

Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

Application of Biochar Technologies to wastewater Treatment

A thesis presented in partial fulfilment of the requirements for the degree of

Doctor of Philosophy

In

Soil Science



Palmerston North, New Zealand.

Kiran Hina
2013

This thesis is dedicated to my saviour and supervisor

Professor Michael James Hedley

Abstract

A review of wastewater treatment options and the properties of biochar (charcoal made from biomass with the intention of carbon sequestration in soil) indicated the potential application of biochar for removal of ammonium-N ($\text{NH}_4^+\text{-N}$) and various organic and inorganic pollutants from wastewaters. This thesis investigates (i) the capacity of alkaline activated and non-activated Pine and Eucalyptus biochars to retain N and P from wastewaters, and (ii) the potential use of these nutrient-rich materials as slow-release fertilisers in soil, thus assisting the recycling of nutrients from waste streams.

The retention of $\text{NH}_4^+\text{-N}$ on different materials, pine bark, pine biochar (produced from wood chips at 550 °C) and zeolite was investigated. When shaken with a 39 mg $\text{NH}_4^+\text{-N L}^{-1}$ influent solution, Zeolite proved to be the best sorbent of $\text{NH}_4^+\text{-N}$, followed by pine biochar and pine bark; $0.71 > 0.38 > 0.27$ mg $\text{NH}_4^+\text{-N g}^{-1}$ sorbent, respectively. Ways of increasing the CEC (cation exchange capacity) and $\text{NH}_4^+\text{-N}$ sorption capacity of biochar were investigated by (i) alkaline activation by tannery waste or (ii) physical activation using steam as pre and post treatment of biochars, respectively to increase their CEC. Washed alkaline activated biochars (Pine and Eucalyptus) showed a significant ($p < 0.05$) increase in the $\text{NH}_4^+\text{-N}$ sorption capacity over corresponding non-activated biochars. Steam activation increased the internal surface area of biochars but did not prove increased retention of $\text{NH}_4^+\text{-N}$. The efficiency of $\text{NH}_4^+\text{-N}$ removal from synthetic NH_4^+ solutions and urban and dairy wastewaters by alkaline activated and non-activated Pine and Eucalyptus biochars was evaluated and compared using batch and column studies under different flow rates and retention times. Greater $\text{NH}_4^+\text{-N}$ sorption was observed in alkaline activated Pine biochar from both the synthetic solution and urban wastewater in column studies @ 2.40 mg N g^{-1} and 2.17 mg g^{-1} $\text{NH}_4^+\text{-N}$ biochar, respectively. Inclusion of Okato tephra with alkaline activated pine biochar proved effective in removing both P and N from urban wastewater.

Finally, the activated pine biochar and tephra loaded with N and P from wastewater treatment were incorporated into two soils (Kiwitea and Manawatu) and the bioavailability of N and P was tested by growing ryegrass in an exhaustive Standford and Dement bioassay. The recovery of N and P was very low and this indicated that it was not economical to use biochar in wastewater treatment for subsequent use as a fertiliser.

Acknowledgements

I would like to acknowledge and thank foremostly Professor Michael J. Hedley, my principle PhD supervisor, for his great supervision, brilliant ideas, guidance and patience throughout this study. His competence in the field of Soil Science and the ocean of knowledge within his great personality has been a constant inspiration and role model in my academic progress in my Post graduate diploma as well as my PhD. My sincere thanks go to my co-supervisors Dr Marta Camps Arbestain and Dr James Hanly for their kindness, efforts, advice and constructive suggestions during my study. A bundle of thanks goes to my friend, Michael Bretherton for his wise suggestions and moral support that helped me to get through the highs and lows of study and life being a single parent. Many thanks to Dr P. Loganathan who accepted my application to work with him in NZ at the very beginning when I was in my home country. This enabled me to get funding from the HEC to come and study in the New Zealand.

Many thanks to Massey University staff; Liza Haarhoff, Ian Furkert, Bob Toes, Glenys Wallace and Ross Wallace. Many thanks to HEC Pakistan government for giving me a chance to see this wonderful world of beautiful and kind people of NZ; as well for the knowledge and learning I attained here from my worthy supervisors and staff at Massey University, NZ.

My appreciation goes to my friends, postgraduate students: Tao Wang, Saman Herath, Neha Jha, Amandeep, Raza Ullah, Sadaf, Saleem Bhatti and Dr Peter Bishop for their support and friendship.

Many thanks to International Student officers of Massey University: Sylvia Hooker, Dianne Reilly and Natalia Benquet for their support during my study.

Last but not least, my immense gratitude to my parents (**M. Younis** and **Khalida Jabeen**), sister (**Dr Iram Shireen**), brother (**M. Nauman**), aunt (**Bushra Akhtar**) and beloved son (**Muhammad Umar**) for their support, strengthening affection and prayers.

Ultimately, I thank our creator, God for bringing into existence the astonishingly wondrous and beautiful world, especially New Zealand, where I come and saw the marvellous sceneries as well as kind and friendly people that made me feel like heaven.

Table of Contents

CHAPTER 1: Introduction.....	1
1.1 Biochar Technology.....	1
1.2 Wastewater discharge and surface water quality.....	1
1.3 Mitigation of adverse effects of wastewater discharge.....	3
1.3.1 Land Treatment.....	3
1.3.2 Filtration, active removal of N and P	3
1.4 Thesis Structure.....	6
CHAPTER 2: Literature Review.....	10
2.1 The biochar Concept and potential applications.....	10
2.2 Manufacture of biochar.....	11
2.2.1 Biochar preparation from agricultural and forestry wastes.....	12
2.3 Stability of biochar.....	13
2.4 Agronomic benefits from amending soils with biochar.....	13
2.5 Soil properties affected by Biochar.....	14
2.5.1 Soil density.....	15
2.5.2 Soil pore size distribution.....	15
2.5.3 Soil Colour.....	15
2.5.4 Soil pH.....	16
2.5.5 Biochar nutrient value.....	16
2.5.6 Biochar and cation exchange capacity (CEC).....	17
2.5.7 Soil Moisture Retention.....	18
2.6 Waste management with biochar.....	18
2.7 Activation of biochar for added value biochar production.....	19
2.8 Wastewaters quality and conventional treatment.....	21

2.8.1	Wastewater treatment systems.....	24
2.8.2	Potential use for biochar in active filtration.....	26
2.9	Summary.....	27
	References.....	30
 CHAPTER 3: Activating biochars with pre (alkaline) and post (steam) treatments		
	of feedstocks and biochars.....	39
3.1	Introduction.....	39
3.2	Materials and Methods.....	40
3.2.1	Materials.....	40
3.2.2	Methods.....	41
3.2.3	Statistical Analyses.....	46
3.3	Results and Discussion.....	46
3.3.1	Composition of feedstocks used.....	46
3.3.2	Characterisation.....	46
3.3.3	Batch sorption study.....	60
3.4	Conclusions.....	61
	References.....	64
 CHAPTER 4: Ammonium retention on biochar: (i) comparison with bark and		
	zeolite, and (ii) effect of biochar particle size.....	68
4.1	Introduction.....	68
4.2	Materials and Methods.....	70
4.2.1	Materials.....	70
4.2.2	Methods.....	70
4.2.3	Statistical Analyses.....	73
4.3	Results and Discussion.....	74

4.3.1 Characterisation of sorbents.....	74
4.3.2 Batch Sorption study comparing zeolite, bark and biochar.....	79
4.3.3 Batch sorption study comparing biochars with different particle sizes.....	79
4.4 Conclusions.....	84
References.....	86
CHAPTER 5: Ammonium sorption and volatilisation from solution by activated and non-activated Biochars.....	88
5.1 Introduction.....	88
5.2 Materials and Methods.....	89
5.2.1 Materials.....	89
5.2.2 Volatilisation studies: Experiment 1 and 2.....	89
5.3 Results and Discussion.....	90
5.3.1 Feedstocks and untreated Biochars.....	90
5.3.2 Sorption of ammonium and volatilisation of ammonia.....	92
5.4 Conclusions.....	98
References.....	99
CHAPTER 6: Ammonium removal from wastewater by Batch and flow through (column) studies.....	100
6.1 Introduction.....	100
6.2 Materials and Methods.....	102
6.2.1 Materials.....	102
6.2.2 Methods.....	103
6.2.3 Statistical Analyses.....	105
6.3 Results and Discussion.....	105

6.4 Conclusions.....	112
References.....	114
CHAPTER 7: Ammonium and phosphorus removal from wastewater using weathered volcanic tephra and biochar mixtures.....	116
7.1 Introduction.....	116
7.2 Materials and Methods.....	117
7.2.1 Materials.....	117
7.2.2 Methods.....	117
7.2.3 Statistical Analyses.....	123
7.3 Results and Discussion.....	121
7.4 Conclusions.....	134
References.....	135
CHAPTER 8: Assessment of N and P bioavailability from biochar and volcanic tephra treated with urban wastewater.....	137
8.1 Introduction.....	137
8.2 Materials and Methods.....	138
8.2.1 Materials.....	138
8.2.2 Establishment of “Stanford and Dement” Bioassay.....	139
8.2.3 Chemical analyses of Soils, tephra and biochars.....	143
8.2.4 Statistical Analyses.....	144
8.3 Results... ..	144
8.4 Discussion.....	159
8.5 Conclusions.....	167
References.....	168
CHAPTER 9: Summary.....	171

9.1 Justification and Organization of work.....	171
9.2 Important Findings.....	173
9.3 Main Conclusions.....	176
9.4 Implications for future Research.....	177
References	178

List of Tables

Table. No	Title	Page No.
Table 2.1	Discharges to water and compliances with proposed water quality standards for N and P in the Manawatu-Whanganui region between 1993 to 2006 at flows less than half median.	24
Table 2.2	Categories of wastewater treatment.	25
Table 3.1	Elemental composition of tannery waste residue.	41
Table 3.2	Values (%) of neutral detergent fibre (NDF), hemicelluloses, cellulose and lignin content of Pine (PI) and Eucalyptus (EU) feedstocks before and after pre-treatment with solid tannery waste (S).	46
Table 3.3	Elemental analysis of feedstocks and biochars.	48
Table 3.4	Values of pH, carboxylic groups and BET surface area.	50
Table 3.5	Normalised area of the peaks corresponding to each oxygen surface group for the different biochars.	57
Table S1	Assignments of absorption peaks and bands in FT-IR spectra.	63
Table 4.1	Chemical and physical characteristics of different sorbents.	75
Table 4.2	Physical and chemical analysis of unwashed biochars.	76
Table 4.3	Electrical conductivity (EC) and pH of leachates collected during a 3-step washing using deionised water prior to the batch sorption-desorption study.	77
Table 4.4	Electrical conductivity (EC) and pH of leachates collected during a 3-step washing using deionised water prior to the column sorption study.	78
Table 4.5	XPS scan of the atomic composition of C, O and N in	79

differently processed unwashed biochars.

Table 5.1	Physical and Chemical Characteristics of activated and non-activated biochars.	91
Table 5.2	Ammonium-N sorbed and volatilised during sorption by washed and unwashed biochars.	93
Table 5.3	Volatilisation of NH ₃ from suspensions of washed and unwashed biochars.	96
Table 6.1	Wastewaters composition.	103
Table 7.1	Typical urban wastewater analysis.	119
Table 7.2	Chemical analysis of tephra before (T) and recovered after the wastewater treatment (WT-T) from all treatments except TE/BC-Mix.	128
Table 7.3	Chemical analysis of biochars before (L PI) and recovered after the wastewater treatment (WT-L PI) from all treatments except TE/BC-Mix.	128
Table 7.4	Fractionation of P in tephra and biochar at time 0 and after wastewater treatment.	133
Table 8.1	Chemical analysis of soils and tephra before (T) and after wastewater treatment (WT-T).	146
Table 8.2	Chemical analysis of biochars (WT-L PI=wastewater treated activated pine biochar, L PI= activated pine biochar, Ctr PI= non activated pine biochar).	146
Table 8.3	Total N and mineral N content of different sorbents.	147

List of Figures

Figure No.	Title	Page No.
Figure 2.1	Pyrolyser used for the manufacture of Biochar (Small, 5 L, rotating, gas fired cylinder).	12
Figure 2.2	Terra preta soils.	16
Figure 2.3	Sources of wastewater.	21
Figure 3.1	FTIR spectra of treated and untreated feedstocks, Pine: A and C, Eucalyptus: B and D.	51
Figure 3.2	FTIR spectra of PI and EU biochars: A) Ctr PI, B) Ctr EU, C) L PI, D) LEU, E) S PI, F) S EU.	53
Figure 3.3	FTIR spectra of PI and EU biochars (Ctr PI, Ctr EU, Steam PI, Steam EU).	54
Figure 3.4	Solid state ¹³ C NMR spectra of feedstocks and biochars: A), Pine, B), Eucalyptus.	55
Figure 3.5	Solid state ¹³ C NMR spectra of biochars.	56
Figure 3.6	C 1s core level spectra obtained for Ctr EU, L EU and S EU biochar samples.	57
Figure 3.7	SEM images of Biochars.	59
Figure 3.8	Sorption and desorption of NH ₄ ⁺ -N in the Pine and Eucalyptus biochars elaborated in this study.	60
Figure 4.1	Materials used in study.	70
Figure 4.2	NH ₄ ⁺ -N sorbed (mg g ⁻¹) on different sorbents using two initial NH ₄ ⁺ -N concentrations (39 and 79 mg L ⁻¹).	80
Figure 4.3	NH ₄ ⁺ -N sorbed (in mg cm ⁻³) on different sorbents using two initial NH ₄ ⁺ -N concentrations (39 and 79 mg L ⁻¹ , Batch study).	81

Figure 4.4	Amount of NH_4^+ -N sorbed and then desorbed by Ion exchange with KCl in the batch sorption study comparing different particle sizes.	82
Figure 4.5	Cumulative amount of NH_4^+ -N sorbed on the different biochars used in the column sorption study comparing different particle sizes.	84
Figure 5.1	Equipment for Volatilisation study.	90
Figure 5.2	Change of EC as biochars are sequentially washed in deionised water.	94
Figure 5.3	Change of pH as biochars are sequentially washed in deionised water.	94
Figure 5.4	Relationship between predicted NH_3 -N and acid trap NH_3 -N.	97
Figure 5.5	Relationship between NH_3 -N in acid trap and pH according to the Henry's model at different influent concentration.	97
Figure 6.1	Isonormal NH_4^+ -N sorption study with synthetic solutions (starting concentrations were 14, 140, 350 $\mu\text{g NH}_4^+$ -N mL^{-1}).	106
Figure 6.2	NH_4^+ -N sorption from FD-A wastewater in batch sorption study.	107
Figure 6.3	Cumulative NH_4^+ -N sorbed from dairy wastewater @ 1 mL/min (column, 11-15 mm diameter) (Column study A).	108
Figure 6.4	Cumulative NH_4^+ -N sorbed from dairy wastewater @ 0.16 mL/min (column, 11-15 mm diameter); (Column study A).	108
Figure 6.5	Desorption of NH_4^+ -N by KCl from different biochars (Column study A).	109
Figure 6.6	Ammonium-N sorption on L PI biochar with urban wastewater under two concentrations @ 0.16 mL min^{-1} (Column study B).	110

Figure 6.7	Ammonium ($\text{NH}_4^+\text{-N}$) sorption on L PI biochar from synthetic $\text{NH}_4\text{-N}$ solution (Column study B, 0.16 mL min^{-1} flow rate, 35 ppm influent solution and 4 g biochar).	111
Figure 6.8	Ammonium-N sorption on L PI biochar in 80 mm diameter columns using urban wastewater with a $\text{NH}_4^+\text{-N}$ concentration of (Column study C).	112
Figure 7.1	Column study setup.	119
Figure 7.2	Cumulative P removed (mg per column) from urban wastewater by different arrangements of biochar and tephra in leaching columns.	122
Figure 7.3	Total P sorbed (mg P /column) in the different treatments.	123
Figure 7.4	pH of the effluents from the column study at different cumulative volumes of wastewater.	124
Figure 7.5	Sorption of $\text{NH}_4^+\text{-N}$ in the different treatments.	125
Figure 7.6	XRD spectra of a). WT- L PI (wastewater treated activated biochar) and b). L PI biochar.	130
Figure 7.7	XRD spectra of a). WT-T (wastewater treated tephra) and b). T (tephra).	131
Figure 8.1	The arrangement of pots a) Two pots technology with upper pot containing sand, and b) after the addition of the upper pot with ryegrass to the lower pot with soil treatments.	140
Figure 8.2	a). “Stanford and Dement” pots at 4 th week after placing top pot on soil treatments, b). A thick rhizosphere root mat has formed in the small volume of soil at the bottom of the pot.	141
Figure 8.3	Different stages of plant bioassay (Stanford and Dement)	142
Figure 8.4	KCl extractable $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ in Kiwitea soil under different treatments.	148

Figure 8.5	pH of incubated Kiwitea soil under different treatments.	149
Figure 8.6	Dry matter yield of ryegrass grown on Kiwitea and Manawatu soils (Ctr) amended with biochars.	150
Figure 8.7	Weight of air dried roots of ryegrass in control soils (Ctr) and soils amended with treatments.	151
Figure 8.8	Percentage P in ryegrass shoots in control soils (Ctr) and soils amended with treatments.	152
Figure 8.9	P uptake (mg P pot^{-1}) in herbage in control soils (Ctr) and soils amended with treatments.	153
Figure 8.10	% N in herbage in control soils (Ctr) and soils amended with treatments.	154
Figure 8.11	N Uptake in herbage in control soils (Ctr) and soils amended with treatments.	155
Figure 8.12	Dry matter yield of ryegrass grown on Kiwitea and Manawatu soils treated with higher levels of biochars.	156
Figure 8.13	Root weights grown on Kiwitea and Manawatu soils treated with higher biochar rates.	156
Figure 8.14	The percentage P in ryegrass herbage grown on Kiwitea and Manawatu soils treated with higher biochar rates.	157
Figure 8.15	P Uptake in ryegrass herbage grown on Kiwitea and Manawatu soils treated with higher biochar rates.	157
Figure 8.16	The percentage N in herbage grown on Kiwitea and Manawatu soils treated with higher biochar rates.	158
Figure 8.17	N content in herbage grown on Kiwitea and Manawatu soils treated with higher biochar rates.	159
Figure 8.18	The percentage P recovered (of that added) from ryegrass plants grown on Kiwitea and Manawatu soils fertilised with wastewater treated tephra WT-T at two rates of application; 10 and 20 t ha^{-1} .	161
Figure 8.19	Bioavailable P indicated by ryegrass plants grown on	162

Kiwitea and Manawatu soils fertilised with wastewater treated tephra (WT-T @ 10 and 20t ha⁻¹) expressed as percentage of P uptake from unfertilised control.

- Figure 8.20** The percentage P recovered (of that added) from ryegrass plants grown on Kiwitea and Manawatu soils fertilised with wastewater treated biochar (WT-L PI) at four rates of application; 10, 20, 40 and 100 t ha⁻¹. 163
- Figure 8.21** The percentage N recovered (of that added) from ryegrass plants grown on Kiwitea and Manawatu soils fertilised with wastewater treated biochar (WT-L PI) at four rates of application; 10, 20, 40 and 100 t ha⁻¹. 163
- Figure 8.22** The percentage bioavailable P as indicated by ryegrass plants grown on Kiwitea and Manawatu soils fertilised with wastewater treated biochar (WT-L PI) at four rates of application; 10, 20, 40 and 100 t ha⁻¹; expressed as % of P uptake in unfertilised soil. 164
- Figure 8.23** The percentage bioavailable N as indicated by ryegrass plants grown on Kiwitea and Manawatu soils fertilised with wastewater treated biochar (WT-L PI) at four rates of application; 10, 20, 40 and 100 t ha⁻¹, expressed as % of N uptake in unfertilised soil. 165
- Figure 8.24** Graphs showing the relationships between the amount of N taken up by ryegrass and two measures of N added; total N (a) and hydrolysable N (b and c) for biochars (Ctr PI, L PI, WT-L PI) applied to the Kiwitea (triangles) and Manawatu (circles) soils. 166

Chapter 1 Introduction

1.1 Biochar Technology

The term biochar has arisen to describe the type of charcoal that results from the thermal treatment (heating) of natural organic feedstocks (such as crop waste, wood chip, municipal waste or manure) in an oxygen-limited environment. The process is termed pyrolysis in which bioenergy may also be produced (Bridgwater, 2003). According to the International Biochar Initiative, the final use of biochar should be for application to soils to achieve an agronomic and/or environmental benefit. For formulating the directions of research undertaken in this thesis, the properties of charcoals manufactured for purposes other than addition to soils, have also been reviewed in this thesis. Due to its aromatic structure, biochar (charcoal) is chemically and biologically more stable than the carbon (C) source from which it is made. This makes biochar difficult to breakdown, remaining stable in soils for hundreds to thousands of years (Krull et al. 2006).

Evidence of past use of biochar is drawn from the discovery and characterisation of patches of dark, highly fertile soils in the Amazonia region developed on acidic Oxisols (Lehmann et al. 2003). These soils were termed “dark soils” or “Terra Preta” and they were created by native people who incorporated biochar into them (Lehmann et al. 2003). Terra Preta soils have high carbon content (a large fraction of which is charcoal), and higher fertility than surrounding soils. Biochar particles comprise two main structural fractions: condensed aromatic C structures and ash (Calvelo Pereira et al. 2011; Wang et al. 2012). Because of the stability of biochar from degradation, it has promise as a technology for mitigating GHG (greenhouse gases) emissions (Lehmann 2007). During the study of charcoal (Glaser et al. 2002) and the role of biochar in soils, researchers have also noted its cation exchange properties (Niggusie and Kissi, 2011).

1.2 Wastewater discharge and surface water quality

Wastewaters from urban origin are rich in nitrogen (N) and phosphorus (P) compounds originating mainly from urine and industrial by-products. The organic forms of N mineralise to ammonium (NH_4^+) (Hedström, 2001), which is a potential pollutant in fresh water resources.

Chapter 1

Enrichment of freshwater lakes and rivers with soluble N and P promote weed and periphyton (algal blooms) growth, which have negative environmental effects such as hypoxia (the depletion of O₂ in water), which reduces oxygen availability to fresh water fish (Nguyen and Tanner, 1998). The proliferation of periphyton also diminishes the aesthetic and recreational value of water (McArthur and Clark, 2007). Some rivers and streams within the Manawatu-Wanganui region currently experience blooms of periphyton growth during periods of high sunlight intensity and extended durations of stable flows (Ausseil and Clark, 2007), which lead to clogging of irrigation and water supply ways.

To reduce the risk of pollution in wastewaters from nutrients, agricultural and urban wastewaters are often treated in oxidation pond systems (Nguyen and Tanner, 1998). However, the ammonium (NH₄⁺) and dissolved reactive phosphorus (DRP) levels in pond effluent discharges are often still excessive and can lead eutrophication of waterways (Oledzka, 2007). There are many towns in New Zealand that continue to discharge pond-treated sewage wastewater into fresh surface waters. For example, in the Manawatu-Wanganui Region there are over 30 towns with sewage wastewater discharges with mean 1700 m³/day discharge (McArthur and Clark, 2007). At some river sites, as it is the case downstream of the Palmerton North and Feilding sewage treatment plant outfalls, sewage wastewater discharges are the predominant source of SIN (soluble inorganic nitrogen), particularly NH₄⁺, and DRP during low river flow conditions.

Historically (pre-2000), most dairy farms in New Zealand also discharged their pond-treated farm dairy wastewater to rivers and lakes. In 1998 over 300 dairy farms discharged their wastewater into the Manawatu River, but by 2010 this number had decreased to only 2, after the widespread adoption of land treatment. However, in some regions, such as the Taranaki Region, a large proportion of farms still use two-pond treatment and discharge their wastewater rich in N, and particularly NH₄⁺, and DRP to fresh water streams and, therefore, contributing to the degradation of water quality (Longhurst et al. 2000; Houlbrooke et al. 2004).

1.3 Mitigation of adverse effects of wastewater discharge

Reducing the levels of NH_4^+ in the wastewater discharges described above is expected to improve river water quality. Improving the effectiveness of aerobic pond treatment, for example by using aerators to increase the nitrification process, is a common method for reducing ammonium levels. However, aerators require a relatively high input of power to operate effectively and typically do not remove all the ammonium. Therefore, it would be an advantage to have an additional treatment method to further remove NH_4^+ from wastewaters.

1.3.1 Land Treatment

Well managed land treatment has been shown to be an effective method for treating wastewaters and is widely used in the dairy industry for treating farm dairy effluent (Houlbrooke et al. 2004). The two-pond treatment system [anaerobic and aerobic (facultative) ponds] is the most prevalent system in small rural towns in New Zealand but is ineffective for N and P removal. However, the cost of operation and maintenance is low under two-pond system, which is the main advantage over other systems.

1.3.2 Filtration, active removal of N and P

Active filters, which include reactive media, have shown promise in removing N and P from wastewater (Kostura et al. 2005; Shilton et al. 2006). A wide variety of substrates have been used in these filters, with gravel, limestone and steel-waste representing just a few examples (Westholm, 2006). Various studies have been conducted using different P adsorbing materials to remove P from wastewaters; this included the use of iron and aluminium oxy-hydroxides (Baker et al. 1998) and allophane (Hanly et al. 2008), commonly present in volcanic tephra. Soils and parent materials derived from tephra (volcanic ash and lapilli) have potential as relatively low cost substrates for use in active filters. Tephra is a term for all the fragmental material erupted explosively from a volcano and is high in amorphous alumina-silicates, which provides tephra with a high P-adsorbing capacity (Ryden and Syers, 1975). The presence of hydrous oxides of iron and aluminium, as a function of the degree of weathering, has been shown to influence the P adsorbing capacity of tephra (Parfitt, 1989). Tephra has been shown to be a successful option to

removing P from synthetic P solutions (Hanly et al; 2008; Liesch, 2010). Liesch 2010 demonstrated that the Okato tephra (<2 mm size fraction) could remove as much as 8 mg P g⁻¹ tephra. A disadvantage of tephra can be its numerous small particles able to clog the flow path of the filter thereby diminishing its hydraulic conductivity. This can generate restricted flow or bypass flow around the outside of material, creating insufficient contact between the media and the wastewater (Drizo et al. 1999), thereby rendering the system inefficient.

Removal of NH₄⁺ from wastewaters is needed if the risk of wastewater discharges in water quality is to be minimised. Several sorbents, such as zeolite (Nguyen and Tanner, 1998, Cooney and Booker et al. 1999) and bark (Bolan et al. 2004; Wieczorek, 2008) have previously been assessed for their ability to remove NH₄⁺ from solution. On saturation, the adsorbent (clinoptilolite zeolite, in case of Perrin et al. 1998) may be applied onto agricultural fields as a fertiliser (Perrin et al. 1998). Mohan and Pittman (2007) reported the use of charcoal produced from woody material (pine bark, oak bark and oak wood) at 400-450 °C for the removal of heavy metals and metalloids (e.g., Cd, Pb and As) from wastewater.

Biochar has been recognized as a good sorbent for different kinds of organic and inorganic pollutants (Chen et al. 2011). Pine needle-derived biochar is reported to adsorb naphthalene, nitrobenzene and m-dinitobenzene effectively (Chen et al. 2008; Chen and Chen 2009). Dairy-manure biochar could effectively remove lead and atrazine simultaneously with little competition effect due to different retention mechanisms of both (Cao et al. 2009).

There has been little previous research carried out with the aim to activate biochar to increase its capacity for cation exchange. Activation of biochar is to treat it with physical and chemical agents to improve the porosity (Azargohar and Dalai, 2008) and increase the acidic functional groups on the mainly aromatic carbon surfaces. One of the challenges of both biochar production and subsequent activation is to keep production costs and the carbon footprint of all processes low, but at the same time produce an added value product that will encourage biochar production and use. Activated biochar with increased acidic functional groups could be used for wastewater treatment. Few studies have conducted steam activation to increase the cation exchange capacity of biochars and thus improve nutrient retention in soils. For example, Singh et al. (2010) studied the impact of pyrolysis temperature and steam activation on the CEC of biochars. The resultant

Chapter 1

effect of activation on the CEC of biochar was variable leaving the conclusion that studies on biochar activation are required for each type of feedstock used. There has been very little research work conducted into other ways of increasing the CEC of biochar, possibly because it is difficult to activate without compromising the energy costs and C (carbon) balance of the process. Biochar enriched with NH_4^+ after treating wastewater may have the potential to be used as N fertiliser for pasture and crop plants and may defray some of these costs. If biochar is combined with materials that have P sorption capabilities then the final mixture may have the potential to remove both N and P from wastewater and produce a combined N and P fertiliser.

There are no trials assessing the nutrient sorbing capacity of activated biochar and tephra in a combined system and use of these materials in soils as slow release fertilisers. Several of the areas mentioned above, offer the opportunity to conduct original research into the manufacture, properties and uses of biochars. These areas are reviewed more extensively in Chapter 2 and subsequent experimental chapters.

1.4 Thesis Structure

This thesis comprises nine chapters including this introduction chapter and a review of literature (Chapter 2). Chapters 3-8 report on the research experiments conducted in this study over a 40 months period of full time PhD research. Each of the six chapters has their own introduction, materials and methods, results and discussion and conclusion sections. A journal article arising from Chapter 3 was published in the Australian Journal of Soil Research (Hina et al. 2010). Some parts/studies from chapters 4, 7 and 8 were presented orally in Biochar Workshop, 2012, Massey University, Palmerston North. The main findings of each of the six research chapters are discussed in a final summary (Chapter 9).

References

- Ausseil O, Clark M (2007) Recommended Water Quality Standards for the Manawatu-Wanganui Region: Technical report to support policy development. *Horizons Regional Council Draft Report*. June, 2007.
- Azargohar R, Dalai A (2008) Steam and KOH activation of biochar: Experimental and modeling studies. *Microporous and Mesoporous Materials*. 110(2), 413-421.

Chapter 1

- Baker MJ, Blowes DW, Ptacek CJ (1998) Laboratory development of permeable reactive mixtures for the removal of phosphorus from onsite wastewater disposal system. *Environmental Science and Technology*. 32, 2308-231.
- Bolan N, Wong L, Adriano D (2004) Nutrient removal from farm effluents. *Bioresource technology*. 94(3), 251-260.
- Bridgwater AV (2003) Renewable fuels and chemicals by thermal processing of biomass. *Journal of Chemical Engineering*. 91, 87-102.
- Calvelo Pereira R, Kaal J, Camps Arbestain M, Pardo Lorenzo R, Aitkenhead W, Hedley M, Macias F, Hindmarsh J, Macia-Agullo JA (2011) Contribution to characterisation of biochar to estimate the labile fraction of carbon. *Organic Geochemistry*. 42, 1331-1342.
- Cao X, Ma L, Gao B, Harris W (2009) Dairy-manure derived biochar effectively sorbs lead and atrazine. *Environmental Science and technology*. 43, 3285-3291.
- Chen B, Chen Z (2009) Sorption of naphthalene and 1-naphthol by biochars of orange peels with different pyrolytic temperatures. *Chemosphere*. 76, 127-133.
- Chen B, Zhou D, Zhu L (2008) Transitional adsorption and partition of non-polar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures. *Environmental Science and Technology*. 42, 5137-5143.
- Chen B, Chen Z, Lv S (2011) A novel magnetic biochar efficiently sorbs organic pollutants and phosphate. *Bioresource technology*. 102,716-723.
- Cooney E, Booker N, Shallcross D, Stevens G (1999) Ammonia removal from wastewaters using natural Australian zeolite. II. Pilot-scale study using continuous packed column process. *Separation Science and Technology*. 34(14), 2741-2760.
- Drizo A, Frost CA, Grace J, Smith KA (1999) Physico-chemical screening of phosphate-removing substrates for use in constructed wetland systems. *Water Research*. 33, 3595-3602.
- Glaser B, Lehmann J, Zech W (2002) Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal. A Review. *Biology Fertile Soils*. 35, 219-230.

Chapter 1

Hanly JA, Hedley MJ, Horne DJ (2008) Evaluation of tephra for removing phosphorus from dairy farm drainage waters. *Australian Journal of Soil Research*. 46, 542-551.

Hedström A (2001) Ion exchange of ammonium in zeolites: A literature review. *Journal of environmental engineering*. 127(8), 673-681.

