Examining the effects of ‘Urban Biochar’ on physical and chemical properties of plant growing media and soil

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Management of municipal waste, such as biosolids and greenwaste, is becoming increasingly problematic with the increase and spread of urban populations. Traditionally such urban resources were viewed as wastes and were often discarded to landfill. More recently these waste resources have been combined, composted and returned to land as a soil conditioner. However, several issues including land availability primarily due to concerns of odour as well as the emission of gases such as ammonia, nitrous oxide and methane limits large scale disposal on land. An alternative way to manage these wastes is to convert them to biochar at a centrally located urban location and use it as a growing media or as a soil amendment.

Biochar is a carbon rich porous solid material, produced as a by-product during thermochemical conversion of biomass under anaerobic conditions, at temperatures above 300 °C. Biochar resembles charcoal but is produced from a wider range of feedstocks such as biosolids and manure and unlike charcoal biochar is not aimed for energy applications. Properties of biochar mainly depend on the pyrolysis temperature and choice of feedstock. The biochar used in this study was slow pyrolysis high temperature (650°C) biochar produced using biosolids and greenwaste in a 2:1 ratio on dry mass basis, called as urban biochar (UB). Although many studies have been conducted to investigate the short term effects of biochar in soils, long term impact of biochar on soil properties remains under studied. Furthermore, the studies conducted to date lack a whole system approach, as they have not investigated the soil - plant system, so do not consider major nutrient loss and use pathways such as: leachate, gaseous loss, storage by soil and plant uptake.

Considering, the high cost of biochar production, commercial application of biochar is feasible only if the biochar is used for high value production systems, such as the growing media
industry. However, there are very limited studies investigating the effects of biochar on physical and chemical properties of growing media. To fill this knowledge gap, in our study, I performed detailed characterization of UB and compared with published values for standard growing media to assess the potential of UB to be used as a growing media substrate. Growing media was then formulated according to the standard industry practice using different rates of UB. To understand the effect of UB on physical and chemical properties of growing media, two laboratory incubation and two glasshouse experiments were conducted. Some key physical and chemical properties tested in the incubation studies were water retention capacity at different matric potential under wetting-drying cycles, air filled porosity, change in bulk density over time, physical breakdown of media particles and nutrient release from UB amended unfertilized growing media mixes. Silverbeet plants were grown in the glasshouse experiment where major nitrogen and phosphorus loss pathways were measured using custom made chambers. Co-composting of UB with food waste was performed to artificially age UB in order to predict long term changes in UB. Suites of chemical and surface analysis were performed to identify the difference between the fresh and aged UB. The fresh and aged UB were then applied to a sandy acidic horticultural soil (Semiaquic Podosol) where important chemical and physical properties were tested to understand nutrient use efficiency and plant growth.

The results of comprehensive characterization of urban biochar and comparison of those results with the published data for growing media substrates indicated that urban biochar has potential to be used as growing media substrate. Incubation studies using different rates of UB in growing media showed UB can completely replace peat from growing media and can be used up to 60% on a volume basis. UB amended media performed better than industry standard media in terms of pH, capacity to supply nutrients, particle size distribution and
greater water holding capacity particularly at lower suction when media dries out. Furthermore, UB amended media proved to be more stable than industry standard media in terms of physical and chemical stability even after being exposed to periodic wetting and drying cycles. UB also reduced the loss of both nitrate and phosphate from growing media. For example 60% UB amended media had 95% less loss of nitrate and 51% less loss of phosphate than the media without UB. Co-composting biochar with food waste showed that co-composting can be used as a tool for artificial ageing of UB as it increases biochar surface oxidation (CEC of UB increased by 37%) and increases the nutrient load of biochar. Addition of 10% UB in composting also accelerated the composting process and improved the germination index. However, application of co-composted/aged UB to soil resulted in lower plant growth (plant growth in fresh UB amended soil was 74% higher than co-composted UB amended soil), lower nutrient use efficiency, greater N2O emission and lower water holding capacity as compared to soil amended with fresh UB.

In conclusion, the present research suggests that i) UB can replace peat and can be used as a growing media substrate when used up to 60% on volume basis; ii) UB improves physical and chemical properties of growing media; iii) Plants grown in UB amended growing media have better growth and greater nutrient use efficiency than industry standard growing media; iv) Co-composting UB with food waste ages the UB, however, it does not have agronomical benefit when applied to sandy acidic horticultural soils.

Keywords: growing media, urban biochar, biosolids, greenwaste, soil, water holding capacity, nutrient use efficiency, co-composted biochar, ageing, food waste, waste management.
DECLARATION

This is to certify that:

I. the thesis comprises only my original work towards the PhD,

II. due acknowledgement has been made in the text to all other material used, and

III. the thesis is fewer than 100,000 words in length, exclusive of tables, maps, bibliographies and appendices.

Bhawana Bhatta Kaudal

March 2017
This thesis is original and based on the studies I have conducted during my PhD candidature (2013-2016) at the University of Melbourne. This thesis is comprised of seven chapters. The first chapter is the introduction, followed by a review of literature which summarizes previous research. The experimental chapters 3–6 are written in manuscript format according to the specific format of individual journals. Connecting statements between these chapters show the progression from one manuscript to the next. Finally, the general discussion and conclusions highlight the key findings of this thesis and suggest areas for further research.

The candidate was the primary author of all manuscripts, and co-authors included are Anthony Weatherley, Deli Chen, Adriana Downie and Dinesh Babu Madhavan. The candidate was responsible for designing and conducting the experiments, collecting and analysing the data, and writing the manuscripts. The co-authors assisted in improving the experimental design, and improving the manuscripts.

The manuscripts included in this thesis are presented in the following order:

Chapter 3


Chapter 4

Chapter 5

Bhawana Bhatta Kaudal, Deli Chen, Anthony Weatherley. Urban biochar amended growing media has improved nutrient supply potential. *Geoderma*, revised and re-submitted on 10\textsuperscript{th} November 2016.

Chapter 6

Co-composting of urban biochar with food waste decreases its efficacy as a soil amendment. Submitted to Pedosphere on 26\textsuperscript{th} October 2016.
Declaration for a thesis with publication

PhD and MPhil students may include a primary research publication in their thesis in lieu of a chapter if:

- The student contributed greater than 50% of the content in the publication and is the "primary author", i.e. the student was responsible primarily for the planning, execution and preparation of the work for publication
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A. PUBLICATION DETAILS (to be completed by the student)

Full title: Pyrolysis of urban waste streams: Their potential use as horticultural media

Authors: Bhawana Bhatta Kaudal, Anthony Weatherley, Deli Chen, Adriana Downie, Dinesh Babu Madhavan

Student's contribution (%): 70%

Journal or book name: Journal of Analytical and Applied Pyrolysis

Volume/page numbers: 112,105–112

Status: ☒ Accepted and in press ☒ Published Date accepted/published: 4/02/2015

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| Full title | An examination of physical and chemical properties of urban biochar for use as growing media substrate |
| Authors | Bhawana Bhatta Kaudal, Anthony Weatherley, Deli Chen, Adriana Downie, Dinesh Babu Madhavan |
| Student’s contribution (%) | 70% |
| Journal or book name | Biomass & Bioenergy |
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| Status | Published | Date accepted/ published 12/11/2015 |

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Co-author’s name: Dr Adriana Downie
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CHAPTER 1

INTRODUCTION

1.1 Research background

Biochar is a carbon rich, porous, solid material produced by thermo chemical conversion of biomass under anaerobic conditions at temperatures above 300 °C. Biochar is similar to charcoal but is produced from a wider range of feedstocks such as biosolids and manure with the primary objective of applying to soil to improve its physical and chemical characteristics (Joseph et al., 2010). Converting biomass to biochar substantially reduces the greenhouse gas emissions that would occur if the biomass were allowed to naturally degrade (IBI, 2015). Biochar is a highly stable form of carbon which can remain in the soil for thousands of years (Nguyen and Lehmann, 2009). Furthermore, during the process of making biochar, energy can also be recovered in the form of syngas and bio-oils (Chun et al., 2013).

More than 330,000 tonnes (t) of biosolids are produced each year in Australia on dry basis, out of which, 59% is applied to land, 20% is stockpiled (mostly in Victoria), around 6% is used for landscaping and around 1% is discharged to the ocean (ANZBP, 2013). In Victoria, three million cubic metres of biosolids, which is equal to 10 years of current national production have been stockpiled (MWC, 2015). Although more than half of the biosolids currently generated are applied to agricultural land, concerns remain in regard to soil and groundwater contamination from nitrogen and phosphorus, heavy metals, organic contaminants, and pathogens. Converting biosolids into biochar involves heating biosolids at high temperatures, eradicating microorganisms, removing odour and making most trace elements unavailable for plant uptake and therefore safer for land application (Park et al., 2011).
Australia has established the Carbon Farming Initiative (CFI) as a commitment to a low carbon economy and this has encouraged biosolids management authorities to invest in green energy and innovative renewable technologies (Government, 2014). The carbon sequestration projects under the CFI are subject to permanence obligations to ensure that the carbon stored is maintained for at least 100 years. Thus, the potential of biochar to sequester carbon in the long term (>100 years), and generate energy during the biochar production process, provides both environmental and economic incentives for waste management authorities to convert biosolids into biochar rather than applying biosolids directly to land (Government, 2014).

Urban garden waste (green waste) is another major waste which is commonly managed through composting, however due to its rapid decomposition in soil and potential emission of nitrous oxide to the atmosphere under anaerobic conditions, it is not considered environmentally friendly (Sohi et al., 2010; Woolf et al., 2010). Green waste also has potential to be converted to biochar for energy generation. For the current study, a novel biochar (Urban Biochar, UB) was produced with a mix of urban waste feedstocks that consisted two parts biosolids and one part of green waste on a dry basis. The primary advantage of this material relates to a potentially higher nutrient (P, Mg, and Ca) content associated with biosolids and carbon sequestration value (both environmental and monetary) associated with carbon rich (C%) green waste.

1.1.1 Biochar characterization

Research shows that biochar properties can vary significantly depending on the feedstock choice and pyrolysis temperature (Downie, 2009). Therefore, it is essential to characterise each biochar and understand its properties in order to determine the suitability of that biochar for any particular use. Biochars produced from manure and biosolids based
feedstocks have high nutrient owing to their high ash content, whereas wood based feedstocks have low ash and more fixed carbon (Zhao et al., 2013). Other chemical properties like pH and CEC also change with feedstock and temperature used to produce biochar (Kloss et al., 2012). Generally, high temperature biochars have low CEC as the carboxylic functional groups responsible for high CEC are destroyed at temperature greater than 250 °C (Kloss et al., 2012). Pyrolysis temperature also affects the concentration and availability of heavy metals from biochar when applied to soil with pyrolysis above 350°C, reduces the availability of those metals making it hard to leach out (He et al., 2010). Also, high temperature biochars have increased specific surface area which helps to retain metals when applied to soil (He et al., 2010; Hwang et al., 2007). The heavy metal availability from biochars produced from different source of biosolid feedstock will vary, therefore, characterization of biochar produced from different biosolids feedstock should be conducted.

1.1.2 Biochar application to soil

Biochar has been widely used in soil as an amendment with the aim of improvement of physical and chemical properties of soil. The impact of biochar on soil properties is also dependent on the type of biochar used and properties of the soil (Kookana et al., 2011). Once biochar is applied to soil, it is likely to stay there for hundreds of years, therefore, it is important to understand the impact of aged biochar in soil properties. There are limited studies looking at the impact of aged biochar to soil. Laboratory based incubation studies have shown a positive impact of biochar ageing on soil properties due to increased surface oxidation of biochar (Nguyen et al., 2009), whereas, field based experiments show little effect of ageing of biochar on improving plant growth (Schmidt et al., 2014) and reducing nitrous oxide emissions (Spokas, 2013). Moreover, field experiments conducted thus far are only few years long. Therefore, further long term studies need to be conducted to understand the
effect of biochar ageing on soil properties. Co-composting biochar with manure and green waste has been used as a tool of artificially accelerating biochar ageing in order to predict long term changes in biochar (Prost et al., 2013). To explore the long term effect of biochar on soil properties and plant growth, the biochar was artificially aged using a co composting procedure.

1.1.3 Biochar application in the horticulture/plant growing media industry

The horticulture industry can be divided into two broad sectors: the production sector, which is largely involved with producing food crops, and the amenity sector, which is involved with growing plants for recreational or ornamental purposes, mainly in nurseries (also called as protected crops). These horticultural industry uses large inputs of fertilizers and water. At the same time the increasing cost of common media components such as peat moss, vermiculite, perlite along with growing environmental concerns about the use of peat moss in particular, is driving the horticultural industry to find an environmentally friendly alternatives. Using biochar can be carbon negative when waste materials are used as feedstock and carbon is sequestered in biochar for long periods of time (Cheng et al., 2008; Gaunt and Lehmann, 2008; Major et al., 2010). One study has suggested an annual carbon sequestration potential of 1200 tonnes from 300 million container grown plants by using 75% biochar on volume basis (Dumroese et al., 2011). These 300 million container plants are the plants used annually for reforestation and conservation planting in the Pacific Northwest USA and British Columbia, Canada. Further if the number of horticulture landscape business that use growing media are considered, and if all of those businesses were to use biochar, there would be a huge potential of sequestering carbon through the normal out planting process. Therefore, the horticulture
industry deserves attention with respect to reductions in greenhouse gas emissions and the potential for long term carbon sequestration (Marble et al., 2011).

Globally, there are large differences in the use of biochar as a growing media substrate. The world’s largest user of biochar amended growing media is the United States where more than 20 companies produce biochar amended growing media with annual production value of $5 billion. Government funded industry programmes on marketing and the formation of state wide working groups has helped to reach out consumers of biochar amended growing media in the United States (Delaney, 2015). In the UK, the government has decided to phase out peat completely from the horticultural industry by 2020. This policy has resulted in an increase in industry based research and also increased the use of biochar as a peat replacement (DEFRA, 2013). In the case of Australia, there is generally a very low adoption of biochar in the horticulture industry which is mainly due to the absence of government policy to provide environment incentives.

Many characteristics of biochar such as the high specific surface area, large water holding capacity, high porosity, adjustable particle size, potential to increase nutrient efficiency, desirable bulk density makes it an attractive option for use in growing media (Licht et al., 2013). In practical situations, it is common for growing media to undergo periodic wetting and drying cycles. Nutrient release from high ash biochar to pore solution and effects of biochar on the properties of growing media under the periodic wetting and drying cycles are unknown. Therefore, further studies need to be conducted to understand the role of high ash biochars on physical and chemical properties under wetting drying cycles. Whist there are few studies that have measured loss of applied nitrogen through leaching from biochar amended growing media in laboratory incubation experiments (Altland and Locke, 2012;
Nemati et al., 2015) and; greenhouse studies investigating plant nutrient uptake (Headlee et al., 2013; Zhang et al., 2014), there have been no studies investigating nutrient use efficiency in biochar amended media with simultaneous measurements of major nitrogen loss pathways including leaching and N\textsubscript{2}O emission in a greenhouse setting. An understanding of the magnitude of N and P leaching and pathways of N gaseous losses in biochar amended media is important for environmentally and economically sustainable management of soilless horticultural enterprises. Therefore, understanding the complete fate of added nitrogen can help to make improved decisions around container plant nutrition and potentially reduce costs through lowered fertilizer use. If biochar can improve water use and nutrient use efficiency in growing media, the use of biochar in the nursery industry could be a financially better choice for nursery operators. Hence, replacing peat from growing media using biochar seems to be a win-win situation where multiple benefits such as, waste management, resource recovery, emission reduction, biomass energy production, reduced transport and carbon sequestration can be achieved (Dumroese et al., 2011). Furthermore, if the biochar is made from locally sourced urban wastes in a location close to the use point, there could be significant savings on the transport cost. An obvious market would be commercial nurseries and parks/gardens on the city fringe. Therefore, this study proposes to convert urban waste (biosolids and green waste) into biochar and then utilize the biochar as a substrate in plant growing media and soil amendment.

1.2 Conceptual framework

The goal of this research is to investigate the effect of application of UB in growing media and soil with five main objectives: (i) Understand the properties of UB (ii) Understand the impact of UB on physical and chemical properties of growing media under typical use conditions of
growing media, (iii) Identify the effects of UB on nutrient use efficiency and plant growth including heavy metal uptake when used as a growing media substrate and in soil, (iv) Identify the best rate of use of UB in growing media and v) Assess the impact of ageing of UB on physical and chemical properties of soil.

To accomplish the first goal, detailed physical and chemical characterization of UB was conducted. Physical properties characterized were surface area, pore properties, particle size distribution and water holding capacity. Chemical properties characterized were pH, EC, CEC, total nutrients, heavy metal and polycyclic aromatic hydrocarbon (PAHs) concentrations. These physical and chemical properties of UB were then compared with the standard growing media properties to determine the potential to use UB as growing media substrate.

To achieve the second goal, two laboratory experiments were conducted. In the first, an incubation experiment, the impact of biochar on the water holding capacity by media at different suctions were established by calculating moisture retention curves. In another incubation experiment, nutrient release from unfertilized UB amended growing media were estimated by analysing nutrient concentration in pore water. Other chemical properties including pH, EC, CEC was also analysed. Results of above experiments enabled understanding of effects of UB on moisture characteristics and nutrient release from UB.

To realize the third goal, a glasshouse experiment was conducted where fertilizer was added in UB amended growing media and silverbeet (Beta vulgaris ssp.cicla) was grown as a test plant. Silverbeet was chosen as the test plant due to its fast growth and high nitrogen requirement. Nitrogen and phosphorus loss pathways were assessed including retention of the fertilizer N and P by growing media, plant uptake, leaching and gaseous loss of nitrogen. Optimal rate of use of UB in growing media was also identified on the basis of this experiment (fourth goal).
To complete the fifth goal, a co-composting experiment was conducted by composting UB with food waste for the purpose of accelerated ageing of UB. Treatments, co-composted UB and fresh UB, were then applied to an acidic soil, collected from a horticultural field. Plant response was evaluated in a greenhouse experiment in order to control the experimental conditions, where sorghum (Sorghum bicolor ssp.MR -Taurus) plants were grown. Sorghum was chosen as it is a common crop grown in acidic sandy soils where low fertilizer use efficiency is a major issue. This combination ensures a nutrient response and enables the impact of biochar on fertilizer use efficiency to be studied. This experiment was a logical progression from growing media and allowed the understanding of the effect of UB on chemical, physical properties of soil along with understanding of the effect of aged UB on nutrient use efficiency and plant growth.

This thesis concludes with an integrated discussion on the application of UB to growing media and horticultural soil along with discussion on composting of UB for purpose of ageing the biochar and its impact on plant growth. Recommendations for the nursery industry and future research on biochar use in growing media and soil are also discussed at the end of the thesis.

1.3  Organization of the thesis

This thesis begins with chapter 1, which covers the research background, conceptual framework, objectives and significance of study. Chapter 2 is a comprehensive literature review on the use of biochar as growing media substrate and soil amendment. Chapter 3 presents characterization of UB exploring potential of UB as a growing media substrate. Chapter 4 explores the impact of addition of various rates of UB on physical and chemical properties of growing media. Chapter 5 investigates the impact of UB on nutrient use efficiency from growing media with main focus on nitrogen and phosphorus. Chapter 6
presents results of co-composting UB with food waste for purpose of ageing UB and compares the performance of plants grown on soil amended with composted biochar, fresh biochar and composted food waste.

This thesis concludes with chapter 7, which presents major findings of the research, implications of the results, limitations of the study, suggestions for nursery industry and future research.

1.4 Significance of the study

This research demonstrates an innovative solution to the utilization of major urban wastes: biosolids, green waste and food waste which may assist waste management authorities to develop waste management plans. The study aims to bring a positive impact on the environment through conversion of wastes into resources called UB and use it to replace an unsustainable resource, peat, from growing media while minimising water and fertilizer costs. This study is also of great benefit to the nursery and other horticultural industries, along with growing media producers, as it helps them to understand the likely physical, chemical and agronomic benefits of added UB. The findings of this study will assist the growing media producers to make decisions on the optimum rate of biochar in growing media. In addition, this study shows the value of co-composting UB with food waste to simulate ageing.
References


Melbourne water corporation, Waste to resources


2.1. Biochar

Biochar is a solid carbonaceous porous product obtained from thermo-chemical conversion of biomass under oxygen depleted conditions at temperatures above 300 °C (Sohi et al., 2010). Biochar may be added to soils with the intention to improve soil function and to reduce emissions from biomass that would otherwise naturally degrade and emit greenhouse gases (Initiative, 2015). Pyrolysis is a controlled process of producing biochar which also yields other by-products such as gases, tars and oils. Modern pyrolysis kilns have ability to capture those by-products which can be used for generating energy (Laird et al., 2009). The yield of biochar and other by-products depends on the length of heating, also called slow (heating for minutes to hours) and fast (heating for seconds) pyrolysis. Slow pyrolysis is optimised for higher yields of biochar and low yield of other by-products, whereas, fast pyrolysis produces high yields of gases and tars with low biochar yield (Sohi et al., 2010).

The oldest description of charred crop waste use in agriculture is in the Japanese textbook entitled ‘Nogyo Zensho’ (Encyclopedia of Agriculture). The so called ‘ash manure’ has been shown to improve yield of major crops (Miyazaki, 1697). However, the recent strong interest on production and use of biochar started after the discovery of charcoal from Amazonian Dark Earths also known as terra preta (Glaser et al., 2002). Terra preta is thought to have formed from a combination of unintentional activities like fires and some intentional activities such as addition of animal wastes to improve soil (Glaser and Birk, 2012). The observed patchiness of terra preta as investigated by archaeologists strongly suggests activities of the pre-Columbian settlement leading to enrichment of soil with organic matter and charcoal from local fires. Patchiness of terra preta has been reported to range from size of less than a
hectare to several square kilometres which also suggests small forest fires as a possible source of fertility of those soils (Kern et al., 2003). It has been found that the terra preta still possess high nutrient status and organic matter to support greater agricultural production relative to the soils found in similar climate region (Novotny et al., 2009). However, it should be noted that the terra preta soils from Amazon were not used for agriculture, and this may have assisted in maintaining the overall nutritional status of the soil. In part, the agronomic use of biochar stems from an attempt to understand the mechanisms behind the fertile soils of terra preta and with the expectation of achieving a similar “terra preta effect” from the application of biochar to soil.

2.1.1 Factors controlling physiochemical properties of biochar

Biochar can be produced from a wide range of feedstocks using different pyrolysis conditions and these determine the properties of the biochar (Downie, 2009).

2.1.1.1 Type of feedstock

A wide range of organic materials, including agricultural and municipal wastes can be converted into biochars. Manure and biosolids derived biochars generally show higher ash contents and soluble macro nutrients compared with wood/greenwaste -derived biochars. The P concentration in biosolids based biochar are also higher (2-6%) than wood based biochars (0.01-0.55%)(Taherymoosavi et al., 2016; Van Zwieten et al., 2010a). Biosolids and manure based biochars are also richer in other macronutrients such as Ca, K, N and Mg. Biochars produced from wood based feedstocks have high C:N ratio (200-557) and high fixed carbon due to the high lignin content, as compared to the manure based biochars which has low C:N ratio (9-26) (Berek and Hue, 2016; Gaskin et al., 2008). Biosolids and manure based biochars have high CEC and EC as compared with wood based biochars (Taherymoosavi et al., 2016; Van Zwieten et al., 2010b; Van Zwieten et al., 2013). Based on chemical properties,
wood and greenwaste based biochars may be beneficial for carbon sequestration due to their high C:N ratio and stability, whereas, manure and biosolids based biochar may be better suited for improving nutrient status of soil owing to high their ash content and high CEC.

2.1.1.2 Pyrolysis temperature

Biochars produced at high temperatures (> 500 °C) are well carbonized, as indicated by their low O/C ratio, consequently making the high temperature biochars more stable in terms of further degradation (Crombie et al., 2013; Nguyen et al., 2010). High temperature biochars are also known to have high specific surface area. On the other hand, low temperature biochars (< 300 °C) have high O/C ratio and low specific surface area due to partial carbonization (Nguyen et al., 2009; Yuan et al., 2015). High temperature during pyrolysis causes volatilization of water molecules, tars and impurities that would otherwise clog the fine pores in biochar which leads to opening up of nano pores (Bagreev et al., 2001; Ma et al., 2016). Production of tars depends on the feedstock source and associated with incomplete carbonization of feedstock. Tars are toxic to the environment, therefore, modern pyrolysis plants are equipped with tar cracker to break down the tars which prevents re-deposition of tars to the biochar surface and also the release of those tars to atmosphere (Downie et al., 2012).

Most of the nitrogen from feedstock is lost during pyrolysis, therefore, biochars have low N content. There is also structural change in the remaining biochar N, with transformation to pyridine like compounds (the so called black N) and this significantly reduces N availability (Hilscher and Knicker, 2011).

Increase in pyrolysis temperature has been shown to increase the concentration of P from 5.6% at 250 °C to 12.8% at 800 °C (Bridle and Pritchard, 2004). Recovery of P from biosolids to biochar was 100% when the pyrolysis temperature was less than 500 °C, however, only
15% of that total P was plant available as observed in the incubation study (Bridle and Pritchard, 2004). In terms of other macronutrients such as Ca and K, about 55% of those nutrients are lost when feedstocks are pyrolyzed between 400- 650 °C (Novak et al., 2014a). The remaining K and Ca from biochar were found to be partly plant available, with about 14% K from biosolids biochar was available to plants (Shinogi and Kanri, 2003).

High temperature pyrolysis also decreases the functional groups associated with the feedstock that provide CEC therefore, low temperature biochars have a relatively higher CEC (Gaskin et al., 2008). A 250 °C biochar may have as much as seven times more CEC than biochar produced at 650 °C (Mukherjee et al., 2011).

2.1.1.3 Kiln residence time

Kiln residence time refers to the time at which the pyrolyzer holds the highest heating temperature. Longer residence time combined with high heating temperature allows complete carbonization of feedstock, producing a biochar with low O/C ratio and high surface area. Therefore, biochar produced using longer kiln residence time and high heating temperature has greater stability (ability of biochar to resist decomposition) and greater nutrient holding capacity (ability of biochar to adsorb nutrients) owing to the higher surface area (Cox et al., 2012).

