Nutrient recycling using biowastes from diverse sources

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Phosphorus is a limiting nutrient in crop growth and thus widely used as an agricultural fertiliser. It cannot be substituted by another element, nor newly synthesized. Hence, global food production is ultimately dependent on it and the demand will increase with global population growth. Most phosphorus is applied to soil as mineral P fertiliser, a non-renewable resource derived from mined phosphate rock and consequently there has been increasing interest in the use of treated biowastes to return P into agricultural soils. This research aimed to establish the physical and chemical properties of hydrochar obtained from biowastes from diverse sources with a view to their eventual use as a P fertiliser in organic farming.

After collecting biowaste samples including biogas slurry, liquid pig manure and struvite the samples were subjected to hydrothermal carbonisation (HTC) treatment. The treated samples were analysed visually with a microscope to estimate grain size, and homogeneity. In the second phase of the research, the chemical properties of the samples were determined. Elemental concentration including phosphorus, nitrogen, potassium, magnesium as well as heavy metals were measured. After this different amendments, including various minerals containing carbonate and phosphate, sea grass, struvite and wood ash, were added to the liquid pig manure to establish whether they influence nutrient concentration as well as P solubility and availability in carbonised pig manure.

The visual analysis indicated that increasing HTC temperature, pressure and processing time resulted generally in more homogeneous particle sizes as well as an increased abundance of smaller pores compared to the unchanged feedstock. The chemical analyses showed that sufficient P is available in all three carbonized biowastes used, thus making them suitable as fertiliser. However, only small differences were found between hydrochars made from the pure liquid pig slurry and those from amended liquid pig manure. The PAH and heavy metal concentrations in the amended and treated biowastes were generally low. P availability was unknown in carbonised pig manure before this research. This researched has shown the potential of biowastes in conventional and organic farming.

Keywords: Biowaste, Phosphorus, Fertiliser, Pig manure, Hydrochar, HTC

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List of Abbreviations

ALK – Alkaline soil type

As - Arsenic

BGSL - Carbonised biogas slurry

CA - Citric Acid extraction method

Cd - Cadmium

C_{DGT} - time averaged concentration at interface of DGT sampler and biowaste solution

CI – confidence interval

Cr – Chromium

Cu - Copper

DGT – Diffusive Gradients in Thin films method

F - Fluoride

Fe - Iron

GFL -Gesellschaft für Labortechnick Gmbh

Hg - Mercury

HTC - Hydrothermal Carbonization

IB – Iron bag method

K - Potassium

LPM - Liquid Pig Manure

MELK – decalcified, neutral soil type

MES – 2-(N-morpholino)-ethanesulfonic acid

Mg - Magnesium

Mn - Manganese

Mo – Molybdenum

MOPS – 3-(N-morpholino)-propanesulfonic acid

N - Nitrogen

Ni - Nickel

P - Phosphorus

PAH - Polycyclic Aromatic Hydrocarbon

Pb - Lead

PR - Phosphate Rock

PW – Process water

S – Sulfur

WHC – Water holding capacity

Zn - Zinc

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Chapter 1

Introduction

The biological availability of phosphorus (P) in many soils is naturally low and most cropping systems need to provide additional P to increase their yield potential. Therefore, various types of P fertilisers are used to increase crop growth and yields on soils where P stocks have been depleted through crop removal (Mullins 2009). While fertilisers represent the greatest use of P in agriculture, they are mostly applied in form of commercially produced chemical supplements. However, the production of these fertilisers relies on finite reserves and limited phosphate rich rock mines making it an expensive product. Furthermore, the production of chemical fertilisers contributes to global warming through releases of greenhouse gases, while the chemical fertiliser itself eliminates diversity in the soil microbial system, decreases soil organic matter, worsens soil structure, reduces biological activities, and therefore decreases soil fertility (Bronick and Lal 2005). The increasing dependence on chemical fertiliser can increase nutrient pollution as evident by eutrophication and decreased water quality through leaching into the groundwater (Zhao et al. 2016). Consequently, there has been an increasing interest in recovering and recycling P from biowaste sources (Schoumans et al. 2015a; Duboc et al. 2017). These sources include: animal manure, sewage sludge, and struvite. Biowaste from these sources can have naturally high concentrations of P and could potentially present a natural substitute to mineral fertiliser (Degryse et al. 2017; Cao et al. 2011). Hence, recovering and recycling P from diverse biowastes is important and shows the need to further research the potential of biowaste as fertiliser in both the organic and conventional agricultural industry.

With increasing livestock farming high quantities of P are accumulated in manure (Bouwman et al. 2013). In Austria 1,739,000 tonnes of animal by-products were measured in 2009 (Agro, 2011). The non-point source might be wasted due to manure storage-related issues as well as direct application of manure could lead to potential risk of P loss since manure contains phosphorous in highly soluble forms (Dai et al. 2015). Due to the high water solubility of P, 50 % of inorganic P in manure, high amounts of P can be lost during rainfall (McDowell et al. 2001). Other naturally occurring P resources can be extracted from slaughterhouse waste, municipal sewage, and waste water (Duboc et al. 2017). These P residues can be either used directly as fertiliser or in carbonised form. However, direct application of biowastes such as sewage sludge is becoming more restricted due to its potential to carry pathogens, heavy metals and other pollutants (Schoumans et al. 2015b; Sartorius, von Horn, and Tettenborn 2012) Furthermore, potential accumulation of heavy metals such as zinc (Zn), copper (Cu), nickel (Ni), cadmium (Cd), lead (Pb), mercury (Hg) and chromium (Cr) also show a need to treat biowastes especially animal manure before application on soil (Choudhary, Bailey, and Grant 1996). Heavy metals have the potential to accumulate in soil as well as becoming toxic to plants. Therefore, the possibility of using raw biowastes is limited. However, the potential of heavy metal accumulation could be avoided by treating biowastes before application (Fytili and Zabaniotou 2008).The heavy metal concentration of the sludge is dependent on its origin.

Various methods have been established to recover P while removing pollutants from biowastes, one of them being the process of carbonisation, where the biowaste is converted into carbon or carbon-containing residue (Sartorius, von Horn, and Tettenborn 2012). Carbonisation processes have become more popular over the recent years due to the positive effects of carbonised substrates on soil water holding capacity, plant nutrient uptake, especially in nitrogen (N), phosphorus and micronutrients while reducing losses through leaching (Moreno-Jiménez et al. 2016). Carbonising biowaste is believed to stabilise and sanitise the product, mobilise nutrients as well as allowing the use of a wider range of biowastes (Schoumans et al. 2015b). With increasing environmental degradation biowastes have the potential to contain higher amounts of heavy metals, organic pollutants and pathogens contamination, hence, it is becoming more necessary to sanitise the product before application (Schoumans et al. 2015b; Sartorius, von Horn, and Tettenborn 2012).

A common carbonisation technique is pyrolysis where organic material (e.g. biowaste) is decomposed thermochemically. Biochar, the product of pyrolysis, has the potential to act as a CO_2 sink as well as soil enhancement although the stability of the char largely depends on multiple factors such as the production method used (Kambo and Dutta 2015). Moreover, pyrolysis produces gases such as carbon monoxide and methane (CH_4) which are well known greenhouse gases, and releases polycyclic aromatic hydrocarbons (PAHs) and oils, that can contaminate soils where carbonised biowastes are applied on (Abdel-Shafy and Mansour 2016). However, this technique cannot be used for liquid waste. Hydrothermal carbonisation technique (HTC) gives the opportunity to treat a wide range of biowastes as well as recycle liquid waste. HTC transforms material such as biowaste into hydrochar within hours using heat and pressure, and the product can be used to provide potential nutrients for plants (Busch and Glaser 2015). Hydrochar is known to be less stable compared to biochar, while showing similar potential to release CH_4, CO_2 and PAHs (Quilliam et al. 2013). However, the HTC process is able to eliminate pathogens and odour compounds, while removing soluble toxic metals (Reza et al. 2013).

Thus far biochar has become a common soil amendment to improve agricultural yields. However, there is a lack of knowledge of the potential of hydrochar in field studies (Brown et al. 2015; Busch and Glaser 2015). In general, using carbonised rather than uncarbonised biowaste has the advantage that it increases soil fertility, stability and its hydraulic properties (Sorrenti et al. 2016). Furthermore, a recent study has shown that phosphorus concentrations increase with increasing HTC temperature applied to the biowaste (Reza et al. 2016). However, to date, most HTC studies have focused on methodology rather than the products, nitrogen rather than phosphorus, and have not considered the potential of hydrochar as fertiliser.

More recent studies focussed on hydrochar produced from liquid animal manure as soil amendment due to high amounts of waste produced in livestock farming. Hence, guidelines for manure management (Ribaudo et al. 2003) as well as methods for P immobilization in manure, including mineral amendments using calcium (Ca) and aluminium (Al) comprising substances were established to diminish P loss from manure (Armstrong et al. 2012; Wilson et al. 2008). Carbonisation of manure results in less soluble P making HTC a potential solution to avoid P loss from biowaste (Liang et al. 2014). Field application of char include manure treatment, soil amendment, carbon sequestration, remediation and crop production. However, although some attention has been given to the characteristics of biochar little is known about the P solubility and availability in manure-derived hydrochar.

1.1 Research aims

Despite existing studies on the transformation of biowaste into char by HTC and pyrolysis, little has been research on a systematic description of the change of P speciation during these treatments (Huang and Tang 2015). This is important as the environmental fate of P in manure is determined partially by the structure of the manure and solubility of the P (Dai et al. 2015). However, some studies have shown that carbonising soil increased total and available P concentrations (Ch'ng, Ahmed, and Ab Majid 2014). This research will explore whether this can be achieved by subjecting certain biowastes to HTC treatment.

There were two principal aims of this research. The first aim was to determine optimal HTC conditions for producing a carbonized biowaste that is homogeneous and could potentially improve the physical characteristics of the soils. The second aim was to determine the concentration, extractability and potential plant bioavailability of the P from different HTC treated biowastes, as well as measuring other parameters relevant to informing their suitability for use as a P fertiliser on agricultural soils.

1.2 Background and Literature review

1.2.1 Groupe Roullier Ltd.

The Groupe Roullier Ltd is a plant, animal and human nutrition specialist. It was founded over 60 years ago and focusses on supplying solutions to the challenges faced in the agricultural industry. The company is organized around five business lines including agro-supplies, food phosphates, magnesia, industrial products and solutions, and the food-industry (Roullier n.d.)

1.2.2 A brief history of biowaste use as a source of phosphorus

Biowaste such as manure, cider and ironmaking slag has been utilised as fertiliser in agricultural practice since 5900 – 2400 B.C. Farmers realised that crop growth increases when animals are nearby. However, the applied manure was not treated thus nutrients such as nitrogen, phosphorus and potassium (K) as well as pollutants including heavy metals and PAHs have been taken up by crops (Bogaard et al. 2013). Polycyclic aromatic hydrocarbons contain only carbon and hydrogen consisting of multiple aromatic rings but are abundant environmental contaminants (Abdel-Shafy and Mansour 2016). They arise during incomplete burning processes such as heating with coke or wood, traffic, industrial emissions and forest fires. To reduce PAHs, other contaminants and pathogen deposition on leaves treatments need to be applied on the material.

Biowaste such as animal manure and sludge are carriers of desired plant nutrients including the major plant nutrient elements, phosphorus, potassium, magnesium (Mg), and sulphur (S) (Rigby and Smith 2014) but do also contain pathogens, heavy metals and organic pollutants including pharmaceutical residues (Albihn and Vinnerås 2007). Biowaste can be a carrier of various harming diseases and bacteria such as *E.coli* and swine fever (Eriksson et al. 2005). Furthermore, antibiotics can be found in pig and chicken biowaste predominantly, diseases are fairly common in livestock and farmers treat their animals with various antibiotics to avoid the risk of spreading diseases (Albihn and Vinnerås 2007). Despite, human influence on potential pollutants, biowaste also naturally contain heavy metals and are therefore contributors of heavy metals to soil (Mortvedt 1995; McBride and Spiers 2001). Cadmium for example, which is mainly present in sludge, is easily taken up by plants and is highly toxic for humans (Linderholm, Tillman, and Mattsson 2012). However, heavy metals such as Cd, Pb, Zn and Cu can be eliminated under the application of high temperatures as they then react with additives including $MgCl_2$ or $CaCl_2$. In contrast, Cr and Ni are not easily dissolved, therefore the importance of having low concentrations of these two trace elements (Linderholm, Tillman, and Mattsson 2012).

Despite the fact that fertilisation in form of manure, compost and animal excrement is more effective due to soil structure improvement and increased ability in water and nutrient holding capacity (Steiner et al. 2007), manure was replaced by mineral fertiliser since the early 19th century. This had two reasons: (1) manure fertilisation is more expensive because of both higher transport and spreading cost as well as (2) less convenient as it was proven by Liebig in his mineral theory (Russel and Williams 1977; van der Salm, van Middelkoop, and Ehlert 2017; Thompson 2009; Nath 1940). Liebig stated that yields are limited by the most limiting nutrient. This means despite high amounts of one nutrient (e.g. nitrogen) plants will only grow as much as the least available nutrient (e.g. phosphorus) permits. He also showed that nitrogen, phosphorus and potassium are essential to plant growth (Aulie 1974).

Increasing urbanisation and industrialisation has led to a growing demand for fertiliser production, as well as the need to substitute coal with biowaste in the energy industry. This had two reasons. Firstly, it was realised that fossil fuel will become scarce and, secondly, the need for a cleaner and more environmentally friendly fuel material (van Wyk 2001). Furthermore, maximizing agricultural output became more important, so in the late 19th century, local P sources were increasingly replaced by more distant P sources, such as guano and mining of phosphate-rich rocks, leading to an imbalance between P taken for crop production and P returned to the soil. Consequently, considerable phosphorus losses occur throughout the food production and consumption system. Substantial amounts of P are lost through leaching, surface erosion from fertilised and agricultural fields (Mullins 2009). Moreover, plant uptake and crop removal from fields upon harvesting also depletes soils from phosphorus.

Mineral phosphorus fertilisers, including phosphate rock (PR), a rock composed of phosphate minerals, are popular soil amendments due to considerable amounts of P (27 – 40 %), Ca (44 – 52 %) and CO_2 concentration of <6 % (Caro and Hill 1956). However, PR is a distant phosphorous source. It is globally mined in the US , Morocco and China (Chien, Prochnow, and Cantarella 2009) with a constant decrease in global availability due to its non-renewable nature (Cordell and White 2011). Since global demands are increasing, it is becoming scarce and expensive (Cordell et al. 2011).

Phosphorus sources containing high P concentrations and low Cd concentrations are close to exhaustion, as phosphate rock becomes depleted, we will be forced to exploit lower quality rock, which will cause more environmental degradation. The high dependence on PR imports can cause high economic damage to countries through supply interruption. Furthermore, mining and export of PR contributes to greenhouse gas emission through the use of machinery. Another issue of P mineral fertiliser is the accumulation of contaminants in soil. Contaminants of great concern include fluorine (F), cadmium, arsenic (As), mercury and lead (Mclaughlin et al. 1996). Moreover, adding mineral fertiliser causes higher mineralisation of soil organic matter, so called *priming effect*, meaning an increase in microbial activity in the soil resulting in a higher organic matter decomposition rate (Marinari et al. 2000). Also, a large portion of soluble inorganic phosphate applied to the soil as chemical fertiliser is immobilised rapidly and becomes unavailable to plants (Chen et al. 2006).

The demand for commercial fertilisers has been rising steadily, with fertiliser use increasing substantially between 1950 and 2000 (Cordell and White 2011). If remaining reserves are not managed well, there is the potential of P becoming scarce in the next 100 years (Childers et al. 2011; Cordell, Drangert, and White 2009). Moreover, remaining PR reserves will become increasingly difficult to access, with increasing costs of extraction and processing, and a decline in quality of the reserves. With 90% of the world's P used for food production, it will be critical to address the problem of limited P availability to meet future nutritional demands of a growing global population (Cordell, Drangert, and White 2009). Hence the realisation that waste in form of organic slurry produced by both agricultural practice and fuel production should be further utilised instead of wasted.

Phosphorus Cycle

Phosphorus is the only element that has virtually no relevant gaseous phase (Cordell and White 2011). Most phosphorus in terrestrial ecosystems is derived from degradation of calcium phosphate minerals, either through natural weathering or at present time by anthropogenic mining of rocks (Figure 1).

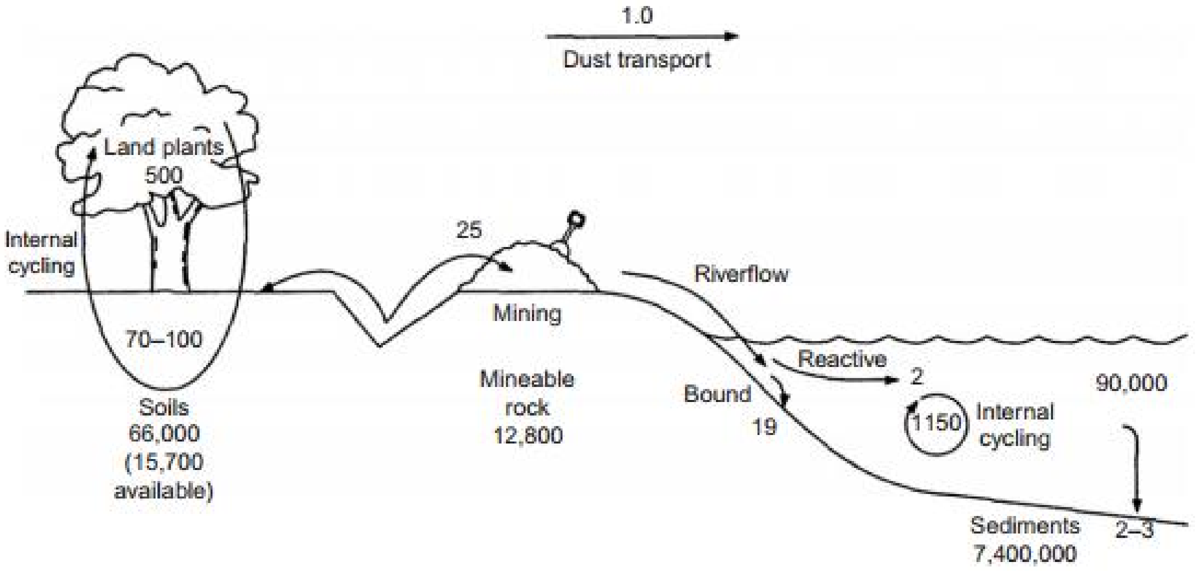

Figure 1 The global phosphorus cycle, showing natural and anthropogenic occurring P. Retrieved from Schlesinger & Bernhardt (2013)

The most common form of phosphorus is inorganic P. In this form the element is taken up by plants and microorganisms, and accounts for a major fraction of the total P in soils (Harrison 1987). Natural deposits of P typically occur as phosphates. During soil formation and weathering processes, phosphates are released from calcium phosphate minerals, mostly apatite ($Ca_5(PO_4)_3OH$) (Kruse et al. 2015). At this stage, P can be absorbed by plants. Phosphorus returns to soil through dead biomass and excretions. In terms of geological time periods the natural P cycle is closed, and those sediments appear back at the earth's surface.

Only a small amount of total phosphorus is available to biota and less than one percent of total P is taken up by plants during plant growth. After plants senescence phosphorus is deposited back to the soil. Thus, recycling P is a well-developed balance both on land and at sea. Recycling, in ultimate analysis, is commonly known as "*trophic chain*". Other P inputs may also derive from atmospheric deposition or, on a long time-scale, uplifting of sedimentary rock from the ocean (Schlesinger 2013).

Phosphorus pools and reactions

Phosphorus exists in diverse chemical forms including organic (P_o) and inorganic P (P_i) and can be bound and cycled in the soil in so-called P pools differing in their reactions with liquid and solid phase and in their availability for microorganisms and plants. In the soil solution, inorganic P (H_2PO_4, HPO_4 and PO_4) can be taken up by plants, incorporated into plant tissue and converted into organic P (as nucleotide phosphates, phospholipids or sugar phosphates) (Filippelli 2008). Phosphorus cycling can be subdivided in inputs, pools & reactions and losses (Figure 2).

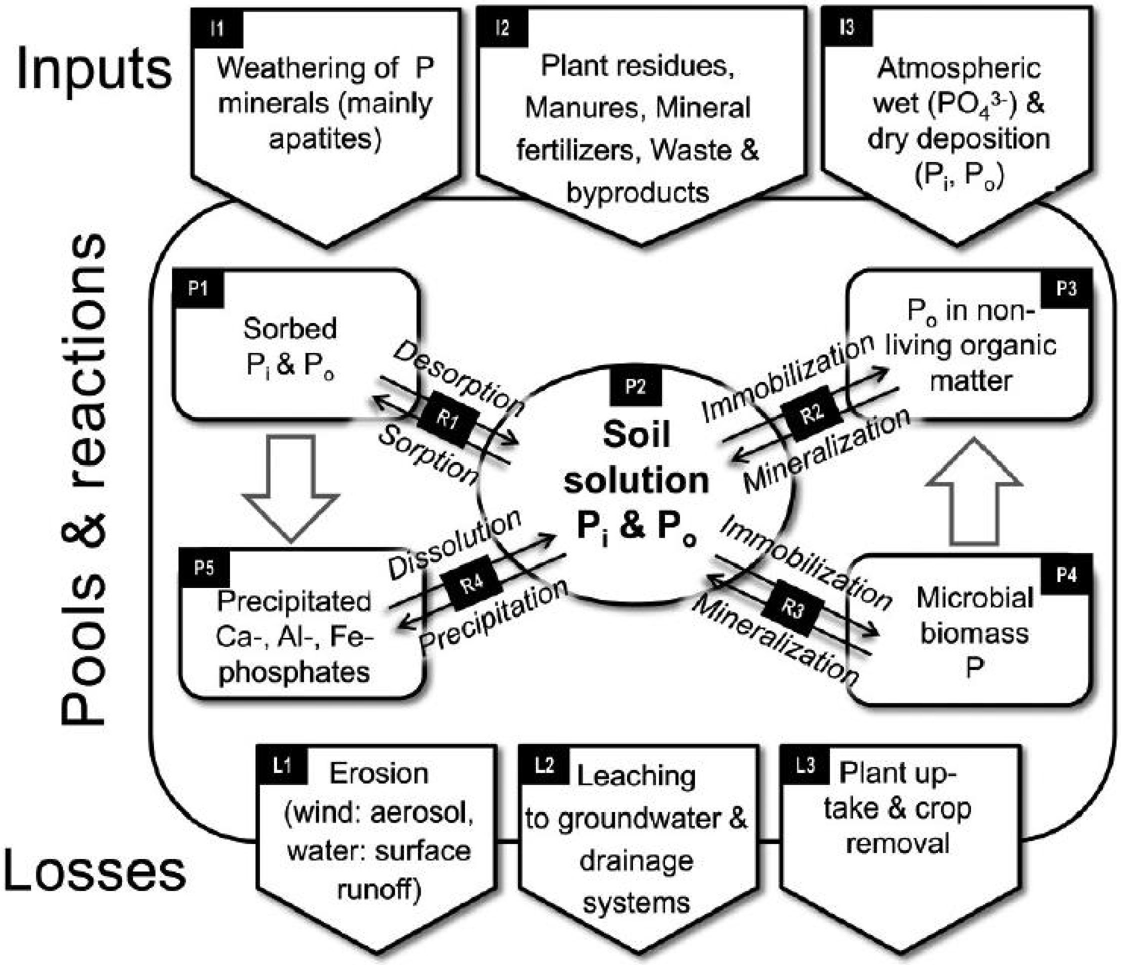

Figure 2. P cycling in soils, showing its inputs, pools and reactions, and losses. Retrieved from Kruse et al (2015).