Hina K, Bishop P, Camps Arbestain M, Calvelo-Pereira R, Maciá-Agulló JA, Hindmarsh J, Hanly JA, Macías F, Hedley MJ. (2010) Producing biochars with enhanced surface activity through alkaline pretreatment of feedstocks. *Australian Journal of Soil Research*. 48, 606-617.

Houlbrooke DJ, Horne DJ, Hedley MJ, Hanly JA, Scotter DR (2004). Minimising surface water pollution resulting from farm-dairy effluent application to mole-pipe drained soils. I. An evaluation of the deficit irrigation system for sustainable land treatment in the Manawatu. *New Zealand Journal of Agricultural Research*. 47, 405-415.

Kostura B, Kulveitová H, Leško J (2005). Blast furnace slags as sorbents of phosphate from water solutions. *Water Resources*. 39 (9), 1795-1802.

Krull ES, Swanston CW, Skjemstad JO, McGowan JA (2006) Importance of charcoal in determining the age and chemistry of organic carbon in surface soils. *Journal of Geophysical Research*. pp. 111.

Lehmann J (2007) Bio-energy in the black. *Frontiers in the Ecology and Environment*. 5, 381-387.

Lehmann J, Kern DC, Glaser B, Woods WI (2003) Amazonian dark earths: Origin, properties, management. Kluwer Academic, Dordrecht.

Liesch AM (2010) Wastewater phosphorus removal by two different types of andesitic volcanic tephra. *Journal of natural resources and Life sciences Education*. 39, 40-44.

Longhurst RD, Roberts AHC, O'Connor MB (2000) Farm dairy effluent: a review of published data on chemical and physical characteristics in New Zealand. *New Zealand Journal of Agricultural Research*. 43, 7-14.

Chapter 1

- McArthur K, Clark M (2007). Nitrogen and Phosphorus Loads to Rivers in the Manawatu-Wanganui Region: *An Analysis of Low Flow State: Technical Report to Support Policy Development*. New Horizons Regional Council. Report No: 2007/EXT/793.
- Mohan D, Pittman CU (2007) Arsenic removal from water/wastewater using adsorbents-a critical review. *Journal of Hazardous Materials*. 142, 1-53
- Nguyen M, Tanner C (1998) Ammonium removal from wastewaters using natural New Zealand zeolites. *New Zealand Journal of Agricultural Research*. 41, 427-446.
- Nigussie A, Kissi E (2011) Impact of Biomass Burning on Physicochemical Properties of Nitisol in the Southwestern Ethiopia. *Asian Journal of Agricultural Research*. 5, 223-233.
- Oledzka M (2007) Substrate selection for Constructed Wetlands. Thesis presented for MSc. Faculty of Bioengineering. Universiteit Gent.
- Parfitt RL (1989). Phosphate reactions with natural allophane ferrihydrite and goethite. *Journal of Soil Science*.19:359-369.
- Perrin T, Drost D, Boettinger J, Norton J (1998) Ammonium-loaded clinoptilolite: A slow-release nitrogen fertilizer for sweet corn. *Journal of plant nutrition*. 21(3), 515-530.
- Ryden JC, Syers JK (1975) Use of tephra for the removal of dissolved inorganic phosphate from sewage effluent. *New Zealand Journal of Sciences*. 18, 3-16.
- Shilton AN, Elmetri I, Drizo A, Pratt S, Haverkamp RG, Bilby SC (2006). Phosphorus removal by an ‘active’ slag filter – a decade of full scale experience. *Water Resources*. 40, 113-118.
- Singh B, Singh BP, Cowie AL (2010) Characterisation and evaluation of biochars for their application as a soil amendment. *Australian Journal of Soil Research*. 48(7), 516-525.
- Van Zwieten L, Kimber S, Morris S, Chan K, Downie A, Rust J, Joseph S, Cowie A (2010) Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. *Plant and Soil*. 327(1), 235-246.

Chapter 1

Wang T, Camps-Arbestain M, Hedley M, Bishop P (2012) Predicting phosphorus bioavailability from high ash biochars. *Plant and Soil*. 1-15.

Westholm LJ (2006). Substrates for phosphorus removal – Potential benefits for on-site wastewater treatment. *Water Resources*. 40, 23-36.

Wieczorek S (2008) Assessing the Influence of Adsorbent Bed (Tree Bark) Parameters on the Reduction of Ammonia Emissions from Animal Husbandry. *Polish Journal of Environmental Studies*. 17(1): 147-154.

Chapter 2

Literature Review

2.1 The Biochar Concept and potential applications

In the natural C cycle, plant debris decomposes very rapidly after the plant dies; with this process, carbon dioxide is released to the atmosphere, leaving the overall natural carbon cycle balance neutral. Biochar technology is designed to ‘uncouple’ the natural C cycle. Instead of allowing the plant material to decompose, biochar technology sequesters C into charcoal, a stable form of C, resistant to decomposition. Biochar technology slows the return of carbon dioxide from the soil to the atmosphere and stores C in a virtually permanent soil carbon pool, making it a carbon-negative process. At the time of preparing the thesis proposal and at the time of writing, the costs associated with biochar manufacture (harvest, charcoal production, transport) cannot be covered by the value of CO₂ credits (under €10 per tonne by EU ETS, European Union emission Trading System; Wikipedia). For adoption of biochar as a GHG mitigation technology, research is required to find other “added value” uses for biochar. The review covers how biochar is made along with its current research.

Biochar technology has more potential for adoption in countries/regions that have large agricultural and/or forestry industries, which produce large quantities of waste biomass for feedstock. Apart from the beneficial effects of drawing CO₂ from the atmosphere, biochar applications to soil are also able to reduce the emissions of other GHGs and improve soil functions (Lehmann et al., 2006). Also, the application of biochar as a soil amendment can, in some circumstances, provide multiple benefits that include increases in i) cation exchange capacity (CEC) of soils (Glaser et al. 2002), ii) soil nutrients (Wang et al. 2012), iii) crop yield (Graber et al. 2010), and iv) soil pH (O’Neill et al. 2009). Biochar is also known to decrease non-CO₂ greenhouse gas (GHG) emissions from soil (Karhu et al. 2011). Biochar also promotes the adsorption of NH₃ and NH₄⁺ on biochar surfaces (Taghizadeh-Toosi et al. 2011), therefore, affecting N ammonification, denitrification, nitrification and volatilisation (Clough and Condon, 2010).

New Zealand features a distinctive greenhouse gas emission profile among industrialised nations. New Zealand's economy heavily relies on its land-based primary industries and the country's pastoral and forestry land-uses are responsible for a major share of its carbon footprint. The agricultural sector alone represents 48 % of total emissions (MfE, 2008). Agricultural GHG emissions are mainly methane from livestock and nitrous oxide derived from ruminant urine patches. Large quantities of forest wastes in NZ have potential as biochar feedstocks. Hence, biochar production could be used to offset agricultural emissions. Early adoption of biochar technology is currently constrained by economic costs (based on the current C credit value), as well as social and environmental issues for example, biochars are dusty and unpleasant to work with and also release poly aromatic hydrocarbons (PAH) during manufacture, respectively (Lehmann and Joseph, 2009). These constraints relate to biochar production costs and the logistics required to operate the technology. To overcome these constraints, researchers are looking to provide evidence that biochar can provide additional productive and economic benefits. This research falls into various categories, such as the use of biochar as a soil amendment to aid nutrient retention, act as a soil conditioner, provide a source of organic carbon or mitigate soil GHG emissions. Rondon et al. (2005) made biochar additions of 0, 7.5, 15, and 30 g charcoal kg⁻¹ soil to a very acid, low-fertility Oxisol (Typic Haplustol). Soybean and tropical grass (*B. humidicola*) yields were increased. After plant growth, they reported increases in soil pH, CEC and availability of various soil nutrients. Methane emissions were suppressed in the grass pots at charcoal additions of 30g kg⁻¹ soil. Nitrous oxide emissions were reduced by up to 50 % when biochar was applied to soybean and by 80 % in grass stands. These low emissions may be explained by better aeration (less frequent occurrence of anaerobic conditions). The lower nitrous oxide evolution may also be a consequence of a slower N cycling (Lehmann et al. 2006).

2.2 Manufacture of biochar

The term pyrolysis is derived from the Greek elements of *pyro* "fire" and *lysis* "separating"; Wikipedia. Pyrolysis is a thermochemical decomposition of organic material at elevated temperatures without the participation of oxygen. It converts biomass into a liquid (bio-oil), a gas and a high carbon, fine grained solid residue, biochar (Lehmann and Joseph, 2009). The distribution of products depends on the heating rate, residence time, surrounding atmosphere and

temperature. In addition, the type of biomass also affects both biomass volatilization and char conversion. Three main factors influencing the properties of biochar are (Glaser et al. 2002a): i) the type of organic matter used for charring ii) the charring environment (e.g temperature and type of atmosphere), and iii) additions during the charring process. The type of feedstock strongly influences the elemental composition of the biochar, its accompanying ash, porous structure and adsorption properties of the resulting activated carbons (Demirbas et al. 2006). The feedstocks used nowadays include wood chip and pellets, tree bark, crop residues (including straw, nut shells and rice hulls), organic wastes including bagasse from the sugarcane industry, olive waste, sewage and paper sludge (Yaman 2004, Kwapinski et al. 2010), chicken litter (Chan et al. 2008) and dairy manure. The moisture contents and particle size of feedstocks are important as wet feedstocks having large particle size will need more energy for pyrolysis (Kwapinski et al. 2010).



Figure 2.1 Pyrolyser used for the manufacture of Biochar (Small, 5 L, rotating, gas fired cylinder)

2.2.1 Biochar preparation from agricultural and forestry wastes

In many agricultural and forestry production systems, waste is produced in significant amounts from residues such as forest residues (logging residues, dead wood, excess saplings, pole trees),

mill residues (pulp, veneers), field crop residues or urban wastes (wood packaging, yard trimmings) (Walsh et al. 1999). Many of the forestry and agricultural residues can be used to produce biochar for application to agricultural soil, to sequester both the C and to improve the yield of crops. The most appropriate materials to produce high yields of biochar have high lignin concentration (Demirbas 2004), such as residues from sawmills, forest residues, or nut shells. The mineral content also plays a role and woody biomass impregnated with potassium (K) and calcium (Ca) yielded up to 15 % more biochar than the original beech wood (Nik-Azar et al. 1997). In 2003 the global accumulation of wood residue was estimated to be of 70.3 Mm³ (FAO, 2004), which is enough biochar to sequester 0.021 Pg C y⁻¹.

2.3 Stability of Biochar

Biochar has the distinguishing properties of high stability in the environment relative to the other types of organic C substances (Nguyen et al., 2008). Plant biomass decomposes over a relatively short period of time in soils, whereas biochar is more stable. Biochar has been estimated to have mean residence time of 10,000 years in soils (Swift, 2001), and also found to remain intact in deep-sea environments for up to 13,900 years (Masiello and Druffel, 1998). Verheijen et al. (2010) reported the residence times for wood biochar in soil is in the order of 10-1000 times longer than for other soil organic matter (SOM). Therefore, biochar addition to soil can be a potential sink of carbon. Given a certain amount of carbon that cycles annually through plants, almost half of it can be taken out of its natural cycle and sequestered in a slower biochar cycle. The stability of biochar is also closely related to the temperature of pyrolysis (Lehmann and Joseph, 2009). The degree of condensation of the aromatic rings provides information regarding its stability in the soil environment.

2.4 Agronomic Benefits from amending soils with biochar

The amount of charcoal/biochar that can be added to soils before it ceases to function as a valuable amendment and becomes detrimental will be the limiting factor in the use of biochar as a soil additive (Woolf, 2008). The strongest proof that high concentrations of charcoal in soil may be useful under some conditions comes from the Amazonian Dark earths, such as Terra Preta and Terra Mulata - charcoal rich soils containing about three times more soil organic matter, N and P than adjacent soils with twice productivity (Glaser, 2007). However, the natural

soils of the area are highly weathered and poor in nutrients. More research needs to be done working on temperate-climate soils.

A number of agronomic benefits have been reported with biochar addition to cropping soils particularly, where soil fertility and productivity is in decline (Novak et al. 2009). Steiner et al (2007) reported a doubling-up of maize grain yield on plots with use of combination of NPK fertiliser with charcoal compared to use of NPK fertiliser alone in fine textured soil with 80% clay in Amazonas, Brasil. The yield fell over the course of four cropping cycles on almost all plots. But the rate of decline in yield was considerably less on charcoal-amended plots than on those that received only mineral fertiliser. The quantity of nutrients K, P, Ca, and Mg remained higher in charcoal-amended plots despite the fact that large amounts of these nutrients had been removed from the soil in the form of harvested plant matter. Lehmann (2007) reported increasing yields with increasing biochar applications of up to 140 Mg C ha⁻¹ (at which rate, the maximum yield had not yet been reached) on highly weathered soils in the humid tropics, for most of their tests. Namgay et al. (2010) conducted a pot experiment (in sandy soil) to investigate the effect of biochar on availability of trace element to maize plant and did not find any significant increase in dry matter yield of maize even at higher rate (15 g kg⁻¹ soil) of application.

Charcoal may exhibit hydrophobicity (Sander and Pignatello, 2005) especially right after its production at high temperature, which makes it well suited to the sorption of organic compounds. Biochar has the capacity to adsorb a variety of compounds including litter decomposition products, plant root exudates and microbial byproducts (DeLuca and Aplet, 2008). Recently formed biochar can adsorb organic compounds that might otherwise be inhibitory to plants or microorganisms (Pietikainen et al. 2000). This capacity to adsorb plant root exudates and litter decomposition products, such as phenolic compounds, may be related to the stimulatory effect of charcoal on nitrification in acidic coniferous forest soils, as reported by DeLuca et al. (2006). He reported that charcoal may alleviate factors that otherwise inhibit the activity of the nitrifying microbial community in forest soils.

2.5 Soil properties affected by biochar

Biochar additions to soil may not only change soil chemical properties of soils, but also affect their physical properties, such as soil water retention and aggregation, bulk density (Lehmann et

Chapter 2

al. 2006) and soil temperature. These effects may enhance the water availability to crops and decrease erosion (Piccolo et al. 1997). Application of biochar into the soil alters physical properties of soils like texture, structure, density and pore size distribution with effects on soil aeration, plant growth, water holding capacity and soil workability (Downie et al. 2009).

2.5.1 Soil Density

The bulk density of biochar is much lower than of soils and therefore, application of biochar can reduce the overall bulk density of mineral soil (Laird et al. 2010), although increases in bulk density are also possible. If biochar particles incorporated into the soil do not fill up existing soil pore space, then a reduction in overall soil bulk density will result. However, if the biochar applied has a low mechanical strength and disintegrates quickly into small particles and fill existing pore spaces in the soil then the dry bulk density of soil can increase (Verheijen et al. 2010).

2.5.2 Soil Pore size distribution

Biochar pore size distribution and connectivity affects the overall porosity of the soil to either increase or decrease following biochar incorporation into soils. There is evidence that suggests that biochar application into soil may increase net soil surface area (Chan et al. 2007) and thereby, may improve soil water retention (Downie et al. 2009). The increase in soil-specific surface area may also benefit native microbial communities, along with the overall sorption capacity of soil (Verheijen et al. 2010). The porosity of the biochar depends on the pyrolysis temperature (i.e. increases with higher temperatures up to 750 °C) (Schimmelpfennig and Glaser, 2011). Pore size ranges from < 2 nm to > 50 nm, with increases in smaller diameter fraction as pyrolysis temperature increases (Downie et al. 2009).

2.5.3 Soil colour

Anthrosols profile pictures (Fig. 2.2) show that high concentrations of biochar in soil darken its colour. Briggs et al. (2005) measured changes in dry soil colour from charcoal additions and found the Munsell value (lightness; from black (value 0) at the bottom, to white (value 10) at the top) to decrease from 5.5 to 4.8 at biochar concentrations of 10 g kg⁻¹, and down to 3.6 at 50 g kg⁻¹. The degree of darkening depends on i) colour of soil prior to biochar addition, ii) biochar

colour, iii) biochar concentration in soil, iv) degree of mixing (related to particle sizes of biochar and soil), v) surface roughness, and vi) change in water retention at the soil surface that accompanies the addition of biochar (Verheijen et al., 2010).



Figure 2.2 Terra preta soils (Anthrosols with charcoal at right) (Birk et al. 2011 or Google Images).

2.5.4 Soil pH

Biochar pH is mostly neutral to basic. The liming effect has been discussed in the literature as one of the important mechanisms behind increases in plant productivity after biochar applications. This reduces the cost of production by reducing the need for a conventional liming operation. Topoliantz et al. (2002) reported increases in soil pH of one unit (from 5.12 to 5.92) when wood biochar was added and mixed in the top 15 cm soil @ 1:3, v:v ratio.

2.5.5 Biochar nutrient value

Biochar has nutrient value supplied either directly by providing nutrients to plants or indirectly by improved soil quality increasing fertiliser use efficiency (Chan et al. 2007; Van Zwiten et al. 2010). Biochar has less mineral N inspite of significant total N (in sewage sludge biochar), but the P content is highly variable among different biochars (Lehmann and Joseph, 2009). Total N and P contents of animal origin (e.g. sewage sludge and poultry litter) biochars are higher than that of the plants origin (Lehmann and Joseph, 2009). Biochar also contains nutrients in ash which may be in a soluble or a more accessible form in biochar than in the feedstock. The

indirect effect of biochar by increasing fertiliser use efficiency on soil P availability and the accessibility of mineral ash (containing K, P and other potentially important nutrients) in the biochar matrix may be important in explaining some short-term impacts of biochar on crop growth, especially since P availability cannot, unlike NH_4^+ , be improved simply by increasing soil organic matter status (Steiner et al. 2007).

2.5.6 Biochar and cation exchange capacity (CEC)

The chemical structure of biochar is aromatic (Schmidt and Noack, 2000), yet there is the possibility of the formation of functional groups with net negative charge on biochar particle surfaces. Since CEC depicts the capacity to retain key nutrient cations in the soil in a plant available form and minimise leaching losses, this is reported as an important property where responses in crop productivity are observed (Sohi et al. 2009). Therefore, the addition of biochar to soil has in some cases shown distinct increases in the availability of major cations. In high leaching conditions in humid tropical Amazonia, Anthrosols enriched with charcoal were found to sustain a higher cation availability (Lima et al. 2002) compared with adjacent forest soils with similar mineralogy. Glaser et al. (2003) suggested the formation of carboxyl groups to be the main reason for observed high CEC. Such formation of carboxyl groups (Liang et al. 2006) and other functional groups with net negative charge at a range of soil pH can be the result of two processes: a) surface oxidation of BC particles themselves and b) adsorption of highly oxidized organic matter onto biochar surfaces once mixed with soil (Lehmann and Rondon, 2005).

Niggusie and Kissi (2011) quoted that, on a mass basis, the intrinsic CEC of biochar is consistently higher than that of whole soil, clays or soil organic matter. An analogy may be drawn to the extremely high CEC of some activated carbons, which is relevant to its function as an adsorption medium for decolourisation and decontamination. This is a function of both enhanced specific surface area and the abundance of carboxyl carbon groups that they display.

Biochar incorporation into soil is expected to enhance overall sorption capacity of soils towards trace anthropogenic organic contaminants (e.g. PAHs, pesticides, herbicides). Yamane and Green (1972), also reported an increase on ametryne sorption on a silty clay soil when charcoal was added. This property may greatly contribute to mitigate

toxicity and transport of common pollutants in soil, it may also reduce the effectiveness of some pesticide treatments (Kookana, 2010).

2.5.7 Soil moisture retention

The use of biochar as means to ameliorate soil physical properties and water holding capacity in specific, has emerged after identification of its high porosity (Liang et al. 2006) and large surface area (Van Zwieten et al. 2009). Biochar has a high surface area due to its porous structure. Kishimoto and Sugiura (1985) estimated inner surface areas of 200-400 m² g⁻¹ of charcoal formed between 400 °C and 1000 °C. As a result, soil water retention increased by 18 % upon addition of 45 % (by volume) charcoal/biochar to a coarse textured sandy soil (Tryon, 1948). Tryon (1948) studied the effect of charcoal on the available moisture percentage in different textured soils. Tryon (1948) showed that the addition of charcoal increased the available moisture only in the sandy soil. In loamy soil no changes were evident, while in a clayey soil the available soil moisture decreased with increase in biochar additions, which might be due to the initial hydrophobicity of the charcoal. Therefore, biochar-soil interactions through aggregation (Brodowski et al. 2006) developed over time by encapsulation of biochar particles in newly formed aggregates, and soil texture, may affect the soil moisture retention pattern of biochar amended soil. However, if the water holding capacity of the soil increases, this may hypothetically reduce the water irrigation volume or frequency.

2.6 Waste management with biochar

As waste management legislation is introduced in many countries, the desired direction of management is towards sustainable strategies, primarily waste minimisation, separation and re-use or recycling of materials and potential production of bio-products (Koutcheiko et al., 2006). These strategies greatly decrease the volume of waste material that needs final disposal and creates sustainable economic opportunities (Popov et al. 2004). Pyrolysis and gasification are alternatives to incineration for recovering useful resources from residual waste (Juniper, 2008). In the agriculture sector, sustainable waste management strategies also have to consider environmental and food safety aspects of recycled manures (Koutcheiko et al. 2006).

2.7 Activation of biochar for added value biochar production

Activated carbons are commercially produced from a variety of carbonaceous materials (e.g. coconut shell, coal, wood, lignocellulosic materials and wood bark) (Junpirom, 2006), and have a well-developed porous structure (Chen et al. 2002). Because of their microporous character and the chemical nature of their surface with acidic functional groups, they have been considered potential adsorbents for the removal of pollutants and nutrients from industrial and sewage wastewaters (Demirbas et al. 2006).

Activated biochars are obtained through one of two general methods (Demirbas et al. 2006): (i) by chemical activation of the precursor with chemicals such as zinc chloride, KOH, NaOH or phosphoric acid (Omar et al. 2003), or (ii) by partial gasification of the primary char with steam or carbon dioxide or a mixture of both to increase their porosity, surface area and surface charge. Chemical additives (AlCl_3 , FeCl_3 , H_3PO_4 , KOH) have an effect by inhibiting hemicellulose decomposition and accelerating cellulose decomposition through the dehydration reaction. Chemical activation by H_3PO_4 at 775 °K (502 °C) proved efficient in producing high quality activated carbon with highly developed porosity and greater adsorption capacity for both organic and inorganic substrates (Demirbas et al. 2006).

Recently, numerous attempts to prepare activated charcoal from solid wastes have been made (Mohan et al. 2004), including activated charcoal developed by pyrolysis of different organic wastes and materials such as sewage sludge (Mui et al. 2004) and nutshells (Johns et al. 1999). Despite the extensive use of activated charcoal for the wastewater treatment, adsorption by charcoal still remains an expensive process and this fact has prompted a growing interest into the production of low cost activated charcoals (biochars) (Koutcheiko et al. 2006). The use of acid and alkaline catalysed pre-treatments has been conducted for the preparation of activated biochar. Hayes (2009) proposed the use of pre-treatments of dilute acids (sulphuric, nitric and hydrochloric acid) and alkaline treatments (sodium, calcium and potassium hydroxide). The increase in oxidation in biochars with activation is associated with the development of acidic functional groups. The activated biochars have potential benefits as acting as filters and sorbents for treating waters and wastes.

Chapter 2

Activated carbon and biochar have been produced to provide adsorbents for different pollutants (Chen et al. 2011). Pine needle biochar is reported to be an effective adsorbent/filter for organic contaminants, like naphthalene and nitrobenzene (Chen and Chen, 2009). Dairy manure biochar have been used to adsorb lead and atrazine efficiently and simultaneously with little competition effect i.e the difference in retention patterns of both (Cao et al. 2009). New Zealand soils have a limited capacity to store mineral N and N-saturated soils, particularly in urine patches of grazing stock, create risks of N leaching into waterways and being emitted to the atmosphere as nitrous oxide (Spokas et al. 2009). Activation of biochar could improve the soils ability retain mineral N in the soil (Chen et al. 2011).

It may also be possible to utilise the adsorptive capacity of activated biochar to remove contamination in wastewater treatment processes. Asada et al. (2002) recorded the effect of pyrolysis temperature on the NH_3 adsorption capacity of bamboo biochar (*Bambusa* sp.) and found greater sorption at 500°C than temperatures of $\geq 700^\circ\text{C}$. This was considered to be due to a decrease in acidic functional groups with increasing temperature, as evidenced from electron spin magnetic resonance spectroscopy, which confirmed the presence of acidic functional groups. Toosi et al. (2011) reported that when NH_3 gas was absorbed on biochar (produced from *Pinus radiata* at 300, 350 and 500°C), much of it remained bioavailable. When incorporated in soils, 11 to 26 % of the added N was recovered in leaf tissues and 6.8 % in roots, depending on different types of biochars. In contrast to other organic matter in soil, biochar also appears to be able to retain H_2PO_4^- , even though it is an anion, although the mechanism is not fully understood (Lehmann, 2007).

The research literature indicates that it is possible to produce biochar that have large internal surface areas. Techniques designed to activate these surfaces to increase their ion retention capacities have mostly involved thermal and chemical oxidation. Certainly the potential exists to use activated biochars to clean up wastewater streams, particularly those associate with New Zealand dairy farms and rural towns close to where biochar feedstocks can be found. Little or no work, however, has been carried out to evaluate low-cost methods of activating biochar and quantify its absorbing capacity for anions, cations and organic compounds. After loading biochars with nutrients from the wastewater, they may have potential as slow-release fertilisers.

2.8 Wastewaters quality and conventional treatment

Ammoniacal N (NH_3 and NH_4^+) and H_2PO_4^- in agricultural and urban wastewaters can promote eutrophication and algal growth of receiving waters (Baker et al. 1998), which has been proven toxic to fish and other aquatic life (Nguyen and Tanner, 1998) thereby declining the environmental quality. The origin of these nutrients should be identified in order to reduce their negative contribution to the aquatic biodiversity (Fig. 2.3) (Roygard and McArthur, 2007).

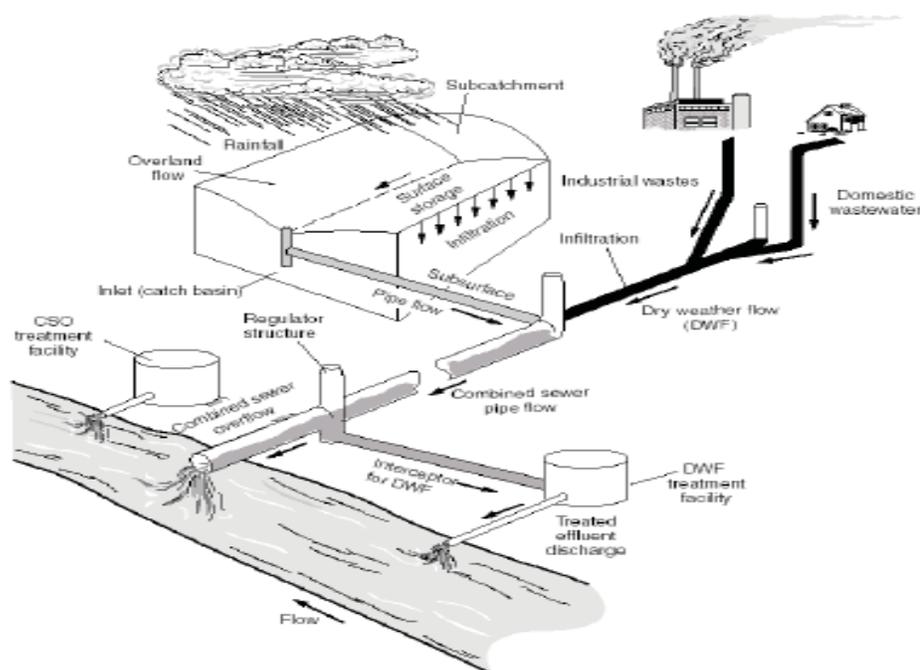


Figure 2.3 Sources of wastewater. Adapted from: Metcalf and Eddy (2003)

To reduce the risk of pollution in wastewaters from nutrients, agricultural and urban wastewaters are often treated in two-pond (anaerobic/aerobic) treatment systems (Nguyen and Tanner, 1998). However, the NH_4^+ and DRP levels in pond effluent discharges are often still excessive and can lead eutrophication of waterways (Oledzka, 2007). Historically (pre-2000), most dairy farms in New Zealand discharged their pond-treated farm dairy wastewater to rivers and lakes. For example, in 1998 over 300 dairy farms discharged their wastewater into the Manawatu River, but by 2010 this number had decreased to only 2, after the widespread adoption of land treatment. However, in some regions, such as the Taranaki Region, a large proportion of farms still use

Chapter 2

two-pond treatment and discharge their wastewater rich in N, and particularly NH_4^+ , and DRP to fresh water streams and, therefore, contributing to the degradation of water quality (Longhurst et al. 2000; Houlbrooke et al. 2004).

There are also many towns in New Zealand that continue to discharge pond-treated sewage wastewater into fresh surface waters like, in the Manawatu-Wanganui Region there are over 30 towns with sewage wastewater discharges (mean $1700 \text{ m}^3/\text{day}$) (McArthur and Clark, 2007). At some river sites, as is the case downstream of the Palmerton North and Feilding sewage treatment plant outfalls, sewage wastewater discharges are the predominant source of SIN (soluble inorganic nitrogen), particularly NH_4^+ , and DRP during low river flow conditions.

McArthur and Clark (2007) reported that DRP loads in the Lower Manawatu and Orua River, a tributary of the Manawatu, were high. Dissolved reactive P also exceeded the proposed standard in Manawatu river at the Hopelands and Opiki sites in almost 75 and 100% of the samples, respectively (McArthur and Clark, 2007). The Manawatu river at Hopelands site also showed SIN concentrations in excess of proposed standards (as mentioned in Introduction) in about 50 % of samples (McArthur and Clark, 2007). Table 2.1 provides a summary of details of the sewage treatment plant (STP) discharges in the Manawatu-Wanganui region that either meet or do not meet proposed water quality standards for SIN and DRP (McArthur and Clark, 2007).

Table 2.1 Discharges to water and compliances with proposed water quality standards for N and P in the Manawatu-Whanganui region, between 1993 to 2006, at flows less than half median (Source: McArthur and Clark, 2007).

Discharge to surface water	SIN		DRP	
	meets SIN standard at MALF	meets SIN standard at ½ median*	meets DRP standard at MALF	meets DRP standard at ½ median*
Norsewood STP	✓	✓	✓	✓
Dannevirke STP	✓	✓	✗	✗
PPCS (Oringi)	✓	✓	✓	✓
Eketahuna STP	✓	✓	✓	✓
Fonterra (Pahiatua)	✓	✓	✓	✓
Pahiatua STP	✓	✓	✗	✗
DB Breweries	✓	✓	✗	✗
Woodville STP	✗	✓	✗	✗
Ashhurst STP	✓	✓	✓	✓
Aokautere STP	✓	✓	✓	✓
PNCC STP	✗	✓	✗	✗
Longburn STP	✓	✓	✓	✓
Fonterra (Longburn)	-	-	-	-
NZ Pharmaceuticals	✓	✓	✓	✓
Kimbolton STP	✓	✓	✓	✓
Affco Manawatu Ltd	✗	✓	✗	✗
Feilding STP	✗	✗	✗	✗
Awahuri STP [®]	-	-	-	-
Rongotea STP [®]	-	-	-	-
Tokomaru STP [®]	-	-	-	-
Shannon STP [®]	-	-	-	-
Foxton STP [®]	-	-	-	-
PPCS (Shannon)	✓	✓	✓	✓
Taihape STP	✓	✓	✗	✗
Mangaweka STP	✓	✓	✓	✓
Hunterville STP	✗	✓	✗	✗
Halcombe STP	✗	✗	✗	✗
Feltex	-	-	-	-
Marton STP	✗	✗	✗	✗
Bulls STP	✓	✓	✓	✓
Riverlands (Manawatu Ltd)	✓	✓	✓	✓
Ohakea STP [®]	-	-	-	-
Sanson STP [®]	-	-	-	-
National Park STP [®]	-	-	-	-
Taumarunui STP	✓	✓	✗	✓
Ohura Prison STP	✓	✓	✓	✓
Pipiriki STP	✓	✓	✓	✓
Winstone Pulp	✓	✓	✗	✗
Waiouru Army Camp STP	✗	✗	✗	✗
Rangataua STP [®]	-	-	-	-
Ohakune STP	✗	✗	✗	✗
Raetihi STP	✗	✓	✗	✗
Pongaroa STP	✓	✓	✗	✓

Key: ✗: Does not meet the standard; ✓: Meets the DRP standard; ✓: Meets the SIN standard

2.8.1 Wastewater treatment systems

Usually wastewater is given primary and secondary treatment for purification, such as in two-pond treatment system previously mentioned. In primary treatment, sedimentation of wastewater proceeds in tanks where sludge usually settles and is removed by mechanical scrapers and left with grease and oil in water. Anaerobic ponds are mainly designed for biological oxygen demand (BOD), oil, grease and suspended solids concentrations removal prior to aerobic treatments (Johns, 1995). In secondary treatment, the biological content of the sewage is subjected to the aerobic biological processes where bacteria and protozoa consume biodegradable soluble organic contaminants. The two-pond treatment system (anaerobic and aerobic; facultative ponds) is most prevalent system in small rural towns in New Zealand but is ineffective for N and P removal.