2.1.2 Engineered biochar

Studies have shown the unique properties of biochars make them more suitable for a particular application than others. For instance, biochars with high surface area are desirable for adsorbing metals from waste water and high C: N ratio biochar are suitable for carbon sequestration (Kookana et al., 2011). Opportunities exist to produce engineered biochars by matching biochar properties to those required for a specific application. Mixing feedstocks
from different streams could be one of the ways to acquire beneficial properties of different feedstocks into biochar. For example, blending biosolids with greenwaste as feedstock for pyrolysis may produce a biochar with high nutrient content and also high carbon content, giving the advantage of increased nutrient content and carbon sequestration. Choosing biosolids as a feedstock and using pyrolysis temperatures of 500 °C, conserves 50% of the feedstock nitrogen, possesses moderate CEC and high specific surface area which makes it a suitable biochar for improving the nutrient status of degraded soils (Bridle and Pritchard, 2004). Hence, by choosing a right feedstock and controlling the pyrolysis temperature, it is possible to produce engineered biochars suitable for specific applications.

2.2 Growing media

Biochar has been widely used as a soil amendment, however, the practical application has been limited owing to the large volume requirement and high production cost of biochar, currently around USD $1000 per tonne (Homagain et al., 2016). A more viable option may be the use in high value applications such as plant/ horticultural growing media which have a higher economic return to offset the production cost.

Growing media are soilless mixture of substrates that are used but not limited to ornamental horticulture container plant production (Handreck and Black, 2010). Other uses of growing media are in green roofs, containerized vegetable production and in parks/gardens. There is no single media that can be used for all purposes but generally, most of the growing media exhibit some of the following characteristics: low bulk density, high porosity, low inherent fertility, neutral pH, high water holding capacity, high cation exchange capacity, high stability, no pathogens and low cost (Handreck and Black, 2010). Organic components of growing media such as peat and compost have the ability to deliver most of the desirable characteristics such has high water holding capacity, high cation exchange capacity and low
bulk density (Landis, 1990). However, relatively faster decomposition of these organic matter rich substrates reduces porosity over time (Landis and Morgan, 2009). Mixing with inorganic bulking materials such as perlite and vermiculite ($USD 250-300 per m$^3$) maintain critical characteristics whilst minimising cost (Auspearl, 2017). Nevertheless, growing environmental concerns about the use of peat moss in particular, is driving horticultural research to find an environmentally friendly alternative to these components which may also save fertilizer and water inputs (Landis and Morgan, 2009). Additionally, heat intensive vermiculite production and non-renewable peat have large carbon footprints (Dumroese et al., 2011). A few studies have examined the use of biochar as an alternative to the peat and vermiculite in growing media (Dumroese et al., 2011; Headlee et al., 2013). Many characteristics of biochar such as the high surface area, increased water holding capacity, high porosity, adjustable particle size, potential to increase nutrient efficiency, desirable bulk density makes it an attractive option for use in media (Licht et al., 2013). It is vital to understand the properties of biochar and the resulting effects of addition of biochar on physical and chemical properties of growing media before recommending biochar as a growing media amendment.

Growing media in containerized plant production is generally used for a relatively short duration (months to year) however it should also be noted that in some of the situations growing media are used for longer term, such as while out planting tree seedlings, in public spaces such as parks and gardens and in green roofs. Resistance of biochar to chemical, physical and biological weathering could be an advantage for these long term applications of growing media.

2.2.1 Impact of biochar on growing media physical properties

2.2.1.1 Water holding capacity
Biochars have high specific surface area which means more water is held at higher negative matric potentials (when biochar gets drier) giving them advantage of high water holding capacity (Basso et al., 2013). At more negative potentials, water retention is controlled mainly by adsorptive forces and is influenced by the total surface area of particles per unit mass (McKenzie et al., 2002). Most of the high temperature manure and wood based biochars (> 500 °C) have high surface area and high porosity (Downie, 2009) which give them the potential to form aggregates with minerals and organic matter, ultimately leading to increased water holding capacity (WHC) (Glaser et al., 2002; Lei and Zhang, 2013). Furthermore, high temperature biochar consists mainly of micropores, which play major role on holding water at higher matric potential. Thus addition of high temperature greenwaste biochar to sand was able to hold and make water available to plants during dry periods (Brockhoff et al., 2010; Devereux et al., 2013; Verheijen et al., 2009). In the case of growing media, Dumroese et al. (2011) found a 3:1 ratio of peat: biochar pellet on dry mass basis (500 °C) improved WHC by 10%. Larger rates of biochar addition have shown to be more beneficial than smaller rates for improving poor structured media (Altland and Locke, 2012; Brockhoff et al., 2010). For instance, adding 25% biochar to sand stored 260% more water when compared with addition of 5% biochar to sand (Brockhoff et al., 2010). In another study, 25% pelleted biochar mixed with peat on a volume basis increased WHC of media (Dumroese et al., 2011). Further studies need to be conducted to determine the optimum rate of use of biochar in growing media to provide optimum WHC whilst maintaining plant performance comparable to the standard growing media.

2.2.1.2 Pore size distribution

Pore size distribution (PSD) is an important property of growing media as it governs the retention and loss of water, which in turn affects WHC (Kevin and Black, 2010). The ability of
growing media to supply oxygen and water to plant roots is determined by the macro and meso pores within the range of 10-450 µm (Drzal et al., 1999). PSD is known to be greatly affected by physical and chemical attributes of growing media such as: particle size distribution, particle size arrangement, aggregate size, porosity, CEC, Ca and Mg content (McKenzie et al., 2002; Talha et al., 1979) Wetting and drying cycles have also been identified as key factors for changes in PSD of soil over time mainly by altering the arrangement of particle size and causing particle breakdown (Bodner et al., 2013). Similarly, wetting and drying cycles of biochar amended growing media may cause changes to surface characteristics and the physical integrity of biochar. Tian et al. (2012) measured the stability of biochar in media by performing particle size analysis of media at the start and end of an incubation experiment and found that biochar improves media stability. They found that the addition of biochar in the media increased the percentage of particles in the desirable range (0.25-2 mm) which is important for sufficient gaseous exchange and water retention. However, measuring physical breakdown without considering the effect of wetting and drying cycles is unlikely to give a realistic estimate of stability both the physical and chemical stability of biochar amended growing media.

2.2.1.3 Bulk density

Bulk density (BD) is an indicator of compaction in growing media which has a direct impact on growth of plant roots (Kevin and Black, 2010). Biochar is a low BD material and may be physiochemically stable for long period of time (Dumroese et al., 2011). In the context of growing media, progressive addition of biochar pellets to replace peat, resulted a slight increase in the BD of media due to relative high BD of biochar in comparison to low BD peat (Dumroese et al., 2011). However, biochar still has lower BD in comparison to other common inorganic bulking substrates such scoria and sand which are generally added to growing media for
longevity (Sohi et al., 2013). Biochar may be able to replace high BD bulking substrates and serve multiple advantages by lowering the BD and providing the long term stability for growing media. A stable BD also means that porosity and drainage capacity of media is not compromised in the longer term (Kevin and Black, 2010). Furthermore, low BD is favourable for growing media due to ease of transportation (Cox et al., 2012). It is vital to have media with lower and stable BD for long growth cycle plants where it is desirable not to top up or replace the media. Stable BD of biochar in growing media is even more important for the applications where the growing media is used for long time such as for green roofs and public parks and gardens.

2.2.2 Impact of biochar on growing media chemical properties

2.2.2.1 Cation exchange capacity and pH

Organic substrates such as peat and composts used in growing media have a higher CEC than biochar, however, other bulking substrates such as sand and pine bark have comparatively lower CEC than that of biochar. CEC of biochar ranges from 3 - 85 cmolc kg\(^{-1}\) depending on the pyrolysis temperature and feedstock (Mukome et al., 2013). Growing media with high CEC is preferred as it can hold nutrients and protect against leaching loss (Handreck and Black, 2010). In case of biochar amended growing media, addition of 25% biochar to peat based media, produces a media with a CEC of 20 cmolc kg\(^{-1}\) which did not change when remeasured after 12 weeks (Headlee et al., 2013). There is only one study looking at the short term CEC changes of biochar amended growing media (Headlee et al., 2013) and no studies on investigating long term changes in CEC of biochar amended media. Depending on the feedstock, most biochars are alkaline (ranges from 7.8-10.9). Most commercial growing media are acidic due to the acidic nature of substrates such as peat and pine bark, therefore, lime is added at the time of formulation of media to bring the pH into
desirable range (Handreck and Black, 2010). The addition of alkaline biochar to acidic growing media may provide a beneficial liming effect.

**2.2.2.2 Nutrient release**

Biochar contains a range of nutrients that reflect feedstock and pyrolysis temperature, and these nutrients become plant available once the biochar is applied to media. Manure and biosolids based biochar have a high ash content, typically range from 30-55% and contain appreciable amounts of macronutrients such as Ca, P, Mg, K, S and other trace elements (Jha et al., 2010). Phosphorus from high ash biochars has been shown to be steadily realised over time indicating that biochar may be a source of slow release P. As might be expected smaller particle size of biochar has been shown to lead to higher release of P, K and Mg (Angst and Sohi, 2013). In a sand based media containing biochar, the concentration of Na, organic C, P and K was increased in the pore water as compared to control sand column without biochar which demonstrates the nutrient release property of biochar (Brockhoff et al., 2010). In an experiment simulating artificial weathering of biochar by exposing biochar to solutions with different pH, Kim et al. (2013) found increase in release of nutrients from biochar at lower pH. Therefore, incorporation of biochar to acidic growing media with pH of 4.5-5 may encourage the release of nutrients from biochar. Nutrient release from biochar amended growing media was also demonstrated in a short term (30 days) laboratory incubation study which showed increasing levels of Fe, K, Na, P, and B in press water extracts with increasing rate of wood based biochar pellets (Dumroese et al., 2011). Although press water extract gives an approximate estimate of how much nutrient can be extracted from the biochar amended media, it is not possible to predict the release of nutrient from biochar and their plant availability by analysing the press water extracts. Press water extracts are measured while the media is under saturated condition, whereas, pore samplers extract water from pores of
media under variable moisture conditions which would normally occur in practical situations. Furthermore, nutrient present in pore water of the growing media is more likely to be plant available, therefore, use of pore water samplers to extract pore water in real time is a more appropriate method to measure plant available nutrients than using press water extract.

2.2.3 Impact of biochar on growing media nutrient dynamics

2.2.3.1 Nutrient sorption and leaching

The capacity of biochar to chemically react with nutrients is due to its high surface area, a function of internal microporosity and, external surface area. The CEC of biochar, also helps to reduce loss of those nutrients via leaching (Hale et al., 2013). Biochars are often steam activated during pyrolysis in order to increase the surface area (Downie, 2009) and this may almost double retention of N and P (Borchard et al., 2012). Sorption and nutrient leaching properties of biochar vary with type of feedstock. For instance, (Hollister et al., 2013) found that oak and corn biochar produced at 350 °C was able to adsorb ammonium, only corn biochar adsorbed nitrate and none of the biochars were able to adsorb phosphate. On the other hand, out of thirteen biochars tested by Yao et al. (2012), they found only nine high temperature (600°C) wood based biochar able to adsorb ammonium and none of the biochars were able to adsorb nitrate and phosphate. These studies indicate presence of permanent negative charge on the biochar surface which enables them to adsorb cations such as ammonium in favour of anions such as phosphate and nitrate. Ability of biochar to store nitrate challenges ionic charge as a mechanism for surface interactions. Further study need to be conducted to investigate the mechanism of nitrate storage in biochar versus phosphate.

There are limited studies on nutrient sorption and subsequent leaching from fertilized biochar amended growing media. However, in one such experiment, there was lower initial nitrate release followed by higher residual nitrate release over time (Altland and Locke, 2012). This
suggests that biochar might be effective in moderating the fluctuations of nitrate levels in growing media over time. In the same experiment, phosphate concentration of the leachate had a similar trend, with higher phosphate concentrations in later leaching events and additional phosphate levels in leachate from biochar amended media as compared to media without biochar. This suggests that biochar can be a modest source of phosphate for growing media (Altland and Locke, 2012).

The effect of biochar on release properties of nitrogen, phosphate and other macronutrients has implications for managing the timing and rate of fertilizer additions to growing media. Therefore there needs to be more in depth studies to understand the nitrogen and phosphorus dynamics in biochar amended growing media in order to improve decision making around container plant nutrition and potentially reduce costs through lowered fertilizer use. Furthermore, the ability of some biochars to adsorb ammonium and phosphate may reduce leaching from containerised plants and thus reduce water pollution (Novak et al., 2014b). This reduction in nitrogen and phosphorus leaching from fertilized media is explored further in this thesis.

2.2.3.2 Nitrogen dynamics

Nitrogen is an essential plant nutrient and research has shown that the addition of biochar to soil affects the transformations of N by influencing nitrification, adsorbing ammonium and altering N₂O and ammonia emissions (Clough and Condron, 2010). Although, N present in low temperature biochars (250-500 °C) has been found to be available for microbes (de la Rosa and Knicker, 2011), availability of nitrogen is drastically reduced once the pyrolysis temperature exceeds 550 °C (Wang et al., 2012a). Nitrogen loss, through volatilization during high temperature pyrolysis is significant, reducing the N concentration of biochars to around 0.5-0.7% N (Downie, 2009). The volatile nitrogen is released either as volatile nitrogen
compounds in the tar phase or as nitrogen containing gaseous species, including N₂, some of which are NOx precursors, and can then be oxidized to NOx during subsequent combustion. This process is more applicable for the feedstock with high nitrogen content so an innovative low NOx emission pyrolysis technology should be used to pyrolyze these high nitrogen feedstocks (Chen et al., 2012). The rest of the feedstock nitrogen is retained in the resultant biochar, mainly in inaccessible form inside the aromatic structure of biochar, which could be the explanation for low levels of N in pore water and leachate of fertilizer free high temperature biochar amended media (Altland and Locke, 2012). There are only handful of studies investigating nitrogen dynamics from biochar amended growing media, with a primary focus on loss of nitrogen through leaching (Altland and Locke, 2012; Headlee et al., 2013).

2.2.3.2.1 Influence of biochar on N₂O emission

Nitrous oxide (N₂O) is one of the pathways for N loss under anaerobic conditions in soil. The N cycle is intrinsically linked to moisture status of soil/media as it controls the substrate (nitrate) through nitrification and microbially mediated denitrification to N₂O and N₂ (Cameron et al., 2013). As biochar improves physical properties of media such as aeration and water holding capacity, it can also affect N₂O emission (Case et al., 2012). Although growing media are naturally freely draining, denitrification may still occur with reports of up to 21% of applied N lost (Agner and Schenk, 2005) compared with 20-45% in soils (Abbasi and Adams, 2000). Anaerobic microsites may occur in the growing media. Currently there are no published studies that investigate the effects of biochar on N₂O emission from growing media.

Any change in N₂O emission depends both on biochar (Van Zwieten et al., 2010c) and soil properties (Spokas et al., 2009; Yoo and Kang, 2012) and thus a decrease in N₂O emission (Angst et al., 2013; Felber et al., 2013; Khan et al., 2013; Lia et al., 2013; Singh et al., 2010b;
Van Zwieten et al., 2010c) and no effect on N$_2$O emission (Case et al., 2014; Díaz-Rojas et al., 2014) have been reported.

Many physical, chemical and biological mechanisms have been suggested for reduced N$_2$O emission from biochar amended soil. In a study with biochar amended sterile soil there was no N$_2$O production which suggests that biotic mechanisms play a significant role in controlling emissions (Cayuela et al., 2013). Some biological related mechanisms responsible for reducing N$_2$O from biochar amended soil are; reduced nitrate availability to denitrifiers (Cayuela et al., 2013; Felber et al., 2013) and the toxic effect of poly aromatic hydrocarbons (PAH) and phenolic compounds to microorganisms (Wang et al., 2013b) resulting in change in microbial community structure (Wang et al., 2013a). A new biological mechanistic explanation is the role of biochar as an electron shuttle, transferring electrons to microorganisms and thus facilitating reduction of N$_2$O emissions (Cayuela et al., 2013). Briones (2012) presented a similar perspective, however, gave importance to synergistic interactions of biochar and humic substances facilitating enhanced electron transfer thus connecting reactive biochar surfaces with the microorganisms.

Some of the proposed chemical mechanisms are: sorption of ammonium by the biochar surfaces (Dempster et al., 2012); presence of volatile compounds (Ameloot et al., 2013); short term retention of nitrate by internal biochar surfaces (Ameloot et al., 2013); an increase in soil pH (Wang et al., 2013a) and; an increase in the buffering capacity of biochar (Cayuela et al., 2013). In a recent study Kammann et al. (2015) have shown nitrate capture as the mechanism for reduced N$_2$O emission from application of co-composted biochar to soil. They also hypothesized that nitrate capture may influence the ratio of electron donors to acceptors (labile organic carbon to nitrate) which promotes nosZ gene activity responsible for complete reduction to N$_2$, thereby lowering N$_2$O/N$_2$ ratios.
On the other hand, a study has shown that N$_2$O is sorbed to the biochar surface (Cornelissen et al., 2013) which suggests physical mechanisms. However, many other competitive factors for sorption sites such as water, CO$_2$, organic matter and their effect on sorption capacity of biochars need further investigation (Kettunen and Saarnio, 2013). Other physical factors related mechanisms that have been suggested for reduced N$_2$O emissions are: increased aeration (Singh et al., 2010b) and improvement in soil moisture due to greater WHC of biochar (Saarnio et al., 2013; Wang et al., 2013a).

It should be taken into consideration that these all mechanisms refer to short term changes; long term N dynamics and mechanisms for N$_2$O reduction under long term agricultural field conditions is still unclear. In addition to this, as every biochar and soil are different, N$_2$O emission from each system needs to be tested before making any recommendations.

2.2.3.3 Impact of biochar on phosphorus dynamics

High ash biochars, particularly those produced from biosolids generally contain 1-2% P, which when applied to soil, steadily release P over time indicating that biochar may be a source of slow release P (Angst and Sohi, 2013; Wang et al., 2012b). Similar release of P has been observed in pore water from an unfertilized sand amended with switchgrass biochar (Brockhoff et al., 2010). Further, in an indirect measure of P availability, with biosolids based biochar, Wang et al. (2012b) found the biochar was to be equally effective as other P fertilizers such as calcium dihydrogen phosphate and phosphate rock even after six harvests of five weeks old ryegrass. Finally an experiment using a risk husk biochar in growing media showed a higher concentration of P in consecutive leaching events, therefore, recommended the biochar as a useful source of P for ornamental plant production (Altland and Locke, 2012).

There are a lack of holistic studies investigating phosphorus use efficiency from biochar.
amended growing media considering the leaching loss, plant uptake and media storage of P. Also the effect of biochar on the availability of sorbed P is not clear.

A number of mechanisms have been postulated for the adsorption of P by biochar amended soils: complexation of P with cations added with biochar such as Ca and Mg (Parvage et al., 2013) and binding of P to positively charged metal complexes formed on biochar surfaces (DeLuca et al., 2009; Yao et al., 2011). Phosphate sorption from aqueous solution by biochar has been associated with the binding of P with nano-sized MgO particles present on the surface of biochar (Yao et al., 2011). According to Pathan et al. (2002) biochar retained P by adsorption on Al- and Fe-oxides and/or by precipitation as Al-P or Fe-P. These mechanisms may also be relevant for adsorption of P by biochars in growing media.

2.3 Plant growth in biochar amended growing media

Most of the studies looked at biochar in growing media have also looked at plant growth parameters. These studies generally show an increase in plant growth with addition of 5-50% biochar on a volume basis (Graber et al., 2010; Tian et al., 2012; Zhang et al., 2013). Some studies also show equivalent plant growth between biochar amended and standard growing media (Headlee et al., 2013; Vaughn et al., 2013). Various mechanisms have been suggested for this increased plant productivity namely: increased retention of nutrients in leaching environments (Headlee et al., 2013; Tian et al., 2012; Zhang et al., 2014b); improved particle size distribution of the media which eventually improves media porosity (Zhang et al., 2014b) and; improved the beneficial plant growth promoting microbial population (Graber et al., 2010). In addition to increased plant growth, biochar application has also found to increase plant tissue concentration of K, N, P and Ca (Biederman and Harpole, 2013). Availability of these nutrients to plant is further improved by the liming effect of biochar (Rajkovich et al., 2012). This increased concentration of nutrients in plant biomass is due to increased
availability of nutrients to plants as biochar reduces loss of those nutrients through leaching (Laird et al., 2010).

2.4 Biochar as a soil amendment

Biochar has been widely used in soil as an amendment with the aim of improving of physical and chemical properties of soil. The impact of biochar on soil properties depends on the type of biochar used and the properties of the soil (Kookana et al., 2011). To date, the most appropriate soils for biochar use appear to be sandy soils and the least appropriate are clayey soils. Generally, the application of biochar to sandy, acidic and tropical soils has been successful in increasing water holding capacity (WHC), increasing nutrient availability and reducing nutrient leaching and greenhouse gas emissions (Jeffery et al., 2011). As acidic, sandy soils have very low pH, cation exchange capacity (CEC) and WHC, application of biochar helps to increase the pH, CEC and WHC, thus improving the soil properties. Field studies show that impact of biochar on nutritional and physical properties of alkaline, temperate and clayey soil is lower than in sandy soil. As alkaline and clayey soils already have higher CEC and more desirable pH, the application of biochar makes little difference to soil properties (Schmidt et al., 2014). Apart from variation on leaching properties with different types of biochar, the effect of biochar on leaching of nutrient also depends on type of soil used (Yao et al., 2012). Nitrate and ammonium leaching was reduced in biochar amended coarse acidic agricultural sand, thus reducing fertilizer requirement (Brockhoff et al., 2010; Dempster et al., 2012). Whereas, biochar application did not have significant effect on leaching loss on clay textured and alkaline soils. Laird et al. (2010) reported 11% and 69% reduction on nitrogen and phosphorus leaching, respectively from sandy soil amended with biochar.

Once biochar is applied to soil, it is likely to stay there for hundreds of years, therefore, it is important to understand the long term impact of biochar on soil properties. Short term lab
incubation based studies show positive impact of biochar ageing on soil properties due to increased surface oxidation of biochar (Nguyen et al., 2009), whereas, field based experiments show ineffectiveness of biochar in improving plant growth (Schmidt et al., 2014) and reducing nitrous oxide emissions (Spokas, 2013) in long term.

2.5 Biochar stability

Due to the recalcitrant chemical structure, biochar is more stable than most other organic matter (Cheng et al., 2008) with estimates of stability of between 100-1000 years (Glaser et al., 2002). These estimates have been obtained using oxygen to carbon ratio method under laboratory conditions. Major et al. (2010) examined the fate of biochars prepared from pruning waste and found they could be rated with a mean residence time (the average time that biochar persists in the soil) of more than 600 years with less than 3% of biochar lost. Proximate analysis (a measure of fixed carbon), O: C ratio and H: C ratio are the three common methods used to determine the stability of biochar. Out of three different methods, O: C ratio had highest correlation with mean residence time of biochar suggesting O: C ratio is the best predictor of the stability of any biochar in soil (Crombie et al., 2013).

Chemical stability refers to the surface oxidation/ surface chemical changes of biochar over time. Spectral analysis of the ‘terra preta’ soils, has shown considerable surface oxidation, nevertheless, the material was not readily mineralized (Liang et al., 2008). This long term stability was further confirmed by Nguyen and Lehmann (2009), showing that oxidation of biochar surfaces mostly occurs in the first 10 years. Surface oxidation has also reported to occur in less than four weeks (LeCroy et al., 2013).

Physical stability is also an important characteristic of biochar and changes in particle size distribution may be used to assess this. A study investigated breakdown of biochar in media using particle size of media before and after the experiment and found the least change in
Many factors affect the overall stability of biochar, mainly pyrolysis temperature, feedstock choice and also soil properties such as soil moisture, soil temperature and soil pH. Mineralization of biochar increased with increase in incubation temperature. Relatively recalcitrant biochar produced at 600 °C was less sensitive to incubation temperature than low temperature biochar. Furthermore, temperature induced oxidation was different with different feedstock with surface of oak biochar more oxidized than corn biochar (Nguyen et al., 2010). Generally wood based biochars are shown to be more stable than biochar from non-wood feedstock due to higher lignin content as measured by the fixed carbon content (Singh and Cowie, 2010).

2.6 Biochar ageing

Although very slowly, biochar does undergo some changes over time (Cheng and Lehmann, 2009). In case of natural ageing, increase of surface negative charges was found with ageing of biochar samples and these changes correlated well with both incubation temperature and incubation time. Among the biochars incubated at range of temperatures from 20-70 °C from period of 1-12 months, the biochar incubated at 70°C for 12 months displayed the highest surface negative charge of 20 cmolc /kg (Cheng and Lehmann, 2009). Other properties such as pH, CEC and carboxylic and phenolic functional groups also increased with ageing over a 12 months period. In the case of ageing of sawdust biochar, for 12 months under field conditions, further laboratory testing showed a reduction of adsorption capacity (Spokas, 2013). This reduction in sorption capacity of aged biochar could be due to clogging of the pores by the organic material present in soil. Addition of aged biochar to soil has been shown to alter nutrient holding capacity and aggregate structure (Nguyen et al., 2009). Therefore, it
is important to understand impact of ageing of biochar on physical and chemical properties of soil.

A common way to predict long term effect of biochar is by artificially ageing the biochar (Hale et al., 2011). Ageing of biochar also leads to surface oxidation which increases the reactivity of biochar (Nguyen et al., 2009). Biochars have been aged artificially using chemical and physical factors (Hale et al., 2011). They found chemical ageing by subjecting biochar to temperatures of around 110 °C increases the biochar CEC by almost 50% and was most effective to change physiochemical properties of biochar. However, significant energy costs associated with this method could be a major drawback.