Phosphorus comes from three different sources including weathering of P minerals, anthropogenic inputs and atmospheric depositions (Figure 2). These inputs influence the P pools and reactions. Phosphorus concentrations differ according to different factors including intensity and type of land use, the stage of weathering, soil texture and the soil horizon. Those factors create the environment in which P binds to different chemical compounds and react with the solid and liquid phase of the soil (Kruse et al. 2015).

Inorganic phosphorus (P_i in Figure 2) consisting of the mineral pool which comprises primary and secondary minerals. Primary minerals are stable and contain apatites (phosphate rocks), strengite and variscite, while secondary contain calcium, aluminium and iron (Fe). Both mineral classes are part of dissolution processes, whereas secondary minerals are also part of precipitation reactions. Primary minerals do not contribute to plant uptake as the weathering process is too slow (Shen et al. 2011). Precipitating with different metal cations, Al and Fe phosphates in acidic soils, Ca phosphates are formed in soils that have neutral to alkaline pH (Hinsinger et al. 2003). Precipitation is also the reaction that influence the solubility of many P fertilisers. Phosphorus availability to plants is limited when soil pH values are below 5.5 or between 7.5 and 8.5 due to fixation with Ca, Al and Fe. The poor mobility and low concentration of plant available phosphorus in P_i requires the use of phosphorus fertilisers to improve crop growth and yield. Application of chemical fertiliser can affect soil physicochemical properties therefore the preference of applying fertiliser produced from organic material (Shen et al. 2011).

30% to 65% of total P in soils is generally contributed by organic phosphorus (P_o in Figure 2) (Harrison 1987). Stabilisation of organic phosphorus in soil is released through mineralisation facilitated by soil organisms and plant roots related to phosphatase release. The P_o processes are mainly influenced by soil physical and chemical properties such as temperature, pH, soil moisture and the redox potential. Furthermore, these transformation have a huge effect on the overall bioavailability of P in soil (Shen et al. 2011). The major causes to P losses are erosion (L1 in Figure 2), leaching to drainage systems and groundwater (L2 in Figure 2) and plant uptake and crop harvesting (Figure 2).

Importance of nutrients to plant growth

The total phosphorous content of most surface soil is low, averaging only 0.6 % P. However, P is essential for all living organisms. It contributes to photosynthesis, respiration, energy storage and transfer as well as cell division, cell enlargement and other processes in plants and animals (Armstrong 1999). Fertilisation requirements can be derived from the Austrian guidelines of sufficient fertilisation (Table 1).

Table 1. Classification of phosphorous content according to the Austrian guidelines of sufficient fertilisation referring to soil extraction with CAL[1]. Content class A being the least desired class and content class C being the most desired class. Over fertilisation starts at content class D.

		cultivated land	pastures
content class	nutrient supply	g kg^{-1}	
A	very low	under 0.026	under 0.027
B	low	0.026 - 0.046	0.026 - 0.047
C	sufficient	0.047 - 0.111	0.047 - 0.068
D	high	0.112 - 0.174	0.068 - 0.174
E	very high	over 0.174	over 0.174

Potassium has multiple functions in plants. In photosynthesis it regulates the opening and closing of stomata, hence it controls the CO_2 uptake and H_2O loss. Potassium also triggers activation of enzymes and is essential for production of adenosine triphosphate (ATP). All in all, K increases crop yield and improves quality. It is important for plant growth processes (Armstrong 1998). According to the Austrian guidelines of sufficient fertilisation soil containing 0.05 – 0.087 g kg^{-1} require fertilisation to

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[1] Calcium acetate lactate (CAL ÖNORM L1087:2005-04--01,2018) extraction.

reach class C, once this is achieved fertilisation can be limited to the annual removal by the plants (Table 2).

Table 2. Classification of potassium content according to the Austrian guidelines of sufficient fertilisation divided by soil texture and land type referring to soil extraction with CAL. Content class A being the least desired class and content class C being the most desired class. over fertilisation starts at content class D.

		cultivated land			pastures
		g kg^{-1}			
content class	nutrient supply	clay content (%)			
A	very low	under 0.05	under 0.066	under 0.083	under 0.05
B	low	0.05 - 0.087	0.066 - 0.112	0.084 - 0.137	0.05 - 0.087
C	sufficient	0.088 - 0.178	0.113 - 212	0.138 - 0.245	0.088 - 0.170
D	high	0.179 - 0.291	0.213 - 0.332	0.246 - 0.374	0.171 - 0.332
E	very high	over 0.291	over 0.332	over 0.374	over 0.332

Magnesium nutrition of plants is frequently overlooked, and shortages will adversely impact plant growth. Many essential plant functions require adequate Mg supplies, the most visible being its role in root formation, chlorophyll and photosynthesis. Many less visible reactions are also dependent on an adequate supply of Mg (Cakmak and Yazici 2010). Fertilisation is required if the soil has < 0.075 g kg^{-1} of Mg (Table 3).

Table 3. Classification of magnesium content according to the Austrian guidelines of sufficient fertilisation divided by soil weight and land type referring to soil extraction with CAL. Content class A being the least desired class and content class C being the most desired class. Over fertilisation starts at content class D.

		g kg^{-1}		
content class	nutrient supply	clay content (%)		
A	very low	-	under 30	under 0.04
B	Low	under 0.05	0.030 - 0.055	0.04 - 0.075
C	Sufficient	0.05 - 0.075	0.056 - 0.105	0.076 - 0.135
D	high	0.076 - 0.150	0.106 - 0.190	0.136 - 0.220
E	very high	over 0.150	over 0.190	over 0.220

Calcium is a central regulator of plant growth and development. Ca^{2+} deficiency can lead to poor root development, leaf curling and necrosis, blossom end rot, bitter pit, poor fruit storage and water soaking. Deficiency especially effects the cell wall where Ca^{2+} plays an essential role in linking acid pectin residues as well as in the cellular membrane system where low Ca^{2+} increases the permeability of the plasma membrane (Hepler 2005). Together with Mg, Ca^{2+} combats Al toxicity in the soil by exerting its protective role in millimolar concentrations. Aluminium has mostly adverse effects on plant growths, especially in acidic soils. Aluminium toxicity mainly effects root cell plasma membrane, predominantly of the root apex (Mossor-Pietraszewska 2001). However, strong interaction of Al^{3+}, the main Al toxic form, with oxygen donor ligands (proteins, nucleic acids, polysaccharides) results in the inhibition of cell division, cell extension, and transport.

While elements including heavy metals such as zinc, copper, molybdenum (Mo), manganese (Mn) and iron as well as the non-metal boron are essential nutrient for plant development, they are only needed in small amounts and can lead to toxic effects when taken up in excess quantities (Nagajyoti, Lee, and Sreekanth 2010). Depending on heavy metal, fertilisation requirements can be derived from table 4 which shows the availability classes measured by an ethylenediaminetetraacetic acid (EDTA) extraction for micronutrients in soil.

Table 4. Classification of trace element content according to the Austrian guidelines of sufficient fertilisation using the extration method EDTA[2]. Over fertilisation is shown in content class E.

		Copper (Cu)	Zinc (Zn)	Manganese (Mn)	Iron (Fe)
content class	nutrient supply	mg kg^{-1}			
A	low	< 2	< 2	< 20	< 20
C	sufficient	± 8	± 8	± 70	± 100
E	high	> 20	> 20	> 200	> 300

Furthermore, according to Eikmann and Kloke (1991) there are different intervention and remediation values depending on heavy metal (Table 16). The intervention value relates to maximum soil concentration of a specific contaminant. Above this value monitoring or land-use changes are required. The remediation value is a threshold value related to land-use above which risk assessment and subsequent remediation is necessary (Lombi, Sletten, and Wenzel 2000). The authors distinguished between land uses of differential susceptibility of the related endpoints (e.g. human, animal, plant) in order to set appropriate thresholds. Hence, the need to assure heavy metals do not exceed trigger values.

Heavy metals (Cu, Zn, Fe, Mn and Mo) have essential biochemical and physiological roles in plants and animals, including (1) contribution to redox reaction, and (2) direct contribution to enzyme chemical structures. Therefore it is important that soil has enough of these to avoid adverse effects (Nagajyoti, Lee, and Sreekanth 2010). Safe limits of heavy metals are set in the European Union guidelines (2002) (Table 5).

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[2] Ethylenediaminetetraacetic acid (EDTA) extraction (Lo and Yang 1999)

Table 5. Values of save limits of heavy metals in agricultural soil according to the guidelines of the European Union (2002).

Sample	Cd	Cu	Pb	Zn	Mn	Ni	Cr
Agricultural soil (µg/g)	3	140	300	300	-	75	150

Copper is an essential nutrient for vascular plants as it contributes to photosynthesis. By readily gaining and losing electrons, Cu is a contributing factor of oxidase, mono- and di-oxygenase and of enzymes part of the removal of superoxide radicals. Zinc, on the other hand, is both required to keep the ribosome in good condition and plays a structural role, therefore it is present in many enzymes (Nagajyoti, Lee, and Sreekanth 2010). Nickel is said to be an important micronutrient to all living organisms as it contributes to enzyme urease. Manganese is also essential in enzyme reactions including metallic dehydrogenase and oxalosuccinic decarboxylase. Furthermore, Mn contributes to water splitting at photosystem II and is needed for superoxide disumutase. Finally, iron is one of the most important heavy metals, it is present in many metabolic processes and is crucial for all organisms. It is a part of heme-containing protein including hemoglobin, myoglobin and cytochrome, and innumerable non-heme iron-containing proteins with important functions in many metabolic processes. Iron and copper are protein components and catalyse redox reactions.

1.2.3 Biowastes used in this research

Pig manure

Worldwide about 1.7 tons of liquid manure is produces annually (Choudhary, Bailey, and Grant 1996). Pig manure is known to contain the essential micronutrients for plant growths. Contritely, it also holds heavy metals such as zinc (1497±91 mg kg^{-}1)and copper (1115±79 mg kg^{-1}) (Zhang et al. 2014) in higher amounts compared to other types of manure and has also the potential to increase leaching of NO_3-N, P and Mg when applied in high amounts (Choudhary, Bailey, and Grant 1996; Liebman et al. 2004). The nutrients and pollutants present depend on place, diet of pigs and other factors. However, it is thought that Zn and Cu do not exceed soil concentrations that are toxic to plants. Therefore, pig manure in form of fertiliser could be a great source of N, P, K, Ca, Mg and Na in the soil (Choudhary, Bailey, and Grant 1996). It is important to note, that pig manure can also contain pathogens and diseases which need to be eliminated before using it as a soil amendment.

Biogas slurry

Biogas slurry discharged from the reactor holds all nutrients initially present in the feeding material including N, P and K (Garg et al. 2005). This shows that biogas slurry usually consisting of maize is a good element to be used as fertiliser. Containing N, P and K makes it also suitable to combat nutrient depletion of many agricultural soils in developing countries. The use of biogas slurry as fertiliser can enhance agriculture production (BIRU 2015).

Struvite

First identified in the 18th century, struvite is a crystalline substance that contains magnesium ammonium phosphate ($MgNH_4PO_4$ $6H_20$). The substance can also be referred to as triple phosphate (Griffith 1978). Containing calcium, magnesium, ammonium, and phosphate, makes it ideal as a plant fertiliser. It is found in human urine and can be extracted from waste water treatment plants (Nongqwenga et al. 2017). Struvite is known to contain low pathogen and heavy metal concentration as well as 5.7 % N, 12.6 % P and 9.9 % Mg by mass, making it ideal as a crop fertiliser (Nongqwenga et al. 2017). However, whilst it has the potential to be used as a fertiliser, it can be a problem in wastewater treatment plants which was discovered in 1939, when struvite was found in the digested sludge supernatant lines. (Doyle and Parsons 2002).

The need to treat biowastes

Besides essential nutrients for plants, biowaste also contains undesired pollutants, including pathogenic microorganisms, antibiotic-resistant bacteria and organic pollutants such as pharmaceutical residues and hormones, as well as a bad odour (Albihn and Vinnerås 2007). Even though biowaste is used as fertiliser since 5900 B.C, it was not a clean nor a safe product, therefore, a hygienic and pollutant free end-product produced from biowaste is required. The potential negative environmental impact of biowastes needs to be eliminated. This can be achieved by applying effective treatment methods to the biowaste in order to prevent the introduction of pathogens and organic pollutants into the agricultural yield (Albihn and Vinnerås 2007). To ensure this, thermal treatment can be applied to biowastes.

1.3 History of hydrothermal carbonisation

Hydrothermal carbonisation (HTC), also called “coalification”, is a process during which liquid feedstock is converted into a solid product called “hydrochar” which can also be referred to as “biochar” (Coronella et al. 2014; Libra et al. 2011; He, Giannis, and Wang 2013) However, it is more common to refer to biochar when the feedstock went through pyrolysis whereas hydrochar is a product of HTC (Figure 3). Furthermore, HTC produces a side product called “process water” which consists of sugar monomer which’s by-product includes organic acids and CO_2. Both processes, pyrolysis and HTC, are procedures during which the carbon concentration, as well as the calorific value of a feedstock, is increased by undergoing a combination of dehydration and decarboxylation (Funke and Ziegler 2010). During carbonisation, the biomass is heated in a low oxygen environment, which leads to an increase of carbon concentration of the biomass (Libra et al. 2011). It is also important to note that charcoal is different from bio- and hydrochar. Although the process of producing biochar and charcoal is the same, bio – and hydrochar are used for nonfuel purposes that make carbon sequestration possible, while charcoal is a fuel (Tenenbaum 2009).

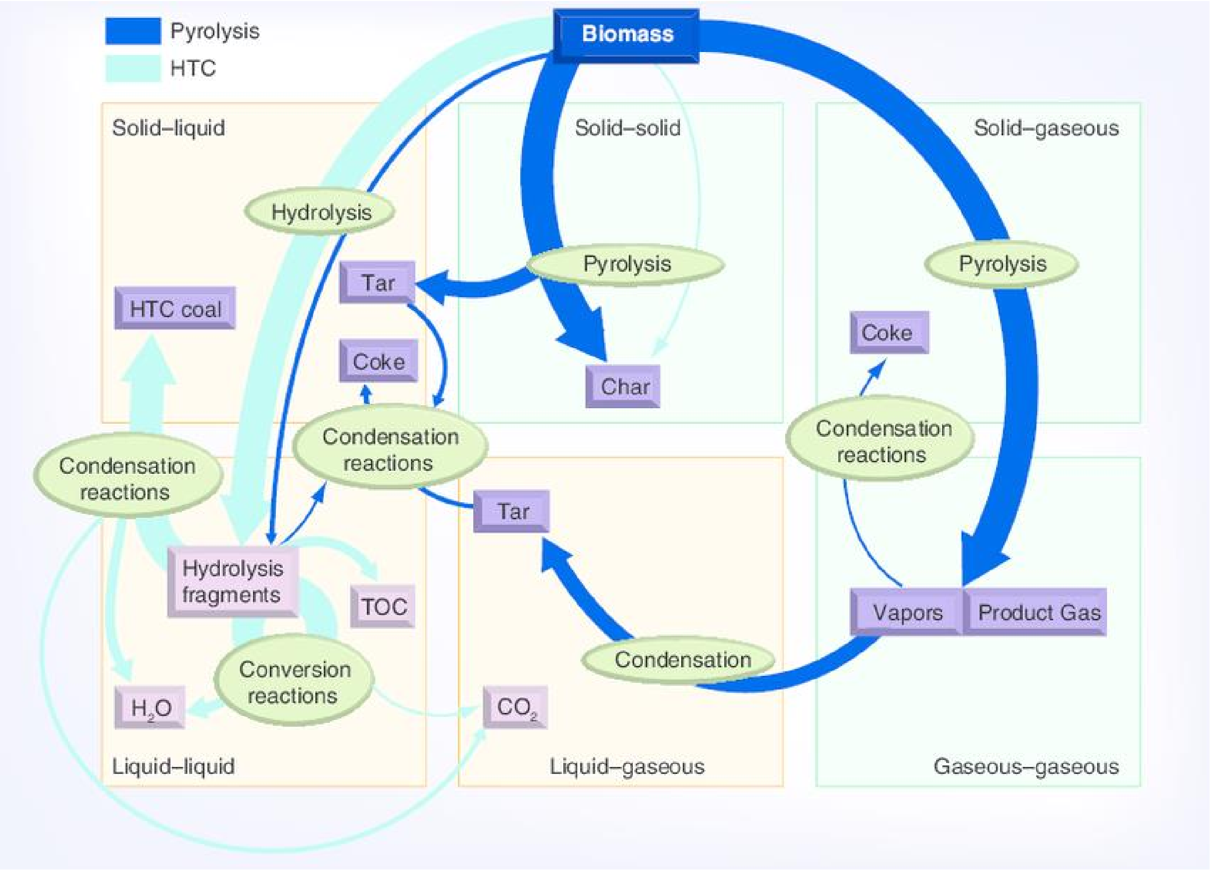


Figure 3. HTC vs Pyrolysis. Retrieved from Libra et al, “Hydrothermal carbonization of biomass residuals: A comparative review of the chemistry, processes and applications of wet and dry pyrolysis”. Here “char” refers to biochar produced through pyrolysis and “HTC coal” refers to hydrochar produced through HTC, Biofuels Journal, 2011.

The first carbonisation experiments were made in 1913 by Friedrich Bergius who received a Nobel Prize for the development of HTC. He heated cellulose under water and pressure and generated a black coal like substance (Haul 1985). In more recent years HTC was recognised as a common process to improve the energy density of biomass. Despite the liquid nature of the samples, the HTC-process generates relatively high yields without needing energy-intensive drying methods (Libra et al. 2011). It has been shown that HTC saves 60 % of thermal energy and 65 % of electric energy on laboratory scale compared to other drying methods of sludge. Additionally, emissions of greenhouse gases are reduced due to the high carbon efficiency of the process (vom Eyser et al. 2015).Thermal and hydrothermal carbonisation methods of biowaste have been recognised as suitable approaches as they eliminate organic pollutants, reduce waste volume and produce valuable by-products (Huang and Tang 2015).

1.3.1 Production of hydrochar

Different temperatures during the process also change the suitability of the end products. For example, at 230 °C under which sugar monomer is produced, it is showing a possible by-product for the conversion of biomass into biofuel. At lower temperatures, most of the organic material is also converted into the solid state, with only small amount of gaseous materials remaining (Libra et al. 2011). The most commonly used temperature lies between 160 - 280 °C, under which possible pathogens can be eliminated (vom Eyser et al. 2015). It is important to reach a certain pressure to avoid evaporation of water during the process. The biomass must be completely covered in water with a water to biomass ratio of 5:1 – 20:1, with a total process time between one minute to 72 hours (Coronella et al. 2014).

Danso-Boaten et al (2015) showed that as the temperature and reaction time increases, the amount of both carbon remaining as hydrochar and the energy yield decrease. They also found, that at higher temperature and reaction time the energy concentration is increased. HTC and pyrolysis differ majorly in all aspects of the process (Figure 3). The biomass used in HTC is liquid, the pressure is high, the temperature relatively low compared to pyrolysis, the environment during the HTC process consists of water, acid and no O_2, and the end-product is hydrochar.

The novelty and advantages of HTC include its suitability for wet biowastes such as wet animal manure, aquaculture and algal residues, municipal solid waste and sewage sludge, which often contain a fair amount of P (Libra et al. 2011), the sterile product which makes it ideal for animal manure, odour improvement, greatly, improved anaerobic digestion of the slurry product, the high energy efficiency, and residual material can be exploited profitably (Heilmann et al. 2014). In contrast, the research process is still at the beginning which makes hydrochar, an unknown but researchable product.

1.3.2 Chemical basis of hydrothermal carbonisation

Various chemical reactions are happening concurrently and sequentially during hydrothermal carbonisation which makes the determination of all intermediate- and final products difficult. Carbonisation is mainly reached through a decrease of oxygen-content as well as a partly decrease of the hydrogen-content (Reza et al. 2014). The most important reaction pathways are shown in figure 4 on an example of lignocellulosic biomass. This will help to understand nutrient concentration differences in feedstock and hydrochar.

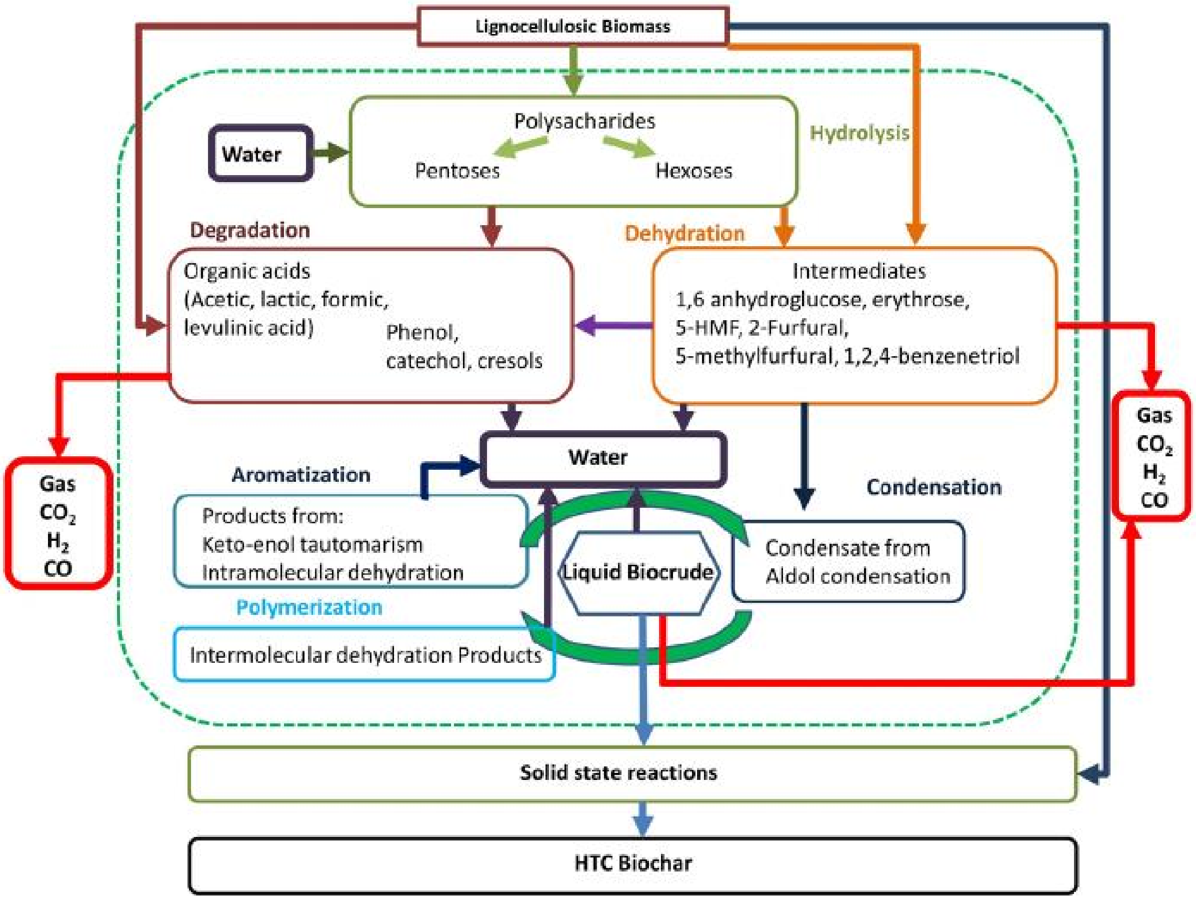


Figure 4. HTC reaction pathways of lignocellulosic biomass. Retrieved from (Reza et al. 2014).