The main disadvantages of the two-pond systems are: i) large land requirement for ponds ii) sludge accumulation will be higher in cold climates when there will be less microbial activity iii) If not designed properly, may cause odour problems (Phuntsho et al., <http://www.eolss.net/Eolss-sampleallchapter.aspx>), iv. Not effective at removing the majority of nutrients, particularly DRP. Constructed wetlands, activated sludge systems and trickling filters are some of the other wastewater treatment systems/options (Johns, 1995).

The treatment involved in the removal of N from wastewater are biological nitrification-denitrification processes. Whereas P removal involves chemical precipitation or adsorption processes (Tchobanoglous, 1991). Nitrogen cannot be precipitated so needs some alternate method for removal from wastewater. The different categories of wastewater treatments are summarised in Table 2.2. The treatment of wastewater with Biochar for nutrient removal falls into the chemical unit under adsorption and precipitation mechanisms.

Table 2.2 Categories of wastewater treatment

Physical unit operations	⇒	<ul style="list-style-type: none"><input type="checkbox"/> Screening<input type="checkbox"/> Comminution<input type="checkbox"/> Flow equalization<input type="checkbox"/> Sedimentation<input type="checkbox"/> Flotation<input type="checkbox"/> Granular-medium filtration
Chemical unit operations	⇒	<ul style="list-style-type: none"><input type="checkbox"/> Chemical precipitation<input type="checkbox"/> Adsorption<input type="checkbox"/> Disinfection<input type="checkbox"/> Dechlorination<input type="checkbox"/> Other chemical applications
Biological unit operations	⇒	<ul style="list-style-type: none"><input type="checkbox"/> Activated sludge process<input type="checkbox"/> Aerated lagoon<input type="checkbox"/> Trickling filters<input type="checkbox"/> Rotating biological contactors<input type="checkbox"/> Pond stabilization<input type="checkbox"/> Anaerobic digestion<input type="checkbox"/> Biological nutrient removal

2.8.2 Potential use for biochar in active filtration

Active filters, which include reactive media, have shown promise in removing N and P from wastewater (Bolan et al. 2004; Kostura et al. 2005; Shilton et al. 2006). Zeolites are expensive substrates for NH_4 removal from wastewater (Nguyen and Tanner, 1998; Cooney et al. 1999) and need special treatment for regeneration of adsorbed N. Bolan et al. (2004) found, working with farm effluents, that the retention of NH_4^+ increased from untreated bark to treated bark (using an alkaline material to increase exchange sites) and to zeolite (clinoptilolite). Perrin et al. (1998) successfully used NH_4^+ saturated zeolite (clinoptilolite) as fertiliser for maize plants. These researchers reported a better performance of small-sized zeolite particles (<0.25 mm) compared to larger particles (2-4 mm), which they attributed to a decrease in the diffusion path length with the former. The NH_4^+ removal capacity of the adsorbents is dependent on (i) the wastewater loading flow rate, (ii) type of wastewater, (iii) media particle size, and (iv) contact time between the wastewater and adsorbent particles (Nguyen and Tanner, 1998). Ammonium retention also depends on (v) the presence of other cations in the aqueous phase and (vi) the initial NH_4^+ concentration (Demir et al. 1998). The NH_4^+ removal procedure is considered viable for wastewater treatment if it is capable of reducing NH_4^+ concentration from 20-60 $\text{mg NH}_4^+ \text{L}^{-1}$ to < 5 mg L^{-1} (Cooney et al. 1999). Use of bark (Bolan et al. 2004; Wieczorek, 2008) or plants to remove N from wastewaters has some de-merits because the entire adsorbed N releases immediately on decomposition, which has more chance of subsequent N loss by leaching or denitrification.

The potential use of biochar to remove organic pollutants (like naphthalene and nitrobenzene) and cations from wastewater has been suggested by several researchers (Chen et al. 2008; Cao et al. 2009; Chen et al. 2009; Chen et al. 2011). Dairy-manure biochar has been shown to effectively remove lead and atrazine simultaneously with little competition effect (Cao et al. 2009). The concept of biochar technologies has arisen because of the need to create sinks for greenhouse gases (GHGs). One of the major environmental challenges for the 21st century is global warming caused by increasing amounts of GHGs (IPCC, 2007). Mohan and Pittman (2007) reported the use of biochars produced from woody material (pine bark, oak bark and oak wood) at 400-450 °C for the removal of heavy metals and metalloids (e.g., Cd, Pb and As) from wastewater. The NH_4^+ -N sorption capacity of biochar has been reported to depend on the acidic

functional groups especially carboxylic groups in the biochars (Asada et al. 2002). Some Removal of the NH_4^+ from water can be attributed to microporous structure of the biochar (Reynolds, 2010). Soto-Garrido et al. (2003) reported that NH_4^+ -N retention is also dependent on the NH_4^+ concentration in the influent solution and increases as the NH_4^+ -N concentration increases by formation of H^+ bonds.

The use of charcoal for water purification (Srivastava and Eames, 1998) to remove unwanted dissolved organic pollutants is well established. However, there has been limited research on the potential for biochar to remove inorganic pollutants, such as NH_4^+ , from water. Due to large volumes of wastewater produced throughout the year, the use of land application, is not feasible particularly during winter and spring when soils are at or close to field capacity. Therefore, a cost effective filtration system that has the potential to lower the levels of N and P in wastewaters would provide a solution to minimize the impacts on surface water quality. The properties of biochar that allow it to adsorb and retain nutrient cations and anions in soils and attract and adsorb organics have the potential to be applied to wastewater treatment, particularly if these properties can be enhanced.

2.9 Summary

Wastewaters from agricultural and urban origin are rich in N and P compounds originating from urine, faeces and industrial by-products. With time, the organic forms of N mineralise to NH_4^+ , which is a potential pollutant in fresh water resources as it can contribute to the eutrophication of the aquatic environment and be potentially toxic to fish species. Moreover, these wastewaters are also rich in DRP, which also poses a threat to quality of water. Removal of NH_4^+ and DRP from wastewaters is thus needed if the risk of wastewater discharges in water quality is to be minimised. Several sorbents, like zeolite, bark and charcoal can be used as sorbents for nutrients removal from wastewaters. Biochar may also have N and P retention capacity and thus its sorption properties should be investigated.

Biochar is a type of charcoal resulting from the thermal treatment (heating) of natural organic materials in an oxygen-limited environment with the final aim of adding it to soils for an environmental and/or agronomic gain. The production process under such conditions is called pyrolysis. A range of temperatures, heating rates, time at final reaction temperature, pressures

and partial pressures of steam/oxygen are used to produce biochars. The structure of the biochar is porous and some may be hydrophobic, therefore, influencing the retention of hydrophobic organic compounds. Activation of biochar by alkaline and acidic treatments enhances its ability to remove hydrophilic pollutants from wastewaters. The presence of acidic functional groups, especially carboxylic groups, is thought to be responsible for these properties. Ammonium removal from wastewaters by alkaline activated biochars should be studied to assess the potential for the high pH of chars to cause volatilisation of ammonia.

This literature review has indicated that considerable research is being conducted on the properties of biochar and its stability in soils as a carbon sink. Associated with this work is detailed research into the chemical and physical properties of biochar and its interactions with soils. Research carried out to present suggest the potential of biochars to adsorb, retain and interact with anions, cations and organics in soils. This sorptive property of biochar has the potential to be applied to wastewater treatment but little research work has been conducted in this area. This area of research study will become the main focus of this thesis.

The main research objectives relating to this thesis are:

1. Review existing literature on the concept of biochar and its potential uses with the objective of identifying research gaps to study in the experimental chapters.
2. Evaluation of the influence of particle size of feedstock on biochars NH_4^+ sorption properties.
3. Study of low cost activation of biochar and its NH_4^+ sorption properties.
4. Characterisation of different activated and non-activated pine (*Pinus radiata*) and eucalyptus (*Eucalyptus Cinerea*) biochars.
5. Assessment of sorption kinetics of NH_4^+ on activated biochars under batch and column studies with urban wastewater.
6. Evaluation of combined biochar and tephra filter for the removal of N and P from urban wastewater in a flow through study.

Chapter 2

7. To quantify the fertiliser value of wastewater-treated biochars and tephra in soils using a bioassay Stanford and Dement exhaustive (1957) pot study.

From here, the term “sorption” will be used to refer to the removal of NH_4^+ from solution, as the exact mechanisms behind this (e.g. physical entrapment, electrostatic retention, etc.) are not known.

References

- Asada T, Ishihara S, Yamane S, Toba T, Yamada A, Oikawa K (2002) Science of bamboo charcoal: Study of carbonizing temperature of bamboo charcoal and removal capability of harmful gases. *Journal of Health Science*. 48, 473-479.
- Baker MJ, Blowes DW, Ptacek CJ (1998) Laboratory development of permeable reactive mixtures for the removal of phosphorus from onsite wastewater disposal system. *Environmental Science and Technology*. 32, 2308-231.
- Birk JJ, Teixeira WG, Neves EG, Glaser B (2011) Faeces deposition on Amazonian Anthrosols as assessed from 5 β -stanols. *Journal of Archaeological Science*. 38 (6), 1209-1220
- Bolan N, Wong L, Adriano D (2004) Nutrient removal from farm effluents. *Bioresource technology*. 94(3), 251-260.
- Briggs CM, Breiner J, Graham RC (2005) Contributions of Pinus Ponderosa Charcoal to Soil Chemical and Physical Properties. The ASA-CSSA-SSSA International Annual Meetings (November 6-10, 2005), Salt Lake City, USA.
- Brodowski S, John B, Flessa H, Amelung W (2006) Aggregate occluded black carbon in soil. *European Journal of Soil Science*. 57, 539-546.
- Cao X, Ma L, Gao B, Harris W (2009) Dairy-manure derived biochar effectively sorbs lead and atrazine. *Environmental Science and technology*. 43, 3285-3291.
- Chan K, Van Zwieten L, Meszaros I, Downie A, Joseph S (2007) Agronomic values of greenwaste biochar as a soil amendment. *Soil Research*. 45(8), 629-634.
- Chan K, Van Zwieten L, Meszaros I, Downie A, Joseph S (2008) Using poultry litter biochars as soil amendments. *Soil Research*. 46(5), 437-444.
- Chen B, Chen Z (2009) Sorption of naphthalene and 1-naphthol by biochars of orange peels with different pyrolytic temperatures. *Chemosphere*. 76, 127-133.
- Chen B, Zhou D, Zhu L (2008) Transitional adsorption and partition of non-polar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures. *Environmental Science and Technology*. 42, 5137-5143.
- Chen X, Jeyaseelan S, Graham N (2002) Physical and chemical properties study of the activated carbon made from sewage sludge. *Waste Management*. 22, 755-760.
- Chen B, Chen Z, Lv S (2011) A novel magnetic biochar efficiently sorbs organic pollutants and phosphate. *Bioresource technology*. 102, 716-723.

- Clough TJ, Condon LM (2010) Biochar and the nitrogen cycle: Introduction. *Journal of Environmental Quality*. 39, 1218-1223.
- Cooney E, Booker N, Shallcross D, Stevens G (1999) Ammonia removal from wastewaters using natural Australian zeolite. II. Pilot-scale study using continuous packed column process. *Separation Science and Technology*. 34(14), 2741-2760.
- DeLuca TH, Aplet GH (2008) Charcoal and carbon storage in forest soils of the Rocky Mountain West. *Frontiers in Ecology and the Environment*. 6:18–24.
- DeLuca TH, MacKenzie MD, Gundale MJ, Holben WE (2006) Wildfire produced charcoal directly influences nitrogen cycling in forest ecosystems. *Soil Science Society of America Journal*. 70, 448-53.
- Demir A, Debik E, Gunay A (1998) Eysel atiksulardan amonyumun gideriminde iyon degitirici olarak dogal zeolit kullaniminin arastirilmasi. *ISKI Projesi Yildiz*, Istanbul.
- Demirbas, A. (2004) Effects of temperature and particle size on bio-char yield from pyrolysis of agricultural residues. *Journal of analytical and applied Pyrolysis*. 72, 243-248.
- Demirbas A, Pehlivan E, Altun T. (2006) Potential evolution of Turkish agricultural residues as bio-gas, bio-char and bio-oil sources. *International Journal of Hydrogen Energy*. 31, 613-620.
- Downie A, Crosky A, Munroe P (2009) Physical properties of biochar. In: *Biochar for Environmental Management: Science and Technology* (Eds. Lehmann J & Joseph S), Earthscan.
- FAO. (2004) FAOSTAT Data, Food and Agriculture Organization of the United Nation. Rome. adapted from URL: <http://apps.fao.org/default.jsp>
- Glaser B (2007) Prehistorically modified soils of central Amazonia: a model for sustainable agriculture in the twenty first century. *Philosophical Transactions of the Royal Society-Biological Sciences*. 362, 1478.
- Glaser B, Guggenberger G, Zech W (2002) Past anthropogenic influence on the present soil properties of anthropogenic dark earths (Terra Preta) in Amazonia (Brazil). *Geoarchaeology*.
- Glaser B, Guggenberger G, Zech W, Ruivo ML (2003) Soil organic matter stability in Amazonian dark earths. In: Lehmann et al (ed.) *Amazonian dark earths: Origin,*

Chapter 2

- properties, management. Kluwer Academic Publishers, Dordrecht, The Netherlands. pp. 141-158.
- Glaser B, Lehmann J, Zech W (2002a) Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal. A Review. *Biology Fertile Soils*. 35, 219-230.
- Graber E, 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.
- Hayes DJ (2009) An examination of biorefining Processes, catalysts and challenges. Adapted from URL: http://www.carbolea.ul.ie/files/DRAFT_PAPER_DAN.pdf.
- Houlbrooke DJ, Horne DJ, Hedley MJ, Hanly JA, Scotter DR (2004). Minimising surface water pollution resulting from farm-dairy effluent application to mole-pipe drained soils. I. An evaluation of the deficit irrigation system for sustainable land treatment in the Manawatu. *New Zealand Journal of Agricultural Research*. 47, 405-415.
- IPCC (2007) Summary for Policymakers. Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Adapted from URL: http://ipcc-wg1.ucar.edu/wg1/Report/AR4WG1_Print_SPM.pdf.
- Johns MR (1995) Development in wastewater treatment in the meat processing industry: A Review. *Bioresource Technology*. 54, 203-216.
- Johns MM, Marshall WE, Toles CA (1999) The effect of activation method on the properties of pecan shell-activated carbons. *Journal of Chemical Technology and Biotechnology*. 74,1037–1044.
- Juniper Consultancy Services Limited, (2008). Briefing document on the pyrolysis and gasification of MSW. Commissioned by improvement and efficiency South East, UK.
- Junpirom S (2006). Activated carbon from longan seed: its activation model and adsorption of water vapour and benzene, PhD. thesis, Suranaree University of Technology, Thailand.

- Karhu K, Mattila T, Bergstrom I, Regina K (2011) Biochar addition to agricultural soil increased CH₄ uptake and water holding capacity, Results from a short-term pilot field study. *Agriculture ecosystems and environment*. 140, 309-313.
- Kishimoto S, Sugiura G (1985) Charcoal as a soil conditioner. *Int Achieve Future*. 5, 12-23.
- Kookana RS (2010) The role of biochar in modifying the environmental fate, bioavailability, and efficacy of pesticides in soils: a review. *Soil Research*. 48(7), 627-637.
- Kostura B, Kulveitová H, Leško J (2005). Blast furnace slags as sorbents of phosphate from water solutions. *Water Resources*. 39 (9), 1795-1802.
- Koutcheiko S, Monreal CM, Kodama H, McCracken T, Kotlyar L (2006) Preparation and characterization of activated carbon derived from the thermo-chemical conversion of chicken manure. *Bioresource Technology*. 98, 2459-2464.
- Kwapinski W, Byrne CMP, Kryachko E, Wolfram P, Adley C, Leahy J, Novotny EH, Hayes MHB (2010). Biochar from biomass and waste. *Waste and Biomass Valorization*. 1(2), 177-189.
- Laird DA, Fleming P, Davis DD, Horton R, Wang B, Karlen DL (2010) Impact of biochar amendments on the quality of a typical Midwestern agricultural soil. *Geoderma*. 158(3-4), 443-449.
- Lehmann J (2007) Bio-energy in the black. *Front Ecology Environment*. 5(7), 381-387.
- Lehmann J, Gaunt J, Rondon M (2006) Biochar sequestration in terrestrial ecosystems- a review. *Mitigation and adaptation Strategies for Global Change*. 11, 403-427.
- Lehmann J, Joseph S (2009) Biochar for environmental management: an introduction. In: Lehmann J, Joseph S. (Eds.), *Biochar for Environmental Management: Science and Technology*. Earthscan, London. 1-12.
- Lehmann CJ, Rondon M (2005) Biochar soil management on highly weathered soils in the tropics. In: Uphoff, N.T. (Ed.). *Biological approaches to sustainable soil systems*. CRC Press. Boca Raton. pp. 517-530.
- Liang B, Lehmann J, Solomon D, Kinyangi J, Grossman J, O'Neill B, Skjemstad JO, Thies J, Luizao FJ, Petersen J, Neves EG (2006) Black carbon increases cation exchange capacity in soils. *Soil Science Society of American Journal*. 70, 1719-1730.

Chapter 2

- Lima HN, Schaefer CER, Mello JWV, Gilkes RJ, Ker JC (2002) Pedogenesis and pre-Colombian land use of "Terra Preta Anthrosols" ("Indian black earth") of Western Amazonia. *Geoderma*. 110, 1–17.
- Longhurst RD, Roberts AHC, O'Connor MB (2000) Farm dairy effluent: a review of published data on chemical and physical characteristics in New Zealand. *New Zealand Journal of Agricultural Research*. 43, 7-14.
- Masiello CA, Druffel ERM (1998) Black carbon in deep sea sediments. *Science*. 280, 1911-1913.
- McArthur K, Clark M (2007) Nitrogen and Phosphorus Loads to Rivers in the Manawatu-Wanganui Region: An Analysis of Low Flow State: Technical Report to Support Policy Development. New Horizons Regional Council. Report No: 2007/EXT/793.
- Metcalf and Eddy (2003) Wastewater Engineering, Treatment and Reuse, 4th Edition (New York: McGraw-Hill).
- MfE (Ministry for the Environment) 2008. Net Position Report 2008. Projected balance of Kyoto Protocol units during the first commitment period. Ministry for the Environment, Wellington.
- Mohan D, Pittman CU (2007) Arsenic removal from water/wastewater using adsorbents-a critical review. *Journal of Hazardous Materials*. 142, 1-53
- Mohan D, Singh KP, Sinha S, Gosh D (2004) Removal of pyridine from aqueous solution using low cost activated carbons derived from agricultural waste materials. *Carbon*. 42, 2409–2421.
- Mui ELK, Ko DCK, McKay G (2004) Production of active carbons from waste tyres – a review. *Carbon*. 42, 2789–2805.
- Namgay T, Singh B, Singh BP (2010) Influence of biochar application to soil on the availability of As, Cd, Cu, Pb, and Zn to maize (*Zea mays* L.). *Soil Research*. 48(7), 638-647.
- Nguyen BT, Lehmann J, Kinyangi J, Smernik R, Riha SJ, Engelhard MH (2008) Long term black carbon dynamics in cultivated soil. *Biogeochemistry*. 89, 295-308.
- Nguyen M, Tanner C (1998) Ammonium removal from wastewaters using natural New Zealand zeolites. *New Zealand Journal of Agricultural Research*. 41, 427-446.

- Nigussie A, Kissi E (2011) Impact of Biomass Burning on Physicochemical Properties of Nitisol in the Southwestern Ethiopia. *Asian Journal of Agricultural Research*. 5, 223-233.
- Nik-Azar M, Hajaligol MR, Sohrabi M, Dabir B (1997) Mineral matter effects in rapid pyrolysis of beech wood. *Fuel Processing Technology*. 51, 7-17.
- Novak JM, Busscher WJ, Laird DL, Ahmedna M, Watts DW, Niandou MAS (2009) Impact of biochar amendment on fertility of a southeastern Coastal Plain soil. *Soil Science*. 174(2), 105.
- Oledzka M (2007) Substrate selection for Constructed Wetlands. Thesis presented for MSc. Faculty of Bioengineering. Universiteit Gent.
- Omar S, Girgis B, Taha F (2003) Carbonaceous materials from seed hulls for bleaching of vegetable oils. *Food Research International*. 36, 11-17.
- O'Neill B, Grossman J, Tsai M, Gomez J, Lehmann J, Peterson J, Neves E, Thies J (2009) Bacterial Community composition in Brazilian Anthrosols and adjacent soils characterized using culturing and molecular identification. *Microbial Ecology*. 58, 23-35.
- Perrin T, Drost D, Boettinger J, Norton J (1998) Ammonium-loaded clinoptilolite: A slow-release nitrogen fertilizer for sweet corn. *Journal of plant nutrition*. 21(3), 515-530.
- Phuntsho S, Shon H, Vigneswaran S, Kandasamy J . Wastewater stabilization ponds (wsp) for wastewater treatment. *Encyclopedia of life support systems (EOLSS)*. 2
- Piccolo A, Pietramellara G, Mbagwu JSC (1997) Use of humic substances as soil conditioners to increase aggregate stability. *Geoderma*. 75, 267-277.
- Pietikainen J, Kiikkila O, Fritze H (2000) Charcoal as a habitat for microbes and its effects on the microbial community of the underlying humus. *Oikos*. 89, 231-242.
- Popov V, Itoh H, Brebbia CA, Kungolos A (2004) Waste Management and the Environment II, WIT Press, Boston.
- Reynolds B (2010) Use of biochar as a nitrogen filter in household wastewater treatment. Användning av biokol som ett kvävefilter i hushållsavloppssystem. A thesis.
- Rondon M, Ramirez J, Lehmann J (2005) Greenhouse gas emissions decrease with charcoal additions to tropical soils. Paper presented at the 3rd USDA symposium on carbon sequestration. Baltimore. 21-24 March, 2005.

- Roygard J, McArthur KJ (2007) A framework for managing non-point source and point source nutrient contributions to water quality: Technical report to support policy development. Horizons Regional Council Report No. 2007/EXT/792.
- Sander M, Pignatello JJ (2005) Characterization of charcoal adsorption sites for aromatic compounds: Insights drawn from single solute and bi solute competitive experiments. *Environmental Science and Technology*. 39, 1606-1615.
- Schimmelpfennig S, Glaser B (2011) one step forward toward characterization: some important material properties to distinguish biochars. *Journal of Environmental Quality*.
- Schmidt MWI, Noack AG (2000) Black carbon in soils and sediments: Analysis, distribution, implications and current challenges. *Global Biogeochemical Cycles*.
- Shilton AN, Elmetri I, Drizo A, Pratt S, Haverkamp RG, Bilby SC (2006). Phosphorus removal by an 'active' slag filter – a decade of full scale experience. *Water Resources*. 40, 113-118.
- 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.
- Soto-Garrido G, Croswell A, Garcia R, Arriagada R (2003) A peach Stone activated carbón chemically modified to adsorb aqueous ammonia. *Journal of the Chilean Chemical Society*. 48, 65-69.
- Spokas KA, Koskinen WC, Baker JM, Reicosky DC (2009) Impacts of woodchip biochar additions on greenhouse gas production and sorption/degradation of two herbicides in a Minnesota soil. *Chemosphere*. 77, 574-581.
- Srivastava N, Eames I (1998) A review of adsorbents and adsorbates in solid–vapour adsorption heat pump systems. *Applied thermal Engineering*. 18(9), 707-714.
- Stanford G, Dement JD (1957) A method for measuring short-term nutrient absorption by plants: I. Phosphorus. *Soil Science society of America Proceedings*. 21, 612-617.
- Steiner C, Teixeira W, Lehmann J, Nehls T, Vasconcelos de Macedo J, Blum W, Zech W (2007) Long term effects of manure, charcoal and mineral fertilization on crop production and fertility on a highly weathered Central Amazonian upland soil. *Plant and Soil*. 291, 1-2.
- Swift RS (2001) Sequestration of carbon by soil. *Soil Science*. 166, 858-871.
- Taghizadeh-Toosi A, Clough TJ, Sherlock RR, Condon L M (2011) Biochar adsorbed ammonia is bioavailable. *Plant and Soil*. 350,57-69.

Chapter 2

- Tchobanoglous G (1991) Wastewater engineering: treatment, disposal and Reuse. (3rd ed.) Metcalf & Eddy, Inc. McGraw Hill, pp. 1-1848.
- Topoliantz S, Ponge JF, Arrouaya D, Ballof S, Lavelle P (2002) Effect of organic manure and endogeic earthworm *Pontoscolex corethrurus* (Oligochaeta: Glossoscolecidae) on soil fertility and bean production. *Biology and Fertility of Soils*. 36, 313–319.
- Tryon EH (1948) Effect of charcoal on certain physical, chemical, and biological properties of forest soils. *Ecology Monographs*. 18, 81–115.
- United Nations (2003) Wastewater treatment technologies, A General Review. *Economic and social Commission for Western Asia*. New York, pp. 2-122.
- Van Zwieten L, Singh BP, Joseph S, Kimber S, Cowie A, Chan KY (2009) Biochar reduces emissions of non CO₂ GHG from soil. In: *Biochar for environmental Management* (eds. Lehmann J, Joseph S). Earthscan, London, UK. pp 227-249.
- Van Zwieten L, Kimber S, Morris S, Chan K, Downie A, Rust J, Joseph S, Cowie A. (2010). Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. *Plant and Soil*. 327(1), 235-246.
- Verheijen F, Jeffery S, Bastos AC, Vander Velde M, Diafas I (2010) Biochar application to soils: A critical scientific review of effects on soil properties, processes and functions. JRC Scientific and technical Reports. Office for the Official Publications of the European Communities. Luxembourg. pp.149
- Walsh ME, Perlack RL, Turhollow A, Ugarte DT, Becker DA, Graham RL, Slinksy SE, Ray DE (1999) Biomass feedstock availability in the united states. 1999 State level Analysis, Oak Ridge National Laboratory. Oak Ridge, TN. Available via bioenergy.ornl.gov.
- Wang T, Camps-Arbestain M, Hedley M, Bishop P (2012) Predicting phosphorus bioavailability from high ash biochars. *Plant and Soil*. 1-15.
- Wieczorek S (2008) Assessing the Influence of Adsorbent Bed (Tree Bark) Parameters on the Reduction of Ammonia Emissions from Animal Husbandry. *Polish Journal of Environmental Studies*. 17(1), 147-154.
- Woolf D (2008) Biochar as a soil amendment: A review of the Environmental implications. Adapted from URL: http://orgprints.org/13268/01/Biochar_as_a_soil_amendment_-_a_review.pdf

Chapter 2

Yaman S (2004) Pyrolysis of biomass to produce fuels and chemical feedstocks. *Energy conversion and Management*. 45, 651-671.

Yamane VK, Green RE (1972) Adsorption of ametryne and atrazine on an oxisom, montmorillonite, and charcoal relation to pH and solubility effects. *Soil Science America Proceedings*. 36, 58-64.



MASSEY UNIVERSITY
GRADUATE RESEARCH SCHOOL

STATEMENT OF CONTRIBUTION
TO DOCTORAL THESIS CONTAINING PUBLICATIONS

(To appear at the end of each thesis chapter/section/appendix submitted as an article/paper or collected as an appendix at the end of the thesis)

We, the candidate and the candidate's Principal Supervisor, certify that all co-authors have consented to their work being included in the thesis and they have accepted the candidate's contribution as indicated below in the *Statement of Originality*.

Name of Candidate: Kiran Hina

Name/Title of Principal Supervisor: Prof M. J. Hedley

Name of Published Research Output and full reference: Title "Producing biochars with enhanced surface activity through alkaline pretreatment of feedstocks". (2010). Australian Journal of Soil Research 48, 606-617.
Authors: Hina K, Bishop P, Camps A, Kersting M, Hedley J.
In which Chapter is the Published Work: Chapter 3

Please indicate either:

- The percentage of the Published Work that was contributed by the candidate: ~30%
and / or
- Describe the contribution that the candidate has made to the Published Work:

The research paper showed that biochars can be activated costeffectively by tannery waste & used for ammonium sorption from waste water.

Kiran
Candidate's Signature

7/2/2013
Date

M. J. Hedley
Principal Supervisor's signature

7/2/2013
Date

Chapter 3

Activating biochars with pre (alkaline) and post (steam) treatments of feedstocks and biochars

This chapter employs the batch sorption technique developed in Chapter 4. The main focus of this chapter is to investigate activation procedures that can be used to potentially increase the NH_4^+ -N sorption capacity of biochars. It gives the detailed characterisation of the chars and the physical and chemical changes induced by activation procedures.

A paper from this study has been published: Hina K, Bishop P, Camps Arbestain M, Calvelo-Pereira R, Maciá-Agulló JA, Hindmarsh J, Hanly JA, Macías F, Hedley MJ (2010) Producing biochars with enhanced surface activity through alkaline pretreatment of feedstocks. Special issue of *Australian Journal of Soil Research*. 48, 606-615.

3.1 Introduction

Biochar, due to its aromatic composition and condensed macromolecular structure, is biologically and chemically more stable than the original biomass sources from which it was produced like bark. Therefore, Biochar loaded with NH_4^+ is a more environmentally suitable addition to soils and long term source of adding sequestered C and some plant available N than zeolite and bark (Chapter 4). In this Chapter research is conducted on activating biochars and evaluating their capacity to sorb NH_4^+ ions. Moreover, the detailed characterisation of biochars used in Chapter 5 is presented.

Current knowledge gained from activated carbon studies could have some application to biochar research. Surface charges on activated carbon are generated by physical and chemical methods (Rodriguez-Reinoso and Molina-Sabio 1992). Physical activation involves the use of oxidizing gases, such as carbon dioxide or water steam, while chemical activation involves the use of inorganic chemicals, such as zinc chloride, phosphoric acid, and potassium or sodium hydroxides (Solano et al. 2008). Sodium hydroxide has been reported to promote a better activation of lignocellulosic materials than potassium hydroxide (Lillo-Rodenas et al. 2007), and this occurs predominantly via a non-intercalation mechanism in the former and through an intercalation process in the latter (Raymundo-Piñero et al. 2005, Lozano-Castelló et al. 2006, Maciá-Agulló et al. 2007).

Bark from pulp mills is a potential feedstock for the production of biochar, because bark is a low cost by-product that is produced in large quantities (Montane et al. 2005). The most common exotic forest species used in New Zealand pulp mills is radiata pine (*Pinus radiata*), followed by Douglas fir (*Pseudotsuga menziesii*) and eucalyptus (*Eucalyptus cinerea*). Softwood and hardwood species have different types of lignin, with softwood (e.g., pine) having lower methoxyl content than hardwood (e.g., eucalyptus). The lignin of softwood (gymnosperms) displays a higher proportion of guaiacyl (G) units and no syringyl (S) units while the lignin of hardwoods (angiosperms) have both G and S units, the latter unit being dominant (Lewis and Yamamoto 1990; Liu et al. 2008). These differences are known to affect the likelihood of internal cross-linking, otherwise hampered by methoxyl groups in S units, and result in a variable reactivity of wood towards alkaline reagents (Tsutsumi et al. 1995) and thermal degradation during pyrolysis (Wang et al. 2009).