2.7 Co-composting biochar

Surface oxidation makes biochar more reactive and this reactivity can be increased due to weathering in soil (Liang et al., 2006; Spokas, 2013). Such weathering/ageing process may be faster if biochar is composted together with organic materials (Vandecasteele et al., 2016). Composting biochar together with other organic matter such as manures, green waste is increasingly used as a tool to condition biochar and to also improve the composting process. The idea of co-composting comes from “terra-preta concept” quote earlier section and use the same terminology (Solomon et al., 2007). A successful method to speed up lab-scale ageing of biochar is to continuously heat biochar at 110 °C for period of eight weeks (Hale et al., 2011). However, heating inhibits microbial processes and also lacks interaction with organic matter and these have been shown to be a very important component of the natural biochar weathering process (Cheng et al., 2006; Hale et al., 2011). Co-composting – a process of composting of biochar with other organic materials, provides all the precursors required for natural ageing with more subdued temperature fluctuation along with interaction with organic matter and increase in microbial activity (Kammann et al., 2015). Such bio-oxidative
environment present in composting caused an almost sixfold increase in CEC of hardwood and poultry litter biochars (Khan et al., 2016; Prost et al., 2013). The mechanism of increased reactivity of biochar during composting appears to be the increase of oxygen containing functional groups mainly phenolic and carboxylic groups (Wiedner et al., 2015) and sorption of organic matter compounds on the biochar surface (Wang et al., 2014). Other than the increase in CEC of biochar, co-composting biochar especially with manure has been shown to increase the concentration of nutrients such as N, P and K on the biochar. Properties of biochar such as stability, nutrient sorption ability and porosity makes it an excellent bulking material for composting (Steiner et al., 2011). Furthermore, biochar also helped the composting process by speeding composting process, optimizing aeration, avoiding compaction of compost piles and helping the compost to maintain optimum moisture content (Sanchez-Garcia et al., 2015; Steiner et al., 2010; Vandecasteele et al., 2016). Biochar has also been shown to adsorb ammonia and water soluble ammonium during composting with poultry manure thus reducing nitrogen loss from the composting process (Steiner et al., 2010). Reduction of ammonia emission during first week was also found during co-composting biochar with sludge and woodchips (Malinska et al., 2014).

Addition of biochar to composts has also been shown to reduce greenhouse gas emission during composting process. Biochar increased porosity of the compost mixture during co-composting of manure and biochar which resulted in reduced activity of methanogens, ultimately reducing methane gas emission during the composting process (Sonoki et al., 2013) found during co-composting of manure and biochar, methane gas emission was reduced as a result of reduction of activity of methanogens because of increase in porosity. In another study involving co-composting biochar with pig manure, emission of N₂O gas was reduced which was attributed to higher abundance of nosZ genes resulting in complete denitrification.
(Wang et al., 2013a). However, the overall result may not be climate neutral as the application of those co-composted biochar to soil increased N₂O emissions by 45% as compared to non-composted biochar due to organic compounds and nitrogen sorbed by biochar during composting (Borchard et al., 2014).

Among various rates of biochar are used for co-composting (from 1% to 30% on volume basis) (Zhang et al., 2014a), 10% seems to be most commonly used rate. In previous studies, biochar has been composted with various organic materials including poultry manure, cattle manure, straw, biosolids, spent mushroom and green waste (Schulz et al., 2013; Zhang and Sun, 2014). There are no studies reported on composting food waste with biochar. High amount of organic acids such as propionic and butyric acids are produced during composting of food waste as compared to other waste streams such as manures and biosolids (Yu and Huang, 2009). Furthermore, low pH of food waste (5 - 6) during initial phase of composting causes low microbial activity (Yu and Huang, 2009). Generally, biochar has high pH (7 - 9), therefore adding biochar to the food waste compost may help the composting process by raising the initial pH of the compost mix and increasing the microbial activity. The organic acids produced during composting of food waste may oxidize the biochar surface causing surface ageing. Therefore, there could be positive synergy of composting food waste with biochar in terms of raising initial compost pH and ageing of biochar surface.

The agronomic effectiveness of composted biochars have given mixed results. Another study with co-composted wood biochar showed a 305% increase in plant growth relative to non-composted biochar due to higher nitrate capture in co-composted biochar which later gets released for use by plants (Kammann et al., 2015). A study looking at improvement in vineyard growth for three year period showed non-significant effect of co-composted wood biochar on vine growth (Schmidt et al., 2014). Although, studies show that the biochar can be
successfully aged and conditioned with respect to CEC and nutrient value by co-composting, this may or may not have agronomic benefits. Therefore, it is important to test the effects of co-composted biochar on soil properties and plant growth before recommending its field application.

2.8 Contaminants in biochar

2.8.1 Organic contaminants

Generally, biochar has some amount of organic contaminants such as PAH, and polychlorinated dibenzodioxins/dibenzofuransdioxins (PCDD/F). The concentration of PAH and PCDD/F in biochars depend on pyrolysis temperature and speed as they are formed during the process of pyrolysis. Thermal breakdown of organic matter together with chlorinated compounds occurs during pyrolysis and when these compounds cool down and condense, the molecular rearrangement causes formation of PCDD/F PCDD/F (Tuppurainen et al., 1998). Maximum formation of PCDD/F occurs at approximately 300 °C (Tuppurainen et al., 1998) and biochars produced between 350-500 °C generally contain high concentration of PAH (Wang et al., 2013b). Higher temperature (> 500°C) and slow pyrolysis conditions tends to produce biochars with below detection levels of PAH (Downie et al., 2012; Hale et al., 2012). Artificial ageing increased concentration of PAH in all 50 biochars tested by Hale et al. (2012) possibly due to removal of hydrophilic compounds therefore exposure of PAH after ageing. However, bioavailability of PAH decreased after ageing and this may be due to increased sorption of PAH to the biochar surface due to ageing induced increased negative charges (Hale et al., 2012).

2.8.2 Inorganic contaminants

Heavy metal concentration of biochar depends on the feedstock source, with greater concentration of heavy metal has been found in biosolids based feedstock as compared to
greenwaste. The concentration of Cd, Ni and As in biosolids ranges from 0.5-85 mg kg⁻¹, concentration of Cu and Cr and Zn ranges from 23-4300 mg kg⁻¹ and Pb from 35-480 mg kg⁻¹ (Agrafioti et al., 2013). In case of greenwaste, although some heavy metals are present, the concentration of those metals are very low. For instance, concentration of heavy metals such as Cd, Cr, Mn and Bo ranges from 0.1- 15 mg kg⁻¹ while Zn concentration ranges from 22- 440 mg kg⁻¹ (Gaskin et al., 2008; Singh et al., 2010a). In general, industrial biosolids have higher heavy metal contents than domestic ones and therefore contain greater concentration of heavy metals in the resulting biochar. Anaerobically digested biosolids had lower heavy metal concentration than fresh biosolids due to loss of heavy metals in the digestion effluent which shows the effect of treatment method of biosolids on the heavy metal concentration (Silveira et al., 2003). As compared to fresh biosolids, biochar produced at 300 °C significantly reduced release of heavy metals such as Pb, Cd, Zn, Cu into soil solution (Agrafioti et al., 2013). It is thought that with pyrolysis above 300 °C, the metals are encapsulated chemically into the aromatic structure (He et al., 2010). Temperatures lower than 300 °C is not sufficient to break the bonds of heavy metal, hence those lower temperatures do not alter the heavy metal speciation in the biochar (Hwang et al., 2007). Moreover, larger specific surface area of the high temperature biochars increases their absorptive capacity and helps to retain metals (He et al., 2010; Hwang et al., 2007). The plant availability of heavy metals present in biochar and further release of those heavy metals from aged biochar are not well studied.
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The comprehensive literature review shows that biochar properties vary considerably depending on the feedstock and temperature used to produce biochar. Therefore, a detailed characterization is appropriate for any new biochar product especially if intended for use as a growing media substrate. In this chapter a detailed characterization of a novel ‘urban’ biochar is conducted. The properties of urban biochar is then compared to the industry standard growing media in this third chapter in order to evaluate its potential as a growing media substrate.
CHAPTER 3

This chapter is based on a published article entitled:

Pyrolysis of urban waste streams: their potential as horticultural growing media. *Journal of analytical and applied pyrolysis* 112, 105-112.
Pyrolysis of urban waste streams: Their potential use as horticultural media

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Abstract
Biochar produced from mixture of biodegradable urban resources such as biosolids and greenwaste was slowly pyrolysed at 650 °C and characterised for its chemical and physical properties. The biochar was then compared to published values for growing media. It was found that this biochar has high surface area, inherent nutrient content, high porosity, high stability, desirable water holding capacity, air filled pore space and bulk density. Comparing the results of characterisation of this biochar with ideal potting substrate showed the highly porous and nutrient rich biochar were desirable however the high salt content was problematic. Fourier transform infrared analysis shows that carboxyl/carbonyl bands were very weak in biochar spectra due to loss of carboxyl groups in the decomposition of carbohydrates in high temperature pyrolysis which also contributed to low cation exchange capacity. The pyrolysis process has multiple advantages such as waste management, energy generation in the form of syngas and long term sequestration of carbon in biochar.

1. Introduction
Municipal wastes such as biosolid and greenwaste are becoming increasingly problematic with the increase and spread of urban populations. Traditionally biodegradable urban resources (BURS) such as greenwaste and biosolids were viewed as wastes and were often discarded to landfill. More recently BURS have been combined, composted and returned to land as a soil conditioner. However, issues of land availability primarily due to objections of odour as well as the emission of gases such as ammonia, nitrous oxide and methane limits large scale disposal on land [1]. In addition there is potential for heavy metal contamination of soils and aquifers. This disposal also often requires long distance transport out of the urban areas into adjacent rural areas which is costly both financially and environmentally. An alternative way of managing BURS is by converting them into biochar by pyrolysis at a centrally located urban location and then utilising the biochar products in urban applications, such as a substrate in growing media for green roofs, potted plants and urban landscaping. Growing medias are also used extensively on the urban fringe in market gardens for producing high value produce such as vegetables and cut flowers. Such BURS derived biochar can be mixed with pine bark, peat and sand for formulation of growing media. This approach offers multiple benefits such as, waste management, resource recovery, emission reduction, biomass energy production, reduced transport and carbon sequestration [2]. A few recent studies have shown that pyrolysed greenwaste and/or manure performs better than composted greenwaste and/or manure when considering nutritional and environmental factors [3–5]. BURS derived biochar, as used in the present study, may provide an innovative way of utilizing greenwaste and biosolids. The biochar product could potentially exhibit the combined benefits of fixed carbon and improved growing media structure from the greenwaste fraction, and nutrient supply from the biosolid residue [6]. Furthermore, the pyrolysis process generates syngas along with biochar, which can be used as an energy source to operate the plant thus making the system energy neutral [7,8].

A number of studies have investigated the suitability of biochar from a range of feedstocks as soil amendment [9–11] as well as a component of growing media [12–17]. Globally, peat is one of the common ingredients used in growing media although this is not
An ideal growing media should exhibit properties such as a balanced supply of nutrients, low bulk density, high water holding capacity, high stability and desirable particle size and air-filled porosity [19]. Studies show that biochar performs better or equal in respect to improving bulk density, stability, porosity and water holding capacity of growing media as compared to peat [14,15,18]. In fact, many characteristics of biochar such as high surface area, increased water holding capacity, high porosity, adjustable particle size, inherent nutrient content, and low bulk density have been shown to fit within the ideal range of substrate properties which may make it an attractive option for use in media [20]. However, there is a limited research on suitability of biochar for growing media substrate.

It is also proven from previous research that biochar produced under high temperature and slow pyrolysis (i.e. heating rates of \(8 \text{K min}^{-1}\)) have high porosity and high surface area [21]. Hence we have chosen the relatively high temperature of 650 \(^\circ\text{C}\) and slow pyrolysis conditions for production of this biochar. Research shows that biochar properties can vary significantly depending on the highest heating temperature, heating rate, and residence time of pyrolysis, and the feedstock characteristics [22]. Therefore, it is valuable to characterise each biochar to determine its suitability for any particular use. The authors are aware of one paper characterising biochar, from gasified wheat straw, for use specifically as growing media [23]. There are no studies on characterising slow pyrolysed biochar produced from a mixture of biosolids and greenwaste to determine its value as a component of growing media substrate.

In this paper we characterised biochar derived from mixture of two BURS, biosolids and greenwaste, by a range of chemical and physical methods to determine its properties in terms of its suitability for use in growth media. This includes analysis of physical properties such as pore size distribution, surface area, surface functional groups, and chemical assessment including major nutrient elements and heavy metals.

2. Materials and methods

2.1. Biochar feedstock

Fresh biosolids were sourced from Bangholme Eastern Treatment Plant (ETP), Victoria. Stabilisation of these biosolids was achieved through settling in primary sedimentation tanks, then pumping to anaerobic digesters. Digested sludge was then dried in sludge drying pans. The dried sludge was harvested during warm weather and stored for 3 years prior to pyrolysis. Moisture content of biosolids as received from treatment plant was 72 wt%. Biosolids and greenwaste were dried in a commercial dryer to a moisture content of 21 wt% and blended at a ratio of 2:1 (on dry basis) in a blender with an internal paddle. Greenwaste composed mainly of municipal softwood garden waste. This ratio was targeted for several reasons including; ensuring sufficient energy content of the feedstock blend on a wet basis, dilution of nutrients and heavy metals, and materials handling characteristics to facilitate processing, whilst keeping the feedstock as high in biosolids concentration as possible.

2.2. Biochar production

Feedstock was pyrolysed in a continuous pyrolyzer by Pacific Pyrolysis at a high heat treatment of 650 \(^\circ\text{C}\) with a residence time of approximately 40 min. Feed rate was controlled at 125 kg h\(^{-1}\).

Biochar used in this experiment is hereafter referred to as Urban Biochar (UB). UB yield was 46% in dry basis. The pyrolysis process was optimised for biochar and syngas production. The syngas were sampled from two points in the pyrolysis plant both before and after syngas cleaning. The syngas was initially passed through a heated particulate filter to remove entrained solids in the line and exclude them from the measured gas. Syngas was then drawn through a solvent to remove tars and oils. After that, the clean syngas was analysed using gas chromatography.

2.3. Feedstock and biochar analysis

The biochar and feedstock was subjected to a range of analysis. Chemical analysis included pH, EC, CEC, ultimate and proximate analysis, elemental and heavy metal composition, polycyclic aromatic hydrocarbons (PAH) and Fourier transform infrared (FTIR) spectroscopy. Physical analysis comprised of particle size distribution, pore size distribution, surface area and surface analysis including scanning electron imaging coupled with electro-dispersive X-ray.

2.3.1. Physical and chemical analysis

pH and EC of samples were measured on a 1:10 ratio of solid to water using a reciprocating shaker at 100 rpm for 18 h [24]. Cation exchange capacity (CEC) was measured according to the method of Rajkovich, et al. [25]. Air filled porosity and water holding capacity were measured as per the Australian Standard (AS) for potting mixes (AS 3743). Bulk density of both UB and feedstock was measured following method of Tian, et al. [17]. Proximate and ultimate analysis was carried out according to AS 1038.3, AS 1038.6.2 and AS 1038.6.1 using dried samples. Mineral and metal analysis for Al, As, Cd, Ca, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, and Zn were performed using samples digested by a modified dry-ash method [26] and quantified using inductive coupled plasma optical emission spectroscopy (Varian 720 ICP-OES). Surface area, pore volume, pore diameter and pore width parameters for a range of pores between 1.7 nm and 300 nm were determined from a nitrogen gas sorption isotherm, which was measured using a Tristar 3000 surface area and porosity analyser (Micrometrics Instrument Corporation, USA) in degassed samples (250 °C for 18 h on a vacuum line) at ~196 °C. The specific surface area of the sample was calculated by a standard multipoint Brunauer–Emmett–Teller (BET) method. Particle size analysis was performed by dry sieving. A 200 g sub sample was passed through vibrating test sieve shaker (The minor, Rowe Scientific Pvt. Ltd.) which had seven sieves with sizes from 4 mm to 65 \(\mu\text{m}\). Sieves were shaken at 3000 vibrations per min for 10 min. Sample remaining in each sieve was weighed and expressed on a mass percentage basis.

2.3.2. Functional group analysis

Diffuse reflectance mid-infrared spectra were recorded using PerkinElmer Spectrum One FTIR spectrometer (PerkinElmer, MA, USA) from 7800 to 450 cm\(^{-1}\) at 8 cm\(^{-1}\) resolution by co-adding the scans for one min. Spectra were corrected for atmospheric water vapour and \(\text{CO}_2\) with a background spectrum collected before running samples. PerkinElmer instrument control software (Spectrum 5.0.1) was used to identify and compare chemical functional groups.

2.3.3. Surface properties

Surface properties of feedstock and UB were analysed using PHI (FEI) XL30 ESEM TMP scanning electron microscope coupled with electro dispersive X-ray (SEM-EDX) operating at 20 kV to which a Si-Li detector EDX system had been interfaced. Samples were sputtered with gold coating prior to analysis.
3. Results and discussion

3.1. Chemical properties

Table 1 indicates the results of proximate and ultimate analysis for UB and feedstock samples on a dry basis. The proximate analysis provides the weight percentage of ash, volatile matter and fixed carbon. The ultimate analysis determines the weight fractions of non-mineral elements: carbon, hydrogen, nitrogen, sulphur and oxygen (by difference). The amount of fixed carbon, which is a function of feedstock source and pyrolysis temperature, shows the amount of stable carbon after all volatile carbon is removed at high temperature of 950 °C. There was an almost fivefold increase in the proportion of fixed carbon after pyrolysis of the feedstock (Table 1).

Table 1: Proximate and ultimate analysis of green waste, biosolids, feedstock (containing 2:1 ratio of biosolid to greenwaste) and urban biochar on dry ash free basis.

<table>
<thead>
<tr>
<th></th>
<th>Ash (%)</th>
<th>Volatile (%)</th>
<th>Fixed carbon (%)</th>
<th>Ultimate analysis (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Greenwaste</td>
<td>0.7</td>
<td>81.2</td>
<td>12.9</td>
<td>C: 46.9; H: 5.6; N: 0.2; S: 0.1; O: 41.3</td>
</tr>
<tr>
<td>Biosolids</td>
<td>49.3</td>
<td>40.0</td>
<td>6.4</td>
<td>C: 23.8; H: 3.7; N: 3.0; S: 0.9; O: 15.0</td>
</tr>
<tr>
<td>Feedstock</td>
<td>20.0</td>
<td>64.2</td>
<td>14.9</td>
<td>C: 39.1; H: 4.90; N: 1.20; S: 0.30; O: 33.3</td>
</tr>
<tr>
<td>Urban biochar</td>
<td>45.1</td>
<td>13.8</td>
<td>41.0</td>
<td>C: 74.4; H: 2.50; N: 0.70; S: 0.10; O: 7.80</td>
</tr>
</tbody>
</table>

This high fixed carbon content suggests that the UB is highly stable. As proximate analysis requires high temperatures (950 °C) for determination of volatile matter, this can inflate the estimate of fixed C by underestimation of ash content [22]. Therefore, molar ratio of O:C is considered a better indicator of stability. Crombie, et al. [27] suggested biochar with a molar O:C ratio in range of 0.2–0.6 could be expected to have mean residence time in soil of 100–1000 years. Our UB had a O:C molar ratio of 0.1 which suggest a mean residence time in soil of around 1000 years. Furthermore, [28] also found an inverse relation between O:C ratio and biochar stability. Therefore, our claim of similar or possibly greater mean residency time is indeed correct. Pyrolysis reduced the volatile content from 64 to 13% with a corresponding increase in fixed carbon in UB. This analysis also reveals that UB contains relatively higher ash (45%) than typical wood or crop residue based biochars [11] which would be expected from the 2:1 biosolid to greenwaste ratio of the feedstock. Wood waste contains mainly lignin and hemicellulose which results in lower ash content, whereas manure and biosolid waste consists of higher inorganic matter which results in higher ash content. The carbon content of the UB (74%), on ash free basis is comparable to other wood based biochars which typically range from 62–75% [11]. This gives UB the advantage of a potentially higher nutrient associated with ash component from biosolid and carbon sequestration value from carbon rich greenwaste, than biochar derived from a single feedstock. A balanced C:N ratio is important to growing media to maintain supply of nitrogen to plants. An ideal C:N ratio for a growing media should be around 30:1 [19]. UB has a high C:N ratio as shown by the proximate analysis (Table 1), however the C is likely to be in the recalcitrant fraction [29] which is inaccessible to microorganisms and this should minimise the potential for N immobilisation. High C:N ratio can also be fixed simply by adding more biosolid to feedstock which will lower the carbon content.

3.2. Nutrient and contaminants characteristics

Major cations, anions and heavy metals from acid digested UB and feedstock samples are shown in Table 2. Results show that heavy metals such as Cd, Pb, Cr, Cu, Ni, Zn are present in UB but at levels below those of the Victorian EPA C2 level classification which may allow unrestricted use of UB to growing media [30] and also within the permissible limit of USA EPA standards for land application of biosolids [31]. Analysis of feedstock components separately, suggests that almost all of the heavy metals originated from biosolid. Although biochars produced from biosolids feedstock are known to have heavy metals [32], Agrafruiti, et al. [33] found that pyrolysis at high temperature impregnates heavy metals in the matrix of biochar which decreases their bioavailability. This may mean that there is no risk of heavy metal contamination of the environment due to the application of UB as a growing media substrate.

Additionally, studies have shown that biochar may also contain poly aromatic hydrocarbons (PAH) [34,35]. Formation of PAH is dependant on pyrolysis temperature, feedstock and the rate of pyrolysis. High temperature slow pyrolysis biochars have lower PAH than low temperature fast pyrolysis biochars [36] and more specifically biochars based on wood and manure have been shown to have PAH levels below detection limits [37]. Consistent with the literature, UB produced through slow pyrolysis at 650 °C, did not contain PAH at the detection limit of 0.5 mg kg⁻¹.

Table 2: Elemental analysis of dry UB and feedstock mix from acid digested samples. Results have been given for individual feedstock components (biosolids and greenwaste) as well as the feedstock mix.

<table>
<thead>
<tr>
<th>Nutrients (mg g⁻¹)</th>
<th>Trace elements (μg g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>Fe</td>
</tr>
<tr>
<td>Biosolids</td>
<td>14.68</td>
</tr>
<tr>
<td>Greenwaste</td>
<td>nda</td>
</tr>
<tr>
<td>Feedstock mix</td>
<td>9.8</td>
</tr>
<tr>
<td>Biochar</td>
<td>11.5</td>
</tr>
</tbody>
</table>

* nda – Below detection level.
important property of biochar for nutrient retention [11]. Generally, the CEC of biochars are in the range of 3–69 cmol (+)/kg depending on feedstock source and pyrolysis temperature [40–42]. The CEC of UB was found to be 10 cmol (+)/kg which lies in the lower side of that range. CEC is temperature dependant with low temperature biochar having greater CEC than high temperature biochars [42]. There is also loss of acidic functional groups (Section 3.5) during pyrolysis at high temperatures which causes development of low CEC [21]. UB being a relatively high temperature biochar, it is not unusual to have a low CEC. Low CEC of UB is consistent with literature when compared to other high temperature biochars with similar feedstock [41].

3.3. Pore properties

UB was found to have a high surface area of 396 m² g⁻¹ and to be rich in mesoporosity, which is evident in average pore width (1.64 nm) and diameter (3.6 nm) values. The cumulative surface area and volume of pores were 23.34 m² g⁻¹ and 0.02 cm³ g⁻¹ respectively. It is known that the porosity of biochar increases with the temperature of pyrolysis mainly due to volatilization of tars present in the pores which cannot be removed under low temperatures [43]. The porosity of biochar also depends on feedstock with higher porosity observed in wood based feedstock due to presence of regular size and arrangement of plant cells [22]. UB was produced at high temperature from fine particles of biosolids, which may explain its high level of porosity, mainly mesoporosity. The high porosity may also help in increasing total air filled pore space (AFPS) of growing media. UB was found to have AFPS of 36.5% which is ideal for growing media [19]. Porosity is considered as an important feature of growing media. Substrate with high porosity allows air movement [19] and also provides habitat for microorganisms [44]. Similarly, water holding capacity of UB is 35% which is ideal for growing media [19].

The observed value for surface area of UB (396 m² g⁻¹) is on higher range when compared to other biochars mentioned in the literature, which range from 14 to 410 m² g⁻¹ [23,45]. This high surface area may be due to pyrolysis parameters such as high temperature and slow pyrolysis rate [21]. Bagreev, et al. [46] reported that surface area increases by almost three times when temperature of pyrolysis is increased from 400 to 950 °C with highest increases occurring after 600 °C.

The pore size distribution curve of UB is shown in Fig. 1. There is significant contribution of mesopores (between 2 and 50 nm) towards the porosity of UB. 67% of pores are between 2 and 50 nm. Only 24% are macropores (50–170 nm) and only 9% of the pores (calculated by difference) are micropores (<2 nm). The ash components of biochar, containing mainly iron, aluminium and silicon oxides have been shown to be the main source of mesoporosity [46]. From EDX spectra results of UB (Fig. 2), we found that it is rich in those inorganic oxides which may be source of the observed high mesoporosity of UB.

3.4. Particle size distribution

Table 3 shows that UB has wide distribution of particle sizes from 4 to 0.063 mm. Particle size distribution is mainly a function of the type of feedstock and pyrolysis temperature [22]. For UB, high temperature pyrolysis and friable feedstock such as biosolid seems to produce favourable conditions for finer particle size. [47] found that for a growing media, particles in the range of 0.25–2.0 mm is most effective in retaining water and also provide sufficient gas exchange to support vigorous plant growth. According to Handreck. [48], media with substrate particles smaller than 0.5 mm, and in particles smaller than 0.25 mm, have the highest influence on porosity and water retention. As 89% of UB is in the optimum range of 0.25–2.0 mm and 20% is below 0.5 mm, it could be an ideal component of growing media according to Handreck’s criteria. On the other hand, feedstock has only 17% particles in the optimum range. So, we found that pyrolysis alters the particle size distribution of feedstock to a more desirable range for growing media. UB also has some fine particles less than 65 μm which may pose some dust issues while mixing the media components. There may also be an issue with loss of media through carry-over, or entrainment during watering events of very small particles. On the positive side, these fine particles may improve water retention due to higher soil water conductivity [49]. Bulk density (BD) of UB was found to be 0.35 g cm⁻³, which falls in the ideal range (0.3–0.6 g cm⁻³) as suggested by Kevin and Black. [19]. Low bulk density is favourable for growing media due to ease of transportation [50].

3.5. Functional group analysis

The diffuse reflectance infrared spectra of UB, feed stock mix and its components, biosolids and greenwaste are shown in Fig. 2. The major intensities in the spectra and the corresponding functional group assignments are mentioned in Table 4. Spectra from feedstock samples were dominated by vegetal macromolecules as O–H bands (3640 cm⁻¹), C–H aliphatic bands (3000–2800 cm⁻¹), lignins moieties (1510–1500 cm⁻¹ and 1380–1330 cm⁻¹), ligno cellulose–hemicellulose complexes (1760–1740 cm⁻¹, 1460–1240 cm⁻¹) and carbohydrate peaks (1160–1040 cm⁻¹). These bands have almost disappeared in UB indicating decomposition of acetyl ester groups, phenols, and polysaccharides after pyrolysis, but were replaced by distinct aromatic bands at 3044, 1610, 1132 and 880–754 cm⁻¹. This indicates that labile compounds were lost in the form of O–H, C=O and C–H bands. ...
Fig. 2. Diffuse reflectance mid-infrared spectra (4000–450 cm⁻¹) of biosolids, green waste (softwood garden waste), feed stock mixture (biosolids + green waste at 2:1 ratio) and UB.

functional groups from the raw materials, possibly in the process of demethoxylation, demethylation and dehydration of lignins [21], which may concurrently lead to increased pore formation due to fused aromatic ring structures [46]. These inferences are in agreement with other results obtained for UB showing higher surface area and mesoporosity and increased proportions of fixed carbon in the form of polyaromatic molecules.

