Biochar as a soil amendment and productivity stimulus for *Eucalyptus nitens* plantations

by

Anna Wróbel-Tobiszewska
(MSci. Envir. Protec.)

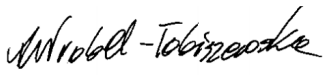
Submitted in fulfilment of the requirements for the degree of Doctor of Philosophy

School of Engineering
University of Tasmania (August 2014)

Supervisors:
Dr Mark Boersma
Dr Jane Sargison
Prof. Stewart Franks

DECLARATIONS

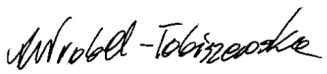
This thesis contains no material that has been accepted for the award of any other degree or diploma in any tertiary institution. To the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference is made in the thesis text. To the best of my knowledge and belief, this thesis contains no material that infringes copyright.



Anna Wrobel-Tobiszewska

Date: 28/08/2014

This thesis may be made available for loan and limited copying in accordance with the *Copyright Act 1968*.



Anna Wrobel-Tobiszewska

Date: 28/08/2014

ABSTRACT

Biochar is a carbon-rich material produced by pyrolysis (heating in the absence of oxygen) of biomass to capture combustible gases and generate heat and electricity. It can be added to soils as a means to sequester carbon and to maintain or improve soil functions. The physical and chemical properties of biochars determine their function as a tool for environmental management. Soil changes and plant response have been analysed on diverse soil types under various climatic conditions, water regimes, chemo-physical environments and on different species. Yet, the exact mechanisms behind the effects of biochar application are not fully understood and productivity gains vary greatly depending on the type of biochar, application rates, crop species and environmental conditions.

Producing biochar from different organic waste materials appears to be a promising method of achieving greater levels of certainty and flexibility for integrating carbon sequestration, managing waste disposal costs and introducing a new solution into soil and yield management in the conventional agricultural and forestry production systems. Biochar, however, is not widely used by farmers or foresters in Australia, mainly due to the lack of certainty concerning long-term consequences, yield gains and a lack of 'know-how' in the field of quality certification, transportation, logistics and cost efficiency.

Forestry is a significant industry in Tasmania, with large scale plantations of radiata pine (*Pinus radiata,* D. Don) and *Eucalyptus* (*E. globulus* and *E. nitens,* H.Deane & Maiden) which play an increasingly important role in supplying for national and international demand for timber. Propagating robust seedlings for planting in the field is an important part of plantation establishment as it influences potential yield, while also being a significant budget component. As biochar has been reported to positively affect desirable soil characteristics (e.g. increased nutrient efficiency, improved water holding capacity or reduced bulk density) and enhance crop productivity, it was hypothesised that it can bring benefits to *Eucalyptus* seedling growth.

The main objectives of this project were to investigate chemical changes of the soil, plant material and soil solution following biochar application; and to determine the optimum biochar dose required to positively influence eucalyptus growth under Tasmanian conditions; both in a controlled nursery environment and during establishment in the field. A secondary aim was to determine if commercial fertiliser rates could be reduced via

biochar application to the growing medium. The final assumption was that biochar can be profitably made from forest residues and utilized within the forest production systems of Tasmania.

The macadamia shell biochar used in this research was characterised as high in potassium and sodium, relatively high in total carbon content and low in total nitrogen (N) and phosphorus (P) content relative to other biochars described in literature. Two experiments were conducted: a pot trial in which *Eucalyptus* seedlings were observed from sowing to 9 months; and a field experiment in the Florentine valley in South West Tasmania where seedling establishment was monitored for 14 months. In both experiments the agronomic characteristics of the seedlings and trees was monitored on a regular basis. Each experiment had 4 sample collection periods when plant material and soil or potting mix samples were collected and analysed. Percolating water was collected from custom-built lysimeters installed in the field plantation.

Agronomic monitoring revealed that in both experiments fertiliser combined with certain doses of biochar influenced the tree growth. The height of seedlings and young trees was comparable between full fertiliser treatment (i.e. when no biochar was applied) and treatments where medium biochar rates were combined with reduced fertiliser amounts. However, biochar application did not result in significantly taller plants. Other agronomic features were not influenced by biochar application in either experiment. The potting mix was high in organic matter and the fertiliser applied at rates reflected industry standards. While fertiliser rates were reduced to simulate a nutritionally poor soil, all other environmental parameters were optimal in the pot trial. As previous reports have indicated that biochar has more noticeable effects on poor quality soils, it is possible that the quality of the potting mix masked the efficacy of biochar in relation to agronomic productivity, although both soil and leachate parameters were influenced. In contrast, under field conditions the biochar doses were applied at rates below that at which soil and leachate parameters were modified in the potting experiment, thus the doses were possibly too low to show a significant effect. The application method could also have influenced biochar efficiency under field conditions.

Chemical and physical changes in the analysed mediums used implied a number of different, in some cases contradictory, mechanisms. Biochar in both experiments increased growing medium pH and released potassium and sodium to the soil. In the plant tissues,

biochar induced changes, yet no clear trends were evident that macadamia biochar has any sizable effect on the nutritional status of *E. nitens* in Tasmania. In most cases, the changes in leaf tissue were correlated with changes in the soil with no evidence that biochar directly influenced plant nutrient uptake.

Biochar did not have a clear effect on percolating water nutritional changes and the only thing that can be concluded with certainty is that application of biochar increased potassium infiltration from the soil. This is most likely connected with significant amount of potassium introduced to the soil when biochar was applied.

While the mechanisms for the reported changes remain unclear, in many cases biochar was responsible for changes in soil and plant material chemical characteristics and a limited agronomic response. It appears that biochar is able to influence nutrients transformations in the soil and therefore influence the soil environment for the *E. nitens* in Tasmania. It also shows significant potential for reduced commercial fertiliser rates both in the forestry plantations and in the forest nurseries.

The financial analysis was based on the trial outcomes and the local operating environment in Tasmania; including current forestry procedures used for managing plantations in Tasmania; and benefits resulting from biochar production and incorporation into Tasmanian soils. The Biochar Scenario assumed on-site biochar making, out of post-harvest forestry residues, and different methods of biochar utilization. The model was built in Microsoft Excel® with help from Forestry Tasmania experts. A number of assumptions were considered concerning: a) production costs, b) savings enjoyed by traditional operations following biochar scenario implementation and c) biochar sale. The analysis revealed a potential annual income of $179,514 resulting from introducing the Biochar Scenario on 270 ha. The sensitivity analysis identified the crucial factors responsible for scenario profitability, namely biochar price and final product distribution.

The findings of this work supported the hypothesis that reducing common fertiliser rates used for seedling establishment in forestry plantations is viable. It has also provided insight into changes in both soil and plant tissue following macadamia shell biochar application to Tasmanian soils. The financial analysis served as a solid background for the realistic implementation of the Biochar Scenario for forestry industry in Tasmania.

ACKNOWLEDGEMENTS

I was told at the beginning of my PhD that I should think carefully about what exactly I would like to work on and choose my topic according to what I really enjoy because at some point I am going to hate my PhD. Throughout those years I had my good and bad moments but never, at any point, could I say I did not enjoy learning and challenging myself every day. I am deeply appreciative of all the people with whom I had the pleasure to work and their skills, of the life circumstances and personal skills I am lucky enough to have, and that I was given an opportunity to learn and develop personally. A gift many people do not have. I did my best.

First, I would like to deeply thank my supervisors, Dr Mark Boersma, Dr Jane Sargison and Prof. Stewart Franks; for their constructive criticism, guidance, encouragement and all the things that they taught me during those years. I am especially grateful to Dr Mark Boersma for endless hours of discussions, his patience with editing and re-reading of my writing, for challenging me constantly and for his enthusiasm to show, teach and share. I consider myself very lucky that I could learn from you.

I would also like to thank Dr Evelyn Krull and Dr Dugald Close for sharing their knowledge and experience with me. I am indebted to Dr Paul Adams for his support and sharing his fabulous forestry knowledge during all the time, from planning the experiments, organizing the trials and for his valuable comments to my work at the end. I would never be able to stay sane with the amount of statistics I had to go through without the help of Dr Alistair Gracie. His patience with explaining things to me can only be compared to my high school physics teacher's patience.

I wish to thank my family for their love and support. My fantastic Dad, for being for me always when I needed it, my aunt Hania for putting a seed of self-criticism in me, my two sisters, Monika and Gabby, who always know how to cheer me up and believe in me more than I do, and my cousin Agata for making me feel at home, far from home. It has been four difficult years being so far from you but we all passed this test and stayed as close as family can be. I am sure Mum is smiling to see it from wherever she is now.

To Marcin, I would not be here without your help and support. Going to the other side of the World so that your partner could follow her dreams is a very big and generous decision.

Not to mention all those weekends doing dirty field work in rain and mud and cutting insane number of rubbish bins to build Lysimeters for my experiments! I would never be able to thank you enough.

Thanks to my friends and fellow students in Australia: Jason, Javad, Gil, Kylee and Sima for their help with boring and dirty field work and their support when I had moments of doubts. Also, to all the postgrad students in the School of Engineering, for making students life cheerful and full of social events. A big Thank You flies to my friends back in Poland: Kasia, Agniesia, Muzzy, Agnieszka and Bartek, for your constant words of reassurance and that you never doubted in me.

I would like to extend my gratitude to:

Crispen Marunda, Kristen Dransfield and other Forestry Tasmania staff for their help with organizing and establishing pot and field trials and for answering my endless questions about forestry operations.

Dr Steven Jarick from Forestry Tasmania for his help with the financial analysis and putting all my thoughts, assumptions and conclusions into the form of a readable model.

Philip Andrews, the glasshouse manager in the Horticultural Research Centre for his help (and teasing) with the pot experiment.

Associate Professor Colin Birch for providing final comments and rescuing me from submitting too early.

Dr Chris Grose from DPIPWE for saving me from determining the soil types myself.

Dr Andrew Measham from the Laboratory in the School of Agricultural Sciences for his significant help with determining the right methods of analysis and invaluable guidance in the Lab.

The Rainbow Bee Eater team: Peter Burgess, Ian Stanley and others for providing biochar for the purposes of my research.

Dr Thomas Rodemann, Dr Karsten Goemann and Dr Sandrin Feig for performing and un-coding the meaning of NMR and SEM-EDS results to me.

Prof. Scott Donne and Dr James Hook for their help with analysing biochar samples.

Finally, I would like to acknowledge School of Engineering and ICT, Tasmanian Institute of Agriculture, Centre for Renewable Energy and Power Systems, Tasmanian Community Fund and TEMCO Billiton for providing funds to conduct this research.

DECLARATIONS II

ABSTRACT III

ACKNOWLEDGEMENTS VI

LIST OF FIGURES XII

LIST OF TABLES XVI

1. INTRODUCTION 1

1.1. THE FUNDAMENTALS OF BIOCHAR 1
1.1. BIOCHAR FOR TASMANIAN FORESTRY 3
1.2. OBJECTIVES AND SCOPE 5
1.3. RESEARCH STRATEGY 6

2. LITERATURE REVIEW 8

2.1. DEVELOPING KNOWLEDGE ABOUT BIOCHAR 8
2.1.1. INTRODUCTION 8
2.1.2. CHEMICAL, PHYSICAL AND BIOLOGICAL CHARACTERISTICS 10
2.1.3. CLASSIFICATION OF BIOCHARS 12
2.1.4. SOIL CHANGES UNDER BIOCHAR APPLICATION 14
2.1.5. EFFECT OF BIOCHAR APPLICATION ON PLANT GROWTH, NUTRIENT UPTAKE AND YIELD 18
2.1.6. APPLICATION RISK AND UNKNOWN EFFECTS 21
2.2. FORESTRY IN TASMANIA 23
2.2.1. PLANTATIONS 23
2.2.2. EUCALYPTUS NITENS 24
2.3. SUMMARY 25

3. MACADAMIA BIOCHAR 27

3.1. INTRODUCTION 27
3.2. ANALYTICAL METHODOLOGY 27
3.3. RESULTS – BIOCHAR CHARACTERISATION 32
3.4. DISCUSSION 43
3.4.1. NUTRITIONAL CHARACTERISTICS 43
3.4.2. SURFACE CHEMISTRY AND POROSITY 44
3.4.3. MAGNETIC RESONANCE 46
3.5. CONCLUSIONS 47

4. GENERAL MATERIAL AND METHODS 48

4.1. INTRODUCTION 48
4.2. GLASSHOUSE POT TRIAL 48
4.2.1. DATA COLLECTION AND PROCESSING 50
4.2.2. PLANT TISSUE ANALYSES 51
4.2.3. SOIL ANALYSES 52

4.3. FIELD TRIAL 52
4.3.1. FIELD SITE LOCATION AND EXPERIMENTAL LAYOUT 53
4.3.2. SOIL AMENDMENTS 55
4.3.3. LYSIMETER INSTALLATION 57
4.3.4. SEASONAL CONDITIONS 57
4.3.5. SAMPLING AND DATA COLLECTION 59
4.3.6. PLANT MATERIAL AND SOIL ANALYSIS 62
4.4. STATISTICAL ANALYSIS 62

5. EFFECTS OF BIOCHAR AND FERTILISER AMENDMENT ON THE SOIL 64

5.1. INTRODUCTION 64
5.2. METHOD 67
5.3. RESULTS 67
5.3.1. ACIDITY 69
5.3.2. NITROGEN, POTASSIUM, PHOSPHORUS 69
5.3.3. ORGANIC CARBON 72
5.3.4. EXCHANGEABLE CATIONS 73
5.3.5. PHYSICAL CHANGES 76
5.4. DISCUSSION 78
5.5. CONCLUSIONS 82

6. PERCOLATING WATER ANALYSIS 84

6.1. INTRODUCTION 84
6.2. METHOD 86
6.3. RESULTS 86
6.3.1. ACIDITY 86
6.3.2. NUTRITION 87
6.4. DISCUSSION 89
6.5. CONCLUSIONS 93

7. EFFECTS OF BIOCHAR AND FERTILISER ON GROWTH RATE AND PLANT NUTRITION 94

7.1. INTRODUCTION 94
7.2. METHOD 95
7.3. RESULTS 96
7.3.1. EMERGENCE 96
7.3.2. SEEDLING GROWTH 96
7.3.3. CHANGES IN PLANT TISSUE ELEMENTAL COMPOSITION 97
***7.4.* DISCUSSION 102**
7.5. CONCLUSIONS 108

8. ECONOMIC ANALYSIS OF BIOCHAR SYSTEM IMPLEMENTATION ON PLANTATION FORESTRY 109

8.1. INTRODUCTION 109
8.2. WOOD CHAR FOR FORESTRY PLANTATIONS, EXAMPLES FROM LITERATURE 110
8.3. CURRENT FORESTRY MANAGEMENT PRACTICES AND COSTS 112
8.3.1. RESIDUE MANAGEMENT 116

8.4. SCENARIO BACKGROUND AND ASSUMPTIONS 117
8.4.1. OUTLINE OF BIOCHAR PRODUCTION AND USE SCENARIO 117
8.4.2. MOBILE PYROLYSIS UNIT 118
8.4.3. DETERMINATION OF SCENARIO COSTS AND BENEFITS 119
8.5. BASE SCENARIO SPECIFIC ASSUMPTIONS 120
8.6. RESULTS 124
8.7. DISCUSSION 126
8.7.1. SENSITIVITY 127
8.7.2. UNACCOUNTED FACTORS 128
8.7.3. POTENTIAL CHANGES 130
8.8. CONCLUSIONS 131

9. FINAL DISCUSSION AND CONCLUSIONS 132

9.1. INTRODUCTION 132
9.2. AGRONOMIC AND CHEMICAL CHANGES 133
9.2.1. SOIL 133
9.2.2. PLANT MATERIAL AND AGRONOMIC RESPONSE 134
9.2.3. LEACHATE 135
9.2.4. SUMMARY 136
9.3. FINANCIAL ASPECTS 136
9.3.1. POTENTIAL IMPLICATIONS OF BIOCHAR PRODUCTION AND USE 136
9.3.2. COMMERCIAL IMPLEMENTATION 138
9.4. WHERE TO FROM HERE? 138

APPENDICES 141

LITERATURE 158

LIST OF FIGURES

Chapter 1

Figure 1.1. Macadamia biochar; the final product (left-hand side), electron microscopy image of the char (right-hand side). 2

Chapter 3

Figure 3.1. Pore size distribution in macadamia biochar, presenting a total volume of certain pore diameter (A). Calculated on Micromeritics® ASAP 2020 Accelerated Surface Area and Porosity System at the University of New South Wales, 2013. 34

Figure 3.2. Electron microscopy image of macadamia biochar. Study performed in CSL in 2013 (Hitachi SU-70 FESEM), samples carbon coated, under a beam energy of 15kV.The distances indicated by arrows show pore diameter (µm). 34

Figure 3.3. Scanning Electron microscope (SEM) images of macadamia biochar particles. Four example particles (A, B, C and D) and their chemical composition (Figure 3.4). Study performed in CSL 2013 (Hitachi SU-70 FESEM), samples carbon coated, under beam energy of 15kV. The white-bordered boxes represent the area where the spectrum was analysed. 35

Figure 3.4. Particular spectra chemical composition in chosen particles of macadamia biochar in electron microscopy scanning image (Hitachi SU-70 FESEM). The spectra analysed (A-I, Spectra 5,6,14-18, 53 and 54) are depicted in Figure 3.3. The peaks represent the approximate quantity of a particular element in the spectrum position. 38

Figure 3.5. Macadamia biochar C13 NMR spectrum acquired using a Bruker Avance III-300 spectrometer operating at 75.4 MHz, and 300 MHz for 13C and 1H. Upper line represents spectrum obtained for all carbons, lower line represents spectrum of non-protonated C. . 41

Chapter 4

Figure 4.1. Eucalyptus nitens glasshouse pot experiment on (A) 29th Jul 2011 and (B) 05th Nov 2011. Horticultural Research Centre, University of Tasmania, Sandy Bay campus. 50

Figure 4.2. Aerial picture of the field experiment area. Florentine valley, Forestry Tasmania coupe 31Z. The red rectangles show the approximate location of the blocks..... 54

Figure 4.3. Design of the field experiment in Florentine Valley, Forestry Tasmania coupe 31Z. Green dots represent seedlings, blue shaded area shows the buffer zones around the blocks, dark green shapes represent the location of the windrows. 54

Figure 4.4. Design of block 1 in the field experimental trial in Florentine valley, Forestry Tasmania coupe 31Z..... 55

Figure 4.5. Custom-built Lysimeter 'LIZZIE' used in the Florentine Valley field trial. 57

Figure 4.6. (A) The total annual rainfall in Tasmania (mm), (B) maximum temperature in Tasmania (°C), and (C) minimum temperature in Tasmania (°C) estimated for the period 01/01/2011 – 31/12/2011. Data acquired from the website of Australian Bureau of Meteorology (Bureau of Meteorology, 2012-2013). The black dot indicates the location of the field experimental plantation. 59

Figure 4.7. Author of the thesis with Eucalyptus nitens seedlings in the field experiment in Florentine valley. January 2012 (left-hand side) and January 2013 (right-hand side). 60

Figure 4.8. Equipment used for collecting water samples from the Lysimeters installed in the field experiment. 61

Figure 4.9. Water samples collected from the field experiment in the Florentine Valley 61

Figure 4.10. Water (above the season bar), plant material and soil (below the season bar) sampling times (presented as days after planting) in the field experiment in Florentine Valley during the duration of the field experiment (Spring 2011- Summer 2013). 61

Chapter 5

Figure 5.1. pH dynamics of the potting mix in Eucalyptus nitens pot experiment in response to: (A) biochar application (0,2,5,10,20,50,80 and 100 t ha^{-1}) (mean across sampling times and fertiliser treatments), (B) time (measured at 135, 177, 219 and 269 days after planting)

(mean across biochar and fertiliser treatments). Error bars indicate the LSD (A-0.11, B-0.16)(p≤0.05). 69

Figure 5.2. Nitrate nitrogen (A, C) and ammonium nitrogen (B, D) level [mg kg^{-1}] in potting mix in response to 8 biochar application rates (0-100 t ha^{-1}) (mean across sampling times and fertiliser treatments)(A, B) and time 135, 177, 219 and 269 days after planting, (C, D) (mean across biochar and fertiliser treatments). Error bars indicate the LSD (A-7.27, B-2.00, C-5.14, 1.41)(p≤0.05) 70

Figure 5.3. Spearman's correlation between (A) Ammonium nitrogen and nitrate nitrogen, (B) pH and nitrate nitrogen, (C) pH and ammonium nitrogen in the potting mix, pooled across 8 biochar treatments (1-100 t ha^{-1}), three fertilisation levels (0, 50 and 100% of the commercially applied dose) and four harvest times (135, 177, 216 and 269 days after planting), p≤0.05..... 70

Figure 5.4. Phosphorus level [mg kg^{-1}] in potting mix in response to 8 biochar application rates (0-100 t ha^{-1}) combined with two fertilisation rates. Error bars indicate the LSD (5.60)(p≤0.05)... 71

Figure 5.5. Potassium level [mg kg^{-1}] in potting mix in response to (A) 8 biochar application rates (0-100 t ha^{-1})(mean across sampling times and fertiliser treatments) and (B) time (135, 177, 219 and 269 days after planting (mean across biochar and fertiliser treatments). Error bars indicate the LSD (A-32.18, B-22.76)(p≤0.05)..... 72

Figure 5.6. Potassium level [mg/kg] in Florentine Valley field experiment soil in response to (A) 6 biochar rates (0, 2, 5, 10, 15, 20 t ha^{-1}) (mean across sampling times and fertiliser treatments), (B) time (95, 216, 338 and 463 days after planting) (mean across biochar and fertiliser treatments), linear regression (Sig. 0.000, r^2=0.320). Error bars indicate the LSD (A-30.47, B-22.9)(p≤0.05). 72

Figure 5.7. Organic carbon level [%] in potting mix in response to (A) 8 biochar application rates (0-100 t ha^{-1})(average data from 135, 177, 219 and 269 days after planting (DAP) and fertilisation at two levels (50 and 100% of the commercially applied dose)) and (B) Rate of decay under 8 biochar application rates (0-100 t ha^{-1}) over time. Error bars indicate the LSD (0.74)(p≤0.05). 73

Figure 5.8. Exchangeable aluminum level [cmol kg^{-1}] in potting mix in response to (A) 8 biochar application rates (0-100 t ha^{-1}) and fertilisation at two levels (50 and 100% of the commercially applied dose)(mean values across sampling times), (B) 8 biochar application rates (0-100 t ha^{-1}) over time (135, 177, 219 and 269 days after planting (DAP)) and (C) Spearman's correlation (rho= -0.924) between exchangeable aluminum and pH (CaCl2) in the potting mix. (D) Spearman's correlation (rho= -0.686) between exchangeable aluminum and exchangeable potassium in the potting mix. Correlation data represents results from all the biochar and fertiliser treatments across time, Error bars indicate the LSD (0.02)(p≤0.05). 74

Figure 5.9. Exchangeable calcium level [cmol kg^{-1}] in potting mix in response to (A) 8 biochar application rates (0-100 t ha^{-1}) and fertilisation at two levels (50 and 100% of the commercially applied dose)(mean across sampling times), (B) time (135, 177, 219 and 269 days after planting) (mean across biochar and fertiliser treatments). Error bars indicate the LSD (A- 0.36, B- 0.26)(p≤0.05)..... 74

Figure 5.10. Exchangeable magnesium level [cmol kg^{-1}] in potting mix in response to (A) 8 biochar application rates (0-100 t ha^{-1}) and fertilisation at two levels (50 and 100% of the commercially applied dose)(means across samplind times), (B) time (135, 177, 219 and 269 days after planting) (mean across biochar and fertiliser treatments). Error bars indicate the LSD (A- 0.27, B- 0.19)(p≤0.05)..... 75

Figure 5.11. Exchangeable sodium level [cmol kg^{-1}] in potting mix in response to (A) 8 biochar application rates (0-100 t ha^{-1})(average data from 135, 177, 219 and 269 days after planting (DAP)) and (B) rate of decay under 8 biochar application rates (0-100 t ha^{-1}). Error bars indicate the LSD (0.02) (p≤0.05)..... 76

Figure 5.12. Exchangeable sodium level [cmol kg^{-1}] in Florentine Valley field experiment soil in response to 6 biochar application rates (0-20 t ha^{-1}) (mean across sampling times and fertiliser treatments). Error bars indicate the LSD (0.02)(p≤0.05). 76

Figure 5.13. Potting mix accumulated water [%] in pot experiment in response to (A) interaction between 8 biochar application rates (0-100 t ha^{-1}) and fertilisation at two levels (50 and 100% of the commercial rate)(mean across sampling times), and (B) time 135, 177, 219,

269 days after planting(mean across biochar and fertiliser treatments). Error bars indicate the LSD (A- 3.71, B- 2.64)(p≤0.05). *77*

Figure 5.14. Gravimetric soil water content [%] in Florentine Valley field experiment soil 95, 216, 338 and 463 days after planting (DAP) in response to 3 fertiliser rates (0, 50 and 100% of the commercially applied dose). Error bars indicate the LSD (3.34)(p≤0.05) *77*

Figure 5.15. Monthly precipitation in Maydena post office meteorological station (Derwent valley, TAS), (Bureau of Meteorology, 2012-2013), white bars indicate the months in which soil samples were collected (95, 216, 338 and 463 DAP). *77*

Chapter 6

Figure 6.1. Soil leachate acidity in Florentine Valley field experiment in response to (A) interaction between 6 biochar application rates (0-20 t ha^{-1}) and fertilization at 3 levels (0, 50 and 100% of the commercial rate)(mean across sampling times); (B) changes in time, 39, 87, 129, 164, 200, 236, 290, 332, 374 and 409 days after planting (mean across biochar and fertilizer treatments). Error bars indicate the LSD (0.24)(p≤0.05). *87*

Figure 6.2. Nitrate nitrogen level in soil leachate [mg L^{-1}] in Florentine Valley field experiment in response to (A) interaction between 6 biochar application rates (0-20 t ha^{-1}) and fertilization at 3 levels (0%, 50% and 100% of the commercial rate)(mean across sampling times); (B)changes in time 39, 87, 129, 164, 200, 236, 290, 332, 374 and 409 days after planting (mean across biochar and fertilizer treatments). Error bars indicate the LSD (A-13.38, B-14.81)(p≤0.05). *88*

Figure 6.3. Ammonium nitrogen level in soil leachate [mg L^{-1}] in Florentine Valley field experiment in response to (A) interaction between 6 biochar application rates (0-20 t ha^{-1}) and fertilization at 3 levels (0%, 50% and 100% of the commercial rate) (mean across sampling times); (B) changes in time 39, 87, 129, 164, 200, 236, 290, 332, 374 and 409 days after planting (mean across biochar and fertilizer treatments). Error bars indicate the LSD (A-0.38, B-0.41)(p≤0.05). *88*

Figure 6.4. Potassium level in soil leachate [mg L^{-1}] in Florentine Valley field experiment in response to (A) interaction between 6 biochar application rates (0-20 t ha^{-1}) and fertilization at 3 levels (0%, 50% and 100% of the commercial rate)(mean across sampling times); (B)changes in time 39, 87, 129, 164, 200, 236, 290, 332, 374 and 409 days after planting (mean across biochar and fertilizer treatments). Error bars indicate the LSD (A- 2.48, B-2.74)(p≤0.05)... *89*

Figure 6.5. Phosphorus level in soil leachate [mg L^{-1}] in Florentine Valley field experiment in response to time of sampling 39, 87, 129, 164, 200, 236, 290, 332, 374 and 409 days after planting (mean across biochar and fertilizer treatments). Error bars indicate the LSD (0.35)(p≤0.05). *89*

Chapter 7

Figure 7.1. Mean height [mm] of E. nitens seedlings in the pot experiment in response to interaction between 8 biochar application rates (0-100 t ha^{-1}) and fertilisation at two levels (50 and 100% of the commercial rate)(mean across sampling times), error bars indicate LSD (15.77)(p≤0.05). *97*

Figure 7.2. E. nitens tree height in Florentine Valley field experiment (mean values from 93-647 days after planting) in response to an interaction between 3 fertiliser rates (0% [F0], 50% [F50] and 100% [F100] of the optimum dose) and 6 biochar rates (0-20 t ha^{-1})(mean across sampling times). Error bars indicate the LSD (52.57)(p≤0.05). *97*

Figure 7.3. Phosphorus concentration [%] in leaf tissue of Eucalyptus nitens seedlings in the pot trial in response to: (A) fertilisation at two levels (50% and 100% of the commercial rate) in partial factorial combination with 8 biochar application rates (0-100 t ha^{-1})(average data from 4 harvests: 135, 177, 219 and 269 days after planting, (B) Days after planting, at 135, 177, 216 and 269, (mean across biochar and fertiliser treatments). Error bars indicate the LSD (A- 0.03, B-0.02)(p≤0.05). *99*

Figure 7.4. Potassium concentration [%] in leaf tissue of Eucalyptus nitens seedlings in the pot trial in response to: (A) fertilisation at two levels (50% and 100% of the commercial rate) in partial factorial combination with 8 biochar application rates (0-100 t ha^{-1})(means across sampling times), (B) Days after planting, 135, 177, 219 and 269, (mean across biochar and fertiliser treatments). Error bars indicate the LSD (p≤0.05). (C)Spearman's correlation

between Colwell potassium level [mg kg^{-1}] in the potting mix and total potassium leaf concentration [%] in E. nitens seedlings in the pot experiment (A- 0.09, B- 0.07)(p≤0.05). 100

Figure 7.5. (A)Calcium and (B)Magnesium concentrations [%] in leaf tissue of Eucalyptus nitens seedlings in the pot experiment in response to 8 biochar application rates (0-100 t ha^{-1}) (mean across sampling times and fertiliser treatments). Error bars indicate the LSD (A-0.04, B- 0.02)(p≤0.05). 100

Figure 7.6. Sodium concentrations [mg kg^{-1}] in leaf tissue of Eucalyptus nitens seedlings in response to (A) 8 biochar application rates (0-100 t ha^{-1}) in the pot experiment (mean across sampling times and fertiliser treatments), (B) fertilisation (50% and 100% of a commercial dose) in time (135, 177, 216 and 269 DAP) in pot experiment (means across biochar rates). Error bars indicate the LSD (A- 0.008, B-0.006)(p≤0.05). 101

Figure 7.7. Manganese concentration [mg kg^{-1}] in leaf tissue of Eucalyptus nitens seedlings in the pot experiment in response to (A) 8 biochar application rates (0-100 t ha^{-1}) (mean across sampling times and fertiliser treatments) and (B) Rate of decay under biochar treatments (B0-B100 – 0-100 t ha^{-1}). Error bars indicate the LSD (75.45)(p≤0.05). 101

Figure 7.8. Boron concentration [mg kg^{-1}] in leaf tissue of Eucalyptus nitens seedlings in the pot experiment in response to (A) 8 biochar application rates (0-100 t ha^{-1}) (mean across sampling times and fertiliser treatments), (B) Days after planting (135, 177, 216 and 269 DAP) (mean across biochar and fertiliser treatments). Error bars indicate the LSD (A-2.02, B-1.44)(p≤0.05). 102

Figure 7.9. Calcium concentrations [%] in leaf tissue of Eucalyptus nitens trees in Florentine Valley field experiment in response to (A) 8 biochar application rates (0-20 t ha^{-1}) (mean across sampling times and fertiliser treatments) and (B) Days after planting (95, 216, 338 and 463 DAP) (mean across biochar and fertiliser treatments). Error bars indicate the LSD (A- 0.05, B- 0.04) (p≤0.05). 102

Chapter 8

Figure 8.1. Map of forestry plantations on State forest land, Tasmania, black areas represent location of plantations (FT database, 2010-2013). 113

Figure 8.2. Bracke mound cultivator used in forest plantations (FT database, 2010-2013). 114

Figure 8.3. Bandicoot spot cultivator used in forest plantations (FT database, 2010-2013). 114

Figure 8.4. Bracke mounder machine in the Forestry Tasmania coupe 116

Figure 8.5. Diagram of the biochar scenario indicating the flow of forestry primary and secondary products. 117

Figure 8.6. Unloading the mobile pyrolyser (MPP20) (EarthSystems, 2013) 119

Figure 8.7. Loaded mobile pyrolyser (MPP20) (EarthSystems, 2013) 119

Figure 8.8. Total benefit of biochar scenario implementation ($) in relation to A) amount of waste wood processed per ha of plantation, B) carbon price per tonne of CO_2 stored, C) price per tonne of biochar. 125

Figure 8.9. Total benefit of the proposed scenario and biochar amount dedicated for sale in relation to percent of total produced biochar, dedicated for sale. Assuming biochar price of $400/tonne. 126

LIST OF TABLES

Chapter 2

Table 2.1. Summary of plant responses and soil chemical changes to biochar application to the soil for a range of horticultural and field crops and woody species grown in a diversity of soils.... 20

Chapter 3

Table 3.1. Macadamia biochar chemical characteristics (element and compounds composition). The methodology for all performed tests described in Chapter 4 as specific for soil and plant tissue samples analyses. Ex.- exchangeable 33

Table 3.2. Chemical composition spectra at random surface locations of 27 biochar particles. (SEM-EDS images and spectra are presented in the Appendix 2.) 39

Table 3.3. Concentration of nutrients introduced to potting mix in the pot experiment [mg kg^{-1}] under different biochar and fertiliser treatments (F50-F100 representing 50% and 100% of a commercial fertiliser dose, B2-B100 representing biochar treatments equivalent to 2-100 t ha^{-1})..... 42

Table 3.4. Amount of nutrients introduced to soil in the Florentine valley experiment [mg kg^{-1}] under different biochar and fertiliser treatments (F50-F100 representing 50% and 100% of a commercial fertiliser dose, B2-B20 representing biochar treatments equivalent to 2-20 t ha^{-1}). 42

Table 3.5. Ranges in the diameter of various soil microorganisms (Thies and Rillig, 2009) 45

Chapter 4

Table 4.1. Fertilisers applied (g per 1L potting mix) in the pot experiment, using standard forestry practice, and analyses of product used. The 50% treatment used half of the fertiliser amounts shown in column 1 (except for dolomite lime, ferrous sulphate and rock gypsum). Calculations are based on the content information provided by the manufacturer..... 49

Table 4.2. The list of treatments applied in the Florentine Valley field experiment. 100% fertiliser rate equalled 200 g Di-ammonium phosphate per seedling. 56

Chapter 5

Table 5.1. Potting mix characteristics P values in response to biochar (B), fertiliser (F) application and time (T) in the pot experiment. Significant values at P≤0.05, n.s. = not significant (OC-organic carbon, ex. Al – exchangeable aluminum, ex. Ca – exchangeable calcium, ex. Mg – exchangeable magnesium, ex. K – exchangeable potassium, ex. Na – exchangeable sodium, P- phosphorus). 68

Table 5.2. Soil characteristics P values (Florentine valley field experiment) in response to biochar (B), fertiliser (F) application and time (T) in the pot experiment. Significant values at P≤0.05 , n.s.= not significant, (OC-organic carbon, ex. Al – exchangeable aluminum, ex. Ca – exchangeable calcium, ex. Mg – exchangeable magnesium, ex. K – exchangeable potassium, ex. Na – exchangeable sodium, P- phosphorus). 68

Chapter 7

Table 7.1. P values of the Eucalyptus nitens leaf tissue elemental composition changes in response to biochar (B), fertiliser (F) application and time (T) in the pot experiment. Significant values at P≤0.05, n.s. = not significant. 98

Table 7.2. P values of the Eucalyptus nitens leaf tissue elemental composition changes in response to biochar (B), fertiliser (F) application and time (T) in the field experiment. Significant values at P≤0.05, n.s. = not significant. 98

Chapter 8

Table 8.1. A summary of the results of studies performed on wildfire-produced charcoal influence on the soil (Stavi, 2013) 111

Table 8.2. List of major plantation forestry establishment and maintenance operations and items generating costs in Tasmania (source: Forestry Tasmania staff personal communication).

Star indicates the cost groups that are likely to change under proposed biochar scenario. 115
Table 8.3. List of potential costs and benefits resulting from biochar scenario implementation. The items in italics were not incorporated into the model. 120
Table 8.4. Assumptions for the Pyrolyser capital, operational costs and technical characteristics used in the model. 122
Table 8.5. Assumptions for the feedstock material used in the model. 122
Table 8.6. Model assumptions for the agronomic benefits based on results from previous chapters. 123
Table 8.7. Different variants of the proposed scenario (MPP40 stands for a CharMaker (Earth Systems®) with a greater capacity to process feedstock (up to 10 t ha^{-1}). 124

SYMBOLS AND ABBREVIATIONS

Symbol	Explanation
Al	Aluminum
Ammonium-N/ NH_4^+	Ammonium nitrogen
B	Boron
BSE	Backscattered electrons
C	Carbon
Ca	Calcium
CEC	Cation exchange capacity
Cl	Chlorine
CL	Cathodoluminescence
CO_2	Carbon dioxide
Cu	Copper
DAP	Days after planting
DiAP	Di-ammonium phosphate
EDS	Energy dispersive spectrometry
ex.	Exchangeable (cations)
Fe	Iron
GHG	Green House Gases
H	Hydrogen
HTT	Highest temperature treatment
K	Potassium
Mg	Magnesium
Mn	Manganese
Mo	Molybdenum
N	Nitrogen
N_2O	Nitrous oxide
Na	Sodium
nitrate-N/ NO_3^-	Nitrate nitrogen
NMR	Nuclear magnetic resonance
O	Oxygen
P	Phosphorus
PAH	Polycyclic aromatic hydrocarbons
PCDD	Polychlorinated dibenzo-p-dioxins
PCDF	Polychlorinated dibenzofurans

PM	Potting mix
S	Sulphur
SE	Secondary electrons
SEM	Scanning electron microscopy
Si	Silicone
SOM	Soil organic matter
SSA	Specific Surface Area
STP	Standard temperature and pressure
Zn	Zinc

1. INTRODUCTION

One of the global challenges of the 21st century is the sustainable management of natural resources, ideally being based on a balance between available reserves and demand for various products. An ongoing discussion about combining the need to protect natural habitats while generating adequate amounts of energy and maintaining the production from systems like agriculture and forestry leads to numerous concepts and ideas to improve sustainability while maintaining the productivity of such systems. Recently there has been a growing interest in biochar, a by-product of renewable energy, and its potential to enhance soil quality, improve crop productivity and sequester atmospheric carbon, thus adding sustainability to environmental production. Biochar (charcoal, agrichar, ecochar) refers to carbon-rich materials produced from the pyrolysis (heating with limited amount of oxygen) of biomass to capture combustible gases (Joseph et al., 2010). A wide range of soil and plant changes have been reported when biochar has been applied in agro-forestry systems. Similarly, the practical feasibility and financial aspects of biochar application are yet to be verified.

1.1. The fundamentals of biochar

The term biochar has previously been used in connection with charcoal production (Demirbas, 2004; Lehmann and Joseph, 2009b) and is often considered to be 'the same thing'. Lehmann and Joseph (2009) established 'biochar' as the appropriate term to use for charred organic matter applied to soil in a deliberate manner, with the intent to improve soil properties and in consequence influence the nutrient composition changes in plant material or ground waters (Figure 1.1). This distinguishes biochar from charcoal that is used as a fuel for heat generation, as a filter, and for other purposes (Lehmann and Joseph 2009). Biochar can be added to soils as a means to sequester carbon (Krull et al., 2003; Lehmann et al., 2006; Nguyen et al., 2009) and maintain or improve soil functions (Amonette and Joseph, 2009; Singh et al., 2010). It has been reported to bring positive changes to desirable soil characteristics but can also cause a negative or no response in both soil and plant material (Chan and Xu, 2009; DeLuca et al., 2009).

The feedstock and pyrolysis conditions determine the biological, physical and chemical properties of biochar (Atkinson et al., 2010; Quilty and Cattle, 2011). Thus its properties are variable, as biochar can be produced from any type of biomass: from animal production

wastes (i.e. chicken litter, cow manure etc.), municipal waste (i.e. sewage sludge, households biodegradable wastes etc.) and agricultural products (i.e. straw) to different types of wooden feedstock (i.e. branches, thinning residues, macadamia shells)(Briens et al., 2008; Lehmann and Joseph, 2009b). Considering the great variability of feedstock and, very often, an opportunity to mix different feedstock types, biochars differ significantly in terms of their chemical and physical properties. The production conditions, especially operating temperature, can be tightly controlled which makes biochar a highly 'engineered' char. This adds to biochar's characteristic variability as the process temperatures range from 350°C to over 700°C and the diversity in residence time and oxygen concentrations may also differ immensely (Amonette and Joseph, 2009; Thies and Rillig, 2009). Many research projects have focused on clarifying differences between biochar types and although some trends have been identified, many questions about biochar heterogeneity as a result of feedstock and production conditions remain unanswered (Roberts et al., 2010).

Figure 1.1. Macadamia biochar; the final product (left-hand side), electron microscopy image of the char (right-hand side).

Biochar has been applied under various environmental conditions both in controlled environments and in the field (Chen et al., 2010; Lehmann et al., 2003; Van Zwieten et al., 2009). It has been reported to increase yield, particularly if added together with organic or mineral fertiliser (Lehmann and Joseph, 2009b). Other plant responses have been analysed on different types of soil, under various climatic conditions and on many agricultural food crops e.g. radish, soybean, wheat, rice and others (Asai et al., 2009; Blackwell et al., 2010; Major et al., 2010). Similar to biochar characteristics, the exact effects of biochar application on plant productivity and yield are not fully understood and require more detailed investigations to allow full explanation of potential mechanisms which putatively

are influenced by biochar application. Considering the known variability in the effects of biochar on soil characteristics and plant responses, a generalized approach to predict biochar effect on soil changes and plant growth seems a very challenging task.

Biochar is a product of the renewable-energy focused pyrolysis technology used to produce biofuels, which may to some extent, displace fossil fuels use (Chan et al., 2007). Unlike fossil fuels, biomass is a renewable source of carbon and using it to produce biochar can release energy with virtually no sulphur or mercury and, very little nitrogen and ash waste. Producing biochar from various biomass waste materials appears to be a promising method of achieving greater levels of certainty and flexibility for integrating carbon sequestration accounting, managing waste disposal costs and renewable energy generation into conventional agricultural production, therefore assisting with moderating the climate change effect (Lehmann 2007, McHenry 2009).

Due to these attributes, there has been much attention given to biochar, and numerous possibilities to introduce it into primary production systems are under investigation. Interest in biochar has generally been driven by two major global issues: mitigation of climate change, and realization of the need for more sustainable soil management (Chan et al., 2007; Chan et al., 2008; Lehmann et al., 2003). Yet, in Australia, biochar is not widely used by farmers, mainly due to the lack of consistent results concerning long-term consequences and yield gains as well as lack of 'know-how' in the fields of transportation, logistics and cost efficiency (Chan et al., 2008; Glover, 2009; Quilty and Cattle, 2011). The variability of the effects of biochar is also a challenging barrier to introducing commercial biochar use in primary productivity systems like agriculture or forestry. Case studies and feasibility reports based on local conditions may serve as a potential remedy to overcome this barrier and allow modelling on a small area scale and consequently lead to larger scale solutions. Therefore, a local scenario may answer the question of feasibility of introducing biochar on a local, Tasmanian scale but also contribute to the challenge of modelling the effects of biochar application on a larger scale.

1.1. Biochar for Tasmanian Forestry

Forestry is a significant industry in Tasmania, with large scale plantations of radiata pine (*Pinus radiata* D. Don) and *Eucalyptus* (*E. globulus* and *E. Nitens* H. Deane &Maiden), the latter playing an increasingly important role in supplying wood to meet national and

international demand for timber products (FT database, 2010-2013; Rothe. A, 2013). Propagating robust seedlings for planting in the field is an important part of plantation establishment, and its success influences potential yield and thus return on a significant budget component.

In most cases newly planted eucalypt seedlings require significant fertiliser input to ensure proper early growth, especially as many forestry plantations in Tasmania are growing on low to medium fertility soils. Biochar is reported to bring about a positive effect on soil through postulated mechanisms such as increased nutrient accumulation, improved water holding capacity or reduced bulk density. Therefore, biochar could be a useful organic amendment as a tool for soil nutrient management in seedling production procedures, assisting the growth of *Eucalyptus* seedlings.

Biochar has potential to serve as a soil amendment enabling the decrease of fertiliser required for young eucalypt plantations. The application of fertilisers to forestry plantations in Tasmania is a significant overall cost connected with plantation establishment. Application of biochar to the soil of *Eucalyptus* plantations may increase soil nutrient retention, decrease chemical leaching and improve fertiliser efficiency. Therefore biochar may reduce costs of plantation establishment.

Production of biochar for use in forest nurseries and during field establishment would be a sustainable system as forestry harvest procedures leave significant amounts of post-harvest residues on site. These residues are either retained or burnt to clear the site for the next rotation (Elliot, 2011; FT database, 2010-2013). Under current commercial procedures processing post-harvest residues is a cost incurred to the forestry industry. Producing biochar from those residues could serve as an alternative to on-site clearing burns, while using the biochar produced as a soil amendment could provide not only agronomic benefits but also financial gains.

While the potential to support a wide range of primary production activities exists, there is little or no research published regarding biochar influence on pastures, fodder shrubs and trees (Santalla et al., 2011; Stavi, 2013; Wrobel-Tobiszewska et al., 2012b). These components of agriculture, agroforestry and forestry could benefit from biochar in the same way as some field crops have done. The possible beneficial effects of biochar on the production of woody biomass may also be important to the potential biomass supply for renewable energy and biochar production itself (Lehmann and Joseph, 2009b). Given the

importance of the forest industry to Tasmania's economy and its contentious role as both a resource and environmental threat, this study looked at using forest residue to increase productivity while enhancing sustainability.

1.2. Objectives and scope

The project was based on two experimental trials and a cost-benefit analysis of producing and utilising biochar in Tasmanian forestry. A pot trial in a controlled environment and a field trial in a local plantation were established to monitor soil changes and agronomic response of young *E. nitens* to biochar application. As no local pyrolysis unit existed and eucalyptus char was unavailable, macadamia biochar was applied in both experiments across a range of rates commonly reported in literature; 0-100 t ha^{-1} (Biederman and Harpole, 2013; Blackwell et al., 2010; Lehmann and Joseph, 2009b). The main hypotheses of the project were:

- That macadamia biochar added to Eucalypt plantation soil under Tasmanian conditions will improve soil nutritional traits, by either introducing nutrients to the soil (release from biochar surfaces) or modifying soil mechanisms to increase nutrient transformation to plant-available forms.

- That macadamia biochar application to the soil will positively influence seedling agronomic response, resulting in better yield and greater height of the trees and seedlings under controlled and field conditions.

- That the medium dose of biochar (10-20 t ha^{-1}) is an optimum dose for seedlings performance, soil quality and nutrition improvements within the soil-plant system to *Eucalyptus nitens* seedlings both under controlled and field conditions.

- That biochar added to plantation soils will decrease nutrient leaching, and therefore increase fertiliser application efficiency and off-site contamination.

- That medium biochar application (10-20 t ha^{-1}) will allow a decrease in fertiliser doses used for the plantations and nurseries with no yield penalty and therefore decrease the overall costs of plantation establishment.

- That biochar produced on a plantation site from post-harvest residues can be used to generate financial benefits in Tasmanian based plantation forestry systems.

1.3. Research strategy

The research objectives addressed characterisation of macadamia biochar, evaluated its effects on soil, plant tissues and agronomic measures, and included a financial assessment of the viability of biochar production and use within a Tasmanian forestry system. The studies included glasshouse, field and a desktop analysis. The thesis is presented in nine chapters, the content of which is outlined below.

Chapter 1- Introduces the topic of biochar in relation to forestry in Tasmania, provides justification for the research and outlines thesis scope and objectives. Specifies the research questions.

Chapter 2- Reviews existing literature about biochars effects on the environment, soil changes, plant agronomic performance and provides more theoretical information about biochar characteristics and classification; it summarizes what is already known about biochar. Presents background of plantation forestry in Tasmania and reviews literature about forestry and char use.

Chapter 3- Presents the results of analyses on the macadamia biochar used in this research. Provides details on the methods used to characterise the product, and discusses the expected effects of biochar application to the soil based on these characteristics.

Chapter 4- Describes methods used in the pot study and field experiment. Outlines the design of the experiments, tests and analyses performed; timing of analyses and detailed procedures are explained.

Chapter 5- Presents and discusses results from both experiments with reference to soil desirable soil characteristics, such as nutritional and physical changes under biochar and fertiliser treatments.

Chapter 6- Presents and discusses the results of biochar and fertiliser effects on soil leachate chemistry in the field experiment.

Chapter 7- Presents and discusses results of plant tissue chemistry changes and agronomic response of seedlings under biochar and fertiliser treatments in the pot and field experiments.

Chapter 8- Introduces a 'Biochar Scenario' based on the idea of using post-harvest residues from forestry plantations in Tasmania to produce biochar. The chapter presents a cost-benefit financial model and a feasibility study based on the model outcomes and the agronomic-chemical outcomes from earlier chapters of this thesis. The presented scenario assumes biochar production from plantation residues on-site and on-site soil application, off-site utilization in forest nurseries and, the introduction of Tasmanian biochar to the market.

Chapter 9 – Summarises the outcome of this research, places the results in perspective, emphasizes the conclusions and identifies research pathways based on the findings of this work.

2. LITERATURE REVIEW

2.1. Developing knowledge about biochar

2.1.1. Introduction

Biochar refers to carbon-rich materials produced from the pyrolysis (heating in the low oxygen conditions) of biomass in order to capture combustible gases and generate heat and electricity (Joseph et al., 2010; Lehmann and Joseph, 2009b). It can be added to soils as a means to sequester carbon (Joseph et al., 2010) and maintain or improve soil functions (Chan et al., 2007; Liang et al., 2006; Shinogi and Kanri, 2003; Singh et al., 2010) and, is a product of the renewable-energy focused pyrolysis technology which produces biofuel (Chan et al., 2007). The positive environmental impacts of biochar are recognized in various areas, including soil, plant tissue, water and even atmospheric changes. Biochar could reduce the degradation of currently used agricultural land by adding to remediation practices and play an important role in groundwater conservation and soil improvement in the future (Chen et al., 2010; Sohi et al., 2009). Due to its ability to influence soil fertility and improve the overall quality it has been suggested that more land would be available (Sarmah et al., 2010; Sohi et al., 2009) to produce food, fibre and forestry products. Sequestering carbon in agricultural soils creates additional benefits for farmers, retains land values by soil conservation, and may improve conventional yields by maintaining soil ecosystems (Klein et al., 2007; McHenry, 2009; Milne et al., 2007).

The term biochar has previously been used in connection with charcoal production (Demirbas, 2004; Lehmann and Joseph, 2009b). Lehmann and Joseph (2009) established and used 'biochar' as the appropriate term where charred organic matter is applied to soil in a deliberate manner, with the intent to improve soil properties. This distinguishes biochar from charcoal that is used for many purposes (Lehmann and Joseph, 2009b). More than 40 million tonnes of biochar were estimated to be produced worldwide per year in 2009 (McHenry, 2009). The current (2014) production intensity has not been estimated, mainly due to the lack in uniformity in biochar production methods, reporting and certification systems however, it is expected to be relatively small in comparison to global CO_2 production. Serious biochar use for C sequestration would require a massive expansion in production and use.

While biochar-charcoal was used many centuries ago in Japan, the recent interest has been stimulated by the topic of 'Terra Preta' (Ogawa and Okimori, 2010). The Terra Preta black soils are found in South America and characterized by high fertility and significant microbial activity (Lehmann and Joseph, 2009). The origin of black soils remains unknown; some theories involve the activity of local volcanoes and ash sediments while others attribute high black earth fertility to human related procedures e.g. cooking, burning and agriculture over many years (Lehmann et al., 2009).

Biochars can be produced from a range of organic materials and under different conditions resulting in products with a diversity of characteristics and properties (Chan et al., 2008; Lei and Zhang, 2013; Nguyen and Lehmann, 2004). It has been suggested that biochar produced in lower temperatures by the process of 'slow' pyrolysis brings more benefits regarding its chemical and physical properties when used as a soil amendment than the product of fast pyrolysis (Joseph et al., 2010; Lehmann, 2007; Lehmann and Joseph, 2009b; Sohi et al., 2009). Singh et al. (2010) performed a study analysing characteristics of biochars produced from different feedstock (*Eucalyptus* wood, poultry litter, cow manure and paper mill sludge) at different temperatures. The results have demonstrated various advantages of using biochar as a soil amendment, including maintaining fertility and improving aeration or water holding capacity. Biochar application to the soil has also been reported to bring both positive and negative effects on plants agronomic performance (Blackwell et al., 2010; Chen et al., 2010; Major et al., 2010).

In the past two decades there has been much interest in biochars, which, apart from discovering Terra Preta, is driven by two major global issues: 1) mitigation of climate change and 2) the realization of the need for more sustainable soil management (Chan and Xu, 2009; Sarkhot et al., 2012; Vaneklaas et al., 2012). Producing biochar from organic waste appears to be a promising method of achieving greater levels of certainty and flexibility for integrating carbon sequestration accounting, managing waste disposal costs and renewable energy generation into conventional agricultural production(Lehmann, 2007; McHenry, 2009). In Australia however, biochar is not widely used by farmers mainly due to the lack of confirmed results concerning the long-term consequences and yield changes as well as lack of 'know-how' in the field of transportation, logistics and cost efficiency (Chan et al., 2008; Quilty and Cattle, 2011).

2.1.2. *Chemical, physical and biological characteristics*

One of the most important features of biochar is its ability to sequester atmospheric carbon in the soil. Increasing atmospheric CO_2 is an important global issue of the 21st century and long-term storage of carbon in soil is considered a vital option to mitigate the increasing level of CO_2 in the atmosphere (Lal, 2008; Singh et al., 2010). The conversion of biomass to biochar leads to sequestration of up to 50% of the initial carbon compared to the low amounts retained after burning (3%) and biological decomposition (10-20%)(Lehmann et al., 2006; McHenry, 2009). Application of charred biomass as an alternative soil amendment to manures or compost seems to be a promising option to maximise carbon storage in soils as charring significantly increases the stability of C against microbial oxidation, however up to approximately 10% of the biochar C can be prone to mineralisation over a few months after application to the soil (Baldock and Smernik, 2002; Laird et al., 2009). Diverting merely 1% of annual net plant uptake (58 Gt year^{-1}) into biochar would mitigate almost 10% of current anthropogenic C emissions (7 Gt year^{-1})(Lehmann and Joseph, 2009b). The ability of biochar to sequester carbon is related to its stability in the soil (Glaser et al., 2001; Lehmann et al., 2009; Lehmann and Joseph, 2009b). The long term-stability and resistance to oxidation is related to biochar structure and recalcitrance to microbial attack (Liang et al., 2008; Nguyen et al., 2009).

The physical and chemical properties of biochars determine their effectiveness in environmental management (Lehmann and Joseph, 2009b). Physical properties of biochar are dependent on feedstock material used and pyrolysis conditions (Lehmann and Joseph, 2009b; Lei and Zhang, 2013), while elemental composition is determined more so by the type of feedstock used. Biological properties and the ability of biochar to interact with soil biota are dependent on the type of soil as well as biochar chemical and physical features.

The exact characteristics of biochars is a function of process conditions (e.g. temperature, moisture, residence time) during production as well as the biomass material used (Krull et al., 2009; Schmidt and Noack, 2000). Biochars are suggested to have a positive influence on soil and plant productivity due to two main processes: release of nutrients from biochar surfaces (this related to cation and anions exchange capacity of the chars), or influencing soil nutrient transformation mechanisms leading to better fertiliser efficiency (Atkinson et al., 2010; Chan and Xu, 2009; DeLuca et al., 2009; Prendergast-Miller et al., 2014; Quilty and Cattle, 2011). It has been suggested that biochars from feedstock consisting of or including

animal faeces and/or sewage sludge contain more nutrients and may, under specific soil conditions, release more of those nutrients to the soil than biochars made from plant material; this related to higher nutrient concentration in animal products in comparison to plant products (Lehmann et al., 2011; Lei and Zhang, 2013). Therefore biochar in some cases can be treated as an organic fertiliser (Chan et al., 2008; Liu et al., 2014; Major et al., 2010). Due to different nutrient content in biochars and different nutrient availability to the plants after biochar application to the soil, it has been implied that the optimum dose of biochar may have to be determined for each soil.