The four main reactions during HTC are hydrolysis, dehydration, aromatisation and polymerisation (Reza et al. 2014). The first step of HTC is hydrolysis where water reacts with cellulose, extractives and hemicellulose causing a breakdown of the initial molecules of the feedstock. An important factor of this reaction is temperature. Depending on biomass type the minimum temperature might vary for sufficient decomposition. Hydrolysis is where the biomass loses its macroscopic structure. Dehydration are reactions where H_2O is separated from the biomass. Carboxyl groups are demerged from the biomass during decarboxylation. For this to happen a process temperature of at least 200°C is needed. Structure is given to the char during aromatisation. During this process potential polycyclic aromatic hydrocarbons can be formed. However, aromatisation usually requires a minimum temperature of 270°C. During polymerisation a recombination of reactive intermediates which were separated from the biomass during depolymerisation is possible. In general, during HTC water, carbon and carbon dioxide is lost, creating a new environment for remaining elements.

Chapter 2

Methodology

2.1 Sample description

For this research, samples including liquid pig manure, biogas slurry and struvite were chosen to represent a range of biowaste products that could be used as potential sources of P. All samples were collected within Austria. The pig farm slurry (liquid pig manure) was collected from a farm in Rath, Upper Austria during two different seasons in 2017: once during the winter months January and February, and the second time during the spring months of May and June. The high moisture concentration in the winter sample meant that drier pig manure had to be added to reduce the moisture concentration before undergoing HTC. The drier pig manure was collected from a farm in Lower Austria. Because of the different compositions of the liquid pig manures, they will be referred to as Liquid Pig Manure (winter) (LPM-w) and Liquid Pig Manure (spring) (LPM-s) from now on. Biogas slurry (BGSL) was collected from Biogas Systems Gmbh Parndorf, Austria during the same winter months as pig manure. It consists of a mixture of organic waste including straw, manure and dry pasture as well as food and other agricultural waste. Five kilograms of struvite (STR) was supplied by Roullier Group Ltd., which was collected from a waste treatment plant. The liquid pig manure (winter), biogas slurry and the struvite were carbonised under different conditions, where temperature, pressure and treatment time were modified (Table 6).

Table 6. HTC condition of the different sample types to determine ideal parameters including temperature and time for soil grain size and homogeneity. HTC was performed by another student; hence some data was withheld.

Sample type/ HTC condition	Temperature (°C)	Time (mins)	Pressure (bar)
LPM-w	200	withheld	withheld
LPM-w	200	30	withheld
LPM-w	200	60	withheld
LPM-w	200	30	18
LPM-w	200	60	21
LPM-w	200	360	25.9
LPM-w	240	30	44
LPM-w	240	60	41
LPM-w	240	360	40.5
BGSL	200	30	withheld
BGSL	200	60	withheld
BGSL	200	120	withheld
BGSL	200	360	24
BGSL	240	60	49
BGSL	240	360	withheld
STR	200	30	withheld
STR	200	60	withheld
STR	200	360	withheld
STR	240	30	36
STR	240	60	36

The methods were divided into two steps (Figure 5). In step 1 both liquid and solid biogas slurry and pig manure (winter) were measured for C, H, N, S and other elemental concentrations. Then struvite, BGSL and LPM-w underwent HTC under differing conditions (temperature and time, Table 6) to establish ideal physical conditions of the samples including grain size and homogeneity. For each carbonisation variation a dry sample (dry sludge), a milled sample and a liquid sample (process water) was provided. Subsequently, the samples were visually assessed to decide with which thermally treated samples to proceed. It was decided to only chemically analyse the samples that underwent HTC at 240°C and 60 min. These carbonised samples from all three biowaste types were then tested for elemental concentrations, P extractability and availability. In order to understand differences in P concentration the uncarbonised feedstock of BGSL and LPM-w were analysed for elemental concentrations.

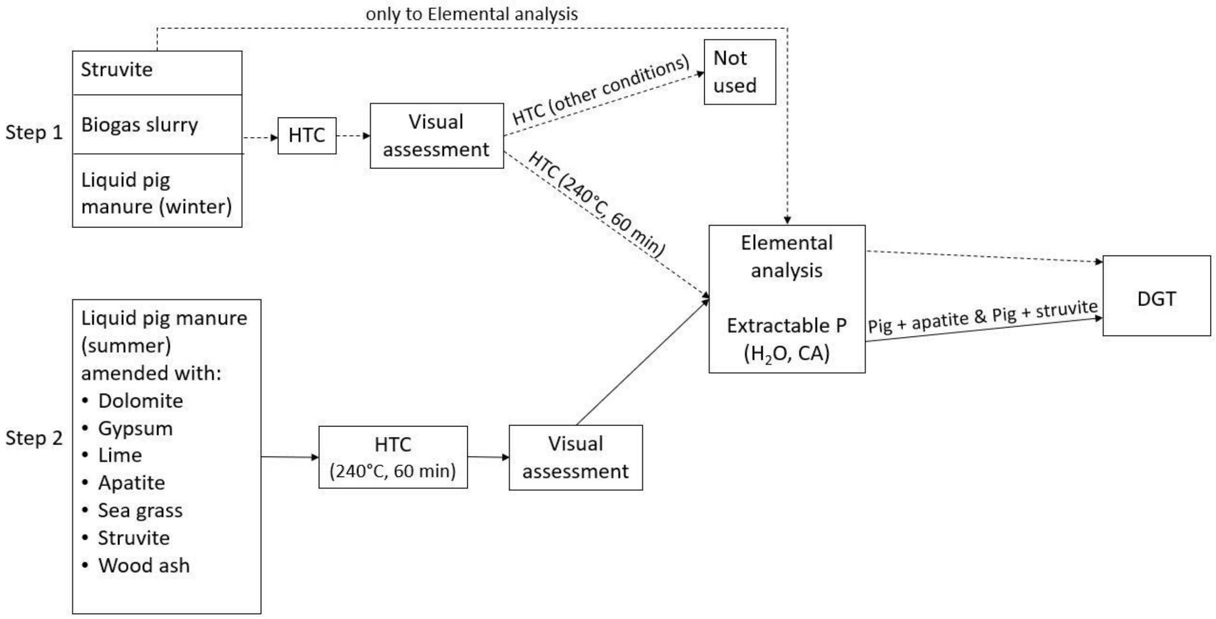


Figure 5. The experimental procedure followed in this research.

In step 2 liquid pig manure (spring) was modified with different amendments as requested by Roullier Ltd. as a potential enhancement of P availability in pig manure. 30 g of each amendment was added to 1 kg of liquid pig manure before undergoing HTC, under the conditions established in step 1. The amendments were: dolomite, gypsum (calcium sulphate $CaSO_4$), lime (calcium carbonate, $CaCO_3$), apatite (rock phosphate), sea grass (*Zostera sp.*), struvite or wood ash each was assigned a three-letter code, given in Table 7. They were then visually assessed and subjected to elemental analysis and tests for extractable P (see later). However, after seeing P solubility results, it was decided to only test LPM-s + APA and LPM-s + STR for bioavailable P.

Table 7. Sample types that underwent HTC including their sample code.

Sample type		**Sample code**
Struvite		STR
Liquid pig manure (winter)		LPM-w
Liquid pig manure (spring)		LPM-s
Biogas slurry		BGSL
Liquid pig manure (spring)	+ Dolomite	LPM-s + DOL
	+ Calcium sulphate	LPM-s + GYP
	+ Calcium carbonate	LMP-s + LIM
	+ rock phosphate	LPM-s + APA
	+ sea weed	LPM-s + SEA
	+ struvite	LPM-s + STR
	+ wood ash	LPM-s + ASH

All samples that underwent the established HTC conditions including STR, LPM-w, BGSL and amended LPM-s were analysed for their carbon, nitrogen, phosphorus and potassium concentrations (see later).

As struvite and some of the amendments originate from commercial suppliers, the origin of materials used cannot be fully disclosed.

2.1.1 Sample preparation

Following guidance from Groupe Roullier Ltd., all processed hydrochars were milled to a fraction between 100 – 200 µm in a vibratory ball mill (Retsch ® MM 200) at 80 Hz using stainless steel grinding apparatus. Individual milling was limited to 3 minutes, then sieved through a 200 µm sieve and then a 100-µm sieve. The material that did not pass through the 200 µm sieve was milled again until it passed through, anything below 100 µm was kept in a separate vial, anything above 100-µm was used for further analysis. This was done to ensure that all analysed hydrochars have a similar grain size. It is important to ensure that all samples are comparable as grain size influences chemical reaction, dissolution rates as well as homogeneity. In general, smaller grain size means more homogenous samples, faster chemical reactions and dissolution. Hydrochars were sieved before physical analysis, to have an indication of grain size.

2.2 Objective 1: Determination of physical properties

2.2.1 Sample and homogeneity, grain size and moisture concentration

A digital microscope (Keyence VHX-5000) was used to assess grain size and other variations of the milled samples compared to their respective unmilled samples. Each sample, in unmilled and milled form, was analysed with a microscope with an image enlargement of x150 under a lens between x20 to x200 enlargement capacity. This enlargement was chosen as it gave the clearest images.

Before starting the analysis, the microscope was calibrated using a calibration scale to enable accurate distance measurements with a specific lens. Then, the sample was placed on a glass petri dish. Afterwards, the desired lens enlargement was chosen and focused in the same manner as before. A function called Z-Stack, which stacks all pixels beginning from the deepest point on the picture in order to obtain a 3D image, was used to focus on the whole image. Homogeneity was visually determined.

The sample moisture concentration was determined by measuring the change in sample weight after 24 h in a 105 °C oven (Gardner et al. ,2000). No replicates were used as it was assumed that moisture concentration would be low after undergoing HTC.

2.3 Objective 2: Determination of chemical properties

From the samples progressed from step 1, only two replicates per sample were analysed for the C and N and elemental concentration as it was more important to obtain a general idea of the suitability of the samples. After physical analysis, struvite, liquid pig manure (winter/spring) and biogas slurry that underwent HTC conditions of 240°C and 60 mins, and all amended samples were analysed using three replicates per sample for the PAHs, iron bag method, H_2O and citric acid extraction and DGT.

2.3.1 Carbon/Nitrogen (C/N) Ratio

To establish the C/N ratio by dry combustion, first a small amount (< 100 mg) of each sieved hydrochar of the fraction 100-200 µm was dried at 105 °C for four hours. The LPM-w, LPM-s, BGSL and LPM-s + amendments derived hydrochars were weighed in at 60 mg per sample, struvite was weighed in at 30 mg per sample and packed in tinfoil before being analysed for their carbon and nitrogen concentration in a NA 1500 Series 2 elemental analyser (Carlo Erba).

2.3.2 Determination of total elemental concentration

Acid digestion with HNO_3/H_2O_2

100 mg of each hydrochar was weighed into Teflon liners and 5 mL 65 % HNO_3 and 1 mL 30 % H_2O_2 was added before digesting them in a Multiwave 3000 microwave system (Anton Paar GmbH, Graz, Austria) under the following conditions: 1400 W, 10 min ramp time, 40 min hold time and 10 min cooling time. Temperature and pressure were set to not exceed 210 °C and 40 bar. For liquid samples (process water (pw) and urine) 2000 µL of sample were pipetted into the Teflon liners (Appendix A).

Elemental analysis

Inductively coupled plasma mass spectrometer (ICP-MS) (Elan DRCe (PerkinElmer, Waltham, MA, USA)) was used to measure Fe, Cu, Zn, Pb, Mo, As, Cd and Cr concentration to identify whether element exceed threshold values to be functioning as nutrients. Each hydrochar and feedstock was diluted by a factor of 10 (1:10) using 1 mL of the sample, 9 mL 2 % HNO_3 and 10 µL indium solution with a concentration of 10 ppb which was meant to act as an 'internal standard'. Inductively coupled plasma optical emission spectrometry (ICP-OES) (Optima 8300, Perkin Elmer, Waltham, Ma, USA) was used to measure P, Al, Ca, K, Mg, Mn and Na concentration of the hydrochars and feedstocks. These elements are important to understand both which nutrients and the amount nutrients available in the hydrochars. Each sample was diluted by a factor of 10 (1:10) using 3 mL of the sample, 6 mL of deionised H_2O and 0.9 mL yttrium solution with a concentration of 1 ppm (the internal standard). Quality control samples containing a reference for each element of interest were included to confirm acceptable analyte recovery (± 10%).

Polycyclic aromatic hydrocarbons

The PAH analysis was undertaken by Eurofins Scientific (Bobritzsch-Hilbersdorf, Germany) accredited by the Deutsche Akkreditierungsstelle GmbH (DAkkS) according to DIN EN ISO/IEC 1702. PAHs were measured according to European standards using extraction with toluene (DIN EN 15527) (GC-MS (DIN CEN/TS 16181). Briefly, 2.5 g of sample was extracted with 50 mL of toluene by reflux for two hours. The extract was then reduced to less than 10 mL. An aliquot was then analysed for PAHs using gas chromatography. The United States Environmental Protection Agency (US EPA) identified 16 PAHs in their Toxic Release Inventory (USEPA, 2016). These PAHs were targeted in this research.

2.3.3 Determination of extractable Phosphorus

Standard sample P extractions

Phosphorus sample extractions were performed according to EN 15920:2011:02 (2% citric acid (CA) soluble P) and EN 15958:2011 (H_2O soluble P). For both extractions 120 mg of each hydrochar was weighed in. The samples were then mixed with either 10 mL of H_2O or CA (depending on extraction) and shaken for 30 mins at 35 RPM and 20 °C in 15 mL vials. Then the samples mixed with either H_2O or CA were diluted at a factor of 5.6 (H_2O extraction) or 20 (CA extraction). The diluted extracts were then filtered using pure cellulose paper filters (Ahlstrom-Munktell, grade 14/N). The CA dilution consisted of 0.5 mL sample and 9.5 mL 0.25 M H_2SO_4, whereas the H_2O dilution contained 1.8 mL sample, 7.2 mL H_2O and 1 mL 0.25 M H_2SO_4.

Ion sink method with ferrihydrite "iron bag" (IB)

The analysis used here is based on the method proposed by the Freese et al. (1995) and measures the available P by driving desorption/dissolution processes from the hydrochars, as opposed to other standard extracts (H_2O and CA) which are based on the assumption of a pseudo-equilibria between P in the solid phase and P in solution. Iron bag method is an infinite sink method utilising iron oxide slurry-filled dialysis tubes as P sinks which provides a quantitative measure of the total water-soluble P in each sample.

In this case it was used to determine P desorption from the hydrochars considered. Dialysis membrane tubes filled with iron oxide slurry were shaken together with the samples in a pH buffer, for a period of about 42 days. P was measured after a period of seven days, then after 21 days and finally after 42 days to establish whether desorption plateaus (expected after 40 days). The constant removal of P from the solution by the iron oxide drives desorption/dissolution processes of P from the hydrochars. This method mimics the basic mechanism by which P is made available from the solid phase of soils.

Preparation

First dialysis membranes were cut and boiled twice for several minutes in an acid washed beaker. Afterwards, the membranes were cooled in deionised water until needed. MOPS (3-(N-morpholino) propane sulfonic acid) was used as a buffer. For 33 samples 5400 mL of buffer was needed. To make the buffer (MOPS) 3.5 L of deionised water was mixed with 2 M NaOH until pH reached 6.8. Ferrihydrite was precipitated by adding 1 M L^{-1} NaOH to 100 g of a ferric nitrate solution mixed with deionised water. The slurry was continuously mixed with a magnetic stirrer until the iron slurry reached a pH between 6.5 -6.8. The ferrihydrite slurry was then centrifuged two times for 3 minutes. Finally, the ferric oxide slurry was resuspended in H_2O and filled up to twice the original volume.

Experimental set up

30 mg of hydrochar, 50 mL deionised water, 100 mL MOPS and micropur™ Katadyn Produkte AG (Kemptthal, Switzerland), a liquid to avoid bacteria accumulation in water, were put into a 250 mL bottle. Each membrane was filled with 20 mL of iron oxide slurry, shut with clips and added to the 250 mL bottle. The bottles were then placed on a GFL overhead shaker 3040™ (Burgwedel, Germany) at 4 RPM. The three samples from the first set, STR, LPM-w and BGLS were measured after seven, 21, and 42 days, the remaining samples, LPM-s and LPM-s + each amendment, were only measured once after 21 days.

Molybdenum blue method (Iron bag, H_2O and CA extraction)

Phosphorus concentration in the extractants was measured with the spectrophotometric molybdenum blue method (Murphy and Riley 1962) at 881 nm. Briefly, a staining reagent was prepared by mixing 10 mL deionized H_2O, 3 mL of 0.009 M ammonium heptamolybdate (99 %, Merck Millipore), and 1 mL of 0.004 M potassium antimony (III) tartrate hydrate (99.95 %, Sigma Aldrich). One millilitre of sample was mixed with 0.14 mL of the staining reagent and 0.06 mL ascorbic acid. After 15-20 minutes the absorbances of the extracts were measured photometrically on a Hitachi U-2000 UV/VIS spectrophotometer (Hitachi High-Technologies Corporation, Tokyo, Japan). Calibration standards were prepared in concentrations ranging from 0.05 to 0.9 mg P L^{-1} in a 0.25 M H_2SO_4 matrix. These were analysed for every batch of samples analysed. If sample's absorbance exceeded that of the highest standard, they were further diluted to remain within the calibration range. The dilution rates ranged between 1:1 to 180:1, depending on the sample.

2.3.4 Diffusive Gradients in Thin Films

The diffusive gradients in thin films (DGT) technique is a passive sampling technique for the measurement of inorganic ion concentrations in water, sediment or soil (Davison, Zhang, and Warnken 2007). It provides an estimate of elemental speciation and bioavailability and has been found to provide a good prediction of plant available P in soils (Six, Smolders, and Merckx 2013; Speirs et al. 2013; L. Burkitt et al. 2015). The DGT method was used to estimate the potential of the used biowaste to serve as a source of P to plants in two different hydrochar-amended soils.

Sample preparation

For this experiment two types of soil were used, one alkaline soil (ALK) and one decalcified, neutral soil (NEU) collected in 2016 in Münchendorf, Austria (48.0296° N, 16.3794° E) and Melk, Austria (48.2265° N, 15.3500° E) respectively (Table 8). The soil samples were air dried,(approximate water content of 2-3 %). In each type of soil, a certain amount of LPM-w, BGSL, STR, LPM-s + APA and LPM-s + STR was added including deionised H_2O (Water holding capacity (WHC) = 60 %) and incubated for 15 days (Table 9). One day before the start of the experiment the percentage of WHC was increased to 90 %. A commercial single superphosphate (DC Superphosphate 18, Timac Agro Düngermittelproduktions- und Handels GmbH, Zwetendorf, Austria) containing 18 % P_2O_2 and 12 % S was applied as a reference material.

Table 8. Characterisation of soil types including soil depth and pH concentration.

	Soil type	Depth	pH H_2O		pH $CaCl_2$	
			Mean	SD	Mean	SD
Neutral soil	Cambisol	0 - 30 cm	7.0	0.0	6.2	0.0
Alkaline Soil	Chernozem	0 - 60 cm	8.0	0.1	7.4	0.1

Table 9. NEU and ALK soil for DGT experiment set-up, with 100 mg P/kg of soil at 60% WHC during incubation of 15 days.

Sample I.D.	g soil /paste (air dry weight)	mg P added to each paste	Fertiliser P concentration (% P DM basis)	Mg Fertiliser /paste "wet" weight	Water to add to MELK at d=0 to the 30g soil (g or ml) (WHC = 60%)	Water to add to ALK at d=0 to the 30g soil (g or ml) (WHC = 60%)
Control	30.54	0	0	0	7.83	12.06
LPM-w	30.54	3	2.09	143.84	7.83	12.06
BGSL	30.54	3	1.45	206.95	7.83	12.06
Struvite	40.72	4	16.15	24.77	10.44	16.08
LPM-s + APA	30.54	3	5.14	58.31	7.83	12.06
LPM-s + STR	30.54	3	7.8	38.44	7.83	12.06
Super phosphate	61.08	6	24.6	24.39	15.66	24.12

Gel preparation

The hydrogels were prepared according to (Zhang and Davison 1995). First, four 0.25 mm and three 0.5 mm thick polyacrylamide hydrogels were prepared, where the thin gels were further prepared to serve as a binding layer and the thick gels as the diffusive layer. The gel solution was mixed with ammonium persulphate (10 %) and TEMED catalyst (N, N, N', N'Tetramethylethylenediamine, 99 %, Sigma Aldrich) and then pipetted into glass plates separated by plastic spacers. For polymerization, the five gels were placed in an oven at 43°C for one hour. The gels were then separately placed in deionised water to rinse off the access reagent. The water was changed three times over a 24-hour period. Gels were then refrigerated in 0.03 M $NaNO_3$.

Precipitation of ferrihydrite gels (binding layer)

The four thin gels were then soaked for two hours in a ferrihydrite solution that consisted of 2.7 g $FeCl_3$ $6H_2O$ and 100 mL deionised H_2O. Afterwards, each gel was transferred to 100 mL 0.05 M 2-(N-morpholino)-ethanesulfonic acid (MES) at pH 6.7 to precipitate. The gels were stirred for at least 30 seconds and shaken for 30 minutes to ensure homogenous precipitation. Gels were then stored in 0.03 M $NaNO_3$. Both types of gels were then cut into discs before starting the experiment (Luo et al. 2010).