The aim/objectives of this study was to produce biochars from pine and eucalyptus feedstocks with increased acidic functional groups, using alkaline tannery waste as activating agent. The effect of different tannery waste dilution was assessed for ammonium sorption/removal from NH_4^+ influent solution, together with the potential distinct response of the two types of wood. Steam activation was also used as post treatment for the activation of biochars. The effectiveness of the different treatments with regard to nutrient retention was also evaluated through an NH_4^+ -N sorption-desorption study. It is proposed that the end use for these activated biochars could be as active filter media for removing nutrients from housed animal and municipal waste streams, and their addition to soils thereafter as slow-release fertilisers.

3.2 Materials and Methods

3.2.1 Materials

Pine and eucalyptus waste barks were supplied, by Carter Holt Harvey NZ Ltd. These wastes were not bark *sensu stricto*, as for eucalyptus, the outer cambium layer was dominant and, for pine, high levels of wood were present. However, these materials will be referred to as “bark” throughout the text to facilitate reading. The pine bark was chipped with a commercial chipper while the eucalyptus bark peelings were used in the received form. The final particle size of the pine chips was irregular, ranging from 3 to 11 mm in length. In order to minimise

processing, no efforts were made to homogenise the size of eucalyptus bark particles. The feedstocks were dried overnight in an oven at 65°C.

Tannery lime float waste slurry was used as an alkaline treatment of the bark feedstocks. This slurry was produced by the tanning industry as a waste from a washing treatment of livestock skins and hides, in which a concentrated solution of Na₂SO₄ and Na₂S is used. The waste consists of hydrolysed proteins and fats, in addition of the original compounds, and is alkaline (pH 13) with a dry matter content of 30%. The composition of the tannery waste is reported in Table 3.1 (analysed by Hill Laboratories, Hamilton, New Zealand).

Table 3.1 Elemental composition of solid tannery waste residue.

Major Elements ^a	(g kg ⁻¹)	Minor elements ^a	(mg kg ⁻¹)
Al	0.2	As	< 2.0
Ca	12.0	Cd	< 0.10
Fe	0.3	Cr	2.2
Mg	0.4	Cu	4.2
P	1.9	Pb	0.5
K	4.2	Zn	49.0
Na	110.0	Ni	< 2.0
OC ^b	430.0	B	79
N	66.0	Co	<0.40
S	62.4	Mn	9.3
		Hg	<0.10
		Mo	<0.40
		Se	<0.20

^a Total concentration values; ^b organic carbon

3.2.2 Methods

Chemical Activation treatments

Chemical activation treatments were carried out through impregnation of the feedstocks either with diluted or undiluted alkaline tannery slurry. The first set of treatments involved impregnating 200 g (dry weight basis) of both feedstocks with diluted tannery slurry (diluted with distilled water in a 1:3 ratio). The impregnation was based on adding to the bark the amount of slurry needed to fill the adsorbent pore volume (Bandosz and Petit 2009). Forty grams (dry weight basis) of tannery slurry diluted with deionised water was needed to impregnate the pine wood (L PI feedstock) and 60 g (dry weight basis) was required for the

eucalyptus bark (L EU feedstock). The second set of treatments involved impregnating 200 g (dry weight basis) of both feedstocks with undiluted tannery slurry (60 and 40 g for S EU and S PI, respectively). Impregnation of feedstocks with both the diluted and undiluted tannery slurry was carried out at room temperature for five hours, before feedstock/tannery slurry mixtures were dried overnight in an oven at 65 °C and then pyrolysed, as described below. Pine and eucalyptus biochars with no tannery slurry treatment were also produced and are referred to as controls treatments (Ctr PI and Ctr EU biochars, respectively). Three replicates were made of each treatment.

Carbonisation processes

For each of PI and EU bark feedstocks, 200 g, either with or without alkaline treatment, were pyrolysed at 550°C by heating at an average heating rate of 28 °C min⁻¹ for an average time of 20 min, for all treatments, in triplicate, using a gas-fired, 5 L stainless steel, rotating drum kiln. When the desired temperature was reached, the kiln was allowed to cool down to room temperature. The mixed char and ash residue was removed and another 2 batches of each feedstock were pyrolysed. The 3 replicates mixed char and ash residues of each treatment were pooled into a single sample. Before sorption studies of the resulting biochar, subsamples of the mixed char and ash residue were washed repeatedly with deionized water until the electrical conductivity decreased to 50 µS cm⁻¹ (Cheng et al. 2006). These washed samples were used for the NH₄⁺ sorption/desorption experiments and BET measurements. Dominant particle-size ranged between 3 to 8 mm for the pine biochars and was < 2 mm for the eucalyptus biochars.

Steam activation

Untreated PI and EU biochars were heated in a muffle furnace to 750 °C, under a constant N₂ flow; then steam was injected for 1 hour into the N₂ gas stream. Non-activated biochars were chosen for steam activation to avoid further C loss from alkaline activated biochars. Thereafter, the steam flow was stopped and the heat source shut down. The biochars were allowed to cool down in the furnace overnight under an N₂ atmosphere. The process was repeated three times. The three replicates were pooled into a single sample thereafter. These biochars were identified as steam-PI and steam-EU, for PI and EU biochars, respectively. The steam activation set-up is shown as follows.

Cellulose, hemicellulose and lignin content

The cellulose, hemicellulose and lignin content of the untreated bark feedstocks were determined using the Fibertec System M (Tecator, Hoganas, Sweden). This method is based on sequential chemical treatments with neutral detergent, acid detergent, 72 % H₂SO₄ and ashing (van Soest 1967). The detergent neutral step washes out the cellular content and the residual fraction is referred to as neutral detergent fibres (NDF). With the acid detergent treatment of NDF, cell walls are broken down and the residual fraction is referred to as acid detergent fibres (ADF). Hemicellulose is estimated as NDF-ADF. With a subsequent H₂SO₄ treatment, cell walls are digested, and an acid detergent lignin (ADL) residue is obtained. Cellulose is estimated as ADF-ADL, and ADL is assumed to be mostly lignin. The analysis was conducted by Food and Nutrition Department, Massey University.

Elemental composition

The total C, H and N content of the different biochars were determined using a TruSpec CHNS analyser (LECO Corp. St. Joseph, MI); total O was determined with an EA elemental analyser (Fisons EA-1108-CHNS-O, Fisons Instruments, Milano, Italy). The C-CO₃ content of biochars was determined using a modification of common static chamber methods (Bundy and Bremner 1972; Tiessen et al. 1983). The organic C was determined as the difference between total C and C-CO₃. The ash content was determined by thermo gravimetric analysis on a TA instrument (Alphatech, SDT Q600 manufactured by TA instruments, Newcastle, Australia). The sample was initially heated from room temperature to 900 °C (at a rate of 5 °C min⁻¹) under a N₂ atmosphere and weight loss recorded (data not shown); thereafter, an air current was provided and the ash was determined when there was no further weight change. Ashes do not contain carbonates, which decarboxylate at temperatures below 900 °C. The elemental composition of steam activated biochars is discussed in chapter 5 of the thesis. The Quality control measures were adopted in analysis of biochars, herbage and soil samples by including external standard samples with known values in each batch of analyses. The analyses of unknown samples and standards were run in duplicate or triplicate to confirm the precision.

pH and surface acid functional groups

Biochar pH was measured using the methodology of Ahmedna et al. (1998), which involved a 1 % (wt/wt) suspension of biochar in deionised water. The suspension was heated in a water bath to about 90 °C and stirred for 20 min to allow dissolution of the soluble biochar

components. After cooling to room temperature, the pH of the biochar suspension was measured. The content of acid groups on the biochar was determined following potentiometric titration (López et al. 2008; Petit et al. 2010). This method involves the suspension of 0.1 g of sample (previously acidified and subsequently dialysed in cellulose bags – pore size 1000 Da – and lyophilised, to eliminate interfering salts) in 50 mL of 0.1 M KNO₃ as the inert electrolyte. Thereafter, biochar suspensions were potentiometrically forward titrated with 0.2 M KOH carbonate-free solution or backward titrated with 0.1 M HCl in order to cover the pH range from 3 to 10. However, pH values of the biochars were buffered close to pH 5; thus with this methodology, functional groups reactive in the pH range of 5 to 10 were estimated. The contents of carboxylic groups in the samples were estimated empirically from the Q (the sample charge) versus pH charge curves as the value of Q at pH = 8. The Q-pH curves were obtained from experimental data points of the potentiometric titrations of the samples. Functional groups analysis was conducted in Spain.

FT-IR

Biochars were ground to 0.1 mm and 0.5 mg of each sample was placed onto the Ge window of a Nicolet 5700 FTIR with an ATR attachment (OMNI Sampler Nexus). Spectra were obtained over 256 scans with a KBr beam splitter. It was set at a resolution of 4 cm⁻¹, covering the range of 4000-700 cm⁻¹ and with an aperture size of 34 cm. The reflectance was measured and analysed using OMNIC v7.1 with Happ-Genzel apodisation and Mertz phase correction. The identification of absorption bands was based on published data and is described at the end of chapter in Table S1.

Solid state CP MAS ¹³C NMR

Solid state, cross polarisation magic-angle spinning ¹³C nuclear magnetic resonance (CPMAS ¹³C NMR) was used to characterise the biochar. All NMR experiments were conducted in the Bruker (Rheinstetten, Germany) AMX 200 Mhz horizontal bore magnet. Samples were packed into a 7 mm diameter rotor and spun at speeds of 5 kHz in a dual resonance magnetic angle spinning (MAS) probe from Doty Scientific. The ¹³C CP/MAS spectra were acquired with a 1H 90° pulse for 5.5 μs, a cross-polarisation contact time of 1000 μs, an acquisition time of 30 ms, relaxation time of 2 sec and 5000 scans. The analysis was done by Jason Hindmarsh from NMR laboratory at Massey University, Palmerston North.

X-ray photoelectron spectroscopy (XPS)

Surface analysis of the eucalyptus samples was conducted using X-ray photoelectron spectroscopy (XPS). This was carried out using a Specs spectrometer, using $MgK\alpha$ (1253.6 eV) radiation emitted from a double anode at 50 W. Binding energies for the high-resolution spectra (C 1s and N 1s) were calibrated by setting C 1s at 284.6 eV. A non-linear least squares curve fitting with a Gaussian-Lorentzian mix function and Shirley background subtraction was used to deconvolute the XPS spectra. The analysis was done by Benito Fuertes from INCAR, CSIC, Spain.

Specific surface area (BET)

Nitrogen gas adsorption measurements for BET measurements were performed using a Micromeritics ASAP 2020 volumetric adsorption system. Samples were previously outgassed at 250 °C for 4 hours. Analysis was done by Dr Ron Etzion from University of Auckland, NZ.

Scanning Electron Microscope (SEM)

The surface physical morphology of the samples was examined by Quanta 200 equipment (FEI, Eindhoven, the Netherlands) after coating the particles with gold using a Bal Tec SCD 500 cool sputting device (Balzers Union, Wallruf, Germany). Analysis was done by Doug Hopcroft from Massey University, Palmerston North, NZ.

Ammonium sorption and desorption

A 10 mL volume of NH_4^+ -N solution, 40 mg N L⁻¹ as $(NH_4)_2SO_4$, was added to 2 g of biochar placed in a 40-mL centrifuge tube and run in triplicates. The NH_4^+ -N solution concentration used was based on the typical levels present in municipal wastewater. The tubes were shaken end-over-end (30 r.p.m) for six hours, then centrifuged for 5 minutes at 7000 rpm and the suspension was filtered (Whatman filter paper 42). This procedure was repeated four times with each sample. Ammonium was determined using a Technicon autoanalyser (Technicon, Dublin). The sorbed concentration was estimated by difference between the initial and final concentration of the NH_4^+ -N. Subsequently, biochars were subjected to desorption of NH_4^+ -N by adding the samples to two separate 10 mL volumes of 2 M KCl solution. The ammonium retention of steam activated biochars is discussed in chapter 3 of the thesis.

3.2.3 Statistical Analysis

The significance of results for the sorption experiment was determined using GraphPad statistical software (GraphPad Prism 5.02 GraphPad Software Inc.). The Student's t test was used to test for significant differences in the results of NH_4^+ -N sorption.

3.3 Results and Discussion

3.3.1 Composition of the feedstocks used

The cellulose content was higher in the eucalyptus bark (51.3 %) compared with the pine bark (39.7 %), whereas the lignin and hemicellulose content were higher in pine bark (26.3 and 17.7 %, respectively) than in eucalyptus bark (10.5 and 15.6 %, respectively) (Table 3.2). The NDF values of the original feedstocks were 77 and 84 % for eucalyptus and pine samples, respectively, which indicates a greater presence of readily degradable cellular contents (RDCC; estimated as $100 - \text{NDF}$) in the eucalyptus bark (Table 3.2).

Table 3.2 Values (%) of neutral detergent fibre (NDF), hemicelluloses, cellulose and lignin content of Pine (PI) and Eucalyptus (EU) feedstocks before and after pre-treatment with solid tannery waste (S).

Sample	NDF	Hemicellulose	Cellulose	Lignin	RDCC ^a
PI feedstock	83.7	17.7	39.7	26.3	16.3
S PI feedstock	63.4	12.8	31.3	19.3	36.6
EU feedstock	77.4	15.6	51.3	10.5	22.6
S EU feedstock	39.6	7.9	26.6	5.1	60.4

^a RDCC, readily degradable cellular contents

Where pine (PI), Eucalyptus (EU), solid tannery waste activated PI biochar (S PI), solid tannery waste activated EU biochar (S EU)

3.3.2 Characterisation

Yield, recovered C and N, C and N contents of Alkaline activated biochars

The yield of the different biochars, defined as the ratio of mass of biochar recovered after pyrolysis and the initial mass of the feedstock (or feedstock + tannery slurry) as a percentage, is reported in Table 3.3. The yield of the three pine biochars (Ctr PI, L PI, S PI) ranged from 26 to 27%, whereas the yield for the three eucalyptus biochars (Ctr EU, L EU, S EU) ranged from 28 to 32% (Table 3.3). The small difference in yields within feedstocks is due to treatments and pyrolysis conditions while difference between pine and eucalyptus can be due to the different type of feedstocks (pine wood chip and eucalyptus bark peelings).

As expected from a carbonisation process, the C content of pine increased from 49 to 78 %, and that of eucalyptus from 46 to 74 % (Table 3.3). Carbon contents of treated biochars included a C-CO₃ fraction (< 3 %) attributed to the formation of carbonates during pyrolysis, as evolved CO₂ became trapped under alkaline conditions. Organic C contents of the treated biochars were lower than the untreated biochars, with values of 70 and 65 % for pine, respectively, and of 56 and 51 % for eucalyptus, respectively (Table 3.3). This lower organic C content could be attributed to the dilution effect caused by the addition of the tannery slurry, as it had a lower C content than the feedstocks (Tables 3.1, 3.3). Recovered C (recovered carbon is amount of biochar C to the amount of feedstock C) ranged between 41-43 % in the pine biochars and between 42-45 % in the eucalyptus biochars (Table 3.3). Biochars treated with diluted tannery slurry had higher H/C ratios than the rest of the samples, this trend being more evident for eucalyptus (data not shown). Pre-treating the feedstocks with tannery waste also increased the ash content of the corresponding biochars, as expected (Table 3.3).

The mass loss of biochar after steam activation – so-called “burn-off” – increased (Table 3.4), as expected (Azargohar and Dalai, 2008), with values of 60.5 and 80 % for the steam-PI and steam-EU biochars. The BET surface area of steam-PI biochar increased (735 m² g⁻¹) compared to the corresponding control (235 m² g⁻¹). A similar trend was observed in the EU biochar, which increased from 2.82 to 457 m² g⁻¹ (Table 3.4). These results confirm the well-established effect of steam activation on increasing the surface area of biochars, in agreement with previous studies (Fan et al. 2004, Nabais et al. 2008, Azargohar and Dalai 2008). This may have a potential for increasing the sorption of cations if accompanied by an increase in negative surface charge (McElligott, 2011), as well as of hydrophobic organic pollutants if no effect on surface charge is achieved (Hu and Srinivasan, 1999). The pH of the biochars decreased with steam activation from 8.3 to 7.8 in the EU biochar, and from 9.3 to 7.9 in the PI biochars, respectively (Table. 3.4). This also could be attributed to the removal of alkaline salts from the biochar.

Table 3.3 Elemental analysis of feedstocks and biochars.

Sample	Chemical composition (wt, %)						C-CO ₃ (%)	Yield (%)	Recovery (%)		
	C ^a	N	H	O	S	Ash ^b			C	N	S
PI feedstock	48.7	0.28	6.39	46.1	<0.05	0.5	n.a. ^c	n.a.	n.a.	n.a.	n.a.
S PI feedstock	42.6	1.81	6.43	40.1	4.1	7.5	n.a.	n.a.	n.a.	n.a.	n.a.
Ctr PI	77.7	0.61	3.69	16.7	<0.05	4.9	0.3	27	43	57	n.a.
L PI	70.4	1.33	3.43	15.4	1.0	8.6	0.8	26	43	19	6
S PI	65.3	1.99	3.11	18.2	1.5	16.9	1.3	27	41	30	10
EU feedstock	45.8	0.33	6.55	48.2	<0.05	4.6	n.a.	n.a.	n.a.	n.a.	n.a.
S EU feedstock	37.5	3.21	6.46	39.2	6.8	14.4	n.a.	n.a.	n.a.	n.a.	n.a.
Ctr EU	73.4	0.56	3.46	12.0	0.2	13.0	0.5	28	45	47	n.a.
L EU	56.0	1.82	3.11	22.6	2.3	27.8	1.8	29	43	16	10
S EU	51.4	2.14	2.53	21.2	2.9	30.1	2.8	32	42	21	13
Steam PI	83.0	0.15	-	-	-	3.7	-	-	-	-	-
Steam EU	79.4	0.23	-	-	-	10.0	-	-	-	-	-

^a organic C= Total C – C-CO₃²⁻; ^b at 900°C; ^c not analyzed/not available.

Where pine (PI), Eucalyptus (EU), non- activated pine biochar (Ctr PI), non- activated Eucalyptus biochar (Ctr EU), liquid tannery waste activated PI biochar or diluted (L PI), solid tannery waste activated PI biochar or un-diluted (S PI), liquid tannery waste activated EU biochar (L EU), solid tannery waste activated EU biochar (S EU); The data in this table was analysed and provided by university from Spain.

The carbonisation process of untreated feedstocks increased the concentration of N in the materials from ~ 0.3 % N prior to pyrolysis, to ~ 0.6 % N, after pyrolysis. The total recovery of N was higher for pine compared to eucalyptus (57% vs. 41 % recovery of N respectively) (Table 3.3). The tannery waste treatments increased the N content of both pine and eucalyptus feedstocks (up to 1.8% and 3.2%, respectively; Table 3.3), as expected, due to the richness of N in raw wastes (Table 3.1). After pyrolysis, the N contents of the materials either slightly increased or decreased, with 2.0 and 2.1 % N for the S PI and S EU biochars, respectively. The recovery of N in the treated biochars was lower than the untreated biochars, with values ranging from 16 to 30 %, thus indicating a greater N loss from the system, compared to untreated biochars (Table 3.3). Further research is required to determine the fate of the unrecovered N. Details of ammonium sorption on steam activated PI and EU are given in Chapter 5 in thesis.

Values of pH and surface charge

The pH values of the biochars ranged from 8.8 for the Ctr EU biochar up to 10.6 for the S EU biochar (Table 3.4). Biochars prepared from alkaline tannery slurry had greater pH values than the corresponding controls. All the analyses were done in duplicate with average values mentioned in Table 3.4. Carboxylic functional groups were more abundant in the Ctr EU treatment than the Ctr PI treatment. The tannery slurry treatments promoted the formation of surface charge in all samples under study, but the response to increasing alkaline concentrations was feedstock-dependent. In the biochars from pine wastes, there was an increase of carboxylic functional groups with increasing concentration of tannery slurry (from 0.006 mmol g⁻¹ in the Ctr PI treatment to 0.080 mmol g⁻¹ in S PI treatment). In the eucalyptus samples, however, the greatest amount of carboxylic groups was generated with the diluted tannery slurry treatment (L EU; 0.164 mmol g⁻¹), which was the highest value of all biochars in this study. The decrease in functional groups observed in the S EU treatment could be due to enhanced degradation of the fibrous structure (Fig. 3.7) of the eucalyptus bark at high alkalinity. Differences between the two feedstocks were mainly attributed to their different types of lignin (David and Shiraishi, 2000).

Table 3.4 Values of pH, carboxylic groups and BET surface area.

Samples	pH	Carboxylic groups (mmol g ⁻¹)	BET (m ² g ⁻¹)	Activation burnoff (%)
Ctr PI	9.8	0.006	235.0	-
LPI	10.3	0.052	3.3	-
S PI	10.5	0.080	9.2	-
Ctr EU	8.8	0.037	135.0	-
L EU	9.6	0.164	2.2	-
S EU	10.6	0.039	2.5	-
Steam PI	7.9	-	735	60.5
Steam EU	7.8	-	457	80.1

Where pine (PI), Eucalyptus (EU), non-activated pine biochar (Ctr PI), non-activated Eucalyptus biochar (Ctr EU), liquid tannery waste activated PI biochar (L PI), solid tannery waste activated PI biochar (S PI), liquid tannery waste activated EU biochar (L EU), solid tannery waste activated EU biochar (S EU)

FT-IR, NMR and XPS spectra

The FT-IR spectra of the two original bark feedstocks (Fig. 3.1 A-B) were similar, although differences were evident when the bands and their intensities were compared. In the FT-IR spectrum of pine feedstock some typical features of a G lignin type bark (Faix et al., 1988) could be identified: $1600\text{ cm}^{-1} \ll 1508\text{ cm}^{-1} \text{ dominant} \gg 1459\text{ cm}^{-1}$, $1270\text{ cm}^{-1} \gg 1223\text{ cm}^{-1}$; a maximum at 1140 cm^{-1} ; $1031\text{ cm}^{-1} > 1223\text{ cm}^{-1}$; two separate bands at 856 and 815 cm^{-1} . The eucalyptus bark feedstock had lower intensity bands at 1508 cm^{-1} (attributed to aromatic C=C or amide II N vibrations, found in fresh litter; Haberhauer et al. 1998) and 1270 cm^{-1} , whereas that at 1600 cm^{-1} , (C=C and/or C=O stretching in conjugated carboxyls; Table S1), was more prominent. In addition, in the eucalyptus bark, a band at 1329 cm^{-1} was evident, indicating C–O stretching vibrations (in relation with syringyl ring; Wang et al. 2009). A single band appeared at 834 cm^{-1} , related to C–H vibrations of syringyl units. Finally, the band at $\sim 1750\text{ cm}^{-1}$ was well defined in both species, although was slightly more pronounced in pine bark, and attributed to C=O stretching (Chiang et al. 2000).

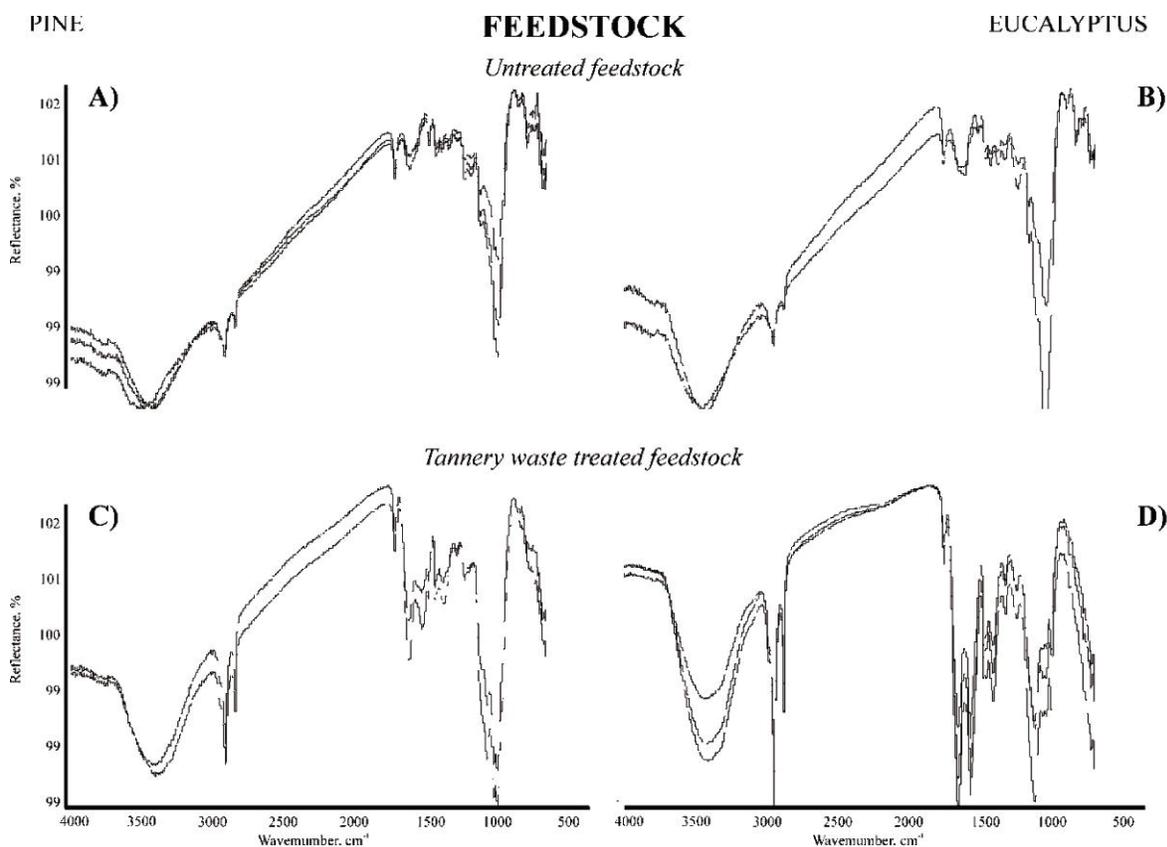


Figure 3.1 FT-IR spectra of activated and non-activated feedstocks, Pine: A and C, Eucalyptus: B and D.

After the tannery slurry treatment, the intensity at 3400 cm^{-1} (H bonded to OH groups; Table S1) decreased in both bark feedstocks (Fig. 3.1C-D). The spectra of both treated bark feedstocks displayed narrow bands at 2950 cm^{-1} and 2830 cm^{-1} , mainly related to C-H stretching of alkyl structures (Gunzler and Bock, 1990), and specifically to methyl (CH_3) and methylene (CH_2) asymmetric stretching, which were both more intense in the eucalyptus than in the pine biochars. This is consistent with the greater amounts of tannery slurry required by the eucalyptus bark to achieve complete impregnation of its fibres. Both bands were also present in the original bark feedstocks, but the intensity was considerably lower (Fig. 3.1A-B). As in the original bark feedstocks, a band at 1750 cm^{-1} , probably related to C=O stretching in esters (Gunzler and Bock, 1990) was observed. The strong band at 1640 and 1550 cm^{-1} were assigned to protein amide I and protein amide II, respectively (Fig. 3.1C-D; Table S1). These were associated with the N compounds present in the tannery slurry, and were more intense in the spectra from the treated eucalyptus. Finally, an increase in the intensity of the band at 1100 cm^{-1} was observed, which was again more evident in the biochar

made from eucalyptus. The presence of a band at 1100 cm^{-1} in both treated feedstocks is related with C–O stretching vibrations (O–CH₃ and C–OH groups; Pradhan and Sandle 1998; Sharma et al. 2004).

A band at $\sim 1400\text{ cm}^{-1}$ corresponding to C–H bending (Smith and Chughtai 1995) was identified in the spectra of the two untreated biochars (Ctr PI and Ctr EU; Fig. 3.2A-B), this band being more pronounced in the case of the eucalyptus. Vibrations at $\sim 1600\text{ cm}^{-1}$, corresponding to C=C stretching (Table S1), were also observed in both samples. The eucalyptus biochar showed a band at 875 cm^{-1} attributed to aromatic C-H out-of-plane (Ibarra et al. 1996), which suggests greater aromaticity of this sample. The pine biochar also showed an additional band at 1157 cm^{-1} , which could be attributed to the stretching of C–O bonds (carboxyl, ester and ether groups) and OH deformations of carboxyl-C (Sharma et al. 2004).

The L EU biochar (Fig. 3.2D) had a FT-IR spectrum similar to that from Ctr EU (Fig. 3.2B), except for the band at 1140 cm^{-1} , which was also pronounced in the L PI biochar (Fig. 3.2C). This could be attributed to stretching of C–O bonds and OH deformation of carboxyl groups, indicating a higher number of oxygen bonds after this treatment in both biochars. Also, a small band at 712 cm^{-1} was detected in the L EU biochar (Fig. 3.2D), which suggested the presence of carbonates, as confirmed by XRD (data not shown). Finally, the S EU and S PI biochars showed spectra very similar to the above ones (Fig. 3.2E-F), the main difference being the bands at 830 and 715 cm^{-1} were more pronounced. The band at 715 cm^{-1} was attributed to the in-plane deformation vibrations of the planar CO₃ units (Tatzber et al. 2007).

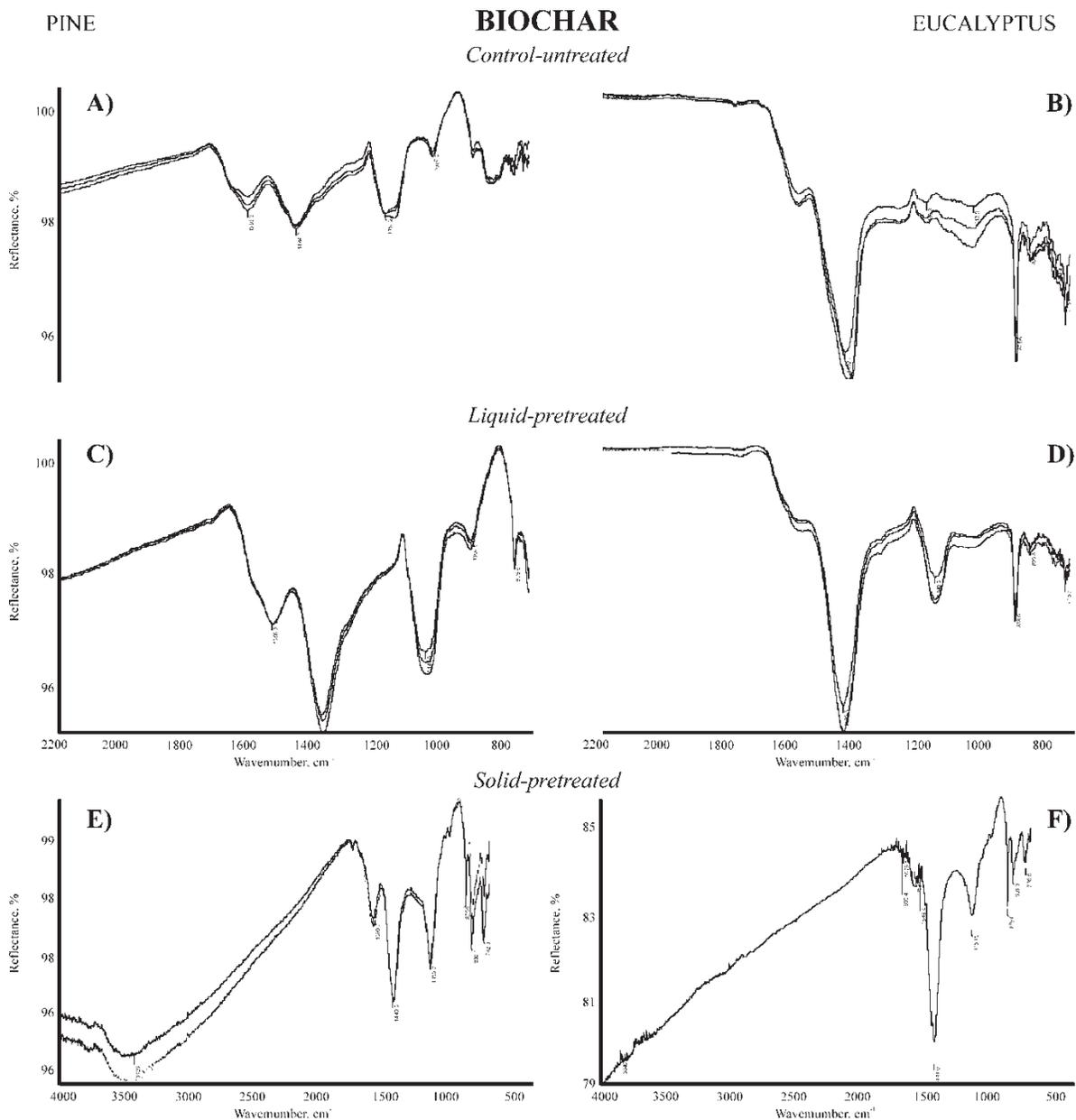


Figure 3.2 FTIR spectra of PI and EU biochars: A) Ctr PI, B) Ctr EU, C) L PI, D) LEU, E) S PI, F) S EU where Ctr, S and L showed non-activated, un-diluted and diluted tannery waste treated.