Biochar has also been proposed to improve soil quality by stimulation of changes in soil chemistry (DeLuca et al., 2009; Jones et al., 2012). The changes have been most often attributed to increased soil pH and cation exchange capacity and therefore improved soil quality and conditions for the plants to grow (Cheng et al., 2006; Liang et al., 2006). Some reports attributed increased nitrification rates (Berglund et al., 2004; Clough and Condron, 2010; Prommer et al., 2014) or phosphorus availability in the soil to the response to biochar application (Cheng et al., 2006; Nelson et al., 2011).

Apart from positive effects that biochars can bring, there are some potentially negative effects that can be caused by introducing biochar to the soil environment. High content of heavy metals have been found in some biochars made from sewage sludge and tannery wastes (Bridle and Pritchard, 2004; Chan and Xu, 2009; Liu et al., 2014; Muralidhara, 1982), and use of these could lead to build up of toxic concentration of heavy metals in soils. Such an outcome could render making of biochars from material with high heavy metal concentrations undesirable or non-viable.

While the chemical characteristics of biochars are strongly related to feedstock and pyrolysis conditions, the physical features of biochar are more related to the latter. At temperatures above 120° Celsius organic materials start to decompose and the original chemical content of feedstock material has a significant influence on physical characteristics of the biochar produced (Downie et al., 2009). Pore structure, size distribution, volume; and total surface area are thus a function of this initial chemistry and pyrolysis conditions. Nano-porosity and macro-porosity of biochars can provide pores for plant root exploration, shelter for microorganisms, affect soil bulk density, porosity and water holding capacity and can be helpful in aeration (Downie et al., 2009; Lehmann et al., 2009). Macropores in biochar play especially important role for plant root exploration.

Several studies have shown the reduction in nutrient runoff following biochar application to soils (Major et al., 2009; Shinogi and Kanri, 2003; Tryon, 1948), presumably because biochar has increased cation exchange capacity (reducing nutrient availability for dissolution in water) or increased water holding capacity of soil (reduces water volume for runoff).

The porosity of biochar influences their ability to stimulate soil microorganisms, and thus plays an important role in whole soil ecology (Thies and Rillig, 2009). The physical and chemical environment of biochars strongly affect soil microbes and in consequence plant productivity, as it is known that microbes (i.e. bacteria, fungi, protozoa) significantly influence the ability of plants to acquire macro and micro nutrients (Lehmann and Joseph, 2009b). Biochar may influence soil micro-biology by two main mechanisms: providing habitat for soil microorganisms and substrates for soil biota (i.e. compounds present on biochar surfaces may provide direct source of bacteria nourishment). The first mechanism is related to chars porosity while the second relates to biochar decomposition in the soil (Dempster et al., 2011; Steinbeiss et al., 2009; Thies and Rillig, 2009). Recent studies have also shown that biochar may stimulate soil microorganisms indirectly, by changing soil environmental conditions (Watzinger et al., 2014).

Considering the numerous types of feedstock utilised, and the wide range of production conditions used, the final products vary significantly and generalization of biochar characteristics becomes a very challenging task. Yet, there have been attempts to classify biochars in order to model soil and plant response under certain products.

2.1.3. Classification of Biochars

As each biochar has its own properties, its introduction to soil should be preceded by an in-depth analysis of potential consequences. Given the variety of biochars and soil types and the unique combination each application makes, the effects of biochar application cannot be fully predicted. It is, however, possible to categorise groups of biochars based on feedstock or the pyrolysis process used (Chan et al., 2008; Joseph et al., 2009; Lei and Zhang, 2013), while pyrolysis temperature and char age categorizations have also been proposed. There are other potential classifiers, for example liming capacity or nutritional properties.

The feedstock divided biochars into two main groups – plant and animal wastes based. Plant-based biochars tend to have higher C content and lower concentrations of total

nitrogen (N), Phosphorus (P), Potassium (K), Sulphur (S), Calcium (Ca), Magnesium (Mg), Aluminium (Al), Sodium (Na), Copper (Cu) and cation exchange capacity (CEC) than animal-based biochars (Chan et al., 2008; Kyoung et al., 2010; Shinogi and Kanri, 2003). Conversely the highest N content found to date is in biochars made from poultry litter and cow manure (Lang et al., 2005; Sarkhot et al., 2012). The highest calcium content was found in biochars made from paper sludge (Singh et al., 2010). Most wood- and nut- based biochars have high C/P and C/N ratios (Kookana, 2010; Krull et al., 2009). Also, biochars from woody materials tend to have lower cation exchange capacity than biochars made from non-woody materials (Chan et al., 2007; Gaskin et al., 2008; Gundale and DeLuca, 2006; Kookana, 2010; Major et al., 2009; Van Zwieten et al., 2010a). Wood-based chars were also reported to increase saturated hydraulic conductivities more than manure-based biochars (Lei and Zhang, 2013) which is a desirable effect in heavy soils.

Biochars may also be classified on age, as the chars properties change with time. 'Aged' biochars (depending on feedstock and pyrolysis conditions 1-5 years old) are characterized by decreased C content, increased O and H content, and higher cation exchange capacity (Kookana, 2010). Increased CEC is a result of oxidation which produces a greater density of negatively charged carboxyl, phenolic, and hydroxyl functional groups on the char surface (Cheng et al., 2008; Cheng et al., 2006; DeLuca et al., 2009).

Pyrolysis temperature can be used to distinguish two main types of biochar – high temperature and low temperature. Biochars from high temperature pyrolysis (>550 °C) are usually richer in carbon and less likely to provide plant nutrients than the low-temperature biochars (Demirbas, 2004; Krull et al., 2009). Biochars produced in temperatures >550 °C, and especially those with high ash content, have intricate surface and internal properties that results in complex physical reactions with soil (Joseph et al., 2010; Lehmann and Joseph, 2009b; Shinogi and Kanri, 2003). Low-temperature pyrolysis (<500 °C), on the other hand, favours greater recovery of carbon (C) that is lost at higher temperatures (Joseph et al., 2010; Keiluweit et al., 2010). Biochar pH may increase with increasing pyrolysis temperature, however this is not universal, and pH has been observed to decline for manure based biochars.

Production temperature can also alter the solubility of certain nutrients and other physical and chemical properties of biochar. The production temperatures range between 300 and 800°C. For example, high-temp biochars tend to have a higher electrical conductivity and

extractable NO_3^-, while low-temp biochars (≥500°C) have in general greater amounts of extractable P, NH_4^+ and phenols (DeLuca et al., 2009; Kookana, 2010). The majority of N and S volatilize above 200 and 374°C respectively while K and P volatilize between 700 and 800°C, which influences the properties of the final product (Kookana, 2010). While high-temperature biochars tend to have greater porosity and SSA, lower temperatures chars may release more nutrients to the soil.

It has been suggested that both specific surface area and microporosity of biochars increase with temperature. Biochars produced at 700°C sorbed more Zinc and cadmium in comparison to the same feedstock biochars produced at 400°C (Melo et al., 2013). In contrast, biochars made at lower temperatures (400-500°C) showed greater sorption of phosphorus in comparison to high temperature biochars (Morales et al., 2013). However, some authors suggest that specific surface area [$m^2\ g^{-1}$] increases only at temperatures up to 700° C (Brown et al., 2006). As this temperature is close to the upper practical limit for pyrolysis, the effects of higher temperatures, if any, on specific surface area will be of little practical importance.

The degree of aromaticity (% of carbon in aromatic rings) is known to increase with increasing charring temperature, hence the C rich biochars made at high temperatures may have greater soil C sequestration value than the low-temperature biochars due to carbon being in a more stabile form (Baldock and Smernik, 2002; Nguyen et al., 2009).

Our understanding of general biochar characteristics based on feedstock type, and production conditions allow us to draw broad conclusions about the potential interaction between char and the soil to which it will be added. However, these should be treated as a guide rather than prescriptive and the physical and chemical features of biochar made using similar methods may still differ markedly.

2.1.4. Soil changes under biochar application

The application of biochar to agricultural soils has the potential to improve soil physical, chemical and biological conditions (Lehmann and Joseph, 2009b). Knowing the extent of the changes that biochar and soil itself undergo is vital for understanding the contribution that biochar can make to soil amelioration and its sustainable management (Lehmann and Joseph, 2009b; Quilty and Cattle, 2011; Shackley and Sohi, 2010). Added to the variability in

the properties of biochar, variability across soil types and the many soil parameters influenced by its application again increases the complexity of the response.

Biochar as a high surface-area, porous, variable-charge organic material has the potential to increase soil water-holding capacity, cation and anion exchange capacity, surface sorption capacity and base saturation (Downie et al., 2009; Hammes and Schmidt, 2009). When added to soil it undergoes several chemical and physical changes, influencing the soil environment at the same time (Glaser et al., 2001; Lehmann et al., 2009; Liang et al., 2006). Hammes et al. (2007) listed the decrease of pore size as one of the most important changes in biochar after application. Biochar also changes chemically; it may interact with different mineral phases, depending on soil and biochar chemistry, and change its elemental composition as a result of oxidation (Krull et al., 2009; Lehmann et al., 2009). Biochar additions also have the potential to alter soil microbial populations, to shift functional groups of soil particles i.e. change soil chemistry and have the potential to reduce soil bulk density (Amonette and Joseph, 2009; Gundale and DeLuca, 2006). Given that biochar is a much stronger sorbent for neutral organic compounds than other forms of organic matter present in most soils, and that biochar is ubiquitous in the environment, it should be expected that biochar naturally present in soil would play an influential role in overall soil sorption properties (Chan and Xu, 2009; DeLuca et al., 2009; Krull et al., 2009). Changes and stability of biochar in the soil is a crucial factor in the framework of biochar use for environmental management. Stability determines how long carbon applied as biochar will remain sequestered and how long biochar can provide benefits to the soil (Lehmann et al., 2009).

As biochars are very porous and improve soil aggregation (Brodowski et al., 2005; Liang et al., 2006), their application to soils should improve soil aeration. Furthermore, improved water-holding capacity and reduced tensile strength have been demonstrated (Chan et al., 2007; Downie et al., 2009). Similar to burned plant residues, biochars can contain varying concentrations of alkaline ash that is directly added into the soil as Ca, Mg, K and Na oxides, hydroxides and carbonates. This soluble form of ash in biochar can be rapidly released into soil and then leaches down the soil profile to ameliorate soil acidity (Gaunt and Cowie, 2009). Increasing soil pH through biochar addition could potentially encourage the activity of N_2O reductase enzymes of denitrifying microorganisms (Gaunt and Cowie, 2009; Yanai et al., 2007). The rate of biochar application, its composition and buffering capacity of the soil

will determine the extent of any change in soil pH. Secondary effects such as those on denitrifying organisms will be partially dependant on pH, but also on other soils characteristics such as aeration, drainage and concentration of labile organic carbon.

Recent studies have demonstrated that the addition of biochar to surface soil may directly influence N transformations by several mechanisms (DeLuca et al., 2009; Van Zwieten et al., 2010a; Wrobel-Tobiszewska et al., 2012a). Biochar has been found to increase net nitrification rates in temperate and boreal forest soils (DeLuca et al., 2006). There is however, no evidence for such an effect on grassland or agricultural soils (DeLuca et al., 2006; Lehmann et al., 2003; Rondon et al., 2006). The rapid response of the nitrifier community to biochar additions in soils with low nitrification activity has led to a number of proposed mechanisms. Biochar may be adsorbing inhibitory compounds from the soil environment, which then allows nitrification to proceed (DeLuca et al., 2009). It has also been suggested that biochar has the potential to catalyse the reduction of N_2O to N_2 during denitrification, potentially reducing the emission of this important GHG to the atmosphere (Gaunt and Cowie, 2009). According to available research biochar increased N_2 fixation when added to nodulating and non-nodulating varieties of common bean (Rondon et al., 2006). Increases in microbial biomass, and a subsequent reduction in available N in soil through immobilization following biochar application can potentially occur by: a) biochar serving as a source of energy for microorganisms, b) providing protection from predation for microorganisms colonizing the pore space; and c) adsorbing labile C substrates and nutrients in soil, consequently increasing metabolic efficiency and growth of microbes proliferating on or around biochar surfaces (Thies and Rillig, 2009).

Several studies have reported enhanced P availability and thus uptake by plants in the presence of biochar, however the mechanisms are not fully understood. Suggested mechanisms include: a) biochar being a source of soluble and exchangeable P; b) biochar modifying soil pH and ameliorating P complexing by the metals Al^{3+}, Fe^{3+2+} and Ca^{2+}; c) biochar may promote microbial activity and P mineralization (Ma and Matsunaka, 2013b; Nelson et al., 2011; Ojekami et al., 2011; Wrobel-Tobiszewska et al., 2012a). Hardwood based biochar has been shown to release P (as well as K and Mg) from its surfaces and providing these nutrients in a plant-available form (Angst and Sohi, 2013). By contrast, biochar has also been reported to adsorb P to its surfaces and lower P plant availability (Chintala et al., 2014). A mixed application of biochar with mineral and organic fertilisers has been suggested to increase nutrients availability in soil and improve crops growth

(Schulz et al., 2013; Widowati and Asnah, 2014). Clearly, there is diversity in findings of the effects of biochar on nutrient availability and thus fertiliser requirements and application practices, so it is not possible to provide a general recommendation on suitable strategies for combined use of biochar and fertiliser.

The amount of plant-essential nutrients lost from the rooting zone in agricultural systems by leaching can be considerable: losses up to 80% of applied N, 172% of applied Ca and 136% of applied Mg have been reported in the field (values greater than 100% indicate that nutrients other than those added were also leached)(Cahn et al., 1993; Lehmann et al., 2003). Phosphorus and other nutrients cause euthrophication when they leach or run off from agricultural land into water bodies (Ojekami et al., 2011; Schachtman et al., 1998). Lysimeter work using a biochar amended clay soil from the Amazon showed that water percolation was related to crop growth: less water percolated from soil/biochar mixtures than pure soil, following increased crop growth (thus more transpiration) when biochar had been added (Lehmann et al., 2003; Major et al., 2009). It has been noted that biochar at high application rates (10% or 20% w/w) can effectively reduce NH^{4+} leaching (Lehmann et al., 2003*)*. Singh et al (2010) demonstrated that while freshly added biochars had little effect on NH^{4+} leaching, upon aging in the soil (approximately 5 months) the wood and poultry litter-based biochars produced at 550 ^{0} C were able to reduce leaching of NH_4^+ by 55-65% in an Alfisol (Kookana, 2010). This can be explained by the fact that most biochars have been found to contain a large proportion (over 95%) of micropores ($<2x10^{-3}$ micrometer), and biochar porosity probably contributes to nutrient adsorption by the trapping of nutrient-containing water held by capillary forces (Major et al., 2009; Tseng and Tseng, 2006; Young et al., 2011).

Recent data (reviewed by (Warnock et al., 2007)) indicate that biochar application is often followed by enhancement of mycorrhizal communities in the rhisosphere, coinciding with improved nutrient uptake by associated plants, thereby potentially reducing leaching. Several other mechanisms have been listed as a potential explanation for limited nutrients leaching from the soil e.g. direct bind or sorption of nutrients, or facilitation of the movement of attached nutrients when fine biochar particles are transported in percolating water (Major et al., 2009; Smernik, 2009). These diverse findings in relation to nutrient retention and release suggest that there may be positive impacts on nutrient leaching and thus adverse environmental outcomes such as eutrophication of water bodies. However,

there is insufficient evidence to make firm conclusions, and it is evident that the outcome is likely to be dependent on numerous soil and biochar characteristics, and soil biology.

As summarised in this chapter biochar has been reported to induce various soil changes. There are numerous mechanisms suggested to be responsible for those and the explanations given are sometimes contradictory. Such observations can be considered a result of great biochar variability and a wide range of soil types and responses. Case studies and results from experiments allow some very general conclusions to be made about biochar influence on soil; however the mechanisms of such are yet to be fully understood.

2.1.5. Effect of biochar application on plant growth, nutrient uptake and yield

Positive and, to a lesser extent, negative yield responses following biochar application have been reported for a wide range of crops and plants in different parts of the world (Asai et al., 2009; Blackwell et al., 2010; Graber et al., 2010; Nigussie et al., 2012; Solaiman et al., 2010). A number of examples with additional details are provided in Table 2.1.

Only some of the positive effects of biochar application were attributed to nutrients supplied directly by biochar (Chan and Xu, 2009; Lehmann et al., 2003). A majority of studies attribute the positive plant responses to other effects of biochar on soil rather than as a direct supplier of nutrients (Chan et al., 2007; Lehmann et al., 2003; Van Zwieten et al., 2010a). The positive responses due to biochar application were attributed to either nutrient savings (decreased leaching) or improved fertiliser-use efficiency (higher yield per unit of fertiliser applied) and can therefore be regarded as an indirect nutrient value of biochars (Blackwell et al., 2010; Chan and Xu, 2009; Chen et al., 2010; Major et al., 2009; Wrobel-Tobiszewska et al., 2012a). Some reasons given for positive crop yield responses include changes in soil water holding capacity, liming effect of biochar, amelioration of pH-induced micronutrient deficiency, improved P, K and Ca availability and indirect effects of improving physical properties in hard-setting soil.

However, biochar can also cause reduction in crop yield or no effects on growth at all, examples being soybean following application of 5 and 15 t ha^{-1} of biochar (Kishimoto and Sagiura, 1985) and for common bean (Rondon et al. 2007)(Table 2.1). Nevertheless, most of the reported effects on yield have been positive, suggesting the negative impacts may be crop, biochar type or site/soil specific, and should be further investigated. An increased N, P

and K uptake has been reported in lettuces while reductions in any nutrients uptake have not been observed.

Most data relates to horticultural and field crops, with the number of studies investigating the effects of biochar application on woody species being very limited (Table 2.1).

Table 2.1. Summary of plant responses and soil chemical changes to biochar application to the soil for a range of horticultural and field crops and woody species grown in a diversity of soils.

Reference	Species, soil, and experimental conditions	Biochar	Results	Comments
(Yamato et al., 2006)	Maize, Cowpea, Peanut on highly weathered infertile tropical soils, field experiment (FE)	Charcoal made of bark of *Acacia mangium* at 260-360°C, applied at the rate of 15 t ha^{-1}.	Positive effects on: root size, yield, colonialization rate of mycorrhizal fungi, pH value, total N and available P_2O_5, CEC	
(Chan et al., 2007)	Radish, alfisol, pot experiment (PE)	Green waste biochar (mix of grass clippings, cotton trash and plant pruning), three rates: 0, 10, 50, 100 t ha^{-1}, mate at 450°C.	Yield increased significantly (up to 266%) with biochar addition at the highest rate with fertiliser.	With no fertiliser, the yield did not respond, and with the lowest rate of biochar the slight decrease in the yield was observed.
(Rondon et al 2007)	Common Bean, oxisol, PE.	Biochar from logs of *Eucalyptus* at 350°C with 15% of oxygen, rates: 0,30,60,90g biochar/kg soil.	N fixation increased and so did biomass production.	Yield decreased when biochar was added at the rate of 90 g/kg, (Colombia).
(Steiner et al., 2008)	Sorghum, highly weathered Ferrosol, FE.	Derived from secondary forest wood, applied at rate 11 Mg/ha (11 t ha^{-1}).	Soil charcoal amendments improved fertiliser efficiency plant growth and doubled grain yield when combined with fertiliser.	
(Chan et al. 2008)	Radish, alfisol and chromosol, PE.	Two biochars made of poultry manure and bedding material, at 450°C and 550°C (rates: 0, 10, 25, 50 t ha^{-1}).	Yield increase mainly due to the N and P availability. Both biochars are useful as an organic amendment.	Yield also increased without fertiliser addition.
(Major et al. 2010)	Soybean-Maize rotation, kaolinic soil, FE.	Wood biochar (rates: 0,8,20 t ha^{-1}).	The yield increased significantly after one year from application (not in the first harvest) and the nutrients uptake was higher.	It is suggested that the yield increase due to higher Ca and Mg availability, (Columbia).
(Chen et al. 2010)	Sugarcane , heavy clay, lysimeter experiment.	Bagasse and biosolid biochars, 600 °C, rates to equal 1% of the total weight.	Use of biochars decreased nitrate-N in percolating water by denitrification of the Nitrate-N and adsorption of ammonium-N by charcoal.	Yield calculated on the basis of equation.
(Van Zwieten et al. 2010)	Wheat, Radish, yellow orthictenosol, PE.	Biochar from whole trees residues produced in 600°C, doses of 0,5,10,20,50 t ha^{-1}.	Biomass increased with high biochar rates but only with low N rates.	Biomass decreased with both high biochar and N rates. Biochar did not influence the soil C but significantly increased microbial activity.
(Blackwell et al. 2010)	Wheat, dryland, south-western Australia, FE.	Biochar rates: 0.07-10 t ha^{-1}. Feedstock: different woody wastes, slow pyrolysis.	Low biochar doses provide positive effect on crops yield and fertiliser requirements.	The prices of biochar which are profitable for the whole production were calculated for particular yield increases over years.
(Graber et al., 2010)	Pepper, Tomato, coconut fibre: tuff growing mix, PE.	Nutrient poor, wood based biochar.	Yield response of pepper improved under biochar. Some response increased in tomato but not the yield.	No differences in plant nutrient content. Effect of shifts in microbial population and/or low doses of phytotoxic chemicals stimulated growth.

(Santalla et al., 2011)	Pinus radiata, humic Umbrisol, FE.	Mixed wood ash (with charcoal), both fly and bottom ash, from *Pinus radiata* bark feedstock. Added with or without P at the rate of 7.5 t ha^{-1}	Nutrients were more available for the trees when charcoal was added with P, however it also caused lower soil N mineralization.	25 years old, second rotation, (Spain).
(Zhang et al. 2011)	Maize, calcareous loamy soil, FE.	Wheat straw biochar produced at350-550°C, rates: 0, 20 and 40 t ha^{-1} with or without N fertilisation.	Maize yield increased by 8.8% to 15.8%, total emissions decreased.	Biochar also decreased soil bulk density and increased total N but had no effect on soil mineral N, (China).
(Nigussie et al., 2012)	Lettuces, chromium polluted soils, PE.	Maize stalk biochar, rates: 0, 5 and 10 t ha^{-1}.	Uptake of N, P and K significantly higher under biochar.	Nutrients from biochar, ash, high surface area and porosity responsible for the changes.
(Ma and Matsunaka, 2013b)	Maize, soils with low P, PE.	Dead dairy cattle biochar, produced at 450°C, different form.	Increased plant growth and dry matter production only when fine biochar was applied.	The effect was promoted by N fertiliser application. Attributed to P release from biochar.
(Schulz et al., 2013)	Oat, washed sand and loamy soil, PE.	Beech wood biochar (350-450°C) mixed with compost.	Biomass production increased with rising biochar and compost amounts.	
(Prendergast-Miller et al., 2014)	Spring barley seedlings, sandy loam soil, PE.	Miscanthus straw (700°C) and willow wood chips (450°C) biochar.	Plants had larger rhisosphere zones in biochar-amended soils.	Biochar as a direct source of nutrients and indirectly altering soil nutrient content.

Biochars differ significantly in terms of physical and chemical conditions and therefore may affect soils and crops in different ways as presented in Table 2.1. More case studies, focusing on biochar application effects are required to investigate its local applicability.

2.1.6. Application risk and unknown effects

The literature identifies many benefits of biochar application to soil but there are also some negative implications beyond that of yield reduction e.g. reduced efficacy of agrochemicals, possibility of introducing toxic elements to soil and water, accumulation and transport of chemicals and/or heavy metals and potential eco-toxicological impacts on soil flora and fauna (Liu et al., 2014; McHenry, 2009; Young et al., 2011).

One of the most discussed topics in biochar literature is the possibility of introducing toxic materials, principally polycyclic aromatic hydrocarbons (PAHs), dioxins and heavy metals into the soil with biochar application. PAHs consist of fused aromatic rings and generally occur in oil, coal and tar deposits, and are by-products of burning fossil fuels and biomass. Dioxin is a general term for a large group of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). So far very little is known about the exact concentration of such organic toxicants in biochars. Brown et al. (2006) analysed a range of

biochars for PAHs content and found that the content showed a strong dependence on the production temperature, with decreasing amount of PAHs with increasing temperature over the range of 450-1000° Celsius (Brown et al., 2006). According to (Singh et al., 2010*)*, who analysed 11 different biochars produced from different feedstock at temperatures ranging from 400 to 550° Celsius, none of the analysed biochars exceeded 0.5 mg kg^{-1}, the Australian guideline value for PAHs in the soil (Kookana, 2010). Due to the fact however, that hydrophobic compounds like PAHs and dioxins are easily sorbed by materials like biochars, more work is needed to confirm the practicality of commercial use of biochars in Australian soils. Re-condensation of pyrolysis vapours from biochar has been reported to bring toxic effects on germination of *Lepidium sativum* but no specific compounds were determined as responsible (Buss and Masek, 2014). Some biochars, especially those based on poultry litter and sewage sludge may contain significant amounts of heavy metals (Chan et al., 2008; Liu et al., 2014). Addition of such biochars to soil may result in high concentration of heavy metals in the soil and potentially toxic effect on plants and soil microorganisms (Kookana, 2010; Shackley and Sohi, 2010).

Another potential risk connected with biochar porosity is altered bioavailability of agrochemicals. Incorporation of small amounts of biochar in soil has been shown to inhibit the microbial degradation of pesticides and thereby to increase their persistence in the environment (Kookana, 2010; Zhang et al., 2011). Yu et al (2009) studied the biodegradation and plant uptake of two insecticides (carbofuran and chlorpyrifos with differing hydrophobicides) on spring onions (*Allium cepa*) after application of biochar. They found that the application of biochar decreased the bioavailability of the pesticides to microorganisms and for a plant uptake (Kookana, 2010).

The majority of biochar studies are based in controlled environments e.g. glasshouses or hothouses. It has been suggested that biochar application on a commercial scale must be preceded by long-term, field-based experiments as the application in controlled environments does not reveal all possible biochar effects (Gurwick et al., 2013). Therefore, field experiments are required to confirm biochar results observed in the controlled environment and to support the proposed feasibility of biochar application in large agro-forestry systems.

The literature reviewed in this section reveals that many mechanisms of biochar effects on soils, plants and microorganisms remain unexplained. Consequently, biochar should be

regarded as potentially having both positive and negative effects and these be considered in relation to characteristics of the soil and site to which it is to be applied. The same conclusion – uncertainty about biochar characteristics and effects – leaves many questions to be answered and mechanisms to be explained.

2.2. Forestry in Tasmania

Forestry is an important industry in Tasmania and its commercial history dates back to 1842 when licences for the felling, removal and sale of timber in Tasmania were granted by legal acts. In the power of the State of Tasmania's Forestry Act 1920, Forestry Tasmania is mandated to manage 1.5 million hectares of state forest as multiple use forest. Sustainable yield logging is currently permitted in approximately one-half of this area. Production of timber, especially high quality saw logs is inseparably connected with generating significant amounts of woody wastes. Currently the residues are either retained on plantation sites or used to produce pulp wood or paper. If utilised alternatively, those wastes could be used as a feedstock for biochar production. The main source of wood supply in Tasmania is plantation based forestry and the majority of woody wastes are generated by these forestry systems. Therefore forestry plantations in Tasmania have very high potential as a feedstock for biochar production.

2.2.1. Plantations

Forestry plantations in Tasmania are managed in 20-25 year rotations to produce high-quality sawlogs. The area covered by forestry plantations in Tasmania (on state land) exceeds 100,000 ha while plantations on private land double this number (FT database, 2010-2013; Rothe. A, 2013). *Eucalyptus nitens*, *Eucalyptus globulus* and *Pinus radiata* are the main plantation species in Tasmania.

A series of operations and preparations must be completed before and during plantation life span to ensure high quality timber production (Elliot, 2011). Plantation management begins with choosing a suitable site and the right species for the site. Land preparation, including cleaning, burning, cultivation and chemical use, significantly affect future plantation development through the soil conditions created in the area to be planted. Before planting the site must be prepared by clearing and cultivation followed by herbicide application to manage weeds. Seedlings about 6 months old grown in nurseries are then planted and fertilised. If required, fertilising might be repeated, this depending on the site

fertility and seedlings/trees performance (Elliot, 2011; FT database, 2010-2013; Wood et al., 2009).

The total yield of forestry plantations is partly dependent on the early growth of tree species which is the result of adequate nutrient supply, water, available sunlight etc. (Duncan et al., 2006; Volker et al., 2006). During the early years, growth of the plants with relatively high nutrient concentration accounts for a major proportion of net primary productivity. This stage of growth is characterized by increasing rates of accumulation of nutrients, which are at a maximum about the time of canopy closure. Tree growth is most likely limited by the supply of nutrients in the soil because of the large demand for nutrients by young seedlings (Attiwill and Adams, 1996). Rapid early growth of tree seedlings is critical to the success of the plantation establishment (Close et al., 2010), therefore different methods are applied to ensure this effect. Specific management procedures and their timing is usually carefully adjusted to plantation location and soil type and quality and planted species (FT, 2013).

Eucalyptus nitens plantations growing on former native forest sites and/or poor quality pasture sites require fertilising as a lack N, P, K may slow seedling growth and influence tree productivity (Volker et al., 2006). Given the purported benefits of biochar, its application in forestry plantations has a potential to facilitate soil nutrition and plantation trees early growth.

2.2.2. Eucalyptus nitens

Eucalyptus nitens H. Deane & Maiden (*Myrtaceae*) is a globally significant plantation species and more than 450,000 ha are now planted across southern Australia (Parsons and Davidson, 2006). *E. globulus* and *E. nitens* plantations are mainly concentrated in southwest Western Australia and the 'Green Triangle' (Tasmania) where mean annual rainfall and temperatures support rapid growth (Close et al., 2005). Both *E. globulus* and *E. nitens* are the main trees grown on forestry plantations in Tasmania. The species characteristics are similar, however, *E. nitens* is more frost tolerant than *E. globulus* and therefore can be planted at higher altitudes and in colder climate (Davidson et al., 2004). *E. nitens* however, is not tolerant to dry sites or poor nutrition (Duncan et al., 2006).

Eucalyptus nitens is commonly known as Shining Gum and is native of Victoria and New South Wales in Australia to an altitude of 1,600 m with a mean annual rainfall 750-1,750

(Boland et al., 1992). It is considered a fast-growing species that can reach a height of 70 m with a trunk diameter of 1-2 m at breast height. Due to its fast growth it is very popular in plantation timber production and significant quantities of woody wastes are generated both during the plantation management practices and after harvest. Currently retained on site the forestry residues could be managed in an alternative manner, and be used as a feedstock for Tasmanian biochar production, while biochar application back into forestry plantations could help address the Eucalypt growth limiting factors (i.e. not sufficient water retention in the soil, nutrient leaching from the soil) issues.

2.3. Summary

Biochar use as a soil amendment is a relatively new topic and the full picture of its utility for different soil types and species as well as the mechanisms of changing soil, increasing crop yield and other positive environmental effects are still to be investigated. However, as discussed early in this chapter the variability in biochar products widens the range of soil and plant material changes to biochar application.

When biochar is applied to soil it undergoes numerous biochemical changes and interactions that are likely to affect their properties over time (Kookana, 2010). Only limited research has focused on long-term effects of biochar on changes in the soil and crop response. Therefore there is a need to perform long term studies under field conditions to investigate biochar impact on soil biota, changes in the soil and agronomic response of the plants.

Biochar has been applied under different conditions and the response of several agricultural species has been observed. There is however very limited knowledge concerning the possibility of using biochar for forestry plantations. The specifics of growing trees on plantation require detailed analyses of the possibilities to use biochar to manage soil condition and possibly enhance growth.

Several knowledge gaps are evident when analysing the available literature concerning biochar use for agricultural and forestry purposes. Given the high variety of feedstock used and production conditions the heterogeneity of available biochars leaves wide range of uncertainty considering its possible use for agro-forestry purposes. The fundamental mechanisms by which biochar could provide beneficial function to soil and the wider

function of the agro-ecosystems are poorly described in terms of providing the predictive capacity that is required (Krull et al., unpublished data).

Forestry Tasmania is required to make available annually a volume of 137,000 cubic meters of eucalypt sawlogs for the veneer and sawmilling industries as part of its multiple-use management of State Forests (FT, 2013). A substantial proportion of this timber volume is planned to come from *Eucalyptus nitens* plantations on State Forest. Management of eucalypt plantations for producing sawlogs is typically intensive, with timely application of value-adding operations such as fertilising, pruning and thinning to ensure the quality and size, respectively, of selected stems within 20-25 year rotations (Wood et al. 2009). Forestry Tasmania is currently focused on applying management regimes, which offer the best return for a site of given quality. Based on current operational costs and market expectations, and given the production goal of high-quality sawlogs (Wood et al. 2009) and alternative solutions could add to the big picture of sustainable forest management.

Biochar effects on agricultural crops under various climatic conditions suggest that it might bring positive influence to soil and plant agronomic response in forestry systems. Establishment and management of forestry plantations involve significant costs. These mainly result from site preparation and chemical application for the next rotation (FT, 2013; FT database, 2010-2013; Lyons et al., 2006). Current knowledge about biochar incorporation into the agricultural systems and implications resulting from previous biochar experiments suggest that biochar may assist in decreasing the costs of establishing forestry plantations in Tasmania. Yet, in order to propose reliable biochar production and application scheme to unique Tasmanian soils, experimental work must be undertaken.

3. MACADAMIA BIOCHAR

3.1. Introduction

The literature contains numerous examples of different biochars made under varying conditions and from a diversity of feedstock (Chapter 2). Taking into account the wide range in the origin of feedstock material and production conditions, biochars will differ in porosity, surface area, chemical composition, surface chemistry and the ability to interact with the soil (Amonette and Joseph, 2009; Chan and Xu, 2009; Downie et al., 2009). It is therefore very important to understand what type of biochar is used and what possible outcomes may arise from biochar application in the soil. This chapter presents the characteristics of macadamia nut shell biochar used in this study.

The biochar was made in South Africa from macadamia nut shells and wheat straw in 2008 (Rainbow Bee Eater Project Pty Ltd 2008). The HTT (highest temperature treatment) was 480° C and residence time was 180 minutes. After arriving in Australia, the biochar was stored in polypropylene containers and shipped to Tasmania in April 2011. Following this, the biochar was stored in a plastic container in a cool, dry place and applied in the pot experiment in May 2011 and in the field trial in September 2011.

3.2. Analytical methodology

Biochar was subjected to comprehensive soil and plant material tests performed at the CSBP Plant and Soil Analyses Laboratory in Western Australia. The tests were alike those performed on soil and plant material, described in full in Chapter 4.

Gas adsorption experiments were conducted using a Micromeritics® ASAP 2020 Accelerated Surface Area and Porosity System at the University of New South Wales, Australia. Before analysis each sample was degassed under vacuum at 300°C for 6 hours. Gas adsorption analysis was conducted using CO_2 as the adsorbate at 273.16 K (0°C; ice-water bath) over a relative pressure (P [Equilibrium pressure]/P_0 [Saturated vapour pressure]) range of 1.0×10^{-5} to 0.03, where P_0 is 24,000 mmHg. The CO_2 adsorption raw data was then converted to the volume of gas adsorbed (V_a; cm^3g^{-1} of material) at standard temperature and pressure (STP) conditions (0°C, 760 mmHg), and an adsorption isotherm

was generated by plotting V_a against P/P_0. From this adsorption isotherm the following information was extracted:

The micropore volume, calculated using the Dubinin-Radushkevich (Dubinin and Radushkevich, 1947) isotherm model (Equation 3.1),

(Eq. 3.1)

$$V_a = V_0 \exp\left\{-\left(\frac{RT}{\beta E}\ln\left(\frac{P_0}{P}\right)\right)^2\right\}$$

(Eq. 3.2)

$$\ln(V_a) = \ln(V_0) - \left(\frac{RT}{\beta E}\ln\left(\frac{P_0}{P}\right)\right)^2$$

where V_0 is the micropore volume ($cm^3 g^{-1}$), R is the gas constant (8.3143 J K^{-1} mol^{-1}), T is the temperature (K), β is the affinity coefficient of the adsorbate, and E is the energy of adsorption (J mol^{-1}). The second form of the equation, a plot of $\ln(V_a)$ versus $\ln(P_0/P)^2$ provides the Y-intercept of $\ln(V_0)$, at which point the volume of gas adsorbed is equivalent to the micro-pore volume.

The specific surface area, calculated using the linearized BET isotherm (Equation 3.3);

(Eq. 3.3)

$$\frac{1}{V_a[(P_0/P)-1]} = \frac{C-1}{V_m}\left(\frac{P}{P_0}\right) + \frac{1}{V_m C}$$

Where V_m is the volume of gas occupying a monolayer across the adsorbent surface ($cm^3 g^{-1}$), and C is the BET constant given by:

(Eq. 3.4)

$$C = \exp\left(\frac{E_{ADS} - E_L}{RT}\right)$$

where E_{ADS} is the heat of adsorption between the adsorbate and adsorbent (J mol^{-1}), and E_L is the heat of liquefaction (J mol^{-1}) for the liquid adsorbate. From a plot of $\left(V_a\left[\left(P_0/P\right)-1\right]\right)^{-1}$ versus P/P_0 , V_m can be determined, from which the cross sectional area of an adsorbing CO_2 molecule (0.17 nm^2) can then be used to then calculate the specific surface area.

Pore size distribution, estimated by first determining pore sizes from the adsorption data. This was calculated by fitting the Frenkel-Halsey-Hill (Hill, 1952) isotherm to the experimental isotherm (Equation 3.5);

(Eq. 3.5)

$$\frac{V_a}{V_m}=\left(\frac{a}{\ln\left(P_0/P\right)}\right)^b$$

where a and b are fitted constants of the model, determined by linear regression. The thickness (t; Å) of the adsorbate layer on the adsorbent surface was then determined using the expression:

(Eq. 3.6)

$$t=3.604\left(\frac{a}{\ln\left(P_0/P\right)}\right)^b$$

where the value 3.604 relates to the size of the adsorbing CO_2 molecule. Added to this is the radius of curvature (r; m) of the adsorbed CO_2 in the pore, as determined from the Kelvin equation;

(Eq. 3.7)

$$r=-\frac{2\gamma V_m}{RT\ln\left(P/P_0\right)}$$

Where γ is the surface tension (Nm^{-1}) between the adsorbing CO_2 and the substrate. At this point the pore radius is the sum of the adsorbate thickness, plus the Kelvin radius. Plotting this data versus the differential of the volume adsorbed gives a pore size distribution.

Scanning electron microscopy (SEM) accompanied by energy dispersive spectrometry (EDS) was performed on both macadamia char and charcoal collected from the field, the latter originating from previous onsite post-harvest woody residues burns. The analyses were performed in the central science laboratory (CSL) at the University of Tasmania. Scanning electron microscopy (SEM) and EDS are closely related techniques for high-magnification imaging and spatially resolved chemical analysis of solid samples. The method employs a finely focussed electron beam exciting a variety of secondary signals: Secondary electrons (SE) show surface morphology, backscattered electrons (BSE) local differences in average atomic number, x-rays are detected by energy dispersive spectrometers (EDS) for chemical analysis. The samples analysed were sputter coated with carbon. The equipment used to carry out analyses was Hitachi® SU-70 FESEM set for 15 kV.

Charcoal from onsite burns (2010) was collected from the soil in the experimental plantation in October 2013. The charcoal was most likely that of *Eucalyptus nitens* residues retained and burnt on site after the previous plantation was harvested. Charcoal was analysed using the SEM-EDS, under similar settings to these used from macadamia biochar analysis.

C^{13}- NMR analysis was performed on macadamia biochar in February 2014 at the NMR facility & Spectroscopy Lab at the University of NSW. Solid-state NMR spectra were acquired using a Bruker Avance III-300 spectrometer (Bruker®) operating at 75.4 MHz, and 300 MHz for 13C and 1H respectively, with a Bruker 4-mm double air-bearing cross-polarisation (CP) probe. The char sample was powdered and ca. 70 mg was packed into 4-mm outside diameter zirconium rotors, and subjected to 'magic-angle spinning' (MAS) at 13 kHz. The spectra were acquired by a directly polarized Hahn echo sequence (DP-echo) with 13C 90° pulse lengths of 4 μs. The tests were run as a pair without and with 75 μs of gated decoupling. Ten second recycle delays were used to equilibrate the 13C magnetization and 2000 transients (scans) were acquired for sufficient signal/noise. High-power SPINAL-64 1H decoupling with field strength of 72 kHz was used during acquisition. The free induction decays were processed with zero-filling to 8 k prior to Fourier transformation with Gaussian broadening.

Macadamia biochar was also analysed for the content of most common Polycyclic Aromatic Hydrocarbons (PAH). The presence and quantification of the following compounds was evaluated: Acenaphthylene, Acenapthene, Anthracene, Benzo-a-anthracene, Benzo-a-

pyrene, Benzo- b&k- fluoranthene, Benzo-ghi-perylene, chrysene, dibenzo-a,h-anthracene, Fluoranthene, Fluorene, Indeno- 1,2,3,cd-pyrene, Naphtalene, Phenanthrene, Pyrene.

A sample of 5 g was mixed with Hydromatrix to create a dry mix. A 100 μL of 100 μg mL^{-1} surrogate standard was added (p-terphenyl-d_{14}) to assess the extraction efficiency. Then 25 mL of 1:1 DCM: acetone was added. The samples were extracted for 3 minutes in an ultrasonic bath and then for 30 minutes on a rotating wheel. The extract was decanted through a filter paper containing anhydrous sodium sulphate into a TurboVap evaporation tube. A second 25 mL 1:1 DCM: acetone extraction was performed as before. A third portion of 20 mL DCM (no acetone) was then used to rinse the tube and sample. All the extracts were combined in the same TurboVap tube. An Internal Standard mix (100 μL of 400 μg mL^{-1}) was added – this contained naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12}. The extract was concentrated to 1 mL using a TurboVap apparatus – this is a water bath which blows gaseous nitrogen over the samples to speed up evaporation. The extracts were transferred to a GC (gas chromatography) vial for analysis. Blanks, Blank recoveries and QC (quality check) samples were run at a rate of 1 per 20 samples. The blank recovery was prepared by spiking blank Hydromatrix with 100 μL of 100 μg mL^{-1} spike mix (containing all 16 PAHs). Standards were prepared at 5, 10, 15 and 20 μg mL^{-1}. GC-MS analysis was conducted using a Varian 3800 GC connected to a Varian Saturn® 2000 MS. The GC column was a Varian VF-5 ms, 30 m x 0.25 mm, 0.25 μm, with 10 m integrated guard column. Injection of 0.6 uL was performed using Pulsed Splitless technique, with the injector at 290° C, and a pressure of 40 psi for 1 min. Column flow was 1.3 mL min^{-1} helium. The MS was operated in scan mode, 90-450 m/z, 0.4 sec scan time.

To understand the concentration of particular nutrients in the soil and the chemical changes over time the quantity of nutrients introduced to the soil with biochar and fertiliser under each biochar*fertiliser treatment was calculated. These calculations were based on the results of biochar chemical analyses and analytical content of the fertiliser gathered from the manufacturer, calculated into particular amount of biochar applied per pot (glasshouse experiment) or tree (field experiment).

3.3. Results – Biochar characterisation

Macadamia biochar has undergone several tests to describe its properties. Both standard plant material methods and standard soil methods were used to determine the nutrient content of the char. Specific surface area, porosity and microscopic analyses were performed to better understand the structure of the char and therefore add to the understanding of biochar effects on soil. The analyses of carbon forms in the char enabled making conclusions about char decay in the soil. Macadamia biochar was characterized as having low content of nitrogen, medium carbon and phosphorus content and high porosity and potassium and sodium. This section presents the detailed results of the analyses.

The chemical analyses results of the char are presented in Table 3.1. The methodology for performed tests is described in Chapter 4 as being specific to soil and plant material analyses.

Table 3.1. Macadamia biochar chemical characteristics (element and compounds composition). The methodology for all performed tests described in Chapter 4 as specific for soil and plant tissue samples analyses. Ex.- exchangeable

BIOCHAR		
Trait	**unit**	**value**
Ammonium Nitrogen	mg kg^{-1}	2
Nitrate Nitrogen	mg kg^{-1}	2
Phosphorus Colwell	mg kg^{-1}	421
Potassium Colwell	mg kg^{-1}	9,388
Organic Carbon	%	4.6
Total carbon	%	57.8
Conductivity	dS m^{-1}	3.6
pH Level (CaCl2)	pH	8.7
pH Level (H2O)	pH	10.1
Ex. Aluminium	cmol kg^{-1}	0.005
Ex. Calcium	cmol kg^{-1}	1.4
Ex. Magnesium	cmol kg^{-1}	1.2
Ex. Potassium	cmol kg^{-1}	22.3
Ex. Sodium	cmol kg^{-1}	2.7
Total Boron	mg kg^{-1}	13.8
Total Calcium	%	0.4
Total Copper	mg kg^{-1}	18.1
Total Iron	mg kg^{-1}	1,212
Total Magnesium	%	0.2
Total Manganese	mg kg^{-1}	108.6
Total Phosphorus	%	0.2
Total Potassium	%	2.2
Total Sodium	%	0.3
Total Sulphur	%	0.1
Total Nitrogen	%	0.4

The specific surface area of Macadamia biochar was calculated at 293.1 $m^2 g^{-1}$ while the micropore volume (< 200 nm in diameter) reached 0.086 $cm^3 g^{-1}$. As presented in Figure 3.1 micropores with diameters of 1.5 to 2.5 µm contributed to approximately half of the pore volume.

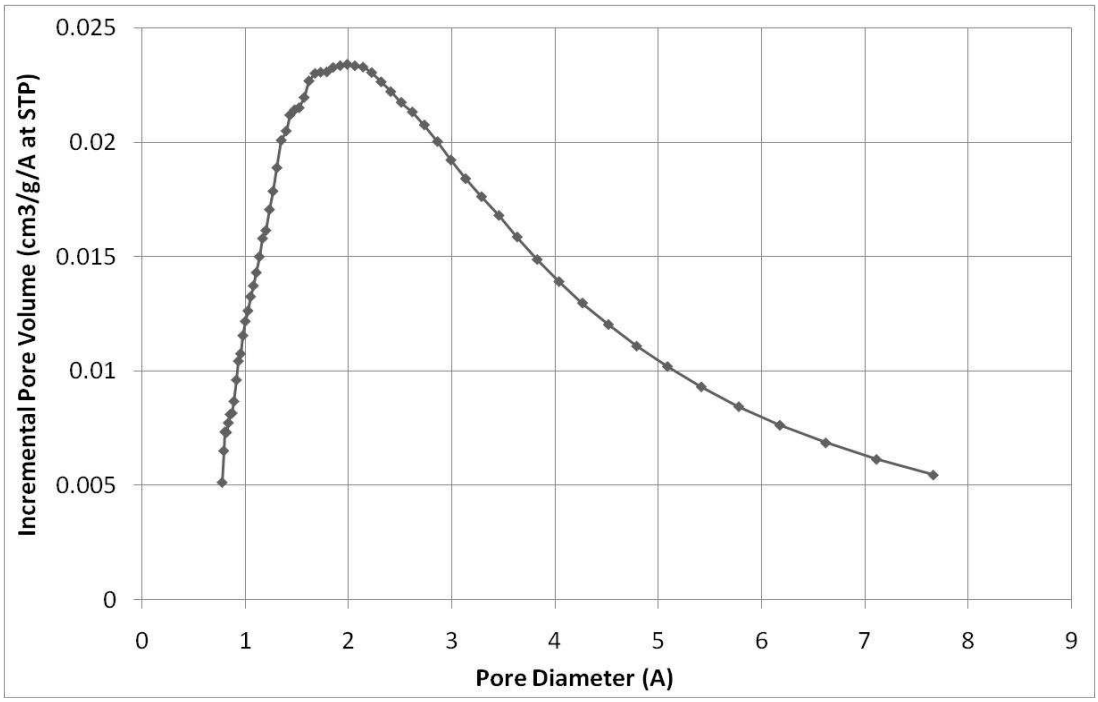


Figure 3.1. Pore size distribution in macadamia biochar, presenting a total volume of certain pore diameter (A). Calculated on Micromeritics® ASAP 2020 Accelerated Surface Area and Porosity System at the University of New South Wales, 2013.

SEM-EDS analysis revealed that macadamia biochar surface and attached particles consisted mostly of C, Si, K, Na and Cl (Table 3.2).

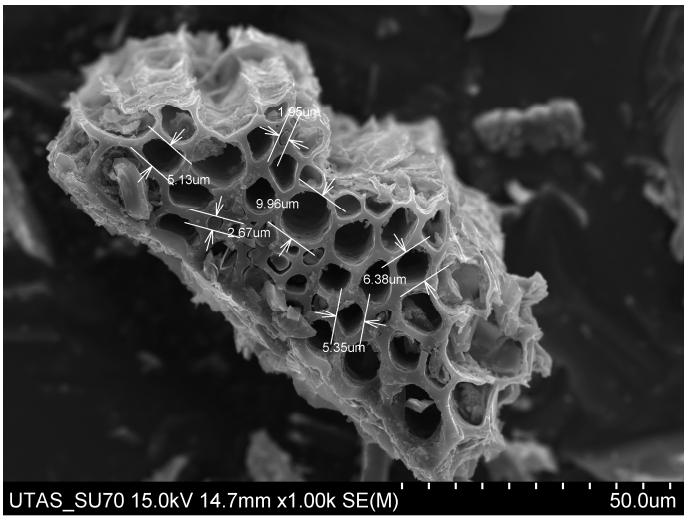


Figure 3.2. Electron microscopy image of macadamia biochar. Study performed in CSL in 2013 (Hitachi SU-70 FESEM), samples carbon coated, under a beam energy of 15kV.The distances indicated by arrows show pore diameter (µm).

The pore diameter measured in a random biochar particle varied between 1.86-9.96 µm (Figure 3.2). However, the image presents only macropores and an assessment of nanoporosity was beyond the equipments capacity.

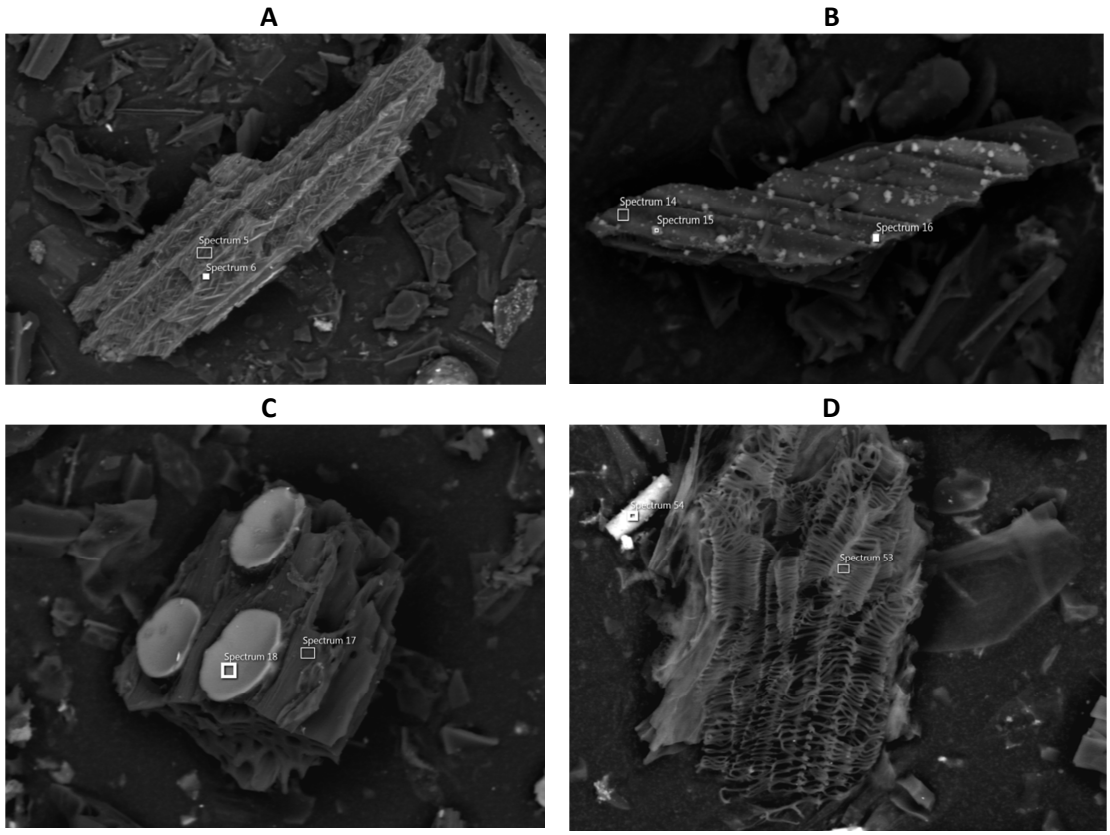
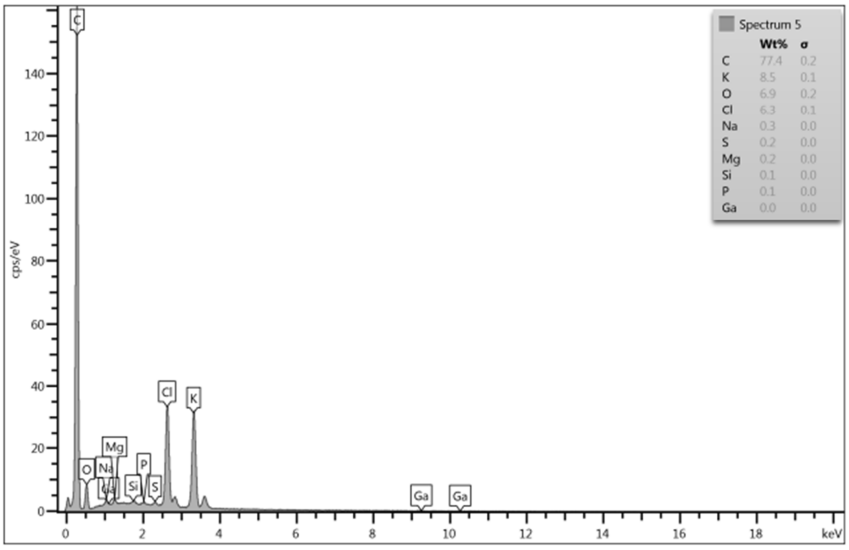
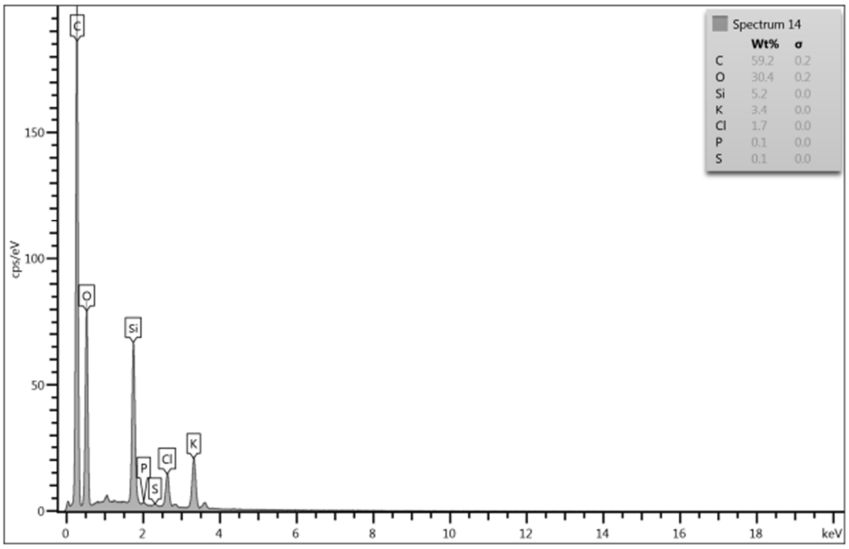


Figure 3.3. Scanning Electron microscope (SEM) images of macadamia biochar particles. Four example particles (A, B, C and D) and their chemical composition (Figure 3.4). Study performed in CSL 2013 (Hitachi SU-70 FESEM), samples carbon coated, under beam energy of 15kV. The white-bordered boxes represent the area where the spectrum was analysed.

