THE UNIVERSITY
of EDINBURGH

This thesis has been submitted in fulfilment of the requirements for a postgraduate degree (e.g. PhD, MPhil, DClinPsychol) at the University of Edinburgh. Please note the following terms and conditions of use:

This work is protected by copyright and other intellectual property rights, which are retained by the thesis author, unless otherwise stated.
A copy can be downloaded for personal non-commercial research or study, without prior permission or charge.
This thesis cannot be reproduced or quoted extensively from without first obtaining permission in writing from the author.
The content must not be changed in any way or sold commercially in any format or medium without the formal permission of the author.
When referring to this work, full bibliographic details including the author, title, awarding institution and date of the thesis must be given.

Contaminant issues in production and application of biochar

Wolfram Buss

Submitted for the degree of Doctor of Philosophy

School of GeoSciences

The University of Edinburgh

2016

Declaration

I confirm that this work has not been previously submitted for any other degree or professional qualification. This thesis has been composed by myself, except where work which has formed part of jointly-authored publications has been included. I was the lead author of the submitted/published manuscripts and was solely responsible for the laboratory work (unless stated otherwise), data analysis and manuscript writing. Co-authors provided guidance and contributed to the editing of the following six published and one submitted manuscripts which are listed in the following according to the order they appear as chapters in this thesis:

1. Buss, W., Graham, M.C., Shepherd, G.J., Mašek, O., 2016. Suitability of marginal biomass-derived biochars for soil amendment. Sci. Total Environ. 547, 314-322. doi: 10.1016/j.scitotenv.2015.11.148
2. Buss, W., Graham, M.C., Shepherd, G.J., Mašek, O., 2016. Risks and benefits of marginal biomass-derived biochars for plant growth. Sci. Total Environ. 569-570. doi: 10.1016/j.scitotenv.2016.06.129
3. Buss, W., Graham, M.C., MacKinnon, G., Mašek, O., 2016. Strategies for producing biochars with minimum PAH contamination. J. Anal. Appl. Pyrolysis 119:24-30. doi: 10.1016/j.jaap.2016.04.001
4. Buss, W., Graham, M.C., Mašek O. Composition of PAHs in biochar and implications for biochar production. J. Anal. Appl. Pyrolysis (submitted)
5. Buss, W., Mašek, O., 2014. Mobile organic compounds in biochar – a potential source of contamination – phytotoxic effects on cress seed (*Lepidium sativum*) germination. J. Environ. Manage. 137, 111-119. doi:10.1016/j.jenvman.2014.01.045
6. Buss, W., Mašek, O., 2016. High-VOC biochar – Effectiveness of post-treatment measures and potential health risks related to handling and storage. Environ. Sci. Pollut. Res. doi: 10.1007/s11356-016-7112-4
7. Buss, W., Mašek, O., Graham, M., Wüst, D., 2015. Inherent organic compounds in biochar–Their content, composition and potential toxic effects. J. Environ. Manage. 156, 150-157. doi:10.1016/j.jenvman.2015.03.035

The digestions of the biochars and feedstocks for publication 1 were conducted by Andy Gray and John Morman. The ICP-OES analyses for publications 1 and 2 were performed by the candidate with the assistance of Lorna Eades and Jessica Shepherd. The schematic of the Stage II pyrolysis unit (Figure 2.2) (in publication 1) was created by Alberto Gonzalez Fernandez. Some of the biochars analysed for (potential) publication 3 and 4 were produced by Peter Brownsort, Kyle Crombie, Clare Peters, Juan Luis Turrion-Gomez and Walter Lowe. The biochar production for publications 5, 6 and 7 was performed by Juan Luis Turrion-Gomez. In addition, the phenol index test in publication 7 was performed by Raphael Pierro at the University of Hohenheim.

Wolfram Buss

May 2016

Lay Summary

Agricultural production is one of the key limitations for human population growth. To sustain more people on the planet, the agricultural output per area needs to be increased, while at the same time it is essential to minimise the environmental impact of agriculture, such as the use of pesticide, fertiliser and irrigation water and the emission of greenhouse gases. Numerous strategies have been suggested to achieve this aim; one of them being the use of so-called biochar, which is a charcoal-like material produced at elevated temperatures in an atmosphere containing limited or no oxygen. This process of thermo-chemical conversion of biomass results in material with unique properties which, when applied to soil or growing media, can improve plant growth and at the same time reduce the amount of fertilisers and irrigation water required and greenhouse gases emitted. However, the feedstocks used for conversion, or the production process itself, can result in contamination of the biochar. Contaminants can result in adverse effects on soil, plants and the environment and it is essential to investigate the formation and fate of different types of contaminants during biochar production and effects after application. Consequently, in this thesis, 90 different biochars were analysed for contaminants which typically occur in biochar. The overall aim was to give recommendations about feedstock and production conditions to create safe biochar. The contaminants in biochar clearly have to be distinguished into two groups, inorganic and organic contaminants, due to their different properties and origins. The concentration of inorganic compounds in biochar, such as the heavy metals copper, cadmium or zinc, is mostly affected by the type of feedstock used for biochar production. In this study, it was demonstrated that even biomass rich in inorganic compounds could be promising, cost-effective feedstocks usable for conversion into biochar. The results also revealed that under normal circumstances, organic contaminants which, in contrast to inorganics, form during the thermo-chemical conversion, are mostly evaporated and separated from biochar during the production process. Consequently, biochars made in well-designed and well-monitored production units had only low concentrations of organic contaminants. Overall, the results from this study are very encouraging for production and application of biochar; most biochars, indeed, can be used safely for environmental management.

Abstract

For widespread use of biochar in agriculture and horticulture, it must be ensured that application will neither adversely affect soil and plants, nor exceed legislated contaminant concentrations. The most relevant groups of contaminants in biochar are potentially toxic elements (PTEs), polycyclic aromatic hydrocarbons (PAHs) and volatile organic compounds (VOC). In this thesis, the concentrations of these groups of contaminants were analysed in 90 different biochars produced by slow pyrolysis. Subsequently, the concentrations were compared to legislation/guideline threshold values and linked to production conditions. The risk these contaminants pose to plant growth was also assessed, to give recommendations on production of safe biochar.

PTEs can neither be formed nor destroyed, which means their presence in biochar is predominantly determined by feedstock type. However, significant levels of Cr, Fe and Ni were introduced into biochar from the furnace steel, whilst PTEs with low boiling points, such as As, Cd and Zn, partially evaporated during pyrolysis. PTEs were not responsible for phytotoxic effects observed for PTE-rich biochars despite biochar's exceedance of available and total PTE threshold values for soil and soil amendments. Although initial tests were promising, the risk that PTE-rich biochars as amendment for soil and growing media pose, needs further investigation.

The PAH concentration in biochar was markedly reduced by increasing carrier gas flow rate, and the type of feedstock also influenced the PAH content. However, there was no clear dependence of pyrolysis temperature on PAH concentrations, which was attributed to PAHs being increasingly formed and evaporated at higher pyrolysis temperatures. Ultimately, condensation of pyrolysis vapours and deposition on biochar was identified as the main risk for biochar contamination with PAHs, as this resulted in elevated concentrations of high-risk, higher molecular weight PAHs.

Weaknesses in the pyrolysis unit design, such as cold zones, resulted in elevated concentrations of VOCs, as well as PAHs, in biochar. Comparing concentrations and phytotoxic potential of both compound groups, it was concluded that observed toxic effects were much more likely caused by VOCs in biochars containing both contaminants. Overall, formation of VOCs and PAHs cannot be prevented, but their presence in biochar resulting from retention and deposition can be minimised.

Acknowledgements

First, I would like to thank my primary supervisor, Dr Ondřej Mašek, for this advice, ideas and guidance during my PhD. Without him I would not have been able to complete this PhD, so thank you a lot. Dr Margaret Graham has always given me excellent feedback on my manuscripts which enabled me to strengthen my scientific writing skills significantly and improve the way I communicate my research to the public. This research was supported by the Scottish Funding Council (SFC) (SRDG Ref: HR08004 Carbon Capture from Power Plant and Atmosphere). In addition, I am very grateful for the financial support for my PhD provided by Derek and Maureen Moss.

Furthermore, I have to thank my co-authors, Jessica Shepherd, Dominik Wüst and Gillian McKinnon for their contributions to our manuscripts and Gillian McKinnon for her willingness to help conducting the necessary lab work for this PhD. Further thanks go to the UKBRC and the people that worked here over the past 3.5 years, in particular Dr Saran Sohi, Dr Clare Peters, Dr Peter Brownsort, Walter Lowe, Dr Andy Cross, Dr Jan Mumme, Franziska Srocke, Dane Dickinson and Alberto Gonzalez Fernandez. Their help in the lab (biochar production), help with organisation and their feedback on my presentations and graphical abstracts made my PhD work so much easier. I also would like to thank the research group of Margaret Graham, in particular Dr Lorna Eades, Michael Muir, Kenneth McGregor and Gavin Sim, the crew lab staff, Andy Gray and John Morman, and the research group around Professor Andrea Kruse at the University of Hohenheim for their help around my PhD thesis lab work. In addition, I would also like to acknowledge following people for their help with the difficult task of sourcing contaminated biomass from various parts of the world: Dr Guido Fellet, Aditya Parmer, Dominik Wüst and Brecht Annicaert.

I am also very grateful for the support and distraction during my PhD from my family and Nick Dobbs, Victor Naden Robinson, Dr Gary McClean and Dr Kyle Crombie and particularly thank Oliver Buß for his help whenever I needed it. Special thanks go to my office mate Jessica Shepherd for all her scientific and emotional support on and off campus.

Table of Contents

List of Tables

List of Figures

List of Abbreviations

AD	anaerobic digestate/digestion
ANOVA	analysis of variance
BBF	British Biochar Foundation
BQM	Biochar Quality Mandate
BTEX	benzene, toluene, ethylbenzene and xylenes
CEC	cation exchange capacity
daf	dry, ash-free basis
db	dry weight basis
DI	deionised
dioxin	polychlorinated dibenzodioxin
EBC	European Biochar Certificate
EC	electrical conductivity
furan	polychlorinated dibenzofuran
GC biochar	gas contaminated biochar
GC-MS	gas chromatography mass spectrometry
GHG	greenhouse gas
HMW	high-molecular weight
HT	heating tape
HTC	hydrothermal carbonisation
HTT	highest treatment temperature
IBI	International Biochar Initiative
ICP-OES	inductively coupled plasma optical emission spectrometry
K_{oc}	soil organic carbon-water partitioning coefficient
LC biochar	liquid contaminated biochar
LMW	low-molecular weight
LOD	limit of detection
LOQ	limit of quantification
m/v	mass per volume
MLV-index	Munoo-Liisa-Vitaility index
n/a	not available
NAP	naphthalene
NC biochar	non-contaminated biochar
non-NAP PAHs	16 US EPA PAHs excluding naphthalene
PAH	polycyclic aromatic hydrocarbon
PA	proximate analysis
PCB	polychlorinated biphenyl
PTE	potentially toxic element
r	Pearson correlation coefficient
RSD	relative standard deviation
RT	residence time

s	standard deviation (in equations)
SD	standard deviation
TEF	toxicity equivalency factor
TEQ	toxic equivalent quantity
TGA	thermogravimetric analysis
UKAS	United Kingdom Accreditation Service
UKBRC	UK Biochar Research Centre
VM	volatile matter
VOC	volatile organic compound
w/w	weight per weight
wt%	weight percent

feedstocks

ADX	*Arundo donax*
DW	demolition wood
FWD	food waste digestate
MC	miscanthus chips
MSP	miscanthus straw pellets
OSR	oilseed rape pellets
PAT	*Paulonia tomentosa*
RH	rice husk
SBI	sugarcane bagasse, India
SLP	*Salix purpurea*
SS	sewage sludge
SWP	softwood pellets
WC	willow chips
WHI	water hyacinth, India
WLB	willow logs, Belgium
WRB	winter rye, Belgium
WSI	wheat straw, India
WSP	wheat straw pellets

Chapter 1 Introduction

1.1 Present challenges in global food producing systems

Under the prospects of a world population of 9.7 billion in 2050, it was predicted that the amount of food produced will need to double relative to 2005 levels to catch-up with the population growth (Campbell et al., 2014; Tilman et al., 2011; United Nations, 2015). Over human history up until the early 20th century, the area used for agriculture expanded and more land was converted into cropland to meet the increasing demand for agricultural products (Amundson et al., 2015). Over recent decades, e.g. between 1985 and 2005, the global crop production increased by around 28%, but only 2.4% of this was attributed to expansion of cropland area as today most of the suitable land is already used for agriculture. Consequently, nearly all of the increase in production of agricultural goods was due to a rise in yields per area which has only been possible since the discovery of the Haber-Bosch process and the application of nitrogen-fertilisers (Amundson et al., 2015; Foley et al., 2011).

Nowadays, external nutrient provision and organic inputs are essential in agriculture because the natural mechanisms that replenish both are very slow, leaving input and output in imbalance (Amundson et al., 2015). In addition, external water supply is vital in many parts of the world and global cereal production is predicted to decrease by 20% without irrigation (Foley et al., 2011). In summary, over the past half-century, the global use of fertiliser has increased by five-fold and the area of irrigated agricultural land has doubled (Foley et al., 2011).

Agricultural intensification has led or contributed to numerous environmental problems, such as soil erosion, climate change (greenhouse gas emission (GHG)), pollution of limnic and marine ecosystems and water degradation (Amundson et al., 2015; Foley et al., 2011; Withers et al., 2014). In addition, while mineral nitrogen-fertilisers can be generated from the air using energy only, the availability of P and K resources is limited, e.g. according to different scenarios P-resources are predicted to run out in 80-1300 years, which has led to increasing prices (Amundson et al., 2015; Reijnders, 2014).

Consequently, the amount of research channelled into “sustainable intensification”, which is the increase of yields per area and simultaneous decrease of the

environmental footprint, is growing (Campbell et al., 2014; Elliott et al., 2013; Foley et al., 2011; Mueller et al., 2012). Various approaches and concepts have been proposed and tested; these aim to increase biodiversity in agricultural areas, decrease GHG emissions, decrease the use and environmental impact of pesticides and mineral fertiliser and at the same time increase the crop yields per area (Brooker et al., 2015; Campbell et al., 2014; Elliott et al., 2013; Tittonell, 2014; Wezel et al., 2014). One management strategy that can tackle several of these issues at the same time is a carbon-rich material called biochar which can contribute to effective nutrient and water management in soil, increase soil biodiversity, promote plant growth directly and help mitigate GHG emissions (Lehmann and Joseph, 2015a).

1.2 Biochar definition and background

Different technologies can be used for biochar production, including slow pyrolysis, fast pyrolysis, gasification and hydrothermal carbonisation (HTC). In all cases, elevated temperatures are applied in the absence or limited presence of oxygen which converts biomass in a thermo-chemical process to a material, called 'char' (Boateng et al., 2015; EBC, 2012a; Lehmann and Joseph, 2015b). Char used as a fuel is called 'charcoal' (Brown et al., 2015; Wiedner and Glaser, 2015), while char used for environmental management is called 'biochar' (EBC, 2012a; Lehmann and Joseph, 2015b). In addition, to distinguish the product of HTC from the remaining chars that are intended for environmental management, the term 'hydrochar' has been established (Libra et al., 2011). More specific definitions for biochar exist which are based on physiochemical properties such as the organic carbon content, H/C ratio, O/C ratio or the parent material (EBC, 2012a; International Biochar Initiative, 2011).

Already centuries ago, char was applied to soil, unintentionally and intentionally, e.g. biochar has been found in the Amazon Basin which resulted in soil patches that were much more fertile than the surrounding soils (Wiedner and Glaser, 2015). The research on these Amazonian dark earths (*Terra Preta de Indio*) led to the re-discovery of biochar and the global interest in using it for environmental management (Glaser et al., 2002, 2001; Lehmann and Joseph, 2015b). Due to the increasing research and commercial interests in biochar and the lack of biochar legislation, national and international non-governmental organisations were founded which established guidelines for the definition, production and use of biochar, the International Biochar Initiative (IBI), the European Biochar Certificate (EBC) and the British Biochar Foundation (BBF).

Nowadays, the perception of biochar goes beyond soil improvement; conversion of waste materials into a stable-carbon product is seen as a waste management alternative. In addition, biochar's aromatic carbon lattice has shown to be very stable against degradation in soil and could contribute to climate change mitigation through the removal of carbon from the atmosphere for a prolonged period (carbon sequestration) (Kuzyakov et al., 2014; Lehmann and Joseph, 2015b; Windeatt et al., 2014; Woolf et al., 2010). While the mean residence time of biochar in soil is one of

the main uncertainties in this area of research and currently a central issue for debate, there is general consensus, that biochar is more stable than its parent material (Ameloot et al., 2013; Lehmann et al., 2015).

1.3 Biochar production

1.3.1 Technologies

Biochar can be produced using different technologies which form solid (char), liquid and gaseous products in varying proportions. Gasification operates at highest treatment temperatures (HTT), which is the maximum temperature the feedstock is exposed to, of 500-1500°C with the addition of small amounts of air which results in partial oxidation of the solids and vapours and the predominant formation of gases (Boateng et al., 2015). Fast pyrolysis is optimised for high liquid yields; HTTs of 400-600°C are applied while using comparatively small feedstock particles (<2 mm) which are heated up very rapidly (<1s) (high heating rates and high heat transfer), resulting in a very low hot vapour residence time in the range of tens of seconds and a solid residence time of seconds to minutes (Boateng et al., 2015; International Energy Agency, 2006; Kuppusamy et al., 2016). Slow pyrolysis, on the other hand, operates at similar HTTs to fast pyrolysis (temperature threshold depends on definition: >250°C (Lehmann and Joseph, 2015b), >350°C (EBC, 2012a)) but the heating rate is lower and the total residence time of the solids at HTT is in the range of minutes to hours (Kuppusamy et al., 2016). This results in maximisation of the solid char yield and consequently, this technology is commonly used for biochar production. Pyrolysis reactors most frequently used for slow pyrolysis are fixed bed reactors, rotary kilns (drums) and screw pyrolysers (Boateng et al., 2015).

1.3.2 Principles of pyrolysis

During biomass pyrolysis, the educts, mostly cellulose, hemicellulose and lignin, are chemically transformed and the products of pyrolysis are char, liquids (aqueous fraction and pyrolysis oils) and non-condensable gases. Generally, lignin conversion into char is reported to be more efficient than hemicellulose and cellulose conversion (Sharma et al., 2004; Yang et al., 2007). Degradation occurs in the range 220-315°C for hemicellulose, 315-400°C for cellulose and in a much wider range for lignin, 160-900°C (Yang et al., 2007). After a particular process temperature is exceeded, pyrolysis is an exothermic process. This activation energy that is needed to start the reactions depends on feedstock, e.g. in the case of wood it is reported that 280°C are needed (Antal and Grønli, 2003).

The pyrolysis liquids which can be used as biofuel consist of a vast variety of intermediate degradation products from the decomposition of biomass which include organic acids, aldehydes, alcohol, ketones, phenols, PAHs, furans and other chemical species (Cordella et al., 2012; Khor et al., 2009; Sánchez et al., 2009). Due to the wide range of possible products, different analytical and separation techniques have been applied to characterise and group the chemical compounds within pyrolysis liquids (Ben and Ragauskas, 2013; Garcia-Perez et al., 2007; Sfetsas et al., 2011; Tessarolo et al., 2013). The main non-condensable gases formed during pyrolysis are H_2, CO_2, CO, H_2O, CH_4, C_2H_4, C_2H_6 and their relative proportion changes with pyrolysis conditions (Crombie and Mašek, 2014; Fagernäs et al., 2012b; Fu et al., 2011; Mahinpey et al., 2009).

The solid input and output materials of pyrolysis have distinctively different chemical and physical properties. During the heat treatment the feedstock is considerably depleted in O and H and partially depleted in N; in contrast, most of the C and P is retained and up to 90% of the final char product can be C, which is strongly aromatic (Antal and Grønli, 2003; Cantrell et al., 2012; Jindo et al., 2014; Lehmann and Joseph, 2015b; Xie et al., 2015). The char loses most of its oxygen-containing functional groups, such as OH and C=O. In addition, aliphatic and aromatic CH-bonds are lost during the conversion, highly condensing the aromatic ring structure, increasingly so with higher HTTs, (Antal and Grønli, 2003). The predominant reactions during char formation are dehydration, elimination, depolymerisation, re-polymerisation and cross-linking (Hajaligol et al., 2001). Char is formed by rearrangements of the molecular carbon structure which results in aromatisation leading to a recalcitrant carbon framework. Initially, primary char formation reactions occur, forming char due to solid-solid interactions. Then secondary char formations take place from reactions of organic vapours/tars with solid carbonaceous material within the particle undergoing pyrolysis (Figure 1.1) and on the gas-solid interface which can enhance the char yield significantly (Antal and Grønli, 2003; Huang et al., 2013; Pattanotai et al., 2013). Various techniques have been used to characterise the changes occurring during the thermo-chemical conversion (e.g. FTIR, SEM, TEM, XRD, BET surface area and proximate analysis (PA)), demonstrating shrinkage and mass loss of the feedstock with increasing

aromaticity and decreasing surface functional groups (Abrego et al., 2009; Bourke et al., 2007; Haas et al., 2009; Keiluweit et al., 2010; Krzesińska et al., 2006; Kwon et al., 2009; Podgorski et al., 2012; Rutherford et al., 2012).

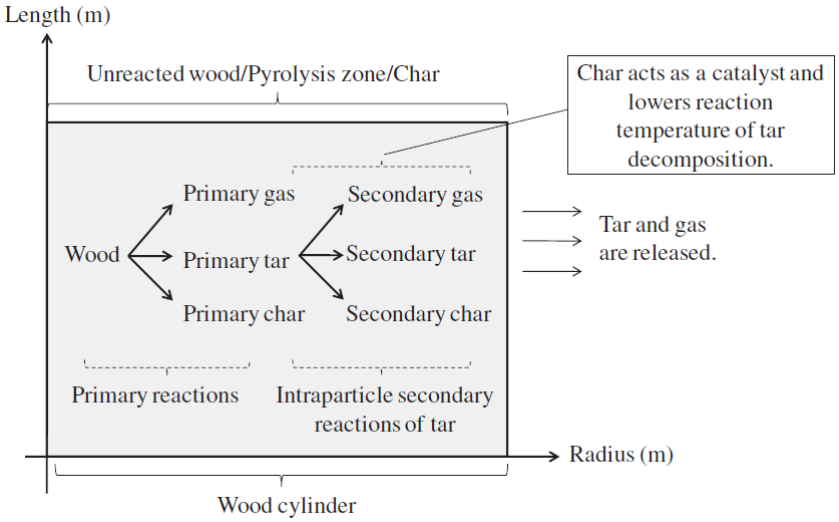


Figure 1.1: Schematic of intraparticle secondary char reactions (at low heating rates) (Pattanotai et al., 2013).

1.3.3 Influence of production parameter on biochar properties

The most important parameters during pyrolysis are: HTT, the residence time at HTT, the carrier gas flow rate and the heating rate (Antal and Grønli, 2003).

HTT is reported to be the parameter with the highest influence on char yield and char properties and, in general, higher HTTs decrease total carbon and char yields (Antal and Grønli, 2003; Enders et al., 2012). Moreover, with increasing HTT, the O/C and H/C ratios of the char decrease, which facilitates the build-up of an aromatic carbon framework, enhances the degree of carbonisation and leads to a higher carbon content in the char (Manyà, 2012). However, some studies have shown that the proportion of carbon stable to thermal and chemical oxidation was nearly independent of HTT (Mašek et al., 2013). Pyrolysis also increases the surface area, pore volume, pH and EC from feedstock to char and these parameters also increase with increasing HTT; in contrast, the average pore diameter is claimed to decrease (Al-Wabel et al., 2013; Cantrell et al., 2012; Jindo et al., 2014; Ronsse et al., 2013; Schimmelpfennig and Glaser, 2012; Zhao et al., 2013). Cation exchange capacity

(CEC) is generally thought to be reduced in chars produced using higher HTTs due to loss of functional groups. Yet, at low HTTs the CEC of biochar is higher than in material exposed to temperatures just below the range defined as pyrolysis (e.g. 200°C) (Gaskin et al., 2008; Harvey et al., 2011; Kloss et al., 2012). In one study, the CEC even increased in biochars from two feedstocks in the whole temperature range investigated, 200°C to 650°C (Zhao et al., 2013).

During slow pyrolysis, variation of the residence time at HTTs of 350°C and 650°C did not result in any considerable effect on biochar properties such as fixed carbon content (carbon fraction remaining after treating char at 900°C in an N_2-atmosphere) or elemental concentrations (Crombie and Mašek, 2015). However, in other studies at 300°C the residence time at HTT did have an impact on biochar parameters such as pH, fixed carbon, total C, biochar yield, H/C ratio and surface characteristics (Ronsse et al., 2013; Rutherford et al., 2012). Generally, increasing carrier gas flow rates reduce secondary char forming reactions, therefore, reduced biochar yields, biochar stable carbon contents and changed the pyrolysis gas composition (Crombie and Mašek, 2015, 2014; Ronsse et al., 2013). While the feedstock heating rate only had a marginal effect on stable carbon content and biochar pH, low heating rates resulted in higher char yields during pyrolysis but the increase occurred asymptotically (Angin, 2013; Antal and Grønli, 2003; Crombie et al., 2014, 2013).

Overall, this shows that there are still some knowledge gaps which need to be addressed before reaching the aim in biochar production research which is the prediction of biochar properties from feedstock and production conditions (Morales et al., 2015).

1.3.4 Feedstocks, feedstock characteristics and biochar properties

Besides unprocessed, virgin biomass, chemically/biologically treated biomass (non-virgin biomass) can be used as feedstock for pyrolysis. The typical feedstocks used for biochar production (virgin as well as non-virgin) are agricultural and forestry residues and manures (Cantrell et al., 2012; Enders et al., 2012; Gaskin et al., 2008; Inyang et al., 2010; Jindo et al., 2014; Kim et al., 2014; Kloss et al., 2012; Mukome et al., 2013; Troy et al., 2013; Windeatt et al., 2014). Furthermore, pyrolysing marine and limnic algae has been investigated because algae have very high growth rates

and do not compete with crops for land resources (agricultural land, nutrients, water). Most algae-derived biochars have high ash contents which can mean high nutrient concentrations but this can also lead to salinity-related issues and low biochar carbon contents (Bird et al., 2011; Kan et al., 2014; Ronsse et al., 2013). However, from an economic perspective, the ideal feedstocks for conversion into biochar are materials of little or no economic value, here referred to as 'marginal biomass', which have no competitive use and partly even gate fees are applied, which are fees companies are charged for waste disposal (Shackley et al., 2011). Therefore, sewage sludge (Abrego et al., 2009; Agrafioti et al., 2013; Liu et al., 2014; Luo et al., 2014; Méndez et al., 2012; Van Wesenbeeck et al., 2014; Zielińska and Oleszczuk, 2015) and anthropogenic wastes (Bernardo et al., 2009; Enders et al., 2012; Kaminsky et al., 1996; Martinez et al., 2013; Oh and Shinogi, 2013; Paradela et al., 2009; Sánchez et al., 2009; Williams and Williams, 1997) have gained a wide interest for use for biochar production.

Various feedstock characteristics can influence the pyrolysis process and the resulting biochar properties. It has been shown that ash/mineral, total organic carbon and fixed carbon content and the C/N ratio of the char are mostly determined by feedstock type, while O/C and H/C ratios are predominantly influenced by pyrolysis conditions (Mukome et al., 2013; Zhao et al., 2013). The moisture content of the feedstock increases the amount of energy and the residence time needed for full carbonisation of the feedstock as the moisture needs to be driven off first (Antal and Grønli, 2003). However, at elevated pressures, elevated feedstock moisture contents (42-62%) can also facilitate char production (Manyà, 2012). Furthermore, minerals in the feedstocks act as catalysts and reduce the volatilisation of organics which promotes the interaction of volatiles and solids resulting in increased char formation (Antal and Grønli, 2003; Sharma et al., 2004; Sharma and Hajaligol, 2003). Feedstock particle size can also influence pyrolysis; bigger particles sizes lead to enhanced intraparticle secondary reactions which resulted in positive charcoal yield responses and decreased tar formation (Manyà, 2012; Pattanotai et al., 2013). However, it was reported that the particle size did not have an influence at slow heating rates (0.17°C s^{-1}), only at fast heating rates (>1000°C s^{-1}) (Asadullah et al., 2010).

1.4 Benefits of biochar in soil

1.4.1 Biochar carbon stability and CO_2 sequestration potential

Pyrolysis increases the persistence of the carbon in biochar against degradation compared to its parent material; this is a central feature that boosts biochar research as the recalcitrance in soil is relevant for carbon sequestration purposes (Lehmann et al., 2015; Woolf et al., 2010).

The high-temperature treatment results in an aromatic carbon lattice which is difficult to be degraded by microorganisms and the stability is reported to increase with HHT and is influenced by feedstock (Ameloot et al., 2013; Calvelo Pereira et al., 2011; Fang et al., 2014; McBeath et al., 2014). Parts of the carbon in biochar is degraded comparatively fast, the so-called "labile carbon" content, while the fraction of "stable carbon" is reported to be degraded much slower, resulting in a bi-phasic degradation profile (Ameloot et al., 2013; Wang et al., 2015). A range of residence times of biochar have been reported in the literature: in one study only 6% of the biochar added to soil was mineralised within 8.5 years in a lab experiment which corresponds to a mean residence time of around 400 years under optimal conditions in the lab and an estimated residence time in the field of ~4000 years (Kuzyakov et al., 2014). Other studies report mean residence times of 90-1600 years (McBeath et al., 2014; Singh et al., 2012; Wang et al., 2015).

Various methods, e.g. elemental analysis, thermogravimetric analysis (TGA) and chemical oxidation, have been used in an attempt to establish easy-to-analyse physiochemical properties as proxies for carbon stability to ultimately estimate the biochar residence time (Calvelo Pereira et al., 2011; Crombie et al., 2013; Cross and Sohi, 2013; Lehmann et al., 2015; Spokas, 2010).

The level of uncertainty regarding biochar's CO_2-sequestration and GHG-mitigation potential increases exponentially when the complexity of the whole biochar-soil system is taken into account. Among others, influencing factors are: variability of field experiments due to soil type and climate, extrapolation beyond the (mostly) short-term studies, potential negative/positive priming of existing soil carbon stocks and the effect of biochar on emission of GHG by microorganisms (Kammann et al.,

2012; Lehmann et al., 2015; Van Zwieten et al., 2015). Figure 1.2 shows a selection of processes and factors influencing the biochar degradation in soil.

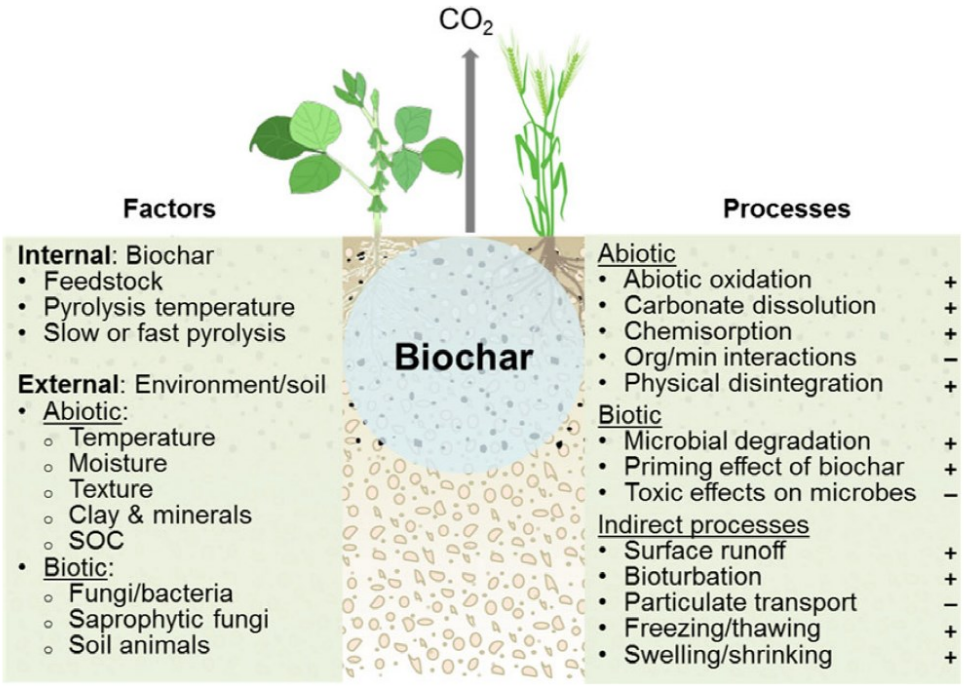


Figure 1.2: Factors and processes affecting biochar degradation in soil (Wang et al., 2015).

Besides simple carbon sequestration, the stability of biochar in soil can also result in long-lasting positive effects on soil properties as observed for Amazonian dark earth; one such potential effect is the remediation of contaminated sites (Beesley et al., 2011; Glaser et al., 2001).

1.4.2 Biochar's use in soil remediation

Contaminated sites, polluted through mining, industrial and commercial activities, inadequate waste disposal and agrochemicals is a global problem; in Europe alone, thousands of contaminated sites exist (World Health Organization regional office for Europea, 2013). Biochar has been used to successfully remediate such sites (Beesley et al., 2015) and consequently, major efforts have been channelled into this area of research. For remediation of contaminated soils it is vital that the treatment results in a permanent immobilisation or removal of contaminants, and the long-term stability of biochar makes it a viable option.

Where biochar has been applied to soil, it decreased the availability and plant uptake of various potentially toxic elements (PTEs) such as Cd, Pb, Cu, Ni and Zn (Beesley et al., 2011; Buss et al., 2012; Karer et al., 2015; Kim, 2015; Kloss et al., 2014a; Méndez et al., 2012; Park et al., 2011; Puga et al., 2015; Uchimiya et al., 2011). The mechanisms responsible for the immobilisation can be separated into: (I) direct mechanisms, e.g. chemical, physical sorption and precipitation; and (II) indirect mechanisms, e.g. increase in pH (Beesley et al., 2015; Uchimiya et al., 2012). Direct immobilisation is mostly influenced by functional groups on the biochar surfaces (Beesley et al., 2015) and the proposed mechanism are inner-sphere complexation, ion exchange and surface complexation, electrostatic attraction, precipitation and π-interactions (Ding et al., 2016). As discussed in 1.3.3, the CEC of biochar decreases with HTT, consequently, so does the ability for direct immobilization of PTEs. The pH of biochar, however, increases with HTT. The effect of pH on PTE mobility is as followed: at lower soil pH, cationic elements such as Pb, Cu, Zn, Co, Ni and Mn are very mobile and an increase in soil pH as caused by biochar leads to nearly complete sorption to oxide surfaces which happens rapidly once a specific pH value is exceeded (Figure 1.3) (Basta et al., 2005). This means that biochars produced at high HTTs increasingly immobilise cationic PTEs through the indirect mechanisms and decreasingly through the direct mechanisms. However, biochar's high pH can also increase the mobility of some elements (Mo, B and As) which can be beneficial as Mo and B are plant micronutrients but can also result in adverse effects on plants (Beesley et al., 2011; Kloss et al., 2014a; Rondon et al., 2007).

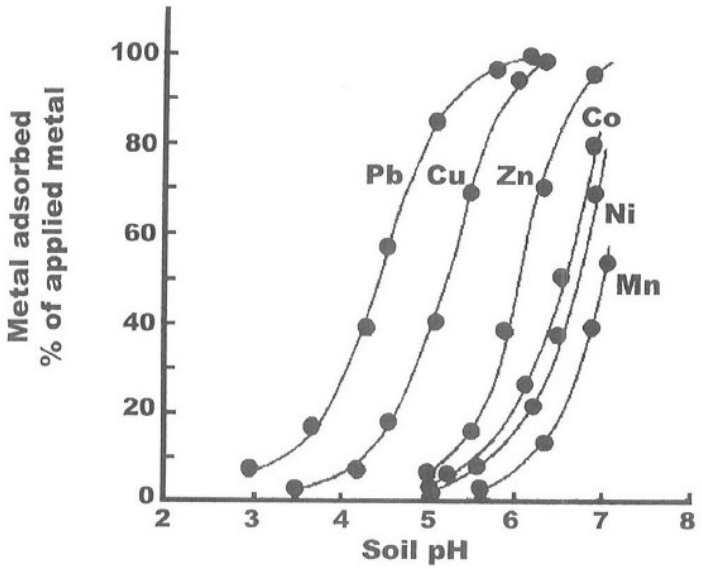


Figure 1.3: Adsorption of cationic PTEs on goethite (Basta et al., 2005).

In addition to PTE, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) have been reported to be immobilised by the application of biochar through surface sorption (Beesley et al., 2011; Chen and Yuan, 2011; Denyes et al., 2012; Huang and Chen, 2010; Ogbonnaya and Semple, 2013; Oleszczuk et al., 2012). Other organic compounds, such as pesticides, can also be immobilised which can be positive as they are not leaching into groundwater but it can also reduce their efficacy (Cabrera et al., 2014; Jones et al., 2011; Kuppusamy et al., 2016; Yao et al., 2011; Yu et al., 2009). Sorption of organic compounds to biochar is complex and consists of different mechanisms (Kupryianchyk et al., 2016; Lattao et al., 2014; Ogbonnaya and Semple, 2013; Wang et al., 2016). The sorption of hydrophobic organic compounds of biochar tends to increases with HTT which is assumed to be caused by the increased surface area of high-temperature biochars (Graber et al., 2012; Kupryianchyk et al., 2016; Wang et al., 2016).

Immobilisation of PTEs and organic contaminants can result in increased crop growth via reduction of phytotoxic effects and so biochar can be used as a soil remediation tool enabling crops for consumption or energy production to be grown on contaminated land (Brennan et al., 2014; Buss et al., 2012; Fellet et al., 2014).

However, biochar can also increase plant growth in more ways than just through a decrease in contaminant toxicity.

1.4.3 Effect of biochar on plant growth

Although biochar addition to soil has resulted in increased plant growth in many studies, in particular in sandy soils with low organic carbon contents, depleted soils or acidic soils, reported effects have been highly variable (Butnan et al., 2015; Cornelissen et al., 2013; Deal et al., 2012; de la Rosa et al., 2014; Hammond et al., 2013; Spokas et al., 2012; Van Zwieten et al., 2010). Due to the immense number of combinations of biochar type (feedstock, production condition, post-treatment), plant species, biochar application rate, additional application (fertiliser, liming, pesticides), climate and soil type, biochar application does not always result in the desired plant growth promotion.

After initial trial-and-error experiments, it became clear that not every biochar fits to every system and that there is the need for fitting a particular biochar to a particular system to gain a desired effect (Novak and Busscher, 2012). Still, meta-analyses from a large number of studies, conducted already in 2011 when most biochar trials were still performed in trial-and-error attempts, showed that on average biochar increased crop growth by around 10% globally (Jeffery et al., 2011). As biochar research only took off this millennia, very few long-term studies exist and the long-term effects of biochar in soil are very difficult to predict, yet, investigations on Amazonian dark earth suggest that biochar indeed can result in positive effect on plant growth even after hundreds of years in the ground (Glaser et al., 2001). Pyrolysis changes the characteristics of the feedstock material majorly, resulting in biochars with unique properties which can improve the nutrient and water status of the soil, change the abundance and composition of soil organisms and decrease the mobility of contaminants in soil (section 1.4.2) which subsequently, can stimulate plant growth.

1.4.3.1 Soil nutrient status

One of the key limitations for crop growth is nutrient availability and biochar can improve the nutrient status of soils in a number of ways (Gunes et al., 2014; Jeffery et al., 2015a; Kloss et al., 2014b). Biochar can reduce the leaching of P and N due to

sorption to its surfaces and consequently, increase the nutrient-use efficiency (de la Rosa et al., 2014; Uzoma et al., 2011). Furthermore, biochar can also increase the CEC in some instances, resulting in increased retention and exchange of cations, such as K (Basso et al., 2013; Deal et al., 2012; Kloss et al., 2014b; Laird et al., 2010; Liang et al., 2006; Van Zwieten et al., 2010). In addition, biochar's high pH can increase the pH of the soils which in turn increases the availability of nutrients such as P, N, Ca, Mg and Mo which were previously 'locked up' within the soil matrix (Jeffery et al., 2015a). However, biochar can also supply nutrients directly originated from the feedstock used for biochar production (Hossain et al., 2011; Ippolito et al., 2015).

1.4.3.2 Soil water regime

In some instances, biochar increased the water holding capacity (WHC) and the plant-available water content, resulting in increased plant growth and a higher plant tolerance against droughts. Yet, a high variability in observed effects has resulted in this topic being highly debated in the literature (Baronti et al., 2014; Basso et al., 2013; Jeffery et al., 2015b; Kammann et al., 2011; Laird et al., 2010; Masiello et al., 2015; Mulcahy et al., 2013; Ojeda et al., 2015; Uzoma et al., 2011). The properties mostly affecting the soil water regime are soil and biochar porosity (pore volume, pore size distribution) and particle size (Gray et al., 2014; Masiello et al., 2015). For example, the intraparticle pore volume decreases when the biochar is ground finely, while the interparticle pore size is affected by interactions of soil and biochar (Masiello et al., 2015). In addition, biochar's hydrophobicity plays an important role on biochar's effect on the water regime in soil which has been reported to be caused by alkyl surface groups in low-temperature biochars and ceases after weathering in soil where the alkyl groups are oxidised and become more hydrophilic (Das and Sarmah, 2015; Eibisch et al., 2015; Gray et al., 2014; Kinney et al., 2012; Masiello et al., 2015; Ojeda et al., 2015). Overall, there are a number of parameters in biochar which interact with soil characteristics and together affect the soil water regime which explains why the observed effects of biochar on soil water regime were so variable in practise.

1.4.3.3 Abundance and composition of soil biota

Biochar can change abundance and composition of soil biota by being a habitat or a substrate for organisms, e.g. for soil microorganisms (Jeffery et al., 2015a; Van Zwieten et al., 2015). Biochar application can increase abundance of mycorrhiza and N_2-fixing bacteria (LeCroy et al., 2013; Masiello et al., 2013; Quilliam et al., 2012; Robertson et al., 2012; Rondon et al., 2007; Warnock et al., 2007). Biochar can also decrease the action of pathogenic species by inducting systemic resistance against pests and therefore, increase the plant performance directly (Elad et al., 2011, 2010).

1.5 Risks of biochar application

1.5.1 Adverse effects of biochar

To gain acceptance with farmers, growers and legislators, consistent growth promoting effects needs to be achieved with biochar application and it needs to be demonstrated that biochar addition to soil does not cause any negative effects. Unfortunately, suppression of plant growth has been observed in many instances; these include various biochars, soils, plant species, under fertilised/unfertilised conditions, in field/pot experiments and using low/high biochar application rates (Butnan et al., 2015; Gell et al., 2011; Jones and Quilliam, 2014; Kloss et al., 2014b; Kwapinski et al., 2010; Lucchini et al., 2014a; Mukherjee et al., 2014; Oleszczuk et al., 2013; Quilliam et al., 2012; Rajkovich et al., 2012; Solaiman et al., 2011; Spokas et al., 2012; Van Zwieten et al., 2010). In addition, negative effects of biochar and biochar extracts were observed in *Vibrio fischeri*, algae, collembolan, protozoa and crustacean (Bernardo et al., 2010, 2009; Domene et al., 2015; Oleszczuk et al., 2013; Smith et al., 2013).

1.5.2 Mechanisms of growth inhibition caused by biochar

Many of biochar's beneficial properties can also be classed as disadvantages as they have the potential to be detrimental to plant growth. Table 1.1 shows the positive and negative implications of the same biochar effect in soil and includes exemplar references. As reported in section 1.4.3, biochar can reduce the losses of N in soil, however, biochar can also lock up N or increase microbial growth resulting in increased N use and lower availability for plants which causes issues, in particular when no extra N is applied with biochar (references in Table 1.1). In addition, biochar's high surface area is predestined to bind and immobilise organics, such as pesticides, when applied to soil. This can reduce the efficacy of pesticides which could reduce crop yields due to pests not being targeted. Furthermore, the increase of soil pH after biochar application is one of the most important benefits of biochar, yet, it can lead to germination and plant growth inhibition by shifting the pH too far into the alkaline range. Similarly, nutrient supply usually increases crop growth but the application of biochars with high-ash contents can result in nutrient imbalances or salinity-related issues causing reduction of plant growth. Finally, biochar can also contain contaminants which are supplied to soil with biochar.

Table 1.1: Biochar effects in soil and their positive and negative implications.

biochar effect in soil	positive implication	negative implication
binding of N in soil	reduced N loss (de la Rosa et al., 2014; Uzoma et al., 2011)	locking up of N (Deenik et al., 2010; Nelissen et al., 2014; Prommer et al., 2014; Rondon et al., 2007; Shenbagavalli and Mahimairaja, 2012)
binding and immobilisation of organic compounds	reduced toxicity of contaminants (Beesley et al., 2011; Buss et al., 2012; Karer et al., 2015; Kim, 2015)	reduced efficacy of pesticides (Cabrera et al., 2014; Cao et al., 2011; Graber et al., 2012; Jones et al., 2011; Kuppusamy et al., 2016; Yu et al., 2009)
increase in soil pH	reduced availability and toxicity of several PTEs and increased P availability (Butnan et al., 2015; Deal et al., 2012; Jeffery et al., 2015a; Kloss et al., 2014b)	potential germination and plant growth inhibition when pH raised into alkaline range (Jeffery et al., 2015a; Shoemaker et al., 1990; Singh et al., 1975)
supply of ash to soil	provision of plant nutrients (Hossain et al., 2011; Ippolito et al., 2015)	nutrient imbalances and salinity-related issues (Butnan et al., 2015; Domene et al., 2015; Gell et al., 2011; Rajkovich et al., 2012)

1.5.3 Adverse effects of contaminants in biochar

Contaminants in biochar were reported to result in toxicity to plants and aquatic and soil organisms. Adverse effects were pinpointed to various inorganic and organic species, yet, in many cases there was a high uncertainty as to what had caused the effects.

Potentially toxic elements (PTEs) is one group of contaminants in biochars that can cause toxic effects, e.g. Cu in biochar inhibited plant growth or Zn reduced growth of the bioluminescent bacteria, *Vibrio fischeri* (Bernardo et al., 2010; Lucchini et al., 2014a). Polycyclic aromatic hydrocarbons (PAHs) in water extracts of high-temperature biochar were suspected to be responsible for inhibitions of growth of

corn (Rogovska et al., 2012). Oleszczuk et al. (2013) and Kołtowski and Oleszczuk (2015) had the same assumption when biochars and biochar extracts caused inhibition of cress growth, *Vibrio fischeri*, algae, crustacean and protozoa. In a different study, radish and lettuce plants showed stunted growth after the addition of pig co-digestate biochar produced at 300°C and the toxicity was associated with high salinity and aliphatic/aromatic hydrocarbons (Gell et al., 2011). In Bernardo et al. (2009) and Bernardo et al. (2010) biochars from different waste mixtures (pine, plastics, tyres) were investigated and toxicity on *Vibrio fischeri* was proposed to be caused by various organic compounds, mostly volatile organic compounds (VOCs). In Rombolà et al. (2015), inhibition of germination of cress (*Lepidium sativum*) by biochar extracts was suspected to be caused by water-soluble degradation products of lipids or proteins. Smith et al. (2013) even went one step further and pinpointed the toxicity of biochar extracts to <500 Da organic molecules with at least one carboxyl group.

The above examples show that organic and inorganic contaminants in biochar can pose a threat to plant growth and other organisms but the responsible chemical species and their interactions are only partially understood and need further investigation.

1.6 Contaminants in biochar

1.6.1 Potentially toxic elements (PTEs)

Potentially toxic elements (PTEs) can be non-essential elements which have no function in plants, such as As, Cd, Cr, Hg, Se and Pb. Some, such as As and Hg, cause plant inhibitions even at very low concentrations, e.g. 0.1 mg L^{-1} Hg in solution and 20 mg kg^{-1} of As in soil inhibited plant growth (Baderna et al., 2015; Davis et al., 1978; Mondal et al., 2015). Plants are, however, less sensitive to Cd than animals and humans which can result in plants not showing any symptoms despite comparatively high concentrations of Cd in their tissues. Consequently, consumption of plants or plant parts grown on Cd-contaminated land can cause toxicity in humans and animals (Gupta and Gupta, 1998; Kabata-Pendias, 2011).

In addition, some PTEs are micronutrients which are essential for plant growth in low amounts, B, Cu, Fe, Mn, Mo, Ni and Zn (Broadley et al., 2011; Gupta and Gupta, 1998). For these elements, the concentration plants are exposed to defines their character as an essential nutrient or toxic element (Davis et al., 1978; Gupta and Gupta, 1998; Kopittke et al., 2010; MacNicol and Beckett, 1985). High concentrations of B and Mn, mainly originating from irrigation water and acidic soil, respectively, have frequently been reported to inhibit plant growth (Gupta and Gupta, 1998). Mo, on the other hand, is more similar to Cd, and can be taken up by plants in high amounts without causing toxic effects but can cause toxicities in grazing animals that ingest the plants (Kabata-Pendias, 2011). Therefore, defining what a nutrient and what a potentially toxic element is and setting clear limit values is not a straight forward approach as some PTEs are essential for plant growth and the supply, e.g. with biochar, can result in plant growth promotion. Nevertheless, establishing PTEs threshold values for biochar when applied to soil is necessary and biochar initiatives have included PTE limit values in their guidelines on biochar quality (British Biochar Foundation, 2013; EBC, 2012a; International Biochar Initiative, 2011).

PTE concentrations have been determined for a wide range of biochars, originating from virgin biomass (Anjum et al., 2014; Freddo et al., 2012; Kloss et al., 2012), as well as non-virgin materials (Bernardo et al., 2010; Evangelou et al., 2014; Farrell et

al., 2013; Jones and Quilliam, 2014; Lucchini et al., 2014a; Qiu et al., 2015; Singh et al., 2010) and in particular from sewage sludge (Agrafioti et al., 2013; Liu et al., 2014; Luo et al., 2014; Méndez et al., 2012; Van Wesenbeeck et al., 2014). In some studies, it was concluded that PTEs in biochars were not of concern for soil and/or plant health (Freddo et al., 2012; Lucchini et al., 2014b). However, biochars from non-virgin feedstocks frequently exceeded PTE guideline values and generally, Zn and Cd were the metals of highest concern (Bernardo et al., 2010; Evangelou et al., 2014; Qiu et al., 2015; Singh et al., 2010; Van Wesenbeeck et al., 2014). In addition, some biochars from Cu-contaminated wastes exceeded Cu threshold values and plant growth inhibitions were associated with a high Cu content (Jones and Quilliam, 2014; Lucchini et al., 2014a).

The availability of PTEs as determined by extracting biochar and its feedstock with weak extractants, such as salt solutions, typically decreased after pyrolysis (Farrell et al., 2013; Khanmohammadi et al., 2015; Kistler et al., 1987; Liu et al., 2014; Meng et al., 2013). Consequently, it is suggested that due to the immobilisation of PTEs during pyrolysis, PTE-rich biochar is safer to use on soil than its feedstock (Agrafioti et al., 2013; Méndez et al., 2012). Elements with low boiling points, e.g. As, Cd, Hg, Pb and Se, can evaporate during pyrolysis to some degree (Evangelou et al., 2014; Kistler et al., 1987; Van Wesenbeeck et al., 2014). This can be beneficial when mentioned non-essential and more toxic elements are lost from the char but it is a drawback when nutrients are evaporated.

In conclusion, there are various factors and parameters to consider when PTE contaminated feedstock is pyrolysed and there is a need for systematic studies that investigate the effect of the pyrolysis process on the PTE content of biochars where the feedstocks are from various PTEs contaminated materials. This is an essential prerequisite in determining their suitability for land application.

1.6.2 Chlorinated aromatic compounds: dioxins, furans and PCBs

Polychlorinated dibenzodioxins (PCDDs; known simply as dioxins), polychlorinated dibenzofurans (PCDFs; known simply as furans) and polychlorinated biphenyls (PCBs) are all chlorinated hydrocarbons which are regarded as persistent organic pollutants and consist of a total of 210 structurally related compounds of dioxins and

furans and 209 PCBs (Environment Agency, 2009; Van den Berg et al., 2006). While dioxins and furans are mostly by-products of different industrial processes, PCBs have been industrially manufactured (Environment Agency, 2009; White and Birnbaum, 2009). In the environment, dioxins, furans and PCBs usually co-exist as mixture of chlorinated aromatic compounds (Van den Berg et al., 2006; White and Birnbaum, 2009). Therefore, the WHO has compiled a list of 7 dioxins, 10 furans and 12 PCBs that have dioxin-like character and introduced toxicity equivalent factors (TEFs) which relate the toxicities of all compounds to the toxicity of 2,3,7,8-TCDD (Environment Agency, 2009; Van den Berg et al., 2006; White and Birnbaum, 2009). Using the TEFs, toxicity equivalent quantities (TEQ) are calculated which is the sum of the concentrations of the individual compounds multiplied by their respective TEFs.

Since chlorinated organic compounds are typically formed in high-temperature processes, biochar initiatives have adopted threshold values for the concentration of various PCBs (mg kg^{-1}) and dioxins/furans (in TEQ) (EBC, 2012a; International Biochar Initiative, 2011). For chlorinated aromatics to be formed, the feedstock naturally needs to contain sufficient chlorine and needs to be exposed to elevated temperatures (Conesa et al., 2009). In an oxygen rich-atmosphere (combustion) the peak of dioxin and furan formation was shown to be at 300-400°C (McKay, 2002; Xhrout et al., 2001). Dioxins and furans contain O in their structure and it was reported that much higher quantities were formed in an oxygen atmosphere (combustion) compared to an oxygen-limited atmosphere (pyrolysis) (Conesa et al., 2009). Consequently, measured concentrations of dioxins and furans in biochars from both, virgin and non-virgin feedstocks, were very low, far below threshold values, in the range of background levels or even below current detectable limits (Downie et al., 2012; Granatstein et al., 2009; Hale et al., 2012; Wiedner et al., 2013). Even chlorine-rich feedstocks such as food waste (2.9% chlorine) resulted in biochars with dioxin concentrations (92 pg g^{-1}) far below threshold values (250 pg g^{-1}) (Hale et al., 2012). In addition, state-of-the-art measurement equipment could not detect available dioxins in a suite of biochar samples (Hale et al., 2012). Furthermore, it was shown that during pyrolysis, feedstock already contaminated with chlorinated compounds lost 99.998% of dioxins and furans when pyrolysed at

800°C for 30 min (Wijesekara et al., 2007) and >75% of PCBs were destroyed at HTT of 450°C (Bridle et al., 1990).

In conclusion, the limited information available suggests that pyrolysis conditions do not favour the formation of chlorinated hydrocarbons. Acknowledging biochar's strong organic compound sorption capacity, overall, it was concluded that the concentrations of dioxins are not of any concern for biochar application (Downie et al., 2012; Hale et al., 2012; Wilson and Reed, 2012) and therefore, chlorinated organic compounds will not be discussed further in this thesis.

1.6.3 Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds with ≥2 aromatic carbon rings that only consist of C and H and are typically formed during incomplete combustion of biomass (Baek et al., 1991). Although more than 100 different PAHs are known, for environmental monitoring purposes, usually only the 16 PAHs of the US EPA priority pollutant list are analysed (Keith, 1979; US Department of Health and Human Services, 1995). Yet, even the 16 US EPA PAHs are a very heterogeneous group possessing variable chemical structures (2-6 rings), chemical properties (from partly water soluble and volatile to non-volatile and hydrophobic) and ecotoxicological, phytotoxic and toxicological effects (The Environmental Applications Group LTD, 1990; US Department of Health and Human Services, 1995). Due to their heterogeneity, as for dioxin-like compounds, TEFs were introduced, comparing the toxicity/carcinogenicity of each PAH to benzo(a)pyrene which is the best investigated and one of the most hazardous PAHs (Nisbet and LaGoy, 1992). Pyrolysis is predestined to promote the synthesis of PAHs and therefore, PAHs are priority pollutants in biochar. Consequently, the EBC and IBI have set 16 US EPA PAH threshold values in biochars based on legislation values which are in the range of 4-20 mg kg^{-1} (EBC, 2012a; International Biochar Initiative, 2011).

The yield of the concentration of 16 US EPA PAHs and the TEQ of PAHs during pyrolysis has been reported to increase with HTT, at least in the temperature range used for biochar production (Figure 1.4) (Aracil et al., 2005; Dai et al., 2014a; McGrath et al., 2001, 2003; Sharma and Hajaligol, 2003; Wei and Lee, 1998).

However, biochar studies show, that the concentrations of PAHs in biochars did not consistently increase with HTT (Bucheli et al., 2015; Dai et al., 2014b; Devi and Saroha, 2015; Hale et al., 2012; Keiluweit et al., 2012). Similarly uncertain are the relationships of PAH concentrations in biochar with other parameters, such as carrier gas flow rate, residence time or feedstock (Bucheli et al., 2015). Several studies found PAH concentrations in biochar which were not regarded as a concern for the environment as they were below threshold values (IBI lower limit value 6 mg kg^{-1}), e.g. 3.3 mg kg^{-1} in Brown et al. (2006), 0.08-5.66 mg kg^{-1} in Freddo et al. (2012) and 0.07-3.27 mg kg^{-1} in Hale et al. (2012). However, in other studies much higher PAH concentrations, exceeding even the upper IBI threshold value (20 mg kg^{-1}), were observed (Table 1.2) (Anjum et al., 2014; Hilber et al., 2012; Keiluweit et al., 2012; Kloss et al., 2012; Kołtowski and Oleszczuk, 2015; Quilliam et al., 2013). Overall, the PAH concentrations in biochars from slow pyrolysis were between 0.07 and 355 mg kg^{-1}.

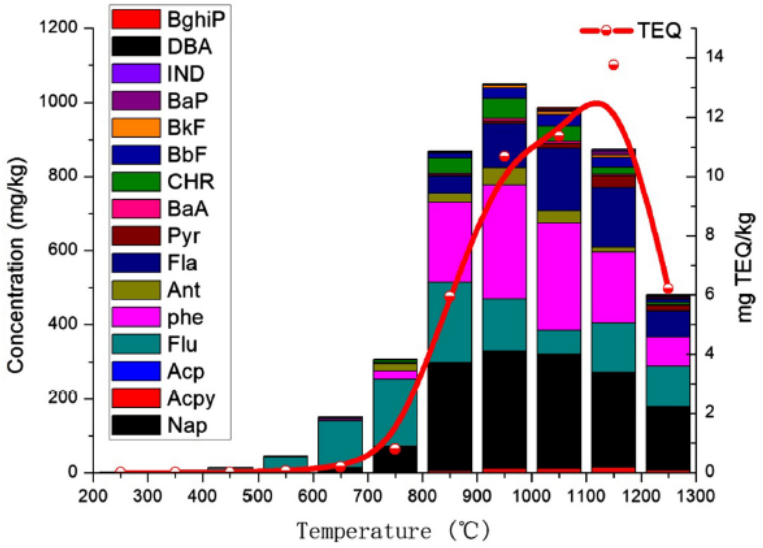


Figure 1.4: Influence of HTT on the PAH concentration and toxicity equivalent quantity (TEQ) of PAHs in pyrolysis vapours of sewage sludge (Dai et al., 2014a).

Since PAHs are mostly hydrophobic, they preferentially attach to soil particles rather than leach into groundwater which makes biochar a good sorbent material to clean-up PAH contaminated soil (Quilliam et al., 2013). Since PAHs sorb strongly to biochar, as expected, the concentrations of available PAHs in biochars have been reported to be in the range of only 0.1% of the total concentration. This meant the available PAH concentrations were mostly under the detection limit of the measurement equipment or in the range of background soil levels and were not regarded as concern for plant growth (Hale et al., 2012; Mayer et al., 2016). Yet, in some studies PAHs in biochar and biochar extracts were claimed to be responsible for toxic effects observed in plants, soil and water organisms (Anjum et al., 2014; Kołtowski and Oleszczuk, 2015; Oleszczuk et al., 2013; Rogovska et al., 2012).

Overall, little is known about the relationship of pyrolysis conditions and feedstocks with PAH concentrations in biochar and the risk associated with PAHs in biochar for plant growth.

Table 1.2 Range of PAH concentrations (mg kg^{-1}) measured in different biochars in the literature.

biochars	PAH concentrations	
International Biochar Initiative threshold	6-20	(International Biochar Initiative, 2011)
pine pyrolysed at 450, 525°C	3.2-3.3	(Brown et al., 2006)
rice, bamboo, redwood, maize pyrolysed at 300, 600°C	0.08-5.66	(Freddo et al., 2012)
~50 slow pyrolysis biochars	0.07-3.27	(Hale et al., 2012)
hemp and wood pellets pyrolysed at 500°C	33.7-34.9	(Anjum et al., 2014)
grapevine wood 600, miscanthus 750, wood 750	9.1-355	(Hilber et al., 2012)
grass and wood pyrolysed at 300, 400, 500, 600, 700°C	0.206-23.0	(Keiluweit et al., 2012)
straw, spruce, poplar pyrolysed at 400, 460, 525°C	1.8-33.7	(Kloss et al., 2012)
miscanthus, willow, wheat straw, HTT unknown	3.5-39.9	(Kołtowski and Oleszczuk, 2015)
wood 450 and rice husk 300-600°C	9.6-64.6	(Quilliam et al., 2013)

1.6.4 Volatile organic compounds (VOCs)

During pyrolysis, vapours are created from the thermochemical conversion which usually separate from the char; however, a proportion of the compounds, which are intermediate degradation products from biomass transformation, remain attached onto the solids. A vast variety of organic compounds has been found in association with biochar but most studies only determined the concentrations of certain chemical groups (Cole et al., 2012; Jamieson et al., 2014; Lin et al., 2012; Norwood et al., 2013; Yu et al., 2012); in others, the analysis was done on individual compounds but only in a qualitative way (Spokas et al., 2011; Yang et al., 2013) or if quantitative analysis were performed it was done only for few compounds (Lievens et al., 2015).

Volatile organic compounds (VOCs), is one of the most important groups to be found in biochar because of their very high mobility and biological activity (Spokas et al., 2011). These are organic compounds with boiling points below 250° and consequently also include the PAH naphthalene (Directive 2004/42/CE of the European parliament and of the council, 2004). VOCs can have both, growth promoting and inhibiting effects; this has been demonstrated in studies of VOCs which (I) occur naturally after forest fires (Brown and Staden, 1997; Keeley and Pizzorno, 1986; Nelson et al., 2012); and (II) originate from biochar (Bargmann et al., 2013; Elad et al., 2011; Smith et al., 2013). Interestingly, the initial biochar guidelines of the EBC from 2012 did not contain threshold values for VOCs but, in the updated version from June 2015, VOCs were incorporated, showing the increasing interest and importance of these compounds in biochar (EBC, 2012a, 2012b).

Very little is known about the magnitude of biochar contamination with VOCs and quantitative assessments are lacking. In addition, the effects of VOCs in biochar and subsequent risks for biochar application are completely unknown. Overall, there is a need for investigating how relevant VOCs are for biochar and its actions in soil.

1.7 Aims and objectives

1.7.1 Thesis objectives

As outlined in this introduction, biochar application to soils has mostly resulted in positive effects on the soil itself and on crop yields. However, the magnitude of observed effects was often highly variable and, in some cases, inhibition of plant growth was also observed; the latter was usually linked to contaminants which were associated with the biochars. To gain commercial, public and governmental acceptance, it needs to be ensured that biochar is safe to be used in food producing systems. Therefore, biochar needs to be thoroughly analysed for potential contaminants and concentrations of these contaminants, both inorganic and organic, must meet guideline and legislation threshold values. Biochar producers need to know which combination of pyrolysis conditions and feedstocks are most suitable for biochar production to be able to offer a safe product. As large-scale biochar application is a recent idea and due to biochar's unique properties that are very different to other environmental samples, besides simply analysing contaminant concentrations, there is a need to assess the risks of analysed concentrations for plant growth, the environment and human health.

Consequently, the aims of this thesis termed "Contaminant issues in production and application of biochar" were:

1. Contaminant issues in biochar production:
    - Identify and quantitatively assess the most relevant groups of contaminants in a variety of biochars, produced from both, virgin and non-virgin feedstocks, and from different production conditions
    - Compare contaminant concentrations with currently available threshold values
    - Link contaminant concentrations to production conditions and feedstocks
    - Where appropriate, assess the suitability of biochar post-treatment measures for reducing contamination
2. Contaminant issues in biochar application:
    - Develop easy-to-perform phytotoxicity screening tests for biochar
    - Assess the potential risk of biochars to plant growth

- Link phytotoxic effects to contaminant concentrations
- Evaluate which groups of contaminants in biochar are of concern to plant growth and to humans and under which circumstances

The overall objective of this thesis was to identify production conditions and feedstocks suitable for the production of biochar safe to be used as soil amendment on the basis of contaminant concentrations and risk of biochars to cause adverse effects.

1.7.2 Chapter structure

These aims have been addressed over the seven experimental chapters of this thesis which have been prepared in journal article format and in one general discussion chapter. The journal article chapters were sub-divided according to three groups of contaminants: Chapter 3 and Chapter 4 deal with PTEs and in particular with biochars from marginal biomass; Chapter 5 and Chapter 6 are about the relationship between PAH concentrations in biochar and various production parameters; in Chapter 7 and Chapter 8 the potential effects of high-VOC biochars on plants and human health and post-treatment measures were investigated; Chapter 9 compares the risk posed by PAHs and VOCs to plant growth.

Chapter 2 Materials and methods

2.1 Overview

Altogether, 90 biochars, produced with the Stage I, Stage II and Stage III pyrolysis units of the UKBRC under highly controlled conditions, monitoring pressure and temperature, were analysed during this PhD project. When inconsistencies during a pyrolysis run were detected, such as high pressure peaks, the biochars were either discarded and the pyrolysis run was repeated, ensuring comparable conditions between runs or the resulting biochars were treated as contaminated (high-VOC biochars, section 2.2.6).

Instead of analysing all 90 (including three post-treated) biochars for all contaminants, groups of biochars were selectively analysed for PTEs, PAHs or VOCs:

- Nineteen biochars from PTE-rich (marginal) feedstocks were analysed for total and 'available' PTEs (and nutrients) by digesting using the "modified dry ashing" procedure and by extraction using NH_4NO_3, followed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) (see section 2.4)
- 84 (including three post-treated) biochars were analysed for PAHs using 36 h Soxhlet extraction followed by gas chromatography-mass spectrometry (GC-MS) (see section 2.5)
    - 46 of these were selected to systematically investigate the effect of different production conditions and feedstocks on sum of 16 US EPA PAHs in biochar
    - All 84 (including post-treated) were analysed for the concentrations of the individual 16 US EPA PAHs to pinpoint specific production conditions resulting in high-risk biochars based on PAH composition
- Three biochars were analysed for VOCs using different extraction and analysis techniques (see section 9.2.2)

In Table 6.1, 84 (including three post-treated) biochars are listed with details on production conditions and feedstocks (all 84 biochars analysed for PAHs including

thirteen marginal biomass-derived biochars) and the remaining six biochars can be found in Table 3.1 (Table with all nineteen marginal biomass-derived biochars).

2.2 Pyrolysis units and biochars

Three pyrolysis units, called 'Stage I, II and III', located at the UK Biochar Research Centre (UKBRC) were used to produce 87 biochars investigated in this PhD project. The Stage I and III pyrolysis units were not run as part of this PhD project but biochars produced in other projects using these units were analysed, while, the Stage II unit was central to biochar production during this PhD project.

2.2.1 'Stage I' pyrolysis unit

The 'Stage I' pyrolysis unit is a small-scale, batch pyrolysis reactor with a vertical quartz tube (inner diameter 50 mm) which has a sample bed depth of around 200 mm and is heated up by a 12 kW infra-red gold image furnace (P610C; ULVAC RIKO, Yokohama, Japan) (Figure 2.1). Depending on feedstock density, different amounts of materials were pyrolysed at varying residence times (RT) (5 to 40 min). The furnace can heat up to 1300°C with a wide range of heating rates, for this project HTTs of 350-700°C and a heating rate of 5°C min^{-1} were adopted. A thermocouple within the sample bed was used to control the pyrolysis temperature during pyrolysis. Nitrogen carrier gas (flow rates 0 to 0.67 L min^{-1}) was injected at the bottom of the quartz tube which ensured an oxygen-limited atmosphere in the reactor. A condensation system (Figure 2.1) was assembled to collect four fractions of condensable gases in a series of traps at different temperatures. The first zone in the condensation system was heated up by heating tapes to ensure that the glass tubes do not block due to excessive condensation of pyrolysis vapours, while the last two traps were cooled with liquid nitrogen. Non-condensable gases were collected in a gas bag after the second cold trap. For this PhD project, however, only the biochars were analysed, not the pyrolysis liquid and gases.

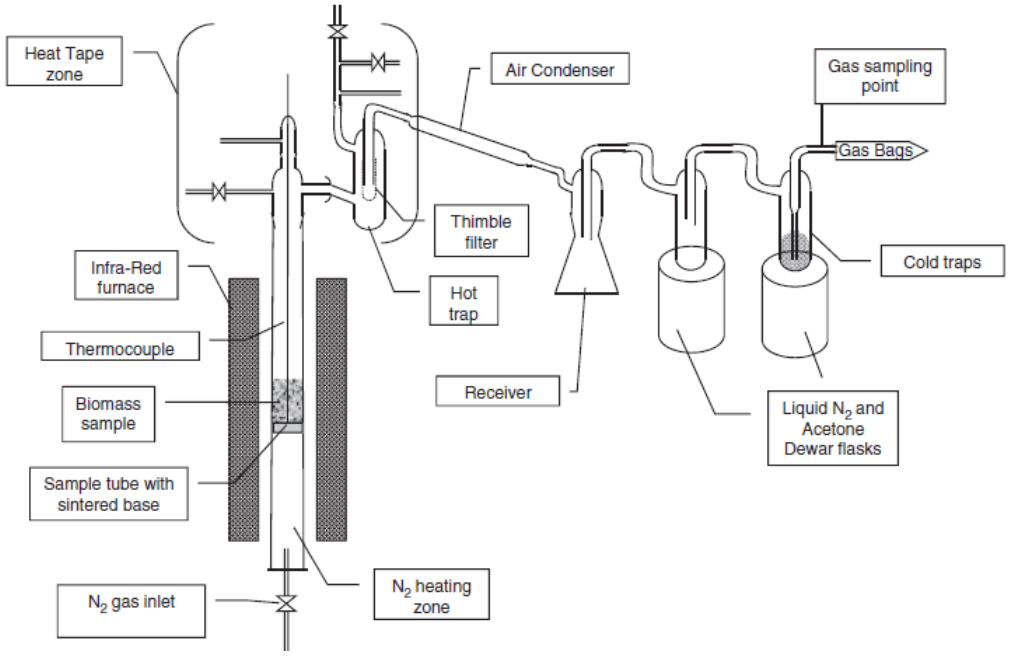


Figure 2.1: Small-scale, batch pyrolysis reactor, 'Stage I', UK Biochar Research Centre (Crombie et al., 2013).

2.2.2 'Stage II' pyrolysis unit

The 'Stage II' unit is a continuous flow pyrolysis unit which is equipped with an electrically heated split-tube furnace. As depicted in Figure 2.2, a feed hopper delivered the feedstock to a rotary valve that prevented syngas to flow back in the feed hopper. When the material passed the rotary valve, it was picked up by the furnace-screw which transported it through the furnace (inner diameter 100 mm). The typical feedstock residence time used corresponds to around 21.5 min in the heated zone. In the discharge chamber adjacent to the furnace, the solid char was separated from the vapours which were drawn up into a propane-fuelled afterburner. A combustion air fan supplied additional air into the afterburner to ensure complete combustion of the syngas. The discharge chamber was heated by two heating tapes, set to 500°C (HT I) and 400°C (HT III). After an initial purge with nitrogen, two injection points delivered nitrogen into the unit during operation: (I) a carrier gas inlet near the feed hopper that was usually set to 1 L min^{-1} and (II) a heated stream of nitrogen (tube goes all the way through the furnace) injected at 4 L min^{-1} at the end point of the furnace. (Figure 2.2). The second carrier gas injection, so-called 'hot purge', delivered hot nitrogen to ensure an oxygen-limited atmosphere in the

discharge chamber area and to further heat the discharge chamber to avoid condensation of syngas on surfaces. The pipes connecting the discharge chamber with the afterburner were heated by an additional heating tape (HT II, 400°C) and were insulated to minimise vapour condensation. After the separation of the pyrolysis vapours and solids, the biochar was collected in a glass vessel and was cooled down under a nitrogen atmosphere.

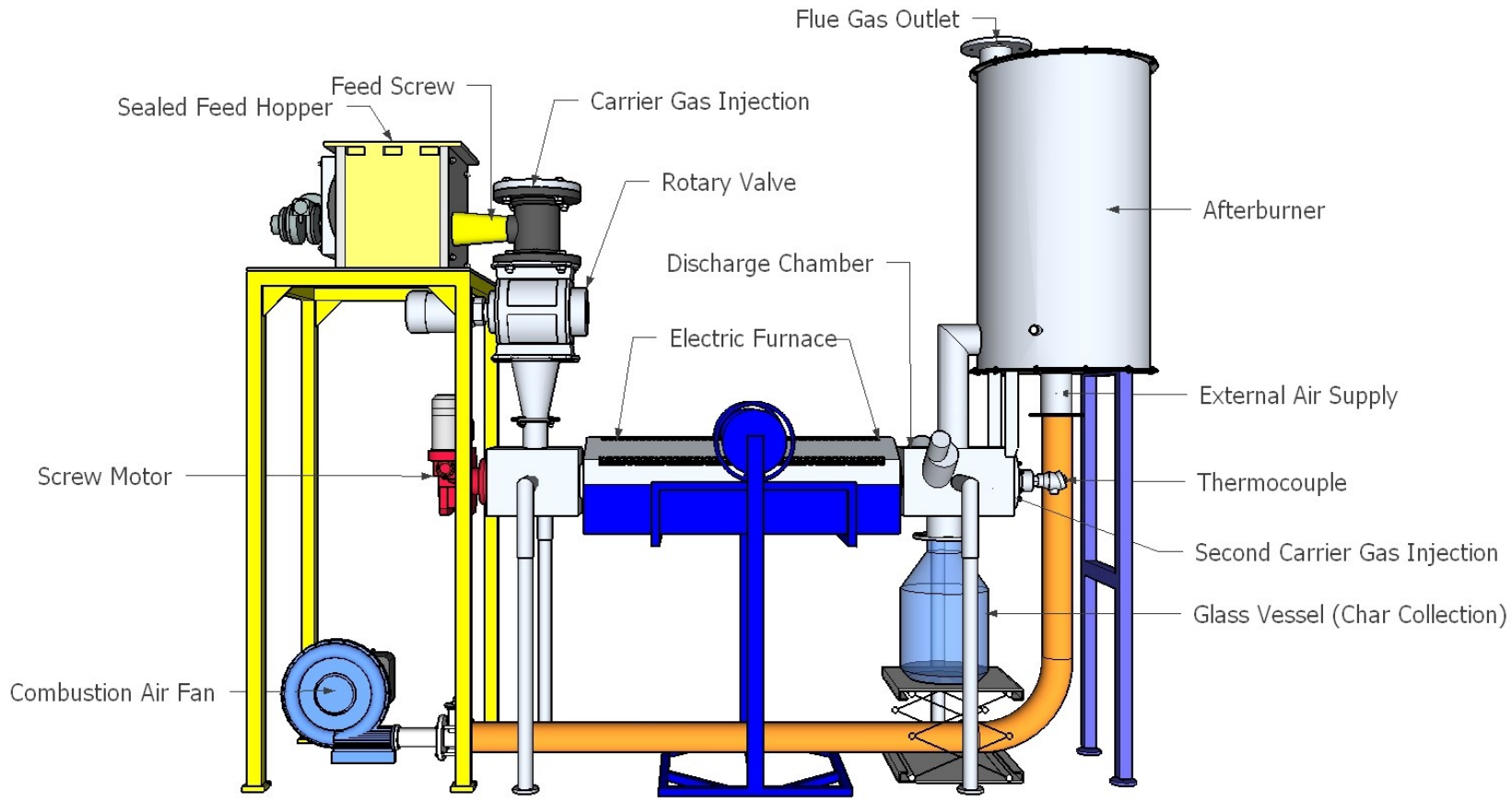


Figure 2.2: Continuous screw-pyrolysis unit, 'Stage II', UK Biochar Research Centre (Buss et al., 2016).

2.2.3 'Stage III' pyrolysis unit

The 'Stage III' pyrolysis unit is a pilot-scale rotary kiln with a heat-tube length of 2.8 m, an inner diameter of 24.4 mm, an angle of 0.5° and a rotational speed of 1-7 rpm (Figure 2.3). The rotary kiln can process between 31-50 kg h^{-1} for high-density feedstocks (wood pellets, density 610 kg m^{-3}) and 4-19 kg h^{-1} for low-density materials (miscanthus straw, density 130 kg m^{-3}). A biomass hopper with a feed screw delivered the feedstock to the rotary kiln where it was heated up to a maximum temperature of 750°C. The discharge chamber separated pyrolysis vapours from solids which dropped on a cooling crew that transported the char to a nitrogen-purged discharge drum. From the discharge chamber, the vapours were channelled into an afterburner where they were combusted with propane and the exhaust gases were released. Temperature and pressure were monitored at different entry points within the heat-tube.

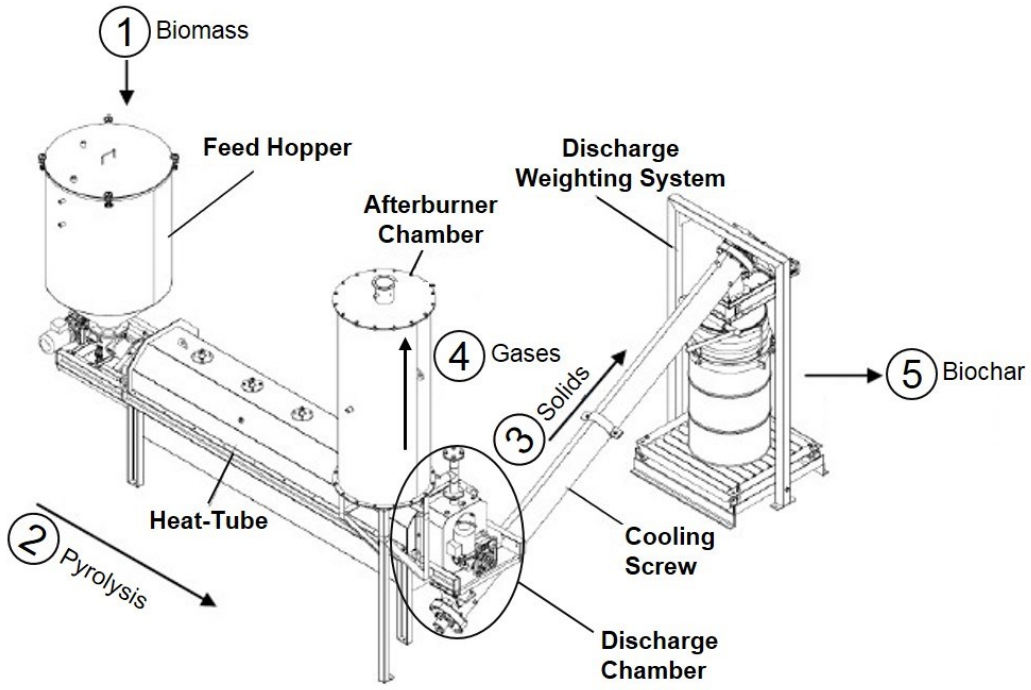


Figure 2.3: Pilot-scale rotary kiln pyrolysis unit, 'Stage III', UK Biochar Research Centre (Buss and Mašek, 2014).