Kloss, et al. [21] ascribed carboxyl/carbonyl groups (1700 cm⁻¹) to contribute negative surface charges and cation retention in soils. As these bands were very weak in UB spectra due to loss of carboxyl groups in the decomposition of carbohydrates in high temperature pyrolysis, they contributed to low CEC in UB. Presence of low carboxyl groups is evident in high temperature pyrolysis biochars. Carboxyl groups are shown to develop on the biochar in the soil environment over time and hence resulting in very high CEC of terra-pret soils [51]. Studies on natural or artificial ageing and surface oxidation of biochar have indicated an increase in O-functionalities such as carboxyl group (1700, 1620 cm⁻¹) which can result in a longer term increase in CEC [52,53].

3.6. Surface properties

The SEM images (Fig. 3a and c) indicates that there are significant differences in surface structure between feedstock and UB. Fig. 3a shows a uniform surface with lesser pores and smooth edges in feedstock. However, after pyrolysis many well-defined small pores can be seen in UB (Fig. 3c). This result is in agreement with the result from pore size distribution and total surface area (Fig. 1) which shows high number of micropores and mesopores in UB. The escape of volatile matter during pyrolysis may help create pores in the biochar giving it high porosity [54]. This loss of volatile matter from feedstock due to pyrolysis is also supported by proximate analysis (Table 1).

The EDX spectra of feedstock and UB (Fig. 3b and d) shows that there is a wide range of nutrients present in UB such as, Ca, Mg, K, P and Fe. High calcium, potassium and iron peaks are consistent with elemental analysis and suggest potential source of those elements. This was consistent with chemical analysis of digested samples (Table 2) which also shows higher percentage of nutrients such as Ca, Mg, K, P and Fe. The amount of nutrients present on the surface of UB as shown by EDX was higher than the feedstock. This may have happened as EDX scans the surface of material and biosolids may have attached to the surface greenwaste woody structure during the process of feedstock mixing which condenses during pyrolysis giving higher concentration of elements.

3.7. Energy recovery

As the pyrolysis process (slow pyrolysis) was optimised to obtain high biochar yield, we observed less energy generated in

<table>
<thead>
<tr>
<th>Wave number (cm⁻¹)</th>
<th>Vibration mode, functional groups and molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td>3696, 3640, 3628</td>
<td>O−H stretch in Si–O–H molecules</td>
</tr>
<tr>
<td>3644</td>
<td>−3440 O−H stretch in phenols, N−H stretch in amides</td>
</tr>
<tr>
<td>2928 and 2854 or 3000–2800</td>
<td>Aliphatic C−H stretch in CH₃ and CH₂</td>
</tr>
<tr>
<td>2928</td>
<td>1760–1740 C−O stretch from esters in lignin, cellulose or hemicelluloses; C−O in ketones, aldehydes and carboxylic acids</td>
</tr>
<tr>
<td>1670–1640</td>
<td>1610–1590 Amide II C−O in primary amides; aromatic C−C ring structures</td>
</tr>
<tr>
<td>1510–1500</td>
<td>1460 Amorphous C−C stretch from lignin moieties</td>
</tr>
<tr>
<td>1426</td>
<td>1380–1330 Aromatic C−O stretch and aliphatic C−H deformation mode; C−O, COO⁻ and O−H stretch in phenolic groups</td>
</tr>
<tr>
<td>1270–1240</td>
<td>1150 C−O stretch in esters and phenols; O−H plane deformation</td>
</tr>
<tr>
<td>1132</td>
<td>1080–1040 C−OH stretch in aliphatic OH; C−O stretch in carbohydrates</td>
</tr>
<tr>
<td>880, 810, 754</td>
<td>50 Aromatic C−O stretch</td>
</tr>
</tbody>
</table>
comparison to other biosolids pyrolysis systems aimed at energy production [7,8,55]. The high heating value (HHV) of UB was found to be 7 MJ/Kg (dry basis) as compared to a HHV of 28 MJ/Kg (dry basis) from wood based biochar produced at 500 °C [56]. This lower HHV can be explained by the high ash content of biosolids feedstock as ash does not have an energy value. Gross calorific value (GCV) of the syngas was found to be 5.822 MJ/kg (dry basis). The pyrolysis process involved the re-use of the syngas in order to directly dry feedstock and to heat the kiln. This utilisation of syngas was shown to be energy neutral for this feedstock blend across the process, with no excess syngas available for electrical energy generation. The greenwaste portion of the feedstock had lower ash content, and therefore higher energy density, than the biosolids. This lower ash content means that the more greenwaste included in the blend the more syngas that will be produced and therefore a larger electrical energy output could also be expected.

4. Conclusion

The results show the UB has properties that are likely to be suitable for application as a major ingredient in growth media for a range of horticultural and plant nursery industries. This provides opportunities for resource recovery of BURS with benefits in terms of commercial production of growth media with environmental benefits from reduce greenhouse gas emissions and carbon sequestration. The process of pyrolyzing BURS generates UB with concurrent production of syngas energy to offset the direct carbon cost and energy used in processing. Analysis of this UB shows heavy metals and PAH’s were not present at a level to be concerned about, however longer term studies should monitor the fate of these contaminants. The ideal properties of growing media largely depend on the purpose of the media. For example, seedling mix has different properties to orchid mix or general growing mix. However, in general, it can be concluded that UB possesses desirable physical properties such as high water holding capacity, low bulk density, air filled pore space and high surface area.

Although the physical properties of UB were suitable for growing media, the chemical properties of UB, specifically the salt load was not ideal. However, this can be modified by using optimum rates of biochar to target EC. Similarly, as the C:N ratio was found to be high, a calculated dose of nitrogen fertilizer could be added to balance the C:N ratio and nutrients levels for plants. UB with low
C:N ratio can also be produced by reducing amount of greenwaste in feedstocks.

Further research is required to understand the interaction of UB with other added nutrients. UB may also bring other chemical, physical and biological changes to growing media such as nutrient mobility, water holding capacity and microbial activity. We are currently conducting experiments by partially replacing non-renewable media substrates with UB and investigating those physio-chemical and biological effects of UB to growing media.

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References


Connecting statements

From the chemical and physical characterization of urban biochar and its comparison with standard growing media properties, it is evident that urban biochar has potential to be used as a growing media substrate.

Fourth chapter further investigates the effects of urban biochar on various physical and chemical properties of a standard growing media. In order to achieve that, results of two laboratory incubation studies, aimed to compare nutrient release and moisture retention curves along with other properties of media amended with various rates of urban biochar with an industry standard media are discussed. Based on those results optimum rate of use of urban biochar for growing media is identified.
CHAPTER 4

This chapter is based on a published article entitled:

An examination of physical and chemical properties of urban biochar for use as growing media substrate. *Biomass and Bioenergy* 84, 49-58.
An examination of physical and chemical properties of urban biochar for use as growing media substrate

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Growing media
Water retention
Wetting–drying cycles

Abstract
The purpose of this study was to evaluate the suitability and optimum rate of addition of Urban Biochar (UB) as an alternative to standard coir peat in plant growing media. UB was prepared through pyrolysis of a 2:1 ratio of biosolids to greenwaste on a dry mass basis. Two incubation experiments are reported both with ﬁve different growing media mixtures which were subjected to periodic wetting and drying. Media mixtures consisted of different rates of UB (100%, 60%, 40%, 20%) mixed with composted pine bark on a volume basis and compared to an industry standard media with 0% UB. The physical and chemical properties of the mixtures were compared pre and post incubation. Substituting coir peat with UB increased media pH, C:N mass ratio, nutrient content, air ﬁlled porosity and bulk density. Furthermore, addition of UB to media also increased the proportion of particles in the desirable range for growing media (0.25–2 mm). UB amended mixes were found to be most stable in terms of both bulk density and resistance to particle breakdown. Fourier transform infrared spectroscopy analysis suggested that periodic wetting and drying enhanced surface oxidation. We found that UB amended substrates, up to 60% biochar on a volume basis, could deliver similar physical and chemical beneﬁts to those of coir peat based industry standard media.

1. Introduction
Growing media are soilless substrates that provide plants with nutrients, air and water, and physical support [1]. Plant growing media must have well-balanced physical and chemical properties such as pH, EC, C:N mass ratio, bulk density (BD), air ﬁlled porosity (AFP), water holding capacity (WHC) and stability. In addition, the growing media must be free of pathogens and toxic chemicals [2]. Growers construct and formulate growing media from a range of substrates such as, pine bark, sphagnum peat, coir peat, compost, perlite and vermiculite [3]. Charcoal has been proved to be an effective substrate and has been used over many years in growing media [4]. In recent years, biochar has emerged as a potential growing media substrate as it resembles charcoal in terms of physical attributes although it is commercially manufactured under reduced oxygen at temperatures above 350 °C from a wider range of feedstocks. Most of the research on the use of biochar in growing media is aimed towards replacing environmentally unfriendly substrates such as peat, vermiculite and perlite from growing media with biochar [5–7]. These studies have shown that biochar improves BD, particle size distribution (PSD) and WHC of growing media. Biochar application to growing media has also known to improve retention of nutrients such as nitrogen and phosphorus [8,9]. Other advantages of using biochar in growing media include improvement of disease resistance [10,11], resistant to drought [12] and improvement of plant growth [13,14]. Furthermore, biochar properties vary depending on their production temperature and feedstock. For instance, biochar cation exchange capacity (CEC) may ﬂuctuate from 0.03 to 0.67 mol kg−1, pH may be between 5.8 and 10.9, surface area may range between 21 and 401 m2 g−1 and C:N mass ratio may vary from 20 to 169 [15]. Hence, it is important to study the impact of particular biochars on vital physical and chemical parameters of growing media before recommending the biochar be used as growing media substrate. We are unaware of any studies of the use of high temperature biochar made from biosolids.
and greenwaste in growing media. Furthermore, it is unclear how the physical (WHC, pore size distribution, BD) and chemical properties (CEC, pH, EC, nutrient release) are influenced by the periodic wetting and drying that occurs in horticultural situations.

Pore size distribution is an important property of growing media as it governs retention and loss of water [2]. Pore size distribution is known to be highly affected by physical and chemical attributes of growing media such as: PSD, particle size arrangement, aggregate size, CEC, Ca and Mg content [16,17]. Wetting and drying cycles have also been identified as key factors for changes in pore size distribution of soil over time mainly by altering the arrangement of particle size and causing particle breakdown [18]. Similar pathways may exist in growing media causing changes to surface characteristics and physical integrity of biochar. Tian, Sun [5] measured the stability of biochar in media by performing particle size analysis at the start and end of media incubation and found that biochar improves media stability. They also found that the addition of biochar in the media increases the percentage of particles in the desirable range (0.25—2 mm) which is important for sufficient gaseous exchange and water retention. However, they measured physical breakdown without considering the effect of wetting and drying cycles on stability. As wetting and drying over a period of time may cause physical breakdown of biochar particles and also cause biochar surface chemical changes, it is clearly important to consider these effects on both physical and chemical stability of biochar.

Most of the high temperature biochar (>500 °C) has large surface area and high porosity [19] which gives it the potential to form aggregates with minerals and organic matter, ultimately leading to increased WHC [20,21]. Biochar (500 °C) has been shown to increase the WHC of soil [22,23] and in the case of growing media, Dumroese, Heiskanen [6] found 3:1 ratio of peat: biochar pellet on dry mass basis (500 °C). Composted pine bark (B0) consisted of, an industry standard, 20% coir peat and 80% fresh biosolids were sourced from Bangholme Eastern Treatment Plant, Victoria. Moisture content of biosolids as received from the treatment plant was 72% as water mass fraction. Biosolids and greenwaste (mainly municipal softwood garden waste chopped to 1.5 cm) were dried in a commercial dryer to a water mass fraction of 21% and blended at a ratio of 2:1 (on dry mass basis).

2. Materials and methods

2.1. Formulation and characteristics of UB

2.1.1. Feedstock

Fresh biosolids were sourced from Bangholme Eastern Treatment Plant, Victoria. Moisture content of biosolids as received from the treatment plant was 72% as water mass fraction. Biosolids and greenwaste (mainly municipal softwood garden waste chopped to 1.5 cm) were dried in a commercial dryer to a water mass fraction of 21% and blended at a ratio of 2:1 (on dry mass basis).

2.1.2. UB production

Feedstock was pyrolyzed in a commercial scale pyrolyzer by Pacific Pyrolysis Pty Ltd. at a high heat treatment of 650 °C with a residence time of 40 min. Feed rate was 125 kg h⁻¹ with a biochar yield of 46% on a dry mass basis.

2.1.3. UB characterization

UB was characterized for its surface area and pore properties by using a Tristar 3000 surface area and porosity analyser (Micrometrics Instrument Corporation, USA) in degassed samples (250 °C for 18 h on a vacuum line) at –196 °C. The specific surface area of the sample was calculated by a standard multipoint Brunauer–Emmett–Teller (BET) method. Chemical properties were analysed by using Fourier transform infrared analysis (FTIR), and elemental analysis was done by ICP-OES after digestion. Some major properties of UB are listed in Table 1 and compared with other typical growing media constituents namely, pine bark and coir peat. Ultimate analysis of UB shows 74% carbon, 2.5% hydrogen, 0.7% nitrogen and 8% oxygen. UB has 14% volatile matter. UB has been characterized in detail by Kaudal et al. [19].

2.2. Media mixes

Five plant growing media (media mixes) were tested. Mix one (B0) consisted of, an industry standard, 20% coir peat and 80% composted pine bark on a volumetric basis. Composted pine bark (3—6 mm grade) was obtained from Debclo Pty Ltd. Coir peat, which are residue from processing of coconut fibre, was sourced from Galuku Pty Ltd. Other mixes completely replaced coir peat with UB and progressively replaced composted pine bark as detailed in Table 2.

2.3. Media analysis

Media mixes were analysed both pre and post incubation. pH and EC of samples were measured by shaking 1 g of media in 20 cm³ of deionized water on a reciprocating shaker at 50 Hz for 1.5 h [32]. CEC was measured according to the method of Rajkovich, Enders [29]. AFP and WHC were measured as per the Australian Standard for potting mixes (AS 3743). Mineral and metal analysis for Al, As, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, and Zn were performed using samples digested by a modified dry-ash method.

...
Table 1
Selected physical and chemical properties of UB, pine bark and coir peat.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Surface area (m² g⁻¹)</th>
<th>EC (dS m⁻¹)</th>
<th>CEC (mol kg⁻¹)</th>
<th>Ash db (%)</th>
<th>pH</th>
<th>Fixed carbon db (%)</th>
<th>Mesopores (%) (between 2 and 50 nm)</th>
<th>Bulk density (g cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UB</td>
<td>396</td>
<td>0.18</td>
<td>0.10</td>
<td>45.1</td>
<td>7.5</td>
<td>41</td>
<td>67</td>
<td>0.31</td>
</tr>
<tr>
<td>Pine bark</td>
<td>190</td>
<td>0.26</td>
<td>0.20</td>
<td>2.9</td>
<td>4.9</td>
<td>25</td>
<td>na</td>
<td>0.31</td>
</tr>
<tr>
<td>Coir Peat</td>
<td>250</td>
<td>0.56</td>
<td>0.31</td>
<td>4.1</td>
<td>5.1</td>
<td>17</td>
<td>na</td>
<td>0.07</td>
</tr>
</tbody>
</table>

na: not assessed, db: dry basis.

Table 2
Composition of media mixes.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Composition (on volume basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B0</td>
<td>Composted pine bark (80%), coir peat (20%)</td>
</tr>
<tr>
<td>B20</td>
<td>Composted pine bark (80%), UB (20%)</td>
</tr>
<tr>
<td>B40</td>
<td>Composted pine bark (60%), UB (40%)</td>
</tr>
<tr>
<td>B60</td>
<td>Composted pine bark (40%), UB (60%)</td>
</tr>
<tr>
<td>B100</td>
<td>UB (100%)</td>
</tr>
</tbody>
</table>

2.4. Experiment design

Two experiments were conducted in parallel using subsamples of the same batch of media mix for each experiment. Experiment 1 assessed nutrient release during wetting and drying cycles, where chemical properties of the media mixes and their nutrient release into pore water and leachate were tested and experiment 2 was conducted to understand the impact of UB on media physical properties, mainly water retention and bulk density.

2.4.1. Experiment 1 — effect of wetting and drying on nutrient release from media

Three replicates of the media mixes were placed in open ended 4 L plastic pots to a fill depth of 20 cm. Two pore samplers (Rhizosphere research products B.V, Netherlands) were inserted into each pot at 5 cm and 15 cm height prior to filling the pots. The pore samplers had ceramic tips to collect media pore water. Pots were incubated in a constant temperature room at 22 °C for 90 days. Wetting and drying cycles were introduced to the experiment by letting media dry for 2 days and then rewetting to their field capacity. Pore water was collected at 12 day intervals which gave a total of 7 collections throughout the experiment. Leachate was also collected in a container at the base of the pot from all mixes. Pore water collected from both samplers at each sampling time were combined and analysed for ammonium, nitrate and P using a Skalar SAN++ segmented flow analyser (Skalar Analytical).

2.4.2. Experiment 2 — effect of wetting and drying on media water retention

To determine water retention curves, media mixes were incubated in stainless steel rings of 5 cm height and 3 cm diameter and placed on individual 6 cm by 6 cm steel plates inside a plastic incubation tray. All rings were filled to the same height and placed in a constant temperature room at 22 °C. There were three replicates of each treatment for each sample time. Wetting and drying cycles were introduced to the experiment by allowing media to dry for 2 days and then rewetting to their field capacity. Fifteen rings (five treatments by three replicates) were randomly selected and removed from the incubation trays at 1, 30, 60, 90 and 150 days to undergo pressure extractions. A pressure chamber was used to determine water held at matric potential of −10 and −20 kPa [34]. For matric potential values of −50, −100, −500, −1000 and −1500 kPa, a pressure plate method was used [34] using a ceramic plate extractor (Soil Moisture Equipment Corp., Santa Barbara, CA, USA). For both methods, the mixes were initially saturated from the bottom up with tap water [35] for 24 h at room temperature of 22 °C. Rings were transferred to the chamber and pressure was applied until rings were at equilibrium (as indicated by the cessation of water draining from the rings). After equilibration at the lowest matric potential, samples were weighed and then the same rings were used for the next higher matric potential. After equilibration of the samples at the highest matric potential, the rings were weighed and volume of media in the rings was measured. Finally, media was oven dried at 105 °C for 12 h and reweighed. Available WHC of each media was determined by calculating the difference in volumetric water content held at −10 and −1500 kPa [23].

2.5. Stability of media

Different parameters of stability were measured for each experiment to determine the physical and chemical stability of the mixes. PSA and functional group analysis were conducted on experiment 1 samples. BD was measured on experiment 2 samples. Media mixes were analysed both pre and post incubation for all the stability tests.

2.5.1. Particle size analysis

PSA was performed using a dry sieving technique. 100 g subsamples of media were placed on a nest of sieves on a vibrating sieve shaker (The minor, Rowe Scientific Pty Ltd). Sieves sizes ranged from 4 mm to 0.063 mm. Sieves were shaken at 3000 vibrations per min for 10 min and the sample remaining in each sieve was weighed.

2.5.2. Functional group analysis

Diffuse reflectance mid-infrared spectra were recorded in finely ground media samples from experiment 1 using a PerkinElmer Spectrum One FTIR spectrometer (PerkinElmer, MA, USA) from 7800 to 450 cm⁻¹ at 8 cm⁻¹ resolution by co-adding the scans for 1 min. 1 g of media sample was diluted with 100 g of KBr before taking the scans. Spectra were corrected for atmospheric water vapour and CO₂ with a background spectrum collected prior to running samples. PerkinElmer instrument software (Spectrum 5.0.1) was used to identify and compare chemical functional groups.

2.5.3. Bulk density

BD was measured from the rings used for the pressure plate analysis (experiment 2) after each sample had equilibrated at the highest matric potential. In total there were five sets of measurements of BD. BD measurements were based on the final volume of the media in the cylinders and their oven dry weight (105 °C). Where media had shrunk, void volumes were calculated by recording the volume of sand required to fill the void. In the case of media expansion, excess media was scraped off and the volume of the media remaining inside the ring was measured.
2.6. Statistical analysis

All data were analysed using Minitab software package (Minitab 16). The significance of differences between mixes and sampling dates were tested by two way ANOVA. Differences between the values were considered statistically significant at $P < 0.001$. Where significant treatment effects were determined, Tukey's test was applied to separate differences between treatment means at a probability level of $P < 0.05$.

3. Results

3.1. Media analysis

Results for properties of all media mixes including pH, EC, CEC, C:N mass ratio and nutrients both pre and post incubation are shown in Table 3. Some physical properties such as BD, AFP and WHC are shown in Table 4. The addition of UB significantly increased the C:N mass ratio, pH and EC values of media mixes ($P < 0.001$). C:N mass ratio for all mixes were significantly different ($P < 0.001$) except for B40 and B60. C:N mass ratio of B100 was twice more than that of the industry standard mix B0. The trend for CEC was exactly opposite to C:N mass ratio. CEC was significantly different for each mix and decreased with increasing rate of UB. Replacing coir peat by UB at 20% on volume basis reduced CEC by 14%. Nutrient values (Ca, K, Mg, Fe, P and S) of all mixes were significantly ($P < 0.001$) different, with higher nutrient loadings in case of B60 and B100. Post incubation, the nutrient content in all media mixes was reduced. BD of the mixes decreased with increasing rate of UB. In contrast, AFP of mixes increased with increasing rate of UB, with B100 exhibiting the lowest value of BD of media mixes was reduced. BD of the mixes decreased with increasing rate of UB, with B100 exhibiting the lowest value of BD of 0.31 g cm$^{-1}$. Similarly, WHC of B0 was highest and decreased with increasing rate of UB. In contrast, AFP of mixes increased with higher rate of UB. All heavy metals in UB were below the Victorian EPA C2 level classification [36] and also within the permissible limit of USA EPA standards for land application of biosolids [37]. Poly aromatic hydrocarbons (PAH) content of UB was below detection limit [19]. For complete detail on PAH and heavy metals of UB refer to [19]. All other mixes (B0, B20, B40 and B60) had below detection level of heavy metals.

3.2. Nutrient dynamics

Ammonium and nitrate concentrations were very low in the pore water of all mixes and in B100 the values were close to the detection limits, hence, we have presented only P results. Fig. 1 shows that all the mixes had a similar pattern of P release over 90 days experiment duration. All the mixes showed P release which is consistent with total P content of media (Table 3). For all mixes there was very little P release at day 1, followed by a spike at second sampling day (day 12) and then a sharp drop. B100 had the highest P value of all mixes at all sampling times except on day 75 and 90 where B20 is higher than B100. B0 had the least P in pore water at all sampling times. After 30 days of experiment, there seems to be lower but sustained release of P from all biochar amended mixes.

For the leachate, loss of nitrogen as nitrate and ammonium (Table 5), was least in B60 and highest in B0. In case of P, B0 had lowest loss in leachate and B40 had the highest.

3.3. Volumetric water content

Water retention curves of all mixes for three representative sampling times are shown in Fig. 2. On day 1, B0 performs significantly better than other mixes to hold water at the drainable porosity range (between 0 and 10 kPa). However, at pressures greater than 10 kPa, the biochar amended treatment, B20, was not significantly different to B0. At day 90 and 150, at pressure greater than 10 kPa, UB amended mixes performed better than at day 1 and their volumetric water content values come closer to B0. Beyond 10 kPa all UB amended mixes (B20, B40 and B60) except B100 were not significantly different to B0 ($P < 0.001$).

3.4. Stability of media

3.4.1. Functional group analysis

Fig. 3 shows the major bands in the FTIR spectra of coir peat and pre and post incubation samples of the media mixes. The broad bands found in all samples around 3400 cm$^{-1}$ could be attributed to hydroxyl group $\text{−OH}$ stretching [24]. The peaks at 2980 and 2852 cm$^{-1}$ indicative of aliphatic C−H stretching [15] were dominant in coir peat and B0 samples, however those aliphatic C−H stretchings declined with increasing UB in the mixes. The bands near 1730 cm$^{-1}$ indicative of C=O stretching vibrations of esters and carboxylic acids [24,38] were intense in coir peat, however these bands had almost disappeared and shifted as a small shoulder near 1700 cm$^{-1}$ in all treatment samples [39]. The strong peaks at $1620−1610$ cm$^{-1}$ are due to the presence of aromatic C=C groups or C=O ring stretching [24]. The aromatic C=C ring vibrations and C−H plane deformations between 1500 and 1430 cm$^{-1}$ and notably a small C=C peak at 1510 cm$^{-1}$ [15] were dominant in coir peat. The band found at 1380 cm$^{-1}$ was indicative of C−O and C−H vibrations in CH$_2$ and CH$_3$, while the bands at 1260−1240 cm$^{-1}$ were from C−O and $\text{−OH}$ phenolic vibrations [15,24]. These bands between 1500 and 1200 cm$^{-1}$ decreased with increasing UB and had almost disappeared in B100, suggesting the disappearance of lignin in the samples. Similarly, sharp peaks in growing media between 1160 and 1040 cm$^{-1}$ due to C−O, $\text{−OH}$, $\text{−COOH}$, $\beta$-glycosidic bonds

Table 3

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Properties</th>
<th>Nutrients (mg kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH</td>
<td>C:N</td>
</tr>
<tr>
<td>Pre incubation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B0</td>
<td>5.30 d</td>
<td>50 a</td>
</tr>
<tr>
<td>B20</td>
<td>5.45 c</td>
<td>75 b</td>
</tr>
<tr>
<td>B40</td>
<td>5.64 bc</td>
<td>89 c</td>
</tr>
<tr>
<td>B60</td>
<td>6.20 b</td>
<td>98 d</td>
</tr>
<tr>
<td>B100</td>
<td>7.65 a</td>
<td>106 e</td>
</tr>
<tr>
<td>Post incubation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B0</td>
<td>5.39 d</td>
<td>42 a</td>
</tr>
<tr>
<td>B20</td>
<td>5.78 c</td>
<td>71 b</td>
</tr>
<tr>
<td>B40</td>
<td>5.84 c</td>
<td>87 c</td>
</tr>
<tr>
<td>B60</td>
<td>6.51 b</td>
<td>94 d</td>
</tr>
<tr>
<td>B100</td>
<td>7.46 a</td>
<td>104 e</td>
</tr>
</tbody>
</table>
in cellulose and hemicellulose or Si–O [15,24,38] declined with increasing proportion of UB. The aromatic C–H out of plane deformation at 898 and 798 cm

\(^{-1}\) that were evident in coir peat also increased from B0 to B100 due to increasing aromatic compounds in the sample. The B100 samples also had a small peak around 3070–3000 cm

\(^{-1}\) originating from aromatic C–H stretching vibration [15]. Comparison of pre and post incubation samples showed no differences in the presence of functional groups, however band specific analysis of spectra revealed that the intensity C–H aliphatic bands at 2926 and 2952 cm

\(^{-1}\) were relatively lower and C–O bands at 1730–1700 cm

\(^{-1}\) and C–O–OH, carboxylic and aromatic bands between 1226 and 1040 cm

\(^{-1}\) were relatively higher in post incubation biochar samples.