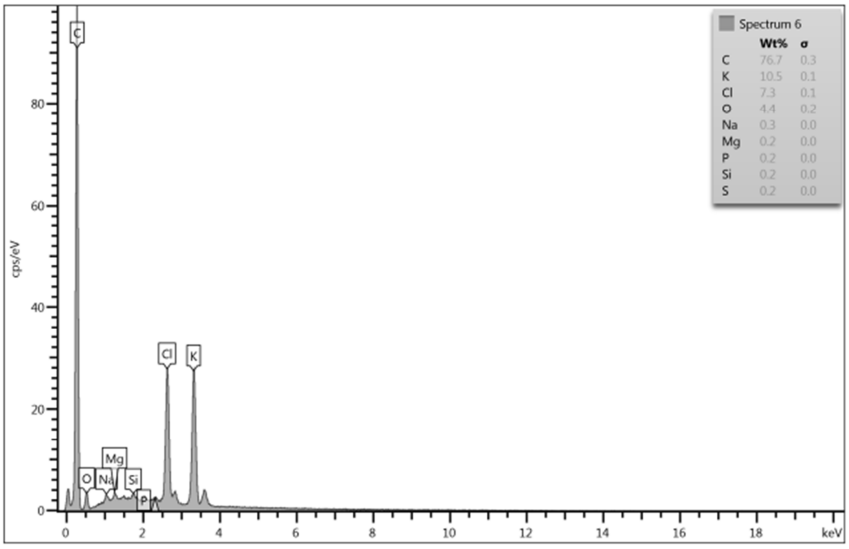
A



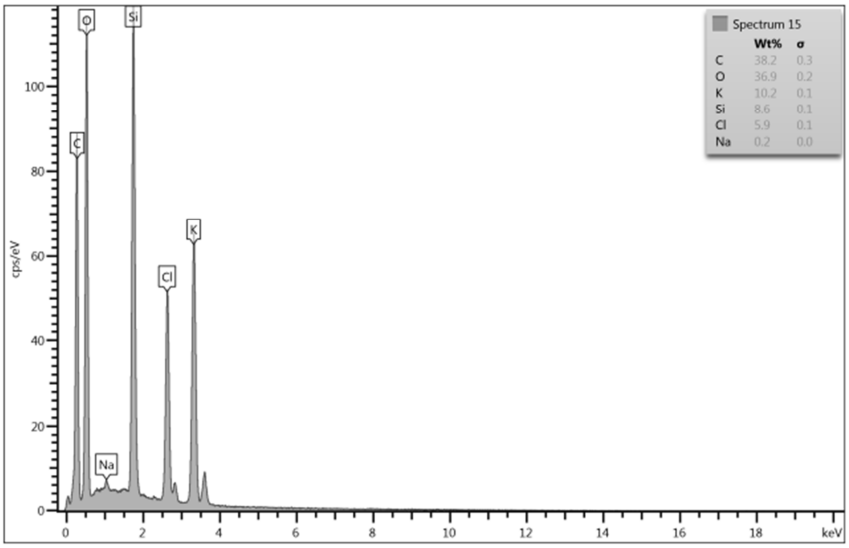
B


Spectrum 14
Wt% σ
C 59.2 0.2
O 30.4 0.2
Si 5.2 0.0
K 3.4 0.0
Cl 1.7 0.0
P 0.1 0.0
S 0.1 0.0
cps/eV
keV
C
O
Si
P
S
Cl
K

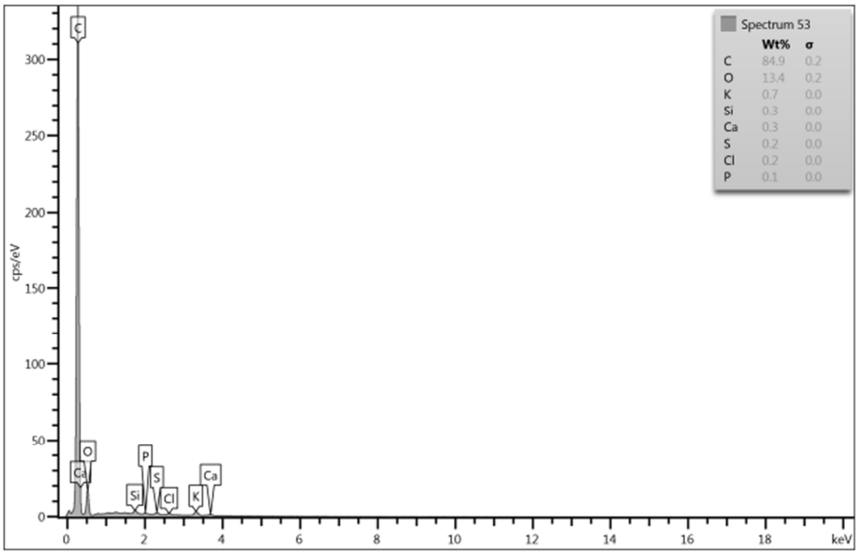
C


Spectrum 6
Wt% σ
C 76.7 0.3
K 10.5 0.1
Cl 7.3 0.1
O 4.4 0.2
Na 0.3 0.0
Mg 0.2 0.0
P 0.2 0.0
Si 0.2 0.0
S 0.2 0.0
cps/eV
keV
C
Cl
K
Mg
O
Na
Si
P

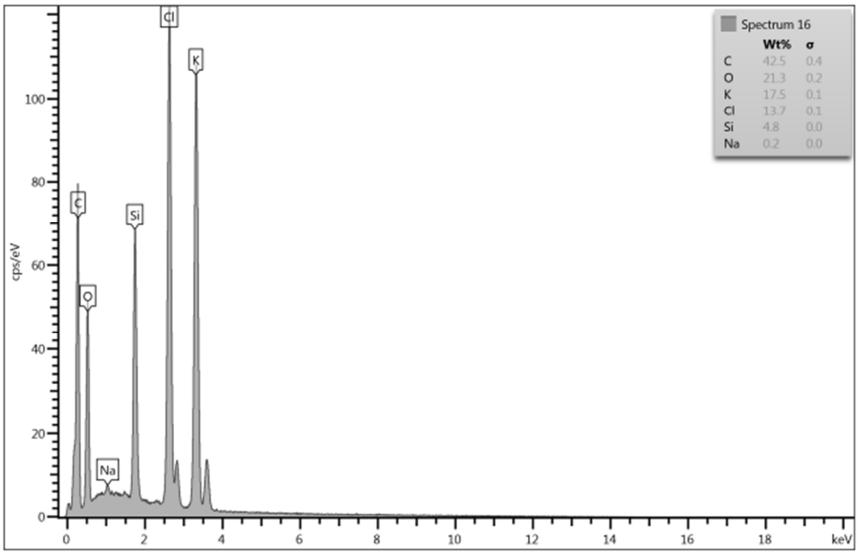
D


Spectrum 15
Wt% σ
C 38.2 0.3
O 36.9 0.2
K 10.2 0.1
Si 8.6 0.1
Cl 5.9 0.1
Na 0.2 0.0
cps/eV
keV
O
Si
C
K
Cl
Na

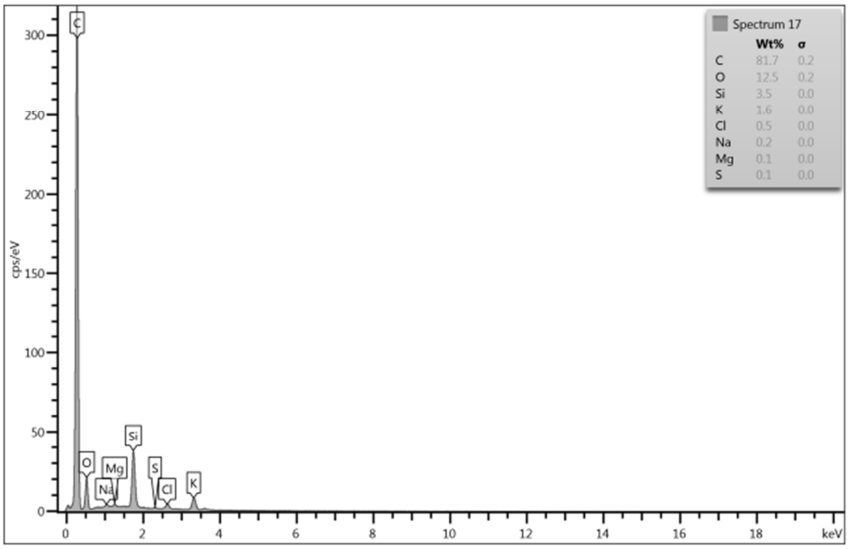
E


Spectrum 53
Wt% σ
C 84.9 0.2
O 13.4 0.2
K 0.7 0.0
Si 0.3 0.0
Ca 0.3 0.0
S 0.2 0.0
Cl 0.2 0.0
P 0.1 0.0
cps/eV
keV

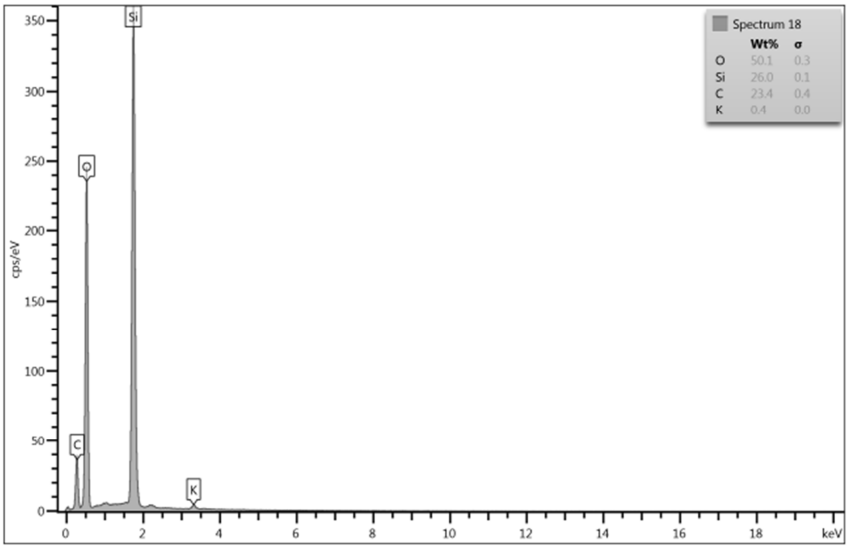
F


Spectrum 16
Wt% σ
C 42.5 0.4
O 21.3 0.2
K 17.5 0.1
Cl 13.7 0.1
Si 4.8 0.0
Na 0.2 0.0
cps/eV
keV

G


Spectrum 17
Wt% σ
C 81.7 0.2
O 12.5 0.2
Si 3.5 0.0
K 1.6 0.0
Cl 0.5 0.0
Na 0.2 0.0
Mg 0.1 0.0
S 0.1 0.0
cps/eV
keV

H



I

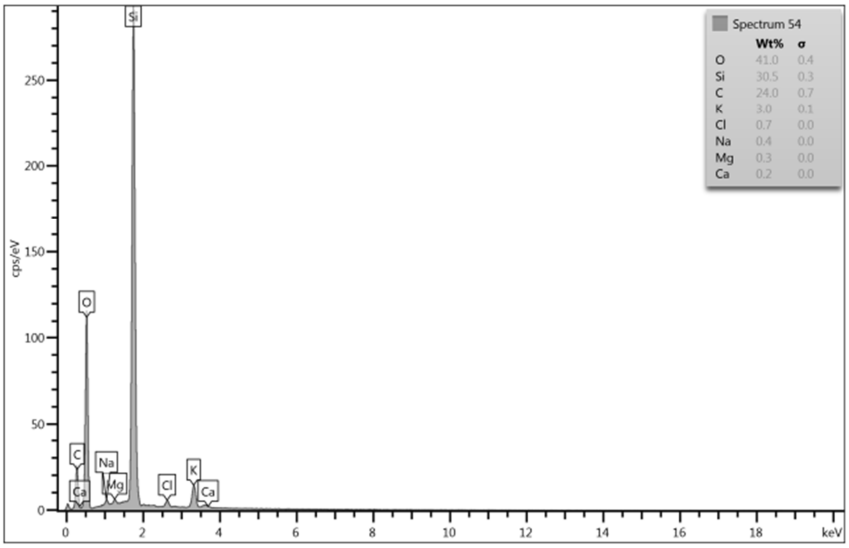


Figure 3.4. Particular spectra chemical composition in chosen particles of macadamia biochar in electron microscopy scanning image (Hitachi SU-70 FESEM). The spectra analysed (A-I, Spectra 5,6,14-18, 53 and 54) are depicted in Figure 3.3. The peaks represent the approximate quantity of a particular element in the spectrum position.

The images and spectra presented in Figures 3.3 and 3.4 are representative from 27 particles and 65 spectra sample positions) and illustrate the most common elements identified on the surface of the macadamia biochar using SEM-EDS. The surface of the macadamia biochar was composed mainly of carbon but Si, K and Cl was widely present, especially in the lighter particles seen adhering to the chars surface (Table 3.2).

Table 3.2. Chemical composition spectra at random surface locations of 27 biochar particles. (SEM-EDS images and spectra are presented in the Appendix 2.)

Particle number	Spectrum number	Main composition	Chemical elements present in minor amounts
1	1	Si, O, Al	K, C, Na, Fe
2	2	C	O, Si, Cl, K
3	3	Cl, K	Si, Al, O
3	4	K, S, O	Si, Cl, P, Na
4	5	C	Cl, K, Mg, Na, P, Si
4	6	C	Cl, K, Mg, Na, Si
5	7	C	Si, Mg, Mo, Na, K, Ca, P
5	8	C	Mg, Si, P, Cl, K, Ca, Na
6	9	C, K	P, Si, Cl, O
6	10	C	P, O, Na, K, Si, Cl
6	11	C	K, S, Cl, P
6	13	C	Si, O, P, S, Cl, K
7	14	C, O, Si	K, Cl, P, S
7	15	O, Si, K, Cl, C	Na
7	16	K, Cl, Si, C, O	Na
8	17	C	Si, Mg, O, Na, S, Cl, K
9	18	Si, O	C, K
10	19	Si	Al, O, K, C, Na
11	21	Cl, K, C	Al, Mg, Na, O, Si, S
12	22	Fe	Mn, C, O, Si, Al, K
13	23	C	Ca, O, Na, Mg, Si, P, S, Cl, K, Ca
14	24	C	O, Na, S, Cl, K
14	25	C	O, Na, Si, P, S, Cl, K
15	32	C	Cl, K, Ca, O, Na, Mo, Br, Si, P
15	33	C	Ca, O, Na, Mg, Si, P, Cl, K
15	34	C, K, Cl	Ca, O, Na, Mg, Si, P
15	35	C	Ca, O, Na, Mg, Si, P, Cl, K
16	36	Si	Co, O, K, Mg, Na, Cl
16	37	C, Si	O, Na, Mg, Cl, K
16	38	Si	C, O, Na, Mg, Al, K
16	39	Si	O, C, Na, K
17	40	C	Ca, O, Co, Mg, Si, P, K, Cl
17	41	C	O, Co, Mg, Si, Cl, K
17	42	C	O, Fe, Mg, Si, Cl, K, Fe
17	43	C	O, Fe,l Mg, Si, Mo, Cl, K, Fe, Co
17	44	C, Si, O	Al, K, Ca, Fe, Na, Mg, P, Cl
18	45	Si	C, O, Ca, Na, Mg, Cl, K, Ca
19	46	C, Si	O, Na, Mg, S, Cl, K
19	47	Si	C, O, Na, Mg, Cl, K
19	48	Si, O	Ca, Na, Mg, P, Cl, K

20	49	C	Ca, O, Si, P, S, Cl, K, Ca
20	50	Si	C, K, O, Na, Mg, Cl
20	51	Si	C, K, O, Na, Mg, Cl
20	52	C, Si	Ca, O, Na, Mg, Cl, K, Ca
21	53	C	Ca, O, Si, P, S, Cl, K, Ca
22	54	Si	O, C, Ca, Na, Mg, Cl, K, Ca
23	55	C	O, Na, S
24	56	C	O, Na, S
25	57	C	O, Na, Mg, Si, P, S, Cl, K
25	58	C	O, Si, Na, Mg, Br, P, S, Cl, K
26 (debris)	59	C, O, Ca, Si	K, Na, S, Mg, P, Cl, Ca
27	60	C	O, Mg, Si, Cl, K
27	61	C, Si	Ca, O, Na, Mg, P, Cl, K, Ca
27	62	K, Cl, C	O, Si
27	63	C	K, Cl, O, Mg, Si, P, S
27	64	C, K, Cl	Si
27	65	C	O, Mg, Si, Mo, Cl, K

The elemental composition of macadamia biochar was predominantly carbon, oxygen, potassium, chloride, sodium and silica. There were minimal amounts of calcium, magnesium, iron, lead, manganese and aluminum detected. Complete data from SEM-EDS analysis on both macadamia biochar and field-collected charcoal can be found in Appendix 3 and 4.

The C^{13}- NMR analyses revealed single peak at 124.7 ppm (Figure 3.5). Carbon in aromatic rings is characterised by peak between 125-150 ppm.

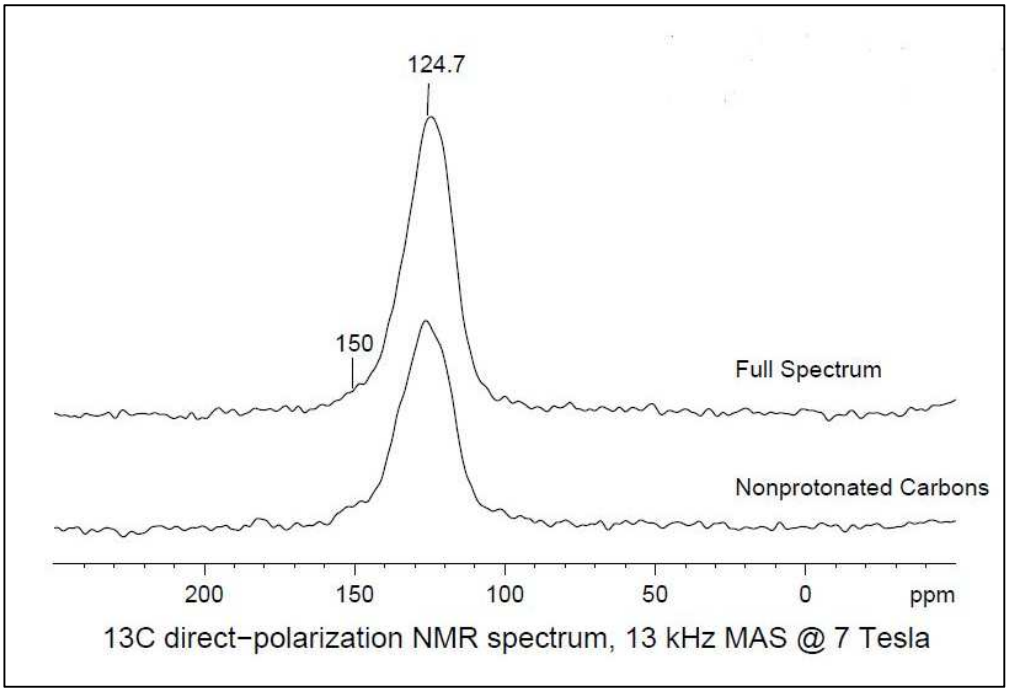


Figure 3.5. Macadamia biochar C13 NMR spectrum acquired using a Bruker Avance III-300 spectrometer operating at 75.4 MHz, and 300 MHz for 13C and 1H. Upper line represents spectrum obtained for all carbons, lower line represents spectrum of non-protonated C.

Screening for PAHs did not detect these compounds in the biochar at concentrations of above 0.1 mg kg^{-1} on a dry matter basis.

Nutrients in the potting mix and field soil were estimated as a concentration for each nutrient introduced through both biochar and fertiliser under each treatment combination (Table 3.3 and 3.4). As the calculations for the concentration of biochar in the field and in the pot experiment were done on the basis of different assumptions (i.e. incorporation depth, soil density) the exact amounts of nutrients introduced to growing mix under the same treatment in pot and field experiment do not equal but correspond to some extent.

Table 3.3. Concentration of nutrients introduced to potting mix in the pot experiment [mg kg^{-1}] under different biochar and fertiliser treatments (F50-F100 representing 50% and 100% of a commercial fertiliser dose, B2-B100 representing biochar treatments equivalent to 2-100 t ha^{-1}).

mg kg^{-1} potting mix										
		B2	**B5**	**B10**	**B20**	**B50**	**B80**	**B100**	**F50**	**F100**
Organic Carbon	C	68.250	168.350	336.700	673.400	1683.50	2693.60	3367.00	n.a.	n.a.
Aluminium	Al	0.001	0.002	0.003	0.007	0.02	0.03	0.03	n.a.	n.a.
Boron	B	0.021	0.051	0.102	0.204	0.51	0.82	1.02	0.61	1.21
Calcium	Ca	5.550	13.690	27.380	54.760	136.90	219.04	273.80	1364.80	1364.80
Copper	Cu	0.028	0.069	0.138	0.275	0.69	1.10	1.38	4.54	9.04
Iron	Fe	1.817	4.483	8.965	17.930	44.83	71.72	89.65	190.27	379.27
Magnesium	Mg	2.550	6.290	12.580	25.160	62.90	100.64	125.80	408.93	450.93
Manganese	Mn	0.163	0.402	0.803	1.607	4.02	6.42	8.03	9.14	18.28
Phosphorus	P	3.600	8.880	17.760	35.520	88.80	142.08	177.60	43.36	86.69
Potassium	K	32.850	81.030	162.060	324.120	810.30	1296.48	1620.60	189.08	377.08
Sodium	Na	4.800	11.840	23.680	47.360	118.40	189.44	236.80	1.17	1.17
Sulfur	S	1.800	4.440	8.880	17.760	44.40	71.04	88.80	436.67	655.33
Total Nitrogen	N	6.450	15.910	31.820	63.640	159.10	254.56	318.20	320.86	640.86
Zinc	Zn	0.042	0.104	0.209	0.417	1.04	1.67	2.09	3.59	7.18

Table 3.4. Amount of nutrients introduced to soil in the Florentine valley experiment [mg kg^{-1}] under different biochar and fertiliser treatments (F50-F100 representing 50% and 100% of a commercial fertiliser dose, B2-B20 representing biochar treatments equivalent to 2-20 t ha^{-1}).

mg kg^{-1} soil								
		B2	**B5**	**B10**	**B15**	**B20**	**F50**	**F100**
Organic Carbon	C	59.150	150.150	300.300	450.450	600.600	600.000	1200.000
Aluminium	Al	0.001	0.001	0.003	0.004	0.006	n.a.	n.a.
Boron	B	0.018	0.046	0.091	0.137	0.182	n.a.	n.a.
Calcium	Ca	4.810	12.210	24.420	36.630	48.840	n.a.	n.a.
Copper	Cu	0.024	0.061	0.123	0.184	0.246	n.a.	n.a.
Iron	Fe	1.575	3.998	7.996	11.994	15.992	50.000	100.000
Magnesium	Mg	2.210	5.610	11.220	16.830	22.440	n.a.	n.a.
Manganese	Mn	0.141	0.358	0.716	1.075	1.433	n.a.	n.a.
Phosphorus	P	3.120	7.920	15.840	23.760	31.680	613.330	1226.670
Potassium	K	28.470	72.270	144.540	216.810	289.080	n.a.	n.a.
Sodium	Na	4.160	10.560	21.120	31.680	42.240	n.a.	n.a.
Sulphur	S	1.560	3.960	7.920	11.880	15.840	73.330	146.670
Total Nitrogen	N	5.590	14.190	28.380	42.570	56.760	600.000	1200.000
Zinc	Zn	0.037	0.093	0.186	0.279	0.372	n.a.	n.a.

3.4. Discussion

The macadamia biochar was high in potassium, silica and sodium in comparison to other biochars. Chemical analyses of the char also revealed that other nutrients were scarce in comparison to non-wood biochars, but within the same range as other wood biochars (Amonette and Joseph, 2009). SEM-EDS showed an abundance of K, Si and Cl element on biochar surfaces which suggest the possibility of potassium chloride and silica compounds on macadamia biochar surface. The high specific surface area results suggest that macadamia biochar may potentially increase soil microbial activity and positively influence soil air and water condition (Downie et al., 2009; Thies and Rillig, 2009). The C^{13} Nuclear Magnetic Resonance analysis presented macadamia biochar as having a moderate number of aromatic rings and varied surface chemistry.

3.4.1. Nutritional characteristics

The pH of the macadamia biochar (8.7) was in the upper range of alkalinity reported in the literature (pH 6.2-9.9)(Chan et al., 2008; Chan and Xu, 2009; Ma and Matsunaka, 2013b). This suggests that biochar added to the soil would have a liming effect and is anticipated to decrease soil acidity. Carbon content was in the middle of the range reported for different biochars (17-90.5%)(Amonette and Joseph, 2009; Krull et al., 2009). Plant available phosphorus in the macadamia biochar was comparatively low (421 mg kg^{-1}) as other biochars may have up to 11,600 mg kg^{-1} (Chan and Xu, 2009). Accordingly it is expected that biochar contribution to P levels in the potting mix or field soil is likely to be small.

Similar to phosphorus, this char's nitrogen content was low when compared to the characterisation of other chars. This has been noticed before in biochars made from woody and other plant based feedstock (Chapter 2)(Chan et al., 2007; Lehmann et al., 2003; Rondon et al., 2006).

The macadamia char's K content was comparatively low with Colwell potassium levels reaching 9,388 mg kg^{-1}. In the literature the range of total K in biochar is quoted between 1,000 and 58,000 mg kg^{-1} which indicates this biochar is a low-potassium char (Atkinson et al., 2010; Quilty and Cattle, 2011; Widowati and Asnah, 2014). However, when the total K was compared to the range of K content in different chars, macadamia biochar appeared to have medium K content (Chan and Xu, 2009). In comparison to oak wood biochar, macadamia char had a K content approximately 75% lower (Amonette and Joseph, 2009;

Bourke et al., 2007). The above suggests that potassium levels in both the potting mix and field soil might change.

Similarly to K content, macadamia char's CEC is expected to bring changes in both experiments. Singh et al. (2010) demonstrated different exchangeable cations capacity of biochars depending on the feedstock material, production temperature and biochar activation (Singh et al., 2010). They analysed biochar made from *Eucalyptus saligna* wood, *E. saligna* leaves, paper sludge, poultry litter and cow manure. As macadamia biochar is a woody material, it might be expected to have exchangeable cation levels close to that of *E. saligna* wood, but exchangeable Mg, Na and K were higher than in *E. saligna* biochar used by Singh et al. (2010)(Ca of 27.7-138.4 mmol kg^{-1}, mg of 1.2-2.0 mmol kg^{-1}, Na of 4.9-13.0 mmol kg^{-1} and K of 3.1-7.3 mmol kg^{-1}).

Not much data are available on the secondary nutrients and microelements content of the various biochars. In comparison to oak wood biochar analysed by Bourke et al. (2007) macadamia biochar had lower content of Ca (Macadamia biochar (MB) 3,700 mg kg^{-1}, Oak wood biochar (OB) 350,000 mg kg^{-1}), Fe (MB 1,211 mg kg^{-1} OB 3,400 mg kg^{-1}), Mg (MB 1,700 mg kg^{-1}, OB 16,000 mg kg^{-1}) and medium content of P (MB 2,400 mg kg^{-1}, OB 5,400 mg kg^{-1})(Bourke et al., 2007). Some researchers (Bridle and Pritchard, 2004) reported a high heavy metal (Cu, Zn, Cr, Ni) content in sewage sludge based biochars, however the level of these nutrients in the macadamia biochar used here was relatively low, as would be expected from a wood based biochar without any animal based additives (Chan et al., 2008). This char is also considered safe as the level of PAHs did not exceed 10 mg kg^{-1} which is considered to be non-toxic (InternationalBiocharInitiative, 2013).

3.4.2. Surface chemistry and porosity

The specific surface area (SSA) of Macadamia biochar was calculated at 293.1 $m^2 g^{-1}$, which is much greater when compared to switch grass biochars made under fast pyrolysis conditions. Surface areas of fast pyrolysed switch grass typically range between 7.7 $m^2 g^{-1}$ and 7.9 $m^2 g^{-1}$. Other biochars have reported surface areas of 92 $m^2 g^{-1}$ (oak feedstock), 48 $m^2 g^{-1}$ (maize hull) and 38 $m^2 g^{-1}$ (maize stover)(Downie et al., 2009; Zhang et al., 2004). The typical sands (coarse and fine) have an SSA of about 0.01-0.1 $m^2 g^{-1}$ while clays SSA range from 5 to 750 $m^2 g^{-1}$ (Downie et al., 2009; Troeh and Thompson, 2005). Therefore if macadamia biochar is added to the sandy soil it is expected to increase the SSA of biochar-soil mixture and positively influence aeration, water holding capacity and microbial activity

in the soil. On the other hand when applying this biochar to loamy or clay soils the consequences are difficult to be estimated as the SSA of such soils are much higher and biochar application might not cause a significant difference.

The pore diameter reported in the gas absorption experiments on macadamia char was 1.5-2.5 µm and the pore diameter of a random biochar particle from SEM analysis equalled 1.86-9.96 µm (not replicated analysis). Rouquerol et al. (Rouquerol et al., 1999) divided pores into three groups in terms of pore diameter: 1) micropores (less than 0.002 µm diameter), 2) mesopores (between 0.002 and 0.05 µm) and macropores (more than 0.050 µm). Macropores play a vital role in soil aeration, hydrology and the movement of the roots in soil (Downie et al., 2009). That suggest that macadamia biochar has substantial potential to provide habitat for soil bacteria as its pores match bacteria diameter range (Table 3.5). Micopores on the other hand contribute more to the SSA of biochar (Amonette and Joseph, 2009). As SSA of macadamia biochar was described as high it might be concluded that this biochar will have a high proportion of micropores. This however could not have be determined by either the SEM analysis or porosity tests due to equipment limitations.

Table 3.5. Ranges in the diameter of various soil microorganisms (Thies and Rillig, 2009)

MICROORGANISM	DIAMETER RANGE (µm)
Bacteria	0.3-3
Fungi	2-80
Protozoa	7-30
Nematodes	3-30

Biochars surface chemistry is often very rich elementally as the heterogeneous composition of feedstock and production temperatures favour this (Amonette and Joseph, 2009). Scanning Electron Microscopy (SEM) performed on the macadamia biochar sample revealed highly porous particles composed mainly of carbon with adhered potassium chloride and silicone particles, and other inbuilt structures were also visible on the biochar surfaces. The potential chemical compounds include potassium chloride (KCl) and Silicates (SiO). Both potassium and silica in the char may result from their content in macadamia nuts feedstock (Marschner, 1995) but this explanation cannot be confirmed due to feedstock material not being available for analysis. It is possible that feedstock material was partially mixed with sand during collection process, which would explain the silica particles presence. In a Hawaiian report (Turn et al., 2002) investigating biomass resources for bioenergy use Macadamia nut shell ash was characterised as having high levels of Si and

K. These have been previously attributed to soil contamination during nut sweeping harvest operations (Turn et al., 2002). Due to the nature of SEM-EDS analysis it was not possible to quantitatively estimate nutrient content in the biochar. However repeatedly observed potassium chloride structures inbuilt on biochar surfaces confirm the chemical biochar tests results of which revealed relatively high K content in macadamia biochar.

SEM-EDS analysis performed on charcoal samples collected from the experimental plantation in Florentine valley revealed a highly carbonized wood material with Si, Al and Fe particles. Also calcium was present on most investigated surfaces. The analysis of charcoal carries some amount of uncertainty. This is first due to the assumption that collected charcoal is made of eucalypt wood residues in the previous on-site burn (2010). Unfortunately it is not possible to confirm either the age or the feedstock material. Despite cleaning of the particles it was not possible to assess if the Al, Si and Ca particles were inbuilt on charcoal surfaces or originated through adhesion of soil particles. The results of chemical analyses did not reveal either high Al or Fe levels, which suggests that these cations were more likely originating from the soil rather than charcoal particles. This could be attributed to charcoal adsorbing these elements from the soil. Any further extrapolations would however be beyond what can be concluded from the results.

3.4.3. Magnetic resonance

NMR results revealed a single, rather wide peak at 124.7 ppm. The frequency of the peak suggests that most carbons in the biochar were SP_2 carbon types i.e. structures in biochar were graphite-like carbon structures with various 1-2 bond types. The additional carbon analysis revealed 30% of the aromatic carbons being protonated. That means other atoms – not carbon – were attached to 30% of carbon in graphite-like structures (person. comm. Dr Thomas Rodemann, Central Science laboratory, UTAS, Tasmania, Australia). The peak frequency also suggests that the aromatic structures were not the majority of biochar carbon structures. The NMR results seem to be confirmed by the other biochar analysis results which revealed a variety of nutrients found on biochar surfaces (e.g. potassium, sodium, etc.) and the PAHs results showed that macadamia biochar PAH content is lower than 10 mg kg^{-1}. It also suggests that this char will be less stable in the soil compared to higher temperature biochars, due to the reactivity associated with the variety of elements bonded to its surface (Amonette and Joseph, 2009; Krull et al., 2009). Therefore macadamia

biochar may be more susceptible to chemical changes and microbial activity in comparison to high temperature biochars.

3.5. Conclusions

The calculations of the amount of nutrients introduced to the potting mix/soil with each fertiliser and biochar rate revealed that significant amounts of Na and K were added to the potting mix and soil under high biochar treatments. Due to different calculation assumptions nutrients amounts applied in the pot experiment do not correspond accurately to nutrient amounts applied in the field experiment under similar biochar treatments. Similarly, fertiliser used in the field trial differed from the one applied in the pot experiment (Chapter 4) so the nutrients introduced to growing mix were applied in different forms and quantities. The most likely effect of biochar application in both experiments is expected to be noticeable in the changes of the above nutrients level. The growth response of plants is usually determined by macronutrients – N, P and K (Atwell et al., 1999). As the only macronutrient applied with biochar in more than minor amounts was K, therefore the changes in plant response are not expected to be substantial.

Macadamia biochar was found with a chemical composition contemporary with other biochars. One of the unique characteristics of char used in this study may have been its potassium content, which is most likely the result of high K level in macadamia nut shells. High Specific Surface area of the char suggests that positive physical changes in some soils might be noticeable. Comparably low level of P and N and relatively low secondary and micronutrients in macadamia biochar implies that this product will not release significant amount of these nutrients to the soil, however due to some variation of char's surface chemistry differences in soil might be observed, especially in K and Na levels. The changes of soil characteristics in both experiments are expected to differ due to the differences in soil and potting mix initial properties. Biochar induced increases in nutrient availability in the growing mediums may possibly influence both plant nutrient uptake and chemical content of soil leachate.

4. GENERAL MATERIAL AND METHODS

4.1. Introduction

This chapter describes the methods used in the research reported in this thesis. The material presented is applicable to results presented and discussed in Chapters 5 to 7, with those chapters containing additional material specific to their content. The chapter describes methods used in a glasshouse pot trial conducted at the Horticultural Research Centre at the University of Tasmania Sandy Bay Campus and a field trial conducted in the Florentine Valley, Forestry Tasmania coupe O031Z in the South-West of Tasmania, Australia. Statistical analyses of both are also described. As the design of both trials applies to all the results presented in the following chapters, the details of the methodology will be presented within this chapter and mentioned briefly again, when presenting specific results.

4.2. Glasshouse Pot Trial

A pot trial was established on the 09/05/2011 in the glasshouse of the Horticultural Research Centre in Sandy Bay campus (Figure 4.1), University of Tasmania, and the final destructive harvest took place 269 days later on 02/02/2012. This study was a partial factorial combination of eight biochar and two fertiliser rates, arranged in a randomised complete block with three replicates of four sample plants. The trial did not have the control-biochar treatments apart from the basic control (0 fertiliser, 0 biochar). The design of the plot is shown in the Appendix 5. The treatments consisted of eight biochar levels (0, 2, 5, 10, 20, 50, 80 and 100 t ha^{-1}) combined with two fertiliser rates (50% and 100% of the optimum rate suggested by Forestry Tasmania nursery specialists). The seeds, potting mix and fertiliser for the trial were provided by Forestry Tasmania nursery in Perth, TAS. The seed line originated from a single open pollinated family harvested in 2008 from a native stand in the central Victorian highlands.

All the pots were kept on the benches to ensure proper aeration and drainage. The glasshouse was equipped with an evaporative cooler and an electric fan heater with perforated polythene-ducting. Temperatures were approximately 20-24° C (winter) and 20-26° C (summer). The trial was under automatic irrigation system and the seedlings received 1.5-3 mm per day in winter and 5 mm per day in summer to match evapotranspiration.

Weed control was carried out regularly until the seedlings reached approximately 30 cm height.

A seed raising mix was prepared by staff at the Forest Nursery (Forestry Tasmania) to emulate the industry standard. The base of this mix consisted of pine bark (72%), washed sand (18%) and peat moss (10%). The fertiliser used was a mix of Osmocote Exact® 3-4 mth (Everris), Osmocote Plus® 8-9 mth (Everris), dolomite lime, ferrous sulphate, Micromax® (Everris) and rock gypsum (Table 4.1). Fertiliser was applied to the pots at 100% and 50% (F50 and F100) of the prescribed rates used by forest nurseries in Tasmania.

Table 4.1. Fertilisers applied (g per 1L potting mix) in the pot experiment, using standard forestry practice, and analyses of product used. The 50% treatment used half of the fertiliser amounts shown in column 1 (except for dolomite lime, ferrous sulphate and rock gypsum). Calculations are based on the content information provided by the manufacturer.

	Fertiliser 100%, F100 (g) per 1 L potting mix	**Fertiliser 50%, F50 (g) per 1 L potting mix**
Osmocote and trace 3-4 mth	1	0.5
Osmocote 8-9 mth	2	1
Dolomite lime fine	2.5	2.5
Ferrous Sulphate	0.5	0.5
Micromax	0.5	0.25
Rock Gypsum	1	1

Biochar, used in the pot study was provided by the Rainbow Bee Eater Project Pty Ltd and produced from Macadamia nut shells at a HTT (highest temperature treatment) of 450-480° C. Detailed chemical characteristic of the product is presented in Chapter 3. Biochar was evenly incorporated within the potting mix at 0, 2, 5, 10, 20, 50, 80 and 100 t ha^{-1} (B0, B5, B10, B20, B50, B80 and B100) calculated on a volumetric basis.

Nine seeds per pot were sown on the 9/05/2011 in a 4 litre pots. The first seed germinated 14 days after planting (DAP) and following that day the number of germinated seeds was counted in each pot daily for 30 days. After that newly germinated seedlings were counted twice a week until the end of July 2011. At 84 DAP seedlings were thinned to leave the strongest three per pot, and after 9 days to the most robust remaining seedling per pot. At 93 DAP the height measurements started and all the seedlings were measured weekly until the end of pot trial.

A B

Figure 4.1. Eucalyptus nitens glasshouse pot experiment on (A) 29th Jul 2011 and (B) 05th Nov 2011. Horticultural Research Centre, University of Tasmania, Sandy Bay campus.

Seedlings were treated with a Previcur fungicide (Propamocarb 600g L^{-1}, Bayer®) immediately after sowing and two weeks following sowing. Plants were also treated with insecticides Azamax (40 ml per 10L) and Eco Oil (40 ml per 10L) on 11/08/2011, 30/09/2011 and 25/10/2011.

Four destructive sampling harvests (H1-H4) took place at 135, 177, 219 and 268 days after planting (DAP). At each harvest one pot from each replicate was destructively sampled for soil and plant analysis. The height measurements were performed on a regular basis during the whole experiment.

4.2.1. Data collection and processing

The germination study was performed as a part of the pot trial study (on the same seedlings) in May and June 2011 so the main procedures were similar as presented in the previous sections. Seeds were put in water for 24 hours prior to sowing then sown manually into each pot by putting each seed 10-15 mm below the soil surface. Immediately after sowing all the pots were watered with a mixture of water and fungicide (Previcur drench (15ml per 10L) at sowing and two weeks following sowing and insecticides: Azamax (40 ml per 10L) and Eco Oil (40 ml per 10L) on 11 Aug (94 DAP), 30 Sep (144 DAP) and 25 Oct (169 DAP) 2011. Emergence was defined as appearance of the cotyledons and was recorded in all the pots every 2 days for the first two months of the pot experiment. The first seedling emerged 14 days after sowing and the last one six months after sowing.

Plant height measurements started 93 DAP and were carried out weekly until the end of the pot trial. The height of each seedling was measured from the potting mix surface level to the stretched upwards end of first pair of juvenile leaves.

Pots were randomly allocated to a harvest date at the beginning of the experiment. At each harvest leaves were stripped from the stem and the leaf area and number from each seedling was measured and recorded. At each harvest all leaves from each seedling were collected and placed on a white sheet of paper. A photo of all the leaves and including a scale marker was taken and then digitally processed in ImageJ® (ver. 1.47) to calculate the total leaf area. Fresh above and below ground biomass was recorded and the leaves and soil samples were sent for an analysis (CSBP Plant and Soil Laboratory) after drying at 60°C for 72 hrs. Dry weight was recorded and the leaves were ground before sub-samples of 3-4 grams were packaged for analysis. Potting mix samples were air-dried at 40° C and the undissolved fertiliser residue manually removed from the samples before analysis.

Plant material at each harvest was quantitatively analysed by Soil and Plant Analysis Laboratory (CSBP) for: boron (B), calcium (Ca), copper (Cu), iron (Fe), magnesium (Mg), manganese (Mn), phosphorus (P), potassium (K), sodium (Na), sulphur (S), total nitrogen (N), zinc (Zn). Soil/PM was analyzed for: ammonium nitrogen (ammonium-N), nitrate nitrogen (nitrate-N), Colwell phosphorus, Colwell potassium, organic carbon, electrical conductivity, pH (1:5 water and $CaCl_2$) and exchangeable cations (aluminum, calcium, magnesium, potassium, sodium). The details of the analyses are presented in following sections.

4.2.2. Plant tissue analyses

Total Nitrogen (TN) was a measure of both inorganic and organic forms of nitrogen. Sample values were determined on a LECO® combustion analyser, where plant samples were loaded into sealed glass combustion tube (at 950˚ C) and flushed with oxygen. This process causes the rapid and complete combustion of the plant material. All gases generated were collected and measured on both an infrared detector and a thermal conductivity cell to measure total nitrogen (CSPB Soil and Plant Analyses Laboratory)(TruSpec).

After complete digestion of the plant material with a combination of nitric acid and hydrogen peroxide at high temperatures, digests were diluted with deionised water to dissolve all precipitates (McQaker et al., 1978). The resulting solutions were subsequently

analysed using Inductively coupled plasma atomic emission spectroscopy (ICP-AES) for determination of the elements B, Cu, Zn, Mn, Fe, Ca, Mg, Na, K, P and S (McQaker et al., 1978; TruSpec).

4.2.3. Soil analyses

Soil nitrate nitrogen and ammonium nitrogen was extracted (shaken) with a 1M potassium chloride solution for 1 hour at 25° C. After dilution the concentration of ammonium nitrogen was determined colorimetrically on a Lachat Flow Injection Analyzer at 420 nm using the indo-phenol blue reaction. Nitrate was reduced to nitrite through a copperized-cadmium column, and measured colorimetrically at 520 nm (Quickchem; Searle, 1984). The Walkley-Black method (Walkley and Black, 1934) was used to determine soil organic carbon content. Here concentrated sulphuric acid was added to soil wetted with dichromate solution. The heat of the acid-based reaction was used to induce oxidation of soil OM. Chromic ions produced were proportional to oxidized OC and were measured colorimetrically at 600 nm on a Multiscan^{TM} GO Microplate Spectrophotometer.

The pH and electrical conductivity of the soil extract was measured using a combination pH electrode. Soils were extracted in deionised water for 1 hour to achieve a soil: solution ratio of 1:5. After water pH and EC were measured, calcium chloride solution was added and after thorough mixing the calcium chloride pH was determined (Rayment and Higginson, 1992). Available P and K were measured using the Colwell method (Colwell, 1965). Soils were extracted with 0.5 M sodium bicarbonate solution, adjusted to pH 8.5 for 16 hours, resulting in a soil: solution ratio of 1:100. The acidified extract was treated with an ammonium molybdate/antimony trichloride reagent and the concentration of phosphorus was measured colorimetrically at 880 nm a flame atomic absorption spectrophotometer. The concentration of potassium was determined using a flame atomic absorption spectrophotometer at 766.5 nm. To determine soil exchangeable cations (Al, Ca, Mg, K and Na) soils were extracted with 0.1M NH_4Cl/0.1M $BaCl_2$ for 2 hours. The exchangeable cations were determined by ICP (Rayment and Higginson, 1992).

4.3. Field trial

A Field trial was established on the 18/10/2011 in the Florentine Valley, south-west Tasmania (42°38'S, 146°27'E; Forestry Tasmania coupe FO031Z). Planting was preceded by site preparation, including disking, installation of field Lysimeters and mixing biochar into

the soil (43 days before planting). The site was a second rotation site, previously used for *Eucalyptus* plantation. The on-site burn was carried out on the 7/04/2010 and was classified as High Intensity Burn (Marsden-Smedley and Whight, 2011). The soil type was defined using the Australian soil classification system, and classed as a Brown Dermosol. The site was sprayed with herbicides prior to plantation establishment, on the 18/05/2012 (Glymac, Macspred® and Associate Agtech®). Due to high weed occurrence site was spot-sprayed again with herbicides on the 29/02/2012 (Roundup® from a backpack sprayer, concentration 360 g L^{-1} glysphosate as an isopropylammonium salt).

Following fertilisation, transplanting was performed by Pottiputki with 6 month old seedlings acquired from a Forestry Tasmania seedling nursery in October 2011. In total 822 seedlings were used to form a trial consisting of 3 blocks. Manual weed control occurred 133 DAP and was followed by Round-Up® spraying (10ml per 1L water) from a backpack sprayer.

4.3.1. Field site location and experimental layout

The trial was located on the northern part of Forestry Tasmania coupe FO031Z in Florentine Valley. Figure 4.2 presents the exact location of the trial. Block 1 was located on the west side of the road while blocks 2 and 3 were located on the east side of the road. The reason for such location was the condition of the field, amount of waste wood left over after harvest and location of windrows. The stacked residue wood from previous harvest, located on the west side of the road enabled the placement of only one block at this location. The reason for locating the two remaining blocks further from the road was the terrain. The first part of the plantation, just next to the road (east side of the road) was steeper so the blocks were located further to the east to avoid the effect of water flowing downhill.

Figure 4.2. Aerial picture of the field experiment area. Florentine valley, Forestry Tasmania coupe 31Z. The red rectangles show the approximate location of the blocks.

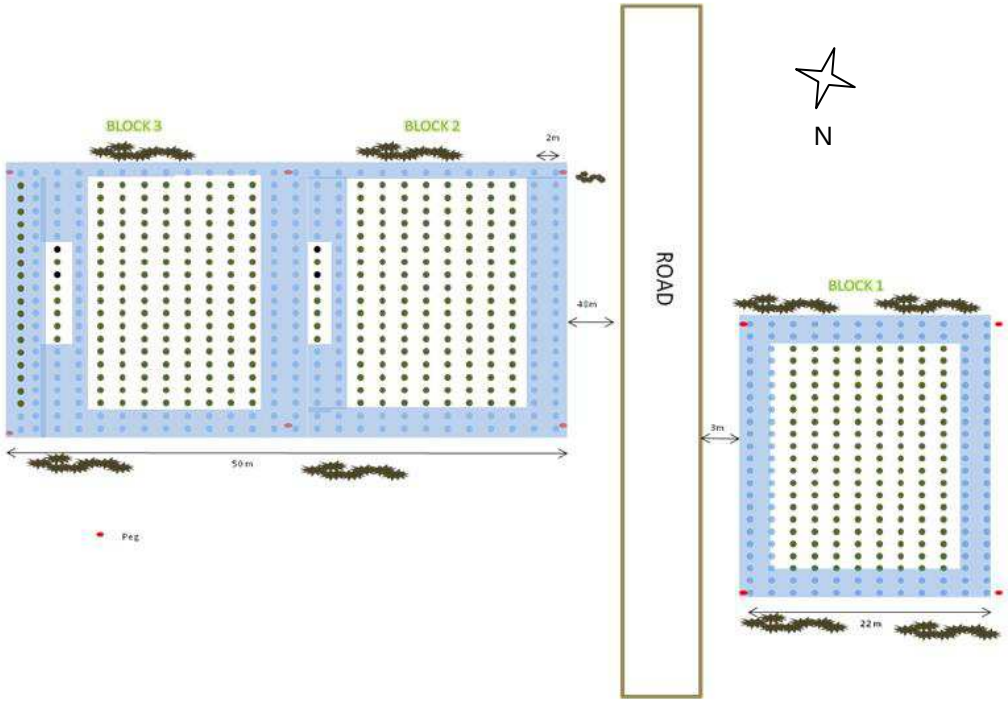


Figure 4.3. Design of the field experiment in Florentine Valley, Forestry Tasmania coupe 31Z. Green dots represent seedlings, blue shaded area shows the buffer zones around the blocks, dark green shapes represent the location of the windrows.

Row spacing in the trial was approximately 3 m while spacing of the seedlings within a row was 2 m (Figure 4.3 and 4.4). Buffer zones were organized around each block and consisted of two rows or two seedlings. On the southern site of blocks 2 and 3 the buffer zone covered only one row of seedlings, this being dictated by the location of windrows. Each

block consisted of 18 rows with treatments allocated randomly to individual rows. Due to not enough number of rows in block 2 and 3 one of the treatments had to be located perpendicularly to the location of other treatments (Appendix 5). The detailed design of an example block and treatments applied is presented in Figure 4.4, the design of the remaining two blocks is presented in Appendix 6.

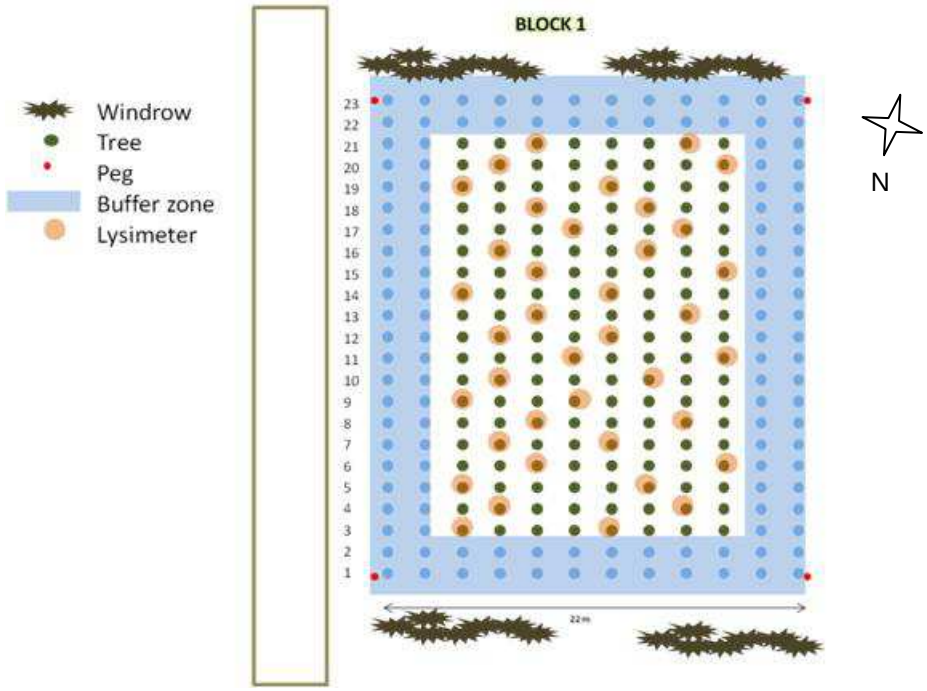


Figure 4.4. Design of block 1 in the field experimental trial in Florentine valley, Forestry Tasmania coupe 31Z.

4.3.2. Soil amendments

Biochar used for the field trial was the same to that used for the pot trial. Full specification of biochar is included in the Appendix 1 while the characteristics of the product used is discussed in Chapter 3. Biochar was applied to eight seedlings within each row at 0, 2, 5, 10, 15 and 20 t ha^{-1} calculated on the basis of soil volume, assuming an incorporation depth of 0.2 m. Biochar was mixed by driving a metal frame (0.4 m x 0.5 m) into the soil, removing soil from within the frames to depth, before placement in a bucket where it was mixed with biochar; after thorough mixing the soil biochar solution was returned to the original location. Where no biochar was applied, similar volume of soil was churned up. Biochar application occurred directly after lysimeters installation, in September 2011.

Phosphorus was applied after biochar incorporation as di-ammonium phosphate (DiAP) (ImpactFertilisers®) at 200 g per seedling (Impact Fertilisers®) in early October 2011. The

dose was calculated on the basis of soil chemical analysis and number of previous rotations in the experiment coupe. Fertiliser was manually mixed into the soil in the radius of 30 cm from the seedling to approximately 20 cm depth. Common forestry practice normally requires fertiliser application by Pottiputki (PUKI) forestry tool (http://en.wikipedia.org/wiki/Pottiputki_(tool)), after planting. However, in this study fertilisation was done manually, before planting to ensure the fertiliser was distributed evenly through the region biochar was placed. To monitor the effects of fertilising method on the results one row in each block was fertilised with PUKI equipment. Fertiliser rates in the trial were 0, 50% and 100% of the commercial dose (200 mg per seedling). The full list of experimental units is presented in table 4.2.

Table 4.2. The list of treatments applied in the Florentine Valley field experiment. 100% fertiliser rate equalled 200 g Di-ammonium phosphate per seedling.

Treatment number	Treatment code	Fertiliser rate (%)	Biochar dose (t ha^{-1})
1	F0B0	0	0
2	F0B2	0	2
3	F0B5	0	5
4	F0B10	0	10
5	F0B15	0	15
6	F0B20	0	20
7	F50B0	50	0
8	F50B2	50	2
9	F50B5	50	5
10	F50B10	50	10
11	F50B15	50	15
12	F50B20	50	20
13	F100B0	100	0
14	F100B2	100	2
15	F100B5	100	5
16	F100B10	100	10
17	F100B15	100	15
18	F100B20	100	20

4.3.3. *Lysimeter installation*

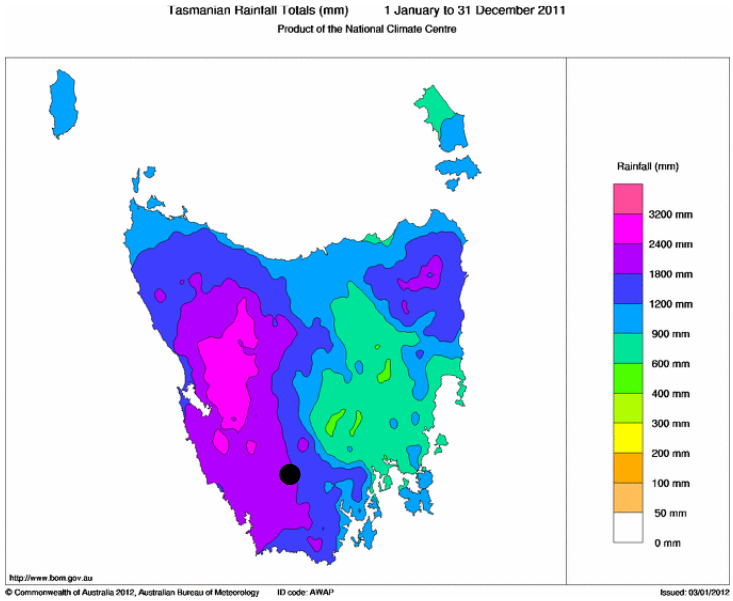
Two zero-tension lysimeters were installed at random position within each treatment (detailed design of the equipment is presented in Appendix 7). Lysimeters were designed and built for the needs of the project following expert advice (Rainbow Bee Eater Pty Ltd)(Figure 4.5). Installation of the equipment in the field was performed with excavator prior to biochar and fertiliser application. In total 114 Lysimeters were installed in September 2011.

Figure 4.5. Custom-built Lysimeter 'LIZZIE' used in the Florentine Valley field trial.

