especially for P400 271.2%, but when corrected with the available-P shift after the first season all amendments with a positive PUE reduced it in the second season. Organic amendment prove to have a higher PUE for P400, SS_{ES}, SS_{ES}-SS_{UK} and P300-SS_{UK} than P-mineral rock (Schröder *et al.*, 2011; Xin *et al.*, 2017). Negative PUE results indicated a higher P uptake in grains grown in control soil. However, this could be due to the high variability of the samples as no significant differences could be found in the first season P uptake for example.

Given this results, acidification of the soil may have had a greater impact on plant development and grain yield than available P in soil. Compared to the previous season the second season had a general increase of the productivity (1-127%), with exception of P300-SS_{UK}, P400-SS_{UK}, SS_{ES}-SS_{UK}, H180-SS_{UK} at 40 t/ha, 6-22% reduction range, the control that maintained it stable (1995 kg/ha). This grain yield is considerably lower to other studies using P fertilisers (1315-2226 kg/ha, from 1229 kg/ha control soil) (Zafar, Rizwan and Shahid, 2017).

5.4 Evaluation of changes in soil conditions

Changes in CEC, surface area, porosity and adsorption capacity are expected to improve water retention in soil however no data is available to confirm if this had an effect on soil conditions over time. However, pH, EC and organic matter content were analysed on initial conditions and after both harvests provided valuable information on soil changes (Chapter 3). Pyrochars improved organic matter over two seasons to 33-528% compared to control soil in season 2, while hydrochars did 37-487% (Appendix Table A 3), maintaining EC under appropriate limits for crop growth (Appendix, Figure A 6). However, pH was reduced by 2 units. Such acidification has not been reported before by the use of hydrochars from sewage sludge to date, although their acidity compared to the feedstock is broadly known (van Zwieten *et al.*, 2010; Kalderis *et al.*, 2014; Cely *et al.*, 2015; Danso-Boateng *et al.*, 2015; Ok *et al.*, 2015; Dai *et al.*, 2017; Chen *et al.*, 2018). Chen *et al.*, (2021) did report the reduction of soil pH of 2 units on a study of pyrochar of Oilseed rape (*Brassica napus* L.) prepared at 500 °C, however this was artificially aged surfactant 2-octanoand. Acidification after using sewage sludge as soil amendment is in accordance to (Antoniadis and Alloway, 2002; McBride, Richards and Steenhuis, 2004).

With the use of pyrochars at higher temperature the acidification was significantly prevented proving that pyrolysis could produce a char with a liming effect compared to the feedstock when added on its own (Chapter 3, Table 0-1). Therefore, after two seasons the hypothesis 3 would be confirmed for pyrochars but not for the rest of amendments, not only for the highest rates but for the lowest too. In the case of pH, the amount added did not produce a significant effect.

On the opposite side, the rate had a predominant effect on the quantity of organic matter, which increased during the second season with a maximum of 7.64% (Chapter 3, Figure 0-5). Overall, there was not a significant difference between the thermal derivatives despite the results of the characterisation, only P400 on its own at the highest rate obtained similar results to combined amendments at the highest rate, even surpassing the result of SS_{ES}. Latare *et al.*, (2014) also reported a built up of OM after the second season of growing wheat with sewage sludge and attributed this to the decomposition of the roots from season to season. Therefore, this could be linked

to the effect of high temperature pyrochars to enhanced root growth from the Zuconi test (Chapter 4, Table 0-2).

Hence, the properties studied for combined amendments and for P400 on its own confirmed hypothesis 3. Sewage sludge and derivatives showed potential as organic amendments where high temperatures of pyrolysis obtained better results and helped to slow down the acidification of the soil.

5.5 Environmental risk assessment

Regarding the potential environmental risks associated with nutrient mobility through the profile, the acid digestion, and the Olsen-P results (Appendix, Table A 5) rejected the hypothesis 4-a. The accumulation of nutrients on the base of the column was not significantly different to the control soil in any of the treatments regardless of their carbon stability. Nonetheless, despite not having produced and analysed any leachate, the analysis performed at the base of the column, provided enough evidence to discard that after 2 seasons the effect of the amendments migrated through the profile. Half a meter underneath the area of application, there were not nutrients or heavy metals accumulated, no significant differences on organic matter or EC and pH remained neutral.

Limitations to use sludge in agricultural land have been reported previously due to Cd accumulation over 30 t/ha (Latare *et al.*, 2014). However, in our experiment Zn would be the limiting factor and not Cd. The acid digestion in Chapter 5 (Table 0-6) indicated that at the highest rates only SS_{UK} on its own could be applied and none of SS_{ES}, their derivatives and combinations, specifically, no combinations of hydrochar with SS_{UK} could be allowed.

It was hypothesised that the risk of accumulated heavy metals in the grains would be less due to their immobilization in the ashes after the carbonization of sludge. Only a significant increment compared to control soil was detected for As for H180 during the first season and Cd H240-SS_{UK} during the first season and SS_{ES}, SS_{ES}+SS_{UK} during the second season. However, both As and Cd were remained under the legal limits in cereal grains (Department of the Environment, 1996).

No significant difference was observed to SS_{ES} during the experiment of heavy metals in the grains. Therefore, there is not enough evidence to support that the carbonization

degree had an impact on preventing heavy metal accumulation after two seasons. If we were to consider application for multiple seasons it is plausible to assume that this may become limiting over time both for grain and soil quality.

Thus, the value of these materials as P fertilisers was compromised by the acidification, the presence of Al and Fe and the slow build-up of available P. More information is needed to address the aging of the chars, the influence of different concentrations of Fe and Al in the sludge used as feedstock and multiple applications over multiple growing seasons.

5.6 Discussion of study limitations and recommendations for future work

The perception of sewage sludge as a source of pollutants partially relies on few studies. As shown in the review presented, the overall outcome was positive with limitations to the rate of amendment. The use of sewage sludge is hampered by the huge diversity of feedstocks and the variability of it depending on the sampling (Zhu *et al.*, 2012). More research needs to be done to provide evidence of the effect of the addition of sludge derivatives for crop production.

It has been reported before that sewage sludge produced different outcomes after the first season, from higher grain yields (Faria *et al.*, 2018b) to higher P uptake (Mackay *et al.*, 2017), the latter confirmed by the present research. However, the extent of the changes remains unpredictable, and the reasons are still based on hypothesis and lack of quantitative evidence as is clear from the results presented and discussed in this thesis.

This thesis has highlighted the need for an assessment of the aging on chars to confirm the new hypothesis presented in this research, and to overcome the challenge of separating all the chars from the soil mixture in order to obtain a representative sample. Changes in porosity, surface area, adsorption capacity, functional groups, organic matter stability and P speciation could prove to be useful for assessing the transformation of the chars in soil.

Limitations of some of the analyses used here became apparent during this study. For example, the Zucconi test often used for phytotoxicity assessment of chars (Álvarez *et al.*, 2017a) didn't provide data that resembled the final germination results on a

small-scale experiment. It should therefore not be considered as a reliable test to determine suitability of chars. The acid digestion was found not to be enough either to provide accurate data on the total elements in raw materials, and soil amended with them and appears to give only an approximation of the concentration of nutrients and heavy metals in the sewage sludge and derivatives (Ma and Matsunaka, 2013). Without a real measurement on the change of porosity, surface area and particle size of the chars after 2 seasons it's quite difficult to directly prove a relationship to the aging of the char to be related to the increment in total elements found in the soil. A comparative study of digestion analysis should be carried out to obtain a more representative picture of the materials studied, possibly expanding to those techniques used in geology, such as reverse aqua regia for a higher recovery rate (Donner *et al.*, 2011; Wang, Baker and Brindle, 2016). This research suggests that in order to provide a solution to P-fertilisers based on sewage sludge as main feedstock, future work should focus on:

- Contrasting the different technologies of P removal and sludge stabilisation used in the Wastewater Treatment Plants;
- Systematically analysing sewage sludge samples for Fe and Al contents, selecting those with low concentrations, for example by opting for a feedstock produced at a Wastewater Treatment Plants that doesn't dose ferric chloride or aluminium chloride, including compostable latrines;
- Providing a readily available form of P along with the chars produced and monitor P-availability changes and testing different concentrations and forms of doping;
- Exploring the possibility of using HTC to remove heavy metals through adjustments in the aqueous medium before using the char for soil amendment;
- Testing pH adjustments, such as combined amendments with lime and applying N through other sources other than ammonia nitrate;
- Evaluating performance of sewage sludge amendments on a longer period of time with special regards to soil acidification;
- Assessing P-efficiency, pH and organic matter content on different types of soil. Analysing nutrient and heavy metal leaching and other soil properties like texture and water holding capacity with other types of soil and irrigation;

- Evaluate changes in rhizosphere studying root morphology and microbiota shifts. Considering an assessment of P uptake mechanisms affected after char amendments including arbuscular mycorrhizal responses.

Finally, it is worth mentioning the economical and accessibility limitations of such materials. At the stage of research, most projects for chars derived from sewage sludge for soil amendments are carried out in small scale which difficult its economic feasibility. While those that focus on the production of chars for energy purposes are more advanced and often include a life cycle assessment that suggests that pyrolysis could be a feasible alternative to incineration with capacity over 2.1 ton per hour of sewage sludge if the char is used partially to maintain the reactor by substitution of fuel (Barry *et al.*, 2019; Kumar, Saini and Bhaskar, 2020).

This thesis sets the basis towards the formulation of a better product to ensure optimal crop productivity and minimum environmental risk. The materials studied won't be an ideal alternative to substitute NPK mineral fertilisers yet. Moreover, the cost of drying, transport and logistics is said to have a great impact on the value of this materials, making pyrolysis an expensive option compared to HTC making them highly dependent on the return's worth (Sohi *et al.*, 2010). According to Akarsu *et al.*, (2019) even HTC would be a very expensive alternative to the current fertilisers in the market making hydrochars better suited for energy purposes of wet biomass conversion. This project highlights the need for more research before such materials derived from sewage sludge reach a larger scale production stage.

5.7 Conclusions and contribution to knowledge

This thesis has provided contribution to knowledge by investigating the potential use and limitations of pyrochars and hydrochars derived from a sewage sludge as P-fertilisers. This was accomplished by:

- Selecting thermal process and temperatures that provide enough statistical differences on structure and physical-chemical characteristics of sewage sludge to best suit a comparative assessment,
- Performing the comparative study of the amendments made with different chars for P availability; in contrast to previous research that focused on N use efficiency or that didn't compare samples obtained from the same feedstock.

- Testing the effect of different rates of amendment on soil properties over two seasons and addressing the influence of sewage sludge applications on soil acidification, which indicated the potential of pyrolysis to prevent or remediate it.
- Evaluating the effect of a combined amendment using equal parts of thermal derivatives and an untreated sewage sludge on P use efficiency.
- Assessing the accumulation of heavy metals in soil and grains over two seasons on a soil that turned acidic. This showed that samples containing Zn could benefit from pyrolysis at higher temperatures.
- Addressing the possible interference of Al and Fe on P availability and its role on the reduction of the performance of the amendments as P-fertilisers to improve spring wheat grain yield.
- Studying the potential enrichment of Fe through sewage sludge amendment to increase grain quality value for malnutrition.

Ultimately, the use of thermal treatments to enhance sewage sludge properties as P-fertiliser proved to have some limitations. Sewage sludge could be an alternative source of available phosphorus that could help to remediate the growing demand of mineral phosphorus reserves, providing at the same time a good base of organic matter for low fertile soils, but the feedstock selected would play an important factor on P use efficiency. Sewage sludge in agriculture must be managed carefully due to its variability in physical-chemical properties and their content of Al, Fe and heavy metals. Acidification of the soil should be avoided in order to obtain better results on P availability. Pyrolysis of sewage sludge may not replace mineral fertilisers, but it could be used to prevent acidification if used as a pre-treatment of sewage sludge, increasing carbon stability and organic matter in loamy sandy soil, immobilizing heavy metals and providing a slow release of P.