2.2.4 Marginal biomass-derived biochars

2.2.4.1 Marginal biomass feedstocks

Ten marginal biomass feedstocks were sourced from five different countries to provide a variety of materials and plant species for biochar production to investigate PTEs in biochar. The feedstocks used were as follows:

Seven biomass samples grown on contaminated land: 1) Wheat straw (*Triticum aestivum*), 'WSI' from the village Madlauda (Panipat, Haryana, India) in the vicinity of Panipat thermal power station (coal fired plant; village Assan, Jind road, Panipat, India) and 2) sugarcane bagasse (Saccharum spp., species unknown), 'SBI' from the vicinity of the river Yamuna close to the village Sarurpur (Uttar Pradesh, India) were sourced from India. Both locations have problems with several PTE (and organic) pollution: Panipat thermal power station (Hajarnavis, 2000) and river Yamuna (Mehra et al., 2000). 3) Winter rye straw (*Secale cereal*) (WRB) and 4) willow logs with bark (salix spp., species unknown), 'WLB' originated from the Campine region in Belgium from heavy metal (Cd, Zn, Pb) contaminated soil (Van Slycken et al., 2013). 5) Whole plant without roots of *Salix purpurea* 'SLP', 6) *Paulonia tomentosa*, 'PAT' and 7) *Arundo donax*, 'ADX' were sourced from Italian industrial waste sites. Salix and Paulonia were grown on a site of an old Zn smelter that covers approximately 50 ha near the city of Crotone, Italy (Marchiol et al., 2013). *Arundo donax* was harvested from an industrial area located in Torviscosa from soil contaminated by various metals (Fellet et al., 2007). PTE concentrations at the various contaminated sites the biomass were sourced from are shown in Table 2.1.

One feedstock grew in contaminated waters: 8) Water hyacinth (whole plant) (*Eichhornia crassipes*), 'WHI' originated from a municipal waste water drain (Rajiv Nagar, Bhalswa, New Delhi, India) flowing close to Bhalswa Landfill Site, New Delhi which is known for its high levels of contamination (Jhamnani and Singh, 2009; Talyan et al., 2008)

Two non-virgin feedstocks were used: 9) Solid residues from anaerobic digestion of food waste, sourced from the UK, denoted 'FWD' and containing a high amount of plastics; and 10) heterogeneous, glued, laminated, painted, coated, or otherwise treated demolition wood (without halogenated compounds), sourced from Germany

and denoted ‘DW’, which included pieces of metal, glass and plastics. The FWD was autoclaved and dried for several days at 80°C while the DW was shredded to <5 mm particle size prior to pyrolysis. A summary of all marginal biomass feedstocks is given in Table 2.2.

Table 2.1: PTE concentrations in soils from the area where the marginal biomass feedstocks used for biochar production were grown. No data for the region of wheat straw (India) was available; water hyacinth (India) was grown in a waste water drain.

plant	location	reference		As	Cd	Cu	Hg	Ni	Pb	Zn
		lower soil limit EU #	mg kg $^{-1}$		1.00	50		30	30	150
		soils limit Germany *	mg kg $^{-1}$	200			5			
sugarcane	Sarurpur, India	(Mehra et al., 2000)	mg kg $^{-1}$		0.46	18		13	16	47
willow, winter rye	campine region, Belgium	(Van Slycken et al., 2013)	mg kg $^{-1}$		6.50					377
Salix purpurea, *Paulonia tomentosa*	Crotone, Italy	(Marchiol et al., 2013)	mg kg $^{-1}$	242	498	1535	32		5802	44048
Arundo donax	Torviscosa, Italy	(Fellet et al., 2007)	mg kg $^{-1}$	20	0.83	73			22	97

EU Council Directive 86/278/EEC, 1986, ANNEX 1 A, on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture

* German Federal Soil Protection and Contaminated Sites Ordinance, 1999, Annex 2, 2.2, Guidance values for contaminant transfer soil-crop on agricultural fields in regards to plant quality

2.2.4.2 Marginal-biomass-derived biochar production

If not stated otherwise in section 2.2.4.1, feedstocks were dried and shredded with a Bosch AXT Rapid 2200 shredder prior to pyrolysis to give a particle size of around <30 mm. When very fine and dusty particles were created during the processing the fraction <2 mm was sieved out and excluded from pyrolysis as the feed and furnace screws were not able to pick up these very fine particles. A sub-sample of the feedstock was dried in an oven at 105°C for 24 h and the moisture content was determined for every run.

The feedstocks were pyrolysed with the Stage II pyrolysis unit with a feeding rate of around 500 g h^{-1} if possible; however, due to the low bulk density of some feedstocks partly lower feeding rates needed to be applied (Table 3.1). Typically between 300-700 g of material was used for the production of one biochar at each HTT. A residence time that corresponds to around 21.5 min in the heated zone was applied for all biochars. Two feedstocks (DW, ADX) were pyrolysed at five temperatures (350, 450, 550, 650, 750°C), one (WLB) at two temperatures (550, 700°C) and the remaining seven feedstocks were pyrolysed at 550°C, the typical HTT for biochar production.

The biochar yield of SBI 550 could not be determined because the furnace screw did not pick up the straw properly and the exact amount of biomass used could not be measured. Consequently, the char yield is not reported in Table 3.1 and mass balances of elements could not be determined.

Table 2.2: Ten marginal biomass feedstocks used for biochar production.

feedstock	abbreviation
seven materials from contaminated land	
wheat straw (*Triticum aestivum*) from Belgium	WSI
sugarcane bagasse (Saccharum spp., species unknown) from India	SBI
winter rye straw (*Secale cereal*) from India	WRB
willow logs with bark (salix spp., species unknown) from Belgium	WLB
whole plant without roots of *Salix purpurea* from Italy	SLP
whole plant without roots of *Paulonia tomentosa* from Italy	PAT
whole plant without roots of *Arundo donax* from Italy	ADX
one material from contaminated water	
water hyacinth (whole plant) (*Eichhornia crassipes*), originated from a waste water drain was sourced from close to Bhalswa Landfill Site (New Delhi, India)	WHI
two non-virgin materials	
solid residues from anaerobic digestion of food waste from Scotland	FWD
demolition wood (heterogeneous, glued, laminated, painted, coated, or otherwise treated wood) from Germany	DW

2.2.5 Various biochars analysed for PAHs

2.2.5.1 Variation of HTT

Different feedstocks were pyrolysed using two pyrolysis units in the typical temperature range used for biochar production (350-750°C). The Stage II pyrolysis unit was used to pyrolyse willow chips (WC) (Koolfuel 40, supplied by Strawsons (Retford, UK)) at three temperatures (350, 550, 750°C) and miscanthus chips (MC) (*Miscanthus x giganteus*) at four temperatures (350, 450, 550, 750°C). Furthermore, sewage sludge (SS) was pyrolysed at five temperatures (350, 450, 550, 650, 750°C) with the Stage III pyrolysis unit.

2.2.5.2 Variation of HTT, residence time, feedstock, carrier gas flow rate

The Stage I pyrolysis unit was used to pyrolyse around 100 g of straw pellets (WSP II) from 50/50 wheat/oilseed rape straw (Crombie and Mašek, 2015) and softwood pellets (SWP II) from 5/95 pine/spruce. Using a constant heating rate of 5°C min^{-1}, two HTTs (350, 650°C), two residence times (10, 40 min) and three carrier gas flow rates (0, 0.33, 0.67 L min^{-1}) were applied, reflecting a diverse but, in industrial terms, significant range of production conditions (Crombie and Mašek, 2015). Twenty-four biochars were produced.

2.2.5.3 Variation of ash and moisture content

For testing the effect of moisture content on PAH concentration, miscanthus chips (MC) were pre-treated and pyrolysed at 450, 550 and 750°C with the Stage II pyrolysis unit. To obtain dry miscanthus chips the feedstock was dried in an oven at 105°C until no change in weight could be determined. To obtain high-moisture feedstock, tap water was sprayed onto the material. On the day the samples were pyrolysed, the moisture contents were (determined again by drying as above): untreated sample 13.4 wt% (same as described in section 2.2.5.1), dried sample 0.28 wt% and wetted sample 23.5 wt%.

The effect of ash content was tested by altering the ash content in miscanthus chips. To obtain low-ash biomass, the chips were washed twice in hot tap water and once with cold DI water over night. To prepare high-ash biomass, K^+ was added in form of an aqueous solution of potassium acetate which was evenly sprayed onto the dried miscanthus chips which restored the original moisture content. The ash contents were (determined using method described in 2.3.1): 4.2 wt% (dry weight basis) for the untreated miscanthus (same as described in section 2.2.5.1), 3.2 wt% for the washed sample and 7.4 wt% for the K-spiked sample. The untreated and two treated samples were pyrolysed at 350, 550 and 750°C with the Stage II pyrolysis unit.

2.2.5.4 Sewage sludge and anaerobically digested sewage sludge

To investigate if anaerobic digestion of the feedstock has an effect on PAH concentration of the resulting biochars, sewage sludge (SS I) and anaerobically digested sewage sludge (AD) from Wessex water (Avonmouth, UK) were pyrolysed at HTTs of 550 and 700°C with the Stage II pyrolysis unit, respectively. No carrier gas flow was applied during biochar production, only for initial purging of the pyrolysis unit. In addition, during the production of SS at 700°C the heating tape I of the pyrolysis' units discharge chamber was faulty and could not be used.

2.2.5.5 Modifications on Stage II pyrolysis unit

It was hypothesised that the set-up of the discharge chamber of the pyrolysis unit can affect the PAH concentration of resulting biochars significantly. Consequently, two biochars were produced from softwood pellets (SWP I) at 550°C with the Stage II pyrolysis unit with modifications to the unit's discharge chamber. Following

modifications were performed: under normal circumstances the discharge chamber, where pyrolysis vapours and solids are separated, was heated up with two heating tapes and the hot air from the nitrogen that streams through the furnace at a rate of 4 L min^{-1} (Figure 2.2). Here, however, the purge gas flow rate was turned down to 2 L min^{-1}, producing 'SWP I - 550 - purge 2 l min^{-1}'. 'SWP I - 550 - no HT III' was produced under identical conditions, however, instead of turning down the nitrogen gas flow, the heating tape III was switched off.

2.2.5.6 Stage comparison

Wheat straw pellets (WSP I) and softwood pellets (SWP I) were pyrolysed at HTTs of 550 and 700°C with all three pyrolysis units using production conditions as comparable as possible. In the two continuous units (Stage II and III), mean residence times (RT) of 20 min were applied. In Stage I, the RT at HTT was varied for WSP I and SWP I and the two HTTs to reflect the RT in the heated areas of the furnace of the continuous units (10 min RT for SWP I 550 and 700, 5 min RT for WSP I 550 and 6 min for WSP I 700). Twelve biochars were produced this way. The biochar 'SWP I 550 - Stage III' is the 'NC biochar' described in section 2.2.6.

2.2.6 High- and low-VOC biochars

Three biochar samples were produced from the same feedstock (softwood pellets, (SWP I)) pyrolysed at the same nominal highest treatment temperature (550°C), with the same mean residence time (20 min) and in the same pyrolysis unit (rotary kiln; Stage III). However, due to production difficulties during the set-up of the unit two biochar batches were contaminated, in different ways, resulting in biochars with high-VOC content. The high-VOC content could be readily detected due to the strong odour of the biochars. To investigate the properties of these contaminated biochars, the two high-VOC biochars, herein described as liquid contaminated (LC) biochar and gas contaminated (GC) biochar were assessed against a low-VOC, non-contaminated (NC) biochar.

LC biochar was contaminated by liquids which condensed on the wall of the discharge chamber, where biochar is separated from pyrolysis vapours, as the temperature of the wall was lower than usual due to improper insulation (Figure 2.3). During a separate pyrolysis run, under the same experimental conditions, fouling had

blocked a pipe that normally leads gases from the discharge chamber to the afterburner, again due to a non-insulated pipe. As a result, pyrolysis gases and vapours filled the discharge chamber and cooling screw (Figure 2.3) and were therefore absorbed by the biochar, resulting in contamination of the GC biochar. NC biochar was obtained following a successful pyrolysis run with no observed blockages or condensation of volatiles after proper insulation of the pyrolysis unit, resulting in odourless, comparably uncontaminated biochar.

For this pyrolysis facility, the degree of condensation and deposition on these high-VOC biochars can be considered as high and unusual; however, it is important to investigate these materials to become aware of potential effects of condensed products, even if at lower concentrations, as highly diverse biochars from numerous and varied pyrolysis units are used for plant studies.

2.2.6.1 Thermally post-treated high- and low-VOC biochars

All three unground biochars (NC, GC, LC biochar) were spread in aluminium trays in one layer and exposed to air at 200°C for 20 h in a laboratory oven.

2.3 Biochar properties

2.3.1 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed on ground biochar samples (~10-15 mg) using a method called proximate analysis with a Mettler-Toledo TGA/DSC1 instrument.

The method used was as follows: from room temperature the temperature was increased at a heating rate of 25°C min^{-1} to 110°C and held for 10 min to drive off moisture. Next, the temperature was increased to 900°C at 25°C min^{-1} and also held for 10 min for removal of volatile matter (VM). Both steps were performed at a nitrogen gas flow rate of 50 mL min^{-1}. For the final step the temperature was hold at 900°C for 20 min but oxygen was introduced to oxidise the remaining carbon content and determine the so-called fixed carbon content and ash content.

2.3.2 Electrical conductivity (EC) and pH

Electrical conductivity (EC) and pH were measured according to Rajkovich et al. (2012) using 1 g of ground biochar (using mortar and pestle) in 20 mL of DI water, which was shaken at 150 rpm for 1.5 h on a bench-top shaker (EC: Hach HQ40d portable meter, conductivity probe meter CDC 401; pH Mettler Toledo FE 30). These analyses were performed in duplicates.

2.4 Analysis of total and available elemental content

2.4.1 Total elemental content: "modified dry ashing"

The biochars were digested according to the "modified dry ashing" method described as the best total elemental analysis method for biochar by Enders and Lehmann (2012). The method was adjusted in two ways (more biochar digested, less DI water added in final step) to yield a higher elemental concentration in order to improve the final ICP-OES analysis. Briefly: 0.5 g of each biochar was weighed into crucibles, heated to 500°C and held at this temperature for 8 h. After cooling, the samples were placed in a steam bath and 5 mL of concentrated (70%) HNO_3 (analytical grade, Fisher Scientific) was added and evaporated to dryness. Again, after cooling, 1 mL HNO_3 and 4 mL H_2O_2 (30%, analytical grade, Fisher Scientific) were added and evaporated to dryness. Next, 2 mL HNO_3 was added to dissolve the solids. The resulting solution was filtered through Whatman No. 41 filter paper and the volume increased to 50 mL with DI water. All biochars, the feedstocks and reagent blanks were prepared using the same method prior to elemental analysis. Using a high-temperature pretreatment means that some of the elements that evaporate easily, such as As and Hg, will be lost during the process (Bridle et al., 1990). Consequently, care needs to be taken when this method is used to prepare samples which have not been previously exposed to such high temperatures (mainly feedstocks) and the focus in the analysis is on elements with low boiling points.

2.4.2 Available elemental content: NH_4NO_3-extraction

In this project, the BS ISO 19730:2008 (2008) method, based on 1 mol L^{-1} NH_4NO_3-extraction, was used for determining the available fraction of nutrients and PTEs. This method was selected as it has been used to establish German soil legislation threshold values for available PTEs to protect crop growth (German Federal Soil Protection and Contaminated Sites Ordinance, 1999) and has been used for extraction of cationic nutrients in soil (Schöning and Brümmer, 2008; Stuanes et al., 1984) and PTEs and nutrients in biochars (Alling et al., 2014; Karer et al., 2015; Kim, 2015; Kloss et al., 2014b; Park et al., 2011).

The method was established for soil samples and needed to be slightly adjusted to reflect the different properties of biochar. According to BS ISO 19730:2008 (2008),

the recommended soil-to-NH_4NO_3-solution ratio is 1:2.5 (m/v); however, due to its low bulk density and high water sorption capacity, the ground biochar did not mix well with the small amount of water and the mixture was too viscous to ensure proper extraction. Different solid-to-solution ratios were tested and thorough mixing of the sample was ensured by using a ratio of 1:10 (m/v). In short, representative samples were taken from each biochar container by taking sub-samples, grinding those with mortar and pestle and taking triplicate aliquots. Next, the samples were weighed into 50 mL centrifuge tubes and suspended in 1 mol L^{-1} NH_4NO_3 (laboratory grade, Fisher Scientific) using a bench-top shaker (150 rpm for 2 h). Afterwards, the samples were centrifuged for 30 min at 3500 rpm and passed through Whatman No. 1 filter papers and then through 0.45 µm membrane filters (Millipore, Watford, UK). Reagent blanks were prepared using the same procedure.

2.4.3 Elemental analysis: ICP-OES

The digests and the NH_4NO_3-extracts were both analysed by ICP-OES (Perkin Elmer Optima 5300DV) for 20 (19) elements. The following elements were analysed: Al, As, B, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, P, Pb, Se and Zn (Na only for digests, not NH_4NO_3-extracts). Most elements were analysed in the axial mode of the instrument, but elements present in high concentrations were analysed in the radial mode. For the digests, Na, Ca, K, Al, Mg, Fe and for the NH_4NO_3-extracts only K was analysed in the radial mode of the instrument. For calibration purposes, the ICP multi-element standard solution IV (Certipur®, Merck) (standard 1) covered most of the elements analysed; the remaining elements (As, Hg, Mo, P, Se) were combined from single ICP standards to form standard 2. Depending on the range in which the element concentrations fell, calibration curves of three standards (calibration blank, 0.01, 0.1 and 1 ppm), four standards (including 10 ppm) or five standards (including 100 ppm) were used. The standards 1 and 2 as well as the ICP multi-element standard solution VI (Certipur®, Merck) were used as internal quality control standards for every batch analysed. Reagent blanks were analysed with each batch of digested and extracted biochars.

The calculation of elemental contents from raw intensity was done the following way for the digests and the NH_4NO_3-extracts:

- Each sample-aliquot was analysed in triplicates by the ICP-OES which automatically calculated the averages
- With the calibration curves, the relative intensities were converted into concentrations for each sample (mg L^{-1})
- The reagent blank was subtracted from the value of the analysed sample
- The concentration was converted into mg kg^{-1} using the exact amount weight in the crucible and the volume of the solution
- Each biochar sample was digested/extracted in triplicates and the averages and standard deviations were calculated, however, negative concentrations were regarded as zero for the averages
- When the average of the triplicate analysis was below the detection limit, '< LOD' was shown

The limit of detection (LOD) was measured/calculated the following way:

- 10 DI water blanks were analysed with the ICP-OES with the methods for the digests and the methods for the extracts, respectively
- The standard deviation of the raw intensities of the 10 DI water blanks was calculated
- Three times the standard deviation was divided by the slope of the respective calibration
- This was done for each element
- The LOD calculated for the solution in mg L^{-1} was then based on:
    - Digests: 0.5 g of material and a volume of 50 mL of solution
    - Available extracts: 1.5 g of material and 15 mL of solution

The LODs for the various elements are stated in Table 2.3 for the methods for digests and available extractions.

Table 2.3: Limit of detection (LOD) of the ICP-OES analysis for twenty elements using two methods. Digests (total elements) and NH_4NO_3-extracts (available elements) of biochars were analysed. n/a, not available.

element	unit	digests	extracts
Al	mg kg^{-1}	0.712	0.105
As	mg kg^{-1}	0.721	0.102
B	mg kg^{-1}	0.356	0.016
Ca	mg kg^{-1}	3.085	0.072
Cd	mg kg^{-1}	0.035	0.161
Co	mg kg^{-1}	0.077	0.008
Cr	mg kg^{-1}	0.489	0.029
Cu	mg kg^{-1}	0.061	0.019
Fe	mg kg^{-1}	0.492	0.009
Hg	mg kg^{-1}	0.232	0.018
K	mg kg^{-1}	7.080	0.830
Mg	mg kg^{-1}	2.011	0.023
Mn	mg kg^{-1}	0.037	0.002
Mo	mg kg^{-1}	0.211	0.061
Na	mg kg^{-1}	5.340	n/a
Ni	mg kg^{-1}	0.095	0.011
P	mg kg^{-1}	0.644	0.103
Pb	mg kg^{-1}	0.739	0.037
Se	mg kg^{-1}	1.401	0.230
Zn	mg kg^{-1}	0.473	0.139

2.4.4 Calculations of total elemental content

2.4.4.1 Relative change of elemental content in % (RECC)

To be able to assess if elements were lost (or gained) during the pyrolysis process, the percentage change of the total elemental content from feedstock to biochar (relative elemental content change (RECC)) in % was determined the following way:

$$RECC\ (\%) = \left(\frac{C_B * Y - C_F}{C_F}\right) * 100$$

$$C_B = total\ elemental\ concentration\ in\ biochar\ (mg\ kg^{-1})$$

$$C_F = total\ elemental\ concentration\ in\ feedstock\ (mg\ kg^{-1})$$

$$Y = biochar\ yield\ during\ pyrolysis$$

The individual changes of the elemental contents were further processed and the average changes after pyrolysis for all biochars and only for the biochars produced at ≥700°C were determined. The geometric mean and geometric standard deviation were calculated to reflect the percentage change appropriately. This was done by converting the RECC into ratios (R):

$$R_{RECC} = \left(\frac{C_B * Y}{C_F}\right) = \frac{(100 + RECC\ (\%))}{100}$$

Next, the natural logarithm was applied, the averages and standard deviations of the transformed values were calculated and the values were converted back:

$$\bar{u}_R = e^{\frac{(\ln R_1 + \ln R + \ln R_3 \ldots + \ln R_n)}{n}}$$

$$\bar{u}_R = geometric\ mean\ (\%)$$

$$n = number\ of\ biochars$$

As described in Bland and Altman (1996), the standard deviation cannot simply be converted back from logarithmic to normal scale because the value would be dimensionless. Thus, the average plus and minus standard deviation in the ln-scale was calculated and then was converted back. The result are unequal standard deviations around the average. In addition, the ln-transformed data were used for one-sample, 2-tailed t-tests to investigate if a significant change ($p < 0.05$) of the elemental content occurred assuming the null hypothesis 0% change. WSI 550 was identified as outlier and was not taken into account for the calculation of the averages as it showed significant mass gains for elements which showed constant mass or mass reductions from feedstock to biochar in the other samples (Zn +620%, Ca +50%, Cu +134%, Mg +43%, Mn +75%, P +88%). A likely explanation for this phenomenon is a cross-contamination or a non-representative sampling of the feedstock used for digestion.

Using the average and standard deviation of the elemental content of feedstocks and biochars analysed in triplicates, the standard deviation for the relative elemental content change (RECC) was calculated through error propagation (standard deviation (s)) according to the following, using partial derivatives:

$$s_{RECC} = \sqrt{\left(\frac{\partial f}{\partial C_B}\right)^2 * s_{C_B}^2 + \left(\frac{\partial f}{\partial C_F}\right)^2 * s_{C_F}^2}$$

$$\frac{\partial f}{\partial C_B} = \frac{Y}{C_F}$$

$$\frac{\partial f}{\partial C_F} = C_B * Y * C_F^{-2}$$

$$s_{RECC} = probagated\ standard\ deviation\ for\ RECC\ (mg\ kg^{-1})$$

$$C_B = total\ elemental\ concentration\ in\ biochar\ (mg\ kg^{-1})$$

$$C_F = total\ elemental\ concentration\ in\ feedstock\ (mg\ kg^{-1})$$

$$Y = biochar\ yield\ during\ pyrolysis$$

Incorporating both equations in the equation above:

$$s_{RECC} = \sqrt{\left(\frac{Y}{C_F}\right)^2 * s_{C_B}^2 + (C_B * Y * C_F^{-2})^2 * s_{C_F}^2}$$

The biochar production was only performed once (no replicates) and therefore, the biochar yield was used as a fixed parameter. Values smaller the LOD were not used for the error propagation as no standard deviation existed.

2.4.4.2 Total change of elemental content in mg kg^{-1} (ECC)

The deviation of the actual concentration (in mg kg^{-1}) from the expected concentration (in mg kg^{-1}) assuming 100% elemental retention was calculated. The elemental content change in mg kg^{-1} (ECC) shows how much of the elemental concentration was lost or gained during pyrolysis in mg kg^{-1}:

$$\text{ECC}\ (mg\ kg^{-1}) = C_B - \left(\frac{C_F}{Y}\right)$$

The LOD was used as described for the RECC (section 2.4.4.1) and the standard deviation (*s*) was calculated as followed, using partial derivatives:

$$s_{ECC} = \sqrt{\left(\frac{\partial f}{\partial C_B}\right)^2 * s_{C_B}^2 + \left(\frac{\partial f}{\partial C_F}\right)^2 * s_{C_F}^2}$$

$$\frac{\partial f}{\partial C_B} = Y$$

$$\frac{\partial f}{\partial C_F} = -1$$

$$s_{ECC} = probagated\ standard\ deviation\ for\ ECC\ (mg\ kg^{-1})$$

$$C_B = total\ elemental\ concentration\ in\ biochar\ (mg\ kg^{-1})$$

$$C_F = total\ elemental\ concentration\ in\ feedstock\ (mg\ kg^{-1})$$

$$Y = biochar\ yield\ during\ pyrolysis$$

Incorporating both equations in the equation above:

$$s_{ECC} = \sqrt{(Y)^2 * s_{C_B}^2 + (-1)^2 * s_{C_F}^2}$$

2.4.5 Calculations of available elemental content

2.4.5.1 Relative/percentage availability of elements in biochars (RAEC)

Calculating the percentage elemental availability was done by dividing the NH_4NO_3-extractable elemental content (in mg kg^{-1}) by the total elemental content (also in mg kg^{-1}). For visualising Figure 4.2 and for calculating the average availability for all biochars, for each element smaller the LOD, where "<" is depicted, 0.5 * the calculated value was used (value varies with total elemental concentration of respective biochar).

The propagated standard deviation (standard deviation (*s*)) for percentage available elemental concentration was calculated in the following way:

$$s_{RAEC} = \sqrt{\left(\frac{1}{C_B}\right)^2 * s_{AC_B}^2 + \left(-\frac{AC_B}{C_B^2}\right)^2 * s_{C_B}^2}$$

$$s_{RAEC} = probagated\ standard\ deviation\ for\ RAEC\ (mg\ kg^{-1})$$

$$C_B = total\ elemental\ concentration\ in\ biochar\ (mg\ kg^{-1})$$

$$AC_B = available\ elemental\ concentration\ in\ biochar\ (mg\ kg^{-1})$$

2.5 PAH analysis

2.5.1 Sampling

To gain representative samples, first the container with the biochar was mixed and around 1/10 of the amount produced was sampled (~10 g) from different areas of the container. The ~10 g sample was ground with mortar and pestle and homogenised, transferred into a sample tube, and mixed again before a 2 g sub-sample was taken. Finally, accurately weighed aliquots (1 g) were used for extraction.

2.5.2 Extraction and analysis

Biochar has a very high sorption capacity for PAHs and studies have shown that a longer extraction duration results in much higher PAH recoveries compared to conventional extraction techniques used for soil (e.g. 6 h Soxhlet extraction) (Fabbri et al., 2013; Hale et al., 2012; Hilber et al., 2012). Since recovery rates reached maximum values after an extraction for 36 h (Fabbri et al., 2013; Hilber et al., 2012), the method recommended in the European Biochar Certificate (EBC, 2012b) is a 36 h Soxhlet extraction using toluene (Hilber et al., 2012), followed by GC-MS analysis which was also applied in this study. 6 h extraction was tested as well on three biochar samples and as reported in the literature, it resulted in much lower PAH recovery (described in Chapter 9).

Each homogenised biochar sample was subjected to a 36 h Soxhlet extraction using approximately 100 mL of toluene. The resulting extract was rotary evaporated to 1 mL and analysed without clean-up for the 16 PAHs on the US EPA priority pollutants list by GC-MS (Agilent 6890 GC plus 5975c MS). Full details including validation of the method can be found in Hilber et al. (2012). The deuterated PAHs (stable isotopes), naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12 and perylene-d12 were used as internal standards. Relative standard deviations (RSDs) of the GC-MS analysis for all individual PAHs were calculated, measuring high and low standards (A Table 1). The LODs for the individual PAHs were 0.10 mg kg^{-1}. The analyses were performed by Northumbrian Water Scientific Services (Newcastle, United Kingdom), accredited by United Kingdom Accreditation Service (UKAS). Several biochars were extracted and analysed in triplicate (separate vials on separate occasions) and RSD values were typically <20% (A Table 2).

2.6 Germination tests

Germination and early seedling growth tests were developed and performed as part of this PhD project as an easy, quick and reproducible phytotoxicity screening method. One tests was specifically developed to investigate the effects of VOCs emitted from biochar ('volatiles only' test). A second test was established to evaluate and differentiate between the effects of volatiles, compounds easily leachable from biochar and biochar in direct contact to be able to narrow down the origin of the observed inhibitions ('all exposure routes').

Both germination tests, i.e., 'volatiles only' and 'all exposure routes' were based on the same principle: a seven day germination test with 30 cress seeds (*Lepidium sativum*) on filter paper in plastic jars at 20-25°C and 24 h light in the lab. The continuous light regime was chosen according to Müller et al. (2006). Cling foil was wrapped around the top of the jars and punctured several times to allow some gas exchange. All tests were performed in triplicates unless stated otherwise. The containers with seeds were placed on a shelf in a randomised design to provide similar growth conditions. Germination rate, root and shoot length were determined (details mentioned in the materials and methods sections of the chapters). As in other studies (El-Darier and Youssef, 2000; Jones-Held et al., 1996), germination was defined here as cracking of seed coating and visibility of root growth.

2.6.1 'Volatiles only' germination test

The test design was adapted from Busch et al. (2012) with the aim of assessing the phytotoxicity of organic compounds that vaporise readily at room temperature (VOCs). Different amounts of ground biochar were placed in an aluminium container (55 mm height, 80 mm diameter) with a stainless metal mesh on top. The mesh supported a filter paper (Whatman No. 1, 70 mm) on which 30 cress seeds (*Lepidium sativum*) were spread and to which two folded filter papers (Whatman No. 1, 110 mm) supplied DI water. This set up was placed within a 1 L plastic storage jar, so that only volatiles released from biochar could access and affect the seeds (Figure 2.4).

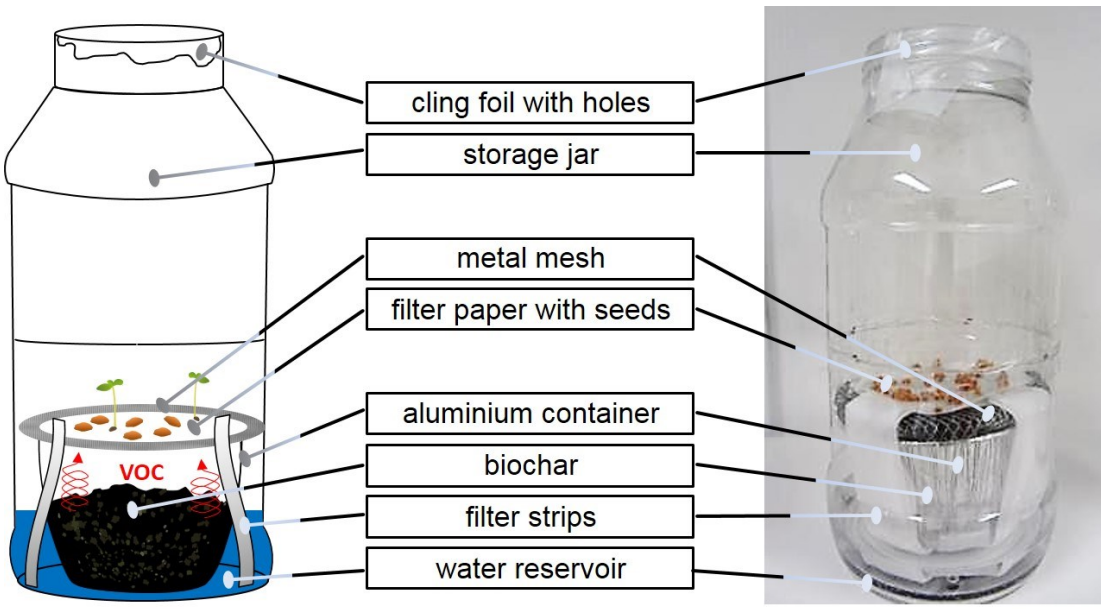


Figure 2.4: Schematic of the experimental setup for the 'volatiles only' germination test for assessing effect of volatiles released from biochar on seed germination (Buss and Mašek, 2014).

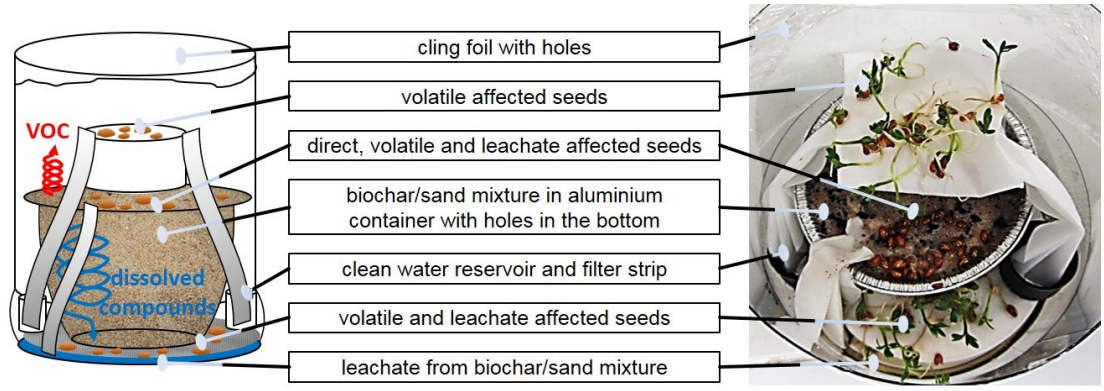


Figure 2.5: Schematic of the experimental setup for the 'all exposure routes' germination test for assessing effect of volatiles released, compounds dissolved by water and direct contact of biochar and seeds (Buss and Mašek, 2014).

2.6.2 'All exposure routes' germination test

The 'all exposure routes' test is based on the setup used by Bargmann et al. (2013) to study the effect of VOCs and direct contact of seeds with biochar-sand, but adds a biochar leachate fraction. This way, the test is designed to assess the effect of contaminants in three different seed-contact systems:

1) Volatiles only

2) Volatiles and leached (dissolved) compounds (in water) and
3) Volatiles, leached (dissolved) compounds and direct contact with biochar

Ground biochar was mixed with sterilised sand (50-70 µm, sterilisation at 500°C for ~2 h) in different ratios (w/w) and 50 g of this mixture was placed in an aluminium container (25 mm height, 70 mm diameter) with holes in the bottom. The control was sterilised sand only. 35 mL of DI water was poured over the mixture which percolated through the sample to dissolve mobile compounds. The design allowed the leachate to flow back towards the biochar-sand mixture through a folded filter paper. Two small lids and two pieces of filter paper supplied clean water to a filter paper on an elevated area on top of the biochar-sand mixture. 30 seeds were spread on the top filter paper, on the biochar-sand mixture and on a filter paper at the bottom on the metal mesh (all Whatman No. 1, 70 mm).

Chapter 3 Fate of PTEs and nutrients during pyrolysis and suitability of marginal biomass-derived biochars for soil amendment

The following chapter is based on the published article:

Buss, W., Graham, M.C., Shepherd, G.J., Mašek, O., 2016. Suitability of marginal biomass-derived biochars for soil amendment. Sci. Total Environ. 547, 314–322. doi: 10.1016/j.scitotenv.2015.11.148

Journal impact factor (2014): 4.099

Number of citations (September 2016): 6

The candidate was solely responsible for data analysis and writing of the article and this chapter. Supervisors provided guidance and supervisors and co-authors contributed to the editing of the manuscript. The experimental work was performed by the candidate, apart from digestion of the biochars and feedstocks which was conducted by Andy Gray and John Morman. The ICP-OES analysis was performed by the candidate with the assistance of Lorna Eades and Jessica Shepherd. The schematic of the Stage II pyrolysis unit (Figure 2.2) was created by Alberto Gonzalez Fernandez.

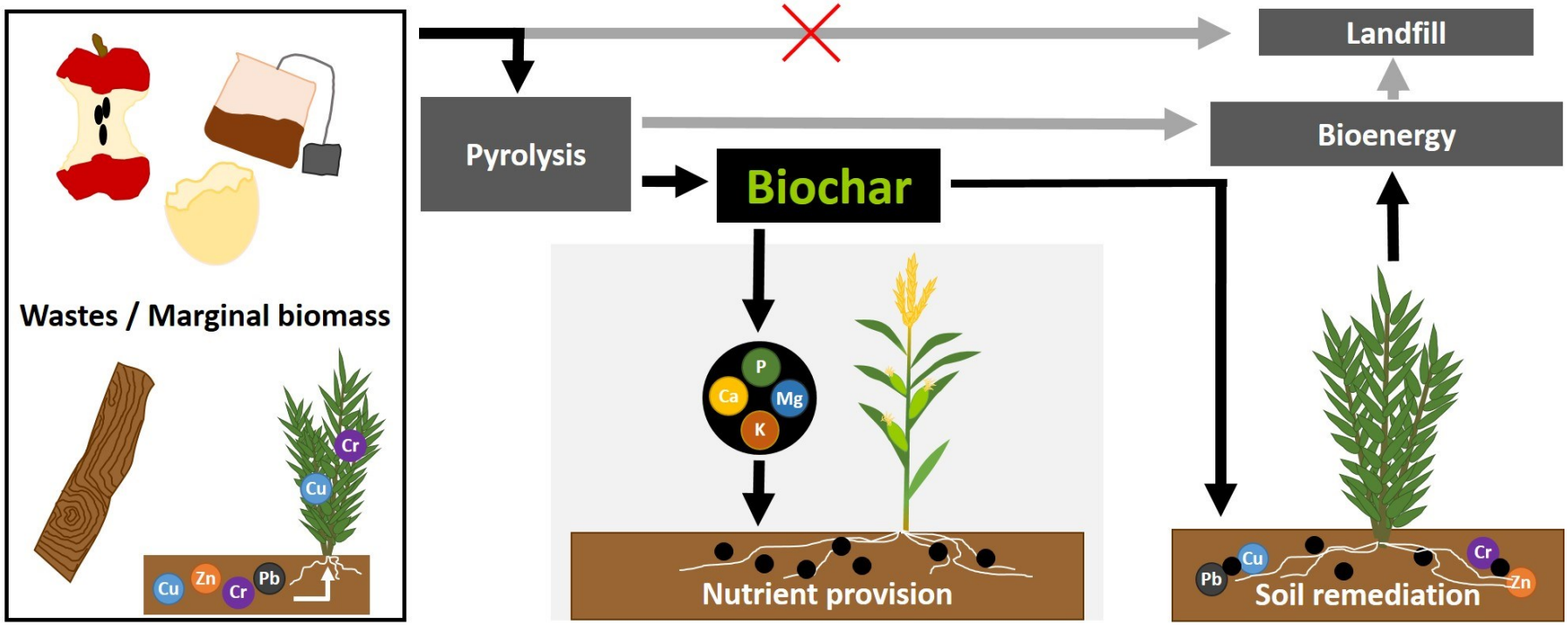


Figure 3.1: Graphical abstract of Chapter 3. Marginal biomass, which are waste feedstocks that often contain contaminants, are landfilled in most cases. Here it was tested if those biochars can be pyrolysed to reduce the amount of material that is landfilled. The pyrolysis gases and liquids from this process could be used for production of energy. It could be shown that many biochars are suitable to be applied to soil for nutrient provision or potential soil remediation. After biochar application, the plants that grow on contaminated land could for example be used for energy production.

3.1 Introduction

To achieve economically viable biochar production in a sustainable context, the use of waste feedstocks is essential. While crop residues fit into this category, they are not considered to be an ideal feedstock (Shackley et al., 2011). On the other hand, plant material from contaminated sites/phytoremediation as well as non-virgin feedstocks (chemically/biologically transformed, amended or treated material (Shackley et al., 2011)) are resources that need additional treatment before re-use, and so these may be more suited to biochar production.

Large areas of land world-wide have been contaminated by inorganic contaminants, whilst the actual size of the area depends on definition. The scale of the problem is still increasing, so the use of plants from this underutilised land for conversion into biochar could be a valuable treatment option (Evangelou et al., 2012). Non-virgin feedstocks, such as food waste (anaerobic digestate (AD)), sewage sludge (AD) or demolition wood are also readily-available materials; in the UK alone, around 200 million tonnes of anthropogenic waste is produced annually (DEFRA, 2015). If such wastes could be converted into a valuable resource through pyrolysis, a wide variety of feedstocks would be accessible in large quantities for biochar production. To describe biomass of little economic value the term ‘marginal biomass’ is used here, taken from the established term “marginal land” for land which, for various reasons, has little agricultural importance (e.g. poor soil quality, pollution) (Peterson and Galbraith, 1932). These marginal biomass feedstocks can be untreated virgin materials such as contaminated plant biomass or non-virgin feedstocks from chemically/biologically transformed materials.

For biochar application to soil to be acceptable, adverse ecosystem effects need to be avoided and contaminant levels kept to a minimum. The contaminants of concern in biochar are organic compounds that are formed during production and can attach loosely or tightly to the biochar framework (PAHs, VOCs, dioxins) (Hale et al., 2012; Spokas et al., 2011) as well as potentially toxic elements (PTEs) originating from the feedstock (Evangelou et al., 2014; Méndez et al., 2012; Van Wesenbeeck et al., 2014). Total PTE concentrations have been analysed in biochars from virgin biomass sources (materials which have not been chemically/biologically

transformed, amended or treated) and the results have not indicated any reasons for concern for soils and plants so far (Freddo et al., 2012; Lucchini et al., 2014b). However, the use of the term 'marginal biomass' here describes materials that have a high probability of being somewhat contaminated and predominantly contain elevated levels of PTEs. Thus, the resulting biochars could exceed legislation values applied to soil amendments. This makes it essential to investigate separately the levels of PTEs in each biochar produced from a new, marginal biomass for compliance with existing regulations. According to the International Biochar Initiative (IBI) (International Biochar Initiative, 2011), arsenic, cadmium, chromium, cobalt, copper, lead, mercury, molybdenum, nickel and zinc are the PTEs of concern in biochar which, with the exception of cobalt and molybdenum, are also part of the priority pollutant list of the US EPA (Environmental Protection Agency, 1982).

Sewage sludge is a marginal feedstock that could be used for biochar production but often contains elevated levels of PTEs. It is available in large quantities and will be so into the future. For example, in 2008 1.6 million t of sewage sludge was produced in the UK (DEFRA, 2011), which could make commercial biochar production viable. Sewage sludge biochar has already been investigated intensively regarding risks and benefits with variable results, mostly related to its heterogeneity and varying composition (Liu et al., 2014; Luo et al., 2014; Méndez et al., 2012; Van Wesenbeeck et al., 2014; Zielińska and Oleszczuk, 2015). In several recent studies, single feedstocks from contaminated biomass were investigated regarding their usefulness for conversion into biochar (Evangelou et al., 2014; Jones and Quilliam, 2014; Lucchini et al., 2014a). However, to my best knowledge, no studies to date have carried out systematic and extensive assessment of PTE in biochars from a range of marginal biomass under different pyrolysis conditions.

Besides PTEs, elements with positive effects on plant growth are present in the ash of feedstocks. The PTEs Cu, Zn, Ni and Mo are phytotoxic in elevated concentrations in soil, in contrast however, low concentrations are needed by plants as micronutrients (Broadley et al., 2011). N, P and K are the major elements in fertilisers and are macronutrients by definition, which means they are the elements needed by plants in high quantities (Hawkesford et al., 2011). All of these nutrients can be found in biochar (Enders and Lehmann, 2012; Mukome et al., 2013).

Therefore, use of nutrient-rich marginal feedstocks for biochar production could be an alternative way of supplying nutrients to plants through application of the resulting biochar to soil.

During pyrolysis, P and K mostly remain in the solid fraction and are, therefore, applied with the biochar to soil. However, N in the feedstock is mostly evaporated, together with most of the organic material and this results in a N-poor material (Antal and Grønli, 2003; Liu et al., 2014). During the high temperature treatment of biomass, part of the mineral matrix evaporates as well (Kistler et al., 1987). The 'loss' of elements from the solid char material can be beneficial when PTEs are concerned, but are a drawback when nutrients are vaporised (Kistler et al., 1987; Nzihou and Stanmore, 2013). Investigation of volatilisation of elements from pyrolysis solids is essential to select the best suitable production conditions of biochar from mineral-rich feedstocks.

The aim of this chapter was to investigate whether feedstocks contaminated with PTEs through various routes: (I) plant uptake through soil, (II) plant uptake through water and (III) direct anthropogenic contamination, are suitable for biochar use in soil in relation to their PTEs compositions. This was evaluated by pyrolysing the mentioned materials and analysing the fate of PTEs (and nutrients) during pyrolysis. Furthermore, the main objective was to identify the best marginal biomass feedstock for conversion into biochar and the most suitable HTT judged on the basis of PTE concentrations (comparison with legislation threshold values), nutrient concentrations and basic biochar characteristics (pH, EC, ash, fixed carbon). For this purpose, nineteen biochars were produced from ten different materials: feedstocks included various plant species that were grown in PTE contaminated soils, a plant grown in contaminated water and two non-virgin feedstocks.

3.2 Materials and methods

3.2.1 Biochars

The ten marginal biomass feedstocks and the production of the nineteen biochars from these feedstocks are described in section 2.2.4.1. An overview of feedstocks and production conditions can be found in Table 3.1. Feedstock effects were studied for all ten materials where pyrolysis at 550°C was used as a typical medium HTT. To study the effects of temperature, two feedstocks (ADX, DW) were pyrolysed at HTTs of 350, 450, 550, 650 and 750°C and one (WLB) was pyrolysed at 550°C and 700°C.

In addition, ten "UKBRC standard biochars" produced with the Stage III pyrolysis unit using softwood pellets (SWP), rice husk (RH), oilseed rape pellets (OSR), miscanthus straw pellets (MSP) and wheat straw pellets (WSP) at 550°C and 700°C were used as a reference for comparison of nutrient concentrations. Detail on the individual biochars can be found at http://www.biochar.ac.uk/standard_materials.php (Mašek, 2014).

3.2.2 Digestion of biochar

The biochars were digested using the "modified dry ashing" procedure (Enders and Lehmann, 2012) and were analysed for the following elements using ICP-OES as described in section 2.4: Al, As, B, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, P, Pb, Se and Zn. The digestions and analyses were performed in triplicates (elements As, B, Hg, K, Mo, Na, Se for feedstocks and biochars of DW, FWD, SBI, WHI and WSI, however, are only available in duplicates).

The relative change of elemental content in % from feedstock to biochar and the change of elemental content in mg kg^{-1} was calculated (section 2.4.4).

3.2.3 Thermogravimetric analysis (TGA), pH, electrical conductivity (EC)

Proximate analysis (PA) using thermogravimetric analysis (TGA), pH and electrical conductivity (EC) measurements were performed as described in section 2.3.

3.3 Results and discussion

Ten marginal biomass samples that either grew on/in PTE contaminated land/waters or were biologically/chemically treated feedstocks sourced from five different countries were converted into biochar using the same pyrolysis unit and very similar process conditions but varying the HTT. Details on yields and production conditions of all biochars are depicted in Table 3.1.

3.3.1 Yields, pH, EC and proximate analysis of biochars

As expected and reported in other studies, the char yield consistently decreased with pyrolysis temperature (Table 3.1) due to increased loss of volatiles (Antal and Grønli, 2003). Proximate analyses showed a decrease of the volatile matter content with temperature and consequently an increase in fixed carbon content (dry ash-free basis) which is again consistent with general observations in other studies (Crombie et al., 2013; Enders et al., 2012; Jindo et al., 2014; Ronsse et al., 2013; Xie et al., 2015).

The pH values of the biochars strongly increased with pyrolysis temperature and were all in the range of 9-10.5, apart from the lower temperature biochars made from demolition wood which had a lower pH (Table 3.1). In a meta-analysis of biochar studies, biochar has shown to increase the soil pH on average (Biederman and Harpole, 2013). Thus, the biochars with a high pH investigated here can be useful for soil pH elevation and the associated benefits of PTE mobility reduction and improvement of P availability (Biederman and Harpole, 2013). The demolition wood biochars had the lowest ash content and pH values; this relationship of low ash content with pH has already been described in Enders et al. (2012). The electrical conductivity (EC) of the biochars (used for approximation of the salinity) increased with HTT and was well correlated with ash content (R^2=0.7538; data not shown). WHI 550 had an ash content of over 40% and the highest EC (8115 µS cm^{-1}) which originated from the uptake of minerals from a waste water drain by the feedstock, water hyacinth. This biochar and some of the others (e.g. WSI 550, WRB 550, FWD 550) could potentially cause negative effects on plants and soil organisms due to their high salinity if applied in high concentrations.

Table 3.1: Selected production conditions and biochar properties of nineteen biochars investigated in this study. Proximate analysis (volatile matter, fixed carbon, ash), pH and electrical conductivity (EC) were performed in duplicates and averages (AV) ± standard deviations (SD) are shown. HTT, highest treatment temperature; FR, feeding rate during pyrolysis; yield, char yield during pyrolysis; db, dry basis; daf , dry ash free basis.

biochar	feedstock	HTT	FR	yield	volatile matter	fixed carbon	ash	pH	EC
		°C	g h^{-1}	% db	% daf		% db		µS cm^{-1}
DW									
DW 350	Demolition wood, Germany	350	500	31.60	28.90 ± 1.63	71.10 ± 1.63	5.35 ± 0.78	7.56 ± 0.39	175 ± 18
DW 450	Demolition wood, Germany	450	500	28.61	23.44 ± 0.91	76.56 ± 0.91	3.51 ± 0.92	7.78 ± 0.30	212 ± 25
DW 550	Demolition wood, Germany	550	500	25.51	14.72 ± 0.26	85.28 ± 0.26	5.32 ± 0.01	7.65 ± 0.08	189 ± 29
DW 650	Demolition wood, Germany	650	500	22.16	10.17 ± 0.52	89.83 ± 0.52	4.97 ± 0.49	8.48 ± 0.11	206 ± 17
DW 750	Demolition wood, Germany	750	500	19.95	8.25 ± 1.78	91.75 ± 1.78	5.70 ± 2.48	9.85 ± 0.27	408 ± 37
ADX									
ADX 350	*Arundo donax,* Italy	350	500	38.69	33.72 ± 0.79	66.28 ± 0.79	12.38 ± 0.90	8.79 ± 0.44	1095 ± 306
ADX 450	*Arundo donax,* Italy	450	500	30.13	21.83 ± 0.55	78.17 ± 0.55	12.62 ± 0.92	9.84 ± 0.11	2165 ± 191
ADX 550	*Arundo donax,* Italy	550	500	26.24	17.13 ± 0.34	82.87 ± 0.34	14.75 ± 0.43	9.68 ± 0.21	2580 ± 85
ADX 650	*Arundo donax,* Italy	650	500	25.49	14.10 ± 1.10	85.90 ± 1.10	16.01 ± 2.47	10.13 ± 0.41	2915 ± 78
ADX 750	*Arundo donax,* Italy	750	500	22.95	10.84 ± 0.22	89.16 ± 0.22	15.51 ± 0.84	10.61 ± 0.64	3430 ± 269
SBI 550	Sugarcane bagasse, India	550	250	*	16.84 ± 0.43	83.16 ± 0.43	12.91 ± 0.48	9.34 ± 0.03	954 ± 153
WHI 550	Water hyacinth, India	550	400	45.20	43.39 ± 3.75	56.61 ± 3.75	42.92 ± 4.16	9.85 ± 0.11	8115 ± 389
WSI 550	Wheat straw, India	550	250	30.74	21.87 ± 1.68	78.13 ± 1.68	24.55 ± 1.10	10.12 ± 0.01	6385 ± 431
WLB									
WLB 550	Willow logs, Belgium	550	500	26.68	16.38 ± 0.14	83.62 ± 0.14	7.22 ± 0.89	9.52 ± 0.16	192 ± 23
WLB 700	Willow logs, Belgium	700	500	23.78	10.85 ± 0.27	89.15 ± 0.27	8.37 ± 1.78	9.52 ± 0.11	620 ± 49
WRB 550	Winter rye straw, Belgium	550	225	20.76	21.93 ± 1.04	78.07 ± 1.04	15.92 ± 1.28	10.10 ± 0.62	6330 ± 42
SLP 550	*Salix purpurea,* Italy	550	350	35.79	27.25 ± 0.39	72.75 ± 0.39	22.21 ± 0.62	10.15 ± 0.49	1678 ± 177
PAT 550	*Paulonia tomentosa,* Italy	550	350	34.40	29.98 ± 2.99	70.02 ± 2.99	21.12 ± 0.21	10.55 ± 1.09	3150 ± 170
FWD 550	Food waste digestate, UK	550	150	28.79	30.07 ± 0.99	69.93 ± 0.99	26.85 ± 0.58	8.88 ± 0.24	5580 ± 438

*not available, see section 2.2.4.2

3.3.2 Nutrients in biochar

In Table 3.2, elements are depicted for which statistically significant changes in mass balance from feedstock to biochar were detected. On average, around 15% and 10% of the macronutrients Ca and Mg were lost during pyrolysis in all biochars (Mg: $p<0.001$, Ca: $p=0.009$) and for the biochars produced ≥700°C around 22.5% of Ca ($p=0.042$) and 15.4% of Mg (non-significant) was lost, respectively. The loss of macronutrients at typical pyrolysis HTTs indicates that lower temperatures are advisable if greater nutrient retention is desired. However, most importantly, P and K were not lost despite previous reports of K being volatilised during pyrolysis to a higher extent than Ca and Mg (Okuno et al., 2005). In this data set, the K concentration even increased significantly ($p=0.041$), however, by 14.1% only (biochars from 8 feedstocks gave mass balances between +20% and -20% (Digital Appendix Table 1), only the two feedstocks pyrolysed at five temperatures had consistently positive mass balances).

The total concentrations of the four macronutrients, P, K, Mg and Ca, are plotted in Figure 3.2 (micronutrient concentrations can be found in Table 3.3). To provide baseline values, besides the biochars from marginal biomass feedstocks investigated in this study, ten "UKBRC standard biochars" from five conventional, uncontaminated feedstocks pyrolysed at 550°C and 700°C were included. The wood biochars (SWP and DW), as expected, had the lowest concentrations of the four reported macronutrients. The elemental content increased with pyrolysis temperature as proportionally more organic material volatilised, while most of the minerals remained in the char. WHI 550 contained a very high concentration of Mg, and while the concentration of Ca was in the same range as for most of the other biochars, P and K concentrations were also elevated. WRB 550 showed comparably high concentrations of P and K but the concentrations of Ca and Mg were in a similar range to most of the other biochars. PAT 550, FWD 550, SLP 550 and WHI 550 all contained levels of macronutrients higher than most of the other biochar samples. In particular, FWD 550 had highly elevated concentrations of P and Ca compared to the other biochars. The total levels of macronutrients in this char were: P 2.0% (w/w), K 2.3%, Ca 9.2% and Mg 0.4%. It has already been shown in early biochar studies that biochar can directly provide nutrients to plants, which can lead to crop yield

increases (Lehmann et al., 2003). The key, however, is nutrient availability, and total concentration can only give an indication of this, if at all. Studies showed that biochar has the potential for suppling high amounts of available K to plants, as well as Ca, Mg and micronutrients (Lehmann et al., 2003; Major et al., 2010; Xu et al., 2013). Phosphorus, on the other hand, is reported to be present in available form in slaughterhouse waste, cattle manure and AD sewage sludge biochars and it has been proposed that there is potential for P-rich biochars to act as slow-release fertilisers (Wang et al., 2014; Zwetsloot et al., 2014). These findings suggests that nutrients-rich biochars, like FWD 550, can be used as fertilisers on arable soils, as long as PTE levels are not of concern. This is discussed in detail in Chapter 4.

Table 3.2: Relative changes of elemental content from feedstock to biochar after pyrolysis (%). Geometric means and geometric standard deviations (SD) were calculated for biochars produced at all temperatures and only the ones produced ≥700°C. One sample, two tailed t-tests were performed to identify significant changes of the ln transformed data (p<0.05). Only the elements that showed significant changes are depicted here. nt, not tested; n, number of biochars.

			Al	Ca	Cr	Fe	K	Mg	Ni	Zn
all biochars	geometric mean	%	-35.0	-14.1	82.8	207.2	14.1	-9.7	226.0	-13.7
	- geometric SD	%	32.3	16.1	108.5	197.0	23.8	12.5	227.7	21.3
	+ geometric SD	%	64.2	19.9	266.9	549.4	30.0	14.5	754.9	28.4
	n		17	17	17	17	17	17	17	17
	p-value		0.013*	0.009*	0.012*	0.000*	0.041*	0.000*'	0.001*	0.056
biochars produced ≥700°C	geometric mean	%	-53.2	-22.5	82.6	161.0	19.5	-15.4	397.5	-37.5
	- geometric SD	%	15.0	6.9	98.9	110.6	35.9	7.6	393.0	9.7
	+ geometric SD	%	22.1	7.5	215.9	192.1	51.3	8.3	1870.3	11.4
	n		3	3	3	3	3	3	3	3
	p-value		0.077	0.042*	0.313	0.095	0.478	0.091	nt	0.040*

* significantly different (p<0.05)

' exponentially back-transformed before statistically analysed

Table 3.3: Total plant micronutrient (Mn, B, Fe) concentrations (mg kg^{-1}) in nineteen biochars and their ten feedstocks with averages and standard deviations.

		Mn	B	Fe
DW	mg kg^{-1}	82.60 ± 2.82	< 0.36	304.82 ± 36.27
DW 350	mg kg^{-1}	234.74 ± 18.49	15.65 ± 5.26	1167.99 ± 101.40
DW 450	mg kg^{-1}	274.44 ± 14.04	17.82 ± 8.59	1730.56 ± 290.66
DW 550	mg kg^{-1}	308.73 ± 20.03	19.00 ± 6.04	2150.04 ± 306.12
DW 650	mg kg^{-1}	360.66 ± 38.81	17.21 ± 0.30	2686.24 ± 699.55
DW 750	mg kg^{-1}	386.90 ± 21.95	16.97 ± 0.27	2260.76 ± 318.36
ADX	mg kg^{-1}	6.60 ± 0.88	< 0.36	76.97 ± 4.46
ADX 350	mg kg^{-1}	34.80 ± 6.23	6.48 ± 4.18	2733.32 ± 249.75
ADX 450	mg kg^{-1}	23.92 ± 3.54	2.55 ± 2.94	1154.50 ± 275.16
ADX 550	mg kg^{-1}	28.76 ± 4.85	3.31 ± 2.83	1615.50 ± 123.36
ADX 650	mg kg^{-1}	32.86 ± 3.12	4.57 ± 1.93	2177.96 ± 761.06
ADX 750	mg kg^{-1}	26.17 ± 5.23	1.98 ± 2.88	904.80 ± 215.72
SBI	mg kg^{-1}	15.59 ± 2.13	< 0.36	365.30 ± 33.06
SBI 550	mg kg^{-1}	122.44 ± 10.62	15.71 ± 5.01	5967.62 ± 2388.56
WHI	mg kg^{-1}	231.55 ± 21.15	42.71 ± 0.23	15391.10 ± 1395.12
WHI 550	mg kg^{-1}	371.27 ± 58.98	82.94 ± 11.22	23957.84 ± 6443.47
WSI	mg kg^{-1}	18.62 ± 4.59	2.53 ± 0.45	970.30 ± 252.90
WSI 550	mg kg^{-1}	105.68 ± 12.61	27.72 ± 2.03	4550.54 ± 748.52
WLB	mg kg^{-1}	15.41 ± 0.55	8.83 ± 1.21	121.19 ± 6.64
WLB 550	mg kg^{-1}	37.30 ± 1.97	29.82 ± 2.24	1033.93 ± 209.92
WLB 700	mg kg^{-1}	52.50 ± 2.63	40.52 ± 4.32	2269.32 ± 199.36
WRB	mg kg^{-1}	28.66 ± 0.33	7.13 ± 4.20	394.55 ± 13.46
WRB 550	mg kg^{-1}	108.56 ± 2.89	17.95 ± 3.73	2676.68 ± 338.39
SLP	mg kg^{-1}	57.26 ± 1.63	42.67 ± 3.26	117.45 ± 6.27
SLP 550	mg kg^{-1}	237.19 ± 5.99	103.47 ± 10.98	14183.85 ± 1089.12
PAT	mg kg^{-1}	42.48 ± 28.50	22.98 ± 3.17	674.23 ± 436.95
PAT 550	mg kg^{-1}	142.28 ± 7.17	107.87 ± 7.59	10099.77 ± 68.40
FWD	mg kg^{-1}	50.97 ± 4.00	26.11 ± 10.70	1549.28 ± 632.03
FWD 550	mg kg^{-1}	184.67 ± 18.09	42.70 ± 1.01	6820.38 ± 469.58

Table 3.4: Potentially toxic element (PTE) concentrations (mg kg^{-1}) of nineteen biochars and their ten feedstocks with averages and standard deviations.

		As	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb	Zn
DW	mg kg^{-1}	< 0.72	< 0.04	0.27±0.18	15.96±8.33	10.36±6.49	< 0.23	< 0.21	1.69±0.94	35.25±29.30	40.29±3.96
DW 350	mg kg^{-1}	< 0.72	0.50±0.46	0.51±0.11	35.86±5.12	34.70±19.62	< 0.23	0.28±0.31	10.18±1.03	48.63±20.46	117.69±15.78
DW 450	mg kg^{-1}	< 0.72	0.22±0.19	1.19±0.97	47.44±8.90	34.71±4.57	< 0.23	< 0.21	8.01±0.48	62.15±12.37	150.15±14.89
DW 550	mg kg^{-1}	< 0.72	0.19±0.18	0.78±0.13	55.92±9.18	35.68±4.18	< 0.23	< 0.21	12.62±3.92	66.50±9.80	167.30±20.34
DW 650	mg kg^{-1}	< 0.72	0.33±0.36	1.02±0.12	94.54±4.99	46.38±2.65	< 0.23	< 0.21	38.48±7.92	149.56±123.82	236.84±136.75
DW 750	mg kg^{-1}	< 0.72	0.12±0.11	2.08±2.18	82.16±15.61	53.16±10.35	< 0.23	< 0.21	16.62±1.30	35.71±8.15	105.91±9.63
ADX	mg kg^{-1}	< 0.72	0.05±0.05	< 0.08	< 0.49	1.58±0.70	< 0.23	< 0.21	0.47±0.25	< 0.74	11.87±3.97
ADX 350	mg kg^{-1}	< 0.72	0.92±0.24	0.25±0.04	6.08±3.91	6.72±0.95	< 0.23	0.56±0.61	8.33±2.37	1.43±2.47	42.02±8.11
ADX 450	mg kg^{-1}	< 0.72	0.11±0.02	0.16±0.04	2.31±2.74	5.89±0.78	< 0.23	0.28±0.49	3.39±0.92	37.70±62.57	38.16±4.36
ADX 550	mg kg^{-1}	< 0.72	0.98±0.12	0.21±0.04	5.67±2.83	6.54±0.66	< 0.23	0.58±0.84	7.06±1.07	5.30±9.18	40.84±4.40
ADX 650	mg kg^{-1}	< 0.72	2.70±0.18	0.28±0.06	8.47±2.08	7.73±0.49	< 0.23	1.40±0.79	9.35±0.43	1.73±2.99	48.85±4.34
ADX 750	mg kg^{-1}	< 0.72	2.64±0.55	0.16±0.05	2.85±2.09	7.46±1.14	< 0.23	0.54±0.47	4.22±0.89	27.22±42.73	37.89±5.64
SBI	mg kg^{-1}	< 0.72	< 0.04	0.37±0.32	4.28±3.74	2.14±0.34	< 0.23	< 0.21	3.26±0.49	19.37±33.55	8.19±2.45
SBI 550	mg kg^{-1}	< 0.72	0.47±0.42	0.90±0.28	24.21±7.42	13.98±6.59	< 0.23	0.92±0.13	37.89±13.74	4.73±1.94	39.77±9.21
WHI	mg kg^{-1}	1.63±0.12	1.24±0.86	9.81±5.15	173.62±29.43	105.57±8.08	< 0.23	6.07±0.37	88.81±1.48	100.86±15.27	262.06±19.83
WHI 550	mg kg^{-1}	< 0.72	0.45±0.39	7.44±0.30	176.42±18.81	118.85±7.41	< 0.23	7.70±0.44	110.59±4.56	215.10±154.13	392.82±35.25
WSI	mg kg^{-1}	< 0.72	< 0.04	0.35±0.05	14.35±12.43	2.17±0.17	< 0.23	2.55±0.21	1.41±0.72	< 0.74	2.65±1.25
WSI 550	mg kg^{-1}	< 0.72	0.05±0.05	1.17±0.20	17.83±13.80	16.55±1.54	< 0.23	8.51±0.35	26.32±1.99	5.98±2.66	62.00±9.03
WLB	mg kg^{-1}	< 0.72	11.46±0.07	0.09±0.02	< 0.49	6.91±0.33	< 0.23	< 0.21	0.36±0.22	16.27±2.15	513.64±64.20
WLB 550	mg kg^{-1}	< 0.72	8.29±0.50	0.29±0.11	3.98±3.56	16.46±0.54	< 0.23	1.65±2.64	16.73±4.42	42.57±7.65	1230.45±98.92
WLB 700	mg kg^{-1}	< 0.72	7.32±0.72	0.48±0.01	9.13±2.25	19.95±0.81	< 0.23	0.31±0.54	45.96±4.52	45.87±17.94	1375.12±30.58
WRB	mg kg^{-1}	< 0.72	2.70±0.03	0.16±0.02	1.60±2.77	9.07±0.30	< 0.23	1.94±0.22	0.48±0.13	24.99±17.78	295.75±33.90
WRB 550	mg kg^{-1}	< 0.72	6.82±0.27	0.42±0.02	6.98±2.90	25.72±1.14	< 0.23	9.48±0.81	14.51±2.62	21.95±5.22	810.89±25.73
SLP	mg kg^{-1}	< 0.72	48.86±3.60	0.57±0.03	0.83±1.44	8.14±0.36	< 0.23	0.52±0.90	0.78±0.10	20.71±27.73	629.87±43.78
SLP 550	mg kg^{-1}	< 0.72	22.00±0.75	2.19±0.09	13.13±3.60	52.22±1.11	< 0.23	7.85±0.54	18.89±2.28	42.03±5.68	1404.33±33.33
PAT	mg kg^{-1}	1.22±0.23	6.71±1.21	0.23±0.05	< 0.49	13.39±2.57	< 0.23	< 0.21	1.07±0.08	29.04±32.54	208.63±33.52
PAT 550	mg kg^{-1}	1.96±0.81	19.13±1.27	1.36±0.08	17.68±3.40	47.71±1.37	< 0.23	5.48±0.23	24.08±3.17	48.06±17.14	544.68±4.39
FWD	mg kg^{-1}	< 0.72	< 0.04	0.49±0.09	6.34±4.22	14.38±0.98	< 0.23	0.51±0.58	15.49±2.35	35.61±42.09	56.41±2.27
FWD 550	mg kg^{-1}	< 0.72	< 0.04	2.76±1.54	25.05±6.33	45.71±2.88	< 0.23	1.15±0.01	10.21±0.74	15.12±4.06	218.77±17.63

Table 3.5: Guideline and legislation threshold values for PTEs.

		As			Cd			Co			Cr			Cu		
IBI biochar guideline (2011)	mg kg^{-1}	12	-	100	1.4	-	39	40	-	150	64	-	1200	63	-	1500
EBC basic grade biochar [+]	mg kg^{-1}				1.5						100			100		
EBC premium grade biochar °	mg kg^{-1}				1						80			100		
compost (EEC No 2092/91*)	mg kg^{-1}				0.7						70			70		
sewage sludge (86/278/EEC [#])	mg kg^{-1}				20	-	40							1000	-	1750

		Hg			Mo			Ni			Pb			Zn		
IBI biochar guideline (2011)	mg kg^{-1}	1	-	17	5	-	20	47	-	600	70	-	500	200	-	7000
EBC basic grade biochar [+]	mg kg^{-1}	1						50			150			400		
EBC premium grade biochar °	mg kg^{-1}	1						30			120			400		
compost (EEC No 2092/91*)	mg kg^{-1}	0.4						25			45			200		
sewage sludge (86/278/EEC [#])	mg kg^{-1}	1.6	-	25				300	-	400	750	-	1200	2500	-	4000

[+] (EBC, 2012a) = German Biowaste Ordinance, 1998 (update 2013), § 4, valid for all biological residues/wastes that are supposed to be applied to soil

° (EBC, 2012a) = Swiss Chemical Risk Reduction Ordinance, 2005 (update 2014), appendix 2.6, organic fertilisers (chromium threshold only in EBC (2012))

* EU Council Regulation (EEC) No 2092/91, 1991 (update 2007), ANNEX II Part A, on organic production of agricultural products; agricultural products and foodstuffs; composted or fermented household wastes

[#] EU Council Directive 86/278/EEC, 1986, ANNEX 1 B, on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture

3.3.3 PTEs in biochar

For comparison of PTE levels in biochar (Table 3.4), legislation and guideline values were used. Here the values reported are from the "German Biowaste Ordinance" (German Biowaste Ordinance, 1998), the "Swiss Chemical Risk Reduction Act" (Swiss Chemical Risk Reduction Ordinance, 2005) adapted as the "EBCC basic" and the "EBCC premium" grade biochar limits (EBC, 2012a), respectively, the European compost and sewage sludge legislation (EU Council Regulation 2092/91/ECC, 1991) and the International Biochar Initiative guidelines (originated from legislation from Australia, Canada, EU, UK and the USA) (summarised in Table 3.5).

Arsenic and Hg concentrations in feedstocks and biochars were mostly below detection limits and did not exceed any of the thresholds (Table 3.4, Table 3.5). Only in WHI and PAT feedstocks and biochar from PAT could As be detected at all (1.63 mg kg^{-1}, 1.22 mg kg^{-1} and 1.96 mg kg^{-1}, respectively). In both biochars, the As concentration was lower than theoretically expected, since enrichment through vaporisation of organic matter should result in higher concentrations of minerals than in the feedstock (WHI biochar below detection limit). This finding shows that As was lost during pyrolysis which can be attributed to its low boiling point of 613°C, and has been observed in other studies (Bridle et al., 1990; Helsen et al., 1997; Kim et al., 2012).

Although Al is not mentioned in any of the reported legislation and regulations, Al toxicity can be a major problem in acidic soils (Delhaize and Ryan, 1995). In this study, the Al content decreased on average from feedstock to biochar significantly by 35.0% ($p=0.013$) for all of the biochars investigated in this study (Table 3.2). A non-significant reduction of 53.2% was observed for the biochars produced at ≥700°C ($p=0.077$) (average of only three biochars) which is confirmed by findings by Chiang et al. (2014). Although Zn was reduced by 37.5% ($p=0.040$) for the three biochars produced at ≥700°C (Table 3.2) which is similar to findings by Chiang et al. (2014) and Koppolu et al. (2003), Zn threshold values were still exceeded (Table 3.4, Table 3.5). However, biochars with similar Zn levels from feedstocks also grown on contaminated land have previously shown to result in positive effects on plant shoots, leading the authors to conclude that the increased Zn levels in shoots were beneficial for growth (Evangelou et al., 2014). Besides virgin feedstocks, non-virgin feedstock,

e.g. sewage sludge, has been shown to contain Zn contents similar to those in this study (1256 mg kg^{-1}) (Srinivasan et al., 2015). Threshold values for Mo exist only in Canada and the US; none are reported in the various European legislation used for comparison in this study. Still, five of the investigated biochars exceeded the reported limit values for Mo (Table 3.4). Furthermore, several biochars surpass the threshold values for Cd, including the biochars produced from feedstocks from the heavily contaminated sites in Italy and Belgium (Table 3.4). Overall, no significant change in Cd mass balance was observed on average for all biochars (data not shown), although Cd levels in four biochars were reduced by more than 80% compared to the feedstock (Digital Appendix Table 1) and the fact that volatilisation of Cd from pyrolysis solids is frequently reported in literature, specifically at temperatures above 600°C (Chiang et al., 2014; Evangelou et al., 2014; Kistler et al., 1987; Luo et al., 2014). Yet, for example in Liu et al. (2014), Cd remained in the char to the highest extent in comparison with various other PTEs (Cu, Pb, Zn, Cr). In general, volatilisation of elements is not simply a function of temperature but differs according to elemental concentrations in the feedstock and is influenced by interactions with the other inorganic and organic components, which explains the high fluctuations of the same elements in different feedstocks in this study, as for example shown for Cd (Digital Appendix Table 1) (Cuypers and Helsen, 2011; Okuno et al., 2005; Olsson et al., 1997; Van Wesenbeeck et al., 2014).

Ni and Cr have also been reported to vaporise during pyrolysis (Kistler et al., 1987; Koppolu et al., 2003). Interestingly however, for these elements and Fe, even significant increases have been observed (Table 3.2). Cr increased by 82.8%, Fe by 207.2% and Ni even by 226.0% on average for all biochars, which indicates contamination during pyrolysis. This can be a result of erosion of small amounts of metal from reactor walls by feedstock and biochar in the continuous pyrolysis unit used in this study. The friction caused by the pressure the moving furnace screw applied onto the material in the furnace most likely eroded small steel particles which contaminated the biochar. As the reactor is made of a high grade stainless steel 253MA (contains 21% chromium and 11% nickel), such a contamination path is probable. It has already been indicated in the EBC quality guidelines that there is potential for this to happen, specifically in new pyrolysis units (EBC, 2012a).

Overall, this is an important point to consider as, for example, DW 650 and 750 would not be allowed to be applied on Swiss soils due only to the exceedance of Cr limit values and SBI 550 due only to Ni exceedance (EBC premium grade limit, Table 3.4).

To further elucidate whether the Ni and Cr exceedances were only attributed to erosion of Ni and Cr from steel in the pyrolysis unit, in contrast to percentage change as above, additional calculations were undertaken. The change in concentration of elements after pyrolysis compared to the expected concentration with the scenario of 100% elemental retention in mg kg^{-1} was calculated (Digital Appendix Table 1). This was done specifically to investigate how much Ni and Cr in the biochars could be attributed to contamination with these elements during the pyrolysis process. The deviation in concentrations expected (100% elemental retention) to actual concentrations for Ni were up to 45 mg kg^{-1} and up to 16-22 mg kg^{-1} for Cr. Considering the legislation/guideline values for Ni of 30-50 mg kg^{-1} and for Cr of 80-100 mg kg^{-1} (Table 3.4), this shows Ni and Cr enrichment from steel during pyrolysis can cause exceedance of threshold values. To overcome this, a rotary drum could be used to replace the furnace screw (which puts a lot of pressure on the furnace metal), or the Ni-Cr steel of the screw could be replaced by a different steel. However, these results show that the exceedance of guideline values (e.g. SBI 550) can be avoided by using a different pyrolysis unit and the feedstock itself is not a concern regarding these PTEs.

In the nineteen biochars investigated here, the PTEs Zn and Cd in particular cause problems with exceedance of threshold values, The highest Zn and Cd concentrations exceed the lowest guideline values (compost guideline) by 7-fold and 31-fold, respectively (Table 3.4, Table 3.5). The feedstocks resulting in biochar that caused exceedances here originated from soil that is known for its contamination with these elements. Pb, Cu, As and Hg did not exceed biochar guideline values despite the fact that some of the land the plants were grown exceed soil guideline values (Table 2.1). A fraction of As, Hg, Zn and Al from feedstocks were lost from pyrolysis solids, which can be beneficial for biochar soil application, yet, it must be ensured that these PTEs are not released into the environment as vapours during pyrolysis. In addition

to Zn and Cd, concentrations of Ni and Cr in some biochars exceed legislation values which can be traced back to the biochar production process itself.

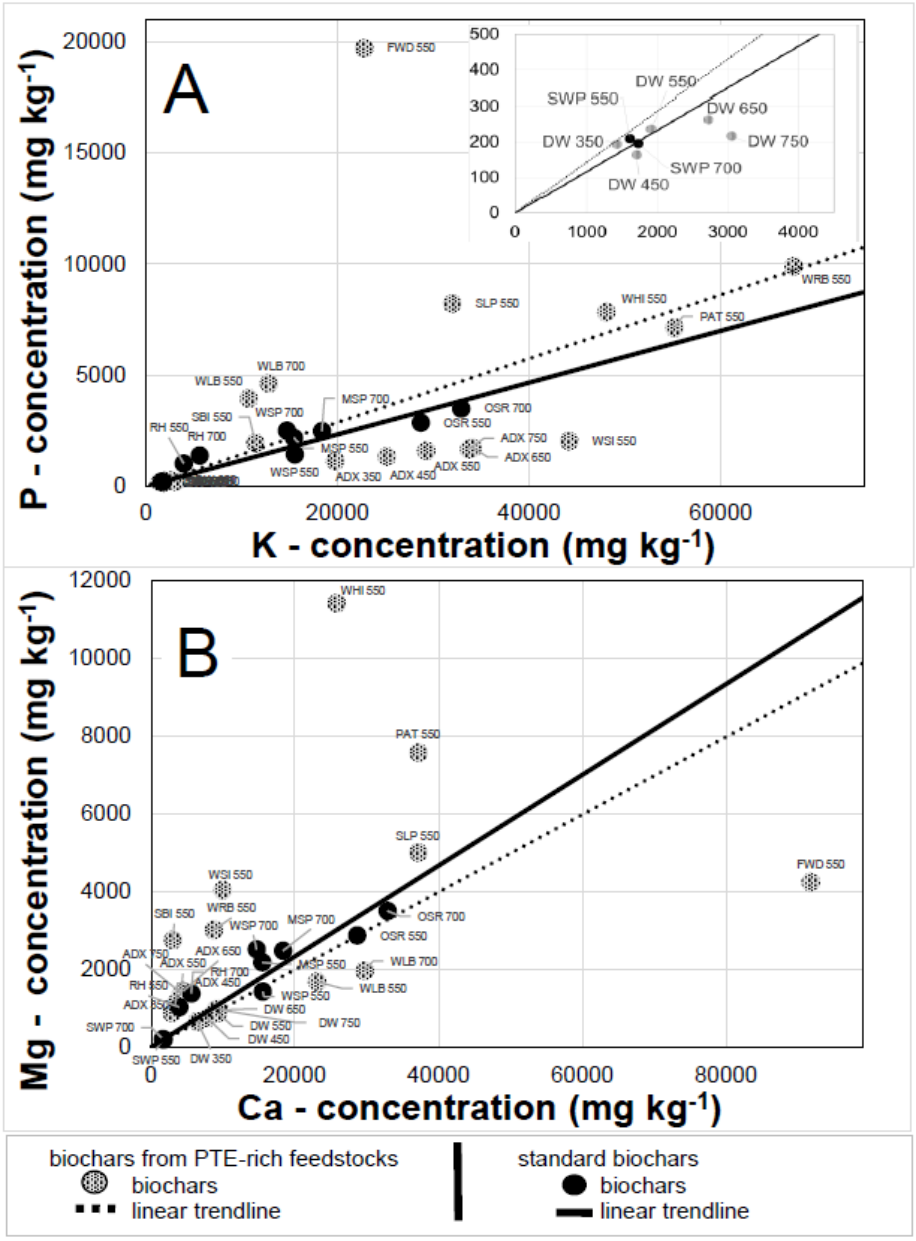


Figure 3.2: Total concentrations (mg kg^{-1}) of macronutrients P and K (upper figure, A) and Mg and Ca (lower figure, B) in nineteen biochars. In addition, ten UKBRC standard biochars are plotted for comparison. Top figure in A shows the same figure in smaller scale. The abbreviations symbolise the different biochars in the way feedstock – pyrolysis temperature.