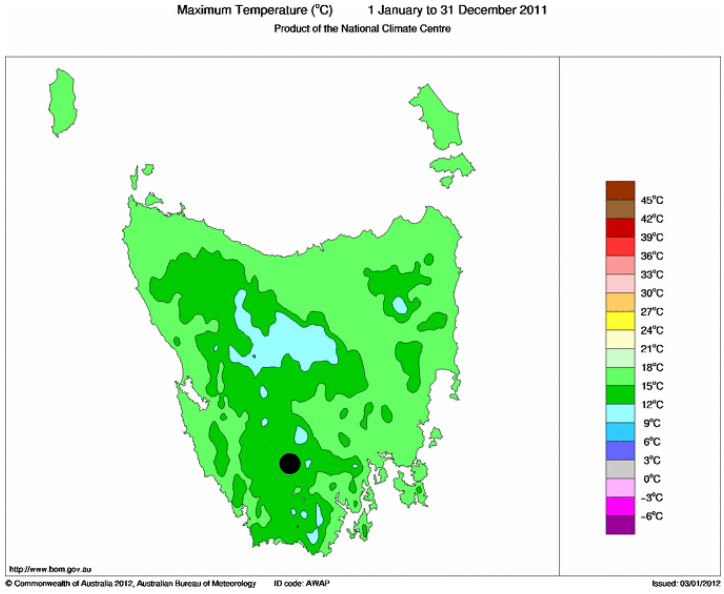
4.3.4. *Seasonal conditions*

The Florentine Valley has an annual average rainfall of 1,178 mm (years 1992-2011) and is located within the second highest rainfall region of Tasmania, the wettest month being August and driest January. Minimum/maximum mean temperatures in Florentine region average 2.4/11.1° C in winter and 8.3/21.3° C in summer. The Maydena weather station located approximately 20 km south from the field trial is the nearest weather station, and was used as a source of weather data for the trial. The use of automatic weather station installed in the field was not available for this project. Figure 4.6 presents the maps of total annual rainfall, maximum and minimum temperatures in Tasmania.

A


Tasmanian Rainfall Totals (mm) 1 January to 31 December 2011
Product of the National Climate Centre
Rainfall (mm)
3200 mm
2400 mm
1800 mm
1200 mm
900 mm
600 mm
400 mm
300 mm
200 mm
100 mm
50 mm
0 mm
http://www.bom.gov.au
© Commonwealth of Australia 2012, Australian Bureau of Meteorology ID code: AWAP
Issued: 03/01/2012

B


Maximum Temperature (°C) 1 January to 31 December 2011
Product of the National Climate Centre
45°C
42°C
39°C
36°C
33°C
30°C
27°C
24°C
21°C
18°C
15°C
12°C
9°C
6°C
3°C
0°C
-3°C
-6°C
http://www.bom.gov.au
© Commonwealth of Australia 2012, Australian Bureau of Meteorology ID code: AWAP
Issued: 03/01/2012

C

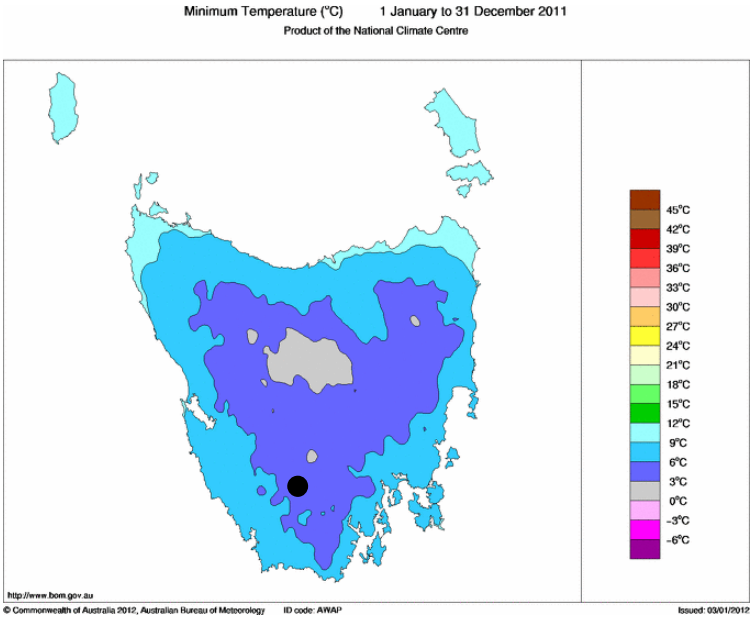


Figure 4.6. (A) The total annual rainfall in Tasmania (mm), (B) maximum temperature in Tasmania (°C), and (C) minimum temperature in Tasmania (°C) estimated for the period 01/01/2011 – 31/12/2011. Data acquired from the website of Australian Bureau of Meteorology (Bureau of Meteorology, 2012-2013). The black dot indicates the location of the field experimental plantation.

4.3.5. Sampling and data collection

Soil and plant material samples were collected from the field at 95, 216, 338 and 463 DAP, the first sampling date being three months after planting and four months after incorporating biochar and fertiliser into the soil.

Soil sampling

Each sample was prepared from the soil collected from three random sites within the row (one treatment). Soil was collected within the 0.2 m radius around the seedling, from 0.1-0.2 m depth. Samples were weighed; air dried in an oven at 40 degrees Celsius and sent for analysis (CSBP Soil and Plant Analysis Laboratory, Western Australia). In between sample preparation and analysis, samples were kept in double sealed plastic bags and stored in a dry and dark store at room temperature.

Plant Tissue

The youngest fully expanded leaves (YFEL) were collected from randomly chosen seedlings within each row (3-5 seedlings) and bulked for analysis to avoid analysing young leaves

which have different nutritional composition (Close and Beadle, 2003). Samples were weighed and then air-dried at 60 degrees Celsius and stored similar to the soil samples.

Seedling height

Seedling height was measured on the 39, 87, 129, 164, 200, 236, 290, 332, 374, 409 and 647 DAP. The height (cm) was measured from the ground to the top of the seedling/tree. Three randomly chosen seedlings per row were measured at each sampling event. At 647 DAP the trunk diameters of 3 trees per treatment were measured at breast height (120 cm).

Figure 4.7. Author of the thesis with Eucalyptus nitens *seedlings in the field experiment in Florentine valley. January 2012 (left-hand side) and January 2013 (right-hand side).*

Soil leachate sampling

Water was pumped up from lysimeters using a drill operated bilge pump powered by a small generator (Figure 4.8). Water from both lysimeters was mixed together and a sample of 40 ml was prepared. Samples (Figure 4.9) were collected every 5-7 weeks and stored at -18°C until the chemical analyses were performed (June-July 2012). Samples were labelled chronologically as A (39 DAP), B (87 DAP), C (129 DAP), D (164 DAP), E (200 DAP), G (236 DAP), H (290 DAP), I (332 DAP), K (374 DAP) and M (409 DAP). The water sampling schedule is presented in Figure 4.10.

Figure 4.8. Equipment used for collecting water samples from the Lysimeters installed in the field experiment.

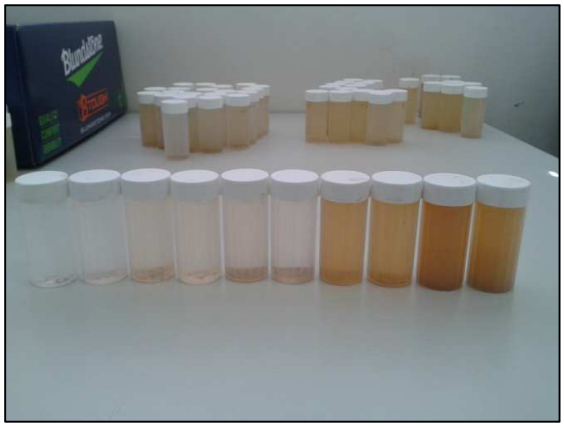


Figure 4.9. Water samples collected from the field experiment in the Florentine Valley

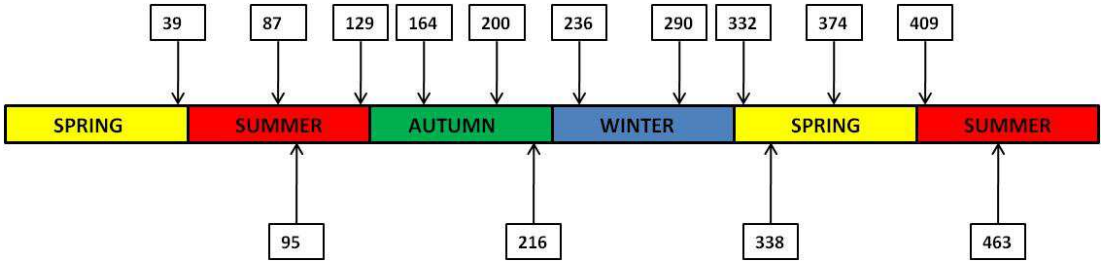


Figure 4.10. Water (above the season bar), plant material and soil (below the season bar) sampling times (presented as days after planting) in the field experiment in Florentine Valley during the duration of the field experiment (Spring 2011- Summer 2013).

Immediately before the analyses were performed, samples were removed from the freezer and thawed. Raw samples were filtered once through Whatman no 1 paper filter. Each sample was filtered with a separate paper filter into a 50 ml clear tube and then analysed for the concentration of ammonium-N, nitrate-N, potassium, phosphorus and pH, as described below.

Acidity, Ammonium and Nitrate

Acidity was measured using a pH electrode attached to a Forston LabNavigator®; the electrode was calibrated against standard solutions of pH 4 and pH 7. After analysing each sample the electrode was rinsed with distilled water. The measurements for ammonium were performed with the ammonium ion selective electrode (Model: NavNH4, Forston Laboratories®) attached to a Forston LabNavigator®. The sensor was calibrated with a 1 mg L^{-1} (low) and 100 mg L^{-1} (high) ammonium standard solution before measuring the samples.

After each sample the electrode was rinsed with distilled water. The nitrate-N measurements were made using a nitrate ion sensor (Model: NavPH, Forston Laboratories®) calibrated with a 1 mg L^{-1} (low) and 100 mg L^{-1} (high) nitrate standard solution.

Potassium

The potassium measurements were performed by Flame Emission Photometric method using a Jenway® Flame Photometer FP7 (direct reading type). Reagents solutions were made prior to measuring the samples: Stock potassium solution of 1 mg K per 1 ml (1.907 g KCL, dried at 110^{o} C for 1h and cooled in desiccator and transferred to 1L volumetric flask), intermediate potassium solution of 0.1 mg K per ml (10 ml Stock potassium solution diluted to 100 ml) and standard potassium solution of 0.01 mg K per ml (10 ml intermediate potassium solution diluted to 100 ml). The flame photometer was calibrated using distilled water and the potassium solution and was every 5-7 samples.

Phosphorus

Phosphorus measurements were performed by the Ascorbic Acid Spectrophotometric method using as spectrophotometer model AXIOSTAR PLUS®. Reagent solutions were prepared immediately prior to P measurements. A set of P standards was also prepared resulting in solutions concentration of 0.01, 0.1, 1 and 10 ppm/P. Samples were analysed in the spectrophotometer at 882 nm. The actual values were read from the graph prepared on the basis of standard solutions readings.

4.3.6. Plant material and soil analysis

Plant and soil samples were analysed in the same manner as that described for the pot trial in sections 4.2.3 and 4.2.4.

4.4. Statistical analysis

The raw data from chemical tests of plant material, soil and percolating leachate, and the agronomic data (height, total biomass, leaf number etc.) water was analysed using Analysis of Variance (ANOVA) and Fisher's Least Significant Difference (LSD) method as a post hoc test. All the Statistical analyses were completed using IBM SPSS® Statistics 19 program and Microsoft Excel® 2007.

A rate of decay analysis (performed on soil and plant tissue data) was calculated on the basis of estimating the parameters 'a' (initial quantity) and 'c' (decay rate) using a fitted exponential decay model. Analysis of variance (ANOVA) was performed on the resulting decay rate parameter (c). In order to check the validity of the exponential rate of decay model, data was transformed into linear form (using a natural logarithm conversion). The exponential and linear regression tests were performed, as all other tests, using IBM SPSS® Statistics 19 program and Microsoft Excel® 2007. The correlation between nutrients levels in analysed mediums was performed using Spearman's correlation method ($p \leq 0.05$).

The pot trial design did not include control biochar treatments (where biochar was applied without fertiliser) other than a basic control (without biochar or fertiliser addition). Therefore the results are to be compared between the treatments not to the control samples results.

The approach of showing the means (across fertiliser or time) was chosen to present the trends of changes following biochar application.

5. EFFECTS OF BIOCHAR AND FERTILISER AMENDMENT ON THE SOIL

5.1. Introduction

Biochar has been suggested as a means to sequester atmospheric carbon and as a potential environmental tool to improve soil quality and enhance plant productivity (Lehmann and Joseph, 2009b). Despite numerous studies where biochar has been effective in influencing the desirable characteristics of horticultural soils, an understanding of the mechanisms and circumstances under which this occurs is still contested, and a number biochar-induced processes are suggested as being responsible (Biederman and Harpole, 2013; Lehmann and Joseph, 2009b). In part the current debate is due to the complexity of feedstock characteristics, pyrolysis process conditions and soil properties that essentially ensure that each application is a unique event. Due to great variation in biochar types as well as differences in the soils characteristics reported, changes after chars application vary broadly and suggested mechanisms influence fertility and soil chemistry in a different manner.

One key soil characteristic influenced by biochar application is pH, where char addition to soil is known to increase alkalinity (Chan et al., 2007; DeLuca et al., 2006; Lehmann and Joseph, 2009a), this effect being attributed to chars having a higher pH than the soil to which they are admixed. Such effect may be observed in the experiments conducted within this research, when admixing macadamia biochar of pH 8.7 ($CaCl_2$) to soil or potting mix (average 4.5-4.9 [$CaCl_2$]). In contrast, pH may decrease, and some researchers postulate that this is facilitated by nitrification, through which H^+ ions are released into the soil solution (Nelson et al., 2011; Unger and Killorn, 2011; Van Zwieten et al., 2010b). In support of this, accelerated nitrification has been observed in several studies (Clough and Condron, 2010; DeLuca et al., 2009; DeLuca et al., 2006; Nelson et al., 2011). DeLuca et al. (2006) suggested that compounds that inhibit nitrification are sorbed to the surface, allowing the reaction to proceed to a greater extent. This may occur through the adsorption of nitrification inhibiting phenols and increased stabilization of inorganic N as proposed by other researchers (Clough and Condron, 2010; DeLuca et al., 2009). Chars can also provide an enriched microbial environment, and Nelson et al. (2011) connected this with increased nitrifying bacteria activity (Nelson et al., 2011). Macadamia biochar was characterized as

having high specific surface area (SSA) which indicates that microbial activity can potentially be stimulated (Chapter 3). Other proposed mechanisms altering N transformations include NH_4^+ adsorption to biochar particle surfaces and subsequent lower ammonium-N levels in the soil solution (Lehmann et al., 2003; Lehmann et al., 2006; Spokas et al., 2011; Steiner et al., 2008; Taghizadeh-Toosi et al., 2011). This mechanism might be observed in experiments presented in this research as macadamia biochar had a moderate cation exchange capacity (CEC)(Chapter 3).

Biochar application can increase soil phosphorus, and it has been proposed that this might be due to stimulation of soil microbial populations through provision of an augmented habitat for phosphate solubilising bacteria (Warnock et al., 2007). The elevated levels of available P have also been attributed to biochar adsorbing free Al^{3+} and Fe^{3+} ions to its negatively charged surface, therefore reducing the PO_4^{3-} immobilization that would otherwise occur through the oxides often formed with these cations (Cheng et al., 2006). For soils that don't have high levels of aluminium or iron, a similar effect may occur as a result of phosphate ions release from char surfaces, as a part of anion exchange capacity of biochars (DeLuca et al., 2009). Phosphorus content of macadamia biochar was identified as low in comparison to other biochars (Chapter 3) which suggests that potential P soil changes might be influenced by a direct phosphate release only to a limited extent.

Changes in available K in soil as a result of biochar application have been observed by Lehmann et al. (2003), Chan et al. (2007) and Major et al. (2010) and ascribed to the release of K ions from the char. Similar increases in exchangeable Na were reported by (Chan et al., 2007) but the reasons for that have not been identified. Macadamia char was described as having moderate CEC and high Na^+ and K^+ content in comparison to other chars (Chapter 3). Additionally both Na^+ and K^+ are among the cations which have low strength of attraction to surfaces when compared to other base cations (Ca, Mg and Al). It is therefore postulated that application of macadamia biochar might increase soil Na and K concentrations.

In contrast to cations release, the adsorption of various ions to char surfaces have been noticed in many experiments (Guo et al., 2014; Lehmann et al., 2003; Nguyen et al., 2009; Tseng and Tseng, 2006; Yamato et al., 2006). Biochars effect on Ca and Mg was noted by Lehmann et al. (2003) in Anthrosol soils, where Ca level increased in response to biochar addition, the authors attributed this effect to Ca adsorption to an exchange complex created by the charcoal additions. Major et al. (2010) reported increases in soil Mg and Ca

and uptake of these nutrients following biochar application, this effect being most likely connected with decreased leaching of Mg and Ca from the soil. Aluminium cation adsorption to biochar surfaces has been reported by Nguyen et al. (2009), where biochar surfaces adsorbed soil Al and Si in the first decade after biochar application, as well as by Yamato et al. (2006) after bark charcoal application to the soil. High surface area and moderate CEC of macadamia biochar imply that the adsorption of different cations might be observed following char application to the soil.

Changes in the mineralization of native soil organic matter (OM) due to the addition of new substrates have been observed in many types of laboratory and field studies and reviewed by Kuzyakov et al. (2000). Most commonly, it is 'positive priming' that is observed, i.e. the accelerated mineralization of a more refractory soil OM components stimulated by the addition of a labile C source (Luo et al., 2011; Wardle et al., 1998; Zimmerman et al., 2011). Luo et al. (2011) attributed this effect to biochar providing a source of labile carbon for the bacterial community and resulting in a positive priming of SOM of the PMs. Zimmerman et al. (2011) reported a similar effect in the soils amended with biochars produced at low temperatures (up to 400° C) and negative priming as a result of high-temperature biochar application. Other negative (Kuzyakov and Domanski, 2000; Liang et al., 2008) changes or no effect of biochar application on soil C (Major, 2010; Major et al., 2010; Novak et al., 2009; Spokas et al., 2011) have been presented for different biochars therefore the direction of macadamia biochar effect of soil C is difficult to be predicted. More changes are expected to be observed in the pot rather than the field trial as the amounts of carbon added with biochar are higher and because OM content was much higher than in the field dermosol.

The characteristics of the macadamia biochar discussed in Chapter 3 suggests that there will be soil and potting mix (PM) changes as a consequence of char application. Significant amounts of Na, K and Ca were applied to the growing media under high biochar treatments; therefore, the most significant effect of biochar application in both experiments is expected to be noticeable in the changes in levels of these nutrients. Potting mix and soil (Chapter 4) attributes imply that the results in both experiments might differ in terms of post-biochar application trends. It is hypothesized that macadamia biochar added to Eucalypt plantation soil and forest nurseries potting mix will increase the availability of essential soil elements, by either introducing these nutrients to the soil (release from

biochar surfaces) or modifying soil mechanisms to increase nutrient transformation to plant-available forms.

5.2. Method

Two experiments were established to monitor the changes of potting mix (PM), field soil and plant material following macadamia biochar application (0-100 t ha^{-1}). The details of experiments design were presented in Chapter 4. In the field experiment soil samples were collected on 4 occasions: at 95, 216, 338 and 463 days after planting (DAP) from the depth of 10 cm. In the pot trial PM samples were collected at 4 destructive harvests which took place at 135, 177, 219 and 269 DAP, from the whole volume of PM within each pot. Samples were analysed for nitrate-N, ammonium-N, carbon, exchangeable cations, electrical conductivity, Colwell potassium and phosphorus. Acidity of the soil was measured both in water (pH_w) and in a 0.01M $CaCl_2$ solution (pH_{CaCl}). Adding $CaCl_2$ to soil results in Ca^{2+} ions displacing H^+ ions ionically bonded to negative surface charges of the soil particles; this forces hydrogen ions into solution increasing their concentration closer to that found in the immediate vicinity of the roots (Rayment and Higginson, 1992). As the $CaCl_2$ method is favoured as more precise only the results from this method will be presented and analysed.

The results of growing medium tests were analysed using SPSS Analysis of Variance (*Sig. 0.05*) and the Rate of Decay analysis (*Sig. 0.05*). The details of the analyses and sample preparations are described in Chapter 4.

5.3. Results

Biochar had an effect on all nutrients and physical soil features assessed in the potting mix (PM) in the controlled environment (pot experiment). Under field conditions the influence of biochar on soil nutrient levels was limited to potassium and sodium.

Higher rates of biochar (50-100 t ha^{-1}) increased PM nitrate-N, P, K and Na and decreased the concentration of ammonium-N, organic carbon, exchangeable Al, Ca and Mg. In the field experiment biochar increased the concentration of potassium and exchangeable sodium in the soil. There was no decrease of any nutrient concentration in the soil found under field conditions. Biochar was suspected to influence the rate of nutrients removal from the soil and an exponential decay analysis (Chapter 4) was used to explore this

hypothesis. Using this approach, only the rate of exchangeable sodium removal from the potting mix (pot experiment) was influenced by biochar. Tables 5.1 and 5.2 summarize the results in both experiments.

Table 5.1. Potting mix characteristics P values in response to biochar (B), fertiliser (F) application and time (T) in the pot experiment. Significant values at P≤0.05, n.s. = not significant (OC-organic carbon, ex. Al – exchangeable aluminum, ex. Ca – exchangeable calcium, ex. Mg – exchangeable magnesium, ex. K – exchangeable potassium, ex. Na – exchangeable sodium, P- phosphorus).

TREATMENT	B	F	T	B*F	B*F*T	B*T	F*T
Ammonium-N	*≤0.001*	*≤0.001*	*≤0.001*	*n.s*	*n.s*	*0.004*	*≤0.001*
OC	*≤0.001*	*n.s.*	*≤0.001*	*n.s.*	*n.s.*	*≤0.001*	*n.s.*
Elec. Cond.	*≤0.001*	*≤0.001*	*≤0.001*	*n.s.*	*n.s.*	*n.s.*	*0.048*
ex. Al	*≤0.001*	*≤0.001*	*≤0.001*	*≤0.001*	*n.s.*	*0.006*	*≤0.001*
ex. Ca	*≤0.001*	*≤0.001*	*≤0.001*	*≤0.001*	*n.s.*	*0.02*	*n.s.*
ex. Mg	*≤0.001*	*≤0.001*	*≤0.001*	*0.005*	*n.s.*	*0.032*	*0.041*
ex. K	*≤0.001*	*n.s.*	*≤0.001*	*n.s.*	*n.s.*	*0.017*	*0.039*
ex. Na	*≤0.001*	*n.s.*	*≤0.001*	*n.s.*	*n.s.*	*≤0.001*	*n.s.*
Nitrate-N	*≤0.001*	*≤0.001*	*≤0.001*	*n.s.*	*n.s.*	*≤0.001*	*≤0.001*
pH (CaCl)	*≤0.001*	*≤0.001*	*≤0.001*	*n.s.*	*n.s.*	*0.039*[*]	*n.s.*
Colwell P	*≤0.001*	*≤0.001*	*≤0.001*	*0.014*	*n.s.*	*n.s.*	*0.002*
Colwell K	*≤0.001*	*0.009*	*≤0.001*	*n.s.*	*n.s.*	*≤0.001*	*≤0.001*

Table 5.2. Soil characteristics P values (Florentine valley field experiment) in response to biochar (B), fertiliser (F) application and time (T) in the pot experiment. Significant values at P≤0.05 , n.s.= not significant, (OC-organic carbon, ex. Al – exchangeable aluminum, ex. Ca – exchangeable calcium, ex. Mg – exchangeable magnesium, ex. K – exchangeable potassium, ex. Na – exchangeable sodium, P-phosphorus).

TREATMENT	B	F	T	B*F	B*F*T	B*T	F*T
Ammonium-N	n.s.	*≤0.001*	*≤0.001*	n.s.	n.s.	n.s.	*≤0.001*
OC	n.s.	n.s.	*0.008*	n.s.	n.s.	n.s.	n.s.
Elec. Cond.	n.s.	*≤0.001*	*≤0.001*	n.s.	n.s.	n.s.	*≤0.001*
ex. Al	n.s.	*≤0.001*	*≤0.001*	n.s.	n.s.	n.s.	*≤0.001*
ex. Ca	n.s.	n.s.	*≤0.001*	n.s.	n.s.	n.s.	n.s.
ex. Mg	n.s.	*0.019*	*≤0.001*	n.s.	n.s.	n.s.	n.s.
ex. K	*≤0.001*	*0.003*	*≤0.001*	n.s.	n.s.	n.s.	*≤0.001*
ex. Na	*≤0.001*	n.s.	*≤0.001*	n.s.	n.s.	n.s.	n.s.
Nitrate-N	n.s.	*≤0.001*	*≤0.001*	n.s.	n.s.	n.s.	*≤0.001*
pH (CaCl)	n.s.	*≤0.001*	*≤0.001*	n.s.	n.s.	n.s.	*0.012*
Colwell P	n.s.	*≤0.001*	n.s.	n.s.	n.s.	n.s.	n.s.
Colwell K	*≤0.001*	*≤0.001*	*≤0.001*	n.s.	n.s.	n.s.	n.s.

5.3.1. *Acidity*

Acidity of the PM decreased in response to high biochar rates (B50-B100)(*p≤0.000*), but this effect was transient, with pH decreasing in time until 219 DAP (Figure 5.1.A and B).

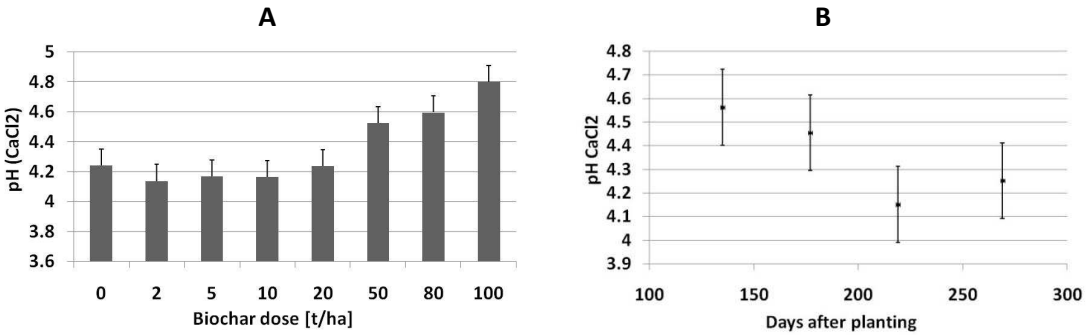


Figure 5.1. pH dynamics of the potting mix in Eucalyptus nitens pot experiment in response to: (A) biochar application (0,2,5,10,20,50,80 and 100 t ha^{-1}) (mean across sampling times and fertiliser treatments), (B) time (measured at 135, 177, 219 and 269 days after planting) (mean across biochar and fertiliser treatments). Error bars indicate the LSD (A-0.11, B-0.16)(p≤0.05).

5.3.2. *Nitrogen, potassium, phosphorus*

Nitrogen

Available soil nitrate-N levels were highest at biochar rates of B50-B100 with no differences (LSD; *p≥0.05*) observed below these rates (Figure 5.2.A). Biochar application diminished soil ammonium-N levels, the magnitude of this response increasing with rate, dropping from 17.5 mg kg^{-1} with no char applied to 13.5 mg kg^{-1} at 100 kg char ha^{-1} (Figure 5.2.B). Nitrate-N concentration in the soil solution declined rapidly in comparison to that of ammonium-N, which although present in lower concentrations, declined at a slower pace (*p≤0.001*)(Figure 5.2.C and D).

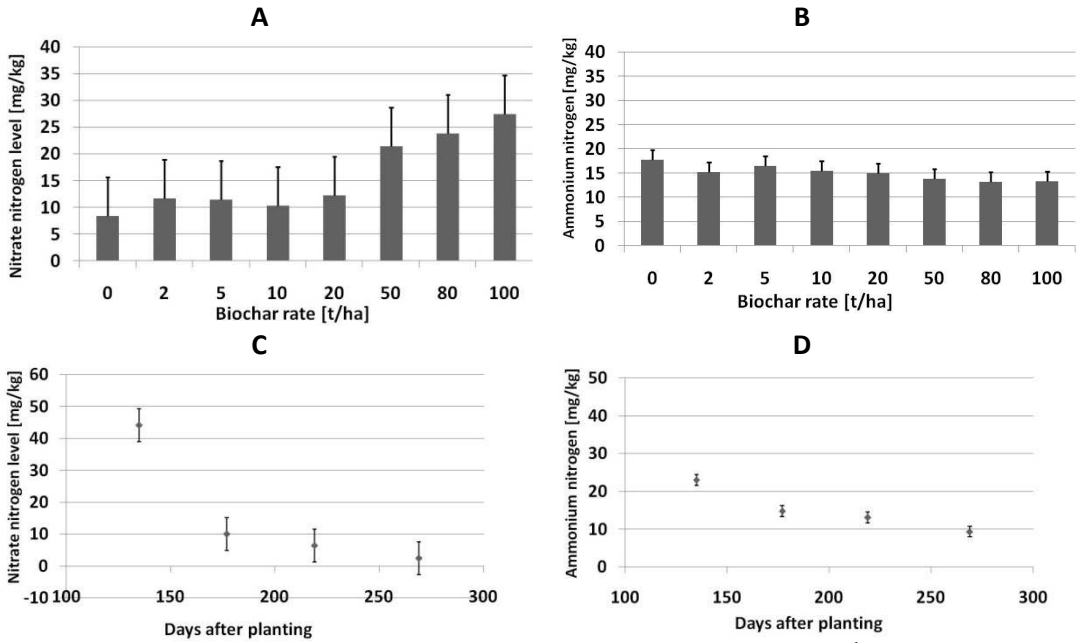


Figure 5.2. Nitrate nitrogen (A, C) and ammonium nitrogen (B, D) level [mg kg^{-1}] in potting mix in response to 8 biochar application rates (0-100 t ha^{-1}) (mean across sampling times and fertiliser treatments)(A, B) and time 135, 177, 219 and 269 days after planting, (C, D) (mean across biochar and fertiliser treatments). Error bars indicate the LSD (A-7.27, B-2.00, C-5.14, 1.41)(p≤0.05)

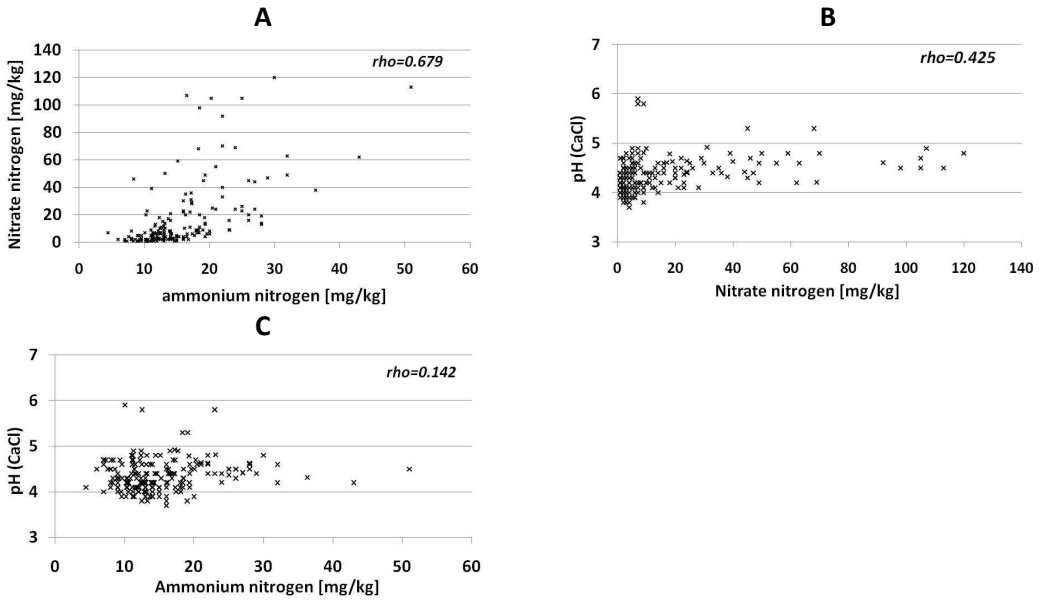


Figure 5.3. Spearman's correlation between (A) Ammonium nitrogen and nitrate nitrogen, (B) pH and nitrate nitrogen, (C) pH and ammonium nitrogen in the potting mix, pooled across 8 biochar treatments (1-100 t ha^{-1}), three fertilisation levels (0, 50 and 100% of the commercially applied dose) and four harvest times (135, 177, 216 and 269 days after planting), p≤0.05

There was a moderately strong positive correlation between ammonium-N and nitrate-N (Figure 5.3.A). A moderate positive correlation was also noticed between PM pH and nitrate while there was little statistical dependence of ammonium N (Figure 5.3.B and C).

Under field conditions both ammonium and nitrate nitrogen did not show any dependance on biochar levels but were only increasing under full fertiliser application rates (data not presented) an effect that decreased in time (*p≤0.001*).

Phosphorus

Biochar added to PM together with 50% fertiliser increased the availability of P, at 80 and 100 t ha^{-1} when compared to the control treatment (*p=0.009*). When biochar was combined with full fertiliser doses it did not elevate P level at any rate but instead decreased available P when biochar was added at the rates of 2, 5 and 20 t ha^{-1} (Figure 5.4). Full fertiliser application increased phosphorus levels during the whole experiment irrespective of biochar dose when compared to the half rate (data not presented).

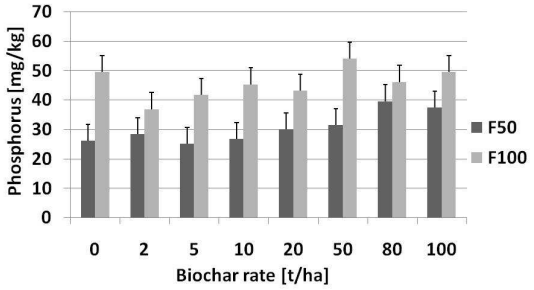


Figure 5.4. Phosphorus level [mg kg^{-1}] in potting mix in response to 8 biochar application rates (0-100 t ha^{-1}) combined with two fertilisation rates. Error bars indicate the LSD (5.60)(p≤0.05).

The response of phosphorus in the field experiment was limited to fertiliser only, resulting in increased available P under higher fertilisation levels; approximately 8 fold under F50 and 16 fold under F100 (*p≤0.001*)(data not presented).

Potassium

Biochar application from B50 to B100 increased available potassium (Colwell) content in the PM (*p≤0.001*)(Figure 5.5.A). By 269 DAP the potassium concentration had dropped by almost 200 mg at F100, and by 100 mg at F50 (data not presented).

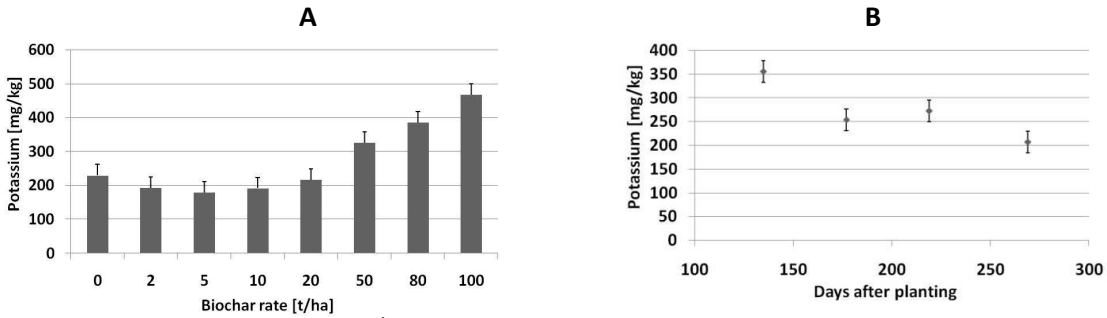


Figure 5.5. Potassium level [mg kg^{-1}] in potting mix in response to (A) 8 biochar application rates (0-100 t ha^{-1})(mean across sampling times and fertiliser treatments) and (B) time (135, 177, 219 and 269 days after planting (mean across biochar and fertiliser treatments). Error bars indicate the LSD (A-32.18, B-22.76)(p≤0.05).

Biochar application increased potassium availability in the field experiment (*p≤0.001*), (Figure 5.6.A). The level of available potassium was however decreasing in time (*p≤0.001*), (Figure 5.6.B) and in response to fertilisation (*p≤0.001)*(data not presented).

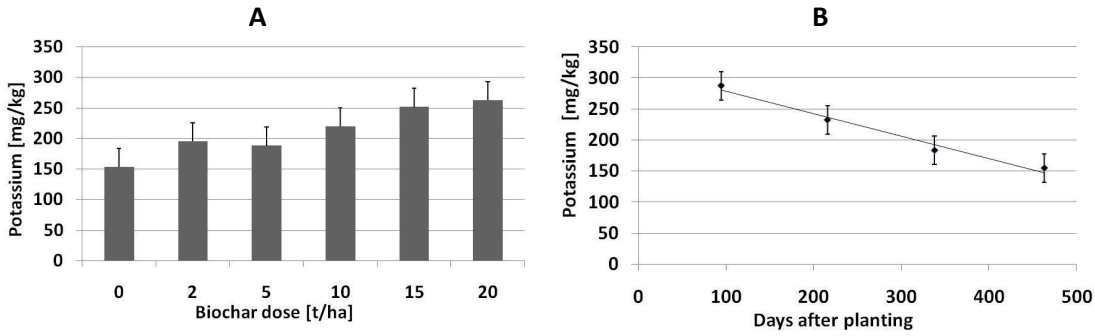


Figure 5.6. Potassium level [mg/kg] in Florentine Valley field experiment soil in response to (A) 6 biochar rates (0, 2, 5, 10, 15, 20 t ha^{-1}) (mean across sampling times and fertiliser treatments), (B) time (95, 216, 338 and 463 days after planting) (mean across biochar and fertiliser treatments), linear regression (Sig. 0.000, r^2=0.320). Error bars indicate the LSD (A-30.47, B-22.9)(p≤0.05).

Exchangeable K in the pot experiment PM behaved similarly to Colwell K so the results will not be presented or discussed separately.

5.3.3. Organic Carbon

Organic carbon in the potting mix decreased in response to biochar application (Figure 5.7.A) while in the field trial there were no changes in total carbon soil concentration under any biochar or fertiliser treatments.

By 400 DAP, the percent carbon dropped by 2.7% in the control treatment and 1.6% under the B5 treatment from the initial modelled concentration. Yet the rate of decay was not significantly different across biochar treatments (Figure 5.7.B) indicating the final

concentration was determined by the initial amounts present. During the whole time of the experiment the highest level of organic carbon was found under no biochar treatment.

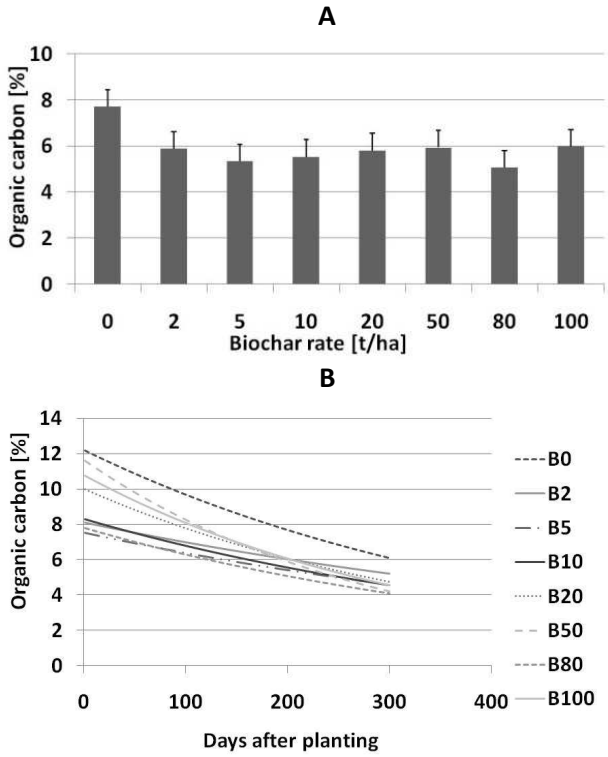


Figure 5.7. Organic carbon level [%] in potting mix in response to (A) 8 biochar application rates (0-100 t ha^{-1})(average data from 135, 177, 219 and 269 days after planting (DAP) and fertilisation at two levels (50 and 100% of the commercially applied dose)) and (B) Rate of decay under 8 biochar application rates (0-100 t ha^{-1}) over time. Error bars indicate the LSD (0.74)(p≤0.05).

5.3.4. Exchangeable cations

Exchangeable Aluminum

Biochar decreased exchangeable aluminum amounts in the PM. Within the same biochar application rate exchangeable aluminum level in PM was higher under full fertiliser treatment in comparison to half fertiliser treatment (*p≤0.001*). The differences were more noticeable for lower biochar treatments (B0-B20)(Figure 5.8.A). The ex. aluminum level increased with time under all the biochar treatments, this more noticeable at lower application rates (B0-B20). There was a negative correlation between the level of exchangeable aluminum in the PM and the mix acidity (Figure 5.8.C) and negative correlation (Spearman's) between ex. Al and ex. K (Figure 5.10.D).

No biochar effect on ex. Al was reported in the field experiment. Biochar did not influence the decay rate of ex. Al in either of the experiments.

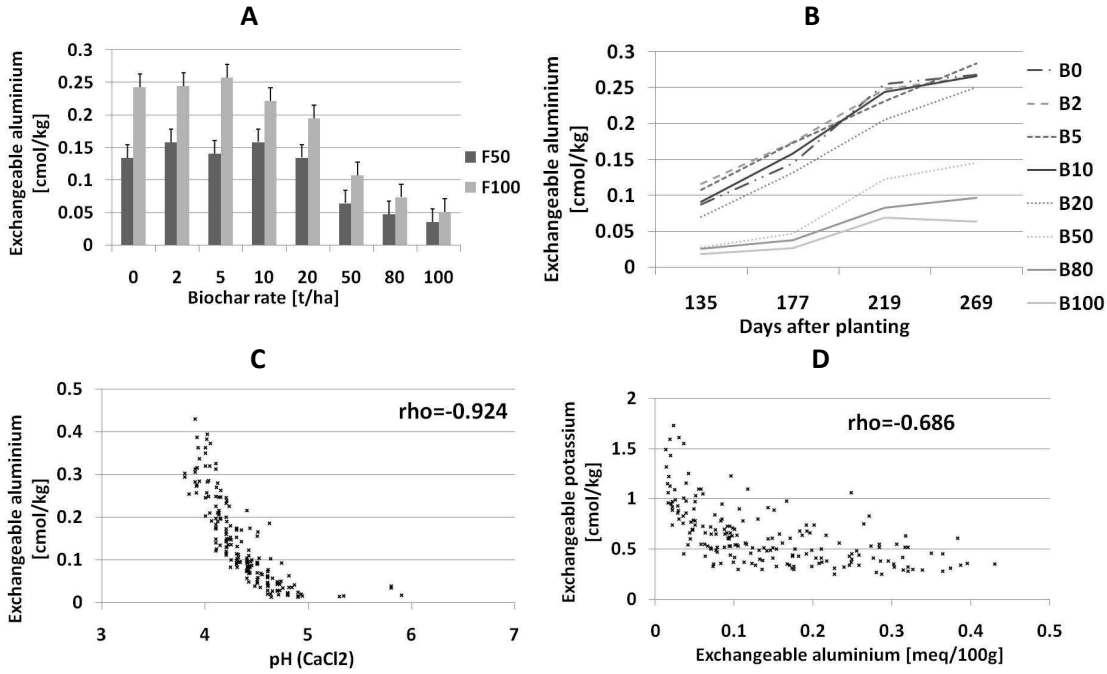


Figure 5.8. Exchangeable aluminum level [cmol kg^{-1}] in potting mix in response to (A) 8 biochar application rates (0-100 t ha^{-1}) and fertilisation at two levels (50 and 100% of the commercially applied dose)(mean values across sampling times), (B) 8 biochar application rates (0-100 t ha^{-1}) over time (135, 177, 219 and 269 days after planting (DAP)) and (C) Spearman's correlation (rho= -0.924) between exchangeable aluminum and pH (CaCl2) in the potting mix. (D) Spearman's correlation (rho= -0.686) between exchangeable aluminum and exchangeable potassium in the potting mix. Correlation data represents results from all the biochar and fertiliser treatments across time, Error bars indicate the LSD (0.02)(p≤0.05).

Exchangeable Calcium

Exchangeable calcium in PM responded to an interaction between fertiliser and biochar, resulting in significantly lower levels when char was applied (*p≤0.001*)(Figure 5.9.A); this trend continued over the length of the experiment. There was no other clear trend between any biochar treatments at any stage of the experiment.

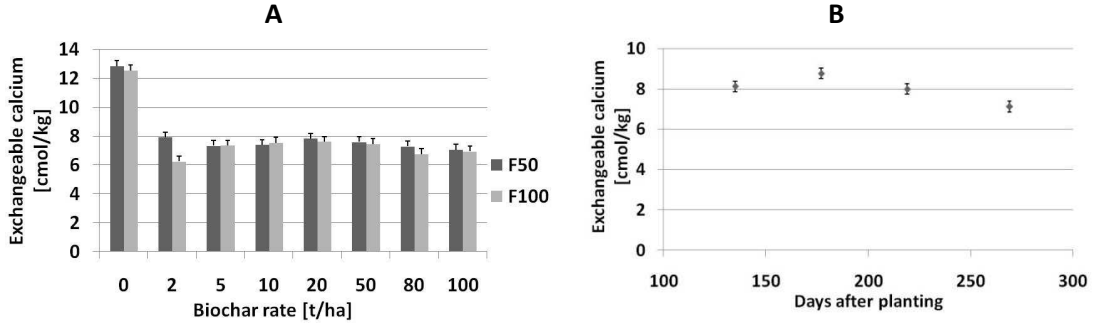


Figure 5.9. Exchangeable calcium level [cmol kg^{-1}] in potting mix in response to (A) 8 biochar application rates (0-100 t ha^{-1}) and fertilisation at two levels (50 and 100% of the commercially applied dose)(mean across sampling times), (B) time (135, 177, 219 and 269 days after planting) (mean across biochar and fertiliser treatments). Error bars indicate the LSD (A- 0.36, B- 0.26)(p≤0.05).

Under field conditions the exchangeable calcium decreased in time and there was no effect of biochar or fertiliser detected.

Exchangeable Magnesium

Similarly to exchangeable calcium, ex. magnesium responded to both interaction between biochar and fertiliser (*p=0.010*) and biochar levels in time (*p=0.033*) resulting in highest ex. magnesium levels under control treatment and no clear trend in between any biochar treatments (Figure 5.10.A).

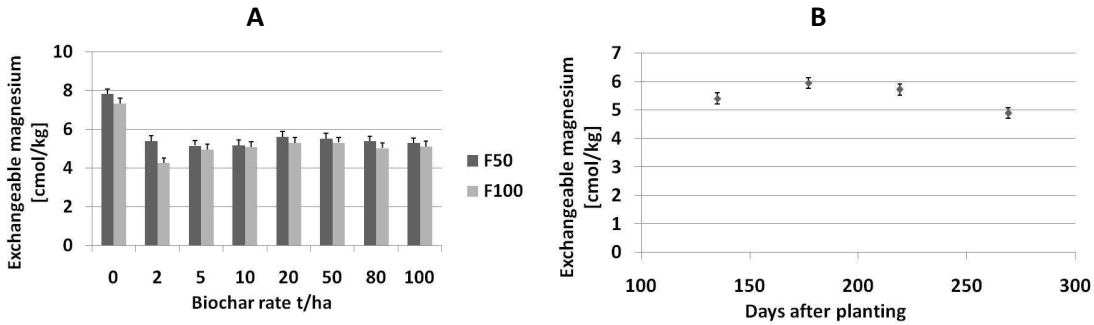


Figure 5.10. Exchangeable magnesium level [cmol kg^{-1}] in potting mix in response to (A) 8 biochar application rates (0-100 t ha^{-1}) and fertilisation at two levels (50 and 100% of the commercially applied dose)(means across samplind times), (B) time (135, 177, 219 and 269 days after planting) (mean across biochar and fertiliser treatments). Error bars indicate the LSD (A- 0.27, B- 0.19)(p≤0.05).

Under field conditions biochar did not influence exchangeable magnesium in the soil. The nutrient was found to decrease in time (*p≤0.001*) and in response to fertilisation (*p=0.019*)(data not presented).

Exchangeable sodium

The effect of biochar application in time on exchangeable sodium in PM was similar to the effect on Colwell potassium resulting in higher levels under B50-B100 (*p≤0.001*)(Figure 5.11.A). At all four harvests the level of ex. sodium was significantly lower in response to low biochar treatments (2-20 t ha^{-1}) in comparison to control treatment.

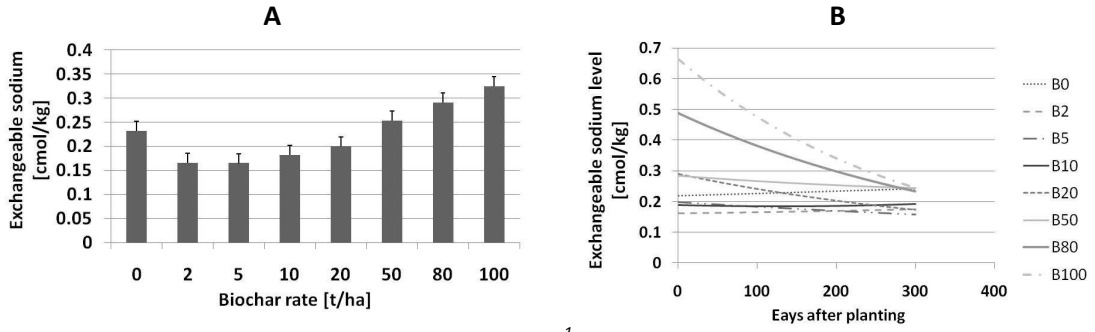


Figure 5.11. Exchangeable sodium level [cmol kg^{-1}] in potting mix in response to (A) 8 biochar application rates (0-100 t ha^{-1})(average data from 135, 177, 219 and 269 days after planting (DAP)) and (B) rate of decay under 8 biochar application rates (0-100 t ha^{-1}). Error bars indicate the LSD (0.02) (p≤0.05).

Exchangeable sodium was the only soil element that declined from the soil at a different rate depending on the amount of biochar applied (Figure 5.11.B). Under B100 and B80 exchangeable Na was declining rapidly in comparison to other biochar treatments. Under B0 and B2 however, a slight increase of ex. Na levels was detected. While the exponential decay coefficient from the model was significantly different for biochar treatments, time as a predictive variable in the model only explained a small component of the variation (R^2=0.026).

Under field conditions ex. Na increased under B15 and B20 in comparison to control treatment but was no different from control under lower biochar rates, namely B2-B10 (*p≤0.001*)(Figure 5.12). The changes in ex. Na, in time were significant, but not clear, increasing and decreasing alternatively (data not presented).

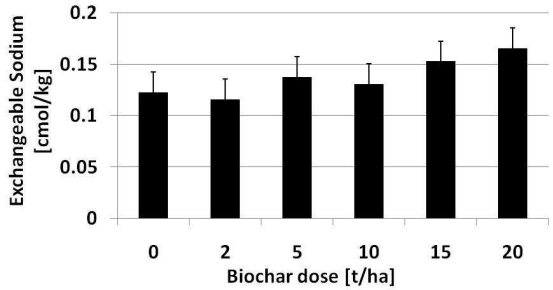


Figure 5.12. Exchangeable sodium level [cmol kg^{-1}] in Florentine Valley field experiment soil in response to 6 biochar application rates (0-20 t ha^{-1}) (mean across sampling times and fertiliser treatments). Error bars indicate the LSD (0.02)(p≤0.05).

5.3.5. Physical changes

Soil conductivity is an indicator of the number of ions present in the soil solution. In the context of other results presented in this chapter it might be considered an auxiliary

indicator of the changes. Therefore it will only be presented and discussed briefly. In the pot experiment the conductivity decreased, on average by 0.05 dS m^{-1}, when biochar was applied at any rate (*p≤0.001*), while the trends in time were not clear. Under field conditions EC decreased in time from 0.27 dS m^{-1} at 95 DAP to 0.06 dS m^{-1} at 463 DAP. In both experiments fertilisation resulted in elevated level of EC (*p≤0.001*).

PM moisture content was influenced by an interaction between fertiliser and biochar (*p=0.003*) and decreased in time (*p≤0.001*) in the pot experiment. Regardless fertiliser level biochar caused decrease in water content of PM (Figure 5.13.B).

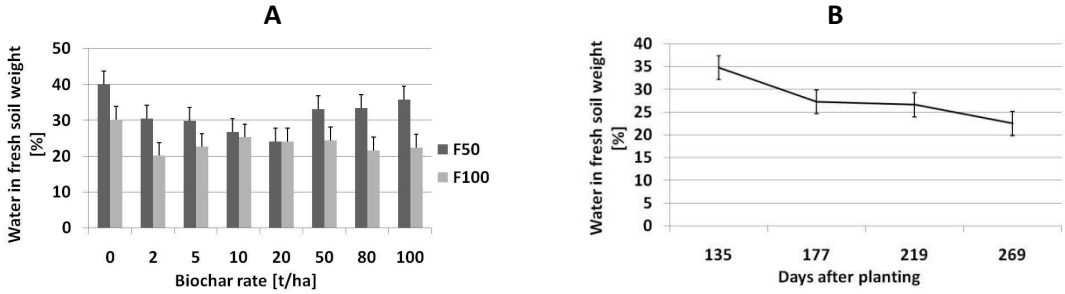


Figure 5.13. Potting mix accumulated water [%] in pot experiment in response to (A) interaction between 8 biochar application rates (0-100 t ha^{-1}) and fertilisation at two levels (50 and 100% of the commercial rate)(mean across sampling times), and (B) time 135, 177, 219, 269 days after planting(mean across biochar and fertiliser treatments). Error bars indicate the LSD (A- 3.71, B-2.64)(p≤0.05).

Biochar did not influence water content in soil during the field experiment. Gravimetric soil water content was influenced by fertilisation in time only (*p=0.038*)(Figure 5.14). The interaction between time and fertilisation resulted in increase of soil water content 216 and 338 DAP and a decrease at the end of experiment (463 DAP)(*p≤0.001*). Monthly precipitation recorded in a weather station in Maydena, Tasmania (20 km from the field plantation location) is presented in Figure 5.15.

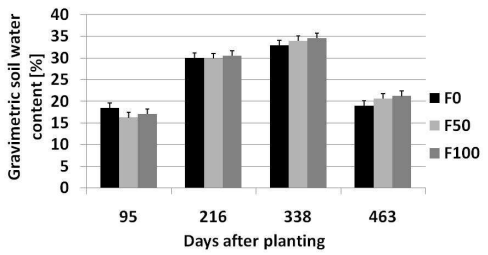


Figure 5.14. Gravimetric soil water content [%] in Florentine Valley field experiment soil 95, 216, 338 and 463 days after planting (DAP) in response to 3 fertiliser rates (0, 50 and 100% of the commercially applied dose). Error bars indicate the LSD (3.34)(p≤0.05)

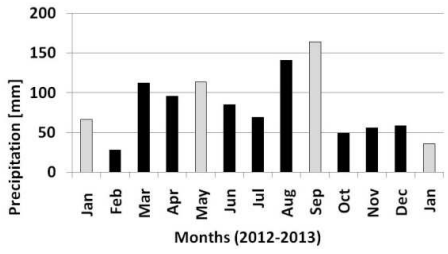


Figure 5.15. Monthly precipitation in Maydena post office meteorological station (Derwent valley, TAS), (Bureau of Meteorology, 2012-2013), white bars indicate the months in which soil samples were collected (95, 216, 338 and 463 DAP).

5.4. Discussion

Macadamia biochar added to the potting mix influenced most of the analysed elements. Ammonium-N, organic carbon, exchangeable magnesium, calcium and aluminum and conductivity levels declined in response to biochar, while nitrate-N, potassium, pH and exchangeable potassium and sodium increased. Phosphorus response was mixed resulting in a slight rise under the highest biochar treatment. In most cases the increase in nutrient concentration was only observed when high biochar doses were applied (B50-B100) with the exception of carbon, ex. Mg and ex. Ca which decreased in response to all biochar treatments. Biochar added to soil in the field experiment at the maximum of 20 t ha^{-1} increased the level of potassium and exchangeable sodium and did not affect any other elements.