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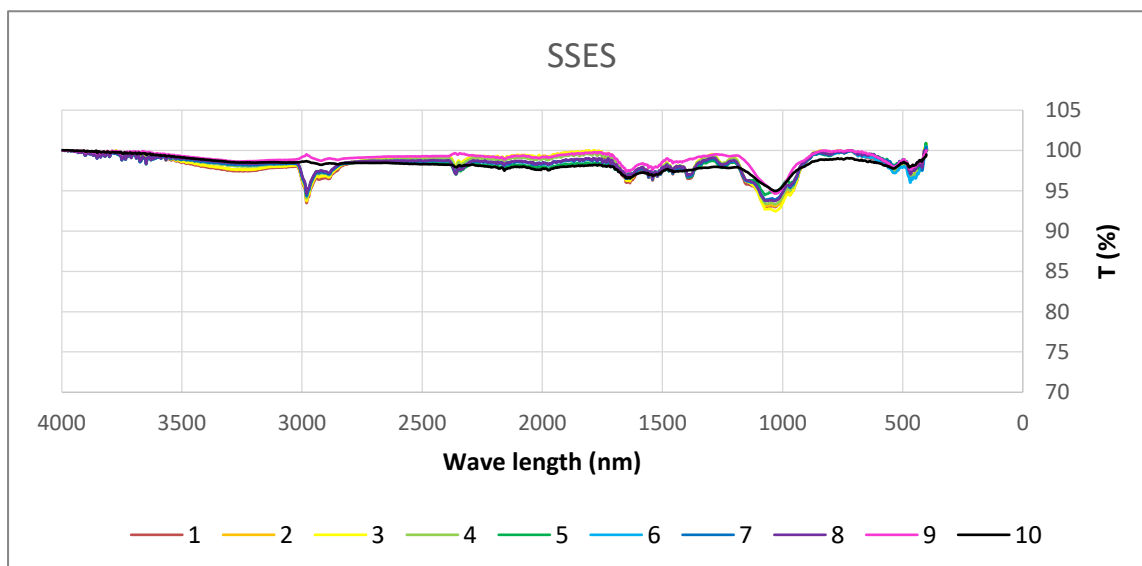
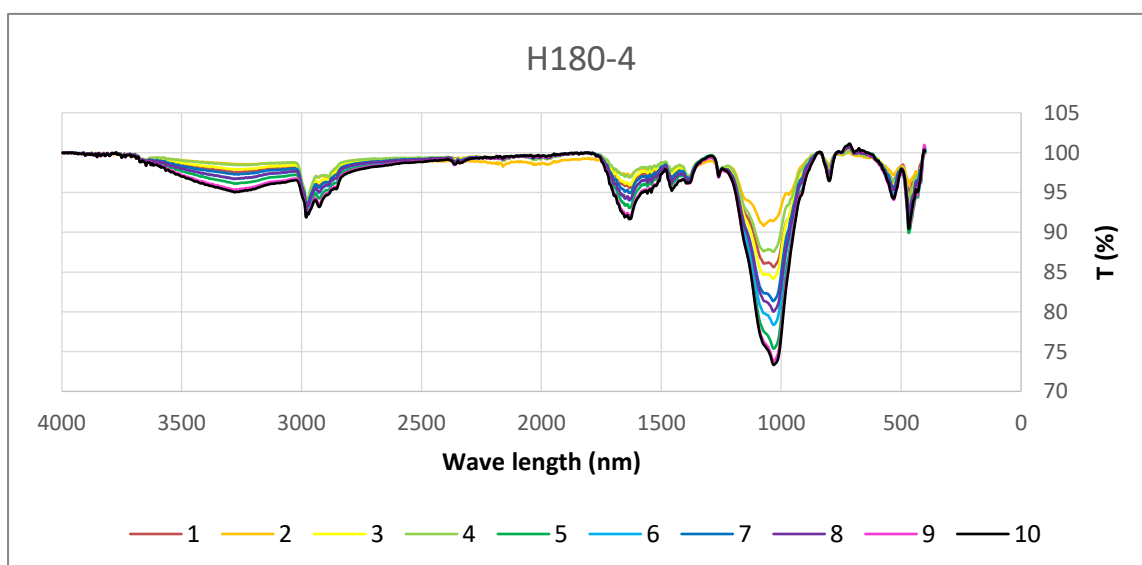
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APPENDICES

Appendix A

A.1 Supplementary information

A.1.1 Characterization.



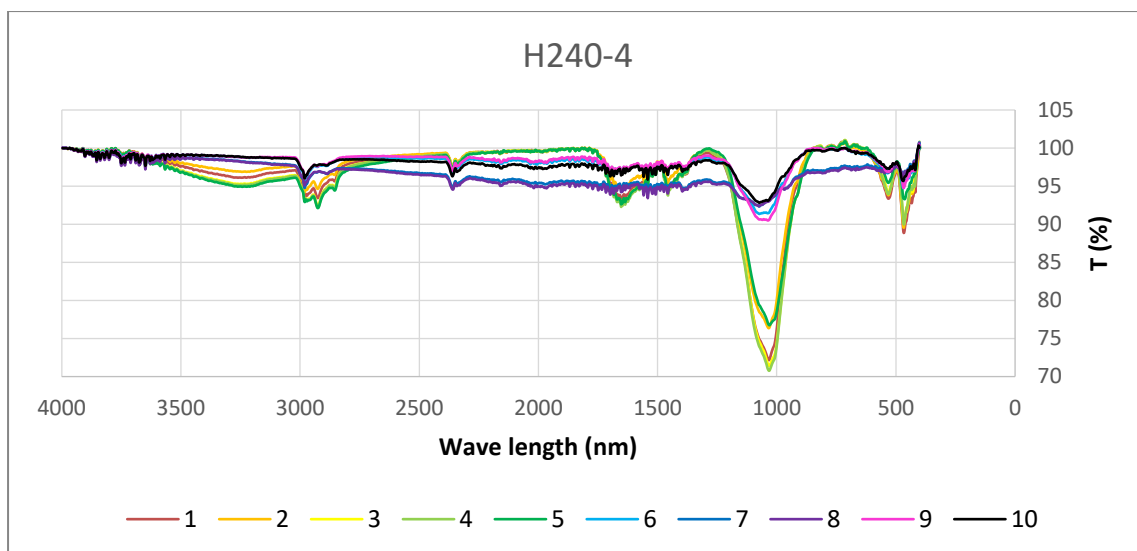
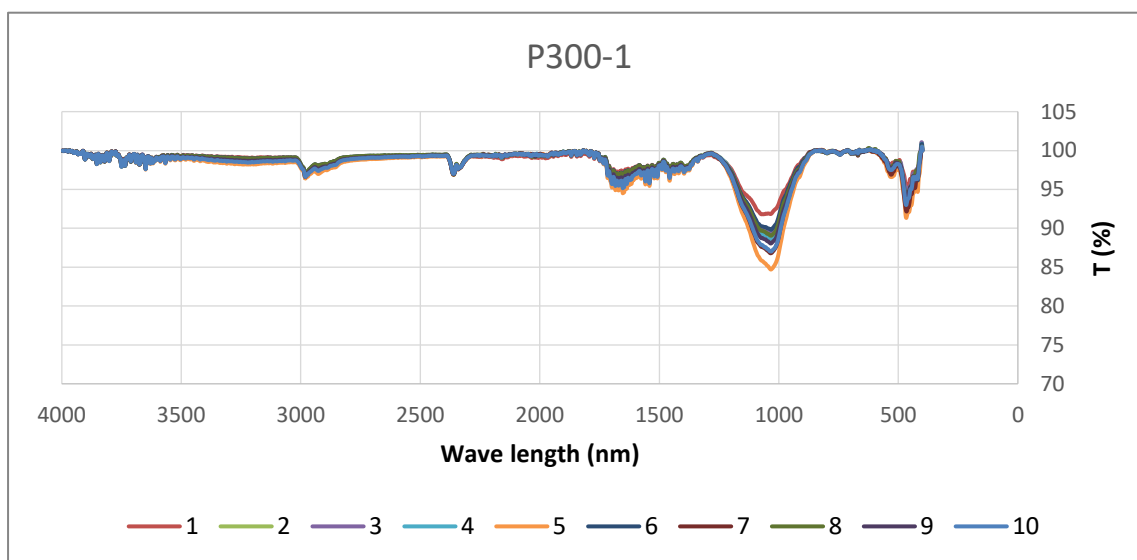
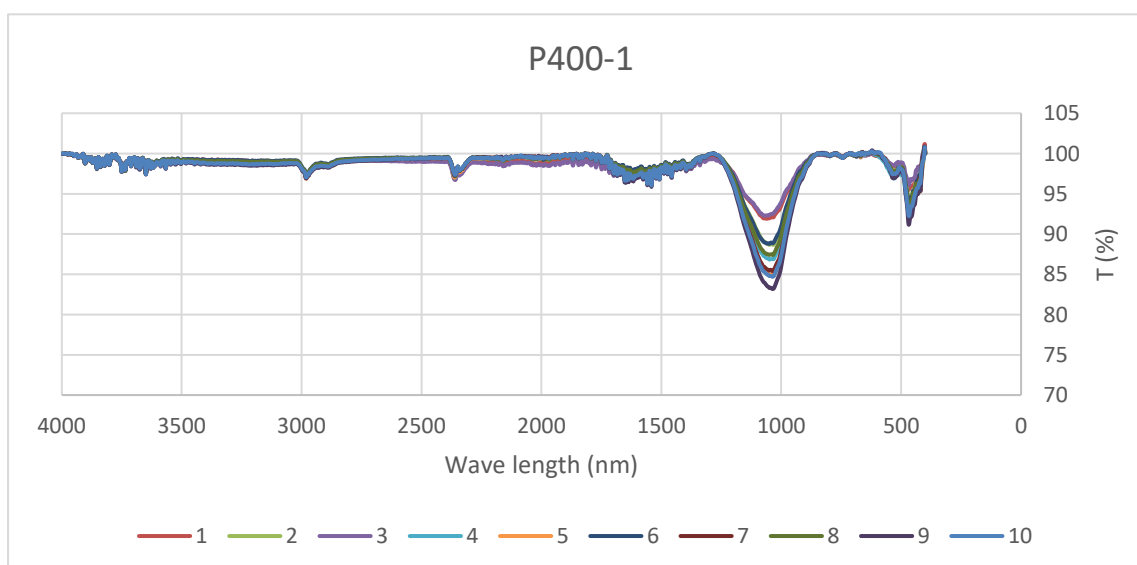


Figure A 1. FTIR analysis, 10 replicates per sample.

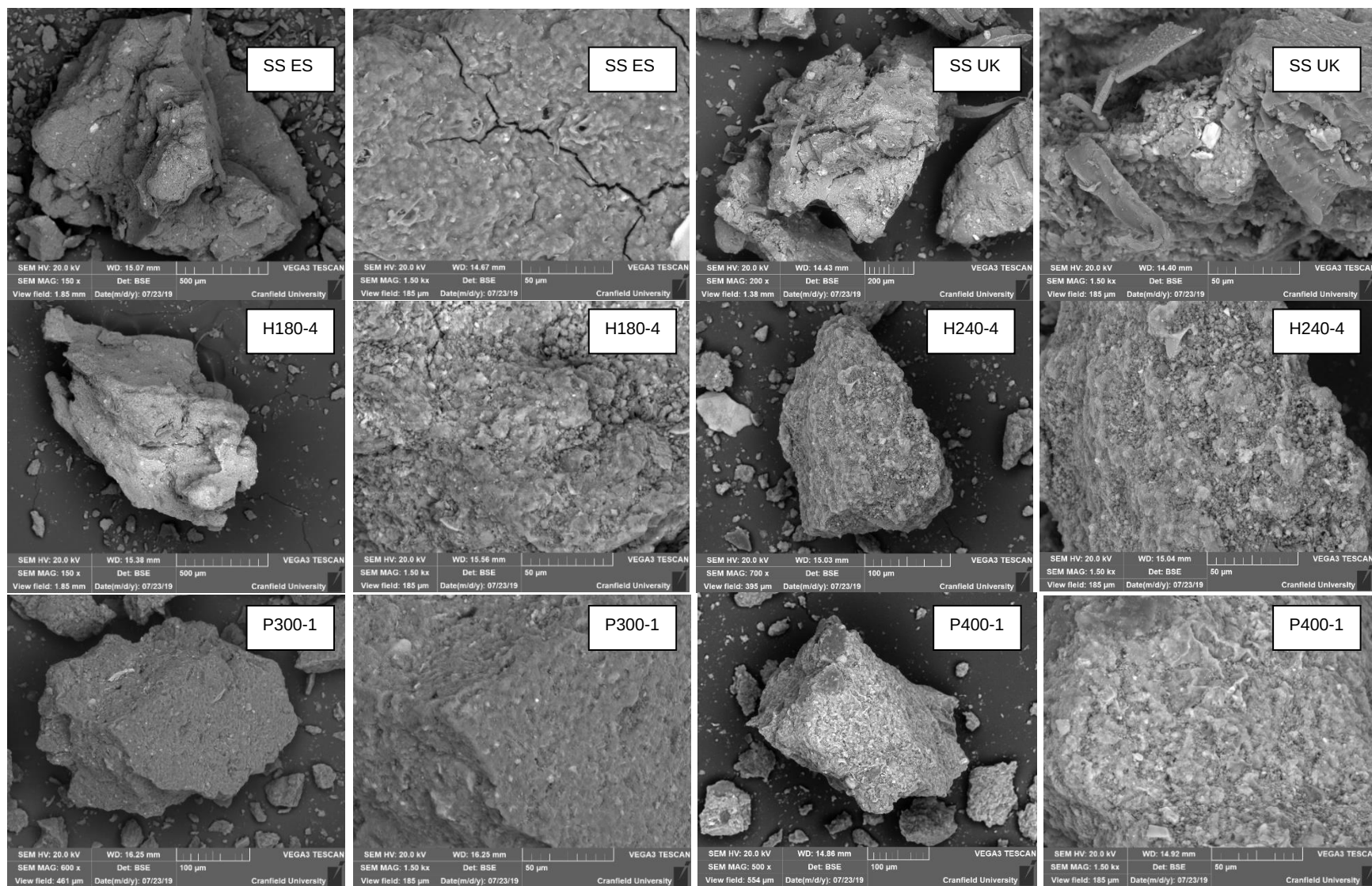


Figure A 2-SEM photographs, from left to right: first Row: SS ES, SS UK; second Row: H180-4, H240-4; third Row: P300-1-P400-1.