3.3.4 Effect of HTT on concentration of PTEs in biochar

One virgin feedstock, *A. donax* (plant biomass from PTE contaminated land), and one non-virgin feedstock, demolition wood, were pyrolysed at five HTTs in the range 350-750°C. As discussed in 3.3.1, increasing pyrolysis temperatures decreased the volatile matter content of the biochars and increased the fixed carbon and ash content (Table 3.1). Volatile organics vaporised, while most of the ash/PTEs remained. This led to enrichment of PTEs in the biochar and a higher concentration of PTEs compared to the feedstock (Table 3.4). However, some PTEs partially evaporated at the applied temperatures, reducing their concentration, e.g. Zn for DW and ADX (Table 3.4). Elements such as Cu did not evaporate and, due to this enrichment, the biochars produced at highest pyrolysis temperatures had the highest Cu concentrations (ADX 650 and 750 not significantly different). Consequently, the effect of HTT on the concentration of PTEs in biochar is not only dependent on the element under investigation but also on the feedstock matrix, which, as discussed in 3.3.3, affects the evaporation behaviour of the elements. However, the parameter which influences the concentration of PTEs in biochar most is their concentration in the initial material. Thus, appropriate selection of feedstock is the most crucial parameter for production of biochar with low total concentrations of PTEs (Kookana et al., 2011).

3.3.5 Environmental implications of marginal biomass-derived biochar

3.3.5.1 Biochars unsuitable for soil application

Although water hyacinth biochar (WHI 550) contained high concentrations of nutrients, it also contained a very high ash content which could lead to salinity-related toxic effects. Despite having lost large amounts of PTEs during pyrolysis (Digital Appendix Table 1), the concentrations of Cr, Cu, Ni, Pb and Zn greatly exceeded threshold values (Table 3.4, Table 3.5). It is known that water hyacinth can take up and accumulate large amounts of toxic substances from water, making it interesting for waste water treatment (Mehra et al., 2000), however, this is a clear disadvantage for its use in biochar production.

Willow logs, winter rye, *Salix purpurea* and *Paulonia tomentosa* all originated from contaminated sites where soil PTE concentrations exceed legislation values (Campine region in Belgium, region of an old Zn smelter in Italy) (Table 2.1) (EU

Council Directive 86/278/EEC, 1986; German Federal Soil Protection and Contaminated Sites Ordinance, 1999). The biochars produced from these feedstocks all exceeded Cd and Zn legislation values and the IBI guideline values for Mo. Again, the ability of willow to accumulate Cd is useful for phytotextraction but here it shows that, when grown on Cd contaminated land, willow is unsuitable to use for biochar production for soil application (Van Slycken et al., 2013).

From this it can be concluded that it is not advisable to use plants grown on soil that already exceeds legislation values or plants from polluted waters for conversion into biochar used for soil amendment, although exceedance of biochar threshold values does not always occur. Specifically, the use of plant species capable of accumulating high amounts of PTEs as feedstock for biochar is problematic. Instead, as described in Evangelou et al. (2012) and Witters et al. (2012), since plants grown on heavily contaminated land are not competing with crops for human consumption they have high potential to be used for sustainable energy production.

3.3.5.2 Biochars with little concern for application

The biochars from wheat straw (WSI) grown at a site close to a thermal power plant (India), and sugarcane bagasse (SBI) that grew close to the highly polluted river of Yamuna (India) in PTE contaminated soil (Table 2.1) comply with regulations and have mostly moderate levels of nutrients along with medium to high pHs. The biochars from the woody materials, demolition wood and *A. donax*, showed rather low concentrations of macronutrients and no relevant exceedances of threshold values, despite *A. donax* having grown on a metal contaminated site with PTE concentrations close to PTE threshold values for soil (Table 2.1).

Overall, as also concluded in Nzihou and Stanmore (2013) for combustion ash from similar materials, biochars from feedstocks grown on less heavily contaminated land and demolition wood biochars seem safe to apply on soil. Therefore, the high temperature biochars from these feedstocks can be suitable for increasing soil pH when applied in high doses (Biederman and Harpole, 2013), for immobilising metals (Uchimiya et al., 2010) and for carbon sequestration due to their recalcitrance indicated by their high fixed carbon contents (which can be used as a proxy for carbon stability (Crombie et al., 2013)). Consequently, these biochars could be used

for remediation of contaminated land (e.g. the land the feedstocks were sourced from) by immobilising PTEs, improving soil properties and subsequently increasing plant yields (Buss et al., 2012).

3.3.5.3 Biochar with high potential for soil application

Anaerobically digested food waste biochar (FWD 550) not only complied with biochar guideline values for heavy metal content in biochar, it also showed high concentrations of all the four macronutrients measured. This is a significant finding as around 16 million tonnes of food waste are produced every year in the UK alone (DEFRA, 2011). However, it is important to keep in mind that the composition of food waste can differ widely. Nevertheless, this makes food waste (AD) a very suitable marginal feedstock that is available in large quantities for the production of biochar and subsequent application on soil, as long as the nutrients in the biochar are plant available which is discussed in Chapter 4.

3.4 Conclusions

In this study, ten marginal biomass-derived feedstocks from either contaminated land/waters or non-virgin biomass were investigated for their suitability for biochar production. First, it was shown that at typical pyrolysis temperatures some PTEs (e.g. As, Al, Zn) and nutrients partially evaporated from the mineral-rich materials. Using higher pyrolysis temperatures was not optimal as the macronutrients Mg and Ca were increasingly lost. Furthermore, it was shown that the long-standing assumption that contamination issues in biochar were either attributed to organic compounds formed during pyrolysis or inorganic PTEs originating in the feedstock is not always valid. Here, it was shown that another source of contaminants can be present, namely contamination by Ni and Cr from high grade steel used in some high-temperature reactors. This finding has important consequences for the design and operation of industrial biochar production units. Overall, feedstocks grown on industrial waste sites and in heavily PTE contaminated water bodies were found to be unsuitable for biochar production due to exceedance of threshold values for total PTE concentrations. Biochars produced from biomass grown in less contaminated soils and two biologically/chemically converted materials did comply with regulations and appear to be safe to apply to soils. Finally, food waste AD was found to be the best marginal feedstock for biochar production tested here due to very high concentrations of plant macronutrients, making the resulting biochar a promising potential organic fertiliser. Yet, from this study it remains uncertain if these macronutrients are present in an available form and whether the biochars exceeding threshold values for total PTEs indeed pose a risk to plant growth. Both is investigated in the next chapter.

Chapter 4 Risks and benefits of marginal biomass-derived biochars for plant growth

The following chapter is based on the published article:

Buss, W., Graham, M.C., Shepherd, G.J., Mašek, O., 2016. Risks and benefits of marginal biomass-derived biochars for plant growth. Sci. Total Environ. 569-570. doi: 10.1016/j.scitotenv.2016.06.129

Journal impact factor (2014): 4.099

Number of citations (September 2016): 0

The candidate was solely responsible for data analysis and writing of the article and this chapter. Supervisors provided guidance and supervisors and co-authors contributed to the editing of the manuscript. The experimental work was performed by the candidate. The ICP-OES analysis was performed by the candidate with the assistance of Lorna Eades and Jessica Shepherd.

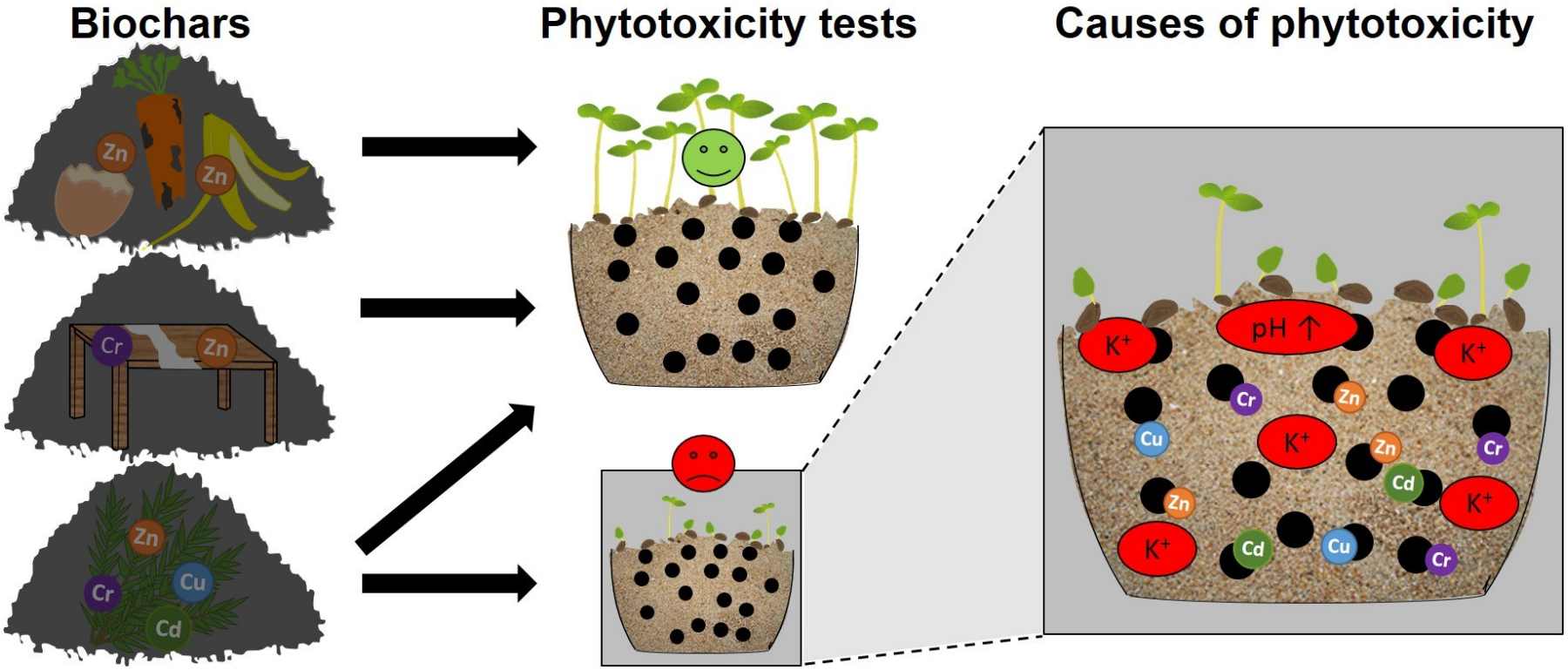


Figure 4.1: Graphical abstract of Chapter 4. Marginal biomass-derived biochars were tested in phytotoxicity tests (germination and early seedling growth assays). Most biochar did not result in any negative effects on cress seedlings. In the few biochars that did result in stunted plant growth, the inhibition were not related to high concentration of available potentially toxic elements, but to high pH and high available K^+ concentration of the biochars.

4.1 Introduction

Biochar can improve soil chemical properties (e.g. pH, CEC), soil biological properties (e.g. stimulate microbial growth) and soil physical properties (e.g. water holding capacity) (Lehmann and Joseph, 2015b) and in addition, supply nutrients directly to the soil (Ippolito et al., 2015). Consequently, among other things, biochar is being tested for plant growth promotion in agriculture, horticulture and viticulture. However, inhibiting effects caused by biochar could negate any positive effects and so biochar should not contain contaminants which pose a risk to plant growth.

The contaminants in biochar which have been reported to be present at sufficient concentrations to affect plant growth are: PAHs, VOCs and PTEs. These can originate from the feedstock (predominantly PTEs) and/or the production process itself (VOCs, PAHs and some metals) (Hale et al., 2012; Hilber et al., 2012; Spokas et al., 2011) (Chapter 3). While process conditions can be adjusted and pyrolysis units can be built to minimise contamination resulting from the production process (Hale et al., 2012) (Chapter 3), contaminants in the feedstock are source-dependent, and therefore, careful selection of biomass is necessary.

From an economic and sustainability perspective, the ideal feedstock for biochar production is biomass or organic waste that would otherwise be landfilled or incinerated (Shackley et al., 2011). However, these materials are likely to contain contaminants, e.g. originating from the soil or water bodies in which the biomass was grown or from direct anthropogenic influences (e.g. wood from demolition sites, sewage sludge and food waste). Such materials of limited economic value are henceforth referred to as ‘marginal biomass’. Biochars produced from marginal biomass containing organic contaminants, e.g. PAHs or dioxins, have been shown to pose a low risk as such contaminants tend to be largely destroyed or evaporated during pyrolysis (Wijesekara et al., 2007; Zielińska and Oleszczuk, 2015).

PTEs, on the other hand, mostly remain in the solids (feedstock/biochar) during biochar production and only a few are partially evaporated (Chapter 3). Consequently, guideline values for total concentrations of PTEs have been introduced and biochars can be tested for compliance against these guidelines (EBC, 2012b; International Biochar Initiative, 2011). However, when biochar is applied to a

soil or a plant growth medium, only a fraction of the PTEs (and nutrients) are present in forms which can be taken up by plants. This proportion is usually termed the 'bioavailable' fraction and, since it usually does not correlate with total elemental content (Ippolito et al., 2015), methods to assess the extent of PTE availability have been developed.

Numerous chemical extraction methods using a wide range of extractants including deionised (DI) water, salt solutions, complexing agents or weak acids have been used to approximate the bioavailable fraction of PTEs (and nutrients) in soils and biochar (Farrell et al., 2013; McLaughlin et al., 2000; Monter Roso et al., 1999; van Raij, 1998). BS ISO 19730:2008 (2008) describes soil extraction with 1 mol L^{-1} NH_4NO_3 for assessing the fraction of trace elements able to interact and affect crop growth and was used to establish German legislation threshold values for PTEs for protecting plant growth and crop quality (German Federal Soil Protection and Contaminated Sites Ordinance, 1999). In addition to extraction of PTEs in soil, the method has also been tested and recommended for extractable cationic nutrients (Schöning and Brümmer, 2008; Stuanes et al., 1984) and for extracting PTEs and nutrients in biochar/biochar-amended soils (Alling et al., 2014; Karer et al., 2015; Kim, 2015; Kloss et al., 2014b; Park et al., 2011). The proportion recovered by such extractants has been described in various ways, e.g. "easily soluble" (BS ISO 19730:2008, 2008), "readily soluble/available" (Gryschko et al., 2004), "mobile" (Schöning and Brümmer, 2008), "exchangeable" (Meers et al., 2007), "extractable" (Kim et al., 2015) or "available" (McLaughlin et al., 2000) fraction. In this study, the term 'available' will be used throughout.

Previous studies, determining the available concentration of PTEs in feedstocks and biochars, have revealed that the pyrolysis process itself can immobilise various PTEs already present in the feedstock; this resulted in pyrolysis being recommended for waste treatment prior to landfilling (Farrell et al., 2013; Hwang and Matsuto, 2008; Khanmohammadi et al., 2015; Liu et al., 2014; Meng et al., 2013). The immobilisation was reported to result from different binding of PTEs to the carbon lattice after pyrolysis and through increase in pH of the material when converted into biochar (Gu et al., 2013; Liu et al., 2014). Yet, it is still unclear if biochars resulting

from feedstocks significantly contaminated with PTEs are suitable for amendment of soil and growing media.

In Chapter 3, the total concentrations of nutrients and PTEs were analysed in nineteen marginal biomass-derived biochars and PTE concentrations were tested for compliance with threshold values for total PTEs. In the current chapter, cress germination and early seedling growth tests were conducted to assess the risk of PTEs in biochar for plant growth. Furthermore, available PTEs were determined using NH_4NO_3 and compared to German legislation threshold values. To complete the risk-benefit analysis of application of marginal biomass-derived biochar to soil and growing media, the availability of nutrients were determined to assess the potential fertiliser value. In addition, the effect of HTT and feedstock on percentage available of total PTEs and nutrients was examined. Ultimately, the available elemental content of the biochars (and biochar pH and EC values) were correlated with phytotoxic effects with the aim to identify the parameter with the greatest potential to affect plant growth adversely.

4.2 Materials and methods

4.2.1 Biochars

Nineteen biochars produced from ten marginal biomass feedstocks were used for this study. All these materials were described in detail in section 2.2.4 and an overview can be found in Table 3.1.

4.2.2 Ammonium nitrate (NH_4NO_3)-extractions

The extractions and analysis are described in section 2.4 and were performed according to BS ISO 19730:2008 (2008).

The results were expressed as the mass of available elemental content relative to the mass of solid biochar (i.e. mg kg^{-1} or g kg^{-1} for elements present at high concentration). The data were also converted to percentage availability using the total elemental concentration data for the same biochar samples (Chapter 3). Details on the calculation can be found in section 2.4.5.

4.2.3 Germination tests

Biochar phytotoxicity screening tests were performed as described in section 2.6 using 7-day 'all exposure routes' cress (*Lepidium sativum*) seed germination tests. Each biochar sample was ground and incorporated in sterilised sand (sterilisation at 500°C for ~2 h) to give a 5% w/w biochar-sand mixture. The control was sterilised sand only. Cress seeds were either in direct contact with the biochar-sand mixture or only exposed to the solution leaching through the mixture (set-up done in triplicates). The effect of volatile organic compounds (VOCs) from the biochars on seedling growth was not tested here as previous work showed no phytotoxic effects even for heavily VOC-contaminated biochars (Chapter 7).

To assess the effect of PTE-rich biochars in the germination tests, following evaluations scheme was used. Seedling growth is reported to be more sensitive to PTEs than seed germination which can lead to seeds with emerged radicle (root) but no growth of the embryo (Li et al., 2005) and consequently, an intermediate stage between germinated seeds and readily developed seedlings was distinguished here, termed 'stunted seedlings'. 'Stunted seedlings' were defined as seeds with visible roots but a root length of <5 mm (which was also used as the limit of quantification (LOQ)); this has also been used by the US EPA (1996) as the threshold for "active

growth by an embryo". For all seeds with root length >5 mm (here called 'healthy, non-stunted seedlings'), shoots and roots were measured using image analysis (ImageJ) and the difference compared to the sand-only control was calculated. Germination rate and root growth was summarised in one parameter by calculating the Munoo-Liisa-Vitality index (MLV-index) which gives the percentage difference of the parameters to performance of the seedlings in the sand only control (European Standard, 2011) (for seedlings with roots <LOQ, 0.5 * LOQ was used).

4.2.4 Removal of available elements from biochar samples prior to germination tests

After the phytotoxicity screening was performed, nine biochars were selected for further testing. These included biochars which caused growth stimulation, growth suppression and no effects. The biochars were extracted with 1 mol L^{-1} NH_4NO_3 as described in section 2.4.2. To remove excess salt solution, this process was followed by addition of 25 mL of DI water and shaking at 150 rpm for 2 h. Filtration was achieved using the protocol described in section 2.4.2 and the biochar samples were pre-dried in an oven overnight at 50°C. The treated biochars were again tested in germination tests as described in section 4.2.3 to predict the effect that could be expected from the biochars after they have been exposed to the environment, e.g. after extractable nutrients and PTEs were removed by natural leaching processes shortly after biochar application.

4.2.5 Statistics

Available concentrations of nineteen elements (if <LOD, 0.5 * LOD was used), pH and EC (pH and EC data both from Chapter 3) were correlated with percentage of healthy, non-stunted seedlings using Pearson correlation (r) in R studio (Version 0.99.484, https://www.rstudio.com/) and regression was performed using the least square method (R^2) in excel.. P-values were calculated and stated as following: p <0.05 are indicated as *, p <0.01 as ** and p-values <0.001 as ***.

4.3 Results and discussion

In this study, the availability of nineteen elements (PTEs and nutrients) in nineteen biochars was determined using 1 mol L^{-1} NH_4NO_3 -extractions followed by elemental analyses. The amount of an element extracted by NH_4NO_3 will be referred to as 'available concentration' when expressed on biochar mass basis (mg kg^{-1}, mg g^{-1}) (Table 4.1) or as 'percentage available' (wt%) when expressed relative to the total concentration of the given element present in each biochar sample.

Table 4.1: NH_4NO_3-extractable (available) PTE concentrations of nineteen biochars (mg kg^{-1}) as average and standard deviation (n=3).

		Al	As	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb	Se	Zn
DW 350	mg kg^{-1}	< 0.11	< 0.10	< 0.16	< 0.01	0.09±0.05	0.12±0.02	< 0.02	< 0.06	0.02±0.01	< 0.04	< 0.23	2.01±0.16
DW 450	mg kg^{-1}	< 0.11	< 0.10	< 0.16	< 0.01	0.11±0.05	0.10±0.05	< 0.02	< 0.06	< 0.01	< 0.04	< 0.23	0.50±0.04
DW 550	mg kg^{-1}	< 0.11	< 0.10	< 0.16	< 0.01	0.10±0.03	0.15±0.06	< 0.02	< 0.06	0.06±0.06	< 0.04	< 0.23	1.16±0.11
DW 650	mg kg^{-1}	< 0.11	< 0.10	< 0.16	< 0.01	0.14±0.01	0.54±0.08	< 0.02	< 0.06	0.22±0.02	< 0.04	< 0.23	1.95±0.16
DW 750	mg kg^{-1}	2.60±0.45	< 0.10	< 0.16	< 0.01	0.52±0.24	1.93±0.21	0.34±0.04	0.18±0.11	0.14±0.02	0.13±0.23	0.34±0.10	3.45±0.42
ADX 350	mg kg^{-1}	2.75±0.49	< 0.10	< 0.16	< 0.01	0.87±0.44	0.29±0.07	0.02±0.02	< 0.06	< 0.01	< 0.04	0.63±0.05	0.21±0.09
ADX 450	mg kg^{-1}	0.49±0.17	< 0.10	< 0.16	< 0.01	0.10±0.09	0.13±0.01	< 0.02	0.06±0.04	< 0.01	< 0.04	< 0.23	< 0.14
ADX 550	mg kg^{-1}	0.88±0.33	< 0.10	< 0.16	< 0.01	0.28±0.12	0.09±0.00	< 0.02	0.20±0.01	< 0.01	< 0.04	< 0.23	< 0.14
ADX 650	mg kg^{-1}	0.96±0.11	< 0.10	0.21±0.03	< 0.01	0.34±0.06	0.15±0.02	< 0.02	0.25±0.05	< 0.01	< 0.04	< 0.23	< 0.14
ADX 750	mg kg^{-1}	2.17±0.01	< 0.10	0.36±0.03	< 0.01	0.98±0.02	0.29±0.01	0.35±0.09	0.35±0.02	0.08±0.04	< 0.04	0.66±0.04	< 0.14
SBI 550	mg kg^{-1}	1.39±0.21	< 0.10	< 0.16	< 0.01	0.44±0.04	< 0.02	< 0.02	0.18±0.08	< 0.01	< 0.04	< 0.23	< 0.14
WHI 550	mg kg^{-1}	1.95±0.27	0.82±0.35	0.27±0.04	< 0.01	0.86±0.10	0.18±0.02	0.09±0.07	0.79±0.01	0.02±0.01	< 0.04	0.69±0.05	1.06±0.25
WSI 550	mg kg^{-1}	1.28±0.43	0.62±0.32	< 0.16±	< 0.01	0.59±0.20	0.14±0.01	0.13±0.02	2.01±0.16	< 0.01	< 0.04	0.99±0.15	< 0.14
WLB 550	mg kg^{-1}	< 0.11	< 0.10	< 0.16	< 0.01	< 0.03	0.17±0.01	0.02±0.04	< 0.06	0.12±0.02	< 0.04	0.44±0.20	24.28±0.81
WLB 700	mg kg^{-1}	1.34±0.27	< 0.10	< 0.16	< 0.01	0.41±0.10	0.14±0.02	< 0.02	< 0.06	0.32±0.11	0.48±0.84	< 0.23	51.48±0.97
WRB 550	mg kg^{-1}	< 0.11	< 0.10	< 0.16	< 0.01	0.03±0.03	0.16±0.01	0.12±0.05	4.54±0.34	< 0.01	< 0.04	0.76±0.11	46.19±2.96
SLP 550	mg kg^{-1}	1.01±0.27	< 0.10	< 0.16	< 0.01	0.22±0.12	0.17±0.03	< 0.02	0.27±0.01	< 0.01	< 0.04	< 0.23	7.47±0.74
PAT 550	mg kg^{-1}	0.64±0.04	< 0.10	< 0.16	< 0.01	0.20±0.05	0.14±0.00	< 0.02	0.50±0.05	< 0.01	< 0.04	0.42±0.19	23.77±1.64
FWD 550	mg kg^{-1}	0.55±0.34	< 0.10	0.24±0.02	< 0.01	0.26±0.23	0.21±0.15	< 0.02	0.16±0.02	0.03±0.05	< 0.04	1.52±0.14	0.66±0.08
BBodSchV*	mg kg^{-1}		0.4	#0.1			1			1.5	0.1		2

***** German Federal Soil Protection and Contaminated Sites Ordinance, 1999; Trigger values in agriculture for As, Cu, Ni and Zn in regards to growth inhibition of crops (Annex 2.4) and Cd, Pb in regards to crop quality (Annex 2.2), using NH_4NO_3 extraction

[#] Action value, if the plant species accumulates Cd strongly, a lower value of 0.04 mg kg^{-1} is defined

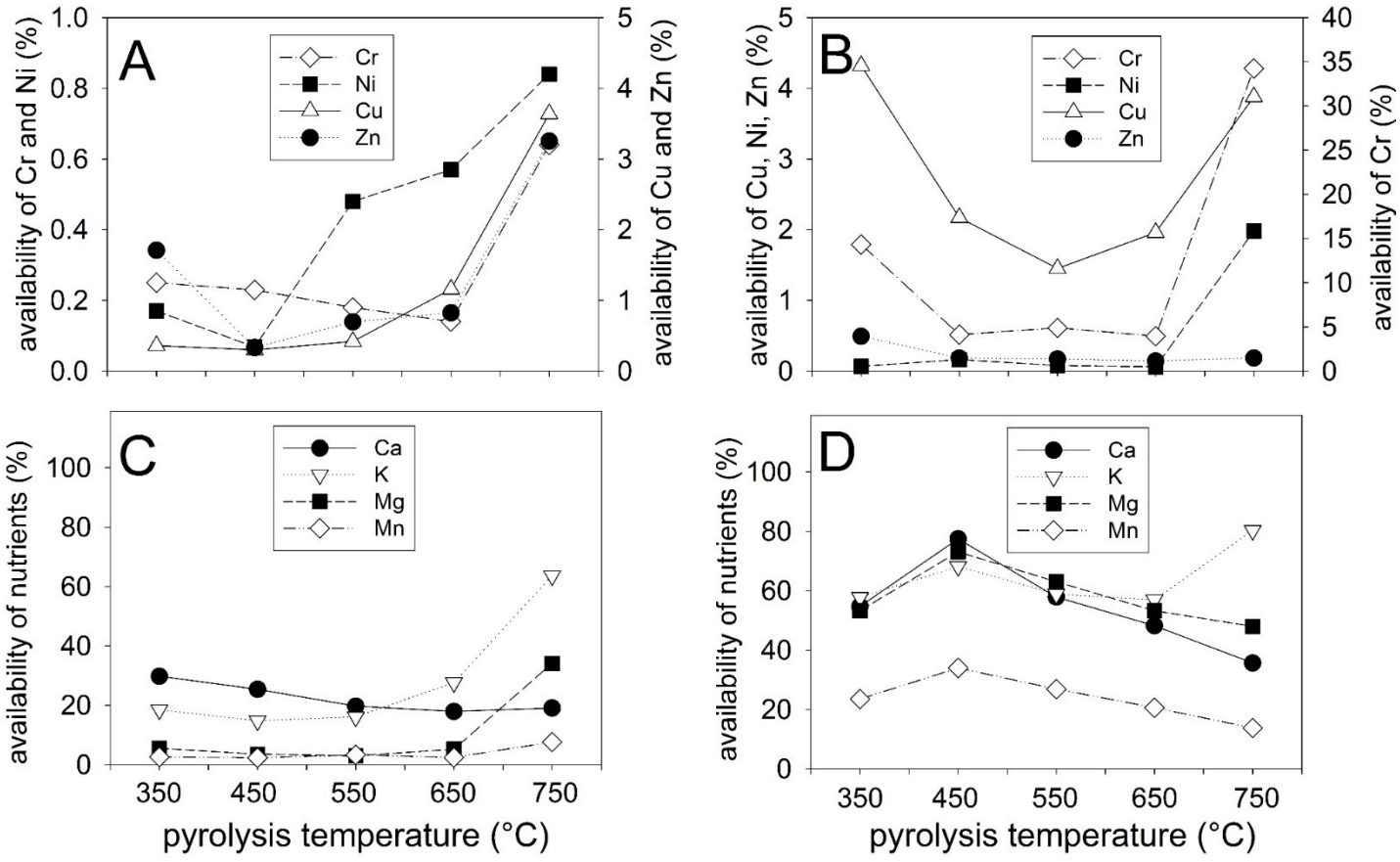


Figure 4.2: Percentage available of PTEs (Cr, Ni, Cu and Zn) (Figure A, B) and nutrients (Ca, K, Mg and P) (Figure C, D). Function of pyrolysis temperature (highest treatment temperature) for biochars produced from demolition wood (A, C) and *A. donax* (B, D). Availability was measured as percentage NH_4NO_3-extractable of the total elemental content.

4.3.1 Effect of pyrolysis HTT on percentage of PTE available

The effects of pyrolysis HTT on percentage availability of typical PTEs (Cr, Cu, Ni and Zn) and nutrients (Ca, K, Mg and P) were studied using biochars from demolition wood (DW) (Figure 4.2A) and a plant (*A. donax*, ADX) grown on contaminated soil (Figure 4.2B). For biochars from both feedstocks, the percentage available of Cr, Ni, Cu and Zn increased sharply when the HTT was increased from 650 to 750°C (Figure 4.2A, B). Khanmohammadi et al. (2015) observed the same behaviour of Cr, Cu, Ni and Zn in sewage sludge biochars pyrolysed at five temperatures between 300 and 700°C; the highest availability (%) was detected at 700°C and it increased in particular after a HTT increase from 600 to 700°C. Confirming this trend, in Meng et al. (2013), Cu and Zn showed a higher percentage of availability in biochars produced at 700°C compared to those produced at 400°C (DTPA extraction) and in Yachigo and Sato (2013), Cd and Zn demonstrated higher percentage availability in biochar produced at 800°C compared with that produced at 300°C (0.1 M HCl extraction).

The influence of HTT on external metal sorption behaviour of biochar has previously been explained as follows: biochars produced at low HTT possess more negative surface charges and functional groups (higher CEC) which are reported to sorb external cations strongly (chemisorption). For biochars produced at higher HTT, however, chemisorption is reduced (due to reduced CEC) and external cations are attached to biochar through electrostatic bonds which are weaker (Beesley et al., 2015). The same mechanisms responsible for sorption of external PTEs onto biochar might also explain the sharp increase in the percentage availability of inherent PTEs within biochar produced at 750°C. More mechanistic studies are needed to confirm this hypothesis.

The curve of percentage availability with HTT displays a different shape in the two feedstocks, ADX-derived biochar showed a higher percentage available for PTEs at a HTT of 350°C which was not visible in DW-biochar (Figure 4.2). This could be related to the fact that the feedstock particle size of ADX prior to pyrolysis was bigger (<30 mm) than for DW (<5 mm) (details on feedstock and biochar production in section 2.2.4) which, due to the relatively short residence time of 20 min, might have resulted in only partial pyrolysis of ADX at 350°C. Indeed, the comparatively

high char yield and volatile matter content of ADX 350 compared to ADX 450 did indicate an incomplete carbonisation (Table 3.1). Concluding from this, it seems that ADX 350 behaved similarly to unpyrolysed material which generally exhibits a higher percentage availability of PTEs compared to the resulting biochar (Farrell et al., 2013).

In summary, it was shown that neither the highest, nor the lowest pyrolysis temperature were suitable for production of biochars from contaminated feedstocks as the percentage availability of PTEs increased in both cases. However, to further assess the risks posed by PTEs in biochar, their availability needs to be compared with the percentage availability obtained for other biochars and soils and, where they exist, with legislative threshold values.

Table 4.2: Percentage available PTEs and nutrients in n biochars as average (AV) and standard deviation (SD) determined as NH_4NO_3-extractable of the total elemental content. The number of biochars used for calculating the percentage availability is listed in the column with heading "n"; for biochars with total and available concentrations below the detection limit, no percentage available could be calculated.

element	unit	AV ± SD	n
PTEs			
Al	%	0.46 ± 0.68	19
Cr	%	4.09 ± 8.02	19
Cu	%	1.27 ± 1.33	19
Mo	%	23.8 ± 23.7	16
Ni	%	0.33 ± 0.48	19
Zn	%	1.32 ± 1.70	19
nutrients			
B	%	13.1 ± 16.1	19
Ca	%	28.3 ± 19.6	19
Fe	%	0.02 ± 0.02	19
K	%	47.7 ± 19.7	19
Mg	%	27.2 ± 22.2	19
Mn	%	4.30 ± 3.10	19
P	%	10.8 ± 10.0	19

4.3.2 Average percentage availability of PTEs in all biochars

In relation to the total elemental content only 1.27±1.33% of Cu, 0.33±0.48% of Ni, 0.02±0.02% of Fe, 1.32±1.70% of Zn and 4.09±8.02% of Cr was available (when the

five biochars from feedstock *A. donax* are not taken into account only 1.18±0.68% of the total Cr was available) (Table 4.2). Two recent studies on total and available PTEs in various biochars obtained comparable results to those in this study; in Khanmohammadi et al. (2015) 0.5-1.4% of the total concentration of Cu, Fe, Ni, Zn and Cr was extractable with 0.005 mol L^{-1} DTPA and in Farrell et al. (2013) less than 1% of Ni, Cu, Cr and Zn was extractable with 1 mol L^{-1} NH_4NO_3. Including this study, typically less than 1.5% of the total concentrations of common PTEs in biochar were available. Clearly, PTEs are typically strongly sorbed to biochars but to place these results in a wider context, further comparison must be made with the average percentage availability of PTEs present in soils.

In Liebe et al. (1997), 335 soil samples from North Rhine-Westphalia (Germany) from different land use types containing comparable total PTE concentrations to the biochars in this study were extracted with 1 mol L^{-1} NH_4NO_3. The pH of the soils varied widely, while the biochar samples in this study all had pHs >7.5 (Table 3.1). Elevated pH decreases the percentage availability of Cu, Cr, Ni and Zn and consequently, the average percentage availability in soils with pH >7.5 was calculated from Liebe et al. (1997). The availability (%) of Cu and Ni in 23 soils with pH >7.5 (average pH 7.93±0.65, organic carbon content 2.94±1.93%) was not significantly different to the average percentage available in the nineteen marginal biomass-derived biochars (p=0.206, p=0.108; two-sample, two-tailed t-test) and the availability (%) of Cr and Zn was even significantly lower in soils (Cr: p=0.037, Zn: p=0.012). From this it was concluded that biochars do not sorb PTEs more strongly than soils do at similar pH values and confirms that the effect of biochar on Cu, Cr, Ni and Zn immobilisation in soil can be mostly attributed to pH increase, e.g. as shown in Houben et al. (2013).

4.3.3 Exceedance of threshold values for available PTEs in biochar

Threshold values for available As, Cd, Cu, Ni, Pb and Zn for soils for protecting crop quality and crop growth were established in the German Federal Soil Protection and Contaminated Sites Ordinance (1999) (Table 4.1). Comparing the available concentrations of As (mg kg^{-1}) for the biochars in this study with the German legislation threshold, only the As concentrations for biochars WHI 550 and WSI 550 exceed the limit (Table 4.1). Both of these biochars showed very high availability of

As (close to 100%). This can be explained by the fact that both biochars have a pH of around ten and the mobility of As is higher at elevated pH. This is a general problem, as addition of biochar and subsequent increase of soil pH, could mobilise As that is already present in the soil. This can lead to increased leaching of As into groundwater and increased uptake by plants (Beesley et al., 2015; Kloss et al., 2014a).

The threshold value for available Cd (0.1 mg kg^{-1}) was exceeded by four biochars (ADX 650, ADX 750, WHI 550 and FWD 550) by a factor of 2-3 (Table 4.1). However, the biochars derived from plant biomass from Cd, Zn and Pb contaminated sites (WLB 550, WLB 700, WRB 550, SLP 550 and PAT 550) and which significantly exceeded biochar guideline values for total Cd (Table 3.4), did not show detectable concentrations of Cd in NH_4NO_3 extracts (LOD 0.16 mg kg^{-1}). The available Zn concentrations (in mg kg^{-1}), however, were far above the limit values for all five biochars despite the fact that the average percent availability of Zn in all biochars was only 1.32±1.70% (Table 4.2). Despite exceeding German soil threshold values for available Zn, application of Zn-rich biochar as soil amendment can be beneficial for plant growth in Zn-deficient soils as Zn is a micronutrient and is intentionally added to some fertilisers (see section 4.3.8) (Beesley et al., 2010; Evangelou et al., 2014; Rogowski et al., 1999).

The concentration of available PTEs is relevant when effect on plants are concerned, yet, legislation and guideline threshold values are mostly based on total concentrations, consequently, the exceedance of threshold values for total and available concentrations were compared for two biochars. DW 750, which only exceeded the threshold value for total Cr (Table 3.4), exceeded the threshold values for available Cu, Pb and Zn (Table 4.1). This might be related to the fact that the metals in demolition wood were concentrated close to the surface, where paints and other coatings were applied and therefore were easy to extract. WHI 550, on the other hand, had the highest values for total concentrations for most PTEs but the available concentrations were very low, only two threshold values were slightly exceeded (As, Cd). These two examples confirm that total concentrations in biochar do not relate to available concentrations and highlight the need to investigate the availability in biochars from different feedstocks separately. For risk assessment, the

available concentrations are to be determined, therefore, threshold values should also be based on available concentrations.

4.3.4 (Percentage) availability of K, Ca and Mg in biochar

Besides PTEs, biochars contain potentially beneficial elements, such as the macronutrients K, Ca and Mg. For assessing the value of biochar as fertiliser, the concentration of available nutrients is of primary importance.

K was the most available of all elements; 47.7±19.7% of the total K was extractable with 1 mol L^{-1} NH_4NO_3 (Table 4.2), which is similar to what was reported in Ippolito et al. (2015) for various biochars and extraction techniques. The percentage availability of K increased when the HTT was increased from 650°C to 750°C in both feedstocks (Figure 4.2). A similar effect was observed by Wu et al. (2011) (300-750°C) and Singh et al. (2010) (400, 550°C). Around 30% of the Mg and Ca in biochar were available (Table 4.2), however, the availability showed different trends with HTT. While the percent of available Ca decreased slightly with increasing HTT in biochars from both feedstocks, the percent of available Mg decreased with increasing HTT in ADX-biochars and remained constant in the range 350-650 for DW-biochars, increasing at 750°C (Figure 4.2).

Available K, Ca and Mg concentrations on biochar mass basis were between 0.3-30 g kg^{-1} (highest for WHI 550, WSI 550 and WRB 550), 1.3-5.6 g kg^{-1} and 0.03-1.2 g kg^{-1}, respectively (Table 4.3) which is in a similar range to cow manure and poultry litter biochars (K 14-18 g kg^{-1}, Ca 0.5-2.5 g kg^{-1} and Mg 0.5-1.3 g kg^{-1}) (Singh et al., 2010).

Ippolito et al. (2015) calculated the application rate of different biochars needed to satisfy the K and P demands of corn plants based on concentrations of available nutrients in biochar ("medium soil", 67 kg ha^{-1} K_2O and P_2O_5), which was between 20 t ha^{-1} (turkey litter biochar) and 145 t ha^{-1} (softwood pellets biochar) for P and 1.8 t ha^{-1} (papermill waste biochar) and 41.4 t ha^{-1} for K (hazelnut biochar). Applied to the biochars from this study, this would correspond to an application rate of only 1.2 to 2.6 t ha^{-1} of ADX 650/750, WSI 550, WHI 550, SLP 550, PAT 550 and FWD 550 to satisfy the K demands of the same corn plants and these biochars would also

provide high amounts of available Ca and Mg. This emphasises the suitability of marginal biomass-derived biochars for provision of cationic nutrients to plants.

4.3.5 (Percentage) availability of P in biochar

Like K, Ca and Mg, P is also a plant macronutrient and is needed by plants in comparatively high amounts (Kirkby, 2011). For the biochars investigated here, the percentage availability of P decreased with pyrolysis HTT (Figure 4.2) which was also reported in literature for biochar produced from swine manure (Meng et al., 2013), *A. donax*, (Zheng et al., 2013) and biosolids (Wang et al., 2012). This was ascribed to assumed structural changes and resulting stabilisation of P/transformation of P into a less soluble form.

Between 0.10 and 34.0% (Digital Appendix Table 2) and on average 10.8±10.0% (Table 4.2) of the total P was available. Although different extraction solvents were used in other studies, the percentage of available P was in the same range: in Singh et al. (2010) Olsen-P per total P was between not detectable to 40% (wood, leave, poultry litter), water soluble concentrations in (composted) swine manure biochars were between 0.3-25.5% (Meng et al., 2013) and for numerous other biochars, available P was between 0.4-34% determined by various extraction methods (Ippolito et al., 2015).

FWD 550 was the biochar with the highest total P concentrations by far (Figure 3.2), but the available concentration was only 20 mg kg^{-1} (Table 4.3), which corresponded to 0.10% of the total P, by far the lowest percentage of P available in all biochars (Digital Appendix Table 2). FWD 550 also had the lowest percentage of available Ca (Digital Appendix Table 2). A plausible explanation for this is as follows: it was reported that P is mostly bound as Ca-phosphates in biochar (Bridle and Pritchard, 2004; Wang et al., 2012) which are initially extracted by the 1 mol L^{-1} NH_4NO_3 solution (pH of solution 4.6). However, with the gradual increase in solution pH due to the high pH of the biochars, it is suggested that Ca-phosphates increasingly precipitated (Goss et al., 2007) and were filtered from the solution during preparation for analysis, which was also observed in Xu et al. (2013). Generally, at high concentrations of Ca and P (FWD had the highest total concentrations of P and Ca), more ions are present in solution to react to form Ca-phosphates. This resulted in a

very low measured percentage availability of P and Ca in FWD 550. The same would not necessarily occur when total biochar Ca and P concentrations are low, as there would be less present to extract and therefore fewer ions in the extraction solution to react and precipitate, resulting in more reliable analysis results. This phenomenon could also be responsible for the generally low measured availability of P in other biochars (particularly those using unbuffered and non-acidic extractants), and the percentage of available P not having exceeded 40% in numerous studies.

While WRB 550 had the highest available P concentrations by far and only 16.6 t ha^{-1} would need to be applied to satisfy the P requirements in a "medium soil" (Ippolito et al., 2015), 1458 t ha^{-1} of FWD 550 would be needed to provide sufficient available P. In contrast, only 2.6 t ha^{-1} of FWD 550 would be needed to supply K (FWD 550 available concentrations: 14 g kg^{-1} K, 5.6 g kg^{-1} Ca, 10 g kg^{-1} Mg and 0.02 g kg^{-1} P). Despite generally comparatively low concentrations of available P in biochar, some studies did show that certain biochar can be used as P-fertiliser with high agronomic efficiencies, in some instances even performing better than mineral fertilisers (Wang et al., 2012; Weber et al., 2014).

Table 4.3: NH_4NO_3-extractable (available) nutrient concentrations of nineteen biochars (mg kg^{-1}) as average and standard deviation (n=3).

		B	Ca	Fe	K	Mg	Mn	P
DW 350	mg kg^{-1}	< 0.02	1911.81 ± 131.84	0.12 ± 0.04	264.04 ± 4.40	36.42 ± 1.57	6.09 ± 0.16	15.36 ± 0.37
DW 450	mg kg^{-1}	< 0.02	1981.25 ± 83.59	< 0.01	247.41 ± 4.08	26.76 ± 1.21	6.47 ± 0.06	14.28 ± 0.13
DW 550	mg kg^{-1}	< 0.02	1828.74 ± 174.81	< 0.01	308.62 ± 14.90	26.54 ± 1.75	10.29 ± 0.63	8.47 ± 0.48
DW 650	mg kg^{-1}	< 0.02	1627.32 ± 52.09	< 0.01	754.54 ± 6.38	49.83 ± 3.29	8.87 ± 0.38	13.21 ± 0.48
DW 750	mg kg^{-1}	6.80 ± 1.14	1731.43 ± 90.58	< 0.01	1945.05 ± 88.55	333.39 ± 22.24	29.52 ± 1.41	4.34 ± 0.23
ADX 350	mg kg^{-1}	1.56 ± 0.57	1566.53 ± 83.58	0.80 ± 0.05	11396.19 ± 567.74	468.17 ± 25.09	3.63 ± 0.40	267.61 ± 17.12
ADX 450	mg kg^{-1}	< 0.02	2625.05 ± 70.22	0.69 ± 0.03	17119.33 ± 222.85	810.66 ± 18.10	1.41 ± 0.04	455.52 ± 9.35
ADX 550	mg kg^{-1}	0.42 ± 0.38	2381.03 ± 92.87	0.59 ± 0.06	17214.35 ± 380.96	841.69 ± 23.84	2.35 ± 0.07	427.48 ± 15.59
ADX 650	mg kg^{-1}	< 0.02	2150.60 ± 47.24	0.38 ± 0.02	19409.80 ± 202.94	768.22 ± 11.50	2.74 ± 0.05	357.60 ± 8.68
ADX 750	mg kg^{-1}	1.16 ± 0.48	1524.37 ± 29.54	0.17 ± 0.06	27071.02 ± 886.79	661.31 ± 4.82	2.26 ± 0.05	230.84 ± 5.73
SBI 550	mg kg^{-1}	0.27 ± 0.47	1323.06 ± 35.58	3.19 ± 0.36	7123.26 ± 242.66	1156.43 ± 98.67	8.59 ± 0.23	390.23 ± 27.71
WHI 550	mg kg^{-1}	6.90 ± 0.16	5118.32 ± 143.48	< 0.01	29827.20 ± 647.63	973.44 ± 37.05	9.08 ± 0.17	158.27 ± 11.68
WSI 550	mg kg^{-1}	3.87 ± 0.15	2109.14 ± 89.68	0.12 ± 0.01	26794.53 ± 461.14	805.64 ± 29.67	1.86 ± 0.04	107.34 ± 0.48
WLB 550	mg kg^{-1}	2.01 ± 0.29	2830.15 ± 163.09	0.25 ± 0.01	2524.05 ± 364.50	228.01 ± 10.12	0.96 ± 0.05	241.54 ± 13.06
WLB 700	mg kg^{-1}	5.58 ± 0.03	2732.63 ± 86.83	0.88 ± 0.76	4511.81 ± 115.88	494.04 ± 13.68	1.68 ± 0.05	212.53 ± 6.22
WRB 550	mg kg^{-1}	6.32 ± 0.51	1496.45 ± 76.67	1.84 ± 0.09	31751.74 ± 715.76	77.51 ± 4.15	0.79 ± 0.04	1759.49 ± 82.86
SLP 550	mg kg^{-1}	12.38 ± 1.08	4608.27 ± 192.06	0.83 ± 0.15	14721.49 ± 790.28	1115.42 ± 65.59	2.73 ± 0.01	238.55 ± 15.11
PAT 550	mg kg^{-1}	14.10 ± 0.66	3794.41 ± 130.56	2.76 ± 0.06	24696.58 ± 719.37	1240.34 ± 27.39	1.91 ± 0.09	70.09 ± 1.94
FWD 550	mg kg^{-1}	2.72 ± 0.26	5582.42 ± 351.53	< 0.01	14123.90 ± 378.96	996.97 ± 49.30	2.96 ± 0.13	20.06 ± 1.40

4.3.6 Effect of biochars on germination and early seedling growth

4.3.6.1 Growth promoting effects of biochars

Of the nineteen biochars tested, eight showed significant shoot growth-promoting effects on cress seedlings in direct contact with the biochar-sand mixture (Figure 4.3B). In four treatments, cress seedlings only exposed to the solution leaching through biochar-sand mixtures also displayed significantly longer shoots (Figure 4.3A). Besides shoot growth, root growth was also stimulated, reflected by >100% Munoo-Liisa Vitality indices (MLV-indices) which takes into account root growth and germination rate (Table 4.4).

Improvements of physical soil properties by biochar can mostly be excluded as the reason for the stimulation of seedling growth, because seedlings also showed improved growth when only exposed to the solution leaching through the biochar-sand-mixture. Although nutrients may have been partially responsible for the growth promoting effects, these cannot explain effects observed in the case of DW biochars. Four of the five DW-biochars significantly increased shoot length, despite having comparatively low available nutrient concentrations (Table 4.3) and in particular, DW 550 showed striking stimulation of shoot growth, which cannot be associated with available nutrients.

Overall, DW 550, SBI 550 and FWD 550 increased shoot length significantly in seedlings in either direct contact with biochar-sand or exposed to biochar leachate. FWD 550 and DW 550 stimulated the growth by 60-80% in the 7-day cress test compared to the control (Figure 4.3A, B). While the biochars from demolition wood produced at five HTTs showed strong growth promoting effects which peaked at medium HTT, ADX-derived biochars inhibited seedling growth with increasing HTT (in ADX 350 seedlings could fully develop, while in ADX 750 100% of the seedling showed stunted growth, Table 4.4).

4.3.6.2 Growth suppression effects of biochars

Germination rate (cracked seed coatings and visible roots) was barely affected by any of the biochars; it was ~100% in almost all cases, with the exception of WRB 550 and PAT 550 where germination rate was only 80-90% (Table 4.5). As also observed in Li et al. (2005), however, early root growth extension was significantly

inhibited by five of the nineteen biochars, all of which were derived from biomass from PTE-contaminated land (ADX 650/750, WSI 550, WRB 550 and PAT 550). This resulted in a reduction of healthy seedlings (roots >5 mm) to only 0-60% when in direct contact with biochar-sand or when exposed to biochar-sand leachate (Table 4.4). Seedlings were able to germinate but their further development was immediately and strongly impeded and the seedlings that did grow further showed reduced shoot (Figure 4.3) and root growth (MLV-indices, Table 4.4).

To test the nature and persistence of the growth-suppressing effects, nine of the biochars, including the ones showing highest suppression, were washed with DI after NH_4NO_3-extraction and re-tested in the same germination experiment. The results revealed that for ADX 750 and WSI 550 the growth suppression was alleviated (germination rate, roots >5 mm and shoot length not significantly different to control; Table 4.6, Figure 4.4). On the other hand, in case of WRB 550 significant inhibitive effects remained, ~50% of the seedlings were stunted and the shoot growth was reduced by around 40%. Generally, the MLV-index was lower in the biochar treatments than in the sand only controls most probably resulting from residues of $NH4^+$ which caused toxicity to the roots of cress which belongs to a plant family that reacts sensitive to $NH4^+$ (Britto and Kronzucker, 2002). Overall, it can be concluded that leaching which would occur under natural conditions does alleviate some, but not all, of the toxic effects caused by the investigated biochars. The next step was to find out what caused the inhibition of growth of cress seeds in the samples in the first place.

Table 4.4: Percentage of seedlings with roots >5 mm ('healthy, non-stunted seedlings') as average and standard deviation, and Munoo-Liisa-Vitality-Index (MLV-index) (%) of nineteen biochars tested in 'all exposure routes' germination tests. Seeds were only affected by leachate from biochar-sand or were in direct contact with the mixture. Results for biochars were compared to the control using two sample, two tailed t-tests. p-value: <0.05 = * , <0.01 = ** , <0.001 = *.**

	leachate affected only		direct contact seeds-biochar	
	roots >5 mm	MLV-index	roots >5 mm	MLV-index
	% %	%	% %	%
DW 350	100.00 ± 0.0	131.1	100.0 ± 0.0	119.8
DW 450	96.3 ± 6.4	107.1	100.0 ± 0.0	117.2
DW 550	100.0 ± 0.0	158.5	98.6 ± 2.4	111.0
DW 650	95.3 ± 4.8	101.6	100.0 ± 0.0	114.5
DW 750	100.0 ± 0.0	142.8	100.0 ± 0.0	96.7
ADX 350	99.0 ± 1.8	142.1	96.5 ± 3.3	172.8
ADX 450	* 86.4 ± 7.1	55.3	75.8 ± 16.2	53.2
ADX 550	76.6 ± 26.5	42.6	76.5 ± 31.0	58.6
ADX 650	* 59.1 ± 24.0	26.2	*** 49.0 ± 3.2	21.2
ADX 750	*** 12.2 ± 10.8	6.5	*** 0.0 ± 0.0	7.5
SBI 550	100.0 ± 0.0	160.1	97.5 ± 4.3	108.8
WHI 550	98.7 ± 2.2	89.5	100.0 ± 0.0	109.3
WSI 550	55.9 ± 33.2	25.7	** 31.4 ± 18.8	18.5
WLB 550	89.6 ± 15.1	81.8	97.8 ± 1.9	101.8
WLB 700	93.5 ± 2.8	58.5	100.0 ± 0.0	85.0
WRB 550	*** 0.0 ± 0.0	3.7	*** 0.0 ± 0.0	7.0
SLP 550	93.2 ± 7.8	51.0	100.0 ± 0.0	93.2
PAT 550	** 21.7 ± 21.4	6.3	*** 0.0 ± 0.0	7.7
FWD 550	96.0 ± 4.2	123.2	100.0 ± 0.0	117.0

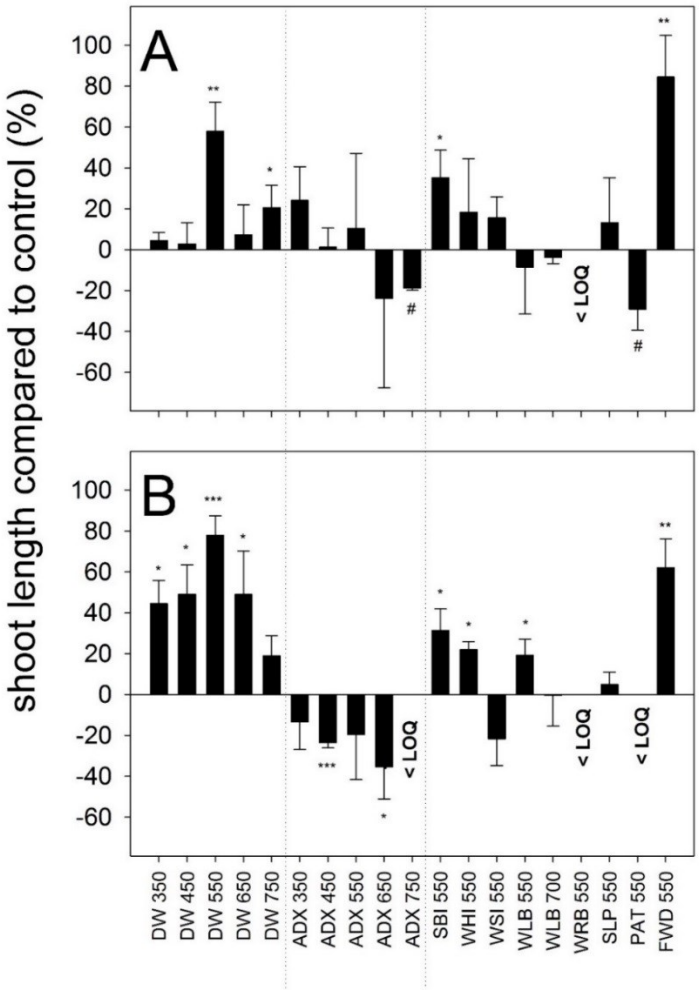


Figure 4.3: Shoot length of cress seedlings compared to control (%) after exposure to 5% biochar in sand for 7 days. (A) shows the results from seeds only being affected by leachate from the mixture and (B) shows the seeds which were exposed to biochar-sand. Results for biochars were compared to the control using two sample, two tailed t-tests. LOQ, limit of quantification; * significant difference with p <0.05, ** with p <0.01, * with p <0.001, # not statistically tested because only two of the replicates showed growth and one replicate had 100% below LOQ.**

Table 4.5: Germination rate (%) of nineteen biochars tested in 'all exposure routes' germination tests with average and standard deviation. Seeds were only affected by leachate from biochar-sand or were in direct contact. p-value: <0.05 = * , <0.01 = ** , <0.001 = *.**

	leachate affected fraction germination rate		direct contact seeds-biochar germination rate	
	%	%	%	%
DW 350	100.0 ±	0.0	98.0 ±	3.4
DW 450	100.0 ±	0.0	100.0 ±	0.0
DW 550	98.7 ±	2.3	100.0 ±	0.0
DW 650	100.0 ±	0.0	100.0 ±	0.0
DW 750	100.0 ±	0.0	100.0 ±	0.0
ADX 350	100.0 ±	0.0	98.8 ±	2.1
ADX 450	97.3 ±	4.6	93.4 ±	4.7
ADX 550	93.8 ±	5.7	96.5 ±	3.6
ADX 650	98.7 ±	2.3	96.1 ±	3.8
ADX 750	98.8 ±	2.1	90.5 ±	10.5
SBI 550	98.4 ±	2.7	100.0 ±	0.0
WHI 550	97.4 ±	4.4	98.8 ±	2.1
WSI 550	92.2 ±	3.7	90.2 ±	5.8
WLB 550	100.0 ±	0.0	100.0 ±	0.0
WLB 700	100.0 ±	0.0	98.9 ±	1.9
WRB 550	*81.0 ±	8.7	**84.2 ±	4.8
SLP 550	100.0 ±	0.0	100.0 ±	0.0
PAT 550	96.2 ±	3.5	*92.5 ±	3.7
FWD 550	100.0 ±	0.0	98.9 ±	2.0

Table 4.6: Germination rate (GR) (%), percentage of seedlings with roots >5 mm ('non-stunted seedlings') and Munoo-Liisa-Vitality-Index (MLV-index) (%) of nine leached biochars tested in 'all exposure routes' germination tests. Seeds were only affected by leachate from biochar-sand or were in direct contact. p-value: <0.05 = * , <0.01 = ** , <0.001 = *.**

	leachate affected fraction					direct contact seeds-biochar				
	GR		roots >5 mm		MLV-index	GR		roots >5 mm		MLV-index
	%	%	%	%	%	%	%	%	%	%
DW 550	98.9 ±	2.0	98.8 ±	2.1	57.7	94.7 ±	4.6	100.0 ±	0.0	65.7
DW 750	98.7 ±	2.2	90.4 ±	8.8	51.7	98.7 ±	2.2	98.9 ±	1.9	62.5
ADX 350	97.6 ±	2.1	* 91.4 ±	3.0	51.1	97.6 ±	2.1	94.5 ±	5.2	43.1
ADX 750	97.4 ±	2.3	89.9 ±	9.7	41.2	96.4 ±	3.5	86.0 ±	9.1	37.3
WHI 550	98.9 ±	2.0	94.0 ±	7.4	57.0	97.7 ±	4.0	90.5 ±	1.9	42.4
WSI 550	98.7 ±	2.2	* 78.8 ±	7.4	34.0	98.7 ±	2.2	90.2 ±	2.5	40.7
WLB 550	98.7 ±	2.3	98.9 ±	1.9	61.4	100.0 ±	0.0	98.9 ±	2.0	49.7
WRB 550	91.3 ±	6.0	*** 14.5 ±	16.1	5.0	93.2 ±	0.4	* 51.8 ±	18.0	13.1
FWD 550	96.3 ±	0.5	93.4 ±	2.9	45.5	98.9 ±	2.0	91.7 ±	5.5	38.4

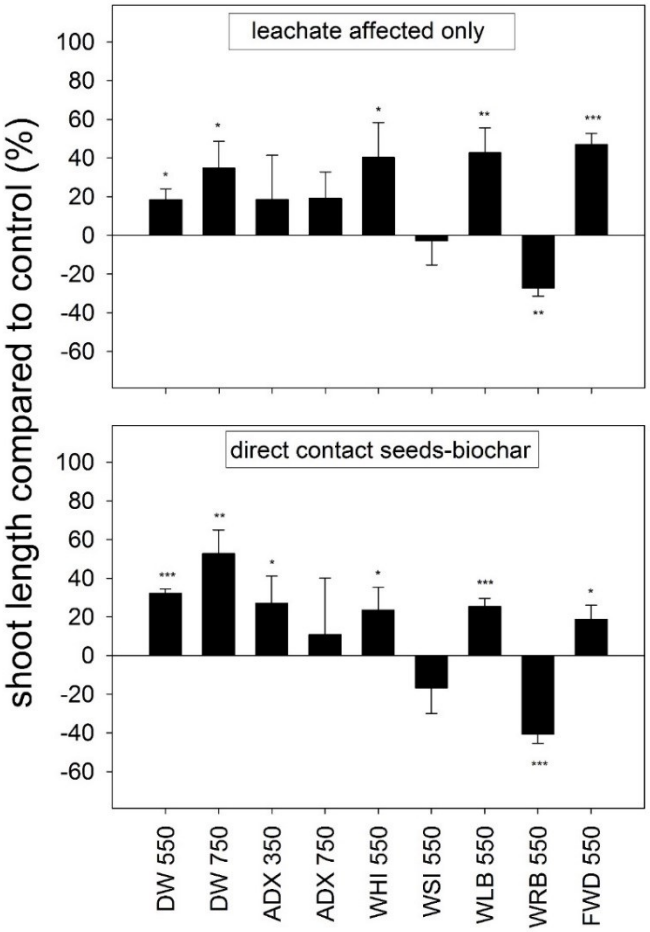


Figure 4.4: Shoot length of cress seedlings compared to control (%) after exposure to 5% biochar in sand for seven days. Top figure shows the results from seeds only being affected by leachate from the mixture and lower figure shows the seeds which were exposed to the biochar-sand mixture. * significant difference with p <0.05, ** with p <0.01, * with p <0.001**

4.3.7 Correlating plant response with biochar characteristics (available elemental concentrations, pH and EC)

Measuring the concentrations of available PTEs and conducting plant tests is a means of risk assessment; to be able to take appropriate risk management measures to avoid the toxic effects of biochar, however, the underlying reasons need to be understood. Consequently, the performance of biochars in cress germination and growth tests (percentage of healthy, non-stunted seedlings) was correlated with the available elemental concentrations of all nineteen elements and with biochar pH and

electrical conductivity (EC) (Table 3.1) to identify the parameter that most likely affected the cress seedling growth adversely.

The effects of ADX-biochars in the plant test were striking; the phytotoxicity increased linearly with HTT (Table 4.4, Figure 4.3). The availability of most PTEs in ADX-biochar, however, did not increase with HTT, except for Mo which increased from <0.06 mg kg^{-1} in ADX 350 to 0.35 mg kg^{-1} in ADX 750 (Table 4.1). Indeed, correlating the percentage of healthy, non-stunted seedlings with available Mo concentrations for the whole set of nineteen biochars showed a significant negative, linear correlation (Table 4.7). It is reported that phytotoxic effects caused by Mo are very uncommon (Gupta and Gupta, 1998; Kabata-Pendias, 2011; Kaiser, 2005; MacNicol and Beckett, 1985), yet, Mo-related inhibitions were observed in some studies: the lowest concentration that showed toxic effects on pea plants and in various other plants in solution was 0.96 mg L^{-1} Mo (0.01 mmol L^{-1}) and 1-2 mg L^{-1}, respectively (Kevresan et al., 2001; McGrath et al., 2010). In the germination tests conducted in this study, a water-to-biochar ratio of 1:14 was used, while the extractions were performed with a ratio of biochar-to-NH_4NO_3-solution of 1:10 and consequently, the Mo concentrations to which the seeds were exposed were comparable to the concentrations detected in the NH_4NO_3-extracts (concentrations in the raw extracts 10 fold lower than in Table 4.1). In the literature inhibitory effects started at ~1 mg L^{-1}, while in this study biochars with Mo concentrations in the NH_4NO_3-extracts of 0.035 mg L^{-1} (ADX 750) totally inhibited early seedling growth in direct contact with biochar. In conclusion, while it cannot be entirely excluded that Mo has contributed to the total inhibition of early seedling growth, it seems highly unlikely. Instead this could be a case of wrongly interpreted cause-effect relationship. The available concentration of Mo is not the cause for the toxicity but it is a symptom of the high pHs of these biochars. Therefore, it is the elevated pHs that caused the observed growth suppression effects. Indeed, biochar pH (Table 3.1) showed a similarly high negative correlation with healthy, non-stunted seedlings as the available Mo concentration observed in this study (Table 4.7).

Henig-Sever et al. (1996) and Singh et al. (1975) showed that solutions with pH in the range 7-9 reduced germination rates in most plant species and by pH of 10-11, total inhibition was observed in most cases. Singh et al. (1975) suggested that the

germination rate-response to pH followed a 2nd order polynomial curve, and therefore, a linear correlation (Pearson) does not describe the relationship between pH and growth response appropriately. Tested on the data from this study, is shows that indeed a 2nd order polynomial curve fitted very well with the plant response (Figure 4.5A: R^2=0.63, Figure 4.5B: R^2=0.68). Investigation of the causes of relatively high pH of the biochar used in this study showed that it can be attributed mainly to potassium salts, e.g. potassium carbonate, as potassium was the element with by far the highest available elemental concentration in all biochars (Table 4.1, Table 4.3).

Consequently, K most likely caused indirect inhibition of plant growth by increasing the pH in solution. Yet, the available K concentration itself shows an even higher significant correlation with seedling growth than pH and a better 2nd order polynomial fit, in fact available K displays the best fit of all parameters tested (r=-0.728, $p<0.001$) (Table 4.7, Figure 4.5C, D). However, the only direct, adverse effect reported for K excess is reduced uptake of other nutrients, which should not affect the early seedling growth, where nutrients are mostly provided by the seed itself (Butnan et al., 2015; Hawkesford et al., 2011). Consequently, the most likely mechanism responsible for growth inhibition caused by available K, as for pH, is an indirect mechanism, an increase in osmotic pressure. El-Darier and Youssef (2000) in their study on effects of different salt concentrations on cress seeds, reported that due to the osmotic pressure of a solution containing >50 mmol L^{-1} NaCl (100 mmol L^{-1} active ions) the shoot and root length were significantly reduced. In the current study, the four biochars that caused the highest inhibition had concentrations of K of ~3,000 mg L^{-1} in NH_4NO_3-extracts (concentrations in the raw extracts ten fold lower than in Table 4.3) which corresponds to 77 mmol L^{-1}. Assuming K dissolution as potassium carbonate or chloride, the active concentrations of ions resulting from this would be 231 and 154 mmol L^{-1}, respectively, which is well in the range where reductions of cress seedling growth have been reported.

As electrical conductivity (EC) is often used as a proxy for osmotic potential of a solution, it was assessed as a potential indicator of plant response. Statistical analysis showed that EC showed a comparatively low Pearson correlation (Table 4.7) and R^2 (not shown) with seedling growth, much lower than that shown by the available K

concentration. This is attributed to the fact that, while ions in solution contribute to EC to different extents, depending on type of ion and its charge, in case of osmotic potential/pressure, which is the actual factor affecting seedling growth, only the quantity of solute per unit volume of solution (molarity) is relevant (Richards, 1954). Consequently, EC is not necessarily a good predictor for the inhibition of germination and early seedling growth, while molarity of the solution is. In conclusion, it was shown that it was the osmotic potential of the solution and partially the high pH (both of which are mostly a result of dissolved K) that were the primary causes of observed phytotoxicity in this study and not the PTEs contained in the biochar.

Table 4.7: Pearson correlation coefficient (r) of available elemental content, pH and EC of nineteen biochars with percentage of seedlings with roots >5 mm ('healthy, non-stunted seedlings') for leachate affected seeds and seeds in direct contact with sand-biochar. Only parameters with significant effect shown. * significant difference with p <0.05, ** with p <0.01, * with p <0.001.**

	leachate affected seeds		direct contact seeds-biochar	
	r	p-value	r	p-value
K	-0.729	***<0.001	-0.749	***<0.001
Mo	-0.660	**0.002	-0.608	**0.006
P	-0.573	*0.010	-0.478	*0.038
EC	-0.471	*0.042	-0.484	*0.036
pH	-0.615	**0.005	-0.627	**0.004

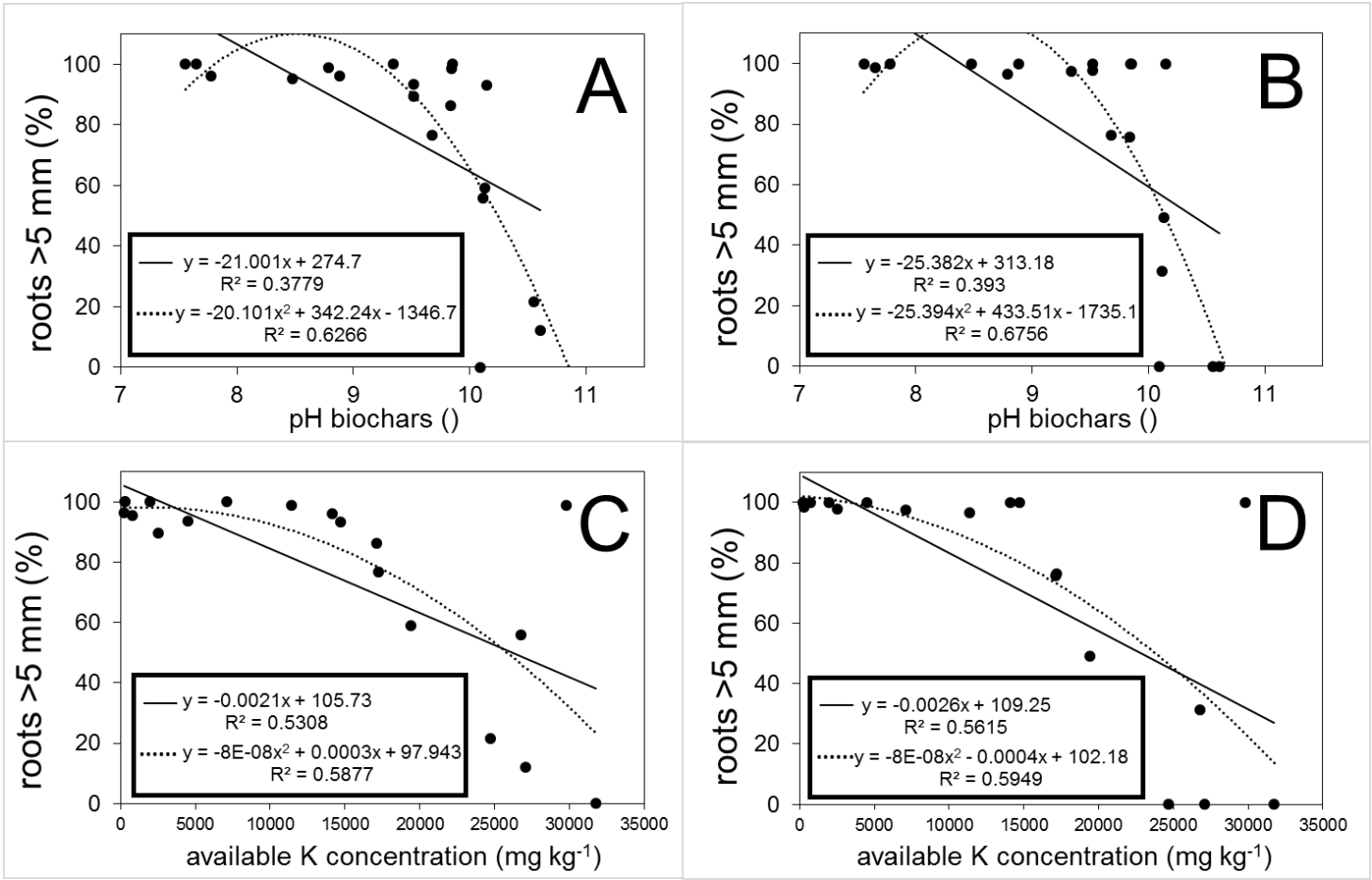


Figure 4.5: Regression of available K concentration and pH of nineteen biochars with percentage of roots >5 mm ('healthy, non-stunted seedlings'). Biochar pH (determined in solution in liquid-to-solid ratio of 20:1) is shown with (A) seedlings affected by biochar-sand leachate and (B) seedlings in direct contact with biochar-sand. Available K concentration in biochar (determined by NH_4NO_3-extraction) is depicted with (C) seedlings affected by biochar-sand leachate and (D) seedlings in direct contact with biochar-sand. The equations in the boxes show the fit of the linear and 2nd order polynomial curves.

4.3.8 Use of biochars from marginal biomass for amendment of soil or as ingredients in growing media

For the use of biochar for amendment of soil and in growing media, biochar has to comply with environmental, health and safety legislations and cannot pose a threat for plant growth. On the contrary, it needs to offer beneficial properties, such as the provision of nutrients.

Overall, in this study, all biochars with agronomically viable concentrations of available cationic nutrients also contained concentrations of available PTEs which exceed the soil threshold values for protection of crop growth of the German Federal Soil Protection and Contaminated Sites Ordinance (1999). However, the threshold values are limits for soil and not soil amendments. Consequently, where pure biochars exceeded threshold values, incorporation in soil at <1% (<20 t ha^{-1}) results in a dilution of 100-fold and consequently, available PTEs would not exceed the limit. Furthermore, comparing the total PTE concentrations to commercially available fertiliser products shows that the concentrations of As, Cd, Cr and Ni are much higher in inorganic fertilisers than in the biochars investigated here and Zn is even added intentionally to inorganic fertilisers to supply Zn for Zn-deficient soils (Rogowski et al., 1999). Therefore, although the compliance/non-compliance of respective biochars with legislation would need to be decided by the responsible governmental bodies, considering the available concentrations, PTEs do not seem to be of any concern. More importantly, the phytotoxic effects observed in this study could not be correlated with available PTEs concentrations.

Five of the nineteen biochars did adversely affect growth in germination tests (linked to high pH and high content of available K), while eight showed significant growth stimulating effects, even in these high application rates (5 wt%, corresponding to >100 t ha^{-1}, depending on soil and application type). Consequently, some of the tested biochars would not be suitable for application in high concentrations, e.g. in growing media, without causing phytotoxic effects. However, the application rates used in this work were unrealistically high from the perspective of agricultural application (these were selected intentionally high to exacerbate negative effects of PTEs) and therefore application in lower, practically relevant application rates (1-10 t ha^{-1}) would result in smaller increases in pH and lower additions of K and would

therefore most likely result in growth stimulating effects. This application rate would also not exceed the available PTE concentrations in soil above the threshold values.

4.4 Conclusions

In this chapter, nineteen biochars produced from marginal biomass feedstocks were investigated to assess their content of available PTE and nutrients, and any growth promoting or suppressing effects. The study confirmed that total concentrations are not good predictors for available concentrations and the potential risk for biochars to cause adverse effects in plants. In addition, it was concluded that in the investigated biochars inherent Cu, Cr, Ni and Zn were bound with similar strength to that of soil at a similar pH (>7.5). The highest HTT applied in this study, 750°C increased the availability of most PTEs and decreased the availability of several nutrients. Eight of the nineteen biochars used in this study significantly increased early seedling growth, while five biochars suppressed growth. The phytotoxic effects showed only poor correlation with available PTEs, but a strong correlation with pH and available K concentration. The available K concentrations most probably resulted in high osmotic pressure which caused the growth inhibition. It is concluded that, although high available K concentrations and high pH were responsible for seedling growth inhibitions in this study using very high biochar application rates, were such biochars used at lower application rates, both factors (available K and pH) would contribute to growth promoting effects and would be among the most important assets of these biochars. Overall, in this chapter it was shown that most marginal biomass-derived biochars have good potential to be used as nutrient source for plants and have low risk to cause adverse effects despite increased content of PTEs. Based on this, revisions of guidelines for application of biochar and other materials to soil is suggested, to reflect the true risks posed by different materials, and not simply base such judgments on the total content of PTEs. Yet, effects of PTE-rich biochars on other plants and soil organisms, as well as long-term fate of PTEs are still uncertain and need to be tested before PTE-rich biochar can be considered safe for soil amendment.

Chapter 5 Influence of production conditions and common feedstock types on total PAH concentrations in biochar

The following chapter is based on the published article:

Buss, W., Graham, M.C., MacKinnon, G., Mašek, O., 2016. Strategies for producing biochars with minimum PAH contamination. J. Anal. Appl. Pyrolysis 119:24-30. doi: 10.1016/j.jaap.2016.04.001

Journal impact factor (2014): 3.564

Number of citations (September 2016): 2

The candidate was solely responsible for data analysis and writing of the article and this chapter. Supervisors provided guidance and supervisors and co-authors contributed to the editing of the manuscript. The experimental work was performed by the candidate apart for production of some biochars which was performed by Peter Brownsort, Kyle Crombie, Clare Peters, Juan Luis Turrion-Gomez and Walter Lowe.

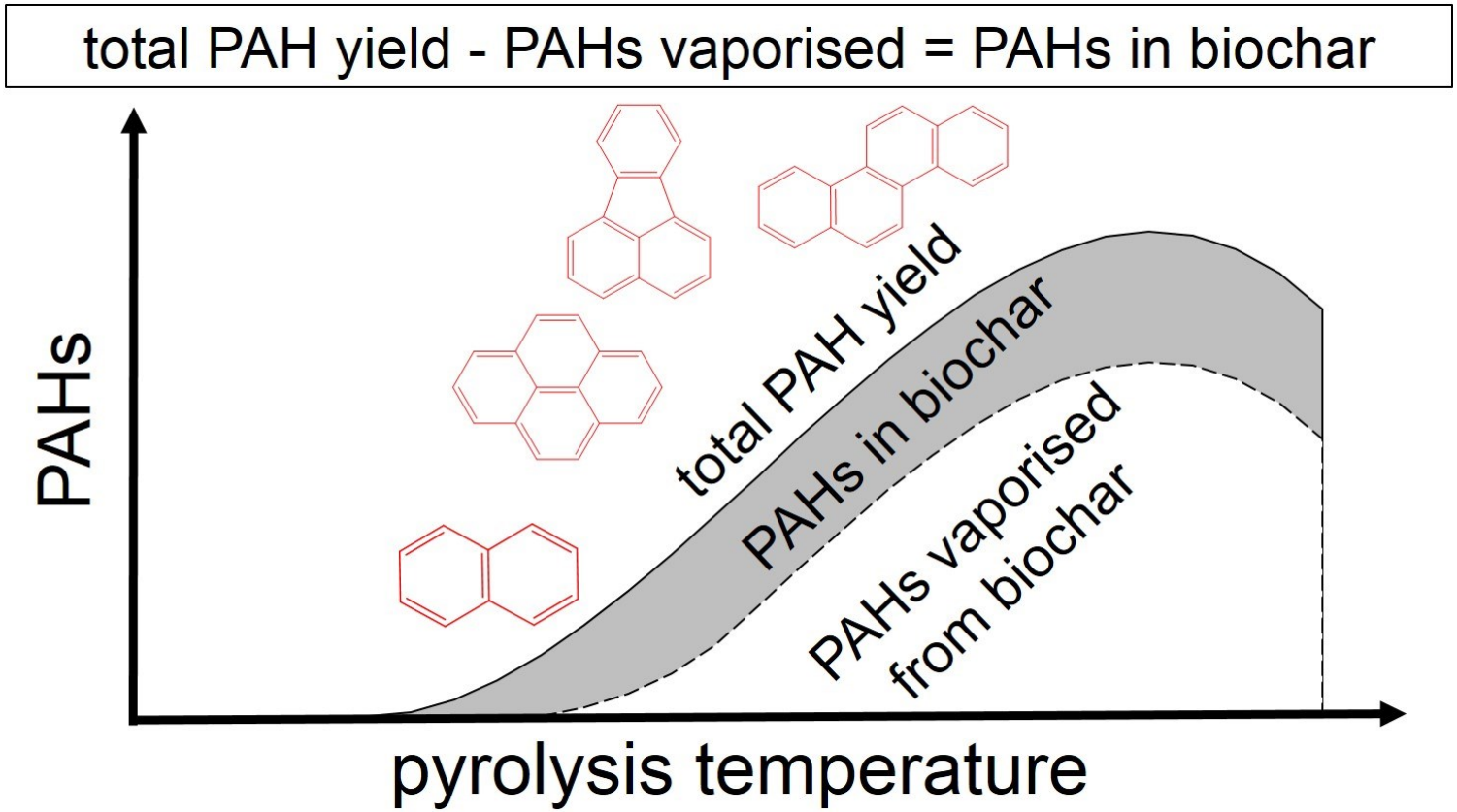


Figure 5.1: Graphical abstract of Chapter 5. The effect of pyrolysis temperature on the polycyclic aromatic hydrocarbon (PAH) concentration in biochar was tested and no relationship could be found. This is explained by the simultaneous increase of PAH yield and increase of vaporisation of PAHs from biochar with increasing pyrolysis temperature. Both effects combined determine the PAH concentration in biochar (grey area – distance between the two graphes which stays the same at all pyrolysis temperatures).