The limited change observed in the field experiment soil in comparison to pot experiment is most likely due to a few factors. Changes in nutrients concentration in the glasshouse were, in most cases, observed only under high biochar application rates (above 50 t ha^{-1}). In the field the highest biochar rate equaled 20 t ha^{-1} and is surmised to be too low to induce as many changes as in the pot trial. Just the same, the application method most likely influenced the magnitude of the results in the field experiment. Biochar was incorporated into known soil volume around each tree. In time however, biochar particles could have been transported with water out of the original region of application, resulting in lower than anticipated biochar concentration in the tested area and therefore reducing the magnitude of expected changes. It must be also acknowledged, that field variability, especially in a plantation replant situation would be expected to affect the results achieved, and may result in different findings. In the pot experiment a high content of PM organic matter had an effect on a few elements concentration and could have masked biochar influence to a certain extent.

At biochar rates above 50 t ha^{-1} PM pH increased, yet the solution remained very strongly acidic (4.5-5.0;Rayment and Lyons, 2011). This effect is surmised to be caused by mixing high pH macadamia char to a lower pH PM and consequently increasing the biochar-soil mix pH. Such explanation appears to be the most intuitive and would be confirmed by repeated experiments; however other mechanisms involved in acidity changes cannot be disregarded. Acidity is the measure of H^+ in solution but Al^{3+} plays an important role in soils as between pH 3.2 and 5.2 ($CaCl_2$), where Al^{3+} reacts with water molecules forming $AlOH^{2+}$,

and $Al(OH)_2^+$, releasing extra H^+ ions. Under high biochar application rates the Al^{3+} ions decreased, this effect being most likely related to Al^{3+} ions sorbed to biochar surfaces. Such mechanism would decrease the Al^{3+} ions concentration and therefore limit the range of said reaction leading to less H^+ free ions in the soil solution and therefore decreased acidity.

The increased availability of nitrate-N and decreased concentration of ammonium-N in response to biochar application suggest that biochar might have stimulated the process of ammonium nitrification. Similar effect reported by other scientists has been attributed to phenols adsorption on biochar surfaces (Clough and Condron, 2010; DeLuca et al., 2009) or increased soil porosity and facilitated environment for bacteria (DeLuca et al., 2006; Nelson et al., 2011). The addition of biochar to PM is suspected to have increased the porosity, this supported by decreased soil gravimetric water content, which makes the second mechanism likely to be in place in the pot experiment. Biochar post-trial and pre-application analyses would be required to confirm the suggested phenol adsorption mechanism.

Lower levels of ammonium-N may be also related to adsorption of NH_4^+ to biochar particle surfaces (Lehmann et al., 2003; Lehmann et al., 2006; Spokas et al., 2011; Steiner et al., 2008), as a result of bonding with organic acidic functional groups on char surfaces (Spokas et al., 2010; Spokas et al., 2011). This mechanism however does not explain increased nitrate PM concentrations and stays in contradiction with the observed correlation between nitrate-N and ammonium-N. Nitrate-N decline in time might either be connected with leaching of this nutrient or uptake by plants, the latter mechanism appearing more likely when considering seedlings early growth stage and high nitrogen requirements.

Biochar did not induce any changes of ammonium-N or nitrate-N when applied to the field soil. It is concluded that biochar rates in the field experiment were too low to stimulate nitrification, or cause any other effect, as in the pot experiment.

The quantity of potassium applied with biochar to PM equalled 32.85- 1,620.6 mg (B2-B100) which is significantly higher in comparison to K applied in the fertiliser: 189 (F50) to 377 (F100) mg. Therefore the effect on PM K concentration is most likely due to K release from biochar surfaces, which was also observed in case of lower K chars (Biederman and Harpole, 2013; Chan et al., 2007; Lehmann et al., 2003; Major et al., 2010). Even though the maximum biochar dose applied in the field was much lower than in the pot trial, increased K concentration was also observed in this experiment. The theory of K release from char

surfaces was supported in the field experiment, where applied fertiliser did not contain any potassium and could not have been a direct K source. The only other than biochar source of K in the field experiment could have been soil itself. Here, the control soil samples (not amended by either biochar or fertiliser) analysed during the experiment did not show large concentration of potassium, which makes the theory of soil being a K source highly unlikely. The theory of biochar releasing K from its surfaces is supported by biochar SEM-EDS analyses (Chapter 3) which revealed large amounts of KCl particles on the surface of macadamia biochar.

The SEM-EDS analysis showed considerable concentration of sodium in various compounds on macadamia biochar surfaces (Chapter 3). Both in the pot and field experiments exchangeable sodium levels increased in response to high biochar application rates. Similarly to K, this effect can be explained by the amounts of Na introduced with biochar: 4.8- 236.8 mg kg^{-1} in the pot experiment (B2- B100) and 4.10-42.24 mg kg^{-1} in the field experiment (B2-B20)[1]; and the release of Na^{+} ions to the soil solution. The analysis of exchangeable sodium changes in time in the pot experiment (rate of decay parameter) shows that biochar application at high rates (B80-B100) stimulated exchangeable Na decline from the PM. This effect is most likely connected with high initial values of ex. Na in the PM and possibly with biochar increasing the porosity of PM and resulting in elevated leachate of certain nutrients, this supported by decreased water content of PM after biochar application. Literature shows sodium as one of the cations which will leach the first, a result of weak strength of attraction to the surfaces of soil or biochar (Manoa, 2014). Sodium decline in time may therefore be a result of leaching from PM, however an increased plant Na uptake cannot be discounted. Leachate and plant material sodium analyses would support this hypothesis.

Biochar increased plant available P in the PM when added at the rates of 50-100 t ha^{-1}. The total quantity of phosphorus contained in the macadamia biochar increased with the application rate from 3.6-177.6 mg P kg^{-1} PM, compared to total P applied by fertiliser of 43 mg P kg^{-1} (F50) and 86 mg P kg^{-1} (F100) PM. The increased level of available P in PM under high biochar rates is most likely explained by soluble P release from biochar (Lehmann and Joseph, 2009). However, decreased immobilization of PO_4^{3-} due to the reduced availability of with Al^{3+} and Fe^{2+}, may have also contributed to increased availability. Similar effect has

[1]Biochar treatments in the pot experiment and field experiment are not corresponding in terms of nutrients applied to the soil with biochar. This is a result of biochar volume calculations vs. soil volume to which it is applied (see chapter 4).

been noticed by Cheng (2006) and the decreased concentration of Al^{3+} when high biochar doses were applied supports such explanation. The mechanism of increased P concentration due to stimulated soil micro-organisms activity, cannot be confirmed or denied in the case of this study as no microbial analyses have been performed in any of the experiments.

In contrast to K, P and Na, exchangeable magnesium and calcium levels were significantly lower at all rates of biochar application. Both Ca and Mg are among the cations which are sorbed to negative surfaces in the first order (Lehmann et al., Wales, 2007) and tend to behave similarly as both are divalent, alkali earth metals with small hydrated radius and in functional group 3 (Sigel and Sigel, 1990). The effect of Mg and Ca retention by biochar in a similar manner has been reported by Lehmann et al. (2003) and Major et al. (2010). In this experiment the decrease of these cations supports strong adsorption to biochar surfaces at the beginning of pot experiment. No differences in ex. Mg and Ca soil levels between biochar treatments suggest that biochar effect on these cations was independent of biochar quantity. This postulate is supported by increases in soil K and Na availability at higher biochar rates. In the pot experiment there were no significant changes in time while under field conditions both exchangeable cations were decreasing which suggest that they were gradually exiting the soil solution either due to the adsorption to biochar surfaces or as a result of plant uptake or leaching.

Similarly to ex. Ca and ex. Mg, ex. Al level was lower under high biochar application rates. Soil aluminum is strongly related to soil pH (Kookana, 2010). The pH increases were shown before to be accompanied by significant reduction in ex. Al by >50% at the higher rates of biochar application due to the adsorption of this cation to char surfaces (Chan et al., 2007). This effect, related to lower concentrations of both Al^{3+} and H^{+}, has been explained when discussing pH changes in the PM and supported by a negative correlation between pH and Al^{3+} in the PM. Looking at the changes in time though it is clear that aluminum levels in soil were increasing which suggests that biochar could have adsorbed the Al cations but started releasing them in time, this effect possibly caused by adsorption of different cations to biochar surfaces. One of these cations could have been K as the level of potassium decreased in time. This effect has not been observed in any other study, but the results of correlation between exchangeable aluminum and potassium seem to support this theory (Spearman's correlation, *rho*=-0.686).

The effect of biochar adsorbing Al cations was not noticed in the field experiment as ex. Al increased in response to higher fertilisation and in time only. It might be speculated that although fertiliser did not contain any aluminum it had an indirect effect on ex. Al increase by elevating soil acidity. More H^+ and Al^{3+} ions were present in the soil solution, which resulted in biochar not being able to adsorb all of them and compensate for that effect.

The level of organic carbon in the pot experiment decreased following biochar application. The decay rate, however, was not statistically different among biochar treatments. Organic carbon level decreasing in the PM may be related to a positive priming effect. Such effect, result of soil OM mineralization following the application of labile C source to the growing medium, has been reported in other studies when biochar was applied (Luo et al., 2011; Wardle et al., 1998; Zimmerman et al., 2011). The chemical analyses of macadamia biochar quantified organic carbon at 4.55% which suggests most of the carbon was in a stabile form. The C^{13} – NMR analyses, however, showed one main peak at 124 ppm (Chapter 3) which is normally attributed to carbon in comparatively less stable alkene compounds (115-140 ppm). The peaks characteristic for carbon in the aromatic rings is usually between 125 and 150 ppm which implies that macadamia biochar did not have much of the latter. The mechanism of positive priming might be more complex and involve both soil and biochar changes (Luo et al., 2011). It is not clear if biochar enhances the loss of soil organic carbon or whether the soil organic content increases the loss of biochar from the soil. High PM organic matter content and carbon analyses in macadamia biochar suggest that both of these mechanisms most likely contributed to decreased organic C levels.

Alternatively, OC drop following biochar application may be related to low biochar OC content in comparison to soil organic carbon and the effect of OC dilution. Consequently the lack of OC changes in the field experiment would be a result of both lower soil organic matter content in comparison to PM and low biochar application rates.

5.5. Conclusions

Biochar applied together with fertiliser both in the pot and field experiment influenced soil nutrient content and physical characteristics, however much more so in the glasshouse experiment. This is concluded to be related to higher biochar rates applied in the pot experiment and biochar incorporation method. The main mechanism involved in soil nutritional changes is directly related to biochar ability to adsorb ions and consequently

influence the ion concentration in the soil solution. It is therefore surmised that biochars selective sorption properties resulted in the displacement of K, Na cations by Mg, Ca, Al and H on macadamia biochar surfaces, the last two correlated with soil acidity decrease. Decreased electrical conductivity in response to biochar supports the fact that less ions were released from biochar than adsorbed. The release of cations was probably accompanied by anions release, namely phosphate but no evidence was found to support this hypothesis. Lowered soil moisture content in the pot experiment suggests the possibility of increased leachate of some ions, namely Na, Ca and Mg. Stimulated nitrification following biochar application was most likely responsible for lower ammonium-N and increased nitrate-N levels. Biochar incorporation may have caused a positive priming effect which is potentially related to interaction and both-way mineralization of soil OM and macadamia biochar. Ideally, biochar would have to be retrieved and analysed after the end of the experiments to confirm proposed mechanisms. Most of the changes were observed only at the beginning of the experiment and beneficial results from biochar application (i.e. increased K soil concentration) did not continue till the end of the experiments. The magnitude of soil changes suggests that agronomic performance differences will be more evident in the controlled environment. Analysis of plant nutrient uptake following biochar induced changes would add to the understanding of macadamia biochar induced changes

6. PERCOLATING WATER ANALYSIS

6.1. Introduction

Biochar can have a positive influence on the physical and chemical soil environment (Amonette and Joseph, 2009; Chan and Xu, 2009; Downie et al., 2009; Krull et al., 2009). Differences reported in the soil environment following biochar application are mainly attributed to a) biochar having an influence on chemical transformations in the soil, b) biochar affecting soil physical properties e.g. porosity, bulk density, water holding capacity etc., c) stimulation of soil microbes (Lehmann and Joseph, 2009b; Major et al., 2009; Troy et al., 2014).

Some changes are however related to decreased leaching or alterations in the chemical composition of the leachate following biochar application (Altland and Locke, 2012; Lehmann et al., 2003). Various types of charred biomass applied to the soil have been demonstrated to affect the leachate, mainly by increasing water holding capacity of the soils and limiting nutrients movement (Altland and Locke, 2012; Guo et al., 2014; Lehmann et al., 2003; Sika and Hardie, 2014; Zhao et al., 2009). These effects have been attributed to biochar increasing soil macro- and nano- porosity and enlarging soil SSA, consequently increasing fertilizer efficiency; as well as direct nutrient release from biochar surfaces (Major et al., 2009; Sika and Hardie, 2014). Various, often contradictory, mechanisms have been proposed to explain changes in nutrient content of leachate.

A decrease in acidity following biochar application has been observed and in most cases attributed to biochar adsorbing both H^+ and Al^{3+} ions and therefore reducing the soil solution pH (Chan et al., 2007; DeLuca et al., 2006; Ma and Matsunaka, 2013b; Nelson et al., 2011). Different chars have been also reported to increase nitrate-N soil concentration, this effect observed by Lehmann et al. (2003) in Ferrosol and Anthrosols when manure based charcoal was applied. Such effect has been ascribed to nitrate-N sorption to biochar surfaces as a result of positive charge sites present on chars surfaces and then nitrate-N release to the leachate as opposed to nitrate being immediately taken up by plants. A similar mechanism for a different effect was proposed by (Altland and Locke, 2012), who found that biochar application decreased nitrate-N leachate and suggested that NO_3^- was bound to biochar surfaces, resulting in slower release to soil solution leachate. Analogous explanation was suggested by (Chan and Xu, 2009; Guo et al., 2014; Lehmann et al., 2003;

Major et al., 2009; Zhao et al., 2009). Nitrate-N leaching increased in sandy soils and decreased in silty soil after beech wood biochar application as a result of soil changes porosity (Borchard et al., 2012). Clearly, there are different propositions in the literature. These differences may be attributed to the type of biochar used, thus differing properties. Therefore different outcomes are likely to occur and the results be specific to biochar-soil combinations used i.e. results are situation specific, and perhaps no general consensus will emerge. Macadamia biochar added to field plantation soil did not induce any changes in either acidity or nitrate-N soil concentration (Chapter 5) yet the earlier studies suggest that it could conceivably alter movement through bulk flow.

Limited ammonium leachate following biochar application was observed by (Lehmann et al., 2003; Sika and Hardie, 2014) and explained by vast increase in sandy soil SSA following pine wood biochar application. On the contrary (Bruun et al., 2012) reported slightly increased ammonium-N leachate when straw and wood based biochars were analysed in repacked sandy soil columns, this effect attributed to reduced nitrification rates, possibly due to toxic compounds in the biochar. This is unlikely to occur from addition of this macadamia biochar for two reasons. There were no signs of toxicity observed in either of the experiments (Chapter 5) and although no N concentration changes were observed in the field trial soil, in the pot experiment stimulated nitrification was proposed as a reason for N changes (Chapter 5). As the field experiment soil ammonium-N changes were not observed under biochar application it is unlikely that the leachate NH_4^+ will change in response to biochar.

Significant increases in K leachate were observed by Lehmann et al. (2003) when manure biochar was applied to two different soils. This effect was attributed to K ions release from biochar surfaces and evidenced by high K content of manure-based biochar; a similar mechanism was postulated by (Altland and Locke, 2012). As biochar application to the PM increased K content, it is expected that soil leachate K concentration may rise as well, this also supported by the fact that K^+ ions have a weak attraction to biochar surfaces and are easily displaced by other base cations. Phosphorus concentration in soil leachate has been reported to both increase (Guo et al., 2014) and decrease (Altland and Locke, 2012; Borchard et al., 2012). Phosphorus level in the forest soil was not influenced by biochar application therefore the differences in soil leachate are not likely. It must be acknowledged though that field variability, especially in a plantation replant situation (as in

Chapter 5) would be expected to affect the results achieved, and that sampling from different locations may result in different findings

Taking into account the range of mechanisms proposed to be involved in various leachate changes it is challenging to predict macadamia biochar induced leachate differences. Macadamia char admixed to field plantation soil resulted in only some elements concentration changes. The availability of potassium and exchangeable sodium increased when biochar was applied at the high rates, while other elements stayed at the same level, regardless of biochar doses. In this study it was hypothesized that macadamia biochar added to brown dermosol field experiment will reduce nutrients leachate mainly due to its high SSA and increased water holding capacity.

6.2. Method

In the field experiment, percolated water was collected in 114 custom-built Lysimeters (LIZ) installed in the *E. nitens* field plantation in Florentine Valley (South-West Tasmania). Two LIZs were installed per biochar*fertilizer treatment and replicated in 3 blocks. The equipment was installed at 1 m (bottom) depth prior to biochar application to the soil, in September 2011. Following transplanting LIZs were emptied every 5-7 weeks for 13 months and in total 10 batches of samples were collected. Samples were stored in the freezer (-18° C) and analysed in the Agricultural Science laboratory at the University of Tasmania. The design of Lysimeters and detailed schedule for sample collection, maintenance as well as the analyses methodology are presented in Chapter 4.

6.3. Results

Macadamia biochar increased soil leachate K concentration when added at the high rates. An interaction between the char and fertilizer affected nitrate-N, ammonium-N and pH but the results did not reveal clear trends. Phosphorus concentrations were unaffected by biochar or fertilizer application.

6.3.1. Acidity

Biochar at the rates of 2, 5, 10 and 15 t ha^{-1} increased soil solution pH when combined with F50. When full fertilization was combined with biochar applied at B2, B10 and B20, pH of the leachate decreased (Figure 6.1.A)(*p=0.024*). Within each biochar level, fertilization in

general increased acidity. pH changes in time showed no apparent trend, other than variability increased markedly after the first 100 DAP (Figure 6.1.B).

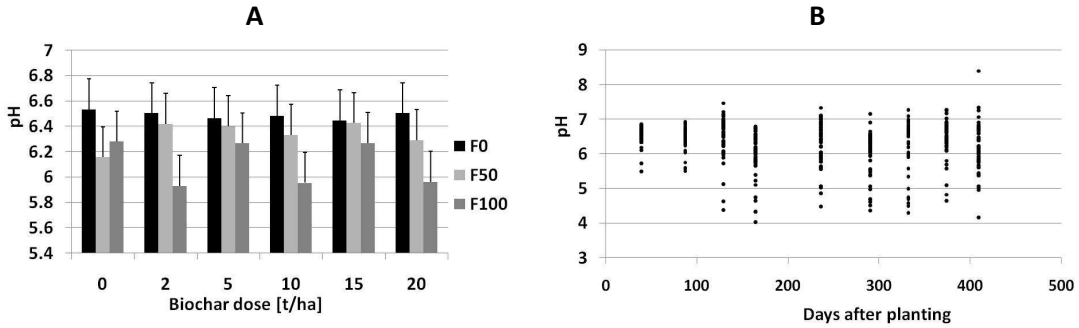


Figure 6.1. Soil leachate acidity in Florentine Valley field experiment in response to (A) interaction between 6 biochar application rates (0-20 t ha^{-1}) and fertilization at 3 levels (0, 50 and 100% of the commercial rate)(mean across sampling times); (B) changes in time, 39, 87, 129, 164, 200, 236, 290, 332, 374 and 409 days after planting (mean across biochar and fertilizer treatments). Error bars indicate the LSD (0.24)(p≤0.05).

6.3.2. Nutrition

Nitrate-N, ammonium-N and phosphorus in the soil water samples did not change in response to biochar application; however both nitrate-N and ammonium-N were influenced by the interaction between biochar and fertilizer (ANOVA, *p≤0.05*, B*F interaction). Of the elements tested, only the concentration of potassium increased when biochar had been applied.

Nitrogen

Biochar interacted with applied fertilizer, influencing the soil water concentration of the negatively charged nitrate concentrations. When 50% fertilizer was applied biochar decreased nitrate concentration at B5 and, when full fertilization was in place the highest biochar dose (B20) also resulted in nitrate decrease (*p≤0.001)*(Figure 6.2.A). Fertilization at both levels increased water nitrate concentration under B0, B2, B10 and B15, but not B20 treatments. Nitrate concentration in water raised with time until 236 DAP and then started diminishing gradually, reaching values close to zero at 374 DAP (*p≤0.001*)(Figure 6.2.B).

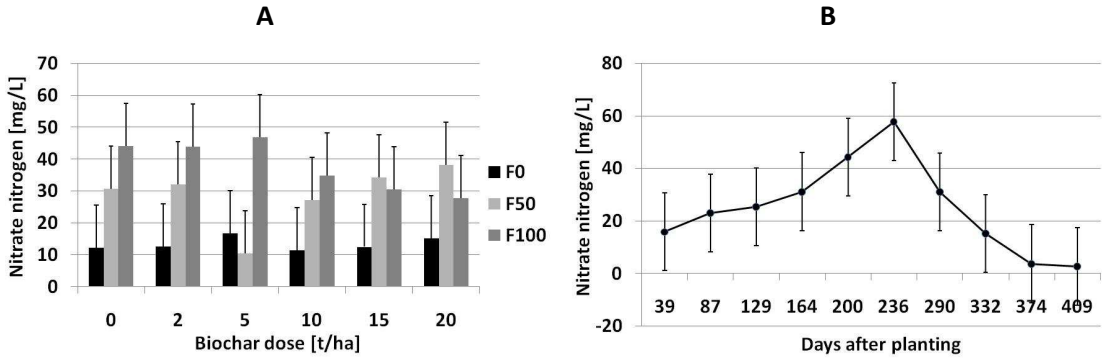


Figure 6.2. Nitrate nitrogen level in soil leachate [mg L^{-1}] in Florentine Valley field experiment in response to (A) interaction between 6 biochar application rates (0-20 t ha^{-1}) and fertilization at 3 levels (0%, 50% and 100% of the commercial rate)(mean across sampling times); (B)changes in time 39, 87, 129, 164, 200, 236, 290, 332, 374 and 409 days after planting (mean across biochar and fertilizer treatments). Error bars indicate the LSD (A-13.38, B-14.81)(p≤0.05).

Biochar did not influence ammonium level when no or 50% fertilizer was applied. Under full fertilization biochar increased concentration of the positively charged ammonium ions when added at the rates of 2 t ha^{-1}, 10 t ha^{-1} and 20 t ha^{-1} (p=0.004)(Figure 6.3.A). Ammonium concentration in percolating water was rising in time, peaking earlier than nitrate at 164 DAP and then lessened to initial levels (*p≤0.001*)(Figure 6.3.B) i.e. near zero.

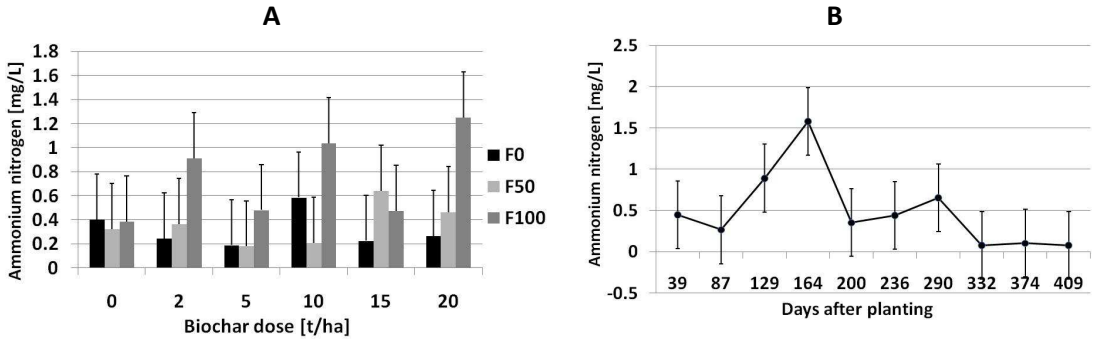


Figure 6.3. Ammonium nitrogen level in soil leachate [mg L^{-1}] in Florentine Valley field experiment in response to (A) interaction between 6 biochar application rates (0-20 t ha^{-1}) and fertilization at 3 levels (0%, 50% and 100% of the commercial rate) (mean across sampling times); (B) changes in time 39, 87, 129, 164, 200, 236, 290, 332, 374 and 409 days after planting (mean across biochar and fertilizer treatments). Error bars indicate the LSD (A-0.38, B-0.41)(p≤0.05).

Potassium

Biochar application increased leachate concentration (by approximately 2.5 mg L^{-1}) of the comparatively less mobile potassium ions when added at the rate of 20 t ha^{-1} (*p≤0.001*). At 50% fertilization biochar added at 2 t ha^{-1} and 20 t ha^{-1} increased potassium concentration while at full fertilization potassium level was similar at all biochar rates (*p≤0.001*)(Figure

6.4.A). The peak in concentration in time, as for phosphorus and ammonia, was noticed at 164 DAP (Figure 6.4.B).

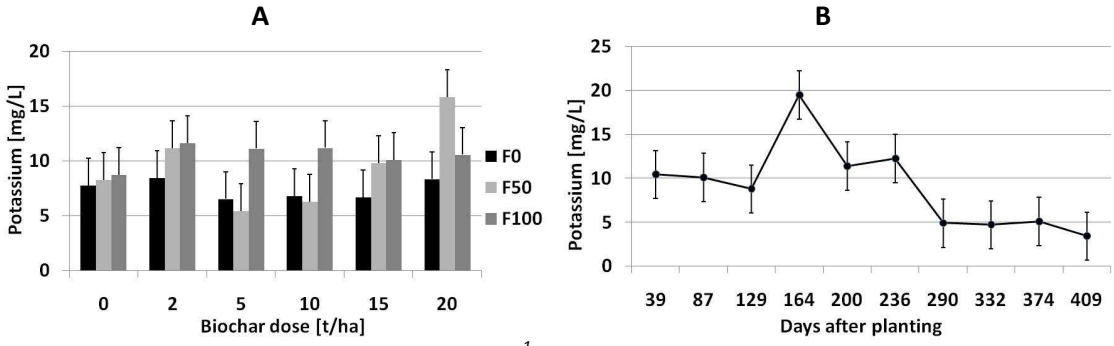


Figure 6.4. Potassium level in soil leachate [mg L^{-1}] in Florentine Valley field experiment in response to (A) interaction between 6 biochar application rates (0-20 t ha^{-1}) and fertilization at 3 levels (0%, 50% and 100% of the commercial rate)(mean across sampling times); (B)changes in time 39, 87, 129, 164, 200, 236, 290, 332, 374 and 409 days after planting (mean across biochar and fertilizer treatments). Error bars indicate the LSD (A- 2.48, B-2.74)(p≤0.05).

Phosphorus

Phosphate concentration in percolating water changed in time and was not influenced by other factors (biochar or fertilizer application). Similar to ammonium, concentrations peaked at 164 DAP; the levels at all other measurement times were similar (*p≤0.001*)(Fig 6.5).

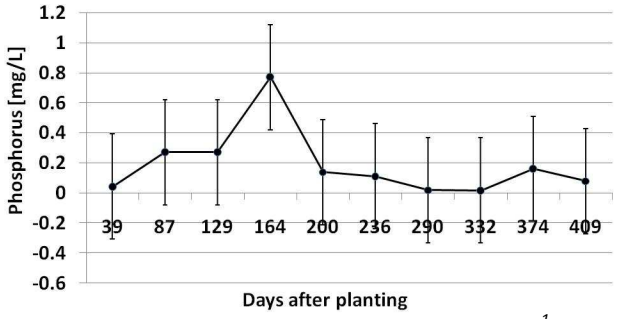


Figure 6.5. Phosphorus level in soil leachate [mg L^{-1}] in Florentine Valley field experiment in response to time of sampling 39, 87, 129, 164, 200, 236, 290, 332, 374 and 409 days after planting (mean across biochar and fertilizer treatments). Error bars indicate the LSD (0.35)(p≤0.05).

6.4. Discussion

Biochar increased K leachate content and when combined with fertilizer it influenced ammonium-N, nitrate-N and leachate acidity. Although counter-intuitive, in most cases observed changes did not follow the ones recorded in the soil. This effect might be related to the methodology of soil and soil leachate analyses. The analysis methods used for

analysing soil leachate were different from the ones applied to analyse soil samples and therefore could have shown the changes which were not detectable in the soil samples. Alternatively the design of Lysimeters and consequently the fact that soil leachate remained in the LIZs for an extended period of time before it was collected could have influenced the leachate nutritional content, particularly N, which might have changed its form. Similarly to biochar induced soil changes it might be assumed that unclear results were a consequence of low biochar rates and application method (Chapter 4 and 5) but also of site-soil-rainfall-biochar specifics, and perhaps site variability. The differences in the magnitude of soil/PM response to biochar application between pot and field experiments (Chapter 5) suggest that much clearer results could have been obtained when analysing pot experiment leachate.

The peak in ammonium-N, phosphorus and potassium concentration in time (164 DAP) is most likely connected with the sampling time. This sampling event was at the end of a very dry season and the amount of water in the LIZs at the time of sampling was estimated 100 times less than usual (Chapter 4), therefore it is surmised that higher concentration of these elements was a result of lower water availability due to low rainfall and water transpiration. Ideally the concentration would be converted to total amounts using the volume of water extracted from the LIZs. This was not possible due to the nature and design of the lysimeters.

The application of biochar increased pH when combined with F50 but resulted in more acidic leachate when F100 was applied. This effect is clearly related to fertilizer acidic nature but also possibly connected with biochar ability to adsorb H^+ and Al^{3+} to its surfaces, reducing concentration of these ions in the soil solution and therefore buffering a decrease in pH, a similar explanation proposed for PM pH changes in the pot experiment (Chan et al., 2007; DeLuca et al., 2006). Even though this effect was not observed when analysing field soil pH (Chapter 5) it is surmised that the methods used for analysing the leachate were more precise and revealed this result. Ideally, similar methods would be used for the soil and leachate tests. The increased leachate acidity when biochar was combined with full fertilization might be related to increased nitrification following biochar application to the soil. Stimulated nitrification after chars application has been reported by (Clough and Condron, 2010; DeLuca et al., 2009; DeLuca et al., 2006; Nelson et al., 2011) and concluded to be responsible for elevated nitrate-N and decreased ammonium-N soil levels in the pot experiment in this study. It is construed that when fertilizer was applied at the full rate

biochar doses were too low to adsorb all extra hydrogen and compensate for its elevated availability in the leachate. Significantly lower leachate pH at 164 DAP supports the explanation connected with very low water level and thus – the high concentration of all nutrients.

Nitrate concentrations in soil water decreased when biochar was applied at 20 t ha^{-1} with fertilizer applied at the full rate and B5 combined with F50. As proposed by Altland and Locke (2012) part of nitrate-N could have been adsorbed to positively charged sites on biochar surfaces, yet this process would have to be confirmed by biochar post-experiment particle analyses. Intuitively, decreased nitrate concentration in the soil solution leachate should be accompanied by increases in nitrate-N concentration in the soil. However this effect was not observed which can be explained either by different soil analysis methods or by increased plant NO_3^- uptake. *E. nitens* trees have been described as more likely to uptake nitrogen from the soil in the form of NH_4^+ rather than NO_3^- which makes the mechanism rather unlikely (Garnett and Smethurst, 1999). Apart from eucalypt seedlings the infestation of weeds in the field plantation was significant. It is therefore suspected that the elevated levels of nitrate-N in the soil could have been compensated by other species uptake, consequently not detectable in the leachate. Weed performance analysis would have to be performed to support or decline this hypothesis.

Biochar added at any rate increased the concentration of ammonium-N in the leachate when combined with full fertilizer, and at 20 t ha^{-1} a 3 fold increase was observed. Brunn et al. (2012) reported slight increases in ammonium-N soil solution leachate concentration and attributed this effect to reduced nitrification rates, following the addition of toxic compounds with biochars application. This explanation is unlikely in the case of this experiment as no signs of macadamia biochar toxicity were observed; this supported by the analysis of PAH levels (Chapter 3). The effect of higher ammonium-N concentration is possibly related to the high amount of NH_4^+ that was introduced to soil with fertilizer (Chapter 4) and increased soil porosity when char was incorporated. Biochar has been presented before as having the ability to increase the porosity of the soil, which in some cases results in better soil nutrients holding capacity (Major et al., 2009). In the other cases it might result in increased leaching as the soil acquires better aeration and water movement capabilities, so down-movement and in consequence leaching of some nutrients may be a result of that (Major et al., 2009; Tryon, 1948). The increasing concentration of ammonia under higher biochar rates was most likely the result of fertilizer application (high

NH_4^+ input) combined with a slight porosity increase, and the fact that such effect was observed only when full fertilizer was applied supports this explanation. The porosity of the soil was not analysed but high SSA as a result of micro-porosity was one of the main characteristics of macadamia biochar (Chapter 3).

Similarly to ammonium-N, leachate potassium levels increased in response to a combined influence of both fertilizer and biochar, and raised in response to most biochar application rates. Biochar used in this experiment was rich in potassium and the maximum dose applied per plant equaled 289.08 mg (Chapter 3). The effect of increased soil Colwell K in both pot experiment and field trial was explained by K ions release from macadamia biochar surfaces (Chapter 5) and is suggested as the most likely explanation of K concentration increase in collected leachate.

Of significance is that the fertilizer did not contain any potassium so leachate K concentration increase in response to fertilization must have been a result of more complex mechanisms. As the only source of potassium in this experiment was biochar, the application of fertilizer must have triggered potassium release from biochar surfaces. Such stimulation could have been an indirect result of high levels of ammonium-N introduced to the soil with fertilizer. Nitrification process in the soil is connected with increased concentration of the H^+ ions in the soil leachate. These however were concluded to be adsorbed in the biochar surfaces and connected with biochar availability to decrease soil pH (Chapter 5). Adsorption of H^+ ions to char surfaces is connected with other cations release from said surfaces and in the case of this experiment the released cations were K^+ and Na^+ (Chapter 5). Therefore the magnitude of ammonium-N application by the fertilizer is likely to be mirrored by K increase in the leachate.

Phosphorus concentration in the leachate did not change in response to either biochar or fertilizer application. Surface runoff is generally regarded as the main pathway for the loss of P from the soil as P has been classified as relatively immobile within the soil (Sims et al., 1998). This is because P is known to strongly interact with both organic and inorganic components resulting in low soil solution P with reduced risk of loss by leaching.

Fertilizer applied in the field contained phosphorus and its application increased P levels in the soil but not in the collected leachate. It appears that PO_4^{3-} from fertilizer must have been taken up by plants and some of P might have runoff. The lack of phosphorus changes can be explained by low P content of biochar and low biochar rates applied in the field

experiment, as well as P tendency to be subject to surface runoff rather than infiltration (Chapter 3 and 5).

6.5. Conclusions

Changes in soil leachate acidity were attributed to increased nitrification process in the soil and biochar abilities to adsorb H^+ ions resulting in increased pH when F50 was applied and more acidic leachate under full fertilizer treatment. Elevated ammonium-N was most likely related to high amounts of NH_4^+ introduced to the soil with fertilizer and increased soil porosity after biochar application while release of K^+ from char surfaces was surmised to be the reason for increases of this element in the leachate. The reasons for decreased nitrate-N leachate were not determined, however the mechanism for nitrate-N uptake by the weeds was proposed. The lack of P changes was attributed to low biochar P content and biochar application rates. In total little leached nutrients changes were detected, which is surmised a result of site variability, supported by large statistics LSD values. It is suspected that biochar application method as well as design of lysimeters played a crucial role in the limited biochar effect on nutrients leachate, however the lack of clear trends in the data due to biochar having had limited effect on soil leachate cannot be disregarded. The results of leachate analysis did not follow changes in the soil in most cases which was ascribed to different methods used to analyze these mediums and/or design of LIZs and leachate residence time before it was collected. Mechanisms attributed to leachate changes would have ideally be confirmed in a column leaching study where the full volume of treated soil and soil leachate can be analyzed.

7. EFFECTS OF BIOCHAR AND FERTILISER ON GROWTH RATE AND PLANT NUTRITION

7.1. Introduction

Different types of charred materials have varied effects on soil quality and plant agronomic performance when added as a soil amendment. The results are influenced by the geographical location of experimental trials, types and quality of soils to which biochar was applied and, the plant species analysed; both increases and decreases in final yield have been reported (Major et al., 2010; Van Zwieten et al., 2010a; Yamato et al., 2006; Zhang et al., 2011). Possible explanations for biochars positive effect include their potential to a) raise soil pH, b) increase soil porosity and therefore increase water holding capacity of the soil, and c) mediate nutrient exchange processes, or d) introduce nutrients to the growing media (Chen et al., 2010). Some of these processes are known to influence transformation of one of the world's most important supplemental elements, nitrogen. Nigussie et al. (2012) found increased N in lettuce leaf tissue following application of a maize stalk biochar. Similarly Van Zwieten et al. (2010) and Chan et al. (2008) reported the effect of biochar on N uptake, in wheat and radish (Chan et al., 2008; Nigussie et al., 2012; Winkler et al., 2009). In these studies, the increase in tissue N was attributed to a high concentration of N in the applied biochar and partly to the stimulation of nitrification in the soil. A meta-analysis performed by Biederman and Harpole (2013) demonstrates most biochars increase above ground yield and plant tissue K concentration across various crops. Increased K, also one of the most commonly applied crop nutrients, has been observed in response to the application of char with soybean (Major et al., 2010) and cowpea (Lehmann et al., 2003). For phosphorus, both a reduction and elevation of plant P concentrations have been reported following biochar application in radish and maize (Chan et al., 2007; Ma and Matsunaka, 2013b). Reductions in tissue concentrations have been attributed to growth dilution when high doses of fertiliser were applied while elevated concentrations have been attributed to phosphate ions release from biochar surface and a subsequent increase in uptake (Ma and Matsunaka, 2013a). From these studies it is clear that depending on the soil type, biochar traits and plant species, char application may affect plant tissue chemical composition and plant growth in a different manner.

While biochar induced leaf tissue changes and proposed mechanisms to explain these vary greatly across different species, in case of eucalyptus leaf tissue analyses, other sources of variation in chemical composition must be considered as well. Close et al. (2005) showed variation in leaf chemical content when whole plant leaves were analysed and suggested that variation between seedlings was higher than variation between treatments (Close et al., 2005). Similarly, Lambdon and Hassall (2005) suggested that changes in chemical composition of leaf tissue with age can be more variable than that between particular plants. These sources of variability must be considered when attributing eucalypt leaf tissue changes in these experiments to biochar related processes.

Changes in soil chemistry following biochar application to the potting mix used in this project revealed increased P, nitrate-N, K, Na and pH. In the field soil, K and Na concentrations were elevated when compared to the zero biochar treatment (Chapter 5). It was expected that these changes would be reflected in increased growth of the *E. nitens* seedlings and young trees, particularly under reduced fertiliser rates, resulting in greater height, better yield and increased leaf tissue nutrient concentration, under both glasshouse and field conditions. The investigation also aimed to determine if medium biochar application rates (10-20 t ha^{-1}) could supplement fertiliser used in both plantations and nurseries while still providing seedlings of equal quality as under full fertiliser application with no biochar addition.

7.2. Method

Two experiments were conducted to determine growth and leaf tissue chemical changes in *E. nitens* in response to biochar applied at up to 100 t ha^{-1}. A basic emergence study was performed on seedlings in a pot trial as an additional experiment. Details concerning data collection were presented in Chapter 4. In both pot and field experiments seedling height was measured on a regular basis and leaf tissue of the youngest fully expanded leaves (YFEL) analysed on four occasions. Total biomass, leaf number, leaf area, leaf water content and below ground biomass were recorded at 4 destructive harvests in a glasshouse pot experiment. The field trial design was a full factorial with 6 levels of biochar (0, 2, 5, 10, 15 and 20 t ha^{-1}), 3 levels of fertiliser (0, 50, 100% of the recommended rate), replicated 3 times, with each experimental unit containing 8 sample plants. The pot trial was an unbalanced factorial design of 8 biochar rates (0, 2, 5, 10, 20, 50 80 and 100 t ha^{-1}) with 3 replicates of 4 sample plants but no biochar control treatments (biochar combined with no

fertiliser) were included. Tables 7.1 and 7.2 summarise macadamia biochars effect on changes in leaf tissue concentrations. Details of the chemical analyses and experimental trials are presented in Chapter 4.

7.3. Results

The effect of biochar was more substantial in the pot experiment, where leaf tissue concentrations of P, K, Na and B all increased. A decrease in leaf tissue Ca was the only effect observed in response to biochar application in the field experiment. In most cases the results are presented as average values across time and fertiliser treatments to emphasize the trends rather than solitary changes.

7.3.1. Emergence

The emergence of the seedlings in the pot experiment was not influenced by either biochar or fertiliser applied at any rate.

7.3.2. Seedling growth

Growth of the eucalypt seedlings in the pot experiment was mostly unaffected by biochar application except, when measured as height. The major changes were observed in response to full fertilisation. In comparison to the controls (B0F50, B0F100), biochar application decreased seedling height when fertiliser was applied at half the commercial rate and, when applied at the highest biochar rates (B50-B100) under full fertilisation ($p \leq 0.05$). Seedling growth was not influenced by biochar application when measured as leaf area, leaf number, above ground biomass or root mass (data not presented).

In the field experiment, biochar application up to 20 t ha^{-1} did not affect seedling growth or the success of establishment (Fig 7.2).

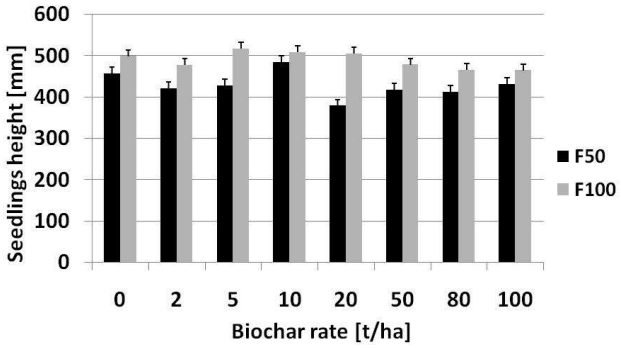


Figure 7.1. Mean height [mm] of E. nitens seedlings in the pot experiment in response to interaction between 8 biochar application rates (0-100 t ha^{-1}) and fertilisation at two levels (50 and 100% of the commercial rate)(mean across sampling times), error bars indicate LSD (15.77)(p≤0.05).

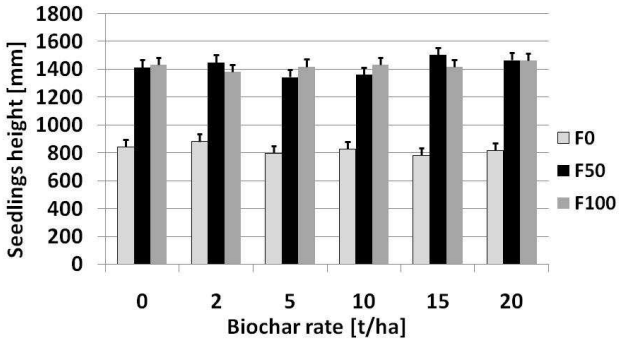


Figure 7.2. E. nitens tree height in Florentine Valley field experiment (mean values from 93-647 days after planting) in response to an interaction between 3 fertiliser rates (0% [F0], 50% [F50] and 100% [F100] of the optimum dose) and 6 biochar rates (0-20 t ha^{-1})(mean across sampling times). Error bars indicate the LSD (52.57)(p≤0.05).

While there was an overall trend for char to decrease plant height in the pot trial, and no response pattern in the field, two anomalies to this were noted (B10F50 in the pot experiment and B15F50 in the field experiment).

7.3.3. Changes in plant tissue elemental composition

A greater response was observed in the pot trial, with only one leaf tissue element concentration changing when biochar was applied in the field.

Of the major nutritional elements (N, P, K, S) only phosphorus and potassium tissue concentrations were influenced by biochar application, with the level of both nutrients increased. While biochar application increased nitrate-N in the potting mix this did not result in higher leaf tissue total N concentration (data not shown). The concentration of the minor nutritional element sodium and the trace element boron increased when biochar was applied, while that of calcium, magnesium and manganese decreased (pot experiment)(table 7.1 and 7.2).

Table 7.1. P values of the Eucalyptus nitens leaf tissue elemental composition changes in response to biochar (B), fertiliser (F) application and time (T) in the pot experiment. Significant values at P≤0.05, n.s. = not significant.

	B	F	T	B*F	B*F*T	B*T	F*T
N	n.s.	*≤0.001*	*≤0.001*	n.s.	n.s.	n.s.	*≤0.001*
P	*≤0.001*	n.s.	*≤0.001*	*0.018*	n.s.	*≤0.001*	*0.033*
K	*≤0.001*	n.s.	*≤0.001*	*≤0.001*	*0.019*	*≤0.001*	n.s.
Ca	*≤0.001*	n.s.	*≤0.001*	n.s.	n.s.	n.s.	*0.004*
Mg	*≤0.001*	*0.032*	*≤0.001*	n.s.	n.s.	n.s.	n.s.
S	n.s.	*≤0.001*	*≤0.001*	n.s.	n.s.	n.s.	n.s.
Na	*≤0.001*	*0.014*	*≤0.001*	n.s.	*0.013*	*≤0.001*	*0.013*
Mn	*≤0.001*	n.s.	*≤0.001*	n.s.	n.s.	n.s.	*≤0.001*
Fe	n.s.	*≤0.001*	*≤0.001*	*0.018*	n.s.	n.s.	*≤0.001*
Cu	n.s.	n.s.	*≤0.001*	n.s.	n.s.	n.s.	n.s.
B	*0.022*	*≤0.001*	*≤0.001*	n.s.	n.s.	n.s.	n.s.
Zn	n.s.	*0.016*	*≤0.001*	n.s.	*≤0.001*	n.s.	*0.004*

Table 7.2. P values of the Eucalyptus nitens leaf tissue elemental composition changes in response to biochar (B), fertiliser (F) application and time (T) in the field experiment. Significant values at P≤0.05, n.s. = not significant.

	B	F	T	B*F	B*F*T	B*T	F*T
N	n.s.	0.044	*≤0.001*	n.s.	n.s.	n.s.	0.002
P	n.s.	*≤0.001*	*≤0.001*	n.s.	n.s.	n.s.	n.s.
K	n.s.	*≤0.001*	*≤0.001*	n.s.	n.s.	n.s.	*≤0.001*
Ca	0.016	n.s.	*≤0.001*	n.s.	n.s.	n.s.	n.s.
Mg	n.s.	n.s.	*≤0.001*	n.s.	n.s.	n.s.	n.s.
S	n.s.	0.009	*≤0.001*	n.s.	n.s.	n.s.	*≤0.001*
Na	n.s.	n.s.	*≤0.001*	n.s.	n.s.	n.s.	n.s.
Mn	n.s.	*≤0.001*	*≤0.001*	n.s.	n.s.	n.s.	n.s.
Fe	n.s.	n.s.	*≤0.001*	n.s.	n.s.	n.s.	0.038
Cu	n.s.	*≤0.001*	*≤0.001*	n.s.	n.s.	n.s.	*≤0.001*
B	n.s.	*≤0.001*	*≤0.001*	n.s.	n.s.	n.s.	0.03
Zn	n.s.	*≤0.001*	*≤0.001*	n.s.	n.s.	n.s.	0.04

Phosphorus in pot trial leaf tissue

Incorporation of phosphorus into the leaf tissue increased at the highest rates of biochar application (*p≤0.001*), with this response greatest where fertiliser was applied at half the full rate (*p=0.018*; B80-B100)(Figure 7.3. A). The level of plant leaf phosphorus decreased over time (*p≤0.001*)(Figure 7.3. B).

A **B**

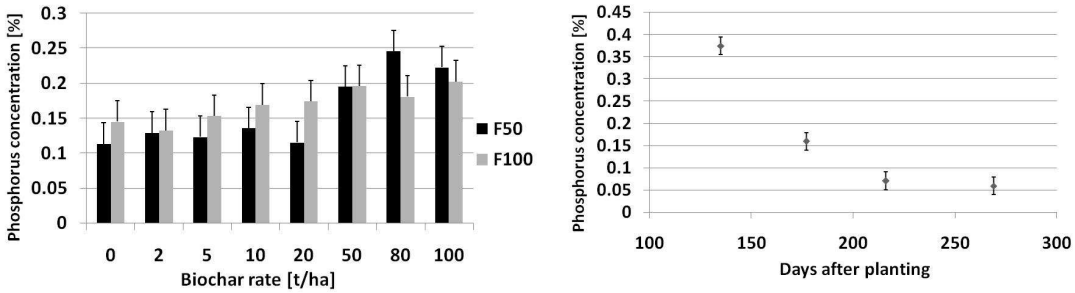


Figure 7.3. Phosphorus concentration [%] in leaf tissue of Eucalyptus nitens seedlings in the pot trial in response to: (A) fertilisation at two levels (50% and 100% of the commercial rate) in partial factorial combination with 8 biochar application rates (0-100 t ha^{-1})(average data from 4 harvests: 135, 177, 219 and 269 days after planting, (B) Days after planting, at 135, 177, 216 and 269, (mean across biochar and fertiliser treatments). Error bars indicate the LSD (A- 0.03, B-0.02)(p≤0.05).

Potassium in the pot trial leaf tissue

Leaf potassium increased when biochar was applied (*p≤0.001*) with the magnitude determined by the rate at which fertiliser was added and the time that had elapsed since application (*p*=0.003). Potassium leaf concentrations were greater than the zero biochar controls (B0F50, B0F100) at biochar rates of 50 to 100 t ha^{-1}, with these higher rates increasing the response at half fertilisation; this response was similar to phosphorus (Figure 7.4. A and B). Leaf tissue K concentration was positively correlated to Colwell K in the potting mix (Spearman's concentration *rho*=0.501, *p ≤0.05*)(Figure 7.4.C)

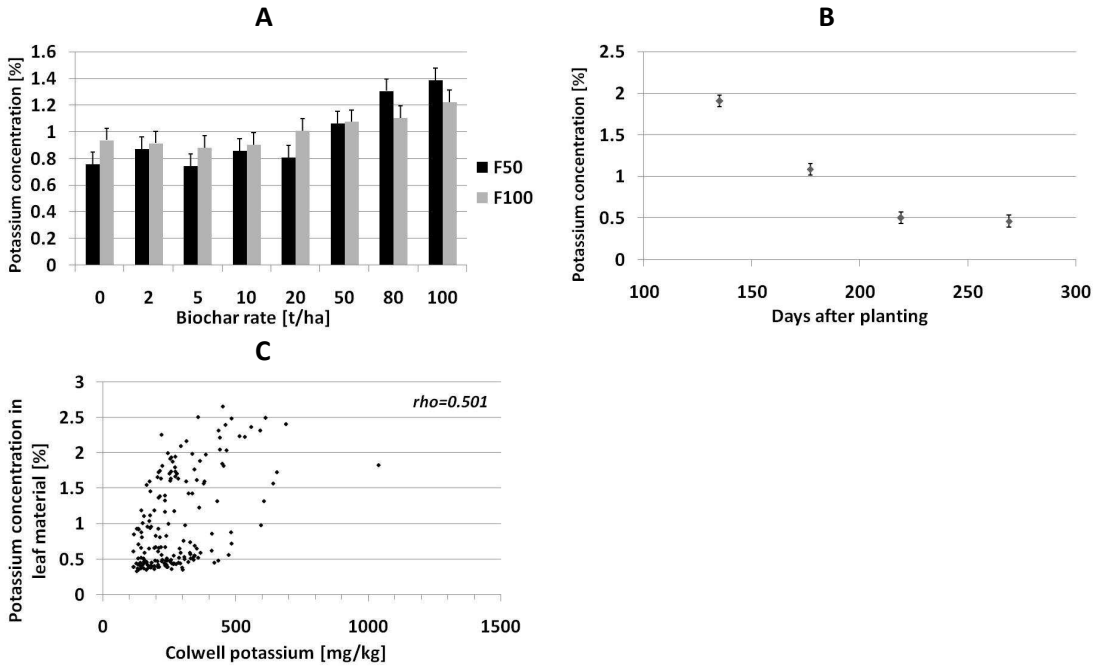


Figure 7.4. Potassium concentration [%] in leaf tissue of Eucalyptus nitens seedlings in the pot trial in response to: (A) fertilisation at two levels (50% and 100% of the commercial rate) in partial factorial combination with 8 biochar application rates (0-100 t ha^{-1})(means across sampling times), (B) Days after planting, 135, 177, 219 and 269, (mean across biochar and fertiliser treatments). Error bars indicate the LSD (p≤0.05). (C)Spearman's correlation between Colwell potassium level [mg kg^{-1}] in the potting mix and total potassium leaf concentration [%] in E. nitens seedlings in the pot experiment (A- 0.09, B- 0.07)(p≤0.05).

Calcium and Magnesium in the pot trial leaf tissue

Calcium in the leaf tissue decreased in response to biochar application of 10 t ha^{-1} or more (*p≤0.001*)(Figure 7.5.A). Magnesium concentration was also lowered under high biochar treatments, namely B80 and B100 (*p≤0.001*)(Figure 7.5.B). Both Mg and Ca decreased in time (*p≤0.001*)(data not presented).

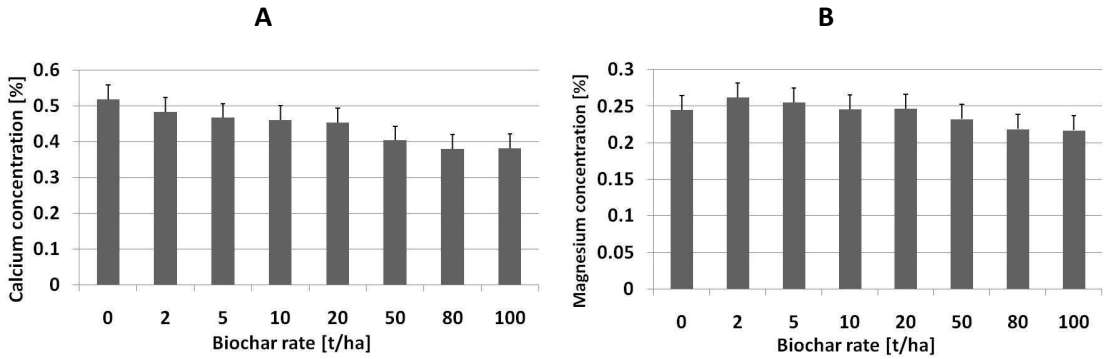


Figure 7.5. (A)Calcium and (B)Magnesium concentrations [%] in leaf tissue of Eucalyptus nitens seedlings in the pot experiment in response to 8 biochar application rates (0-100 t ha^{-1}) (mean across sampling times and fertiliser treatments). Error bars indicate the LSD (A-0.04, B- 0.02)(p≤0.05).

Micronutrients in the pot trial leaf tissue

Sodium

Sodium concentration responded to biochar application, increasing under higher biochar treatments (B50-B100)(*p≤0.001*)(Figure 7.6.A). The Na level decreased until 219 DAP and did not change after that (Figure 7.6.B). The level of Na was lower under F100 in comparison to F50, but this effect was noticed only at the beginning of the experiment (135 DAP)(Figure 7.6.B).

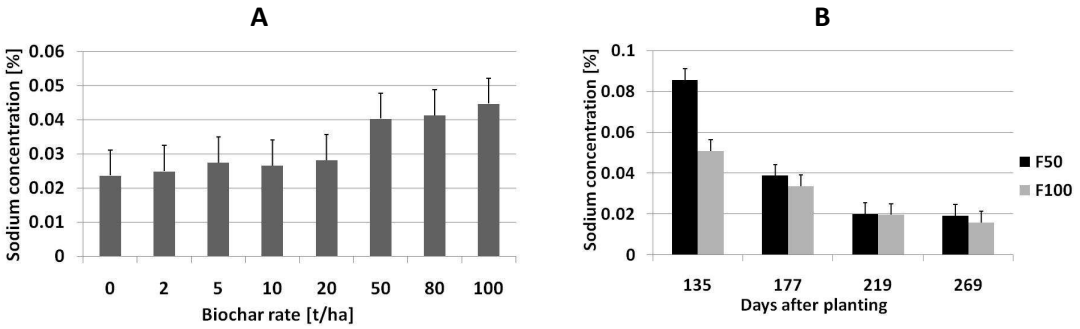


Figure 7.6. Sodium concentrations [mg kg^{-1}] in leaf tissue of Eucalyptus nitens seedlings in response to (A) 8 biochar application rates (0-100 t ha^{-1}) in the pot experiment (mean across sampling times and fertiliser treatments), (B) fertilisation (50% and 100% of a commercial dose) in time (135, 177, 216 and 269 DAP) in pot experiment (means across biochar rates). Error bars indicate the LSD (A- 0.008, B-0.006)(p≤0.05).