Principal Components: on Correlations

Correlations

	LOI (%)	CEC	C/N	H/C	O/C
LOI (%)	1.0000	0.8052	-0.4153	0.9100	0.9076
CEC	0.8052	1.0000	-0.0746	0.9320	0.9409
C/N	-0.4153	-0.0746	1.0000	-0.0446	-0.1875
H/C	0.9100	0.9320	-0.0446	1.0000	0.9597
O/C	0.9076	0.9409	-0.1875	0.9597	1.0000

The correlations are estimated by Row-wise method.

Summary Plots

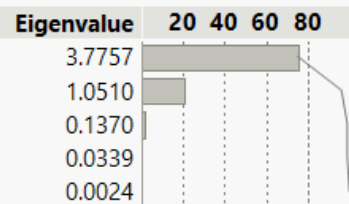
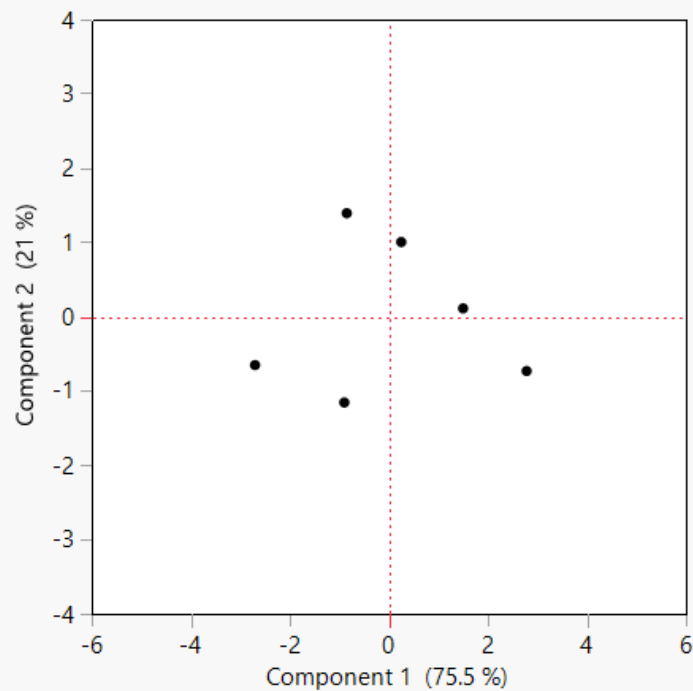
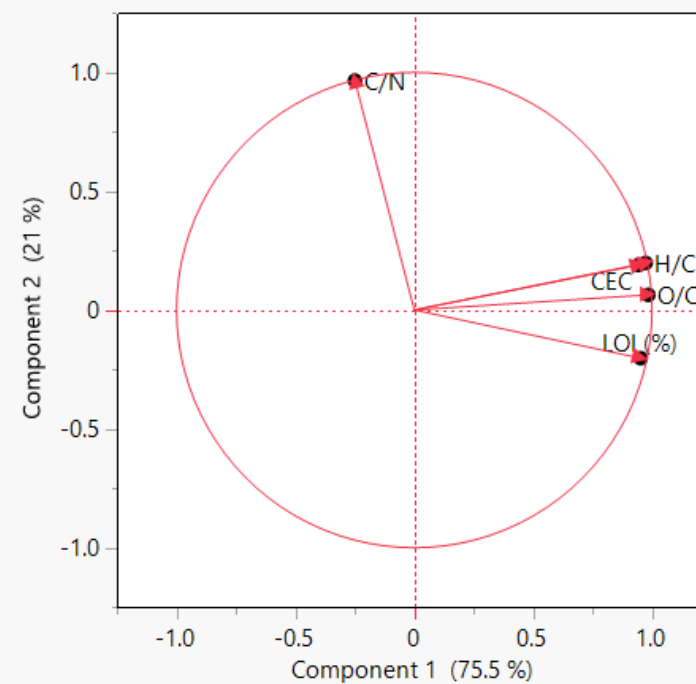


Figure A 3 PCA raw materials, Chapter 2.

Multivariate																													
Correlations																													
	Temperature	TimepH (1:10)	H2OEC (µS cm-1)	Olsen-P (mg kg-1)	CEC Average of Na Average of Mg Average of Ca Average of K Average of Mn										C	H	N	O	O/C	H/C	C/N HHV (MJ kg-1)	LOI (%)	Ash (%)	H2O (%)	CaCO3 (%)	Surface area (m2/g)			
Temperature	1.0000	-0.8088	0.3206	-0.8799	-0.4922	-0.9237	-0.3733	-0.5845	-0.6143	-0.1591	0.5931	0.2460	-0.9492	0.0613	-0.9680	-0.9751	-0.9825	-0.0111	-0.5628	-0.8685	0.8024	-0.5257	-0.5124				0.4803		
Time	-0.8088	1.0000	0.2447	0.7492	0.3855	0.7991	0.4484	0.5498	0.7540	0.1523	-0.4407	-0.1881	0.7733	0.2750	0.8939	0.8918	0.7931	-0.4034	0.3943	0.8047	-0.8538	0.6500	0.6989				-0.7572		
pH (1:10) H2O	0.3206	0.2447	1.0000	-0.0811	0.1372	-0.0994	0.4261	0.2428	-0.0612	0.3529	0.5402	0.1118	-0.2469	0.6727	-0.1083	-0.1197	-0.2718	-0.7920	-0.2183	-0.0321	0.1150	-0.1271	0.0239				-0.4028		
EC (µS cm-1)	-0.8799	0.7492	-0.0811	1.0000	0.8249	0.9684	0.7388	0.8506	0.2890	0.5846	-0.2933	-0.2927	0.8925	0.0261	0.8646	0.8831	0.9310	-0.0772	0.5305	0.8143	-0.5123	0.1508	0.1538				-0.3766		
Olsen-P (mg kg-1)	-0.4922	0.3855	0.1372	0.8249	1.0000	0.7587	0.9192	0.9520	-0.2233	0.9273	0.2625	-0.3200	0.5407	0.0857	0.4986	0.5311	0.5878	-0.1410	0.2694	0.5052	0.0254	-0.3887	-0.3644				-0.0684		
CEC	-0.9237	0.7991	-0.0994	0.9684	0.7587	1.0000	0.6340	0.8112	0.4311	0.4790	-0.2874	-0.4143	0.8702	-0.0286	0.9143	0.9409	0.9320	-0.0746	0.4063	0.8052	-0.5957	0.2831	0.2683				-0.3788		
Average of Na	-0.3733	0.4484	0.4261	0.7388	0.9192	0.6340	1.0000	0.9416	-0.2435	0.9376	0.3097	-0.0259	0.5095	0.4375	0.4612	0.4656	0.5028	-0.4655	0.3944	0.5641	-0.0074	-0.3865	-0.2648				-0.3342		
Average of Mg	-0.5845	0.5498	0.2428	0.8506	0.9520	0.8112	0.9416	1.0000	-0.0762	0.8718	0.2238	-0.1725	0.6515	0.3199	0.6513	0.6654	0.6722	-0.3846	0.3943	0.6896	-0.1709	-0.2368	-0.1406				-0.3411		
Average of Ca	-0.6143	0.7540	-0.0612	0.2890	-0.2233	0.4311	-0.2435	-0.0762	1.0000	-0.5020	-0.6796	-0.2718	0.4528	-0.0850	0.6323	0.6350	0.4947	-0.0522	0.0782	0.4343	-0.9011	0.9802	0.9236				-0.5210		
Average of K	-0.1591	0.1523	0.3529	0.5846	0.9273	0.4790	0.9376	0.8718	-0.5020	1.0000	0.5326	-0.1315	0.2725	0.2666	0.2087	0.2297	0.2885	-0.2911	0.1795	0.2996	0.3079	-0.6453	-0.5673				-0.0095		
Average of Mn	0.5931	-0.4407	0.5402	-0.2933	0.2625	-0.2874	0.3097	0.2238	-0.6796	0.5326	1.0000	-0.0685	-0.5686	0.2660	-0.4920	-0.4717	-0.5498	-0.3398	-0.5007	-0.4201	0.7475	-0.7450	-0.6665				0.3207		
C	0.2460	-0.1881	0.1118	-0.2927	-0.3200	-0.4143	0.3097	-0.0259	-0.1725	-0.2718	-0.1315	-0.0685	1.0000	0.0223	0.7002	-0.1393	-0.2286	-0.1526	-0.4771	0.6123	0.1819	-0.0060	-0.1379				-0.4654		
H	-0.9492	0.7733	-0.2469	0.8925	0.5407	0.8702	0.5095	0.6515	0.4528	0.2725	-0.5686	0.0223	1.0000	0.1528	0.9450	0.9301	0.9845	-0.1329	0.7805	0.9527	-0.7497	0.3842	0.4427				-0.5984		
N	0.0613	0.2750	0.6727	0.0261	0.0857	-0.0286	0.4375	0.3199	-0.0850	0.2666	0.2660	0.7002	0.1528	1.0000	0.1700	0.1021	0.0257	-0.9572	0.4425	0.4246	-0.1545	-0.0780	0.2225				-0.7673		
O	-0.9680	0.8939	-0.1083	0.8646	0.4986	0.9143	0.4612	0.6513	0.6323	0.2087	-0.4920	-0.1393	0.9450	0.1700	1.0000	0.9957	0.9589	-0.2378	0.5876	0.9382	-0.8421	0.5367	0.5877				-0.6588		
O/C	-0.9751	0.8918	-0.1197	0.8831	0.5311	0.9409	0.4656	0.6654	0.6350	0.2297	-0.4717	-0.2286	0.9301	0.1021	0.9957	1.0000	0.9597	-0.1875	0.5259	0.9076	-0.8195	0.5277	0.5557				-0.5996		
H/C	-0.9825	0.7931	-0.2718	0.9310	0.5878	0.9320	0.5028	0.6722	0.4947	0.2885	-0.5498	-0.1526	0.9845	0.0257	0.9589	0.9597	1.0000	-0.0446	0.6642	0.9100	-0.7400	0.4040	0.4910				-0.5071		
C/N	-0.0111	-0.4034	-0.7920	-0.0772	-0.1410	-0.0746	-0.4655	-0.3846	-0.0522	-0.2911	-0.3398	-0.4771	-0.1329	-0.9572	-0.2378	-0.1875	-0.0446	1.0000	-0.2604	-0.4153	0.2114	-0.0184	-0.2191				0.7734		
HHV (MJ kg-1)	-0.5628	0.3943	-0.2183	0.5305	0.2694	0.4063	0.3944	0.3943	0.0782	0.1795	-0.5007	0.6123	0.7805	0.4425	0.5876	0.5259	0.6642	-0.2604	1.0000	0.7967	-0.4897	0.1112	0.2785				-0.6250		
LOI (%)	-0.8685	0.8047	-0.0321	0.8143	0.5052	0.8052	0.5641	0.6896	0.4343	0.2996	-0.4201	0.1819	0.9527	0.4246	0.9382	0.9076	0.9100	-0.4153	0.7967	1.0000	-0.7582	0.3679	0.5078				-0.7764		
Ash (%)	0.8024	-0.8538	0.1150	-0.5123	0.0254	-0.5957	-0.0074	-0.1709	-0.9011	0.3079	0.7475	-0.0060	-0.7497	-0.1545	-0.8421	-0.8195	-0.7400	0.2114	-0.4897	-0.7582	1.0000	-0.8848	-0.9203				0.7463		
H2O (%)	-0.5257	0.6500	-0.1271	0.1508	-0.3887	0.2831	-0.3865	-0.2368	0.9802	-0.6453	-0.7450	-0.1379	0.3842	-0.0780	0.5367	0.5277	0.4040	-0.0184	0.1112	0.3679	-0.8848	1.0000	0.9517				-0.5116		
CaCO3 (%)	-0.5124	0.6989	0.0239	-0.1538	-0.3644	0.2683	-0.2648	-0.1406	0.9236	-0.5673	-0.6665	0.1067	0.4427	0.2225	0.5877	0.5557	0.4190	-0.2911	0.2785	0.5078	-0.9203	0.9517	1.0000				-0.7308		
Surface area (m2/g)	0.4803	-0.7572	-0.4028	-0.3766	-0.0684	-0.3788	-0.3342	-0.3411	-0.5210	-0.0095	0.3207	-0.4654	-0.5984	-0.7673	-0.6588	-0.5996	-0.5071	0.7734	-0.6250	-0.7764	0.7463	-0.5116	-0.7308				1.0000		
Adsorption average pore width (A) (nm)	-0.1011	-0.2395	-0.6991	-0.2772	-0.5650	-0.2478	-0.6063	-0.4816	0.1432	-0.6515	-0.5234	0.5017	0.1348	-0.0744	0.0316	-0.0181	0.0543	0.2506	0.4114	0.1142	-0.2737	0.2951	0.3311				-0.0780		
MicroPore < 2-10 nm (%)	-0.6563	0.9123	0.4329	0.6717	0.4065	0.6635	0.5995	0.6201	0.5200	0.2912	-0.2738	0.1679	0.7401	0.6268	0.6706	0.6972	-0.6884	0.5794	0.8600	-0.7356	0.4951	0.6040	-0.9169				-0.9169		
MesoPore 10-20 nm (%)	0.0483	0.1174	0.2451	-0.2638	-0.3911	-0.2224	-0.1296	-0.1147	0.1565	-0.2965	-0.0142	0.7573	0.0786	0.7767	0.1301	0.0524	-0.0511	-0.7075	0.3919	0.3291	-0.3327	0.2440	0.5023				-0.6908		
MesoPore 20-50 nm (%)	0.5356	-0.8363	-0.5895	-0.6903	-0.5774	-0.6529	-0.7772	-0.7456	-0.3170	-0.5256	0.0404	-0.0923	-0.6366	-0.6480	-0.6970	-0.6772	-0.6064	0.7266	-0.4719	-0.7619	0.5201	-0.2046	-0.3683				0.8030		
MesoPore 10-50 nm (%)	0.5641	-0.8171	-0.5222	-0.7938	-0.7204	-0.7419	-0.8383	-0.8011	-0.2727	-0.6360	0.0367	0.1561	-0.6256	-0.4062	-0.6703	-0.6758	-0.6376	0.5095	-0.5333	-0.6708	0.4222	-0.1287	-0.2106				0.5932		
MacroPore > 50 nm (%)	0.1972	-0.2146	0.1428	0.1927	0.5543	0.1132	0.4085	0.3022	-0.4744	0.6157	0.4442	-0.5982	-0.2417	-0.4307	-0.2865	-0.2179	-0.1397	0.3575	-0.4378	-0.3833	0.6044	-0.5866	-0.7444				0.6315		
Mo	0.6640	-0.5917	-0.1280	-0.8292	-0.7868	-0.7550	-0.8581	-0.9041	0.0051	-0.7000	0.0320	-0.1938	-0.8147	-0.5054	-0.7448	-0.7225	-0.7701	0.4757	-0.7389	-0.8779	0.3645	0.1048	-0.0632				0.5866		
Hg	-0.4017	-0.0135	-0.4006	0.5996	0.6944	0.4610	0.5964	0.6227	-0.4564	0.6381	-0.0261	0.1561	0.5571	0.0028	0.3235	0.3176	0.5254	0.1489	0.6415	0.4658	0.1078	-0.4976	-0.4495				0.0567		
Cr	0.6640	-0.5917	-0.1280	-0.8292	-0.7868	-0.7550	-0.8581	-0.9041	0.0051	-0.7000	0.0320	-0.1938	-0.8147	-0.5054	-0.7448	-0.7225	-0.7701	0.4757	-0.7389	-0.8779	0.3645	0.1048	-0.0632				0.5866		
Pb	0.7457	-0.8804	-0.0077	-0.4663	0.0476	-0.5714	0.0037	-0.1529	-0.9446	0.3158	0.6715	0.0769	-0.6644	-0.1637	-0.8048	-0.7890	-0.6694	0.2636	-0.3546	-0.6910	0.9845	-0.9148	-0.9420				0.7435		
Ni	0.9276	-0.6583	0.3432	-0.9246	-0.6495	-0.8876	-0.5995	-0.7071	-0.3023	-0.3846	0.4889	0.0562	-0.9754	-0.0344	-0.8882	-0.8843	-0.9747	0.0029	-0.7460	-0.8913	0.6056	-0.2222	-0.2522				0.4264		
Co	0.8432	-0.5976	0.2680	-0.8303	-0.5884	-0.7812	-0.5749	-0.7024	-0.2057	-0.3861	0.4056	-0.1962	-0.9529	-0.2675	-0.8506	-0.8243	-0.9093	0.1954	-0.8626	-0.9395	0.5798	-0.1512	-0.2627				0.5553		
Cd	0.5293	-0.5216	-0.0775	-0.5011	-0.2836	-0.4220	-0.4863	-0.4948	-0.1467	-0.2363	0.3045	-0.6461	-0.7415	-0.7104	-0.6435	-0.5757	-0.6196	0.5913	-0.9242	-0.8641	0.5464	-0.1547	-0.3938				0.8298		
Zn	0.9266	-0.6912	0.0510	-0.8194	-0.4408	-0.8467	-0.4672	-0.6234	-0.6089	-0.1852	0.5113	-0.0328	-0.9511	-0.3104	-0.9838	-0.9636	-0.9343	0.3454	-0.6909	-0.9780	0.8615	-0.5345	-0.6299				0.7670		
Cu	0.8807	-0.9005	-0.0792	-0.8234	-0.5049	-0.8461	-0.5																						