3.4.2. Particle size distribution

Fig. 4 shows the particle size distribution (PSD) of all mixes from experiment 1. Comparing the difference of particles at each sieve size, pre and post incubation, for all mixes, there is increase in percentage of fine particles which is greatest for B0 and least for B100. Furthermore, the percentage of particles in the desirable range of 0.25–2 mm is highest in B100 followed by B60, B40 B20 and B0.

3.4.3. Bulk density

Bulk density of all mixes from experiment 2 over the period of 190 days are shown in Fig. 5. Addition of UB reduced BD of media. As the experiment progressed, BD of all mixes reduced due to compaction and setting of media with the least change happening in B100. During the course of the whole experiment, BD of treatment B0 reduced significantly and quickly from 0.38 to 0.24 g cm

\(^{-3}\). BD of B60 remained the highest through the incubation. B100 was best in terms of BD as it remained relatively stable in comparison to B0.

4. Discussion

4.1. Media properties

High CEC is important for nutrient retention [40], so media with high CEC could be an advantage. Although CEC of media decreases with addition of UB, CEC values of all UB amended mixes (Table 3) are within desirable media range of 5 mol kg

\(^{-1}\) to 50 mol kg

\(^{-1}\). B0 has high organic matter rich coir peat, which is likely responsible for its high CEC. This is supported by organic functional groups in the FTIR spectra from cellulose and carbohydrates at 3400, 1160–1040 cm

\(^{-1}\), fats, wax and lipids at 2926 and 2952 cm

\(^{-1}\), carboxylic acids and lignin at 1730, 1600, 1500–1260 cm

\(^{-1}\) [41]. CEC of coir peat and pine bark is higher than UB, hence, there is systematic decrease in CEC with the increase of UB in the media mixes. The slight increase in CEC of all media mixes after the incubation is likely due to surface oxidation which is verified by the increase in carboxylic functional groups (1730–1700 cm

\(^{-1}\) and 1200–1000 cm

\(^{-1}\) ) as indicated by FTIR analysis (Fig. 3). The pH of B0 is not within the ideal media range (5.5–6). The addition of 20% biochar to the media brings the pH inside the ideal range although B60 and B100 are outside this range owing to high pH of biochar (7.46). In most commercial growing media the addition of fertilizer may cause a decrease in pH so the addition of biochar would have a beneficial liming effect in those systems.

In contrast to the pH trend, nutrient values in all mixes, mainly Ca, K, Fe, and P, are higher in pre incubation samples of experiment 1 than post incubation samples. This is likely due to the release of nutrients from the media substrates as seen in the pore water analysis results (Fig. 1) where UB amended mixes have higher P in pore water and some nitrate and ammonium in the leachate (Table 5). As the heavy metal composition of UB was well below the permissible limits of Victorian EPA and USA EPA standards and there were negligible levels of heavy metals present in the media mixes, these substrates should be suitable for unrestricted use in growing media.

C:N mass ratio of UB amended mixes were relatively more stable than B0 for the duration of the experiment due to their higher aromatic carbon content. This was evident from FTIR spectra showing a reduction in aliphatic C–H and aromatic ring C=C vibrations.
derived from lignin functional groups (3000—2800 cm\(^{-1}\) and 1500—1240 cm\(^{-1}\)) and increase in aromatic functional groups from higher C—H deformations (800—600 cm\(^{-1}\)) from B20 to B100. C:N mass ratio of all mixes were above the desirable range for growing media (30:1). Although C:N mass ratio of the UB mixes (B20, B40 and B60, B100) were higher than the recommended range for growing media, this should not be a problem as the carbon present is UB is aromatic and not readily available for microbial degradation. Furthermore, high C:N mass ratio can also be rectified by adding mineral nitrogen when formulating the media [42].

Higher AFP in UB amended media is likely to be due to its high mesoporosity (Table 1). Development of porosity in biochar has been shown to be positively correlated to pyrolysis temperature [43]. As UB is high temperature biochar (650 °C), it has developed high porosity [19] which may contribute towards total porosity of the media mixture. Biochars with fine particle size can result in higher aeration of media [9]. As more than 70% of UB is below 2 mm particle size, UB amended media has high AFP.

WHC of mixes were measured using the standard method of Kevin and Black [2] by soaking samples in water for 2 h. This was sufficient time for coir peat to adsorb water but the UB, due to its fine pore network, may not have had enough time to become completely saturated with water, hence the WHC values of UB may be underestimated. Hence, we recommend using longer soaking time for media amended with biochar. A similar trend was also observed by Dumreose et al. [6] where short exposure to water led peat to absorb more water and longer exposure led more water to be absorbed by biochar amended treatment. Although, WHC of all UB mixes are lower than B0, these values still lie within the desirable range for growing media (>20% by volume) [2]. Furthermore, WHC of UB amended mixes are higher than B0 at the higher matric potential which is shown in Fig. 2 and discussed in more detail in Section 4.3.

4.2. Nutrient dynamics

As the first pore water sample was taken immediately after starting incubation (day 1), an initial lag phase in the release of P was observed (Fig. 1). This could be due to time taken by soluble P to be dissolved in pore water. As the soluble P from all mixes dissolves in water with time, there is a flush of P from all mixes observed by the second sampling (day 12). The highest P release is consistent with the high total P value in the B100 treatment [23]. have found similar flush of P in day 1 pore water from 25% biochar amended sand. The higher P values in UB amended mixes in addition to the low but sustained P release into pore water over period of 90 days shows that UB may act as a modest source of slow release P supplement when added to growing media. This sustained release of P is consistent with leaching experiment done by Angst et al. [30] who found rapid decline of potassium and magnesium but 45% P still being released after a sixth extraction with deionized water. An experiment in soilless media [28] which showed higher concentration of P in the consecutive leaching
events recommends their biochar as a useful source of P for ornamental plant production. In an experiment with a similar biochar (1:1 ratio of biosolids to greenwaste on dry mass basis, 550°C) Wang, Camps-Arbestain [31] found the product was equally effective as other P fertilizers such as calcium dihydrogen phosphate and phosphate rock even after six harvests. Additionally, Mukherjee and Zimmerman [44] found there is a positive correlation between extractable P and biochar ash content. Hence, we can assert that high P release properties of UB are a consequence of its high ash content (45%) likely form the biosolids component.

Elemental analysis of UB shows it contains only 0.7% N [19]. Although, N present in low temperature biochars (250–500 °C) is found to be available for microbes [45], availability of nitrogen is drastically reduced once pyrolysis temperature exceeds 550 °C [46]. Hence, UB being high temperature biochar, the nitrogen present in it could be in inaccessible forms which could be the reason for low levels of N in pore water and leachate. From nursery grower’s perspective, they prefer media with low inherent fertility as they can manipulate the nutrient status of media as per the demand of the plant [6]. Low nitrogen availability in the mixes also means there will be decrease in nitrogen runoff to the waterways. Reduction in concentration of nitrogen in runoff water was found in green roof substrate amended with 7% biochar [8]. Therefore, low nitrogen availability on pore water of media mixes could be an advantage both from growers and an environmental point of view.

4.3. Media water retention

Adding biochar to pure sand and sandy soil has been found to improve water retention capacity [22]. In our experiment, B0 consist of coir peat which is known to have high WHC [2] which cannot be matched by the biochar amended mixes especially at lower matric potentials. It can be inferred that performance of biochar is better in media with low organic matter than in the industry standard media (B0) containing high organic matter coir peat. Similar water retention curves to our experiment were found in a study done by Dumreose et al. [6] using various mixtures of peat and pelleted biochar where peat had the highest water retention at lower matric potential and adding 25% pelleted biochar exceeded water retention of peat only on higher matric potential (>1000 kPa). These results are very similar to our results where, addition of biochar seems to have a positive effect on matric potential over 91 days have been observed after addition of biochar in sandy soil by Basso, Miguez [22]. The authors observed that WHC was not significantly different between biochar amended

![Fig. 4. Percentage of particles of various sizes for all mixes. Incubation 1 and 2 represent pre-incubation and post-incubation particle sizes respectively.](image)

![Fig. 5. Change in bulk density of all mixes over 190 days. Bars are one standard error from the mean (n = 3).](image)
mixes and the control on day 1 and 15 whereas on day 29 and 91 all biochar amended mixes performed better than the control. We assume that this may have been caused by the fine pore size distribution of biochar particles. The standard method for measuring WHC by using pressure plates states to saturate samples for 24 h, however, as in general, biochar has large number of micropores, it could take more than 24 h for water to enter into all the pores and completely saturate the biochar. Hence on day 1 we see trend of low water retention by UB. After 90 and 150 days in incubation, water may have got into all the fine pores of UB which gave it higher water retention capacity. As UB is a high temperature biochar and has fine pores (67% of pores between 2 and 50 nm and many pores below 2 nm) [19], it may take longer time for them to fill. Another explanation for our results may be improvement of pore accessibility from the movement and breakdown of particles which leads to improvement in WHC in UB amended mixes at day 90 and 150 (Fig. 2). Increase in water retention at higher matric potential in UB amended mixes (−1000 and −1500 kPa), where water is held by adsorptive and capillary forces, suggests that adding UB in media may lead to a secondary pore size maximum which improves water stored at that high matric potential.

Many mechanisms for increase in WHC after biochar application are suggested such as increases in biochar polarity, improved soil aggregation and changes in porosity, especially microporosity [26,47,48]. The explanation for increase in micropores of biochar is the dissolution of ash present in the pores of biochar after a few watering events, [48]. Larger surface area of biochar and improved aggregation and structure of soil are also proposed as a mechanism for improved WHC [21]. As we have found that UB has high ash content (45%) and high surface area (396 m² g⁻¹), we think dissolution of ash from UB and high surface area could be two main mechanisms for WHC of UB. An increase in WHC at higher matric potential means that the additional volume of water stored in the micropores of UB may become available as the media dries and the micropores increase making UB amended media more advantageous for drier situations.

4.4. Stability of media

4.4.1. Functional group analysis

Aromatic carbon is the recalcitrant component that provides stability to biochar in soil, while aliphatic C, carboxyl and carbohydrate bands observed in FTIR spectra may present a relatively labile component of biochar [49]. In this study, increasing proportion of biochar in the media mixes from B20 to B100, led to increase in fused aromatic functional groups in the FTIR spectra in the form of C=C, COO⁻ and C–H ring structures at 3044, 1610, 1132, 800–600 cm⁻¹ it [19,24]. Furthermore, B20 to B100 showed a gradual reduction in readily decomposable C=O and C–H bands from lignin and polysaccharide groups at 2926, 2952 and 1510–1264 cm⁻¹ when compared to B0 which contained spectral features almost similar to organic forms in coir peat. These results were consistent with increasing C:N mass ratio, pH and porosity and suggest that the media mixes from B20 to B100 were in the increasing order of physical and chemical stability.

4.4.2. Particle size distribution

PSD is a very important property of growing media as it determines available pore space, gas exchange capacity and water holding capacities [50]. According to Handreck [1], media substrates with particles smaller than 0.50 mm have the highest influence on porosity and water retention. For a growing media, particles in the range of 0.25–2.0 mm are most effective in retaining water and also provide sufficient gas exchange to support vigorous plant growth [51]. B100 has the highest amount of particles in the favourable range while B0 has least. In other words, adding UB to growing media increased the percentage of particles in this favourable range. The amount of particles in this desirable range increases in all mixes after incubation, however, B100 still has the highest amount of particles in that range. It is also known that a balance of coarse and fine particles is very important [51]. More than 75% of coarse particles (>1 mm) may cause problem of excessive drainage and low WHC [51] while large amount of fine particles may clog the media pores and reduce air filled porosity. Media with some fine particles may also have an issue of loss of media through carry-over, or entrainment of very small particles during watering events. On the positive side, these fine particles may improve water retention due to higher soil water conductivity [52]. Hence the UB amended media have an advantage over B0.

Comparison of PSD pre and post incubation has also been used as a measure of physical stability of media [5]. As the physical stability of growing media substrates is very important to maintain BD and water retention properties of media [1], a media with stable PSD is an advantage. Our results show that adding UB to media makes media more stable in terms of physical breakdown which maintains the PSD over a period of 90 days. This stability of UB amended media may be due to physical strength of UB and its resistance to microbial degradation as compared to coir peat in B0.

4.4.3. Bulk density

BD, which is an indicator of compaction in media, is an important parameter for growth of plant roots [2]. Lower BD is preferable as it limits compaction of media. Addition of biochar has been shown to decrease BD of soil [22]. In context of growing media, progressive addition of biochar pellets to replace peat, showed a slight increase in BD [6]. UB addition to media made media more stable in terms of reducing the change in BD over 190 days of experiment. This may be due to physical ability of UB to resist compaction and due to low BD of biochar itself [43]. A stable BD also means that porosity and drainage capacity of media is not compromised [2]. Therefore, in respect to growing media, having a media with stable BD throughout a longer period of 190 days is a strong advantage. Furthermore, low BD is favourable for growing media due to ease of transportation [53]. It is also important to have media with lower and stable BD in applications such as roof gardens or long growth cycle plants where it is desirable not to top up or replace the media.

4.5. Media comparison

In order to visualize how properties of UB compare with ideal media, media mixes used on our experiments were compared with ideal media properties (C:N mass ratio 30, balanced supply of nutrients, at least 20% of particles between 0.25 and 2 mm, CEC between 0.05 and 0.50 mol kg⁻¹, pH between 5.5 and 6.0, EC < 2.5 dS m⁻¹, WHC >20% by volume, BD between 0.3 and 0.6 g cm⁻³ and AFP between 7 and 50% by volume) as listed by Kevin and Black [2]. All of the mixes comfortably fit within those ideal media property ranges for all criteria except for C:N mass ratio and pH. However, this should not be a problem as the carbon present is UB is aromatic and not readily available for microbial degradation. High C:N mass ratio can also be addressed by adding mineral nitrogen when formulating the mixes [42]. Furthermore, high pH of UB can make media alkaline thus help reduce use of lime. It should also be noted that the ideal properties for any media will depend on the use of that media. For example seedling mix will have different ideal properties than an orchid mix [2].
5. Conclusion

Comparing our media mixes with ideal media, most of the properties of UB amended media match or exceed specifications for growing media. As the UB possesses physical properties such as greater WHC at drier situations (higher suction), low bulk density, high air-filled pore space and high surface area which are desirable for growing media, media amended with UB has performed comparably to our industry standard treatment, B0. UB amended mixes exceed B0 in terms of pH, supply of nutrients, PSD and WHC at higher matric potentials. Stability of UB amended mixes are greater when compared to B0, even after introducing periodic wetting and drying cycles. We also found that it takes longer time for water to get into all pores of UB than coir peat hence UB amended media mixes need to be wet and stored before use especially for water sensitive applications. The best rate of use of UB in growing media is using 40% on volume basis as the properties of B40 were similar to B0 in terms of physical and chemical properties with all the properties of B40 lying within the desirable range. However, if the aim is to make use of maximum amount of UB in growing media, we found that UB can replace coir peat up to 60% on volume basis and still achieve comparable physical and chemical benefit from the growing media when compared to B0. We are conducting further experiments to understand fertilizer utilization efficiency and plant performance in the UB amended media.

Acknowledgements

B. Bhatta would like to acknowledge the financial support from Australian Postgraduate Award Scholarship.

References


Connecting statements

Results of laboratory incubation studies discussed in previous chapter (Chapter 4) showed 60% V/V as an optimum rate of use of urban biochar in growing media. The results also indicated that urban biochar amended growing media can have comparable physical and chemical properties to those of industry standard media. However, it is not feasible to come to a conclusion on effectiveness of urban biochar as growing media substrate without assessing plant growth and nutrient uptake. Under practical situations, the feasibility of the use of urban biochar amended growing media would occur most likely be in greenhouse settings. Furthermore, in Chapter 4, the incubation studies were conducted with unfertilized growing media, therefore, effects of urban biochar on fertilizer use efficiency could not be determined. Therefore, conduct a greenhouse study is conducted in order to test the plant performance and fertilizer use efficiency from fertilized urban biochar amended growing media and also assess major nutrient loss pathways (Chapter 5).
CHAPTER 5

This chapter is based on a submitted article entitled:

Urban biochar amended growing media has improved nutrient supply potential. *Geoderma*, revised and re-submitted on 10th November 2016.
Urban biochar amended growing media has improved nutrient supply potential

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Abstract

The purpose of this study was to evaluate the nutrient supply potential of plant growing media amended with urban biochar (UB) as a sphagnum peat substitute. UB was produced from the pyrolysis at 650 °C of a 2:1 ratio of biosolids to greenwaste. We compared three mixes: 20% sphagnum peat mixed with pine bark; 20% UB mixed with pine bark and; 60% UB mixed with pine bark, for their ability to promote plant growth and minimise leaching losses in a greenhouse experiment using silverbeet (*Beta vulgaris* ssp.cicla). Plants were grown in 4.0 L custom made chambers with the capacity to collect leachate and measure N₂O gas flux. Substituting sphagnum peat with 20% UB (B20) and 60% UB (B60) increased media pH, air filled porosity, bulk density and nutrient content. Sphagnum peat based media, B0 had highest cation exchange capacity and electrical conductivity. UB based mixes, B20 and B60 had no significant effect on silverbeet biomass after 11 weeks of growth but had higher nitrogen and phosphorus use efficiency than B0. These results indicate that UB can replace sphagnum peat from growing media and can be used at the rate of 60% on volume basis while improving nutrient supply potential.

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1. Introduction

Growing media are soilless substrates used for growing plants in pots for horticulture and are primarily composed of a blend of organic and inorganic materials such as peat, vermiculite, perlite, pine bark and sand (Handreck and Black, 2010). Peat is considered a premium substrate mainly because of its low bulk density and high water holding capacity (Gruda, 2012). Ecological concerns surrounding the harvest and use of peat (Verhagen, 2009), is driving research to find peat replacements. In the past decade this research has focused on the use of industrial and urban waste by-products as replacement growing media substrates such as: greenwaste (Nieto et al., 2016; Zhang et al., 2014); biosolids (Jayasinghe et al., 2010; Zhang et al., 2013); coir husk (Abad et al., 2002; Hongpakdee and Ruamrungsri, 2015); poultry manure (Bustamante et al., 2008; Zhang et al., 2013); wheat straw (Raviv et al., 2005; Vaughn et al., 2013) and; composted food waste (Farrell and Jones, 2010; Landis and Morgan, 2009).

Biochar, a solid by-product produced during the heating of biomass in a low oxygen environment, can be made from all these waste feedstocks and, when the carbon balance is considered, biochar is generally carbon positive as a large proportion of the carbon in the waste is retained in the product (Gaunt and Lehmann, 2008). The conversion of urban waste into biochar has additional benefits such as waste reduction, resource recovery and emission reductions (Kaudal et al., 2015). The replacement of peat in growing media with urban waste biochar is a potential win-win situation if biochar is at least as good a substrate as peat. Studies have shown the potential of biochar to replace peat from growing media mainly involve improvement of bulk density (BD), particle size distribution (PSD) and water holding capacity (WHC) of growing media (Dumroese et al., 2011; Headlee et al., 2013; Kaudal et al., 2015). Furthermore, fertilizers are routinely applied in containerized plant production systems to achieve near optimum plant growth (Landis, 1990) and often, nursery growers use...
more fertilizer than required and this results in higher operating costs and negative effects on
the environment due to eventual leaching loss of N and P into waterways (Novak et al., 2015).
Reduced efficiency of added N fertilizer due to loss of N by leaching is a common problem in
growing media (Shober et al., 2010) and some experiments have shown as much as 48% of
applied N fertilizer is lost as nitrate in leachate (Zhu et al., 2007). Denitrification in peat and
rice husk based growing media is another loss pathway with reports of up to 21% of applied
N lost (Agner and Schenk, 2005).
The impact of biochar on leaching of nutrients from soils and media is not uniform and this
depends mainly on type of biochar and fertilizer used (Yao et al., 2012). A number of
experiments have shown biochar decreases N and P losses from soil by increased sorption
and also reducing nitrous oxide emissions (Angst et al., 2013; Felber et al., 2013; Khan et al.,
2013; Li et al., 2013; Singh et al., 2010; Van Zwieten et al., 2010). Laird et al. (2010) reported
11% and 69% reduction in N and P leaching respectively from sandy soil columns amended
with biochar. Whilst there are a few studies that have measured loss of applied nitrogen
through leaching from biochar amended growing media in: laboratory incubation
experiments (Altland and Locke, 2012; Nemati et al., 2015) and; greenhouse studies
investigating plant nutrient uptake (Headlee et al., 2013; Zhang et al., 2014), there have been
no studies investigating nutrient supply potential from biochar amended media with
simultaneous measurement of nitrogen loss pathways including leaching and N₂O emission in
a greenhouse setting.
Leaching losses of up to 80% of P from growing media have been reported using soluble
phosphatic fertilizers (Yeager and Barrett, 1985). This P leaching is mainly due to the low P
fixation capacity of peat (Marconi and Nelson, 1984) and pine bark (Williams et al., 2000)
which is the main bulking substrate in growing media.
An understanding of the magnitude of both leaching (of N and P) and gaseous (N) loss pathways in biochar amended media is important for environmentally and economically sustainable management of soilless horticultural enterprises. Understanding the complete fate of added nitrogen can help to make improved decision making around container plant nutrition and potentially reduce costs through lowered fertilizer use.

In this greenhouse study, we grew silverbeet plants in custom made chambers designed to allow the measurement of the effect of systematic replacement of sphagnum peat by urban biochar in growing media on the nitrogen budget under a leaching regime. We also determined plant nitrogen use efficiency and heavy metal uptake to understand the suitability of urban biochar amended growing media for plant growth.

2. Materials and Methods

2.1. Feedstock and characteristics of UB

Biosolids and greenwaste (mainly municipal softwood garden waste chopped to 1.5 cm) were used as feedstock for producing UB which were dried in a commercial dryer to a moisture content of 21 wt% and blended at a ratio of 2:1 (on a dry basis). Fresh biosolids were sourced from Bangholme Eastern Treatment Plant, Victoria. The Eastern Treatment Plant at Bangholme is sited on 1,100 hectares and treats about 330 million litres of sewage a day, which is about 40% of Melbourne’s total sewage. Historically, the plant has received little waste from industry primarily owing to the youth of the plant and strict EPA regulation. Therefore these biosolids contain lower amounts of inorganic and organic contaminants (MW, 2017). The moisture content of biosolids, as received from the treatment plant, was 72 wt% dry basis. The feedstock was pyrolyzed in a commercial scale pyrolyzer by Pacific Pyrolysis Pty Ltd. at a high heat treatment of 650 °C with a residence time of 40 minutes. The feed rate was 125 kg hr⁻¹ with a biochar yield of 46 wt% dry basis. Pyrolysis parameters were
set as above in order to achieve a biochar with high surface area, high fixed carbon content (high stability), high porosity and high yield. Further details can be found in Kaudal et al. (2015).

UB was characterized for its surface area and pore properties using the Brunauer-Emmett-Teller (BET) nitrogen adsorption method. Some of the properties of UB are listed in Table 1 and 2 along with the other growing media constituents namely, composted pine bark and sphagnum peat. This UB has been characterized in detail by Kaudal et al. (2015)

2.2. Media mixes

Three plant growing media (media mixes) were tested: B0 consisted of an industry standard 20% sphagnum peat (peat) and 80% composted pine bark on a volumetric basis; B20 comprised 80% composted pine bark combined with 20% UB using a cement mixer and; B60 contained 60% UB combined with 40% composted pine bark also using a cement mixer. Composted pine bark (3-6 mm grade) was obtained from Debco Pty Ltd, Victoria, Australia. Peat was sourced from Lameque quality group Ltd, Canada.

2.3. Media and plant analysis

pH and EC of media (both substrates and mixes) were measured by shaking 1 g of media in 20 ml of deionized water on a reciprocating shaker at 100 rpm for 1.5 h (IBI, 2015). Cation exchange capacity (CEC) of media was measured according to the method of Rajkovich et al. (2012). Media air filled porosity (AFP) and water holding capacity (WHC) were measured as per the Australian Standard for potting mixes (AS 3743). For the bulk density measurement, a stainless steel cylinder with a volume of 50 cm$^3$ was filled with the sample. To ensure even packing of the cylinder for all samples, the cylinder was first filled to half and then dropped (free fall) from a height of 5 cm to the table 5 times, the cylinder was then filled to full height and again dropped twice (Handreck and Black, 2010). Bulk density measurements were based
on the final volume of the media in the cylinders and their oven dry weight (105 °C). Mineral N was determined by 2M KCl extraction of the media as per (Bremner, 1965) and NO3⁻ and NH4⁺ in the supernatant was measured using a segmented flow auto analyser (Skalar SAN plus System, Breda, The Netherlands).

Both plant and media samples were digested using a modified dry-ash method (Enders and Lehmann, 2012) and elements quantified (Al, Ca, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, and Zn) using inductively coupled plasma optical emission spectroscopy (Optima 8300 DV, PerkinElmer, Boston, USA). Total carbon and nitrogen of plant and media samples were measured using a mass spectrometer (SERCON Co, Crewe, UK) and then C:N ratio was calculated. All plant analyses were determined on finely ground samples dried at 60 °C.