Experiment

The incubator was set to 20°C and wet tissues were placed inside to humidify the atmosphere in order to avoid drying out of the samples during the experiment. Diffusive gradients thin films were assembled using both types of gels as well as protective discs including (1) ferrihydrite binding gel, (2) polycarbonate membrane to separate the layers, (3) diffusive gel, and (4) polyether sulfone membrane as the protective layer. For each sample and soil combination, three DGTs were deployed. After deployment in the incubator for exactly 24 hours, soil paste was carefully removed. The DGT device was cleaned thoroughly to avoid particle contamination. The ferrihydrite binding gels were removed and the bound P was eluted in 5 mL 0.25 M H_2SO_4. The samples were then measured using the molybdenum blue method with a dilution factor of 1:1. Results are expressed in C_{DGT}:

$$(1)\ C_{DGT=}\frac{M\Delta g}{DAt}$$

This formula calculates the time-average soil solution concentration at the sampler-soil interface (C_{DGT}) and considers the mass M of P accumulated over a period of 24 hours on the sample, Δg is the diffusive layer thickness (cm), and D is the phosphate diffusion coefficient in the diffusive layer ($cm^2\ s^{-1}$), A is the sampling area (cm^2) and t is the deployment time (s) (Duboc et al. 2017).

2.3.5 Data analysis

To understand the effect of the different treatments on the capacity of the different biowastes to supply nutrients, the data from the different experiments underwent statistical analysis. ANOVA with a post-hoc Turkey's analysis of sample means was applied to test for differences between different treatments applied to the samples, and differences in hydrochar types (STR, LPM-w and BGSL) using IBM Statistics SPSS 20™ with a confidence interval (CI) of 0.95.

Chapter 3

Results

3.1 Chemical properties

3.1.1 C/N ratio

The C/N ratio was generally lower in STR compared to LPM-w and BGSL (Table 10). The LPM-s hydrochars containing different amendments have a similar C/N ratio to the LPM-s hydrochar. Aside from STR, the carbon concentration of all hydrochars ranges between 27 – 49 %, with a low N concentration. The C/N ratio ranges between 0.52 to 19.46, with STR having the lowest C/N ratio and LPM-s + LIM the highest.

Table 10. Total C and N in percentage, and C/N ratio of all hydrochars.

Sample type	N	C	C/N ratio
	%		
STR	3.80	1.98	0.52
LPM-w	2.26	40.74	18.04
BGSL	3.08	48.33	15.70
LPM-s + DOL	2.16	35.05	16.25
LPM-s + GYP	2.01	30.92	15.38
LPM-s + LIM	1.67	32.47	19.46
LPM-s + APA	2.07	31.88	15.37
LPM-s + SEA	2.96	45.25	15.30
LPM-s + STR	2.03	31.35	15.46
LPM-s + ASH	1.60	27.48	17.17
LPM-s	2.74	45.77	16.71

3.1.2 Elemental concentration

Comparing the feedstock solid BGSL and liquid BGSL shows a difference in both the C and the N concentration (Table 11). The hydrogen concentration does not show major variation between dry and liquid BGSL feedstock. The main component of BGSL are a combination of other elements (Table 11). The difference between solid and LPM-w feedstock is substantial. While LPM-w feedstock has a C concentration 26 – 29 %, solid PM-w has over 10 % more Carbon. The N concentration however only differs <1%. Like BGSL feedstock the main component of PM-w is compounded by other elements. Sulphur is for both feedstock types and both phases < 0.5%.

Table 11. Elemental concentration of BGSL and LPM-w feedstock. All concentrations are related to their original fresh sample and are depicted in mass %.

Sample type	wet weight	DM	C	H	N	S	other	Total
	g	[%]	(w/w) Mass %					
BGSL (solid)	69.5	15.54	44	5.65	2.25	<05	47.7	99.6
BGSL (liquid)	38	10.26	42.4	5.25	3.73	<0.5	48.5	99.88
BGSL (liquid)	41.7	10.55	42.3	5.25	3.71	<0.5	48.7	99.96
LPM -w	53.7	1.12	28.5	3.73	2.87	<0.5	64.8	99.9
LPM -w	49.3	0.41	26.7	3.39	2.65	<0.5	66.9	99.64
PM - w (solid)	43.6	66.74	39.7	5.4	2.93	<0.5	51.9	99.93
PM - w (solid)	81.2	54.56	40.7	5.6	3.03	<0.5	50.6	99.93

LPM-s + ASH has the highest amount of Fe followed by LPM-w (Table 12). It is noticeable that LPM -w feedstock has low iron concentrations compared to the carbonised LPM-w, however, there is also a difference in Fe concentration in LPM-w and LPM-s. The remaining amended LPM-s hydrochars have a similar Fe concentration (1258 – 1832 mg/kg^{-1}). Copper and zinc are most predominant in LPM-s and vary slightly across the amended pig manure hydrochars depending on composition of the amendment. The least desired heavy metals including lead, molybdenum, arsenic and chromium are present in small amounts. In general, there is a difference of elemental concentration between LPM-w and LPM-s as well as lower amounts of Fe, Cu and Fe in the LPM-w feedstock. Struvite has low amounts of most elements whereas BGSL has a comparable amount of Zn and Cu but is very low in Fe.

Table 12. Comparison of the different hydrochars' average elemental concentrations including Fe, Cu, Zn, Pb, Mo, As, Cr and Cd measured on the ICP-MS. Mean ± SE. Including thresholds for heavy metals in biochars according to Germany’s Federal Soil protection act derived from European Biochar Certificate (EBC) referring to the biochar’s total dry mass (DM) and the Austrian fertilisation regulation 2004 referring to DM, and values of save limits of heavy metals in agricultural soil according to the guidelines of the European Union (2002).

	Iron	Copper	Zinc	Lead	Molybdenum	Arsenic	Chromium	Cadmium
	mg kg^{-1}							
STR	1670 ± 11.7	6 ± 0.45	11 ± 0.07	1 ± 0	0.1 ± 0	2 ± 0.02	2 ± 0.05	0 ± 0.01
LPM-w	2212 ± 3.28	52 ± 0.09	218 ± 2.81	3 ± 0.02	1 ± 0.01	0.5± 0.02	7 ± 0.16	0.1 ± 0.03
BGSL	622 ± 0.07	18 ± 0.85	267 ± 3.94	0.5 ± 0	1 ± 0.02	0.1 ± 0.01	8 ± 0.02	0.1 ± 0.01
LPM-s + DOL	1576 ± 2.12	37 ± 0.38	158 ± 2.21	2 ± 0.03	1 ± 0.03	0.4 ± 20.01	5 ± 0.21	0.2 ± 0.01
LPM-s + GYP	1641 ± 0.55	43 ± 1.23	152 ± 0.86	6 ± 0.14	2 ± 0.04	0.3 ± 0.01	4 ± 0.05	0.1 ± 0.01
LPM-s + LIM	1258 ± 10.18	38 ± 0.77	138 ± 0.67	3 ± 0.12	1 ± 0.04	0.2 ± 0.01	4 ± 0.10	0.1 ± 0.01
LPM-s + APA	1832 ± 2.36	40 ± 0.27	187 ± 8.44	3 ± 0.01	2 ± 0.05	1 ± 0.04	14 ± 0.04	1.2 ± 0
LPM-s + SEA	1773 ± 111.41	47 ± 0.11	155 ± 5.42	4 ± 0.04	2 ± 0.07	4 ± 0.01	6 ± 0.16	0.2 ± 0.01
LPM-s + STR	1610 ± 4.74	75 ± 1.11	262 ± 1.16	2 ± 0.02	1 ± 0.02	1 ± 0.02	4 ± 0.07	0.1 ± 0
LPM-s + ASH	5233 ± 81.01	52 ± 1.64	218 ± 3.23	9 ± 0.25	1 ± 0	1 ± 0.01	21 ± 0.72	0.3 ± 0.01
LPM-s	1550 ± 1	87 ± 0.58	305 ± 3.94	3 ± 0.06	2 ± 0.02	0.3 ± 0.02	4 ± 0.14	0.1 ± 0
LPM-w feedstock	822 ± 3.67	13 ± 0.07	101 ± 3.44	1 ± 20.02	1 ± 0.03	0.2 ± 0.01	2 ± 0.08	0.1 ± 0.01

EBC thresholds	n/a	< 100	< 400	< 100	n/a	n/a	< 90	< 1.5
Austrian fertilisation regulation	n/a	n/a	n/a	100	n/a	40	2	3
EU guidelines		140	300	300			150	3

Comparing the hydrochars to the EBC and Austrian fertilisation thresholds (Table 12) shows that no thresholds are exceeded in the hydrochar. Despite the increase in As, Cd, Cr and Pb through carbonisation, the As, Cd and Pb concentrations in all LPM hydrochars are below threshold values, whereas Cd concentrations exceed the threshold according to the Austrian fertilisation regulation in all hydrochars but STR. The LPM-w feedstock has a Cd concentration equalling the threshold.

Comparing the heavy metal values in all hydrochars with the EU guidelines shows that all but LPM-s (Zn) are below the save limit values given by the EU (Table 12). One interesting observation of the LPM-s is that pure it shows more zinc and copper than in amended form. This, however, might be due to dilution by the amendments if it is assumed that the latter have lower heavy metal concentrations. In general, all elements are present in amounts to be functioning as nutrients and not pollutants. This is important as most heavy metals excluding Pb, Cr and Cd, play an important role in plant development.

Struvite has the highest amount of P followed by LPM-s + STR and LPM-s + APA (Table 13). It is noticeable that struvite has almost a tenfold amount of P compared to the other hydrochars excluding LPM-s + APA and LPM-s + STR. LPM-s and LPM-w have in general higher concentrations of P than the amended LPM-s samples (Table 13). Aluminium is most predominant in LPM-s + SEA, and lowest in LPM-s + ASH. Calcium is present in high amounts in hydrochars that include calcium rich amendments such as calcium phosphate, calcium carbonate and rock phosphate. The other samples vary in Ca concentration depending on their chemical composition.

Table 13. Comparison of the different samples' average elemental concentrations including P, Al, Ca, K, Mg, Mn and Na measured on the ICP-OES. Mean ± SE.

	Phosphorus	Aluminium	Calcium	Potassium	Magnesium	Manganese	Sodium
			g kg^{-1}			mg kg^{-1}	
STR	162 ± 2.32	1 ± 0.01	29 ± 0.24	1 ± 0.013	158 ± 1.134	564 ± 7.42	57 ± 0.17
LPM-w	22 ± 0.28	5 ± 0.16	36 ± 0.55	5 ± 0.08	8 ± 0.09	430 ± 8.14	1026 ± 15.79
BGSL	15 ± 0.28	4 ± 0.03	19 ± 0.24	16 ± 0.17	13 ± 0.14	196 ± 4.98	54 ± 1.73
LPM-s + DOL	15 ± 0.1	4 ± 0.11	83 ± 0.35	5 ± 0.01	37 ± 0.11	448 ± 4.44	1020 ± 5.52
LPM-s + GYP	11 ± 0.05	5 ± 0.04	116 ± 0.4	4 ± 0.03	8 ± 0.02	361 ± 2.72	670 ± 4
LMP + LIM	11 ± 0.34	5 ± 0.13	165 ± 0.68	4 ± 0.08	9 ± 0.02	360 ± 5.84	739 ± 16.73
LPM-s + APA	51 ± 0.51	3 ± 0.06	123 ± 0.86	5 ± 0.03	8 ± 0.03	495 ± 6.04	1393 ± 9.58
LPM-s + SEA	11 ± 0.1	18 ± 0.13	29 ± 0.21	7 ± 0.05	9 ± 0.05	393 ± 0.84	2510 ± 4.98
LPM-s + STR	78 ± 0.42	5 ± 0.01	42 ± 0.21	4 ± 0.013	67 ± 0.45	771 ± 4.65	883 ± 4.69
LPM-s + ASH	11 ± 0.17	0.3 ± 0.35	90 ± 1.32	9 ± 0.19	15 ± 0.23	2209 ± 38.17	1180 ± 30.89
LPM-s	20 ± 0.24	8 ± 0.06	36 ± 0.32	4 ± 0.04	10 ± 0.08	634 ± 7.93	703 ± 30.89

LPM feedstock	15 ± 0.16	2 ± 0.01	26 ± 0.15	7 ± 0.06	6 ± 0.03	191 ± 3.28	3668 ± 0.85
BGSL feedstock	8 ± 0.21	0 ± 0.00	9 ± 0.02	2 ± 0	6 ± 0.02	126 ± 0.02	120 ± 2.71

Potassium is three times higher in BGSL compared to almost all other hydrochars. Magnesium concentration in STR derived hydrochar shows the highest difference compared to other hydrochars, it is at least ten times higher. Sodium is highest in LPM-s + SEA and lowest in BGSL. Manganese is at least a fivefold higher in LPM-s + ASH compared to all other hydrochars.

3.1.3 Polycyclic aromatic hydrocarbons

Both carbonised BGSL and LPM-w contain a marginal amount of PAHs (Table 14). Trigger values set by the European biochar foundation are set for basic quality standards at less than 12 mg kg^{-1} and for premium quality standards at less than 4 mg kg^{-1}. Both carbonised biowastes are below the premium quality standard threshold for all PAHs.

Table 14. PAHs measured in carbonised BGSL and LPM-w showing all PAHs being under the trigger threshold value (4 – 12 mg kg^{-1}).

Parameter	LPM-w mg kg^{-1}	BGSL
Naphthalin	0.2	0.2
Acenaphthylene	< 0.1	0.2
Acenaphthene	< 0.1	0.3
Fluorene	< 0.1	0.3
Phenanthrene	< 0.1	< 0.1
Anthracene	< 0.1	< 0.1
Fluoranthene	< 0.1	0.8
Pyrene	< 0.1	< 0.1
Benzo[a]anthracene	< 0.1	< 0.1
Chrysene	< 0.1	0.2
Benzo[b]fluoranthene	< 0.1	< 0.1
Benzo[k]fluoranthene	< 0.1	< 0.1
Benzo[a]pyrene	< 0.1	< 0.1
Indenol[1,2,3-cd] pyrene	< 0.1	0.1
Dibenzo[ghi]anthracene	< 0.1	< 0.1
Benzo[ghi]perylene	< 0.1	< 0.1
Sum	0.2	2.1

3.1.4 P solubility from the iron bag method and other extractions

Almost 100 % of P was extracted from STR by day seven (Figure 6), another 2 % by day 21 and another 1 % by day 42. BGSL and LPM-w follow a similar trend, while during the first measurement most P was extracted (between 50 – 65 %), both samples still show that a further 10-20 % was extracted by day 21 and slightly more (2 -5 %) by day 42.

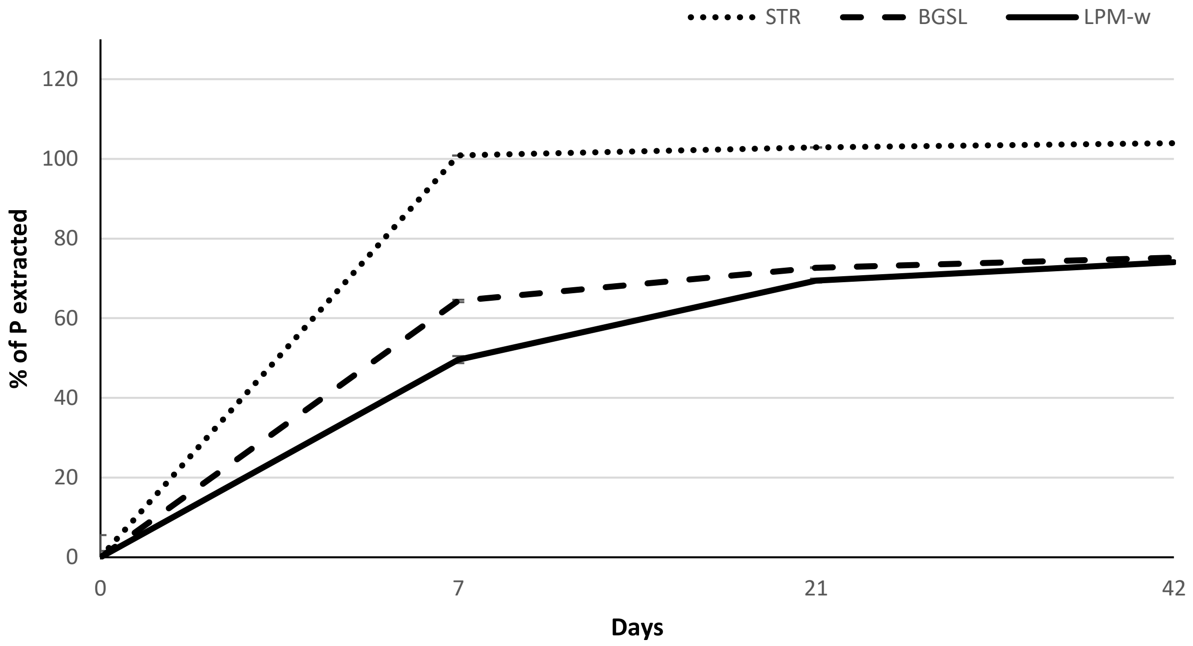


Figure 6. Comparison of average values of Struvite, Biogas slurry, and Pig manure extracted after 7, 21, and 42 days. Mean (n=3) + SE.

When comparing the percentage of total P extracted using the iron bag method, it becomes apparent that the highest proportion of total P was extracted from STR and LPM-s + STR (Figure 7). The least P was extracted from LPM-s + APA. While LPM-w, LPM-s and BGSL have a similar amount of soluble P, the LPM-s + amendments do not differ vastly from them, showing that LPM-s does probably not need amendments as they do not supply more soluble P. The error bars show that there is not much variability within the samples. LPM-s + DOL and LPM-s + GYP have higher variability as in each case one replicate was damaged during the experiment. There are significant differences between struvite and all other samples but LPM-s + APA and vice versa.

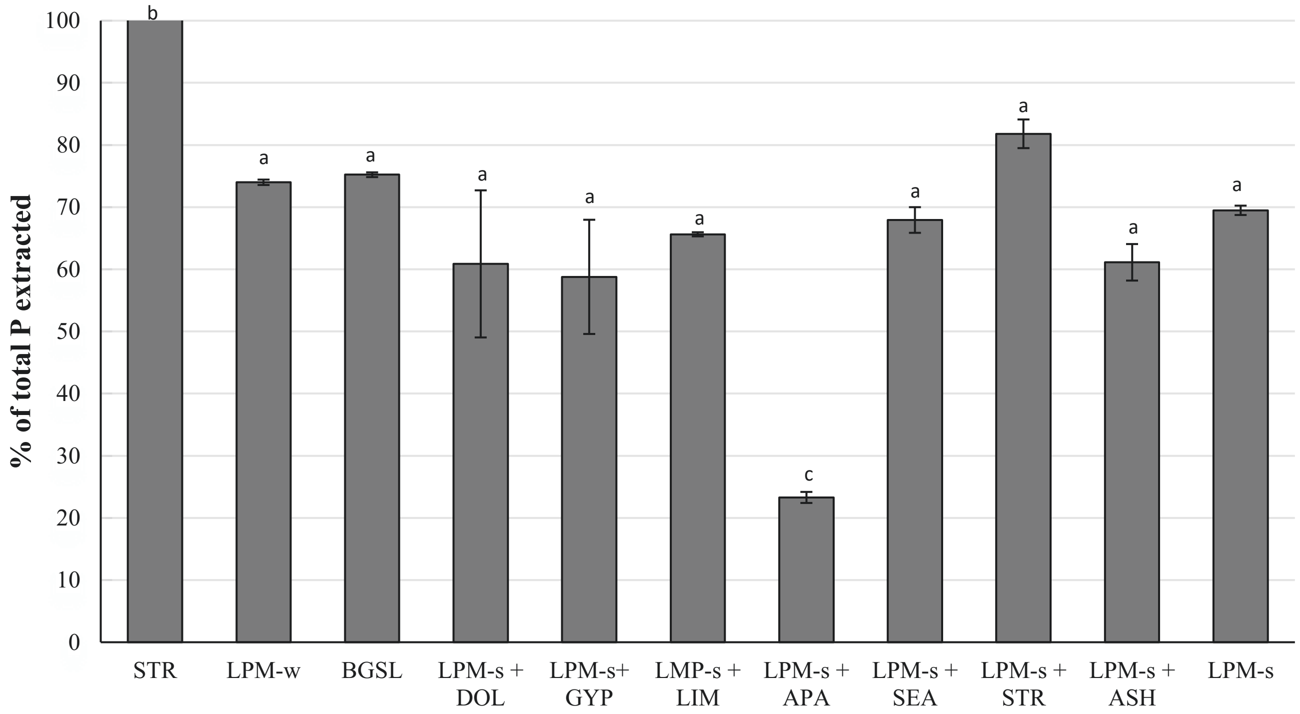


Figure 7. Average percentage of total P extracted from the different samples using the iron bag method. Error bars showing the standard error (*n*=3). Values with the same letters are not significant different ($p < 0.05$).

The comparison of the iron bag method and H_2O extraction show significant differences ($p < 0.05$) in P extractability. In Figure 8 the percentage of total P extracted by the iron bag method is compared to a H_2O extraction, showing a similar trend as above. Most hydrochars cluster between 60 - 80 % of extractable P by IB and have a similar water solubility. However, the highest water-soluble P was found in STR, LPM-s + STR and BGSL. However, all hydrochars have rather low water solubility.

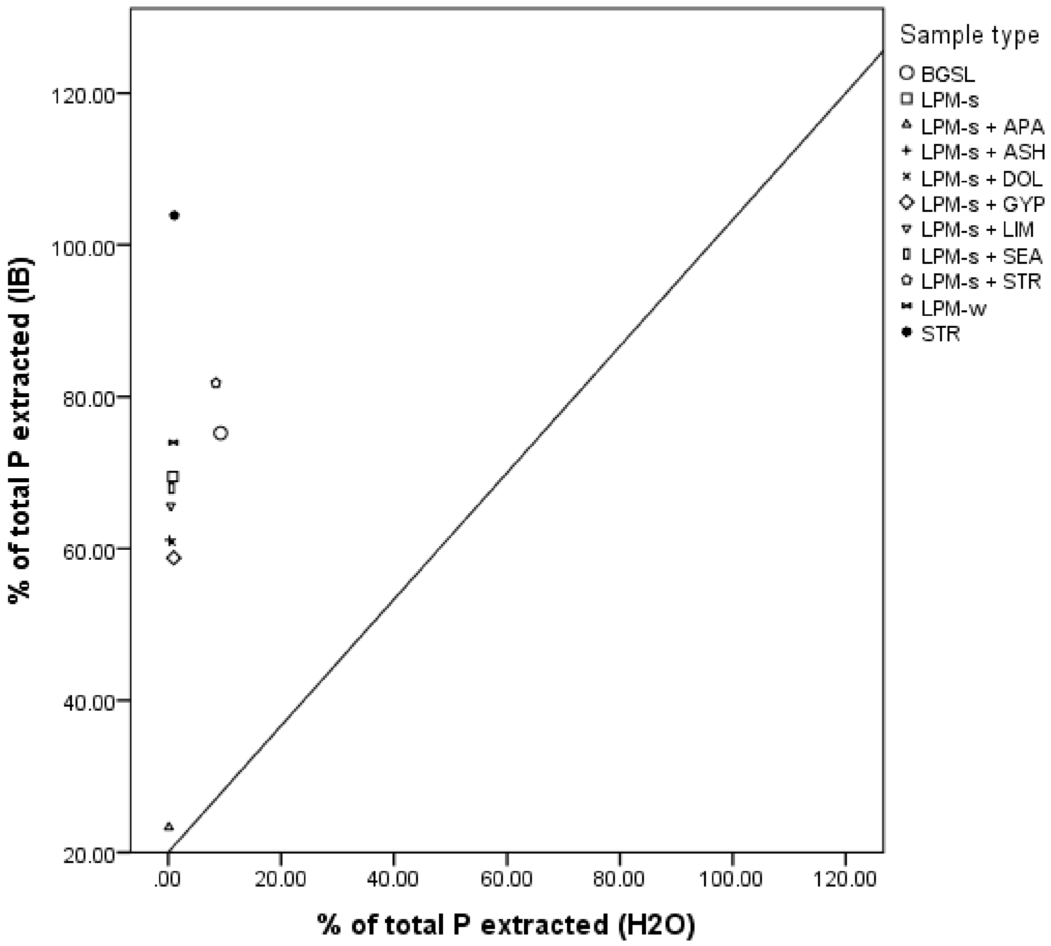


Figure 8. Comparison of average percentage (n = 3) of total P extracted with iron bag (IB) and H_2O extraction. The line shows how the graph would look like if the same amount of P would be extracted from IB and H_2O extraction.