Correlations																												
		h (A) (nm)MicroPore 2-10 nm (%)MesoPore 10-20 nm (%)MesoPore 20-50 nm (%)MesoPore 50-100 nm (%)MacroPore >50 nm (%)																										
Temperature																												
Time																												
pH (1:10) H2O																												
EC (µS cm ⁻¹)																												
Olsen-P (mg kg ⁻¹)																												
CEC																												
Average of Na																												
Average of Mg																												
Average of Ca																												
Average of K																												
Average of Mn																												
C																												
H																												
N																												
O																												
O/C																												
H/C																												
C/N																												
HHV (MJ kg ⁻¹)																												
LOI (%)																												
Ash (%)																												
H2O (%)																												
CaCO3 (%)																												
Surface area (m ²)																												
Adsorption ave																												
MicroPore 2-10																												
MesoPore 10-20																												
MesoPore 20-50																												
MesoPore 50-100																												
MacroPore >50																												
Mo																												
Hg																												
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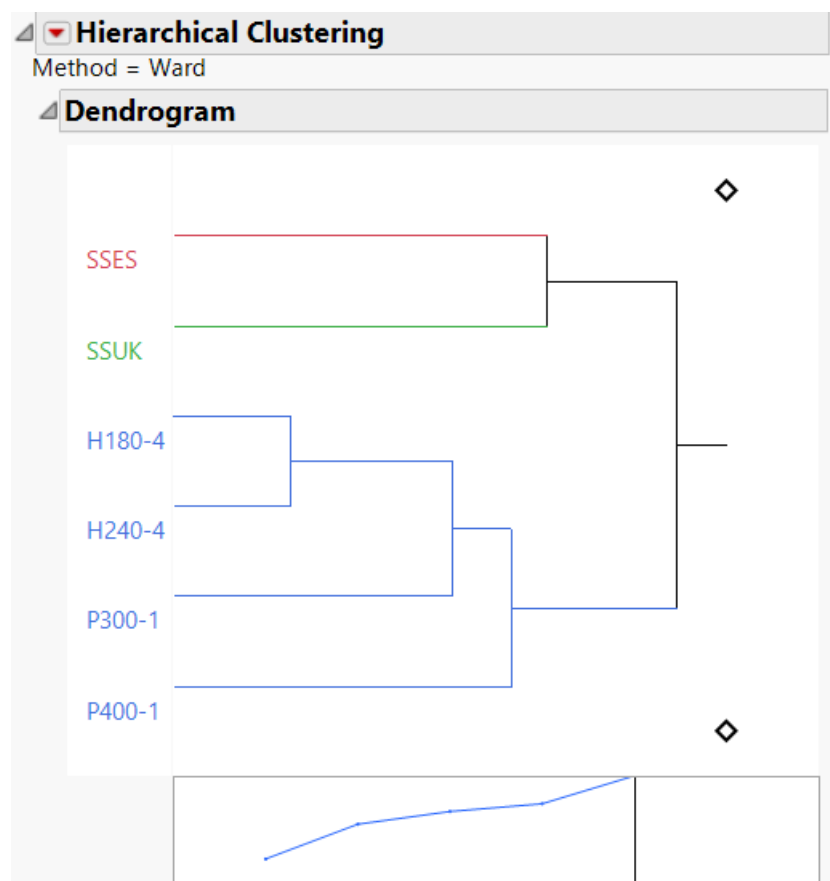


Figure A 5 Hierarchy of raw materials.

A.1.2 Soil properties changes derived from the glasshouse experiment.