5.1 Introduction

Biochar is the solid product of thermochemical conversion of biomass under an atmosphere with reduced content of free oxygen or its complete absence, i.e. pyrolysis and gasification (Lehmann and Joseph, 2009). During such conversion, biomass undergoes extensive devolatilisation and develops a solid carbonised matrix (Bridgwater, 2003). This is accompanied by formation of polycyclic aromatic hydrocarbons (PAHs), an important class of organic contaminants, associated with environmental problems (Baek et al., 1991). PAHs can have acute adverse effects on human health, plants and the wider ecosystem with some displaying carcinogenic, mutagenic and teratogenic effects (US Department of Health and Human Services, 1995).

PAHs are defined as aromatic structures that consist of two or more linked carbon rings and only contain the elements carbon and hydrogen (Baek et al., 1991). PAHs are formed during incomplete combustion of any type of biomass and biomass-derived material. Thus, PAHs are present in the environment naturally through forest fires and volcanic eruptions, with UK rural soils containing a mean PAH concentration of 2.2 mg kg^{-1} (Creaser et al., 2007). However, human actions increase PAH concentrations locally and the average PAH concentrations in UK urban soils were reported to be 14.2 mg kg^{-1} (Creaser et al., 2007). In soil they are known to accumulate as they are difficult to degrade, associate with organic matter and have low water solubility (half-life of PAHs of more than three rings >20 to hundreds of days) (US Department of Health and Human Services, 1995).

There are two main pathways by which PAHs are known to form: at lower conversion temperatures Diels-Alder reactions take place which involve dehydrogenation, polymerisation, cyclisation and aromatisation of hydrocarbons to form PAHs (Chiang et al., 2014; Keiluweit et al., 2012; McGrath et al., 2003). At temperatures above 400-500°C, the alternative is a pyrosynthetic pathway consisting of demethylation, demethoxylation and dehydroxylation of lignin, cellulose and hemicellulose to form phenol, alkyl-phenols and BTEX. This is followed by deoxygenation/dehydrogenation, connecting single compounds and condensing these into larger compounds which end up as polyaromatic networks (PAHs or pyrolytic

carbon) (Chiang et al., 2014; Hajaligol et al., 2001; McGrath et al., 2003; Sharma and Hajaligol, 2003).

Research effort regarding anthropogenic pollution with PAHs used to focus on reducing PAH emissions from fossil fuel and biomass combustion (Baek et al., 1991). Studies that dealt with PAHs and pyrolysis mostly investigated PAH formation and concentrations in pyrolysis liquids/gases (McGrath et al., 2001, 2003; Sharma and Hajaligol, 2003; Wei and Lee, 1998; Zhou et al., 2014b). Recently, attention has shifted to PAH concentrations in pyrolysis solids because of the potential application of biochar to soil for soil improvement, soil remediation and carbon sequestration (Dai et al., 2014b; Devi and Saroha, 2015; Freddo et al., 2012; Hale et al., 2012; Keiluweit et al., 2012; Kloss et al., 2012; Rogovska et al., 2012). In order to avoid possible negative effects on soil ecosystems and to comply with environmental legislation, it is essential to produce biochars with low PAH concentrations. Biochar guideline values have been established which are based on current legislation. For example, the European Biochar Certificate (EBC) allows up to 12 mg kg^{-1} of 16 US EPA PAHs for basic grade and up to 4 mg kg^{-1} for premium grade biochar which was adopted from the Swiss Chemical Risk Reduction Act (EBC, 2012b). The International Biochar Initiative (IBI) guidelines use threshold values of 20 mg kg^{-1} and 6 mg kg^{-1} based on the Austrian Compost Ordinance (International Biochar Initiative, 2011).

The few systematic studies on dependence of PAH concentrations on pyrolysis conditions that exist, provide different perspectives and no overall trend is observed (Brown et al., 2006; Dai et al., 2014b; Devi and Saroha, 2015; Freddo et al., 2012; Hale et al., 2012; Keiluweit et al., 2012; Kloss et al., 2012; Rogovska et al., 2012). In Hale et al. (2012), the effects of highest treatment temperature (HTT-maximum temperature material is exposed to), residence time and feedstock was investigated by analysing 59 biochars, however, due to the highly variable technologies used for biochar production only limited conclusions could be drawn. This shows the absolute need for a systematic study on the relationship of pyrolysis conditions and feedstock with PAHs in biochars produced from highly controlled, slow pyrolysis units.

Consequently, in this chapter the effects of two common feedstock types (wood and straw) and typical pyrolysis parameters (residence time, HTT and carrier gas flow rate) were investigated to determine their effect on total concentrations of 16 US EPA PAHs in resulting biochars. The overall objective was to provide recommendations to produce pyrolysis solids (biochar) with minimal PAH contamination based on a data set of biochars produced from highly controlled pyrolysis units.

5.2 Materials and methods

5.2.1 Biochar production

Forty-six biochars were produced under highly controlled pyrolysis conditions using three different slow pyrolysis units that are located at the UK Biochar Research Centre (UKBRC). Production parameters, such as HTT (350-750°C), residence time (10, 20, 40 min) and carrier gas flow (0, 0.33, 0.67 L min^{-1}) were varied. The carrier gas flows under standard conditions were 10 L min^{-1} for Stage III (inner diameter 244 mm), 1 L min^{-1} for Stage II (inner diameter 100 mm) and 0.3 L min^{-1} for Stage I (inner diameter 50 mm). When inconsistencies during a pyrolysis run were detected, such as high pressure peaks, the biochars were discarded and the pyrolysis run was repeated ensuring comparative conditions between runs. An overview of all the biochars including production conditions and feedstocks can be found in Table 5.1. More details on feedstocks and biochar production are described in section 2.2.5, 2.2.4 and 2.2.6, here is a short overview of the biochars analysed in this chapter.

5.2.1.1 Highest treatment temperature (HTT)

To be able to find overall trends of the influence of HTT on the total PAH concentration in biochar, different feedstocks were pyrolysed using two pyrolysis units in the typical temperature range used for biochar production (350-750°C). Stage II pyrolysis unit was used to pyrolyse demolition wood and *A. donax* at five temperatures (350, 450, 550, 650, 750°C), willow chips at three temperatures (350, 550, 750°C) and miscanthus chips at four temperatures (350, 450, 550, 750°C). Furthermore, sewage sludge was pyrolysed at five temperatures (350, 450, 550, 650, 750°C) with the Stage III pyrolysis unit.

5.2.1.2 Carrier gas flow rate, HTT, feedstock, and residence time at HTT

The Stage I pyrolysis unit was used to pyrolyse straw pellets (WSP II) and softwood pellets (SWP II) at two HTTs (350, 650°C), two residence times (10, 40 min) and three carrier gas flow rates (0, 0.33, 0.67 L min^{-1}). In total, 24 biochars were produced. The feedstocks and production conditions were chosen as typical feedstocks and production conditions for biochar production. More details on the feedstocks, such as elemental content (ultimate analysis) and biomass components, can be found in Crombie and Mašek (2015).

5.2.2 PAH analysis

The analyses were performed by Northumbrian Water Scientific Services (Newcastle, United Kingdom), accredited by United Kingdom Accreditation Service (UKAS). More details can be found in section 2.5. The sum of 16 US EPA priority PAHs is reported for 46 biochars.

5.2.3 Statistics

Results were evaluated statistically using two-sample, two-tailed t-tests and Analysis of Variance (ANOVA) followed by Student-Newman-Keuls post hoc tests performed with SigmaPlot 12 (Systat Software Inc., Chicago, IL). Significant differences are stated with a p-value <0.05.

5.3 Results and discussion

Production conditions and total PAH concentrations for all 46 biochars used in this work are shown in Table 5.1. The 16 US EPA PAH concentrations detected in the 46 biochars analysed in this study were between 1.2 and 100 mg kg^{-1}. This falls in the range of PAH concentrations detected in published studies which employed various solvents and extraction durations (but all used Soxhlet extractions), 0.07-355 mg kg^{-1} (Anjum et al., 2014; Fabbri et al., 2013; Granatstein et al., 2009; Hale et al., 2012; Hilber et al., 2012; Kloss et al., 2012; Schimmelpfennig and Glaser, 2012). However, comparison of the measured values against guideline values for acceptable PAHs concentrations in biochar for soil application showed that out of the 46 biochars tested 59% exceeded the EBC premium grade PAH limit (4 mg kg^{-1}), 46% were above the EBC basic grade limit (12 mg kg^{-1}) and 43% were higher than the IBI threshold (20 mg kg^{-1}) (Table 5.2).

Table 5.1: Production conditions and total 16 US EPA concentrations (mg kg^{-1}) of 46 biochars investigated in this study. HTT, highest treatment temperature; RT, residence time at peak temperature; HR, heating rate (batch process only); CGF, carrier gas flow; n/a, not available.

biochar	Feedstock	pyrolysis unit	HTT	RT	HR	CGF	PAHs
			°C	min	°C min^{-1}	L min^{-1}	mg kg^{-1}
DNX - 350	*Arundo donax*	Stage II	350	20	n/a	1	2.9
DNX - 450	*Arundo donax*	Stage II	450	20	n/a	1	3.9
DNX - 550	*Arundo donax*	Stage II	550	20	n/a	1	5.5
DNX - 650	*Arundo donax*	Stage II	650	20	n/a	1	7.8
DNX - 750	*Arundo donax*	Stage II	750	20	n/a	1	67
DW - 350	Demolition wood	Stage II	350	20	n/a	1	2.2
DW - 450	Demolition wood	Stage II	450	20	n/a	1	1.5
DW - 550	Demolition wood	Stage II	550	20	n/a	1	3.6
DW - 650	Demolition wood	Stage II	650	20	n/a	1	3.4
DW - 750	Demolition wood	Stage II	750	20	n/a	1	48
MC - 350	Miscanthus chips	Stage II	350	20	n/a	1	27
MC - 450	Miscanthus chips	Stage II	450	20	n/a	1	44
MC - 550	Miscanthus chips	Stage II	550	20	n/a	1	26
MC - 750	Miscanthus chips	Stage II	750	20	n/a	1	52
SS - 350	Sewage sludge	Stage III	350	20	n/a	10	31
SS - 450	Sewage sludge	Stage III	450	20	n/a	10	21
SS - 550	Sewage sludge	Stage III	550	20	n/a	10	26
SS - 650	Sewage sludge	Stage III	650	20	n/a	10	21
SS - 750	Sewage sludge	Stage III	750	20	n/a	10	37
WC - 350	Willow chips	Stage II	350	20	n/a	1	20
WC - 550	Willow chips	Stage II	550	20	n/a	1	45
WC - 750	Willow chips	Stage II	750	20	n/a	1	100
SWP II-350-10-0	Softwood pellets II	Stage I	350	10	5	0.00	2.9
SWP II-350-10-0.33	Softwood pellets II	Stage I	350	10	5	0.33	2.1
SWP II-350-10-0.66	Softwood pellets II	Stage I	350	10	5	0.67	2.2
SWP II-350-40-0	Softwood pellets II	Stage I	350	40	5	0.00	5.3
SWP II-350-40-0.33	Softwood pellets II	Stage I	350	40	5	0.33	2.3
SWP II-350-40-0.66	Softwood pellets II	Stage I	350	40	5	0.67	1.3
SWP II-650-10-0	Softwood pellets II	Stage I	650	10	5	0.00	13
SWP II-650-10-0.33	Softwood pellets II	Stage I	650	10	5	0.33	1.9
SWP II-650-10-0.66	Softwood pellets II	Stage I	650	10	5	0.67	1.4
SWP II-650-40-0	Softwood pellets II	Stage I	650	40	5	0.00	8.5
SWP II-650-40-0.33	Softwood pellets II	Stage I	650	40	5	0.33	1.9
SWP II-650-40-0.66	Softwood pellets II	Stage I	650	40	5	0.67	1.3
WSP II-350-10-0	Straw pellets II	Stage I	350	10	5	0.00	52
WSP II-350-10-0.33	Straw pellets II	Stage I	350	10	5	0.33	38
WSP II-350-10-0.66	Straw pellets II	Stage I	350	10	5	0.67	5.7
WSP II-350-40-0	Straw pellets II	Stage I	350	40	5	0.00	33
WSP II-350-40-0.33	Straw pellets II	Stage I	350	40	5	0.33	25
WSP II-350-40-0.66	Straw pellets II	Stage I	350	40	5	0.67	3.4
WSP II-650-10-0	Straw pellets II	Stage I	650	10	5	0.00	34
WSP II-650-10-0.33	Straw pellets II	Stage I	650	10	5	0.33	1.4
WSP II-650-10-0.66	Straw pellets II	Stage I	650	10	5	0.67	3.0
WSP II-650-40-0	Straw pellets II	Stage I	650	40	5	0.00	53
WSP II-650-40-0.33	Straw pellets II	Stage I	650	40	5	0.33	4.5
WSP II-650-40-0.66	Straw pellets II	Stage I	650	40	5	0.67	2.0

Table 5.2: Biochars exceeding PAH guideline values. The values depicted are for biochar soil application according to European Biochar Certificate (EBC, 2012b) and International Biochar Initiative (International Biochar Initiative, 2011) and number and percentage of biochars out of the set of 46, exceeding these guideline values.

		EBC premium	EBC basic	IBI
threshold	mg kg $^{-1}$	4	12	20
exceedance	biochars	27	21	20
	%	59	46	43

5.3.1 Effect of highest treatment temperature (HTT) on PAHs in biochar

Four different feedstocks were pyrolysed with Stage II pyrolysis unit and one with Stage III pyrolysis unit in the temperature range 350-750°C (Figure 5.2). For production temperatures of up to 650°C, biochars from both pyrolysis units showed some variations in the PAH concentrations, but, taking all feedstocks and both pyrolysis units into account, there was no significant change in the range 350-650°C (one-way ANOVA). However, on average, the biochars produced at 750°C showed significantly higher PAH concentrations than biochars produced at any of the lower temperatures (one-way ANOVA). Yet, the PAH concentrations of the biochar produced at 750°C with the Stage III pyrolysis unit was only 1.2 fold higher than the biochar from the same feedstock produced at 350°C, while the PAH concentrations in the biochars produced at 750°C with the Stage II pyrolysis unit were 1.9 fold to 23.3 fold higher than the 350°C-biochars (DW 21.8 fold, ADX 23.3 fold, MC 1.9 fold and WC 5.0 fold) (Figure 5.2).

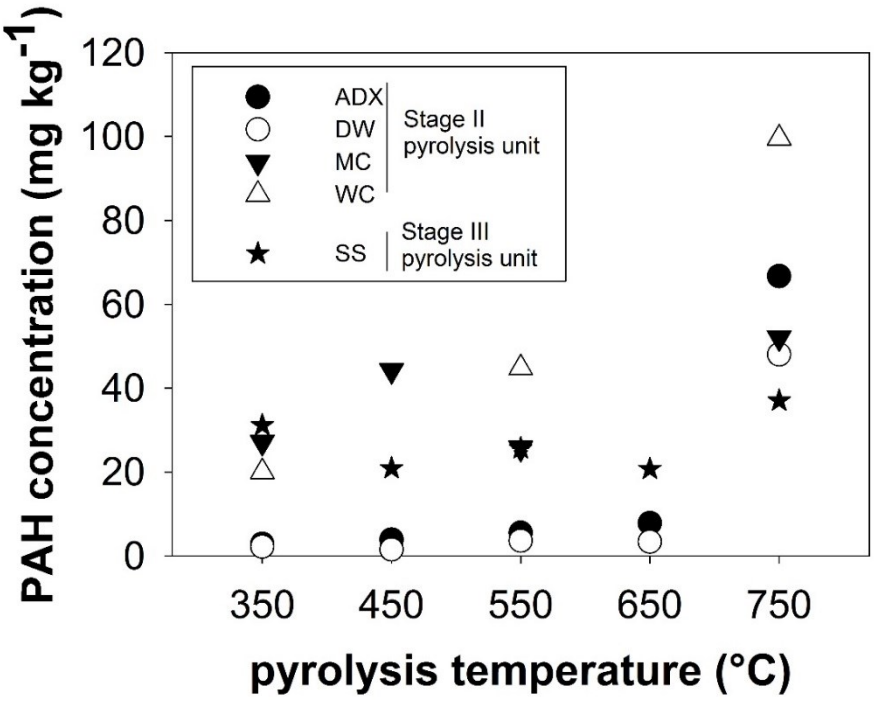


Figure 5.2: Effect of pyrolysis temperature on 16 US EPA PAH concentration in biochar (mg kg^{-1}). The biochars were produced from four different feedstocks in Stage II pyrolysis unit (ADX, *Arundo donax*; DW, demolition wood; MC, miscanthus chips; WC, willow chips) and one feedstock in Stage III pyrolysis unit (SS, sewage sludge). For all the feedstocks combined, the PAH concentration in the biochars produced at 750°C is significantly different to all the other pyrolysis temperatures (HTTs) (one-way ANOVA).

So far, no satisfactory explanation has been given in the literature regarding the relationship of PAH concentrations in biochar and pyrolysis HTT (Bucheli et al., 2015). Brown et al. (2006) (450-1000°C) and Freddo et al. (2012) (300, 600°C) reported decreasing PAH concentrations with increasing temperature. Kloss et al. (2012) (400-525°C) did not observe any temperature dependence, while Rogovska et al. (2012) (450-850°C) and Zielińska and Oleszczuk (2015) (500-700°C) found that PAH concentrations increased with increasing pyrolysis temperature. In the current study, the PAH concentrations were not significantly different in biochars produced in the temperature range 350-650°C. At 750°C, however, a significant increase in PAH concentration was observed. Although most published studies did not investigate biochar produced at temperatures ≥700°C, those that did, did not report any marked increase in PAH concentrations at temperatures ≥700°C (Brown et al., 2006; Dai et al., 2014b; Devi and Saroha, 2015; Hale et al., 2012; Keiluweit et al.,

2012). Several studies observed maximum PAH concentrations in biochars produced at lower pyrolysis temperatures than 750°C, e.g. Hale et al. (2012) over the range 350-550°C using various feedstocks; Devi and Saroha (2015) at 500°C with sewage sludge; Keiluweit et al. (2012) at 500°C with wood and grass and Dai et al. (2014b) at 600°C with sewage sludge.

Although there appears to be no clear trend in biochar PAH concentrations with temperature, PAH yield in all pyrolysis products, i.e. solids, liquids and gases, has been shown to increase with temperature (at least in the temperature range suitable for biochar production) (Aracil et al., 2005; Dai et al., 2014a; McGrath et al., 2001, 2003; Sharma and Hajaligol, 2003; Wei and Lee, 1998; Zhou et al., 2014b). The PAH yield at a particular temperature consists of PAH formation and destruction (conversion of PAHs into lighter hydrocarbons/gases (Dai et al., 2014b; McGrath et al., 2001) and condensation to form high molecular weight PAHs/pyrolytic carbon (Keiluweit et al., 2012; Sharma and Hajaligol, 2003; Zhou et al., 2014b)). This concept is illustrated in Figure 5.3. However, during fast/slow pyrolysis the particle that is heated up goes through all the different temperature phases in rapid/slow succession until the highest treatment temperature (target) is reached, e.g. as shown in Huang et al. (2013). Consequently, what is actually determined when the total PAH concentration in pyrolysis solids, liquids and gases is measured is the PAH yield integrated over temperature which is the accumulation of all PAHs produced from starting to highest treatment temperature. Consequently, the peak of PAH yield (Figure 5.3A) indicates the temperature where the highest accumulated yield increase is reached (slope change Figure 5.3B). At even higher temperatures, the PAH yield decreases until PAH destruction equals PAH formation (PAH yield is zero) and the maximum accumulated PAH yield is reached (Figure 5.3A, B) which is between 750-900°C (Aracil et al., 2005; Dai et al., 2014a, 2014b; Zhou et al., 2014b).

However, neither PAH formation, nor accumulated PAH yield alone are the key for elucidating the relationship between pyrolysis temperature and PAH concentrations in biochar; the distribution of PAHs into the pyrolysis fractions is a highly important contributing factor. Since PAHs are reported to be mostly formed at the gas-solid interphase (Bucheli et al., 2015; Hajaligol et al., 2001; Keiluweit et al., 2012; McGrath et al., 2003; Zhou et al., 2014b), most PAHs created are easily vaporised at

typical pyrolysis temperatures (>99% end up in pyrolysis liquids/gases) (Dai et al., 2014b; Fagernäs et al., 2012a). Naturally, increasing pyrolysis temperature leads to higher PAH vaporisation from pyrolysis solids which counteracts the increasing amount of accumulated PAH yield at higher temperatures. The difference between PAHs formed and PAHs vaporised is the actual concentration of PAHs in biochar, which is illustrated in Figure 5.3C. It is hypothesised that simultaneous increase in PAH formation and PAH vaporisation with temperature is the reason why no general trend of PAHs in biochar with pyrolysis temperature has been reported in literature as the effects are counteracting, one resulting in increased and one in decreased PAHs in biochar (Figure 5.3C).

This explanation is supported by the PAH concentrations in biochars produced in the temperature range 350-650°C (Table 5.2) where no significant changes were seen. Yet, the significantly higher PAH concentrations observed in biochars produced at 750°C (with the Stage II pyrolysis unit) in the current study could be seen as contradictory. However, a plausible explanation of this unit-specific effect, is that it is caused by the pyrolysis unit design and operation, resulting in distribution of temperatures that allowed cooling of volatiles at the discharge end of the unit. Due to the pyrolysis unit design, where pyrolysis vapours (containing >99% of the produced PAHs (Dai et al., 2014b; Fagernäs et al., 2012a)) travel concurrently through the pyrolysis chamber and into a discharge chamber where biochar is separated, extensive contact between biochar and vapours is possible. Therefore, if at any point the reactor or material temperature drops below the dew point of the tars, including PAHs in the pyrolysis vapours, these would condense onto the biochar. This effect has been described in section 2.2.6. The discharge chamber of the Stage II pyrolysis unit is actively heated up with heating tapes which are fixed at a certain temperature irrespective of the pyrolysis temperature. This can result in a major difference in furnace and discharge chamber temperature and condensation of pyrolysis vapours, including PAHs. The discharge chamber of the Stage III pyrolysis unit, however, is heated by the furnace and released vapours/gases and consequently, the temperature of the discharge chamber is increasing with the furnace temperature. The difference in set-up of the discharge chamber may be the reason for the difference in PAH

concentration observed for the biochars produced at 750°C with the Stage II and III pyrolysis unit.

5.3.2 Effect of carrier gas flow and residence time on PAHs in biochar

The effects of carrier gas flow rate, HTT, and residence time at HTT on PAH concentrations were tested by pyrolysing two feedstocks (straw, wood) at twelve different conditions in a batch pyrolysis reactor (Stage I), respectively (Figure 5.4). Straw pyrolysis yielded biochar with much higher PAH concentrations than wood (further discussed in section 5.3.3). The biochars that only differed in residence time showed very similar PAH concentrations (Figure 5.4), confirming previous observations that in these samples residence time at HTT in the range investigated had negligible effect on resulting biochars (energy content of pyrolysis products and carbon sequestration potential tested in Crombie and Mašek (2015)).

It is also apparent that the concentration of PAHs in biochar decreased with increasing carrier gas flow rate irrespective of HTT and residence time from 43.1 mg kg^{-1} to 17.3 mg kg^{-1} and 3.5 mg kg^{-1} for biochars produced from WSP and 7.4 mg kg^{-1} to 2.0 mg kg^{-1} and 1.5 mg kg^{-1} for biochars produced from SWP (Figure 5.4, averages in Table 5.3). For biochars from both feedstocks this meant a significant reduction of PAHs due to increased carrier gas flow rates from 0 to 0.33 L min^{-1} (two-sample, two-tailed t-test; WSP II: p-value=0.046, SWP II: p-value=0.048) and from 0 to 0.67 L min^{-1} (WSP II: p-value=0.0003, SWP II: p-value=0.035). At 650°C the effect was more pronounced, with a sharp decline with increase of carrier gas flow rate from 0 to 0.33 L min^{-1} for both feedstocks. At 350°C the decrease with flow rate was more gradual, ultimately reaching concentrations similar to those obtained for the 650°C biochar when the carrier flow rate was increased to 0.67 L min^{-1}. Most importantly both feedstocks resulted in biochars with PAH concentrations of less than 6 mg kg^{-1} (IBI lower guideline value) at higher carrier gas flow rate, and wood pellets biochars even stayed below the premium grade biochar limit (4 mg kg^{-1}) at low carrier gas flow rate. It was shown that increasing carrier gas flow through the bed of biomass undergoing pyrolysis in a fixed bed reactor decreased the PAH concentrations in biochar. On the other hand, residence time of biomass at HTT in the fixed bed did not have any discernible effect on PAH concentrations.

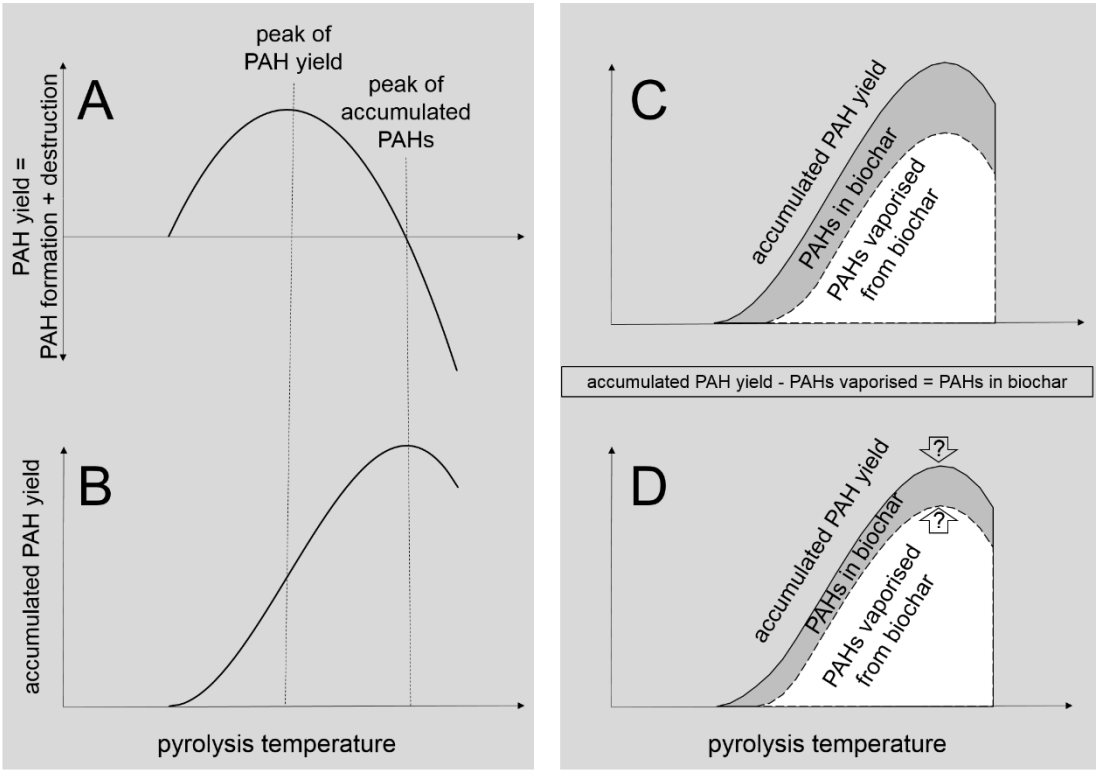


Figure 5.3: Schematic illustration of conceptual relationship of PAHs and pyrolysis temperature. (A) shows PAH yield consisting of PAH formation and destruction, regarding each individual pyrolysis temperature separately. (B) is the integral of (A) and shows the total yield accumulated over the whole temperature range up to the highest treatment temperature, i.e. the PAH yields from each temperature step summed up. (C) shows the concentration of PAHs in biochar at each pyrolysis temperature as the difference between accumulated PAH yield (as in (B)) and PAHs vaporised (released from solids to gas phase). (D) shows which effect increased carrier gas flow had on PAHs in biochar which was either caused by a decreased PAH yield or an increased PAH vaporisation from the solid (indicated as arrows with question marks in the schematic).

Table 5.3: Average concentration of PAHs (mg kg^{-1}) in biochars produced from straw pellets (WSP II) and softwood pellets (SWP II) using the same carrier gas flow. On the right side the results from two-sample, two-tailed t-tests comparing the different treatments is shown. Significant differences are shown in bold.

	PAH concentration			p-value	
carrier gas flow	WSP II	SWP II	carrier gas flow	WSP II	SWP II
L min^{-1}	mg kg^{-1}	mg kg^{-1}	comparison		
0	43.1	7.4	0 vs 0.33	**0.046**	**0.048**
0.33	17.3	2.0	0.33 vs 0.67	0.167	0.064
0.67	3.5	1.5	0 vs 0.67	**0.0003**	**0.035**

PAHs are mainly formed through secondary reactions of vapours, and similar reaction pathways also form biochar through combining PAHs to higher molecular weight PAHs and further combine these to build pyrolytic carbon (Hajaligol et al.,

2001; McGrath et al., 2001; Sharma and Hajaligol, 2003). It is reported that the magnitude of secondary (char) reactions is mainly influenced by the intensity and duration of contact of vapours with feedstock/biochar (Connor, 2008; Huang et al., 2013) as longer vapour residence times increase biochar yields (Zaror et al., 1985). This means that reduced hot vapour residence time, besides reducing biochar formation (Crombie and Mašek, 2015), should also reduce PAH formation as already speculated in McGrath et al. (2003) and shown in Dai et al. (2014a).

Residence time of feedstock in the heated zone, however, must be clearly differentiated from hot vapour residence time. During fast pyrolysis, vapour residence time indeed is influenced by residence time of the feedstock in the heated zone and has a major effect on PAH yield (McGrath et al., 2001). Residence time during slow pyrolysis, on the other hand, is in the range of minutes (10 and 40 min tested here) to hours and hot vapour residence time in the range of seconds, which is much longer than during fast pyrolysis (Bridgwater, 2013). Consequently, during slow pyrolysis in a batch reactor, variation of the residence time of the feedstock in the heated zone has much less effect on hot vapour residence time. This could explain why no effect of residence time on PAH concentration has been observed in this study. However, it needs to be stressed that this has only been investigated in a batch reactor and in a continuous pyrolysis reactor the system is quite different. In a continuous unit, pyrolysis vapours can interact with pyrolysis solids further down-stream within the pyrolysis unit on their way to the gas outlet (e.g. after-burner) (Huang et al., 2013). Therefore, in a continuous unit a change of residence time could also have an effect on secondary char reaction and on PAH concentration in biochar.

Carrier gas flow rate also affects the vapour-solid interaction. In a batch-reactor with no carrier gas flow, the gas-solid residence time for secondary reactions to take place is maximised (Crombie and Mašek, 2015; Zaror et al., 1985). Higher carrier gas flow decreases the hot vapour residence time which results in decreased PAH formation (Dai et al., 2014a). In addition, carrier gas flow rate increases the driving force for physical removal of PAHs from the solids (biochar). Thus, carrier gas flow increases PAH vaporisation from biochar and decreases PAH formation which is illustrated in Figure 5.3D, however, it is unclear which is the dominant factor. Considering the

small proportion of PAHs that attached to pyrolysis solids without carrier gas flow in the Fagernäs et al. (2012) study (0.6% = 24 mg kg^{-1}), a small change in the distribution of PAHs in solids and liquids/gases could have a large effect on total PAH concentrations in biochar. The phenomenon that carrier gas flow has a major effect on PAH concentrations in biochar could explain parts of the high fluctuations of PAH concentrations reported in literature and increased PAH concentrations in biochars produced under field conditions (no carrier gas flow) (Hale et al., 2012). Again, this has only been investigated in a batch reactor and needs to be tested for continuous units.

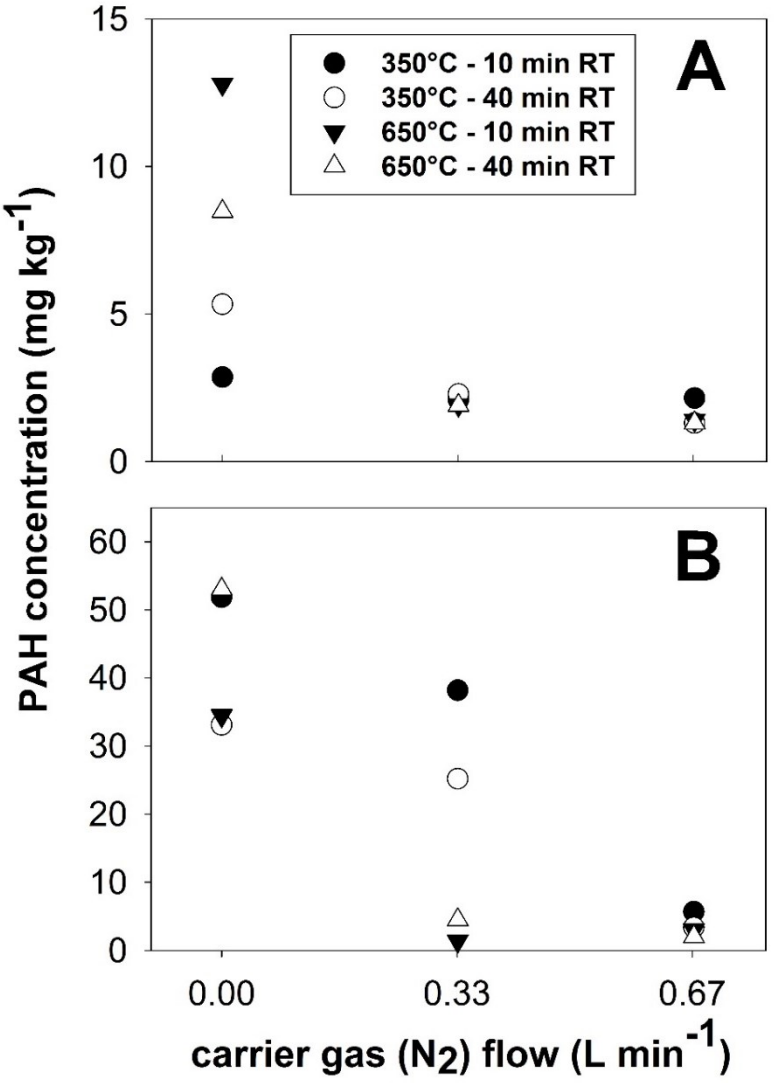


Figure 5.4: Effects of HTT, residence time (RT) and carrier gas flow rate on 16 US EPA PAH concentration in biochar (mg kg^{-1}). Biochars were produced from (A) softwood pellets (SWP II) and (B) straw pellets (WSP II) in Stage I pyrolysis unit.

5.3.3 Effect of biomass type on PAHs in biochar: wood – straw

As already indicated above in Figure 5.4, there is a notable difference in scale for total PAH concentrations for (A) wood- and (B) straw-derived biochars produced at twelve different pyrolysis conditions, respectively. The results showed that straw pyrolysis yielded biochars with significantly higher PAH concentrations compared to softwood pellets (two-sample, two-tailed t-test, p-value=0.007), on average the PAH concentration in straw biochar was 5.8 fold higher than in wood biochar (Table 5.4). The difference in PAH concentrations between straw and wood biochar was most apparent at low carrier gas flow rates, but were almost undetectable at the highest carrier gas flow rate in the range investigated.

Table 5.4: Total PAH concentrations (mg kg^{-1}) of biochars produced under varying pyrolysis conditions from two feedstocks (WSP II, straw pellets; SWP II, softwood pellets). Production conditions are highest treatment temperature (HTT), residence time (RT) and carrier gas flow rate (CGF). On average WSP-derived biochar had 5.8 times higher PAH concentrations than SWP II-derived biochar.

production conditions			PAH concentration	
HTT	RT	CGF	WSP II	SWP II
°C	min	L min^{-1}	mg kg^{-1}	mg kg^{-1}
350	10	0	52	2.9
350	40	0	33	5.3
650	10	0	34	13
650	40	0	53	8.5
350	10	0.33	38	2.1
350	40	0.33	25	2.3
650	10	0.33	1.4	1.9
650	40	0.33	4.5	1.9
350	10	0.66	5.7	2.2
350	40	0.66	3.4	1.3
650	10	0.66	3.0	1.4
650	40	0.66	2.0	1.3
	average		21.3	3.6
			average difference 5.8	
two-sample, two-tailed t-test, p-value: 0.007				

The findings that straw-derived biochar contained 5.8 times more PAHs than wood-derived biochar are similar to those obtained by Keiluweit et al. (2012) who reported four times higher concentrations of PAHs in grass-derived biochar produced at 500°C, compared to wood biochar. Similarly, Kloss et al. (2012) observed considerably higher PAH concentrations in straw-derived biochar compared to

spruce-derived biochar and Fabbri et al. (2013) reported that slow pyrolysis of woody biomass resulted in the lowest PAH concentrations compared to various other feedstocks.

In general, lignin-rich feedstocks have been observed to produce biochars with less PAHs than those which are comprised mainly of pectin and cellulose (Sharma et al., 2004; Sharma and Hajaligol, 2003). Yet, the opposite was observed by Zhou et al. (2014a). As the lignin content of straw pellets and wood pellets used in the current study was very similar (~22%, analysed in Crombie and Mašek (2014)), the content of lignin cannot explain the trends observed in the current study. Besides lignin content, the composition of lignin, which is very different between straw and woody biomass (Burhenne et al., 2013; del Río et al., 2012) could be at least partly responsible for differences in PAH content, however, insufficient studies on this are available. In addition, the C, H, N, O-elemental contents and cellulose and hemicellulose content of the feedstocks varied greatly (Crombie and Mašek, 2014) which could explain the different PAH contents after pyrolysis. Zhou et al. (2014a) observed non-additive, synergistic effects of biomass components, i.e. of cellulose, hemicellulose and lignin, on the formation of PAHs during pyrolysis, making prediction of PAH concentrations in biomass based on feedstock composition very challenging.

5.4 Conclusions

From data collected on the 46 biochars investigated in this study, it is concluded that residence time at peak temperature (slow pyrolysis, batch reactor) did not influence the PAH concentration in biochar. On the other hand, it was observed that pyrolysis of woody biomass yielded biochar with considerably lower PAH contents than straw biomass, at least in the units and operating conditions deployed in this study. Overall, this work showed how complex the matter of effects of feedstock characteristics on PAH concentrations in biochar is and how many factors could have an influence. This study presents a significant contribution to the limited body of knowledge on feedstock effects on PAHs in biochar and shows that: (I) feedstock selection is a critical parameter and (II) careful matching with conversion technology is necessary to ensure production of biochars with low PAH concentration. Based on the extensive data set collected in this study, it is not possible to recommend particular HTTs for production of biochar with low PAH content. This research showed that HTT alone did not seem to be the main influencing factor of PAH concentration in biochar. The HTT should be considered in conjunction with the specific design of the pyrolysis unit used, as this study indicates that it is the combined effect that determines the PAH concentrations in resulting biochar. Besides HTT, the flow of carrier gas in the pyrolysis reactor has an important effect and in general, higher carrier gas flow rate resulted in biochars with lower PAH concentrations (independent of HTT, residence time and feedstock). However, even low carrier gas flow rates can be sufficient for production of biochar with PAH concentrations below guideline values, for certain feedstock, HTT and unit design. Overall, it may not be possible to completely eliminate formation of PAHs during biomass pyrolysis, but it is possible to minimise contamination of produced biochar by suitably combining feedstock with conversion unit and operating parameters. In this study, it was shown that ‘clean’ biochar, i.e., with low PAH content, can be produced from a range of feedstock and in different units. Furthermore, this study provides critical information for bringing us one step closer to production of biochar with low PAH contamination from diverse biomass using different production processes. However, an assessment of the risk of PAHs for human health and plant growth is lacking which will be conducted in Chapter 6 and Chapter 9.

Chapter 6 Composition of PAHs in biochar and implications for recommendations for biochar production

The following chapter is based on the submitted manuscript:

Buss, W., Graham, M.C., Mašek O. Composition of PAHs in biochar and implications for biochar production. J. Anal. Appl. Pyrolysis (submitted)

Journal impact factor (2014): 3.564

The candidate was solely responsible for data analysis and writing of the article and this chapter. Supervisors provided guidance and supervisors and co-authors contributed to the editing of the manuscript. The experimental work was performed by the candidate apart for production of some biochars which was performed by Peter Brownsort, Kyle Crombie, Clare Peters, Juan Luis Turrion-Gomez and Walter Lowe.

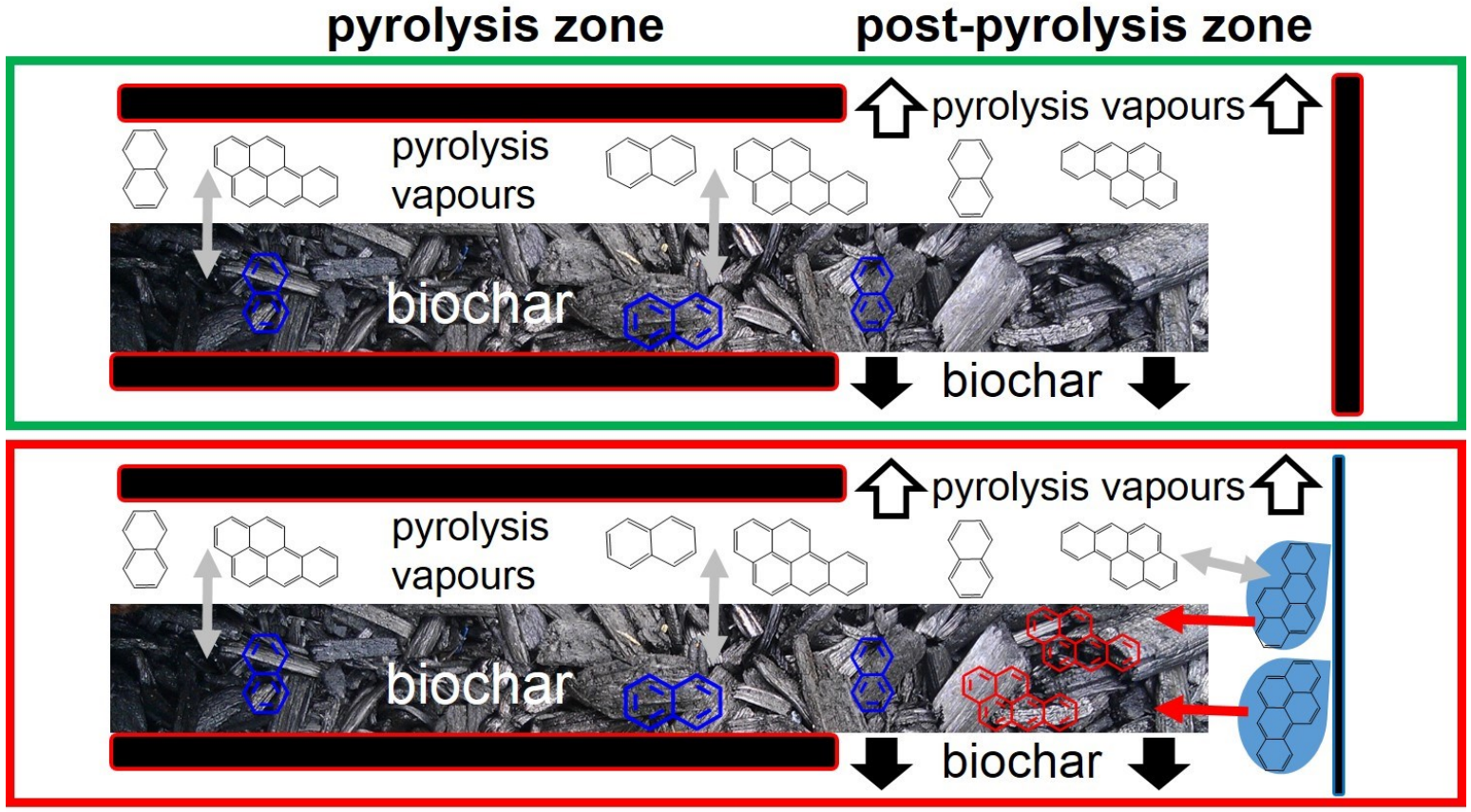


Figure 6.1: Graphical abstract of Chapter 6. The effect of condensation of pyrolysis vapours due to cold zones in the post-pyrolysis area is presented. Biochar is transported from the left to the right. In the post-pyrolysis zone pyrolysis vapours and biochar are separated. The green box shows biochar production in a well-insulated post-pyrolysis zone which does not result in significant condensation of pyrolysis vapours on the wall of the pyrolysis unit. Consequently, the biochar produced with this unit contains only a low concentration of PAHs. The post-pyrolysis zone of the pyrolysis unit in the red box is not insulated sufficiently. Therefore, during biochar production vapour condensation occurs which results in increased concentration of PAHs, in particular of higher molecular weight PAHs.

6.1 Introduction

Exposing biomass to high temperatures in an oxygen-limited atmosphere, results in the formation of potentially toxic substances. A variety of intermediate, primary and secondary degradation products of cellulose, hemicellulose and lignin and newly synthesised hydrocarbons are formed during pyrolysis. These compounds can either be further transformed into so-called secondary char or get released into the vapour phase (Cordella et al., 2012; Fagernäs et al., 2012b; Huang et al., 2013).

Polycyclic aromatic hydrocarbons (PAHs) is one of the groups of hydrocarbons that form during pyrolysis. PAHs are commonly defined as organic compounds composed of polycyclic aromatic networks containing only C and H and at least two aromatic rings (Baek et al., 1991). Previous studies reported that >99% of the PAHs formed will end up in the pyrolysis liquid and gas fraction in the whole temperature range suitable for biochar production (Dai et al., 2014b). PAHs have been shown to cause short-term adverse effects in humans and plants, but their long-term effects are of particular concern causing carcinogenic, mutagenic and teratogenic effects (The Environmental Applications Group LTD, 1990; US Department of Health and Human Services, 1995). Although a huge variety of PAHs exists (US Department of Health and Human Services, 1995), in most cases legislation threshold values are given for the sum of 16 US EPA PAHs as published in the priority pollutant list of the US EPA proposed in the late 1970s (Keith, 1979).

PAH threshold values have been established for various soil and soil amendments, such as soils in residential areas (20 mg kg^{-1}) (Australia National Environment Protection Council, 1999), for compost made from waste (6 mg kg^{-1}) (Austrian Compost Ordinance, 2001) and for compost and digestate (4 mg kg^{-1}) (Swiss Chemical Risk Reduction Ordinance, 2005) which are all based on the sum of the concentrations of the 16 US EPA PAHs. Several biochar guideline values, proposed for safe biochar production, are based on the mentioned legislation and consequently, PAH limit values in the International Biochar Initiative (IBI) guidelines, European Biochar Certificate (EBC) and in the Biochar Quality Mandate (BQM) are also based on the sum of 16 US EPA PAHs (British Biochar Foundation, 2013; EBC, 2012b; International Biochar Initiative, 2011).

A number of studies have investigated the total concentration of PAHs in various biochars and overall, the PAH concentrations varied greatly, from 0.07 and 355 mg kg^{-1} (Freddo et al., 2012; Hale et al., 2012; Hilber et al., 2012; Kloss et al., 2012). Despite the relatively large number of biochar types analysed, it has so far been challenging to give specific recommendations regarding production conditions and feedstocks for production of biochars with low PAH concentrations (below threshold values).

Although the EPA identified 16 priority PAHs as the main PAHs of concern, the chemical structures of these compounds vary greatly, and so do their properties and toxicities. Among the 16 US EPA PAHs, naphthalene (NAP) is the only one with two aromatic rings, it is the least toxic one and, according to some definitions, it actually does not belong to the PAH category (Delistraty, 1997). NAP is not considered to be carcinogenic, nor genotoxic, the LD 50 (lethal dose to kill half of the population) for mice and rats is as high as 350-9500 mg kg^{-1} body weight (European Commission Scientific Committee on Food, 2002). NAP is also the most volatile PAH and evaporates significantly when present in soil (US Department of Health and Human Services, 1995). Furthermore, the half-life of NAP in soil was reported to be only two days, the shortest of eleven PAHs tested and in some cases NAP can be degraded in hours, e.g. in sediment that has previously been contaminated with PAHs and where microbial communities have adapted (US Department of Health and Human Services, 1995).

The different status of NAP compared with the rest of the 16 US EPA PAHs has been recognised and after recommendation by the European Scientific Committee on Food in 2005, the EU Commission established a list of 15 priority pollutants for investigation in food which did not include NAP (nor some other lower toxicity PAHs such as phenanthrene) (EU Commission Recommendation, 2005). The PAH-related risk associated with biochars containing similar total PAH concentration can vary greatly, depending on PAH composition; NAP plays an important role as it typically comprises ≥40% of the total PAH concentrations in biochar (Bucheli et al., 2015; Freddo et al., 2012; Hilber et al., 2012; Khalid and Klarup, 2015; Kloss et al., 2012; Quilliam et al., 2013; Yargicoglu et al., 2015). It is clear that even biochar with a high content of total 16 US EPA PAHs may not pose environmental or health risk

if NAP is the major PAH component. Previous studies have shown, however, that the NAP content in biochar can vary widely, e.g. in Fabbri et al. (2013) the percentage of NAP was between 14 and 63% and in Freddo et al. (2012) between 11 and 83%. Significantly, very few biochar studies to date have considered the different composition of PAHs and the implications for biochar production and utilisation (Dai et al., 2014a) and even existing guidelines for biochar use fail to take into account the discrepancy between sum of PAH concentrations, individual composition of PAHs and risk. This highlights the need for a risk-based evaluation of PAHs in biochars based on PAH concentration and composition, rather than total content.

While in the previous chapter only total PAH concentrations were investigated, in this chapter, the relative concentrations of 16 US EPA PAHs were investigated in 84 biochars produced from various feedstock and production conditions, in three slow pyrolysis units of different scales. This extensive set of biochar samples and the fact that different technologies with well-monitored production conditions and at different scales were used, makes this data set unique. The objective was to develop recommendations for production of biochar with low PAH-related risk. In particular, the aim was to investigate, whether high concentrations of non-NAP 16 US EPA PAHs in biochars can be linked to particular pyrolysis conditions. Consequently, the ten of the 84 biochars with the highest non-NAP PAH concentrations were studied to pinpoint the reasons for the high concentrations, based on detailed and in-depth understanding of the production processes.

6.2 Materials and methods

6.2.1 Biochars

84 biochars were produced from fourteen different feedstocks in three different pyrolysis units at the UKBRC (rotary kiln, auger reactor and fixed bed reactor). The parameters controlled during the production include: HTT, residence time and carrier gas flow rates. Some of the materials also reflected changes to the pyrolysis unit set-up. In addition, four different feedstock pre-treatments (K^+-doping, washing, drying, increase of moisture content), and one biochar post-treatment (treatment at 200°C for 20 h) were applied. Overall, as many parameters as possible were covered that could potentially affect the concentration and composition of PAHs in biochar.

All biochars described in section 2.2.5 and 2.2.6 and thirteen of the nineteen biochars described in section 2.2.4 (ADX 350-750, DW 350-750, WHI 550, WSI 550, FWD 550) were analysed in this study. An overview of all biochars and their production conditions can be found in Table 6.1.

6.2.2 PAH analysis

Representative samples were taken from all biochar samples, ground biochars were extracted using a 36 h extraction with toluene and the resulting extracts were analysed by GC-MS. The analyses were performed by Northumbrian Water Scientific Services (Newcastle, United Kingdom), accredited by United Kingdom Accreditation Service (UKAS). More details can be found in section 2.5. The individual concentrations of 16 US EPA PAHs in 84 biochars are reported.

6.3 Results and discussion

The 16 US EPA PAH concentration without NAP in the following will be referred to as 'non-NAP PAHs'. The individual concentrations of all 16 US EPA PAHs in the 84 biochars are shown in Digital Appendix Table 3.

Table 6.1: Production conditions, total 16 US EPA (mg kg^{-1}), naphthalene (NAP) and non-NAP PAH concentration of 84 biochars. HTT, highest treatment temperature; RT, residence time at peak temperature; HR, heating rate (batch process only); CGF, carrier gas flow; bdl, below detection limit.

biochar	feedstock	unit	HTT	RT	HR	CGF	PAHs	NAP		non-NAP
			°C	min	°C min^{-1}	L min^{-1}	mg kg^{-1}	mg kg^{-1}	%	mg kg^{-1}
DNX - 350	*Arundo donax*	Stage II	350	20	n/a	1	2.9	2.5	87	0.36
DNX - 450	*Arundo donax*	Stage II	450	20	n/a	1	3.9	3.4	88	0.47
DNX - 550	*Arundo donax*	Stage II	550	20	n/a	1	5.5	4.4	80	1.1
DNX - 650	*Arundo donax*	Stage II	650	20	n/a	1	7.8	5.5	70	2.3
DNX - 750	*Arundo donax*	Stage II	750	20	n/a	1	67	26	39	41
DW - 350	Demolition wood	Stage II	350	20	n/a	1	2.2	2.2	100	0
DW - 450	Demolition wood	Stage II	450	20	n/a	1	1.5	1.5	100	0
DW - 550	Demolition wood	Stage II	550	20	n/a	1	3.6	2.6	72	1.0
DW - 650	Demolition wood	Stage II	650	20	n/a	1	3.4	2.7	80	0.67
DW - 750	Demolition wood	Stage II	750	20	n/a	1	48	18	37	30
MC - 350	Miscanthus chips	Stage II	350	20	n/a	1	27	24	89	3.1
MC - 350 - high ash	Miscanthus chips	Stage II	350	20	n/a	1	16	15	91	1.4
MC - 350 - low ash	Miscanthus chips	Stage II	350	20	n/a	1	42	34	80	8.5
MC - 450	Miscanthus chips	Stage II	450	20	n/a	1	44	44	99	0.24
MC - 450 - dry	Miscanthus chips	Stage II	450	20	n/a	1	34	21	61	13
MC - 450 - wet	Miscanthus chips	Stage II	450	20	n/a	1	35	35	99	0.38
MC - 550	Miscanthus chips	Stage II	550	20	n/a	1	26	25	97	0.74
MC - 550 - dry	Miscanthus chips	Stage II	550	20	n/a	1	30	30	99	0.29
MC - 550 - high ash	Miscanthus chips	Stage II	550	20	n/a	1	14	14	100	0
MC - 550 - low ash	Miscanthus chips	Stage II	550	20	n/a	1	22	22	99	0.3
MC - 550 - wet	Miscanthus chips	Stage II	550	20	n/a	1	36	36	100	0.14
MC - 750	Miscanthus chips	Stage II	750	20	n/a	1	52	44	85	8.1
MC - 750 - dry	Miscanthus chips	Stage II	750	20	n/a	1	26	21	82	4.5
MC - 750 - high ash	Miscanthus chips	Stage II	750	20	n/a	1	49	26	53	23
MC - 750 - low ash	Miscanthus chips	Stage II	750	20	n/a	1	168	55	33	113
MC - 750 - wet	Miscanthus chips	Stage II	750	20	n/a	1	53	37	70	16
SS II - 350	Sewage sludge II	Stage III	350	20	n/a	10	31	24	77	7.2
SS II - 450	Sewage sludge II	Stage III	450	20	n/a	10	21	17	81	3.9
SS II - 550	Sewage sludge II	Stage III	550	20	n/a	10	26	20	78	5.6
SS II - 650	Sewage sludge II	Stage III	650	20	n/a	10	21	18	87	2.7
SS II - 750	Sewage sludge II	Stage III	750	20	n/a	10	37	32	87	5.0

SWP II-350-10-0	Softwood pellets II	Stage I	350	10	5	0	2.9	2.7	94	0.16
SWP II-350-10-0.33	Softwood pellets II	Stage I	350	10	5	0.33	2.1	1.9	91	0.19
SWP II-350-10-0.66	Softwood pellets II	Stage I	350	10	5	0.67	2.2	1.5	70	0.65
SWP II-350-40-0	Softwood pellets II	Stage I	350	40	5	0	5.3	4.9	92	0.43
SWP II-350-40-0.33	Softwood pellets II	Stage I	350	40	5	0.33	2.3	2.0	87	0.29
SWP II-350-40-0.66	Softwood pellets II	Stage I	350	40	5	0.67	1.3	1.3	100	0
SWP II-650-10-0	Softwood pellets II	Stage I	650	10	5	0	13	11	86	1.8
SWP II-650-10-0.33	Softwood pellets II	Stage I	650	10	5	0.33	1.9	1.8	94	0.11
SWP II-650-10-0.66	Softwood pellets II	Stage I	650	10	5	0.67	1.4	1.4	100	0
SWP II-650-40-0	Softwood pellets II	Stage I	650	40	5	0	8.5	7.5	89	0.97
SWP II-650-40-0.33	Softwood pellets II	Stage I	650	40	5	0.33	1.9	1.9	100	0
SWP II-650-40-0.66	Softwood pellets II	Stage I	650	40	5	0.67	1.3	1.3	100	0
WC - 350	Willow chips	Stage II	350	20	n/a	1	20	13	65	7.0
WC - 550	Willow chips	Stage II	550	20	n/a	1	45	42	94	2.8
WC - 750	Willow chips	Stage II	750	20	n/a	1	100	28	28	72
WSP II-350-10-0	Straw pellets	Stage I	350	10	5	0	52	37	71	15
WSP II-350-10-0.33	Straw pellets	Stage I	350	10	5	0.33	38	38	99	0.21
WSP II-350-10-0.66	Straw pellets	Stage I	350	10	5	0.67	5.7	5.7	100	0
WSP II-350-40-0	Straw pellets	Stage I	350	40	5	0	33	32	97	1.1
WSP II-350-40-0.33	Straw pellets	Stage I	350	40	5	0.33	25	25	99	0.21
WSP II-350-40-0.66	Straw pellets	Stage I	350	40	5	0.67	3.4	3.4	100	0
WSP II-650-10-0	Straw pellets	Stage I	650	10	5	0	34	31	90	3.5
WSP II-650-10-0.33	Straw pellets	Stage I	650	10	5	0.33	1.4	1.4	100	0
WSP II-650-10-0.66	Straw pellets	Stage I	650	10	5	0.67	3.0	3.0	100	0
WSP II-650-40-0	Straw pellets	Stage I	650	40	5	0	53	52	98	1.0
WSP II-650-40-0.33	Straw pellets	Stage I	650	40	5	0.33	4.5	4.5	100	0
WSP II-650-40-0.66	Straw pellets	Stage I	650	40	5	0.67	2.0	2.0	100	0
SWP I - 550 - GC	Softwood pellets I	Stage III	550	20	n/a	10	53	8.2	15	45
SWP I - 550 - LC	Softwood pellets I	Stage III	550	20	n/a	10	28	9.9	35	18
SWP I - 550 - Stage III - NC	Softwood pellets I	Stage III	550	20	n/a	10	6.1	4.3	71	1.8
SWP I - 550 - GC - 200 T	Softwood pellets I	Stage III	550	20	n/a	10	2.8	2.5	90	0.29
SWP I - 550 - 200 T	Softwood pellets I	Stage III	550	20	n/a	10	1.8	1.5	84	0.29
SWP I - 550 - LC - 200 T	Softwood pellets I	Stage III	550	20	n/a	10	1.2	0.95	79	0.26
AD - 550	Sewage sludge AD	Stage II	550	20	n/a	0*	19	17	90	1.8
AD - 700	Sewage sludge AD	Stage II	700	20	n/a	0*	22	14	63	8.3
SS I - 550	Sewage sludge I	Stage II	550	20	n/a	0*	21	20	96	0.88
SS I - 700 - no HT I	Sewage sludge I	Stage II	700	20	n/a	0*	232	25	11	207
FWD - 550	Food waste AD	Stage II	550	20	n/a	1	9.8	5.5	56	4.3
WHI - 550	Water hyacinth, India	Stage II	550	20	n/a	1	39	37	95	2.1
WSI - 550	Wheat straw, India	Stage II	550	20	n/a	1	11	8	70	3.5
SWP I - 550 - no HT III	Softwood pellets I	Stage II	550	20	n/a	1	17	17	99	0.24
SWP I - 550 - purge 2 L min^{-1}	Softwood pellets I	Stage II	550	20	n/a	1	14	13	96	0.5
SWP I - 550 - Stage I	Softwood pellets I	Stage I	550	10	80	0.3	21	21	99	0.2
SWP I - 550 - Stage II	Softwood pellets I	Stage II	550	20	n/a	1	25	25	99	0.15

SWP I - 700 - Stage I	Softwood pellets I	Stage I	700	10	87	0.3	23	23	100	0
SWP I - 700 - Stage II	Softwood pellets I	Stage II	700	20	n/a	1	20	19	97	0.5
SWP I - 700 - Stage III	Softwood pellets I	Stage III	700	20	n/a	10	20	20	100	0
WSP I - 550 - Stage I	Wheat straw pellets	Stage I	550	5	80	0.3	54	54	100	0.23
WSP I - 550 - Stage II	Wheat straw pellets	Stage II	550	20	n/a	1	67	67	99	0.5
WSP I - 550 - Stage III	Wheat straw pellets	Stage III	550	20	n/a	10	57	55	97	2.0
WSP I - 700 - Stage I	Wheat straw pellets	Stage I	700	6	80	0.3	94	73	78	21
WSP I - 700 - Stage II	Wheat straw pellets	Stage II	700	20	n/a	1	54	53	98	1.3
WSP I - 700 - Stage III	Wheat straw pellets	Stage III	700	20	n/a	10	46	46	100	0

*no carrier gas flow during operation of unit

Table 6.2: 16 US EPA PAH concentration, naphthalene concentration, proportion of naphthalene and toxicity equivalent quantity (TEQ) of 84 biochars, the ten biochars with the highest non-NAP PAH concentration (group 1) and the remaining 74 biochars (group 2).

	PAHs total		naphthalene				TEQ	
	AV	SD	AV	SD	AV	SD	AV	SD
	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	%	%	B(a)P eqi	B(a)P eqi
all 84 biochars	28	35	20	17	84	218	1.33	3.95
group 1	89	64	31	20	40	22	8.49	8.52
group 2	20	18	18	17	90	12	0.37	0.89

6.3.1 PAH composition in 84 biochars

The concentration of 16 US EPA PAHs in all 84 biochars investigated in this study was between 1.2 and 232 mg kg^{-1} and on average 28±35 mg kg^{-1} (Table 6.2) which is similar to reports for various biochars in other studies, e.g. 0.07-355 mg kg^{-1} (Anjum et al., 2014; Fabbri et al., 2013; Granatstein et al., 2009; Hale et al., 2012; Hilber et al., 2012; Kloss et al., 2012; Schimmelpfennig and Glaser, 2012). The proportion of NAP of the total PAH concentration was 84±21% (Table 6.2) and overall, the proportion ranged between 11 and 100%. Similarly high proportions of NAP were reported in other studies, e.g. in Fagernäs et al. (2012a) and in the higher temperature biochars (525°C) in Kloss et al. (2012) the proportion of NAP of the (16 US EPA) PAHs was also >80%. In a review, taking into account many biochars, rotary kilns were reported to produce biochars with a proportion of NAP of 30-80% (Bucheli et al., 2015). The average NAP proportion in this thesis is still slightly exceeding this range which is attributed to the way the proportion was calculated with individual PAH concentrations <LOD (which was 0.10 mg kg^{-1}) considered as zero. Using the LOD instead of zero results in an average proportion of NAP of 72±21% which is

well in the range reported for other biochars. The reason for the high concentration of NAP in biochars in general, could be that NAP, being the smallest PAH, has access to very small biochar pores other PAHs do not have access to where it is trapped and accumulated.

The PAH concentrations and NAP proportion for all 84 biochars is displayed in Figure 6.2. Most biochars possessed very high proportions of NAP (grey bars) and barely any other PAHs. However, some biochars stood out, as they contained very high concentrations of non-NAP PAHs (black bars) and comparatively low proportions of NAP (Figure 6.2). To investigate this phenomenon further, ten biochars with the highest non-NAP concentrations were selected and the average proportion of NAP in this group of biochar (group 1; n=10) was calculated. The resulting value was compared to the average NAP/total PAH ratio of all remaining biochars (group 2; n=74). This comparison revealed stark differences between the two groups; while in biochar group 1 NAP represented only 40% of the PAHs measured, in group 2 it represented 90% (Table 6.2). In group 1, the NAP concentration did not increase proportionally with the concentration of total PAHs, while it did for group 2 (Figure 6.3).

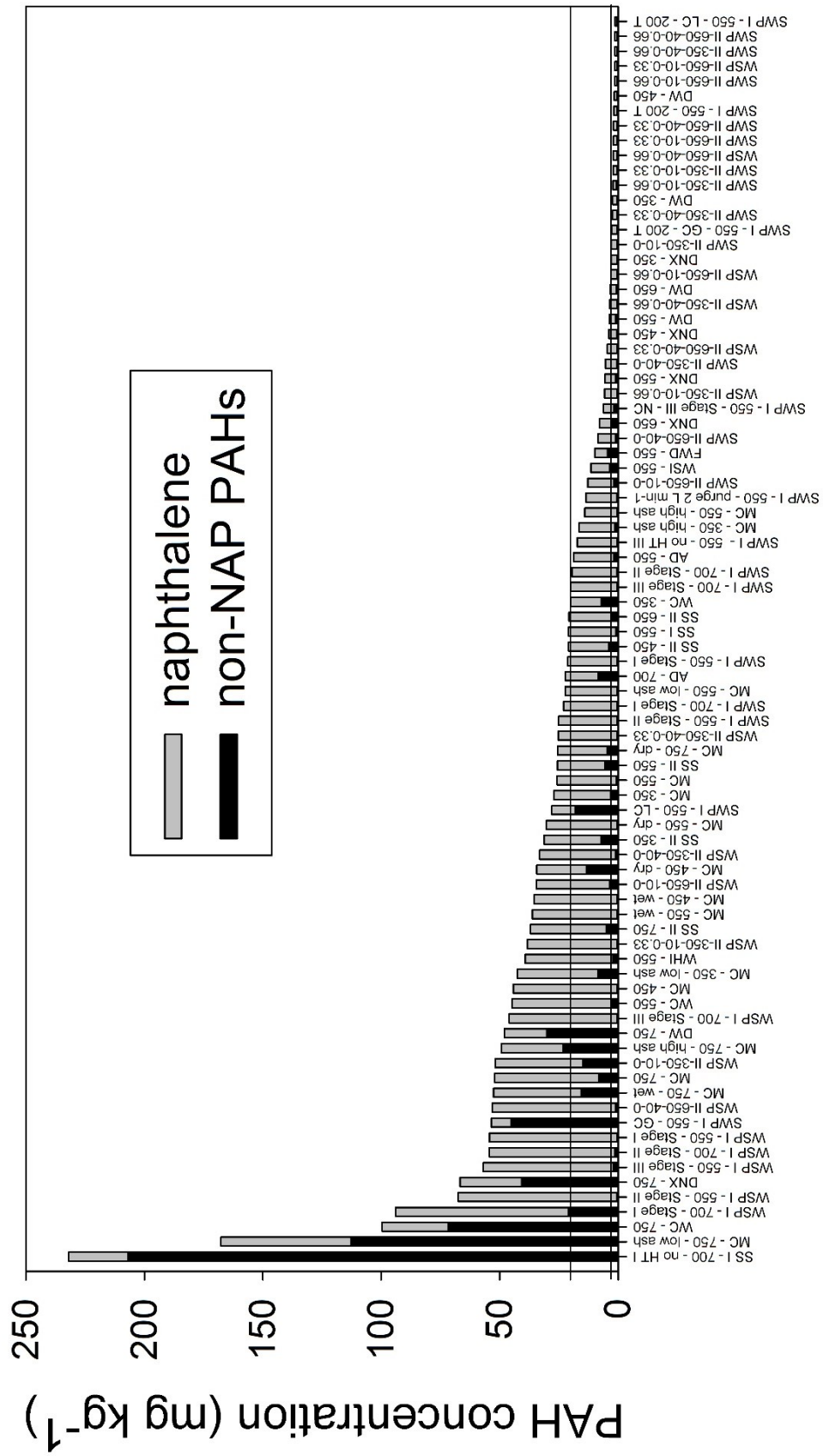


Figure 6.2: 16 US EPA PAH concentration (mg kg^{-1}) in 84 biochars. The proportions of naphthalene and non-NAP PAHs are indicated, respectively. Biochars are abbreviated in the following way: feedstock - HTT - further production conditions or pre-/post-treatments. Following PAH threshold values are indicated: upper line IBI threshold values of 20 mg kg^{-1} and lower line EBC premium quality threshold values of 4 mg kg^{-1}.

Investigating the composition of PAHs in individual biochars proved to be challenging as in most biochars individual PAH compound concentrations were under the detection limit of 0.10 mg kg^{-1} (Digital Appendix Table 3). Consequently, detailed analysis of individual PAHs was conducted only for the ten biochars in group 1. The results showed that, with the exception of the biochar with the highest PAH concentration ('SS I - 700 - no HT I'), NAP was the compound with highest concentration of all individual PAHs (Figure 6.4). The PAH with the second highest concentration in this set of ten biochars was phenanthrene which was also the PAH with the second highest concentration on average in all 84 biochars in this study (average 1.8 mg kg^{-1}) and in biochars in other studies (Fabbri et al., 2013; Hilber et al., 2012; Quilliam et al., 2013). The concentrations of the other 3-ring PAHs and more toxic 5- and 6-ring PAHs were typically slightly lower than the concentrations of 4-ring PAHs (Figure 6.4) which was also reported for other biochars (Fabbri et al., 2013; Freddo et al., 2012; Hale et al., 2012). However, 'WSP I 700' produced with the Stage I unit contained only NAP, 5- and 6-ring PAHs and surprisingly barely any PAHs with 3 and 4 rings; therefore, the composition of PAHs of this biochar is very different to all the other biochars (Figure 6.4).

In conclusion, the biochars with the highest concentration of non-NAP PAHs (group 1) had a proportionally lower concentration of NAP than the remaining biochars (group 2) (Figure 6.3). There are a number of possible causes for this distribution of PAHs in biochar and these are discussed in detail in the following section, together with options for avoiding high-non-NAP PAH biochar production.

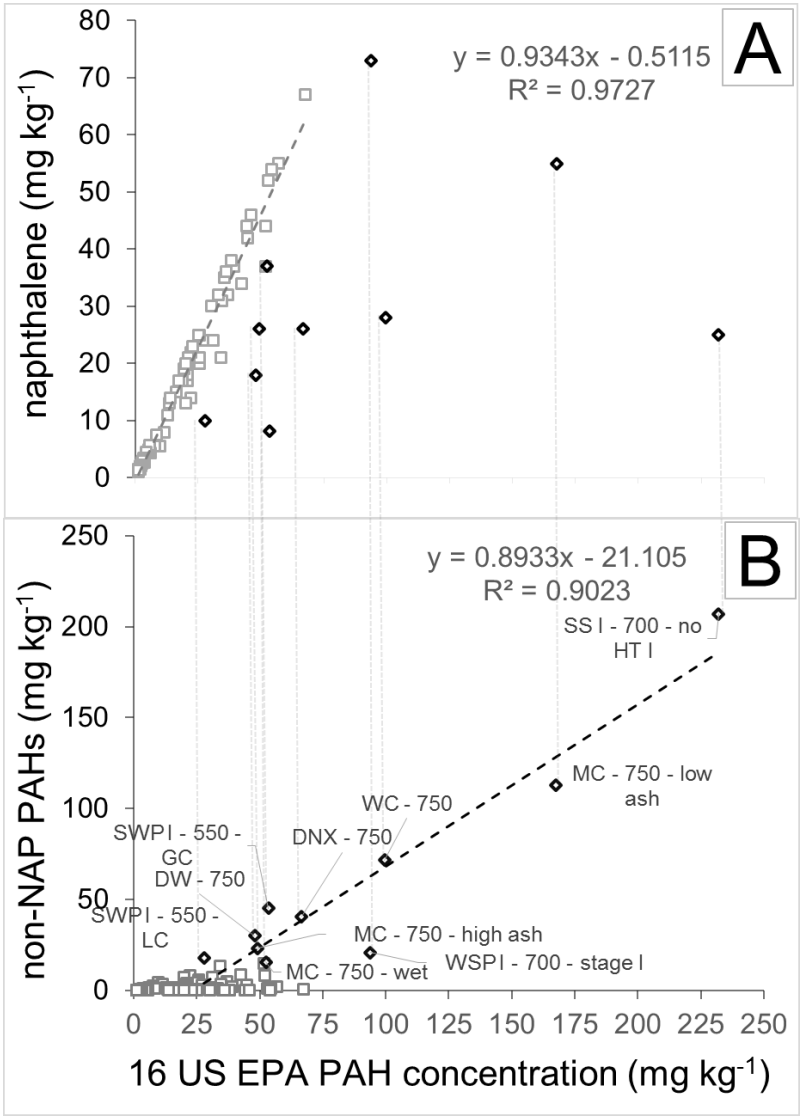


Figure 6.3: Naphthalene (A) and non-NAP PAH (B) concentrations of 84 biochars plotted with total 16 US EPA PAH concentrations, respectively. The black squares show group 1 which are the ten biochars with the highest non-NAP PAH concentrations, while the grey squares are the remaining biochars (group 2). The equations show the fit of a linear curve with group 2 in (A) and group 1 in (B).

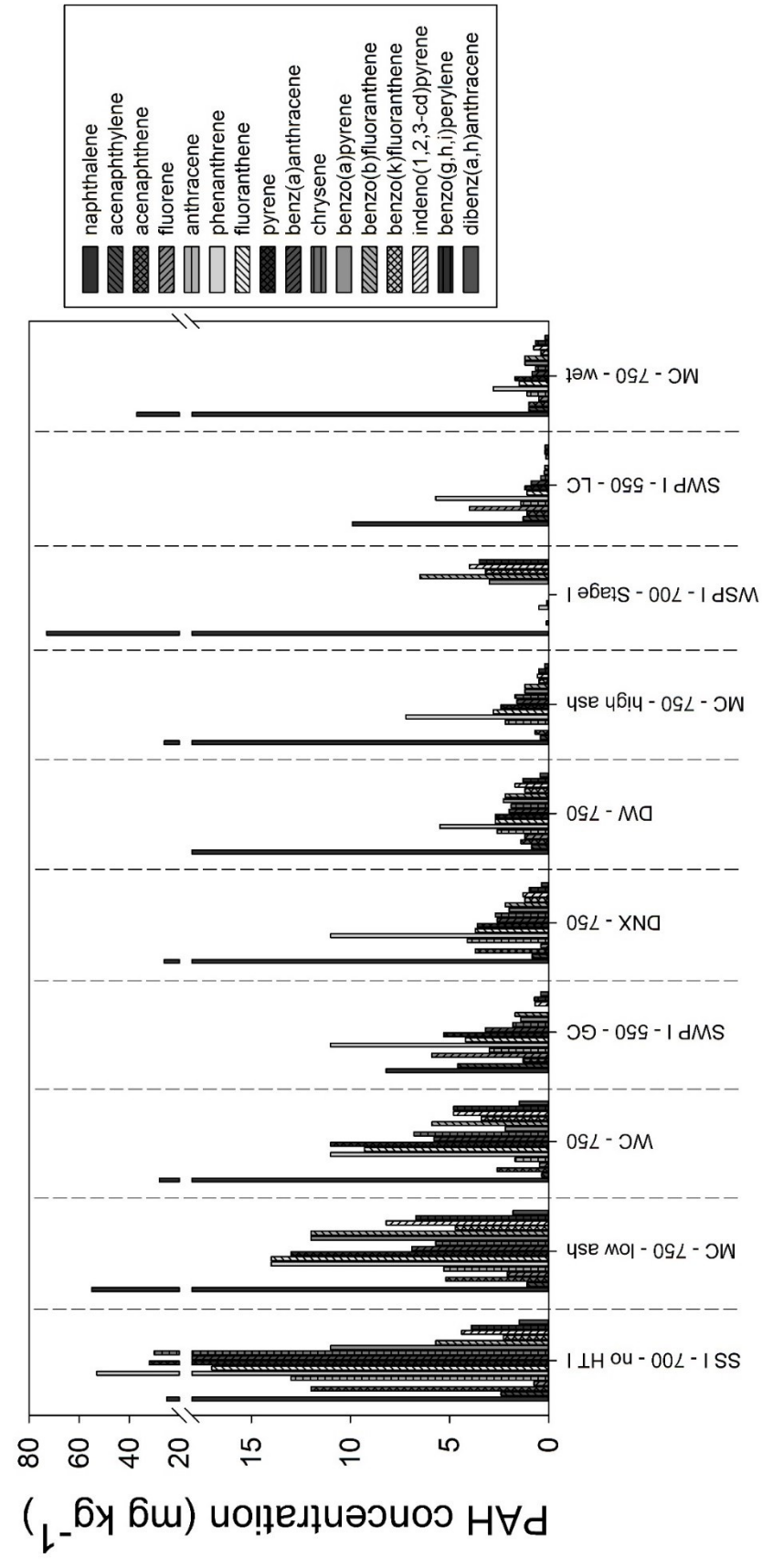


Figure 6.4: Individual concentration of 16 US EPA PAHs (mg kg^{-1}) in the ten biochars with highest non-NAP PAH concentrations (group 1). Biochars are abbreviated in the following way: feedstock - HTT - further production conditions or pre-/post-treatments.

Table 6.3: The ten biochars with the highest non-NAP PAH concentration and the feature most likely responsible for the high concentration.

biochar	non-NAP	PAH total	NAP		feature most likely responsible for high non-NAP PAHs
	mg kg $^{-1}$	mg kg $^{-1}$	mg kg $^{-1}$	%	
SS I - 700 - no HT I	207	232	25	10.8	faulty heating tape - cold spots
MC - 750 - low ash	113	168	55	32.8	750°C Stage II unit - low-temperature discharge chamber
WC - 750	72	100	28	28.1	750°C Stage II unit - low-temperature discharge chamber
SWP I - 550 - GC	45	53	8.2	15.4	pipe not insulated - cold spot in pyrolysis unit
DNX - 750	41	67	26	39.0	750°C Stage II unit - low-temperature discharge chamber
DW - 750	30	48	18	37.5	750°C Stage II unit - low-temperature discharge chamber
MC - 750 - high ash	23	49	26	52.9	750°C Stage II unit - low-temperature discharge chamber
WSP I - 700 - Stage I	21	94	73	77.7	?
SWP I - 550 - LC	18	28	9.9	35.5	discharge chamber not insulated - cold spot in pyrolysis unit
MC - 750 - wet	16	53	37	70.4	750°C Stage II unit - low-temperature discharge chamber

6.3.2 Reasons for high concentrations of non-NAP PAHs in biochar

When comparing the production conditions and feedstocks of the ten biochars with the highest non-NAP PAH concentrations, it becomes apparent that the high concentrations of PAHs cannot be associated with a particular feedstock type. Both virgin biomass, such as softwood pellets, wheat straw pellets, miscanthus and willow and non-virgin biomass (sewage sludge, demolition wood) yielded biochars with high concentrations of non-NAP PAHs under certain production conditions (Table 6.3). Furthermore, the increased non-NAP PAHs content could not be unanimously ascribed to a particular pyrolysis temperature, nor pyrolysis unit. The causes of production of biochar with increased non-NAP PAHs are complex and depend on more than simple feedstock, HTT or pyrolysis unit type. Specific causes identified for the ten biochar are discussed in the following.