The FT-IR analyses of steam-PI and steam-EU biochars (Fig. 3.3) showed the lack of development of acid functional groups with this treatment. Steam PI, Steam EU, CtrPI, Ctr EU and L P had a low intensity band at 850 cm^{-1} (attributed to the C-H out of plane; Ibarra et al. 1996). In the steam-EU biochar, a band was detected at 1400 cm^{-1} and was attributed to C-H bending (Smith and Chughtai, 1995).

Steam activated biochars

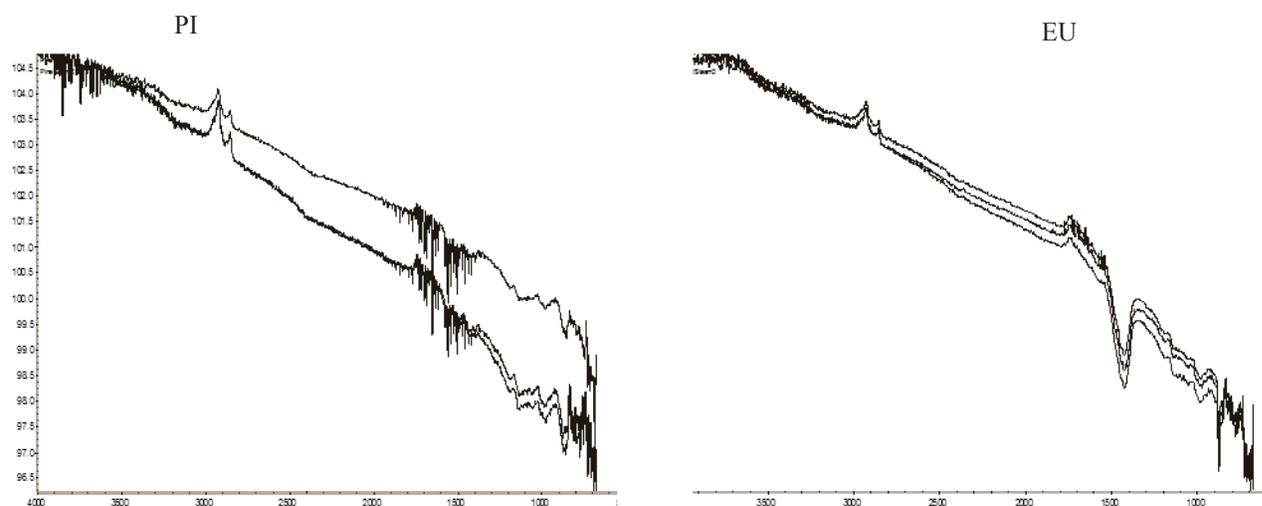


Figure 3.3 FTIR spectra of PI and EU biochars: Steam PI (steam pine), Steam EU (steam eucalyptus)

The CPMAS ^{13}C NMR spectra of both pine and eucalyptus bark feedstocks before charring (Fig. 3.4) were dominated by a signal in the *O*-alkyl C regions (45–110 ppm), reflecting the dominance of cellulose (Preston et al. 1998; Baldock and Smernick 2002). A methoxyl (also produced by α -amino groups) carbon signal at 56 ppm and several signals in the aryl C region (110–165 ppm) indicated the presence of lignin and/or that of hydrolysable tannin. Weak signals were observed in the alkyl (0–45 ppm) and carboxyl (165–210 ppm) regions. In contrast, the CP spectra of the Ctr EU and Ctr PI biochar treatments were dominated by peaks in the aromatic/unsaturated region (110–165 ppm). Both of these biochars showed signals from the aromatic spinning side bands. The aryl peak was centred at 130.5 ppm for the Ctr PI and at 129.3 ppm for the Ctr EU treatment. The Ctr PI biochar had a shoulder at \sim 155 ppm attributed to *O*- or *N*- substitutes aryl groups. The CP spectra of the treated biochars, either with diluted (liquid treatment) or undiluted (solid treatment) tannery slurry, showed a similar pattern to that of the control except for the size of the aromatic peak of the biochar from eucalyptus. The eucalyptus biochar had a less intense aryl peak than that of the pine, which could be related to the lower C content of the former (Fig. 3.4; Table 3.3). Overall, the results reflect the strong aromaticity of the biochars produced in this experiment (both treated and controls).

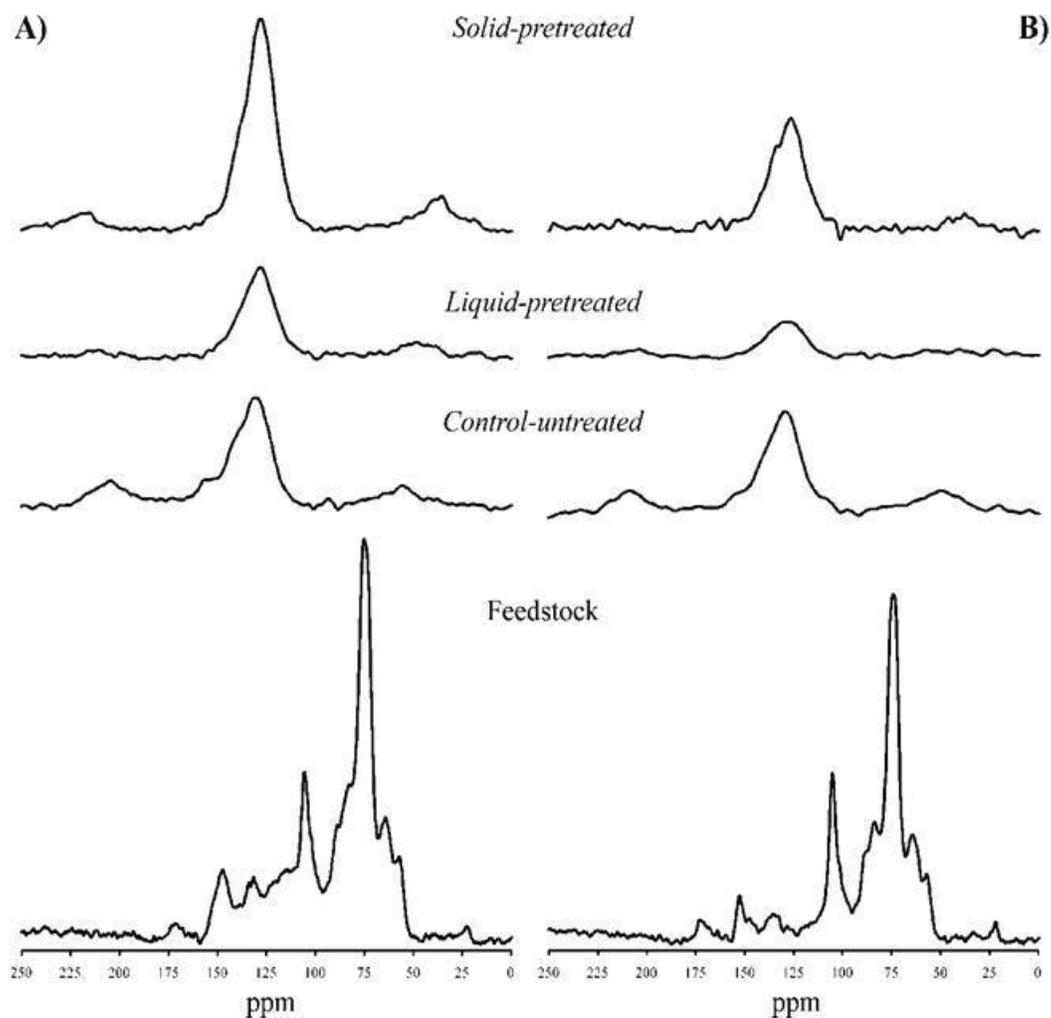


Figure 3.4 Solid state ^{13}C NMR spectra of feedstocks and biochars: A), Pine, B), Eucalyptus.

The CPMAS ^{13}C NMR spectra of the steam activated biochars were dominated by a well pronounced peak in the aryl C region (100-160 ppm) (Fig. 3.5) just like the control biochars without any activation. This was attributed to the C- and H- substituted aromatic C. The next largest peaks in the spectra, mostly evident in the EU samples, were also related to this peak; these are spinning side bands (SSBs) that occur when the rate of magic angle spinning is insufficient compared with the chemical shift anisotropy of the signal.

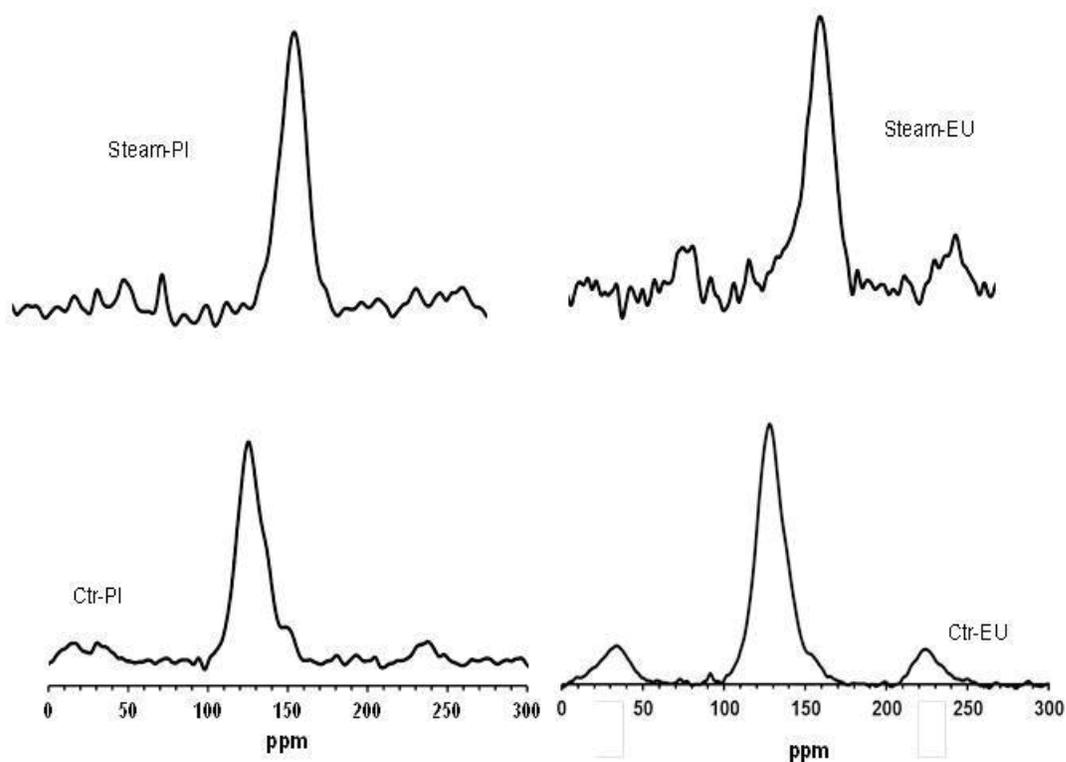


Figure 3.5 Solid state ^{13}C NMR spectra of biochars (Ctr PI (non-activated pine), Ctr EU (non- activated eucalyptus), Steam PI (steam pine), Steam EU (steam eucalyptus)).

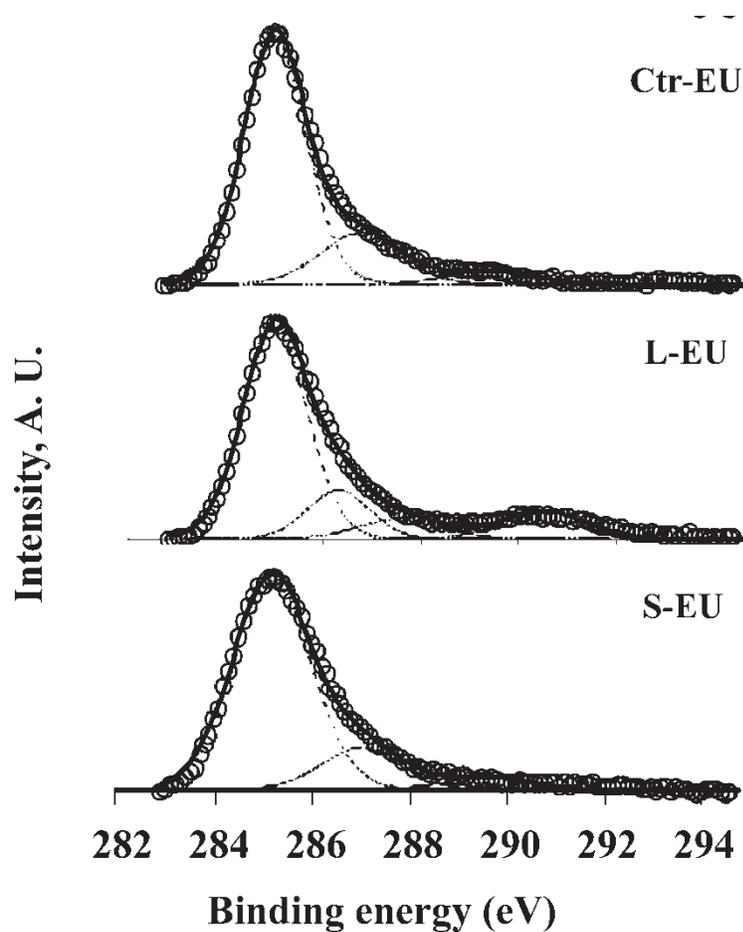
The C 1s core level spectra obtained with XPS spectroscopy for Ctr EU, S EU and L EU biochar samples are shown in Fig. 3.6 and the normalised area of the peaks corresponding to each O-containing surface group for the different biochars are presented in Table 3.5. The spectra of the three samples displayed signals attributed to the aliphatic/aromatic carbon group (CH_x , C-C/C=C) (284.6 eV), hydroxyl groups ($-\text{C-OR}$) (285.7-286.3 eV), and carboxylic groups, esters or lactones ($-\text{COOR}$) (289-290 eV). The spectrum of the S EU treatment had the highest content of hydroxyl groups, whereas that from the L EU treatment contained the highest carboxylic group proportion. In addition, the spectrum of the latter treatment showed a signal corresponding to carbonyl groups ($>\text{C=O}$) (287.2 eV). Overall, the results indicate the presence of more oxygen-rich functional groups in the L EU and S EU biochars than the Ctr EU biochar, particularly in the diluted alkaline treatment. This finding agrees with the FT-IR spectra and the acidic functional groups determined by titration.

Table 3.5 Normalised area of the peaks corresponding to each oxygen surface group for the different biochars.

Sample	-C-OR	>C=O	-COOR
L EU	0.146	0.084	0.111
S EU	0.197	0.057	<d.l. ^a
Ctr EU	0.163	0.050	<d.l.

^a <d.l., below detection limit

Where Eucalyptus (EU), liquid tannery waste activated EU biochar (L EU), solid tannery waste activated EU biochar (S EU).

**Figure 3.6** C 1s core level spectra obtained for Ctr EU, L EU and S EU biochar samples.

Structural characteristics of biochars

Adsorption of N₂ in the Ctr PI and Ctr EU biochar samples displayed a type I isotherm, according to the IUPAC classification (data not shown); this indicates that the samples are essentially microporous (pore size < 2 nm). The surface area of the Ctr EU biochar (135 m² g⁻¹) was smaller than that of the Ctr PI biochar (235 m² g⁻¹) (Table 3.4). The treated biochars showed type II isotherms, which are typical of non-porous materials, and the values of specific surface area calculated are only due to the external surface (< 9 m² g⁻¹, Table 3.4). A decrease in the surface area of biochars after alkaline activation was also observed in other studies (Chiang et al. 2000). However, this decrease did not imply a reduction in surface charge, as shown above. Finally, the SEM images of untreated biochars (Fig. 3.7) showed the presence of numerous hollow channels originated from plant cells with honey comb structures. Biochars made from eucalyptus were especially affected by the alkaline tannery slurry treatments, with a collapse of the former structure, rendering a highly disorganised appearance (Fig. 3.7).

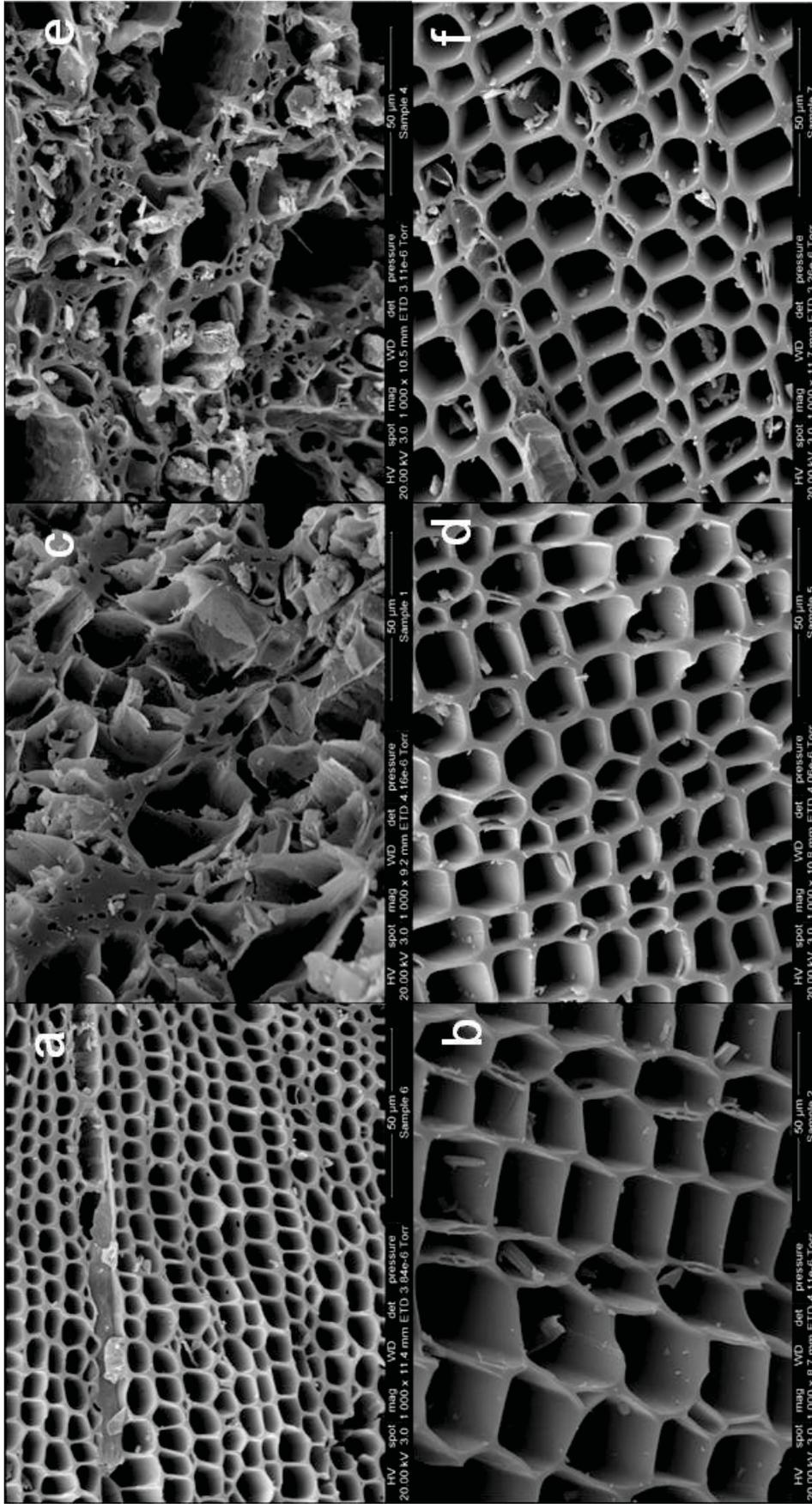


Figure 3.7 SEM images of unwashed biochars. Where a. EU control, b. PI control, c. EU pre-liquid, d. PI pre-liquid, e. EU pre-solid, f. PI pre-solid

3.3.3 Batch sorption Study of Alkaline activated biochars

Sorption of $\text{NH}_4^+\text{-N}$ after 4 additions of $\text{NH}_4^+\text{-N}$ solutions of 40 mg L^{-1} was significantly ($P < 0.05$) greater for the Ctr EU treatment than in the Ctr PI treatment, with average values of 0.036 and 0.025 mmol N g^{-1} , respectively (Fig. 3.8), which represented 61 and 41% of the total amount of N added. Treatment of feedstocks with alkaline tannery slurry increased the $\text{NH}_4^+\text{-N}$ sorption capacity of the resulting biochar, with the increase being highest for the undiluted tannery slurry treatment. The highest sorption was achieved by the S EU treatment, with a value of 0.047 mmol N g^{-1} , which represented 83 % of the total amount added. Therefore, sorption did not appear to be directly related to the total amount of surface charge present in the biochar. However, as the amount of $\text{NH}_4^+\text{-N}$ added was 2-30 times lower than the estimated total amount of carboxylic acid groups (Table 3.4), the role of the total amount of surface charge present on $\text{NH}_4^+\text{-N}$ sorption is difficult to evaluate. The present results also provide evidence of the lack of influence of surface area on $\text{NH}_4^+\text{-N}$ sorption. Others studies have also observed a reverse correlation between surface area and the sorption of NH_3 and NH_4^+ (Lee and Reucroft, 1999; Vassileva et al. 2008).

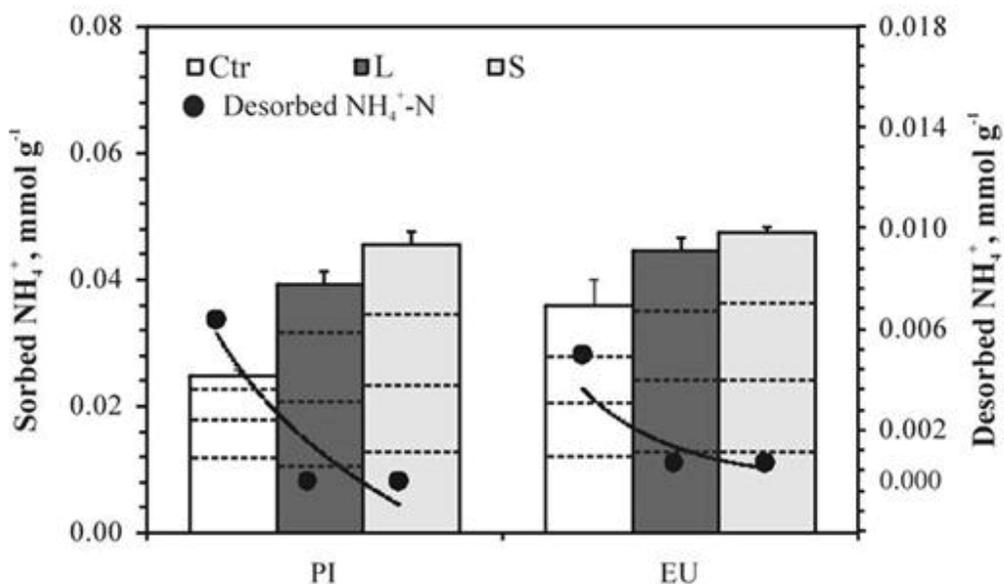


Figure 3.8 Sorption and desorption of $\text{NH}_4^+\text{-N}$ in the Pine and Eucalyptus biochars elaborated in this study where Ctr, L and S denotes non-activated, liquid tannery waste activated and solid tannery waste activated, respectively).

Ammonium desorption from the different biochars was low, being 14 and 27 % of that added, for Ctr EU and Ctr PI biochar treatments, and < 2% for the treated biochars (Fig. 3.8). Therefore, the alkaline feedstock treatment increased the NH_4^+ -N retention strength of the biochar. This could be attributed to an increase in coulombic forces that prevented a fast desorption. However, other mechanisms could also be involved in NH_4^+ -N retention, such as chemisorption-ammonia fixation (Stevenson, 1982) or the role of acidic S-functional groups i.e. sulfonate groups (Petit et al. 2010) developed from sulphide in tannery waste. The mechanism of ammonium sorption on biochars was considered to be non-specific (CEC e.g. carboxylic groups, and sulphonate groups). If the sorption was because of CEC, then it must desorb maximum NH_4^+ -N back into solution by KCl extraction. However, it did not happen so it is considered some immobilisation, either physical (micropore) or chemical formation of amides occur (Petit et al. 2010).

Analyses of N 1s core level were carried out in two samples (Ctr EU and S EU) after the sorption experiments. Only the S EU sample had enough N (an atomic percentage of 1.9 %) to be detectable by XPS (data not shown), and the latter mainly originated from the tannery waste. After deconvolution its N 1s core level spectrum provides evidence for three species (Raymundo-Piñero et al. 2002): imine-pyridine (398.5 eV), neutral amine (399.4 eV), and pyrrole-pyridone and charged N (400.5 eV). These results do not provide enough evidence to determine the type of mechanism causing NH_4^+ -N retention, as the amount added in the sorption experiment was probably too low to be detectable using XPS. However, these results do provide evidence for the presence of non-available forms of N in this treated biochar.

3.4 Conclusion

Pyrolysis of pine and eucalyptus barks to a final temperature of 550 °C produced highly aromatic biochars with large internal microporous structure. The final recovery accounted for 43 and 45% of the initial C, respectively, and 57% and 47% of the initial N, respectively. Pre-treatment of the barks with alkaline tannery slurry prevented the development of internal microporous surfaces of the biochars. Despite this reduction in internal surface area, the treated biochars developed increase in surface functional groups (particularly carboxyl and carbonyl groups) and greater NH_4^+ sorption capacity than the untreated chars. Desorption of the sorbed NH_4^+ -N was low, especially for treated biochars compared to untreated biochars. This confirmed the results of

Chapter 3

batch sorption study in Chapter 4 where desorption of NH_4^+ -N was very less compared to sorption. However, the steam activation of biochar did not show any presence of acidic functional groups with FT-IR spectra and proved to be a non promising activation technique for ammonium sorption which was confirmed in batch study in Chapter 5. Pre-treatment of feedstock with alkaline tannery slurry represents a low cost methodology for surface activation of biochars to improve their NH_4^+ sink strength for wastewater treatment. The resultant activated biochar, has potential as a product for the treatment of waste streams and, once saturated with NH_4^+ -N, it could be disposed to soils, which may add value to the original biochar. However, as the desorption of NH_4^+ -N was very low by KCl extraction, the idea of slow release fertiliser may not be feasible in soils.

So far, the batch studies have been conducted in Chapter 3, 4 and 5 to evaluate the biochars for NH_4^+ -N sorption capacity. In Chapter 6 flow through studies with actual wastewater are conducted to determine the NH_4^+ -N sorption trend under more practical conditions.

Table S1. Assignments of absorption peaks and bands in FTIR spectra, indicating functional groups associated.

Wavenumber (cm ⁻¹)	Assignment	References
3300, 3400	H bonded OH groups (alcohols, phenols, organic acids)	Chen et al. (2002); Cheng et al. (2006)
2950	Methyl CH asymmetric –CH ₃	Gunzler and Bock (1990);Chiang et al. (2000)
2830, 2855	Methylene symmetric stretch –CH ₂	Gunzler and Bock (1990)
1750	C=O stretching	Chiang et al. (2000)
1620	Aromatic and oleifinic C=C, C=O of bonded conjugated ketones, quinine.	Duggan and Allen (1997)
1600	C=C, C=O stretching conjugated to the aromatic ring	Guo and Bustin (1998); Wang et al. (2009)
1500, 1508	Aromatic ring (C=C) vibrations; amide II vibrations	Sharma et al. (2004); Haberbauer et al., 1998
1433, 1459	C-H deformations, asymmetric in CH ₃ and CH ₂	Sharma et al. 2004
1400, 1420	Aromatic ring vibrations combined with C–H in plane deformation	Smith and Chughtai. (1995)
1329	Syringyl ring with C–O stretching	Wang et al. (2009)
1270	Guaiacyl ring with C–O stretching	Wang et al. (2009)
1223, 1220	C–C plus C-O, C=O stretching	Wang et al. (2009)
1220	C–C or C=O stretching	Wang et al. (2009)
1133, 1140,1157	C-O stretching vibrations of C-O-C groups	Sharma et al. (2004)
1100	C–O stretch for O–CH ₃ and C–OH groups	Pradhan and Sandle (1998); Sharma et al. (2004)
1031	Aromatic CH deformation and C=O stretching	Wang et al. (2009)
1010, 1000	C–O–C groups	Arriagada et al. (1997)
875,878	Carbonate ion, CO ₃	Chiang et al. (2000)
712,715	Deformation vibrations of planar CO ₃	Tatzber et al. (2006)

References

- Ahmedna M, Marsall WE, Rao RM (1998) Production of granular activated carbon from select agricultural by-products and evaluation of their physical, chemical and adsorption properties. *Bioresource Technology*. 71, 113-123.
- Arriagada R, Garcia R, Molina-Sabio M, Rodriguez-Reinoso F (1997) Effect of steam activation on the porosity and chemical nature of activated carbons from Eucalyptus globules and peach stones. *Microporous Materials*. 8, 123-130.
- Azargohar, R., & Dalai, A. (2008) Steam and KOH activation of biochar: Experimental and modeling studies. *Microporous and Mesoporous Materials*, 110 (2-3), 413-421.
- Baldock JA, Smernick, RJ (2002) Chemical composition and bioavailability of thermally altered *Pinus resinosa* (red pine) wood. *Organic Geochemistry*. 33, 1093-1109.
- Bandosz TJ, Petit C (2009) On the reactive adsorption of ammonia on activated carbons modified by impregnation with inorganic compounds. *Journal of Colloid and Interface Science*. 338, 329-345.
- Bundy LG, Bremner JM (1972) A Simple Titrimetric Method for Determination of Inorganic Carbon in Soils. *Soil Science Society of America Journal*. 36(2), 273-275.
- Chen X, Jeyaseelan S, Graham N (2002) Physical and chemical properties study of the activated carbon made from sewage sludge. *Waste Management*. 22, 755-760.
- Cheng CH, Lehmann J, Thies JE, Burton SD, Engelhard MH (2006) Oxidation of black carbon by biotic and abiotic processes. *Organic Geochemistry*. 37, 1477-1488.
- Chiang HL, Tsai JH, Tsai CL, Hsu YC (2000) Adsorption characteristics of alkaline activated carbon exemplified by water vapour, H₂S and CH₃SH Gas. *Separation Science and Technology*. 35, 903-918.
- David N, Shiraishi N (2000) Pulping Chemistry. In 'Wood and Cellulosic Chemistry'. pp. 859-899. (Mercel Dekker Inc. NY)
- Duggan O, Allen SJ (1997) Study of the physical and chemical characteristics of a range of chemically treated, lignite based carbons. *Water Science and Technology*. 35, pp. 27.
- Emmerich FG, Luengo CA (1996) Babassu charcoal: A sulfurless renewable thermo-reducing feedstock for steelmaking. *Biomass and Bioenergy*. 10, 41-44.
- Faix O, Jakab E, Till F, Szekely T (1988) Study on low mass thermal degradation products of milledwood lignins by thermogravimetry-mass-spectrometry. *Wood Science Technology*. 22, 131-137.
- Fan M, Marshall W, Daugaard D, Brown RC (2004) Steam activation of chars produced from oat hulls and corn stover. *Bioresource Technology*. 93, 103-107.