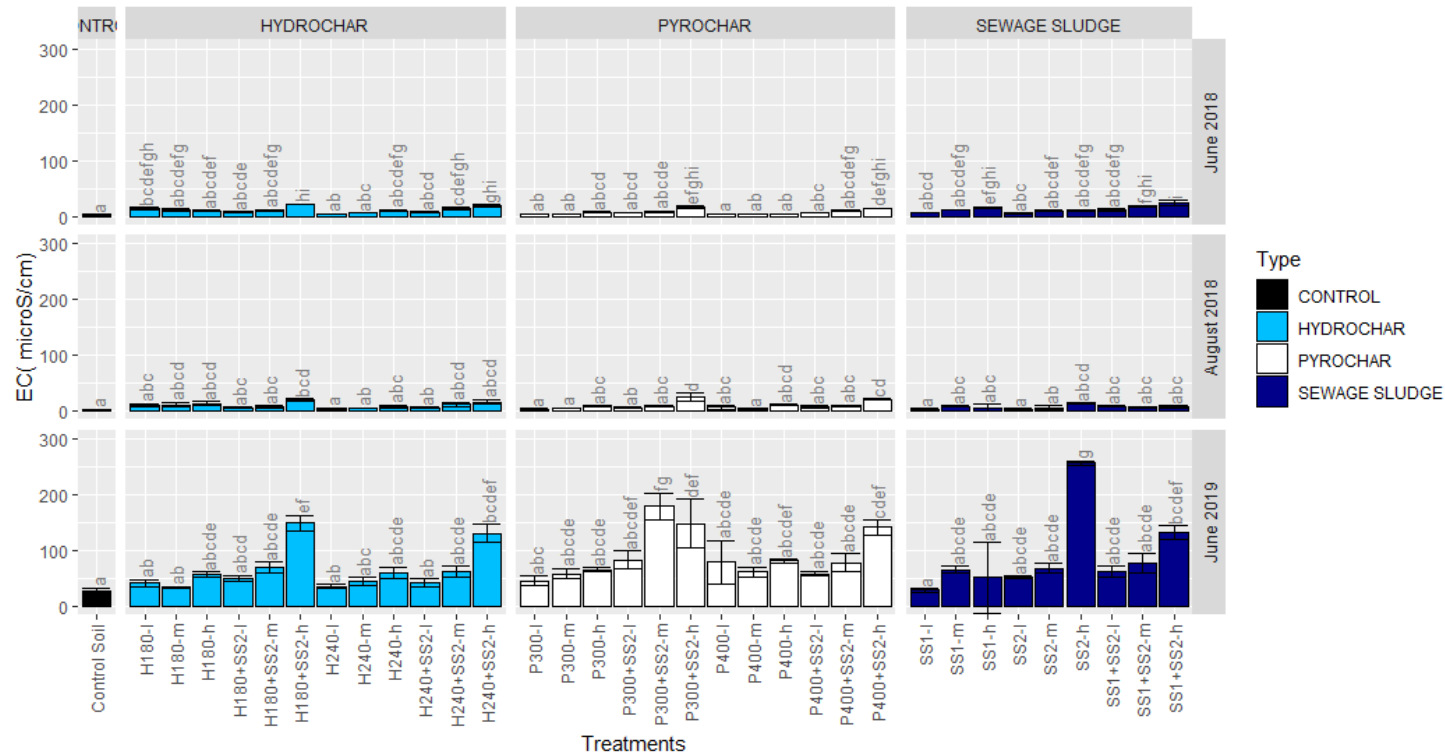
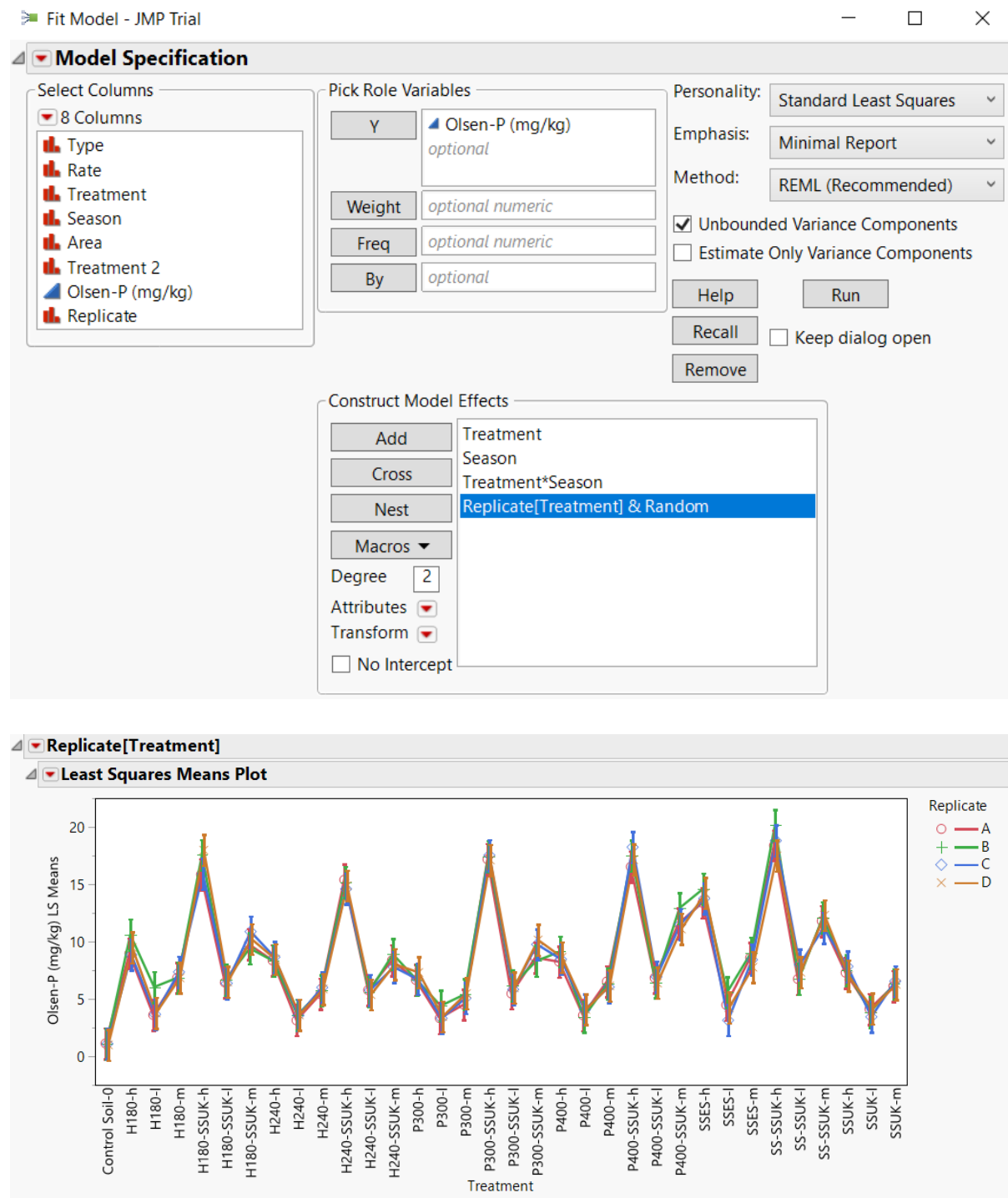
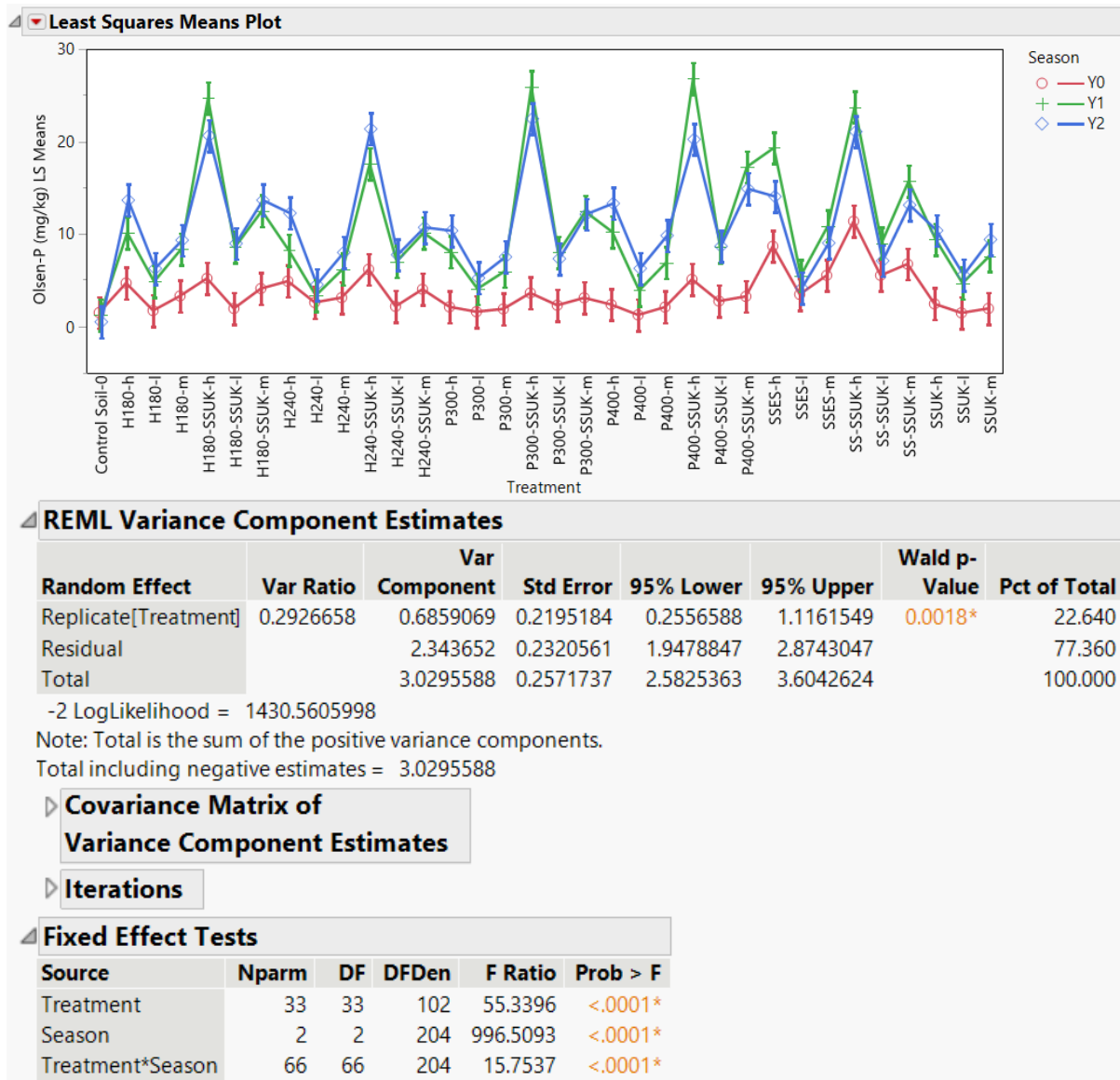


Figure A 6 Changes in soil EC after amendments with SS_{ES} (SS1) derivatives and SS_{UK} (SS2) mixed in the combined treatments.

Letters show significant differences ($p < 0.05$) according to a one-way analysis of variance followed by a Tukey's honestly significant difference (HSD) multiple-means comparison of data from the same year Statistica program. SS_{ES} stands for Sewage Sludge (Spain) dried 105°C. 48h; H180-4 hydrochar from SS_{ES} at 180°C for 4h; H240-4 hydrochar from SS_{ES} at 240°C for 4h; P300-1 pyrochar from SS_{ES} at 300°C for 1h; P400-1 pyrochar from SS_{ES} at 400°C for 1h; SS_{UK} Commercialized Sewage Sludge (UK) used for combined treatments 72% moisture. Example: H180- SS_{UK} I indicates a combined treatment (50:50) at the lowest rate of H180-4 (5t/ha) mixed with wet SS_{UK} (5t/ha). giving a total of 10 t/ha applied. *(EC) Limit between a normal and a saline soil is 400 μ S/cm.

Repeated Measures Analysis (Mixed Model) REML on Olsen-P:





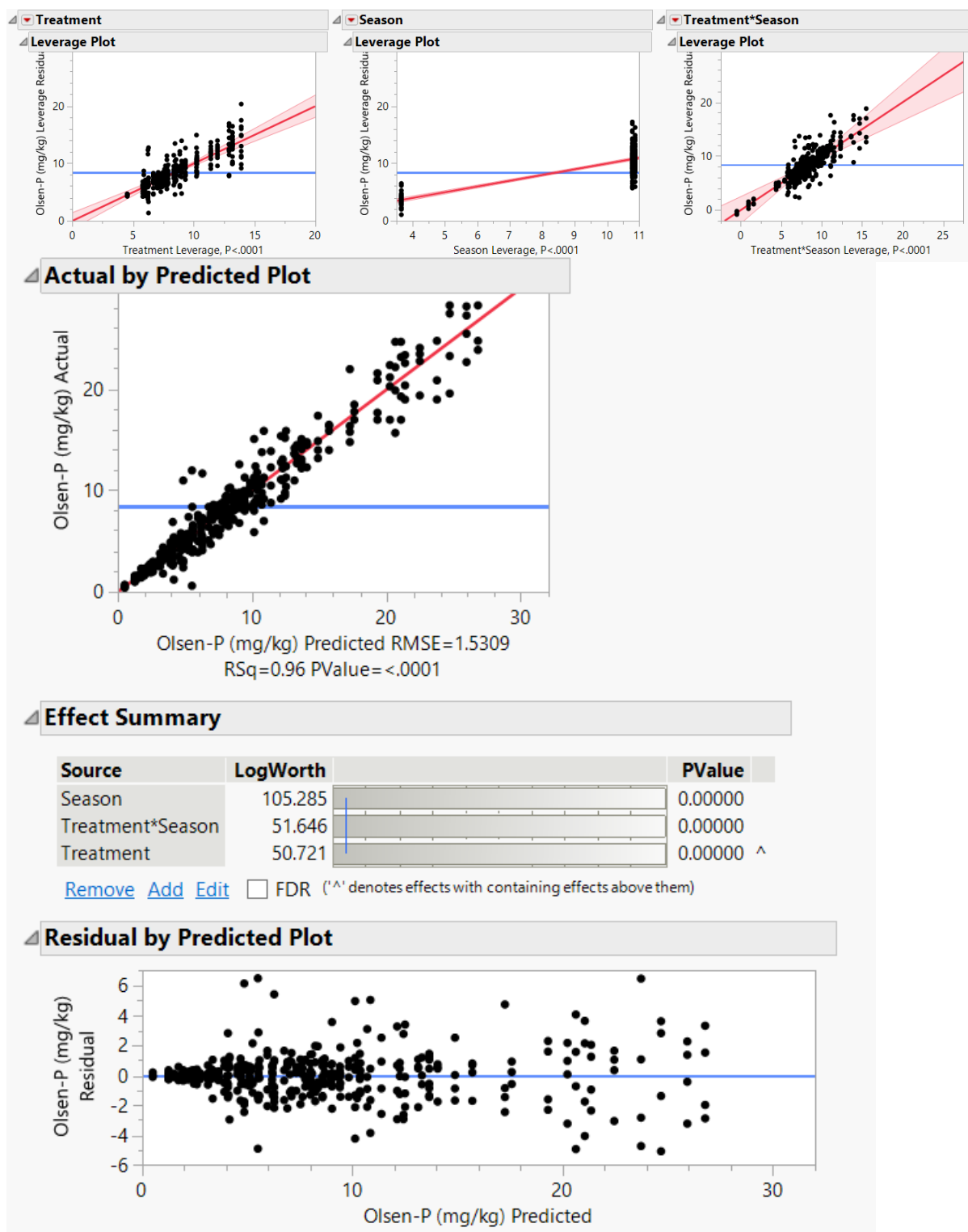


Figure A 7 Changes in soil Olsen-P after amendments with SS_{ES} derivatives and SS_{UK} mixed in the combined treatments

Table A 1 Olsen-P in soil, all seasons, Tukey test.