6.3.2.1 Biochars produced at 750°C with Stage II

Six of the ten biochars with the highest non-NAP PAH concentration were produced at HTT of 750°C in the Stage II pyrolysis unit. Analyses of total PAHs in these and other biochar samples as reported in section 5.3.1 showed that biochar produced in the Stage II unit at 750°C had significantly higher total PAH concentrations than biochar produced at lower temperatures. This marked increase in PAH content with HTT increase to 750°C became even more prominent when only non-NAP PAHs were considered (Figure 6.5). Compared to the non-NAP PAH concentrations of the biochars produced at 350°C, the biochars produced at 750°C had 300 fold (DW), 113 fold (DNX), 2.6 fold (MC) and 10.2 fold (WC) higher concentrations. This trend is in direct contrast to that observed for biochar produced in the other continuous pyrolysis unit (the Stage III pyrolysis unit), where the non-NAP PAH concentration in biochar produced at 750°C compared to the content of the biochar produced at 350°C decreased from 7.2 to 5.0 mg kg^{-1} (Figure 6.5).

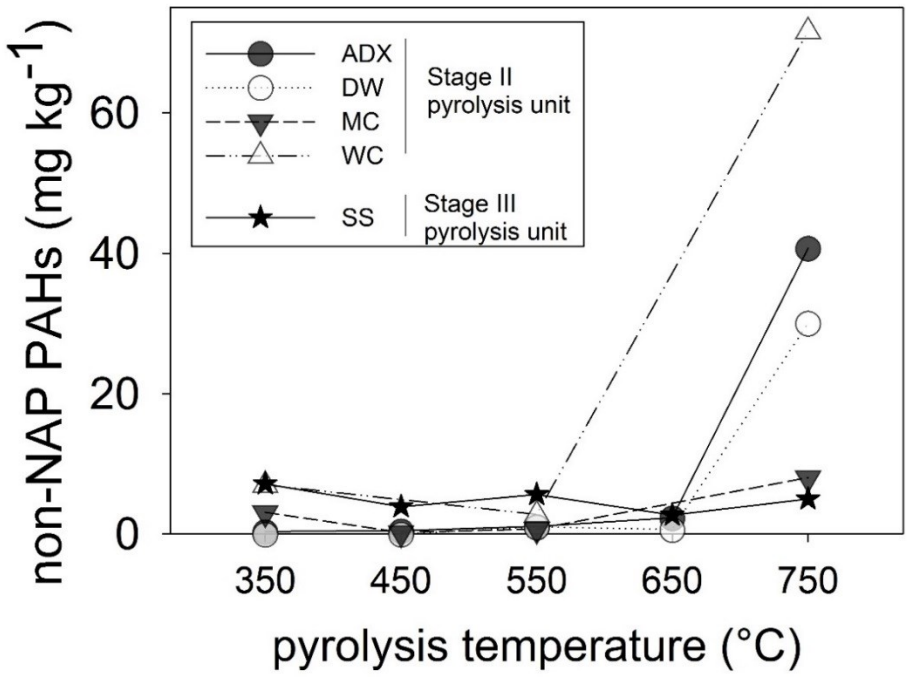


Figure 6.5: Effect of pyrolysis temperature on non-NAP PAH concentrations (mg kg^{-1}) in different biochars. The biochars were produced from four different feedstocks in Stage II pyrolysis unit (ADX, *Arundo donax*; DW, demolition wood; MC, miscanthus chips; WC, willow chips) and one feedstock in Stage III pyrolysis unit (SS, sewage sludge).

As reported in section 5.3.1, after detailed investigations, the fixed temperatures of the heating tapes in the discharge chamber of the Stage II pyrolysis unit were identified as source of the high PAH concentrations of biochars produced at 750°C with the Stage II unit. The heating tapes, which were fixed at 500°C and 400°C, resulted in the discharge chamber walls being cool enough for pyrolysis vapour condensation and deposition on biochar. In addition, it was reported that the PAH yield during pyrolysis increased drastically at temperatures >700°C (Aracil et al., 2005; Dai et al., 2014a, 2014b; Font et al., 2003; Zhou et al., 2014b). This means that pyrolysis vapours formed at HTTs of 750°C contained much higher PAH concentrations than vapours produced at lower HTT, e.g. vapour generated at 650°C. However, in the Stage II pyrolysis unit, the temperature in the discharge chamber was the same at all HTTs due to the fixed temperature of the heating tapes and consequently, a higher amount of PAHs condensed from the vapours produced at 750°C compared to the vapours produced at lower HTTs (650°C as example) which is illustrated in Figure 6.6.

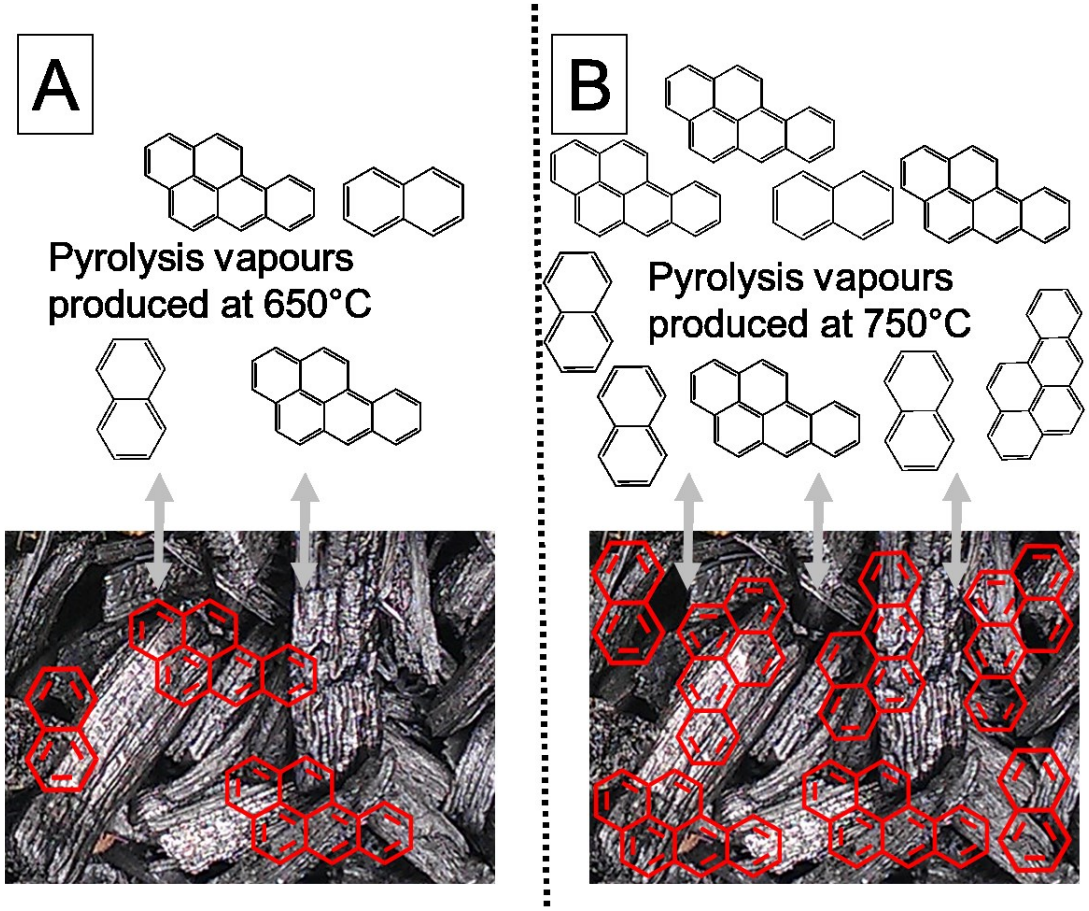


Figure 6.6: Schematic illustration of contamination of biochars by condensation of high-vapour pressure and low-vapour pressure PAHs in the discharge chamber of a pyrolysis unit which uses heating-tapes to heat up the post-pyrolysis zone. Generally, the concentrations of PAHs in pyrolysis vapours produced at 750°C (B) are much higher than the concentration of PAHs in pyrolysis vapours produced at lower temperatures, here reflected by 650°C (A). In this pyrolysis unit, the temperature in the discharge chamber is set by heating tapes and is the same at both pyrolysis temperatures. Therefore, the ratio of PAHs in the vapour phase and condensed on biochar is the same in (A) and (B), but it is different for low-vapour pressure PAHs (here reflected by naphthalene) and high-vapour pressure PAHs (here reflected by benzo(a)pyrene). Due to the higher PAH concentration in the pyrolysis vapours produced at 750°C, the concentration of PAHs in biochar is much higher in (B) and most of those PAHs are high-vapour pressure PAHs.

6.3.2.2 'SS I-700' biochar

The biochar produced from anaerobically digested sewage sludge at 700°C ('AD-700') had a PAH concentration of 22 mg kg^{-1} which mostly consisted of NAP and barely differed from PAH concentrations in biochar produced from AD and SS I produced at 550°C (Figure 6.7). However, SS I pyrolysed at 700°C had a total PAH

concentration of 232 mg kg^{-1} and all of the additional PAHs compared to the other three biochars are non-NAP PAHs (207 mg kg^{-1}).

During production of this particular biochar, one of the heating tapes in the discharge chamber was faulty (HT I) and consequently, the temperature in the discharge chamber was much lower than in comparable pyrolysis runs (side of the discharge chamber of Stage II pyrolysis unit: 'AD-700' 198°C, 'SS I-700' 113°C). Most likely, due to the lower temperature in the discharge chamber, PAHs condensed and deposited on biochar. This example illustrates that PAH contamination through condensation and deposition is a common phenomenon in biochar production and can occur even due to small modifications of the pyrolysis unit set-up.

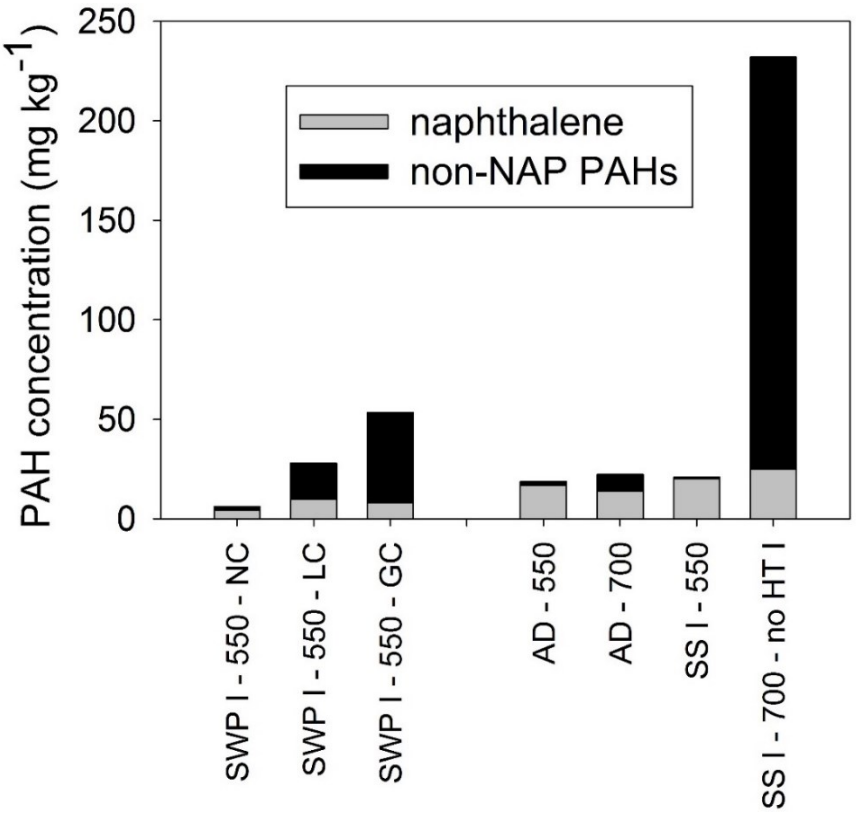


Figure 6.7: 16 US EPA PAH concentration (mg kg^{-1}) in seven biochars. The proportions of naphthalene and non-NAP PAHs are indicated, respectively. The first three biochars were produced under the same condition from the same feedstock (SWP, softwood pellets) with the Stage III pyrolysis unit, but two biochars were contaminated with pyrolysis vapours during production (LC and GC). The second group of biochars was produced from two different feedstocks (SS I, sewage sludge; AD, anaerobic digestate of sewage sludge) at two different temperatures (550, 700°C) with the Stage II pyrolysis unit, but during the pyrolysis run of the 'SS I – 700' one of the heating tapes (HT I) which heats up the discharge chambers was faulty.

6.3.2.3 GC and LC biochars

The GC (gas contaminated) and LC (liquid contaminated) biochars were produced from softwood pellets at 550°C with the Stage III pyrolysis unit and are described and characterised in more detail in Chapter 7, Chapter 8 and Chapter 9. The particular pyrolysis runs took place after the pyrolysis unit was set-up initially and run for the first time. Irregularities during the production led to contact of biochar with pyrolysis vapours/liquids (section 2.2.6). During the 'GC biochar'-production, a tube was blocked due to a build-up of tars while during 'LC biochar'-production the discharge chamber was much cooler than the pyrolysis vapours. In both cases improper insulation and resulting cold zones in the pyrolysis unit caused condensation of pyrolysis vapours on biochar. This resulted in marked increases of PAH concentrations and in particular increases in non-NAP PAHs. Another biochar was produced under the same production conditions and from the same feedstock after the discharge chamber and the previously blocked tube were insulated and very low PAH concentrations were detected in this biochar (NC biochar; Figure 6.7).

In conclusion, all the biochars with high concentrations of non-NAP PAHs most likely were contaminated with pyrolysis vapours in a similar way during production. Cold zones in the post-pyrolysis stage caused condensation which resulted in high PAH concentrations in biochars. However, it still remains unclear why the proportion of NAP is smaller in these biochars compared to the remaining biochars and this will be discussed further in the sections below.

6.3.3 Post-pyrolysis PAH contamination and its consequences

The pyrolysis process itself is very effective in separating PAHs from pyrolysis solids; <1% of the PAHs synthesised during pyrolysis were found in biochar, the remaining proportion was detected in pyrolysis liquids and gases (Dai et al., 2014b; Fagernäs et al., 2012a). The elevated temperatures are favourable for PAHs formed on the biochar surface or in the biochar structure to be evaporated and also, result in PAHs synthesised at the solid-gas interface to remain in the gas phase. However, condensation of pyrolysis vapours onto its parent material still occurs frequently during pyrolysis. Under high temperatures in the furnace, vapours containing PAHs and other organics can react with the char in so-called secondary char formation reactions which are responsible for a significant part of the char formation (Huang et

al., 2013; Pattanotai et al., 2013). However, when condensation of pyrolysis vapours happens in the post-pyrolysis stage, in areas colder than the furnace and compounds such as PAHs (or VOCs) deposit on biochar, they are not transformed but physically sorb to the biochar matrix and contaminate the materials.

The processes determining the concentrations of PAHs in biochar within the furnace area (formation and evaporation) are very complex (section 5.3). However, as displayed in Figure 6.8 (and discussed in section 6.3.4) for wheat straw biochar vs. wood-derived biochars, the feedstock only influenced the concentration of NAP, while the non-NAP concentration changed only marginally. As for feedstock type, the carrier gas flow also only influenced the concentration of NAP in biochar, at least in most cases (Table 6.1). Consequently, the different pyrolysis conditions and feedstock types mainly affect the NAP concentration; contamination in the post-pyrolysis stage, however, mostly increased the concentration of non-NAP PAHs which can be explained as follows.

In the case of lower temperatures in the post-pyrolysis stage, formation and transformation reactions of organic compounds are strongly reduced and instead the extent of contamination of biochar with PAHs (and VOCs) depends on: (I) the concentration of the respective PAH in the gas phase; (II) the (equilibrium) vapour pressure of the PAH (boiling point); and (III) the temperature difference between the gases and the surface for potential condensation (inner surfaces of the pyrolysis unit or biochar). In the post-pyrolysis area, the PAH concentration in the vapour phase and the condensed phase reach a thermodynamic equilibrium which is dependent on the equilibrium vapour pressure of the PAH. NAP has a boiling point of 218°C and a much higher vapour pressure than higher molecular weight (HMW) PAHs, such as benzo(a)pyrene (boiling point 495°C). This means that a bigger proportion of benzo(a)pyrene present in the gas phase will condense and deposit as liquid in comparison to NAP which is more volatile and remains in the gas phase to a higher extent (illustrated in Figure 6.6). This resulted in biochars with high non-NAP PAH concentrations and a smaller proportion of NAP than observed in biochars not contaminated by post-pyrolysis condensation.

This phenomenon does happen to some extent in every biochar production run; consequently, the biochars investigated here cannot be clearly differentiated into two groups (biochar contaminated by condensation and biochars not contaminate by condensation) since the ratios of NAP/total PAH concentration are continuous (Table 6.1). Yet, as shown in section 6.3.2, the concentrations for biochars in group 1 were clearly more strongly affected than other biochars. To investigate if this process is influenced by the different pyrolysis technologies, the three pyrolysis units under investigation were directly compared.

To test how comparable PAH concentrations in biochars from different, but highly controlled, pyrolysis units are, two feedstocks (softwood pellets and wheat straw pellets) were pyrolysed at two temperatures (550, 700°C) with the batch and the two continuous pyrolysis units. The same residence times in the heated area were applied to result in pyrolysis conditions as comparable as possible. And indeed, as depicted in Figure 6.8, non-NAP PAH concentrations were very comparable in biochars from different pyrolysis units, except for 'WSP I 700' from Stage I which had very high PAH levels. As already discussed in 6.3.1, the composition of this biochar is very different to all the other biochars and it can be concluded that the biochar was contaminated in a different way. The PAHs present in this biochar are typical for the heavy tars which are collected in a "hot trap" (assembly described in Crombie et al. (2013)). During the production run, the system is nitrogen purged and it is rather unlikely that the contamination occurred. However, it is likely that the biochar got in contact, either with the content of the heavy tar trap or with tars condensing at the top of the glass tube that contains the biochar after production which caused the contamination with HMW PAHs only.

In summary, the 16 US EPA PAH and non-NAP PAH concentrations were comparable between all three pyrolysis units, which demonstrates that biochar production can, in principle, be done on different scales and using different technologies without negative effects on PAH concentrations in biochar.

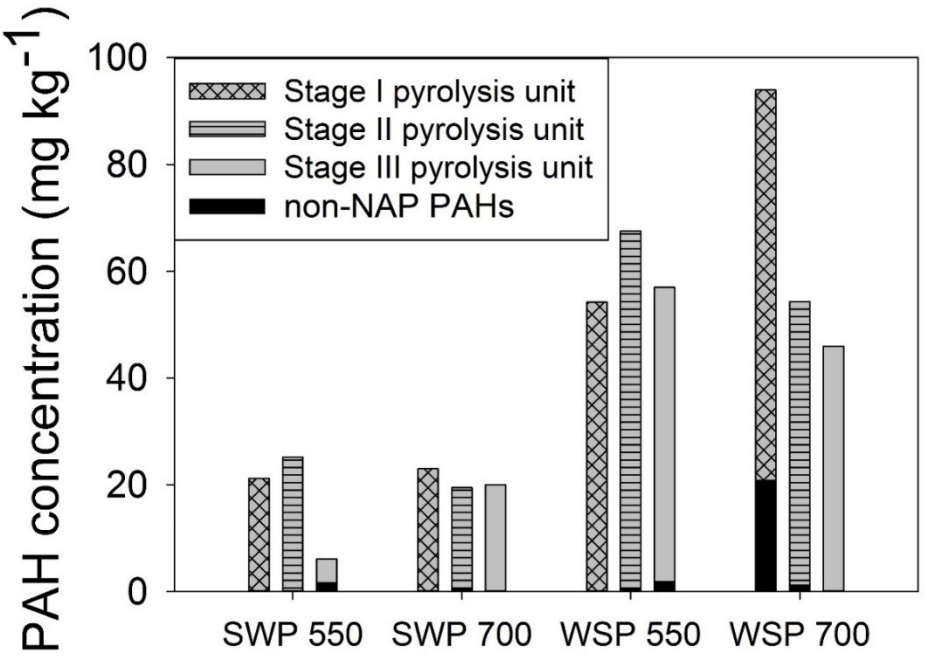


Figure 6.8: 16 US EPA PAH concentrations (mg kg^{-1}) in twelve biochars from two feedstocks (SWP, softwood pellets; WSP, wheat straw pellets) produced at two HTTs (550, 700°C) in three different pyrolysis units. The proportion of non-NAP PAHs is indicated, respectively.

6.3.4 Recommendations for biochar production and future studies

It was concluded that the high concentrations of non-NAP PAHs mostly resulted from condensation and deposition of PAH in cold zones of the post-pyrolysis area. This shows the importance of proper insulation of the pyrolysis unit to avoid cold zones and the crucial role of the design of biochar discharge arrangements in the pyrolysis unit. Generally, where pyrolysis gases and solids travel in the same direction through the pyrolysis unit, the discharge chamber, which separates pyrolysis solids and vapours, needs to be maintained at temperatures as close to the HTT used in the pyrolysis process as possible. Another option would be to separate pyrolysis vapours from solids already within the pyrolysis reactor, e.g. by using a counter-current arrangement, where pyrolysis gases are extracted close to the feedstock entry point, i.e. on the opposite end from the biochar discharge. Such counter-current arrangement would have an impact not only on the quality of the biochar, yielding biochar with lower PAHs concentrations, but could also reduce the yield of biochar, due to reduced secondary char formation (Huang et al., 2013). This

work emphasises the importance of monitoring and controlling of the pyrolysis process beyond just simple HTT in the pyrolysis reactor, to achieve production of good quality biochar.

In the literature, effects of various pyrolysis parameters on PAHs concentrations in biochar were reported; in particular, numerous different effects were observed of HTT on PAHs in biochar (Dai et al., 2014b; Devi and Saroha, 2015; Freddo et al., 2012; Hale et al., 2012; Keiluweit et al., 2012; Rogovska et al., 2012). Despite significant efforts, these studies did not provide a general relationships between biochar PAH concentrations and pyrolysis parameters. Based on the investigations is this chapter, it is suggested that this is due to the fact that important aspects of biochar production were not sufficiently addressed by these studies, to allow development of such general understanding. In this study, it was demonstrated that weaknesses in design, or in operation of biochar production units, in particular the post-pyrolysis area, can have a striking effect, resulting in high concentrations of non-NAP PAHs in biochar. This effect was much more important and surpassed the effects of HTT, carrier gas flow or feedstock. In Hale et al. (2012), it was reported that the PAH concentrations were highest in biochars from "uncontrolled field conditions" which confirms the need for highly controlled and monitored pyrolysis units. When studying relationships between biochar PAHs concentrations as a function of feedstock and different pyrolysis parameters, it is critical to ensure that these are compared on the same basis, i.e. that there is sufficient information on all the relevant aspects of the production, so that certain effects (such as deposition of PAHs) are not misinterpreted as effects of, for example, pyrolysis temperature.

6.3.5 PAH composition in biochar and threshold values

For a risk-based assessment of biochars, changes in the concentration of NAP is of little relevance due to naphthalene's low carcinogenicity, low toxicity and rapid degradability in soil (European Commission Scientific Committee on Food, 2002; Nisbet and LaGoy, 1992; US Department of Health and Human Services, 1995). However, comparing with legislation and guidelines values which are based on the sum of the 16 US EPA PAHs, it is clear that the concentration of NAP takes in a crucial part concerning compliance/non-compliance of biochar PAH concentrations with threshold values.

Table 6.4: The number and percentage of biochars out of the set of 84, exceeding guideline values. Total PAHs and non-NAP PAHs were considered separately. The threshold values depicted were established for biochar soil application according to (EBC, 2012b) and International Biochar Initiative (2011).

		EBC premium 4 mg kg^{-1}	IBI upper limit 20 mg kg^{-1}
total PAHs	biochars	62	45
	%	73.8	53.6
non-NAP PAHs	biochars	21	8
	%	25.0	9.5

In Figure 6.2 and Table 6.4 the lowest and the highest of the PAH guideline values from IBI, EBC and BQM are shown, both based on national legislation (20 mg kg^{-1} Australian legislation=IBI upper PAH limit, 4 mg kg^{-1} Swiss legislation=EBC lower limit/premium grade biochar). When NAP is taken into account, 45 (53.6%) and 62 (73.8%) biochars of the set of 84 exceed the IBI upper limit and the EBC lower limit values, respectively. However, when NAP is excluded, only eight biochars (9.5%) exceeded the IBI upper limit and 21 biochars (25.0%) exceed the EBC lower limit guideline values, respectively. This shows the disadvantage of using the sum of the 16 US EPA PAHs for evaluating the risk of PAH contamination in biochar as individual toxicity is not taking into account and consequently, alternative ways of evaluating the risk of PAHs in biochar should be established.

Table 6.5: Number and percentage of 84 biochars exceeding benzo(a)pyrene threshold values of the German Federal Soil Protection and Contaminated Sites Ordinance (1999) for certain land use types.

		agricultural soils	children's playgrounds	residential areas	parks	industrial areas
	threshold	1 mg kg^{-1}	2 mg kg^{-1}	4 mg kg^{-1}	10 mg kg^{-1}	12 mg kg^{-1}
exceedance	biochars	10	6	2	2	0
	%	11.9	7.1	2.4	2.4	0.0

Benzo(a)pyrene is the most investigated PAH and is often used as reference point to compare the toxicities of all 16 US EPA PAHs (Delistraty, 1997). Its average concentration in all 84 biochars was 0.53 mg kg^{-1} but most biochars showed concentrations below the limit of detection (Digital Appendix Table 3). In the

German Federal Soil Protection Ordinance, benzo(a)pyrene is used as an indicator for PAHs and the limit value for protection of plant growth is 1 mg kg^{-1}. Comparing with this limit value, it shows that only ten of the 84 biochars exceed it and apart from two, all of these are part of the biochars of group 1 with identified vapour-condensation during production (Table 6.5) (German Federal Soil Protection and Contaminated Sites Ordinance, 1999). Benzo(a)pyrene soil threshold values were also established for children's playgrounds, residential areas, parks and industrial areas (2, 4, 10 and 12 mg kg^{-1}) which are only exceeded by 6, 2, 2, and 0 biochars, respectively (Table 6.5). Benzo(a)pyrene is well-correlated with the non-NAP PAH concentrations in this study (data not shown) and consequently, could be used as an indicator for non-NAP PAHs and PAH associated risk as already established for food products in the EU (EU Commission Recommendation, 2005).

In addition, Nisbet and LaGoy (1992) used benzo(a)pyrene to set up toxicity equivalent factors (TEFs) based on carcinogenicity of benzo(a)pyrene. Using these to calculate the average toxicity equivalent quantity (TEQ) for all 84 biochars in this study, the TEQ was 1.33 benzo(a)pyrene-TEQ kg^{-1} (Table 6.2) and varied from 0 to 24.7 benzo(a)pyrene-TEQ kg^{-1}. While the TEQ of group 1 (8.49 benzo(a)pyrene-TEQ kg^{-1}) was higher than the value for UK urban soils (1.37) (Creaser et al., 2007), the average values in group 2 was only 0.37 benzo(a)pyrene-TEQ kg^{-1} which is lower than the average TEQ of PAHs in rural soils in the UK (0.44 benzo(a)pyrene TEQ kg^{-1}) (Creaser et al., 2007).

Overall, it does not seem advisable to use threshold values based on the sum of the concentration of 16 US EPA PAHs as they comprise of both, compounds which pose low risk for humans and the environment, such as naphthalene, and highly carcinogenic compounds, such as benzo(a)pyrene. For biochar this is a particular issue as NAP is the dominant compound and its concentration fluctuates widely and so total PAH concentrations do not reflect the risk associated with biochars appropriately. Instead, the concentration of benzo(a)pyrene or the TEF-approach could be used. Alternatively, different threshold values could be established individually for NAP and the sum of the remaining 15 US EPA PAHs as done in the German Federal Soil Protection Ordinance for the soil-groundwater interface (German Federal Soil Protection and Contaminated Sites Ordinance, 1999).

6.4 Conclusions

In this chapter, involving 84 biochars, post-pyrolysis contact of pyrolysis vapours with biochar was the most significant factor determining the concentration of non-NAP PAHs in biochar. Weaknesses in pyrolysis unit design can result in cold zones in the post-pyrolysis area and condensation and physical deposition of PAHs on biochar, in particular HMW PAHs due to their lower vapour pressure. Biochars affected by PAH-deposition had a high concentration of heavier, high-risk PAHs, such as benzo(a)pyrene, and a lower concentration of the 2-ring, highly volatile PAH, naphthalene. As a result, such biochars pose a higher risk to humans and plants after application. This effect is not limited to any particular technology or unit, as demonstrated using three units based on different designs (rotary kiln, auger reactor and fixed bed reactor). Therefore, appropriate construction and operation of pyrolysis units focussed on reduction of PAH deposition is critical. The observed differences in total PAH concentrations in biochar, but even more importantly, the distribution of individual PAHs, highlighted issues with using the 16 EPA PAHs as a measure of quality or of the risk posed by biochar, due to the often disproportionally large contribution of NAP to the total PAH content. More than half of the biochars investigated in this study exceeded the PAH limit values proposed in biochar guideline values based on the sum of 16 US EPA PAHs. Yet, very few biochars exceeded legislation threshold values for soil, based on the concentration of the highly toxic PAH, benzo(a)pyrene. This illustrates the discrepancy of biochar guideline value for PAHs in biochar and actual PAH-associated risk and shows that the current state of biochar guidelines do not reflect the risk of PAHs in biochar and should be adapted accordingly.

Chapter 7 Impact of high-VOC biochars and post-treatment measures on plant growth

The following chapter is based on the published article:

Buss, W., Mašek, O., 2014. Mobile organic compounds in biochar – a potential source of contamination – phytotoxic effects on cress seed (*Lepidium sativum*) germination. J. Environ. Manage. 137, 111–119. doi:10.1016/j.jenvman.2014.01.045

Journal impact factor (2014): 2.723

Number of citations (September 2016): 36

The candidate was solely responsible for data analysis and writing of the article and this chapter. Ondřej Mašek provided guidance and contributed to the editing of the manuscript. The experimental work was performed by the candidate, apart from the biochar production which was performed by Juan Luis Turrion-Gomez.

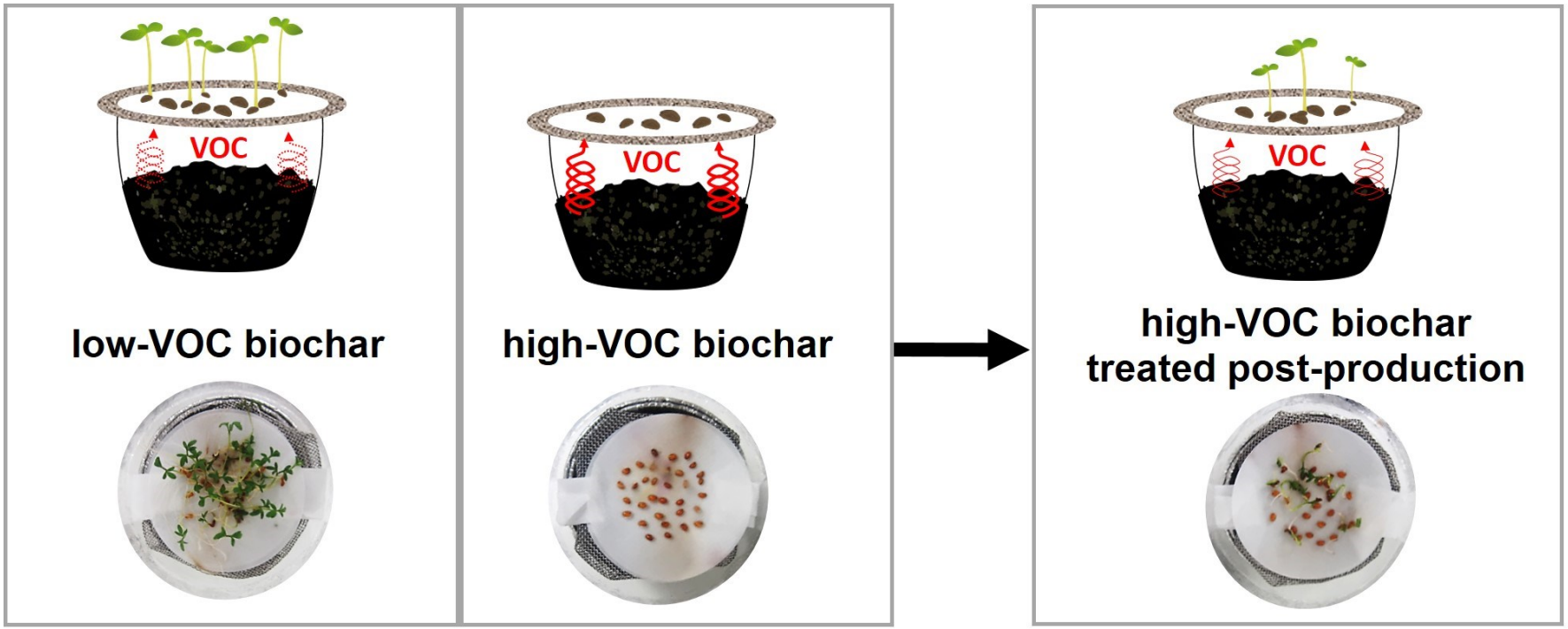


Figure 7.1: Graphical abstract of Chapter 7. Low- and high-VOC biochars were tested in cress germination and early seedling growth tests. Vapours of low-VOC biochar did not have any effect on plant growth, while vapours of high-VOC biochar strongly inhibited growth. Post-production treatments of high-VOC biochar resulted in improved germination and early seedling growth.

7.1 Introduction

For future large-scale application of biochar, it is important to ensure that biochar will neither show toxic effects nor otherwise pose a short or long-term threat to soil and the environment, e.g. in form of bound contaminants. Most research on contaminants in biochar focus on the latter, on bound and rather non-bioavailable potentially toxic elements (PTEs) and polycyclic aromatic hydrocarbons (PAHs) (Fabbri et al., 2013; Freddo et al., 2012; Hale et al., 2012; Hilber et al., 2012; Oleszczuk et al., 2013; Rogovska et al., 2012; Singh et al., 2010). Nevertheless, volatile and/or easily leachable organic compounds exist within biochar and can cause positive (Elad et al., 2011) as well as negative effects (Smith et al., 2013).

Few studies have been published in which the composition and impact of residual tars and other organic compounds from pyrolysis on direct and acute toxicity has been assessed (Smith et al., 2013; Spokas et al., 2011; Yang et al., 2013). Pyrolysis liquids primarily consist of low-molecular weight (LMW) degradation products of cellulose, hemicellulose and lignin (Cordella et al., 2012) and the compound classes that are covered are mainly organic acids, aldehydes, furans, ketones, alcohols and phenols, however, PAHs can be found as well (Cordella et al., 2012; Sánchez et al., 2009; Sfetsas et al., 2011). Most of those are VOCs which are compounds with boiling points ≤250°C (Directive 2004/42/CE of the European parliament and of the council, 2004).

Depending on production conditions and pyrolysis technology, condensation and deposition of pyrolysis liquids and gases on biochar occurs (Spokas et al., 2011). As contamination of char with organic compounds is not an issue in systems focused on electricity/biofuel production, this aspect has not been a focus of extensive research. It is, yet, a critical consideration in designing units for production of biochar. Furthermore, due to the high variability of vapour condensation and deposition on biochar and the influence of post-handling on concentrations and composition of residues of pyrolysis vapours, it is difficult to draw conclusions about their impact on plant growth and the ecosystem. Thus, to be able to determine the potential impact of biochar-derived mobile organic compounds on seed germination, this study

investigated biochar samples containing high concentrations of VOCs and other organic compounds as a result of irregularities during production.

Several studies have looked at different methods for reducing the toxicity of biochar/hydrochar (char from hydrothermal carbonisation) vapours (Bargmann et al., 2013; Busch et al., 2012). Busch et al. (2012) demonstrated significant improvement of germination performance when exposed to hydrochar vapours after the hydrochar had been kept in closed storage and were dried. Furthermore, washing of hydrochar and biochar with water or an organic solvent has been successfully tested to reduce phytotoxicity of solids or extracts (Bargmann et al., 2013; Bernardo et al., 2010; Rogovska et al., 2012).

Another potential method for VOC toxicity mitigation is to use low-VOC biochar to sorb contaminants from high-VOC biochar. Biochar has proven to sorb organic and inorganic compounds from soil (Buss et al., 2012; Gomez-Eyles et al., 2011; Huang and Chen, 2010; Ogbonnaya and Semple, 2013). Furthermore, Rogovska et al. (2012) showed that biochar can sorb allelochemicals from corn residues in solution and reduces their toxicity on seedling growth. As shown for activated carbon, which is used in practice for effluent gas cleaning (Rodríguez-Mirasol et al., 2005), biochar might be able to sorb VOCs, thus, reduce toxicity of VOCs.

Therefore, in this chapter, biochar contaminated by pyrolysis vapours during production (high-VOC) were investigated for chemical characteristics (pH, ash, volatile matter, fixed carbon content) and their phytotoxicity and compared to a biochar not contaminated by pyrolysis vapours produced under the same conditions (low-VOC). This chapter focussed on the effect these biochars have on germination and early seedling growth of cress. Storage and blending of high- with low-VOC biochars were tested as measures to reduce the phytotoxicity, because these methods are easy to perform, cheap and reasonable to be used in practical applications. The aim of the chapter was to assess the extent of phytotoxicity of VOCs, to determine whether high-VOC biochar can be safely used in practice and whether toxicity can be reduced/mitigated.

7.2 Materials and methods

7.2.1 High- and low-VOC biochars

For this study, the NC, GC and LC biochars were used as described in section 2.2.6. Two of the biochars (GC and LC) were high-VOC biochars, contaminated during production and one biochar (NC biochar) was not contaminated and resulted from a production run without irregularities during production.

7.2.2 Characterisation of biochars

Proximate analysis and pH measurements were performed on LC, GC and NC biochar according to the method described in section 2.3.

7.2.3 Germination tests

'Volatiles only' germination tests were performed (section 2.6.1) using a range of amounts of crushed LC, GC and NC biochars (30, 10, 5, 2, 1, 0.5, 0.25 g). For evaluation of the tests, the germination rate was calculated and the shoot and root length was measured manually with a ruler.

'All exposure routes' germination test were performed with 1, 2 and 5% GC, LC and NC biochar in sand (section 2.6.2). The roots of the seedlings were categorised into three groups (<15 mm, between 15 and 60 mm and above 60 mm) and the percentage of seedlings with a particular roots length was calculated.

The pH of the filter paper on which the seeds were placed was measured using universal indicator paper.

7.2.4 Biochar post-treatments

Different biochar post-treatments were performed to assess their suitability for reducing the release of volatiles from contaminated biochars and the treated biochars were subsequently assessed in 'volatile only' germination tests.

NC, GC and LC biochar samples were stored at ambient temperature in aluminium trays for four weeks, covered by a paper tissue to avoid contamination from particles from the air. To prevent an initial peak release of volatiles in the germination tests, stored biochar samples were crushed after storage to release any desorbed, gaseous VOCs trapped within the biochar structure. The biochars were assessed in different

amounts (0.25, 0.5, 1, 2, 5, 10, 30 g) in 'volatile only' germination tests in three replicates.

In addition to storage, blending of biochar samples was also investigated. Low-VOC biochar (NC) was blended with high-VOC biochars (LC, GC) to test if low-VOC biochar was able to mitigate the release of VOC associated with the high-VOC biochar via sorption. 10 g samples of biochar containing 1 and 2 g (w/w) LC or GC biochar were tested using a 'volatile only' germination test in five replicates. In the following they are referred to as GCB 1:9, GCB 2:8, LCB 1:9 and LCB 2:8.

7.2.5 Statistics

Results were evaluated statistically using Analysis of Variance (ANOVA) performed with SigmaPlot 12 (Systat Software Inc., Chicago, IL) followed by Student-Newman-Keuls post hoc tests. In addition, t-tests were used to determine differences between the treatments. Different letters in the figures indicate significant differences between the treatments ($p < 0.05$). The p-values in the legends of the figures indicate the error probability of an effect of the treatments on a respective parameter.

7.3 Results and discussion

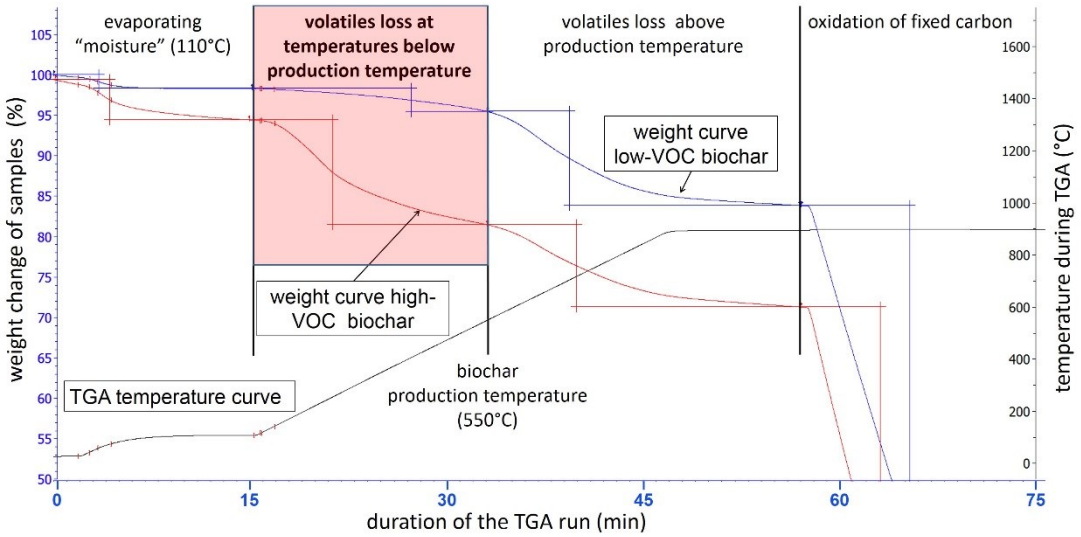


Figure 7.2: Temperature and weight loss curves of low-VOC and high-VOC (LC) biochar during thermogravimetric analysis (TGA).

Table 7.1: Characteristics of low-VOC and two high-VOC biochars. Proximate analysis performed by TGA. The pH was determined in solution. RT, residence time; % daf, % dry, ash-free basis.

biochar	VOC	feedstock	temperature	RT	pH	moisture	ash	fixed C	volatile matter		
			°C	min		%	%	% daf	% daf		
									total VM	<550°C*	>550°C#
non-contaminated (NC)	low	softwood pellets	550°C	20 min	7.12	1.71	1.67	85.05	14.95	2.95	12.37
gas contaminated (GC)	high	softwood pellets	550°C	20 min	3.64	4.47	1.93	73.67	26.33	15.48	12.85
liquid contaminated (LC)	high	softwood pellets	550°C	20 min	3.64	4.96	1.21	75.43	24.57	13.90	12.39

* volatile matter content released <550°C calculated based on dry, ash free basis

volatile matter content released >550°C calculated based on total mass at TGA temperature of 550°C (excluding moisture, ash and volatiles lost <550°C)

7.3.1 Characterisation of biochars

Results for proximate analysis of LC, GC and NC biochar can be found in Table 7.1. Proximate analysis showed NC biochar had a volatile matter (VM) content of 14.7% and a fixed carbon content of 83.6%. The NC biochar contained low VM-levels compared to values found in literature for the VM content of pine biochar (pyrolysis temperature 450-600°C; VM 17-37%) (Crombie et al., 2013; Mukome et al., 2013; Ronsse et al., 2013).

The thermo-gravimetric analysis (TGA) revealed weight loss in the liquid contaminated and gas contaminated biochar at 110°C of 5% and 4.5% respectively, but only 1.7% in the NC biochar. In proximate analyses, this weight loss is attributed to moisture but in this case a component of this figure could be attributed to condensed organic compounds that vaporised at low temperatures.

Table 7.1 indicates nearly the same relative amount of volatiles-release above the pyrolysis process temperature of the biochars (550°C) for all biochar samples. This is also depicted in Figure 7.2, where the slopes of low-VOC biochar and high-VOC biochar weight loss curves above the pyrolysis temperature are the same (in Figure 7.2 only LC is depicted but GC biochar showed the same pattern). However, during heating of the samples to the pyrolysis HTT (i.e. between 110-550°C), the contaminated biochars lost more weight compared to the low-VOC biochar. Obviously, as already described, the contamination of the two biochars occurred due to compounds that vaporised during the pyrolysis process to 550°C initially, but condensed onto the solid product because of low temperature in certain areas of the unit. LC and GC biochar contained a 10% higher proportion of VM than NC biochar and potentially organic compounds disguised within the “moisture fraction”.

As shown in Table 7.1, NC biochar had a pH of 7.12, whereas the contaminated biochars had a pH of 3.64. Typically, the pH of wood biochar produced at mid-pyrolysis temperatures is between 6.7-7.9 (Calvelo Pereira et al., 2011; Mukome et al., 2013; Ronsse et al., 2013), but in one instance, a pine biochar (<450°C, fast pyrolysis) was stated to have a pH of only 3.9 (Smith et al., 2013). The acidic nature of the condensed pyrolysis liquids is the reason for the low pH of contaminated biochars (Fagernäs et al., 2012a), which originated from the degradation of cellulose,

hemicellulose and lignin and the formation of acetic acid and other organic acids during pyrolysis (Fagernäs et al., 2012a; Spokas et al., 2011).

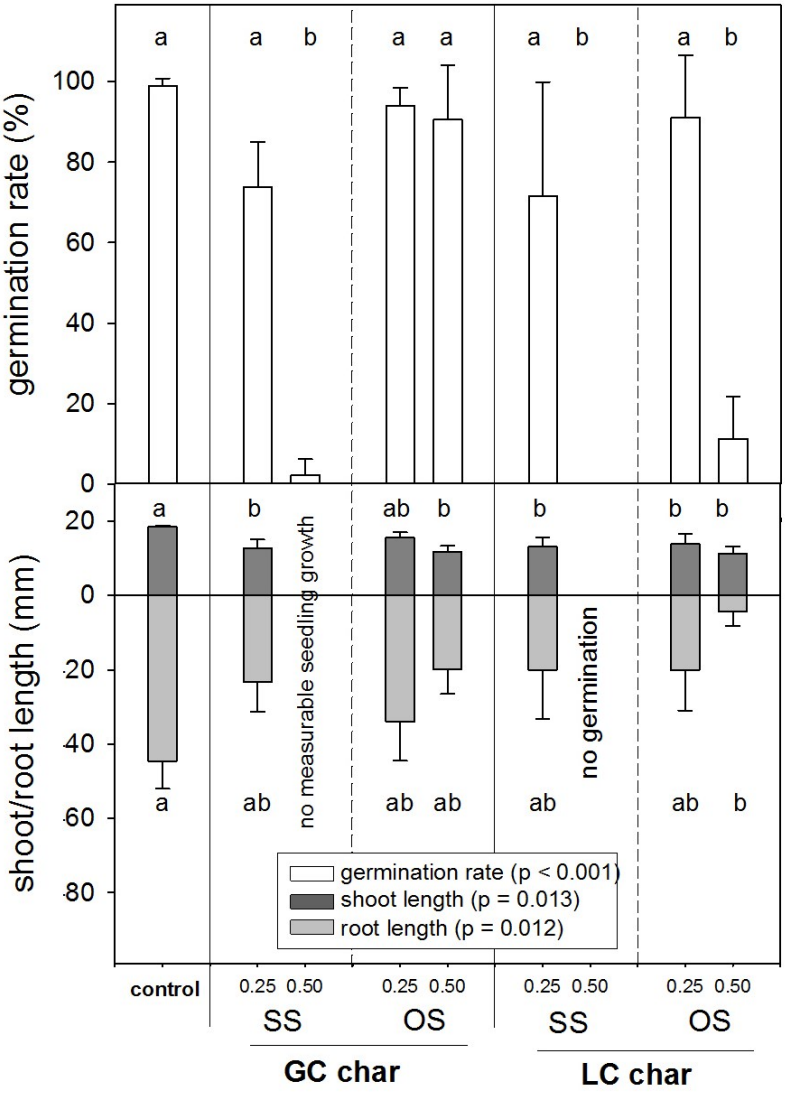


Figure 7.3: Germination rate (%) and shoot/root length (mm) of cress tested in a 'volatiles only germination' test using different amounts of biochar. LC and GC biochar were tested using sealed storage (SS) and open storage (OS) for four weeks. Different letters indicate significant differences between the treatments.

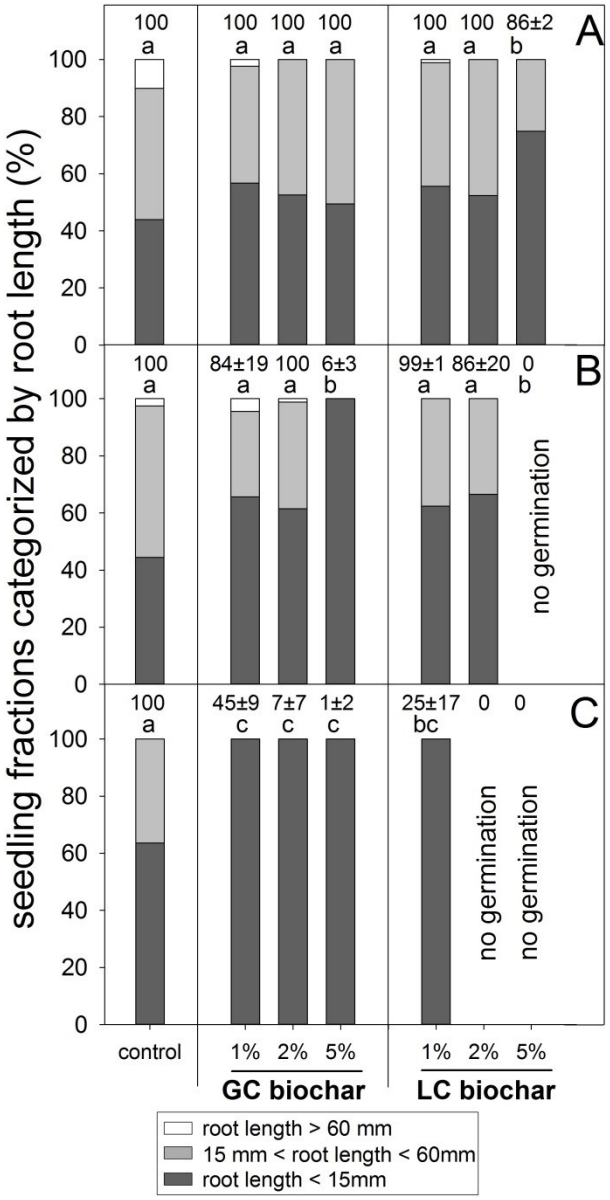


Figure 7.4: Germination rate (%) (values above bars) and seedling fractions (%) with root growth <15 mm, between 15 and 60 mm and above 60 mm as bars are depicted. 'All exposure routes' germination test was performed assessing toxicity of gaseous compounds released (A), leachable compounds (B) and direct contact of seeds and biochar (C). Two high-VOC biochars (GC and LC) were tested in sand (w/w). Germination rate is given as averages with standard deviation and letters indicate significant differences of germination rate between the treatments.

7.3.2 Assessment of phytotoxicity of VOCs and mitigation methods

7.3.2.1 Effect of volatiles

Germination rate for 'volatile only' tests can be seen in Table 7.2. The vapours released from NC biochar showed no toxic effect on cress seeds and germination rates were close to 100% in all NC biochar treatments and in the controls (controls

not shown in Table 7.2). Yet, the vapours emitted from LC and GC biochars were highly inhibitive to germination. The use of biochar amounts >0.5 g fully suppressed the germination of cress seeds (Table 7.2). Even 0.5 g of high-VOC biochars led to significant reductions in the rate of germination compared to the control (GC: $p < 0.001$; LC: $p < 0.001$), while 0.25 g resulted in a non-significant reduction in germination rate (GC: $p = 0.164$; LC: $p = 0.150$) (Figure 7.3). There were no toxic effects identified in the volatile fraction of the 'all exposure routes' germination test, except for a slight but significant decrease of germination for the highest LC treatment (LC 5% compared to control: $p = 0.014$) (Figure 7.4). This can be explained by the fact that biochar was incorporated into sand and leached with water, which reduced the potential of VOC to be vaporised.

The impact of volatiles on seed germination from high temperature biochars (800-860°C) produced from different feedstocks has been tested on barley seed germination and no inhibition was observed (Bargmann et al., 2013). Nevertheless, proximate analyses have shown that high-temperature biochars possess a lower VM content compared to biochar produced at lower temperatures and so less/no toxic effects would be expected for high temperature biochars (Ronsse et al., 2013). In a similar pyrolysis experiment carried out by Busch et al. (2012), peanut hull biochar produced at 500°C did show inhibition of germination and on hypocotyl (shoot) growth, however, this was attributed to adverse effects caused by a moisture shortage and not due to toxicity (Busch et al., 2012). Furthermore, in the study one year old biochar was used and therefore a large amount of VOCs might have dispersed over the time of storage (Busch et al., 2012).

Simple storage

It has been stated that processing, handling and storage of biochar led to reduction of VOCs and these seem to be the most relevant factors which determine the profile of VOCs sorbed to biochar (Spokas et al., 2011). Thus, biochar storage was chosen as a suitable parameter to investigate effects on mitigation of VOC toxicity. The 0.5 g GC biochar treatment showed a significant improvement from close to 0% germination for fresh samples to nearly 100% for stored biochar ($p < 0.001$) (Figure 7.3). In the LC treatment this effect was less pronounced. Storage did not mitigate toxicity or

improve germination rates in treatments with more than 0.5 g biochar, all showed total inhibition of germination (apart from 1 g stored GC biochar which improved germination rate to 4%) (Table 7.2). Tests with 0.5 g of stored GC biochar showed similar toxicity as 0.25 g non-stored GC biochar treatment and an increase in amounts of biochar in both treatments decreased germination strongly, thus, a twofold reduction of toxicity was achieved while the storage of LC biochar showed a smaller improvement.

It is clear that this type of storage of contaminated biochars was a poor measure to reduce toxicity and it is unlikely that the contaminated biochars would release vapours continuously in high amounts even after four weeks (further investigated in Chapter 8). This indicates that even small amounts of vapours released after four weeks of storage are highly toxic or the introduction of stored biochar into the germination test jars led to an additional peak of vapour release. A reason for desorption of VOCs after storage could be the increased moisture content due to the water reservoir in the closed jars used during the germination tests. It has been shown for soil that a water saturated nitrogen/helium stream desorbs a higher fraction of compounds than a dry stream, due to displacement of VOC by water (Thibaud et al., 1993; Yeo et al., 1997). However, in the case of activated carbon, sorption/desorption behaviour showed both no influence (Delage et al., 1999) and decreased sorption (thus increased desorption) (Li et al., 2008) due to increased relative humidity. Only when water has a higher affinity to the solid material than the respective VOC, is it able to displace VOCs and facilitate desorption (hydrophobicity of the solid and the kind of VOC determine these affinities). Soil has a higher affinity to water than to VOCs (Thibaud et al., 1993) and for activated carbon it is reported to be the opposite due to hydrophobic surfaces (Delage et al., 1999). It remains unclear if biochar rather has a higher affinity to water or to VOCs, therefore, if relative humidity increases VOC desorption.

The use of short term storage (four weeks) was deemed to be unsuitable to reduce toxicity of biochars with very high VOC content. Potentially, storage parameters could be improved to result in higher performance, e.g. by increasing temperature (investigated in Chapter 8).

Blending of low- and high-VOC biochar

The potential for low-VOC biochar to sorb organic vapours from contaminated biochar and consequently, reduce their inhibition of germination was tested through the blending of LC and GC biochars with NC biochar. The 'volatiles only' germination tests showed a reduction in toxicity due to blending (Table 7.2, Figure 7.5). While, treatments of 1 and 2 g LC and GC biochar without blending led to total inhibition of germination (Table 7.2), blending of 1 g of GC biochar with 9 g of NC biochar (GCB 1:9) resulted in a similar germination rate as the control, but 2 g GC blended with 8 g NC (GCB 2:8) did not improve the plant growth (Figure 7.5). In addition, LCB2:8 did not improve germination rate, while LCB 1:9 did, the germination rate increased to around 50% when blended (Table 7.2, Figure 7.5).

The 0.25 g non-blended GC biochar (Figure 7.3) treatment was slightly more toxic than 1 g blended treatment (Figure 7.5), thus, the toxicity was reduced by at least a factor of four due to blending. For LC biochar the toxicity was reduced to a smaller degree.

Di Lonardo et al. (2013) observed that biochar (poplar, 550°C, pyrolitic stove) decreased concentrations of gaseous ethylene in closed glass vials and decreased negative influences on plant growth. The same effect could explain the reduced toxicity when LC and GC samples were blended with NC biochar, due to the ability of low-VOC biochar to adsorb more toxic VOCs (further investigated in Chapter 8).

Blending of contaminated biochars with low-VOC biochars appears to reduce the toxicity of VOCs from contaminated biochars. Nonetheless, as the large standard deviation of germination rate in the LCB 2:8 treatment shows (Figure 7.5) the effect can be highly variable. An explanation for this variability could be that only one or a few compounds are responsible for germination inhibition and could already effect germination in low concentrations. As soon as biochar cannot adsorb any more compounds, germination inhibition occurs. The adsorption capacity in the LCB 2:8 treatment could have reached this limit and in some replicates, when highly toxic VOCs could not be trapped anymore, they were released and caused near total inhibition of germination. Yet, poor blending of the two biochars could also have caused non-consistent release of VOCs during the replicate runs.

Volatiles effect in practice

Major negative effects on seed germination by VOC were noted, however, it is difficult to assess what impact VOCs from biochar will have on plant germination and growth in practice. Biochar handling does have a major impact on amounts and composition of volatiles in biochar (Spokas et al., 2011). It has been reported that vapours released from hydrochar caused toxicity in closed containers but not when free gas exchange was ensured (Bargmann et al., 2013). The 'all exposure routes' experiment confirmed that vapours from fresh contaminated biochars in a wetted sand-mixture caused little toxicity, which indicates this could also be the case if applied in agricultural soil. Still, it has been reported that in hydrochar most vapours causing toxicity are water soluble (Bargmann et al., 2013). This also seems to be the case for contaminated biochars, as leaching reduced toxicity of the volatile fraction strikingly. The toxicity of the resulting leachate and biochar is discussed in the following section.

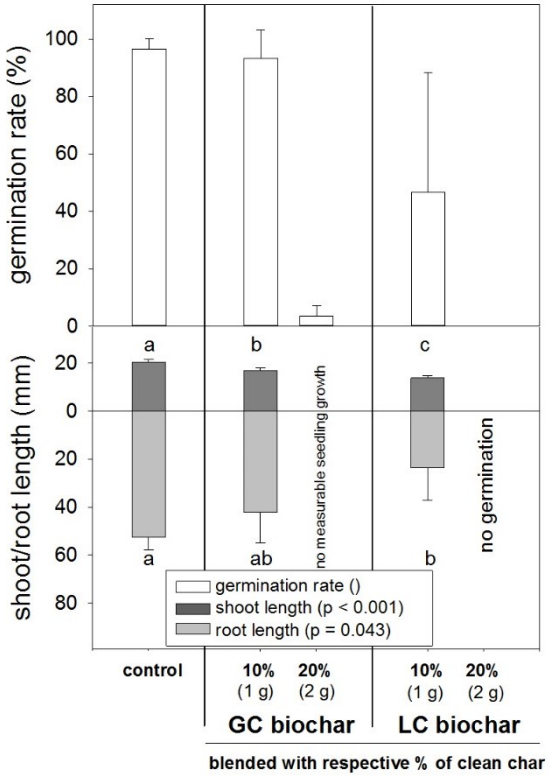


Figure 7.5: Germination rate (%) and shoot/root length (mm) of cress tested in a 'volatiles only germination' test. High-VOC biochars (LC and GC) were blended with low-VOC biochar as measure to reduce phytotoxicity in a ratio of 1g to 9g (GCB 1:9, LCB 1:9) and in a ratio of 2g to 8g (GCB 2:8, LCB 2:8). Different letters indicate significant differences between the treatments. No statistical analysis was performed for parameter germination rate.

7.3.2.2 Effects of water soluble compounds and direct biochar contact

The fraction in the 'all exposure routes' germination test affected by volatiles as well as by the leachate from the biochar-sand mixture showed very strong negative effects on germination (Figure 7.4). In the highest treatment (5%), both contaminated biochars inhibited germination almost completely (6% GC; 0% LC) which clearly shows that water soluble compounds from biochar can cause high toxicity on seed germination. In the 1% and 2% LC biochar treatments, in which no significant effect on germination could be detected, a shift of root length fraction to a greater proportion of smaller roots was visible. Seeds exposed to leachate from NC biochar showed 100% germination rate in all biochar concentrations (A Table 3). Furthermore, positive effects of NC biochar on plant growth (roots) was observed, agreeing with reports for most biochars (Jeffery et al., 2011; Lehmann and Joseph, 2009) (A Figure 2).

In the 'solid fraction', seeds were in direct contact with biochar and were additionally exposed to dissolved compounds and released gases. As expected due to exposure to all toxic routes, this treatment demonstrated the highest level of germination inhibition with 1% of contaminated biochar in soil leading to detrimental effects on germination rate (45% GC; 25% LC) and growth (entire roots smaller 15 mm).

It can be clearly seen (Figure 7.4) that direct contact with seeds increased biochar toxicity compared to seed contact only with leachates. It needs to be noted, however, that the seed-contact-systems were different, therefore, water supply might have been different and might have influenced germination. Yet, the controls on filter paper and on biochar-sand mixture all showed 100% seed germination rate, indicating that the contact system did not have any (negative) influences.

Table 7.2: Effect of GC and LC biochar amounts on the germination rate (%) during 'volatile only' germination tests with cress. Samples were either stored in sealed containers or openly for 4 weeks.

biochar	storage	amount used (g)				
		30	10	5	2	1
		germination rate (%)				
non-contaminated (NC)	sealed	98	97	98	99	97
	open	99	100	100	98	100
gas contaminated (GC)	sealed	0	0	0	0	0
	open	0	0	0	0	4
liquid contaminated (LC)	sealed	0	0	0	0	0
	open	0	0	0	0	0

Table 7.3: Determination of pH of filter paper from 'volatiles only' germination tests using openly stored (OS) and sealed (SS) LC and GC biochar in different amounts. nt, not tested.

amount	low-VOC biochar		GC biochar		LC biochar	
g	SS	OS	SS	OS	SS	OS
0.25	nt	nt	7.0	6.5	7.3	6.8
0.5	nt	nt	6.5	6.5	6.7	6.8
1	6.8	6.7	6.2	6.3	5.5	6.0
2	7.0	7.0	6.2	6.3	5.3	5.5
5	6.7	6.0	6.0	6.3	5.3	5.5
10	6.8	6.2	5.0	5.2	4.5	4.5

7.3.3 Nature of toxicity

It has been shown that high phytotoxic effects are associated with mobile compounds from biochar, but how does this affect plant growth and which factors are responsible?

In the 'volatiles only' germination test, four treatments showed a significant reduction of shoot length compared to the control (GC SS 0.25: $p=0.024$; GC OS 0.5: $p=0.013$; LC SS 0.25: $p=0.028$; LC OS 0.5: $p=0.023$) and LC OS 0.5 showed a significant reduction on root length ($p=0.009$) (Figure 7.3). This could be attributed to direct negative effects on growth after germination but it was observed that the listed treatments showed delayed germination; except in the control case no visible germination was detected after 48 h (A Figure 1). Delayed germination, which was also seen for barley seeds exposed to volatiles from hydrochar (unsealed conditions) (Bargmann et al., 2013), could have resulted in reduced time for growth and so

reduced shoot and root length. This shows that the most sensitive parameter for toxicity of mobile compounds from biochar is germination rate and changes in shoot and root length only seem to be a result of inhibition of germination.

One potential underlying cause for reduced germination caused by vapours from biochar could be low pH of <5, leading to total or close to total inhibition of seed germination on filter paper for various plant species (Shoemaker et al., 1990). By measuring the pH of filter paper it was identified that in the 'volatile only' germination test the filter paper of the high biochar treatments (10 g) had a pH of around 4.5 (Figure 7.4). Nevertheless, in the lower treatments (1, 2, 5 g), the pH increased and reached neutral values (5.3-7.0), but still no germination was observed. In a study of eight plant species, it was reported that a pH of 5.5 to 7.5 is the optimum pH for germination (Shoemaker et al., 1990). This clearly shows that the reduced pH in the experiments outline here might have contributed to the inhibition of seed germination, but is not the sole cause. A pine wood biochar extract with a pH of 3.9 showed toxic effects on algae; yet, even when the pH was neutralised the toxic effects still occurred (Smith et al., 2013). This confirms that mobile compounds from biochar can cause direct toxicity as reported in Smith et al. (2013).

Seeds in direct contact with biochar and affected by biochar leachate were even stronger inhibited than seeds only exposed to biochar vapours. Gell et al. (2011) demonstrated that biochar produced from digested pig manure at 300°C caused major toxicity on germination due to salt stress and/or dissolvable phytotoxic organic compounds. However, adverse effect due to the salt-stress caused by the ash in biochar, as also suggested in Busch et al. (2012), can be excluded as LC, GC and NC biochars had ash contents of less than 2%. The toxic effects of water extracts from biochar have been investigated before with extracts from VM-rich charcoal (macadamia nut shell, 430°C), demonstrating reduced germination of radish and corn seeds (Deenik et al., 2010). It has been reported that three out of six biochar extracts from different feedstocks and HTTs decreased seedling growth but did not have an influence on germination rate (Rogovska et al., 2012). In another study, pine biochar extracts (biochar produced at 450°C) exhibited toxic effects on blue-green and green algae (Smith et al., 2013). Furthermore, biochar extracts from different feedstocks showed variable negative impacts on aquatic species of several organism groups

(bacteria, algae, crustacea, protozoa) which was attributed to organic compounds in biochar (Oleszczuk et al., 2013).

These studies confirm that biochar can possess readily water soluble compounds that can have a negative impact on different organisms. In all four above mentioned studies, biochar was extracted by shaking with water. Yet, in this study, biochar was simply leached by water that percolated through a biochar-sand mixture and still this resulted in highly toxic leachates. These results show that acute toxic compounds in biochar of organic origin can be dissolved easily into water and could potentially be readily transported into soil, leached into groundwater and also taken up by organisms. It is difficult, however, to assess the degree of which condensation and deposition affects biochar produced in other pyrolysis units and if mobile organic compounds might have been responsible for some of the variable results of plant response in field and greenhouse trials (Biederman and Harpole, 2013; Spokas et al., 2011) as no studies on these factors could be found. Which particular organic compounds might have caused the toxic effects observed here will be further discussed in Chapter 9.

7.4 Conclusions

In this study, condensation and deposition of liquids and gases during pyrolysis resulted in biochar with a high content of organic compounds that were released below HTT. These volatiles were highly mobile and showed strong toxic effects on cress seed germination, both in vapour form and dissolved in water, indicating potential problems in the use of this type of biochar for soil amendment. Two methods, storage and blending, for reducing toxicity of high-VOC biochar were tested. The results showed that despite the high potential of VOC to vaporise/to be released, simple open-air storage proved insufficient for toxicity reduction, at least within the range investigated. On the other hand, blending of high-VOC biochar with low-VOC biochar showed positive synergy and effective reduction of toxicity was demonstrated in some cases. Due to the limited efficacy of tested post-treatment measures, the VOC-release and post treatment measures were further investigated in the next chapter. It was concluded that the phytotoxic effects of the biochar samples might be attributed partly to a reduction in pH caused by volatiles and dissolved compounds. However, it does not explain the toxic effects in all cases. Since salt and water stress were excluded as causes for the inhibition, it was deduced that mobile organic compounds were most likely responsible for the undescribed adverse effects on germination. Variable plant responses observed in previous studies might be explained by this phenomenon of mobile organic compounds and therefore it is very important to continue research in this area. Consequently, in Chapter 9 it is further discussed which compounds caused the toxicity. In addition, there is a need to investigate the condensation and deposition of pyrolysis vapours for different pyrolysis facilities as the degree is unique to the individual unit. Findings in this work open up a new area of research of high importance to biochar development and application.

Chapter 8 Mechanisms of post-treatment measures and potential human health effects of high-VOC biochars

The following chapter is based on the published article:

Buss, W., Mašek, O., 2016. High-VOC biochar – Effectiveness of post-treatment measures and potential health risks related to handling and storage. Environ. Sci. Pollut. Res. doi: 10.1007/s11356-016-7112-4

Journal impact factor (2014): 2.828

Number of citations (September 2016): 0

The candidate was solely responsible for data analysis and writing of the article and this chapter. Ondřej Mašek provided guidance contributed to the editing of the manuscript. The experimental work was performed by the candidate, apart from the biochar production which was performed by Juan Luis Turrion-Gomez.

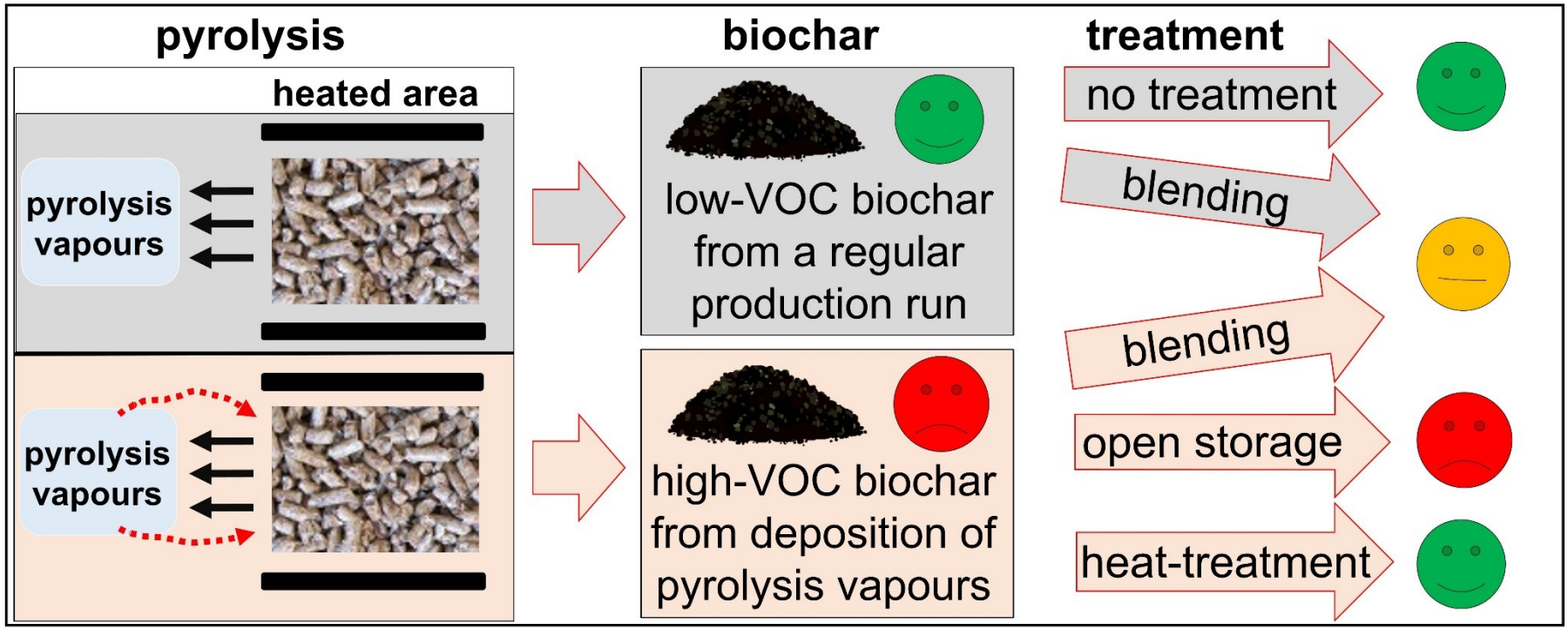


Figure 8.1: Graphical abstract Chapter 8. Two biochars were produced, one of those was contaminated with pyrolysis vapours due to problems during production. Different post-treatments were investigated regarding their effect on reduction of VOC emissions from the high-VOC biochar. Open storage was not sufficient to mitigate VOC emissions completely. Blending of high- with low-VOC biochar was more successful, while heat-treatments fully mitigated VOC emissions.

8.1 Introduction

Biochar has shown to possess a range of beneficial properties which make it suitable for various purposes, e.g. carbon storage, soil remediation, soil improvement and wastewater treatment (Lehmann and Joseph, 2015b). However, in some studies biochar has been shown to cause negative effects on plants and soil organisms (Deenik et al., 2010; Domene et al., 2015; Gell et al., 2011; Oleszczuk et al., 2013; Rajkovich et al., 2012; Rogovska et al., 2012; Smith et al., 2013). High salinity and nitrogen immobilisation after biochar application have been suggested to be two of the factors having caused adverse effects (Deenik et al., 2010; Domene et al., 2015; Gell et al., 2011; Rajkovich et al., 2012), yet, the majority of studies identified contaminants to be responsible for observed phytotoxicity (Gell et al., 2011; Jones and Quilliam, 2014; Oleszczuk et al., 2013; Smith et al., 2013). For application of biochar to soil, as well as for general handling of biochar, it needs to be ensured that biochar does not pose any excessive risk to plants, humans and the ecosystem. Consequently, conducting phytotoxicity tests and analysing contaminants in biochar is essential and different groups of contaminants have been found; inorganics, as well as organics.

Potentially toxic elements (PTEs) in biochar most often originate from the feedstock but sometimes also from materials used for construction of the processing equipment (Chapter 3). Organic contaminants in biochar are a more complex issue, as these are formed in elaborate reactions during the high-temperature treatment in pyrolysis units; the relevant groups are volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs) and dioxins. It has been shown that, while total concentrations of dioxins are typically below threshold values for soils (Bucheli et al., 2015; Hale et al., 2012), concentrations of PAHs can, in some cases, exceed values recommended in current legislation (Hale et al., 2012; Hilber et al., 2012). However, concentrations of available dioxins were below the detection limit of analytical equipment and available PAH levels were lower than clean urban sediments (Hale et al., 2012). The third category, i.e. VOCs, on the other hand, are not studied very well in biochar, but the studies that exist indicate that a wide selection of VOCs are present with considerable potential for negative or positive impact on plants and soil due to their high mobility (Elad et al., 2011; Spokas et al.,

2011). Consequently, phytotoxicity tests were conducted investigating the effect of vapours from VOC-rich biochars and indeed strong inhibitions were observed (Chapter 7). Post-treatment measures showed only partially to be successful in alleviating negative effects and there is a need for understanding the VOC-removal mechanisms and for developing more effective methods for post-treating biochars.

VOCs are defined as organic compounds that have boiling points of ≤250°C and due to their volatility are often considered contaminants that can threaten air quality (Directive 2004/42/CE of the European parliament and of the council, 2004). During handling or storage of VOC-rich biochars, people involved could be exposed to VOCs which could be a health and safety hazard. Depending on the use of biochars, different threshold values for human health would apply. When used at a work place, occupational exposure limit values regulate the VOC concentration thresholds, which exist in most countries (Aussschuss für Gefahrstoffe, 2006; EU Commission Directive 91/322/ECC, 1991; US Department of Health and Human Services, 2007). When biochar is used privately e.g. in growing media, VOCs released from biochar would have to be evaluated differently. E.g. in Germany, guideline values for indoor air pollution in private and public buildings were introduced to assess the toxicological risk for long-term exposure to VOCs (Arbeitsgemeinschaft Ökologischer Forschungsintitute, 2013) or to regulate the maximum permissible VOC release of construction products which was also partially implemented in EU legislation (Ausschuss zur Gesundheitlichen Bewertung von Bauprodukten, 2012; European Union Joint Research Centre, 2013). To my knowledge compliance of biochar with existing VOC threshold values has not been tested before which could be highly relevant for human health and safety.

Continuing the investigations of Chapter 7, this chapter focused on the release mechanisms of VOCs from biochar to understand the effects of vapours from VOC-rich biochars on plant growth and the way the post-processing affected the VOC-release in the previous chapter. In addition, further post-treatment measures for reducing the VOC concentrations in biochar to levels not affecting plant growth were investigated. Furthermore, the potential impact of VOCs from biochar on human health was assessed by comparing VOC concentrations with threshold values. The

release of VOCs from two types of biochar during open storage was investigated: (I) biochar contaminated during production with pyrolysis vapours (high-VOC) and (II) comparable biochar (same feedstock and pyrolysis conditions) with low concentration of VOCs (low-VOC). Mass change of the biochars during open storage was measured to see if it is possible to use this easy-to-perform method to assess the volatile carbon fraction that is already emitted at room temperature and if this can be correlated with VOC concentration in the head-space of the samples measured with a VOC analyser. Furthermore, potential mitigation measures, such as sorption of VOCs onto low-VOC biochar, and low-temperature oxidation were tested. The objective of this research was to assess the release dynamics of VOCs from contaminated biochars and to develop effective post-treatment measures for reducing VOC concentrations.

8.2 Materials and methods

An overview of all the experiments that were conducted in this chapter can be found in Figure 8.2.

8.2.1 Biochars

Liquid contaminated (LC) biochar and gas contaminated (GC) biochar were assessed against a low-VOC, non-contaminated (NC) biochar. Details on the biochars can be found in section 2.2.6.

8.2.2 VOC measurements

For the VOC measurements, a miniRAE lite VOC analyser (RAE Systems, Inc, San Jose, California) with a photoionisation detector and a 10.6 eV gas-discharge lamp was used. The instrument has a flow rate of around 0.5 L min^{-1} and detects VOCs with a resolution of 0.1 ppm. A two point calibration using fresh air (0 ppm) and isobutylene standard reference gas (100 ppm) was performed. As control, the air in the lab was sampled for each measurement.

8.2.3 VOC emissions of fresh biochar samples

To analyse the initial VOC release of the three biochars, 10 g of 'fresh' (stored in a sealed container after production) NC, GC and LC biochar pellets were added into 125 mL glass jars and the VOC concentration in the head-space above the biochar samples was measured. The biochars were not ground prior to analysis to be able to measure the VOC concentration released from the undisturbed samples (the same for thermally treated samples in 8.2.6). The concentration in the head-space of the biochar samples was measured for 10 s and the peak VOC concentration within this time period was reported. Triplicate analysis were performed by measuring the VOC concentration in the head-space of the container after 5 min sealed storage (open container, measure for ~10 s, close container for 5 min, open container and measure for ~10s, repeat all).

8.2.4 Time series measurements of VOC release dynamics

Three different experiments were performed to investigate the VOC release dynamics by high- and low-VOC biochars when openly stored (exposed to air), after storage in sealed containers since the day of production. The VOC concentration in the head-space above the samples, the change of mass of the samples and the change

of pH of a water reservoir surrounding the samples was determined (grey underlined area in Figure 8.2). For the following time series of VOC measurements during open storage the samples were ground using pestle and mortar. 2 g of ground NC, GC and LC biochar were filled in 125 mL glass vials, respectively.

8.2.4.1 VOC measurement in the head-space of biochar

Prior to the first VOC measurement, the samples were stored openly for 5 min because the VOC concentrations of the freshly ground samples fluctuated significantly. To investigate the release of VOCs during open storage, the VOC concentration in the head-space of the biochar samples were measured every 30 min over the course of 50 h using the miniRAE lite VOC analyser as described. To eliminate short-term fluctuations, instead of taking one measurement every 30 min, at each stage the concentration was measured four times within 40 s and an average was reported. Cross-contamination was avoided by conducting the experiments with different biochars individually, at different days. The temperature was kept at ~17±1°C. Afterwards, the samples were stored openly in the lab for 2 month (17-22°C) before the VOC concentration in the head-space was measured again. A summary of all the VOC measurements conducted can be found in Table 8.1.