Using a one-way ANOVA test including a Turkey's post hoc analysis revealed very high standard deviations in the iron bag data of LPM-s + DOL and LPM-s + GYP. This however could be explained by membrane breakage at day 21. Homogeneity of variances was violated, as assessed by Levene's Test of Homogeneity of Variance (*p* = 0.001 (IB) and p= 0 (H_2O)). For example, the comparison of sample types with similar compositions such as LPM-s + LIM and LMP-s + GYP shows statistical significance in the iron bag and H_2O extraction methods.

Hydrochars containing struvite or added phosphorus (e.g. PR) have higher amounts of P, however, that does not mean that theses sample have the highest amount of extractable P, as shown in Table 15. LPM-s + APA is a good example of this, while it contained over 5 % of total P, it had the least amount of extractable P.

Table 15. Average total P measured (n=3) in fertiliser with ICP-OES, and the % of total P extracted with the iron bag method for each sample type.

Sample type	Ave. total P. in sample (% of DM)	P extracted (% of total)	Absolute SD of P extracted
LPM-s + LIM	1.07	65.63	0.57
LPM-s + GYP	1.07	58.78	15.91
LPM-s + SEA	1.12	67.93	3.58
LPM-s + ASH	1.14	61.13	5.09
BGSL	1.45	75.21	1.15
LPM-s + DOL	1.50	60.87	20.50
LPM-s	2.03	69.49	1.31
LPM-w	2.09	74.06	1.31
LPM-s + APA	5.14	23.30	1.54
LMP + STR	7.80	81.81	4.00
STR	16.15	103.93	3.26

Comparing the different extraction methods, CA, H_2O and IB, it becomes apparent that the IB extraction removed the most P,while CA and H_2O extractions removed progressively less (Figure 9). Again standard errors are highest in LPM-s + DOL and LPM-s + GYP because of the broken membranes during the IB experiment. LPM-w, BGSL and LPM-s follow similar patterns in all three extraction types, whereas the amended LPM-s hydrochars show less soluble P unless struvite was added. A two-sided ANOVA showed significant ($p < 0.05$) differences between all three methods.

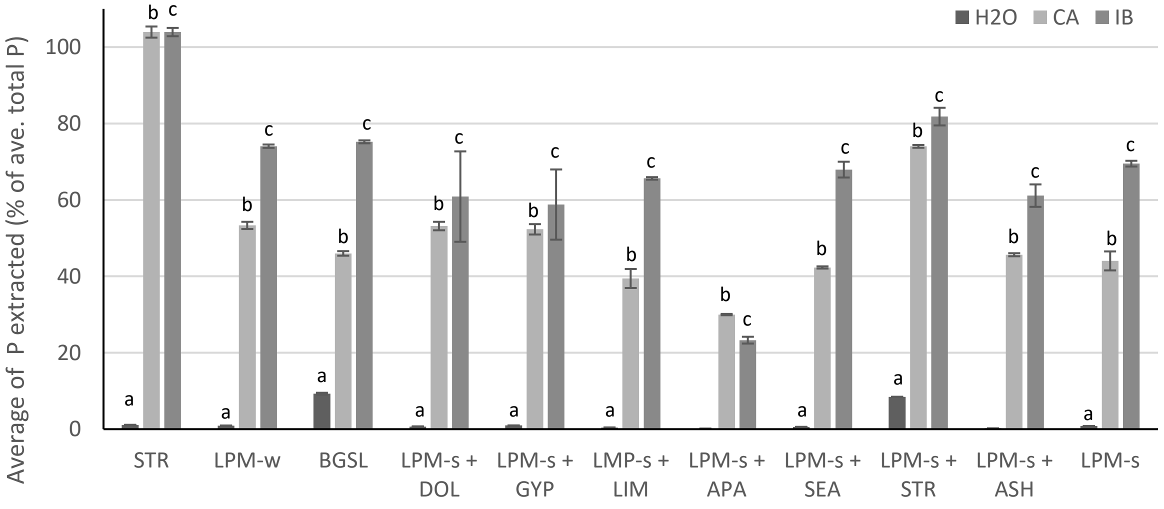


Figure 9 Comparison of all three extraction methods showing that IB is the most effective method for soluble P. Error bars showing the standard error of the mean (n = 3). H2O = H2O extraction, CA = citric acid extraction, IB = iron bag method.

3.1.5 DGT

It was found that most P is bioavailable in neutral soil in STR and least available in alkaline soil in the LPM-s + APA hydrochar (Figure 10). The single super phosphate (SSP), commercial mineral fertiliser, was used as a benchmark sample. In general, the results show that all hydrochars have higher (at least 13 % up to 35 %) C_{DGT} results in in neutral soils than alkaline soils. This means that the time averaged concentration at interface of DGT sampler and biowaste solution is higher in neutral soil. Again, most P is available in hydrochars that contain struvite. LPM-w and BGSL have similar amounts of C_{DGT} in both soils (NEU = 22.61 – 22.95 µg L^{-1} and ALK= 6.97 – 7.99 µg L^{-1}).

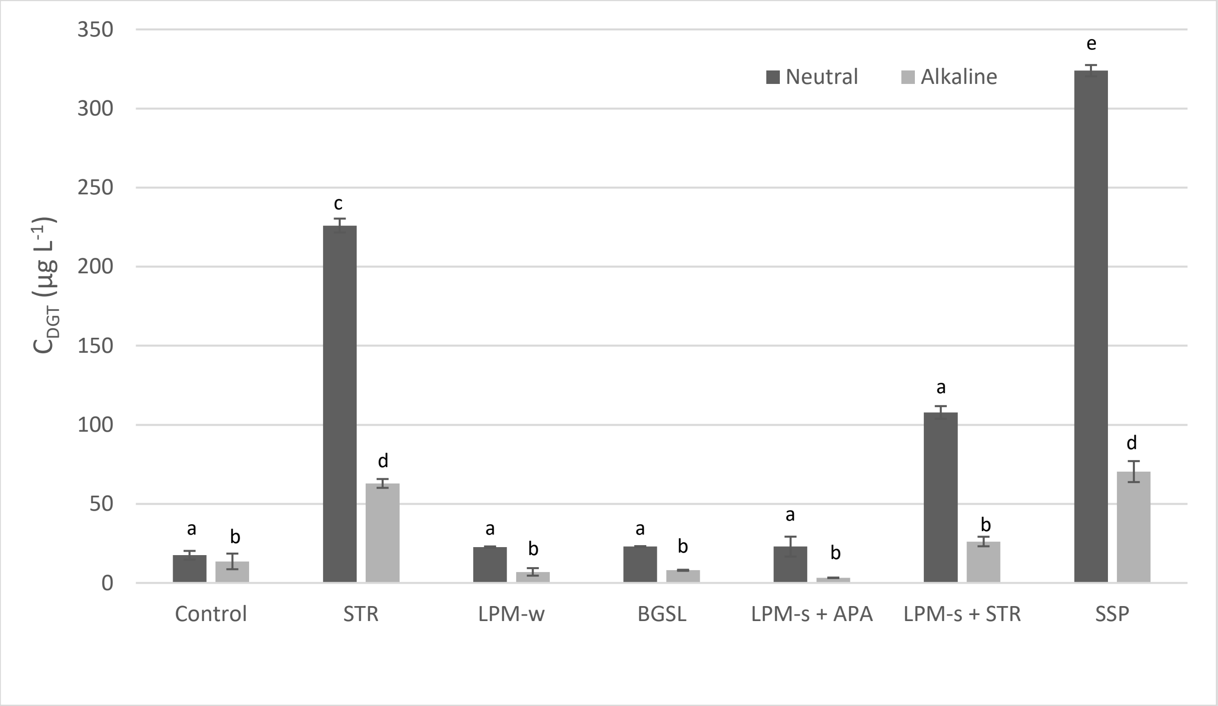


Figure 10. Comparison of sample types' C_{DGT} in alkaline and neutral soil. Error bars indicating the standard error of the mean (n=3). Values with the same letter are not significantly different.

Results show that there is a significant difference in P bioavailability between neutral and alkaline soil.

3.2 Physical properties

3.2.1 Soil porosity, grain size and homogenity

Grain size and homogeneity were visually analysed. Overall, increasing HTC temperature, pressure and/or processing time in most cases resulted in more homogeneous particle size and increased abundance of smaller pores (Figure 11 - 15) as compared to the unaltered feedstock (Appendix B). Furthermore, the observed samples decrease in particle size with increased intensity of HTC treatment goes along with increased surface area, which may be considered beneficial for its use as carrier of nutrients or other compounds. While LPM-w and BGSL show similar changes in homogeneity depending on HTC conditions, STR does not show relevant changes in response to HTC treatment (Figure 15). At least visually not much change is expected because struvite as a mineral is not containing much organic matter that could be converted during HTC. There may be some chemical (solubility) changes, however, those could only be detected if unaltered struvite had been included in the chemical analysis.

For LPM-w and BGSL, Figure 11 - 14 show that the higher the temperature and the longer the samples are carbonised the more likely homogeneity is reached. However, in both milled and unmilled samples, the samples do not differ substantially between 60 min and anything longer than 60 minutes, whereas the highest temperature tested (240°C) in combination with 60 minutes provided the most homogeneous samples.

The modified LPM-s hydrochars (Appendix B) show similar changes compared to LPM-w, meaning that increasing HTC conditions also result in more homogeneous particle size and increased abundance of smaller pores. This shows that LPM-s with any of the amendments does not differ much from LPM-w with regards to physical properties.

Pig manure

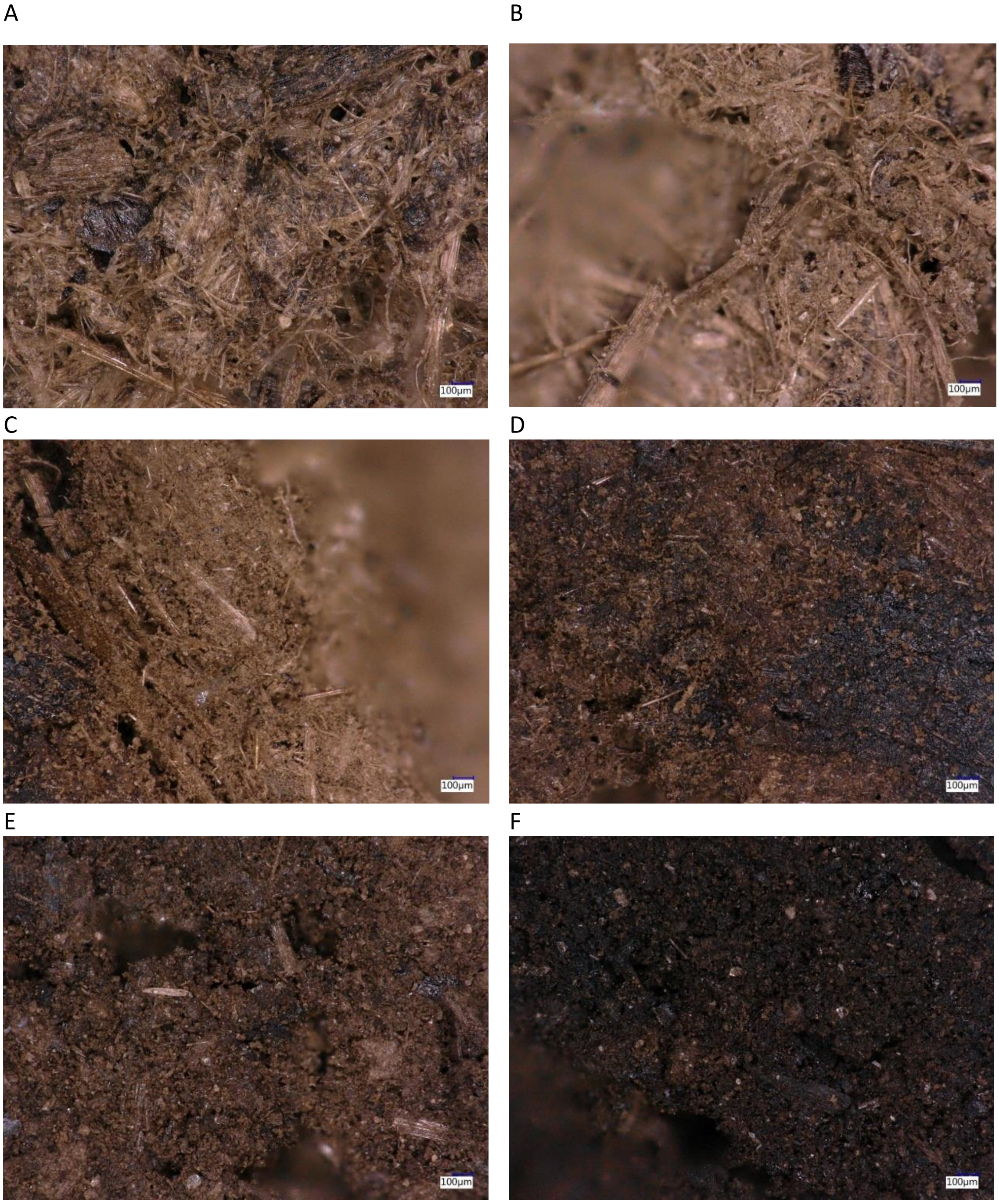


Figure 11. Digital microscopy of unmilled hydrochars produced from pig manure at various process conditions: A – 200°C, 30 min; B – 200°C, 60 min; C – 200°C, 120 min; D –200°C, 360 min, 24 bar; E- 240°C, 60 min, 49 bar; F - 240°C, 360 min.

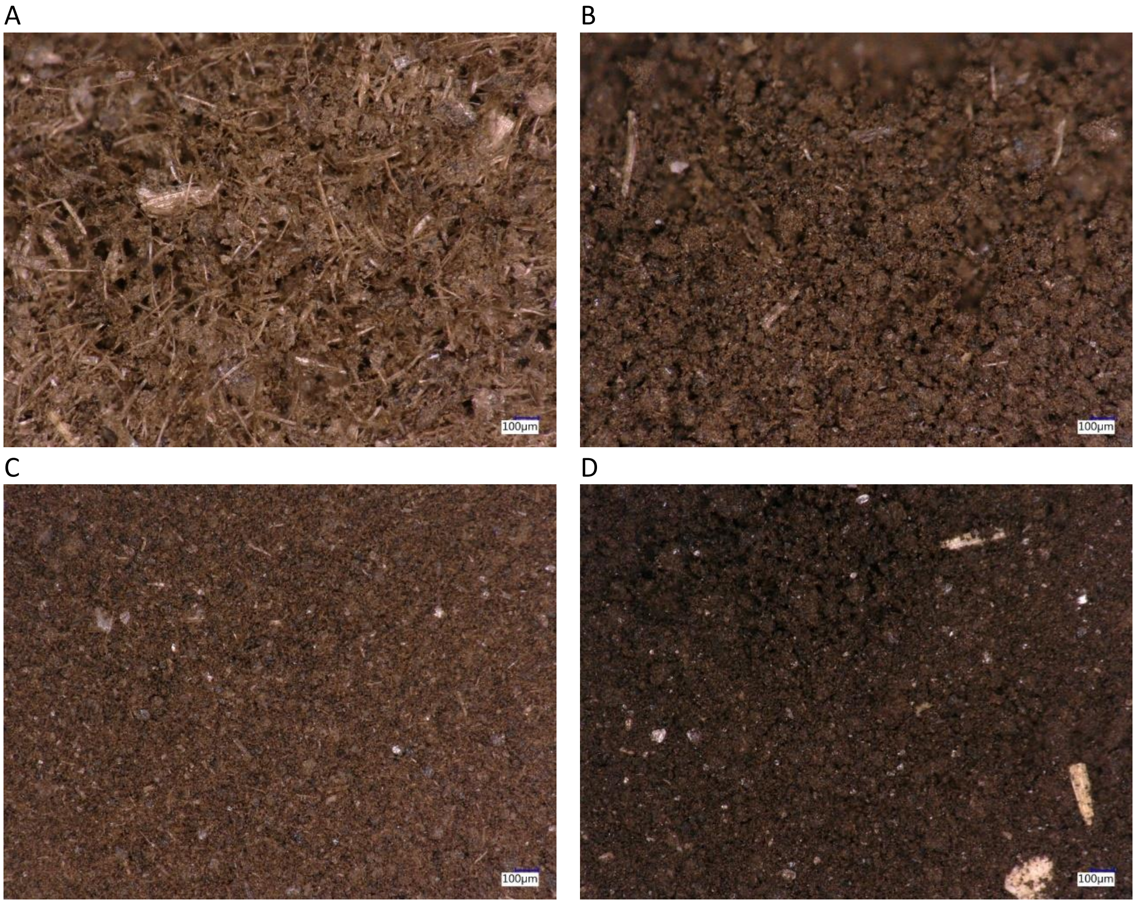
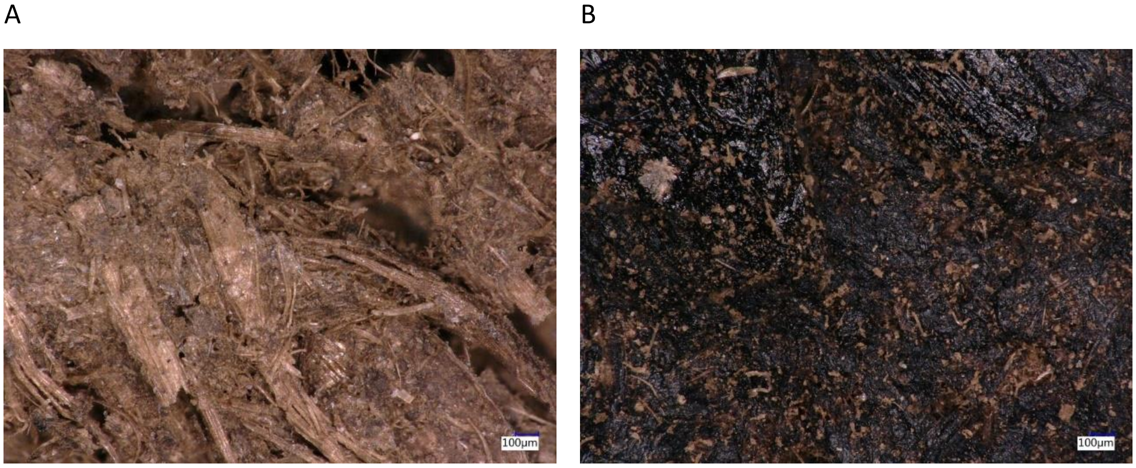


Figure 12. Digital microscopy of milled hydrochars produced from pig manure at various process conditions: A – 200°C, 60 min; B – 200°C, 360 min; C –240°C, 30 min, 24 bar; D- 240°C, 60 min, 49 bar.

Biogas slurry



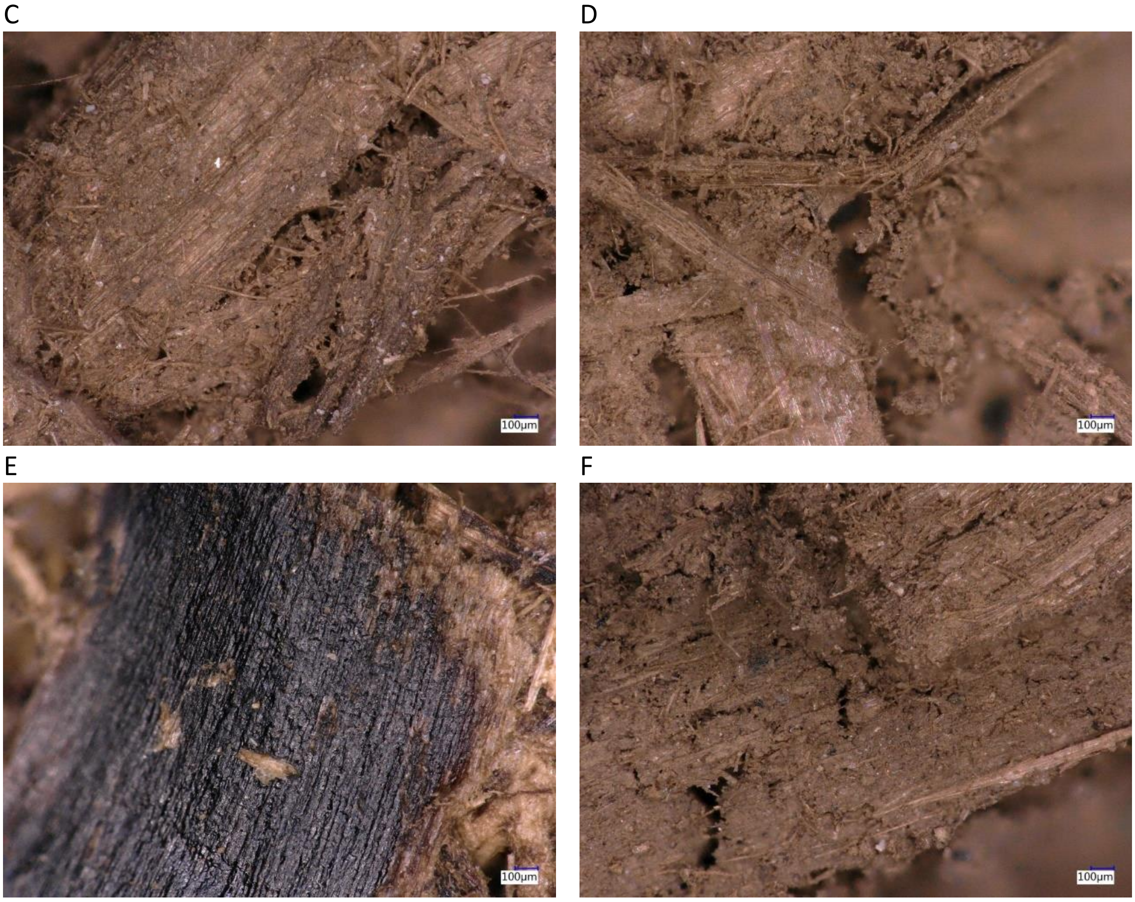


Figure 13. Digital microscopy of unmilled hydrochars produced from biogas slurry at various process conditions: A – 200°C, 30 min; B – 200°C, 60 min; C – 200°C, 120 min; D –200°C, 360 min, 24 bar; E- 240°C, 60 min, 49 bar; F - 240°C, 360 min.