Level	Letters Tuckey Test	Least Sq Mean Olsen-P (mg/kg)
Control Soil-0,Y0	L1M1N1O1P1	1.5
Control Soil-0,Y1	N1O1P1	1.25
Control Soil-0,Y2	P1	0.5
H180-h,Y0	XYZA1B1C1D1E1F1G1H1I1J1K1L1M1N1O1P1	4.7
H180-h,Y1	JKLMNOPQRSTUVWXYZ	10.125
H180-h,Y2	GHIJKL	13.65
H180-l,Y0	K1L1M1N1O1P1	1.725
H180-l,Y1	WXYZA1B1C1D1E1F1G1H1I1J1K1L1M1N1O1P1	4.85
H180-l,Y2	STUVWXYZA1B1C1D1E1F1G1H1I1J1K1L1M1N1O1	6.275
H180-m,Y0	B1E1F1G1H1I1J1K1L1M1N1O1P1	3.3
H180-m,Y1	LMNOPQRSTUVWXYZA1C1D1	8.35
H180-m,Y2	KLMNOPQRSTUVWXYZ	9.325
H180-SSUK-h,Y0	VWXYZA1B1C1D1E1F1G1H1I1J1K1L1M1N1O1P1	5.2
H180-SSUK-h,Y1	ABC	24.675
H180-SSUK-h,Y2	BCDE	20.625
H180-SSUK-l,Y0	J1K1L1M1N1O1P1	1.95
H180-SSUK-l,Y1	LMNOPQRSTUVWXYZA1B1C1	8.575
H180-SSUK-l,Y2	KLMNOPQRSTUVWXYZ	8.975
H180-SSUK-m,Y0	YZA1B1C1D1E1F1G1H1I1J1K1L1M1N1O1P1	4.1
H180-SSUK-m,Y1	GHIJKLMNO	12.5
H180-SSUK-m,Y2	GHIJKL	13.65
H240-h,Y0	WXYZA1B1C1D1E1F1G1H1I1J1K1L1M1N1O1P1	4.9
H240-h,Y1	MNOPQRSTUVWXYZA1B1C1D1	8.225
H240-h,Y2	GHIJKLMNOPQ	12.25
H240-l,Y0	F1G1H1I1J1K1L1M1N1O1P1	2.6
H240-l,Y1	A1B1C1D1E1F1G1H1I1J1K1L1M1N1O1P1	3.35
H240-l,Y2	XYZA1B1C1D1E1F1G1H1I1J1K1L1M1N1O1P1	4.525
H240-m,Y0	D1G1H1I1J1K1L1M1N1O1P1	3.125
H240-m,Y1	STUVWXYZA1B1C1D1E1F1G1H1I1J1K1L1M1N1O1	6.2
H240-m,Y2	MNOPQRSTUVWXYZA1B1C1E1F1	8
H240-SSUK-h,Y0	STUVWXYZA1B1C1D1E1F1G1H1I1J1K1L1M1N1O1	6.175
H240-SSUK-h,Y1	DEFG	17.575
H240-SSUK-h,Y2	BCD	21.35
H240-SSUK-l,Y0	I1L1M1N1O1P1	2.175
H240-SSUK-l,Y1	PQRSTUVWXYZA1B1C1D1E1F1G1H1J1K1	7.025
H240-SSUK-l,Y2	NOPQRSTUVWXYZA1B1C1D1E1F1G1	7.75
H240-SSUK-m,Y0	YZA1B1C1D1E1F1G1H1I1J1K1L1M1N1O1P1	4.025
H240-SSUK-m,Y1	JKLMNOPQRSTUVWXYZ	10.125
H240-SSUK-m,Y2	IJKLMNOPQRSTU	10.7
P300-h,Y0	I1J1K1L1M1N1O1P1	2.125
P300-h,Y1	MNOPQRSTUVWXYZA1B1C1D1E1	8.075
P300-h,Y2	IJKLMNOPQRSTU	10.35
P300-l,Y0	L1M1N1O1P1	1.6
P300-l,Y1	YZA1B1C1D1E1F1G1H1I1J1K1L1M1N1O1P1	4.075
P300-l,Y2	VWXYZA1B1C1D1E1F1G1H1I1J1K1L1M1N1O1P1	5.25

P300-m,Y0	K1L1M1N1O1P1	1.9
P300-m,Y1	TUVWXYZA1B1C1D1E1F1G1H1I1J1K1L1M1N1O1	5.95
P300-m,Y2	OPQRSTUVWXYZA1B1C1D1E1F1G1H1I1	7.525
P300-SSUK-h,Y0	ZA1B1C1D1E1F1G1H1I1J1K1L1M1N1O1P1	3.625
P300-SSUK-h,Y1	AB	25.925
P300-SSUK-h,Y2	ABCD	22.45
P300-SSUK-l,Y0	H1K1L1M1N1O1P1	2.3
P300-SSUK-l,Y1	MNOPQRSTUVWXYZA1B1C1D1E1F1	8
P300-SSUK-l,Y2	OPQRSTUVWXYZA1B1C1D1E1F1G1H1I1J1	7.325
P300-SSUK-m,Y0	D1E1F1G1H1I1J1K1L1M1N1O1P1	3.1
P300-SSUK-m,Y1	GHIJKLMNOP	12.425
P300-SSUK-m,Y2	HIJKLMNOPQR	12.125
P400-h,Y0	G1H1I1J1K1L1M1N1O1P1	2.375
P400-h,Y1	JKLMNOPQRSTUVWXYZ	10.225
P400-h,Y2	GHIJKLM	13.3
P400-l,Y0	O1P1	1.25
P400-l,Y1	ZA1B1C1D1E1F1G1H1I1J1K1L1M1N1O1P1	3.9
P400-l,Y2	STUVWXYZA1B1C1D1E1F1G1H1I1J1K1L1M1N1	6.275
P400-m,Y0	J1M1N1O1P1	2.1
P400-m,Y1	QRSTUVWXYZA1B1C1D1E1F1G1H1I1K1L1	6.9
P400-m,Y2	JKLMNOPQRSTUVWXYZ	9.825
P400-SSUK-h,Y0	VWXYZA1B1C1D1E1F1G1H1I1J1K1L1M1N1O1P1	5.1
P400-SSUK-h,Y1	A	26.775
P400-SSUK-h,Y2	CDEF	20.225
P400-SSUK-l,Y0	E1F1G1H1I1J1K1L1M1N1O1P1	2.75
P400-SSUK-l,Y1	LMNOPQRSTUVWXYZA1B1C1	8.575
P400-SSUK-l,Y2	KLMNOPQRSTUVWXYZA1B1	8.675
P400-SSUK-m,Y0	C1D1E1F1G1H1I1J1K1L1M1N1O1P1	3.25
P400-SSUK-m,Y1	DEFGH	17.25
P400-SSUK-m,Y2	FGHIJ	14.875
SSES-h,Y0	LMNOPQRSTUVWXYZA1B1	8.675
SSES-h,Y1	CDEF	19.3
SSES-h,Y2	GHIJK	14.05
SSES-l,Y0	A1B1C1D1E1F1G1H1I1J1K1L1M1N1O1P1	3.475
SSES-l,Y1	TUVWXYZA1B1C1D1E1F1G1H1I1J1K1L1M1N1O1P1	5.5
SSES-l,Y2	YZA1B1C1D1E1F1G1H1I1J1K1L1M1N1O1P1	4.15
SSES-m,Y0	UVWXYZA1B1C1D1E1F1G1H1I1J1K1L1M1N1O1P1	5.525
SSES-m,Y1	IJKLMNOPQRST	10.85
SSES-m,Y2	KLMNOPQRSTUVWXYZ	9.025
SS-SSUK-h,Y0	IJKLMNOPQRS	11.375
SS-SSUK-h,Y1	ABC	23.725
SS-SSUK-h,Y2	BCDE	21.05
SS-SSUK-l,Y0	TUVWXYZA1B1C1D1E1F1G1H1I1J1K1L1M1N1O1P1	5.525
SS-SSUK-l,Y1	KLMNOPQRSTUVWXYZ	9.025
SS-SSUK-l,Y2	OPQRSTUVWXYZA1B1C1D1E1F1G1H1I1J1K1	7.1
SS-SSUK-m,Y0	RSTUVWXYZA1B1C1D1E1F1G1H1I1J1K1L1M1	6.75
SS-SSUK-m,Y1	EFGHI	15.7
SS-SSUK-m,Y2	GHIJKLMN	13.125
SSUK-h,Y0	G1H1I1J1K1L1M1N1O1P1	2.45
SSUK-h,Y1	KLMNOPQRSTUVWXYZ	9.425

SSUK-h,Y2	IJKLMNOPQRSTU	10.375
SSUK-I,Y0	M1N1O1P1	1.475
SSUK-I,Y1	XYZA1B1C1D1E1F1G1H1I1J1K1L1M1N1O1P1	4.675
SSUK-I,Y2	TUVWXYZA1B1C1D1E1F1G1H1I1J1K1L1M1N1O1P1	5.575
SSUK-m,Y0	J1K1L1M1N1O1P1	1.95
SSUK-m,Y1	OPQRSTUVWXYZA1B1C1D1E1F1G1H1	7.625
SSUK-m,Y2	KLMNOPQRSTUVWXYZ	9.4

Table A 2 **Olsen-P in soil** (mg/kg), Tukey test by season.

Treatment	Yo		Y1		Y2		Increment Y1 from Yo	Increment Y2 from Y1
Control Soil	1.5	ab	1.2	a	0.5	a	-17%	-57%
H180-SSUK-l	2.0	abcd	8.6	bcde	9.0	cdefgh	335%	4%
H180-SSUK-m	4.1	fghijk	12.5	efgh	13.7	ijk	204%	9%
H180-SSUK-h	5.2	jklm	24.7	kl	20.6	l	371%	-16%
H180-l	1.7	abcd	4.8	abcd	6.3	bcde	178%	30%
H180-m	3.3	bcdefghij	8.3	bcde	9.3	defghi	154%	12%
H180-h	4.7	ghijkl	10.1	cdef	13.6	ijk	115%	35%
H240-SSUK-l	2.2	abcdef	7.0	abcde	7.8	bcdefg	224%	10%
H240-SSUK-m	4.0	efghijk	10.1	cdef	10.7	efghijk	152%	6%
H240-SSUK-h	6.2	lm	17.6	hij	21.3	l	185%	21%
H240-l	2.6	abcdef	3.4	ab	4.5	abc	30%	34%
H240-m	3.1	bcdefgh	6.2	abcde	8.0	bcdefg	98%	29%
H240-h	4.9	hijklm	8.2	bcde	12.3	ghijk	69%	49%
P300-SSUK-l	2.3	abcdef	8.0	bcde	7.3	bcde	247%	-9%
P300-SSUK-m	3.1	bcdefgh	12.5	efgh	12.1	fghijk	301%	-3%
P300-SSUK-h	3.6	defghijk	25.9	kl	22.5	l	611%	-13%
P300-l	1.6	abc	4.1	abc	5.3	bcd	155%	29%
P300-m	1.9	abcd	5.9	abcde	7.5	bcdef	212%	27%
P300-h	2.1	abcde	8.1	bcde	10.4	efghijk	283%	28%
P400-SSUK-l	2.8	bcdefg	8.6	bcde	8.7	bcdefgh	211%	1%
P400-SSUK-m	3.3	bcdefghi	17.3	ghij	14.9	k	429%	-14%
P400-SSUK-h	5.1	ijklm	26.8	k	20.2	l	425%	-24%
P400-l	1.3	a	3.9	abc	6.3	bcde	211%	60%
P400-m	2.1	abcde	6.9	abcde	9.8	defghij	232%	43%
P400-h	2.4	abcdef	10.2	cdef	13.3	hijk	327%	30%
SSES-SSUK-l	5.5	klm	9.0	bcde	7.1	bcde	64%	-21%
SSES-SSUK-m	6.8	mn	15.7	efghi	13.1	hijk	132%	-16%

SSES-SSUK-h	11.4	o	23.7	jkl	21.1	l	108%	-11%
SSUK-l	1.5	ab	4.7	abcd	5.6	bcd	220%	18%
SSUK-m	2.0	abcd	7.6	abcde	9.4	defghi	288%	23%
SSUK-h	2.4	abcdef	9.4	bcdef	10.4	efghijk	287%	10%
SSES-l	3.5	cdefghij	5.5	abcd	4.2	ab	59%	-24%
SSES-m	5.5	klm	10.8	defg	9.0	cdefghij	96%	-17%
SSES-h	8.7	mn	19.3	ijk	14.1	jk	122%	-27%

Letters show significant differences ($p < 0.05$) according to a one-way analysis of variance followed by a Tukey's honestly significant difference (HSD) multiple-means comparison of data from the same year Statistica program.

Yo: Initial conditions of soil mixed with amendments after application; Y1: After first harvest, Y2: After second harvest.

Table A 3 Organic matter in soil (%).

Treatment	YO		Y2		Increment Y2 from Yo	Improvement to control soil YO	Improvement to control soil Y2
Control Soil	13.0	a	12.1	a	-7%		
H180-SSUK-l	16.2	ab	26.8	abcde	66%	24%	122%
H180-SSUK-m	23.6	ab	34.3	bcde	45%	81%	184%
H180-SSUK-h	25.8	ab	70.9	h	175%	98%	487%
H180-l	15.0	ab	16.5	ab	10%	16%	37%
H180-m	19.1	ab	29.1	abcde	53%	46%	141%
H180-h	28.2	abc	37.3	bcdef	32%	117%	209%
H240-SSUK-l	14.1	ab	28.1	abcde	98%	9%	132%
H240-SSUK-m	22.9	ab	36.3	bcde	59%	76%	200%
H240-SSUK-h	24.3	ab	58.3	fgh	140%	87%	383%
H240-l	15.1	ab	16.9	ab	12%	16%	40%
H240-m	16.2	ab	22.2	abcd	37%	25%	84%
H240-h	23.3	ab	39.0	cdef	68%	79%	223%
P300-SSUK-l	15.1	ab	26.2	abcde	74%	16%	117%
P300-SSUK-m	26.1	ab	32.9	abcde	26%	101%	172%
P300-SSUK-h	46.4	cd	75.8	h	63%	257%	528%
P300-l	15.9	ab	20.2	abc	27%	22%	67%
P300-m	19.0	ab	27.6	abcde	45%	46%	128%
P300-h	26.5	ab	42.0	defg	59%	103%	248%
P400-SSUK-l	14.1	ab	25.4	abcde	80%	8%	110%
P400-SSUK-m	20.6	ab	36.3	bcde	76%	58%	201%
P400-SSUK-h	31.9	bcd	62.4	gh	95%	145%	416%
P400-l	14.6	ab	16.1	ab	10%	12%	33%
P400-m	18.3	ab	22.9	abcd	25%	41%	90%
P400-h	24.8	ab	74.7	h	201%	91%	518%
SSES-SSUK-l	16.5	ab	23.9	abcd	45%	27%	98%
SSES-SSUK-m	28.3	abc	46.2	efg	63%	117%	283%
SSES-SSUK-h	47.7	d	69.1	h	45%	266%	472%
SSUK-l	14.4	ab	16.8	ab	16%	11%	39%
SSUK-m	17.8	ab	27.0	abcde	51%	37%	123%
SSUK-h	22.1	ab	45.5	efg	106%	70%	276%
SSES-l	14.0	ab	20.0	abc	42%	8%	65%
SSES-m	15.8	ab	41.2	cdefg	161%	21%	241%
SSES-h	22.9	ab	73.5	h	221%	76%	509%

A.1.3 Position in the glasshouse.