Manganese

The concentration of plant Mn decreased in response to medium and high biochar doses (B20-B100)(*p≤0.001*) but within each application rate, the concentrations increased over time (rate of decay analysis)(Figure.7.7. A and B).

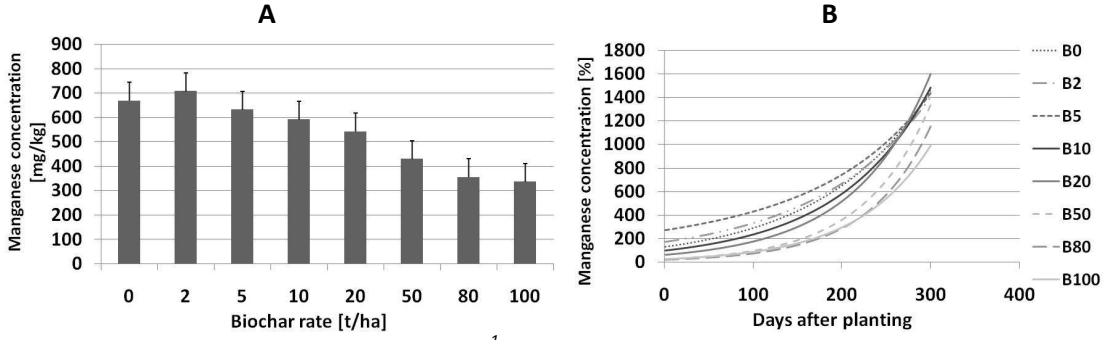


Figure 7.7. Manganese concentration [mg kg^{-1}] in leaf tissue of Eucalyptus nitens seedlings in the pot experiment in response to (A) 8 biochar application rates (0-100 t ha^{-1}) (mean across sampling times and fertiliser treatments) and (B) Rate of decay under biochar treatments (B0-B100 – 0-100 t ha^{-1}). Error bars indicate the LSD (75.45)(p≤0.05).

Boron

Boron concentration in plant material of the pot experiment only increased under B50 in comparison to control treatment (p=0.022) (Figure 7.8. A). A higher concentration of boron was also found under the half fertiliser treatment rather than at the full rate and, similar to manganese, increased over time (data not presented)(Figure 7.8.B).

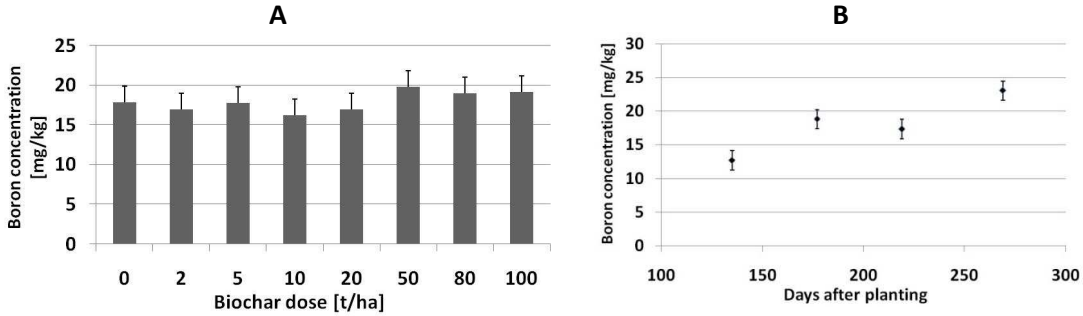


Figure 7.8. Boron concentration [mg kg^{-1}] in leaf tissue of Eucalyptus nitens seedlings in the pot experiment in response to (A) 8 biochar application rates (0-100 t ha^{-1}) (mean across sampling times and fertiliser treatments), (B) Days after planting (135, 177, 216 and 269 DAP) (mean across biochar and fertiliser treatments). Error bars indicate the LSD (A-2.02, B-1.44)(p≤0.05).

Calcium in the field trial leaf tissue

Biochar applied at any rate decreased calcium concentration in the plant tissue (*p=0.016*)(Figure 7.9.A), with a comparable response across all rates. Contrary to the pot trial, leaf tissue calcium in the field increased with time (*p≤0.001*)(Figure 7.9.B).

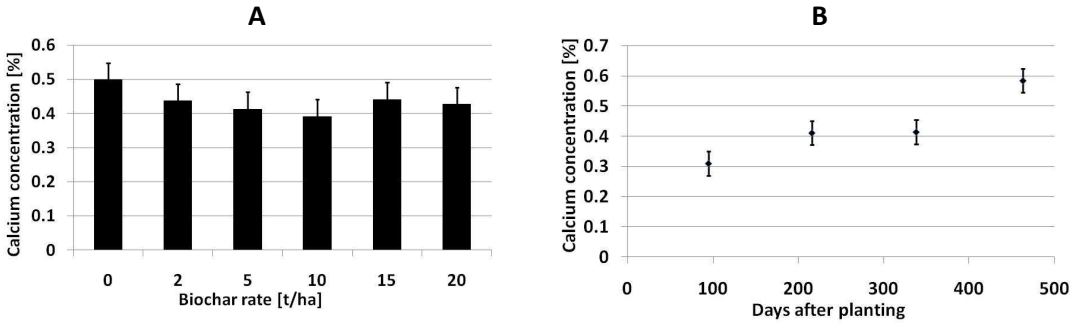


Figure 7.9. Calcium concentrations [%] in leaf tissue of Eucalyptus nitens trees in Florentine Valley field experiment in response to (A) 8 biochar application rates (0-20 t ha^{-1}) (mean across sampling times and fertiliser treatments) and (B) Days after planting (95, 216, 338 and 463 DAP) (mean across biochar and fertiliser treatments). Error bars indicate the LSD (A- 0.05, B- 0.04) (p≤0.05).

7.4. Discussion

Biochars are known to change the nutrient content of plant tissue, and this effect has been attributed to improved soil physical and nutritional characteristics and a subsequent

increased uptake by plants (Major et al., 2010; Nigussie et al., 2012; Yamato et al., 2006) following biochar application. Variations in nutrient concentration in leaf material have been reported both to result in increased crop yield and, to have had no effect on a plants agronomic performance (Blackwell et al., 2010; Ma and Matsunaka, 2013b; Schulz et al., 2013). In this pot experiment phosphorus, potassium, boron and sodium leaf concentration increased after biochar application while calcium, magnesium and manganese concentrations decreased. Under field conditions biochar decreased leaf calcium only. Both in the pot and field experiments the analysis of *E. nitens* growth revealed some biochar and fertiliser effects, however in most cases the changes were limited to 1-4 biochar rates and revealed clear trends only in case of some nutrients concentrations.

More changes were observed in the pot experiment than under field conditions and this is most likely due to methodology. The rates of biochar applied in the pot experiment were higher than in the field trial, and most of the observed changes in PM occurred under the higher biochar doses (B50-B100). In the field biochar was applied within a limited area and depth around the plants, and the eucalypt roots would have outgrown the treated soil volume, where biochar potentially influenced nutrient uptake. The concurrent effect of these factors may have resulted in limited nutritional changes under field conditions, but could not have affected the response in the pot experiment seedlings.

A limited collection of work has reported both rises in and, inhibition of germination, this varying greatly and dependent on the soil type and pyrolysis conditions associated with the biochars production (Kookana, 2010). Some experimental outcomes indicate that biochars may contain phytotoxic compounds that can decrease plant germination and growth (Rogovska et al., 2012). Paper mill waste biochar added at 10 kg ha^{-1} has been shown to improve wheat germination but not that of radish or soybean on a Ferrosol soil in NSW, Australia, however the same char added to a Calcarosol had no influence on the germination of all three species (Van Zwieten et al., 2010a). On the contrary, negative results on germination have been observed by Kwapinski et al. (2010) who showed that *Miscanthus* biochar made at 400 °C inhibited the growth of maize (*Zea mays* L.). The application of the macadamia shell biochar used in this study did not influence seedlings emergence and given the high rates used, indicates that this char did not contain phytoxic compounds. Although increased concentrations of P and K were observed in plant tissues early in the experiment, these interactions between this char and the growing media used did not provide any measured advantage to the success of seed germination.

Biochar application in the pot experiment increased plant K uptake, and this phenomena following the application of charcoal has been reported for soybean (Major et al., 2010) and cowpea (Lehmann et al., 2003), though the mechanisms of this effect have not been fully understood. In the pot trial, increased available potassium in the PM correlated (Spearman's correlation) with increases in leaf potassium. Consequently, it would seem increased availability of K in the soil solution through release from biochar was the main mechanism leading to changes in the leaf tissue. Both chemical and SEM-EDS analyses showed a high concentration of potassium in the macadamia biochar (Chapter 3), thus K release into the potting mix and a consequent increase in leaf tissue under high char application rates appears a reasonable explanation. This effect was however not observed in the field experiment, despite soil exchangeable K levels increasing, which is most likely a result of roots outgrowing the biochar application region, discussed before (Chapter 5). Cation release from biochar surfaces might also partly explain the increased uptake of Na and B by the plants.

Similarly to potassium, sodium leaf tissue concentration in the pot experiment increased under high biochar rates. Sodium was introduced to the potting mix at 236.8 mg kg^{-1} PM when biochar was applied at the rate of 100 t ha^{-1} with SEM-EDS analysis revealing a large amount of Na in various compounds on the biochar surfaces (Chapter 3). The increase in leaf tissue Na suggests that as with K, increased sodium availability in the PM due to release from biochar surfaces increased availability and elevated the leaf tissue content. Analysis of the rate of decay in the field experiment revealed a significant difference under one of the treatments (B5) while no changes were observed for other biochar rates. An analysis of the *ln* transformed exponential model revealed a poor fit (R^2=0.282) which suggests that the rate of decay model did not represent this particular data set well, and that elevated Na concentration of the leaves was determined by initial quantities of sodium introduced with the biochar, rather than biochar induced transformations.

In the same way, the initial quantities of boron introduced to the soil with biochar and subsequently increased availability to the root systems is the most likely reason for increased leaf concentrations of this element. Even though the quantity of boron applied to the soil with biochar was not large, a maximum of approximately 1 mg kg^{-1} (B100), this could have been enough to increase plant tissue B concentration (Sakya et al., 2002), especially given the increase was not large and observed only under one biochar rate. An

uptake calculation based on the total plant weight and total tissue boron concentration would have to be carried out to support this explanation.

The increase in leaf boron could however have been driven simultaneously by a separate mechanism. Similarly to other nutrients, much of the soil available B lies within the root zone where mycorrhizas are common (Sakya et al., 2002). Different types of biochar have been reported to increase mycorrhizal activity in the soil (Solaiman et al., 2010; Warnock et al., 2007) and this activity might be connected with increased boron uptake following biochar application. Mycorrhizas changing the B uptake capacity of other genus species, silver birch (*Betula pendula*)(Lehto et al., 2004) have been observed. Similar effect would have to be explored in *Myrtaceae* family to determine if there is a relationship between mycorrhiza, boron uptake and eucalypt. The fact that boron increase was relatively small and observed only under B50 implies that there were no clear trends or basis for further speculations.

For the other elements analyzed, net availability in the growing mix did not explain changes in leaf tissue. For these elements other mechanisms such as ionic charge may have played a role. Concentrations of the divalent calcium and magnesium decreased in the pot experiment leaf tissue, and in the field, leaf Ca was diminished. To maintain balanced charge following the release of K, Na and B, other cations such as Mg and Ca and Mn could have been adsorbed to char surfaces to compensate for the positively charged ions release (Chapter 5). Additionally, various biochars have been reported to adsorb Mg and Ca through electro-static attraction to their negatively charged surfaces (Lehmann et al., 2009). The results presented in this study showed decreased levels of exchangeable Mg and Ca in the potting mix (Chapter 5). The decrease of leaf tissue Ca and Mg concentration suggests that plant uptake could have mirrored the decreased growing mediums availability following biochar application. While the results of both experiments support this conclusion, as with boron, other mechanisms cannot be discarded. If plants have abundant supplies of potassium at their disposal, their magnesium content will be relatively low (Bear, 1965; White, 2012), this mechanism postulated to result from a reduction in net translocation of Mg rather than decreased uptake of Mg by root cells (Sigel and Sigel, 1990). As soil Colwell K increased under high biochar doses this mechanism may well have lowered leaf Mg concentration, root cells analyses would be required to confirm that.

The decrease in Mn leaf concentration in response to biochar application has not been reported before, and again, may be a result of more than one mechanism. Organic soils are more likely to show manganese deficiencies as this metal ion is readily chelated by organic molecules, making it less available (Broadley et al., 2012; Hong et al., 2010). Biochar has been reported to be an excellent adsorber of organic molecules through the chelation of various metal ions (Al^{3+}, Fe^{3+}, Ca^{2+})(DeLuca et al., 2009; Zimmerman et al., 2011). In this experiment, the potting mix contained large amounts of organic matter and application of biochar could have resulted in increased chelation on biochar surfaces, decreasing availability, and consequently leaf Mn concentration. This explanation fits the observations of the field experiment, where organic matter soil content was lower in comparison to potting mix; here the effect of Mn decrease was not observed. Detailed post-application biochar analyses and paired experiments in the controlled environment would have to be carried out to confirm this hypothesis.

Manganese not chelated would have been present as an exchangeable fraction of the soil solution in the same way as other cationic nutrients (Peverill et al., 1999) and as with other ions, this may have influenced availability. Manganese, being usually a divalent cation is likely to behave in this case similarly to Ca and Mg (Hong et al., 2010; White, 2012). The decreased Mn concentration under moderate and high doses of biochar may therefore be connected with both chelation and biochars capacity to sorb Mn cations to its surface, therefore making it less available for plant uptake.

As with other nutrients, the increased P concentration in plant material may have resulted from elevated PO_4^{3-} availability in the potting mix following biochar application. This has previously been attributed to adsorption of Al^{3+} and Fe^{2+} cations at the interface of the biochar surface, subsequently limiting their ability to immobilize phosphate (Chapter 5). On the other hand, phosphate uptake by plants is stimulated by mycorrhizal fungi (Schachtman et al., 1998). Since various chars have been reported to stimulate mycorrhizal root colonialization, it can be hypothesised that the increased leaf tissue P concentration is partly caused by this effect. Although biochar increased leaf P levels, its application did not influence above or below ground seedling biomass, nor the leaf area or seedling growth. This effect is possibly explained by plan cell phosphorus storage. Veneklaas et al. (2012) suggested that the inorganic orthophosphate form of P may be stored in vacuoles by plants to buffer changes of P concentration in cytoplasm (Schachtman et al., 1998). Vacuoles are not responsible for cell expansion and it is possible that higher levels of phosphorus in leaf

tissue were buffered by vacuoles. Detailed leaf tissue microscopy analyses would add to the understanding of this effect.

The combination of high biochar rates (B80-B100) and full fertiliser resulting in lower P and K plant concentrations when compared to F50, suggests that there must have been another factor mitigating the uptake of these ions. It is counter-intuitive that at the same rate of char application, P and K concentration would be greater at F50 than at F100. The pattern in P and K leaf accumulation did not reflect that of the soil at high biochar rates, which suggests that char application could have influenced uptake mechanisms at the root soil interface. Decreased uptake in both cases could be related to concentrations above sufficiency for these nutrients in plant material and the risk of toxicity. This however seems unlikely as K and P leaf concentrations were optimal or close to optimum according to published literature (Reuter and Robinson, 1997). This was observed during the whole experiment and no signs of limited seedling growth or toxicity were observed. Chan et al. (2007) reported lower P concentrations in radish plant tissue in the presence of N fertiliser when compared to nil fertiliser treatments, relating this to P dilution by the larger dry mass (DM) production (growth dilution). This explanation can be disregarded in the experiment presented here as the differences in DM production by seedlings under different biochar treatments were not significant ($p>0.05$) at any time. More detailed analysis focused on anionic P and cationic K uptake would be required to determine a mechanism responsible for these changes.

In both experiments certain doses of biochar combined with halved fertilisation resulted in similar or greater seedlings height as under full fertiliser treatment with no biochar added. However, there were no clear trends and this was only noticed with B15 in the field experiment and B10 in the pot trial, which does not allow drawing any definite conclusions. Even though more nutritional changes were observed in the pot trial they were obviously not mitigating the reduction of fertiliser as effectively as in the field experiment. It suggests that an unaccounted factor was at work affecting seedlings growth. Nevertheless, observed similarities in height suggests lower fertiliser doses can be used in forest plantation establishment while still sustaining seedlings quality, providing more detailed experiments are carried out to present clear trends in both leaf nutrition and seedlings growth.

In general the limited leaf tissue nutrient content changes in *E. nitens* following biochar application are most likely a result of direct nutrient release and adsorption to biochar

surfaces. This explanation is supported by the fact that the Rate of Decay analysis did not reveal significant changes in the nutrient leaf concentration. Observed results suggest that biochar has a potential to assist forest plantations nutritional management and productivity but more experimental results are required to determine the exact mechanisms of biochar effects and the possible changes in forestry procedures.

7.5. Conclusions

The results of both pot and field experiments show that the addition of macadamia biochar to growing mix together with fertiliser affected seedlings and young trees leaf chemical composition. Biochar did not increase plants growth when added to growing medium at any dose, with the exception of two isolated treatments. This effect did not reveal any clear trends but suggests it may be possible to reduce commercial fertiliser rates while maintaining seedlings agronomic quality if further experiments are established to investigate biochar-eucalypt productivity pattern. Increased plant K, Na and B uptake was most likely related to ion release from biochar surfaces and increased soil availability and plant uptake of these ions. Lower concentration of eucalypt leaf tissue Mg, Ca and Mn was attributed to decreased soil availability of these cations due to biochar sorption properties, however in both increase and decrease of nutrient concentration in leaf tissue further experimental work would be required to support the above explanations. Elevated concentration of tissue P was related to increased phosphate availability, resulting from different mechanisms, but did not at any point increase plant growth. Chemical changes in leaf tissue are mainly attributed to elevated or decreased availability of particular cations in the growing mediums, however, alternative mechanisms in case of P, B, Mn and Mg were proposed as being partly responsible for the chemical changes. The limited response to biochar application in the field was related to lower biochar rates, application method and soil type. Biochar post experimental analyses and further experimental work would allow establishing greater understanding of discussed mechanisms.

8. ECONOMIC ANALYSIS OF BIOCHAR SYSTEM IMPLEMENTATION ON PLANTATION FORESTRY

8.1. Introduction

The development of forestry plantations on State owned land in Tasmania commenced in the early twentieth century with *Pinus radiata* (Don, 1836). The goal was to secure a source of softwood timber for doors, windows and other building uses, as local hardwoods were considered unsuitable for these purposes and large quantities of softwood timber were being imported into the State (Elliot, 2011). The first hardwood plantations were established in the late 1930's, mainly in the north-west of the State. Most of these were small *Eucalyptus* plantings within patches of native forest as a trial to evaluate species performance. Today, there are over 100,000 hectares of plantations on State forest land in Tasmania, with approximately 53,000 ha of soft woods and 56,000 ha of hardwoods. These plantations are used to supply timber to local and interstate industries. The current hardwood plantation estate comprises two main species: *E. nitens* (85%) and *E. globulus* (15%).

The post harvest residues from eucalyptus plantations are currently retained or burned on-site. An alternative use of these residues, namely biochar production, will be investigated in this chapter. This will be done on the basis of presenting a financial model, built to estimate costs and benefits connected with introducing biochar systems into plantation forestry in Tasmania. The model described in this thesis assumes using post-harvest residues to produce biochar on-site and different methods of dealing with the product e.g. immediate application to the soil, storage, use in nurseries or sale. The background and rationale for model implementation are presented in the next sections, while the detailed assumptions of the model are discussed in section 9.4. The results of the model are then presented and discussed. The whole cycle of plantation production and insight into current knowledge about char application to forestry systems will be addressed, with an emphasis in the residue management, and this necessitates a brief description of standard (current) practices and assessment of costs of them, as a basis on which to consider changes on the introduction of biochar into the system as well.

8.2. Wood char for forestry plantations, examples from literature

Biochar has been presented earlier (Chapter 2) as a potential soil conditioner, improving both soil nutrient and water retention leading to increased productivity. It has also been suggested as a practical means to manage nutrition of the soil and a potential solution for decreasing fertiliser input for forestry plantations (Chapters 5, 6, 7). Despite the dominant use of biochar in agriculture only few studies have investigated its utilisation in forestry and other tree-based systems (Stavi, 2013). There are however, a number of papers that discuss the effects of wildfires on forest soils and can be used as indicators for biochar influence on forest soils (Bell, 1994; DeLuca et al., 2006). Although this topic has been investigated in Chapter 2 of this thesis, some more examples of char application in forestry systems are presented in Table 8.1. Increased shoot-to-root ratio in Silver birch (*Betula pendula*) and Scots Pine (*Pinus sylvestris*) as an effect of charcoal from wildfires mixed with substrates from microhabitats has been reported in a glasshouse study in north Sweden (Wardle et al., 1998). De Luca et al. (DeLuca et al., 2006) reported increased nitrification rates in the soil after application of wildfire-produced charcoal mixed with ammonium salts. The results differ significantly and are dependent on multiple factors, such as soil pH, texture, climate and char specifics. The summary of these and other results are presented in table 8.1.

Table 8.1. A summary of the results of studies performed on wildfire-produced charcoal influence on the soil (Stavi, 2013)

LOCATION	CLIMATE	SOIL TYPE	TREE SPECIES	RESULT	EFFECT ON TREES	SOURCE
Sweden	cold	Various	Silver birch, Scots pine	charcoal stimulated microbial biomass in some cases and affected litter decomposition	Increased shoot-to-root ratio, greater growth of silver birch	(Wardle et al., 1998)
USA (Montana)	temperate	Typic Dystrocryepts	Ponderosa Pine	Charcoal mixed with ammonium increased nitrification rate	decreased solution concentrations of plant phenolics	(DeLuca et al. 2006)
USA (Montana)	temperate	Lithic Dystrustept	Ponderosa pine	Charcoal increased sorbing of litter-phenols and augmented litter nitrification		(MacKenzie and DeLuca, 2006)
Sweden	cold	?	Scots pine	Charcoal mixed with humus increased mass loss of humus through either respiration or leaching of soluble compounds		(Wardle et al., 2008)
USA (Idaho)	temperate	?	Ponderosa pine, douglas-fir	Charcoal mixed in mineral soils augmented abundance of ammonia-oxidizing bacteria and increased nitrification rates		(Ball et al., 2010)
Switzerland	temperate	Cambisol	various	Charcoal mixed with organic materials in mineral soil did not increase decomposition rate of litter		(Abiven and Andreoli, 2011)
Russia	cold	Brown taiga	Gmelin larch	Charcoal increased soil pH, water content and available P	increased germination of Scots Pine	(Makoto et al., 2011)

Although biochar has been shown earlier in this thesis to be not a significant factor in improving *Eucalyptus nitens* growth, its potential to reduce fertiliser inputs in a plantation

remains an important characteristic. The productivity of the young forestry plantations (expressed as seedling height, total biomass and stem diameter) remained at the same level under full fertiliser treatment with no biochar added, as the treatments receiving combined fertiliser and biochar application.

Similarly, there is a potential to use biochar produced from forestry residues for different purposes. For example it might be returned to the site in order to condition the soil, improve water retention and possibly decrease the rates of required fertilisation. Some biochar can be used in forest nurseries as a growing medium/additive to growing medium for seedling production and/or replace the organic matter content (usually bark) used currently in the forest nurseries growing mixes. Biochar can also be stored for an extended period as well as sold immediately after production. However, the biochar market is still in the development stage and there may not be many wholesalers in operation.

8.3. Current forestry management practices and costs

There are approximately 56,000 ha hardwood plantations on Tasmanian State forest (Figure 8.1). The typical plantation is being managed for 25 years to produce high value pruned logs for industry. Within the next five years (2014 – 2019) it is expected that an average area of 2000 hectares will be harvested and replanted each year. Approximately 75% of the replanting will occur in the north of the state (FT, 2013). Eucalypt plantations are managed primarily for the production of high-value pruned logs for industry and export; however, unpruned saw logs, peelers, poles, posts and pulp are also produced. The standard management unit is the plantation coupe and management practices are adjusted according to conditions on the coupe, such as soil type and fertility, location and terrain, species and silviculture regime.

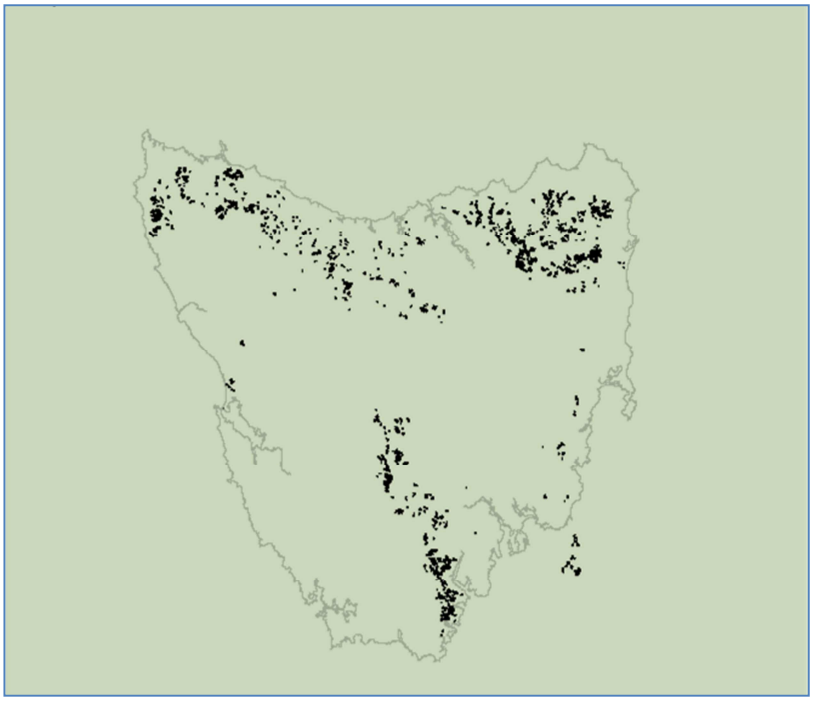


Figure 8.1. Map of forestry plantations on State forest land, Tasmania, black areas represent location of plantations (FT database, 2010-2013).

Plantations have been established on sites that were previously native forests (ex-native forest), on cleared agricultural land (ex-agriculture), or following a previous plantation crop of the same or different species (second rotation, 2R). Replacement of native forests by plantations (native forest conversion) is no longer practiced. Typical maintenance procedures to prepare the ground for plantation establishment include: harvesting and clearing the slash (harvest residues) from previous plantation rotation, soil cultivation and chemical application (i.e. herbicides and insecticides).

Clearing the harvest residues on a coupe can be done by a number of methods depending on the volume and size of residues, the soil type and quality, location of the coupe and slope. Typically, the residues are windrowed by gathering all the course woody residues into large rows with an inter row distance ranging from 15-60 m. The large windrows are normally associated with ex-native forest sites where large volumes of residues (not utilised by industry) needed to be arranged on-site in uniform rows to allow machinery access for establishing the plantation crop. These windrows were usually burnt to reduce their size and allow seedlings to be planted within them. Now, when second rotation plantations are established on sites that have these existing large windrows, the harvest residues are usually re-stacked in the old windrows, and they are crushed and burnt again. This reduces the size of the windrows even further. On sites that do not have these large windrows, it is a standard practice to arrange the harvest residue into small windrows spaced 10 – 15 m

apart and these are left unburnt on-site and gradually decompose. Burning is avoided where possible in order to conserve organic matter.

Soil cultivation is traditionally done by a mound cultivator, pulled behind a tractor which creates continuous mounds on top of which the seedlings are planted (Figure 8.2). There is however a new method being implemented now. The method utilises spot cultivation which is combined with waste transport to the existing windrows and formation of waste wood heaps in between windrows (Figure 8.3). The waste heaps might be burnt in order to clear the site and condition soil with ash and burnt organic matter. Burning across the site (broadcasting) is not a preferred method in the current practices.

Prior to planting the ground is usually sprayed with herbicide to avoid extensive competition from weeds. Spraying is done either by ground-based machines or aerially and might be repeated at later stages if required.

Figure 8.2. Bracke mound cultivator used in forest plantations (FT database, 2010-2013).

Figure 8.3. Bandicoot spot cultivator used in forest plantations (FT database, 2010-2013).

Seedlings are grown in the nursery until they are about six months old then they are transported to the coupes for planting in spring (Sept – Oct) using the Pottiputki forestry tool (described in Chapter 4). Planting is followed by manual fertilisation (spot fertilisation) 4 – 6 weeks later, with the application rate determined by the soil fertility and rotation. A new spot cultivator however, might be equipped with a mounting suitable for automatic fertilisation.

Management of plantation after the establishment (2 years) includes operations such as additional fertilising where needed, insect and browsing monitoring and control, refill planting (if required), pruning and thinning. The production of high-value pruned logs

involves high pruning to 6.4 m between age 3 to 5 years followed by production thinning, typically between age 8 to 12 years. The timing and intensity of these operations is adjusted to local conditions and requirements. The estimated costs of plantation establishment and management during the 20 – 25 year rotation are presented in Table 8.2, which also provides an indication of practices, and therefore costs, that are likely to change in a system using biochar. Costs associated with these items are reassessed later in this chapter.

Table 8.2. List of major plantation forestry establishment and maintenance operations and items generating costs in Tasmania (source: Forestry Tasmania staff personal communication). Star indicates the cost groups that are likely to change under proposed biochar scenario.

ITEM/SERVICE	COST [$] PER UNIT	COST [$] PER HA
Seedling✶	0.15-0.20/seedling	190
Planting	160/ha	160
Herbicide spraying	100/ha	100
Site prep- windrowing ✶	800/ha	800
Site prep- cultivation ✶	500/ha/mean from spot and mound	700
Fertilisation ✶	80-120/ha labour	100
Fertiliser ✶	[2]220/ha	220
Browsing monitoring	48/hour	25
Insect monitoring	46/hour	10
Shooting	48.43/hour	200
Maintenance costs	40/ha/4 years	200
Pruning	1.70/tree/lift (3 lifts)	1530
ADDITIONAL OPERATIONS		
[3]Site prep- burning ✶	100/ha	100
[4]Post-plant herbicide spraying ✶	102/ha	102
[5] Infill planting costs ✶	36/hour	80
TOTAL COST OF ESTABLISHING AND MANAGING PLANTATION PER HECTARE **(Plus additional costs of $282/ha)**		$4229

[2]200g of Di-Ammonium Phosphate per seedling

[3]Burning is not the preferred method of managing harvest slash because the aim is to conserve organic matter to protect the productive capacity of each site after harvest. However, where slash loads are very heavy and impede operations broadcast burning may be warranted; or where old windrows are to be re-burnt by re-packing with harvest slash, then windrow burning may be carried out. Of the 47 coupes planted over the 3 years site preparation operations that included burning occurred in approx. 70% of the coupes.

[4]Post plant herbicide spraying is done where it is required and currently occurs on 9% of plantations on average.

[5]Re-planting is only done if 85% or more of the planted seedlings do not survive the first 6 months of growth. During the last years (2011-2014) replanting was done only on 3% of all the plantations in Tasmania.

8.3.1. *Residue management*

Currently residues from plantation harvest are used in two ways. They are either stacked within the existing windrows and burnt onsite to produce charcoal and ash which is considered to condition the soil or, they are left on site (without burning) to decay and contribute to the soil organic matter. These two methods and the actual residue volume dedicated for each use can be combined and adjusted depending on site requirements.

Figure 8.4. Bracke mounder machine in the Forestry Tasmania coupe

Residue management is influenced by cultivation method chosen for the site depending on the volume of residue onsite, the slope and terrain, and whether row orientation is to be changed from the previous crop (FT, 2013). The current range of methods for managing post-harvest residues enables proper site clearance and preparation for planting of next rotation seedlings (Figure 8.4). Nutrients from residue wood are returned to soil when the residues are left on site to decay. Ash from on-site burns of windrows and heaps can condition soil as has been recognized in forestry and agriculture for centuries (FT, 2013; Greaves and May, 2012; Rothe. A, 2013).

In the next chapters however, an alternative method for dealing with post-harvest residues while preparing the site for the next rotation planting will be presented and discussed.

8.4. Scenario background and assumptions

8.4.1. Outline of biochar production and use scenario

The scenario proposed in this analysis assumes using post-harvest residues and a mobile unit to perform the process of pyrolysis of woody residues on-site in order to produce biochar which can be applied to the site. The scenario assumes three uses of the final product: (a) on-site application, (b) use in the forest nurseries and (c) commercial sale of the char. Figure 8.2 presents a graphical explanation of the proposed biochar scenario. Fifty percent of the harvest residue is retained on site at time of harvest. The other fifty percent is used to make biochar, with 60% of this biochar returned to the site, 30% sold onto the open market and 10% made available for use in plant nurseries.

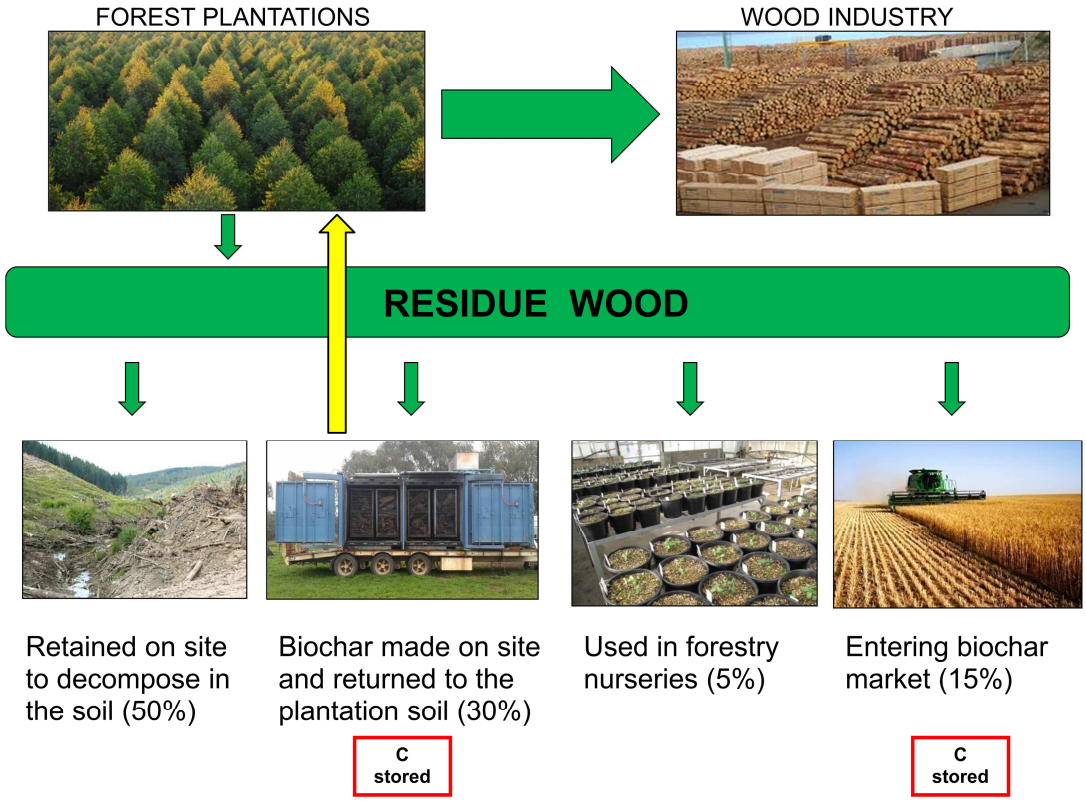


Figure 8.5. Diagram of the biochar scenario indicating the flow of forestry primary and secondary products.

The amount of post-harvest residues retained on site varies depending on the site productivity, age of trees at harvest and machinery used for harvesting. On average it has been estimated (Sadanandan Nambiar, CSIRO, pers. comm.) that the amount of organic residues, specifically slash (coarse and fine woody debris) and litter, vary between 10 and

70 t ha^{-1}. For the modeling purposes an average value of 30 t woody residues per hectare has been assumed.

Typical residues retained on site after harvest consists of branches and small logs not exceeding 200 mm diameter with lengths less than 2.4 m (FT, 2013). Stumps and root systems are also retained on-site after harvest. It is very difficult to estimate waste material moisture content as it is dependent on weather conditions at the time of harvest and in months following. Typical freshly cut wood moisture content oscillates around 30%. When left on site and air-dried for several months it is likely to decrease to approximately 12% (FT, 2013; Greaves and May, 2012). At this moisture content (12%) wood residues are considered suitable to be burnt on site or in a kiln to produce energy (Rothe. A, 2013).

In the current site clearing and preparation process heavy machinery e.g. excavators, tractor mounted cultivators and /or mounders are widely used to move and stack residue wood. This machinery could also be used to transport the target residues from within the coupe to the edge where a mobile pyrolysis plant could be located. Additionally, the harvest method could be modified to deliver appropriate residues to the coupe edge for later collection for processing by pyrolysis.

8.4.2. Mobile pyrolysis unit

There are different mobile pyrolysers available on the market. In this analysis the CharMaker MPP20 mobile pyrolysis plant from the Earth Systems® was considered as the most suitable for the proposed scenario.

The mobile pyrolysis unit is designed for low cost disposal of woody materials in remote areas. The unit is designed around a standard 6 m (20 feet) shipping container and can be easily transported on a truck or trailer. The unit is intended to operate on large pieces of material (up to 2 m length) in order to by-pass the need for on-site chipping of large volumes of woody matter. The CharMaker MPP20 is equipped with primary heating and emission control (after-burner) systems supplied by diesel oil during start-up. It can operate unattended and has the potential to sequester several kilo-tonnes of carbon dioxide equivalent (CO_2e) per annum through char production (EarthSystems, 2013).

Figure 8.6. Unloading the mobile pyrolyser (MPP20) (EarthSystems, 2013)

Figure 8.7. Loaded mobile pyrolyser (MPP20) (EarthSystems, 2013)

The unit can process up to 4 tonnes of waste wood (moisture content up to 35%) per batch and produce approximately 1 tonne of biochar after 4 hours operation. The process temperature ranges between 350 and 600°C. The CharMaker normally operates on 3 batches per day. Assuming that only 50% of waste wood will be used for making biochar it leaves the State with approximately 30,000 tonnes of waste wood to be processed per year and resulting 7,500 tonnes[6] of biochar made a year.

After biochar is made in the mobile unit it can be left on site until arrangements are made to apply it into the soil. The most suitable solution for that seems to be incorporation of biochar to the soil during cultivation. The two current cultivation methods could accommodate a hopper and delivery device for applying the biochar and have been presented and discussed in the previous sections. Detailed assumptions and the model for cost-benefit analysis are presented in section 8.5.

8.4.3. Determination of scenario costs and benefits

Plantation management inputs and costs were presented and discussed in section 8.1 (Table 8.1). This section is aimed at presenting and analysing costs and benefits resulting from proposed biochar scenario. While some of the costs and benefits are easily estimated, others – especially environmental and social benefits, can only be discussed in concept terms, as it is difficult to quantify the monetary values for these in a financial model. Table 8.3 presents identified costs and benefits arising from the proposed biochar scenario.

[6]Assuming 56,000ha of plantation forestry in Tasmania (Eucalyptus), 2,000ha harvested annually, 4:1 wood :biochar production rate.

Table 8.3. List of potential costs and benefits resulting from biochar scenario implementation. The items in italics were not incorporated into the model.

COSTS
Pyrolyser capital and operating costs
Feedstock collection
Feedstock preparation
Labour costs for pyrolyser operation
Biochar application/transport and storage
Chemical treatment of the site
BENEFITS
Savings resulting from minimised clearing of the site
Decreased fire risk
Decreased cost of windrowing
Decreased fertiliser amounts in the field
Carbon sequestration
Biochar use in the nurseries – decreased cost of seedlings production
Better seedlings resistance to drought
Limited costs of second fertilising
Revenue from biochar sale
Community approval and new jobs

Potential benefits from the scenario such as carbon sequestration, less fertiliser use for plantation establishment, drought management or lowered site clearance costs are presented as monetary values and implemented into the model. There is however another group of benefits which cannot be quantified in monetary terms; these include community approval and decreased fire risk which will be discussed in the last section of this chapter. Pyrolyser costs are estimated on the basis of technical information provided by one of the manufacturers (Earth Systems®, Australia). Feedstock collection, preparation and biochar application back to the site is calculated on the basis of equipment, heavy machinery and labour costs. Detailed assumptions are presented in the following section while formulas used in the model are listed in Appendix 8.

8.5. Base Scenario specific assumptions

For the purpose of estimating the costs and benefits from the biochar scenario a model was built in Microsoft Office Excel® (ver. 2007) and a set of assumptions made to meet the specific conditions of this analysis. For the cost modeling purposes some base assumptions for the pyrolyser, operating costs and forestry coupes have been made and incorporated into the model. The detailed assumptions are presented further in this chapter.

The model consists of several formulas (Appendix 8) calculating the assumed values into the total annual benefit. The total benefit calculated by the model is based on three main components:

1) savings on standard operations, calculated on the basis of decreased costs connected with the need for in-fill planting, fertilisation, site clearing/preparation after plantation harvest and requirements for herbicide spraying following biochar application,

2) potential benefits or disadvantages arising directly from biochar production and application calculated with respect to carbon prices, current market prices of biochar and financial benefits of using biochar in the forest nurseries and;

3) facility and process costs associated with incorporation, namely pyrolyser capital cost, operating costs and costs involved in handling feedstock and biochar.

Pyrolyser

The lifespan of the pyrolyser was estimated to be 10 years and the annual maintenance costs were assumed to equal 4% of the capital cost. More detailed assumptions are presented in Table 8.4. This type of equipment was chosen mainly due to its mobility and the fact that it can be easily transported between forestry coupes.

Table 8.4. Assumptions for the Pyrolyser capital, operational costs and technical characteristics used in the model.

Pyrolyser	Assumption	Justification
Mobile pyrolyser capital cost	$250,000	Including the delivery
Mobile pyrolyser useful life	10 years	Assumed as advised by manufacturer
Finance interest rate per annum	10%	Standard financial assumptions
Labour cost per batch	$30/hour	The costs of a tractor operator
Diesel used per batch	10 L	Following manufacturer recommendations
Diesel ($/L)	$0.8	An average price for bulk purchases
Pyrolyser maintenance ($/year)	4% capex	Following manufacturer recommendations
Machine hire to feed pyrolyser	$15/t of feedstock	Standard prices and time required to load the pyrolyser
Cost of moving pyrolyser between example -coupes	$300	Labour involved in loading pyrolyser onto the truck and transport over 20 km (average distance in between example coupes)
Operation per year	330 days	Based on the holidays and annual leave of the employees, assuming some days off-duty for maintenance purposes
Average number of batches per day	3	Manufacturer's recommendations

A set of assumptions has been made for the feedstock amount and processing methods, the assumptions are listed and explained in Table 8.5.

Table 8.5. Assumptions for the feedstock material used in the model.

Feedstock and area	Assumption	Justification
Model coupe size	30 ha	Estimated in co-operation with Forestry Tasmania
Waste wood per hectare	30 t	Estimated in co-operation with Forestry Tasmania
Waste wood pyrolysed per hectare	15 t	Based on wood moisture and limitations in terms of waste wood required to be left over for the soil nutrition purposes
Average batch size	4 t	Pyrolyser capacity
Cost of delivering waste to the edge of coupe	$10/tonne	Assumed with regards to machinery operation and time required
Waste wood moisture content after seasoning	15%	Estimated in co-operation with Forestry Tasmania
Feedstock to produced biochar ratio	4:1	Average from available technologies and the manufacturer's recommendation
Equivalent tonnes of CO_2 stored in one tonne of biochar applied in the soil	3	Assumed on the basis of available literature(Rothe. A, 2013)

Assumptions concerning agronomic benefits have been made with respect to the rate of biochar applied to the soil and potential benefits/costs arising from it. Different values were used for the benefits connected with raising seedlings, site preparation, fertilisation and post-planting herbicide spraying (Table 8.6). Detailed formulas describing the relationship used in the model can be found in Appendix 8.

Table 8.6. Model assumptions for the agronomic benefits based on results from previous chapters.

Products and agronomic benefits	Assumption	Justification
Raising seedlings saving	$10/ha	Biochar application rate of 1-5 t ha^{-1}, supporting the early growth of seedlings and increased drought resistance resulting in lower seedlings mortality
Site preparation savings	$200/ha	≥15 t wood processed per hectare
Fertilisation savings	$45/ha	Application rate of 1.5-3 t ha^{-1}
Post-plant spraying effect	-$10/ha	Application rate of 1.5-3 t ha^{-1}
Final product distribution (onsite : nurseries : sale)	60% : 10% : 30%	Based on the forestry needs and market demand
Price for CO_2	$10/tonne	Assumed price
Biochar : CO_2	1 : 3	Estimated on the basis of available literature of CO2 equivalents
Nurseries savings	$50/t biochar	Considers the costs of raising seedlings in the nurseries, potting mix composition and fertiliser required, based on agronomic results from previous chapters
Biochar price	$1000/t	Current average biochar price in Australia
Distance from the coupe to biochar collection site	100km	Plantation distribution in Tasmania (average)
Extra costs of incorporating biochar to the field	$30/coupe	Biochar incorporation into the soil will be done during cultivation. Extra time might be needed to reload biochar containers, unblock blockages

A sensitivity analysis was performed to determine the effect of particular assumptions on the total benefit of the scenario. To keep the analysis simple only the influence of a single factor change was investigated at the time. The influence of biochar production scale (pyrolyser capacity, pyrolyser number, and amount of processed wood) and external factors (prices per 1 tonne of biochar and 1 tonne of CO_2 storage) were investigated and discussed.

8.6. Results

The model was run with the assumptions outlined in section 8.5 showing a net annual benefit of $179,514.

It is considered that due to the innovation of the discussed scenario costs and benefits may vary significantly depending on many factors. In order to understand the relationship between the total net benefit and particular assumptions as well as to determine the critical factors for the total benefit of the proposed scenario, a sensitivity analysis was performed. Table 8.7 presents the results of total benefits when changing assumptions of the model. Even though no down-ward scenarios were directly analysed, certain factors, e.g. production capacity, biochar price, carbon price were thoughtfully investigated and the pessimistic outcomes presented (later in this section).

Table 8.7. Different variants of the proposed scenario (MPP40 stands for a CharMaker (Earth Systems®) with a greater capacity to process feedstock (up to 10 t ha^{-1}).

No	Scenario	Total benefit	Change to base
0	**Base assumptions**	**$179 514**	-
1	Bigger pyrolyser (MPP40, capacity of up to 10 t/batch)(capital cost $350 000)	$375 029	$195 515 (117%)
2	Working days increased to 350	$197 414	$24 850 (14%)
3	Final product distribution 70 :10 :20	$83 284	-$96 230 (52%)
4	Increasing amount of processed wood/ha to 30 t	$179 514	-
5	Increasing carbon price to $20	$ 189 844	$10 330 (10%)
6	Biochar price $2000	$ 460 546	$281 032 (167%)
7	3* MPP40	$1 124 270	$944 756 (552%)

Scenario 1 presumes the use of a larger pyrolyser, capable of processing up to 10 tonnes of feedstock per batch instead of 4 tonnes per batch in the base scenario. The capital costs and operating costs increase but the total benefit from implementing this scenario rises as well, which is connected with the cost per unit processed wood and biochar produced. Increasing the number of operating days per year (scenario 2) raises the total benefit of the venture by 15%. Changes presented in scenario 3 include differences in production distribution, increasing field application by 10% with a corresponding decrease in sale distribution and in consequence decrease the total benefit of implementing the project to $83,284. Increasing the quantity of processed waste wood by 100% did not change the

benefits of implementing the scenario which is connected with increasing costs of feedstock processing (Table 8.7, Figure 8.8.A). Increases in carbon price as well as the price per tonne of biochar would lead to significant increases in the total economic benefits (10 to 166%). The last scenario presents the benefit achievable when three pyrolysers of a bigger size (MPP40, capable of processing 8 tonnes of wood per batch)) are used to process waste biomass.

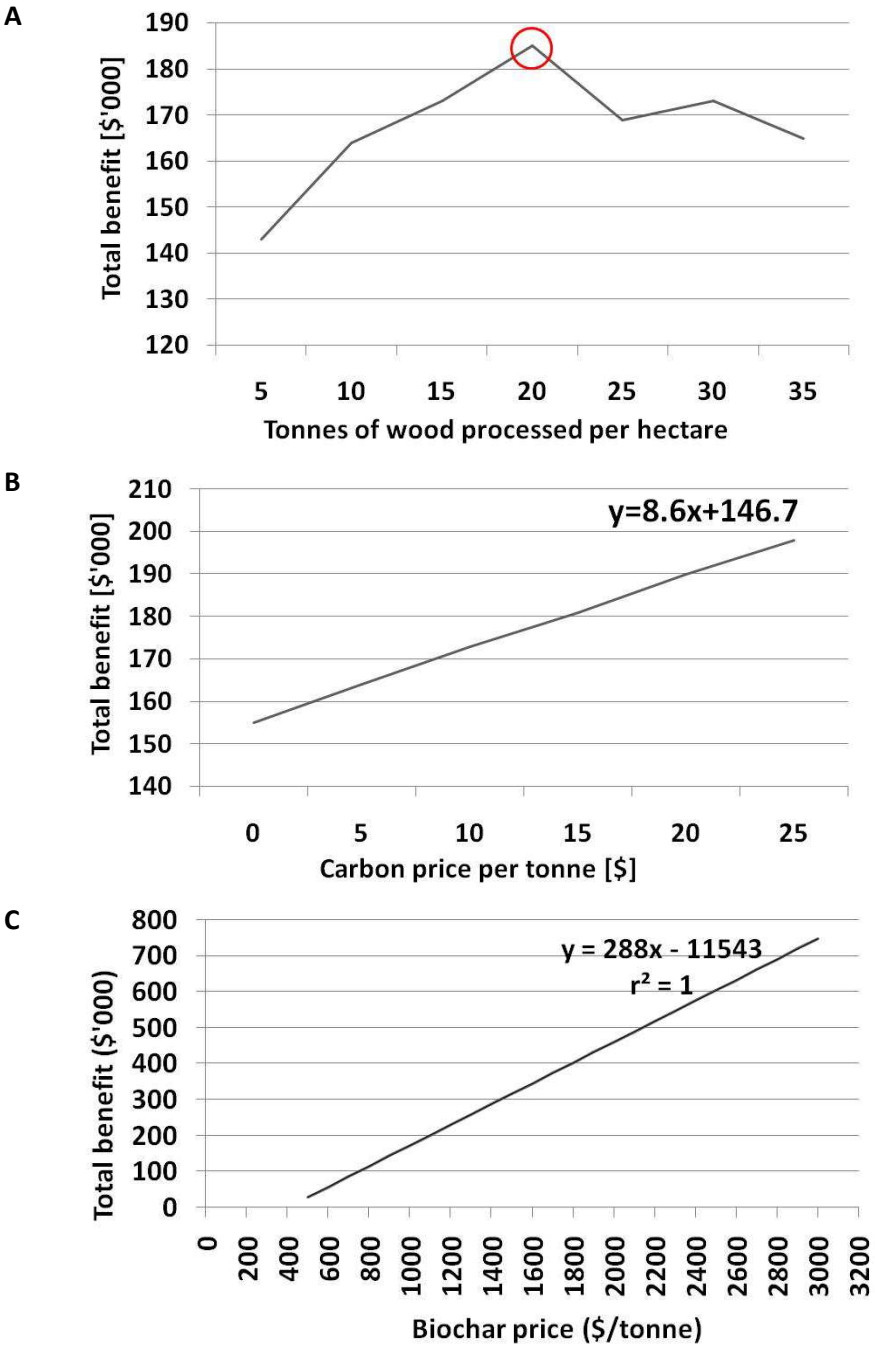


Figure 8.8. Total benefit of biochar scenario implementation ($) in relation to A) amount of waste wood processed per ha of plantation, B) carbon price per tonne of CO_2 stored, C) price per tonne of biochar.

As presented in Figure 8.8.A. the optimum amount of residue wood to be processed per hectare, under assumptions used in the model equals 20 tonnes. Lower or higher amounts result in a decreased total benefit. Figures 8.8.B and 8.8.C present a strong linear dependence of total benefit of the project on the price of carbon and biochar. Figure 8.8.B however, reveals that if carbon price equals zero, the total benefit of the project will equal $155,300, which suggests that the carbon price is not a crucial factor for project financial feasibility under current assumptions. Figure 8.8.C shows a linear, steep dependence of total project benefit to biochar market price. Biochar net benefit per tonne of $600 more, comparing to base scenario, doubles the benefits of the project while biochar price falling to less than $400 per tonne results in negative economic returns.

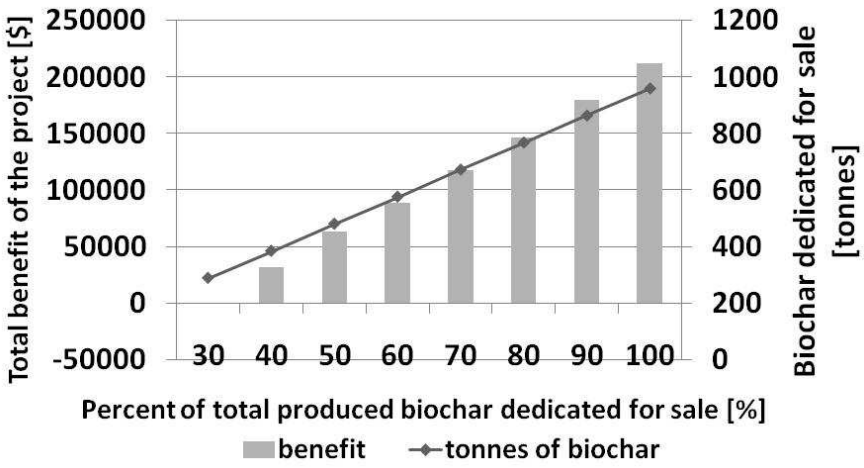


Figure 8.9. Total benefit of the proposed scenario and biochar amount dedicated for sale in relation to percent of total produced biochar, dedicated for sale. Assuming biochar price of $400/tonne.

Figure 8.9 presents the total benefit of the scenario and the total amount of biochar for sale, assuming a different final product distribution (between nurseries, field application and sale) and a constant biochar price of $400 per tonne. The total benefit of the project increases rapidly when a larger share of biochar is dedicated for sale. Depending on the biochar production scale total amount of biochar produced to enter the market varies between 288 and 966 tonnes per annum.

8.7. Discussion

Tasmania has a sustainable supply of forest biomass for different use of at least 3 M green t y^{-1}, which would be sourced predominantly from plantations, with a smaller fraction coming from native forest re-growth harvest (Rothe. A, 2013). The biochar scenario proposed in this study has been shown to have potential to provide financial benefits under specific

assumptions. The most crucial factor for scenario feasibility was found to be biochar market price. Therefore the developing biochar market in Australia has to be investigated in details prior to scenario implementation.

8.7.1. Sensitivity

The sensitivity analysis determined which factors were critical to the scenario and how stabile the scenario was in terms of financial feasibility. Both scenarios assuming the use of a larger capacity pyrolyser (10 t per batch) are connected with significant increase in biochar production and consequently more final product to make use of. The base scenario assumes production of biochar exceeding 1000 t per year for the sale. The increased capacity pyrolyser scenario doubles this amount while the scenario of using more feedstock to produce biochar (scenario 4) assumes biochar production six times greater than the base scenario. Introducing such quantities of biochar to the Australian market may be difficult in terms of finding potential purchasers (Glover, 2009; Joseph, 2009; McCarl et al., 2009) and would have to be preceded by more detailed market studies to ensure that there will be enough interest from traders and purchasers (Glover, 2009).

Increasing the number of operation days per year (scenario 2) and presuming higher price for tonne of CO_2 stored (scenario 5) did not change the total project benefit significantly (+/- 15% of the base scenario benefits) which means neither the number of days nor the carbon price qualifies as highly influencing factors comparing to biochar price or pyrolyser capacity. Similarly assuming the number of operation days to be 280 per year decreased the total benefit of the project by 20% (data not presented). The linear relationship between the total benefit of the project and biochar price per tonne can be assumed to be critical for the project feasibility. Therefore the early development stages of biochar market in Australia and Worldwide must be considered when preparing the scenario for the implementation on a commercial scale (Glover, 2009).