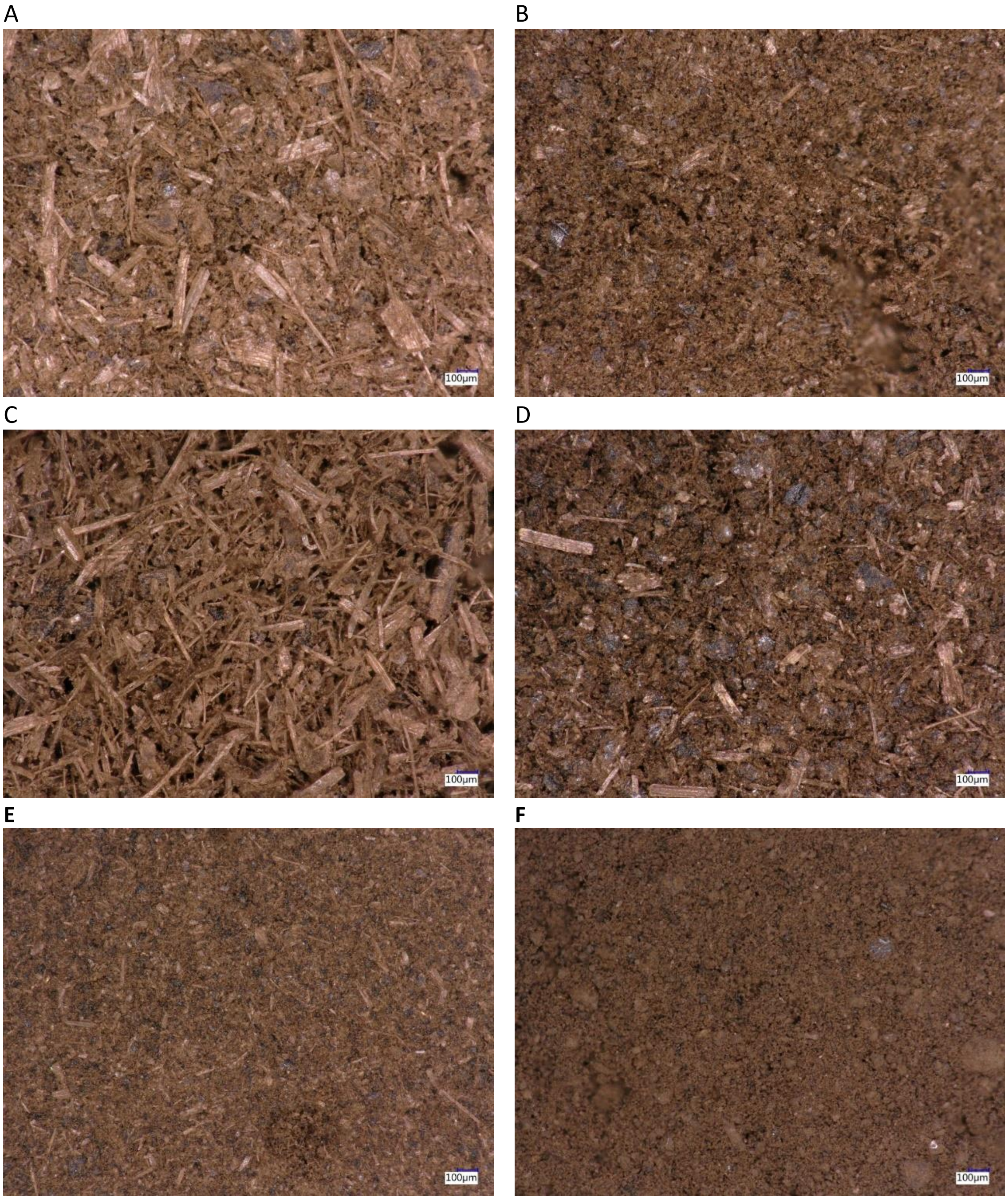


Figure 14. Digital microscopy of milled hydrochars produced from biogas slurry at various process conditions: A – 200°C, 30 min; B – 200°C, 60 min; C – 200°C, 120 min; D –200°C, 360 min, 24 bar; E- 240°C, 60 min, 49 bar; F - 240°C, 360 min.

Struvite

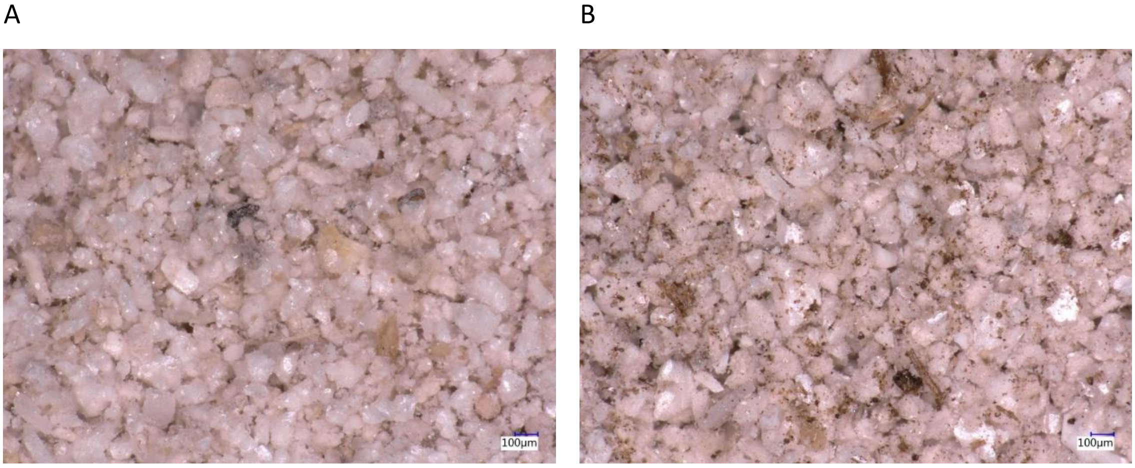


Figure 15.Digital microscopy of milled hydrochars produced from struvite at various process conditions: A – 200°C, 60 min; B – 240°C, 60 min, 36 bar.

All hydrochars have a residual water concentration of <2.5% (Appendix C)

Chapter 4

Discussion

The objective of this research was to determine whether different types of carbonised biowastes are suitable as fertilisers. Phosphorus concentration, as well as the solubility and availability of P in the amendments were analysed, and appropriate HTC conditions were sought for desired physical properties. Furthermore, the difference between feedstock and hydrochar was compared as well as LPM -s with amended LPM-s.

4.1 Chemical properties

4.1.1 Chemical characteristics

Certain chemical characteristics of biowastes should be avoided before being used as fertiliser, namely excess of moisture, low C/N ratio and nutrient concentration and excess pollutants (Bernal, Alburquerque, and Moral 2009). Therefore, appropriate biowaste handling is required in order to attain quality fertiliser. In the following the mentioned chemical characteristics are compared to guidelines and previous studies to establish the biowastes' potential as fertiliser.

Nutrients and Pollutants

Many studies have measured both P concentration and availability in different types of manure and proven that manure application to soil increases crop yield due to higher P availability (Cao et al. 2011). Comparing the LPM feedstock measurements with LPM-w shows that HTC has mostly increased the samples' nutrient concentration.

Compared to the Austrian fertilisation regulations and EBC, all hydrochars measured can be considered suitable as fertiliser for all nutrient concentrations. The hydrochars contain between 10.7 – 161.5 g kg^{-1} of phosphorus (Table 1 & Table 14). Struvite was used as a reference as it is known to contain a sufficient amount of P, while LPM-w and LPM-s have also a high amount of P at 20.9 and 20.3 g kg^{-1}, making it more than suitable as fertiliser material. During the process of HTC carbon and oxygen are lost in form of water and gas, while P is relatively well retained, resulting in an apparent increase in P concentration. The feedstock is dehydrated and changes the environment for and speciation of phosphorus, hence the different concentrations of P in feedstock and hydrochar. Furthermore, in fact some P is lost, but not as much as water (dehydration) and carbon. This has also been shown in previous studies (Pedersen, Rubæk, and Sørensen 2017). Nitrogen losses appear to be relatively low during HTC as indicated by the data (feedstocks versus products, Tables 11 and 13). The same applies for potassium. The different hydrochars contained between 0.5 – 16 g kg^{-1} of K (Table 13). The highest amount was found in BGSL which may be due to the K concentration in maize which is often used in the production of biogas. In the Austrian guidelines of sufficient fertilisation, the K concentration needed to be suitable as a fertiliser depends on the clay content. However, comparing the measured samples to the guidelines shows that all samples have sufficient K in order to be used (Table 2). Measured K in manure from previous studies showed differing results. Potassium measured in different feedstocks varied between 11.33 g kg^{-1} (Antoniadis, Koutroubas, and Fotiadis 2015) – 75.5 g kg^{-1} (Sager 2007). Sager (2007) measured nutrient concentrations in different types of biowaste showing that highest concentrations of potassium were found in pig manure and biogas slurry (50–80 g kg^{-1}). However, he depicted the dry weight nutrient concentration. Hence, the much lower measured K concentrations in this research. Furthermore, potassium concentration depends on type of biowaste (Smith, Singh, and Ross 2016). The same applies for other nutrients.

The different samples measured show Mg concentrations between 8.1 – 158 g kg^{-1} which is above previously measured Mg concentrations in animal manure (Huang et al. 2008). Magnesium is especially important as it combats aluminium toxicity in plants. Hence, the relatively low aluminium concentrations ranging between 0.3 – 17.6 g kg^{-1} were desired. The highest Al concentration is found in LPM-s + SEA, which was expected due to its environment (Prange and Dennison 2000). Compared to guideline values all the samples are within the range of recommended concentrations. All hydrochars contain traces of copper (6- 75 mg kg^{-1}) and zinc (11-267 mg kg^{-1}) in amounts that are not toxic but can enhance plant growth. Compared to measurements of cow dung and pig manure in previous studies the concentration of Cu is lower, but the concentration of Zn is higher in the hydrochars of this study (Lv, Xing, and Yang 2016). Especially the pure LPM-w and -s hydrochars show a higher amount of Cu compared to LPM-s with amendments derived hydrochars which could be due to the small concentrations of Cu in the amendments leading to dilution in LPM-s when amendments were added. In contrast, the amount of zinc does not vary considerably between the hydrochars, and is present in high enough amounts, showing that all hydrochars are in that sense suitable to be used as fertiliser. Comparing the Pb concentration of LPM-w and LPM-s to the study of raw manure by Lv et al. (2016) shows less Pb in the hydrochars here. This is probably due to natural variability between samples (Song and Guo 2012).

Animal manure enhances soil by adding Mn, Zn, Cu and Co. Due to the small concentrations of heavy metals measured in the hydrochars, they are unlikely to pose a threat to agricultural soils. Although, it is always important to ensure that heavy metal accumulation in soil is avoided by applying the right amount of fertiliser. Accumulations of heavy metals in hydrochars have been suspected as causing adverse effects to plant growth (Reza et al. 2014), nevertheless the results of ecotoxicological studies have not confirmed this theory (Reza et al. 2014). A hypothetical scenario for potential heavy metal accumulation of samples used here was calculated using the following equation

Heavy metal accumulation in soil = $C_{soil}+((C_{biowaste}*rate)/p*v))$;

with C_{soil} being the concentration (mg kg^{-1}) of heavy metal present in soil, $C_{biowaste}$ being the concentration (mg kg^{-1}) of heavy metal present in the hydrochar, rate being the application rate of each biowaste in order to supply 30 t P ha^{-1} to the soil (Table 16), p the soil bulk density (t m^{-3}) and v the volume of soil (m^3). Bulk density was chosen according to Liebhard (1994) at 1.3 t m $^{-3}$ for soil at 20 cm depth (v = 2000 m^3). Elemental concentration of Austrian soil was taken from the Amt der Niederösterreichischen Landesregierung (1994), the trigger values[3] for heavy metals was taken from the Austrian Environmental Agency (2003) (Table 17).

Table 16. Application rate (t/ha) needed for each soil to apply 30 t P/ha using P concentrations of each hydrochar.

	Application rates to provide 30 t P /ha
STR	49
LPM-w	379
BGSL	545
LPM-s + DOL	525
LPM-s + GYP	738
LMP + LIM	741
LPM-s + APA	153
LPM-s + SEA	703
LPM-s + STR	101
LPM-s + ASH	691
LPM-s	388

Table 17. Elemental concentration in Lower Austrian soil (0-20 cm) [mg kg^{-1}], and trigger values [mg kg^{-1}] taken from the Austrian Environmental Agency (2003).

	As	Cd	Cu	Ni	Pb	Zn
Conc. in soil	7.54	0.17	19.9	22.3	11.81	73.6
Trigger value[3]	20	1	100	60	100	300

The calculations show that even with added hydrochar, the heavy metal accumulation in soil does not exceed the Austrian trigger value (Figure 16). Furthermore, Cd concentration remains at a very low concentration, showing that the soil amendment does barely add any cadmium.

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[3] Trigger value: value that triggers the need for further investigation with regards to toxicity.

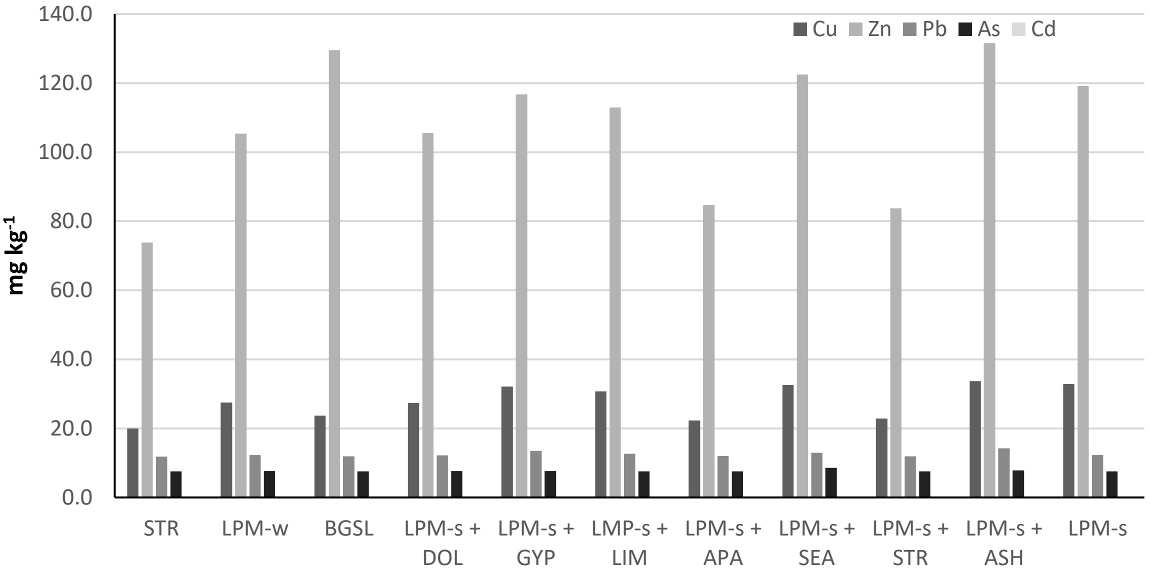


Figure 16. Potential heavy metal accumulation in Austrian soil using p=1300 t/m^{3}and v=2000 m^3, after 1 year of application.

Nonetheless, there is a small leeway before heavy metal thresholds for the soils might be exceeded if the amendments are applied at a certain rate (Figure 16). Zinc trigger values are exceeded after 5 years application of BGSL, after ten years of application, all hydrochars but STR and LPM-s + STR exceed the Zn trigger values in soils. Cupper trigger values are exceeded after 10 years of application by applying LPM-s + GYP, LPM-s + LIM, LPM-s + SEA, LPM-s + ASH and LPM-s. All other heavy metal trigger values are not exceeded after 10 years of application. This shows that long-term the tested amendments need to be further investigated before applications especially in terms of Cu and Zn accumulation. However, the calculation is only based on P fertilisation and has not included other factors, such as losses of the heavy metals from the soils through plant uptake, leaching or erosion.

PAHs

Comparing the measured PAHs to the check list for the evaluation of organic soil contaminants (Leidraad Bodemsanering, 1988, cited in Rosenkranz et al., 1994) (Appendix D) shows that neither the PAHs in LPM-w nor in BGSL reach the reference value. Very few PAHs were found unlike in other types of soil amendments such as biochar and lignite (Liu et al. 2015; Gomez-Eyles et al. 2011; Liu et al. 2013). HTC seems to be a suitable technology that permits product that can be almost PAH free, meaning that there is no threat to contribute to ecotoxicology (Reza et al. 2014). However, this only holds true if a process temperature of < 270°C is used.

C/N ratio

The C/N ratio of soils is normally about 10–12:1 (Sparks 2003). Furthermore, according to the Test Methods for the Examination of Composting and Compost (TMECC 2002) the C/N ratio of manure should be below 25 to reach maturity. Disregarding struvite, the C/N ratios of the hydrochars measured are between 15-20 parts of C to 1 part of N. In addition, biomass with a low N concentration or high C/N ratio is more stable than biomass with high N concentration and low C/N ratio (Masunga et al. 2016). All amendments decreased the carbon concentration of the samples while the N concentration was only decreased by a small fraction. The difference between LPM-w and LPM-s is most probably due to natural variability between samples, as has been identified previously (Song and Guo 2012).

Phosphorus solubility and availability

Comparing P availability to previous studies depicts higher P availability in the carbonised LPM-w compared to feedstock (Cao et al. 2011). Furthermore, biochar has been said to be a suitable soil improvement (Heilmann et al. 2014), applying this to potential soil fertilisers also shows enhancement. Comparing BGSL hydrochars produced for this research to measurements done by Duboc (2016, personal communication) shows higher P solubility in the hydrocharsF considered here (Appendix E). Furthermore, comparing the BGSL hydrochar produced for this researched to previously measured biochar produced by pyrolysis shows higher values of soluble P in hydrochar (75 % extracted P) than biochar (69.4 %) (Duboc, 2016 personal communication) (Appendix E).

Water soluble P is reduced during HTC. A previous study suggested that this was caused by the formation of insoluble Ca-P (Dai et al. 2015) . Therefore, it was important to use a method where more P can be extracted. In general, most P was extracted from STR, BGSL and LPM-w in the first seven days of the IB experiment. On the one hand this is due to the high affinity of phosphorus to ferric form of the ferrihydrite (Shen et al. 2011). On the other hand, the reaction velocity from day zero to day seven influenced P release, suggesting that most of the soluble PO_4^{3-} was available to react with the ferrihydrite within the first week. The differences in P solubility in the different hydrochars depended on P availability and speciation, hence the higher amount of extracted P in struvite compared to BGSL and LPM. The LPM-s + amendment such as LPM-s + APA showing less extracted P due to 'locked-up' P unavailable for sorption, meaning phosphorus is chemically bound to particles.

The low C_{DGT} results in the alkaline soil may be explained by the high pH of the soil. P availability to plants is limited when soil pH values are between 7.5 and 8.5 due to fixation with Ca, Al and Fe minerals (Shen et al. 2011). Compared to other C_{DGT} studies measuring fertilised soil (Santner et al. 2015) the values measured in this work in the neutral soil are low. In three different neutral soils (pH 7.1-7.8) Santner et al. (2011) measured 238, 260 and 11.9 µg L^{-1} of available soil P fractions, where the first two soils were fertilised with liquid pig manure as well as mineral P. The third soil had not been fertilised since 2001, meaning that LPM-w and BGSL in this study could potentially have double extractable P when applied to the neutral soil. Adding superphosphate shows the high potential of extractable P when adding efficient fertilisers to soil. P solubility depends not only on pH but on total P present, P forms i.e. it is normal to find this kind of variation in P availability across different soils of similar pH.

Generally, the availability of fertiliser P in alkaline soils is more limited due to formation of sparingly soluble P-Ca minerals. Also the added P is clearly more immobilised (even for highly soluble fertilisers such as SSP) in the alkaline soil as shown in results. There is some small increase of P availability after addition of the hydrochars in the neutral soil but a tendency to decrease in the alkaline soil. The hydrochar may interact with the available P present in the soil and at least initially leads to immobilisation. Perhaps this is an effect of added surface area and/or of compounds such as Ca, Fe, Al that are added with the char and may bind P present in the soil. Overall, this warrants further investigations.

4.1.2 Differences between three biowaste types overall

While BGSL and liquid LPM-w show overall similar patterns, STR contains higher phosphorus concentrations. This was expected as previous studies have shown high P concentration in struvite (Ghosh, Mohan, and Sarkar 1996; Massey et al. 2009). Comparing all three biowaste hydrochars to the Austrian guidelines of sufficient fertilisation shows that P concentration of all three samples falls into the concentration class C and exceed the value needed by at least a tenfold hinting towards management requirement for appropriate application rates. Whereas BGSL and STR have been tested before for fertilisation purposes and proven to be suitable (Massey et al. 2009; Nkoa 2014), there is very little literature on P solubility in pig manure. However, previous studies have shown an increase of P availability through manure application to soil (Schoumans et al. 2015b). It was expected that LPM-w and BGSL would behave in a similar manner due to similar behaviour of manure and biogas slurry in previous studies (Nkoa 2014). In most case this is correct, differences found included PAHs as well as nutrient concentration. Total PAHs measured in LPM-w were small which makes it even more appealing as fertiliser. The percentage of P extracted using IB from LPM-w and BGSL also showed similar results, however, P concentration in LPM-w was slightly higher, meaning that actual P extracted is also higher in LPM-w. Furthermore, P bioavailability in LPM-w and BGSL is very similar to the control samples, showing that more tests are needed here to obtain conclusive results. The differences between STR and BGSL and LPM-w in P solubility can be explained by the high magnesium concentration of struvite as Mg can reduce the adsorption of P by $CaCO_3$.

4.1.3 Feedstock vs carbonised samples

Previous studies on HTC of manures have shown that most phosphorus was preserved in the hydrochar after HTC (Heilmann et al. 2014). This study shows increases in P concentration in all hydrochars. The formation of insoluble phosphate was previously related to metal ions such as aluminium, calcium, magnesium and iron present in manures due to binding to proteins or colloidal forms (Ekpo et al. 2016). This was confirmed in this study. LPM-w shows higher concentrations of Al, Ca, Mg and Fe in the hydrochars compared to its feedstock. Previous studies also claim calcium as the main factor controlling the solubility of phosphorus in the solid residue and conclude that the solubility of phosphorus might be a result of apatite-P formed during HTC (Dai et al. 2015). Ekpo et al (2016) showed a Ca:P ratio of 2.44, 1.44 and 1.44 for pig manure, digestate and chicken manure respectively, arguing that this may explain the extraction of P.

A similar trend was observed. Calcium rich samples such as LPM-s + LIM, LPM-s + GYP and LPM+ ASH are the least soluble compared to magnesium rich samples such as LPM+ STR and STR. This is due to the tendency of calcium rich samples binding to inorganic anions leading to immobilisation of P. In contrast, the magnesium rich samples are almost instantly soluble (see STR). In contrast, LPM+ APA contains the least amount of soluble P. This could be affiliated with a higher calcium concentration in rock phosphate itself as Dai et al (2015) argued. However, comparing Ca:P ratio between carbonised LPM-w and feedstock shows little difference. In general, this means that it could be beneficial to add magnesium rich samples to pig manure as they are not only more soluble, but their nutrients would also add to the potential fertiliser.