2.4 Greenhouse experiment

The experiment was conducted at the University of Melbourne (Burnley campus) greenhouse maintained at day temperature of 24 °C and night temperature of 18 °C. A randomized complete block design with four replicates of each treatment was used. Plants were grown in custom made polypropylene chambers with three compartments: a lower/leachate chamber; a middle/growth chamber and; an upper/gas collection chamber. A tap was fitted to the base of lower chamber for the purpose of leachate collection. The lower and middle compartments were separated by a perforated polypropylene insert that was covered with a geofabric (Geofabric Australasia Pty Ltd, Victoria, Australia) to retain the media and to separate the leachate. The lower and middle chamber were constructed from a single polypropylene tube with an internal diameter of 17 cm and height of 18 cm. The upper chamber (internal diameter 24 cm and height 35.5 cm), with a gas sampling valve, could be securely fitted to the middle chamber to accommodate plant shoots and maintain an air-tight seal for routine gas sampling. At the beginning of the experiment the middle chamber was filled to 3 cm below
its top with each media mix and chambers were filled using the free fall method (Handreck and Black (2010). Chambers were watered every day to maintain a constant moisture status of 85% water filled pore space (WFPS). Watering was increased to 125% WFPS during leaching events with leachate collected each week and stored in a freezer prior to analysis. Water required for 85% and 125% WFPS was based on the bulk density of the media in each chamber. A basal dose of a micronutrient solution (Mn, Bo, Fe, Cu, Zn at rates of 50, 20, 18, 18, 18 kg ha\(^{-1}\) equivalents) as Cl and SO\(_4\) salts was applied to each chamber on the first day of the experiment. Weekly doses of N (as NH\(_4\)NO\(_3\)), P (as KH\(_2\)PO\(_4\)) and K (as KH\(_2\)PO\(_4\) and KCl) (89, 33, 39 kg ha\(^{-1}\) equivalents) were applied to each chamber according to department of agriculture, Western Australia recommendations for vegetable crops (Burt, 2005). Three silverbeet seeds (Beta vulgaris ssp.cicla) were sown at a depth of 1.5 cm into the mixes on day 1 and these were later thinned to the single strongest seedling. 20 ml of gas was taken using a syringe from the headspace of the upper chamber of each treatment once a week from week 3 onwards at intervals of 0, 60, 120 and 180 minutes after the chamber was closed and the gas sample transferred to pre-evacuated 12 ml glass vials. N\(_2\)O was determined with an Agilent 7890 Gas Chromatograph (Agilent Technologies, Santa Clara, USA) with the electron capture detector. Columns used are HayeSep Q80/100 which run isothermally at 60 °C using hydrogen as the carrier gas at 21 ml min\(^{-1}\) in constant pressure mode. Sample introduction was by loop injection of 1 ml at 100 °C. Gas concentrations were tested for linearity to determine the best flux and converted to N\(_2\)O flux ha\(^{-1}\)day\(^{-1}\) using the flux calculation equation developed by Ruser et al. (1998). Plant size prevented gas sampling after week 9 and the plants were harvested at week 11. Roots were hand-picked from the media at harvest. All plant material was dried at 60 °C and then weighed prior to further analysis.

2.5 Nutrient use efficiency
Nitrogen use efficiency (NUE) of plants grown on each mix was calculated by dividing total nitrogen uptake by the shoots by the added mineral nitrogen input (as liquid fertilizer) and expressed as a percentage. Phosphorus use efficiency (PUE) was calculated by dividing total phosphorus uptake by the shoots by the mineral phosphorus input and expressed as a percentage.

2.6 Particle size analysis

Particle size distribution of mixes was determined at the beginning (from retained material) and end of the experiment (from material recovered from the chambers) using a dry sieving technique. 100 g sub samples of media were placed on a nest of sieves on a vibrating sieve shaker (Endecotts, minor 200, London, UK). Sieves sizes ranged from 4 mm to 0.063 mm. Sieves were shaken at 3000 vibrations per minute for 10 minutes and the sample remaining in each sieve was then weighed.

2.7 Statistical analysis

All data were analysed using Minitab software (Minitab 16). The significance of differences between mixes and samples taken at different dates were tested using two way ANOVA. Differences between the values were considered statistically significant at $P < 0.05$. Where significant treatment effects were determined, Tukey's test was applied to separate differences between treatment means at a probability level of $P < 0.05$. Pearson correlations were performed to check the relationships between nitrogen use efficiency with air filled porosity and pH of the mixes at $P < 0.05$ level.

3. Results and Discussion

3.1 Media and substrate properties
Selected physical and chemical properties of the substrates and the media mixes are given in Tables 1 and 2, respectively. As expected the BD of peat was much lower than both UB and pine bark. Among the mixes, BD’s increased in the following order: B0, B60 and B20. B0 consisted of 20% peat (low BD substrate), therefore it has lower BD than B60 which consisted of 60% UB with a relatively higher BD. Out of three mixes, B0 has the highest WHC while B60 has the highest air filled porosity (AFP). All the values for AFP, BD and WHC of the mixes fall within the range for ideal growing media (Kaudal et al., 2015). As UB is mesoporous, with more than 67% of pores between 2 and 50 nm (Kaudal et al., 2015), adding UB to the media increased porosity of B20 and B60 and this should ensure greater oxygen availability to the roots and increased drainage. Addition of UB to the media brings the pH close to the ideal range (5.5-6) for potting media owing to the high pH of UB. The CEC values of both UB mixes (Table 2) are within the desirable media range of 5-50 cmolc kg$^{-1}$ however, these values are considerably lower than those of organic matter rich peat. As UB had the lowest CEC among the substrates (pine bark and peat), the CEC of B60 is also the lowest. There was a slight increase in the CEC of all media after the experiment which was likely due to surface oxidation of the substrates (Nguyen et al., 2009). The C:N ratio of UB amended mixes were unchanged over the duration of the experiment probably due to their high aromatic carbon content (Kaudal et al., 2015). Although the C:N ratio of all mixes were above the desirable range for growing media (30:1), this should not pose an issue for the UB mixes as much of the carbon present in UB is aromatic and not readily available for microbial use. The EC of all the substrates and mixes, both at the beginning and after the experiment, were within the ideal range for growing media (0.3-1.5 dS m$^{-1}$) (Handreck and Black, 2010). The EC of all mixes decreased after experiment, probably due to the leaching regime imposed on the chambers.
Table 1. Physical properties of the substrates and media mixes at the beginning of the experiment.

<table>
<thead>
<tr>
<th></th>
<th>Bulk Density (g cm(^{-3}))</th>
<th>Air filled Porosity (%)</th>
<th>Water Holding Capacity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peat</td>
<td>0.08</td>
<td>14</td>
<td>69</td>
</tr>
<tr>
<td>Pine Bark</td>
<td>0.37</td>
<td>14</td>
<td>45</td>
</tr>
<tr>
<td>UB</td>
<td>0.31</td>
<td>36</td>
<td>35</td>
</tr>
<tr>
<td>B0</td>
<td>0.27</td>
<td>11</td>
<td>55</td>
</tr>
<tr>
<td>B20</td>
<td>0.41</td>
<td>16</td>
<td>44</td>
</tr>
<tr>
<td>B60</td>
<td>0.35</td>
<td>18</td>
<td>41</td>
</tr>
</tbody>
</table>

3.2 Nitrogen use efficiency

NUE and fate of nitrogen for all mixes is shown in Table 4. B60 had highest NUE followed by B20 and B0. The results show that most of the N input was stored in the media (89% for B0, 94% for B20 and 96% for B60). The leachate loss of N was 1.7%, 0.3% and 0.01% for B0, B20 and B60, respectively. The N accounted for, which is the percentage of N in the media initially plus the inorganic N applied divided by the N in the media at the end of the experiment plus leachate and \(N_2O\) loss, from the mixes was 97%, 99% and 99% for B0, B20 and B60 respectively. This shows that the chambers used in this experiment were able to capture all significant N losses from the system. A strong positive correlation was found between the NUE with each of pH and AFP of the mixes with Pearson correlation coefficients of 0.864 (\(P = 0.003\)) and 0.822 (\(P = 0.006\)), respectively. This shows that the pH and AFP of the mixes play an important role in the ability of plants to uptake nitrogen.

3.3. Plant growth

There were no significant differences (\(p < 0.05\)) in silverbeet dry weights between treatments although there was a tendency for shoot and root dry weight to be highest for B60 followed by B0 and B20 (Figure 1). Thus replacing peat from B0 with 60% UB on a volume basis is at least as good and potentially better in terms of plant growth. This result is similar to Vaughn.
et al. (2013) who showed plant growth in a wood based biochar amended sand was comparable to a standard peat amended sand. Other studies have observed increase in plant growth with addition of 5-50% biochar on volume basis to growing media (Graber et al., 2010; Headlee et al., 2013; Tian et al., 2012; Zhang et al., 2014). Various mechanisms have been suggested for this increased plant productivity namely: increased retention of nutrients (Headlee et al., 2013); improved particle size distribution of the media leading to improved media porosity (Zhang et al., 2014) and; increased population of the beneficial plant growth promoting microbes (Graber et al., 2010). We propose the higher nutrient retention (Figure 2, 3 and Table 2) and higher AFP (Table 1) in B60 to be the main reasons for the improved plant biomass. B0 and B20 have a lower AFP than B60 (Table 1) which may have resulted in relatively lower plant biomass. Higher nutrient retention by B60 means there could be more nutrient available for plant uptake over the duration of the experiment. Also, higher AFP of B60 helps to improve the physical properties of growing media by providing better aeration and drainage. Higher nutrient retention may also help to reduce fertilizer requirements for the biochar amended media.
Figure 1. Root and shoot dry weight for silverbeet plants grown for 11 weeks on all mixes.

Error bars indicate the standard error of the mean (n=4)

Table 2. Selected chemical properties of the media mixes at the beginning and after the experiment. Ammonium and nitrate are from the KCl extract of the substrates and media mixes. For comparisons within columns, values are significantly different ($P < 0.001$) if they do not share a common letter.

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>C:N</th>
<th>EC (dS m$^{-1}$)</th>
<th>CEC (cmol kg$^{-1}$)</th>
<th>Ammonium-N (mg kg$^{-1}$)</th>
<th>Nitrate-N (mg kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Beginning Experiment</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peat</td>
<td>3.9a</td>
<td>54a</td>
<td>0.17a</td>
<td>23.3a</td>
<td>440.21a</td>
<td>20.15a</td>
</tr>
<tr>
<td>Pine Bark</td>
<td>4.9b</td>
<td>101b</td>
<td>0.25b</td>
<td>10.2b</td>
<td>50.29b</td>
<td>10.25a</td>
</tr>
<tr>
<td>UB</td>
<td>8.0c</td>
<td>84c</td>
<td>0.10c</td>
<td>4.7c</td>
<td>20.54b</td>
<td>10.24a</td>
</tr>
<tr>
<td>B0</td>
<td>4.7b</td>
<td>36d</td>
<td>0.35d</td>
<td>12.0d</td>
<td>26.75b</td>
<td>16.60a</td>
</tr>
<tr>
<td>B20</td>
<td>5.3d</td>
<td>56a</td>
<td>0.46e</td>
<td>8.8e</td>
<td>27.82b</td>
<td>4.91a</td>
</tr>
<tr>
<td>B60</td>
<td>6.2e</td>
<td>90e</td>
<td>0.21f</td>
<td>7.5f</td>
<td>27.40b</td>
<td>6.35a</td>
</tr>
<tr>
<td><strong>After Experiment</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B0</td>
<td>5.1a</td>
<td>33a</td>
<td>0.10a</td>
<td>12.8a</td>
<td>346.78c</td>
<td>27.93a</td>
</tr>
<tr>
<td>B20</td>
<td>6.2b</td>
<td>47b</td>
<td>0.03b</td>
<td>10.1b</td>
<td>123.65d</td>
<td>51.33a</td>
</tr>
<tr>
<td>B60</td>
<td>6.6b</td>
<td>69c</td>
<td>0.04b</td>
<td>8.5c</td>
<td>40.87b</td>
<td>109.77b</td>
</tr>
</tbody>
</table>
3.4 Nitrate leaching

Figure 2 shows the cumulative leaching loss of nitrate from all mixes over the 11 week growth period. B0 has highest loss of nitrate in leachate among all mixes. B60 has 20 times less loss of nitrate as compared to B0 and six times less as compared to B20. All the mixes showed a sigmoidal trend for nitrate leaching, with retardation of N in leachate during the first six weeks followed by an increase in nitrate leaching. Many studies have found between 5% and 80% reduction in the loss of nitrate in leachate after addition of biochar in soil (Borchard et al., 2012; Laird et al., 2010). These studies have also shown that this leaching loss of nitrate is rate dependent, with lower loss of nitrate in leachate observed from the soil where high rates of biochar was applied. In case of growing media, Altland and Locke (2012) found that biochar has been shown to attenuate nitrate release curves and 10% biochar to be most effective in reducing leachate loss of nitrate as compared to 1% and 5% addition of biochar. Similar results were observed by Nemati et al. (2015) with 11% reduction of leaching loss of nitrate from biochar amended media as compared with peat based media due to higher nitrogen retention by biochar amended media.

The inorganic N content, as determined by KCl extraction, (Table 2) shows that all of the mixes had low levels of nitrate prior to the pot experiment. After the experiment, B60 is able to capture 75% more nitrate than B0 and 58% more nitrate than B20. Similar high nitrate capture by biochar has also been observed by Kammann et al. (2015). The trend in ammonium concentration of the mixes measured after the experiment is exactly opposite to nitrate. In the case of ammonium, B0 has 85% higher ammonium than B60 and 62% higher ammonium than B20. The high CEC of the peat in B0 is likely to be the mechanism behind the high ammonium loading in B0.
Figure 2. Cumulative loss of NO3-N in leachate from all mixes over 11 weeks of the greenhouse experiment. N was applied as ammonium nitrate in equal additions at the end of each week for 11 weeks. Error bars indicate the standard error of the mean (n=4)

3.5 P leaching

Cumulative P leached from all mixes over 11 weeks is shown in Figure 3. As observed for nitrate the highest leaching of P was from B0 and lowest from B60. B60 has 50% less loss of P than B0 and 13% less P loss than B20. Yeager and Barrett (1985) have shown that as much as 80% of water soluble P fertilizer can be lost in leachate from growing media. P readily leaches from pine bark (Williams et al., 2000) and peat (Marconi and Nelson, 1984) based substrates owing to their low P fixation capacities. A number of mechanisms have been postulated for the adsorption of P to biochar: flocculation of P with cations added with biochar such as Ca and Mg (Parvage et al., 2013) and binding of P to positively charged metal complexes formed on biochar surfaces (DeLuca et al., 2009; Yao et al., 2012). According to Pathan et al. (2002)...
sludge biochar retained P by adsorption on Al- and Fe-oxides and/or by precipitation as Al-P or Fe-P. The high proportion (66%) of ferro-alumino silicate in the ash component of UB (Kaudal et al., 2015) is consistent with this mechanism. Phosphate sorption from aqueous solution by biochar has also been associated with the binding of P with nano-sized MgO particles present on the surface of biochar (Yao et al., 2012). SEM-EDX spectra of UB (not shown) revealed around 0.3% of MgO on the surface of UB and this may result in increased P sorption.

Additionally, the concentration of P in plant biomass (Table 3) indicates a higher uptake of P from B60 (380 mg) followed by B20 (152 mg) and least by B0 (140 mg) which inversely corresponds to the amount of P available in the leachate and suggests that UB reduces the leaching loss of P and the conserved P is also available for plant uptake.
Figure 3. Cumulative loss of P as leachate from all mixes over 11 weeks of the greenhouse experiment. P was applied as potassium dihydrogen phosphate at the end of each week for 11 weeks. Error bars indicate the standard error of the mean (n=4).

3.6. Nitrous oxide fluxes

Figure 4 shows cumulative fluxes of N$_2$O gas for all mixes over the period of 9 weeks. Overall, the gaseous emissions are low for all mixes and this is a minor loss pathway in our system. The small fluxes of N$_2$O from our growing media are not unexpected as the high porosity and free draining nature of the media increase aeration and inhibit denitrification. N$_2$O fluxes increased over time with emission from B0 significantly higher ($P<0.05$) than B20 and B60 for first few weeks. The initial higher flux of N$_2$O from B0 could be attributed to higher labile organic matter which may have encouraged microbial activity. In comparison, B20 and B60 are dominated by relatively recalcitrant organic material. Volatile compounds present in biochar are known to shift the microbial population structure towards microbes responsible for complete denitrification, therefore, reducing N$_2$O emission from soil (Ameloot et al., 2013; Wang et al., 2013). In our experiment, the observed initial reduction of N$_2$O by UB for first few weeks could be due to the presence of such volatile compounds in UB. As the experiment progressed, the concentration of those volatile compounds may have decreased causing an increase in N$_2$O fluxes from B60 after week 8. Similar trends were observed in a field experiment with wood biochar where higher fluxes of N$_2$O were observed after a few weeks of the experiment (Spokas, 2013). Much higher N$_2$O fluxes have been reported for soil based biochar amended cropping systems ranging from 0.4-108 mg N$_2$O-N kg$^{-1}$ soil over period of 12 days (Cayuela et al., 2013).

3.7. Nutrient elements and trace elements
The total macronutrients and heavy metal concentrations of the substrates, media mixes and plant biomass are shown in Table 3. Heavy metals such as Cd, Se, As were below detection (< 0.01 g kg\(^{-1}\)) for all samples (mixes, plant biomass), therefore not reported in Table 3. UB is relatively richer in nutrients mainly Ca, Fe, Mg, K and P than peat and pine bark although the addition of a complete nutrient solution is likely to mask any positive effect of these macronutrients. At the beginning of the experiment B60 had the highest concentration of those nutrients. After the experiment, these nutrient concentrations were lower due to plant uptake and/or leaching as suggested by the N and P leaching results (Figure 2 and 4). The corresponding phosphorus use efficiency is 16%, 20%, 25% for B0, B20 and B60, respectively which is consistent with the nitrogen results. It should be noted that biochars are generally stable for long periods and therefore the total nutrient present may be released slowly through time (Nguyen and Lehmann, 2009). However for ash rich biochars produced from biosolids, nutrients such as Ca, K, P and S have been shown to be released even in short term (Yao et al., 2010). The plant biomass figures for Ca, Mg, and P for the high ash content (45%) biochar used in our study (Table 3) support this observation.

Heavy metal concentration of all mixes, both at the beginning and end of the experiment are all within the Victorian EPA C2 level classification and within acceptable limits of USA EPA (EPA, 1993; Victoria, 2004) which suggests UB can be safely used in growing media. Furthermore, heavy metal uptake by plants is very much lower than total heavy metal content of UB, which shows that the heavy metals present in UB are largely unavailable to plants.
Table 3. Macro nutrient and heavy metal content in media and plant biomass. Mixes followed by start and end denotes measurement taken at the beginning and the end of experiment respectively.

<table>
<thead>
<tr>
<th>Macro nutrients (g kg(^{-1}))</th>
<th>Heavy metal (g kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>Fe</td>
</tr>
<tr>
<td>Pine Bark</td>
<td>8.5</td>
</tr>
<tr>
<td>Peat</td>
<td>1.7</td>
</tr>
<tr>
<td>UB</td>
<td>10.5</td>
</tr>
<tr>
<td>B0-Start</td>
<td>9.3</td>
</tr>
<tr>
<td>B20-Start</td>
<td>13.5</td>
</tr>
<tr>
<td>B60-Start</td>
<td>19.2</td>
</tr>
<tr>
<td>B0-End</td>
<td>6.2</td>
</tr>
<tr>
<td>B20-End</td>
<td>10.9</td>
</tr>
<tr>
<td>B60-End</td>
<td>15.7</td>
</tr>
<tr>
<td>B0-shoot</td>
<td>8.2</td>
</tr>
<tr>
<td>B0-root</td>
<td>7.6</td>
</tr>
<tr>
<td>B20- shoot</td>
<td>6.8</td>
</tr>
<tr>
<td>B20-root</td>
<td>8.1</td>
</tr>
<tr>
<td>B60-shoot</td>
<td>9.2</td>
</tr>
<tr>
<td>B60-root</td>
<td>10.8</td>
</tr>
</tbody>
</table>

nd=not detected (detection limit < 0.01 g kg\(^{-1}\))

Table 4. Use efficiency and fate of nitrogen for all mixes over the duration of the experiment. Numbers in brackets indicate the standard error of the mean (n=4)

<table>
<thead>
<tr>
<th>Mixes</th>
<th>N mineral input</th>
<th>Total media (beginning)</th>
<th>N leached</th>
<th>Total media (end)</th>
<th>N</th>
<th>N(_2)O</th>
<th>N biomass (Shoot + root)</th>
<th>N use efficiency (NUE) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>B0</td>
<td>1960</td>
<td>4128 (29)</td>
<td>105 (29)</td>
<td>5442 (116)</td>
<td>0.3 (0.01)</td>
<td>382 (27)</td>
<td>19 (1.2)</td>
<td></td>
</tr>
<tr>
<td>B20</td>
<td>1960</td>
<td>8262 (39)</td>
<td>30 (9)</td>
<td>9751 (41)</td>
<td>0.2 (0.01)</td>
<td>442 (47)</td>
<td>22 (2.1)</td>
<td></td>
</tr>
<tr>
<td>B60</td>
<td>1960</td>
<td>13,086 (157)</td>
<td>5 (2)</td>
<td>14,461 (616)</td>
<td>0.4 (0.01)</td>
<td>474 (50)</td>
<td>24 (2.6)</td>
<td></td>
</tr>
</tbody>
</table>
3.8. Particle size analysis

At the start of the experiment, the percentage of particles in the desirable range of 0.25-2mm for growing media is highest in B60 (71%) followed by B20 (59%) and B0 (49%). At the end of the experiment the percentage of particles in the desirable range changed for all mixes but remained highest for B60 (69%) followed by B20 (56%) and B0 (53%) (data not shown). According to Handreck (1983) for a growing media, particles in the range of 0.25-2.0mm are most effective in retaining water and also provide sufficient gas exchange to support vigorous plant growth. This particle size data also support the porosity results (Table 1) which shows the highest porosity in B60 followed by B20 and B0. Therefore, B60 has advantage over B20 and B0 in terms of greater porosity due to its desirable particle size.
5. Conclusion

To our knowledge, this is the first study that investigates the effect of biochar on nutrient supply potential from growing media using custom made chambers and considering major nutrient loss pathways for nitrogen and phosphorus including quantification of N₂O gases. Addition of biochar reduced loss of both N and P in leachate and had positive effect on plant nitrogen and phosphorus use efficiency. As B60 had ideal physical and chemical properties together with higher nutrient supply potential and plant yield comparable to standard peat based media, we recommend the use of 60% UB on volume basis as replacement of peat for growing media. Using a higher rate of biochar in growing media has the additional advantage of sequestering more carbon and, reducing urban waste streams and landfill costs.

Acknowledgements

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References


composted dairy manure solids as a peat substitute in substrate. Hortscience 45(10), 1516-1521.


Based on the Chapters 3-5, it is evident that urban biochar can be a valuable addition to growing media in terms of plant growth and environment benefits. There is evidence that biochar has additional benefits as it ages. The experiments reported to date have necessarily been short term as the shelf life of a growing media is generally few months to a year. It is in soil that the longer term benefits have been demonstrated partly because of the increased weathering that can occur in these environments. Therefore, in order to study the longer term benefit of urban biochar the focus of this thesis shifts to soil rather than growing media in the sixth Chapter. Naturally ageing urban biochar in field would take many years, hence, artificial aging of urban biochar is performed by co-composting urban biochar with food waste. After that the co-composted (aged) biochar is applied to a sandy acidic horticultural soil in order to investigate the changes in urban biochar due to composting induced ageing and the agronomical benefit of the aged biochar as compared with fresh biochar.
CHAPTER 6

This chapter is based on a submitted article entitled:

Co-composting of urban biochar with food waste decreases its efficacy as a soil amendment.

Under revision with Pedosphere from 26th October 2016.
Co-composting of urban biochar with food waste decreases its efficacy as a soil amendment

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Abstract

A co-composting experiment was conducted to artificially age urban biochar (UB). UB was produced through the pyrolysis of 2:1 ratio of biosolids and green waste and then composted with food waste (10% v/v) until compost maturity at around 70 days. A portion of the UB was also placed in litterbags within the compost in order to examine the effects of co-composting more closely. The agronomic value of UB and the finished composts (co-composted UB + food waste and food waste only) was evaluated in a greenhouse pot experiment with sorghum plants on a Semiaquic Podosol. Co-composting UB with food waste accelerated the composting process. As measured from the litter bags, co-composting increased CEC, pH, EC and nitrogen loading relative to the un-composted/fresh UB. However, the composting process reduced BET surface area and porosity of UB most probably due to clogging of pores within the UB. Results of the greenhouse experiment showed higher plant growth, lower emission of N₂O and higher nitrogen use efficiency in soil amended with un-composted UB than the soil amended with either co-composted UB or composted food waste.

Keywords: Ageing, Biosolids, Cation exchange capacity, Nutrient use efficiency, Surface oxidation.

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Introduction

Management of organic municipal wastes such as food waste, green waste and biosolids is becoming problematic in urban areas of many countries due to the rapid increase in population and policies preventing the landfill of organic wastes. There is great potential to reuse these urban organic wastes to create both biochar and compost for use as soil amendments. The biochar used in this study was produced from two significant urban waste streams, greenwaste and biosolids, hence called “urban biochar”. Many studies have shown that addition of biochar to soil improves short term physical and chemical properties (Basso et al., 2013; Brockhoff et al., 2010; Van Zwieten et al., 2010). Over longer term biochar undergoes surface oxidation (ageing) in soil (Liang et al., 2006; Spokas, 2013) and this is thought to make biochar agronomically more effective. Ageing is defined as the changes to the biochar properties as a result of long term interaction of biochar with environmental or edaphic factors. Ageing of biochar has been simulated under laboratory condition by continuous heating at 110 °C for a periods up to eight weeks and such artificial ageing increased the cation exchange capacity (CEC) of biochar by 50% (Hale et al., 2011). However, these heating processes inhibit microbes and also exclude the interaction with soil organic matter, both of which have been shown to be very important for the natural weathering of biochar (Cheng et al., 2006; Hale et al., 2011). On the other hand, co-composting – a process of composting of biochar with various organic substrates, provides all the precursors required for natural ageing: a low temperature environment; interaction with organic matter and; enhanced microbial activity (Kammann et al., 2015). Natural ageing is the oxidation of biochar when left in nature/field as opposed to laboratory/chemical oxidation. The co-composting process provides bio-oxidative environments which have been shown to cause an almost six fold increase in the CEC of biochar derived from wood products (Khan et al., 2016; Prost et al., 2013). The mechanism for the increased reactivity of biochar after composting appears to be the increase of oxygen containing functional groups mainly phenolic and carboxylic groups (Wiedner et al., 2015) and sorption of organic compounds to the biochar surface (Wang et al., 2014). Other than the increase in CEC of biochar, co-composting biochar especially with manure, has been shown to increase the concentration of nutrients with concomitant reduction in the surface area of biochar possibly due to clogging of the micropores.
by compost derived materials (Prost et al., 2013). The study of the effects of co-composting on biochar is hampered by the ability to effectively recover the biochar from the compost. Hand picking had been most commonly used (Jindo et al., 2012; Wiedner et al., 2015), however there is a distinct bias towards coarser particle sizes. More recently studies have used litterbags in biochar co-composting experiments which allowed analysis of the composted biochar sample and that was representative of the biochar in the compost mix (Khan et al., 2014; Prost et al., 2013).