8.2.4.2 Change of mass of biochar sample

To determine the change in biochar mass as a result of VOC release, ~2 g of each of NC, GC and LC biochar was added to pre-weighed aluminium foil cups (25 mm height, 70 mm diameter at the top, 40 mm at the bottom) and the mass was measured over 50 h. Variations of relative humidity in the lab led to significant fluctuations of the mass of the samples and to account for this, the same experiment was performed with samples that were stored in the lab for several weeks prior to the experiment (no net change of mass). The change in mass of these samples was subtracted from the fresh samples for the different points in time. The analyses were performed in triplicates.

8.2.4.3 Change of pH of water reservoir affected by biochar vapours

To investigate the acidity of the vapours released, the change of pH of a water reservoir surrounding, but not in direct contact with the biochar samples, was measured. Again 2 g of ground NC, GC and LC biochar was added to aluminium

cups and placed into plastic jars on an elevated platform above 100 mL of a 0.1 mol L^{-1} KCl solution. The KCl was added because resistance errors can occur measuring the pH of distilled water and the resulting value can differ significantly (Youmans, 1972). The pH was measured with a pH meter (Mettler Toledo FE 30) over the course of 50 h. The change in H^+ concentration was calculated from the pH. The analyses were performed in triplicates.

8.2.5 Blending of low-VOC and high-VOC biochars

To evaluate if low-VOC biochar had the ability to sorb measurable amounts of VOCs from high-VOC biochar, fresh samples of LC biochar were mixed in ratios of 1 g to 9 g and 2 g to 8 g with NC biochar (same ratio as used in the germination test in Chapter 7). The biochars were ground, mixed together and 10 g of the mixture was placed into a 125 mL glass jar. In the following, the blends will be referred to as LCB 1:9 and LCB 2:8. The VOC concentration in the head-space was measured (section 8.2.3). The experiment was not performed for 50 h as for the experiment with the unblended biochars, but for 60 h as the VOC concentration was still changing after 50 h.

8.2.6 Thermal post-treatment

Samples of all three uncrushed biochars (NC, GC and LC biochar) were spread in aluminium trays in one layer and exposed to air at 200°C for 20 h in a laboratory oven. 10 g of each of the thermally treated biochars was placed in a 125 mL glass jar and the VOC concentration in the head-space was measured as described in 8.2.3. The treated samples were used for germination tests (section 8.2.7) and parts were stored openly for 14 days and the VOC emission was measured again.

8.2.7 Germination tests

‘Volatiles only’ and ‘all exposure routes’ cress seed germination tests (section 2.6) were performed using 1, 2 and 5 g of ground NC, GC and LC biochar treated at 200°C for 20 h (for ‘volatiles only’ test) and 1, 2 and 5% of the three biochars in sand (for ‘all exposure routes’ test). In the 'volatiles only' germination test, seeds were not directly exposed to the biochar but only to its vapours. In the 'all exposure routes' germination test, seeds were either only exposed to the vapours from a biochar-sand mixture, exposed to the vapours and leachate from the mixture or were

in direct contact with biochar. For the 'volatiles only' germination test, length of shoots and roots were determined, while in the 'all exposure routes' germination test the roots were categorised in three fractions (roots <15 mm, roots between 15-60 mm and roots >60 mm). More details can be found in section 2.6. The tests were performed in triplicates.

8.2.8 PAH analysis

Concentrations of total and water extractable PAHs were determined using 36 h Soxhlet extraction with toluene and shaking of biochar in DI water with a ratio of 1:10, respectively. PAH analyses were performed by Northumbrian Water Scientific Services (Newcastle, United Kingdom), laboratories accredited by United Kingdom Accreditation Service (UKAS). More details can be found in section 2.5.

8.2.9 Statistics

Freundlich-langmuir sorption isotherms were fitted to the data for VOC release and change of H^+ concentration according to a best fit model. R^2 was used to show the deviation of the data from this fit. For the evaluation of the germination tests the difference to the control was determined using one-way ANOVAs in SigmaPlot 12.5 (Systat Software Inc).

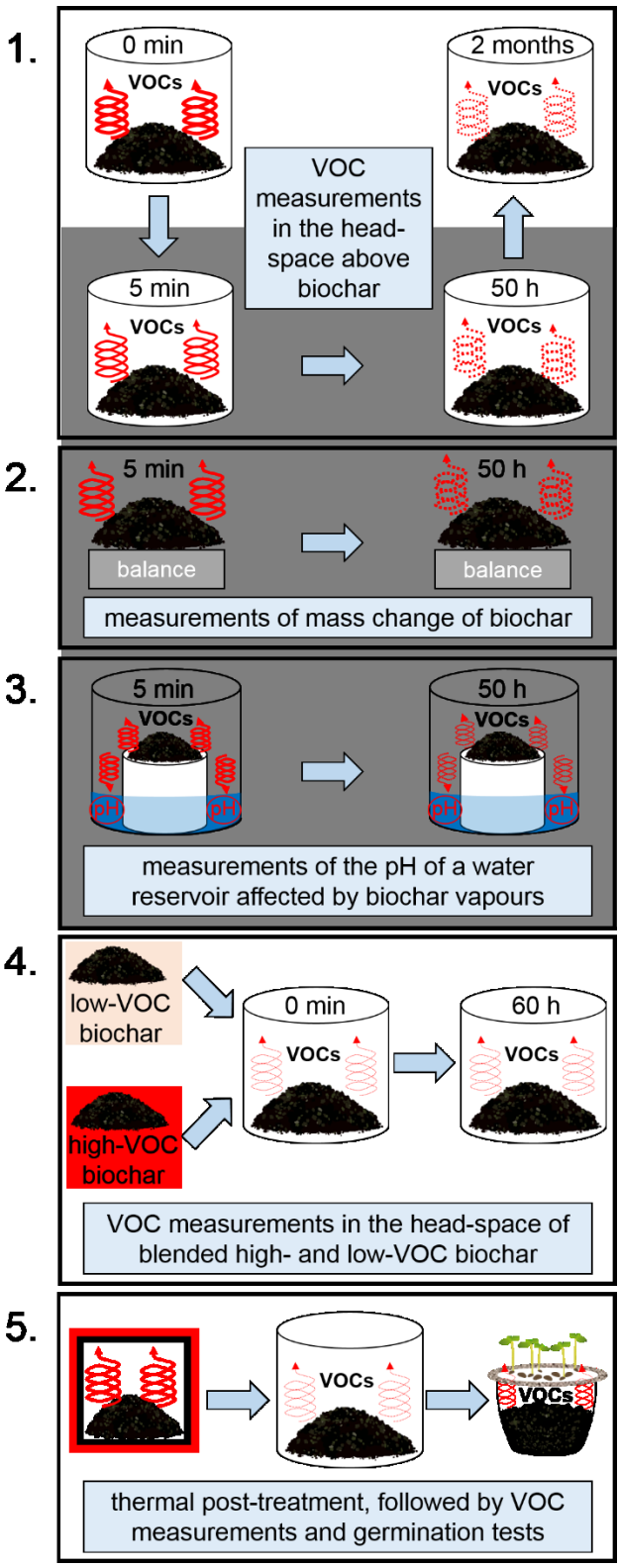


Figure 8.2: Schematic of the experiments conducted in this chapter. The low-VOC biochar and the two high-VOC biochars were tested in all five tests. Results for experiment 1 can be found in Table 8.1, the results for the grey underlined experiments which were all performed on the same time scale are depicted in Figure 8.3, the results of experiment 4 are shown in Figure 8.4 and results of experiment 5 can be found in Table 8.1 and in the Figure 8.5 and Figure 8.6. More details about the experiments can be found in section 8.2.

8.3 Results and discussion

8.3.1 VOC release of fresh and stored biochars

To investigate the VOC release of biochars, two high- and one low-VOC biochar were tested in three times series experiments conducted over 50 h. The experimental set-ups can be found in Figure 8.2 (grey underlined area). VOC release characteristics of GC, LC and NC biochars were investigated by measuring the head-space VOC concentration, the change of mass of the biochars and the change of the pH of a water reservoir surrounding the samples (measured as change of H^+ concentration). The results are shown in Figure 8.3.

The low-VOC, NC biochar increased in mass rapidly within the first 5-6 h of open storage, saturation was reached at around 6% with barely any additional weight change until the end of the experiment (freundlich-langmuir sorption isotherm, R^2=0.999). The mass gain can be attributed to uptake of moisture from the air which is typical for hygroscopic, porous carbons (Li et al., 2008). Measurement of concentrations of VOCs in the head-space showed that the NC biochar did not release any detectable levels of VOCs and there was also no noticeable change in the pH of the water reservoir surrounding it (Figure 8.3).

Unlike the NC, both the GC and LC biochar released considerable amount of VOCs. The head-space concentrations of VOCs for fresh (crushed) samples were 2.9 ppm for GC and 8.5 ppm for LC biochar (Table 8.1) which reduced dramatically with exposure to air, dropping to 1 ppm after 10 h open storage and then to 0.4 ppm until the end of the experiment (50 h) for GC biochar (Figure 8.3). For LC biochar the concentration declined to 1.8 ppm after 10 h exposure to air and in the following 40 h it decreased slowly to 0.7 ppm. During the 50 h VOC release period under ambient conditions, the GC biochar sample increased in mass by around 2% while the mass of LC biochar remained constant. This could mean that LC in contrast to NC biochar did not take up any moisture and the mass of the VOCs released was too small to be captured with the balance. However, in Chapter 7 using thermogravimetric analysis it was shown that, when heated to 110°C for 15 min, there was an extra mass loss of ~5% in the LC biochar sample compared to the NC biochar indicating that measurable amount of VOCs were released. This 5% extra loss of mass of the LC

biochar matches the 6% mass uptake of the NC biochar very closely, suggesting that VOC release and moisture uptake happened simultaneously and to a similar extent in LC biochar, overall, resulting in no change in mass. In addition, the mass gain curve (moisture uptake) of the NC sample and the VOC release curve of the LC sample are inversely correlated (Figure 8.3), which means moisture uptake and VOC release happened at a similar rate. Overall, the simultaneous release of VOCs and uptake of moisture resulted in constant weight of the LC biochar confirming that moisture uptake masked the release of VOCs. This highlights an issue with using gravimetric methods for simple assessment of VOC release in biochar.

Table 8.1: VOC concentrations (ppm) in the head-space of low-VOC (NC) and two high-VOC (GC and LC) biochars treated in different ways as average (AV) and standard deviation (SD).

		low-VOC		high-VOC			
		NC biochar		GC biochar		LC biochar	
treatment	unit	AV	SD	AV	SD	AV	SD
* fresh (0 min)	ppm	0.0	0.0	7.3	0.9	13.7	2.2
# crushed and stored for 5 min	ppm	0.0	0.0	2.9	0.2	8.5	0.7
# open storage for 50 h	ppm	0.0	0.0	0.4	0.0	0.7	0.0
# open storage for 2 months	ppm	0.0	0.0	0.2	0.1	0.3	0.1
* 200°C for 20 h from fresh	ppm	0.0	0.0	0.0	0.0	0.7	0.2
* + 14 days of storage	ppm	0.0	0.0	0.0	0.0	0.0	0.0

* 10 g of uncrushed biochar were measured in 125 mL vials in triplicates

2 g of crushed biochar was measured in 125 mL vials in quadruplicates

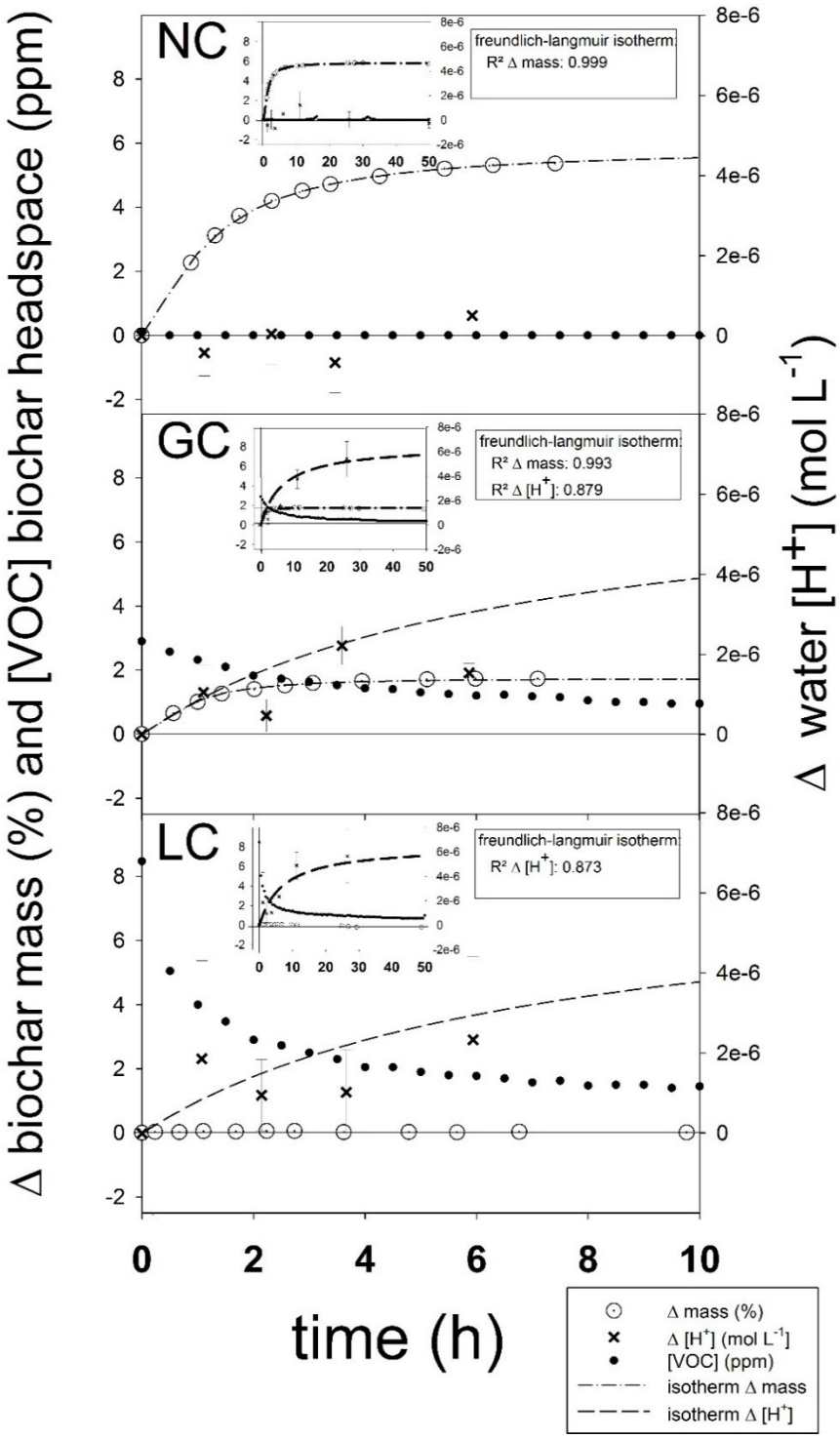


Figure 8.3: Mass change (%), VOC concentration in the head-space (ppm) (both left axis) of non-contaminated (NC), gas contaminated (GC) and liquid contaminated (LC) biochar when exposed to air and the change of H^+ concentration (mol L^{-1}) of a water reservoir surrounding the samples is shown (right axis). H^+ concentration change and mass change are given with standard deviation (n=3). R^2 are depicted where freundlich-langmuir sorption isotherms were fitted to the data. The small graphs in each figure show the same data over the whole duration of the experiment, i.e. 50 h.

Furthermore, the high-VOC biochars (GC, LC), increased the H^+-concentration in the water reservoir surrounding the samples (this corresponds to a pH decrease) (Figure 8.3). The VOC release and change of H^+-concentration were inversely correlated, which in addition to high concentrations of LMW aliphatic acid detected in the samples (Chapter 9), strongly indicates that the pH change indeed originated from VOCs emitted by biochar. The change of the pH of the water reservoir was very similar for both high-VOC biochars (~$6*10^{-6}$ mol L^{-1}) which showed to have the same pH (3.64) and very similar amounts of volatile, LMW, aliphatic acids (~1600 mg kg^{-1}) (Chapter 7 and Chapter 9) (the higher amounts of phenols detected in LC biochar is the likely cause for the difference in head-space VOC concentrations). The starting pH in the tests varied slightly, nevertheless, change of H^+ concentration of $6*10^{-6}$ mol L^{-1} corresponds to a pH decrease of 1.8 units when starting at a pH of 7. Here it was shown that VOCs emitted by biochar indeed have the ability to change the pH of a water reservoir to a significant extent which means emissions of VOC from biochars could lead to corrosion of metal containers or metal structures close to the area these biochars are stored.

Overall, after 50 h of storage in open air and even after open storage for 2 months in the lab, still, VOC emissions from GC and LC biochars were at detectable levels (Table 8.1). It shows the ineffectiveness of simple, open storage as post-treatment for removing VOCs from these specific biochars. In Busch et al. (2012), on the contrary, storage of char from hydrothermal carbonisation for 2 weeks showed to reduce VOC emissions successfully and cress seeds were able to grow unhampered. The phenomenon of constant release of VOCs shown by the two highly contaminated biochars, even after long-term storage could be a hazard for application of such biochar to soil. However, previously, it was shown that incorporation of biochars into wet sand or washing of biochar alleviated phytotoxic effects of VOCs to a large extent (Bargmann et al., 2013) (Chapter 7). Consequently, under natural conditions, biochar will be exposed to natural weathering and precipitation/irrigation which will reduce effects of VOCs significantly.

8.3.2 Blending of low-VOC and high-VOC biochars as a measure for mitigating risk for plant growth

In this experiment, it was tested, whether low-VOC biochar can sorb measureable amounts of VOCs from high-VOC biochar. The initial (0 h) VOC concentration in the head-space above LC biochar samples amended with low-VOC (NC) biochar was 0 ppm for both blends (LCB 1:9 and LCB 2:8) (Figure 8.4). Compared to the initial concentration of VOCs above the pure 2 g LC sample (8.5 ppm, added in Figure 8.4), it shows that blending with NC was effective and that NC biochar was able to sorb most, if not all, of the VOCs released by LC biochar. However, after a few hours the VOC concentration in the head-space of LCB 2:8 increased and a peak concentration of 0.9 ppm after around 14 h was detected. Consequently, it seems that NC biochar reached its maximum sorption capacity and could not take up more of the VOCs. Subsequently, the VOC concentration slowly decreased until it reached 0.1 ppm after 52 h. The situation was different for the LCB 1:9, which showed no detectable VOC release for the duration of the experiment, confirming NC biochar's ability to prevent VOC release from the LC sample at lower concentrations (Figure 8.4).

In the case of activated carbon, the VOC sorption capacity in two studies was tested with gaseous benzene and different activated carbons were able to take up around 0.4 g benzene/g on average (Chiang et al., 2001; Rodríguez-Mirasol et al., 2005). The biochars investigated here clearly did not have the capacity to sorb an amount as high. Still, blending high-VOC and low-VOC biochars could be used to help to control the desorption rate of VOCs, providing more time for their degradation in soil or for deliberate release of small amounts of VOCs to trigger positive effects on plant growth as observed in several studies (Elad et al., 2011; Keeley and Pizzorno, 1986; Kwapinski et al., 2010).

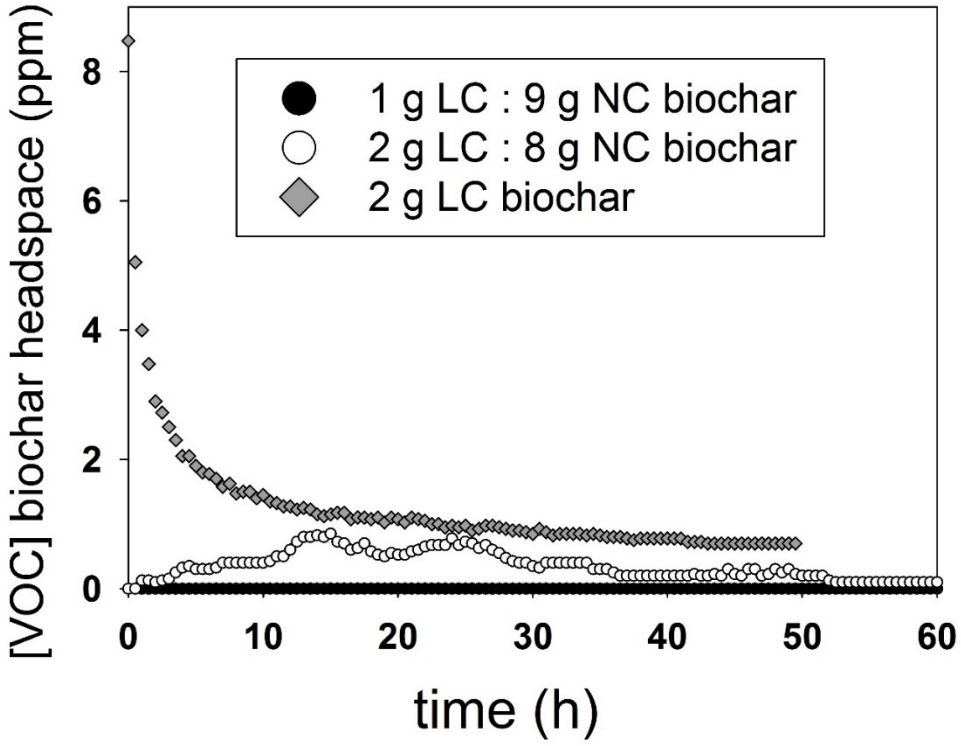


Figure 8.4: VOC concentration (ppm) in the head-space of LC biochar samples blended in different ratios when openly stored for 60 h. 1 g of LC biochar was mixed with 9 g of NC biochar (LCB 1:9) and 2 g LC mixed with 8 g NC biochar (LCB 2:8). For comparison, the VOC concentration in the head-space of 2 g LC biochar as in Figure 8.3 is shown (measured for 50 h).

8.3.3 Thermal post-treatment as measure for VOC-removal and alleviation of phytotoxic effects

As long-term open-storage did not show to be promising in terms of VOC release mitigation, and blending was effective only at relatively low concentrations of contaminated biochar, low-temperature oxidation/devolatilisation (200°C for 20 h) as another method for VOC content management was investigated. Thermal treatment reduced the VOC content in the head-space in GC biochar to 0 ppm and in LC biochar to 0.7 ppm (Table 8.1). In combination with open-air storage for 14 days, the VOC concentration in the head-space of LC biochar also dropped to 0 ppm.

In Kołtowski and Oleszczuk (2015), a similar thermal treatment approach was tested for removal of PAHs in biochars with similar PAH concentration (3.5, 20 and 40 mg kg^{-1}) as determined in the biochars investigated in this study (6, 28 and 53 mg kg^{-1}) (PAH results shown in Chapter 9). As in Kołtowski and Oleszczuk (2015), thermal

treatment effectively reduced the total concentrations of PAHs to 1.79 mg kg^{-1} for NC, 2.79 mg kg^{-1} for GC and 1.21 mg kg^{-1} for LC biochar and the water-extractable concentrations to below 0.001 mg kg^{-1} (Table 8.2) (fresh GC biochar contained 1.6 and LC 2 mg kg^{-1} water extractable PAHs (Chapter 9)). This shows that 200°C treatment for 20 h can remove VOCs as well as PAHs from biochar.

The thermally treated biochars were tested in 1, 2 and 5 g in 'volatiles only' cress seed germination tests and where vapours from fresh and 4 week-stored biochars resulted in 100% germination inhibition (Chapter 7), low-temperature treatment alleviated all toxic effects (Figure 8.5) (100% germination rate was observed in all treatments and the shoot and root growth did not differ statically from the control). Testing all three biochars in 'all exposure routes' seed germination tests revealed the same, seeds affected by vapours, seeds affected by the leachate from biochar-sand and seeds in direct contact with biochar-sand showed no inhibition of germination rate and early seedling growth compared to the control (Figure 8.6). In Kołtowski and Oleszczuk (2015), thermal treatment did remove PAHs, however, the thermally treated biochars showed inconclusive effects (positive and negative) on growth of shoots and roots in the same plant species as tested here, suggesting that other than VOC or PAH effects were responsible for the toxicity.

Overall, in the current study, thermal treatment showed to be effective in reducing PAHs and VOCs of both contaminated biochars (GC and LC biochar) and in alleviating previously observed phytotoxicity.

Table 8.2: Concentrations of PAHs in low-temperature biochars extracted by toluene in 36 h Soxhlet extraction (total) and by DI water.

	low-VOC		high-VOC			
	NC biochar		GC biochar		LC biochar	
	total	water	total	water	total	water
	µg g^{-1}	µg g^{-1}	µg g^{-1}	µg g^{-1}	µg g^{-1}	µg g^{-1}
naphthalene	1.5	<0.001	2.5	<0.001	0.95	<0.001
acenaphthylene	<0.10	<0.001	<0.10	<0.001	<0.10	<0.001
acenaphthene	<0.10	<0.001	<0.10	<0.001	<0.10	<0.001
fluorene	<0.10	<0.001	<0.10	<0.001	<0.10	<0.001
phenanthrene	<0.10	<0.001	<0.10	<0.001	<0.10	<0.001
anthracene	<0.10	<0.001	<0.10	<0.001	<0.10	<0.001
fluoranthene	<0.10	<0.001	<0.10	<0.001	<0.10	<0.001
pyrene	<0.10	<0.001	<0.10	<0.001	<0.10	<0.001
benz(a)anthracene	0.29	<0.001	0.29	<0.001	0.29	<0.001
chrysene	<0.10	<0.001	<0.10	<0.001	<0.10	<0.001
benzo(b)fluoranthene	<0.10	<0.001	<0.10	<0.001	<0.10	<0.001
benzo(k)fluoranthene	<0.10	<0.001	<0.10	<0.001	<0.10	<0.001
benzo(a)pyrene	<0.10	<0.001	<0.10	<0.001	<0.10	<0.001
indeno(1,2,3-cd)pyrene	<0.10	<0.001	<0.10	<0.001	<0.10	<0.001
dibenz(a,h)anthracene	<0.10	<0.001	<0.10	<0.001	<0.10	<0.001
benzo(g,h,i)perylene	<0.10	<0.001	<0.10	<0.001	<0.10	<0.001
16 USEPA	**1.79**	**<0.001**	**2.79**	**<0.001**	**1.21**	**<0.001**

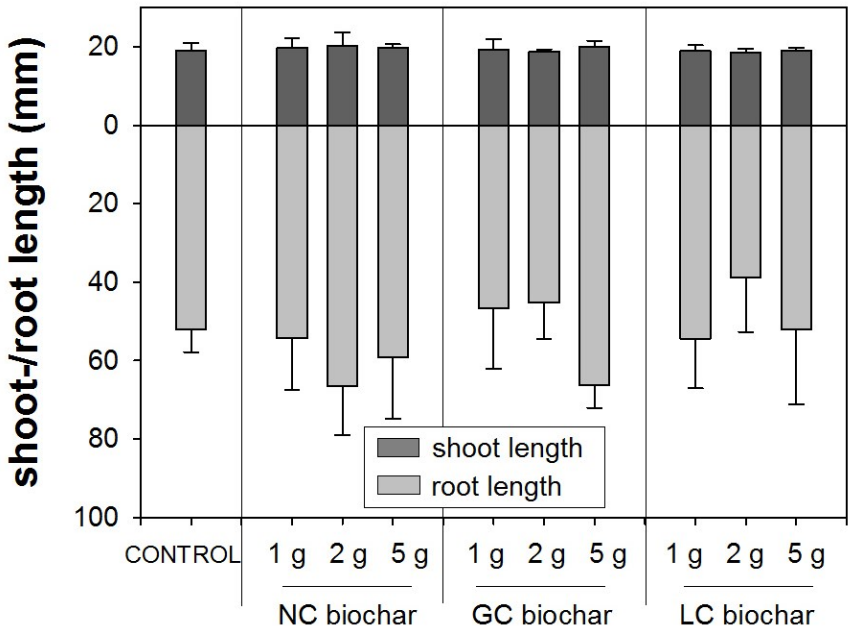


Figure 8.5: Shoot and root length of cress seeds tested in 'volatiles only' germination tests with 1, 2 and 5 g low-temperature treated NC, GC and LC biochar. Shoot and root length of the treatments are not statistically different to the control (one-way ANOVA).

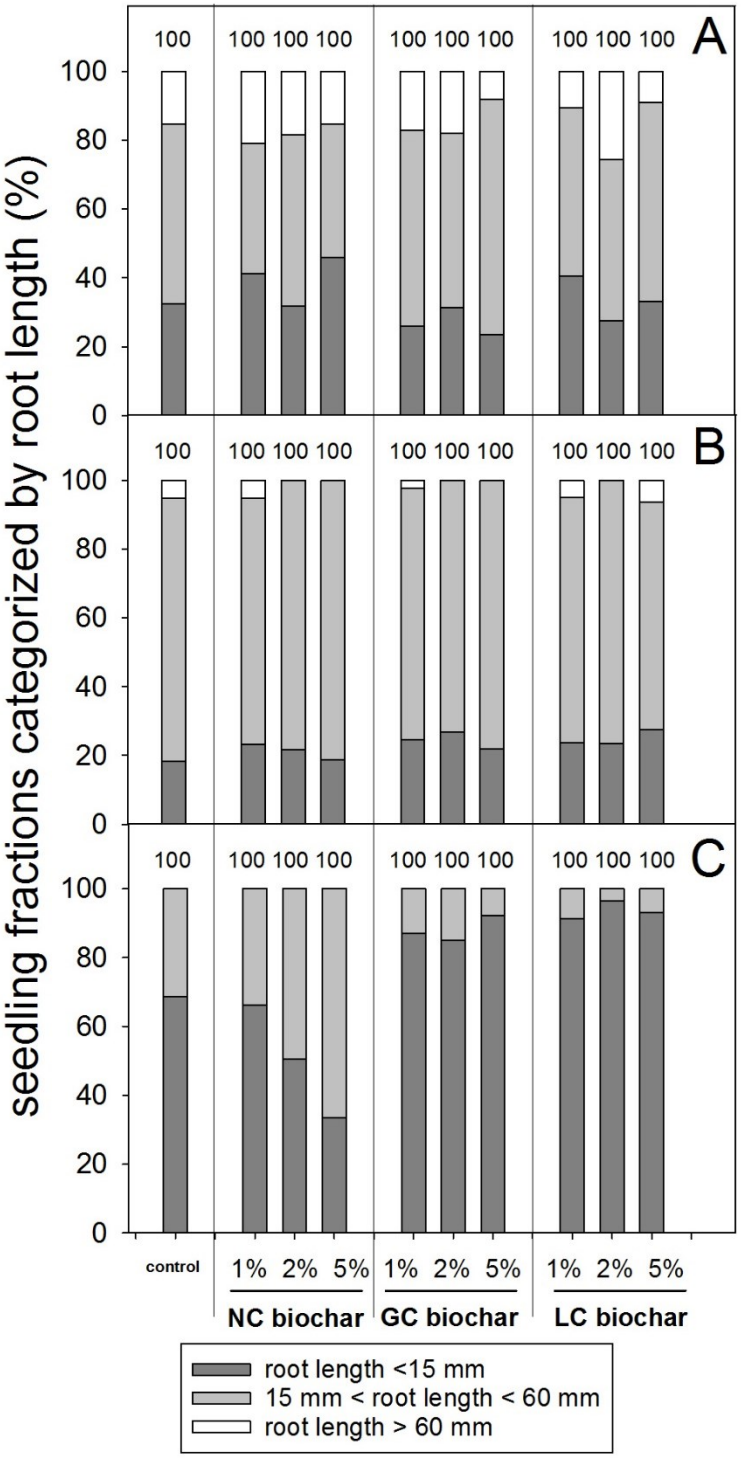


Figure 8.6: 'All exposure routes' germination test assessing toxicity of gaseous compounds released (A), leachable compounds (B) and direct contact of seeds and biochar (C). Seven day germination test using low-temperature treated NC, LC and GC biochar mixed in three concentrations in sand (1, 2 and 5%). Germination rates are depicted above the bars; bars show percentage of seedlings with root growth <15 mm, between 15 and 60 mm and above 60 mm.

Table 8.3: Threshold values for individual VOCs based on German, EU and US guidelines and legislations.

	occupational exposure limits				indoor air quality	
	short-term		40 h-week		GV II	LCI
	[1]EU	[2]NIOSH	[1]EU/[3]TRGS	[2]NIOSH	[4]AGÖF 2013	[5]AgBB 2012
	ppm	ppm	ppm	ppm	ppm	ppm
phenol	4	[+]15.6	2	5	0.052	
cresol				2.3	*0.011	
naphthalene		15	0.1	10	0.006	0.0001
formic acid			5	5		0.66
acetic acid		15	10	10		0.13
propionic acid	20	15	10	10		0.12
$TVOC_3$						2.6
$TVOC_{28}$						0.26

* sum of three cresols

[+] ceiling value: should not be exceeded at any time

[1] EU Commission Directive 2000/39/EC, 2000; EU Commission Directive 2006/15/EC, 2006; EU Commission Directive 2009/161/EU, 2009; EU Commission Directive 91/322/ECC, 1991. Occupational exposure limits based on weighted-averages in a 40 h work-week and short-term (15 min) exposure limits. Lower of the EU/German occupational limit value depicted.

[2] US Department of Health and Human Services, 2007, "Pocket Guide to Chemical Hazards". Occupational exposure limits based on weighted-averages in a 40 h work-week and short-term (15 min) exposure limits.

[3] Aussschuss für Gefahrstoffe, 2006 (Germany), "Technische Regeln für Gefahrenstoffe, Arbeitsplatzgrenzwerte". Occupational exposure limits based on weighted-averages in a 40 h work-week. Lower of the EU/German occupational limit value depicted.

[4] Arbeitsgemeinschaft Ökologischer Forschungsintitute, 2013 (Germany), "Guidance Values for Volatile Organic Compounds in Indoor Air". GV II, reference value, for indoor air quality of private and public homes, based on toxicological studies, when exceeded countermeasures to be taken. Values in µg m^{-3} were converted into ppm based on 25°C and 1 bar pressure.

[5] Ausschuss zur Gesundheitlichen Bewertung von Bauprodukten, 2012 (Germany), "Health-related evaluation procedure for volatile organic compounds emissions (VOC and SVOC) from building products". LCI, lowest concentration of interest, threshold value emitted by construction products in a test chamber after 28 days. $TVOC_3$, total VOCs after 3 days. $TVOC_{28}$, total VOCs after 28 days. Values in µg m^{-3} were converted into ppm based on 25°C and 1 bar pressure, for $TVOC_3$ and $TVOC_{28}$ in addition the molecular weight of phenol was used.

8.3.4 Potential human health and safety risks associated with VOC release from fresh and treated biochars

During handling and storage of contaminated biochar, such as GC and LC used in this study, relatively high amounts of VOCs can be released, leading to risk of exposure for anyone working with these materials, particularly in enclosed areas with poor ventilation. Fresh LC and GC biochar resulted in head-space concentrations of VOCs of up to 13.7 ppm (LC) and 7.3 ppm (GC) directly after removing from closed containers. In Chapter 9, the individual composition of LMW-hydrocarbons in GC and LC biochar are listed and the effects on plant growth were discussed. Although measured in water extracts from the samples, a very similar composition can be assumed in the head-space above the biochars as the identified compounds are typical VOCs which partly vaporise at room temperature. Methanol, phenol, cresols and LMW aliphatic acids were the compounds in the highest concentrations; naphthalene was also present but in comparably low concentrations (Chapter 9).

According to EU and US legislation, short-term occupational exposure limits for workers for the described VOCs are in the range of 4-20 ppm (Table 8.3). The exposure to phenol should not exceed 4 ppm for 15 min and 15.6 ppm should never be exceeded. Naphthalene, acetic acid and propionic acid short-term exposure threshold values, as defined by the US National Institute for Occupational Safety and Health, were set to 15 ppm (US Department of Health and Human Services, 2007). Based on results obtained in this study, 13.7 and 7.3 ppm release of a mixture of VOCs by high-VOC biochar, it seems feasible for short-term exposure values for certain VOC constituents to be exceeded under certain conditions, especially during handling. Risks related to long-term exposure can also be foreseen, as limits in this case are much lower than for short-term exposure, e.g. phenol should not exceed 2-5 ppm, acetic acid 5 ppm and cresol 2.3 ppm (Table 8.3). Overall, long-term exposure could be an issue where, for example, VOC-contaminated biochar would be stored openly next to a work place. Considering that biochars stored for 50 h showed head-space concentrations of VOCs of 0.4 ppm (GC) and 0.7 ppm (LC) (Table 8.1), it seems rather improbable that threshold values would be exceeded. Furthermore, low-VOC biochar, e.g. NC biochar in this study, did not emit any detectable

concentrations of VOCs and would definitely comply with occupational exposure limits.

In addition to risks to workers handling contaminated biochar, public and private indoor air quality could also become an issue for use of high-VOC biochar. This could be the case, for example, if such contaminated biochar was used in growing media used for potted plants in residential or commercial buildings. VOC-rich biochars stored for 2 months still emitted measurable amounts of VOCs (0.2, 0.3 ppm) (Table 8.1) which could exceed the toxicological reference values for phenol (0.052 ppm), sum of the three cresols (0.011) and naphthalene (0.006) of indoor air quality guidelines in Germany (Table 8.3). Another concept for monitoring indoor air quality which could apply for biochar, is VOC testing of building products in a ventilated test chamber after 3 and 28 days (Ausschuss zur Gesundheitlichen Bewertung von Bauprodukten, 2012). As an example, in Germany, the total values of VOCs emitted by construction products (materials used in buildings and furniture) as well as so-called "lowest concentration of interest (LCI)" for individual VOCs were established and were partly incorporated into EU legislation (Ausschuss zur Gesundheitlichen Bewertung von Bauprodukten, 2012; European Union Joint Research Centre, 2013). In this study, high-VOC biochar openly stored for 50 h (0.4, 0.7 ppm) did not exceed the total VOC threshold value for 3 days (2.6 ppm) but biochars stored for 2 months (0.2, 0.3 ppm) exceeded the value for 28 days (0.26 ppm). Again, the low-VOC biochar did not show any VOC emissions, therefore, did not exceed any of the threshold values for VOC exposure and in fact can act as a sorbent for VOCs, subsequently, improving indoor air quality.

Overall, it shows that handling of high-VOC biochar, as well as the use in closed spaces can pose hazards to human health, and where handling of contaminated biochar cannot be avoided, appropriate measures need to be implemented. Further processing of such high-VOC biochar is highly recommended to allow safe handling and use, such as, blending with low-VOC biochar or thermal post-treatment.

8.4 Conclusions

In this study, the VOC release dynamics from biochars contaminated by deposition of pyrolysis vapours during biochar production was investigated and the effectiveness of potential post-treatment measures aimed at reducing VOC contamination were assessed. It was shown that simply measuring the mass change of biochar samples when openly stored is not a sufficient indicator for assessing changes in VOC content due to the simultaneous uptake of water vapour. From three measures for reducing VOC content in contaminated biochar reported in this study, open air storage proved to be the least effective as biochar even released VOCs after several weeks of storage. As already shown in Chapter 7, blending of contaminated biochar with clean biochar yielded promising results and showed biochar's ability to take up VOCs from its surroundings. However, for the biochar studied this method was effective only at relatively low concentrations of contaminated biochar (1 g high-VOC biochar in 9 g of low-VOC biochar). The most effective post-treatment method was thermal treatment at relatively low temperature (200°C), as such treatment removed VOCs and previously observed phytotoxic effects. Furthermore, it was shown that under certain circumstances, high-VOC biochars can pose a risk to human health. However, this is limited only to extreme cases and in general most biochars are likely to sorb VOCs from the environment rather than to release them.

Chapter 9 PAHs vs. VOCs – Quantitative assessment and potential for plant growth inhibition in high-VOC biochars

The following chapter is based on the published article:

Buss, W., Mašek, O., Graham, M., Wüst, D., 2015. Inherent organic compounds in biochar–Their content, composition and potential toxic effects. J. Environ. Manage. 156, 150–157. doi:10.1016/j.jenvman.2015.03.035

Journal impact factor (2014): 2.723

Number of citations (September 2016): 14

The candidate was solely responsible for data analysis and writing of the article and this chapter. Supervisors provided guidance and supervisors and co-authors contributed to the editing of the manuscript. The experimental work was performed by the candidate, apart from the biochar production which was performed by Juan Luis Turrion-Gomez. In addition, the phenol index test was performed by Raphael Pierro at the University of Hohenheim.

Figure 9.1: Graphical abstract of Chapter 9. In biochars contaminated with pyrolysis vapours, both, VOCs and PAHs, were detected in concentrations high enough to cause phytotoxic effects. However, it was concluded that with a high probability VOCs were responsible for previously observed plant inhibitions caused by these biochars. This was attributed to the higher mobility and phytotoxicity of VOCs compared to PAHs.

9.1 Introduction

It is well known that char from natural forest fires and organic compounds released from such processes can promote seed germination and plant growth (Brown and Staden, 1997; Keeley and Pizzorno, 1986). However, negative effects of compounds generated during forest fires have also been observed and various organic compounds like phenolics and naphthalene can be responsible (Nelson et al., 2012). Recent work has shown that biochar can be used to improve soil properties, to remediate soil contamination and for long-term carbon storage (Buss et al., 2012; Lehmann and Joseph, 2009). Similar to natural char, besides positive effects of biochar, negative effects have also been reported (Bernardo et al., 2010; Gell et al., 2011; Kloss et al., 2014b; Oleszczuk et al., 2013; Quilliam et al., 2012; Rogovska et al., 2012; Smith et al., 2013), however, detailed understanding of causes of such negative effects is yet lacking. In Chapter 7, it showed that pyrolysis vapours condensed on biochar can have toxic effects on plants; and this chapter further investigated the causes of this toxicity resulting from this contamination pathway.

Contaminants within biochar may present a risk following application to soil, therefore, several studies have determined the total and bioavailable concentrations of potentially toxic elements (PTE) (e.g., Cd, Cu, Pb, Zn) and polycyclic aromatic hydrocarbons (PAHs) in biochars from various feedstocks and produced under various pyrolysis conditions. As low total levels and much lower levels of bioavailable PAHs and PTEs have generally been detected in biochars, these are not usually considered as a threat to plants and the environment (Hale et al., 2012; Singh et al., 2010). Nevertheless, in some studies, PAHs in biochar were suspected to have been responsible for acute toxicity to various organisms (Oleszczuk et al., 2013; Rogovska et al., 2012).

During pyrolysis, organic matter is broken down and new compounds are formed that are either transformed and incorporated into char or are volatilised and end up in the pyrolysis liquid/gas phases (Antal and Grønli, 2003; Spokas et al., 2011). Small amounts of compounds with a boiling point lower than the pyrolysis temperature naturally end up in the solid pyrolysis fraction, depending on the extent and nature of interaction between pyrolysis gases and solids. However, condensation, deposition

and trapping in biochar pores are among the mechanisms responsible for enhancing biochar's concentration of compounds that are normally associated with the pyrolysis liquid fraction (Fagernäs et al., 2012a; Spokas et al., 2011). The amount of condensation is highly variable and is related to the design of different pyrolysis units, where influences such as cold spots can cause vapour-condensation and a contamination by liquids (Gundale and DeLuca, 2006; Spokas et al., 2011). A huge variety of organic thermal degradation intermediates of various chemical classes have been found in pyrolysis liquids (Cordella et al., 2012; Sánchez et al., 2009). Among these are volatile organic compounds (VOCs), e.g. low molecular weight (LMW) organic acids, alcohols, ketones and phenols (Cordella et al., 2012). In addition, PAHs have also been reported in pyrolysis liquids and biochar, in much higher levels in the former than the latter (less than 1% of the total PAHs produced are present in pyrolysis solids) (Fagernäs et al., 2012a). Although levels of VOCs in biochar show a decrease with a rise in pyrolysis temperature (more volatilisation from solid product), the picture for PAHs is more complex (Fabbri et al., 2013; Hale et al., 2012) (Chapter 5).

Since there are only a limited number of reported studies on the topic of VOCs and biochars and to my knowledge no quantitative studies, there is a need to investigate the composition and concentration of organics sorbed to biochar. This is especially important since highly varied responses have been reported for biochar application to soil (Jeffery et al., 2011) and mobile organic compounds within the biochar may be responsible for some of the positive and negative effects that cannot be explained by factors like nutrients, pH or soil structure improvements (Elad et al., 2011; Nelson et al., 2012; Spokas et al., 2011).

In this chapter, biochars contaminated by a high dose of condensed pyrolysis liquids and gases (high-VOC biochars) were analysed for low-molecular weight (LMW) organics and priority PAHs as potentially toxic compounds and compared to a low-VOC biochar. These samples represent the worst-case scenario of uncontrolled pyrolysis and production in poorly designed or operated pyrolysis units. In Chapter 7, phytotoxicity of these high-VOC biochars on cress seeds was already demonstrated and the mechanisms investigated. The objectives of the current chapter were to assess the nature of condensed compounds on biochar, to identify classes of

compounds with the highest potential for adverse impact after soil application and to explain the toxic effects of this specific set of biochars observed in Chapter 7. The two working hypotheses behind this research were as follows: (I) condensation of pyrolysis vapours on biochar simultaneously increases concentration of two classes of organic contaminants, PAHs and VOCs; (II) VOCs, not PAHs are responsible for the main negative effects of biochar affected by pyrolysis vapour-condensation.

9.2 Materials and methods

9.2.1 Biochars

NC, GC and LC biochars were all produced from the same feedstock and process conditions, but NC and GC biochars were contaminated during production by pyrolysis vapours. More details are described in section 2.2.6.

9.2.2 Extractions and analyses

The concentrations stated in this study are not reported on a dry weight basis due to the high-VOC content of two of the samples. It was not possible to either remove the biochar moisture content without releasing VOCs or to determine the moisture content of the samples. The following extractions and analyses were performed for the NC (low-VOC) biochar and the two high-VOC biochars. If not stated otherwise the analysis were performed by Northumbrian Water Scientific Services (Newcastle, United Kingdom), laboratories accredited by United Kingdom Accreditation Service (UKAS). Validation/quality control of the analyses are stated in A Table 1 as percentage standard deviation of the concentration of (low, high) standards analysed in replicates.

9.2.2.1 Total PAH extraction and analysis

The total concentrations of the 16 US EPA PAHs were determined according to Hilber et al. (2012) by 6 h and 36 h Soxhlet extractions using toluene, followed by a GC-MS analysis (6890 GC plus autosampler and Agilent 5975c MS). Both extractions were performed to compare the extractability of different PAHs with time and to compare total PAH levels with literature values based on the same extraction duration. The limit of detection for PAHs was 0.10 µg g^{-1}.

9.2.2.2 Water extractable phenols

According to the method of Hildebrand (1979), 5 g solid material was extracted with 500 mL DI water (solid-to-liquid ratio of 1:100) for 12 h in a closed bottle to prevent the loss of volatiles. Instead of using a Soxhlet apparatus, a magnetic stirrer was used since it resulted in higher phenol recoveries and gave results with lower standard deviations. The mixtures were filtered under vacuum and the LCK 345 phenol index test (Hach, Loveland, Colorado, USA) was used for analysis of the phenol index in the extracts using a DR5000 Spectrophotometer UV-VIS (Hach, Loveland,

Colorado, USA). Furthermore, the samples were analysed for methylated and chlorinated phenols according to BS EN 12673:1999 / BS 6068-2.65:1999 (2008) using a Restek Rxi-XLB column in an Agilent 7890 GC-5975c MS. Analyses were performed by EUROFINS Umwelt West (Wesseling, Germany), accredited laboratory by Germany's National Accreditation Body (DakkS). Compounds below the detection limit and phenol index results from a different solid-to-liquid ratio than 1:100 are stated in A Table 4 and A Table 5**,** respectively.

9.2.2.3 Water extractable PAHs, organic acids, alcohols and ketones

10 g of biochar was extracted with 100 mL of DI water (solid-to-liquid ratio of 1:10) for 24 h on a reciprocal shaker at 150 rpm. Samples were then vacuum filtered using Whatman No. 1 filter paper.

Water extractable PAHs

Aqueous samples were extracted with dichloromethane and the extracts analysed for the 16 US EPA PAHs by GC-MS (6890 GC plus autosampler and Agilent 5975c MS). The detection limit was 0.1 µg L^{-1} for the extracts, therefore 0.001 µg g^{-1} for the biochar samples.

Water extractable organic acids

Aqueous samples were analysed by ion-exchange chromatography (KOH mobile phase, Dionex IonPac® AS15 column) and a conductivity detector (Dionex DX-320). Acetic, formic, propionic and butyric acids were analysed. The detection limits for the different compounds are stated in A Table 6.

Water extractable alcohols and ketones

Head-space GC-FID (Varian 450-GC-FID with Varian PAL head-space autosampler) analysis was used for alcohols and ketones (listed in Table 9.1). Again the respective detection limits are stated in A Table 6.

9.2.2.4 VOC scan

To identify additional mobile organic compounds, a semi-quantitative scan for a large series of organic compounds in organic solvent extracts was undertaken. 1 g of biochar was extracted with 10 mL of toluene-d8 spiked carbon disulphide for 1 h and occasionally agitated before injection onto a capillary GC column (Varian 3900 GC

fitted with a Restek RTX-VMS, 20 m, 0.18 mm ID, 1 μm film column). The extract was analysed by a Varian Saturn 2100 ion trap MS run in full scan mode.

Compounds were identified from a suit of around 60 VOCs according to NIST library of mass spectra and the concentrations are approximated from the response factor of toluene as an internal standard. The detection limit of these tentatively identified compounds was 20 $\mu g\ g^{-1}$. Compounds below this limit are not listed in Table 9.1.

9.2.3 Data analysis

As described in section above (9.2.2.2, 9.2.2.3), the water extractions were performed using a biochar solid-to-liquid ratio of 1:10 and 1:100. In Chapter 7, high- and low-VOC biochars were mixed at varying ratios in sand (A Table 7), a fixed amount of water was added and the resulting leachates were tested on their effect on seed germination. An overview of the theoretical concentrations of the compounds present in the leachates according to the solid-to-liquid ratios used can be found in A Table 7. For this study, it is assumed that all compounds extracted in both 1:10 and 1:100 ratios were also present in the leachates. However, since the biochars were not actually extracted in the germination tests, where the water percolated through the mixture instead, the levels stated represent a worst-case scenario.

9.3 Results and discussion

Table 9.1: Concentrations of various organic compounds expressed per mass of biochar (µg g^{-1}), extracted from high- and low-VOC biochars in different ways. Alcohols, ketones and LMW aliphatic acids extracted in water in a solid-to-liquid ratio of 1:10 and phenols in 1:100. 16 US EPA PAHs extracted by toluene (6 h and 36 h) and DI water (solid-to-liquid ratio 1:10). VOC scan performed by carbon disulphide extraction and semi-quantitative analysis with an internal standard. bdl, below detection limit.

		low-VOC	high-VOC	
		NC biochar	GC biochar	LC biochar
alcohols and ketones				
acetone	µg g^{-1}	bdl	bdl	bdl
butan-1-ol	µg g^{-1}	bdl	bdl	bdl
butan-2-ol	µg g^{-1}	bdl	bdl	bdl
ethanol	µg g^{-1}	bdl	20.0	46.0
isobutanol	µg g^{-1}	bdl	bdl	bdl
methanol	µg g^{-1}	bdl	380.9	250.1
methyl ethyl ketone (MEK)	µg g^{-1}	bdl	bdl	bdl
methyl isobuthyl ketone (MIBK)	µg g^{-1}	bdl	bdl	bdl
propan-1-ol	µg g^{-1}	bdl	bdl	bdl
propan-2-ol	µg g^{-1}	bdl	bdl	bdl
LMW aliphatic acids				
acetate as acetic acid	µg g^{-1}	97.0	771.9	730.3
acetic acid	µg g^{-1}	97.0	771.9	730.3
butyric acid	µg g^{-1}	bdl	210.5	150.1
formic acid	µg g^{-1}	85.0	541.3	500.2
propionic acid	µg g^{-1}	bdl	37.1	260.1
phenols				
phenol index (n = 3)	µg g^{-1}	5.45	2165	3265
phenol	µg g^{-1}	bdl	190	310
2-methylphenol (o-cresol)	µg g^{-1}	0.005	240	380
3-methylphenol (m-cresol)	µg g^{-1}	bdl	160	240
4-methylphenol (p-cresol)	µg g^{-1}	bdl	150	220
2,6-dimethylphenol	µg g^{-1}	bdl	43	47
2,5-dimethylphenol	µg g^{-1}	bdl	42	58
2,4-dimethylphenol	µg g^{-1}	0.017	300	260
3,5-dimethylphenol	µg g^{-1}	bdl	31	60
2,3-dimethylphenol	µg g^{-1}	bdl	18	24
3,4-dimethylphenol	µg g^{-1}	bdl	21	28
2,4,6-trimethylphenol	µg g^{-1}	bdl	20	30
2,3,6-trimethylphenol	µg g^{-1}	bdl	4.4	8
2,3,5-trimethylphenol	µg g^{-1}	bdl	13	12
3,4,5-trimethylphenol	µg g^{-1}	bdl	2.0	3
2-chlorophenol	µg g^{-1}	bdl	0.066	0.120
2,4/2,5-dichlorophenol	µg g^{-1}	bdl	0.40	0.770

16 US EPA PAHs				
DI water extraction	µg g^{-1}	<0.001	1.6	2.0
6 h toluene extraction	µg g^{-1}	0.34	29	17
36 h toluene extraction	µg g^{-1}	6.1	53	28
VOC scan (various organics)				
phenol	µg g^{-1}	bdl	49	110
3-methyl-1,2-cyclopentadione	µg g^{-1}	bdl	60	91
2-methylphenol	µg g^{-1}	bdl	60	130
3/4-methylphenol	µg g^{-1}	bdl	92	200
3,4-dimethylphenol	µg g^{-1}	bdl	120	240
2-methoxy-5-methylphenol	µg g^{-1}	bdl	23	bdl
4-ethylphenol	µg g^{-1}	bdl	61	110
3-ethyl-5-methylphenol	µg g^{-1}	bdl	20	64
4-ethyl-3-methylphenol	µg g^{-1}	bdl	59	110
1,2-benzenediol	µg g^{-1}	bdl	49	66
4-methyl-1,2-benzenediol	µg g^{-1}	bdl	31	45

Three biochars were investigated in this study, one biochar from a regular pyrolysis run (NC biochar) and two biochars that were contaminated by condensation and deposition during pyrolysis (GC and LC biochar). These biochars were previously characterised by proximate analysis, pH measurements and phytotoxicity tests (Chapter 7). It was revealed that the NC biochar was non-toxic while the GC and LC biochars contained a high content of VOCs and caused adverse effects on seed germination.

9.3.1 Origin, levels and mobility of organic compounds

9.3.1.1 VOCs

GC and LC biochar were extracted with an organic solvent (carbon disulphide) followed by a GC-MS analysis which indicated high concentrations of methylated and ethylated phenols; phenol, 2-methylphenol, 3/4-methylphenol, 3,4-dimethylphenol, 4-ethylphenol and 4-ethyl-3-methylphenol were most abundant (Table 9.1). In addition, biochar water extracts showed that acetic acid, methanol, formic acid, butyric acid, propionic acid, phenol, o-, m-, p- cresol and 2,4-dimethylphenol, were the dominant compounds, all present at levels higher than 100 µg g^{-1} (Table 9.1). The low-VOC biochar, on the contrary, did not show any of these compounds in concentrations above 100 µg g^{-1}. Very few studies have dealt with quantitative determination of the mentioned compounds in biochar. However, a study

by Gundale and DeLuca (2006) detected lower water extractable concentrations of phenols for wood charcoal (30-40 μg g^{-1}) than observed here. The heavier, organic fraction of pyrolysis liquids mainly consists of phenol, methylated phenols and longer chain organic acids (Ogunjobi and Lajide, 2013; Sánchez et al., 2009), while the lighter aqueous fraction has been shown to contain compounds such as acetic acid and methanol (Elliott, 1986). All of these compounds have been identified in this study, indicating that the high-VOC biochars have been contaminated by both, the organic and aqueous pyrolysis liquid fractions. In Chapter 7, it was shown that the pHs of the high-VOC biochars were low (pH 3.64, respectively). In the study of Ogunjobi and Lajide (2013) the organic pyrolysis liquid fraction had a pH of around 5.3, while the aqueous fraction had a pH of around 3, the latter explained by high concentrations of LMW organic acids which could be the same reason for the low pH of the LC and GC biochars.

9.3.1.2 PAHs

As shown in Figure 9.2, LMW PAHs were most abundant in the high-VOC biochars investigated in this study. Naphthalene was identified in the highest concentrations, followed by phenanthrene as already discussed in Chapter 6. Reported concentrations for total 16 USEPA PAHs associated with slow pyrolysis biochars vary greatly (<0.1-355 μg g^{-1}) (Fabbri et al., 2013; Hale et al., 2012; Hilber et al., 2012; Singh et al., 2010), however, the extraction method has been identified as having a large influence on measured PAH levels in biochar (Fabbri et al., 2013; Hilber et al., 2012). For this reason, in this study 6 h and 36 h toluene extractions were performed to assess the effect of extraction length on the concentration of PAHs extracted. Hale et al. (2012) investigated over 50 biochars using 6 h Soxhlet extraction with toluene, reporting concentrations between 0.07 and 3.27 μg g^{-1}. These levels are much lower than the ones for high-VOC biochars contaminated by vapour-condensation in this study (29 μg g^{-1} for GC biochar; 17 μg g^{-1} for LC biochar; Table 9.1) but in the same range as the low-VOC, NC biochar (0.34 μg g^{-1}). Concentrations of PAHs for biochars extracted for 36 h, were 6.1 μg g^{-1} for NC, 53 μg g^{-1} for GC and 28 μg g^{-1} for LC biochar (Table 9.1). Again the concentrations of PAHs for GC and LC biochar in this study revealed to be higher than for most other biochars extracted for 36 h (1.2-19 μg g^{-1}) (Fabbri et al., 2013) but equivalent to a miscanthus biochar

produced at 750°C (Hilber et al., 2012). Guideline values for PAHs from the International Biochar Initiative (6-20 μg g^{-1}) are exceeded by both contaminated biochars, especially the GC biochar, and the NC biochar levels are just at the lower threshold (International Biochar Initiative, 2011).

The concentrations of PAHs after 6 h extraction were then compared in more detail with those obtained after 36 h (A Table 8). The ratio of extractability of 6 h to 36 h varied for the different PAHs between 30-85% (GC biochar) and 50-95% (LC biochar). This means that some PAHs showed only 30% of the levels when biochar was extracted for 6 h compared to the levels they showed after 36 h extraction. This not only shows, in agreement with Hilber et al. (2012), a 36 h extraction is a much more suitable method for extracting the total PAHs content of biochar, but it also shows the dissimilarity in PAH extractability in the two high-VOC biochars. No relationship was identified between extractability and molecular weight of the PAHs, with some high molecular weight (HMW) PAHs having similar levels with 6 h and 36 h extraction (A Table 8).

Although the concentration of water extractable PAHs for NC biochar was below the analytical detection limit, the values were 1.6 and 2.0 μg g^{-1} for the GC and LC biochars, respectively (Table 9.1). Although not directly comparable, these concentrations are around 1000 times higher than the levels of PAHs sorbed to passive samplers in a study by Hilber et al. (2012) (~2 ng g^{-1}). Also, while the proportion of PAHs determined by passive samplers relative to total PAHs (6 h toluene extraction) was around 0.05% in that study (Hale et al., 2012), in this work the ratio of water extractable to 6 h toluene extraction was as much as 5.5% and 12.3% for the GC and LC biochars, respectively (data not shown). This shows that contamination with condensing vapours results in higher availability of the PAHs deposited onto the biochar surfaces (A Table 8). In addition, contamination by condensation also resulted in unexpected patterns in extractability of different PAHs. As HMW PAHs have a higher soil organic carbon-water partitioning coefficient (log K_{oc}), they are less soluble in water and more extensively attach to organic surfaces than LMW PAHs (A Table 8). Despite this, the percentage of water extractable of the total concentration of individual PAHs in this study did not simply decrease with increasing molecular weight. For example, several 5- and 6-ring PAHs showed

similar or slightly greater water extractability than naphthalene. This may be an artefact of the analysis as the results for water and solvent extraction both turned out to be very close to the detection limit of the measurement equipment. But as the varying extractability of 6 h compared to 36 h for the individual PAHs described above, it could also signal a different distribution and therefore availability of different PAHs in the porous biochar structure. Due to the external nature of contamination (from gas phase surrounding biochar particles), the distribution of PAHs within biochar would be determined by their ability to diffuse into the porous structure, and therefore the HMW PAHs could potentially be closer to the particle surface and therefore be more readily available. To understand these results further, additional investigations such as surface and pore analysis of biochar to physically locate PAH sorption sites and to link this to PAH properties are needed. However this was beyond the scope of this study and will be considered in future work. The log K_{oc} does, however, explain the very high water extractability of acenaphthylene (24% GC biochar, 61% LC biochar) (A Table 8). This shows that acenaphthylene in biochar should be monitored more closely due to its high mobility as this makes it a potential compound to leach into groundwater.

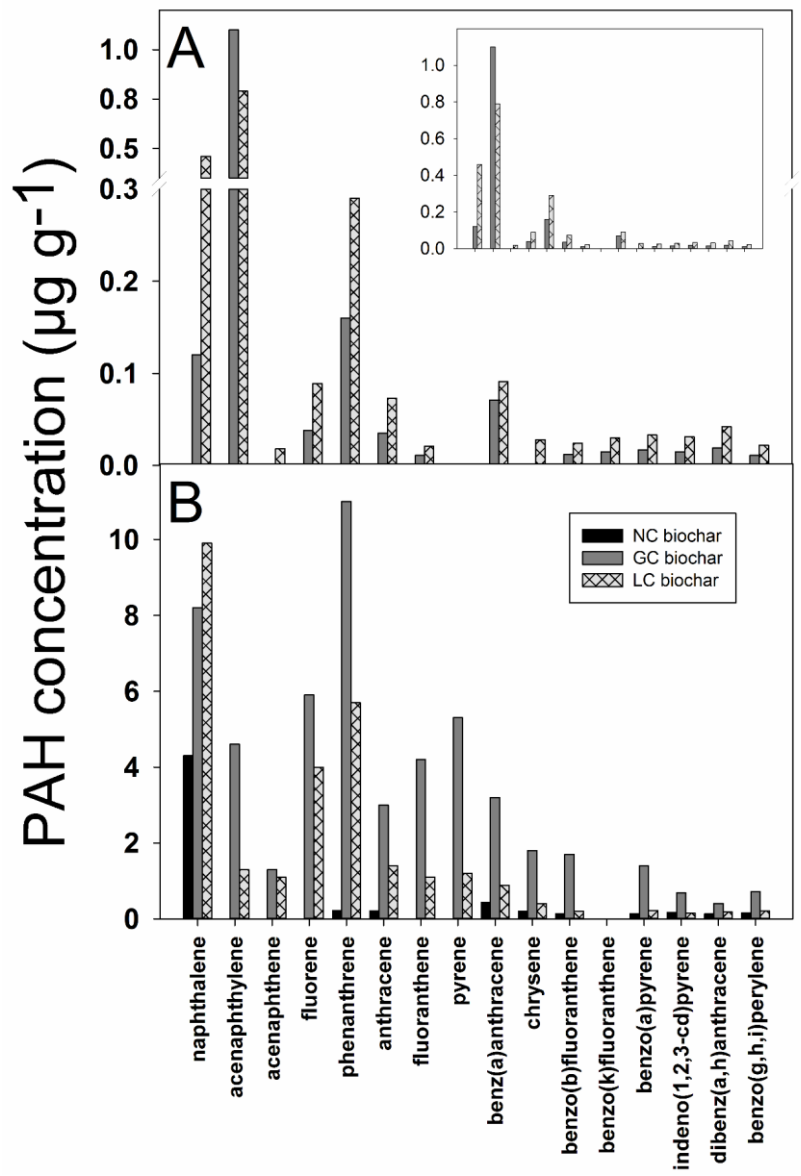


Figure 9.2: Water extractable (A) and 36 h toluene extractable (B) concentrations of individual 16 US EPA PAHs in NC, LC and GC biochars (µg g^{-1}). The small figure at the top right shows figure A in full view.

9.3.2 Phytotoxic potential of analysed contaminants

In Chapter 7, it was shown that cress seeds were strongly inhibited by a 5% high-VOC biochar-sand-composite, exposed to a leachate from this mixture and by vapours of pure biochar. It was concluded that the inhibition was caused by toxic compounds but it could not be pin-pointed specifically which compounds were responsible for the effects. However, the analyses in this study makes it feasible to link the detected concentrations in water extracts (Table 9.1) to the biochar-sand

leachates in the germination test of Chapter 7 (A Table 7) (further explanation section 9.2.3). This was done to discuss the toxicity of the individual compounds in the investigated leachates and to be able to relate the levels to literature values and generally identify which compound class in the concentrations detected here has the highest potential to cause adverse effects as observed in Chapter 7. Therefore, in the following, levels for 5% biochar treatment refers to the calculated concentrations in the 5% biochar-sand leachate that showed toxic effects in Chapter 7.

9.3.2.1 Phytotoxic potential of VOCs: phenols, organic acids, alcohols

Related to the 5% biochar treatment (explanation beginning 9.3.2), the concentrations of phenol were 13.6 mg L^{-1} (GC biochar) and 22.4 mg L^{-1} (LC biochar) and the concentrations for o-cresol 17.1 mg L^{-1} (GC biochar) and 27.1 mg L^{-1} (LC biochar) as two typical compounds of the class of 'phenols' (A Table 7). In a study by Feng et al. (1996), the inhibition of root elongation by phenols was tested in Chinese cabbage. Effective concentration for 50% reduction (EC_{50}) of roots for phenol was 125.6 mg L^{-1} and for o-cresol 54.9 mg L^{-1}. In Bargmann et al. (2013), *L. sativum* was used as the test organism and only 60 mg L^{-1} phenol was applied, which did not negatively affect germination and root elongation. However, the data above show that individual phenols present in concentrations slightly higher than those calculated for the highly toxic leachate in Chapter 7 caused inhibitory effects on seed germination and plant growth in other studies. Taking into account that the extracts from the biochars in this study contain a mixture of various phenols, it is very likely that they pose a serious threat to plant growth and were at least partly responsible for the phytotoxic effects observed in the germination tests of Chapter 7. An aqueous leachate from a char produced by pyrolysis of waste performed in a closed container, allowing direct contact of pyrolysis solids with liquids and gases, showed a complex mixture of benzene, toluene, ethylbenzene, and xylenes (BTEX), and methylated phenols in similar concentrations to those detected in this study (Bernardo et al., 2010). The eluate was toxic to bioluminescent bacteria (*Vibrio fischeri*) which suggests the detrimental effects of compounds emanating from the char probably originated from the pyrolysis liquids. However, after washing with an organic solvent (dichloromethane) to remove aromatics like phenols and BTEX, a water extract from this char still demonstrated toxic effects. This indicates that compounds

insoluble in organic solvents, such as LMW organic acids and alcohols, were responsible for a significant part of the observed growth inhibition (Bernardo et al., 2010).

The concentrations of formic, acetic, propionic and butyric acid in the 5% LC biochar treatment were 35.7, 52.2, 18.6 and 10.7 mg L^{-1}, respectively (A Table 7). These levels are only slightly lower than the individual concentrations reported to have caused toxic effects to plants in various other studies (Lynch, 1980; Rao and Mikkelsen, 1977). Acetic acid, for example, inhibited growth as follows; 25% inhibition of root extension at 300 mg L^{-1} (Lynch, 1980) and 60 mg L^{-1} significant reduction of root growth in rice seedlings (Rao and Mikkelsen, 1977). 1600 mg L^{-1} acetic acid caused impediment of root length of *Lepidium sativum* but had no effect on germination (Bargmann et al., 2013). However, as discussed for phenols above, besides acetic acid, various other potentially toxic organic acids were present in the water extracts and thus, in the leachates in the germination tests of Chapter 7 and as such, the phytotoxic influences of the different compounds are expected to accumulate. Generally, the adverse effects of LMW organic acids have been reported to increase with increasing number of carbon atoms (Lynch, 1980). But more importantly, the pH of the solution/soil influences the toxicity of the acids investigated (Lynch, 1980; Rao and Mikkelsen, 1977). Stronger effects were seen at lower pH as a larger fraction of the acids were present in their undissociated form, which is more toxic (Rao and Mikkelsen, 1977). This is important to note as the pH of the high-VOC biochars (determined in Chapter 7) was 3.64 and as indicated in Table 9.1, all of the acetate in the water extracts was indeed present as acetic acid, thus, undissociated. Furthermore, not only might the organic acids be directly responsible for toxicity but the low pH itself, caused by the above mentioned LMW organic acids and other acids, could have at least partly contributed to the inhibition.

The concentrations of alcohols and ketones identified in water extracts were mostly below detection limits, with the exceptions of ethanol and methanol, which related to the 5% biochar treatment were present in concentrations of less than 30 mg L^{-1} (A Table 7). Toxic concentrations of these compounds reported in the literature are much higher; around 2000 mg L^{-1} for ethanol and 8000 mg L^{-1} for methanol resulted in delayed germination of *Euphorbia heterophylla* after 24 h (Kern et al., 2009).

Even these effects proved to be short-term only. There are many other compounds, especially aromatic compounds, that are also typical products of thermal degradation of biomass that show partially toxic effects in similar concentrations as the phenols reported above (Lynch, 1980). Yet, due to the vast quantities of compounds present, not all could be analysed in detail in this study.

To summarise, individual VOCs have been shown to cause phytotoxic effects at concentrations not much greater than the concentrations detected in this study. Furthermore, the boiling points of the above discussed compounds are below 200°C and they can be considered as volatile (Dreisbach and Shrader, 1949). Taken their mobility into account, overall, this suggests that the complex mixture of LMW organic acids and phenols detected are very likely to cause phytotoxic effects and have caused the acute toxic effects of biochar, biochar leachate and vapours from biochar revealed in Chapter 7. Although the effects of VOCs are likely to be short-lived due to their degradability and natural volatility it is important to measure their concentration in biochar. In order to analyse and monitor concentrations the BS EN ISO 16703:2011 (2011) method could be used, but strong odour and a low pH of the biochars after production can also be used as a likely indicator of high concentrations of condensed pyrolysis vapours.

9.3.2.2 Phytotoxic potential of PAHs

PAHs effects in solution

As done for VOCs, the water extractable amounts of PAHs in the biochars were compared with the treatments in Chapter 7. In the 5% LC biochar treatment (explanation beginning 9.3.2), naphthalene (2 rings) was found at levels of 32.9 µg L^{-1}, phenanthrene (3 rings) at 20.7 µg L^{-1}, chrysene (4 rings) at 2.0 µg L^{-1} and benzo(a)pyrene (5 rings) at 2.4 µg L^{-1} (A Table 7). The concentrations of naphthalene and phenanthrene are around 900 times and 60 times lower than the maximum possible, based on their water solubilities, respectively, whereas the concentrations of chrysene and benzo(a)pyrene are in the same range (maximum water soluble concentrations: naphthalene 30,000 µg L^{-1}, phenanthrene 1,200 µg L^{-1}, chrysene 2.8 µg L^{-1}, benzo(a)pyrene 2.3 µg L^{-1}, A Table 7). In the work of Loibner et al. (2004), the effects of saturated aqueous solutions of each of the 16 US EPA PAHs were tested on bioluminescence of *V. fischeri* individually. It was discovered that

only two and three aromatic ring PAHs inhibited bioluminescence, whereas HMW PAHs did not show any toxicity (Loibner et al., 2004). Henner et al. (1999) also studied the influence of maximum water soluble amounts of each individual PAH on germination of several plant species in petri dishes. They found that naphthalene and phenanthrene delayed germination by 24 h but after five days the germination rate of the affected seeds was the same as the control. For chrysene and benzo(a)pyrene no toxicity was reported for concentration very similar as detected in this study (maximum water soluble concentrations).

Overall, it becomes clear that only LMW PAHs, when present in levels close to their maximum soluble concentrations, are able to cause negative effects on seed germination due to their higher solubility in water. The concentrations of PAHs in water extracts in the high-VOC biochars were exceptionally high for biochar (the NC biochar taken as a reference for a typical concentration of PAHs) but still far below the reported toxic concentrations of each individual PAH (A Table 7 and Figure 9.2). Additionally, in another study it has been shown that the effect of PAH mixtures proved to be cumulative and not synergistic (or antagonistic) (Loibner et al., 2004). This shows that phytotoxic influences of high-VOC biochar leachates on seed germination are very unlikely to be related to PAHs.

PAHs effects in soil

Total concentrations of PAHs as depicted in Figure 9.2 and Table 9.1 were 53 μg g^{-1} for GC biochar and 28 μg g^{-1} for LC biochar. These levels are above concentrations that are reported to have caused toxic effects in soil. Somtrakoon and Chouychai (2013) identified negative impacts on sweet corn seed germination in soil that had been freshly contaminated with 2 μg g^{-1} of anthracene, fluorene or fluoranthene (Somtrakoon and Chouychai, 2013). These concentrations are mostly exceeded by the high-VOC biochars in this study (Figure 9.2). It seems that solid material contaminated with PAHs exhibits a higher potential to cause adverse effects in plants than PAH-containing solutions. PAHs are mostly hydrophobic and have high K_{oc}'s (Marchal et al., 2014; US Department of Health and Human Services, 1995); this means high levels of PAHs can accumulate on/in organic material. However, to cause negative effects in plants, PAHs must be able to interact with the plant, which is not possible when they are strongly attached to soil organic matter. Uptake of

dissolved compounds via soil solution and gaseous uptake via leaves and shoots are the two mechanisms by which toxic compounds can affect plants (US Department of Health and Human Services, 1995), thus, solubility in water and volatility are the main factors that determine plant uptake. Consequently, LMW PAHs are more likely to gain access to plants to cause adverse effects (Somtrakoon and Chouychai, 2013). Yet, besides these two mechanisms, PAHs can be adsorbed onto root surfaces as plant tissue is organic matter (Marchal et al., 2014). It has been shown that after washing of roots, the overall PAH concentration of the root tissue decreased, indicating an association of PAHs with root surfaces (Vácha et al., 2010). Due to their low water solubility, HMW PAHs do not cause toxic effects in solution (Loibner et al., 2004), still, an accumulation in soil and adsorption to roots (high log K_{oc}) poses a risk.

On the other hand, in Lors et al. (2010), coal-tar contaminated soil after 6 months of biotreatment, still showing PAHs concentrations of 345 mg kg^{-1} (mainly 4-ring PAHs) did not cause phytotoxic effects (on *Lactuca sativa*). This could indicate that PAHs ready to interact with living organisms had been degraded and only PAHs that associated with soil particles very strongly retained which did not affect the plants. However, it could also have been the case that the PAH concentrations were too low to cause toxic effects in this plant species as the negative effects of PAHs reported in soil vary strongly, depending on the plant tested. One species (waxy corn) showed no germination inhibition even when exposed to concentrations of individual PAHs as high as 400 µg g^{-1} (Somtrakoon and Chouychai, 2013). Oleszczuk et al. (2014) showed root growth of *L. sativum* was inhibited by different soils contaminated with varying PAH concentrations of up to 100 µg g^{-1}. However, in the same study a soil sample with less than 0.5 µg g^{-1} PAHs showed even higher toxicity than the 100 µg g^{-1} sample, indicating that contaminants other than PAHs in the soil were responsible for the observed effects. All this shows how complex the topic of PAH toxicity in soil is and gives an indication of the magnitude of complexity of PAH effects in even less well investigated biochar.

PAHs effects in biochar

As a result of the cause of contamination by condensation, PAH concentrations in the high-VOC biochars are high and PAHs are rather loosely sorbed to biochar surfaces

which makes them more readily available (high concentrations in water extracts). Despite this, naphthalene is the only PAH that has been detected in the head-space above PAH contaminated sites (Henner et al., 1999) and therefore, is the only one that can be considered volatile under environmental conditions. Taking into account the low toxicity of naphthalene (Henner et al., 1999; Loibner et al., 2004), it seems highly unlikely that PAHs are causing toxic effects in the vapour phase. Furthermore, maximum soluble amounts of PAHs in water are considered only to be of low risk to plant growth. Since the total and available PAH concentrations in these high-VOC samples are already worst-case scenarios, leachates from biochars from a pyrolysis run without condensation are even much less likely to pose any threat to plants.

However, the acute, short-term toxic effects caused by direct contact with the contaminated biochars described in Chapter 7 may have been partially caused by PAHs when the high concentrations observed and the fact that mixtures of PAHs already influence plants negatively in $\mu g\ g^{-1}$ levels in soil are taken into account. But generally, it is difficult to transfer the conclusions of PAH toxicity in artificially contaminated soils to PAHs in biochar. One reason for this is that biochars sorb PAHs much stronger than soil, and this is why biochar can be used for remediation of PAH contaminated soils (Chen and Yuan, 2011). Secondly, the reason for the observed low availability and strong attachment of PAHs in biochar after pyrolysis (Hale et al., 2012) is probably not only the high sorption capacity of biochar, but also attributed to the fact that weaker attached PAHs vaporise during the pyrolysis process (at least if they are not contaminated by condensed pyrolysis vapours). As discussed for soil above, this removal of available PAHs might only leave very inactive PAHs behind that, even if present in high concentrations, do not pose a threat to plants (Lors et al., 2010). Furthermore, the largest proportion of PAHs in biochar has been shown to be allocated to naphthalene which is mobile but little toxic (Fabbri et al., 2013; Hilber et al., 2012) (Chapter 6). This shows that total levels of PAHs are not necessarily a good indicator for potential adverse effects but rather the individual PAH concentrations need to be taken into account as already discussed in Chapter 6. Koltowski and Oleszczuk (2015) demonstrated toxic effects of biochars, but they were not able to correlate PAH concentrations in (thermally treated) biochars to shoot and root inhibition of *L. sativum*. In Busch et al. (2013), it

was shown that a biochar with similar PAH concentration as in this study (62.7 µg g^{-1} (Hilber et al., 2012)), did not result in any negative influences on germination or biomass weight of *Brassica rapa* and *Zea mays*, even in levels of 10% in soil, supporting the hypothesis of little concern of high PAH concentration in biochar regarding short-term, acute plant effects.

Long-term PAH effects

However, since PAHs also have mutagenic properties and could be a long-term risk, to conclude the potential negative influences of PAHs in the high-VOC biochars this topic is shortly discussed here. In the study of Busch et al. (2013), despite no visible influences on plant growth, biochar increased DNA damage in pollen cells. Nevertheless, it could not be proven that these effects were due to the presence of PAHs. Anjum et al. (2014) conducted a study using hemp and wood biochar (batch unit, 500°C, 30 min residence time), both with similar concentrations of PAHs, but hemp biochar contained higher concentrations of LMW PAHs. Significant higher mutagenic effects were observed in the hemp biochar treatments compared to the wood biochar and it was concluded that this was due to the higher concentration of LMW PAHs. However, LMW PAHs have been reported to have lower mutagenic potential (Nisbet and LaGoy, 1992), thus, using the toxicity equivalency factors (TEF) to calculate the toxic equivalent quantity (TEQ) of the PAH levels compared to benzo(a)pyrene, hemp biochar turns out to have 0.22 benzo(a)pyrene-TEQ and wood biochar a 2.5 fold higher value of 0.55 benzo(a)pyrene-TEQ. But it needs to be mentioned that the TEFs were derived from toxicological and not plant studies, and might differ for plants. Still, this shows that no correlation of TEQ and mutagenic effect exists and it seems very unlikely that PAHs were responsible for the effects in that study. Interestingly, the phenol concentrations in the more mutagenic hemp biochar were much higher (55 µg g^{-1}) than phenols in the wood biochar (8.3 µg g^{-1}), indicating that phenols and other VOCs might have caused these effects instead.