Column	Treatment	Cluster S1	Cluster S2	Column	Treatment	Cluster S1	Cluster S2	Column	Treatment	Cluster S1	Cluster S2
1	H180-SSUK-m C	6	3	45	SSES-SSUK-l B	9	2	91	P300-SSUK-m B	9	5
2	P400-SSUK-m A	11	12	46	P300-SSUK-l D	9	6	92	H240-SSUK-l B	3	5
3	H180-SSUK-l C	9	10	47	H180-m D	10	2	93	SSUK-l A	3	2
4	P400-SSUK-l A	6	1	48	P300-h C	10	2	94	P400-SSUK-m B	9	2
5	P400-h D	9	1	49	P400-SSUK-h B	6	1	95	P300-m D	3	5
6	H180-SSUK-l D	9	1	50	P400-m B	10	3	96	P400-l D	10	4
7	H180-SSUK-m D	6	8	51	H240-SSUK-h C	6	3	97	H240-m D	10	2
8	H240-h A	10	8	52	H180-l C	3	1	98	P400-SSUK-l D	3	2
9	SSES-SSUK-l C	9	9	53	H240-SSUK-m B	10	2	99	SSES-h B	6	4
10	H180-m A	9	10	54	P300-SSUK-l C	10	1	100	H240-m C	10	2
11	H180-SSUK-h D	11	11	55	SSUK-h A	6	1	101	H240-l B	10	3
12	H180-SSUK-h A	12	8	56	SSES-h C	7	8	102	P300-SSUK-h C	6	7
13	CONTROL A	9	12	57	P400-SSUK-m D	9	12	103	SSES-SSUK-m D	9	3
14	P400-SSUK-h C	6	8	58	H240-l D	10	1	104	SSUK-h C	9	3
15	P400-SSUK-h D	11	8	59	SSES-h D	6	3	105	P300-SSUK-m C	9	3
16	H180-SSUK-l A	9	12	60	H240-m A	10	3	106	H240-SSUK-l D	10	2
17	P400-SSUK-m C	9	8	61	SSES-SSUK-h D	12	3	107	H240-l A	10	2
18	SSUK-h D	1	4	62	H240-l C	10	1	108	SSUK-m A	9	8
19	SSES-l B	3	4	63	P300-l A	9	1	109	SSES-SSUK-h A	8	3
20	H240-SSUK-m A	9	3	64	CONTROL D	9	1	110	P400-SSUK-h A	6	4
21	P400-m A	9	4	65	P400-SSUK-l C	9	8	111	H180-l A	3	8
22	SSES-SSUK-m B	4	4	66	SSES-SSUK-h B	12	4	112	SSES-SSUK-h C	2	4
23	H240-SSUK-h D	4	4	67	H240-SSUK-m D	9	3	113	H180-SSUK-m B	9	1
24	P300-SSUK-l B	6	2	68	H180-l B	6	3	114	SSUK-m D	9	8
25	SSES-SSUK-m A	9	4	69	H240-SSUK-l C	9	12	115	H240-h D	10	8
26	H180-m C	3	2	70	P300-l C	10	8	116	SSUK-l B	6	1
27	P300-h A	10	3	71	SSUK-l C	6	1	117	P300-m B	10	3
28	H180-SSUK-l B	9	2	72	P300-l B	9	1	118	H240-SSUK-l A	3	8
29	SSUK-l D	6	12	73	SSES-l C	9	12	119	SSES-m A	6	1
30	SSES-m B	9	8	74	H180-SSUK-m A	9	12	120	H180-l D	10	1
31	H240-SSUK-h B	9	1	75	P400-m D	6	8	121	CONTROL C	10	8
32	H180-h D	9	12	76	P300-l D	10	3	122	SSES-l D	10	1
33	P400-m C	3	1	77	P300-SSUK-l A	9	2	123	P400-l A	10	1
34	P300-SSUK-m D	9	8	78	SSES-l A	9	3	124	P300-SSUK-h D	6	3
35	H180-m B	9	3	79	SSES-h A	5	7	125	H240-m B	3	3
36	P300-SSUK-h A	12	8	80	SSES-SSUK-m C	6	3	126	P400-h C	6	2
37	P400-h B	9	3	81	H180-h B	9	3	127	SSES-m D	10	3
38	H240-SSUK-h A	6	4	82	SSES-SSUK-l A	9	1	128	P300-m A	10	3
39	SSUK-m B	9	12	83	SSUK-h B	9	1	129	P300-SSUK-m A	9	4
40	P400-l C	6	1	84	P300-h B	10	1	130	H240-h B	10	3
41	P300-SSUK-h B	11	4	85	H240-SSUK-m C	10	1	131	SSUK-m C	10	1
42	H180-h C	9	8	86	H180-h A	9	1	132	P300-h D	10	3
43	H240-h C	9	1	87	SSES-SSUK-l D	9	3	133	SSES-m C	10	3
44	H180-SSUK-h B	1	1	88	CONTROL B	6	8	134	P400-l B	10	12
				89	H180-SSUK-h C	6	8	135	P400-h A	10	3
				90	P300-m C	10	8	136	P400-SSUK-l B	10	12

Figure A 8 Glasshouse map and cluster season 1 season 2 to yield.

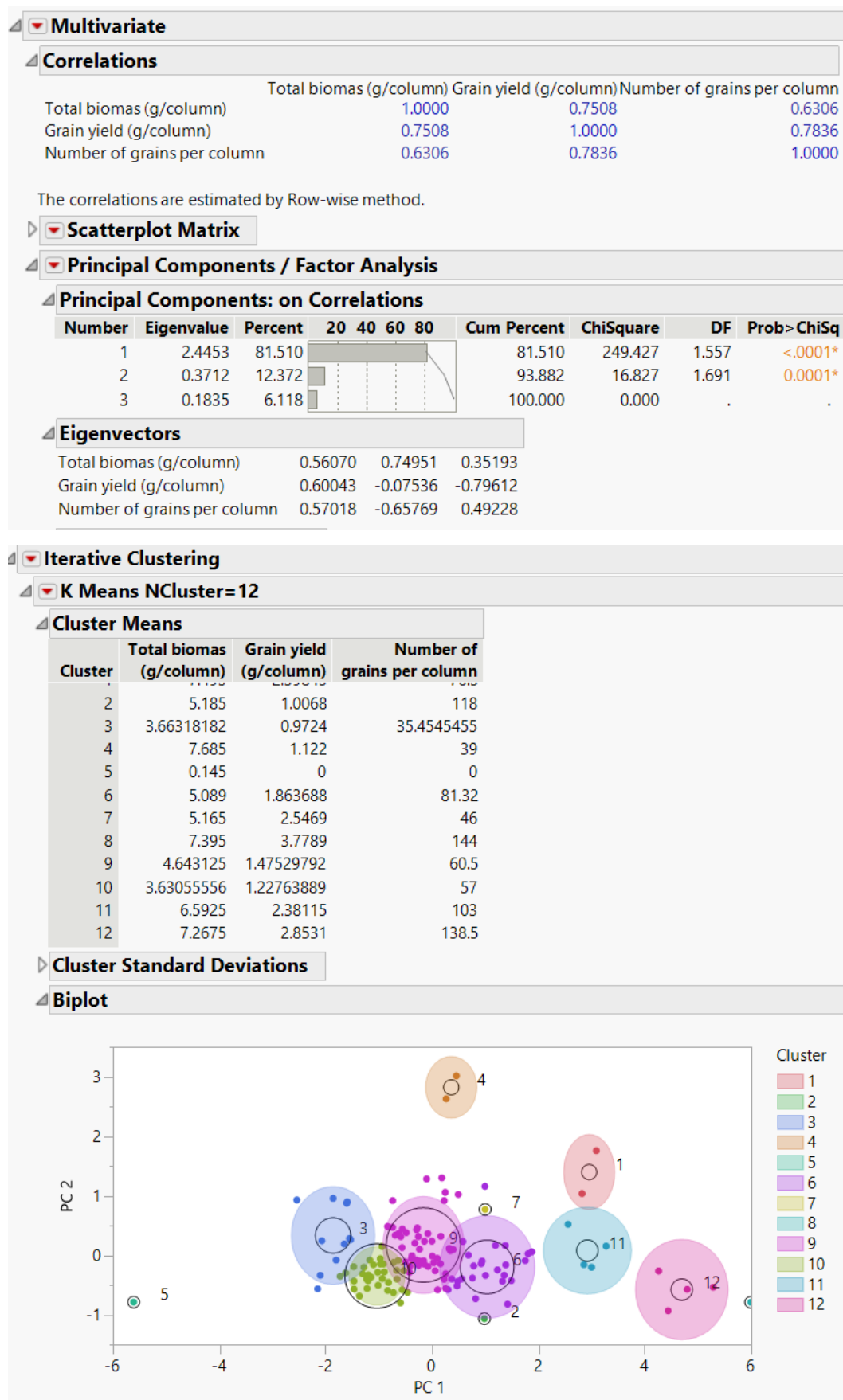


Figure A 9 PCA season 1 yield.

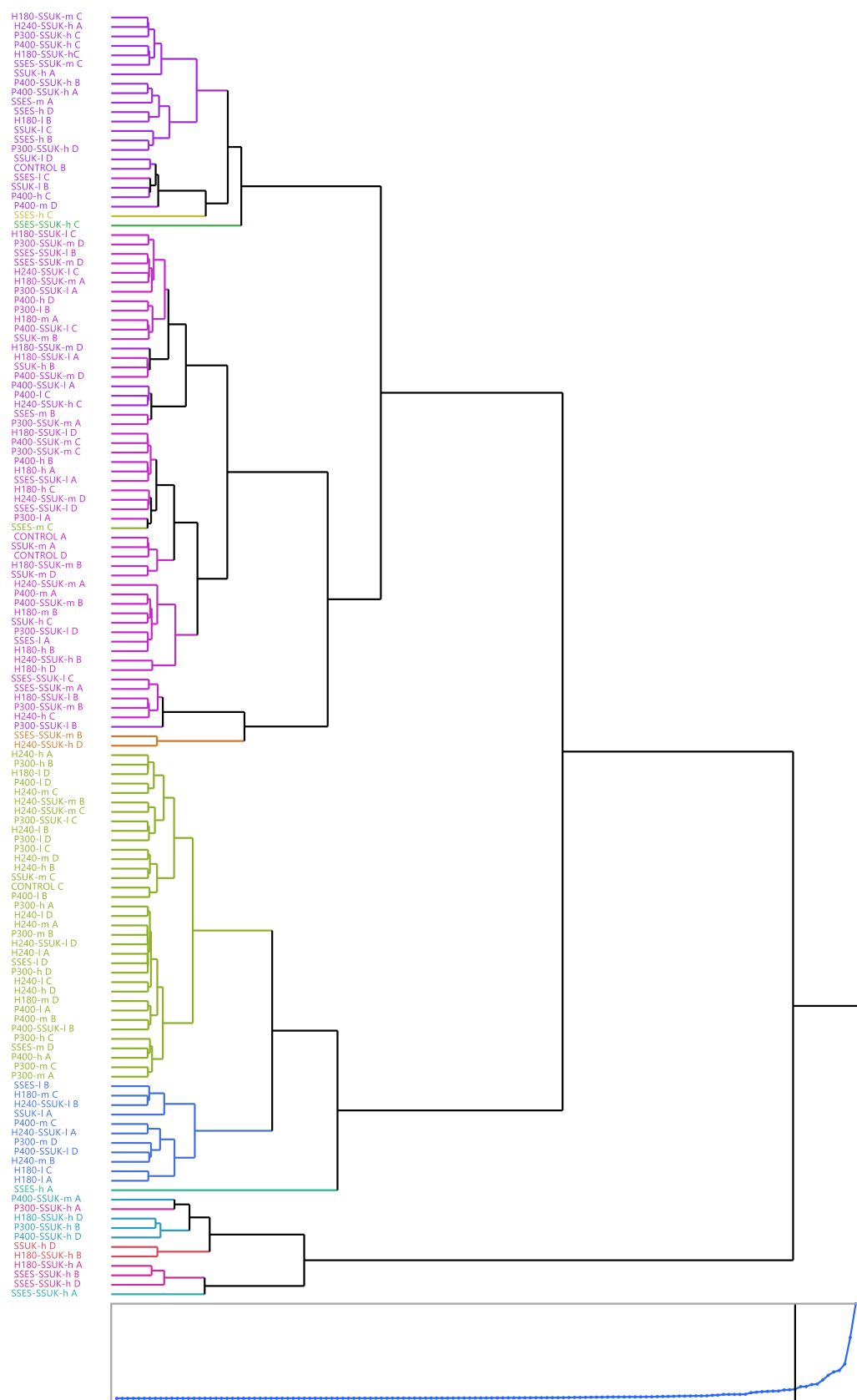


Figure A 10 Hyerarchy season 1 yield.