In addition to the changes in biochar, adding biochar to compost also brings changes to the composting process. The properties of biochar such as high stability, high nutrient sorption capacity, micro porosity, high water holding capacity and low bulk density makes it an excellent bulking material for composting (Steiner et al., 2011). Biochar addition to poultry manure compost has been shown to reduce ammonia emissions due to its ability to adsorb ammonium during the composting process (Steiner et al., 2010). Reduction of ammonia emissions has also been observed during the first week of co-composting of biochar with sewage sludge and woodchips (Malinska et al., 2014). Furthermore, biochar aids the composting process by increasing the compost pH, accelerating the composting process, achieving a balanced C:N ratio, optimizing aeration, avoiding compaction of compost mixes and helping the compost to maintain an optimum moisture content (Sanchez-Garcia et al., 2015; Steiner et al., 2011; Vandecasteele et al., 2016). Co-composting of biochar with pig manure, has also been shown to reduce the emission of N₂O gas and this was attributed to the complete denitrification of substrate (Wang et al., 2013a). Although, biochar may reduce the emission of N₂O during the composting process, application of the co-composted biochar to soil has been shown to increase N₂O emissions by 45% as compared to non-composted biochar due to greater availability of organic compounds and nitrogen sorbed by biochar during composting process (Borchard et al., 2014; Vandecasteele et al., 2016).

In previous studies, biochar has been co-composted with various organic materials including poultry manure, cattle manure, straw, biosolids, spent mushroom and green waste (Schulz et al., 2013; Zhang and Sun, 2014). There are no studies reported on the co-composting of biochar with food waste. The composting of food waste produces high amounts of organic acids such as lactic, propionic and butyric acids which contrasts to composts produced from manures (Yu and Huang, 2009) and these organic
acids may stimulate ageing of the biochar. However, the low pH of food waste (5 - 6) during composting inhibits microbial activity (Yu and Huang, 2009) and therefore the addition of biochar (pH of 7-9) may stimulate microbial activity. Therefore, co-composting of food waste and biochar are complementary process, accelerating ageing of the biochar surface whilst increasing microbial activity.

The application of co-composted biochar to soil both in field and greenhouse based studies has shown to give mixed agronomic outcomes. In a greenhouse study, without a leaching regime, improvement of plant growth of up to 305% was observed with the application of co-composted biochar to a sandy loam soil which was attributed to increased availability of nutrients, mainly nitrogen (Kammann et al., 2015). A field study looking at three year vineyard growth on a sandy clay loam soil showed a non-significant effect of co-composted biochar on vine growth (Schmidt et al., 2014). Whereas, Bass et al. (2016) found a 24% reduction in papaya yield due to the application of co-composted biochar in a sandy loam soil as compared to fresh biochar.

Of the nitrogen related studies looking at co-composting of biochar, the main focus has been on the changes in biochar, the composting process and plant growth after applying co-composted biochar in soil. However, these studies generally lack a whole system approach. Our study aims at investigating the whole soil - plant system by looking at major nitrogen loss pathways: leaching, gaseous loss, storage by soil and plant uptake with a focus on nutrient use efficiency. Our study is the first to explore the extent of ageing of biochar due to co-composting with food waste.

2 Methodology

2.1 Biochar and compost production

2.1.1. Urban biochar feedstock and production

Fresh biosolids (72 wt% moisture) were sourced from Bangholme Eastern Treatment Plant, Victoria. Biosolids and green waste (mainly municipal softwood garden waste chopped to 1.5 cm) were dried in a commercial dryer to a moisture content of 21 wt% and blended at a ratio of 2:1 (on dry basis). Feedstock was pyrolyzed in a commercial scale pyrolyzer by Pacific Pyrolysis Pty Ltd. at the high heat treatment of 650 °C with a residence time of 40 minutes which are optimum conditions to produce
biochar with high surface area and aromaticity. Feed rate was 125 kg hr\(^{-1}\) with the biochar yield of 46 wt% dry basis.

2.1.2 Compost production

Food waste comprised mainly used coffee grounds, fruit (citrus, watermelon, pineapple) and vegetable (lettuce, celery, carrot) scraps with no meat or dairy products from the University of Melbourne student canteen. The C:N ratio of food waste feedstock was 18, which is below the desirable level for composting (C:N ratio of 30), hence commercially purchased sawdust with high C:N ratio of 295 was used to adjust the C:N ratio of each compost mix to around 30:1 according to Augustin and Rahman (2010). There were 2 compost mixes with 3 replications in the compost production. The composting mixes were prepared using the following feedstocks on a volume basis:

Food waste compost (FW compost): 95% food waste, 5% sawdust

Urban biochar compost (UB compost): 85% food waste, 10% UB, 5% sawdust.

The compost mixes were composted in a commercial composter bins, roto twin composters (composting home, Canada) which held 70 litres of compost in each compartment. The composter bins were turned 5 times every day to ensure mixing and aeration of the compost mixture. The composter bins were kept in an automated greenhouse with day and night temperature of 24 and 18 °C, respectively. The composting process was conducted for 10 weeks during which temperature and moisture were monitored to keep the moisture within the range of 40-55%. Temperature of the compost mixes were recorded every our using iButton temperature loggers placed in the middle of the mix (Thermochron, DS1922T-F5). We used a 10% biochar rate for co-composting as an earlier study evaluating rates from 1% to 30% on volume basis (Zhang et al., 2014a) suggested this to be the most effective rate. Seed germination index, ability to reach optimum Carbon: Nitrogen ratio (C: N) and peak thermophilic stage were used as maturity indices for the composts (Khan et al., 2014). Total carbon and nitrogen of the compost subsamples were measured using a mass spectrometer (Sercon, Crewe, UK). Seed germination index was calculated using method of Van Zwieten et al. (2010). At the end of composting the 3 replicates were combined for use in the greenhouse pot experiment with subsamples of the bulked material retained for chemical and physical analysis.
2.1.3 Biochar litterbags in compost

To enable recovery of composted UB from the compost mixes, a 5-6 g subsample of oven dried UB was placed in nylon litterbags (10 cm length and 10 cm width) and then placed in the compost mixes. The litterbags were made from 100% polyester fabric with an average porosity of 30 µm for unrestricted movement of composting liquids and microbes. 20 litterbags were placed in each of the co-compost mixes at the start of composting. Composted litterbag urban biochar is referred to as LUB and un-composted UB referred to as fresh UB hereafter.

2.2 Greenhouse pot experiment

The experiment was conducted at the University of Melbourne, Burnley campus greenhouse maintained at day temperature of 24 °C and night temperature of 18 °C. Topsoil (0-20 cm) of a previously unfertilised Semiaquic Podosol (sandy texture) from Clyde, Victoria with 2% organic carbon was air dried and sieved less than 4 mm. The Clyde soil was an unfertilized sandy acidic soil managed under native vegetation which was the main motive behind the site selection. Selected properties of the soil are given in Table 1. The treatments (Table 2) were then mixed with the soil in bulk from which the chambers (described below) were filled. Plants were grown in custom made polypropylene chambers with three compartments: a lower/leachate chamber; a middle/growth chamber and; an upper/gas collection chamber. A tap was fitted to the base of lower chamber for the purpose of leachate collection. The lower and middle compartments were separated by a perforated polypropylene insert that was covered with a geofabric (Geofabric Australasia Pty Ltd, Victoria, Australia) to retain the media and to separate the leachate. The lower and middle chambers were constructed from a single polypropylene tube with an internal diameter of 17 cm and height of 18 cm. The upper chamber (internal diameter 24 cm and height 35.5 cm), with a gas sampling valve, could be securely fitted to the middle chamber to accommodate plant shoots and maintain an air-tight seal for routine gas sampling. At the beginning of the experiment the lower chamber was filled to 3 cm below its top with each treatment. All treatments were then pre-incubated in the greenhouse for 4 weeks with a constant moisture content of 40% water filled pore space (WFPS) in order to stabilize the microbial population in the treatments (OECD, 2002). A randomized complete block design with four replicates of each treatment was used. After the pre-
incubation, all the treatments were watered daily to maintain a constant moisture status of approximately 75% WFPS. Some leachate was evident during the experiment and this was collected and analysed for NH$_4^+$ and NO$_3^-$ using a segmented flow auto analyser (Skalar SAN ++ System, Breda, The Netherlands). A basal dose of the mineral form of nutrients (Mg, S, Ca, Fe, B, Mn, Zn, Cu, Mo, Co) at rates equivalent to 30, 25, 35, 7, 2, 5, 4, 3, 0.4, 0.1 kg ha$^{-1}$ was applied to all chambers after the pre-incubation period. Weekly doses of N (as NH$_4$NO$_3$), P (as KH$_2$PO$_4$) and K (as KH$_2$PO$_4$ and KCl) (89, 33, 39 kg ha$^{-1}$ equivalents) were applied as solutions to each chamber. Three sorghum seeds (variety MR -Taurus) were pre-germinated for 4 days on filter paper and then inserted at a depth of 1.5 cm into the soil on day 1 and these were later thinned to the two strongest seedlings. 20 ml of gas was taken from the headspace of each chamber once a week at intervals of 0, 20, 40, 60 and 80 minutes after the chamber was closed the sampled gas was emptied into pre-evacuated 12 ml glass vials. Agilent 7890 Gas Chromatograph (Agilent Technologies, Santa Clara, USA) fitted with the electron capture detector was used for nitrous oxide determination. Columns used were HayeSep Q80/100 run isothermally at 60 °C with hydrogen as a carrier gas at 21 ml min$^{-1}$ in constant pressure mode. Gas concentrations were tested for linearity to determine the best flux and converted to N$_2$O flux ha$^{-1}$day$^{-1}$ using the flux calculation equation developed by (Ruser et al., 1998). Plant size prevented gas sampling after week 5 and the plants were harvested at week 7. After the harvest, roots were hand-picked from the soil. Both roots and shoots were weighed and dried at 60 °C for further analysis.

2.3 Chemical and physical analysis

pH and EC of soil and compost and greenhouse treatments were measured by shaking 5 g of soil in 25 ml of deionized water for 1 hour. pH and EC of biochar samples were measured on 1 g biochar in 20 ml deionized water (IBI, 2015). Cation exchange capacity (CEC) of soil, compost and greenhouse treatments were measured according to the method of Rajkovich et al. (2012). Inorganic-N (NO$_3^-$ and NH$_4^+$) was extracted from 10 g samples as per Pathan et al. (2002) and NO$_3^-$ and NH$_4^+$ in the extracted sample was measured using a segmented flow auto analyser (Skalar, SAN ++ System, the Netherlands). For LUB and fresh UB samples, entrained inorganic N was measured using a sequential washing procedure (Kammann et al., 2015). In brief, 1.5 g of sample was shaken with 10 ml 2M KCl on a
reciprocating shaker, filtered and the filtrate retained for inorganic N analysis. This step was repeated with the following sequence of solutions (1) 1 h with volume distilled water, (2) 24 h with a new volume of distilled water, (3) 1 h with a volume of 2 M KCl and (4) 24 h with a new volume of 2 M KCl. All filtrates were analysed for NO$_3^-$ and NH$_4^+$ in the supernatant using a segmented flow auto analyser (Skalar, SAN ++ System, the Netherlands).

All plant, greenhouse treatments and compost samples were digested using a wet digestion method (Enders and Lehmann, 2012) and elements quantified (Al, Ca, Fe, K, Mg, Mn, Na, P, Pb, S and Zn) using inductively coupled plasma optical emission spectroscopy (Optima 8300 DV, PerkinElmer, Boston, USA). The C: N ratio of plant, soil and compost samples were measured by using a mass spectrometer (SERCON Co, Crewe, UK). All of these chemical properties (total C and N, CEC, elemental analysis, pH, EC) were measured both pre and post pot experiment. Organic carbon of soil was measured using walkley-black method and particle size was determined by using the hydrometer method. Available water holding capacity (AWHC) and field capacity (FC) of all greenhouse treatments were measured as per the ASTM D6836 (ASTM, 2008). Bulk density measurements of the greenhouse treatments were measured before pre-incubation according to Kaudal et al. (2016)

Surface area, pore volume, pore diameter and pore width parameters of UB and LUB was determined from a nitrogen gas sorption isotherm, which was measured using a Tristar 3000 surface area and porosity analyser (Micrometrics Instrument Corporation, USA) in degassed samples (250 °C for 18 h on a vacuum line) at -196 °C. The specific surface area of the sample was calculated by a standard multipoint Brunauer-Emmett-Teller (BET) method. To further examine the effect of composting on LUB, a subsample was washed with analytical grade acetone to remove surface and dissolved organics from the sample. In brief, 2 g sub sample of LUB was mixed with 30 ml of acetone in a glass vial and shaken on a reciprocating shaker for 10 minutes and then filtered using a Whatman 42 filter paper. This process was repeated three times and after the third washing, the LUB retained in the filter paper was dried at 40°C re-analysed for surface area. Surface characteristics of LUB and fresh UB were observed using PHILIPS (FEI) XL30 ESEM TMP scanning electron microscope operating at 20 kV. Comparative images for UB and LUB was selected on the basis of particle size of biochar. Biochar
particle with similar size was scanned before and after the composting process. UB has been characterized in detail by Kaudal et al. (2015).

2.4. Functional group analysis

Diffuse reflectance mid-infrared spectra of fresh UB and LUB were recorded using PerkinElmer Spectrum One FTIR spectrometer (PerkinElmer, MA, USA) from 7800 to 450 cm\(^{-1}\) at 8 cm\(^{-1}\) resolution by co-adding the scans for one minute. Spectra were corrected for atmospheric water vapour and CO\(_2\) with a background spectrum collected prior to running samples. PerkinElmer instrument control software (Spectrum 5.0.1) was used to identify and compare chemical functional groups.

2.5 Nitrogen use efficiency

Nitrogen use efficiency (NUE) of each mix was calculated by dividing the total nitrogen uptake by the shoots by the mineral nitrogen input and expressed as a percentage.

2.6 Statistical analyses

All data were analysed using Minitab software (Minitab 17). The significance of differences between treatments were tested using a two-way ANOVA. Differences between the values were considered statistically significant at \( P < 0.05 \). Where significant treatment effects were determined, Tukey's test was applied to separate differences between treatment means at a probability level of \( P < 0.05 \).

3 Results and discussion

3.1 Composting process

The temperature of all the compost mixes showed an initial high temperature of 55 \(^\circ\)C within the first two weeks followed by reduced temperature of 23-25 \(^\circ\)C for the remaining composting period (data not shown). Furthermore, UB compost reached the highest temperature (55 \(^\circ\)C), five days sooner than the FW compost. This could be due to increased aeration improving conditions for microbial growth in the UB amended compost mixes. The C:N ratio of the compost mixes reduced during the composting process to values appropriate for matured compost (C:N ratio <21) (USCC, 2002). In agreement with this, seed germination was 95% and 85% for composted UB and FW, respectively. The positive results for this suite of compost maturity tests confirmed that each of the compost mixes were mature.

3.2 Properties of finished composts
Selected properties of finished composts are listed in Table 1. The pH of both finished compost mixes were around 8, which is also an optimum pH for composting microorganisms (Khan et al., 2014). FW compost has slightly higher pH, N, EC, CEC, K and S than UB compost and this is likely a dilution effect of UB on values for FW compost. UB compost is richer in C, Ca, Mg and P than FW compost owing to the high concentration of those elements in UB (Table 1). As the food waste used for this composting study consists mostly of citrus fruits and vegetable scraps which are known to have around 0.9- 1.4 g kg\(^{-1}\) of K (Lasztity, 2009), the both FW compost reflects this high K content.

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>N</th>
<th>C</th>
<th>EC</th>
<th>CEC</th>
<th>Ca</th>
<th>Fe</th>
<th>Mg</th>
<th>K</th>
<th>P</th>
<th>S</th>
<th>Al</th>
<th>Na</th>
<th>Pb</th>
<th>Mn</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>UB compost</td>
<td>8.1</td>
<td>2.8</td>
<td>48</td>
<td>2.21</td>
<td>8.2</td>
<td>4.4</td>
<td>3.5</td>
<td>2.4</td>
<td>24.8</td>
<td>9.4</td>
<td>2.6</td>
<td>0.631</td>
<td>0.167</td>
<td>0.011</td>
<td>0.117</td>
<td>0.054</td>
</tr>
<tr>
<td>FW compost</td>
<td>8.5</td>
<td>3.5</td>
<td>40</td>
<td>3.55</td>
<td>8.4</td>
<td>4</td>
<td>3.4</td>
<td>1.5</td>
<td>38.4</td>
<td>7.1</td>
<td>5.4</td>
<td>0.714</td>
<td>0.351</td>
<td>Nd</td>
<td>0.171</td>
<td>0.296</td>
</tr>
<tr>
<td>Soil</td>
<td>5.2</td>
<td>0.2</td>
<td>3</td>
<td>0.02</td>
<td>2.5</td>
<td>0.4</td>
<td>0.7</td>
<td>Nd</td>
<td>Nd</td>
<td>0.3</td>
<td>Nd</td>
<td>3.053</td>
<td>Nd</td>
<td>0.015</td>
<td>0.045</td>
<td>0.024</td>
</tr>
<tr>
<td>UB</td>
<td>7.7</td>
<td>0.7</td>
<td>59</td>
<td>0.28</td>
<td>4.2</td>
<td>11.1</td>
<td>4.4</td>
<td>4.6</td>
<td>5.4</td>
<td>24.7</td>
<td>2.6</td>
<td>3.695</td>
<td>0.118</td>
<td>0.054</td>
<td>0.319</td>
<td>0.83</td>
</tr>
<tr>
<td>LUB</td>
<td>9.3</td>
<td>1.8</td>
<td>56</td>
<td>1.96</td>
<td>7.0</td>
<td>9.9</td>
<td>4.2</td>
<td>3.8</td>
<td>22.4</td>
<td>9.9</td>
<td>1.9</td>
<td>2.147</td>
<td>3.565</td>
<td>0.019</td>
<td>0.144</td>
<td>0.414</td>
</tr>
</tbody>
</table>

Nd: not detected (detection limit <0.01 g kg\(^{-1}\))

UB: Fresh urban biochar, LUB: biochar in litterbags, UB compost: UB co-composted with food waste,

FW compost: food waste compost

Table 2. Composition of treatments used in greenhouse pot experiment.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Composition of treatments (on volume basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UB-P</td>
<td>Soil + 10% UB (without plants)</td>
</tr>
<tr>
<td>UB+P</td>
<td>Soil + 10% UB (with plants)</td>
</tr>
<tr>
<td>CUB</td>
<td>Soil + 10% UB compost (with plants)</td>
</tr>
<tr>
<td>FW</td>
<td>Soil + 10% FW compost (with plants)</td>
</tr>
</tbody>
</table>

UB: Fresh urban biochar, UB compost: urban biochar co-composted with food waste, FW compost: food waste compost.

3.3 Ageing of UB due to composting with food waste
3.3.1 Surface properties

The BET surface area of UB reduced from 396 m² g⁻¹ to 12 m² g⁻¹ as a result of co-composting with food waste. We hypothesize, in our experiment, the organics released during the composting process have clogged the surface pores of UB, and therefore, blocked the entry of nitrogen gas during the measurement of BET surface area resulting in a lower surface area value for LUB. The total volume of pores less than 124 nm diameter was also reduced from 0.16 cm³ g⁻¹ in fresh UB to 0.02 cm³ g⁻¹ in LUB. An increase of average pore width from 1.6 nm in fresh UB to 4.7 nm in LUB suggests blocking of micropores during composting. Jindo et al. (2012) suggested similar reduction in surface area of biochar due to sorption of dissolved organic substances produced during the composting process. To examine this hypothesis we washed LUB with acetone in order to remove the organics and remeasured the BET surface area. BET surface area of acetone washed LUB showed higher surface area of 76 m² g⁻¹. However, the acetone washed surface area of LUB was still four times smaller than fresh UB and other unexplained mechanisms must be responsible for the reduction in surface area of UB. Particle breakdown during composting and subsequent movement of those small particles into the small pores of UB could be another mechanism for the clogging of surface pores of UB. This blocking of the surface pores of LUB is further supported by SEM results (Fig 1) where there are only a few visible surface pores in LUB as compared to clear surface pore structures of UB. This loss of visible surface pores on LUB also supports the observed decrease of surface microporosity of LUB as indicated by the nitrogen gas sorption method.
3.3.2 FTIR spectra

The FTIR spectra of UB and LUB are shown in Fig 2. The spectra of UB shows distinct aromatic bands at 3044, 1610, 1132 and 880–754 cm⁻¹ and a relatively small peak at 1700 cm⁻¹ for carboxyl C stretching (Cheng et al., 2006). Co-composting biochar with food waste resulted in some changes in functional groups of biochar. For LUB, the peaks for the carboxyl functional group (1700 cm⁻¹) and the peaks for the carboxylic O-H group (1270 cm⁻¹) became slightly stronger compared to that of UB. The spectrum of UB shows very small peaks at 1700 cm⁻¹ for carboxyl C stretching (Cheng et al., 2006). High temperature pyrolysis generally leads to loss of carboxyl groups (Kaudal et al., 2015) leading to low CEC in the UB (Table 1) and this is reflected in the very weak bands at 1700 cm⁻¹. Studies of co-composting biochar with other substrates have also shown an increase in carboxyl functional groups on the surface of composted biochar (Khan et al., 2016). Carboxyl groups of charcoal surface are known to increase over time due to chemical and biotic oxidation and hence resulting in the very high CEC of naturally occurring charcoal in terra-preta soils (Liang et al., 2006). We hypothesize, that the enlargement of peaks for carboxyl functional groups of LUB (1270 cm⁻¹) is likely a result of biotic and abiotic oxidation of UB during composting process. In our study, high temperature thermophilic stage combined with ability of biochar to sorb organic compounds produced during composting may have
caused surface oxidation of biochar as shown by the increase of carboxyl functional groups of LUB and also supported by the observed increase in the CEC of LUB (Table 1).

![FTIR spectra of fresh UB (UB) and litterbag urban biochar (LUB)](image)

**Fig 2. FTIR spectra of fresh UB (UB) and litterbag urban biochar (LUB)**

### 3.3.3 Chemical properties

Chemical properties of fresh UB and LUB are listed in Table 1. Co-composting strongly increased the alkalinity of the UB. EC of LUB has increased most possibly due to sorption of salts from the food waste during composting. Nitrogen loading of LUB increased nearly three folds during the composting process. Co-composting has also increased the CEC of UB by 37%. Similar increase in CEC after composting of biochar has also been reported by Khan et al. (2016). This increase in CEC of LUB is consistent with FTIR results which show an increase in the intensity of carboxyl functional groups (fig 2). Organic acids produced during the composting of FW may have helped to oxidize the surface of UB. Thus, increased the CEC of UB which led to adsorption of ammonium and concomitantly dissolve Ca and P present in the ash component of UB as shown by lower concentration of Ca and P in LUB.

### 3.4 Greenhouse experiment

#### 3.4.1 Physical properties
Among the treatments, the UB compost amended treatment (CUB) had the lowest bulk density. AWHC shows an opposite trend to bulk density, with the highest AWHC for fresh UB amended soil (UB+P) and the lowest for CUB (Table 3). Soil used in the experiment has low AWHC (8%) which is significantly ($P > 0.05$) improved by the addition of fresh UB. Fresh UB addition increases AWHC of soil by 75% while addition of UB compost and FW compost has only slight improvement in the soil AWHC (13%).

Table 3. The change in selected chemical and physical properties of each of the treatments imposed during the greenhouse pot experiment. For comparisons within columns, values are significantly different ($P < 0.05$) if they do not share a common letter.

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>N (%)</th>
<th>C (%)</th>
<th>EC (dS m$^{-1}$)</th>
<th>CEC (cmolc kg$^{-1}$)</th>
<th>BD (g cm$^{-3}$)</th>
<th>AWHC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Start of experiment</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UB-P/UB+P</td>
<td>5.62ef</td>
<td>0.282a</td>
<td>8.01a</td>
<td>0.06ef</td>
<td>5.02d</td>
<td>1.22a</td>
<td>14a</td>
</tr>
<tr>
<td>CUB</td>
<td>6.41de</td>
<td>0.293a</td>
<td>5.04b</td>
<td>0.23def</td>
<td>4.61d</td>
<td>1.04b</td>
<td>9b</td>
</tr>
<tr>
<td>FW</td>
<td>6.96de</td>
<td>0.256a</td>
<td>5.43b</td>
<td>0.28d</td>
<td>4.22d</td>
<td>1.09b</td>
<td>9b</td>
</tr>
<tr>
<td><strong>End of experiment</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UB-P</td>
<td>6.01e</td>
<td>0.487b</td>
<td>8.57a</td>
<td>0.07ef</td>
<td>7.05c</td>
<td>NM</td>
<td>NM</td>
</tr>
<tr>
<td>UB+P</td>
<td>6.11e</td>
<td>0.491b</td>
<td>8.26a</td>
<td>0.07ef</td>
<td>7.14c</td>
<td>NM</td>
<td>NM</td>
</tr>
<tr>
<td>CUB</td>
<td>5.97e</td>
<td>0.417b</td>
<td>5.44b</td>
<td>0.18def</td>
<td>5.13d</td>
<td>NM</td>
<td>NM</td>
</tr>
<tr>
<td>FW</td>
<td>6.85d</td>
<td>0.403b</td>
<td>5.91b</td>
<td>0.11def</td>
<td>5.04d</td>
<td>NM</td>
<td>NM</td>
</tr>
</tbody>
</table>

NM- not measured

UB-P: Soil + 10% UB (without plants), UB+P: Soil + 10% UB, CUB: Soil + 10% UB compost, FW: Soil + 10% FW compost.