While this study did not focus on bioavailable P of feedstock, it would be beneficial to do so in order to understand whether HTC increases the bioavailability of P in biowaste samples. Especially because the C_{DGT} results do not show significant differences in carbonised LPM-w and BGSL and the control. This might mean that carbonising the samples does not increase bioavailability or that P was immobilised due to high temperatures during hydrothermal carbonisation (Ekpo et al. 2016).

4.1.4 Comparison of pig manure samples

Increasing P concentration, solubility and bioavailability by adding different amendments to LPM-s was only partially succeeded. It was expected that especially P solubility and availability will be increased by adding different amendments. The LPM-s amendments did not change the P solubility significantly. While adding calcium substrates to LPM-s possibly resulted in less soluble P due to a probable reaction of Ca & P forming insoluble Ca-P which is not readily available to plants. Adding the chosen amendments to LPM-s did not increase P concentration and solubility in LPM-s. For this reason, P bioavailability was not tested all LPM + amendments.

Apart from that, adding different amendments means also that these could contribute to certain soil P pools and thus provide further nutrients to plant growth. For example, adding primary minerals such as apatite to pig manure was expected to improve LPM-s as a P fertiliser, however, the weathering is too slow contribute to plant uptake (Shen et al. 2011). Hence, the low amount of P bioavailability of LPM-s + APA compared to the other samples. In contrast, adding amendments such as LIM and GYP containing secondary minerals was expected to increase P solubility as they are part of precipitation which positively influence the solubility of many P fertilisers. However, this was not the case.

4.2 Physical properties

4.2.1 Influences of process parameter on end product

Qualitative assessment of physical parameters

The visual assessment of grain size and homogeneity did not give clear enough results. A quantification of gran size and homogeneity alongside the microscope picture would have been necessary to accurately state the physical properties. Despite reaching a scale of 100 – 1000 µm and achieving minimum size as shown by microscope images, the microscope enlargement of x150 did not give the desired details to clearly observe the physical properties needed, however, it gave an estimate of changing properties with changing HTC conditions. Here, it is important to provide a complementary quantification method such as physical stability (Naisse et al. 2015), WHC (Song and Guo 2012) and specific surface area using BET (Brunauer-Emett-Teller) surface area method (Song and Guo 2012). Therefore, visual observations are used to provide complementary qualitative evidence to support chemical measurements.

While LPM-w and -s (with and without amendments) and BGSL similar changes in homogeneity depending on HTC conditions, struvite does not show changes in response to HTC treatment. This shows that LPM and BGSL can be treated similar in the process of HTC, whereas it is not necessary to carbonise struvite to obtain better performance. A big difference between LPM by itself and amended LPM samples is visible in the pictures taken with the microscope. The amendments are clearly visible in the pictures (Appendix B) and may also affect physical as well as chemical structures of the samples.

Generally, hydrochar can improve soils because of its porosity and large surface area. Its porous structure indicates good storage space for nutrients and sorption capacity, while encourages microbial colony growth (Reza et al. 2014). However, physical parameters are dependent on both HTC conditions which effect polymerisation and feedstock type (Reza et al. 2014) This improves both nutrient and water availability of the soil. Furthermore, WHC of hydrochar is much higher due to is high meso- and macro porous surface as well as its carbon structure, potentially improving the fertility of sandy soil (Reza et al. 2014) To sum up, smaller particle size and increased homogeneity provide improved properties for further use of the products in the formulation of fertilisers, soil amendments or bio effectors.

4.2.2 Water concentration

While liquid pig manure and biogas slurry are very water rich materials it was expected that the hydrochar will contain nearly no water. This is because after carbonising the samples most of the water is lost and kept as process water. However, tests showed that only little phosphorus is lost to process water (Appendix F). Afterwards the remaining char is further dried before analysis, meaning a further loss of water.

4.3 The potential for different types of HTC-treated biowastes for use on agricultural soils

Hydrothermal carbonisation has a wide scope of potential use. One of the most important aspects is the recycling of biowastes produced in livestock farming as well as biofuel production. In Austria the waste produced from livestock farming is steadily increasing. In 2016 46.8 % of Austria's overall production came from livestock farming, 10.6 % of them being from pig farming (Statistik 2018). Due to storage issues and high leaching potential of manure recoverable phosphorus might be lost. However, hydrochar is still not allowed to be used as fertiliser in Austria as it has not been added to the fertilisation regulation (§2 Abs. 1 Düngemittelverordnung). The potential use is possible in some individual cases, nonetheless, due to its high potential as fertiliser the regulations within Austria should be updated to incorporate hydrochar in their fertilisation directive.

The high potential of the biowastes used as fertiliser is especially apparent in its high P concentrations. To be functional as fertiliser EBC and Austrian regulation demand low heavy metal concentrations. Considering LPM-w as a fertiliser a farmer would need a small amount of LPM-w hydrochar for sufficient crop fertilisation (Table 16). However, considering the small amount of bioavailability of the LPM-w, the biowaste needs to be further tested for suitability as sufficient fertiliser. In this sense, one might suspect that using SSP would be advantageous to hydrochar fertiliser due to its excellent solubility. Yet, it has been replaced due to its low P concentrations. Advantages of SSP included high solubility, simple management and low cost (Plotegher and Ribeiro 2016). However, the production of SSP highly relies on phosphate rock which is becoming increasingly scarcer. Hence, the need of a shift to the use of biowastes that contain more P and with slight alteration (HTC) can replace mineral fertilisers. As shown in the results and heavy metal accumulation potential calculation all biowastes used here have sufficient amounts of nutrients and no concerning amounts of pollutants. Furthermore, the high P concentrations (Table 13) could reduce fertiliser costs and also stop heavy metal accumulation from mineral fertilisers derived from phosphor rock (Al Mamun et al. 2016).

In terms of nutrient content and solubility hydrochar seems to be more cost effective. Yet, there are no HTC plants that exist and could operate to meet fertilisation demands, therefore, it is uncertain whether it is economic feasible (Al Mamun et al. 2016). According to Al Mamun et al. (2016) the investment into a reactor big enough to produce at commercial scale will be the main expenditure. Thinking about biowastes produced in Austria this might be a worthwhile investment in order to push a shift back into both fertiliser produced from biowaste and recycling of resources. The cost effectiveness calculation of Al Mamun et al. (2016) shows that costs will be saved despite the requirement of monitoring at the beginning due to the yet little researched application of hydrochar as fertiliser. Cost will be saved because the use of biowaste is not reliant on imports such as commercially produced chemical fertilisers dependend on non-renewable sources. Furthermore, in order to fertilise a 2000 m^3 field with 30 t P/ha a farmer does not require a considerable amount of hydrochar in order to meet fertilisation demands. Compared to compost and application rates, the hydrochar application rates needed are lower due to HTC. Furthermore, the little impurities it has with regards to PAHs and heavy metal content makes hydrochar even more competitive. The shift to organic recycled material would decrease both Austria's dependency on phosphate rock and waste produced in the agricultural sector. Furthermore, farmers might be very likely to use hydrochar fertiliser produced from farmyard manure as they will be going back to the roots and trust the fertiliser feedstock that came from other farms. Despite the few limitations in establishing large enough HTC plant, hydrochar might be the right step into less dependent fertilisation on non-renewable resources as well as recycling nutrient rich biowastes.

Chapter 5

Conclusion

This study has shown the suitability of biogas slurry and liquid pig manure as fertiliser. While LPM-w and -s and BGSL showed higher P concentrations in carbonised form, amending the LPM-s did not enhance the material as P fertiliser. Furthermore, the research did show that PAHs and heavy metal are decreased when carbonising samples.

On the one hand, due to the unknown source and extraction method of the struvite used in this research, the applicability of using struvite as a fertiliser might be decreased if all struvite came from the same plant. Furthermore, it would have been important to apply the same methods on the feedstock of all products to allow for comparison between hydrochar and its feedstock. Physical parameters need to be quantified in order to gain more conclusive results. To understand practical implications of plant uptake, a pot experiment would be needed.

On the other hand, this research showed that carbonised LPM-w and BGSL enhance P concentration, and show high amounts of extractable P. However, P availability was not enhanced by applying HTC to liquid biowastes as samples showed similar results as the controls. The LPM collected at different times of the year show deviating results, meaning that seasonality might be a factor in P concentration. HTC treatment also showed increasing homogeneity with increasing temperature (up to 240°C) and time (plateau at 60 min).

Appendix A

Acid digestion details of all hydrochars

Table A. List of acid digested biowastes using HNO_3/H_2O_2.

Sample type	HTC conditions (°C, bar, mins)	Weight (mg)	Actual weight after acid digestion (g)	Temperature (°C) during digestion	Colour of Samples After digestion	Particles
BGSL	200, n/a, 30	100.5	86.87	168	Light yellow	Brown particles
BGSL	200, n/a, 60	109.8	**86.871**	**170**	Clear	Grey Particles
BGSL	200, n/a, 120	99.2	86.911	162	Clear	Grey particles
BGSL	200, n/a, 120	100.1	86.916	181	Clear	Grey Particles
BGSL	200, n/a, 60	100.2	**86.877**	**201**	Clear	No
BGSL	dry uncarbonised manure	101.3	86.878	169	Clear	Grey Particles
Activil 106	n/a	99.4	86.911	190	Clear	Grey Particles
Blank	n/a	n/a	**86.873**	**176**	Clear	Grey Particles
BGSL	200, n/a, 30	99.9	86.912	178	Clear	No
BGSL	200, n/a, 60	104.9	**86.875**	**161**	Clear	Grey Particles
BGSL	200, n/a, 120	100.5	86.913	189	Clear	Grey particles
BGSL	200, n/a, 120	99.3	86.915	171	Clear	Grey Particles
BGSL	200, n/a, 60	99.5	86.871	175	Light yellow	Brown particles
LPM	dry uncarbonised manure	104.4	**86.876**	**162**	Clear	Grey Particles
Activil 106	n/a	102.1	86.918	183	Clear	Grey Particles
Blank	n/a	n/a	86.914	190	Clear	Grey Particles
LPM	200,60, 21	100.1	**86.907**	178	Clear	Grey Particles
LPM	200,60,21	99.5	**86.917**	180	Clear	Grey Particles
LPM	dry uncarbonised manure	99.2	86.869	176	Clear	Grey Particles
LPM	dry uncarbonised manure	100.3	86.913	177	Clear	Grey Particles
LPM	dry uncarbonised manure	99.8	**86.91**	163	Clear	Grey Particles
LPM	dry uncarbonised manure	101.8	86.874	177	Clear	Grey Particles
LPM	240,30,44	99.5	**86.877**	186	Clear	Grey Particles

Sample type	HTC conditions (°C, bar, mins)	Weight (mg)	Actual weight after acid digestion (g)	Temperature (°C) during digestion	Colour of Samples After digestion	Particles
LPM	240,30,44	100.1	86.87	182	Clear	Grey Particles
BGSL	240,60,49	99.6	86.859	213	Clear	Grey Particles
BGSL	240,60,49	99.4	86.876	171	Clear	Grey Particles
BGSL	240,360, n/a	100.3	86.911	184	Light yellow	Grey Particles
BGSL	240,360, n/a	99	86.916	178	Clear	Grey Particles
BGSL	n/a	101.8	**86.876**	190	Clear	Brownish particles
Activil106	n/a	99.2	86.914	181	Clear	Brownish particles
Blank	n/a	n/a	86.911	165	Clear	No
Blank	n/a	n/a	86.911	175	Clear	No
BGSL	200,360,24	99	86.912	157	Clear	Grey Particles
BGSL	200,360,24	99	86.873	168	Clear	Grey Particles
BGSL	dry uncarbonised slurry	99.2	86.879	172	Clear	Grey particles
BGSL	Trocken	99.3	**86.877**	177	Clear	Grey particles
LPM	240,60,41	99.2	86.882	178	Clear	Grey Particles
LPM	240,60,41	99.4	**86.916**	177	Clear	Grey Particles
LPM	dry uncarbonised manure	99.1	86.912	190	Clear	Grey Particles
LPM	dry uncarbonised manure	100.2	86.914	178	Clear	Grey Particles
BGSL	dry uncarbonised slurry	99.8	**86.916**	177	Clear	No
BGSL	dry uncarbonised slurry	99.4	86.868	184	Clear	No
BGSL	withheld	103.6	86.876	161	Clear	Grey particles
BGSL	withheld	100.9	86.872	183	Clear	Grey particles
Activil106	n/a	99.8	86.922	213	Clear	Brownish Particles
Activil106	n/a	99.4	86.911	197	Clear	Brownish Particles
Blank	n/a	n/a	86.875	168	Clear	no
Blank	n/a	n/a	86.784	161	Clear	No
STR	200, 30, n/a	99.1	**86.851**	171	Clear	No

Sample type	HTC conditions (°C, bar, mins)	Weight (mg)	Actual weight after acid digestion (g)	Temperature (°C) during digestion	Colour of Samples After digestion	Particles
STR	200, 30, n/a	99.6	86.916	187	Clear	No
STR	200, 60, n/a	99.2	86.918	184	Clear	Grey particles
STR	200, 60, n/a	99.3	**86.872**	164	Clear	Grey particles
STR	200,360,n/a	99.3	86.875	173	Clear	No
STR	200,360,n/a	99.5	86.91	178	Clear	No
STR	200,60,n/a	100	86.865	173	Clear	No
STR	200,60,n/a	99.3	86.869	195	Clear	No
STR	240,30,36	101.1	86.858	176	Clear	No
STR	240,30,36	99.5	**86.908**	213	Clear	No
STR	240,60,36	100.2	86.912	182	Clear	Grey particles
STR	240,60,36	99.2	86.91	176	Clear	Grey particles
STR	n/a	103.2	**86.873**	203	Clear	Brownish particles
Activil106	n/a	100.2	86.861	175	Clear	Brownish particles
Blank	n/a	n/a	**86.913**	175	Clear	No
Blank	n/a	n/a	86.876	166	Clear	No
LPM	200,30,18	99	86.861	179	Clear	Grey Particles
LPM	200,30,18	100.5	86.86	195	Clear	Grey Particles
LPM	240,360,40.5	99.1	**86.865**	179	Very light yellow	Grey Particles
LPM	240,360,40.5	99.8	86.879	165	Very light yellow	Grey Particles
Sunflower Raw (Pyrolyse Coy)	n/a	101.8	86.87	180	Dark yellow	Grey particles
Sunflower Raw (Pyrolyse Coy)	n/a	99	86.854	215	Very light yellow	Grey particles
Sunflower Raw (Pyrolyse Coy)	n/a	99.8	**86.855**	176	Dark yellow	Grey particles
Sunflower Husk (Pyrolyse Coy)	n/a	99.7	86.863	188	Yellow	Grey Particles
Sunflower Husk (Pyrolyse Coy)	n/a	100.2	86.873	183	Yellow	Grey Particles

Sample type	HTC conditions (°C, bar, mins)	Weight (mg)	Actual weight after acid digestion (g)	Temperature (°C) during digestion	Colour of Samples After digestion	Particles
Sunflower Husk (Pyrolyse Coy)	n/a	99.9	86.876	172	Yellow	Grey particles
Animal meal (Pyrolyse Coy)	n/a	99.4	86.855	171	Yellow	Grey particles
Animal meal (Pyrolyse Coy)	n/a	99.9	86.86	191	Very light yellow	Grey particles
Animal meal (Pyrolyse Coy)	n/a	99.1	86.86	202	Clear	Grey particles
BGSL	n/a	100	86.917	167	Clear	Grey particles
Blank	n/a	n/a	86.859	109	Clear	No
Blank	n/a	n/a	**86.914**	86	Clear	No
charcoal sludge	n/a	100.9	86.913	212	Clear	Grey particles
charcoal sludge	n/a	100	86.914	190	very light yellow	Grey particles
charcoal sludge	n/a	99.2	86.914	205	Clear	Grey particles
charcoal sludge	n/a	100.2	86.87	191	very light yellow	Grey particles
charcoal coarse	n/a	102.1	86.919	210	very light yellow	Grey particles
charcoal coarse	n/a	99.6	86.927	194	Yellow	Grey & orange particles
charcoal coarse	n/a	100	86.911	210	very light yellow	Grey particles
charcoal coarse	n/a	99.1	86.871	203	very light yellow	Grey particles
charcoal coarse	n/a	99	86.871	195	very light yellow	Grey particles
charcoal coarse	n/a	99.8	86.882	193	very light yellow	Grey particles
charcoal coarse	n/a	99	86.881	204	very light yellow	Grey particles
charcoal coarse	n/a	99.8	86.912	187	very light yellow	Grey particles
BGSL	n/a	100	86.873	195	Clear	white particles
BGSL	n/a	99.4	86.874	203	Clear	white particles
Blank	n/a	n/a	86.871	168	Clear	no
Blank	n/a	n/a	86.92	213	Clear	no
Urine	n/a	1943.1	86.875	152	Clear	No
Urine	n/a	1958.9	86.912	132	Clear	No

Sample type	HTC conditions (°C, bar, mins)	Weight (mg)	Actual weight after acid digestion (g)	Temperature (°C) during digestion	Colour of Samples After digestion	Particles
Urine	n/a	2002	86.913	150	Clear	No
Urine	n/a	1959.8	86.911	200	Clear	No
Urine	n/a	2019.8	86.914	161	Clear	No
Urine	n/a	1997.9	86.883	146	Clear	No
Urine	n/a	1929.6	86.873	160	Clear	No
Urine	n/a	2018.3	86.914	157	Clear	No
Urine	n/a	1996.6	86.874	149	Clear	No
Urine	n/a	1939.2	86.87	149	Clear	No
Urine	n/a	1986.8	86.878	149	Clear	No
Urine	n/a	1993.1	86.911	172	Clear	No
Urine	n/a	2100.8+251.1	86.878	146	Clear	No
Urine	n/a	2157.2+248.9	86.912	147	Clear	No
Blank	n/a	n/a	86.918	170	Clear	No
Blank	n/a	n/a	86.873	142	Clear	No
Charcoal finely ground	n/a	99.9	86.873	213	Clear	Grey Particles
Charcoal finely ground	n/a	99.4	86.922	181	Very light yellow	Grey Particles
Charcoal finely ground	n/a	99.7	86.871	204	Very light yellow	Grey Particles
Charcoal finely ground	n/a	99.8	86.916	173	Very light yellow	Grey Particles
Charcoal finely ground	n/a	100.4	86.91	195	Clear	Grey Particles
Charcoal finely ground	n/a	99.8	86.877	168	Very light yellow	Grey Particles
Charcoal finely ground	n/a	99.9	86.871	191	Clear	Grey Particles
Charcoal finely ground	n/a	99.6	86.872	197	Very light yellow	Grey Particles
charcoal sludge	n/a	99.6	86.875	192	Very light yellow	Grey Particles

Sample type	HTC conditions (°C, bar, mins)	Weight (mg)	Actual weight after acid digestion (g)	Temperature (°C) during digestion	Colour of Samples After digestion	Particles
charcoal sludge	n/a	101.5	86.873	186	Very light yellow	Grey Particles
charcoal sludge	n/a	99.9	86.917	200	Very light yellow	Grey Particles
charcoal sludge	n/a	99.7	86.913	183	Very light yellow	Grey Particles
BGSL	n/a	99.3	86.883	184	Clear	Grey Particles
BGSL	n/a	99.6	86.915	195	Clear	Grey Particles
Blank	n/a	n/a	86.912	161	Clear	No
Blank	n/a	n/a	86.915	212	Clear	No
STR pw	n/a	1953.6	86.872	165	Clear	No
STR pw	n/a	1979.7	86.871	167	Clear	No
STR pw	n/a	1971.8	86.91	156	Clear	No
STR pw	n/a	1961.4	86.911	162	Clear	No
LPM pw	n/a	1974.8	86.873	216	Clear	No
LPM pw	n/a	2008	86.911	173	Clear	No
LPM pw	n/a	1984.1	86.869	161	Clear	No
LPM pw	n/a	1977.9	86.913	177	Clear	No
BGSL pw	n/a	1990.1	86.872	169	Clear	No
BGSL pw	n/a	1994.6	86.871	175	Clear	No
BGSL pw	n/a	1990.6	86.875	177	Clear	No
BGSL pw	n/a	1996.6	86.91	152	Clear	No
Blank	n/a	n/a	86.908	161	Clear	No
Blank	n/a	n/a	86.872	180	Clear	No
Blank	n/a	n/a	86.91	183	Clear	No
Blank	n/a	n/a	86.873	168	Clear	No
LPM-s + DOL pw	n/a	1980.5	86.96	216	Clear	No
LPM-s + DOL pw	n/a	2012.7	86.964	161	Clear	No
LPM-s + DOL pw	n/a	1992.4	86.964	169	Clear	No
LPM-s + GYP pw	n/a	1975.4	86.962	181	Clear	No
LPM-s + GYP pw	n/a	1965.9	86.959	157	Clear	No

Sample type	HTC conditions (°C, bar, mins)	Weight (mg)	Actual weight after acid digestion (g)	Temperature (°C) during digestion	Colour of Samples After digestion	Particles
LPM-s + GYP pw	n/a	1992.8	86.961	180	Clear	No
LPM-s + LIM pw	n/a	1989.9	86.915	163	Clear	No
LPM-s + LIM pw	n/a	2010.8	86.96	181	Clear	No
LPM-s + LIM pw	n/a	1988.3	86.918	164	Clear	No
LPM-s + APA pw	n/a	1880.6	86.919	157	Clear	No
LPM-s + APA pw	n/a	1996.3	86.918	155	Clear	No
LPM-s + APA pw	n/a	2010.5	86.915	150	Clear	No
Blank	n/a	n/a	86.912	181	Clear	No
Blank	n/a	n/a	86.958	182	Clear	No
Blank	n/a	n/a	86.92	163	Clear	No
Blank	n/a	n/a	86.958	159	Clear	No
LPM-s + SEA pw	n/a	1990.5	86.911	216	Clear	No
LPM-s + SEA pw	n/a	2002.7	86.91	161	Clear	No
LPM-s + SEA pw	n/a	2009	86.957	169	Clear	No
LPM-s + STR pw	n/a	1988.3	86.957	181	Clear	No
LPM-s + STR pw	n/a	1997	86.954	157	Clear	No
LPM-s + STR pw	n/a	1986.1	86.911	180	Clear	No
LPM-s + ASH pw	n/a	1978.3	86.91	163	Clear	No
LPM-s + ASH pw	n/a	1989.3	86.915	181	Clear	No
LPM-s + ASH pw	n/a	1990.7	86.958	164	Clear	No
LPM-s pw	n/a	1978.3	86.955	157	Clear	No
LPM-s pw	n/a	1944.3	86.954	155	Clear	No
LPM-s pw	n/a	1986.3	86.955	150	Clear	No
Blank	n/a	n/a	86.914	181	Clear	No
Blank	n/a	n/a	86.913	182	Clear	No
Blank	n/a	n/a	86.956	163	Clear	No
Blank	n/a	n/a	86.913	159	Clear	No
LPM-s + DOL	240, 60, withheld	100.1	86.974	148	clear	yes