- Gunzler H, Bock H (1990) IR-Spektroskopie. Verlag Chemie. Weinheim, Germany.
- Guo Y, Bustin RM (1998) FTIR spectroscopy and reflectance of modern charcoal and fungal decayed woods: Implications for studies of Inertinite in coals. *International Journal of Coal Geology*. 37, 29-53.
- Haberhauer G, Rafferty B, Strebl F, Gerzabek MH (1998) Comparison of the composition of forest soil litter derived from three different sites at various decompositional stages using FTIR-spectroscopy. *Geoderma*. 83, 331-342.
- Hu Z, Srinivasan MP (1999) Preparation of high surface area activated carbons from coconut shell. *Microporous and Mesoporous Materials*. 27, 11-18.
- Ibarra JV, Munoz E, Moliner R (1996) FTIR study of the evolution of coal structure during coalification process. *Organic Geochemistry*. 24, 725-735.
- Lee W, Reucroft P (1999) Vapor adsorption on coal-and wood-based chemically activated carbons (III) NH₃ and H₂S adsorption in the low relative pressure range. *Carbon* .37, 21-26.
- Lehmann J (2007) Bio-energy in the black. *Frontiers in the Ecology and Environment*. 5, 381-387.
- Lewis NG, Yamamoto E (1990) Lignin: occurrence, biogenesis and biodegradation. *Annual Review of Plant Biology*. 41, 455-496.
- Liu C, Shao Y, Jia DM (2008) Chemically modified starch reinforced natural rubber composites. *Polymer*. 49, 2176–2181.
- López R, Gondar D, Iglesias A, Fiol S, Antelo J, Arce F (2008) Acid properties of fulvic and humic acids isolated from two acid forest soils under different vegetation cover and soil depth. *European Journal of Soil Science*. 59, 892–899.
- Lozano-Castelló D, Maciá-Agulló JA, Cazorla-Amorós D, Linares-Solano A, Müller M, Burghammer M, Riekkel C (2006). Isotropic and anisotropic microporosity development upon chemical activation of carbon fibers, revealed by microbeam small-angle X-ray scattering. *Carbon*. 44, 1121-1129.
- Maciá-Agulló JA, Moore BC, Cazorla-Amorós D, Linares-Solano A (2007) Influence of carbon fibres crystallinities on their chemical activation by KOH and NaOH. *Microporous and Mesoporous Materials*. 101, 397-405.
- McElligott KM (2011) Biochar amendments to forest soils: effects on soil properties and tree growth (A thesis submitted for requirement of Master of Science). University of Idaho.

- Montane D, Torne-Fernandez V, Fierro V (2005) Activated carbons from lignin: kinetic modeling of the pyrolysis of Kraft lignin activated with phosphoric acid. *Chemical Engineering Journal*. 106, 1-12.
- Nabais JMV, Nunes P, Carrott PJ M, Ribeiro Carrott MML, García AM, Díaz-Díez M (2008) Production of activated carbons from coffee endocarp by CO₂ and steam activation. *Fuel Processing Technology*. 89(3), 262-268.
- Petit C, Kante K, Badosz TJ (2010) The role of sulphur-containing groups in ammonia retention on activated carbons. *Carbon*. 48, 654-667.
- Pradhan BK, Sandle NK (1998) Effect of different oxidizing agent treatments on the surface properties of activated carbons. *Carbon*. 37, 1323-1332.
- Preston CM, Trofymow JA, Niw J, Fyfe CA (1998) ¹³CPMAS-NMR spectroscopy and chemical analysis of coarse woody debris in coastal forests of Vancouver Island. *Forest Ecology and Management*. 111, 51-68.
- Raymundo-Piñero E, Cazorla-Amorós D, Linares-Solano A, Find J, Wild U, Schlögl R (2002). Structural characterization of N-containing activated carbon fibers prepared from a low softening point petroleum pitch and a melamine resin. *Carbon*. 40, 597-608.
- Raymundo-Piñero E, Azaïs P, Cacciaguerra T, Cazorla-Amorós D, Linares-Solano A, Béguin F (2005). KOH and NaOH activation mechanisms of multiwalled carbon nanotubes with different structural organisation. *Carbon*. 43, 786–795.
- Rodriguez-Reinoso F, Molina-Sabio M (1992) Activated carbons from lignocellulosic materials by chemical and/or physical activation: an overview. *Carbon*. 30, 1110-1118.
- Sharma RK, Wooten JB, Baliga VL, Lin X, Chan WG, Hajaligol MR (2004) Characterization of chars from pyrolysis of lignin. *Fuel*. 83, 1469-1482.
- Smith DM, Chughtai A R (1995) The surface structure and reactivity of black carbon. *Colloids and Surfaces*. 105, 47-77.
- Solano LA, Lozano-Castello D, Lillo-Rodenas MA, Cazorla-Amoros D (2008) Carbon Activation by Alkaline Hydroxides: Preparation and Reactions, Porosity and Performance. *Chemistry and Physics of Carbon*. 30, 1.
- Stevenson FJ (1982) Ammonia reactions. In: 'Humus Chemistry. Genesis Composition; Reactions'. (Wiley Interscience publication. New York), pp. 101-105.

- Tatzber M, Stemmer M, Spiegel H, Katzlberger C, Haberhauer G, Gerzabek MH (2007) An alternative method to measure carbonate in soils by FT-IR spectroscopy. *Environmental Chemistry Letters*. 5, 9-12.
- Tiessen H, Roberts T, Stewart J (1983) Carbonate analysis in soils and minerals by acid digestion and two-endpoint titration. *Communications in Soil Science and Plant Analysis*. 14(2), 161-166.
- Tsutsumi Y, Kondo R, Sakai K, Imamura H (1995) The difference of reactivity between syringyl lignin and guaiacyl lignin in alkaline systems. *Holzforschung*. 49, 423-428.
- Van Soest PJ (1967) Development of a comprehensive system of feed analysis and the application to forages. *Journal of Animal Science*. 26, 119-128.
- Vassileva P, Tzvetkova P, Nickolov R (2008) Removal of ammonium ions from aqueous solutions with coal-based activated carbons modified by oxidation. *Fuel*. 88, 387-390.
- Wang SK, Wang K, Liu Q, Gu Y, Luo Z, Cen K, Fransson T (2009) Comparison of the pyrolysis behavior of lignins from different tree species. *Biotechnology Advances*. 27, 562-567.

Chapter 4

Ammonium retention on biochar: (i) comparison with bark and zeolite, and (ii) effect of biochar particle size

In Chapter 3, the role of using different activated and non-activated biochars with significant cation exchange properties to sorb ammonium (NH_4^+) ions from synthetic NH_4^+ solution was introduced. This chapter reports on further preliminary research conducted to compare the sorption of NH_4^+ by biochar, produced from pine wood chips, with the NH_4^+ sorption potential of pine bark and zeolite (clinoptilolite), which have been used in previous studies by other authors.

4.1 Introduction

Biochars can be efficient sorbents for different types of charged ions (Chapter 3, 5) and organic pollutants. Washing of biochars to reduce their ash content proved an important step towards increasing sorption capacity of biochars especially in chemically activated biochars (Chapter 5). Pine needle-derived biochar has been reported to effectively adsorb naphthalene, nitrobenzene and m-dinitrobenzene (Chen et al. 2008; Chen and Chen 2009; Chen et al. 2011). Dairy-manure biochar has been shown to effectively remove lead and atrazine simultaneously with little competition effect (Cao et al. 2009). However, no studies have been published that compare the NH_4^+ sorption properties of biochar with those of other materials currently used to treat wastewaters. The effect of biochar particle size on the effectiveness of the removal of NH_4^+ from NH_4^+ rich waters also is unknown.

Wastewaters from dairy and urban origin are rich in nitrogen (N) compounds originating from urine, faeces and industrial by-products. With time, the organic forms of N mineralise to NH_4^+ (Hedstrom, 2001), which is a potential pollutant in fresh water resources as it can contribute to the eutrophication and is also potentially toxic to fish. Removal of NH_4^+ from wastewaters is, thus, needed if the risk of wastewater discharges to water quality is to be minimised. Several materials, such as zeolite (Nguyen and Tanner, 1998, Cooney and Booker, 1999) and bark (Bolan et al. 2004; Wieczorek, 2008), have been proposed to be used as wastewater filters. On saturation, the sorbent could be applied to soil as N fertiliser.

Bolan et al. (2004), working with farm effluents, found that the retention of NH_4^+ increased from untreated bark to treated bark (using an alkaline material to increase exchange sites) and to zeolite (clinoptilolite). Perrin et al. (1998) successfully used NH_4^+ saturated zeolite (clinoptilolite) as fertiliser for maize plants. These researchers reported greater NH_4^+ sorption performance of small sized zeolite particles (<0.25 mm) compared to larger particles (2-4 mm), which they attributed to a decrease in the diffusion path length with the former.

The NH_4^+ removal capacity of the sorbents is dependent on (i) the wastewater loading flow rate, (ii) type of wastewater, (iii) particle size, and (iv) contact time between the wastewater and sorbent particles (Nguyen and Tanner, 1998). Ammonium retention also depends on (v) the presence of other cations in the aqueous phase and (vi) the initial NH_4^+ concentration (Demir et al., 1998).

The NH_4^+ removal procedure is considered viable for wastewater treatment if it is capable of reducing NH_4^+ -N concentration from 20-60 mg N L^{-1} to 5 mg N L^{-1} (Cooney and Booker, 1999). In Chapter 5, it was found that biochars made from tannery waste pre-treatment of Pine and Eucalyptus bark peeling, after washing to remove residual ashes, could sorb 0.56 and 0.52 mg N g^{-1} as NH_4^+ -N, respectively, from the influent NH_4^+ -N concentration of 37 mg N L^{-1} with final solution concentrations of 9 and 11 mg N L^{-1} , respectively.

In this chapter, the use of biochar, produced from pine wood chips (Ctr PI), for the removal of NH_4^+ from NH_4^+ -rich waters is compared to the performance of pine bark and zeolite (clinoptilolite). The effect of particle size of biochar was also investigated. In this document, the term “sorption” was used to refer to the removal of NH_4^+ from solution, as the mechanisms behind this (e.g. physical entrapment, electrostatic retention, or acidic functional groups) were not investigated.

The objectives of this study were:

- 1) To measure NH_4^+ sorption capacity of Pine biochar relative to other common sorbents.
- 2) To determine the effect of particle size of pine feedstock and biochar on NH_4^+ sorption capacity.

4.2 Material and Methods

4.2.1 Materials

Comparative study using different sorbents: (i) clinoptilolite zeolite (< 2 mm), supplied by Blue Pacific Minerals (NZ), (ii) pine bark (2-3 mm), (iii) biochar produced from pine wood chips (3-8 mm) (Fig. 4.1).

Biochar particle-size study: Biochar was produced from pine wood chips. These were previously chipped with a commercial chipper and then separated/sieved into different particle size fractions as follows: (i) bulk feedstock (2.0-11.2 mm) (BULK), (ii) a large particle size feedstock (5.6-11.2 mm) (LAR), and (iii) the same LAR particle size feedstock, but crushed and sieved to < 2 mm (LAR-CR) prior to pyrolysis. Feedstocks were oven-dried at 65 °C before pyrolysis. Biochars were washed repeatedly with deionised water prior to the sorption studies to reduce the ash content of the biochars.



Figure 4.1 Materials used in this study

4.2.2 Methods

Carbonisation Processes

Two hundred grams of each pine feedstock were pyrolysed in a gas-fired, 5 L, stainless steel, rotating drum kiln, using an average heating rate of 28 °C min⁻¹ to reach a maximum temperature of 550 °C. When the desired temperature was reached, the kiln was allowed to cool down to room temperature. Three batches of biochar were produced from each feedstock and, thereafter, pooled into a single sample. Details of biochar carbonisation and characterisation are discussed in Chapter 3.

Chemical Analyses

pH, Elemental Composition and Ash Content.

Biochar pH was measured using the methodology of Ahmedna et al. (1997), which involved a 1 % (wt/wt) suspension of crushed biochar in deionised water. The suspension was heated in a water bath to about 90 °C and stirred for 20 min to allow the dissolution of highly water-soluble biochar components. After cooling to room temperature, the pH of the biochar suspension was measured. Biochars contain soluble salts entrapped in pores so needed to be analysed for pH by method described above. The pH of bark was measured after shaking a suspension of 5 g bark in 25 mL of deionised water for 2 hours.

Total C, N and H contents of the different materials were determined using a TruSpec CNHS Analyser (LECO Corp, St Joseph, MI, USA). The ash content was determined by thermogravimetric analysis on a TA instrument (Alphatech, SDT Q600; TA instruments, Newcastle, Australia) following the methodology described by Calvelo-Pereira et al. (2011), after Sevilla and Fuertes (2010). The sample was initially heated from room temperature to 900 °C (at a rate of 5 °C min⁻¹) under a N₂ atmosphere and weight loss was recorded (data not shown); thereafter, an air current was provided and the ash weight was determined when there was no further weight change. All analyses were carried out in duplicate.

X-ray Photoelectron Spectroscopy.

Surface analysis of some biochar samples was conducted using X-ray photoelectron spectroscopy (XPS). This was carried out using an ESCALAB 220i-XL spectrometer (Thermo VG Scientific Ltd., UK), using Al K α for which the energy of the electron is 1486.6 eV. The spot size used in this analysis was ~ 1 mm in diameter. XPS spectra were collected over an energy range of 0-1100 eV. The results are expressed at “atomic percent” in which the signal from each element is normalized against the total amount of all the detected elements, which is taken as almost 100%. Further details are provided in Chapter 3.

Exchangeable Cations of Zeolite and Bark.

A 0.5 g sample of each sorbent, in triplicate, was placed in a 40-mL centrifugation tube and shaken with 25 mL NH₄⁺-acetate solution in an end-over-end shaker for two hours and then analysed for displaced cations on an atomic adsorption spectrophotometer (AAS, GBC

904AA, Australia). Cation exchange capacity (CEC) was considered the sum of displaced cations in $\text{cmol}^+ \text{kg}^{-1}$ of material (Blakemore, 1987).

Cation Exchange Capacity of Biochar.

Determination of CEC of biochar was conducted by using a 0.2 g sample taken in small columns filled with sand and leached with 0.01 M and 0.001 M SrCl_2 followed by 0.5 M HCl (up to 45 minutes in each leaching @ 1 mL/min) to desorb the Sr (strontium) from exchange sites (Matsue and Wada, 1985). The first leachate was analysed for exchangeable cations and after the second leaching, the char was leached with 45-50 ml of 0.5 M HCl. Strontium concentration in the 0.5 M HCl extract/leachate was measured for CEC determination. The reasoning behind the use of a different methodology for the biochar was the fact that soluble salts were present in the ash fraction, and these interfered with the measurement of exchangeable cations.

Batch Study Comparing Zeolite, Biochar and Bark.

The NH_4^+ sorption study using zeolite, biochar and bark was carried out as follows: A 20-mL aliquot of $(\text{NH}_4)_2\text{SO}_4$ solution at two different concentrations, 39 and 79 mg N L^{-1} (nominally as 40 and 80 ppm) (equivalent to a load of 0.78 and 1.56 mg N g^{-1} sorbent, respectively), was added to 1 g of sorbent sample (zeolite, pine bark and washed pine biochar) previously placed in a 40-mL centrifuge tube and run in triplicate. The NH_4^+ solution concentrations chosen were based on the typical levels present in dairy and municipal wastewater. The tubes were shaken end-over-end (30 rpm) for 24 hours and then filtered with Whatman filter paper 42. Ammonium was determined using a Technicon autoanalyser (Technicon, Dublin). The NH_4^+ retained was determined by difference between the initial and final solution concentration of NH_4^+ . A separate study (Chapter 5) had shown that the amount of NH_4^+ volatilised during sorption studies using sorbents with a pH in the range of 8.01-10.3 was < 4.10%. The methodologies adopted for batch and column studies were developed independently and not from previous references.

Biochar Batch Study Comparing Biochar Particle Sizes.

For the particle-size study, three types of feedstocks were used (BULK, LAR and LAR-CR pine wood chips), resulting in three different biochars (BULK-PY, LAR-PY and LAR-CR-PY). In addition, a subsample of the LAR-PY biochar was crushed and sieved to < 2 mm to produce a fourth type of biochar, which was termed LAR-PY-CR. Prior to the batch study, a

washing step was carried out to reduce the ash and tar content of the biochars. For this, 2 g of each biochar were placed in centrifugation tubes in triplicate followed by 25 mL of distilled water. The biochar were repeatedly shaken (three times) on an end-over-end shaker for half an hour and then centrifuged at 7000 rpm in a centrifuge (RC5C, Sorvall Instruments, Du Pont, Supplied by Watson Victor Ltd NZ). The supernatant was collected and analysed for electrical conductivity (EC) and pH. After this washing step, 10 mL of $(\text{NH}_4)_2\text{SO}_4$ solution, with a $\text{NH}_4^+\text{-N}$ concentration of 40 mg N L^{-1} , was added to the centrifugation tubes. The tubes were shaken overnight, centrifuged at 7000 rpm, filtered and $\text{NH}_4^+\text{-N}$ concentration determined using Technicon II autoanalyser (Technicon, Dublin). Ammonium removal was determined based on the difference between the influent and effluent concentrations of the $\text{NH}_4^+\text{-N}$. The biochar was then washed with 15 mL deionised water by shaking (for 1 hour) in an end-over-end shaker followed by centrifugation (desorption). The supernatant was decanted and 10 mL 2 M KCl solution was added to the tubes to desorb NH_4^+ by ion exchange. The supernatant was collected after shaking and centrifuging, as above. This step with KCl was repeated twice and, thus, two KCl extracts were collected separately. Desorbed (removed by ion exchange) $\text{NH}_4^+\text{-N}$ concentration was determined in the filtrates using the above-mentioned autoanalyser.

Biochar Column Study Comparing Biochar Particle Sizes.

The retention of NH_4^+ in biochars of different particle sizes was also assessed in a column study using small columns of 11-15 mm \O and 13 cm height, in duplicate. A filter paper was placed at the bottom of the column; this was then filled by 3 g of silica sand followed by 1 g of biochar. Deionised water was first pumped through the columns to reduce ash and tar contents using a peristaltic pump at a flow rate of 0.23 mL min^{-1} . The effluent was collected after every 15 minutes up to a maximum of fifteen times. The EC and pH were determined for all the leachates. A solution containing $38 \text{ mg NH}_4^+\text{-N L}^{-1}$ was pumped through the columns and leachate was collected in 3.45 to 4 mL aliquots in 35 mL plastic vials. Collection was continued for approximately 4 hours, with almost 2 pore volumes per leachate. The $\text{NH}_4^+\text{-N}$ concentration of leachates was determined using the autoanalyser. All sorption studies were conducted at ambient temperature.

4.2.3 Statistical Analyses

The data was analysed using ANOVA and comparison of means using Tukey's test by SAS 2010 statistical software.

4.3 Results and Discussion

4.3.1 Characterisation of the sorbents

Comparative study of sorbents: The bulk density of pine bark was higher than that of the pine biochar (0.31 vs. 0.23 g cm⁻³) while the pH was acidic in the former (4.3) and alkaline in the latter (8.2) (Table 4.1). The ash content (4.9 %) in unwashed biochar was three-fold that of bark (1.4%), which is consistent with the two-third mass loss during carbonisation. Zeolite had the maximum CEC (27.5 cmol_c kg⁻¹), followed by biochar with the pine bark having the least (6.4 cmol_c kg⁻¹).

Table 4.1 Chemical and physical characteristics of different sorbents.

	K (cmol+ kg^{-1})	Mg (cmol+ kg^{-1})	Na (cmol+ kg^{-1})	Ca (cmol+ kg^{-1})	CEC ¹ ($\text{cmol}_c \text{ kg}^{-1}$)	Bulk density (g cm^{-3})	C (g kg^{-1})	N (g kg^{-1})	pH	Ash (%)
Zeolite	2.16	1.68	2.91	20.8	27.5	0.665	-	-	5.7	-
Bark	1.64	0.83	0.72	3.2	6.4	0.310	561	0.9	4.3	1.4
Biochar³	n.a. ²	n.a.	n.a.	n.a.	17.6	0.225	777	6.1	8.9	4.9

¹For zeolite and bark CEC was estimated from the sum of cations displaced with NH_4^+ -acetate; for biochar the CEC was determined using SrCl_2 following the methodology of Matsue and Wada (1985).

²n.a.: non available data.

³Biochar=Ctr PI(unwashed)

Biochar particle-size study: Some physical and chemical characteristics of the unwashed biochar samples are reported in Table 4.2. The ash content in the biochar produced from the bulk pine wood chips (BULK-PY) was 4.9 %, while those produced from the large particle-size material had similar ash content (2.0-2.1 %). BULK-PY biochar had a lower C content (78 %) than the rest of biochars studied (83-84 %), and this was attributed to the greater ash content of the former. The ash content also had influence on the pH of the biochars, the greatest value being that of the biochar from the bulk pine wood chips (9.8), as expected. The pH of the other three biochars was in the range of 7.9 and 8.8. The biochar with the lowest bulk density was the LAR-PY (0.15 g cm⁻³), which was the one that did not undergo any crushing step and originated from a large particle-size feedstock. The bulk densities of the other biochars ranged between 0.21 and 0.25 g cm⁻³. Biochar yield (%) was significantly different between the treatments with maximum in BULK-PY followed by LAR-PY and LAR-CR-PY (Table 4.2), thereby showing a trend of decreasing yield with finer particle size of biochar feedstock.

Table 4.2 Physical and chemical analysis of unwashed biochars.

Treatment	C (%)	N (%)	H (%)	pH	Yield* %	Ash content %	Bulk Density (g cm ⁻³)
LAR-PY	83	0.30	3.41	8.30	26.78B	2.0	0.150
LAR-PY-CR	84	0.27	3.36	8.76	26.75B	2.0	0.214
BULK-PY	78	0.61	3.39	9.80	27.25A	4.9	0.252
LAR-CR-PY	83	0.32	3.40	7.93	26.32C	2.1	0.240

Where BULK-PY stands for biochar from bulk feedstock (particle sizes ranging from 2.0 to 11.2 mm), LAR-PY for biochar from a large particle size feedstock (5.6 to 11.2 mm); LAR-PY-CR for the LAR-PY biochar crushed to < 2 mm; LAR-CR-PY for the biochar produced after crushing the large feedstock to < 2 mm prior to pyrolysis; * shows Tukey lettering.

Table 4.3 Electrical conductivity (EC) and pH of leachates collected during a 3-step washing using deionised water prior to the batch sorption-desorption (ion exchange) study.

Treatment	Leachate 1 EC ($\mu\text{S cm}^{-1}$)	Leachate 2 EC ($\mu\text{S cm}^{-1}$)	Leachate 3 EC ($\mu\text{S cm}^{-1}$)	Leachate 1 pH	Leachate 2 pH	Leachate 3 pH
LAR-PY	76.8	75.0	65.6	8.07	8.08	8.02
LAR-PY-CR	119.0	93.3	85.3	8.37	8.78	8.75
BULK-PY	182.5	143.0	102.6	7.47	8.11	8.49
LAR-CR-PY	85.8	84.6	68.3	6.86	7.29	7.46

Where BULK-PY stands for biochar from bulk feedstock (particle sizes ranging from 2.0 to 11.2 mm), LAR-PY for biochar from a large particle size feedstock (5.6 to 11.2 mm); LAR-PY-CR for the LAR-PY biochar crushed to < 2 mm; LAR-CR-PY for the biochar produced after crushing the large feedstock to < 2 mm prior to pyrolysis.

In preparation for the batch sorption experiments the biochars were washed. The EC and pH of the leachates produced, after the initial washing step with deionised water, is reported in Table 4.3. The EC of the biochar leachates decreased with progressive washing. The high electrical conductivity (EC) indicates the greater presence of salts readily soluble in the wash water from the BULK-PY biochar and is in agreement with its greater ash content (Table 4.2). The final pH values of the leachates were > 8.0 for the LAR-PY, LAR-PY-CR and BULK-PY biochars, and 7.46 for the LAR-CR-PY. Jensen et al. (2000) pointed out that some minor amounts of inorganic matter may be lost during pyrolysis because of the convective transport of small particles caused by the liberated gas. This may thus explain the loss of alkalinity during the pyrolysis of the crushed feedstock (LAR-CR-PY), but more research is needed to prove this hypothesis.

In preparation for the column sorption experiments the biochars were flushed with deionised water. The EC and pH of the leachates produced after the initial flushing step is reported in Table 4.4. The successive flushings with deionised water carried out in the column study exhibit a different pattern from that of the batch study in that no clear relationship was found between EC values and the ash content of the biochars (Table 4.4). Moreover, the pH values of the leachates tended to remain around neutrality after the washing step. The different amount of water added (52:1 vs. 25:2; v:wt ratio; column vs. batch experiment) together with

the different displacement technique used, may explain the differences in results between the two sorption experiments.

Table 4.4 Electrical conductivity (EC) and pH of leachates collected during a 3-step washing using deionised water prior to the column sorption study.

Treatment	1st EC ($\mu\text{S cm}^{-1}$)	2nd EC ($\mu\text{S cm}^{-1}$)	3rd EC ($\mu\text{S cm}^{-1}$)	1st pH	2nd pH	3rd pH
LAR-PY	90.2	77.8	49.8	6.97	7.34	7.25
LAR-PY-CR	169.1	118.4	73.5	7.12	7.50	7.41
BULK-PY	168.1	121.6	74.3	7.91	7.71	7.35
LAR-CR-PY	173.5	138.1	58.5	6.97	7.63	7.14

Where

BULK-PY stands for biochar from bulk feedstock (particle sizes ranging from 2.0 to 11.2 mm), LAR-PY for biochar from a large particle size feedstock (5.6 to 11.2 mm); LAR-PY-CR for the LAR-PY biochar crushed to < 2 mm; LAR-CR-PY for the biochar produced after crushing the large feedstock to < 2 mm prior to pyrolysis.

Results obtained with XPS spectroscopy for the LAR-PY, LAR-PY-CR, BULK-PY and LAR-CR-PY are reported in Table 4.5. Data indicates that the surface of the biochars consist mostly of C (87-88 %) and O (7.2-7.9 %), with an atomic O/C ratio < 0.15. The amount of N at the surface was < 0.4% (atom %). Surfaces of the four biochars were thus very similar. Subtle differences were detected with the BULK-PY biochar, this having slightly less C and slightly more O at the surface than the other biochars. The lower C content of this biochar is in agreement with the elemental analysis. The spectra of the four samples displayed signals attributed to the aliphatic/aromatic carbon groups (CH_x, C-C/C=C) (285 eV) (74-76%), hydroxyl groups (-C-OR) (286.6 eV) (9.3-9.9%), carbonyl groups (-C=O) (1.6-1.9%) and carboxylic groups, esters, or lactones (-COOR) (289 eV) (1.7-1.8%). The XPS results indicate that almost no differences in surface functional groups were produced by crushing before pyrolysis or after pyrolysis (LAR-PY-CR vs LAR-CR-PY). Moreover, the fact that the distribution of functional groups in the LAR-PY and LAR-PY-CR samples was similar denotes a complete carbonization of the charcoal particles to their core during pyrolysis, independently of the particle size used.

Table 4.5 XPS scan of the atomic composition of C, O and N in differently processed unwashed biochars.

Transition	Assigned structure	Peak energy	LAR-PY	LAR-PY-CR	BULK-PY	LAR-CR-PY
		eV	At%	At%	At%	At%
C1s	C-C/C=C	285.0-285.1	75.1	75.5	74.1	75.2
	C-O	286.6	9.4	9.6	9.9	9.3
	C=O	288.0	1.9	1.6	1.7	1.9
	COO	289.2-289.3	1.7	1.8	1.8	1.8
Subtotal C1s			88.0	88.6	87.2	88.2
O1s	C-O-C	533.4-533.7	7.3	7.6	7.9	7.2
	C=O, C-OH, C-O-C	532.0-532.3	4.3	3.7	4.2	4.3
Subtotal O1s			11.6	11.2	12.1	11.5
N1s	Pyrolic N	400.7-400.8	0.2	0.1	0.2	0.2
	Pyridinic N in O- containing struct.					
	>N pyridinic	398.9-399.2	0.1	0.1	0.2	0.1
Subtotal N1s			0.3	0.2	0.4	0.4
O/C ratio			0.13	0.13	0.14	0.13

Where C1s, N1s, and O1s are binding energies/functionalities for carbon, nitrogen and oxygen.

4.3.2 Batch Sorption Study Comparing Zeolite, Bark and Biochar

The results from the batch sorption study are reported in Fig. 4.2. Sorption of NH_4^+ -N when added at a dose of $39 \text{ mg NH}_4^+\text{-N L}^{-1}$, followed the order zeolite > biochar > bark, with values of 0.71, 0.38 and $0.27 \text{ mg NH}_4^+\text{-N g}^{-1}$ sorbent, respectively. This corresponded to 91, 49 and 35% sorption, differences being significant at $p < 0.05$. The sorption of NH_4^+ -N was 16-33 % of respective CECs of all sorbents. When the dose of NH_4^+ -N was doubled ($79 \text{ mg NH}_4^+\text{-N L}^{-1}$), the order was zeolite > biochar ~ bark, with values of 1.40, 0.52 and 0.47 mg

$\text{NH}_4^+\text{-N}$ g^{-1} sorbent, respectively. This corresponded to 89, 33 and 30% sorption, with sorption on zeolite being significantly higher ($p < 0.05$) than that of the other two materials under study. The results obtained also indicated that doubling the incoming $\text{NH}_4^+\text{-N}$ concentration increased the retention of $\text{NH}_4^+\text{-N}$ at the surface of the biochar particles by 37%. The other two materials studied displayed an increase in the amount of $\text{NH}_4^+\text{-N}$ retained of greater than 70% (Fig. 4.2).

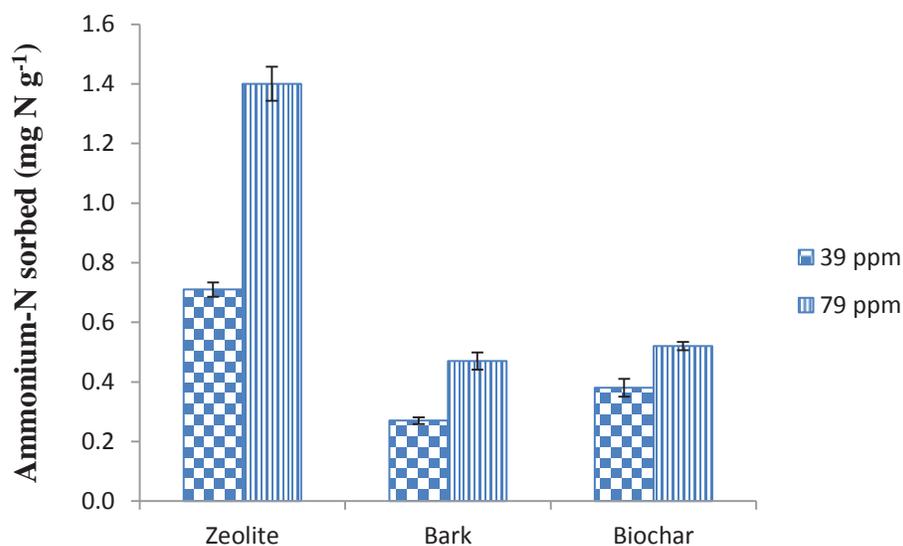


Figure 4.2 $\text{NH}_4^+\text{-N}$ sorbed (mg g^{-1}) on different sorbents using two initial $\text{NH}_4^+\text{-N}$ concentrations (39 and 79 mg L^{-1}).

In the present study, biochar proved to significantly remove ($p < 0.05$) greater amounts of $\text{NH}_4^+\text{-N}$ than bark at 39 mg L^{-1} influent concentration, but not at 79 mg L^{-1} . This reflects (i) the existence of different affinities of $\text{NH}_4^+\text{-N}$ for these two surfaces, and/or (ii) the occurrence of different retention mechanisms. Furthermore, the different pH of the two materials (acidic for bark and alkaline for biochar) may have had an influence on their different behaviour. It should also be noted that whereas bark has an important fraction of C available to microbes and, therefore, N immobilisation by microbes can be a dominant process, this is not the case for the C in biochar. Several researchers have shown that materials rich in labile C such as saw dust and bark – are effective in removal of $\text{NO}_3\text{-N}$ from wastewaters and drainage effluents through this process (Blowes et al., 1994; Schipper and Vojvodic-Vukovic, 2000, Christianson et al. 2011).