9.3.3 VOCs vs. PAHs – Relevance in environmental samples

In the above discussion it was concluded that due to the concentrations, toxicity and mobility of individual organics in these specific biochars, VOCs pose a greater concern for plant growth than PAHs. The concentrations of both compound classes are likely to be exaggerated by the nature of these specific biochars, however, it

clearly demonstrates that even in biochar with lower concentrations of organic contaminants, VOCs are likely to play a significant role, and that these compounds can help to explain previous observations reported in literature.

In their work, Eom et al. (2007), Manzo et al. (2008) and Oleszczuk et al. (2014) all investigated soils contaminated with PAHs and in all of these studies the authors concluded that observed toxicity (mostly) could not be correlated with PAH concentrations and the adverse effects were rather caused by non-PAH compounds. Loibner et al. (2004) showed that in leachates from soil contaminated with PAHs by gasification and incineration processes contaminants other than PAHs were responsible for inhibition of *V. fischeri*. It shows that in soils compounds co-occurring with PAHs can be a greater risk than PAHs themselves. In this chapter, it was now shown that this can be the case for biochar as well.

Among the products of pyrolysis, PAHs tend to concentrate in pyrolysis liquids. Therefore, if as a result of the design or operation of a pyrolysis unit, biochar is extensively exposed to pyrolysis vapours or condensing liquids, it is likely to be heavily contaminated with PAHs, as well as VOCs. Therefore, as shown in Chapter 6, when biochar contains high amounts of PAHs, it often is a result of contamination by condensed pyrolysis vapours and consequently, such biochars, when fresh, would contain high amounts of VOCs in addition to the PAHs originating from pyrolysis liquids. This hypothesis holds true for the biochars in the current study, but needs to be proven for other biochars. However, fresh biochars are necessary to investigate this hypothesis due to the high volatility of VOCs.

Overall, VOCs in biochar are much more likely to be responsible for phytotoxic effects observed in other biochar studies than PAHs. This is supported by the fact that in longer-term studies, the observed negative influence of fresh biochar showed to be only short-lived, which could be a result of VOCs in biochar naturally dispersing with time (Gell et al., 2011; Kloss et al., 2014b; Quilliam et al., 2012). Similarly, it has been reported that many of the biochars showing adverse influences had a low pH value (Bernardo et al., 2010; Gell et al., 2011; Oleszczuk et al., 2013; Smith et al., 2013) which could be related to LMW organic acids and other acids from pyrolysis liquids.

9.4 Conclusions

The high-VOC biochars investigated in this study contained compounds typically present in the pyrolysis liquids fraction, confirming their contamination by pyrolysis vapours during production. Water-soluble concentrations of both compound groups, VOCs and PAHs, were comparatively high. It was shown for the first time that the more mobile VOCs, co-occurring with PAHs, are a bigger threat to plant growth than PAHs. Water extractable LMW organic acids and phenols have been found in biochars contaminated by condensed pyrolysis vapours in concentrations that can cause phytotoxic effects and hence, most probably caused the inhibitions of plant growth observed in Chapter 7. However, their mobility also makes VOCs prone to be leached, vaporised and degraded after application of VOC-rich biochar to soil and will, consequently, not pose a long-term threat. Concentrations of VOCs in biochar with minimal, if any, pyrolysis vapour contamination were mostly below detection limits, explaining why no adverse effects on plant growth were observed in Chapter 7. In contrast to biochars contaminated by pyrolysis vapours during production, the water-extractable concentrations of PAH in non-contaminated biochar were also below the detection limit, showing that PAHs in biochar pose very little risk to plants and soil. In general, the concentration of VOCs in biochar could be a good indicator for potential phytotoxic effects but this research area needs further investigation. This is an important finding providing strong evidence based on which VOCs content in biochar should be included among criteria for quality assessment of biochar and in biochar guidelines. From this study, however, it remains unknown how pyrolysis production parameter affect the VOC concentrations in biochar. In addition, although high concentrations of PAHs and VOCs were found in biochars in this study, it cannot be foreseen if both compound groups always correlate in biochar. VOCs have much lower boiling points than most PAHs (although naphthalene can be considered a VOC) which could mean that the VOC and PAH concentrations in biochar are affected differently by pyrolysis conditions, such as carrier gas flow or HTT. This is a very interesting research area, however, it requires the analysis of fresh biochar samples due to the high potential for VOCs to dissipate.

Chapter 10 Discussion, conclusions and further research

The aim of this thesis was to investigate contaminants in biochar and give recommendations for production of biochar safe to be used for environmental management. Feedstocks and production conditions most suitable for biochar production were assessed on the basis of contaminant concentrations (compliance with threshold values) and potential and actual effects of contaminants in biochars on plant growth. The results from this research are essential for biochar producers to be able to adjust production conditions and use suitable feedstocks to produce biochars with minimum contamination and to ensure users that respective biochars are safe to be applied.

Three groups of priority contaminants in biochar were identified and analysed: potentially toxic elements (PTEs), polycyclic aromatic hydrocarbons (PAHs) and volatile organic compounds (VOCs). All are diverse groups which were investigated separately, yet, due to their similar behaviour during pyrolysis, VOCs and PAHs were also discussed together.

10.1 Potentially toxic elements (PTEs)

Potentially toxic elements (PTEs) are of particular concern as they are indestructible and therefore, very persistent in the environment, can inhibit plant growth and can cause adverse effects in humans and animals ingesting PTE-containing biomass (Kabata-Pendias, 2011). However, PTE concentrations in biochars produced from typical feedstocks, such as wastes from forestry or agriculture, were shown previously not to exceed threshold value and not to be of any concern for plant growth (Freddo et al., 2012; Lucchini et al., 2014b). Consequently, studying the worst case scenario, PTEs were investigated in a set of PTE-rich biochars from marginal biomass which is material of little/no economic value.

10.1.1 PTE concentrations and pyrolysis conditions

As expected, the concentrations of PTEs in biochar were mostly dependent on the concentrations of PTEs in the feedstock used for biochar production. However, the pyrolysis unit also contributed to contamination with PTEs due to erosion of Cr, Ni and Fe from the furnace steel of the screw-pyrolysis unit. To avoid this contamination pathway, different materials of construction should be used for critical parts of the pyrolysis unit or a different reactor design that reduces erosion, e.g. a rotary kiln can be used. This needs to be taken into account in the design of biochar production units.

With increasing highest treatment temperature (HTT), an increasing amount of organic compounds were vaporised, while most of the minerals remained in the pyrolysis solids and therefore, PTE concentrations were enriched from feedstock to biochar. Yet, depending on boiling point, PTEs, such as As, Cd, Hg, Se or Zn, did evaporate from the solids to some extent and both, the HTT and feedstock type, influenced the extent of evaporation. For some feedstocks that are contaminated with one or several PTEs with low boiling points, the use of high HTT seem to be a suitable way to produce biochar with minimum PTE-contamination. However, the evaporated PTEs will, subsequently, contaminate pyrolysis liquids or gases. When the pyrolysis liquids and gases are used to fuel the pyrolysis process, the exhaust gases would need to be treated to remove the respective PTEs. Upgrading of PTE-contaminated pyrolysis liquids to biofuel could be even more problematic. In

addition, it was shown that the macronutrients Ca and Mg increasingly evaporated at high HTTs which would decrease biochar's fertiliser value. Most importantly, despite evaporation of various elements with increasing HTT, the available concentration of most PTEs (mg kg^{-1}) was highest at the highest HTT investigated (750°C). Consequently, applying high pyrolysis temperatures to remove PTEs cannot be recommended as the remaining proportion of the PTEs left in biochar showed to be highly available.

Overall, the easiest way to avoid contamination of biochar with PTEs is the use of feedstocks with low PTE concentrations. Yet, PTE-rich feedstocks can have economic benefits as the materials often have little or no (marginal) economic value. Pyrolysing PTE-rich feedstocks in the range 350-750°C, the availability of PTEs was lowest at medium HTTs. Consequently, the most suitable way to convert PTE-contaminated feedstocks into biochar, is the pyrolysis in a reactor made from PTE-free stainless steel at temperatures of 450-550°C.

10.1.2 PTE concentrations, limit values and potential effects

Biochars produced from biomass grown on heavily contaminated soil exceeded legislation threshold values for soil amendments and biochar guidelines values. The biochars from both anthropogenic wastes investigated here, demolition wood and food waste digestate, complied with European threshold values for biochar and soil amendments. However, the composition and PTE-content of most anthropogenic wastes varies majorly and consequently, biochars made from different feedstock sources need to be investigated individually regarding compliance with threshold values.

Besides total concentrations of PTEs, legislation values exist for available concentrations of PTEs, such as the NH_4NO_3-extractable PTE limit values in the German Federal Soil Protection and Contaminated Sites Ordinance (1999), which reflect the risk of PTEs to cause adverse effects more appropriately. Compared to these limit values, a very different picture to the comparison with threshold values for total PTEs was shown. The contrasting results highlight the difficulty to conclude about the legality of biochar application to soil.

Phytotoxic effects, as observed for some biochars in this thesis in small scale, short-term germination and growth tests, could not be correlated with available (and total) PTE concentrations. Some biochars with concentrations of PTEs exceeding threshold values for available PTEs even resulted in growth promoting effects. Consequently, PTEs in biochars might not be a concern for plant growth at all. Yet, it is unknown what happens to PTEs in biochar on long-term after application to soil. When the PTEs are bound to inorganic compounds, they could be immobilised permanently. However, when they are bound to organic compounds, they will become available eventually, when the organic material is degraded (McBride, 1995). Biochars from waste feedstocks containing PTEs have not been applied for long enough to investigate long-term effects in soil and it was not possible to investigate this in the limited time frame of this PhD. However, relatively high amounts of PTEs have been applied to arable land within the past decades via the application of sewage sludge and despite a long history of investigating the (long-term) fate of PTEs in soil applied with sewage sludge, many uncertainties remain, while it is generally agreed that, the (long-term) risks of PTEs in soil should not be underestimated (McBride, 2003, 1995; McGrath et al., 1995).

Overall, it cannot be clearly concluded if the use of biochar from PTE-rich feedstocks for environmental management is safe. The risks and benefits of the respective biochar and application scenarios need to be assessed separately. For example, blending PTE-rich biochars with growing media and using the mixture for growing plants in pots might be less problematic as only the plant performance and potentially the PTE concentration in respective plant parts used for consumption need to be evaluated. Some marginal biomass-derived biochars strongly increased the plant performance in 5% in sand and could be suitable to be used for amendment of growing media, while some biochars strongly inhibited the growth in the same application scenario. Incorporation of biochar into soil, however, can have unforeseen consequence, e.g. the long-term availability of PTEs applied with biochar to soil are completely unknown, so are the effects on soil flora and fauna. Testing the biochars in short-term phytotoxicity tests and measuring the total and available concentration can only be the start to ensure safe application to soil.

10.2 PAHs

PAHs are an important group of organic contaminants, in particular due to their carcinogenic properties and their ubiquitous presence and increasing concentration in soils world-wide from anthropogenic sources (Jones et al., 1989; US Department of Health and Human Services, 1995; Wilcke, 2007). PAHs are typically formed during incomplete combustions and consequently, are also priority pollutants in biochar. A large range of biochars were investigated for PAHs in previous studies with various claims regarding the effects of pyrolysis conditions on PAH concentrations and the risk of PAHs in biochar (Anjum et al., 2014; Brown et al., 2006; Freddo et al., 2012; Hale et al., 2012; Keiluweit et al., 2012; Kloss et al., 2012; Kołtowski and Oleszczuk, 2015; Oleszczuk et al., 2013).

To help close these knowledge gaps, in this thesis, the 16 US EPA PAH concentrations were analysed in 84 biochars. The effect of various process conditions and common feedstock types on total PAH concentrations in biochar was investigated in a systematic set of 46 biochars. In addition, the composition of PAHs in these biochars and additional 38 biochars was analysed to identify particular process conditions and feedstocks resulting in high-risk biochars based on a particular PAH composition. Finally, three biochars were tested in toxicity tests to assess the risk of PAHs to cause adverse effects in plants.

10.2.1 PAH concentrations, PAH composition and pyrolysis conditions

In a batch pyrolysis unit, increasing carrier gas flow rates decreased the PAH concentrations in biochar. It is hypothesised, this happened both, due to decreased PAH forming reactions (resulting from decreased hot vapour residence time) and increased evaporation of PAHs (resulting from elevated driving force for physical PAH removal). Woody biomass resulted in much lower PAH concentrations in biochar than straw-based material, yet, the underlying reasons could not be identified. Neither residence time, nor HTT displayed clear effects on the PAH concentration in biochar. The fact that the PAH concentration did not significantly change with HTT was explained by a simultaneous increase in formation and evaporation of PAHs with increasing HTT.

On average, in all biochars the proportion of NAP of the sum of PAHs was very high (84.1%). The most likely reason for the high percentage of NAP was that NAP, being the only 2-ring PAH and the smallest molecule, was trapped in small biochar pores which opened up during pyrolysis. This is confirmed by a comparatively low percentage of water-extractable of the total NAP concentration, described in section 9.3.1.2. Overall, the strongest effect on the concentration of PAHs in biochar was attributed to the pyrolysis unit itself, to weaknesses in the pyrolysis unit design and its operation.

Contact of biochar with pyrolysis vapours, which contain >99% of the PAHs synthesised during pyrolysis (Dai et al., 2014b; Fagernäs et al., 2012a), outside the furnace area, in colder parts of the pyrolysis units (discharge chamber) resulted in condensation and deposition of PAHs on biochar. The composition of PAHs in biochars contaminated via this pathway showed high concentrations of total and water-extractable PAHs, and in particular, very high total concentrations of non-NAP PAHs. This shift in PAH composition to a lower proportion of NAP in biochars contaminated by condensing pyrolysis vapours was attributed to the lower vapour pressure of NAP compared to the other PAHs which meant NAP mostly remained in the gas phase, while the HMW PAHs condensed and deposited on biochar.

Overall, the best way to ensure low concentration of PAHs in biochar is to avoid condensation of pyrolysis vapours which contain most of the PAHs. Pyrolysis solids and vapours need to be effectively separated in the discharge chamber of the pyrolysis unit by ensuring high temperatures and by avoidance of cold spots in the post-pyrolysis set-up. This is best achieved by a well-insulated discharge chamber or in case the discharge chamber is heated up actively, an adjustment of the temperature of the heating tapes according to the furnace temperature. Yet, even when condensation of pyrolysis vapours did not take place, high NAP concentrations were found in some biochars, e.g. biochars from wheat straw, which cannot be avoided easily. Overall, the biochar with the lowest 16 US EPA PAH concentrations were produced from wood pellets at a high carrier gas flow rate. Post-treatment at 200°C showed to be effective in removing PAHs and could be used for strongly PAH-contaminated biochars.

10.2.2 Potential toxic effects and fate of PAHs in biochar

Generally, PAHs in soil and solution can result in short-term adverse effects on plant growth, yet, in particular due to their low water solubilities and therefore low uptake into plants, plant growth inhibitions happen rather infrequently (Chapter 9). Two biochars that were highly contaminated with pyrolysis vapours in the post-pyrolysis process and showed high water-soluble concentrations of PAHs, inhibited plant growth strongly in short-term germination and growth studies. It was concluded, however, that VOCs, co-occurring with PAHs and being highly mobile, caused the observed phytotoxic effects. Biochars not contaminated by condensation of pyrolysis vapours showed water-extractable PAH concentrations below the detection limit and very low PAH availability was also shown in various studies in the literature which is predicted to stay low also on long-term (Hale et al., 2012; Jonker et al., 2005; Mayer et al., 2016). Therefore, it can be concluded that PAHs in biochar pose a low risk to cause adverse effects on plants.

Despite the strong sorption of PAHs to biochar, rapid loss of PAHs, in particular three and four ring PAHs, from biochar incorporated in soil was observed in Kuśmierz et al. (2016) and it was hypothesised that biodegradation and leaching was responsible for the loss. The concentration of PAHs in soil, which was elevated due to the application of biochar, decreased to the level of the control within the two and a half years of the experiment. The concept that the desorption rate of PAHs from organic matter is the factor mostly influencing the rate of degradation of PAHs in soil was the general consensus, yet, many biochar studies do not support this (Anyika et al., 2015; Shuttleworth and Cerniglia, 1995). Marchal et al. showed that the sorption of PAHs to biochar limits its degradation in biochar-amended soils but not in pure biochar (Marchal et al., 2013a, 2013b). In Khalid and Klarup (2015), the PAH concentration in biochar was strongly reduced by exposure to sun light and water addition which is encouraging as it suggests that PAH concentrations in biochar can be reduced rapidly in the environment after soil application despite being strongly sorbed.

In conclusion, PAHs in biochar neither seem to pose a threat to plant growth and the ecosystem on short-term, nor on long-term. Nevertheless, biochars still need to comply with existing PAH legislation and guideline values.

10.2.3 PAH concentrations, PAH composition and limit values

More than 50% and nearly ¾ of the 84 biochars investigated in this study, exceeded the upper limit of the IBI guideline (20 mg kg^{-1}) and the lower limit of the EBC (premium grade, 4 mg kg^{-1}) guideline, respectively (EBC, 2012a; International Biochar Initiative, 2011). Generally, it is difficult to recommend particular process conditions to guarantee biochars with PAH concentrations under biochar guideline values. Yet, using a high carrier gas flow rate, seven of eight biochars produced from two feedstocks, two HTTs and two residence times in a batch pyrolysis unit complied with the EBC premium grade threshold value. This clearly shows that an increase in carrier gas flow rate can be a suitable measure to produce biochars that comply with threshold values for 16 US EPA PAHs, at least in a batch pyrolysis unit. However, comparing the sum of the 16 US EPA PAHs does not take into account the different properties and toxicities of the various PAHs which is essential for a risk assessment of PAHs in biochar.

NAP is the PAH that is most different from all the other PAHs: it is highly volatile, easily degradable in soil, not considered carcinogenic and genotoxic and shows low toxicity in mammals (European Commission Scientific Committee on Food, 2002; US Department of Health and Human Services, 1995). The high proportion of NAP in biochar results in NAP being the crucial compound that decides about non-/compliance with threshold values in many biochars. Excluding the NAP concentration from the sum of PAHs, only 10% and ¼ of previous 50% and ¾ of the biochars exceeded the IBI upper limit and EBC premium grade biochar threshold value. In addition, all of the biochars that exceeded the IBI upper limit threshold value when only the non-NAP PAH concentration is taken into account in this study, were shown to be contaminated with pyrolysis vapours during biochar production caused by weaknesses of the pyrolysis unit design.

Threshold values based on the sum of all 16 US EPA PAHs do not adequately reflect the risk posed by PAHs to cause adverse effects. Instead, alternative evaluation schemes should be applied such as: (I) the TEF-approach, (II) threshold values only for benzo(a)pyrene as an indicator for toxic PAHs (III) separate threshold values for NAP and non-NAP PAHs. All of these methods are proven, used in practise for other materials and could easily be applied for biochar as well (Delistraty, 1997; EU

Commission Recommendation, 2005; German Federal Soil Protection and Contaminated Sites Ordinance, 1999; Wisconsin Department of Natural Resources Bureau of water quality, 2015). Overall, the results on PAHs in this thesis are very encouraging, however, guideline and legislation values will need to be adjusted to reflect the risk associated with PAHs in biochar appropriately.

10.3 Volatile organic compounds (VOCs)

Generally, volatile organic compounds (VOCs) are organic compounds with a boiling point below 250°C (Directive 2004/42/CE of the European parliament and of the council, 2004). Many VOCs are highly water soluble and due to their low boiling points, partially vaporise already at room temperature which makes them highly mobile in the environment. In addition, VOCs can be highly toxic, therefore, they are potential high risk compounds for plants, human health and the ecosystem (Cordella et al., 2012). However, very little is known about concentrations, composition and potential toxic effects of VOCs in biochar.

In this thesis, VOCs in biochar were examined and potential post-treatment measures for VOC removal were tested on three biochars produced under nominally same process conditions but, due to irregularities during production, two of the biochars were contaminated with pyrolysis vapours after production (high-VOC biochars). Comparing biochars from the same feedstock and same production conditions meant that observed differences in effects could clearly be attributed to the contamination with pyrolysis vapours.

10.3.1 Potential toxic effects of VOCs in biochar

It was shown that vapours from the high-VOC biochars inhibited germination and early seedling growth of cress. The adverse effect could clearly be attributed to the high volatility and toxicity of VOCs and it was concluded that compounds, such as phenols and LMW organic acids, caused the inhibition. In addition, seeds in direct contact with biochar and seeds exposed to the leachate from a biochar-sand mixture were strongly inhibited. Besides, high concentrations of mobile VOCs, the biochars also contained high concentrations of water-extractable PAHs and it was more difficult to pinpoint phytotoxicity in the seeds affected by the leachate and in direct contact with biochar to either group. Still, after an extensive literature review, it was concluded that the observed inhibitory effects were much more likely caused by the LMW organic acids and phenols due to their high mobility and easy uptake by plants (Chapter 9). However, the high mobility also results in VOCs being easily degraded by soil microorganism and lost through volatilisation and leaching (Takijima, 1964; van Schie and Young, 2000; Wilson and Jones, 1996). Consequently, no long-term

negative effects of VOCs on plant growth are expected, even if strong inhibitory effects are present in the short-term.

Due to their high volatility and as a result exposure of humans to VOCs during biochar processing, handling and storage, the potential human health effects of VOCs from biochar, such as phenols, cresols, LMW organic acids and methanol, were investigated. The concentration of the individual VOCs in the head-space above biochar were estimated and compared to occupational exposure limits and public and private indoor air quality guidelines. It was concluded that short-term occupational exposure limits for individual VOCs could be exceeded by VOC-rich biochars, yet, due to the fast volatilisation of VOCs, it seems rather improbable that long-term exposure limits would be exceeded. However, the lower indoor air quality guideline values could be surpassed by compounds such as phenol or cresols. In addition, the maximum allowable VOC-emissions from building products could be exceeded by VOC-rich biochars. However, only the two high-VOC, contaminated biochars posed a potential risk to human health, the clean biochar did not emit any detectable VOCs at all. VOC-rich biochar, consequently, needs to be handled with care and any processing should be done with face masks equipped with organic filters.

10.3.2 VOCs and biochar production

In the highly controlled pyrolysis unit under investigation, only irregularities in the area that separates pyrolysis solids and vapours (discharge chamber) resulted in biochars with high VOC concentrations. However, uncontrolled pyrolysis units and low-tech units might also result in biochars with high VOC concentrations in normal operation. This makes the topic of VOCs in biochars and their adverse effects in soils highly important as some traditional, very rudimentary techniques are used for the production of biochar (Wiedner and Glaser, 2015). The concentrations of VOCs in biochars from different pyrolysis techniques, units and conditions need further investigations to give recommendations for production of biochar with minimum VOC contamination. The difficulty with investigating VOCs is the need for freshly produced biochar as VOCs volatilise very easily and consequently, the set of 84 biochars used for investigating PAHs in this thesis could not be used to investigate VOC concentrations.

From the limited sets of biochars tested here, it can be concluded that for highly-controlled pyrolysis units, pyrolysis runs resulting in high-VOC biochar are identified easily due to significant excursions of production parameters from the design parameters. Examples of such excursions can be smoke in the unit/unit-outlet, lower than usual temperatures in different parts of the unit and strong odour of resulting biochars. As discussed for PAHs, for minimising contamination with VOCs, pyrolysis units need to be properly designed by avoiding cold spots which could result in vapour condensation and deposition on biochar.

Due to the high volatility of VOCs, relatively simple post-treatment of biochar could be sufficient to reduce contaminant concentrations. Among the methods tested, simple open air storage under ambient conditions for two months was not sufficient to remove VOCs completely and treated biochars still demonstrated inhibitory effects. In addition, blending of high-VOC biochars with low-VOC biochar, even at a ratio of 2:8 still resulted in VOC emissions and phytotoxic effects of the vapours. Yet, blending at a ratio of 1:9 showed considerable suppression of VOC emissions and mitigated the previously observed toxicity. To a limited extent, blending could be used to control the desorption rate of VOCs, for example during biochar storage. Low temperature oxidation treatment at 200°C in air for 20 h resulted in biochars that did not emit detectable levels of VOCs. Although, the priority should be to avoid VOC contamination of biochar in the first place, 200°C treatment in air is a suitable method that could be used for VOC removal in practise.

Overall, biochar contamination with VOCs is preventable, however, it is uncertain how strong VOC contamination of biochar in other pyrolysis units and under varying conditions is. Due to the significant toxic effects observed for high-VOC biochar here and potential human health effects, VOC levels should be monitored closely (in particular when fresh biochar is handled) and incorporated in biochar guideline values as recently done for the European Biochar Certificate (EBC, 2012a).

10.4 Conclusions

There are two main groups of contaminants in biochar, inorganic contaminants (PTEs) and organic contaminants (PAHs and VOCs). Inorganic contaminants mostly originate from the feedstock and organic contaminants are synthesised during the production process itself. Generally, careful feedstock selection is necessary to avoid contamination with PTEs, while pyrolysis unit and production conditions need to be optimised to avoid contamination with organic contaminants.

The type of feedstock used is the main factor that determines the concentration of PTEs in biochar, yet, the type of material used for critical parts of the pyrolysis unit, in contact with biomass or biochar, can also contribute to PTE contamination. The use of high HTTs to evaporate PTEs from pyrolysis solids cannot be recommended as the resulting biochars showed elevated availability of the remaining PTEs. However, despite high concentrations of PTEs in biochar and high biochar application rates, PTEs in biochar did not cause phytotoxic effects in this study. This is encouraging, yet, the biochars need to be exposed to further testing to confirm the safety of PTE-rich biochars for soil application as unexpected long-term effects or harmful effects on soil flora and fauna could occur. The risks and benefits of a specific PTE-rich, marginal biomass-derived biochar need to be evaluated individually for the particular application scenario (including evaluating economic factors) before making a decision about biochar application.

Two main groups of organic contaminants were identified in biochar, VOCs and PAHs, which are both intermediate degradation products of biomass constituents and under normal circumstances during pyrolysis, they are either further transformed into char or are evaporated and form the pyrolysis liquids and gases. The pyrolysis process is very effective in separating pyrolysis solids from PAHs and VOCs, yet, due to weaknesses in the pyrolysis unit design or operation, strong contamination with PAHs and VOCs through condensation and deposition can occur. Biochar contaminated by pyrolysis vapours, contained comparatively high concentrations of PAHs, in particular non-NAP PAHs and VOCs and were highly phytotoxic. Yet, the phytotoxicity was mainly attributed to VOCs. It remains unclear if in fresh biochar, the concentrations of both compound groups always correlate or whether they co-

occur only in some instances (differences in boiling points). Post-treatment at 200°C was successful in removing both compounds groups, yet, avoidance of the contamination in the first place is more effective than post-treatments. Most importantly, biochars produced under normal circumstances, which were not contaminated by condensation and deposition of pyrolysis vapours in the post-pyrolysis stage, showed not to be a risk to plant growth and human health as they contained very low concentrations of VOCs and the PAHs were mostly composed of naphthalene and not water extractable. Consequently, these biochars can be considered safe to be used for environmental management.

10.5 Further research

- The availability of PTEs in biochars increased at the highest HTT investigated (750°C), yet, it can only be speculated what the underlying mechanisms were (decreased CEC with increasing HTT which decreased the binding force for PTEs). Consequently, the mechanisms of availability of PTEs in biochar and how pyrolysis affects the availability need further investigation.
- It was concluded, based on availability of PTEs and the short-term effects on cress seedling growth, that PTE-rich biochars do not present a risk when applied in the right application rate. However, the effects of PTEs in biochars from heavily PTE contaminated materials on other plant species and soil organisms should be investigated, both, in short-term and long-term studies. In particular the long-term availability of PTEs in biochar and the effect of biochar aging on availability is unknown. This knowledge is essential to assess the risk of application of PTE-rich biochars to soil.
- In this study, the effects of pyrolysis conditions, such as residence time and carrier gas flow rate on the PAHs concentrations in biochar were investigated for a batch pyrolysis unit only. To be able to give general recommendation for biochar production with minimum PAH contamination, respective pyrolysis parameters should also be investigated regarding their effect in continuous pyrolysis units of different designs.
- Using literature data, it was concluded that PAHs are of rather low concern for plant growth in comparison to VOCs. This could be further confirmed by studying the effect of PAH-rich biochars with low VOC concentration on plant growth.
- It was hypothesised that PAHs and VOCs co-occur in biochars as they showed similar contamination pathways. This was confirmed for the two biochars investigated in this study, but needs to be further investigated for other biochars. However, biochars need to be analysed for VOCs immediately after production as VOCs vaporise and dissipate easily. In addition, the VOC concentrations of various fresh biochars should be correlated with pyrolysis technique, unit and conditions to give further

recommendations for production of biochar with minimum VOC contamination.

- It has been shown that VOCs can have significant adverse effects on plant growth, yet, in the literature various VOCs have also been reported to result in growth-promoting effect, if present in the right concentration. Consequently, the growth-promoting properties of VOCs originating from biochar should be investigated further.

References

Abrego, J., Arauzo, J., Sanchez, J.L., A, G., Cordero, T., Rodriguez-Mirasol, J., 2009. Structural changes of sewage sludge char during fixed-bed pyrolysis. Ind. Eng. Chem. Res. 48, 3211–3221. doi:10.1021/ie801366t

Agrafioti, E., Bouras, G., Kalderis, D., Diamadopoulos, E., 2013. Biochar production by sewage sludge pyrolysis. J. Anal. Appl. Pyrolysis 101, 72–78. doi:10.1016/j.jaap.2013.02.010

Alling, V., Hale, S.E., Martinsen, V., Mulder, J., Smebye, A., Breedveld, G.D., Cornelissen, G., 2014. The role of biochar in retaining nutrients in amended tropical soils. J. Plant Nutr. Soil Sci. 177, 671–680. doi:10.1002/jpln.201400109

Al-Wabel, M.I., Al-Omran, A., El-Naggar, A.H., Nadeem, M., Usman, A.R.A., 2013. Pyrolysis temperature induced changes in characteristics and chemical composition of biochar produced from conocarpus wastes. Bioresour. Technol. 131, 374–379. doi:10.1016/j.biortech.2012.12.165

Ameloot, N., Graber, E.R., Verheijen, F.G.A., De Neve, S., 2013. Interactions between biochar stability and soil organisms: Review and research needs. Eur. J. Soil Sci. 64, 379–390. doi:10.1111/ejss.12064

Amundson, R., Berhe, A.A., Hopmans, J.W., Olson, C., Sztein, A.E., Sparks, D.L., 2015. Soil and human security in the 21st century. Science 348, 1261071. doi:10.1126/science.1261071

Angin, D., 2013. Effect of pyrolysis temperature and heating rate on biochar obtained from pyrolysis of safflower seed press cake. Bioresour. Technol. 128, 593–597. doi:10.1016/j.biortech.2012.10.150

Anjum, R., Krakat, N., Toufiq Reza, M., Klocke, M., 2014. Assessment of mutagenic potential of pyrolysis biochars by Ames Salmonella/mammalian-microsomal mutagenicity test. Ecotoxicol. Environ. Saf. 107, 306–312. doi:10.1016/j.ecoenv.2014.06.005

Antal, M.J., Grønli, M., 2003. The art, science, and technology of charcoal production. Ind. Eng. Chem. Res. 42, 1619–1640. doi:10.1021/ie0207919

Anyika, C., Abdul Majid, Z., Ibrahim, Z., Zakaria, M.P., Yahya, A., 2015. The impact of biochars on sorption and biodegradation of polycyclic aromatic hydrocarbons in soils—a review. Environ. Sci. Pollut. Res. 22, 3314–3341. doi:10.1007/s11356-014-3719-5

Aracil, I., Font, R., Conesa, J.A., 2005. Semivolatile and volatile compounds from the pyrolysis and combustion of polyvinyl chloride. J. Anal. Appl. Pyrolysis 74, 465–478. doi:10.1016/j.jaap.2004.09.008

Arbeitsgemeinschaft Ökologischer Forschungsintitute, 2013. AGÖF Guidance Values for Volatile Organic Compounds in Indoor Air. Springe-Eldagsen.

Asadullah, M., Zhang, S., Li, C.-Z., 2010. Evaluation of structural features of chars from pyrolysis of biomass of different particle sizes. Fuel Process. Technol. 91,

877–881. doi:10.1016/j.fuproc.2009.08.008

Ausschuss zur Gesundheitlichen Bewertung von Bauprodukten, 2012. Health-related evaluation procedure for volatile organic compounds emissions (VOC and SVOC) from building products.

Aussschuss für Gefahrstoffe, 2006. TRGS 900, Technische Regeln für Gefahrstoffe. Bundesarbeitsblatt 1, 41–55.

Australia National Environment Protection Council, 1999. Assessment of site contamination, Schedule B (1) Guideline on the investigation levels for soil and groundwater.

Austrian Compost Ordinance, 2001. Bundesgesetzblatt für die Republik Österreich, 292. Verordnung: Kompostverordnung.

Baderna, D., Lomazzi, E., Pogliaghi, A., Ciaccia, G., Lodi, M., Benfenati, E., 2015. Acute phytotoxicity of seven metals alone and in mixture: Are Italian soil threshold concentrations suitable for plant protection? Environ. Res. 140, 102–111. doi:10.1016/j.envres.2015.03.023

Baek, S.O., Field, R.A., Goldstone, M.E., Kirk, P.W., Lester, J.N., Perry, R., 1991. A review of atmospheric polycyclic aromatic hydrocarbons: Sources, fate and behavior. Water. Air. Soil Pollut. 60, 279–300. doi:10.1007/BF00282628

Bargmann, I., Rillig, M.C., Buss, W., Kruse, A., Kuecke, M., 2013. Hydrochar and biochar effects on germination of spring barley. J. Agron. Crop Sci. 199, 360–373. doi:10.1111/jac.12024

Baronti, S., Vaccari, F.P., Miglietta, F., Calzolari, C., Lugato, E., Orlandini, S., Pini, R., Zulian, C., Genesio, L., 2014. Impact of biochar application on plant water relations in Vitis vinifera (L.). Eur. J. Agron. 53, 38–44. doi:10.1016/j.eja.2013.11.003

Basso, A.S., Miguez, F.E., Laird, D.A., Horton, R., Westgate, M., 2013. Assessing potential of biochar for increasing water-holding capacity of sandy soils. GCB Bioenergy 5, 132–143. doi:10.1111/gcbb.12026

Basta, N.T., Ryan, J. a, Chaney, R.L., 2005. Trace element chemistry in residual-treated soil: key concepts and metal bioavailability. J. Environ. Qual. 34, 49–63.

Beesley, L., Moreno-Jiménez, E., Fellet, G., Melo, L., Sizmur, T., 2015. Chapter 20: Biochar and heavy metals, in: Biochar for Environmental Management: Science and Technology and Implementation, Second Edition. Earthscan Ltd., London., pp. 563–594.

Beesley, L., Moreno-Jiménez, E., Gomez-Eyles, J.L., 2010. Effects of biochar and greenwaste compost amendments on mobility, bioavailability and toxicity of inorganic and organic contaminants in a multi-element polluted soil. Environ. Pollut. 158, 2282–2287. doi:10.1016/j.envpol.2010.02.003

Beesley, L., Moreno-Jiménez, E., Gomez-Eyles, J.L., Harris, E., Robinson, B., Sizmur, T., 2011. A review of biochars' potential role in the remediation, revegetation and restoration of contaminated soils. Environ. Pollut. (Oxford, U.

K.) 159, 3269–3282. doi:10.1016/j.envpol.2011.07.023

Ben, H., Ragauskas, A.J., 2013. Comparison for the compositions of fast and slow pyrolysis oils by NMR characterization. Bioresour. Technol. 147, 577–84. doi:10.1016/j.biortech.2013.07.151

Bernardo, M., Lapa, N., Gonçalves, M., Barbosa, R., Mendes, B., Pinto, F., Gulyurtlu, I., 2010. Toxicity of char residues produced in the co-pyrolysis of different wastes. Waste Manage. 30, 628–635. doi:10.1016/j.wasman.2009.10.015

Bernardo, M.S., Lapa, N., Barbosa, R., Gonçalves, M., Mendes, B., Pinto, F., Gulyurtlu, I., 2009. Chemical and ecotoxicological characterization of solid residues produced during the co-pyrolysis of plastics and pine biomass. J. Hazard. Mater. 166, 309–317. doi:10.1016/j.jhazmat.2008.11.031

Biederman, L.A., Harpole, W.S., 2013. Biochar and its effects on plant productivity and nutrient cycling: a meta-analysis. GCB Bioenergy 5, 202–214. doi:10.1111/gcbb.12037

Bird, M.I., Wurster, C.M., de Paula Silva, P.H., Bass, A.M., de Nys, R., 2011. Algal biochar - production and properties. Bioresour. Technol. 102, 1886–1891. doi:10.1016/j.biortech.2010.07.106

Bland, J.M., Altman, D.G., 1996. Transformations, means, and confidence intervals. BMJ 312, 1079.

Boateng, A.A., Garcia-Perez, M., Mašek, O., Brown, R., del Campo, B., 2015. Chapter 4: Biochar production technology, in: Biochar for Environmental Management: Science and Technology and Implementation, Second Edition. Earthscan Ltd., London., pp. 53–66.

Bourke, J., Manley-Harris, M., Fushimi, C., Dowaki, K., Nunoura, T., Antal, M.J.J., 2007. Do all carbonized charcoals have the same chemical structure? 2. A model of the chemical structure of carbonized charcoal. Ind. Eng. Chem. Res. 46, 5954–5967.

Brennan, A., Moreno Jiminez, E., Alburquerque, J.A., Knapp, C.W., Switzer, C., 2014. Effects of biochar and activated carbon amendment on maize growth and the uptake and measured availability of polycyclic aromatic hydrocarbons (PAHs) and potentially toxic elements (PTEs). Environ. Pollut. (Oxford, U. K.) 193, 79–87. doi:10.1016/j.envpol.2014.06.016

Bridgwater, A., 2003. Renewable fuels and chemicals by thermal processing of biomass. Chem. Eng. J. 91, 87–102. doi:10.1016/S1385-8947(02)00142-0

Bridgwater, A., 2013. Fast pyrolysis of biomass for the production of liquids, in: Biomass Combustion Science, Technology and Engineering. Woodhead Publishing, pp. 130–168.

Bridle, T.R., Hammerton, I., Hertle, C.K., 1990. Control of heavy metals and organochlorines using the oil from sludge process. Water Sci. Technol. 22, 249–258.

Bridle, T.R., Pritchard, D., 2004. Energy and nutrient recovery from sewage sludge via pyrolysis. Water Sci. Technol. 50, 169–175.

British Biochar Foundation, 2013. Biochar Quality Mandate (BQM), v. 1.0.

Britto, D.T., Kronzucker, H.J., 2002. NH4+ toxicity in higher plants: a critical review. J. Plant Physiol. 159, 567–584. doi:10.1078/0176-1617-0774

Broadley, M., Brown, P., Cakmak, I., Rengel, Z., Zhao, F., 2011. Function of nutrients: micronutrients, Marschner's Mineral Nutrition of Higher Plants: Third Edition. Academic Press. doi:10.1016/B978-0-12-384905-2.00007-8

Brooker, R.W., Jones, H.G., Paterson, E., Watson, C., Brooker, R.W., Bennett, A.E., Cong, W., Daniell, T.J., George, T.S., Hallett, P.D., Hawes, C., Iannetta, P.P.M., Jones, H.G., Karley, A.J., Li, L., Mckenzie, B.M., 2015. Improving intercropping: a synthesis of research in agronomy, plant physiology and ecology. New Phytol. 206, 107–117.

Brown, N.A.C., Staden, J. Van, 1997. Smoke as a germination cue: a review. Plant Growth Regul. 22, 115–124.

Brown, R.A., Kercher, A.K., Nguyen, T.H., Nagle, D.C., Ball, W.P., 2006. Production and characterization of synthetic wood chars for use as surrogates for natural sorbents. Org. Geochem. 37, 321–333. doi:10.1016/j.orggeochem.2005.10.008

Brown, R., del Campo, B., Boateng, A.A., Garcia-Perez, M., Mašek, O., 2015. Chapter 3: Fundamentals of biochar production, in: Biochar for Environmental Management: Science and Technology and Implementation, Second Edition. Earthscan Ltd., London., pp. 39–61.

BS EN 12673:1999 / BS 6068-2.65:1999, 2008. Water quality - Gas chromatographic determination of some selected chlorophenols in water.

BS EN ISO 16703:2011, 2011. Soil quality — Determination of content of hydrocarbon in the range C 10 to C 40 by gas chromatography.

BS ISO 19730:2008, 2008. Extraction of trace elements from soil using ammonium nitrate solution.

Bucheli, T.D., Hilber, I., Schmidt, H.P., 2015. Chapter 21: Polycyclic aromatic hydrocarbons and polychlorinated aromatic compounds in biochar, in: Biochar for Environmental Management: Science and Technology and Implementation, Second Edition. Earthscan Ltd., London., pp. 595–624.

Burhenne, L., Messmer, J., Aicher, T., Laborie, M.P., 2013. The effect of the biomass components lignin, cellulose and hemicellulose on TGA and fixed bed pyrolysis. J. Anal. Appl. Pyrolysis 101, 177–184. doi:10.1016/j.jaap.2013.01.012

Busch, D., Kammann, C., Grünhage, L., Müller, C., 2012. Simple biotoxicity tests for evaluation of carbonaceous soil additives: establishment and reproducibility of four test procedures. J. Environ. Qual. 41, 1023–1032. doi:10.2134/jeq2011.0122

Busch, D., Stark, A., Kammann, C.I., Glaser, B., 2013. Genotoxic and phytotoxic risk assessment of fresh and treated hydrochar from hydrothermal carbonization compared to biochar from pyrolysis. Ecotoxicol. Environ. Saf. 97, 59–66. doi:10.1016/j.ecoenv.2013.07.003

Buss, W., Graham, M.C., Shepherd, G.J., Mašek, O., 2016. Suitability of marginal biomass-derived biochars for soil amendment. Sci. Total Environ. 547, 314–322. doi:doi:10.1016/j.scitotenv.2015.11.148

Buss, W., Kammann, C., Koyro, H.-W., 2012. Biochar reduces copper toxicity in Chenopodium quinoa Willd. in a sandy soil. J. Environ. Qual. 41, 1157–1165. doi:10.2134/jeq2011.0022

Buss, W., Mašek, O., 2014. Mobile organic compounds in biochar – a potential source of contamination – phytotoxic effects on cress seed (Lepidium sativum) germination. J. Environ. Manage. 137, 111–119. doi:10.1016/j.jenvman.2014.01.045

Butnan, S., Deenik, J.L., Toomsan, B., Antal, M.J., Vityakon, P., 2015. Biochar characteristics and application rates affecting corn growth and properties of soils contrasting in texture and mineralogy. Geoderma 237–238, 105–116. doi:10.1016/j.geoderma.2014.08.010

Cabrera, A., Cox, L., Spokas, K., Hermosín, M.C., Cornejo, J., Koskinen, W.C., 2014. Influence of biochar amendments on the sorption-desorption of aminocyclopyrachlor, bentazone and pyraclostrobin pesticides to an agricultural soil. Sci. Total Environ. 470–471, 438–443. doi:10.1016/j.scitotenv.2013.09.080

Calvelo Pereira, R., Kaal, J., Camps Arbestain, M., Pardo Lorenzo, R., Aitkenhead, W., Hedley, M., Macías, F., Hindmarsh, J., Maciá-Agulló, J.A., 2011. Contribution to characterisation of biochar to estimate the labile fraction of carbon. Org. Geochem. 42, 1331–1342. doi:10.1016/j.orggeochem.2011.09.002

Campbell, B.M., Thornton, P., Zougmoré, R., van Asten, P., Lipper, L., 2014. Sustainable intensification: What is its role in climate smart agriculture? Curr. Opin. Environ. Sustain. 8, 39–43. doi:10.1016/j.cosust.2014.07.002

Cantrell, K.B., Hunt, P.G., Uchimiya, M., Novak, J.M., Ro, K.S., 2012. Impact of pyrolysis temperature and manure source on physicochemical characteristics of biochar. Bioresour. Technol. 107, 419–428. doi:10.1016/j.biortech.2011.11.084

Cao, X., Ma, L., Liang, Y., Gao, B., Harris, W., 2011. Simultaneous immobilization of lead and atrazine in contaminated soils using dairy-manure biochar. Environ. Sci. Technol. 45, 4884–4889. doi:10.1021/es103752u

Chen, B., Yuan, M., 2011. Enhanced sorption of polycyclic aromatic hydrocarbons by soil amended with biochar. J. Soils Sediments 11, 62–71. doi:10.1007/s11368-010-0266-7

Chiang, H.L., Lin, K.H., Lai, N., Shieh, Z.X., 2014. Element and PAH constituents in the residues and liquid oil from biosludge pyrolysis in an electrical thermal furnace. Sci. Total Environ. 481, 533–541. doi:10.1016/j.scitotenv.2014.02.083

Chiang, Y., Chiang, P., Chang, P.E., 2001. Effects of Surface Characterisitics of Activated Carbons on VOC adsorption. J. Environ. Sci. 54–62.

Cole, D.P., Smith, E.A., Lee, Y.J., 2012. High-resolution mass spectrometric characterization of molecules on biochar from pyrolysis and gasification of switchgrass. Energy Fuels 26, 3803–3809. doi:dx.doi.org/10.1021/ef300356u

Conesa, J.A., Font, R., Fullana, A., Martin-Gullon, I., Aracil, I., Galvez, A., Molto, J., Gomez-Rico, M.F., 2009. Comparison between emissions from the pyrolysis and combustion of different wastes. J. Anal. Appl. Pyrolysis 84, 95–102. doi:10.1016/j.jaap.2008.11.022

Connor, M., 2008. Improving charcoal kiln performance - do fundamental studies have a role?, in: Progress in Thermochemical Biomass Conversion. Blackwell Science Ltd, pp. 1603–1618.

Cordella, M., Torri, C., Adamiano, A., Fabbri, D., Barontini, F., Cozzani, V., 2012. Bio-oils from biomass slow pyrolysis: a chemical and toxicological screening. J. Hazard. Mater. 231–232, 26–35. doi:10.1016/j.jhazmat.2012.06.030

Cornelissen, G., Martinsen, V., Shitumbanuma, V., Alling, V., Breedveld, G., Rutherford, D., Sparrevik, M., Hale, S., Obia, A., Mulder, J., 2013. Biochar effect on maize yield and soil characteristics in five conservation farming sites in zambia. Agronomy (Basel, Switz.) 3, 256–274. doi:10.3390/agronomy3020256

Creaser, C.S., Wood, M.D., Alcock, R., Copplestone, D., Crook, P.J., 2007. UK Soil and Herbage Pollutant Survey - UKSHS Report No. 8. UK Environment Agency.

Crombie, K., Mašek, O., 2014. Investigating the potential for a self-sustaining slow pyrolysis system under varying operating conditions. Bioresour. Technol. 162, 148–156. doi:10.1016/j.biortech.2014.03.134

Crombie, K., Mašek, O., 2015. Pyrolysis biochar systems, balance between bioenergy and carbon sequestration. GCB Bioenergy 7, 349–361. doi:10.1111/gcbb.12137

Crombie, K., Mašek, O., Cross, A., Sohi, S., 2014. Biochar - synergies and trade-offs between soil enhancing properties and C sequestration potential. GCB Bioenergy 1–15. doi:10.1111/gcbb.12213

Crombie, K., Mašek, O., Sohi, S.P., Brownsort, P., Cross, A., 2013. The effect of pyrolysis conditions on biochar stability as determined by three methods. GCB Bioenergy 5, 122–131. doi:10.1111/gcbb.12030

Cross, A., Sohi, S.P., 2013. A method for screening the relative long-term stability of biochar. GCB Bioenergy 5, 215–220. doi:10.1111/gcbb.12035

Cuypers, F., Helsen, L., 2011. Pyrolysis of chromated copper arsenate (CCA) treated wood waste at elevated pressure: Influence of particle size, heating rate, residence time, temperature and pressure. J. Anal. Appl. Pyrolysis 92, 111–122. doi:10.1016/j.jaap.2011.05.002

Dai, Q., Jiang, X., Jiang, Y., Jin, Y., Wang, F., Chi, Y., Yan, J., 2014a. Formation of PAHs during the pyrolysis of dry sewage sludge. Fuel 130, 92–99. doi:10.1016/j.fuel.2014.04.017

Dai, Q., Jiang, X., Jiang, Y., Jin, Y., Wang, F., Chi, Y., Yan, J., Xu, A., 2014b. Temperature influence and distribution in three phases of PAHs in wet sewage sludge pyrolysis using conventional and microwave heating. Energy and Fuels 28, 3317–3325. doi:10.1021/ef5003638

Das, O., Sarmah, A.K., 2015. The love-hate relationship of pyrolysis biochar and water: A perspective. Sci. Total Environ. 512–513, 682–685. doi:10.1016/j.scitotenv.2015.01.061

Davis, R.D., Beckett, P.H.T., Wollan, E., 1978. Critical levels of twenty potentially toxic elements in young spring barley plants. Plant Soil 49, 395–408.

Deal, C., Brewer, C.E., Brown, R.C., Okure, M.A.E., Amoding, A., 2012. Comparison of kiln-derived and gasifier-derived biochars as soil amendments in the humid tropics. Biomass and Bioenergy 37, 161–168. doi:10.1016/j.biombioe.2011.12.017

de la Rosa, J.M., Paneque, M., Miller, A.Z., Knicker, H., 2014. Relating physical and chemical properties of four different biochars and their application rate to biomass production of Lolium perenne on a Calcic Cambisol during a pot experiment of 79 days. Sci. Total Environ. 499, 175–184. doi:10.1016/j.scitotenv.2014.08.025

Deenik, J.L., McClellan, T., Uehara, G., Antal, M.J., Campbell, S., 2010. Charcoal volatile matter content influences plant growth and soil nitrogen transformations. Soil Sci. Soc. Am. J. 74, 1259–1270. doi:10.2136/sssaj2009.0115

Delage, F., Pascaline, P., Le Cloirec, P., 1999. Effect of moisture on warming of activated carbon bed during VOC adsorption. J. Environ. Sci. 1160–1167.

del Río, J.C., Rencoret, J., Prinsen, P., Martinéz, Á.T., Ralph, J., Gutiérrez, A., 2012. Structural characterization of wheat straw lignin as revealed by analytical pyrolysis, 2D-NMR, and reductive cleavage methods. J. Agric. Food Chem. 60, 5922–5935. doi:dx.doi.org/10.1021/jf301002n

Delhaize, E., Ryan, P.R., 1995. Aluminum toxicity and tolerance in plants. Plant Physiol. 107, 315–321. doi:107/2/315

Delistraty, D., 1997. Toxic equivalency factor approach for risk assessment of polycyclic aromatic hydrocarbons. Toxicol. Environ. Chem. 64, 81–108.

Denyes, M.J., Langlois, V.S., Rutter, A., Zeeb, B. a, 2012. The use of biochar to reduce soil PCB bioavailability to Cucurbita pepo and Eisenia fetida. Sci. Total Environ. 437, 76–82. doi:10.1016/j.scitotenv.2012.07.081

Department for Environment Food and Rural Development, 2011. Anaerobic digestion strategy and action plan.

Department for Environment Food and Rural Development, 2015. Digest of waste

and resource statistics – 2015 Edition.

Devi, P., Saroha, A.K., 2015. Effect of pyrolysis temperature on polycyclic aromatic hydrocarbons toxicity and sorption behaviour of biochars prepared by pyrolysis of paper mill effluent treatment plant sludge. Bioresour. Technol. 192, 312–320. doi:10.1016/j.biortech.2015.05.084

Di Lonardo, S., Vaccari, F.P., Baronti, S., Capuana, M., Bacci, L., Sabatini, F., Lambardi, M., Miglietta, F., 2013. Biochar successfully replaces activated charcoal for in vitro culture of two white poplar clones reducing ethylene concentration. Plant Growth Regul. 69, 43–50. doi:10.1007/s10725-012-9745-8

Ding, Y., Liu, Y., Liu, S., Li, Z., Tan, X., Huang, X., Zeng, G., Zhou, Y., Zheng, B., Cai, X., 2016. Competitive removal of Cd(II) and Pb(II) by biochars produced from water hyacinths: performance and mechanism. RSC Adv. 6, 5223–5232. doi:10.1039/C5RA26248H

Directive 2004/42/CE of the European parliament and of the council, 2004. on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain paints and varnishes and vehicle refinishing products and amending Directive 1999/13/EC. Off. J. Eur. Union L143, 87–96.

Domene, X., Enders, A., Hanley, K., Lehmann, J., 2015. Ecotoxicological characterization of biochars: Role of feedstock and pyrolysis temperature. Sci. Total Environ. 512–513, 552–561. doi:10.1016/j.scitotenv.2014.12.035

Downie, A., Munroe, P., Cowie, A., Van Zwieten, L., Lau, D.M.S., 2012. Biochar as a geoengineering climate solution: hazard identification and risk management. Crit. Rev. Environ. Sci. Technol. 42, 225–250. doi:10.1080/10643389.2010.507980

Dreisbach, R.R., Shrader, S.A., 1949. Vapor pressure–temperature data on some organic compounds. Ind. Eng. Chem. 41, 2879–2880. doi:10.1021/ie50480a054

EBC, 2012a. European Biochar Certificate: Guidelines for a sustainable production of biochar, v. 6.1, June 19th 2015. doi:10.13140/RG.2.1.4658.7043

EBC, 2012b. European Biochar Certificate: Guidelines for biochar production, v. 4.2, June 13th 2012. doi:0.13140/RG.2.1.4658.7043

Eibisch, N., Durner, W., Bechtold, M., Fuß, R., Mikutta, R., Woche, S.K., Helfrich, M., 2015. Does water repellency of pyrochars and hydrochars counter their positive effects on soil hydraulic properties? Geoderma 245–246, 31–39. doi:10.1016/j.geoderma.2015.01.009

Elad, Y., Cytryn, E., Harel, Y.M., Lew, B., Graber, E.R., 2011. The biochar effect: plant resistance to biotic stresses. Phytopathol. Mediterr. 50, 335–349.

Elad, Y., David, D.R., Harel, Y.M., Borenshtein, M., Kalifa, H. Ben, Silber, A., Graber, E.R., 2010. Induction of systemic resistance in plants by biochar, a soil-applied carbon sequestering agent. Phytopathology 100, 913–21. doi:10.1094/PHYTO-100-9-0913

El-Darier, S.M., Youssef, R.S., 2000. Effect of soil type, salinity, and

allelochemicals on germination and seedling growth of a medicinal plant Lepidium sativum L. Ann. Appl. Biol. 136, 273–279. doi:10.1111/j.1744-7348.2000.tb00035.x

Elliott, D.C., 1986. Analysis and comparison of biomass pyrolysis/gasification condensates - final report prepared for the Biofuels and Municipal Waste Technology Division, US Department of Energy. Richland, Washington.

Elliott, J., Firbank, L.G., Drake, B., Cao, Y., Gooday, R., 2013. Land use policy group: Exploring the concept of sustainable intensification.

Enders, A., Hanley, K., Whitman, T., Joseph, S., Lehmann, J., 2012. Characterization of biochars to evaluate recalcitrance and agronomic performance. Bioresour. Technol. 114, 644–653. doi:10.1016/j.biortech.2012.03.022

Enders, A., Lehmann, J., 2012. Comparison of wet-digestion and dry-ashing methods for total elemental analysis of biochar. Commun. Soil Sci. Plant Anal. 43, 1042–1052. doi:10.1080/00103624.2012.656167

Environment Agency, 2009. Science Report SC050021/Dioxins SGV: Soil guideline values for dioxins, furans and dioxin-like PCBs in soil. doi:SCHO0909BQYQ-E-P

Environmental Protection Agency, 1982. Federal Register / Vol . 47 , No . 224 / Friday , November 19 , 1982 / Rules and Regulations. Fed. Regist. 47, 52290–52309.

Eom, I.C., Rast, C., Veber, A.M., Vasseur, P., 2007. Ecotoxicity of a polycyclic aromatic hydrocarbon (PAH)-contaminated soil. Ecotoxicol. Environ. Saf. 67, 190–205. doi:10.1016/j.ecoenv.2006.12.020

EU Commission Directive 2000/39/EC, 2000. establishing a first list of indicative occupational exposure limit values in implementation of Council Directive 98/24/EC on the protection of the health and safety of workers from the risks related to chemical agents at work. Off. J. Eur. Communities L142, 47–50. doi:http://eur-lex.europa.eu/pri/en/oj/dat/2003/l_285/l_28520031101en00330037.pdf

EU Commission Directive 2006/15/EC, 2006. establishing a second list of indicative occupational exposure limit values in implementation of Council Directive 98/24/EC and amending Directives 91/322/EEC and 2000/39/EC. Off. J. Eur. Union L 38, 36–39.

EU Commission Directive 2009/161/EU, 2009. establishing a third list of indicative occupational exposure limit values in implementation of Council Directive 98/24/EC and amending Commission Directive 2000/39/EC. Off. J. Eur. Union L338, 87–89.

EU Commission Directive 91/322/ECC, 1991. on establishing indicative limit values by implementing Council Directive 80/1107/EEC on the protection of workers from the risks related to exposure to chemical, physical and biological agents at work. Off. J. Eur. Communities L 177, 22. doi:2004R0726 - v.7 of 05.06.2013

EU Commission Recommendation, 2005. on the further investigation into the levels of polycyclic aromatic hydrocarbons in certain foods (2005/108/EC). Off. J. Eur. Union 34, 43–45.

EU Council Directive 86/278/EEC, 1986. on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture. Off. J. Eur. Communities 4.7.86, 6–12.

EU Council Regulation 2092/91/ECC, 1991. on organic production of agricultural products and indications referring thereto on agricultural products and foodstuffs.

European Commission Scientific Committee on Food, 2002. Opinion on the scientific committee on food on the risk to human health of polycyclic aromatic hydrocarbons in food.

European Standard, 2011. BS EN 16086-2:2011: Soil improvers and growing media - Determination of plant response - Part 2: Petri dish test using cress.

European Union Joint Research Centre, 2013. Report No 29: Harmonisation framework for health based evaluation of indoor emissions from construction products in the European Union using the EU-LCI concept.

Evangelou, M.W.H., Brem, A., Ugolini, F., Abiven, S., Schulin, R., 2014. Soil application of biochar produced from biomass grown on trace element contaminated land. J. Environ. Manage. 146, 100–106. doi:10.1016/j.jenvman.2014.07.046

Evangelou, M.W.H., Conesa, H.M., Robinson, B.H., Schulin, R., 2012. Biomass production on trace element–contaminated land: a review. Environ. Eng. Sci. 29, 823–839. doi:10.1089/ees.2011.0428

Fabbri, D., Rombolà, A.G., Torri, C., Spokas, K.A., 2013. Determination of polycyclic aromatic hydrocarbons in biochar and biochar amended soil. J. Anal. Appl. Pyrolysis 103, 60–67. doi:10.1016/j.jaap.2012.10.003

Fagernäs, L., Kuoppala, E., Simell, P., 2012a. Polycyclic aromatic hydrocarbons in birch wood slow pyrolysis products. Energy Fuels 26, 6960–6970. doi:10.1021/ef2018836

Fagernäs, L., Kuoppala, E., Tiilikkala, K., Oasmaa, A., 2012b. Chemical composition of birch wood slow pyrolysis products. Energy Fuels 26, 1275–1283. doi:10.1021/ef2018836

Fang, Y., Singh, B., Singh, B.P., Krull, E., 2014. Biochar carbon stability in four contrasting soils. Eur. J. Soil Sci. 65, 60–71. doi:10.1111/ejss.12094

Farrell, M., Rangott, G., Krull, E., 2013. Difficulties in using soil-based methods to assess plant availability of potentially toxic elements in biochars and their feedstocks. J. Hazard. Mater. 250–251, 29–36. doi:10.1016/j.jhazmat.2013.01.073

Fellet, G., Marchiol, L., Perosa, D., Zerbi, G., 2007. The application of phytoremediation technology in a soil contaminated by pyrite cinders. Ecol.

Eng. 31, 207–214. doi:10.1016/j.ecoleng.2007.06.011

Fellet, G., Marmiroli, M., Marchiol, L., 2014. Elements uptake by metal accumulator species grown on mine tailings amended with three types of biochar. Sci. Total Environ. 468–469, 598–608. doi:10.1016/j.scitotenv.2013.08.072

Feng, L., Wang, L., Zhao, Y., Song, B., 1996. Effects of substituted anilines and phenols on root elongation of cabbage seed. Chemosphere 32, 1575–1583. doi:10.1016/0045-6535(96)00067-7

Foley, J.A., Ramankutty, N., Brauman, K.A., Cassidy, E.S., Gerber, J.S., Johnston, M., Mueller, N.D., Connell, C.O., Ray, D.K., West, P.C., Balzer, C., Bennett, E.M., Sheehan, J., Siebert, S., Carpenter, S.R., Hill, J., Monfreda, C., Polasky, S., Rockstro, J., Tilman, D., Zaks, D.P.M., 2011. Solutions for a cultivated planet. Nature 478, 337–342. doi:10.1038/nature10452

Font, R., Aracil, I., Fullana, A., Martín-Gullón, I., Conesa, J.A., 2003. Semivolatile compounds in pyrolysis of polyethylene. J. Anal. Appl. Pyrolysis 68–69, 599–611. doi:10.1016/S0165-2370(03)00038-X

Freddo, A., Cai, C., Reid, B.J., 2012. Environmental contextualisation of potential toxic elements and polycyclic aromatic hydrocarbons in biochar. Environ. Pollut. (Oxford, U. K.) 171, 18–24. doi:10.1016/j.envpol.2012.07.009

Fu, P., Yi, W., Bai, X., Li, Z., Hu, S., Xiang, J., 2011. Effect of temperature on gas composition and char structural features of pyrolyzed agricultural residues. Bioresour. Technol. 102, 8211–8219. doi:10.1016/j.biortech.2011.05.083

Garcia-Perez, M., Chaala, A., Pakdel, H., Kretschmer, D., Roy, C., 2007. Characterization of bio-oils in chemical families. Biomass and Bioenergy 31, 222–242. doi:10.1016/j.biombioe.2006.02.006

Gaskin, J.W., Steiner, C., Harris, K., Das, K.C., Bibens, B., 2008. Effect of low-temperature pyrolysis conditions on biochar for agricultural use. Trans. Am. Soc. Agric. Biol. Eng. 51, 2061–2069.

Gell, K., van Groenigen, J., Cayuela, M.L., 2011. Residues of bioenergy production chains as soil amendments: immediate and temporal phytotoxicity. J. Hazard. Mater. 186, 2017–2025. doi:10.1016/j.jhazmat.2010.12.105

German Biowaste Ordinance, 1998. Verordnung über die Verwertung von Bioabfällen auf landwirtschaftlich, forstwirtschaftlich und gärtnerisch genutzten Böden (Bioabfallverordnung - BioAbfV).

German Federal Soil Protection and Contaminated Sites Ordinance, 1999. Bundes-Bodenschutz- und Altlastenverordnung (BBodSchV).

Glaser, B., Haumaier, L., Guggenberger, G., Zech, W., 2001. The “Terra Preta” phenomenon: a model for sustainable agriculture in the humid tropics. Naturwissenschaften 88, 37–41. doi:10.1007/s001140000193

Glaser, B., Lehmann, J., Zech, W., 2002. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal - A review. Biol. Fertil. Soils 35, 219–230. doi:10.1007/s00374-002-0466-4

Gomez-Eyles, J.L., Sizmur, T., Collins, C.D., Hodson, M.E., 2011. Effects of biochar and the earthworm Eisenia fetida on the bioavailability of polycyclic aromatic hydrocarbons and potentially toxic elements. Environ. Pollut. (Oxford, U. K.) 159, 616–622. doi:10.1016/j.envpol.2010.09.037

Goss, S.L., Lemons, K.A., Kerstetter, J.E., Bogner, R.H., 2007. Determination of calcium salt solubility with changes in pH and PCO2, simulating varying gastrointestinal environments. J. Pharm. Pharmacol. 59, 1485–1492. doi:10.1211/jpp.59.11.0004

Graber, E.R., Tsechansky, L., Gerstl, Z., Lew, B., 2012. High surface area biochar negatively impacts herbicide efficacy. Plant Soil 353, 95–106. doi:10.1007/s11104-011-1012-7

Granatstein, D., Collins, H., Garcia-Perez, M., Yoder, J., 2009. Use of biochar from the pyrolysis of waste organic material as a soil amendment, Final project report. Center for Sustaining Agriculture and Natural Resources, Washington State University, Wenatchee, WA.

Gray, M., Johnson, M.G., Dragila, M.I., Kleber, M., 2014. Water uptake in biochars: The roles of porosity and hydrophobicity. Biomass and Bioenergy 61, 196–205. doi:10.1016/j.biombioe.2013.12.010

Gryschko, R., Kuhnle, R., Terytze, K., Breuer, J., Stahr, K., 2004. Soil extraction of readily soluble heavy metals and As with 1 M NH4NO3-solution - Evaluation of DIN 19730. J. Soils Sediments 2004, 1–6. doi:10.1065/jss2004.10.119

Gu, Z., Wu, M., Li, K., Ning, P., 2013. Variation of heavy metal speciation during the pyrolysis of sediment collected from the Dianchi Lake, China. Arab. J. Chem. doi:10.1016/j.arabjc.2013.07.053

Gundale, M.J., DeLuca, T.H., 2006. Charcoal effects on soil solution chemistry and growth of Koeleria macrantha in the ponderosa pine/Douglas-fir ecosystem. Biol. Fertil. Soils 43, 303–311. doi:10.1007/s00374-006-0106-5

Gunes, A., Inal, A., Taskin, M.B., Sahin, O., Kaya, E.C., Atakol, A., 2014. Effect of phosphorus-enriched biochar and poultry manure on growth and mineral composition of lettuce (Lactuca sativa L. cv.) grown in alkaline soil. Soil Use Manag. 30, 182–188. doi:10.1111/sum.12114

Gupta, U.C., Gupta, S.C., 1998. Trace element toxicity relationships to crop production and livestock and human health: implications for management. Commun. Soil Sci. Plant Anal. 29, 1491–1522. doi:10.1080/00103629809370045

Haas, T.J., Nimlos, M.R., Donohoe, B.S., 2009. Real-time and post-reaction microscopic structural analysis of biomass undergoing pyrolysis. Energy and Fuels 23, 3810–3817. doi:10.1021/ef900201b

Hajaligol, M.R., Waymack, B., Kellogg, D., 2001. Low temperature formation of aromatic hydrocarbon from pyrolysis of cellulosic materials. Fuel 80, 1799–1807.

Hajarnavis, M.R., 2000. Studies of trace metals in acidic fly ash. J. Sci. Ind. Res. (India). 381–388.

Hale, S.E., Lehmann, J., Rutherford, D., Zimmerman, A.R., Bachmann, R.T., Shitumbanuma, V., O'Toole, A., Sundqvist, K.L., Arp, H.P.H., Cornelissen, G., 2012. Quantifying the total and bioavailable polycyclic aromatic hydrocarbons and dioxins in biochars. Environ. Sci. Technol. 46, 2830–2838. doi:10.1021/es203984k

Hammond, J., Shackley, S., Prendergast-Miller, M., Cook, J., Buckingham, S., Pappa, V.A., 2013. Biochar field testing in the UK: outcomes and implications for use. Carbon Manag. 4, 159–170. doi:10.4155/cmt.13.3

Harvey, O.R., Herbert, B.E., Rhue, R.D., Kuo, L.J., 2011. Metal interactions at the biochar-water interface: Energetics and structure-sorption relationships elucidated by flow adsorption microcalorimetry. Environ. Sci. Technol. 45, 5550–5556. doi:10.1021/es104401h

Hawkesford, M., Horst, W., Kichey, T., Lambers, H., Schjoerring, J., Møller, I.S., White, P., 2011. Functions of macronutrients, Marschner's Mineral Nutrition of Higher Plants: Third Edition. Elsevier Ltd. doi:10.1016/B978-0-12-384905-2.00006-6

Helsen, L., Van den Bulck, E., Van den Broeck, K., Vandecasteele, C., 1997. Low-temperature pyrolysis of CCA-treated wood waste: Chemical determination and statistical analysis of metal input and output; mass balances. Waste Manage. 17, 79–86. doi:10.1016/S0956-053X(97)00040-8

Henig-Sever, N., Eshel, A., Ne'eman, G., 1996. pH and osmotic potential of pine ash as post-fire germination inhibitors. Physiol. Plant. 96, 71–76. doi:10.1034/j.1399-3054.1996.960111.x

Henner, P., Schiavon, M., Druelle, V., Lichtfouse, E., 1999. Phytotoxicity of ancient gaswork soils. Effect of polycyclic aromatic hydrocarbons (PAHs) on plant germination. Org. Geochem. 30, 963–969. doi:10.1016/S0146-6380(99)00080-7

Hilber, I., Blum, F., Leifeld, J., Schmidt, H.-P., Bucheli, T.D., 2012. Quantitative determination of PAHs in biochar: a prerequisite to ensure its quality and safe application. J. Agric. Food Chem. 60, 3042–3050. doi:10.1021/jf205278v

Hildebrand, E.E., 1979. Erfassung und Charakterisierung von Polyphenolen als potentiellen Wuchshemmstoffen in kompostierten Siedlungsabfällen. Mitteilung der Dtsch. Bodenkundlichen Gesellschaft 29, 609–622.

Hossain, M.K., Strezov Vladimir, V., Chan, K.Y., Ziolkowski, A., Nelson, P.F., 2011. Influence of pyrolysis temperature on production and nutrient properties of wastewater sludge biochar. J. Environ. Manage. 92, 223–228. doi:10.1016/j.jenvman.2010.09.008

Houben, D., Evrard, L., Sonnet, P., 2013. Mobility, bioavailability and pH-dependent leaching of cadmium, zinc and lead in a contaminated soil amended with biochar. Chemosphere 92, 1450–7. doi:10.1016/j.chemosphere.2013.03.055

Huang, W., Chen, B., 2010. Interaction mechanisms of organic contaminants with burned straw ash charcoal. J. Environ. Sci. (Beijing, China) 22, 1586–1594. doi:10.1016/S1001-0742(09)60293-X

Huang, Y., Kudo, S., Mašek, O., Norinaga, K., Hayashi, J.I., 2013. Simultaneous maximization of the char yield and volatility of oil from biomass pyrolysis. Energy and Fuels 27, 247–254. doi:10.1021/ef301366x

Hwang, I.H., Matsuto, T., 2008. Evaluation of carbonization as a thermal pretreatment method for landfilling by column leaching tests. Waste Manage. 28, 3–14. doi:10.1016/j.wasman.2006.11.007

International Biochar Initiative, 2011. Standardized product definition and product testing guidelines for biochar that is used in soil, v. 1.1, April 11th 2013.

International Energy Agency, 2006. IEA bioenergy annual report 2006. doi:10.1111/j.1365-2338.2007.01172.x

Inyang, M., Gao, B., Pullammanappallil, P., Ding, W., Zimmerman, A.R., 2010. Biochar from anaerobically digested sugarcane bagasse. Bioresour. Technol. 101, 8868–8872. doi:10.1016/j.biortech.2010.06.088

Ippolito, J.A., Spokas, K.A., Novak, J.M., Lentz, R.D., Cantrell, K.B., 2015. Chapter 7: Biochar elemental composition and factors influencing nutrient retention, in: Biochar for Environmental Management: Science and Technology and Implementation, Second Edition. Earthscan Ltd., London., pp. 139–163.

Jamieson, T., Sager, E., Gu??guen, C., 2014. Characterization of biochar-derived dissolved organic matter using UV-visible absorption and excitation-emission fluorescence spectroscopies. Chemosphere 103, 197–204. doi:10.1016/j.chemosphere.2013.11.066

Jeffery, S., Abalos, D., Spokas, K., Verheijen, F.G.A., 2015a. Chapter 12: Biochar effects on crop yield, in: Biochar for Environmental Management: Science and Technology and Implementation, Second Edition. Earthscan Ltd., London., pp. 207–226.

Jeffery, S., Meinders, M.B.J., Stoof, C.R., Bezemer, T.M., van de Voorde, T.F.J., Mommer, L., van Groenigen, J.W., 2015b. Biochar application does not improve the soil hydrological function of a sandy soil. Geoderma 251–252, 47–54. doi:10.1016/j.geoderma.2015.03.022

Jeffery, S., Verheijen, F.G.A., van der Velde, M., Bastos, A.C., 2011. A quantitative review of the effects of biochar application to soils on crop productivity using meta-analysis. Agric., Ecosyst. Environ. 144, 175–187. doi:10.1016/j.agee.2011.08.015

Jhamnani, B., Singh, S.K., 2009. Groundwater Contamination due to Bhalaswa Landfill Site in New Delhi. Int. J. Civ. Environ. Eng. 1, 121–125.

Jindo, K., Mizumoto, H., Sawada, Y., Sonoki, T., 2014. Physical and chemical characterization of biochars derived from different agricultural residues. Biogeosciences 11, 6613–6621. doi:10.5194/bg-11-6613-2014

Jones, D.L., Edwards-Jones, G., Murphy, D.V., 2011. Biochar mediated alterations in herbicide breakdown and leaching in soil. Soil Biol. Biochem. 43, 804–813. doi:10.1016/j.soilbio.2010.12.015

Jones, D.L., Quilliam, R.S., 2014. Metal contaminated biochar and wood ash negatively affect plant growth and soil quality after land application. J. Hazard. Mater. 276, 362–370. doi:10.1016/j.jhazmat.2014.05.053

Jones, K.C., Stratford, J.A., Tidridge, P., Waterhouse, K.S., 1989. Polynuclear aromatic hydrocarbons in an agricultural soil: long-term changes in profile distribution. Environ. Pollut. (Oxford, U. K.) 56, 337–351.

Jones-Held, S., VanDoren, M., Lockwood, T., 1996. Brassinolide Application to Lepidium sativum Seeds and the Effects on Seedling Growth. J. Plant Growth Regul. 22, 63–67.

Jonker, M.T.O., Hawthorne, S.B., Koelmans, A. a, 2005. Extremely slowly desorbing polycyclic aromatic hydrocarbons from soot and soot-like materials: evidence by supercritical fluid extraction. Environ. Sci. Technol. 39, 7889–95.

Kabata-Pendias, A., 2011. Trace elements in soils and plants, CRC Press. doi:10.1201/b10158-25

Kaiser, B.N., 2005. The Role of Molybdenum in Agricultural Plant Production. Ann. Bot. 96, 745–754. doi:10.1093/aob/mci226

Kaminsky, W., Schlesselmann, B., Simon, C.M., 1996. Thermal degradation of mixed plastic waste to aromatics and gas. Polym. Degrad. Stab. 53, 189–197.

Kammann, C., Ratering, S., Eckhard, C., Muller, C., 2012. Biochar and Hydrochar Effects on Greenhouse Gas (Carbon Dioxide, Nitrous Oxide, and Methane) Fluxes from Soils. J. Environ. Qual. 41, 1052–1066. doi:10.2134/jeq2011.0132

Kammann, C.I., Linsel, S., Gößling, J.W., Koyro, H.W., 2011. Influence of biochar on drought tolerance of Chenopodium quinoa Willd and on soil-plant relations. Plant Soil 345, 195–210. doi:10.1007/s11104-011-0771-5

Kan, T., Grierson, S., De Nys, R., Strezov, V., 2014. Comparative assessment of the thermochemical conversion of freshwater and marine micro- and macroalgae. Energy and Fuels 28, 104–114. doi:10.1021/ef401568s

Karer, J., Wawra, A., Zehetner, F., Dunst, G., Wagner, M., Pavel, P., Puschenreiter, M., Friesl-hanl, W., Soja, G., 2015. Effects of Biochars and Compost Mixtures and Inorganic Additives on Immobilisation of Heavy Metals in Contaminated Soils. Water, Air, Soil Pollut. 226, 1–12. doi:10.1007/s11270-015-2584-2

Keeley, S.C., Pizzorno, M., 1986. Charred Wood Stimulated Germination of Two Fire-Following Herbs of the California Chaparral and the Role of Hemicellulose. Am. J. Bot. 73, 1289–1297.

Keiluweit, M., Kleber, M., Sparrow, M.A., Simoneit, B.R.T., Prahl, F.G., 2012. Solvent-extractable polycyclic aromatic hydrocarbons in biochar: influence of pyrolysis temperature and feedstock. Environ. Sci. Technol. 46, 9333–41. doi:10.1021/es302125k

Keiluweit, M., Nico, P.S., Johnson, M.G., 2010. Dynamic Molecular Structure of Plant Biomass-Derived Black Carbon (Biochar). Environ. Sci. Technol. 44, 1247–1253.

Keith, L.H., 1979. Priority pollutants: I - a perspective view. Environ. Sci. Technol. 13, 416–23.

Kern, K.A., Pergo, E.M., Kagami, F.L., Arraes, L.S., Sert, M.A., Ishii-Iwamoto, E.L., 2009. The phytotoxic effect of exogenous ethanol on Euphorbia heterophylla L. Plant Physiol. Biochem. 47, 1095–1101. doi:10.1016/j.plaphy.2009.07.002

Kevresan, S., N, P., M, P., J, K., 2001. Nitrogen and protein metabolism in young pea plants As affected by different concentrations of nickel, cadmium, lead and molybdenum. J. Plant Nutr. 24, 1633–1644. doi:10.1081/PLN-100106026

Khalid, F.N.M., Klarup, D., 2015. The influence of sunlight and oxidative treatment on measured PAH concentrations in biochar. Environ. Sci. Pollut. Res. 22, 12975–12981. doi:10.1007/s11356-015-4469-8

Khanmohammadi, Z., Afyuni, M., Mosaddeghi, M.R., 2015. Effect of pyrolysis temperature on chemical and physical properties of sewage sludge biochar. Waste Manag. Res. 33, 275–283. doi:10.1177/0734242X14565210

Khor, K.H., Lim, K.O., Zainal, Z.A., Pinang, P., Tebal, N., 2009. Characterization of Bio-Oil : A By-Product from Slow Pyrolysis of Oil Palm Empty Fruit Bunches School of Physics , School of Mechanical Engineering , Engineering Campus , 6, 1647–1652.