Similarly, the change in production distribution, presented in scenario 3 also reveals a significant difference in total project benefits in comparison to base scenario (52%). This effect is most likely connected with benefits arising from biochar application to the field being not commensurable to benefits arising from biochar sale.

The sensitivity analysis performed within this model was based only on one factor-change at the time. To fully understand the effect of particular factors and the benefits resulting

from different scenarios a more detailed sensitivity analysis, including simultaneous factors values fluctuations, would have to be performed (Pearce et al., 2006).

8.7.2. Unaccounted factors

The model presented in this thesis required some simplifications dictated by the objectives of the thesis and the chapter. The model was aimed at investigating the financial possibilities for incorporating biochar as standard forestry practice however more complex financial analyses would be required to confirm the outcomes of this model on a wider industrial scale. One of the main simplifications used in the model was the assumption that only post-harvest residue wood is used for biochar production. Other available residues include:

- Plantations that do not grow as expected during the first years and are terminated to be replaced by other species or dedicated for other purposes,
- Thinning residues, a common residue in plantation management (currently used for pulpwood production),
- Private forestry plantations resources,
- Wood processing industry (i.e. Sawmill waste),
- Native forests management practices residues.

(Greaves and May, 2012; Rothe. A, 2013)

The scenario of biochar on-site production is one of the possible solutions of processing woody residues but its main disadvantage is the lack of pyrolysis gases recovery and consequently missed opportunity on generating energy. The choice of mobile pyrolyser to be included in the proposed biochar production scenario was based on the simplicity of this equipment and avoided feedstock transportation logistics and costs. Stationary systems, based on residues delivery from the vicinity are under research and pilot implementations have been investigated in Australia. Some of these systems assume combined production, focused rather on renewable energy generation (heat and syngas) treating biochar more as a by-product. Some of the currently researched systems are based on local conditions and placed next to facilities, where all of the pyrolysis process products can be used immediately (in example glasshouse using heat for heating purposes, biochar as growing media and syngas to produce electricity used in the glasshouse laboratory)(data confidential).

When considering the feasibility of pyrolysing forest residues, of importance are factors that may provide possible benefits that could not be considered in the model. These include benefits resulting from community approval to limited on-site burns, decreased fire risk and reduced smoke disruption to local communities (Greaves and May, 2012; Rothe. A, 2013).

On-site burns in the plantations to process post-harvest residues are always performed very carefully but even when preserving all the safety measures the fire risk of an open-controlled fire must be considered (Marsden-Smedley and Whight, 2011; Wood et al., 2009). Currently, Forestry Tasmania staff prepares fire risk assessments according to the conditions and site location. Regardless of the diligence in performing these burns there is always some risk of fire burning out of control. Pyrolysis is a controlled and contained process carrying a much lower fire risk and can be terminated at any point if necessary. Thus it can be argued that combustion in a mobile pyrolyser involves a lower risk of uncontrolled fire and should be considered even though it is not possible to reliably transform this effect into monetary value.

Many forestry operations have opponents in the local communities and more general society. Protests are often connected with harvesting natural forests which is not directly joined with the topic of forestry plantations. However, the objections also rise to the on-site burns and smoke which is being produced and affects local communities (Pearce et al., 2006). In the proposed scenario the effects of smoke produced during on site burns will be significantly reduced or avoided as waste wood will not be burnt on site but in the pyrolyser in the controlled, clean process, during which the smoke and exhaust gases are managed and let into the atmosphere in a controlled manner. The community approval might be also expressed due to the fact that a sustainable, environmentally friendly approach is being taken as biochar is produced from the residues and returned to the soil. Similarly, it has been suggested that in addition to its environmental benefits, the practice of biochar application to the soil could also lead to economic and social advantages by establishing new businesses, opening new job positions and in consequence facilitating small, rural communities (Joseph, 2009; Ogawa et al., 2006).

The aspects mentioned above, together with an overall community approval connected with producing environmentally sustainable product and an environmental method of dealing with residue wood should be considered when assessing the scenario feasibility.

Again, similarly to the case of two previous factors it is not possible to transform these benefits into actual value to be included in the model. Taking into consideration current public protests about some forest operations in Tasmania, the above should be accounted for when making a decision about the implementation of the scenario.

While the potential benefits discussed above may be difficult to quantify monetarily, many of these issues, such as controlled and uncontrolled burns, are of immense importance to the forest industry and community and therefore should be considered along with the measurable benefits resulting from the biochar scenario.

8.7.3. Potential changes

It is important to note that the assumptions used in this model were average from data available about plantations, management, growth response and local conditions in Florentine valley. The model is environmentally sensitive and the resulting cost and benefits values are expected to change in regards to micro-climate, soil type and other similar factors (Joseph, 2009).

Fertilising operations on forestry plantations in Tasmania are currently under transformation in order to utilize a new generation and better efficiency fertiliser type. The agronomic data used within this model was based on fertilising the plantations with standard di-ammonium phosphate (DiAP)(Chapter 4). It must be considered that the new fertiliser type is likely to interact with applied biochar unlike DiAP and result in significantly different final outcome (trees height, nutrient efficiency from fertiliser). A pilot experimental trial would be required to estimate expected results of new type of fertiliser in combination with biochar.

Equally, the topic of increasing nutrients release from biochar would be interesting to investigate. Certain organic additives (i.e. chicken litter, farm animals manure) have been shown to increase biochar ability to introduce nutrients to the soil (Sarkhot et al., 2012). An opportunity to collect animal manure and litter from local farms and its addition to woody feedstock during the pyrolysis process might decrease fertiliser rates required for the plantations and could be used on a wider scale as a nutrient-application method in the future. In northern Tasmania there is a large scale dairy industry which could provide interesting possibilities for making biochar enriched by animal manure.

Tasmania has been presented as an Australian state with a significant potential to use forest residues for generating bio-energy and bio-products (Greaves and May, 2012; Rothe. A, 2013). With the current production of 300,000 m^3 (Wood et al., 2009) of eucalypt sawlog and other forestry-related industries the potential arising from primary and secondary forests products and residues cannot be overestimated. Biomass estimating reports however, are based on woody residues used mainly for energy generation purposes while biochar has been discussed very briefly in proposed solutions. Co-operating with other authors and working on the basis of already existing biomass reports but introducing biochar scenario on a wider scale could provide interesting solutions for proceeding woody residues under Tasmanian conditions.

8.8. Conclusions

The evaluation of this model shows that biochar production from forest residues may be feasible dependent on receiving a minimum of $400 per tonne when 30% of the produced char is sold into a commercial market. The proposed operation was most sensitive to the market biochar price and the amount of biochar dedicated to enter the market, which are both considered highly changeable in the developing Australian biochar market. Model assumptions included only one source of residues, namely plantation post-harvest residue wood while other sources of biochar feedstock (i.e. thinnings and native forest woody residues) could enlarge the scale of biochar scenario incorporation, if considered in the analysis. Similarly, the opportunities connected with pyrolysis gasses production were not considered in the model due to the type of pyrolyser used. Other unaccounted benefits include community advantages resulting from creating new jobs or environmental benefits like decreased fire risk or on-site burns smoke management. The results of this scenario would be best confirmed by a practical biochar production and utilisation system based in Tasmania.

9. FINAL DISCUSSION AND CONCLUSIONS

9.1. Introduction

The objectives of this research were to test the agronomic and financial feasibility of biochar application to Tasmanian soils and forestry plantations. Two experiments (pot and field experiments) were established and monitored in order to gather data to support hypotheses that macadamia biochar can bring beneficial effects to soil quality, plant nutrition and agronomic response in *E. nitens* seedlings as well as allow decreasing common fertiliser rates used in forestry plantations (Chapter 1). Results from the experimental analyses were incorporated into the financial model, along with market assumptions and local economic and environmental suppositions, to investigate financial feasibility of producing and incorporating biochar on Tasmanian-based forestry plantations.

The results have shown initially increased availability of potassium, sodium, nitrate-N and phosphorus; elevated pH in the potting mix and higher concentration of sodium and potassium in the field plantation soil (Chapter 5), though over time the effect was diminished. The leaf tissue concentration in response to biochar in both experiments revealed P, K and Na increase in the pot trial and in some, although not all cases, some clear trends were evident (Chapter 7). Biochar application in the field increased potassium leachate which was attributed to higher K availability in soil following biochar application (Chapter 6). Char application did not result in significantly taller trees or greater biomass production in general, but two biochar application rates combined with halved fertilisation resulted in seedlings of similar quality (height) to the ones produced under full fertiliser rate with no biochar applied (Chapter 7). These results indicated a potential of decreasing fertiliser rates commercially used in forestry plantations in Tasmania if supported by further research.

The financial model based on the idea of on-site biochar production from the post-harvest residues revealed a potential annual income of nearly $180,000 based on processing post-harvest residues from 270 ha (Chapter 8). The sensitivity analysis showed that a critical factor for model financial feasibility is biochar market demand and price, which is presently unstable in the developing biochar market in Australia.

9.2. Agronomic and chemical changes

9.2.1. Soil

While in some cases the trends in nutrients levels were consistent with existing theory and explicable (Colwell potassium, pH, and exchangeable sodium, magnesium, aluminium and calcium), some of the nutrient dynamics could not be clearly related to any particular known mechanism.

Some changes in the soil were less noticeable than anticipated. Macadamia biochar did not have an effect on soil electrical conductivity or pH under field conditions. The EC in the potting mix was lowered by biochar application, which was concluded to be an effect of cation adsorption from the soil solution to biochar surfaces. Some evidence of accelerated nitrification in the PM and increased potassium content in the field soil suggested that macadamia biochar influenced both the direct release of nutrients and affected nutrient transformation mechanisms (Chapter 5). The high SSA of macadamia biochar (Chapter 3) was suspected to influence soil microbial activity and result in readily noticeable changes in bacteria- related nutrient levels (mainly N and P), especially in the field experiment. Stimulated microbial activity could have been a case in this experiment, however, as it was not analysed and there were few changes in soil that would allow any conclusion about its potential importance, this aspect must remain unresolved and possibly be the subject of further research.

Biochar influence was much more evident in the pot experiment in comparison to the field trial changes. This is most likely the effect of the comparatively low biochar rates used in the field study. The highest biochar rate applied in the glasshouse equalled 100 t ha^{-1} while in the field the maximum dose was equivalent to 20 t ha^{-1}. Most of the PM changes in the controlled environment were reported for high biochar rates (50-100 t ha^{-1}) which provides a potential explanation that low char rates applied in the field were responsible for the lack of substantial effects of biochar.

The positive influence of biochar on soil condition and plant growth is sometimes related to the effect of biochar aging in soil (Nguyen et al. 2009, Atkinson et al. 2010). As biochar ages, its overall chemical and physical characteristics change, including surface charges and bulk density and others (Chapter 2). It is possible that the duration of both pot and field experiments were too short to reveal the differences resulting from long-term biochar

induced changes in soil. However, the extractable nutrient concentrations decline to close to initial values in around 1 year suggests that there are likely to be limited long term effects. Despite this, a longer-term study with higher rates of biochar application would help to understand changes to soil nutrient availability and transformation mechanisms as a result of biochar application.

Although biochar induced changes were the most noticeable in the potting mix the full extent of potential transformations in growing media may have been mitigated by this mix's inherent properties. The PM used in the experiment contained a large proportion of organic matter (Chapter 4) and might have masked the effects of biochar application. For instance, the high proportion of peat in the potting mix would have imbued an already substantial CEC capacity before the char was added. This observation might be extended to hypothesis that biochar may be used in the commercial potting mix for growing Eucalypt seedlings and replace, to some extent, pine bark or other high organic matter components of growing mixes. Further research would however be required to formulate firm recommendations.

9.2.2. Plant material and agronomic response

Although biochar application did not result in higher trees or increased biomass production by *Eucalyptus nitens*, two treatments bucked the trend (or lack thereof) where biochar combined with decreased fertiliser inputs resulted in similar or greater seedlings height as full fertilisation with no biochar addition. Even though not showing a clear trend or repeatability under more than one biochar rate (10 t ha^{-1} in the pot and 15 t ha^{-1} in the field) this result might be considered very important from practical point of view as it implies a possibility of reducing commercial fertiliser application rates with no negative effect on wood quality. As discussed in Chapter 9 establishing forestry plantations is inevitably connected with significant expenses and can only be supported by a financial effectiveness. The possibility of substantially reducing commercial fertiliser rates on a big scale would considerably decrease the costs connected with plantation establishment and early management. The results of this research revealed that producing seedlings of similar quality under biochar application can be achievable in the early stages of *E. nitens* growth. However, to confirm these conclusions similar experiments using a range of growth media and soil types would be required.

Biochar rate and application method may have been responsible for the lack of response in the field trials – the highest rate (20 t ha^{-1}) had little effect in the glasshouse trial, hence it was probably inadequate in the field. The application of biochar to a restricted volume of soil, though increasing the effective rate of application, may mean that it was not present in the volume of soil explored by eucalypt roots. Additional research would be needed to explore this possibility. Alternatively, the possibility that the site was simply unresponsive has to be recognised.

The differences in seedlings height between full fertilizer treatments and half- fertilizer treatments combined with biochar rates, however limited to two biochar application rates, suggests that even though biochar did not stimulate trees growth or resulted in greater biomass production, its application has a potential to decrease fertilisation rates used in the commercial forest plantations. The analysis of leaf tissue nutrient concentration did not reveal many significant differences either, which suggests that half-fertilisation combined with biochar results in similar nutrient uptake by *E. nitens* trees as full fertilization treatment. That supports the hypothesis concerning biochar having a high potential for decreasing commercial rates of fertiliser. On the contrary, the full rate of fertiliser may have been a luxury rate, or compensatory supplies of nutrients arose from the biochar. Though unlikely, as the biochar had little available nutrient (other than potassium and sodium) is it, it may be a contributor, especially at high rates of biochar addition.

9.2.3. Leachate

The increase in soil leachate potassium in the field experiment when biochar was applied was attributed to K release from surface deposits on the biochar surfaces and subsequently an increased concentration of this cation in the soil. On the contrary to results observed in this experiment, various biochars have been reported to decrease runoff of soil nutrients, this effect being attributed to increased SSA in soil-biochar mixture, and mostly reported mainly for sandy soils. The soil in the field experiment most likely did not benefit from increased SSA to an extent sandy or loamy soils would, as clay soils are in general characterised by high SSA (Chapter 6). Therefore it is concluded that biochar added on its own may not have caused any positive changes in terms of better holding of nutrients to soil and biochar surfaces in our field experiment. It might however be speculated that the same biochar added to the plantations with sandy soils could limit nutrients runoff, thus

raising questions about biochar application suitability on different soil types and plantation species in Tasmania.

9.2.4. Summary

Although biochar applied to the soil in combination with fertiliser induced some changes, specific trends were not always evident. Biochars ability to serve as a direct source of nutrients was possibly responsible for increased levels of K, P and Na in the soil and K in the soil leachate. The adsorption of cations was most likely the mechanism responsible for decreased Mg, Ca and Al concentrations, post-experimental biochar analyses and specific studies using growing mixes in a laboratory setting would support this explanation. Other changes in the soil and leaf tissue were thought to result from an increased growing medium pH, its influence on solubility of various ions in co-operation with a group of different mechanisms resulting from biochar properties (Chapters 3, 5 and 6) as well as the effect of agronomic variability (field experiment) and other unaccounted factors.

In general, in comparison to what was expected, a few factors were concluded to contribute to biochar limited effects. The potting mix and soil characteristics (organic matter content and high surface area, respectively) were most likely responsible for limited biochar influence on stimulating soil transformations. Low application rates and biochar application methods in the field experiment may have contributed to the limited plant response. With both experiments, the relatively short time-frame would not have detected later changes that may occur as a result of the char properties changing with age, as reported in some studies (Cheng et al., 2008; Qian and Chen, 2014). It is unfortunate that biochar, due to its form (dust) could not have been analysed after retrieving from the soil/potting mix since hypotheses concerning nutrient adsorption to its surfaces or microbial activities could have been confirmed.

9.3. Financial aspects

9.3.1. Potential implications of biochar production and use

The financial model was run under assumptions presented and discussed in Chapter 9, including a) direct revenues from biochar utilisation, b) savings arising from changed traditional forestry operations and c) capital and operating costs of biochar production machinery and equipment. While the model was built based on a case study and *E. nitens*

plantations, the number of assumptions and the outcomes of sensitivity analysis clearly show that particular segments of the model can be adjusted to suit local conditions and demand. Assumptions concerning agronomic benefits or transport-related costs can be changed to fit different plantation scenarios, including area, location, soil type, response to biochar and species.

The model was based on the case scenario of a Forestry Tasmania coupe, located on Permanent Timber Production Zone Land (PTPZL). Apart from Forestry Tasmania there are other forestry based industries, and significant portion of the State's plantations are located on private land in Tasmania. While this project has only considered State forest plantations operations, the model could be expanded to include other Tasmanian-based wood industries. With the large volume of forest residues generated in Tasmania, cross-industry opportunities related to biochar production would be an interesting subject for exploration.

Biochar type might play an important role in the feasibility equation. The agronomic assumptions used in the model were based on the results of macadamia biochar influence on forestry plantations, which provided little agronomic advantage. In the proposed scenario however, Eucalypt-based biochar is planned as the main char product. While both macadamia and eucalypt chars, being wood-based biochars, are expected to have similar general characteristics, it is not possible to predict the exact effects of eucalypt biochar on forestry plantations and an experimental approach would have to be employed to assess the effects of eucalyptus biochar under realistic field conditions.

The total project benefit was calculated on the basic assumption of making only one product, namely biochar. One of the scenario's main components is the employment of a mobile pyrolyser to produce biochar on site, potentially reducing the costs connected with residue transport. The pyrolysis process also generates significant amounts of heat and gases which could be utilised for different purposes. This however, cannot be done with current mobile equipment and a stationery pyrolyser would have to be considered. From one perspective, such solution would certainly increase the feedstock transport-related expenses, but the benefits of for instance capturing the emitted gases and their sale could potentially compensate for that. A pyrolyser type and local market focused analysis would add to the investigation of these issues.

9.3.2. Commercial implementation

The total financial outcome of the model implementation was found to be strongly dependant on the amount of biochar produced for sale and biochar market price. The developing biochar market in Australia and Worldwide does not guarantee either a stabile price or demand for biochar. Therefore the most crucial factors of the assumed scenario are also the most unpredictable, elevating the risks associated with biochar production and use. It is important to mention that the Tasmanian or Australian demand for biochar was not investigated, to make assumptions within the proposed scenario and only the supply side was considered. A detailed exploration of demand, especially based on local needs would certainly add to the models reliability.

An analysis of potential sites locations and logistic issues in Tasmania would allow minimization of the risk when applying the scenario in practice. Considering the diversity of plantations location, soil types, species and nutritional needs, the inevitable variation in response to biochar, as well as local and national supply-demand relations, the model can be adjusted to be applicable under different environmental and market conditions.

9.4. Where to from here?

The research results presented here answer some questions surrounding biochar applicability on Tasmanian soils, but also leave questions to be answered. Biochar application for forestry purposes has not received much attention in the past, nor has application of biochar in Tasmania and the results of this research contribute to filling both gaps.

A number of issues remain unsolved or incompletely resolved and would require more attention to be supported. Biochar characteristics could be investigated further to determine its physical and chemical properties to a greater detail. As mentioned before, Tasmanian eucalypt biochar would need to undergo thorough analyses to assess the level of its suitability for particular regions in Tasmania. Some of the soil changes following biochar implementation could not be attributed to particular mechanisms and more research would be required to understand processes that occur.

Many environmental benefits were mentioned within this project but not investigated deeply. The GHG emissions reduction resulting from biochar application to the soil has been reported before. This topic has not been explored within the scope of this research, however could add significant environmental profits to the big picture of biochar production and application in Tasmania. Carbon sequestration potential has been included in the cost-benefit analysis model, but the assumptions were general and not based on soil types or particular biochar carbon content and in consequence its ability to sequester carbon. Detailed topic-based studies would be needed to provide more information about the potential of carbon sequestration in Tasmania.

The timeframe of the experiments was limited in relation to biochar stability in the soil as well as the changes chars undergo in the soil environment (Chapter 2). This aspect is also an important factor when considering the forestry plantation rotation timeframe. The results of this research focused on the establishment stage of plantations, both in the nurseries and under field conditions. The long-term effects of biochar and use of multiple applications arise as possibilities for further research.

Although forestry practices and methods to manage harvest residues have been practiced for decades, there is a growing interest in alternative use of forestry and agricultural residues in Tasmania, and elsewhere. From the practical point of view several actions could be taken following a dissemination of the results from this study. A demonstration trial, involving mobile pyrolyser and eucalypt biochar production could prove the practicability of the proposed scenario and feasibility of biochar generation and use in Tasmania. Gradual implementation of the scenario in different regions of Tasmania would ensure the model development as it would be adjusted to local conditions and changing financial circumstances.

The results of this research allow me to conclude that wood-based biochar may serve as a potential environmental and forestry tool in Tasmania, if manufactured and used according to needs and requirements dictated by local conditions. However, more information is needed to be able to make strong recommendations on its use.

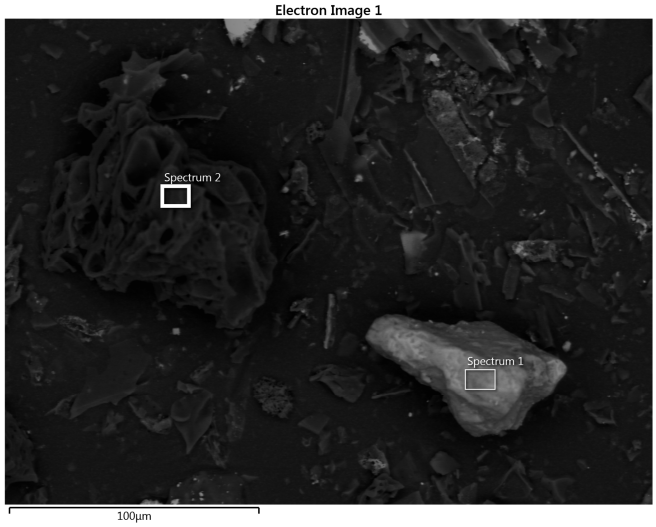
APPENDICES

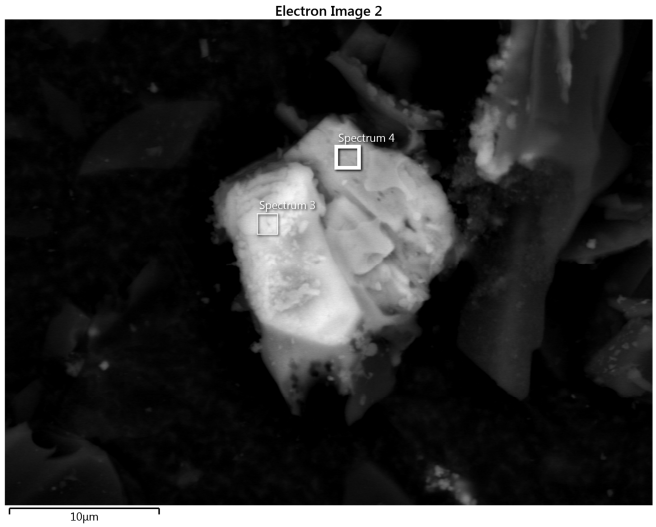
Appendix.1. Full specification of Macadamia shells biochar used in pot and field trials.

Biochar full specification		
test	**unit**	**result**
Temp made	C degrees	450-480
Electrical Conductivity	mS/cm	0.59
Water holding capacity		77.00
pH(H2O)		8.76
pH(CaCl2)		8.07
CEC-pH7	CEC/100g C	3.03
CEC-pH7	CEC/100g	2.38
Nitrogen	%	0.57
Carbon	%	57.76
Organic carbon	%	4.5
C/N Ratio		136.00
NH4-N	mg/L	3.5
NOx-N	mg/L	0.1
Mineral N	mg/L	3.6
LOI	%	97.9
Al	mg/kg	165
As	mg/kg	< 10
B	mg/kg	11.4
Ca	mg/kg	1380
Cd	mg/kg	< 10
Co	mg/kg	< 10
Cr	mg/kg	< 10
Cu	mg/kg	11.2
Fe	mg/kg	786
K	mg/kg	2430
Mg	mg/kg	597
Mn	mg/kg	98.7
Mo	mg/kg	< 10
Na	mg/kg	1620
Ni	mg/kg	< 10
P	mg/kg	424
Pb	mg/kg	6.34
S	mg/kg	457
Zn	mg/kg	33
Acenaph- thylene	mg/kgDMB	<0.10
Acenaphthene	mg/kgDMB	<0.10
Anthracene	mg/kgDMB	<0.10
Benzo[a] anthracene	mg/kgDMB	<0.10
Benzo[a] pyrene	mg/kgDMB	<0.10

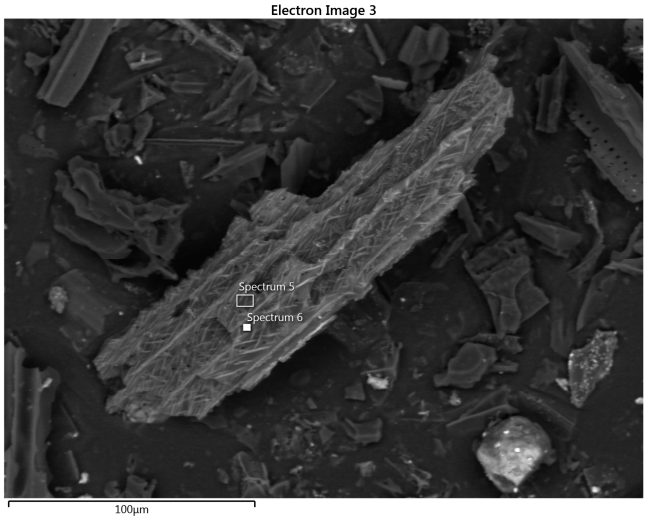
Benzo[b&k] fluoranthene	mg/kgDMB	<0.10
Benzo[ghi] perylene	mg/kgDMB	<0.10
Chrysene	mg/kgDMB	<0.10
Dibenzo[a,h] anthracene	mg/kgDMB	<0.10
Fluoranthrene	mg/kgDMB	<0.10
Fluorene	mg/kgDMB	<0.10
Indeno[1,2,3-cd]pyrene	mg/kgDMB	<0.10
Naphthalene	mg/kgDMB	<0.10
Phenanthrene	mg/kgDMB	<0.10
Pyrene	mg/kgDMB	<0.10

Appendix.2. Macadamia biochar Electron Microscopy spectra sites (SEM-EDS), refer to Chapter 3 for element composition.

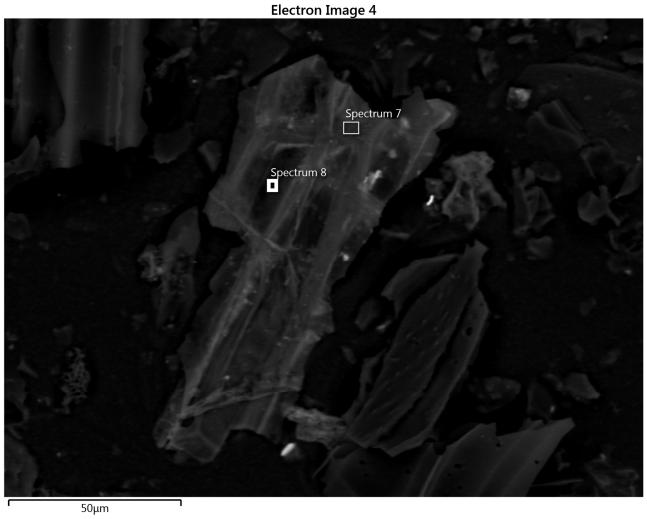




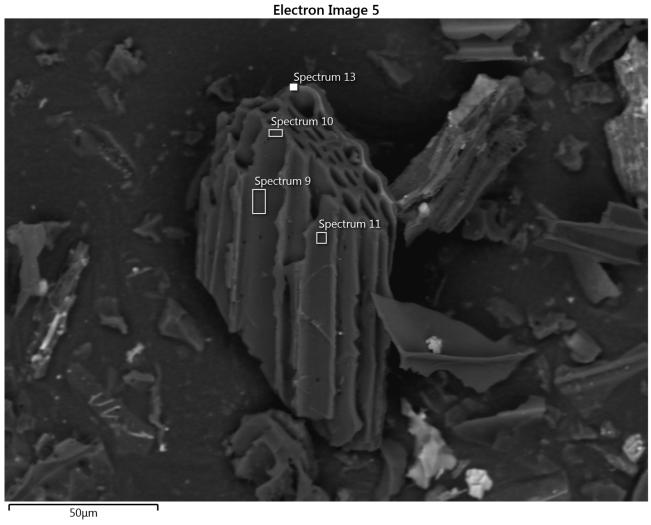
Electron Image 3



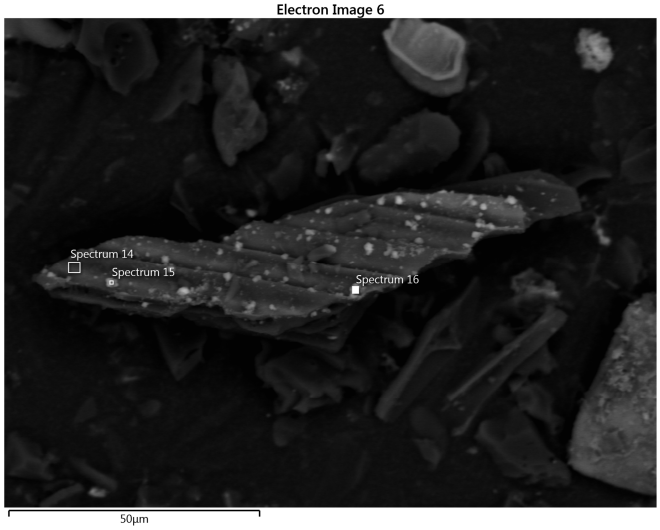
Electron Image 4



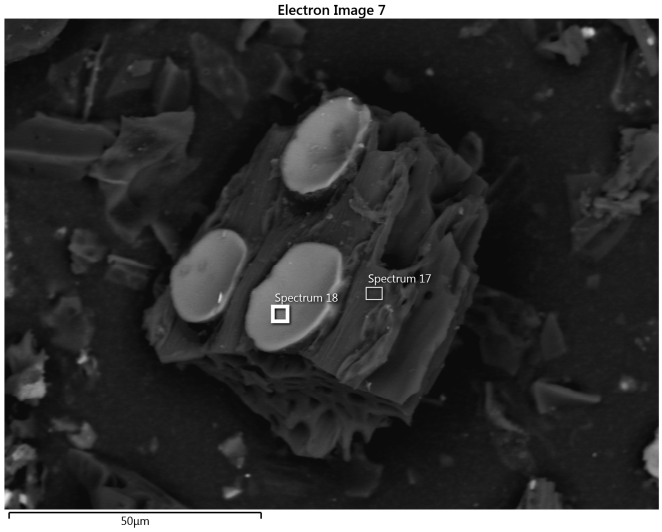
Electron Image 5



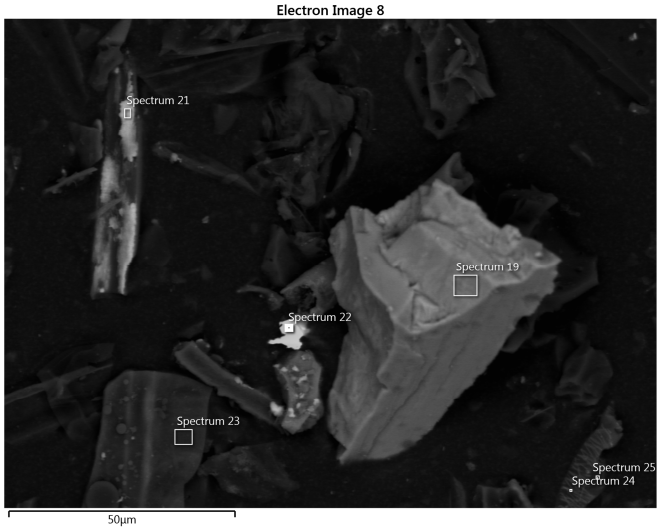
Electron Image 6



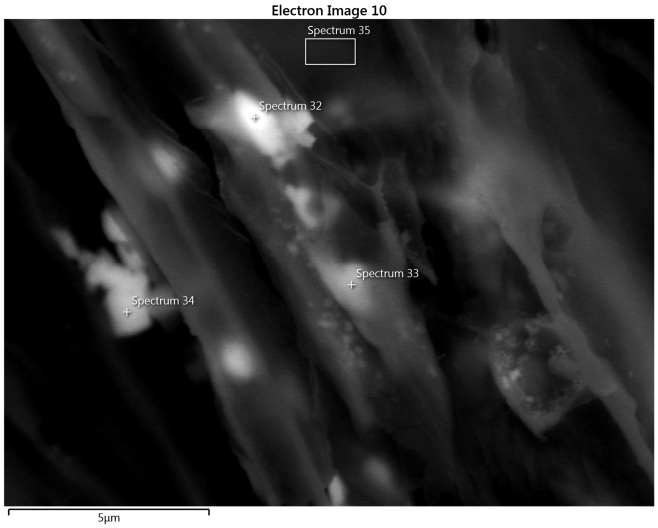
Electron Image 7



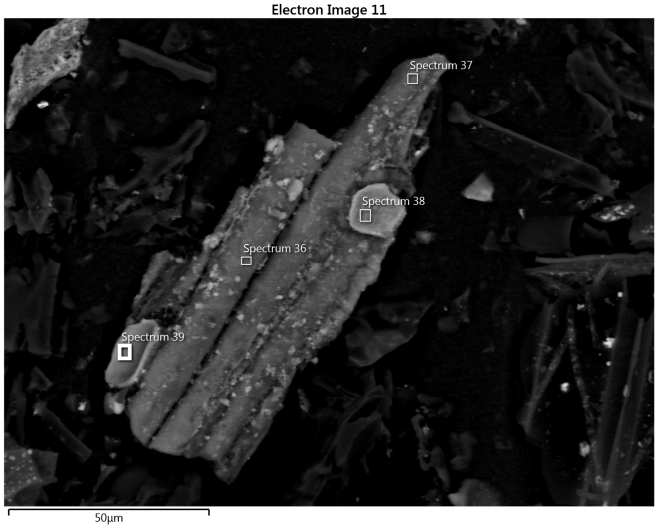
Electron Image 8



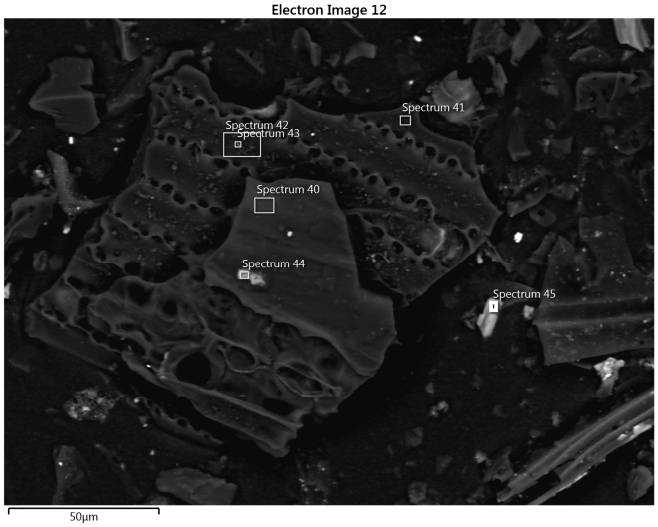
Electron Image 10



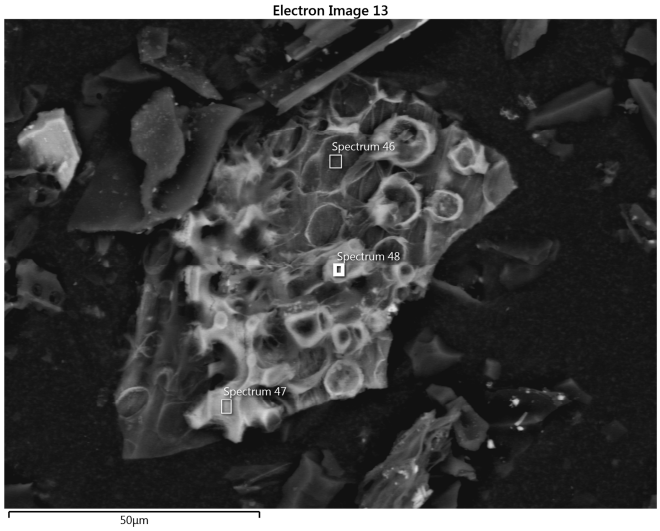
Electron Image 11



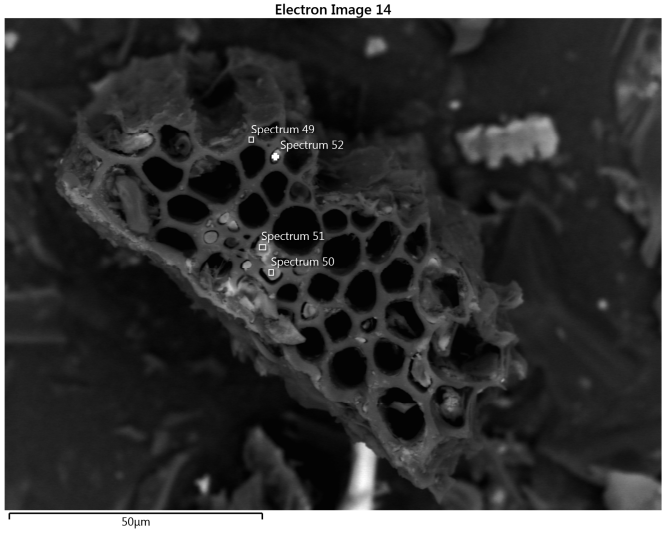
Electron Image 12



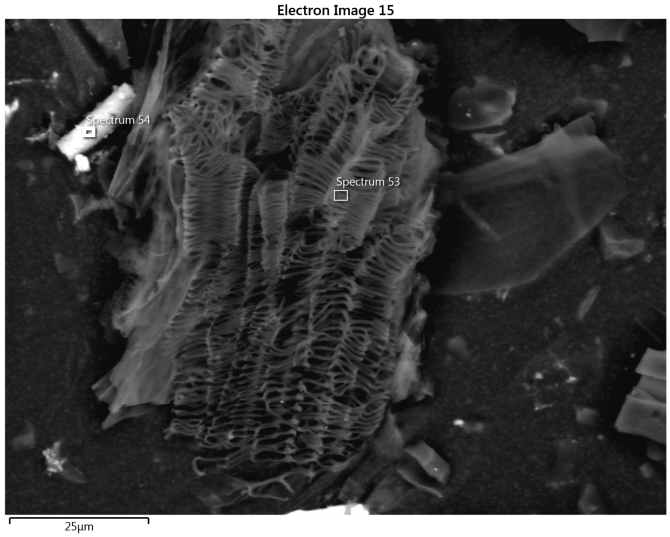
Electron Image 13



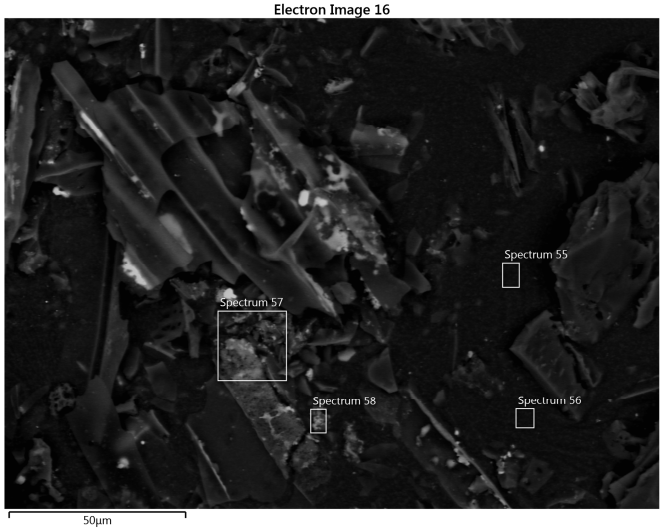
Electron Image 14



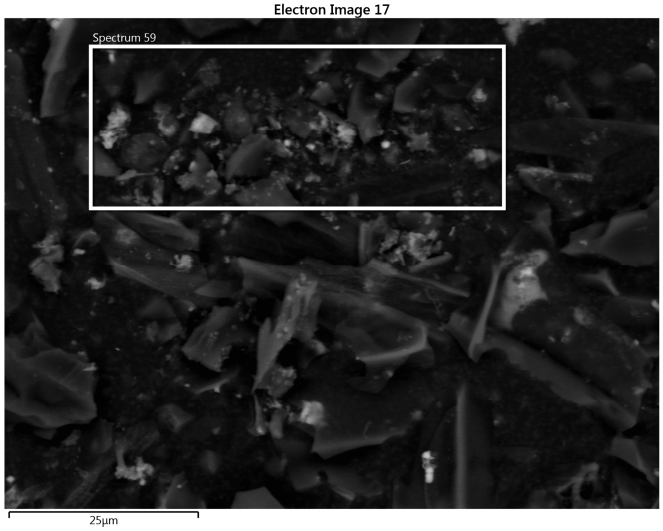
Electron Image 15



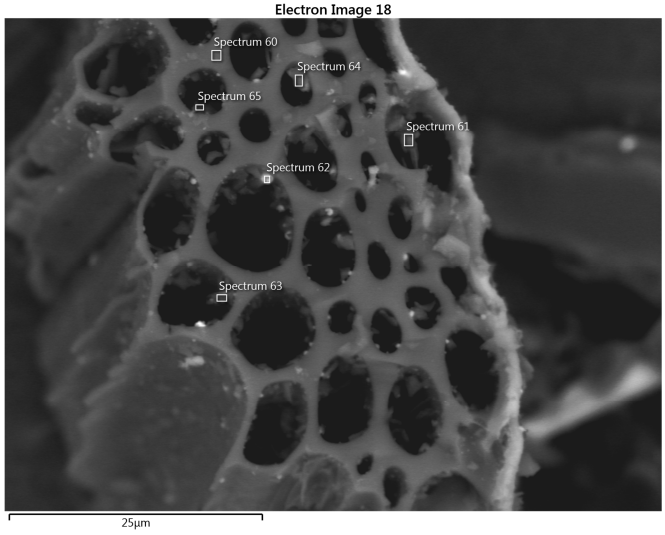
Electron Image 16

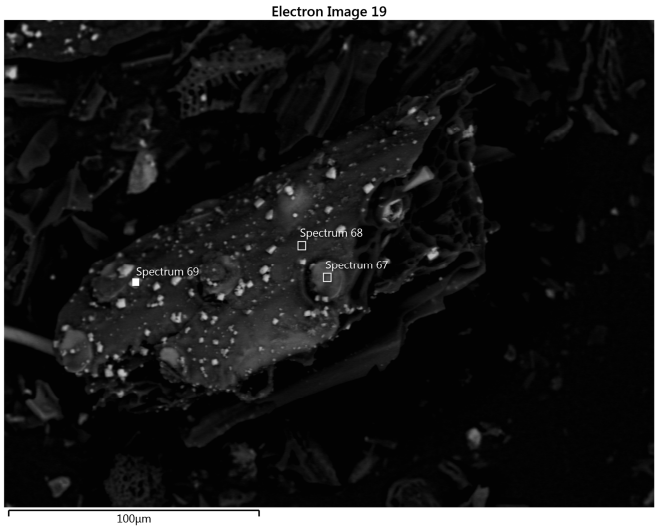


Electron Image 17



Electron Image 18



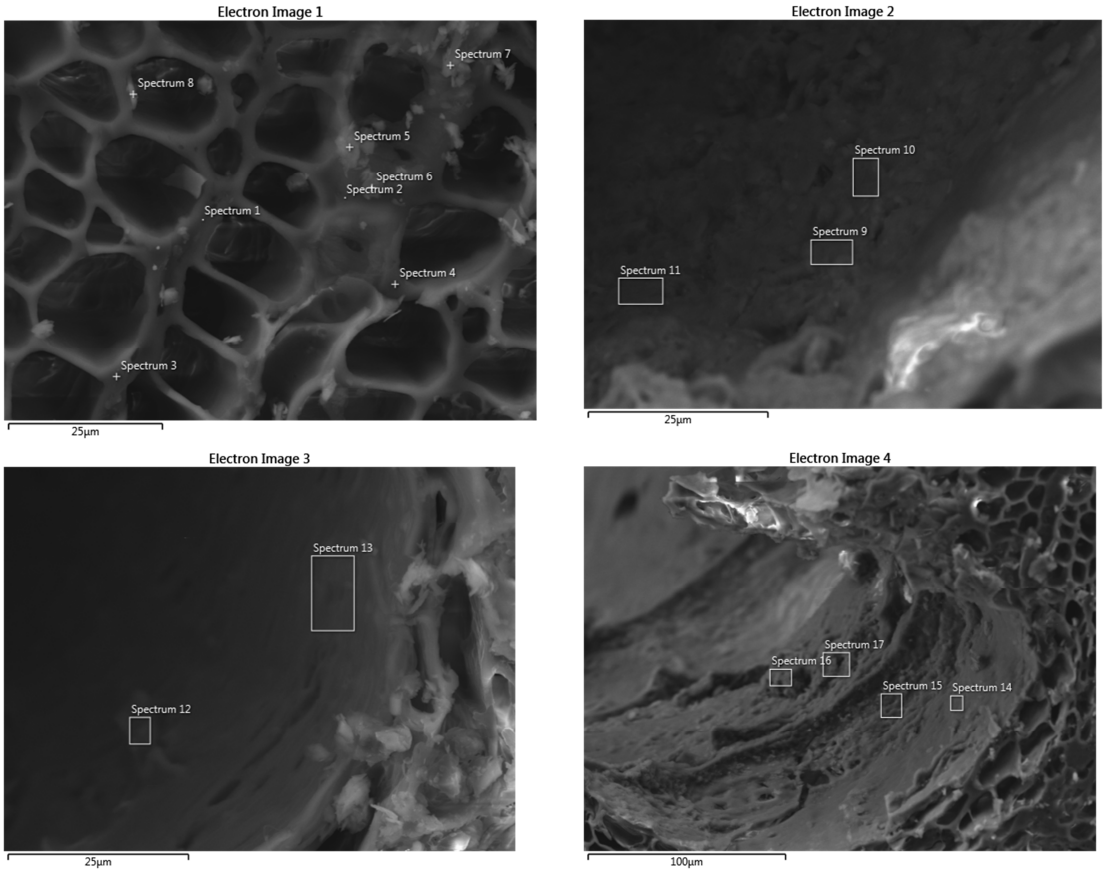


Appendix. 3 Charcoal derived from the soil on the plantation in Florentine valley (2013) chemical composition following the SEM-EDS analysis. The charcoal was most likely produced during onsite burn of the residues after Eucalyptus plantation harvest (2005).

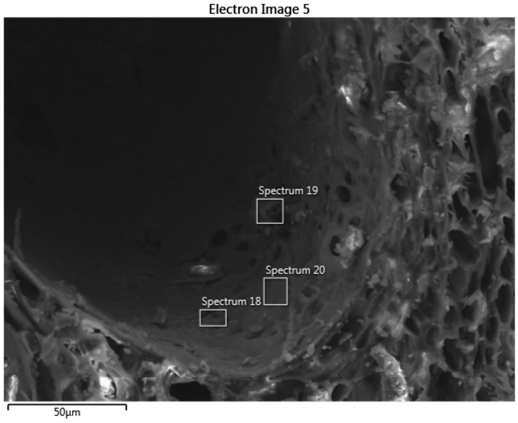
Spectrum number	Main composition	Chemical elements present in minimal amount
1	C	Al, Ca, K, Mg, P, Fe, O
2	C	Al, Ca, K, Mg, Fe, O
3	C	Al, Ca, K, Mg, Fe, O
4	C	Al, Ca, K, Mg, Fe, O
5	Si, O, Al, C	Na, Mg, Fe, Ca, K,
6	Si, O, Al, C	Mg, Fe, Ca, K,
7	C	O, Si, Na, Fe, Al, Mg, Mn, Ca, K,
8	Si, O, C	Ca
9	Si, O	Al, Mg, Fe, C, K
10	Si, K	Al, O, C, Fe, Ti,
11	Si, K	C, O, Al, Fe
12	C	O, Fe, Ca, Br, Si,
13	C, O	Ca, Fe, Al, K
14	C, O	Ca, Fe, Al, Si, K
15	C, O	Ca, Fe, Al, Si, K
16	C, O	Ca, Fe, Al, Si, K
17	Fe, C	O, Ca, Al, Si, K
18	C	O, Mg, Na, Fe, Ca, Al, P, Si, K
19	C, Fe	O, Si, K, Al
20	C, O	Ca, Fe, Al, Si, K
21	O	Mn, C, Si, P, Al, Pb, K
22	C	O, Mg, Na, Fe, Ca, Al, K
23	Si, Al, O	C, Fe, Mg, Ti, Ca, K
24	C	O, Ca, Fe, K

25	C	O, Ca, Mg, Al, K
26	Mn, O	C, P, Si, Al, Pb, K
27	C	O
28	C	O, Na
29	C	O, Na
30	C	O, Na
31	C	Ca, O
32	C	Ca, O, Mg, Al, Si
33	O, C	Si, Al, Fe, K, Ca, Mg
34	C	O, Ca, Al, Si, Fe, K
35	C	O, Fe, Ca, Al, Si, K
36	C, O	Si, Al, Fe, K, Ca, Mg
37	Fe	K, Ca, C, O, Si
38	C	O, Cl
39	C	O, Cl
40	C	O, Cl

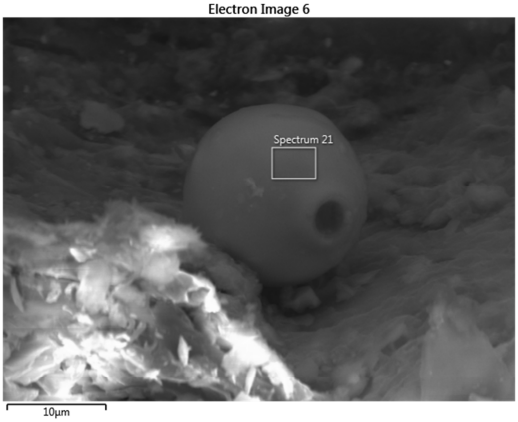
Appendix 4. Electron Microscopy spectra sites (SEM-EDS) of charcoal derived from forestry coupe 31Z in Florentine Valley. Analysed in Central Science Laboratory, UTAS, 2014.