Zeolite sorption capacity was found to be in accordance with its high internal surface and CEC (Nguyen and Tanner, 1998), although the estimated CEC was considerably smaller than that reported by other researchers (Perrin et al. 1998; Kithome et al. 1999; Bolan et al. 2004). Bolan et al. (2004) working with the sorption of NH_4^+ from synthetic solutions on zeolite and bark and with an influent solution with up to 500 mg N L^{-1} , reported much higher sorption of 21.8 and $13.4 \text{ mg g}^{-1} \text{ NH}_4^+\text{-N}$ by zeolite and untreated bark, respectively. The sorption of NH_4^+ in zeolite was almost equal to its CEC, thus showing the simple ion-exchange to be responsible for the adsorption. In case of bark, the adsorption exceeded the CEC showing the possibility of immobilization of NH_4^+ to organic N. When sorption is expressed on a volume basis the low bulk density sorbents bark and biochar sorb much lower amounts than zeolite (Fig. 4.3).

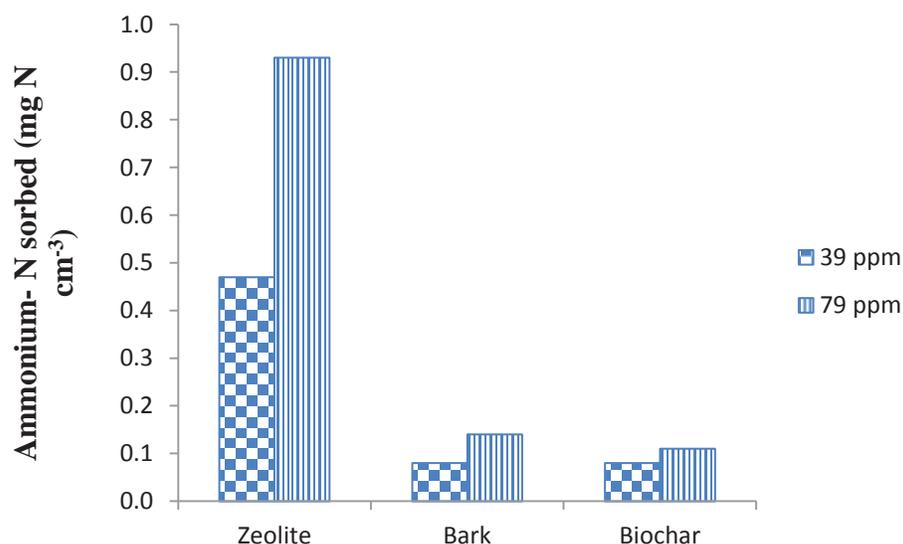


Figure 4.3 $\text{NH}_4^+\text{-N}$ sorbed (mg cm^{-3}) on different sorbents using two initial $\text{NH}_4^+\text{-N}$ concentrations (39 and 79 mg L^{-1} , Batch study).

4.3.3 Batch Sorption Study Comparing Biochars with Different Particle-sizes

Ammonium sorption was lowest in the LAR-CR-PY treatment ($0.10 \text{ mg NH}_4^+\text{-N g biochar}$) (Fig. 4.4); this biochar was the only one to which a crushing step was made prior to pyrolysis. This corresponded to a removal of 54% of the added $\text{NH}_4^+\text{-N}$. The other three treatments showed a similar behaviour among them sorbing $0.16 \text{ mg NH}_4^+\text{-N g biochar}$ each, which corresponded to a removal of 79% of the added $\text{NH}_4^+\text{-N}$. Ammonium retention through ion exchange reactions is affected by pH, increasing as pH rises through the creation of additional negative charge (Kithome et al. 1999); however, the ionized forms of NH_4^+ will tend to diminish at high pH values. The lower amount of cation exchange sites at a lower pH

values may be expected to explain the different pattern of NH_4^+ sorption observed in the LAR-CR-PY treatment, compared to the rest of treatments, however no relationship was found between NH_4^+ sorption and the pH of the biochar suspension or column leachate (data not shown).

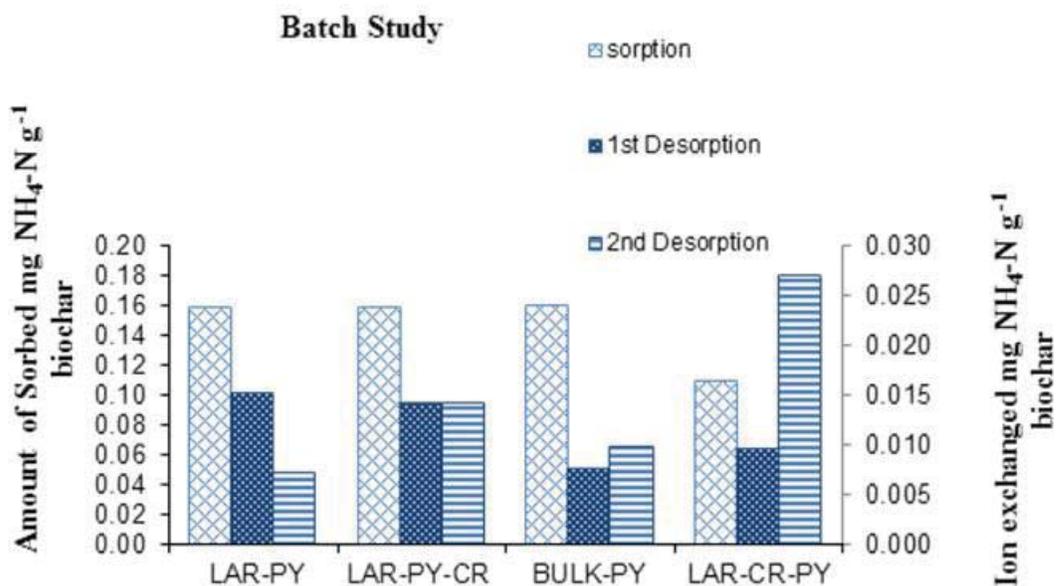


Figure 4.4 Amount of NH_4^+ -N sorbed and then desorbed by ion exchange with KCl in the batch sorption study comparing different particle sizes.

Where BULK-PY stands for biochar from bulk feedstock (particle sizes ranging from 2.0 to 11.2 mm), LAR-PY for biochar from a large particle size feedstock (5.6 to 11.2 mm); LAR-PY-CR for the LAR-PY biochar crushed to < 2 mm; LAR-CR-PY for the biochar produced after crushing the large feedstock to < 2 mm prior to pyrolysis.

Decreasing the particle size of biochar by crushing after pyrolysis did not affect the NH_4^+ -N sorption properties of these biochars (e.g., LAR-PY vs. LAR-PY-CR) in the batch study (Fig. 4.4). It should be noted that the batch study was carried out by shaking the samples in an end-over-end rotator for 24 hrs. It is thus possible that, under such conditions, the effect of surface area of biochar particles on NH_4^+ -N sorption was minimized and NH_4^+ -N was probably able to readily diffuse within biochar pores.

Between the sorption and desorption procedures the biochars were washed with water and the eluent removed in order to measure the NH_4^+ retained by ion exchange. The amount of NH_4^+ -N desorbed (over 1 hour shaking in two steps) corresponded to 11-33% of the amount sorbed in the sorption phase (Fig. 4.4). Values are in the same range as those reported in Chapter 5

working with similar biochars under similar conditions (14-27%), although some different patterns were observed among the treatments under study here. The LAR-CR-PY biochar displayed a different behaviour in that it desorbed 33% of the amount sorbed, whereas, desorption in the other three biochars ranged from 11 to 18%. Moreover, modifying the particle size before pyrolysis had an effect on the desorption of $\text{NH}_4^+\text{-N}$, as the smaller particle sizes (LAR-PY-CR and LAR-CR-PY) were able to desorb significantly greater amounts of this cation ($p < 0.05$). BULK-PY, which produced the maximum yield of biochar (Table 4.2), had equal sorption as that of LAR-PY (Fig. 4.4). No significant difference was found in sorption ability with reduced particle sizes of biochar, so pre-crushing is not recommended for future sorption studies. Zheng et al. (2010) studied the sorption of two triazine pesticides by greenwaste biochar at different particle sizes (0.053-0.250 mm). They reported that the biochar with small particle size needed less time to reach sorption equilibrium, however, they did not highlight any significant difference in sorption capacity with change in particle size of biochar.

Biochar Column Study

The cumulative sorption of $\text{NH}_4^+\text{-N}$, 0.17-0.23 mg $\text{NH}_4^+\text{-N g}^{-1}$ biochar, calculated by analysing the fifteen volume fractions of column effluent collected, was greater (Fig. 4.5) than that observed in the batch study experiment (0.10-0.16 mg $\text{NH}_4^+\text{-N g}^{-1}$ biochar) (Fig. 4.4). This illustrates the greater ability of biochar to retain $\text{NH}_4^+\text{-N}$ with a continuous application of a 38 mg L^{-1} $\text{NH}_4^+\text{-N}$ influent solution in the column study compared with that in the batch study where the $\text{NH}_4^+\text{-N}$ solution concentration decreased with time as this cation became sorbed. However, the efficiency of $\text{NH}_4^+\text{-N}$ removal from the influent solution was smaller in column study than that of the batch study. No significant differences ($p < 0.05$) were found among treatments except for the LAR-PY treatment, which displayed a lower NH_4^+ removal capacity. This was attributed to the smaller surface contact of influent solution with loosely packed large particle-sized biochar (11.20-5.60 mm); this effect was overcome in the batch study through the end-over-end shaking process. In this study, the LAR-CR-PY biochar displayed a similar sorption behaviour than the other two treatments (BULK-PY and LAR-PY-CR).

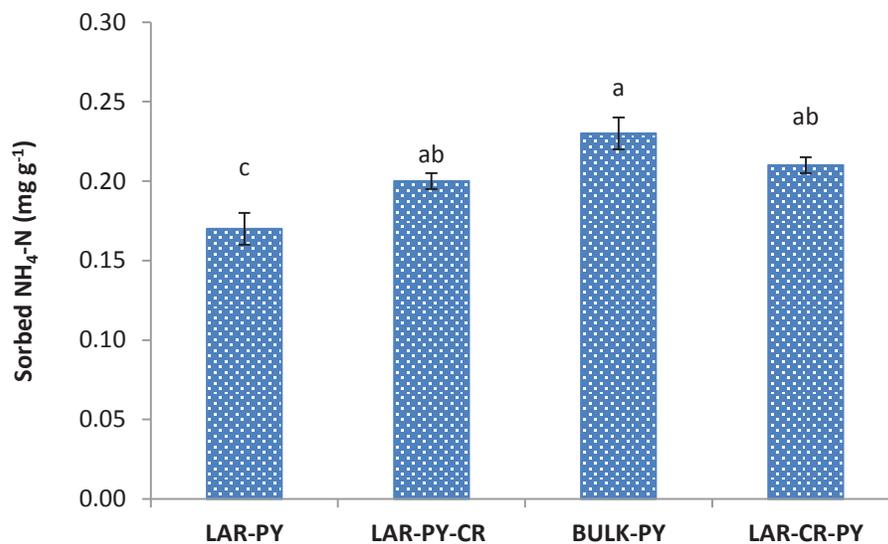


Figure 4.5 Cumulative amount of NH₄⁺-N sorbed on the different biochars used in the column sorption study comparing different particle sizes (Tukey lettering).

Where BULK-PY stands for biochar from bulk feedstock (particle sizes ranging from 2.0 to 11.2 mm), LAR-PY for biochar from a large particle size feedstock (5.6 to 11.2 mm); LAR-PY-CR for the LAR-PY biochar crushed to < 2 mm; LAR-CR-PY for the biochar produced after crushing the large feedstock to < 2 mm prior to pyrolysis.

4.4 Conclusion

The results obtained in this study led to the following conclusions:

Comparison among different sorbents

Zeolite had the greater ability to sorb NH₄⁺ from wastewaters, followed by biochar and bark. Zeolites sorbed almost 89 % of NH₄⁺ added at higher concentration so proved to be the best sorbent for wastewater treatment for NH₄⁺. Although commercially available, zeolites are expensive adsorbents, therefore, may need to be regenerated by desorbing the NH₄⁺ which need some special treatment and salt to get rid of it for use again. Bark and biochar are less expensive options, which after use for sorbing NH₄⁺ from wastewaters can be added directly to soil. On application to soil, bark loaded with NH₄⁺-N will decompose and potentially immobilise or release the sorbed N. Biochar, due to its aromatic composition and condensed macromolecular structure, is biologically and chemically more stable than the original biomass sources from which it was produced like bark. Therefore, biochar loaded with NH₄⁺ may be a more environmentally suitable addition to soils and long-term source of adding sequestered C and some plant available N. Further research on the agronomic value of NH₄⁺ loaded barks and biochar as soil amendments is required.

Comparison among biochars of different particle sizes

Feedstock particle size was found to affect the yield of the biochar with maximum in BULK-PY followed by large pieces of feedstock (5.6-11.2 mm). The results obtained here suggest that pyrolysis of large pieces of feedstock (5.6-11.2 mm) led to a similar degree of carbonisation as that of small pieces of feedstock (size < 2 mm). No significant differences in sorption were observed with crushing of biochars, so no need to crush.

A batch method with an overnight shaking may not be adequate to study the influence of biochar particle size on NH_4^+ -N sorption, as the effect of particle size on NH_4^+ diffusion to the inner biochar microporous structure, may take long time to reach equilibrium. Particle size of the feedstock did not give any significant differences in NH_4^+ -N sorption capacity of biochars.

Further research is required to investigate how the NH_4^+ -N sorption power and capacity of biochar can be increased and its use as an environmentally safe option for removing NH_4^+ -N from wastewater treatment is evaluated. These aspects are covered in the following Chapters.

References

- Ahmedna M, Marsall WE, Rao RM (1998) Production of granular activated carbon from select agricultural by-products and evaluation of their physical, chemical and adsorption properties. *Bioresource Technology*. 71, 113-123.
- Blakemore LC, Searle PL, Daly BK (1987) Methods for chemical analysis for soils. *NZ Soil Bureau Scientific report*. 80, 78–79
- Blowes DW, Robertson WD, Ptacek CJ, Merkley C (1994) Removal of agricultural nitrate from tile drainage effluent water using in line bioreactors. *Journal of Contaminant Hydrology*. 15, 207-221.
- Bolan N, Wong L, Adriano D (2004) Nutrient removal from farm effluents. *Bioresource technology*. 94(3), 251-260.
- Calvelo Pereira R, Kaal J, Camps-Arbestain M, Pardo Lorenzo R, Aitkenhead W, Hedley M, Macias F, Hindmarsh J and Macia-Agullo JA (2011) Contribution to the chemical characterisation of biochars for the prediction of their carbon lability. *Organic Geochemistry*, 42,1331-1342.
- Cao X, Ma L, Gao B, Harris W (2009) Dairy-manure derived biochar effectively sorbs lead and atrazine. *Environmental Science and technology*. 43, 3285-3291.
- Chen B, Chen Z (2009) Sorption of naphthalene and 1-naphthol by biochars of orange peels with different pyrolytic temperatures. *Chemosphere*. 76, 127-133.
- Chen B, Chen Z, Lv S (2011) A novel magnetic biochar efficiently sorbs organic pollutants and phosphate. *Bioresource Technology*. 102, 716-723.
- Chen B, Zhou D, Zhu L (2008) Transitional adsorption and partition of non-polar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures. *Environmental Science and Technology*. 42, 5137-5143.
- Christianson LE (2011) Design and performance of denitrification bioreactors for agricultural drainage. PhD Thesis and dissertation, US, pp. 1-86.
- Cooney E, Booker N, Shallcross D, Stevens G (1999) Ammonia removal from wastewaters using natural Australian zeolite. II. Pilot-scale study using continuous packed column process. *Separation Science and Technology*. 34(14), 2741-2760.
- Demir A, Debik E, Gunay A (1998) Eysel atiksulardan amonyumun gideriminde iyon degitirici olarak dogal zeolit kullaniminin arastirilmesi. *ISKI Projesi Yildiz*, Istanbul.

- Hedström A (2001) Ion exchange of ammonium in zeolites: A literature review. *Journal of Environmental Engineering*. 127, 673-681.
- Jensen PA, Frandsen FJ, Dam-Johansen K, Sander B, (2000) Experimental investigation of the transformation and release to gas phase of potassium and chlorine during straw pyrolysis. *Energy Fuels*. 14, 1280-1285.
- Kithome M, Paul JW, Lavkulich LM, Bomke AA (1999) Effect of pH on ammonium adsorption by natural zeolite clinoptilolite. *Communications in Soil Science and Plant analysis*. 30, 1417-1430.
- Matsue N, Wada K (1985) A new equilibrium method for cation-exchange capacity measurement. *Soil Science Society of America Journal*. 49, 574-578.
- Nguyen M, Tanner C (1998) Ammonium removal from wastewaters using natural New Zealand zeolites. *New Zealand Journal of Agricultural Research*. 41, 427-446.
- Perrin T, Drost D, Boettinger J, Norton J (1998) Ammonium-loaded clinoptilolite: A slow-release nitrogen fertilizer for sweet corn. *Journal of Plant Nutrition*. 21(3), 515-530.
- Schipper LA, Vojvodic-Vukovic M (2000) Nitrate removal from groundwater and denitrification rates in a porous treatment wall amended with sawdust. *Ecological Engineering*. 14, 269-278.
- Sevilla M, Fuertes AB (2010) Graphitic carbon nanostructures from cellulose. *Chemical Physics Letters*. 490, 63-68.
- Wieczorek S (2008) Assessing the Influence of Adsorbent Bed (Tree Bark) Parameters on the Reduction of Ammonia Emissions from Animal Husbandry. *Polish Journal of Environmental Studies*. 17(1), 147-154.
- Zheng W, Guo M, Chow T, Bennett DN, Rajagopalan N (2010) Sorption properties of greenwaste biochar for two triazine pesticides. *Journal of Hazardous Materials*. 181, 121-126

Chapter 5

Ammonium sorption and volatilisation from solution by activated and non-activated Biochars

5.1 Introduction

In this Chapter, preliminary experiments are reported that were conducted to select methodologies suitable for studying the removal of ammonium (NH_4^+) from wastewaters using biochar. In the introduction to this thesis (Chapter 1), the concept of using materials with significant cation exchange capacity such as zeolite (Nguyen and Tanner, 1998; Cooney et al. 1999), bark (Bolan et al. 2004; Wieczorek, 2008) and biochar, or activated biochar, to strip NH_4^+ from agricultural waste streams was discussed.

Depending upon the feedstock used, the method of activation and the extent of pyrolysis, the biochar produced can have a range of ash content (Lehmann et al. 2009). High-ash content biochars increase the pH of waters that they are in contact with. In addition, wastewaters from dairy and urban origin, that are rich in nitrogen (N), decompose during storage or processing releasing NH_4^+ (Hedstrom, 2001), which raises the pH of the wastewater. There is the risk that if treated with high ash biochars, the elevated pH of the waste stream may cause ammonia (NH_3) volatilisation. Ammonia volatilisation presents itself as a potential problem when trying to measure the NH_4^+ sorption capacity of alkaline sorbents by the commonly used methodology, such shaking or leaching the substrate with NH_4^+ containing solutions. Sorbed NH_4^+ is estimated from the difference between the influent and effluent NH_4^+ concentrations multiplied by the flow rate, or the volume, of the solution. Such methodology, used by Bolan et al. (2004), does not account for potential NH_3 volatilisation, which would attribute volatilised N to the pool sorbed by the sorbent. To be suitable as a sorbent of NH_4^+ , the sorbing active filter must not raise the pH of the waste stream to a value that accelerates NH_3 volatilisation. A study by Poach et al. (2002) highlights the ammonia volatilisation that occurs in wetlands treating swine wastewater and found that 7% to 16% of the nitrogen (N) load to the wetlands was removed through NH_3 volatilisation. In this Chapter, equipment capable of measuring both NH_3 volatilisation and NH_4^+ sorption was designed and used to measure NH_4^+ removal from wastewaters by biochar.

The key objectives of this chapter are:

- 1) To assess the NH_4^+ sorption capacity of low ash and high ash biochars.
- 2) To assess the volatilisation of NH_3 from low ash and high ash biochars during NH_4^+ sorption experiments.

The hypothesis tested was that high ash biochars will increase solution pH and cause NH_3 volatilisation.

5.2 Material and Methods

5.2.1 Materials

Biochars, manufactured from pine wood chip (Ctr PI) and eucalyptus log peelings (Ctr EU), used in the sorption and volatilisation studies are fully characterised and described in detail in Chapter 3. These Biochars also include those made by pre-treating pine (L PI) and eucalyptus log peelings (L EU) with alkaline tannery waste to create activated biochar with increased cation exchange capacity. The production of steam activated biochar is described in Chapter 3.

Carbonisation and Biochar washing

Two hundred grams of each feedstock were pyrolysed at 550 °C and heated at an average heating rate of 28 °C min⁻¹ using a gas-fired, 5 L, stainless steel, rotating drum kiln. (Details of the pyrolysis process are given in Chapter 5). Subsamples of the different biochars were stored for analysis (unwashed biochars). After unwashed samples of tannery waste activated biochars caused ammonia volatilisation, additional subsamples were washed repeatedly with deionized water until the electrical conductivity; EC (EC meter No. HI 8633 by Hanna Instruments, Singapore) decreased to 50 $\mu\text{S cm}^{-1}$. The pH of the washing solution ranged between 8.0 and 10.1 (Fig. 5.3). Washing was done in the same water : biochar ratio (20:1) as that of sorption study. Sub samples of washed pine biochar (washed PI) were steam activated (details of steam activation are presented in Chapter 3). The particle-sizes of the biochars produced ranged between 2 to 3 mm for the PI biochars and was < 2 mm for the EU biochars.

Chemical Analyses

The methodology for the chemical and physical analysis of biochars is described in detail in chapter 5.

5.2.2 Volatilisation studies: Experiment 1 and 2

A sample of finely ground biochar (1 g) (unwashed; Experiment 1 and washed; Experiment 2 with deionised water) was weighed in a 50-mL beaker in duplicate and placed into an AGEE preserving jar with a screw on sealed cap. A 40-mL tube containing 10 mL of 0.025 M H_2SO_4

was also placed into the jar to trap any volatilised NH_3 . After sealing the jar, 20 mL of $37 \text{ mg L}^{-1} \text{NH}_4^+\text{-N}$ solution as $(\text{NH}_4)_2\text{SO}_4$ was injected with a syringe into the beaker through a septum. The beaker was then swirled gently for 15 minutes with an automatic stirrer to mix the biochar / NH_4^+ solution suspension adequately. A control jar with no biochar, also in duplicate, was treated as previously described. After allowing the AGEE jar to stand at room temperature ($20\text{-}25 \text{ }^\circ\text{C}$) for 6 hours, the biochar-solution suspensions were filtered and transferred to the vials for NH_4^+ analysis using a Technicon autoanalyzer (Pulse Instrumentation Ltd. Canada). The same equipment was used to determine NH_4^+ concentration in the acid trap. The NH_4^+ sorbed was determined by difference between the initial and final solution, after correcting for volatilised NH_3 (i.e. the NH_4^+ measured in the acid trap)

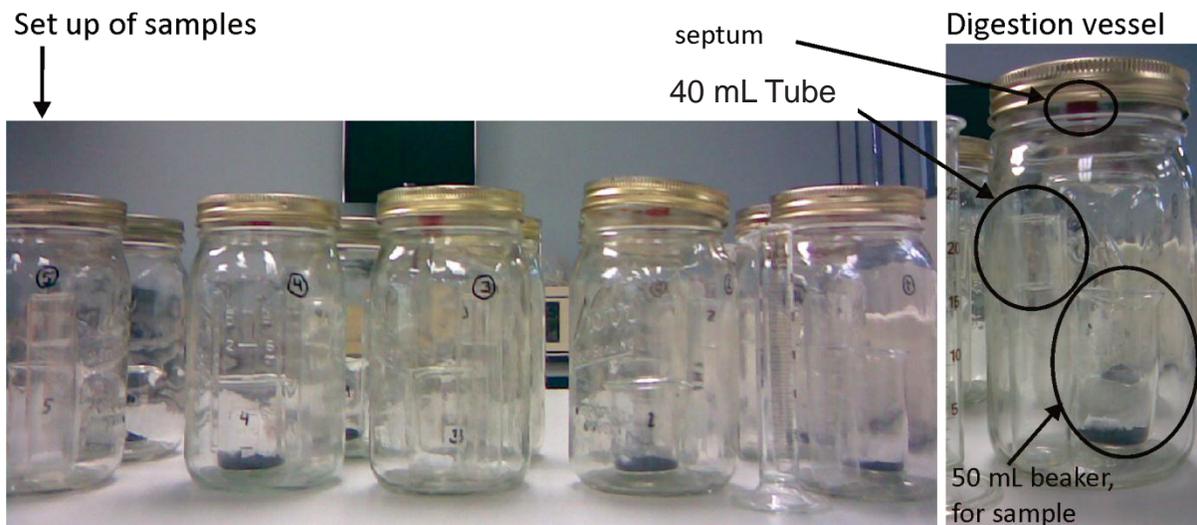


Figure 5.1 Equipment used in the NH_3 volatilisation study.

Statistical Analyses

Simple one way ANOVA and Tukey's test were used to test for significant differences in the results of NH_4^+ sorption and NH_3 volatilisation at $p < 0.05$ (SAS statistical software, SAS 2002-2010 by SAS Institute, USA).

5.3 Results and Discussion

5.3.1 Feedstocks and Untreated Biochars

The C content of the PI feedstock increased from 487 to 777 g kg^{-1} after the carbonisation process, and that of EU from 460 to 760 g kg^{-1} (Table 3.1). Similarly, the N content in PI and

EU materials increased from 2.8 to 6.1 g kg⁻¹ and 3.0 to 6.7 g kg⁻¹, respectively. The ash content also increased with carbonisation, from < 10 g kg⁻¹ to 50 and 70 g kg⁻¹ for Ctr PI and Ctr EU biochars, respectively (Table 5.1). Biochars treated with diluted tannery slurry had higher H/C ratios compared to the other samples.

Table 5.1 Physical and Chemical Characteristics of activated and non-activated biochars.

S.No**	Treatment	Carbon (g kg ⁻¹) *	Nitrogen (g kg ⁻¹)	H (%)	Org. C (%)	pH	Ash (g kg ⁻¹)	BET (m ² /g)
1	PI feedstock	487G	2.8E		-	-	5.0	-
2	EU feedstock	460H	3.0E		-	-	7.0	-
3	Ctr PI (unwashed)	777C	6.1D	3.6	77.4	9.8	50	235
4	Ctr EU (unwashed)	760C	6.7C	2.8	75.4	8.8	70	2.8
5	L PI (unwashed)	704E	13.3B	3.4	69.6	10.3	90	3.3
6	L EU (unwashed)	550F	21.0A	2.7	54.1	8.9	248	2.2
7	L PI (washed)	753C	11.4B	2.7	-	8.3	55	2.7
8	L EU (washed)	637D	20.4A	2.9	-	8.0	170	1.6
7	Steam PI	830A	1.5G	-	-	7.9	37	735
8	Steam EU	794B	2.3F	-	-	7.8	100	457

*Letters show Tukey's test groupings.

**Numbers show the chronological sequence

Pre-treating feedstocks with tannery waste (L) increased the ash contents relative to the Ctr EU and Ctr PI biochars from 50 to 90 and 70 to 248 g kg⁻¹, for L PI and L EU biochars, respectively (Table 5.1). The L EU biochar had more than double ash content than that of the

L PI on average over the treatments. The pH values of the pre-treated biochars were greater than the untreated ones, with values ranging from 8.9 to 10.3 in the former and from 8.8 to 9.8 in the latter (Table. 5.1).

Steam Activation

Steam activation increased the C content of the treated biochars (830 and 794 g kg⁻¹ in steam-PI and steam-EU, respectively) compared to the respective controls (777 and 760 g kg⁻¹ in Ctr PI and Ctr EU, respectively) (Table 3.1), which could be due to the solubilisation of the ashes in the biochar during steam activation (See Chapter 3, for details on Steam activation).

5.3.2 Sorption of ammonium and volatilisation of ammonia

Experiment 1

The amount of NH₄⁺-N sorbed by biochars in Experiment 1 (Table 5.2a) ranged between 0.13 to 0.43 mg NH₄⁺-N g⁻¹. All the eucalyptus biochars sorbed significantly more NH₄⁺-N compared to the pine biochars. For example, the Ctr EU (washed) biochar sorbed 0.31 mg NH₄⁺-N/g biochar (or 41.9 % of NH₄⁺-N added) compared to 0.13 mg NH₄⁺-N/g biochar (or 17.3 % of NH₄⁺-N added) for the Ctr PI (washed) biochar. However, the difference between the control and steam-activated biochars was not large enough to be significantly different. The quantity of NH₄⁺-N estimated to have been removed from solution via NH₃ volatilisation was relatively small for all the biochars, ranging from 0.14 – 4.09%, with the highest level of volatilisation occurring with the alkaline tannery pre-treated (unwashed) biochars.

Table 5.2 Ammonium-N sorbed and volatilised during sorption by washed and unwashed biochars.

Treatments	NH ₄ ⁺ -N Sorptior (mg N g ⁻¹ biochar) *	% NH ₄ ⁺ -N sorbed on biochar/amount added	Acid trap NH ₄ ⁺ -N (mg N L ⁻¹)	% NH ₄ ⁺ -N In acid trap/amount added
<i>a) Experiment 1</i>				
Ctr PI (washed)	0.13C	17.3	0.21	0.28
Ctr EU (washed)	0.31B	41.9	0.87	1.18
L PI (unwashed)	0.18C	17.5	4.05	4.05
L EU (unwashed)	0.43B	43.5	4.09	4.09
Steam PI	0.13C	17.6	0.47	0.64
Steam EU	0.35B	47.6	0.10	0.14
<i>b) Experiment 2</i>				
L PI (washed)	0.56A	75.7	0.30	0.40
L EU (washed)	0.52A	70.3	0.14	0.18

* Treatments are significant at (p<0.05) and letters show the Tukey's test groupings.

Experiment 2

Biochars made by activating pine or eucalyptus feedstock with alkaline tannery waste were washed sequentially with deionised water and the electrical conductivity (EC) of the washings is shown in Fig. 5.2. A different number of washings were required for each type of biochar to achieve a solution EC reading of 50 $\mu\text{S cm}^{-1}$ (Cheng et al. 2006). The Ctr EU, Ctr PI, L EU and L PI biochars required 3, 4, 11 and 12 washings, respectively. Washing also reduced suspension pH (Fig. 5.3).

Ammonium sorption and volatilisation was tested using washed activated biochars (L PI and L EU), which showed higher sorption as well as lower volatilisation (Table 5.2), compared to the unwashed biochars. For example, the L PI (washed) biochar sorbed 0.56 mg NH₄⁺-N g⁻¹ biochar, which was over 3-fold higher than the quantity sorbed by the unwashed version. This amount of sorbed NH₄⁺-N represented 75.7% of the NH₄⁺-N added in solution.

Volatilisation only accounted for 0.40% of NH_4^+ removed from solution, compared to 4.05% for the unwashed L PI biochar.

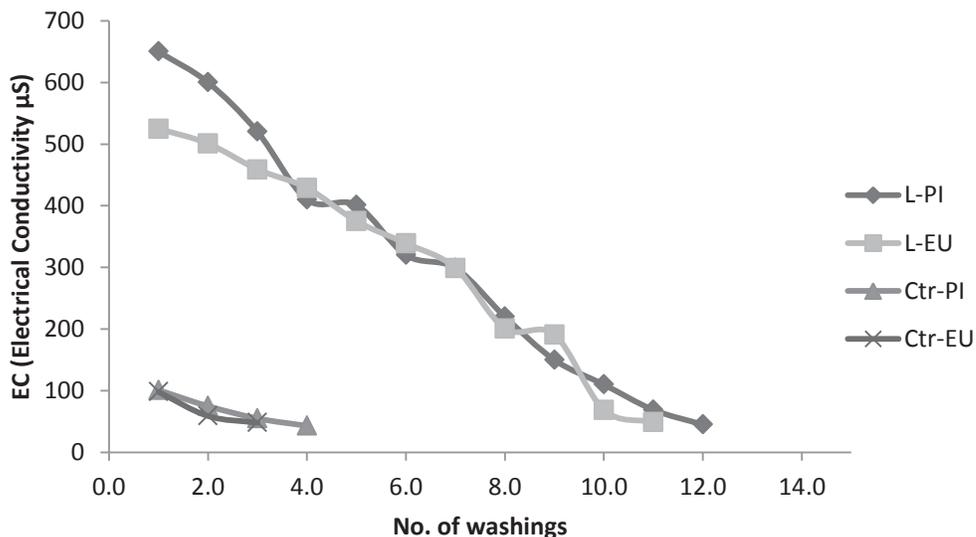


Figure 5.2 Change of EC of washing water as biochars are sequentially washed in deionised water.