3.4.2 Chemical properties

After eleven weeks of incubation, the pH of soil with the composted materials (CUB and FW) slightly decreased whilst the pH of soil with fresh UB amendment (UB-P and UB+P) slightly increased (Table 3), although this was not significantly different ($P > 0.05$). C: N ratio of all treatments were significantly reduced ($P > 0.05$) due to nitrogen retention in the amended soil (Table 3). The CEC of UB+P and UB-P increased significantly ($P > 0.05$) which suggests an interaction between the acidic Podosol and the UB. Podosols are known to have between 1 and 8% humic acid (Vialykh et al., 2014). In a study...
investigating growing media properties amended with biochar and humic acids, amendment of biochar and humic acid together resulted in the highest increase of CEC of the media mixture as compared to the addition of biochar and humic acid separately (Zhang et al., 2014b). This supports the idea that humic acid present in otherwise unreactive sandy soil may affect the biochar surface and increase the CEC of UB-P and UB+P. A similar increase in CEC of sandy soil amended with wood based high temperature biochar has also been shown in another short term study (Partey et al., 2014). The concentration of nutrients such as Ca, Mg, Fe and K measured at the end of experiment for all treatments were slightly lower than the concentration of those elements at the start of the experiment, despite the application of basal nutrients and this is consistent with uptake of those nutrients by plants (Table 4). Although fresh UB contains some heavy metals (Table 1), the concentration of those heavy metals for all treatments and plant biomass are within the Victorian EPA C2 level classification which allows safe application to land (EPA, 2004). Furthermore, heavy metals, Cd and Mo were below detection for all treatments tested, therefore not shown on the Table 4.

Table 4. Total nutrient elements and heavy metal content in treatments and plant biomass for the greenhouse experiment. Treatment names followed by ‘start’ and ‘end’ denote measurements taken at the start and the end of experiment respectively.

<table>
<thead>
<tr>
<th>Nutrient elements (g kg⁻¹)</th>
<th>Heavy metals (g kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca Fe Mg Al Na K P S Pb Mn Ni Zn</td>
<td>Ca Fe Mg Al Na K P S Pb Mn Ni Zn</td>
</tr>
<tr>
<td>UB-P/UB+P start</td>
<td>9.7 3.8 2.5 2.4 2.5 0.1 1.4 0.237 0.011 0.072 0.011 0.053</td>
</tr>
<tr>
<td>CUB start</td>
<td>5.4 2.7 1.4 1.6 2.1 0.8 0.6 0.115 0.013 0.061 Nd 0.035</td>
</tr>
<tr>
<td>FW start</td>
<td>2.0 2.1 0.9 2.5 3.5 1.2 0.4 0.152 0.011 0.044 0.021 0.044</td>
</tr>
<tr>
<td>UB-P end</td>
<td>1.8 2.0 0.5 2.7 0.1 0.3 1.6 0.214 0.016 0.081 0.012 0.068</td>
</tr>
<tr>
<td>UB+P end</td>
<td>1.8 1.4 0.3 1.5 Nd 0.1 1.4 0.335 0.014 0.082 0.014 0.051</td>
</tr>
<tr>
<td>CUB end</td>
<td>1.0 0.1 0.1 0.6 Nd 0.6 0.5 0.225 0.013 0.062 0.016 0.032</td>
</tr>
<tr>
<td>FW end</td>
<td>0.9 Nd 0.1 Nd Nd 0.8 0.3 0.241 0.011 0.054 0.017 0.025</td>
</tr>
<tr>
<td>UB+P shoot</td>
<td>2.7 Nd 5.1 Nd 0.1 34.3 8.5 1.634 Nd 0.012 Nd 0.077</td>
</tr>
<tr>
<td>CUB shoot</td>
<td>2.4 Nd 3.2 Nd Nd 36.5 7.5 1.361 Nd 0.111 Nd 0.081</td>
</tr>
<tr>
<td>FW shoot</td>
<td>1.7 Nd 3.2 Nd Nd 43.8 7.2 1.912 Nd 0.061 Nd 0.062</td>
</tr>
<tr>
<td>UB+P root</td>
<td>3.7 7.0 3.1 6.7 2.4 14.4 12.7 3.224 0.012 0.154 0.024 0.073</td>
</tr>
<tr>
<td>CUB root</td>
<td>2.4 5.5 1.4 4.2 0.7 11.8 9.1 1.139 0.013 0.178 0.043 0.074</td>
</tr>
<tr>
<td>FW root</td>
<td>1.9 5.9 0.7 2.9 0.8 12.7 9.5 1.352 0.011 0.143 0.048 0.051</td>
</tr>
</tbody>
</table>
3.4.3 Plant growth, nutrient uptake and leaching loss

Both root and shoot biomass of the UB+P treatment was significantly higher ($P < 0.05$) than CUB and FW (fig 3). Shoot biomass of plants grown in UB+P was 74% and 70% higher and the root biomass was 43% and 64% higher than the plants grown on CUB and FW, respectively. Studies have found mixed results on plant growth after application of co-composted biochar to soil. A greenhouse study investigating effects of application of 2% co-composted wood biochar (composted with manure) on a sandy loam soil found improved plant growth (Kammann et al., 2015) while plant growth was reduced under field conditions after application of similar co-composted wood biochar to a sandy clay loam soil (Schmidt et al., 2014). A greenhouse study showed that the plant growth in a sandy loam soil amended with fresh biochar was three times higher than co-composted biochar (prepared by co-composting of wood based biochar and sewage sludge) (Schulz et al., 2013). Our results also show a fourfold increase in shoot biomass and a threefold increase in root biomass for fresh biochar amended soil when compared to co-composted biochar. The reduction in root and shoot biomass of plants grown in FW treatment may be due to low AWHC of the treatment (Table 3). Characterization of fresh UB from our previous study (Kaudal et al., 2016) shows fresh UB has high AWHC (25%) which is higher than the treatments of our greenhouse experiment (Table 3). In the treatments UB-P and UB+P, 10% fresh UB was added as compared to addition of 1% co-composted biochar in CUB. Therefore, UB-P and UB+P may have a greater AWHC than FW and CUB, simply due to the difference in their application rates.

The average amount of inorganic nitrogen (sum of $\text{NO}_3^-$ and $\text{NH}_4^+$) lost in leachate from UB+P, FW, UB-P and CUB were 8, 158, 254, 417 mg pot$^{-1}$ respectively. The significantly smaller loss of N from UB+P as compared to other treatments may be due to the higher CEC of the UB (Table 3). Similar results were observed in a study where there was large loss of inorganic nitrogen from soil amended...
with compost as compared to soil amended with fresh biochar (Sorrenti and Toselli, 2016). Both UB-P and UB+P had a similar CEC (Table 3), however, as there were no plants grown in UB-P, there was no plant nitrogen uptake, and therefore greater (Table 4) leaching loss.

![Fig 3](image-url)

**Fig 3.** Root and shoot dry weight for sorghum plants grown for 7 weeks with the indicated treatments. Error bars indicate the standard error of the mean (n=4).

### 3.4.4 Cumulative N₂O emission

Cumulative N₂O emission from all treatments (Fig 4) shows a significantly higher emission than from CUB treatment than the other treatments ($P < 0.05$) and is probably due to higher levels of ammonium and nitrate (Fig 5), and thus greater substrate for denitrification. To our knowledge, there are only two published studies which have compared N₂O emissions from composted and fresh biochar amended soils and these also showed higher N₂O emission from soil amended with co-composted biochar. These authors speculated that this was most likely due to the greater microbial activity due to higher
availability of organic carbon and nitrogen sorbed by biochar during composting (Borchard et al., 2014; Vandecasteele et al., 2016).

A number of mechanisms have been suggested for reduced N₂O emissions after fresh biochar is applied to soil, such as increased aeration (Singh et al., 2010), reduced nitrate availability to denitrifiers (Cayuela et al., 2013), the toxic effect of PAH and phenolic compounds to microorganisms (Wang et al., 2013b), sorption of ammonium onto the biochar surface (Dempster et al., 2012), improvement in soil moisture (Saarnio et al., 2013), increase in soil pH (Wang et al., 2013a) and change in microbial community structure (Harter et al., 2013). In our study, it is unlikely that the adsorption of ammonium by fresh UB is the mechanism for reduced N₂O emission because the KCl soil extract showed that UB-P and UB+P had consistently lower concentration of ammonium during the experiment (Fig 5) while having the lowest N₂O emissions when compared with FW and CUB (Fig 4). More recently, a new mechanism for the ability of biochar to reduce N₂O emissions from soils has been postulated by Kammann et al. (2015). They have suggested that biochar has the ability to capture nitrate which is only partly available, thereby substrate availability to the denitrifying bacteria is reduced. Furthermore, they have also shown that the captured nitrate is only partially recovered by the traditional extraction method. To test that hypothesis and to understand the magnitude of nitrate captured by fresh UB and LUB, we performed sequential extraction according to the method of Kammann et al. (2015). The results of sequential extraction show that the total nitrate recovered from the extraction procedure is small when compared with the weekly additions of nitrogen to the experiment, therefore, it is unlikely to play a big role on reducing the substrate availability for microbes. However, we do agree with Kammann et al. (2015) that the traditional extraction method of nitrate, which is by shaking biochar in 2M KCl for one hour, is not vigorous enough to extract all nitrate present in fresh and co-composted biochar. Our results of sequential extraction (Fig 6) showed that the first extraction step, which is equivalent to the traditional extraction method, recovered only 6% nitrate and 50% ammonium from fresh UB; recovered only 1% nitrate and 30% ammonium from LUB. There is highest recovery for nitrate from LUB (53%) which occurs during the last step of extraction. Therefore, according to our results the traditional extraction
method of shaking biochar 1 hour is not effective for complete recovery of nitrate and ammonium present in the biochar.

Fig 4. Cumulative emission of nitrous oxide gas from all treatments over 5 weeks. Error bars indicate the standard error of the mean (n=4). UB-P: Soil + 10% UB (without plants), UB+P: Soil + 10% UB, CUB: Soil + 10% UB compost, FW: Soil + 10% FW compost

3.5 Nitrogen use efficiency

NUE and nitrogen balance for all treatments are shown in Table 5. NUE of all treatments are significantly different ($P < 0.05$) with the highest NUE from UB+P which is approximately three times higher than CUB followed by FW. Most of the N applied was stored in the amended soil at the end of the experiment (84% for UB-P, 79% for UB+P, 87% for CUB and 79% for FW). The N accounted for was defined as the percentage of N in the treatment initially plus the inorganic N applied divided by the N in the treatment at the end of the experiment plus leachate and N$_2$O loss from the treatments. N accounted for was 85%, 81%, 91% and 81% for UB-P, UB+P, CUB and FW respectively which shows that the chambers used in this experiment were able to capture all significant N losses from the system.
Table 5. Use efficiency and fate of Nitrogen for all treatments over the duration of the experiment.

Numbers in brackets indicate the standard error of the mean (n=4)

<table>
<thead>
<tr>
<th>Treatments</th>
<th>N mineral input</th>
<th>Total N treatment (start)</th>
<th>N leached</th>
<th>Total N treatment (end)</th>
<th>N$_2$O</th>
<th>N biomass (shoot + root)</th>
<th>N use efficiency (NUE) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>UB-P</td>
<td>800</td>
<td>18,860 (53)</td>
<td>254 (26)</td>
<td>16,428 (235)</td>
<td>0.171 (0.04)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>UB+P</td>
<td>800</td>
<td>19,106 (80)</td>
<td>84 (3)</td>
<td>15,891 (513)</td>
<td>0.105 (0.01)</td>
<td>294 (26)</td>
<td>37 (1.7)</td>
</tr>
<tr>
<td>CUB</td>
<td>800</td>
<td>10,818 (69)</td>
<td>342 (90)</td>
<td>10,090 (248)</td>
<td>0.356 (0.08)</td>
<td>84 (13)</td>
<td>12 (2.1)</td>
</tr>
<tr>
<td>FW</td>
<td>800</td>
<td>14,452 (113)</td>
<td>158 (28)</td>
<td>12,150 (125)</td>
<td>0.102 (0.01)</td>
<td>80 (19)</td>
<td>20 (9.2)</td>
</tr>
</tbody>
</table>

UB-P: Soil + 10% UB (without plants), UB+P: Soil + 10% UB, CUB: Soil + 10% UB compost, FW: Soil + 10% FW compost

Fig 5. Ammonium and nitrate in KCl extract of all treatments used in the greenhouse pot experiment at the start and end of the experiment. Error bars indicate the standard error of the
mean (n=4). UB-P: Soil + 10% UB (without plants), UB+P: Soil + 10% UB, CUB: Soil + 10% UB compost, FW: Soil + 10% FW compost

Fig 6. Ammonium and nitrate release from fresh UB and LUB after sequential extraction. The sequential extraction was performed after completion of the composting process. Step 1- 1 h washing with deionized water, step 2- 24 h washing with deionized water, step 3- 1 h washing with 2M KCl, step 4- 24 h washing with 2M KCl.

4. Conclusions

Co-composting urban biochar with food waste improved the composting process by reducing composting time and improving seed germination index. Co-composting also increased the CEC and nitrogen content of fresh UB. However, there was a significant reduction in the surface area of the biochar due to clogging of the pores by the organics and fine particles present in the compost. The greenhouse experiment showed better plant growth and greater nitrogen uptake and lower N2O emission from the soil amended with fresh UB than the soil amended with co-composted UB and food waste compost. This study verifies that co-composting can be used to artificially age biochar. Although some of the composting parameters and UB properties are improved by co-composting UB with food waste,
fresh UB is found to be better than co-composted UB for plant growth, plant nitrogen uptake and for reducing nitrous oxide emission.

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Connecting statements

Detail characterization of urban biochar and four experiments were conducted to examine the effects of urban biochar on the physical and chemical properties of growing media and soil. In the following chapter, the major findings of individual experiments are presented and implications of the findings are discussed.
CHAPTER 7

GENERAL DISCUSSION AND CONCLUSIONS

7.1 Major findings

Comprehensive characterization of urban biochar (UB) and comparison with published data for growing media substrates indicated that UB has potential to be used as a growing media substrate (Chapter 3). Further examination of the effects of UB on physical and chemical properties of growing media and on that basis showed that UB can completely replace peat from growing media and can be used up to 60% UB (V/V). UB amended media generally maintained more favourable conditions for plant growth than industry standard media (peat and pine bark based media) in terms of pH, capacity to supply nutrients, particle size distribution and higher water holding capacity particularly, at lower suctions when media dries. Furthermore, UB amended media proved to be more stable than industry standard media in terms of physical and chemical stability even after being exposed to periodic wetting and drying cycles (Chapter 4). Growing media with 60% UB on volume basis (B60) has highest nitrogen and phosphorus use efficiency with reduced loss of both nitrate and phosphate in the leachate as compared with industry standard media without biochar (B0) (Chapter 5). The ability of B60 to capture 78% more nitrate than B0 was the reason for reduced loss of nitrate in leachate.

Co-composting biochar with food waste accelerated the ageing of UB due to the presence of an assumed bio-oxidative environment in the composting process, resulting in an increase of oxygen containing functional groups (mainly phenolic and carboxylic groups) on the UB surface. Co-composting also accelerated the composting process, increased CEC and the nutrient load of UB. Co-composting process reduced the surface area of UB due to clogging
of the surface pores presumably by the organics produced during composting which resulted in lower water holding capacity of the co-composted UB amended soil as compared to the soil amended with fresh UB. Additionally, nutrients present in co-composted UB were only partly available for plant uptake. Therefore, application of compost mixture containing aged/co-composted UB to the soil resulted in poorer plant growth, lower nutrient use efficiency, greater N₂O emission and lower water holding capacity as compared to the soil amended with fresh/un-composted UB (Chapter 6).

7.2 Implications of the study

7.2.1 Environmental benefit

Municipal wastes such as biosolids and greenwaste are becoming increasingly problematic with the increase in volume of waste generated associated with growing urban population. Traditionally greenwaste and biosolids have been viewed as wastes and were discarded to landfill. Recently, government policy has changed towards zero waste which aims to divert organic waste from landfill and encourages resource recovery (Victoria 2012). Alternative use for these waste streams have been sought including composting and returning to land as a soil conditioner. Contamination of biosolids by heavy metals limits large scale disposal on land. This disposal also requires long distance transport out of the urban areas into adjacent rural areas which is costly and environmentally unfriendly. However, the availability of land close to cities, objections to odour, as well as the emission of gases such as ammonia, nitrous oxide and methane limit urban composting. Biochar is an alternative way of managing those urban wastes through their pyrolysis at a centrally located urban location and then utilising the biochar products in urban applications, such as a substrate in growing media, urban landscaping and also as an amendment for urban horticultural soils. In case of Australia, more
than 330,000 tonnes of biosolids are produced each year, out of which, 20% is stockpiled (ANZBP 2013). If biochar is produced from the waste stream, there should be enough waste, mainly biosolids and greenwaste, sitting in stockpiles which can be converted to biochar to meet the horticulture industry demand. Pyrolysis plants can be established near feedstocks which will reduce cartage costs. Other substrates (peat and pine bark) will always need to be transported to the ‘market’. Also, nearly 60% of the horticultural industries are close to the urban populations of the major cities of Australia (Prince 2014).

Converting biosolids to biochar eliminates the odour and also eradicates harmful organisms from the biosolids. This approach offers multiple benefits such as waste management, resource recovery, emission reduction, reduced transport and carbon sequestration (Gaunt and Lehmann 2008). Conversion of biosolids to biochar using high temperature pyrolysis (>350°C), substantially reduces the availability of heavy metals (He et al. 2010). Therefore the risk to environment due to heavy metal contamination associated with land application of biosolids is greatly reduced once it is converted to biochar. Furthermore, the pyrolysis process generates syngas and bio-oils along with biochar, which can be used as an energy source to operate the pyrolysis plant thus making the system energy neutral (Gaunt and Lehmann 2008). UB used in the present study, provides an innovative way of utilizing urban wastes like greenwaste and biosolids by converting waste into biochar for use as plant growing media substrate and soil amendment. O: C ratio is used as an indicator of stability and biochars with O:C of <0.1 are considered stable for over 100 years (Crombie et al. 2013). As UB has O:C of <0.1 and 41% fixed carbon, UB has the potential of sequestering carbon in growing media and soil for a long time. On the other hand, when UB is applied to growing media, it reduces the loss of N and P in leachate which in turn helps to reduce the water pollution and protects environment.
Peat and vermiculite are one of the common growing media substrates. Peat is a non-renewable resource and there are environmental concerns related to emission of greenhouse gases from drained peat bog and harm to local ecology resulting from harvest of peat (Landis and Morgan 2009). Vermiculite is also a limited resource which is first mined and then heated to high temperatures of 800-1000 °C in order to make it ready to be used for industrial purposes (Landis and Morgan 2009). Replacing peat and vermiculite from growing media with a renewable resource such as UB makes growing media more environmentally friendly. The use of peat and vermiculite may be cheaper ($50-68 ton⁻¹) than biochar ($500-1500 ton⁻¹), but these substrates also have an indirect cost to the environment and ecology over long term. Nonetheless, biochar can be produced at lower cost if it is produced from waste streams and the energy generated during pyrolysis is captured (Sohi et al. 2013).

7.2.2 The need for characterization of each biochar

Each biochar varies in its physical and chemical properties depending on the temperature and feedstock used for producing biochar (Downie et al. 2009). Biochars produced at higher temperature, like in our study, have lower CEC, higher pH, higher surface area and higher porosity. All of these properties affect the performance of biochar in the growing media, hence a detail characterization of biochar should be done before recommending its use as a growing media substrate.

7.2.3 Implications for nursery industry

Australian nursery and garden industry’s sustainability relies on the availability and affordability of suitable quality water for the production and ongoing care of plants (NGIA 2010). Drought is a huge issue in Australia and likely to remain so in the future. During periods of drought, water restrictions for individuals and organizations impact on the watering regime
for the nursery industry. There is potential for the nursery industry to use sustainable substrates like biochar in the growing media which can reduce water use while increasing nutrient retention and reducing loss of nutrient to waterways. This study has shown that UB, when compared to industry standard media, has ability to increase storage of water in the media especially at the lower suction when the media gets dry. Out of six water management best practice guidelines outlined by Nursery and Garden Association of Australia, adding biochar to growing media meets four guidelines; efficient water use to minimise the business demand on the water resource, maximise the retention of nutrients to improve efficiency of production, maintain water quality and effective management of sediment and litter (NGIA 2010).

Most of the large scale nurseries recycle the irrigation runoff by using combination of filtration systems, reed beds and chemical treatment (Allender 2010). This sort of water treatment process minimizes the risk of natural water pollution and saves water but are also expensive to manage. Small scale nurseries and general households do not practice recycling of irrigation runoff. Under those circumstances where water is not recycled, the ability of biochar to reduce nutrient leaching can be of advantage. This study found that UB amendment increases retention of nutrients (N and P) in the media and thereby reduces loss of these nutrients through leaching. Reduction of these nutrients in leachate also helps to protect the waterways from possible pollution and eutrophication. Therefore, UB addition to growing media, has the potential to help industry to save operating costs by reducing use of water and fertilizer.

The nursery industry also uses unsustainable amendments such as peat and vermiculite to formulate growing media. UB can be more sustainable alternative as it is produced from
waste stream and can be produced locally. Furthermore, syngas generated during production of biochar can be reused to dry the feedstock making the pyrolysis process energy neutral (Gaunt and Lehmann 2008). Using UB in nursery production has another potential advantage for long term carbon sequestration at little or no additional cost. For instance, if 1000 container pots (pot volume of 4,000 cm³) were filled with growing media containing 60% UB (on a volume basis) were sold annually by each nursery for tree plantation purposes, the carbon sequestration potential is 0.5 tonnes carbon/annum. It should be noted that the carbon sequestration potential estimation from this study is higher than proposed by Dumroese et al. (2011). The parameters used to calculate the carbon sequestration in this study are; pot volume, percentage of biochar in the media and the fixed carbon content of biochar which are all higher than the study of Dumroese et al. (2011) which leads to the higher carbon sequestration potential for UB in this study. Further, if large horticultural landscape businesses used biochar, there would be a huge potential of sequestering carbon through normal out planting process. Some of the large scale nurseries dump their used growing media into landfill. Under those circumstances, biochar amended growing media can sequester carbon for long time while in landfill.

7.3 Limitations of the study and suggestions for further work

In this study only one biochar was investigated. Further studies should be conducted on characterizing other biochars from wide range of feedstocks and production temperatures, which will enable to link the biochar functional properties to feedstock, pyrolysis parameters leading to biochar classification, making it easier to choose a specific biochar for a particular use. Defining a ‘standard’ for biochar used in different types of growing media would broaden
the use of biochar in growing media. Furthermore, the standards for chemical analysis of biochar are not fully developed and tested for different biochar types, we used available biochar analysis methods from International Biochar Initiative and adapted some methods from soil chemical analysis. Recently, a book has been published by biochar experts which provides guidelines for biochar specific analytical methods (Singh et al. 2017) In future, more studies should also be conducted on development and validation of methods for chemical analysis of biochar.

A study to understand long term effects biochar in growing media would be beneficial. The experiments investigating effects of UB on growing media properties (Chapters 4 and 5) ranged from 3-5 months, which is a short period to understand long term changes in UB. Although, in most of the situations, lifespan of growing media in nurseries range from few months to a year. However, in some cases, trees and shrubs are grown in growing media for longer period. Long term effect of application of biochar on soil properties is not well understood due to the lack of field based long term studies. Therefore, a long term experiment, conducted in the field for different types of soils, would help to further understand the long term impact of biochar on properties of various soils.

We were unable to look at the impact of biochar on plant performance for an entire growth of sorghum (Chapter 6) as the plants were harvested before the flowering formation stage. Hence, this study could not come to a conclusion on effects of biochar on grain yield. Nonetheless, in this 10 weeks long experiment, the plants reached the boot stage (one stage earlier than flowering), which gives good indication on efficacy of UB and other amendments for plant performance.
Further research is also required to investigate the afterlife of used biochar amended growing media. Biochar amended growing media is physically stable, therefore there is an option of re-using the media after sterilization. Studies need to be conducted to investigate the efficacy of biochar amended growing media when it is recycled multiple times. Most of the growing media users landfill their used media and some of them compost the used media with other nursery greenwaste. Any possibility of release of heavy metals over time from the biochar dumped in the landfill should also be investigated. Another option for management of used biochar amended growing media is regeneration through pyrolysis to create new biochar, thereby providing a sterile substrate for formulation of new growing media. Under the circumstances of reuse of the biochar amended media, further research needs to be conducted to evaluate if the heavy metals from biochar becomes available in long term.

Like any new industry, biochar use in horticultural industry faces several barriers. Lack of policy incentives (tax rebates, credit for sequestering carbon) for biochar use, lack of biochar product standardization and an incomplete understanding of end-user customer needs, as well as a lack of life cycle assessment projects to understand the economics of biochar use are some of the industry barriers. Currently these barriers hamper market demand for biochar. Furthermore, current evidence for the potentially beneficial effects of biochar as growing media substrate are poorly communicated to the growers. The evidence that exists resides mainly in the scientific literature which is not accessible to the growing media users. The studies conducted with biochar amended growing media lacks economic analysis. A life cycle assessment of use of biochar (produced from various streams of feedstock) on growing media would give more confidence to the growers to make a decision based on use of biochar. Currently, the cost of production of biochar is high ($500-1500 ton⁻¹), which is one of the major limitations for the commercial use of biochar in growing media. Therefore, further
studies need to be conducted to identify measures to reduce the production cost of biochar.

The use of unsustainable substrates such as peat and vermiculite may be cheaper than biochar but they also have indirect cost to the environment and ecology over long term. Furthermore, greater nutrient retention capacity and greater water holding capacity of biochar could potentially save fertilizer and irrigation cost to the growers. In future, studies should compare economics of using biochar and other common substrates such as peat and vermiculite using life cycle assessment methodology with particular focus on the potential harm to the environment that may incur further cost to society.

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Plate 1 Media incubated in stainless steel cylinders for experiment 1 (Chapter 4)

Plate 2 Measurement of water retention at different suctions using pressure plate (Chapter 4)
Plate 3 Incubation of media in pots with pore samplers to collect pore water and leachate (Chapter 4)

Plate 4 Custom designed chamber used for experiments in Chapters 4 and 5
Plate 5 Lower part of the custom made chamber used in Chapters 4 and 5

Plate 6 Roto Twin composter used for composting experiment in Chapter 6.
Plate 7 Sorghum plants grown on treatments consisting of fresh UB and co-composted UB and composted foodwaste respectively (from left) (Chapter 6).
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