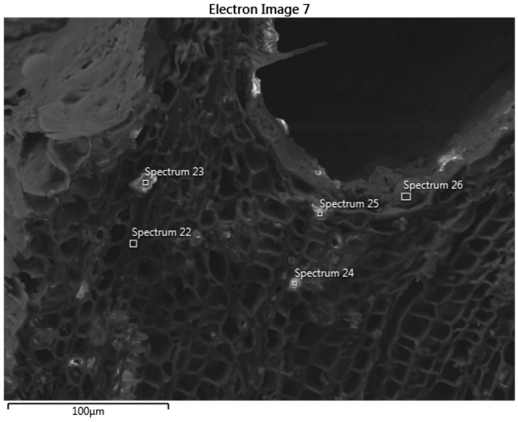
Electron Image 5



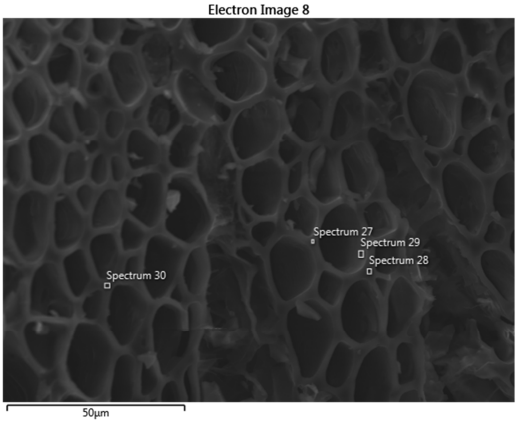
Electron Image 6



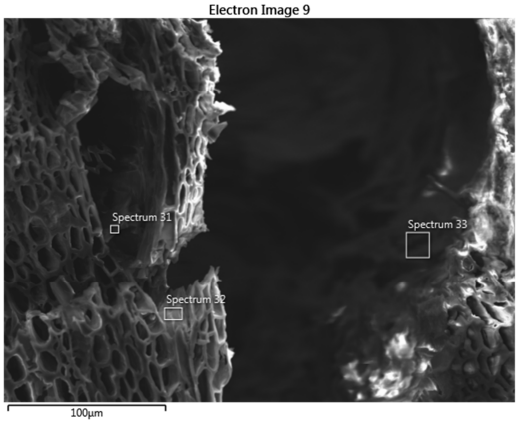
Electron Image 7



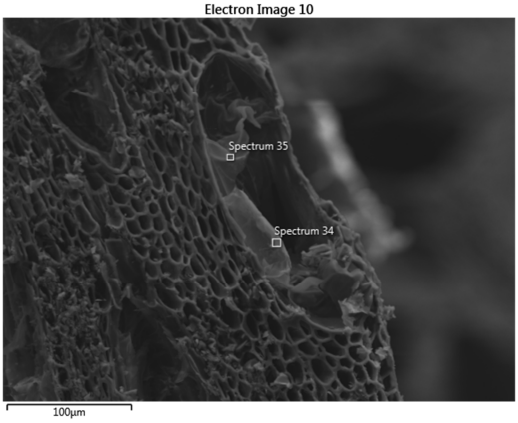
Electron Image 8



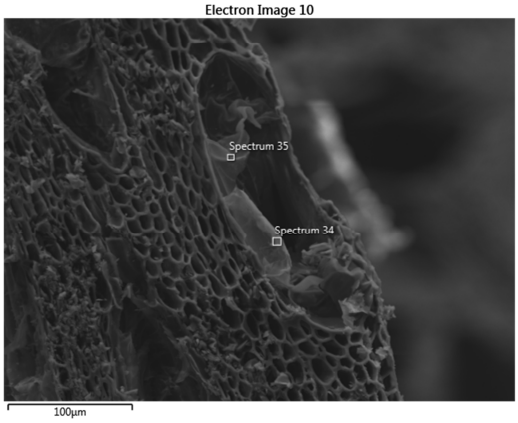
Electron Image 9



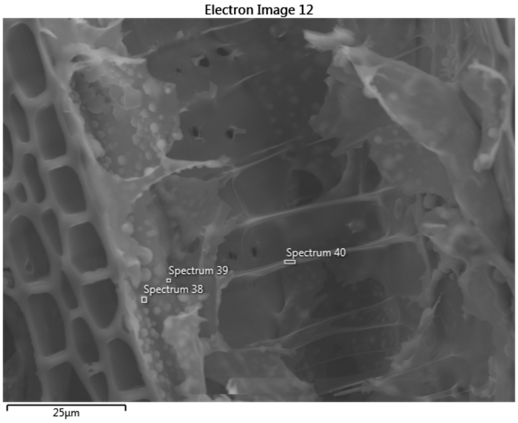
Electron Image 10



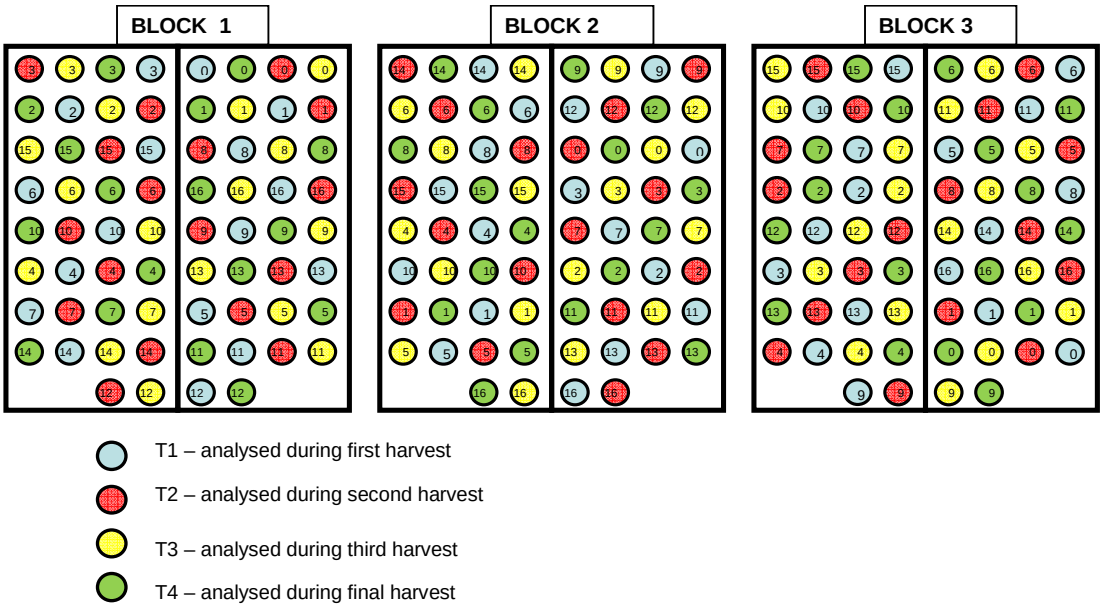
Electron Image 10



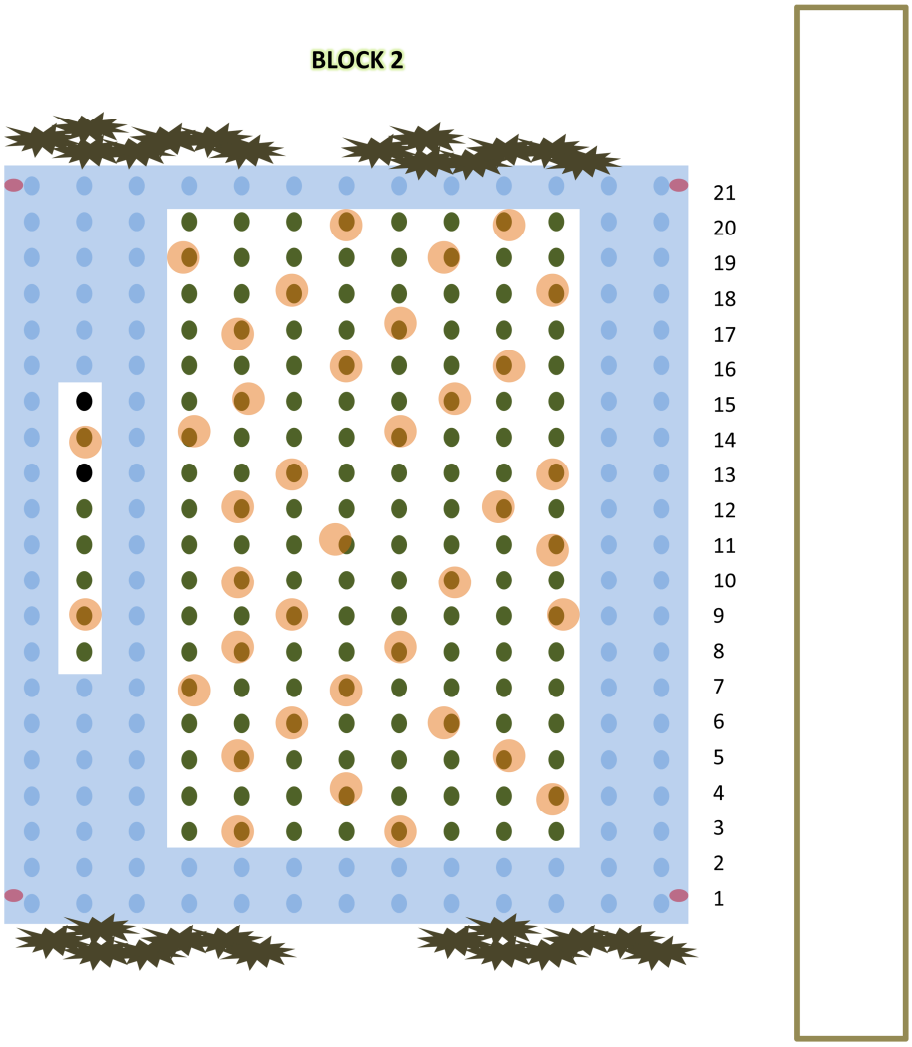
Electron Image 12

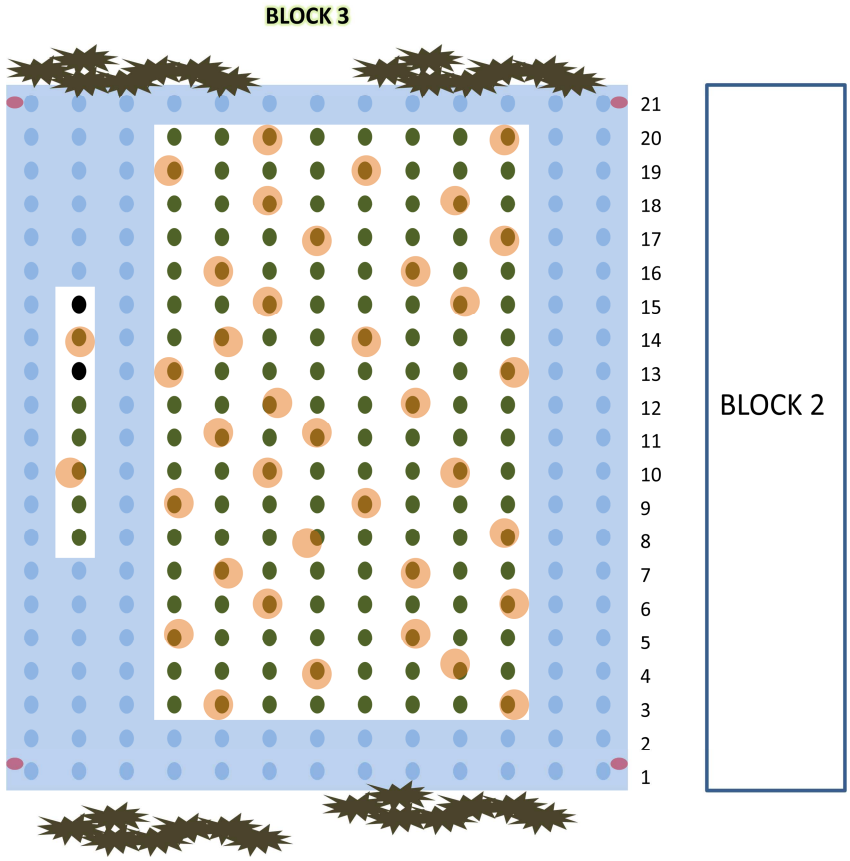


Appendix. 5. Spatial design of treatments in the *Eucalyptus nitens* pot trial, May 2011



Appendix 6. Spatial design of block 2 and 3 in the experimental plantation of *E. nitens* in Florentine Valley, September 2011.





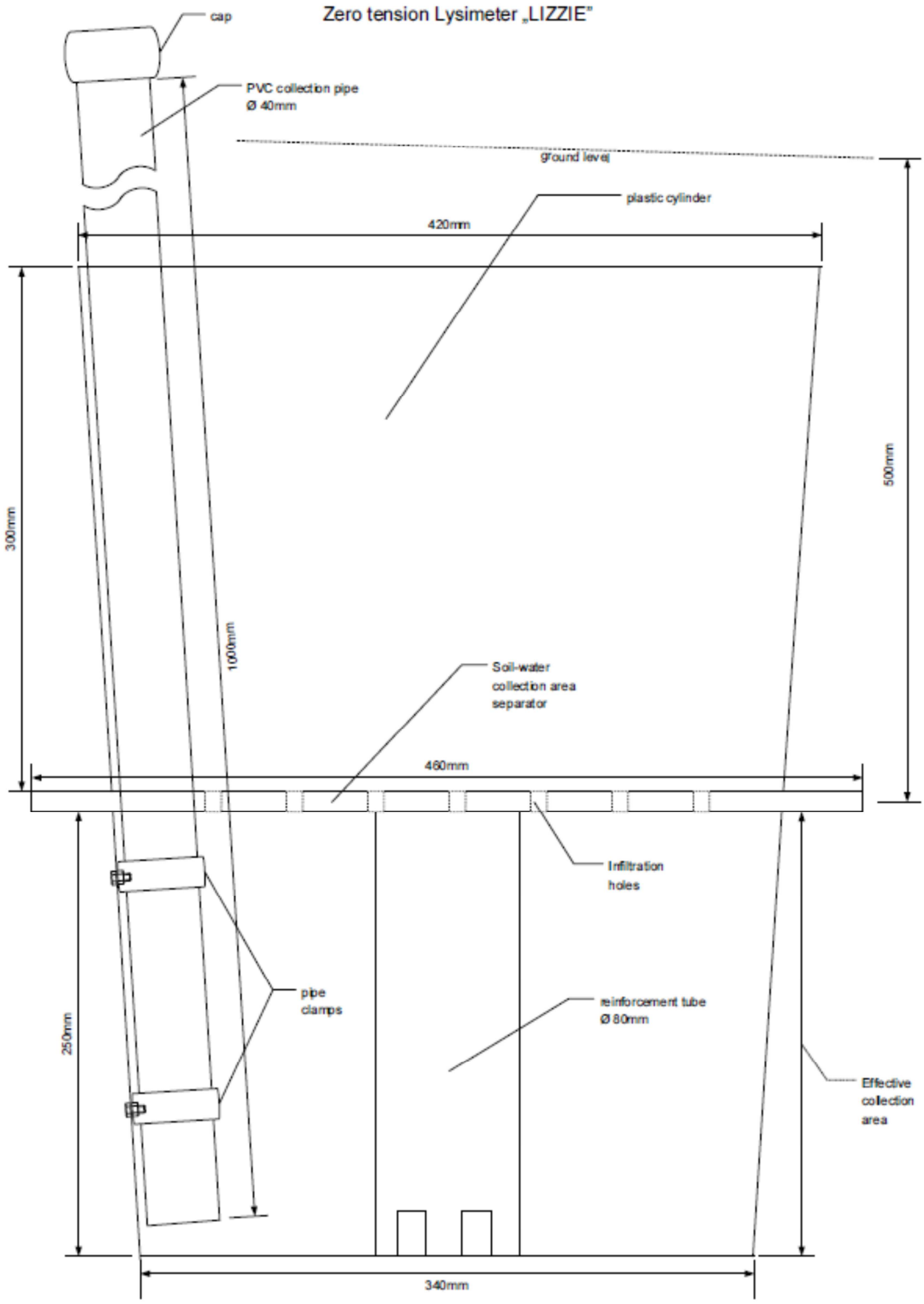
T1 – analysed during first harvest

T2 – analysed during second harvest

T3 – analysed during third harvest

T4 – analysed during final harvest

Appendix 7. Design of zero-tension Lysimeter 'Lizzie' installed in the field experiment in Florentine Valley.



Appendix 8. Major formulas in the Microsoft Excel financial model presented and discussed in Chapter 8.

1. Number of coupes per annum (M17) = number of operating days per year * number of tones processed per year / total tones processed in example coupe
2. Diesel cost per coupe (E16) = example coupe number batches * diesel used per batch in litres * cost of diesel per litre
3. Pyrolyser maintenance cost per annum (E19) = unit capital cost * maintenance cost per annum as % of capex
4. Seedling raising saving per hectare (E26) = if biochar is applied at the rate of 10 t ha^{-1} or more it equals $20, if biochar is applied at the rate of 5-10 t ha^{-1} it equals $15, if biochar is applied at the rate of 1-4 t ha^{-1}, it equals $10, if the application rate is lower there is no saving.
5. Site preparation savings per ha (E27) = If tones of wood processed per hectare is 30 or more, it equals $400, If tones of wood processed per hectare is 20-29, it equals $300, If tones of wood processed per hectare is 15-19, it equals $200, If tones of wood processed per hectare is 10-14, it equals $100, if there is less than 5 tonnes processed there is no saving.
6. Fertilisation savings per hectare (E28) = if biochar is applied in the field at the rate of 3 t ha^{-1} or more, it equals $90, if biochar is applied in the field at the rate of 1.5-2.9 t ha^{-1}, it equals $45, If biochar is applied at the lower rate than 0.5 t ha^{-1} there are no savings.
7. Second spraying effect per ha (E29) = if biochar is applied in the field at the rate of 3 t ha^{-1} or more, it equals -$20, if biochar is applied in the field at the rate of below 3 t ha^{-1}, it equals -$10.
8. Total savings per hectare (E30) = sum of: a)seedlings raising saving per hectare (E26), b)site preparation, windrowing, clearing etc (E27), c)fertilisation saving per hectare (E28), second spraying effect per hectare (E29).
9. Tonnes of biochar in the field per hectare (M30) = tonnes of wood processed in example coupe * biochar produced per tonnes of wood processed * onsite % distribution of production / number of hectares in example coupe.
10. Tonnes of biochar made in coupe for transport and sale/storing (M32) = number of hectares in example coupe * tonnes of wood processed per hectare * biochar produced per tonnes of wood processed * (to nursery distribution of production +sales distribution of production)
11. Total biochar produced per year (M37) = example number coupes per annum * tonnes processed in example coupe * biochar produced per tonne of wood processed.

12. Total biochar for sale per year (M38) = total biochar produced per year * sales distribution of production
13. Example coupe on site revenue (E38) = tonnes processed in example coupe * biochar produced per tone of wood processed * onsite distribution of production * onsite biochar price * tonnes of CO2 in 1 tonne of biochar.
14. Example coupe nurseries revenue (E39) = tonnes processed in example coupe * biochar produced per tonne of wood processed * to nursery distribution of production * to nursery biochar price.
15. Example coupe commercial revenue (E40) = tonnes processed in example coupe * biochar produced per tonne of wood processed * for sale distribution of production * market biochar price.
16. Annual revenue (G43) = total example coupe revenue * number of coupes harvested per annum.
17. Savings enjoyed by traditional operations per annum (G46) = total savings per hectare * number of hectares in an example coupe * number of coupes harvested per annum.
18. Annual costs all coupes (G53) = total operating and capital costs of biochar production per coupe * number of times pyrolyser is moved between example number of coupes per annum.

Appendix. 9. Interface of the Excel cost-benefit scenario model with base assumptions

Biochar Economics - direct biochar process costs and revenues plus biochar induced coupe savings

Assumptions

Mobile pyrolyzer capital cost	$250,000	Number of ha's in example coupe	30
Number of years useful life	10	Tonnes of wood processed per ha	15
Finance interest rate p.a.	10%	Tonnes processed in example coupe	450
Principal + interest repays p.a.	$39,836	Average batch size in tonnes	4
		Number of batches in example coupe	113
Mobile pyrolyzer operating costs:			
Example coupe number batches	113	Number of operating days per year	330
Person cost per batch	$30	Number of tonnes processed per day	12
Labour cost per coupe	$3,375		
		Cost of delivering waste to coupe	
Diesel used per batch in litres	10	edge per tonne	$10
Cost of diesel per litre	$0.80		
Diesel cost per coupe	$900	Number of times pyrolyzer moved in	
		example number coupes per annum	9
Maintenance cost p.a. As % of capex	4.0%	Pyrolyzer transport cost per move	$300
Maintenance cost per annum	$10,000		
		Biochar produced per tonne of wood	
Machine hire to feed pyrolyzer per t	$15	processed	0.25 tonnes
		Tonnes of CO2 in 1 tonne of biochar	3
		number of batches processed per day	3

Savings enjoyed by traditional operations

with biochar operating, derived from comparative table:

Seedling raising saving per ha	$10
Site prep, w'rowing, clearing etc per ha	$200
Fertilisation saving per ha	$45
Second spraying effect per ha	-$10.00
Total saving per ha	$245.00

Market:

	On site	To Nurser	Commercial Sales
% distribution of producti	60%	10%	30%
Sales price per tonne	$10 (carbon price)	$50 (at forest)	$1,000 (at forest)

tonnes of biochar in the field per ha	2.25
tonnes of biochar made in coupe for transport	45
cost of biochar transport per tonne per 100 km	$40

Biochar Economics - direct biochar process costs and revenues plus biochar induced coupe savings

Revenue

Example coupe **on site** revenue	$2,025	
Example coupe **nurseries** revenue	$563	
Example coupe **commercial** revenue	$33,750	
Total example coupe revenue	$36,338	
Number of coupes harvested per annum	9	
Annual Revenue		$319,770

total biochar produced per year [t]	990
total biochar for sale per year	297

Savings enjoyed by traditional operations per annum

Derived from $ savings per ha, ave coupe size & qty of	$64,680

Costs - biochar operating and capital

Labour cost per coupe	$3,375	
Diesel cost per coupe	$900	
Total costs per coupe	$4,275	
Annual costs all coupes		$37,620
Annual maintenance costs of capex		$10,000
Annual cost to deliver waste to coupe edge		$39,600
Annual machine hire to feed pyrolyzer		$59,400
Annual cost of moving pyrolyzer		$2,640
Annual finance cost of pyrolyzer		$39,836
Annual cost of biochar transport		$15,840
Net annual benefit in cost/benefit analysis		**$179,514**

1

Literature

[1] Abiven S., Andreoli R. (2011) Charcoal does not change decomposition rate of mixed litters in a mineral cambisol: a controlled conditions study. Biology and Fertility of Soils 47:111-114.

[2] Altland J.E., Locke J.C. (2012) Biochar affects macronutrient leaching from a soilless substrate. Horticultural Science 47:1136-1140.

[3] Amonette J.E., Joseph S. (2009) Characteristics of biochar: microchemical properties, in: J. Lehmann and S. Joseph (Eds.), Biochar for Environmental Management, Earth Scan, London.

[4] Angst T.E., Sohi S.P. (2013) Establishing release dynamics for plant nutrients from biochar. Bioenergy 5:221-226.

[5] Asai H., Samson B.K., Stephan H.M., Songyikhangsuthor K., Homma K., Kiyono Y., Inoue Y., Shiraiwa T., Horie T. (2009) Biochar amendment techniques for upland rice production in Northern Laos: soil physical properties, leaf SPAD and grain yild. Field Crop Research 111:81-84.

[6] Atkinson C.J., Fitzgerald J.D., Hipps N.A. (2010) Potential mechanisms for achieving agricultural benefits from biochar application to temperate soils: a review. Plant and Soil 337:1-18. DOI: 10.1007/s11104-010-0464-5.

[7] Attiwill P.M., Adams M.A. (1996) Nutrition of Eucalypts CSIRO Publishing Australia.

[8] Atwell B.J., Kriedemann P.E., Turnbull C.G.N. (1999) Chapter 3. Gaining water and nutrients: root function, in: B. J. Atwell, et al. (Eds.), Plants in action, Macmillan Education Australia Pty Ltd., http://plantsinaction.science.uq.edu.au/edition1/?q=content/contents-page.

[9] Baldock J.A., Smernik R.J. (2002) Chemical composition and bioavailability of thermally alerted *Pinus resinosa* (red pine) wood. Org. Geochem. 33:1093-1109.

[10] Ball P.N., MacKenzie M.D., DeLuca T.H., Holben W.E. (2010) Wildfire and charcoal enhance nitrification and ammonium-oxidizing bacterial abundance in dry montane forest soils. Journal of Environmental Quality 39:1243-1253.

[11] Bear F.E. (1965) Soils in Relation to Crop Growth Reinhold Publishing Corporation, Agricultural College&Experiment Station, Rutgers- the State University, New Brunswick, New Jersey, USA.

[12] Bell D.T. (1994) Interaction of Fire, temperature and light in the germination response of 16 species from the *Eucalyptus marginata* forest of South-western Australia. Australian Journal of Botany 42:501-509.

[13] Berglund L.M., DeLuca T.H., Zackrisson O. (2004) Activated carbon amendments to soil alters nitrification rates in Scots pine forests. Soil Biology and Biochemistry 36:2067-2073.

[14] Biederman L.A., Harpole W.S. (2013) Biochar and its effects on plant productivity and nutrient cycling: a meta-analysis. Bioenergy 5:202-214.

[15] Blackwell P., Krull E., Butler G., Herbert A., Solaiman Z. (2010) Effect of banded biochar on dryland wheat production and fertilizer use in south-western Australia: an agronomic and economic perspective. Australian Journal of Soil Research 48:531-545.

[16] Boland D.J., Brooker M.I.H., Chippendale G.M., Hall N., Hyland B.P.M., Johnson R.D., Kleinig D.A., Turner J.D. (1992) Forest trees of Australia CSIRO, Canberra.

[17] Borchard N., Wolf A., Laabs V., Aeckersberg R., Scherer H.W., Moeller A., Amelung W. (2012) Physical activation of biochar and its meaning for soilb fertility and nutrient leaching - a greenhouse experiment. Soil use and management 28:177-184.

[18] Bourke J.M.H., Fushimi C., Dowaki K., Nunoura T., Antal M.J.J. (2007) Do all carbonized charcoals have the same chemical structure?2. A model of the chemical structure of carbonized charcoal. Industrial and Engineering chemistry Research 46:5954-5967.

[19] Bridle T.R., Pritchard D. (2004) Energy and nutrient recovery from sawage sludge via pyrolysis. Water science and technology 50:169-175.

[20] Briens C., Piskorz J., Berruti F. (2008) Biomass Valorization for Fuel and Chemicals Production – a Review. International Journal of Chemical Reactor Engineering 6.

[21] Broadley M.R., Brown P., Cakmak I., Rengel Z., Zhao F. (2012) Function of nutrients: Micronutrients, in: H. Marschner (Ed.), Mineral nutrition of higher plants, Elsevier Ltd, USA.

[22] Brodowski S., Amelung W., Haumaier L., Abetz C., Zech W. (2005) Morphological and chemical properties of black carbon in physical soil fractions as revealed by scanning electron microscopy and energy-dispersive x-ray spectroscopy. Geoderma 128:116-129.

[23] Brown R.A., Kercher A.K., Nguyen B.T., Nagle D.C., Ball W.P. (2006) Production and characterization of synthetic wood chars for use as surrogates for natural sorbents. Organic geochemistry 37:515-522.

[24] Bruun E.W., Petersen C., Strobel B.W., Hauggaard-Nielsen H. (2012) Nitrogen and carbon leaching in repacked sandy soil with added fine particulate biochar. Soil Science Society American Journal 76:1142-1148.

[25] Bureau of Meteorology A.G. (2012-2013) Monthly weather reviews, http://www.bom.gov.au/climate/mwr/.

[26] Buss W., Masek O. (2014) Mobile organic compounds in biochar- a potential source of contamination- phytotoxic effect on cress seed (Lapidium sativum) germination. Journal of Environmental Management 137:111-119.

[27] Cahn M.D., Bouldin D.R., Cravo M.S., Bowen W.T. (1993) Cation and nitrate leaching in an oxisol of the Brazilian Amazon. Acta Amazonica 18:97-107.

[28] Chan K.Y., Van Zwieten L., Meszaros I., Downie A., Joseph S. (2007) Agronomic values of greenwaste biochar as a soil amendment. Australian Journal of Soil Research 45:629. DOI: 10.1071/sr07109.

[29] Chan K.Y., Van Zwieten L., Meszaros I., Downie A., Joseph S. (2008) Using poultry litter biochars as a soil amendments. Australian Journal of Soil Research 48:526-530

[30] Chan K.Y., Xu Z. (2009) Biochar: Nutrient properties and their enhancement, in: J. Lehmann and S. Joseph (Eds.), Biochar for environmental management, Earthscan, London.

[31] Chen Y., Shinogi Y., Taira M. (2010) Influence of biochar use on sugarcane growth, soil parameters and groundwater quality. Australian Journal of Soil Research 48:526-530

[32] Cheng C.H., Lehmann J., Engelhard M.H. (2008) Natural oxidation of black carbon in soils: Changes in molecular form and surface charge along a climosequence. Geochimica et Cosmochimica Acta 72:1598-1610.

[33] Cheng C.H., Lehmann J., Thies J., Burton S.D., Engelhard M.H. (2006) Oxidation of black carbon by biotic and abiotic. Organic geochemistry 37:1477-1488.

[34] Chintala R., Schumacher T.E., McDonald L.M., Clay D.E., Malo D.D., Papiernik S.K., Clay S.A., Julson J.L. (2014) Phosphorus Sorption and availability from biochars and soil/biochar mixtures. Clean soil air water 42:626-634.

[35] Close D.C., Bail I., Hunter S., Beadle C.L. (2005) Effects of exponential nutrient-loading on morphological and nitrogen characteristics and on after-planting performance of *Eucalyptus globulus* seedlings. Forest Ecology and Management 205:397-403. DOI: 10.1016/j.foreco.2004.10.041.

[36] Close D.C., Beadle C.L. (2003) Chilling-dependent photoinhibition, nutrition and growth analysis of *Ecalyptus nitens* seedlings during establishment. Tree Physiology 23:217-226.

[37] Close D.C., Davidson N.J., Churchill K.C., Corkrey R. (2010) Establishment of native *Eucalyptus pauciflora* and exotic *Eucalyptus nitens* on former grazing land. New Forests 40:143-152. DOI: 10.1007/s11056-010-9189-9.

[38] Clough T.J., Condron L.M. (2010) Biochar and nitrogen cycle: Introduction. Journal of Environmental Quality 39:1218-1223.

[39] Colwell J.D. (1965) An automatic procedure for the determination of Phosphorus in sodium hydrogen carbonate extracts of soils. Chemistry Industry:893-895.

[40] Davidson N.J., Battaglia M., Close D.C. (2004) Photosynthetic responses to overnight frost in *Eucalyptus nitens* and *E. globulus*. Trees - Structure and Function 18:245-252. DOI: 10.1007/s00468-003-0298-3.

[41] DeLuca T.H., MacKenzie M.D., Gundale M.J. (2009) Biochar effects on soil nutrient transformation, in: J. Lehmann and S. Joseph (Eds.), Biochar for Environmental Management, Earthscan, London.

[42] DeLuca T.H., MacKenzie M.D., Gundale M.J., Holben W.E. (2006) Wildlife-produced charcoal directly influences nitrogen cycling in Ponderosa pine forests. Soil Science 70:448-453.

[43] Demirbas A. (2004) Effects of temperature and particle size on biochar yield from pyrolysis of agricultural residues. J. Anal. Appl. Pyrol. 72:243-248.

[44] Dempster D.N., Gleeson D.B., Solaiman Z.M., Jones D.L., Murphy D.V. (2011) Decreased soil microbial biomass and nitrogen mineralisation with *Eucalyptus* biochar addition to coarse textured soil. Plant Soil. DOI: 10.1007/S11104-011-1067-5.

[45] Downie A., Crosky A., Munroe P. (2009) Physical properties of biochar, in: J. Lehmann and S. Joseph (Eds.), Biochar for environmental management, Earthscan, London, UK.

[46] Dubinin M.M., Radushkevich L.V. (1947) The equation of the characteristic curve of the activated charcoal. Proc.Academ.Sci, USSR Psych. Chem. Sect. 55:331-337.

[47] Duncan F., Hawkins C., Leech M., Parker N., Davidson N., McArthur C., Walsh A., Beadle C., Chuter C. (2006) Managing native farm forests, in: N. Davidson, et al. (Eds.), Farm Forestry: A technical and business handbook, Monotone Art Printers Pty, Ltd, Hobart.

[48] EarthSystems. (2013) Personal communication, expert advice and quote.

[49] Elliot H. (2011) The early history of plantation forestry on State-owned land in Tasmania. Tasforests 19.

[50] FT. (2013) Personal Communication.

[51] FT database. (2010-2013) Forestry Tasmania database, on request from Forestry Tasmania experts.

[52] Garnett T.P., Smethurst P.J. (1999) Ammonium and nitrate uptake by *Eucalyptus nitens*: effects of pH and temperature. Plant and soil 214:133-140.

[53] Gaskin J.W., Steiner C., Harris K., Das K.C., Bibens B. (2008) Effects of low temperature pyrolysis conditions on biochars for agricultural use. ASABE 51:2061-2069.

[54] Gaunt J.L., Cowie A. (2009) Biochar, Greenhouse gas accounting and emissions trading, in: J. Lehmann and S. Joseph (Eds.), Biochar for environmentla management, EarthScan, London.

[55] Glaser B., Haumaier L., Guggenberger G., Zech W. (2001) The 'Terra Preta' phenomenon: A model for sustainable agriculture in the humid tropics. Naturwissenschaften 88:37-41.

[56] Glover M. (2009) Taking Biochar to market: some essential concepts for commercial success, in: J. Lehmann and S. Joseph (Eds.), Biochar for environmental management, Earthscan, London.

[57] Graber E.R., Meller Harel Y., Kolton M., Cytryn E., Silber A., Rav David D., Tsechansky L., Borenshtein M., Elad Y. (2010) Biochar impact on development and productivity of pepper and tomato grown in fertigated soilless media. Plant and Soil 337:481-496. DOI: 10.1007/s11104-010-0544-6.

[58] Greaves B., May B. (2012) Australian secondary wood products and their markets, Forest&Wood products Australia.

[59] Gundale M.J., DeLuca T.H. (2006) Temperature and source material influence ecological attributes of ponderosa pine and Douglas-fir charcoal. Forest Ecology and Management 231:86-93.

[60] Guo Y., Tang H., Li G., Xie D. (2014) Effects of cow dung biochar amendment on adsorption and leaching of nutrient from an acid yellow soil irrigated with biogas slurry. Water, Air, & Soil Pollution: Focus 225:1820.

[61] Gurwick N.P., Moore L.A., HKelly C., Elias P. (2013) A systematic review of biochar research, with a focus on its stability in situ and its primise as a climate mitigation strategy. Plos one 8.

[62] Hammes K., Schmidt M.W.I. (2009) Changes of biochar in soil, in: J. Lehmann and S. Joseph (Eds.), Biochar for environmental management, EarthScan, London.

[63] Hill T.L. (1952) Theory of physical adsorption. Adc. Cat.4:211-258.

[64] Hong E., Ketterings Q., McBride M. (2010) Manganese, Agronomy Fact Sheet Series: Manganese, Cornell University

[65] College of Agriculture and Life Sciences.

[66] InternationalBiocharInitiative. (2013) Standarized Product Definition and Product Testing Guidelines for Biochar That Is Used in Soil, in: I.

B. Initiative (Ed.), www.biochar-international.org/characterizationstandard.

[67] Jones D.L., Rousk J., Edwards-Jones G., DeLuca T.H., Murphy D.V. (2012) Biochar-mediated changes in the soil quality and plant growth in a three year field trial. Soil Biology and Biochemistry:113-124.

[68] Joseph S. (2009) Soci-economic assessment and implementation of small-scale biochar projects, in: J. Lehmann and S. Joseph (Eds.), Biochar for environmental management, Earthscan, London.

[69] Joseph S., Peacocke C., Lehmann J., Munroe P. (2009) Developing a biochar classification and test methods, in: J. Lehmann and S. Joseph (Eds.), Biochar for Environmental management, EarthScan, London.

[70] Joseph S.D., Camps-Arbestain M., Lin Y., Munroe P., Chia C.H., Hook J., Van Zwieten L., Kimber S., Cowie A., Singh B.P., Lehmann J., Foidl N., Smernik R.J., Amonette J.E. (2010) An investigation into the reactions of biochar in soil. Australian Journal of Soil Sciences 48:501-515.

[71] Keiluweit M., Nico P.S., Johnson M.G., Kleber M. (2010) Dynamic molecular structure of plant biomass-derived black carbon (biochar). Environ Sci Technol 44:1247-1253.

[72] Kishimoto S., Sagiura G. (1985) Charcoal as a soil conditioner. Symposium on forest products research, international achievements for the future 5:12-23.

[73] Klein R.J.T., Huq S., Denton F., Downing T.E., Richels R.G., Robinson J.B., Toth F.L. (2007) Interrelationships between adaptation and mitigation. In Climate change 2007: Impacts, Adaptation and vulnerability., in: C. U. Press (Ed.), Contribution of working group II to he Fourth Assessment report of the Intergovernmental panel on Climate Change, Cambridge, United Kingdom.

[74] Kookana R.S. (2010) The role of biochar in modifying the environmental fate, bioavailability, and efficacy of pesticides in soils: a review. Australian Journal of Soil Research 48:627-637.

[75] Krull E., Baldock J.A., Skjemstad J.A.N., Smernik R. (2009) Characteristics of biochar: organo-chemical properties, in: J. Lehmann and S. Joseph (Eds.), Biochar for environmental management, EarthScan, London.

[76] Krull E.S., Baldock J.A., Skjemstad J.O. (2003) Importance of mechanisms and processes of the stabilisation of soil organic matter for modelling carbon turnover. Functional Plant Biology 30:207-222.

[77] Kuzyakov Y., Domanski G. (2000) Carbon input by plants into the soil. Review. Plant nutrition and soil science 163:421-431.

[78] Kyoung S., Cantrell K.B., Hunt P.G. (2010) High-Temperature Pyrolysis of blended animal manures for producing renewable energy and value-added biochar. Industrial and Engineering chemistry Research 49:10125-10131.

[79] Laird D., Brown R.C., Amonette J.E., Lehmann J. (2009) Review of the pyrolysis platform for coproducing bio-oil and biochar. Biofuels, Bioproducts and Biorafineries 3:547-562.

[80] Lal R. (2008) Carbon sequestration. Philos Trans R Soc 363:815-830.

[81] Lang T., Jensen A.D., Jensen P.A. (2005) Retention of organic elements during solid fuel pyrolysis with emphasis on the peculiar behaviour of nitrogen. Energy & Fuels 19:1631-1643

[82] Lehmann J. (2007) Bio-energy in the black. Front. Ecol. Environ 5:381-387

[83] Lehmann J., Czimczik C., D. L., Sohi S. (2009) Stability of biochar in the soil, in: J. Lehmann and S. Joseph (Eds.), Biochar for environmental Management, EarthScan, London.

[84] Lehmann J., Da Silva J.P., Steiner C., Nehls T., Zech W., Glaser B. (2003) Nutrient availability and leaching in an archaeological Anthrosol and a Ferrasol of the Central Amazon basin:fertilizer, manure and charcoal amendments. Plant and Soil 249:343-357.

[85] Lehmann J., Gaunt J., Rondon M. (2006) Bio-char Sequestration in Terrestrial Ecosystems – A Review. Mitigation and Adaptation Strategies for Global Change 11:395-419. DOI: 10.1007/s11027-005-9006-5.

[86] Lehmann J., Joseph S. (2009a) Biochar for Environmental Management Earthscan, Uk and USA.

[87] Lehmann J., Joseph S. (2009b) Biochar for environmental management: An Introduction, in: J. Lehmann and S. Joseph (Eds.), Biochar for Environmental Management, EarthScan, London.

[88] Lehmann J., Rillig M.C., Thies J., Masiello C.A., Hockaday W.C., Crowley D. (2011) Biochar effect on soil biota - A review. Soil Biology and Biochemistry 43:1812-1836.

[89] Lehto T., Lavola A., Kallio E., Aphalo P.J. (2004) Boron uptake by ectomycorrhizas of silver birch. Mycorrhiza 14:209-212.

[90] Lei O., Zhang R. (2013) Effects of biochars derived from different feedstock and pyrolysis temperatures on soil physical and hydraulic properties. Soil Sediments 13:1561-1572.

[91] Liang B., Lehmann J., Solomon D., Kinyangi J., Grossman J., O'Neill B., Skjemstad J.O., Thies J., Luizao F.J., Petersen J., Neves E.G. (2006) Black carbon increases cation exchange capacity in soils. Soil Science Society of America Journal 70:5.

[92] Liang B., Lehmann J., Solomon D., Sohi S., Thies J.E., Skjemstad J.O., Luizão F.J., Engelhard M.H., Neves E.G., Wirick S. (2008) Stability of biomass-derived black carbon in soils. Geochimica et Cosmochimica Acta 72:6069-6078. DOI: 10.1016/j.gca.2008.09.028.

[93] Liu T., Liu B., Zhang W. (2014) Nutrients and heavy metals in biochar produced by sewage sludge pyrolysis: its application in soil amendment. Journal of Environmental Studies 23:271-275.

[94] Luo Y., Durenkamp M., De Nobili M., Lin Q., Brookes P.C. (2011) Short term soil priming effects and the mineralization of biochar following its incorporation to soils of different pH. Soil Biology and Biochemistry 43:2304-2314.

[95] Lyons A., Horne M., Taylor P., Wilkinson G., Smith S.E., Lord J., Gilfedder L., Valker P., Leech M., Hawkins C. (2006) The business of farm forestry, in: N. Davidson, et al. (Eds.), Farm Forestry, a technical and business handbook, Monotone Art printers Pty, Ltd, Hobart.

[96] Ma Y.L., Matsunaka T. (2013a) Biochar derived from dairy cattle carcasses as an alternative source of phosphorus and amendment for soil acidity. Soil Science and Plant Nutrition 59:628-641. DOI: 10.1080/00380768.2013.806205.

[97] Ma Y.L., Matsunaka T. (2013b) Biochar derived from dairy cattle carcasses as an alternative source of phosphorus and amendment for soil acidity. Soil Science and Plant Nutrition 59:628-641.

[98] MacKenzie M.D., DeLuca T.H. (2006) Charcoal and shrubs modify soil processes in ponderosa pine forests of western Montana. Plant and Soil 287:257-266. DOI: 10.1007/s11104-006-9074-7.

[99] Major J. (2010) Biochar impact on soil carbon losses, IBI Research Summary, International Biochar Initiative.

[100] Major J., Rondon M., Molina D., Riha S.J., Lehmann J. (2010) Maize yield and nutrition during 4 years after biochar application to a Colombian savanna oxisol. Plant and Soil 333:117-128. DOI: 10.1007/s11104-010-0327-0.

[101] Major J., Steiner C., Downie A., Lehmann J. (2009) Biochar Effects on Nutrient Leaching, in: J. Lehmann and S. Joseph (Eds.), Biochar for Environmental Management, EarthScan, London.

[102] Makoto K., Hirobe M., DeLuca T.H., Brayanin S.V., Procopchuk V.F., Koike T. (2011) Effects of fire-derived charcoal on soil properties and seedlings regeneration in a recently burned *Larix gmelini/Pinus sylvestris* forest. Journal of Soils and Sediments 11:1317-1322.

[103] Manoa U.o.H.a. (2014) Soil-nutrient management for Maui Country, http://www.ctahr.hawaii.edu/mauisoil/c_relationship.aspx.

[104] Marschner H. (1995) The mineral nutrition of higher plants Acadamic Press, San Diego, CA.

[105] Marsden-Smedley J.B., Whight S. (2011) Planned burning in Tasmania. II. Fire risk assessment and the development of standarised Burn Risk Assessment Tool (BRAT). Tasforests 19:109-121.

[106] McCarl B.A., Peacocke C., Chrisman R., Kung C., Sands R.D. (2009) Economics of Biochar production, utilizatiopn andf greenhouse gas offsets, in: J. Lehmann and S. Joseph (Eds.), Biochar for Environmental Management, Earthscan, London.

[107] McHenry M.P. (2009) Agricultural bio-char production, renewable energy generation and farm carbon sequestration in Western Australia: Certainty, uncertainty and risk. Agriculture, Ecosystems & Environment 129:1-7. DOI: 10.1016/j.agee.2008.08.006.

[108] McQaker N.R., Brown D.F., Kluckner P.D. (1978) AOAC Official Methods of analysis 15 Ed. Analitical chemistry 51.

[109] Melo L.C.A., Coscione A.R., Abreau C.A., Puga C.A., Camargo O.A. (2013) Influence of pyrolysis temperature on cadmium and zinc sorption capacity of sugar cane straw-derived biochar. Bioresources 8:4992-5004.

[110] Milne E., Powlson D.S., Cerri C.E. (2007) Soil carbon stocks at regional scales. Agriculture, Ecosystems & Environment 122:1-2. DOI: 10.1016/j.agee.2007.01.001.

[111] Morales M.M., Comerford N., Guerrini I.A., Falcao N.P.S., Reeves J.B. (2013) Sorption and desorption of phosphate on biochar and biochar-soil mixtures. Soil use and management 29:306-314.

[112] Muralidhara H.S. (1982) Conversion of tannery waste to useful products. Resources and conservation 8:43-59.

[113] Nelson N.O., Agudelo S.C., Yuan W., Gan J. (2011) Nitrogen and Phosphorus availability in biochar-amended soils. Soil Science 176.

[114] Nguyen B.T., Lehmann J. (2004) Black carbon decomposition under varying water regimes. Org. Geochem 40:846-853.

[115] Nguyen B.T., Lehmann J., Kinyangi J., Smernik R., Riha S.J., Englehard M.H. (2009) Long-term black carbon dynamics in cultivated soil. Biochemistry 92:163-176.

[116] Nigussie A., Kissi E., Misganaw M., Ambaw G. (2012) Effect of Biochar Application on soil properties and nutrient uptake of Lettuces (Lectuca sativa) grown in chromium polutted soils. American-Eurasian Journal Agricultural &Environmental Sciences 12:369-376.

[117] Novak J.M., Busscher W.J., Laird D.L., Ahmedna M., Watts D.W., Niandou M.A.S. (2009) Impact of Biochar Amendment on Fertility of a Southeastern Coastal Plain Soil. Soil Science 174:105-112. DOI: 10.1097/SS.0b013e3181981d9a.

[118] Ogawa M., Okimori Y. (2010) Pioneering works in biochar research, Japan. Australian Journal of Soil Sciences 48:489-500

[119] Ogawa M., Okimori Y., Takahashi F. (2006) Carbon Sequestration by Carbonization of Biomass and Forestation: Three Case Studies. Mitigation and Adaptation Strategies for Global Change 11:421-436. DOI: 10.1007/s11027-005-9007-4.

[120] Ojekami A., Ige D., Hao X., Akinremi O. (2011) Phosphorus mobility in a soil with long term manure application. Journal of Agricultural Science 3.

[121] Parsons M.G.M., Davidson J. (2006) Australia's plantations, Bureau of rural sciences, Canberra.

[122] Pearce D., Atkinson G., Maurato S. (2006) Cost-benefit analysis and the environment OECD Publishing.

[123] Peverill K.I., Sparrow L.A., Reuter D.J. (1999) Soil analysis: an interpretation manual CSIRO publishing, Australia.

[124] Prendergast-Miller M.T., Duvall M., Sohi S.P. (2014) Biochar-root interactions are mediated by biochar nutrient content and impacts on soil nutrient availability. European Journal of Soil Science 65:173-185.

[125] Prommer J., Wanek W., Hofhansl F., Trojan D., Offre P., Urich T., Schleper C., Sassmann S., Kitzler B., Soja G., Hood-Nowotny R.C. (2014) Biochar decelerates soil organic nitrogen cycling but stimulates soil nitrification in a temperate arable field. Plos One 9.

[126] Qian L., Chen B. (2014) Interactions of Aluminum with Biochars and Oxidized Biochars: Implications for the Biochar Aging Process. J Agric Food Chem. DOI: 10.1021/jf404624h.

[127] Quickchem. Methods manual for the 'Quickchem' automated ion analyser, Lachat instruments.

[128] Quilty J.R., Cattle S.R. (2011) Use and understanding of organic amendments in Australian agriculture: a review. Soil Research 49:1-26.

[129] Rayment G.E., Higginson F.R. (1992) Australian Laboratory Handbook of Soil and Water Chemical Methods.

[130] Rayment G.E., Lyons D.J. (2011) Soil chemical methods – Australasia, CSIRO Publishing, Collingwood, Victoria.

[131] Reuter D.J., Robinson J.B. (1997) Plant Analysis:an interpretation manual. 2nd ed. CSIRO Publishing, Australia.

[132] Roberts K., Gloy B.A., Joseph S., Scott N.R., Lehmann J. (2010) Life Cycle Assesment of Biochar Systems: Estimating the energetic,

economic and climate change potential. Environment, Science and technology 44:827-833.

[133] Rogovska N., Laird D., Cruse R.M., Trabue S., Heaton E. (2012) Germination tests for assessing biochar quality. Journal of Environmental Quality 41:1014-1022.

[134] Rondon M.A., Lehmann J., Ramírez J., Hurtado M. (2006) Biological nitrogen fixation by common beans (Phaseolus vulgaris L.) increases with bio-char additions. Biology and Fertility of Soils 43:699-708. DOI: 10.1007/s00374-006-0152-z.

[135] Rothe. A. (2013) Forest Biomass for energy: Current and potentuial use in Tasmania and a comparison with European experience, Weihenstephan- Triesdorf, University of Applied Sciences, Zentrum Wald Forst Holz Weihenstephan.

[136] Rouquerol F., Rouquerol I., Sing K. (1999) Adsorption by Powders and porous solids Acadamic Press, London, UK.

[137] Sakya A.T., Dell B., Huang L. (2002) Boron requirements for *Eucalyptus globulus* seedlings. Plant and Soil 246:87-95.

[138] Santalla M., Omil B., Rodríguez-Soalleiro R., Merino A. (2011) Effectiveness of wood ash containing charcoal as a fertilizer for a forest plantation in a temperate region. Plant and Soil 346:63-78. DOI: 10.1007/s11104-011-0794-y.

[139] Sarkhot D.V., Berhe A.A., Ghezzehei T.A. (2012) Impact of biochar enriched with dairy manure effluent on carbon and nitrogen dynamics. Journal of Environmental Quality 41:1107-1114.

[140] Sarmah A.K., Srinivasan P., Smernik R.J., Manley-Harris M., Antal M.J., Downie A., Van Zwieten L. (2010) Retention capacity of biochar-amended New Zealand dairy farm soil for an estrogenic steroid hormone and its primary metabolite. Australian Journal of Soil Research 48:648-658.

[141] Schachtman D.P., Reid R.J., Ayling S.M. (1998) Phosphorus Uptake by Plants: From Soil to Cell. Plant Physiol 116:447-453.

[142] Schmidt M.W.I., Noack A.G. (2000) Black carbon in soils and sediments: analysis, distribution, implications and current cha;;enges. Global biochaemical cycles 14:777-793.

[143] Schulz H., Dunst G., Glaser B. (2013) Positive effects of composed biochar on plant growth and soil fertility. Agronomic sustainable development 33:817-827.

[144] Searle P.L. (1984) The Bertholet or indophenol reaction and its use in the analytical chemistry of Nitrogen. Analyst 109:549-568.

[145] Shackley S., Sohi S. (2010) An assessment of the benefits and issues associated with the application of biochar to soil, UK Biochar Research Centre.

[146] Shinogi Y., Kanri Y. (2003) Pyrolysis of plant, animal and human waste: physical and chemical characterization of the pyrolytic products. Bioresour. Technol 90:241-247

[147] Sigel H., Sigel A. (1990) Metal Ions in biological systems, Compendium on Magnesium and its role in Biology, Nutrition and physiology, Institute of Inorganic Chemistry, Basel.

[148] Sika M.P., Hardie A.G. (2014) Effect of pine wood biochar on ammonium nitrate leaching and availability in a South African sandy soil. European Journal of Soil Science 65:113-119.

[149] Sims J.T., Simard R.R., Joern B.C. (1998) Phosphorus loss in agricultural drainage: historical perspective and current research. Journal of Environmental Quality 27:277-293.

[150] Singh B., Singh B.P., Cowie A. (2010) Characterization and evaluation of biochars for their application as a soil amendment. Australian Journal of Soil Research 48:516-525.

[151] Smernik R.J. (2009) Biochar and sorption of organic compound, in: J. Lehmann and S. Joseph (Eds.), Biochar for environmental management, EarthScan, London.

[152] Sohi S., Lopez-Capel E., Krull E., Bol R. (2009) Biochar, climate change and soil: A review to guide future research, CSIRO Land and Water Science Report

[153] Solaiman Z.M., Blackwell P., Abbott L.K., Storer P. (2010) Direct and residual effect of biochar application on mycorrhizal root colonialization, growth and nutrition of wheat. Australian Journal of Soil Research 48:546-554.

[154] Spokas K.A., Baker J.M., Reicosky D.C. (2010) Ethylene: potential key for biochar amendment impacts. Plant and Soil 333:443-452. DOI: 10.1007/s11104-010-0359-5.

[155] Spokas K.A., Novak J.M., Venterea R.T. (2011) Biochar's role as an alternative N-fertilizer: ammonia capture. Plant and Soil 350:35-42. DOI: 10.1007/s11104-011-0930-8.

[156] Stavi I. (2013) Biochar use in forestry and tree-based agro-ecosystems for increasing climate change mitigation and adaptation. International Journal of Sustainable Development & World Ecology 20:166-181.

[157] Steinbeiss S., Gleixner G., Antonietti M. (2009) Effect of biochar amendment on soil carbon balance and soil microbial activity. Soil Biology and Biochemistry 41:1301-1310. DOI: 10.1016/j.soilbio.2009.03.016.

[158] Steiner C., Glaser B., Teixeira W.G., Lehmann J., Blum W.E.H., Zech W. (2008) Nitrogen retention and plant uptake on a highly weathered central Amazoniam ferrasol amended with compost and charcoal. Soil Science 171:893-899.

[159] Taghizadeh-Toosi A., Clough T.J., Sherlock R.R., Condron L.M. (2011) Biochar adsorbed ammonia is bioavailable. Plant and Soil 350:57-69. DOI: 10.1007/s11104-011-0870-3.

[160] Thies J.E., Rillig M.C. (2009) Characteristics of Biochar: Biological properties, in: J. Lehmann and S. Joseph (Eds.), Biochar for Environmental Management, Earth Scan, London.

[161] Troeh F.R., Thompson L.M. (2005) Soils and soil fertility Blackwell Publishing, Iowa, US.

[162] Troy S.M., Lawlor P.G., O'Flynn C.J., Healy M.G. (2014) The impact of biochar addition on nutrient leaching and soil properties from tillage soil amended with pig manure. Water, Air, & Soil Pollution: Focus 225:1900.

[163] TruSpec. CN Carbon Nitrogen Determinator Instruction Manual Software version 1.6 x Part number 200 to 288.

[164] Tryon E.H. (1948) Effect of charcoal on certain physical, chemical and biological properties of soils. Ecological Monographs 18:81-115.

[165] Tseng R.L., Tseng S.K. (2006) Characterization and use of high surface area activated carbons prepared from cane pith for liquid-phase adsorption. Journal of hazardous materials B136:671-680.

[166] Turn S.Q., Keffer V., Staackmann M. (2002) Analysis of hawaii Biomass Energy Resources for Distributed Energy Applications, University of Hawaii, School of Ocean and Earth Sciences and Technology Hawaii, USA.

[167] Unger R., Killorn R. (2011) Effect of three different qualities of biochar on selected soil properties. Communications in soil science and plant analysis 42:2274-2283.

[168] Van Zwieten L., Kimber S., Downie A., Morris S., Petty S., Rust J., Chan K.Y. (2010a) A glasshouse study on the interaction of low mineral ash biochar with nitrogen in a sandy soil. Australian Journal of Soil Sciences 48:569-576.

[169] Van Zwieten L., Kimber S., Morris S., Chan K.Y., Downie A., Rust J., Joseph S., Cowie A. (2009) Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. Plant and Soil 327:235-246. DOI: 10.1007/s11104-009-0050-x.

[170] Van Zwieten L., Kimber S., Morris S., Downie A., Berger E., Rust J., Acheer C. (2010b) Influence of biochars on flux of N2O and CO2 from Ferrosol. Australian Journal of Soil Sciences 48:555-568.

[171] Vaneklaas E.J., Lambers H., Bragg J., Finnegan P.M., C.E. L., Plaxton W.C., Price C.A., Scheible W.R., Shane M.W., White P.J., Raven J.A. (2012) Opportunities for improving phosphorus-use efficiency in crop plants. New Phytologist, Tansley Reviews 195.

[172] Volker P., Castley P., Lyons A., Beadle C., Battaglia M., Bower D., Smethurst P.J., Close D.C., Hall M., Medhurst J., Elek J., Davidson N. (2006) Plantation forestry on farms, in: N. Davidson, et al. (Eds.), Farm Forestry: a technical business handbook, Monotone Art Printers Pty, Ltd, Hobart.

[173] Walkley A., Black I.A. (1934) An examination of the Degtjareff Method for Determining Soil Organic Matter and a proposed modification of the chromic acid titration method. Soil Science 37:29-38.

[174] Wardle D.A., Nilsson M.C., Zackrisson O. (2008) Fire-derived charcoal causes loss of forest humus. www.sciencemag.org 320.

[175] Wardle D.A., Zackrisson O., Nilsson M.C. (1998) The charcoal effect in Boreal forests: mechanisms and ecological consequences. Oecologia 115:419-426.

[176] Warnock D.D., Lehmann J., Kuyper T.W., Rillig M.C. (2007) Mycorrhizal responses to biochar in soil – concepts and mechanisms. Plant and Soil 300:9-20. DOI: 10.1007/s11104-007-9391-5.

[177] Watzinger A., Feichtmair S., Kitzler B., Zehetner F., Kloss S., Wimmer B., Zechmeister-Boltenstern S., Soja G. (2014) Soil microbial communities responded to biochar application in temperate soils and slowly metabolized 13C-labelled biochar as revealed by 13C PLFA analyses: results from a short-term incubation and pot experiment. European Journal of Soil Science 65:40-51.

[178] White P.J. (2012) Ion uptake mechanisms of individual cells and roots: short-distance transport, in: H. Marschner (Ed.), Mineral Nutrition of higher plants, Elsevier, Ltd, USA. pp. 26.

[179] Widowati, Asnah. (2014) Biochar can enhance potassium fertilization efficiency and economic feasibility of maize cultivation. Journal of Agricultural Science 6.

[180] Winkler J.B., Lang H., Graf W., Reth S., Munch J.C. (2009) Experimental setup of field lysimeters for studying effects of elevated ozone and below-ground pathogen infection on a plant-soil-system of juvenile beech (*Fagus sylvatica L.*). Plant and Soil 323:7-19. DOI: 10.1007/s11104-009-9936-x.

[181] Wood M.J., McLarin M.L., Volker P.W., Syme M. (2009) Management of Eucalypt plantations for profitable sawlog production in Tasmania, Australia. Tasforests 18.

[182] Wrobel-Tobiszewska A., Boersma M., Sargison J., Adams P., Close D.C. (2012a) Nitrogen, phosphorus and potassium dynamics in potting mix and plant material under biochar and fertilizer combination amendments in nine-months *Eucalyptus nitens* pot experiment.

[183] Wrobel-Tobiszewska A., Boersma M., Sargison J., Close D.C., Krull E., Adams P. (2012b) Macadamia biochar as a growth stimulus for *Eucalyptus nitens* forestry nurseries, Soil Science Conference, Hobart.

[184] Yamato M., Okimori Y., Wibowo I.F., Anshori S., Ogawa M. (2006) Effects of the application of charred bark ofAcacia mangiumon the yield of maize, cowpea and peanut, and soil chemical properties in South Sumatra, Indonesia. Soil Science and Plant Nutrition 52:489-495. DOI: 10.1111/j.1747-0765.2006.00065.x.

[185] Yanai Y., Toyota K., Okazaki M. (2007) Effects of charcoal addition on N2O emissions from soil resulting from rewetting air-dried soil in short-term laboratory experiments. Soil science and plant nutrition 53:181-188.

[186] Young E.A., Hea S.B., Soon I.K., Myung H.K., Young-Joon A. (2011) Hazardous effects of eight years of application of four organic waste materials on earthworm numbers and biomass in field lysimeters. Arch Environ Contam Toxicol 60:99-106.

[187] Zhang A., Liu Y., Pan G., Hussain Q., Li L., Zheng J., Zhang X. (2011) Effect of biochar amendment on maize yield and greenhouse gas emissions from a soil organic carbon poor calcareous loamy soil from Central China Plain. Plant and Soil 351:263-275. DOI: 10.1007/s11104-011-0957-x.

[188] Zhang A., Walawender W.P., Fan M., Fan L.T., Daugaard D., Brown R.C. (2004) Preparation of activated carbon from forestr and agricultural residues through CO2 activation. Chemical Engineering Journal 105:53-59.

[189] Zhao C., Hu C., Huang W., Sun X., Tan Q., Di H. (2009) A lysimeter study of nitrate leaching and optimum nitrogen application rates for intensively irrigated vegetable production systems in Central China. Journal of Soils and Sediments 10:9-17. DOI: 10.1007/s11368-009-0063-3.

[190] Zimmerman A.R., Gao B., Mi-Youn A. (2011) Positive and negative carbon mineralization priming effects among a variety of biochar-amended soils. Soil Biology and Biochemistry 43:1169-1179.