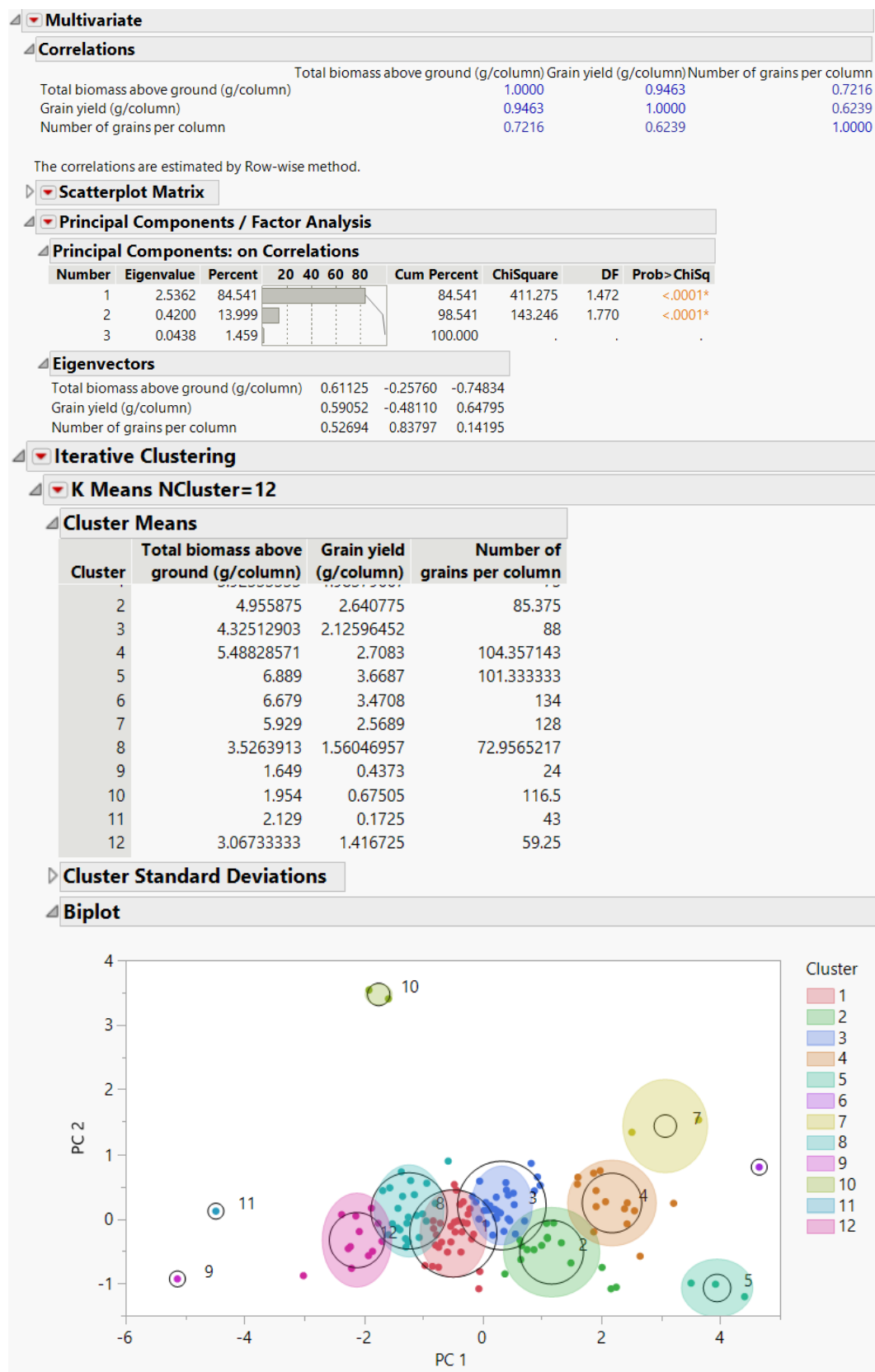


Figure A 11 PCA season 2 yield.

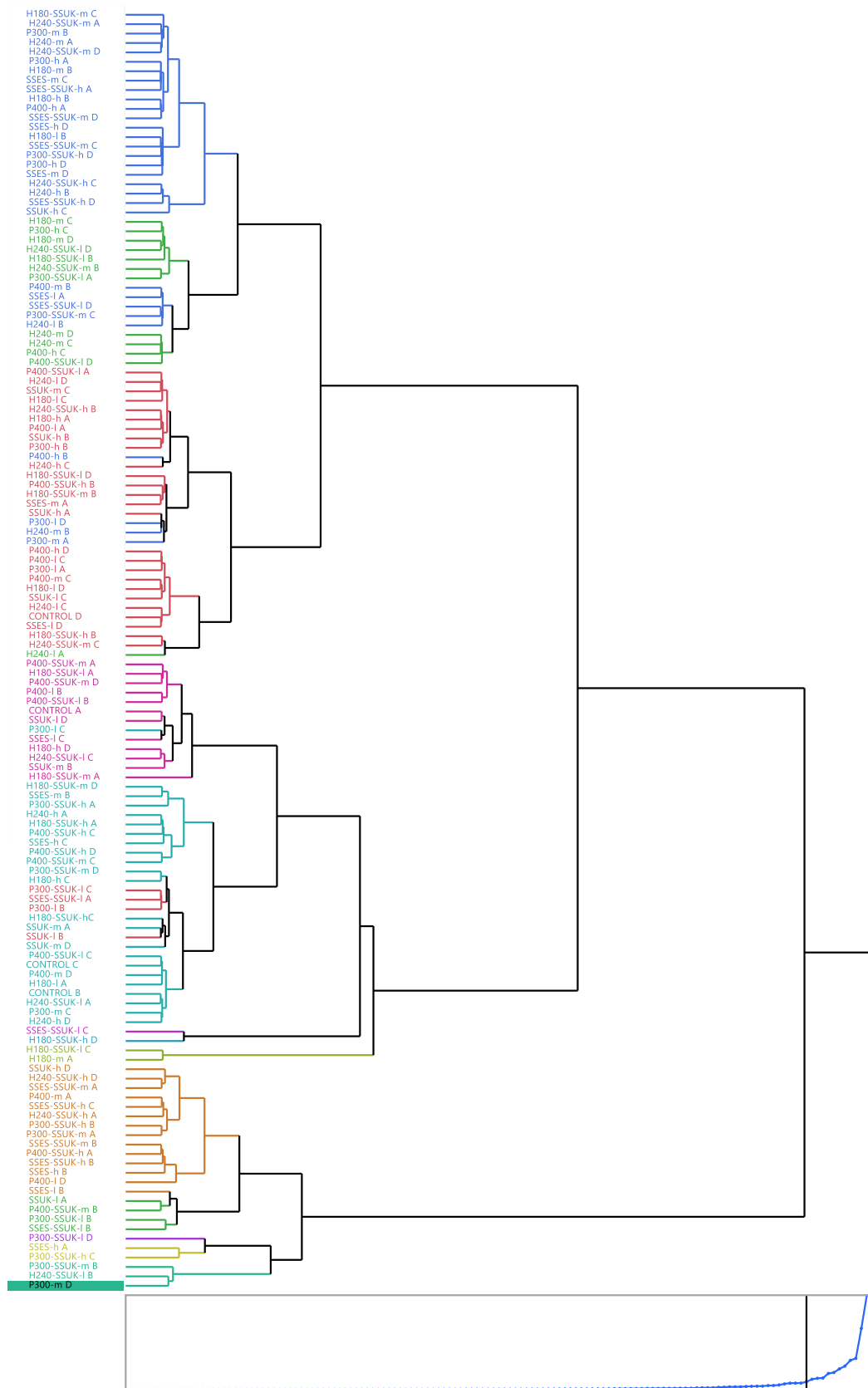


Figure A 12 Hyerarchy season 2 yield.

A.1.4 Environmental risk, analysis of bottom layer.

Table A 4 Bottom layer analysis acid digestion rest of elements (mg/kg).

	B	Pb	Hg	Cd	As	Mo	Na	Mg	K	Ca	Cr	Cu	Ni	Zn	Co	Mn
SS _{ES}	8.4	13.9	0.1	0.1	11.9	0.4	28.3	530.9	518.0	992.4	13.2	6.4	2.2	22.5	4.6	177.4
SS _{UK}	6.5	12.6	0.0	0.1	12.0	0.4	19.0	445.3	381.5	947.5	11.4	6.1	22.6	23.7	4.5	174.1
SS _{ES} -SS _{UK}	7.4	9.9	0.0	0.1	11.6	0.4	17.4	456.9	447.5	864.4	11.2	5.6	11.7	20.9	4.5	154.6
H180-SS _{UK}	5.6	8.9	0.2	0.1	11.3	0.4	17.7	397.8	400.9	602.8	9.8	5.2	1.6	20.2	3.9	145.4
H180-SS _{UK}	6.8	9.1	0.0	0.1	11.3	0.3	12.4	389.4	361.5	725.4	10.5	4.9	5.0	18.5	3.9	133.1
H240	4.8	9.8	0.1	0.1	9.7	0.3	26.1	390.9	420.6	780.4	8.5	5.2	0.1	18.7	3.4	134.3
H240-SS _{UK}	4.9	11.2	0.0	0.1	10.4	0.3	22.7	417.9	327.6	1128.6	9.5	5.7	11.2	21.3	4.2	162.6
P300	5.6	9.1	0.1	0.1	11.5	0.4	21.6	414.9	431.9	651.9	9.9	5.3	7.1	19.4	4.1	155.2
P300-SS _{UK}	6.7	16.3	0.1	0.1	11.5	0.5	32.9	539.5	385.8	1583.1	11.3	7.2	15.3	25.5	4.8	178.9
P400	6.0	9.1	0.0	0.1	11.5	0.4	19.3	424.4	438.0	635.9	9.7	5.3	3.2	20.1	3.9	156.0
P400-SS _{UK}	6.5	10.9	0.0	0.1	13.6	0.4	9.7	437.1	360.3	711.9	11.3	6.0	6.4	23.7	5.1	175.4
Control Soil	7.4	10.5	0.1	0.1	11.7	0.5	21.6	437.2	430.8	742.5	11.8	5.5	5.3	21.2	5.2	174.7

Table A 5 Bottom layer analysis (mg/kg).

	pH (1:10)		EC μS/cm		LOI mg/kg		Olsen-P mg/kg		Total P mg/kg		Total K mg/kg		Total Fe mg/kg		Total Al mg/kg	
Control Soil	7.8	b	41.0	a	11741.0	a	1.49	a	250.0	ab	430.8	ab	12252.7	a	3472.5	ab
H180-SS _{UK}	7.7	b	119.5	a	7058.2	a	2.06	a	223.1	a	361.5	ab	10676.7	a	3054.3	ab
H180	7.8	b	70.5	a	12767.1	a	1.86	a	230.1	a	400.9	ab	11030.0	a	3243.5	ab
H240-SS _{UK}	7.3	a	290.9	a	15707.0	a	1.61	a	256.6	ab	327.6	a	9902.2	a	2659.6	a
H240	7.8	b	118.8	a	15949.0	a	2.24	a	247.1	ab	420.6	ab	9528.7	a	3319.0	ab
P300-SS _{UK}	7.5	ab	282.5	a	11159.8	a	1.84	a	289.4	b	385.8	ab	11870.9	a	3722.0	ab
P300	7.8	b	91.7	a	16590.4	a	1.48	a	236.6	ab	431.9	ab	11311.8	a	3493.9	ab
P400-SS _{UK}	7.7	ab	59.4	a	9719.7	a	1.45	a	272.4	ab	360.3	ab	13752.9	a	3042.6	ab
P400	7.9	b	57.4	a	15261.5	a	1.44	a	235.1	ab	438.0	ab	11039.2	a	3539.5	ab
SS _{ES} -SS _{UK}	7.7	b	122.1	a	13518.4	a	1.70	a	252.1	ab	447.5	ab	11409.0	a	3544.5	ab
SS _{ES}	7.6	ab	142.9	a	12941.5	a	2.19	a	277.1	ab	518.0	b	12673.5	a	4129.4	b
SS _{UK}	7.6	ab	152.7	a	25479.1	a	2.08	a	274.1	ab	381.5	ab	11547.3	a	3223.8	ab

Letters show significant differences ($p < 0.05$) according to a one-way analysis of variance followed by a Tukey's honestly significant difference (HSD) multiple-means comparison of data from the same year Statistica program.