Sample type	HTC conditions (°C, bar, mins)	Weight (mg)	Actual weight after acid digestion (g)	Temperature (°C) during digestion	Colour of Samples After digestion	Particles
LPM-s + DOL	240, 60, withheld	100	86.921	145	light yellow	yes
LPM-s + DOL	240, 60, withheld	99.8	86.933	162	clear	yes
LPM-s + GYP	240, 60, withheld	100.7	86.971	170	clear	yes
LPM-s + GYP	240, 60, withheld	100.8	86.918	163	clear	yes
LPM-s + GYP	240, 60, withheld	100	86.919	171	clear	yes
LPM-s + LIM	240, 60, withheld	101.2	86.925	169	clear	yes
LPM-s + LIM	240, 60, withheld	100	86.92	162	clear	yes
LPM-s + LIM	240, 60, withheld	100.2	86.963	171	clear	yes
LPM-s + APA	240, 60, withheld	100.8	86.97	159	clear	yes
LPM-s + APA	240, 60, withheld	101.1	86.963	166	clear	yes
LPM-s + APA	240, 60, withheld	99.8	86.979	147	clear	yes
BGSL	n/a	100.1	86.925	184	clear	yes
BGSL	n/a	99	86.973	185	clear	yes
Blank	n/a	n/a	86.999	214	clear	no
Blank	n/a	n/a	86.986	145	clear	no
LPM+ SEA	240, 60, withheld	100.8	86.965	168	clear	yes
LPM+ SEA	240, 60, withheld	99.8	86.915	168	clear	yes
LPM+ SEA	240, 60, withheld	99.5	86.96	183	clear	yes
LPM+ STR	240, 60, withheld	99.2	86.963	179	clear	yes
LPM+ STR	240, 60, withheld	99.4	86.964	173	clear	yes
LPM+ STR	240, 60, withheld	100.4	86.963	175	clear	yes
LPM+ ASH	240, 60, withheld	99.4	86.962	174	clear	yes
LPM+ ASH	240, 60, withheld	100.1	86.959	172	clear	yes
LPM+ ASH	240, 60, withheld	99.3	86.916	185	clear	yes
LPM-s	240, 60, withheld	101.2	86.962	171	clear	yes
LPM-s	240, 60, withheld	100.2	86.959	173	clear	yes
LPM-s	240, 60, withheld	99.3	86.964	165	clear	yes
BGSL	n/a	100.4	86.918	189	clear	no

Sample type	HTC conditions (°C, bar, mins)	Weight (mg)	Actual weight after acid digestion (g)	Temperature (°C) during digestion	Colour of Samples After digestion	Particles
BGSL	n/a	99.7	86.959	194	clear	yes
Blank	n/a	n/a	86.96	214	clear	no
Blank	n/a	n/a	86.964	172	clear	no
LPM feed	240, 60, withheld	99.2	86.961	172	clear	yes
LPM feed	240, 60, withheld	99.8	86.961	175	clear	yes
LPM feed	240, 60, withheld	99.2	86.915	190	clear	yes
STR	240, 60, withheld	99.9	86.917	188	clear	no
STR	240, 60, withheld	100.9	86.964	176	clear	no
STR	240, 60, withheld	100.7	86.963	180	clear	no
LPM	240, 60, withheld	99.1	86.96	173	clear	yes
LPM	240, 60, withheld	99.8	86.957	185	clear	yes
LPM	240, 60, withheld	99.1	86.964	193	clear	yes
BGSL	240, 60, withheld	99.2	86.958	173	clear	yes
BGSL	240, 60, withheld	100.2	86.919	169	clear	yes
BGSL	240, 60, withheld	101.1	86.922	176	clear	yes
BGSL	n/a	99.1	86.913	193	pinkish	yes
BGSL	n/a	99.3	86.958	193	pinkish	yes
Blank	n/a	n/a	86.914	213	clear	no
Blank	n/a	n/a	86.96	159	clear	no

Appendix B Pictures of LPM-s + amendments hydrochars

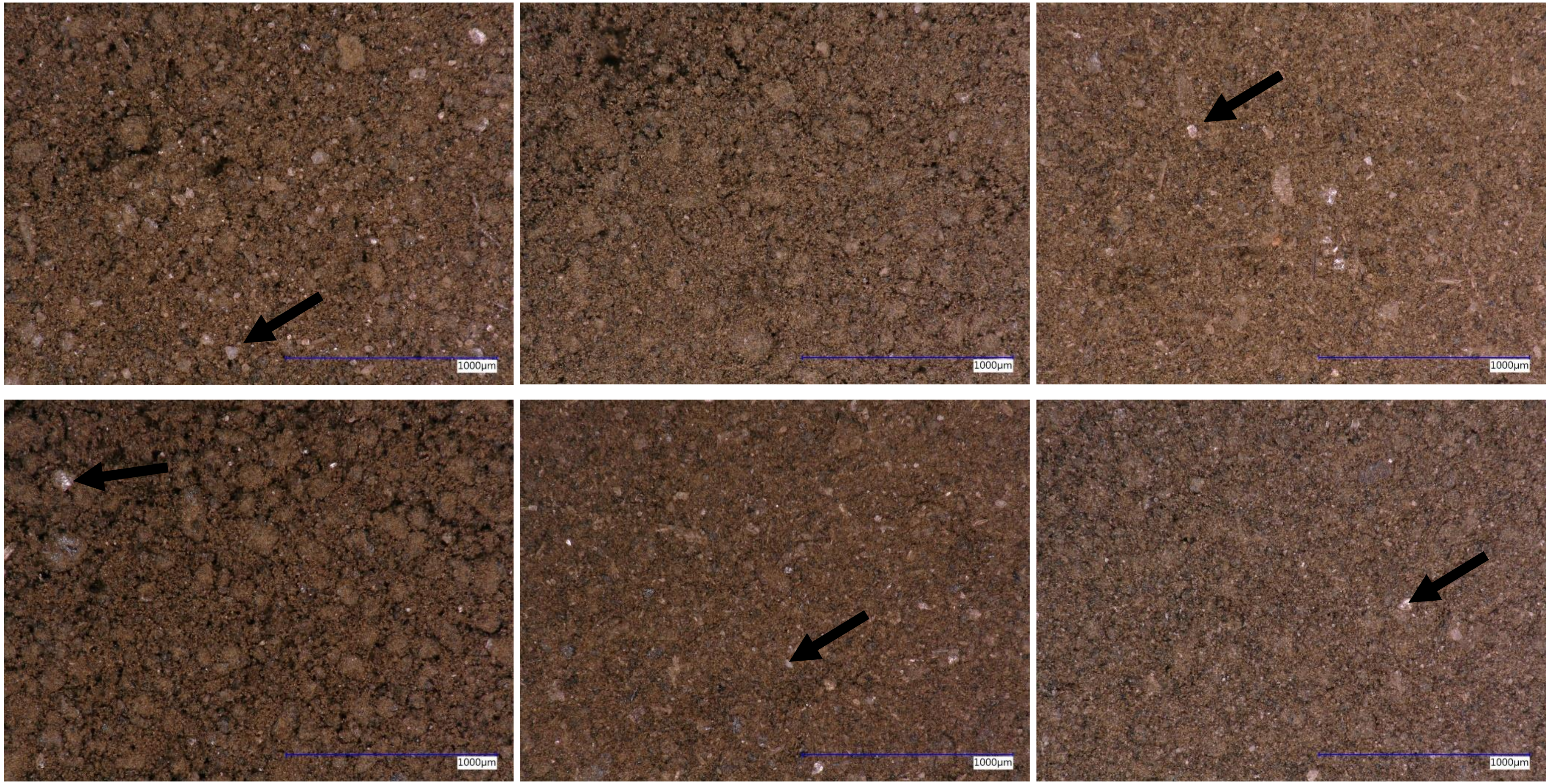


Figure A. Digital microscopy of milled hydrochars produced from LPM-s + amendments at process conditions of 240°C, 60 min: From top left to bottom right: LPM-s + DOL, LPM-s + GYP, LPM-s + LIM , LPM-s + APA, LPM-s + SEA, LPM-s + ASH. Errors indicating amendments.

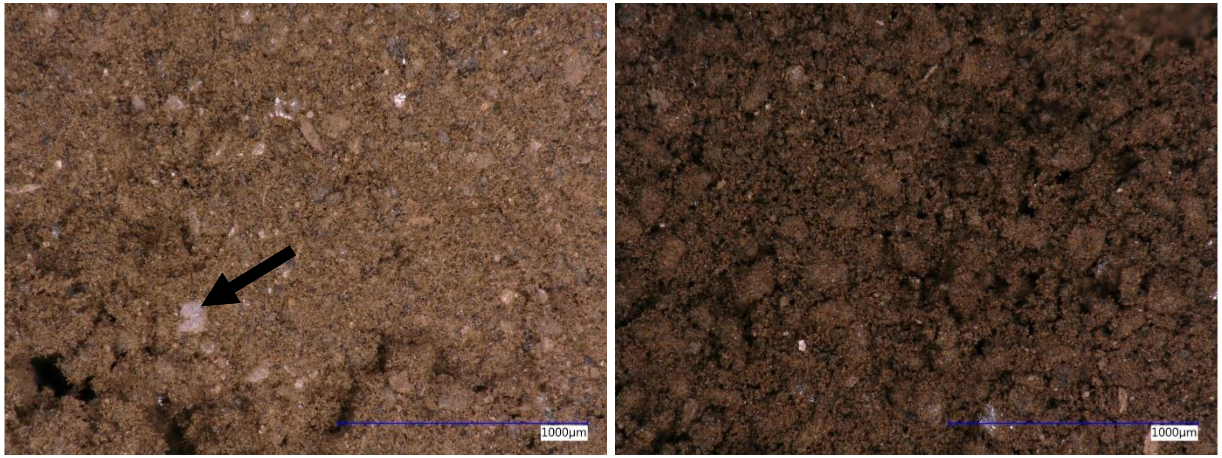


Figure B. Digital microscopy of milled hydrochars produced from LPM-s + amendments at process conditions of 240°C, 60 min: From left to right: LPM-s + STR and LPM-s. Errors indicating amendments.

Appendix C

Water content

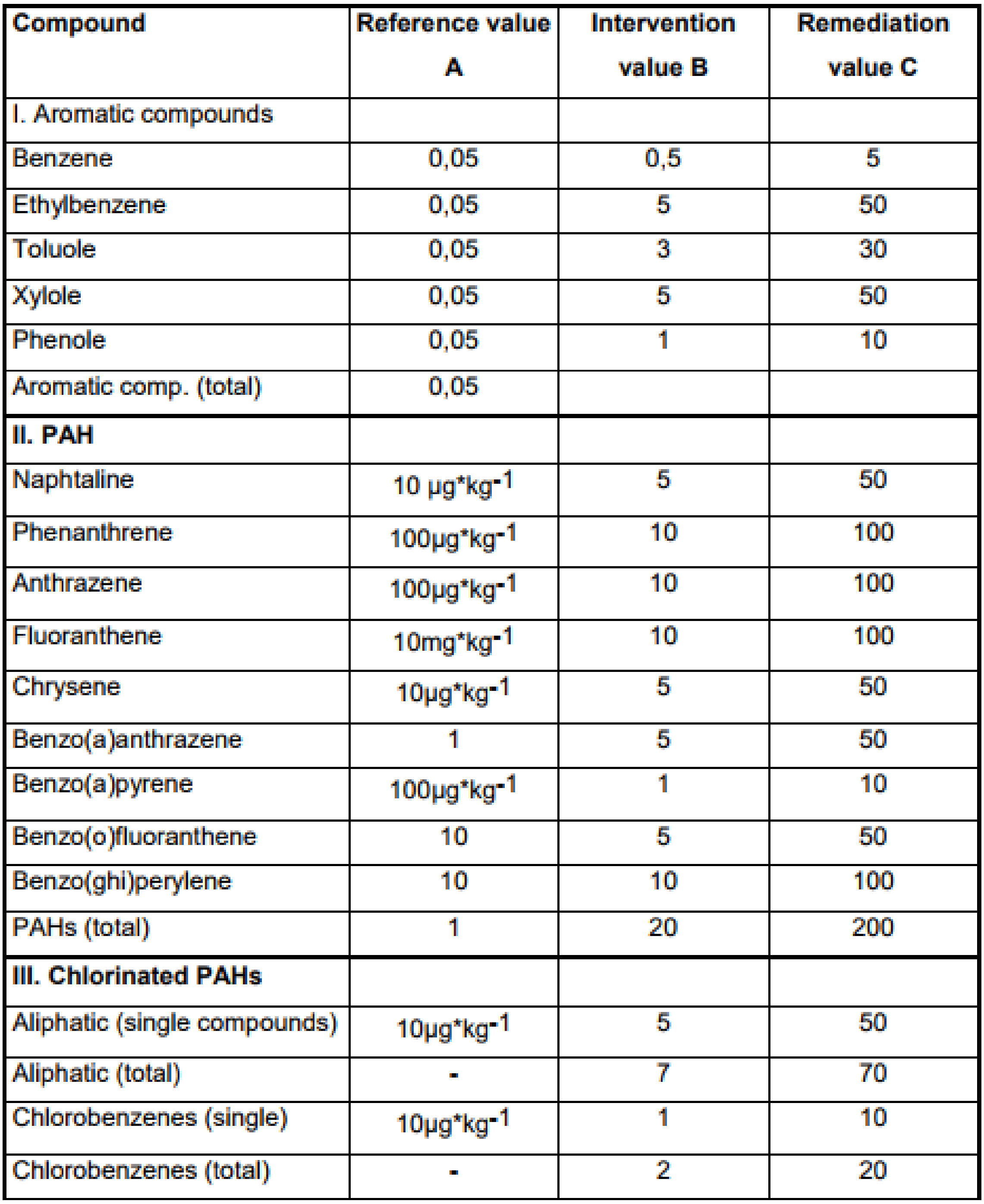
Table I. Water content and dry mass of hydrochars in percentage.

Sample type	DM (%)	Water content (%)
STR	98.82	1.18
LPM	98.54	1.46
BGSL	99.63	0.37
LPM-s + DOL	98.11	1.89
LPM-s + GYP	98.59	1.41
LPM-s + LIM	98.71	1.29
LPM-s + APA	98.23	1.77
LPM-s + SEA	97.93	2.07
LPM-s + STR	98.38	1.62
LPM-s + ASH	98.96	1.04
LPM-s	98.22	1.78

Appendix D

Reference values for PAHs

Table J. Reference, intervention and remediation values of polycyclic aromatic hydrocarbons according to USEPA. Toxic Release Inventory Public Data Release.Washington, D.C.: Office of Environmental Information, United States Environmental Protection Agency; 2016. Retrieved 29/01/2018 from https://www.epa.gov/toxics-release-inventory-tri-program/tri-listed-chemicals



Compound	**Reference value A**	**Intervention value B**	**Remediation value C**
I. Aromatic compounds			
Benzene	0,05	0,5	5
Ethylbenzene	0,05	5	50
Toluole	0,05	3	30
Xylole	0,05	5	50
Phenole	0,05	1	10
Aromatic comp. (total)	0,05		
II. PAH			
Naphtaline	10 µg*kg^{-1}	5	50
Phenanthrene	100µg*kg^{-1}	10	100
Anthrazene	100µg*kg^{-1}	10	100
Fluoranthene	10mg*kg^{-1}	10	100
Chrysene	10µg*kg^{-1}	5	50
Benzo(a)anthrazene	1	5	50
Benzo(a)pyrene	100µg*kg^{-1}	1	10
Benzo(o)fluoranthene	10	5	50
Benzo(ghi)perylene	10	10	100
PAHs (total)	1	20	200
III. Chlorinated PAHs			
Aliphatic (single compounds)	10µg*kg^{-1}	5	50
Aliphatic (total)	-	7	70
Chlorobenzenes (single)	10µg*kg^{-1}	1	10
Chlorobenzenes (total)	-	2	20

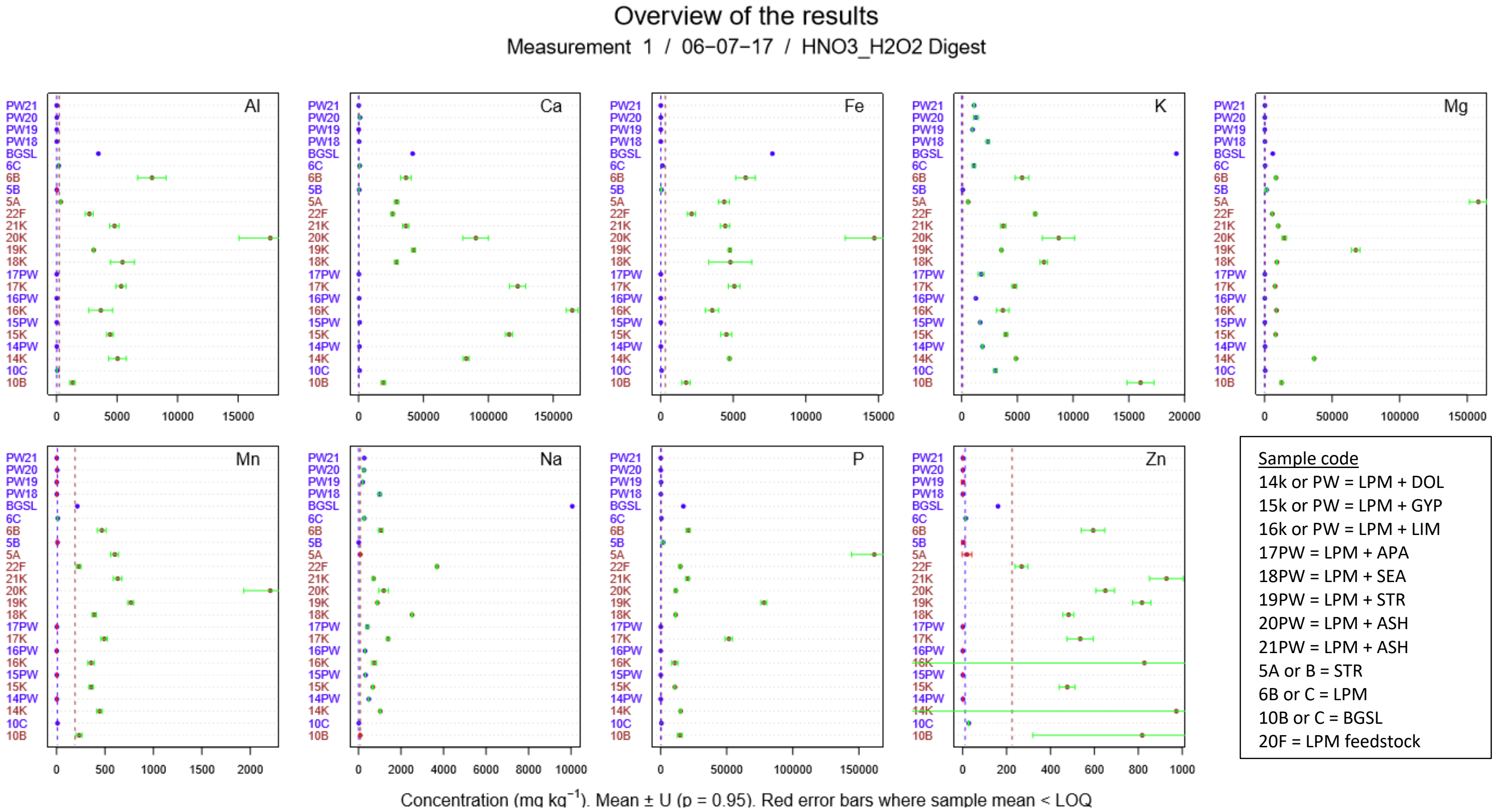
Compound	**Reference value A**	**Intervention value B**	**Remediation value C**
III. Chlorinated PAHs (continued)			
Chlorophenoles (single)	100µg*kg^{-1}	0,5	5
Chlorophenoles (total)	-	1	10
PCBs (total)	50 µg*kg^{-1}	1	10
EOCl (total)	0,1	8	80
VI. Plant Protectives			
Organic chlorinated compounds (single)	1µg*kg^{-1}	0,5	5
Organic chlorinated compounds (total)	-	1	10
Non-chlorinated compounds (single)	10µg*kg^{-1}	1	10
Non-chlorinated compounds (total)	-	2	20
V. Other contaminants			
Tetrahydrofurane	0,1	4	40
Pyridine	0,1	2	20
Tetrahydrothiophene	0,1	5	50
Cyclohexanone	0,1	6	60
Styrene	0,1	5	50
Phtalates (total)	0,1	50	500
Oxidated PAHs (total)	0,1	200	2.000
Mineral oils	50	1.000	5.000

Appendix E Hydrochars vs. Biochars

Table K. HTC and pyrolysis data from different assignments in the laboratory in Tulln, Austria (University of Life Science, Vienna, Austria) showing P solubility (IB and H_2O) in hydro- and biochar. Mean ± SD.

Product type	**Fraction analysed / pretreatment**	**Laboratory**	**Date of analysis / experiment**								Type of conversion	Time	Temperature
				Iron bag 10 or 17 days			Iron bag 37 or 40 days		H2O extract				
				% of total P			% of total P		% of total P				
Biochar	Milled to < 200 µm	BOKU, Tulln	Nov 15 - Apr 16	**41.5**	±	0.2	**55.8**	± 0.2	**2.31**	± 0.02	Pyrolysis	withheld	withheld
Biochar	Milled to < 200 µm	BOKU, Tulln	Apr - July 16	**56.7**	±	1.0	**67.7**	± 0.9	**5.7**	± 0.4	Pyrolysis	withheld	400
Biochar	Milled to < 200 µm	BOKU, Tulln	Apr - July 16	**59.9**	±	2.7	**69.4**	± 1.7	**4.8**	± 0.2	Pyrolysis	withheld	500
Hydrochar	Milled to < 200 µm	BOKU, Tulln	Apr - July 16	**37.5**	±	0.8	**60.8**	± 2.9	**1.9**	± 0.1	HTC	225	200
Hydrochar	Milled to < 200 µm	BOKU, Tulln	Apr - July 16	**51.2**	±	2.1	**68.0**	± 1.8	**2.6**	± 0.1	HTC	225	200
Hydrochar	Milled to < 200 µm	BOKU, Tulln	Apr - July 16	**34.8**	±	2.0	**62.7**	± 3.8	**2.8**	± 0	HTC	390	175

Appendix F Elemental concentration in the HTC process water



Sample code
14k or PW = LPM + DOL
15k or PW = LPM + GYP
16k or PW = LPM + LIM
17PW = LPM + APA
18PW = LPM + SEA
19PW = LPM + STR
20PW = LPM + ASH
21PW = LPM + ASH
5A or B = STR
6B or C = LPM
10B or C = BGSL
20F = LPM feedstock

Figure B. Elemental concentration (mg kg^{-1}) of the HTC process water (PW, B, C), all hydrochars (k, A, B) and feedstock (F). Mean ± U.

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