Kim, J.Y., Kim, T.S., Eom, I.Y., Kang, S.M., Cho, T.S., Choi, I.G., Choi, J.W., 2012. Characterization of pyrolytic products obtained from fast pyrolysis of chromated copper arsenate (CCA)- and alkaline copper quaternary compounds (ACQ)-treated wood biomasses. J. Hazard. Mater. 227–228, 445–452. doi:10.1016/j.jhazmat.2012.05.052

Kim, K., 2015. Examination of three different organic waste biochars as soil amendment for metal-contaminated agricultural soils. Water, Air, Soil Pollut. 226, 1–11. doi:10.1007/s11270-015-2556-6

Kim, M.S., Min, H.G., Koo, N., Park, J., Lee, S.H., Bak, G.I., Kim, J.G., 2014. The effectiveness of spent coffee grounds and its biochar on the amelioration of heavy metals-contaminated water and soil using chemical and biological assessments. J. Environ. Manage. 146, 124–130. doi:10.1016/j.jenvman.2014.07.001

Kim, R.-Y., Yoon, J.-K., Kim, T.-S., Yang, J.E., Owens, G., Kim, K.-R., 2015. Bioavailability of heavy metals in soils: definitions and practical implementation—a critical review. Environ. Geochem. Health 37, 1041–1061. doi:10.1007/s10653-015-9695-y

Kinney, T.J., Masiello, C. a., Dugan, B., Hockaday, W.C., Dean, M.R., Zygourakis, K., Barnes, R.T., 2012. Hydrologic properties of biochars produced at different temperatures. Biomass and Bioenergy 41, 34–43.

doi:10.1016/j.biombioe.2012.01.033

Kirkby, E., 2011. Introduction, definition and classification of nutrients, Marschner's Mineral Nutrition of Higher Plants: Third Edition. Elsevier Ltd. doi:10.1016/B978-0-12-384905-2.00001-7

Kistler, R.C., Widmer, F., Brunner, P.H., 1987. Behavior of chromium, nickel, copper, zinc, cadmium, mercury, and lead during the pyrolysis of sewage sludge. Environ. Sci. Technol. 21, 704–708. doi:10.1021/es00161a012

Kloss, S., Zehetner, F., Dellantonio, A., Hamid, R., Ottner, F., Liedtke, V., Schwanninger, M., Gerzabek, M.H., Soja, G., 2012. Characterization of slow pyrolysis biochars: effects of feedstocks and pyrolysis temperature on biochar properties. J. Environ. Qual. 41, 990–1000. doi:10.2134/jeq2011.0070

Kloss, S., Zehetner, F., Oburger, E., Buecker, J., Kitzler, B., Wenzel, W.W., Wimmer, B., Soja, G., 2014a. Trace element concentrations in leachates and mustard plant tissue (Sinapis alba L.) after biochar application to temperate soils. Sci. Total Environ. 481, 498–508. doi:10.1016/j.scitotenv.2014.02.093

Kloss, S., Zehetner, F., Wimmer, B., Buecker, J., Rempt, F., Soja, G., 2014b. Biochar application to temperate soils: Effects on soil fertility and crop growth under greenhouse conditions. J. Plant Nutr. Soil Sci. 177, 3–15. doi:10.1002/jpln.201200282

Kołtowski, M., Oleszczuk, P., 2015. Toxicity of biochars after polycyclic aromatic hydrocarbons removal by thermal treatment. Ecol. Eng. 75, 79–85. doi:10.1016/j.ecoleng.2014.11.004

Kookana, R.S., Sarmah, A.K., Van Zwieten, L., Krull, E., Singh, B., 2011. Chapter Three: Biochar application to soil: agronomic and environmental benefits and unintended consequenes, in: Advances in Agronomy, Volume 112. Earthscan Ltd., London., pp. 103–135.

Kopittke, P.M., Blamey, F.P.C., Asher, C.J., Menzies, N.W., 2010. Trace metal phytotoxicity in solution culture: A review. J. Exp. Bot. 61, 945–954. doi:10.1093/jxb/erp385

Koppolu, L., Agblevor, F.A., Clements, L.D., 2003. Pyrolysis as a technique for separating heavy metals from hyperaccumulators. Part II: Lab-scale pyrolysis of synthetic hyperaccumulator biomass. Biomass and Bioenergy 25, 651–663. doi:10.1016/S0961-9534(03)00057-6

Krzesińska, M., Pilawa, B., Pusz, S., Ng, J., 2006. Physical characteristics of carbon materials derived from pyrolysed vascular plants. Biomass and Bioenergy 30, 166–176. doi:10.1016/j.biombioe.2005.11.009

Kuppusamy, S., Thavamani, P., Megharaj, M., Venkateswarlu, K., Naidu, R., 2016. Agronomic and remedial benefits and risks of applying biochar to soil: Current knowledge and future research directions. Environ. Int. 87, 1–12. doi:10.1016/j.envint.2015.10.018

Kupryianchyk, D., Hale, S., Zimmerman, A.R., Harvey, O., Rutherford, D., Abiven,

S., Knicker, H., Schmidt, H.P., Rumpel, C., Cornelissen, G., 2016. Sorption of hydrophobic organic compounds to a diverse suite of carbonaceous materials with emphasis on biochar. Chemosphere 144, 879–887. doi:10.1016/j.chemosphere.2015.09.055

Kuśmierz, M., Oleszczuk, P., Kraska, P., Pałys, E., Andruszczak, S., 2016. Persistence of polycyclic aromatic hydrocarbons (PAHs) in biochar-amended soil. Chemosphere 146, 272–279. doi:10.1016/j.chemosphere.2015.12.010

Kuzyakov, Y., Bogomolova, I., Glaser, B., 2014. Biochar stability in soil: Decomposition during eight years and transformation as assessed by compound-specific 14C analysis. Soil Biol. Biochem. 70, 229–236. doi:10.1016/j.soilbio.2013.12.021

Kwapinski, W., Byrne, C.M.P., Kryachko, E., Wolfram, P., Adley, C., Leahy, J.J., Novotny, E.H., Hayes, M.H.B., 2010. Biochar from biomass and waste. Waste and Biomass Valorization 1, 177–189. doi:10.1007/s12649-010-9024-8

Kwon, S.M., Kim, N.H., Cha, D.S., 2009. An investigation on the transition characteristics of the wood cell walls during carbonization. Wood Sci. Technol. 43, 487–498. doi:10.1007/s00226-009-0245-6

Laird, D., Fleming, P., Wang, B., Horton, R., Karlen, D., 2010. Biochar impact on nutrient leaching from a Midwestern agricultural soil. Geoderma 158, 436–442. doi:10.1016/j.geoderma.2010.05.012

Lattao, C., Cao, X., Mao, J., Schmidt-Rohr, K., Pignatello, J.J., 2014. Influence of molecular structure and adsorbent properties on sorption of organic compounds to a temperature series of wood chars. Environ. Sci. Technol. 48, 4790–4798. doi:10.1021/es405096q

LeCroy, C., Masiello, C.A., Rudgers, J.A., Hockaday, W.C., Silberg, J.J., 2013. Nitrogen, biochar, and mycorrhizae: Alteration of the symbiosis and oxidation of the char surface. Soil Biol. Biochem. 58, 248–254. doi:10.1016/j.soilbio.2012.11.023

Lehmann, J., Abiven, S., Kleber, M., Pan, G., Singh, B., Sohi, S., Zimmerman, A., 2015. Chapter 10: Persistence of biochar in soil, in: Biochar for Environmental Management: Science and Technology and Implementation, Second Edition. Earthscan Ltd., London., pp. 169–182.

Lehmann, J., Joseph, S., 2009. Biochar for Environmental Management: Science and Technology, first Edition. Earthscan Ltd., London.

Lehmann, J., Joseph, S., 2015a. Biochar for Environmental Management: Science and Technology and Implementation, second Edition. Earthscan Ltd., London.

Lehmann, J., Joseph, S., 2015b. Chapter 1: Biochar for environmental managment: an introduction, in: Biochar for Environmental Management: Science and Technology and Implementation, Second Edition. Earthscan Ltd., London., pp. 1–13.

Lehmann, J., Pereira da Silva, J., Steiner, C., Nehls, T., Zech, W., Glaser, B., 2003.

Nutrient availability and leaching in an archaeological Anthrosol and a Ferralsol of the Central Amazon Basin: fertilizer, manure and charcoal\amendments. Plant Soil 249, 343–357.

Li, J., Li, Z., Liu, B., Xia, Q., Xi, H., 2008. Effect of relative humidity on adsorption of formaldehyde on modified activated carbons. Chin. J. Chem. Eng. 16, 871–875. doi:10.1016/S1004-9541(09)60008-2

Li, W., Khan, M. a., Yamaguchi, S., Kamiya, Y., 2005. Effects of heavy metals on seed germination and early seedling growth of Arabidopsis thaliana. Plant Growth Regul. 46, 45–50. doi:10.1007/s10725-005-6324-2

Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O'Neill, B., Skjemstad, J.O., Thies, J., Luizão, F.J., Petersen, J., Neves, E.G., 2006. Black carbon increases cation exchange capacity in soils. Soil Sci. Soc. Am. J. 70, 1719. doi:10.2136/sssaj2005.0383

Libra, J.A., Ro, K.S., Kammann, C., Funke, A., Berge, N.D., Neubauer, Y., Titirici, M.-M., Fühner, C., Bens, O., Kern, J., Emmerich, K.-H., 2011. Hydrothermal carbonization of biomass residuals: a comparative review of the chemistry, processes and applications of wet and dry pyrolysis. Biofuels 2, 71–106. doi:10.4155/bfs.10.81

Liebe, F., Welp, G., Bruemmer, G.W., 1997. Mobilität anorganischer Schadstoffe in Böden Nordrhein-Westfalens, in: Materialien Zur Altlastensanierung Und Zum Bodenschutz, Landesumweltamt Nordrhein-Westfalen.

Lievens, C., Mourant, D., Gunawan, R., Hu, X., Wang, Y., 2015. Organic compounds leached from fast pyrolysis mallee leaf and bark biochars. Chemosphere 139, 659–664. doi:10.1016/j.chemosphere.2014.11.009

Lin, Y., Munroe, P., Joseph, S., Henderson, R., Ziolkowski, A., 2012. Water extractable organic carbon in untreated and chemical treated biochars. Chemosphere 87, 151–157. doi:10.1016/j.chemosphere.2011.12.007

Liu, T., Liu, B., Zhang, W., 2014. Nutrients and heavy metals in biochar produced by sewage sludge pyrolysis: Its application in soil amendment. Polish J. Environ. Stud. 23, 271–275.

Loibner, A.P., Szolar, O.H.J., Braun, R., Hirmann, D., 2004. Toxicity testing of 16 priority polycyclic aromatic hydrocarbons using Lumistox. Environ. Toxicol. Chem. 23, 557–564. doi:10.1897/03-59

Lors, C., Ponge, J.-F., Martínez Aldaya, M., Damidot, D., 2010. Comparison of solid-phase bioassays and ecoscores to evaluate the toxicity of contaminated soils. Environ. Pollut. 158, 2640–7. doi:10.1016/j.envpol.2010.05.005

Lucchini, P., Quilliam, R.S., DeLuca, T.H., Vamerali, T., Jones, D.L., 2014a. Increased bioavailability of metals in two contrasting agricultural soils treated with waste wood-derived biochar and ash. Environ. Sci. Pollut. Res. 21, 3230–3240. doi:10.1007/s11356-013-2272-y

Lucchini, P., Quilliam, R.S., DeLuca, T.H., Vamerali, T., Jones, D.L., 2014b. Does

biochar application alter heavy metal dynamics in agricultural soil? Agric., Ecosyst. Environ. 184, 149–157. doi:10.1016/j.agee.2013.11.018

Luo, F., Song, J., Xia, W., Dong, M., Chen, M., Soudek, P., 2014. Characterization of contaminants and evaluation of the suitability for land application of maize and sludge biochars. Environ. Sci. Pollut. Res. Int. doi:10.1007/s11356-014-2797-8

Lynch, J.M., 1980. Effects of organic acids on the germination of seeds and growth of seedlings. Plant, Cell Environ. 3, 255–259. doi:10.1111/1365-3040.ep11581824

MacNicol, R.D., Beckett, P.H.T., 1985. Critical tissue concentrations of potentially toxic elements. Plant Soil 85, 107–129.

Mahinpey, N., Murugan, P., Mani, T., Raina, R., 2009. Analysis of bio-oil, biogas, and biochar from pressurized pyrolysis of wheat straw using a tubular reactor. Energy Fuels 23, 2736–2742. doi:10.1021/ef8010959

Major, J., Rondon, M., Molina, D., Riha, S.J., Lehmann, J., 2010. Maize yield and nutrition during 4 years after biochar application to a Colombian savanna oxisol. Plant Soil 333, 117–128. doi:10.1007/s11104-010-0327-0

Manyà, J.J., 2012. Pyrolysis for biochar purposes: a review to establish current knowledge gaps and research needs. Environ. Sci. Technol. 46, 7939–54. doi:10.1021/es301029g

Manzo, S., De Nicola, F., De Luca Picione, F., Maisto, G., Alfani, A., 2008. Assessment of the effects of soil PAH accumulation by a battery of ecotoxicological tests. Chemosphere 71, 1937–1944. doi:10.1016/j.chemosphere.2007.12.026

Marchal, G., Smith, K.E.C., Mayer, P., Wollesen de Jonge, L., Karlson, U.G., 2014. Impact of soil amendments and the plant rhizosphere on PAH behaviour in soil. Environ. Pollut. 188, 124–31. doi:10.1016/j.envpol.2014.02.008

Marchal, G., Smith, K.E.C., Rein, A., Winding, A., Trapp, S., Karlson, U.G., 2013a. Comparing the desorption and biodegradation of low concentrations of phenanthrene sorbed to activated carbon, biochar and compost. Chemosphere 90, 1767–1778. doi:10.1016/j.chemosphere.2012.07.048

Marchal, G., Smith, K.E.C., Rein, A., Winding, A., Wollensen De Jonge, L., Trapp, S., Karlson, U.G., 2013b. Impact of activated carbon, biochar and compost on the desorption and mineralization of phenanthrene in soil. Environ. Pollut. (Oxford, U. K.) 181, 200–210. doi:10.1016/j.envpol.2013.06.026

Marchiol, L., Fellet, G., Boscutti, F., Montella, C., Mozzi, R., Guarino, C., 2013. Gentle remediation at the former “Pertusola Sud” zinc smelter: Evaluation of native species for phytoremediation purposes. Ecol. Eng. 53, 343–353. doi:10.1016/j.ecoleng.2012.12.072

Martinez, J.D., Puy, N., Murillo, R., Garcia, T., Navarro, M.V., Mastral, A.M., 2013. Waste tyre pyrolysis - A review. Renew. Sustain. Energy Rev. 23, 179–213.

doi:10.1016/j.rser.2013.02.038

Mašek, O., 2014. UKBRC Standard Biochars [WWW Document]. http://www.biochar.ac.uk/standard_materials.php, accessed 07/04/2016.

Mašek, O., Brownsort, P., Cross, A., Sohi, S., 2013. Influence of production conditions on the yield and environmental stability of biochar. Fuel 103, 151–155. doi:10.1016/j.fuel.2011.08.044

Masiello, C.A., Chen, Y., Gao, X., Liu, S., Cheng, H.Y., Bennett, M.R., Rudgers, J.A., Wagner, D.S., Zygourakis, K., Silberg, J.J., 2013. Biochar and microbial signaling: Production conditions determine effects on microbial communication. Environ. Sci. Technol. 47, 11496–11503. doi:10.1021/es401458s

Masiello, C.A., Dugan, B., Brewer, C.E., Spokas, K., Novak, J.M., Liu, Z., Sorrenti, G., 2015. Chapter 19: Biochar effects on soil hydrology, in: Biochar for Environmental Management: Science and Technology and Implementation, Second Edition. Earthscan Ltd., London., pp. 341–358.

Mayer, P., Hilber, I., Gouliarmou, V., Hale, S.E., Cornelissen, G., Bucheli, T.D., 2016. How to determine the environmental exposure of PAHs originating from biochar. Environ. Sci. Technol. acs.est.5b05603. doi:10.1021/acs.est.5b05603

McBeath, A. V., Smernik, R.J., Krull, E.S., Lehmann, J., 2014. The influence of feedstock and production temperature on biochar carbon chemistry: A solid-state 13C NMR study. Biomass and Bioenergy 60, 121–129. doi:10.1016/j.biombioe.2013.11.002

McBride, M.B., 1995. Toxic metal accumulation from agricultural use of sludge: are USEPA regulations protective? J. Environ. Qual. 24, 5. doi:10.2134/jeq1995.00472425002400010002x

McBride, M.B., 2003. Toxic metals in sewage sludge-amended soils: Has promotion of beneficial use discounted the risks? Adv. Environ. Res. 8, 5–19. doi:10.1016/S1093-0191(02)00141-7

McGrath, S.P., Chaudri, A.M., Giller, K.E., 1995. Long-term effects off metals in sewage sludge on soils, microorganisms and plants. J. Ind. Microbiol. 14, 94–104.

McGrath, S.P., Micó, C., Zhao, F.J., Stroud, J.L., Zhang, H., Fozard, S., 2010. Predicting molybdenum toxicity to higher plants: Estimation of toxicity threshold values. Environ. Pollut. (Oxford, U. K.) 158, 3095–3102. doi:10.1016/j.envpol.2010.06.027

McGrath, T., Sharma, R.K., Hajaligol, M.R., 2001. An experimental investigation into the formation of polycyclic-aromatic hydrocarbons (PAH) from pyrolysis of biomass materials. Fuel 80, 1787–1797. doi:10.1016/S0016-2361(01)00062-X

McGrath, T.E., Chan, W.G., Hajaligol, M.R., 2003. Low temperature mechanism for the formation of polycyclic aromatic hydrocarbons from the pyrolysis of cellulose. J. Anal. Appl. Pyrolysis 66, 51–70. doi:10.1016/S0165-

2370(02)00105-5

McKay, G., 2002. Dioxin characterisation, formation and minimisation during municipal solid waste (MSW) incineration: Review. Chem. Eng. J. 86, 343–368. doi:10.1016/S1385-8947(01)00228-5

McLaughlin, M.J., Zarcinas, B.A., Stevens, D.P., Cook, N., 2000. Soil testing for heavy metals. Commun. Soil Sci. Plan Anal. 31, 1661–1700.

Meers, E., Samson, R., Tack, F.M.G., Ruttens, A., Vandegehuchte, M., Vangronsveld, J., Verloo, M.G., 2007. Phytoavailability assessment of heavy metals in soils by single extractions and accumulation by Phaseolus vulgaris. Environ. Exp. Bot. 60, 385–396. doi:10.1016/j.envexpbot.2006.12.010

Mehra, A., Farago, M.E., Banerjee, D.K., 2000. A study of Eichhornia crassipes growing in the overbank and floodplain soils of the river Yamuna in Delhi, India. Environ. Monit. Assess. 60, 25–45.

Méndez, A., Gómez, A., Paz-Ferreiro, J., Gascó, G., 2012. Effects of sewage sludge biochar on plant metal availability after application to a Mediterranean soil. Chemosphere 89, 1354–1359. doi:10.1016/j.chemosphere.2012.05.092

Meng, J., Wang, L., Liu, X., Wu, J., Brookes, P.C., Xu, J., 2013. Physicochemical properties of biochar produced from aerobically composted swine manure and its potential use as an environmental amendment. Bioresour. Technol. 142, 641–646. doi:10.1016/j.biortech.2013.05.086

Mondal, N.K., Das, C., Datta, J.K., 2015. Effect of mercury on seedling growth, nodulation and ultrastructural deformation of Vigna radiata (L) Wilczek. Environ. Monit. Assess. 187, 241. doi:10.1007/s10661-015-4484-8

Monter Roso, C., Alvarez, E., Fernandez Marco, M.L., 1999. Evaluation of Mehlich 3 reagent as a multielmnent extractant in mine soils. L. Degrad. Dev. 47, 35–47.

Morales, V.L., Pérez-Reche, F.J., Hapca, S.M., Hanley, K.L., Lehmann, J., Zhang, W., 2015. Reverse engineering of biochar. Bioresour. Technol. 183, 163–174. doi:10.1016/j.biortech.2015.02.043

Mueller, N.D., Gerber, J.S., Johnston, M., Ray, D.K., Ramankutty, N., Foley, J.A., 2012. Closing yield gaps through nutrient and water management. Nature 490, 254–257. doi:10.1038/nature11420

Mukherjee, A., Zimmerman, A.R., Hamdan, R., Cooper, W.T., 2014. Physicochemical changes in pyrogenic organic matter (biochar) after 15 months of field aging. Solid Earth 5, 693–704. doi:10.5194/se-5-693-2014

Mukome, F.N.D., Zhang, X., Silva, L.C.R., Six, J., Parikh, S.J., 2013. Use of chemical and physical characteristics to investigate trends in biochar feedstocks. J. Agric. Food Chem. 61, 2196–2204. doi:10.1021/jf3049142

Mulcahy, D.N., Mulcahy, D.L., Dietz, D., 2013. Biochar soil amendment increases tomato seedling resistance to drought in sandy soils. J. Arid Environ. 88, 222–225. doi:10.1016/j.jaridenv.2012.07.012

Müller, K., Tintelnot, S., Leubner-Metzger, G., 2006. Endosperm-limited Brassicaceae seed germination: abscisic acid inhibits embryo-induced endosperm weakening of Lepidium sativum (cress) and endosperm rupture of cress and Arabidopsis thaliana. Plant Cell Physiol. 47, 864–877. doi:10.1093/pcp/pcj059

Nelissen, V., Ruysschaert, G., Müller-Stöver, D., Bodé, S., Cook, J., Ronsse, F., Shackley, S., Boeckx, P., Hauggaard-Nielsen, H., 2014. Short-term effect of feedstock and pyrolysis temperature on biochar characteristics, soil and crop response in temperate soils. Agronomy (Basel, Switz.) 4, 52–73. doi:10.3390/agronomy4010052

Nelson, D.C., Flematti, G.R., Ghisalberti, E.L., Dixon, K.W., Smith, S.M., 2012. Regulation of seed germination and seedling growth by chemical signals from burning vegetation. Annu. Rev. Plant Biol. 63, 107–30. doi:10.1146/annurev-arplant-042811-105545

Nisbet, I.C., LaGoy, P.K., 1992. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). Regul. Toxicol. Pharmacol. 16, 290–300. doi:10.1016/0273-2300(92)90009-X

Norwood, M.J., Louchouarn, P., Kuo, L.-J., Harvey, O.R., 2013. Characterization and biodegradation of water-soluble biomarkers and organic carbon extracted from low temperature chars. Org. Geochem. 56, 111–119. doi:10.1016/j.orggeochem.2012.12.008

Novak, J.M., Busscher, W.J., 2012. Selection and use of designer biochars to improve characteristics of southeastern USA coastal plain degraded soils, in: Advanced Biofuels and Bioproducts. pp. 69–96.

Nzihou, A., Stanmore, B., 2013. The fate of heavy metals during combustion and gasification of contaminated biomass-A brief review. J. Hazard. Mater. 256–257, 56–66. doi:10.1016/j.jhazmat.2013.02.050

Ogbonnaya, U., Semple, K., 2013. Impact of biochar on organic contaminants in soil: a tool for mitigating risk? Agronomy (Basel, Switz.) 3, 349–375. doi:10.3390/agronomy3020349

Ogunjobi, J.K., Lajide, L., 2013. Characterisation of bio-oil and bio-char from slow-pyrolysed Nigerian yellow and white corn cobs. J. Sustain. Energy Environ. 4, 77–84.

Oh, T.-K., Shinogi, Y., 2013. Characterization of the pyrolytic solid derived from used disposable diapers. Environ. Technol. 34, 3153–60. doi:10.1080/09593330.2013.808240

Ojeda, G., Mattana, S., Àvila, A., Alcañiz, J.M., Volkmann, M., Bachmann, J., 2015. Are soil-water functions affected by biochar application? Geoderma 249–250, 1–11. doi:10.1016/j.geoderma.2015.02.014

Okuno, T., Sonoyama, N., Hayashi, J.I., Li, C.Z., Sathe, C., Chiba, T., 2005. Primary release of alkali and alkaline earth metallic species during the pyrolysis of pulverized biomass. Energy and Fuels 19, 2164–2171. doi:10.1021/ef050002a

Oleszczuk, P., Hale, S.E., Lehmann, J., Cornelissen, G., 2012. Activated carbon and biochar amendments decrease pore-water concentrations of polycyclic aromatic hydrocarbons (PAHs) in sewage sludge. Bioresour. Technol. 111, 84–91. doi:10.1016/j.biortech.2012.02.030

Oleszczuk, P., Jośko, I., Kuśmierz, M., 2013. Biochar properties regarding to contaminants content and ecotoxicological assessment. J. Hazard. Mater. 260, 375–382. doi:10.1016/j.jhazmat.2013.05.044

Oleszczuk, P., Jośko, I., Kuśmierz, M., Futa, B., Wielgosz, E., Ligęza, S., Pranagal, J., 2014. Microbiological, biochemical and ecotoxicological evaluation of soils in the area of biochar production in relation to polycyclic aromatic hydrocarbon content. Geoderma 213, 502–511. doi:10.1016/j.geoderma.2013.08.027

Olsson, J.G., Ja, U., Pettersson, J.B.C., 1997. Alkali metal emission during pyrolysis of biomass. Energy Fuels 11, 779–784. doi:10.1021/ef960096b

Paradela, F., Pinto, F., Ramos, A.M., Gulyurtlu, I., Cabrita, I., 2009. Study of the slow batch pyrolysis of mixtures of plastics, tyres and forestry biomass wastes. J. Anal. Appl. Pyrolysis 85, 392–398. doi:10.1016/j.jaap.2008.09.003

Park, J.H., Choppala, G.K., Bolan, N.S., Chung, J.W., Chuasavathi, T., 2011. Biochar reduces the bioavailability and phytotoxicity of heavy metals. Plant Soil 348, 439–451. doi:10.1007/s11104-011-0948-y

Pattanotai, T., Watanabe, H., Okazaki, K., 2013. Experimental investigation of intraparticle secondary reactions of tar during wood pyrolysis. Fuel 104, 468–475. doi:10.1016/j.fuel.2012.08.047

Peterson, G.., Galbraith, J.K., 1932. The concept of marginal land. J. Farm Econ. 14, 295–310. doi:10.2307/1230112

Podgorski, D.C., Hamdan, R., McKenna, A.M., Nyadong, L., Rodgers, R.P., Marshall, A.G., Cooper, W.T., 2012. Characterization of pyrogenic black carbon by desorption atmospheric pressure photoionization Fourier transform ion cyclotron resonance mass spectrometry. Anal. Chem. 84, 1281–7. doi:10.1021/ac202166x

Prommer, J., Wanek, W., Hofhansl, F., Trojan, D., Offre, P., Urich, T., Schleper, C., Sassmann, S., Kitzler, B., Soja, G., Hood-Nowotny, R.C., 2014. Biochar decelerates soil organic nitrogen cycling but stimulates soil nitrification in a temperate arable field trial. PLoS One 9. doi:10.1371/journal.pone.0086388

Puga, A.P., Abreu, C.A., Melo, L.C.A., Beesley, L., 2015. Biochar application to a contaminated soil reduces the availability and plant uptake of zinc, lead and cadmium. J. Environ. Manage. 159, 86–93. doi:10.1016/j.jenvman.2015.05.036

Qiu, M., Sun, K., Jin, J., Han, L., Sun, H., Zhao, Y., Xia, X., Wu, F., Xing, B., 2015. Metal/metalloid elements and polycyclic aromatic hydrocarbon in various biochars: The effect of feedstock, temperature, minerals, and properties. Environ. Pollut. (Oxford, U. K.) 206, 298–305. doi:10.1016/j.envpol.2015.07.026

Quilliam, R.S., Marsden, K.A., Gertler, C., Rousk, J., DeLuca, T.H., Jones, D.L., 2012. Nutrient dynamics, microbial growth and weed emergence in biochar amended soil are influenced by time since application and reapplication rate. Agric., Ecosyst. Environ. 158, 192–199. doi:10.1016/j.agee.2012.06.011

Quilliam, R.S., Rangecroft, S., Emmett, B. a., Deluca, T.H., Jones, D.L., 2013. Is biochar a source or sink for polycyclic aromatic hydrocarbon (PAH) compounds in agricultural soils? GCB Bioenergy 5, 96–103. doi:10.1111/gcbb.12007

Rajkovich, S., Enders, A., Hanley, K., Hyland, C., Zimmerman, A.R., Lehmann, J., 2012. Corn growth and nitrogen nutrition after additions of biochars with varying properties to a temperate soil. Biol. Fertil. Soils 48, 271–284. doi:10.1007/s00374-011-0624-7

Rao, D.N., Mikkelsen, D.S., 1977. Effects of acetic, propionic, and butyric acids on rice seedling growth and nutrition. Plant Soil 47, 323–334. doi:10.1007/BF00011491

Reijnders, L., 2014. Phosphorus resources, their depletion and conservation, a review. Resour. Conserv. Recycl. 93, 32–49. doi:10.1016/j.resconrec.2014.09.006

Richards, L., 1954. Agriculture Handbook No 60: Diagnosis and improvement of saline and alkali soils. US Department of Agriculture.

Robertson, S.J., Rutherford, P.M., Lo, J.C., Massicotte, H.B., 2012. Biochar enhances seedling growth and alters root symbioses and properties of sub-boreal forest soils. Can. J. Soil Sci. 92, 329–340. doi:10.4141/CJSS2011-066

Rodríguez-Mirasol, J., Bedia, J., Cordero, T., Rodríguez, J.J., 2005. Influence of water vapor on the adsorption of VOCs on lignin-based activated carbons. Sep. Sci. Technol. (Philadelphia, PA, U. S.) 40, 3113–3135. doi:10.1080/01496390500385277

Rogovska, N., Laird, D., Cruse, R.M., Trabue, S., Heaton, E., 2012. Germination tests for assessing biochar quality. J. Environ. Qual. 41, 1014–1022. doi:10.2134/jeq2011.0103

Rogowski, D., Golding, S., Bowhay, D., Singleton, S., 1999. Final Report - screening survey for metals and dioxins in fertilizer products and soils in Washington State. Ecol. Publ. 99–309, 177.

Rombolà, A.G., Marisi, G., Torri, C., Fabbri, D., Buscaroli, A., Ghidotti, M., Hornung, A., 2015. Relationships between Chemical Characteristics and Phytotoxicity of Biochar from Poultry Litter Pyrolysis. J. Agric. Food Chem. 63, 6660–6667. doi:10.1021/acs.jafc.5b01540

Rondon, M.A., Lehmann, J., Ramirez, J., Hurtado, M., 2007. Biological nitrogen fixation by common beans (Phaseolus vulgaris L.) increases with bio-char additions. Biol. Fertil. Soils 43, 699–708. doi:10.1007/s00374-006-0152-z

Ronsse, F., van Hecke, S., Dickinson, D., Prins, W., 2013. Production and characterization of slow pyrolysis biochar: influence of feedstock type and

pyrolysis conditions. GCB Bioenergy 5, 104–115. doi:10.1111/gcbb.12018

Rutherford, D.W., Wershaw, R.L., Rostad, C.E., Kelly, C.N., 2012. Effect of formation conditions on biochars: Compositional and structural properties of cellulose, lignin, and pine biochars. Biomass and Bioenergy 46, 693–701. doi:10.1016/j.biombioe.2012.06.026

Sánchez, M.E., Menéndez, J.A., Domínguez, A., Pis, J.J., Martínez, O., Calvo, L.F., Bernad, P.L., 2009. Effect of pyrolysis temperature on the composition of the oils obtained from sewage sludge. Biomass and Bioenergy 33, 933–940. doi:10.1016/j.biombioe.2009.02.002

Schimmelpfennig, S., Glaser, B., 2012. One step forward toward characterization: some important material properties to distinguish biochars. J. Environ. Qual. 41, 1001–1013. doi:10.2134/jeq2011.0146

Schöning, A., Brümmer, G.W., 2008. Extraction of mobile element fractions in forest soils using ammonium nitrate and ammonium chloride. J. Plant Nutr. Soil Sci. 171, 392–398. doi:10.1002/jpln.200625169

Sfetsas, T., Michailof, C., Lappas, A., Li, Q., Kneale, B., 2011. Qualitative and quantitative analysis of pyrolysis oil by gas chromatography with flame ionization detection and comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry. J. Chromatogr. A 1218, 3317–3325. doi:10.1016/j.chroma.2010.10.034

Shackley, S., Hammond, J., Gaunt, J., Ibarrola, R., 2011. The feasibility and costs of biochar deployment in the UK. Carbon Manag. 2, 335–356. doi:10.4155/cmt.11.22

Sharma, R.K., Hajaligol, M.R., 2003. Effect of pyrolysis conditions on the formation of polycyclic aromatic hydrocarbons (PAHs) from polyphenolic compounds. J. Anal. Appl. Pyrolysis 66, 123–144. doi:10.1016/S0165-2370(02)00109-2

Sharma, R.K., Wooten, J.B., Baliga, V.L., Lin, X., Geoffrey Chan, W., Hajaligol, M.R., 2004. Characterization of chars from pyrolysis of lignin. Fuel 83, 1469–1482. doi:10.1016/j.fuel.2003.11.015

Shenbagavalli, S., Mahimairaja, S., 2012. Characterization and Effect of Biochar on Nitrogen and. Intern. J. Adv. Biol. Res. 2, 249–255.

Shoemaker, C.A., Carlson, W.H., Hort, B., Hook, I., 1990. pH affects seed germination of eight bedding plant species. HortScience 25, 762–764.

Shuttleworth, K.L., Cerniglia, C.E., 1995. Environmental aspects of PAH degradation. Appl. Biochem. Biotechnol. 54, 291–302.

Singh, B., Singh, B.P., Cowie, A.L., 2010. Characterisation and evaluation of biochars for their application as a soil amendment. Aust. J. Soil Res. 48, 516–525. doi:10.1071/SR10058

Singh, B.P., Cowie, A.L., Smernik, R.J., 2012. Biochar carbon stability in a clayey soil as a function of feedstock and pyrolysis temperature. Environ. Sci. Technol. 46, 11770–11778. doi:10.1021/es302545b

Singh, V.P., Mall, S.L., Billore, S.K., 1975. Effect of pH on germination of four common grass species of Ujjain (India). J. Range Manag. 28, 497–498.

Smith, C.R., Buzan, E.M., Lee, J.W., 2013. Potential impact of biochar water-extractable substances on environmental sustainability. ACS Sustain. Chem. Eng. 1, 118–126. doi:10.1021/sc300063f

Solaiman, Z.M., Murphy, D. V., Abbott, L.K., 2011. Biochars influence seed germination and early growth of seedlings. Plant Soil 353, 273–287. doi:10.1007/s11104-011-1031-4

Somtrakoon, K., Chouychai, W., 2013. Phytotoxicity of single and combined polycyclic aromatic hydrocarbons toward economic crops. Russ. J. Plant Physiol. 60, 139–148. doi:10.1134/S1021443712060155

Spokas, K.A., 2010. Review of the stability of biochar in soils: predictability of O:C molar ratios. Carbon Manag. 1, 289–303. doi:10.4155/cmt.10.32

Spokas, K.A., Cantrell, K.B., Novak, J.M., Archer, D.W., Ippolito, J.A., Collins, H.P., Boateng, A.A., Lima, I.M., Lamb, M.C., McAloon, A.J., Lentz, R.D., Nichols, K.A., 2012. Biochar: a synthesis of its agronomic impact beyond carbon sequestration. J. Environ. Qual. 41, 973–989. doi:10.2134/jeq2011.0069

Spokas, K.A., Novak, J.M., Stewart, C.E., Cantrell, K.B., Uchimiya, M., Dusaire, M.G., Ro, K.S., 2011. Qualitative analysis of volatile organic compounds on biochar. Chemosphere 85, 869–882. doi:10.1016/j.chemosphere.2011.06.108

Srinivasan, P., Sarmah, A.K., Smernik, R., Das, O., Farid, M., Gao, W., 2015. A feasibility study of agricultural and sewage biomass as biochar, bioenergy and biocomposite feedstock: Production, characterization and potential applications. Sci. Total Environ. 512–513, 495–505. doi:10.1016/j.scitotenv.2015.01.068

Stuanes, A.O., G., O., M, O., 1984. Ammonium nitrate as extractant for soil exchangeable cations, exchangeable acidity and aluminium. Commun. Soil Sci. Plan Anal. 15, 773–778.

Swiss Chemical Risk Reduction Ordinance, 2005. Verordnung zur Reduktion von Risiken beim Umgang mit bestimmten besonders gefährlichen Stoffen , Zubereitungen und Gegenständen (Chemikalien-Risikoreduktions-Verordnung, ChemRRV) #814.81.

Takijima, Y., 1964. Studies on organic acids in paddy field soils with reference to their inhibitory effects on the growth of rice plants. Soil Sci. Plant Nutr. 10, 14–21. doi:10.1080/00380768.1964.10431135

Talyan, V., Dahiya, R.P., Sreekrishnan, T.R., 2008. State of municipal solid waste management in Delhi, the capital of India. Waste Manag. 28, 1276–87. doi:10.1016/j.wasman.2007.05.017

Tessarolo, N.S., dos Santos, L.R.M., Silva, R.S.F., Azevedo, D.A., 2013. Chemical characterization of bio-oils using comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry. J. Chromatogr. A 1279, 68–75. doi:10.1016/j.chroma.2012.12.052

The Environmental Applications Group LTD, 1990. The Environmental toxiciology of polycyclic aromatic hydrocarbons, prepared for the Ontario Ministry of the Environment.

Thibaud, C., Erkey, C., Akgerman, A., 1993. Investigation of the effect of moisture on the sorption and desorption of chlorobenzene and toluene from soil. Environ. Sci. Technol. 27, 2373–2380. doi:10.1021/es00048a010

Tilman, D., Balzer, C., Hill, J., Befort, B.L., 2011. Global food demand and the sustainable intensification of agriculture. Pnas 108, 20260–4. doi:10.1073/pnas.1116437108

Tittonell, P., 2014. Ecological intensification of agriculture-sustainable by nature. Curr. Opin. Environ. Sustain. 8, 53–61. doi:10.1016/j.cosust.2014.08.006

Troy, S.M., Nolan, T., Leahy, J.J., Lawlor, P.G., Healy, M.G., Kwapinski, W., 2013. Effect of sawdust addition and composting of feedstock on renewable energy and biochar production from pyrolysis of anaerobically digested pig manure. Biomass and Bioenergy 49, 1–9. doi:10.1016/j.biombioe.2012.12.014

Uchimiya, M., Bannon, D.I., Wartelle, L.H., 2012. Retention of Heavy Metals by Carboxyl Functional Groups of. J. Agric. Food Chem. 60, 1798–1809. doi:10.1021/jf2047898

Uchimiya, M., Lima, I.M., Thomas Klasson, K., Chang, S., Wartelle, L.H., Rodgers, J.E., 2010. Immobilization of heavy metal ions (CuII, CdII, NiII, and PbII) by broiler litter-derived biochars in water and soil. J. Agric. Food Chem. 58, 5538–5544. doi:10.1021/jf9044217

Uchimiya, M., Wartelle, L.H., Klasson, K.T., Fortier, C.A., Lima, I.M., 2011. Influence of pyrolysis temperature on biochar property and function as a heavy metal sorbent in soil. J. Agric. Food Chem. 59, 2501–2510. doi:10.1021/jf104206c

United Nations, 2015. World population prospects, the 2015 revision, key findings and advance tables. doi:10.1017/CBO9781107415324.004

US Department of Health and Human Services, 1995. Toxicological profile for polycyclic aromatic hydrocarbons. Atlanta, Georgia.

US Department of Health and Human Services, 2007. NIOSH Pocket guide to chemical hazards, DHHS (NIOSH) Publication No. 2005-149. Cincinnati, Ohio.

US Environmental Protection Agency, 1996. Ecological effects test guidelines: OPPTS 859.4200, seed germination/root elongation toxicity test.

Uzoma, K.C., Inoue, M., Andry, H., Zahoor, A., Nishihara, E., 2011. Influence of biochar application on sandy soil hydraulic properties and nutrient retention. J. Food, Agric. Environ. 9, 1137–1143.

Vácha, R., Čechmánková, J., Skála, J., 2010. Polycyclic aromatic hydrocarbons in soil and selected plants. Plant Soil Environ. 56, 434–443.

Van den Berg, M., Birnbaum, L.S., Denison, M., De Vito, M., Farland, W., Feeley,

M., Fiedler, H., Hakansson, H., Hanberg, A., Haws, L., Rose, M., Safe, S., Schrenk, D., Tohyama, C., Tritscher, A., Tuomisto, J., Tysklind, M., Walker, N., Peterson, R.E., 2006. The 2005 World Health Organization reevaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. Toxicol. Sci. 93, 223–241. doi:10.1093/toxsci/kfl055

van Raij, B., 1998. Bioavailable tests: alternatives to standard soil extractions. Commun. Soil Sci. Plant Anal. 29, 1553–1570. doi:10.1080/00103629809370049

van Schie, P.M., Young, L.Y., 2000. Biodegradation of phenol: mechanisms and applications. Bioremediat. J. 4, 1–18. doi:10.1080/10588330008951128

Van Slycken, S., Witters, N., Meiresonne, L., Meers, E., Ruttens, A., Van Peteghem, P., Weyens, N., Tack, F.M.G., Vangronsveld, J., 2013. Field evaluation of willow under short rotation coppice for phytomanagement of metal-polluted agricultural soils. Int. J. Phytoremediation 15, 677–689. doi:10.1080/15226514.2012.723070

Van Wesenbeeck, S., Prins, W., Ronsse, F., Antal, M.J., 2014. Sewage sludge carbonization for biochar applications. Fate of heavy metals. Energy Fuels 140622102204000. doi:10.1021/ef500875c

Van Zwieten, L., Kimber, S., Morris, S., Chan, K.Y., Downie, A., Rust, J., Joseph, S., Cowie, A., 2010. Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. Plant Soil 327, 235–246. doi:10.1007/s11104-009-0050-x

Van Zwieten, L., Singh, B., Joseph, S., Kimber, S., Cowie, A., Chan, K.Y., 2015. Chapter 13: Biochar and emissions of non-CO2 greenhouse gasses from soil, in: Biochar for Environmental Management: Science and Technology and Implementation, Second Edition. Earthscan Ltd., London., pp. 227–250.

Wang, J., Xiong, Z., Kuzyakov, Y., 2015. Biochar stability in soil: Meta-analysis of decomposition and priming effects. GCB Bioenergy 1–12. doi:10.1111/gcbb.12266

Wang, T., Camps-Arbestain, M., Hedley, M., 2014. The fate of phosphorus of ash-rich biochars in a soil-plant system. Plant Soil 375, 61–74. doi:10.1007/s11104-013-1938-z

Wang, T., Camps-Arbestain, M., Hedley, M., Bishop, P., 2012. Predicting phosphorus bioavailability from high-ash biochars. Plant Soil 357, 173–187. doi:10.1007/s11104-012-1131-9

Wang, Z., Han, L., Sun, K., Jin, J., Ro, K.S., Libra, J.A., Liu, X., Xing, B., 2016. Sorption of four hydrophobic organic contaminants by biochars derived from maize straw, wood dust and swine manure at different pyrolytic temperatures. Chemosphere 144, 285–291. doi:10.1016/j.chemosphere.2015.08.042

Warnock, D.D., Lehmann, J., Kuyper, T.W., Rillig, M.C., 2007. Mycorrhizal responses to biochar in soil – concepts and mechanisms. Plant Soil 300, 9–20. doi:10.1007/s11104-007-9391-5

Weber, B., Stadlbauer, E.A., Schlich, E., Eichenauer, S., Kern, J., Steffens, D., 2014. Phosphorus bioavailability of biochars produced by thermo-chemical conversion. J. Plant Nutr. Soil Sci. 177, 84–90. doi:10.1002/jpln.201300281

Wei, Y.L., Lee, J.H., 1998. Formation of priority PAHs from polystyrene pyrolysis with addition of calcium oxide. Sci. Total Environ. 212, 173–181. doi:10.1016/S0048-9697(98)00004-7

Wezel, A., Casagrande, M., Celette, F., Vian, J.F., Ferrer, A., Peigné, J., 2014. Agroecological practices for sustainable agriculture. A review. Agron. Sustain. Dev. 34, 1–20. doi:10.1007/s13593-013-0180-7

White, S., Birnbaum, L., 2009. An overview of the effects of dioxins and dioxin-like compounds on vertebrates, as documented in human and ecological epidemiology. J. Environ. Sci. Heal. Part C, Environ. Carcinog. Ecotoxicol. Rev. 27, 197–211. doi:10.1080/10590500903310047.An

Wiedner, K., Glaser, B., 2015. Chapter 2: Traditional use of biochar, in: Biochar for Environmental Management: Science and Technology and Implementation, Second Edition. Earthscan Ltd., London., pp. 13–32.

Wiedner, K., Rumpel, C., Steiner, C., Pozzi, A., Maas, R., Glaser, B., 2013. Chemical evaluation of chars produced by thermochemical conversion (gasification, pyrolysis and hydrothermal carbonization) of agro-industrial biomass on a commercial scale. Biomass and Bioenergy 59, 264–278. doi:10.1016/j.biombioe.2013.08.026

Wijesekara, S., Navarro, R.R., Zhan-bo, H., 2007. Simultaneous treatment of dioxins and heavy metals in Tagonoura harbor sediment by two-step pyrolysis. Soil Sediment Contam. 16, 569–584. doi:10.1080/15320380701623412

Wilcke, W., 2007. Global patterns of polycyclic aromatic hydrocarbons (PAHs) in soil. Geoderma 141, 157–166. doi:10.1016/j.geoderma.2007.07.007

Williams, E.A., Williams, P.T., 1997. The pyrolysis of individual plastics and a plastic mixture in a fixed bed reactor. J. Chem. Technol. Biotechnol. 70, 9–20.

Wilson, B.K., Reed, D., 2012. IBI white paper implications and risks of potential dioxin presence in biochar.

Wilson, S.C., Jones, K.C., 1996. The fate and behavior of volatile aromatic hydrocarbons in sewage sludge-amended soil, in: Volatile Organic Compounds in the Environment, ASTM STP 1261. pp. 119–123.

Windeatt, J.H., Ross, A.B., Williams, P.T., Forster, P.M., Nahil, M.A., Singh, S., 2014. Characteristics of biochars from crop residues: Potential for carbon sequestration and soil amendment. J. Environ. Manage. 146, 189–197. doi:10.1016/j.jenvman.2014.08.003

Wisconsin Department of Natural Resources Bureau of water quality, 2015. PAH group of 10 calculation of concentration using toxicity equivalent factors, guidance number: 3400-2015-01.

Withers, P.J.A., Neal, C., Jarvie, H.P., Doody, D.G., 2014. Agriculture and

eutrophication: Where do we go from here? Sustain. 6, 5853–5875. doi:10.3390/su6095853

Witters, N., Mendelsohn, R.O., Van Slycken, S., Weyens, N., Schreurs, E., Meers, E., Tack, F., Carleer, R., Vangronsveld, J., 2012. Phytoremediation, a sustainable remediation technology? Conclusions from a case study. I: Energy production and carbon dioxide abatement. Biomass and Bioenergy 39, 454–469. doi:10.1016/j.biombioe.2011.08.016

Woolf, D., Amonette, J.E., Street-Perrott, F.A., Lehmann, J., Joseph, S., 2010. Sustainable biochar to mitigate global climate change. Nat. Commun. 1, 1–9. doi:10.1038/ncomms1053

World Health Organization regional office for Europea, 2013. Contaminated sites and health, report of two WHO workshops.

Wu, H., Yip, K., Kong, Z., Li, C.Z., Liu, D., Yu, Y., Gao, X., 2011. Removal and recycling of inherent inorganic nutrient species in mallee biomass and derived biochars by water leaching. Ind. Eng. Chem. Res. 50, 12143–12151. doi:10.1021/ie200679n

Xhrout, C., Pirard, C., De Pauw, E., 2001. De novo synthesis of polychlorinated dibenzo-p-dioxins and dibenzofurans on fly ash from a sintering rrocess. Environ. Sci. Technol. 35, 1616–1623.

Xie, T., Reddy, K.R., Wang, C., Yargicoglu, E., 2015. Characteristics and applications of biochar for environmental remediation: A review. Crit. Rev. Environ. Sci. Technol. 45, 939–969. doi:10.1080/10643389.2014.924180

Xu, G., Wei, L.L., Sun, J.N., Shao, H.B., Chang, S.X., 2013. What is more important for enhancing nutrient bioavailability with biochar application into a sandy soil: Direct or indirect mechanism? Ecol. Eng. 52, 119–124. doi:10.1016/j.ecoleng.2012.12.091

Yachigo, M., Sato, S., 2013. Leachability and vegetable absorption of heavy metals from sewage sludge biochar, in: Soriano, M.C.H. (Ed.), Soil Processes and Current Trends in Quality Assessment. InTech, pp. 399–416. doi:10.5772/45835

Yang, H., Kudo, S., Hazeyama, S., Norinaga, K., Mašek, O., Hayashi, J., 2013. Detailed analysis of residual volatiles in chars from the pyrolysis of biomass and lignite. Energy Fuels 27, 3209–3223. doi:10.1021/ef4001192

Yang, H., Yan, R., Chen, H., Lee, D.H., Zheng, C., 2007. Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel 86, 1781–1788. doi:10.1016/j.fuel.2006.12.013

Yao, Y., Gao, B., Inyang, M., Zimmerman, A.R., Cao, X., Pullammanappallil, P., Yang, L., 2011. Biochar derived from anaerobically digested sugar beet tailings: Characterization and phosphate removal potential. Bioresour. Technol. 102, 6273–6278. doi:10.1016/j.biortech.2011.03.006

Yargicoglu, E.N., Sadasivam, B.Y., Reddy, K.R., Spokas, K., 2015. Physical and chemical characterization of waste wood derived biochars. Waste Manage. 36,

256–268. doi:10.1016/j.wasman.2014.10.029

Yeo, S.-D., Tuncer, E., Akgerman, A., 1997. Adsorption of volatile organic compounds on soil and prediction of desorption breakthroughs. Sep. Sci. Technol. (Philadelphia, PA, U. S.) 32, 2497–2512. doi:10.1080/01496399708000782

Youmans, H.L., 1972. Measurement of pH of distilled water. J. Chem. Educ. 49, 429.

Yu, X.-Y., Ying, G.-G., Kookana, R.S., 2009. Reduced plant uptake of pesticides with biochar additions to soil. Chemosphere 76, 665–71. doi:10.1016/j.chemosphere.2009.04.001

Yu, Y., Liu, D., Wu, H., 2012. Characterization of water-soluble intermediates from slow pyrolysis of cellulose at low temperatures. Energy Fuels 26, 7331–7339.

Zaror, C.A., Hutchings, I.S., Pyle, D.L., Stiles, H.N., Kandiyoti, R., 1985. Secondary char formation in the catalytic pyrolysis of biomass. Fuel 64, 990–994. doi:10.1016/0016-2361(85)90156-5

Zhao, L., Cao, X., Mašek, O., Zimmerman, A., 2013. Heterogeneity of biochar properties as a function of feedstock sources and production temperatures. J. Hazard. Mater. 256–257, 1–9. doi:10.1016/j.jhazmat.2013.04.015

Zheng, H., Wang, Z., Deng, X., Zhao, J., Luo, Y., Novak, J., Herbert, S., Xing, B., 2013. Characteristics and nutrient values of biochars produced from giant reed at different temperatures. Bioresour. Technol. 130, 463–471. doi:10.1016/j.biortech.2012.12.044

Zhou, H., Wu, C., Meng, A., Zhang, Y., Williams, P.T., 2014a. Effect of interactions of biomass constituents on polycyclic aromatic hydrocarbons (PAH) formation during fast pyrolysis. J. Anal. Appl. Pyrolysis 110, 264–269. doi:10.1016/j.jaap.2014.09.007

Zhou, H., Wu, C., Onwudili, J.A., Meng, A., Zhang, Y., Williams, P.T., 2014b. Polycyclic aromatic hydrocarbon formation from the pyrolysis/gasification of lignin at different reaction conditions. Energy Fuels 28, 6371–79.

Zielińska, A., Oleszczuk, P., 2015. The conversion of sewage sludge into biochar reduces polycyclic aromatic hydrocarbon content and ecotoxicity but increases trace metal content. Biomass and Bioenergy 75, 235–244. doi:10.1016/j.biombioe.2015.02.019

Zwetsloot, M.J., Lehmann, J., Solomon, D., 2014. Recycling slaughterhouse waste into fertilizer: How do pyrolysis temperature and biomass additions affect phosphorus availability and chemistry? J. Sci. Food Agric. 95, 271–288. doi:10.1002/jsfa.6716

Appendix 1 Supplementary information

A 1.1 Supplementary information for Chapter 2

A Table 1: Validation/quality control of chemical analyses performed in this study in percentage standard deviation of the concentration of (low, high) standards analysed in replicates.

	standard deviation (%)	
	low standard	high standard
acetone	17.72	7.06
butan-1-ol	18.64	7.11
butan-2-ol	18.61	6.80
ethanol	17.97	7.49
isobutanol	18.06	6.83
MEK	18.08	7.21
methanol	16.90	7.25
MIBK	17.79	8.67
propan-1-ol	18.24	7.27
propan-2-ol	18.18	7.06
acetic acid	5.33	6.45
formic acid	7.73	9.42
propionic acid	5.73	6.67
butyric acid	5.97	7.61
naphthalene	1.69	1.16
acenaphthylene	5.54	4.48
acenaphthene	2.06	1.30
fluorene	3.54	3.78
phenanthrene	1.79	1.41
anthracene	5.64	2.63
fluoranthene	6.52	7.35
pyrene	5.20	8.39
benz(a)anthracene	7.83	3.08
chrysene	2.64	1.98
benzo(b)fluoranthene	9.41	8.95
benzo(k)fluoranthene	8.23	9.11
benzo(a)pyrene	9.57	9.19
indeno(1,2,3-cd)pyrene	9.17	5.88
dibenz(a,h)anthracene	9.64	6.53
benzo(g,h,i)perylene	8.64	6.16
phenol	45.00	
2,4-dimethylphenol (as marker for alkylphenols)	17.00	
pentachlorophenol (as marker for chlorophenols)	51.00	
VOC scan		semi-quantitative only
PAHs in solids	no standard / reference for biochar exists yet	

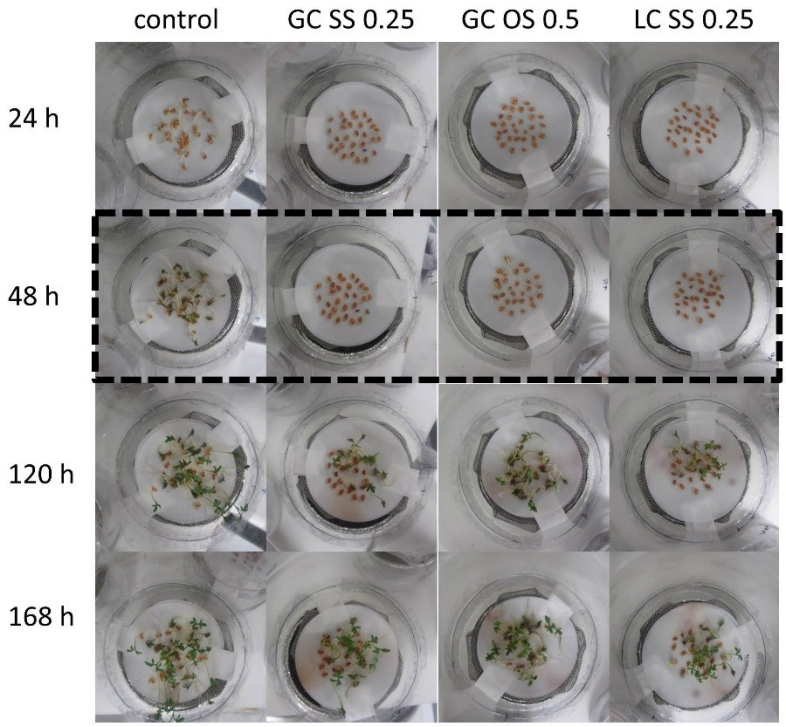
A Table 2: 16 US EPA PAHs in three biochars analysed in triplicates, respectively. Extraction and analysis was done on separate vials on different occasions. Average (AV) and standard deviation (SD) (in mg kg^{-1} and %) is shown. n/a, not available.

sample ID	date analysed	unit	acenaphthene	acenaphthylene	anthracene	benz(a)anthracene	benzo(a)pyrene	benzo(b)fluoranthene	benzo(g,h,i)perylene	benzo(k)fluoranthene	chrysene	dibenz(a,h)anthracene	fluoranthene	fluorene	indeno(1,2,3-cd)pyrene	phenanthrene	pyrene	naphthalene	sum 16 USEPA PAHs	sum non-NAP PAHs
29-20120705/350	Dec-14	mg kg^{-1}	0.15	0.8	0.53	0.4	0.34	0.3	0.21	0.1	0.32	<0.10	0.66	0.51	0.24	1.7	0.89	24	31.2	7.2
29-20120705/350	May-15	mg kg^{-1}	0.13	0.59	0.52	0.47	0.41	0.38	0.23	0.12	0.47	<0.10	0.69	0.4	0.24	1.6	0.95	n/a	n/a	7.2
29-20120705/350	May-15	mg kg^{-1}	0.19	0.94	0.7	0.51	0.41	0.39	0.22	0.12	0.47	<0.10	0.85	0.63	0.24	2.1	1.1	n/a	n/a	8.9
AV		mg kg^{-1}	0.16	0.78	0.58	0.46	0.39	0.36	0.22	0.11	0.42		0.73	0.51	0.24	1.80	0.98			7.7
SD		mg kg^{-1}	0.03	0.18	0.10	0.06	0.04	0.05	0.01	0.01	0.09		0.10	0.12	0.00	0.26	0.11			1.0
		%	19.5	22.7	17.3	12.1	10.5	13.8	4.5	10.2	20.6		13.9	22.4	0.0	14.7	11.0			12.6
35-1012/97/700	Dec-14	mg kg^{-1}	<0.10	<0.10	<0.10	0.11	0.11	<0.10	0.11	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	0.17	<0.10	19	19.5	
35-1012/97/700	Feb-15	mg kg^{-1}	<0.10	<0.10	<0.10	0.16	0.18	0.26	0.19	0.14	0.13	<0.10	<0.10	<0.10	0.22	0.16	0.1	27	28.5	
35-1012/97/700	Feb-15	mg kg^{-1}	<0.10	<0.10	<0.10	<0.10	<0.10	0.11	0.15	<0.10	<0.10	<0.10	<0.10	<0.10	0.15	<0.10	<0.10	20	20.4	
AV		mg kg^{-1}				0.14	0.15	0.19	0.15						0.19	0.17		22	22.8	
SD		mg kg^{-1}				0.04	0.05	0.11	0.04						0.05	0.01		4.4	5.0	
		%				26.2	34.1	57.3	26.7						26.8	4.3		19.8	21.8	
16-1011/23/750	Dec-14	mg kg^{-1}	0.69	0.42	2.2	1.6	1.2	1.2	0.51	0.49	1.7	0.21	2.8	<0.10	0.57	7.2	2.4	26	49.19	23.2
16-1011/23/750	Apr-15	mg kg^{-1}	0.73	<0.10	0.45	1	0.47	3.6	1.3	1.5	1.9	0.47	2.4	<0.10	1	7.9	1.9	47	71.62	24.6
16-1011/23/750	May-15	mg kg^{-1}	0.81	0.24	1	1.6	0.96	3.4	1.7	1.5	2.5	0.68	3.5	<0.10	1.7	8.6	2.9	n/a	n/a	31.1
AV		mg kg^{-1}	0.74	0.33	1.22	1.40	0.88	2.73	1.17	1.16	2.03	0.45	2.9		1.1	7.9	2.4			26.3
SD		mg kg^{-1}	0.06	0.13	0.89	0.35	0.37	1.33	0.61	0.58	0.42	0.24	0.6		0.6	0.7	0.5			4.2
		%	8.2	38.6	73.6	24.7	42.4	48.7	51.8	50.1	20.5	51.9	19.2		52.3	8.9	20.8			16.0

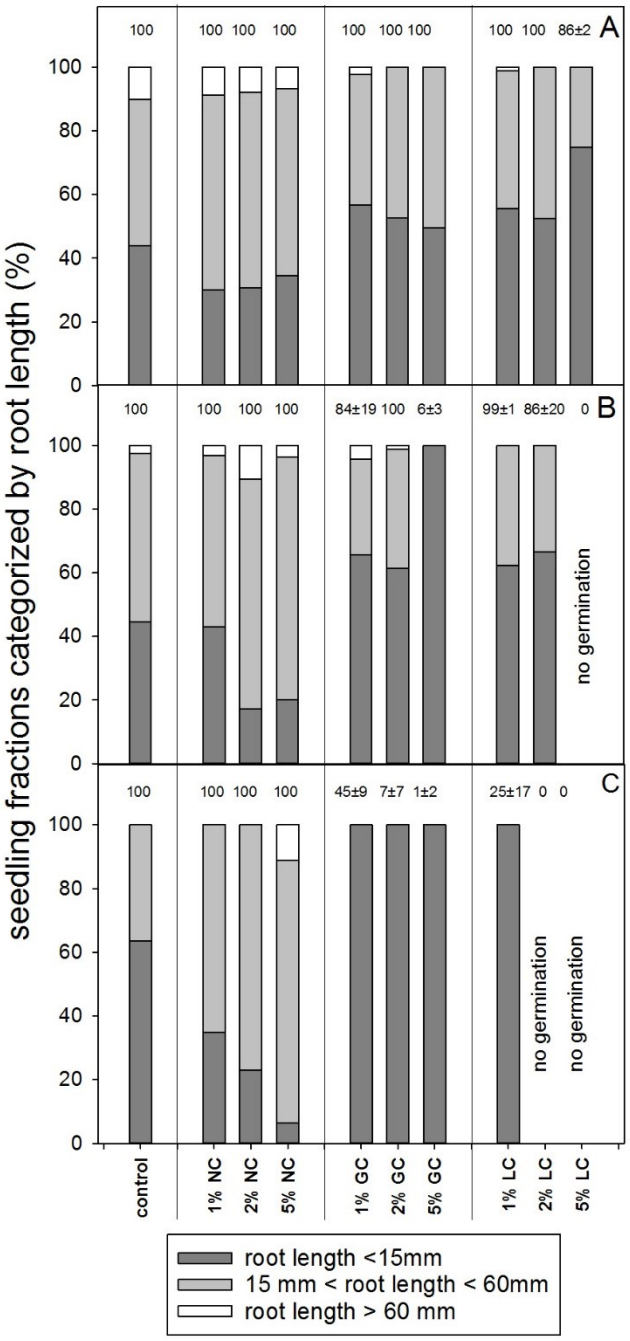
A 1.2 Supplementary information for Chapter 7

A Table 3: Germination rate (%) from 'all exposure routes' germination tests including low-VOC biochar treatments in average (AV) and standard deviation (SD).

	volatiles only		leachate affected		direct contact seed-biochar	
biochar	AV	SD	AV	SD	AV	SD
control	1.00	0.00	1.00	0.00	1.00	0.00
1% NC	1.00	0.00	1.00	0.00	1.00	0.00
2% NC	1.00	0.00	1.00	0.00	1.00	0.00
5% NC	1.00	0.00	1.00	0.00	1.00	0.00
1% GC	1.00	0.00	0.84	0.19	0.45	0.09
2% GC	1.00	0.00	1.00	0.00	0.07	0.07
5% GC	1.00	0.00	0.06	0.03	0.01	0.02
1% LC	1.00	0.00	0.99	0.01	0.25	0.17
2% LC	0.98	0.03	0.67	0.47	0.00	0.00
5% LC	0.86	0.02	0.00	0.00	0.00	0.00



A Figure 1: Progression of cress seeds from the start of 'volatiles only germination' test using different amounts of biochar. 0.25 g gas contaminated biochar sealed storage (GC SS 0.25), 0.5 g gas contaminated biochar four weeks open storage (GC OS 0.5) and 0.25 liquid contaminated biochar sealed storage (LC SS 0.25) are depicted.



A Figure 2: 'All exposure routes' germination test assessing toxicity of gaseous compounds released (A), leachable compounds (B) and direct contact of seeds and biochar (C). Seven-day germination test using NC, LC and GC biochar mixed in three concentrations with sand. Germination rates are depicted above the bars; bars show percentage of seedlings with root growth <15 mm, between 15 and 60 mm and above 60 mm.

A 1.3 Supplementary information for Chapter 9

A Table 4: Phenols with concentrations below 0.005 µg g^{-1} biochar from water extracts (solid-to-liquid ratio 1:100) in low- and high-VOC biochars.

phenols	phenols
3-chlorophenol	2,3,5-trichlorophenol
4-chlorophenol	2,4,5-trichlorophenol
2,6-dichlorophenol	2,3,4-trichlorophenol
3,4-dichlorophenol	3,4,5-trichlorophenol
3,5-dichlorophenol	2,3,5,6-tetrachlorophenol
2,3-dichlorophenol	2,3,4,6-tetrachlorophenol
2,4,6-trichlorophenol	2,3,4,5-tetrachlorophenol
2,3,6-trichlorophenol	pentachlorophenol

A Table 5: Concentrations of water extractable phenols determined by a phenol index test in NC, GC and LC biochar using two different solid-to-liquid extraction ratios. The extraction with solid-to-liquid extraction ratio of 1:100 was performed in triplicates and averages ± standard deviation are shown. Percentage extracted shows the fraction of 5/500 already extracted by 9/100 ratio

			low-VOC	high-VOC	
	solid-to-liquid ratio		NC biochar	GC biochar	LC biochar
phenol index	5 g / 500 mL	µg g^{-1}	5.45	2165	3265
phenol index	9 g / 100 mL	µg g^{-1}	<45	1797	2734
percentage extracted		%	-	83.02	83.74

Water-extractable phenols were extracted in a solid-to-liquid ratio of 1:100 to follow the method Hildebrand (1979). However, in the germination tests in Chapter 7 ratios of biochar-to-water of 1:14 (5% biochar), 1:35 (2% biochar) and 1:70 (1% biochar) were used. Thus, it was tested if it is possible to extract all phenols with lower solid-to-liquid ratios by extracting with a ratio of 1:9 and analyse the phenol index. 83% of the phenols extracted by a 1:100 ratio were already extracted by a ratio of 1:9 which indicates that the concentrations measured for individual phenols by the 1:100 ratio can be scaled-up to the solid-to-liquid ratio of 1:9 and to the ratios used in the germination tests accordingly.

A Table 6: Detection limits (LOD) for alcohols, ketones and LMW aliphatic acids.

alcohols and ketones		
acetone	µg g^{-1}	10.0
butan-1-ol	µg g^{-1}	12.0
butan-2-ol	µg g^{-1}	12.0
ethanol	µg g^{-1}	13.0
isobutanol	µg g^{-1}	10.0
methanol	µg g^{-1}	14.0
methyl ethyl ketone (MEK)	µg g^{-1}	5.0
methyl isobuthyl ketone (MIBK)	µg g^{-1}	2.0
propan-1-ol	µg g^{-1}	11.0
propan-2-ol	µg g^{-1}	10.0
LMW aliphatic acids		
acetic acid	µg g^{-1}	12.0
butyric acid	µg g^{-1}	10.0
formic acid	µg g^{-1}	15.0
propionic acid	µg g^{-1}	12.0

A Table 7: Concentrations of organic compounds in low- and high-VOC biochars. The grey areas show the concentrations in the water extracts (solid-to-liquid ratio of 10 or 100) as determined. The remaining columns depict the extracted concentrations up or down scaled according to the leachates in the germination tests in Chapter 7. Three different concentrations of biochar in sand were used, all with the same amount of water. According to these solid-to-liquid ratios, the expected concentrations in the leachates were calculated.

										5% BC		2% BC		1% BC	
			high-VOC			1:100		1:10		1:14		1:35		1:70	
		NC	GC	LC		5 g : 500 mL		10 g : 100 mL		2.5 g : 35 mL		1 g : 35 mL		0.5 g : 35 mL	
alcohols and ketones						GC	LC	GC	LC	GC	LC	GC	LC	GC	LC
acetone	µg g^{-1}	bdl	bdl	bdl	mg L^{-1}										
butan-1-ol	µg g^{-1}	bdl	bdl	bdl	mg L^{-1}										
butan-2-ol	µg g^{-1}	bdl	bdl	bdl	mg L^{-1}										
ethanol	µg g^{-1}	bdl	20.0	46.0	mg L^{-1}	0.20	0.46	2.0	4.6	1.4	3.3	0.6	1.3	0.29	0.66
isobutanol	µg g^{-1}	bdl	bdl	bdl	mg L^{-1}										
methanol	µg g^{-1}	bdl	380.9	250.1	mg L^{-1}	3.81	2.50	38.1	25.0	27.2	17.9	10.9	7.1	5.44	3.57
methyl ethyl ketone (MEK)	µg g^{-1}	bdl	bdl	bdl	mg L^{-1}										
methyl isobuthyl ketone (MIBK)	µg g^{-1}	bdl	bdl	bdl	mg L^{-1}										
propan-1-ol	µg g^{-1}	bdl	bdl	bdl	mg L^{-1}										
propan-2-ol	µg g^{-1}	bdl	bdl	bdl	mg L^{-1}										
LMW aliphatic acids															
acetic acid	µg g^{-1}	97.0	771.9	730.3	mg L^{-1}	7.72	7.30	77.2	73.0	55.1	52.2	22.1	20.9	11.03	10.43
butyric acid	µg g^{-1}	bdl	210.5	150.1	mg L^{-1}	2.11	1.50	21.1	15.0	15.0	10.7	6.0	4.3	3.01	2.14
formic acid	µg g^{-1}	85.0	541.3	500.2	mg L^{-1}	5.41	5.00	54.1	50.0	38.7	35.7	15.5	14.3	7.73	7.15
propionic acid	µg g^{-1}	bdl	37.1	260.1	mg L^{-1}	0.37	2.60	3.7	26.0	2.6	18.6	1.1	7.4	0.53	3.72

phenols															
phenol index	µg g^{-1}	5.45	2165	3265	mg L^{-1}	21.65	32.65	216.50	326.50	154.64	233.21	61.86	93.29	30.93	46.64
phenol	µg g^{-1}	bdl	190	310	mg L^{-1}	1.90	3.10	19.00	31.00	13.57	22.14	5.43	8.86	2.71	4.43
2-methylphenol (o-cresol)	µg g^{-1}	0.005	240	380	mg L^{-1}	2.40	3.80	24.00	38.00	17.14	27.14	6.86	10.86	3.43	5.43
3-methylphenol (m-cresol)	µg g^{-1}	bdl	160	240	mg L^{-1}	1.60	2.40	16.00	24.00	11.43	17.14	4.57	6.86	2.29	3.43
4-methylphenol (p-cresol)	µg g^{-1}	bdl	150	220	mg L^{-1}	1.50	2.20	15.00	22.00	10.71	15.71	4.29	6.29	2.14	3.14
2,6-dimethylphenol	µg g^{-1}	bdl	43	47	mg L^{-1}	0.43	0.47	4.30	4.70	3.07	3.36	1.23	1.34	0.61	0.67
2,5-dimethylphenol	µg g^{-1}	bdl	42	58	mg L^{-1}	0.42	0.58	4.20	5.80	3.00	4.14	1.20	1.66	0.60	0.83
2,4-dimethylphenol	µg g^{-1}	0.017	300	260	mg L^{-1}	3.00	2.60	30.00	26.00	21.43	18.57	8.57	7.43	4.29	3.71
3,5-dimethylphenol	µg g^{-1}	0.008	31	60	mg L^{-1}	0.31	0.60	3.10	6.00	2.21	4.29	0.89	1.71	0.44	0.86
2,3-dimethylphenol	µg g^{-1}	bdl	18	24	mg L^{-1}	0.18	0.24	1.80	2.40	1.29	1.71	0.51	0.69	0.26	0.34
3,4-dimethylphenol	µg g^{-1}	bdl	21	28	mg L^{-1}	0.21	0.28	2.10	2.80	1.50	2.00	0.60	0.80	0.30	0.40
2,4,6-trimethylphenol	µg g^{-1}	bdl	20	30	mg L^{-1}	0.20	0.30	2.00	3.00	1.43	2.14	0.57	0.86	0.29	0.43
2,3,6-trimethylphenol	µg g^{-1}	bdl	4.4	8	mg L^{-1}	0.04	0.08	0.44	0.82	0.31	0.59	0.13	0.23	0.06	0.12
2,3,5-trimethylphenol	µg g^{-1}	bdl	13	12	mg L^{-1}	0.13	0.12	1.30	1.20	0.93	0.86	0.37	0.34	0.19	0.17
3,4,5-trimethylphenol	µg g^{-1}	bdl	2.0	3	mg L^{-1}	0.02	0.03	0.20	0.29	0.14	0.21	0.06	0.08	0.03	0.04
2-chlorophenol	µg g^{-1}	bdl	0.066	0.120	mg L^{-1}	0.00	0.00	0.01	0.01	0.00	0.01	0.00	0.00	0.00	0.00
2,4/2,5-dichlorophenol	µg g^{-1}	bdl	0.40	0.770	mg L^{-1}	0.00	0.01	0.04	0.08	0.03	0.06	0.01	0.02	0.01	0.01

PAHs															
naphthalene	µg g^{-1}	bdl	0.12	0.46	µg L^{-1}	1.20	4.60	12.00	46.00	8.57	32.86	3.43	13.14	1.71	6.57
acenaphthylene	µg g^{-1}	bdl	1.10	0.79	µg L^{-1}	11.00	7.90	110.00	79.00	78.57	56.43	31.43	22.57	15.71	11.29
acenaphthene	µg g^{-1}	bdl	0.001	0.018	µg L^{-1}	0.01	0.18	0.10	1.80	0.07	1.29	0.03	0.51	0.01	0.26
fluorene	µg g^{-1}	bdl	0.038	0.089	µg L^{-1}	0.38	0.89	3.80	8.90	2.71	6.36	1.09	2.54	0.54	1.27
phenanthrene	µg g^{-1}	bdl	0.16	0.29	µg L^{-1}	1.60	2.90	16.00	29.00	11.43	20.71	4.57	8.29	2.29	4.14
anthracene	µg g^{-1}	bdl	0.035	0.073	µg L^{-1}	0.35	0.73	3.50	7.30	2.50	5.21	1.00	2.09	0.50	1.04
fluoranthene	µg g^{-1}	bdl	0.011	0.021	µg L^{-1}	0.11	0.21	1.10	2.10	0.79	1.50	0.31	0.60	0.16	0.30
pyrene	µg g^{-1}	bdl	bdl	bdl	µg L^{-1}										
benz(a)anthracene	µg g^{-1}	bdl	0.071	0.091	µg L^{-1}	0.71	0.91	7.10	9.10	5.07	6.50	2.03	2.60	1.01	1.30
chrysene	µg g^{-1}	bdl	bdl	0.028	µg L^{-1}		0.28		2.80		2.00		0.80		0.40
benzo(b)fluoranthene	µg g^{-1}	bdl	0.012	0.024	µg L^{-1}	0.12	0.24	1.20	2.40	0.86	1.71	0.34	0.69	0.17	0.34
benzo(k)fluoranthene	µg g^{-1}	bdl	0.015	0.030	µg L^{-1}	0.15	0.30	1.50	3.00	1.07	2.14	0.43	0.86	0.21	0.43
benzo(a)pyrene	µg g^{-1}	bdl	0.017	0.033	µg L^{-1}	0.17	0.33	1.70	3.30	1.21	2.36	0.49	0.94	0.24	0.47
indeno(1,2,3-cd)pyrene	µg g^{-1}	bdl	0.015	0.031	µg L^{-1}	0.15	0.31	1.50	3.10	1.07	2.21	0.43	0.89	0.21	0.44
dibenz(a,h)anthracene	µg g^{-1}	bdl	0.019	0.042	µg L^{-1}	0.19	0.42	1.90	4.20	1.36	3.00	0.54	1.20	0.27	0.60
benzo(g,h,i)perylene	µg g^{-1}	bdl	0.011	0.022	µg L^{-1}	0.11	0.22	1.10	2.20	0.79	1.57	0.31	0.63	0.16	0.31
16 USEPA	µg g^{-1}	bdl	1.62	2.04	µg L^{-1}	16.24	20.42	162.40	204.20	116.00	145.86	46.40	58.34	23.20	29.17

A Table 8: Mobility/extractability of 16 US EPA PAHs. The first three columns contain the fraction of PAHs extracted by toluene after 6 h compared to the total amount of PAHs after 36 h extraction. In the next columns, the percentage concentrations of PAHs extracted by water in relation to the total (36 h toluene extracted) PAHs are depicted. The last four columns show literature values on several properties of PAHs. n/a, not available.

	NC extractability	GC water/36 h	LC	NC extractability	GC 6 h/36 h	LC	literature values			
	%	%	%	%	%	%	boiling point °C	solubility mg L^{-1}	log K_{ow}	log K_{oc}
PAHs										
naphthalene	n/a	1.46	4.65	5.35	48.78	56.57	218[*]	30[#]	3.30[§]	2.97[+]
acenaphthylene	n/a	23.91	60.77	n/a	52.17	63.08	265-275	3.93	4.07	1.4
acenaphthene	n/a	0.08	1.64	n/a	30.77	53.64	96.2	1.93	3.98	3.66
fluorene	n/a	0.64	2.23	n/a	38.98	50.00	295	1.68-1.98	4.18	3.86
phenanthrene	n/a	1.45	5.09	50.00	43.64	56.14	340	1.2	4.45	4.15
anthracene	n/a	1.17	5.21	n/a	43.33	59.29	342	0.076	4.45	4.15
fluoranthene	n/a	0.26	1.91	n/a	57.14	80.91	375	0.2-0.26	4.9	4.58
pyrene	n/a	n/a	n/a	n/a	64.15	91.67	393	0.077	4.88	4.58
benz(a)anthracene	n/a	2.22	10.22	n/a	81.25	88.76	400	0.01	5.61	5.3
chrysene	n/a	n/a	7.00	n/a	72.22	75.00	448	0.0028	5.16	5.3
benzo(b)fluoranthene	n/a	0.71	12.00	n/a	82.35	95.00	481*	0.0012	6.04	5.74
benzo(k)fluoranthene	n/a	n/a	n/a	n/a	n/a	n/a	480	0.00076	6.06	5.74
benzo(a)pyrene	n/a	1.21	15.00	n/a	85.71	68.18	495	0.0023	6.06	6.74
indeno(1,2,3-cd)pyrene	n/a	2.17	20.67	n/a	76.81	66.67	530	0.062	6.58	6.2
dibenz(a,h)anthracene	n/a	4.63	23.33	n/a	51.22	n/a	524[*]	0.0005	6.84	6.52
benzo(g,h,i)perylene	n/a	1.53	10.48	n/a	70.83	n/a	550	0.00026	6.5	6.2
total 16 USEPA	n/a	3.04	7.31	5.58	54.66	59.25				

Kow, octanol-water partitioning coefficient
Koc, soil organic carbon-water partitioning coefficient
n/a, not available, one/both concentrations was/were under the detection limit
references: all from US Department of Health and Human Services (1995) apart from the following
* Alves de Lima Ribeiro and Ferreira (2003)
# Shiu and Ma (2000)
§ Sangster (1989)
+ Lee (2010)

References

Alves de Lima Ribeiro, F., Ferreira, M.M.C., 2003. QSPR models of boiling point, octanol–water partition coefficient and retention time index of polycyclic aromatic hydrocarbons. J. Mol. Struct. 663, 109–126. doi:10.1016/j.theochem.2003.08.107

Hildebrand, E.E., 1979. Erfassung und Charakterisierung von Polyphenolen als potentiellen Wuchshemmstoffen in kompostierten Siedlungsabfällen. Mitteilung der Dtsch. Bodenkundlichen Gesellschaft 29, 609–622.

Lee, B.-K., 2010. Sources , Distribution and Toxicity of Polycyclic Aromatic Hydrocarbons (PAHs) in Particulate Matter, in: Villanyi, V. (Ed.), Air Pollution. InTech, p. 370.

Sangster, J., 1989. Octanol-water partition coefficients of simple organic compounds. J. Phys. Chem. Ref. Data 18, 1111–1227.

Shiu, W.-Y., Ma, K., 2000. Temperature dependence of physical–chemical properties of selected chemicals of environmental interest. I. Mononuclear and polynuclear aromatic hydrocarbons. J. Phys. Chem. Ref. Data 29, 41. doi:10.1063/1.556055

US Department of Health and Human Services, 1995. Toxicological profile for Polycyclic Aromatic Hydrocarbons.

Appendix 2 Digital appendix

Following documents can be found on the flash drive supplied with the PhD thesis:

- One excel file, called “Digital Appendix_PhD thesis_Wolfram Buss“, containing the following three tables:
    - Digital Appendix Table 1: Concentration (mg kg^{-1}), relative change (%) and total change of the elemental content after pyrolysis (mg kg^{-1}) (assuming 100% retention) for twenty elements in eighteen biochars.
    - Digital Appendix Table 2: Percentage available of the total elemental content for nutrients and PTEs in nineteen biochars.
    - Digital Appendix Table 3: Concentration of individual and total 16 US EPA PAH concentrations in 84 biochars.
- The published manuscripts included in this PhD thesis.