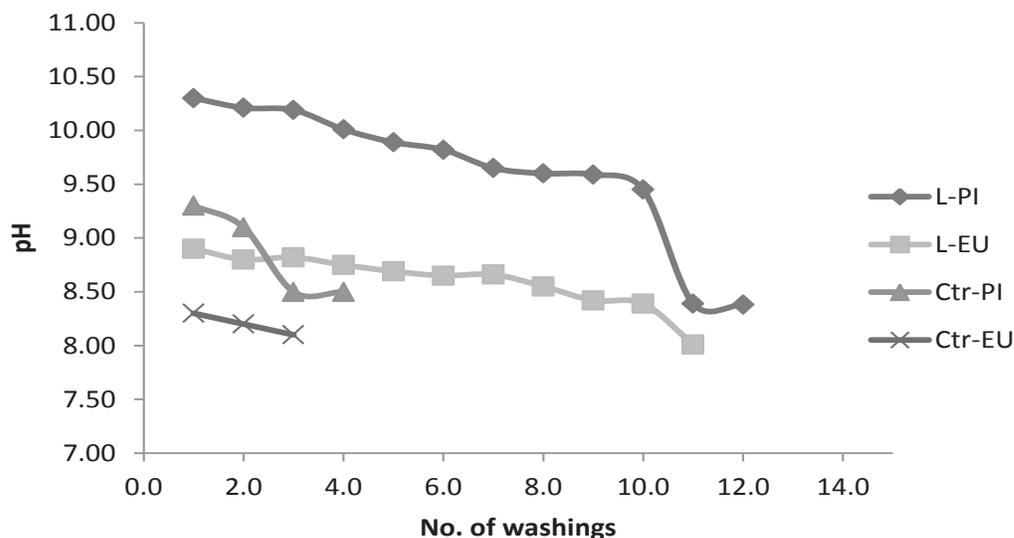


Figure 5.3 Change of pH of washing water as biochars are sequentially washed in deionised water.

In both experiments 1 and 2, NH_4^+ -N sorption followed the order L PI (washed) ~ L EU (washed) > Ctr EU ~ L EU (unwashed) ~ Steam EU > Ctr PI ~ L PI (unwashed) ~ Steam PI (“~” denotes no significant differences at $p < 0.05$). Therefore, there was no clear improvement in sorption from steam activation. It showed that no significant differences were observed between the NH_4^+ sorption on steam PI and steam EU biochars compared with non-activated PI and EU biochars. Pre-treating feedstocks with tannery waste (L PI and L

EU) increased the ash contents of both the EU and PI biochars compared to untreated feedstocks, which resulted in higher NH₃ volatilisation but did not increase NH₄⁺ sorption significantly. Washing the L PI and L EU decreased volatilisation and increased sorption.

It would be useful if the pH supported by a biochar in aqueous suspension could be used to predict whether NH₃ volatilisation is likely to occur. Ammonia volatilisation in these systems should obey simple pH equilibria rules. The dissociation constant of ammonium is defined according to the following equation:

$$K_{\text{NH}_4} = \frac{[\text{H}^+][\gamma\text{NH}_3]}{[\gamma\text{NH}_4^+]} \quad \text{Eq 1.}$$

Where γ is the activity coefficient for NH₃ and NH₄⁺ in solution. The amount of NH₃ was expressed as percentage of total NH₄⁺-N added to the biochar in the sorption flask. Ammonia gas lost to atmosphere was calculated using Henry's Law (Montes et al. 2009):

$$K_h = \frac{[\text{NH}_3]_{\text{gas}}}{\gamma[\text{NH}_3]_{\text{solution}}} \quad \text{Eq 2.}$$

Where $K_h = 0.00062$ at 21 °C. The concentration of [NH₃]_{gas} in solution is determined by the dissociation constant (K_a) in solution, which is sensitive to solution pH. Both (K_h) and (K_a) are also sensitive to the ionic strength of the solution, which can be calculated from the EC of the solution (Montes et al. 2009). Unwashed biochars produce EC values of > 500 $\mu\text{S cm}^{-1}$ in the sorption flask and washed chars < 300 $\mu\text{S cm}^{-1}$. Using these values, ionic strength (I) (Montes et al. 2009) was calculated by following equation:

$$I = 1.6 \times 10^{-2} (\text{EC}) \quad \text{Eq 3.}$$

Where EC is in millimhos cm^{-1} or mS cm^{-1} . The ionic strength of the biochar suspensions was between 0.05 to 0.70 mS cm^{-1} .

Activity coefficient for NH₄⁺ can be calculated from equation 4.

$$\text{Log} \gamma_{\text{NH}_4^+(\text{aq})} = -0.5(c^2) \left[\frac{I}{\sqrt{1+I}} - 0.31 \right] \quad \text{Eq 4.}$$

The activity coefficients (Eq4) for the range of I values estimated from equation 3 did not change significantly from 1. Moreover, c denotes the charge and is 1 for ammonium.

The standard equations for K_a and K_h (0.00062) were used to produce a range of [NH₃]_{gas} for each trial. For simplicity it was assumed that the flux of volatilised NH₃ obeyed Fick's first law of diffusion:

$$J = -D \delta[C]/\delta x \quad \text{Eq 5.}$$

Flux of diffusing material = Diffusion coefficient \times concentration gradient

Where J is diffusive flux in per unit area per unit time, D is diffusion coefficient or diffusivity, and $\delta[C]/\delta x$ is the ammonia gas concentration in one dimension. Diffusion coefficient of ammonia in air is $0.259 \text{ cm}^2/\text{s}$.

The equation can be re-written as

$$J = -D \cdot SA \cdot t \cdot [C_A - C_B] / \delta x \quad \text{Eq 6.}$$

The concentration of NH_3 gas at the surface of the sorption beaker (C_A) was given by the dissociation constant (Eq. 1) and Henry's law (Eq. 2). In order to model the observed values of NH_3 volatilised, a concentration gradient of 1.5% had to be assumed for a stagnant gas layer to a point 1cm (point B) above the liquid surface in the biochar suspension beaker of surface area (SA), where the concentration was $C_B = 0.985C_A$ (Eq. 6). The complete volatilisation model was constructed numerically in an excel spread sheet with a time step (t) of 1 minute. The volatilisation values, both as theoretical and actual (calculated from Model based on Henry law) are shown in Table. 3.3 and compared in Fig 5.4).

The influent $\text{NH}_4^+\text{-N}$ concentration of $50 \mu\text{g}/\text{mL}$ gave a significant amount of ammonia volatilisation ($>4\%$; Table 5.2) at pH range of 8.12-10.19 in unwashed biochar suspensions, which was predicted by the model as well. The fact that the pH remained high in the suspensions and did not reduce with NH_3 volatilisation suggests that there is a pH buffering effect caused by the biochar ash.

Table 5.3 Volatilisation of NH_3 from suspensions of washed and unwashed biochars.

	Suspension pH	Initial $\text{NH}_4\text{-N}$ conc. ($\mu\text{g mL}^{-1}$)	Predicted $\text{NH}_3\text{-N}$ Volatilisation ($\mu\text{g N}$)	Actual $\text{NH}_3\text{-N}$ Volatilisation ($\mu\text{g N}$)*	Post sorption $\text{NH}_4\text{-N}$ Conc. ($\mu\text{g mL}^{-1}$)
L PI					
washed	8.32	37	3.4	3.0(0.40)	9.0
unwashed	10.19	50	37.0	37.0(3.7)	43.1
L EU					
washed	8.12	37	2.2	1.3(0.17)	11.2
unwashed	9.45	50	26.0	39.0(3.9)	30.0

*Values in brackets showed the % ammonia volatilized of that added.

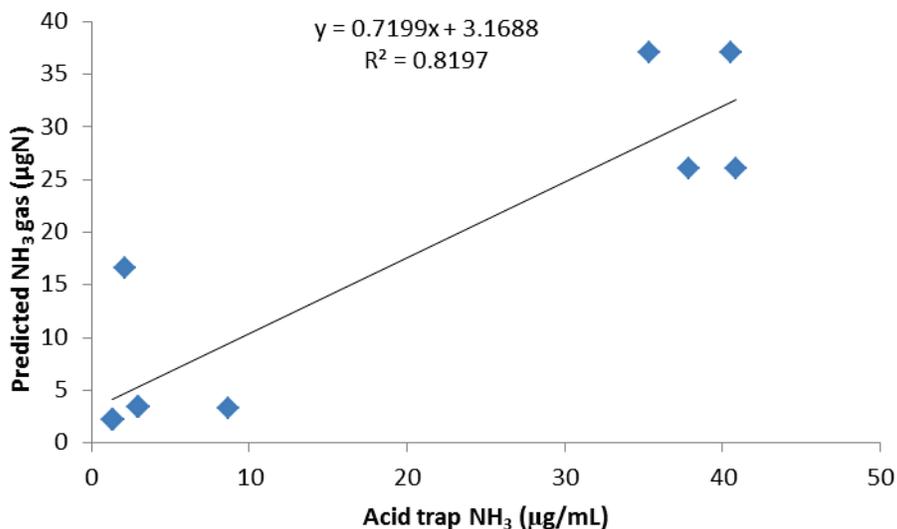


Figure 5.4 Relationship between predicted NH₃-N and acid trap NH₃-N.

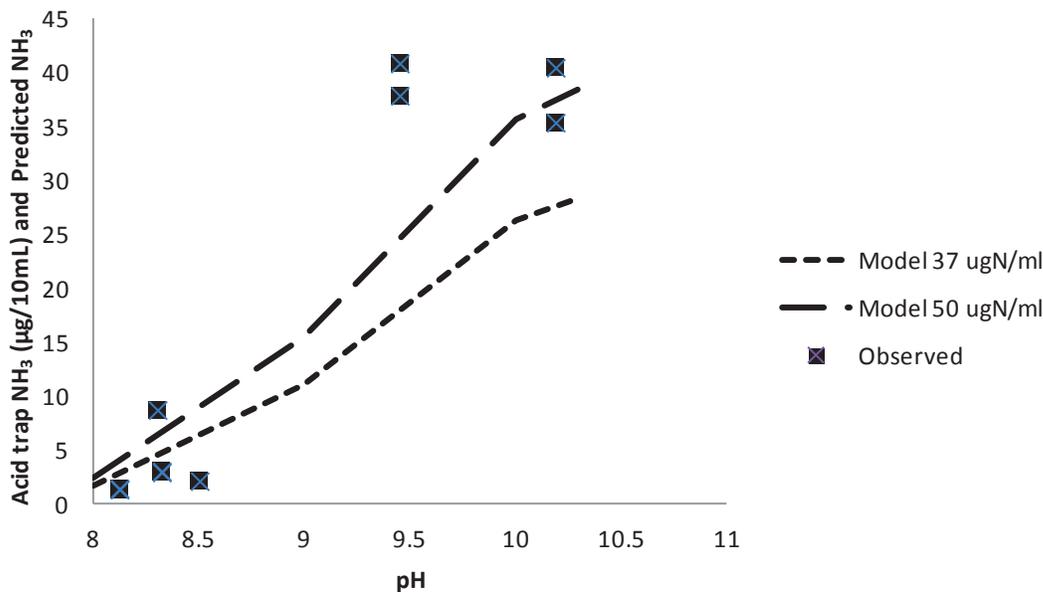


Figure 5.5 Relationship between NH₃-N in acid trap and pH according to the Henry's model at different influent concentration.

The relationship between predicted NH₃-N and acid trap NH₃-N was almost linear with R² value of 0.819 (Fig. 5.4). It confirmed the hypothesis that increased pH in solution caused volatilisation of ammonia in high ash alkaline biochars and that pH supported by a char in aqueous suspension and influent NH₄⁺-N concentration can be used to predict the approximate extent of NH₃ volatilisation. The relationship of pH and predicted ammonia volatilisation by Henry's law at two influent concentrations is showed in Fig. 5.5. It confirms the effect of pH and influent ammonium concentration on the volatilisation of ammonia.

The physical and chemical properties relevant to the sorption of NH_4^+ ions on different biochars are examined and discussed in detail in other Chapters. However, high ash content and EC posed problems for enhanced NH_4^+ -N sorption on biochars. In the current study, this could be due to the presence of cations/soluble salts from tannery waste use in activation (Chapter 3) which saturate the porous structure of biochar, thereby binding pores from NH_4^+ sorption. The presence of these competing cations in the unwashed biochars seemed to be responsible for the less sorption of NH_4^+ -N than that in washed biochars (Table 5.2).

5.4 Conclusions

Influent NH_4^+ concentration and pH affect the amount of ammonia volatilisation occurring during studies of NH_4^+ sorption on biochar. The amounts of ammonia volatilisation could be predicted using a semi-empirical model and the predicted amounts were consistent with those observed in acid traps in the current study. Pre-treating feedstocks with tannery waste increased the ash contents of both the EU and PI biochars compared to untreated feedstocks. It does not increase the sorption of NH_4^+ -N on the unwashed treated biochars but increased NH_4 -N volatilisation during the sorption phase. Buffering of high pH values in the biochar suspensions could be the reason for the enhanced volatilisation of ammonia in the unwashed/high ash biochars. Washing the activated biochars until the EC of the effluent reaches $50 \mu\text{S cm}^{-1}$ enhanced the sorption capacity of biochars to greater than the unwashed activated biochars. This is caused by removal of ashes or cations binding or competing with NH_4^+ sorption sites in the porous structure of biochar. Chemically activated washed biochars proved better NH_4^+ sorbents than the unwashed biochars. It is thereby recommended that chemically activated biochars be washed prior to sorption of cations or pollutants for better results.

References

- Bolan N, Wong L, Adriano D (2004) Nutrient removal from farm effluents. *Bioresource Technology*. 94(3), 251-260.
- Cheng CH, Lehmann J, Thies JE, Burton SD, Engelhard MH (2006) Oxidation of black carbon by biotic and abiotic processes. *Organic Geochemistry*. 37(11), 1477-1488.
- Cooney E, Booker N, Shallcross D, Stevens G (1999) Ammonia removal from wastewaters using natural Australian zeolite. II. Pilot-scale study using continuous packed column process. *Separation Science and Technology*. 34(14), 2741-2760.
- Hedström A (2001) Ion exchange of ammonium in zeolites: A literature review. *Journal of Environmental Engineering*. 127(8), 673-681.
- Lehmann J, Joseph S (2009) Developing a biochar classification and test methods. J. Lehmann, S. Joseph (Eds.), *Biochar for Environmental Management: Science and Technology*, Earthscan, London, pp. 107-117.
- Montes F, Rotz CA, Chaoui H (2009) Process Modeling of ammonia volatilization from ammonium solution and manure surfaces: A review with recommended Models. *Transactions of the ASABE. American Society of Agricultural and Biological Engineers*. 52, 1707-1719.
- Nguyen M, Tanner C (1998) Ammonium removal from wastewaters using natural New Zealand zeolites. *New Zealand Journal of Agricultural Research*. 41, 427-446.
- Poach ME, Hunt PG, Sadler EJ, Matheny TA, Johnson MH, Stone KC, Humenik FJ, Rice JM. (2002) Ammonia volatilization from constructed wetlands that treat swine wastewater. *Transactions of the ASAE*. 45, 619-627.
- Wieczorek S (2008) Assessing the Influence of Adsorbent Bed (Tree Bark) Parameters on the Reduction of Ammonia Emissions from Animal Husbandry. *Polish Journal of Environmental Studies*. 17(1), 147-154.

Chapter 6

Ammonium removal from wastewater by Batch and flow through (column) studies

6.1 Introduction

In Chapter 3, different chemically and steam activated biochars were characterised and chemically activated biochars were evaluated for NH_4^+ -N sorption from ammonium salt solutions. In this Chapter further research is conducted to compare the sorption of NH_4^+ -N from chemically complex wastewaters by biochars produced from activated and non-activated pine wood chips and eucalyptus bark using batch and column studies (flow through studies).

When urban and agricultural wastewaters are discharged to fresh water lakes and streams, eutrophication can result. Although these wastewaters are often treated in two-pond (an anaerobic pond followed by an aerobic pond) treatment systems, they can still contain excessive levels of nitrogen (N) and phosphorus (P), which have negative effects on the receiving waters (Longhurst et al. 2000; Oledzka, 2007; McArthur and Clark, 2007).

There are many towns in New Zealand that continue to discharge pond-treated sewage wastewater into fresh surface waters. For example, in the Manawatu-Wanganui Region, there are over 30 towns with sewage wastewater discharges (mean 1700 m³/day, McArthur and Clark, 2007). At some river sites, for example downstream of the Palmerton North and Feilding sewage treatment plant outfalls, sewage wastewater discharges are the predominant source of SIN (soluble inorganic nitrogen), particularly ammonium (NH_4^+), during low river flow conditions. Ammoniacal N (ammonia and ammonium) in wastewaters can promote eutrophication of receiving waters, which has been proven toxic to fish and other aquatic life (Nguyen and Tanner, 1998).

Historically, most dairy farms in New Zealand also discharged their pond-treated farm dairy wastewater to rivers and lakes. In 1998 over 300 dairy farms discharged their wastewater

into the Manawatu River. However, by 2010 this number had decreased to only 2, which was primarily due to the widespread adoption of land treatment. However, in some regions, such as the Taranaki Region, a large proportion of farms still use two-pond treatment and discharge their wastewater to fresh water streams. As previously discussed two-pond treated wastewaters can be high in N, particularly ammonium, so can contribute to degrading water quality (Longhurts et al. 2000; Houlbrooke et al. 2004).

Reducing the levels of NH_4^+ in the wastewater discharges described above is expected to improve river water quality. Improving the effectiveness of aerobic pond treatment, for example by using aerators to increase the nitrification process, is a common method for reducing NH_4^+ levels. However, aerators require a relatively high input of power to operate effectively and typically don't remove all the NH_4^+ . Therefore, it would be an advantage to have an additional treatment method to further remove NH_4^+ from wastewaters. Active filters, which include reactive media, have shown promise in removing N from wastewater (Chang et al. 2002). Sorption of NH_4^+ on various adsorbents such as coal, bark and zeolites has been reported (Cooney et al. 1999; Bolan et al. 2004). Bolan et al. (2004) observed a maximum adsorption for NH_4^+ ion by the untreated bark, treated bark (treated with industrial waste product i.e. slaked fluidized bed boiler ash-FBA) and zeolite at 10.4, 14.6 and 16.9 g NH_4^+ -N kg^{-1} , respectively.

Biochars, such as wood charcoals and crop residue-derived chars, refer to the carbon-rich residues from pyrolysis of biomass in absence of oxygen (Chen et al. 2008). Agricultural wastes or residues including corncob, elephant grass and rapeseed oil cake, are widely available low-cost raw materials used to produce biochar, as well as bio-oil and gases (Strezov et al. 2008; Ucar and Ozkan, 2008; Zhang et al. 2009). Dairy-manure biochar effectively removed lead and atrazine simultaneously with little competition effect due to the different retention mechanisms of both (Cao et al. 2009). Taghizadeh-Toosi et al. (2011) exposed biochars to ^{15}N enriched ammonia (NH_3) and obtained a final ^{15}N enrichment of 5.36 atom%. These authors reported that when NH_3 gas was absorbed on biochar (produced from *Pinus radiata* at 300, 350 and 500 °C), a considerable fraction of it (11-26 % in leaves) remained bioavailable, thereby showing the biochar's potential use as fertiliser.

It has been proposed that activated biochar with increased acidic functional groups could be used for wastewater treatment. However, there have been very few studies conducted with the aim to activate biochar and enhance its sorption capacity. Some studies have used steam activation to increase the cation exchange capacity of biochars and, thus, improve nutrient retention in soils. In the previous chapter of this thesis (Chapter 3), biochars from pine and eucalyptus wood were activated with alkaline tannery waste and steam activation, and some improvement regarding acidic functional groups (tannery waste treatment) and BET surface area (Steam activation) were measured. The objective of this paper was to evaluate the effectiveness of tannery waste treated biochars and untreated biochars at removing the NH_4^+ -N from aerobic pond treated farm dairy and town sewage wastewaters.

6.2 Materials and Methods

6.2.1 Materials

Pine (PI) and Eucalyptus (EU) waste barks used in this study were supplied by Carter Holt Harvey NZ Ltd. The PI bark was chipped with a commercial chipper while the EU bark was used after chipping with a laboratory chipper. The particle size range for chipped PI bark was 3-11 mm in length and chipped EU was 2-5 mm. These feedstocks were oven-dried at 65 °C. Acid washed sand was collected from Ajax Fine chem. Pty Ltd, NZ.

Liquid tannery lime float waste was used as an alkaline pre-treatment of both bark feedstocks, prior to pyrolysis (Chapter 5). The biochars made with pre-treatment PI and EU bark are referred to here after as L PI and L EU biochars, respectively. Biochars made with untreated PI and EU bark (Control) are referred to as Ctr PI and Ctr EU biochars, respectively.

Two different types of wastewaters, farm dairy (FD) and town sewage treatment plant (STP) wastewaters were used for this study. The FD wastewater was collected from the aerobic treatment pond at Massey University's No. 4 Dairy Farm, near Palmerston North (NZ), on June (FD-A) and August (FD-B) 2010, with NH_4^+ -N concentrations of 20 and 80 $\mu\text{g N mL}^{-1}$, respectively (Table 6.1). Sewage treatment plant wastewater was collected from the Ashhurst (NZ) wastewater treatment ponds on September, 2010 (STP-C) and January 2011, (STP-D) with NH_4^+ -N concentrations of 11.87 and 6 $\mu\text{g N mL}^{-1}$, respectively.

Table 6.1 Wastewaters composition.

Sample (Collection date)	K ($\mu\text{g mL}^{-1}$)	Na ($\mu\text{g mL}^{-1}$)	Ca ($\mu\text{g mL}^{-1}$)	Mg ($\mu\text{g mL}^{-1}$)	S ($\mu\text{g mL}^{-1}$)	$\text{NH}_4^+\text{-N}$ ($\mu\text{g mL}^{-1}$)
FD-A (June 2010)	146.3	24.7	59.58	18.6	3.2	20
FD-B (August 2010)	175.7	30.5	68.9	23.4	2.7	80
STP-C (September 2010)	103.9	26.4	31.6	5.3	7.1	11.8
STP-D (January 2011)	90	30	29	10	-	6.0

6.2.2 Methods

Carbonisation Processes.

Details of biochar carbonisation and characterisation are provided in full in Chapter 5.

Ammonium removal studies

All of the biochar treatments were ground and sieved to 2 mm particle size range and evaluated for their ability to remove $\text{NH}_4^+\text{-N}$ in all experiments except 2-3 mm size was used in column study C. Both batch (isonormal sorption) and flow through (leaching column) experiments were conducted at ambient temperature ($21 \pm 1^\circ\text{C}$).

Batch sorption study

Each biochar treatment (2 g per sample) was shaken for 20 hours, on an end-over-end shaker, with 20 mL of one of four different solutions (in 30 mL centrifugation tubes); three different isonormal ammonium chloride-sodium and potassium chloride ($\text{NH}_4\text{Cl} - \text{NaCl} \& \text{KCl}$ [1:1]) solutions: total 0.1 M) and one type of wastewater (FD-A; Table 6.1). Each biochar:solution combination was replicated three times. The NH_4Cl and $\text{NaCl} - \text{KCl}$ concentration in these isonormal solutions were 0.001, 0.01, 0.025 M NH_4Cl (containing 14, 140, 350 ppm $\text{NH}_4\text{-N}$) and 0.099, 0.090, and 0.075 M $\text{NaCl} - \text{KCl}$ (1:1), respectively, which maintained a constant ionic strength. The FD-A wastewater was also included as an additional treatment in this batch experiment to assess $\text{NH}_4^+\text{-N}$ sorption from a natural wastewater. The filtrates from this experiment were analysed for $\text{NH}_4^+\text{-N}$ calorimetrically (Blakemore et al. 1987) with a Technicon II segmented-flow autoanalyser.

Flow through (Column) Studies

The retention and sorption of $\text{NH}_4^+\text{-N}$ by all biochar treatments were assessed in replicated column studies. The influence of column size, influent flow rate, and influent solution type were also assessed and is described below:

1) In the first column study (Column study A), columns (10 mL) measuring 11-15 mm in diameter (15 mm diameter at top and tapering down to 11 mm at the bottom) and 130 mm in height (16 and 100 mL/min for equivalent of 1 litre filter @ 0.16 and 1 mL/min flow rate, respectively) were used for this study. Filter paper was placed at the bottom of the columns, and then each was filled with 3 g of acid-washed silica sand and 1 g of biochar on top. Each biochar treatment was used in three replicated columns. Deionized water was pumped through the columns, by the peristaltic pump at two flow rates (1 mL min^{-1} and 0.16 mL min^{-1}), until electrical conductivity (EC) of the effluent solution was 50 $\mu\text{S cm}^{-1}$ to minimise the ash and tar present in the biochars. The effluent was collected hourly for three hours and EC was determined on each sample. The FD-A wastewater was then pumped into each of the columns also at the two flow rates previously mentioned. At the flow rate of 1 mL min^{-1} leachates were collected every 15 minutes. At the 0.16 mL min^{-1} flow rate leachates were collected every 6 minutes (i.e. 1 mL) for up to 2 pore volumes (3.5 mL was one pore volume) and then every 30 minutes (i.e. 5 mL) subsequently. Experiments were also conducted with columns being treated with the FD-B wastewater, but only at the lower flow rate (0.16 mL min^{-1}). Leachates were collected until the effluent $\text{NH}_4^+\text{-N}$ concentration was the same as the influent concentration. The columns were then pumped with deionised water for one hour and then with a 1 M KCl solution, at a 0.16 mL min^{-1} flow rate, to quantify $\text{NH}_4^+\text{-N}$ desorption. All samples in this experiment were analysed for $\text{NH}_4\text{-N}$ calorimetrically (Blakemore et al. 1987) with a Technicon II segmented-flow autoanalyser.

2) In a second column study (Column study B), columns (60 mL) measuring 29 mm in diameter and 130 mm in height (2.67 mL/min for equivalent of 1 litre filter) were used. Each column had filter paper placed at the bottom, and was then filled with 3 g of silica sand, followed by with 6 g biochar and a flow rate of 0.16 mL min^{-1} . The $\text{NH}_4^+\text{-N}$ sorption properties of L PI biochar were investigated using two concentrations ($\text{NH}_4^+\text{-N}$; 11.87 and 5.38 $\mu\text{g mL}^{-1}$; diluted wastewater) of the same urban wastewater (STP-C) in columns. An

artificial ammonium salt solution containing $35 \mu\text{g N mL}^{-1}$ was also tested under similar conditions.

3) In a final column study (Column study C), larger columns (300 mL) measuring 80 mm in diameter and 140 mm in height (2.67 mL/min for equivalent of 1 litre filter) were used. A polyethylene cloth based perforated sieve was fixed at the bottom of each column and a total of 40 g of L PI biochar was added. Sand was not used in this study. The STP-D wastewater (Table 6.1, $6 \mu\text{g NH}_4^+\text{-N mL}^{-1}$) was fed through each column at a flow rate of 0.8 mL min^{-1} . Leachates were sampled once per day and analysed for $\text{NH}_4^+\text{-N}$ until the influent $\text{NH}_4^+\text{-N}$ concentrations were equal to the effluent concentrations, which indicated that $\text{NH}_4^+\text{-N}$ sorption had ceased.

6.2.3 Statistical Analysis

The data was analysed using ANOVA by SAS statistical software. The standard error calculations were calculated using Excel 2010 (Microsoft Corporation).

6.3 Results and Discussion

Batch sorption study

In the batch sorption study, $\text{NH}_4^+\text{-N}$ sorption by the biochars increased with increasing $\text{NH}_4^+\text{-N}$ solution concentration (Fig. 6.1). The maximum $\text{NH}_4^+\text{-N}$ sorption capacity, of $2.80 \text{ mg NH}_4^+\text{-N g}^{-1}$ biochar (40.1% of the $\text{NH}_4^+\text{-N}$ added), was achieved by the L PI treatment with the 0.025 M solution ($350 \mu\text{g mL}^{-1} \text{ NH}_4^+\text{-N}$). The other treated biochar (L EU) achieved the second highest level of $\text{NH}_4^+\text{-N}$ sorption of 2.60 mg N g^{-1} biochar (37% of added $\text{NH}_4^+\text{-N}$). The untreated biochars achieved lower levels of sorption, approximately: 2.2 mg g^{-1} from $0.025 \text{ M NH}_4^+\text{-N}$ solution, which was approximately 80% of the $\text{NH}_4^+\text{-N}$ sorption of their respective activated counterparts (L PI and L EU). The higher $\text{NH}_4^+\text{-N}$ sorption ability of the activated biochars was found to be dependent on the influent NH_4^+ concentration. The alkaline activated biochars showed development of acidic functional groups and enhanced sorption capacity of $\text{NH}_4^+\text{-N}$ (Chapter 5).

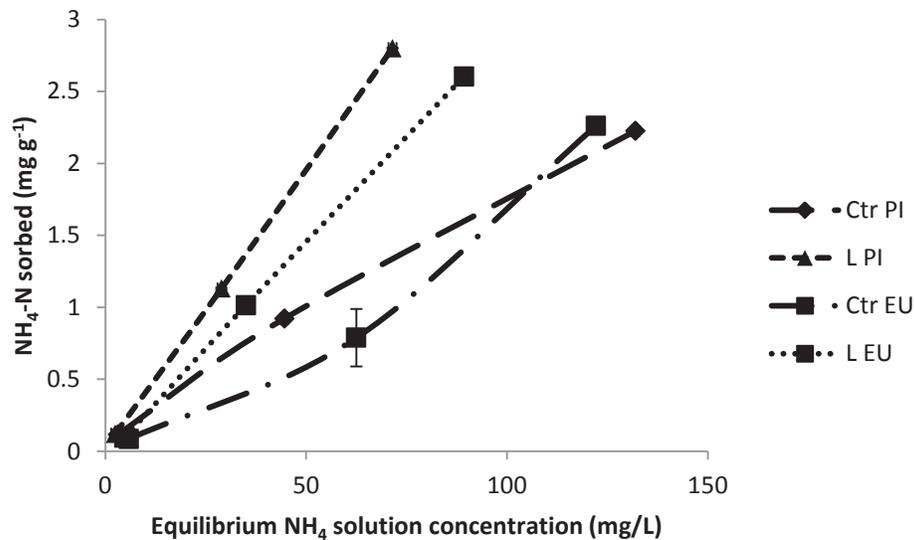


Figure 6.1 Isonormal NH_4^+ -N sorption study with synthetic solutions (starting concentrations were 14, 140, 350 $\mu\text{g NH}_4^+$ -N mL^{-1}).

where Ctr PI=control pine biochar, L PI=liquid tannery waste pre-treated biochar, Ctr EU=control Eucalyptus biochar, L EU=liquid tannery waste pre-treated biochar;(Error bars show the SE); Equilibrium solution concentration is final solution concentration.

The L PI biochar also achieved the highest sorption of NH_4^+ -N from the FD-A (20 $\mu\text{g NH}_4^+$ -N mL^{-1}) wastewater, with total sorption of 0.16 mg N g^{-1} biochar (Fig. 6.2), which was 41% of the NH_4^+ -N added. For this biochar, this was lower compared to the quantity of NH_4^+ -N sorbed from the 350 and 141 $\mu\text{g NH}_4^+$ -N mL^{-1} ammonium salt solutions, but similar to the amount sorbed from the 14.5 $\mu\text{g NH}_4^+$ -N mL^{-1} solution. The Ctr EU and L EU biochar achieved similar levels of sorption as the L PI biochar. However, the Ctr PI biochar achieved a level of sorption substantially lower than the other biochars, being 0.058 mg N g^{-1} biochar, which was only 14 % of the NH_4^+ -N added.

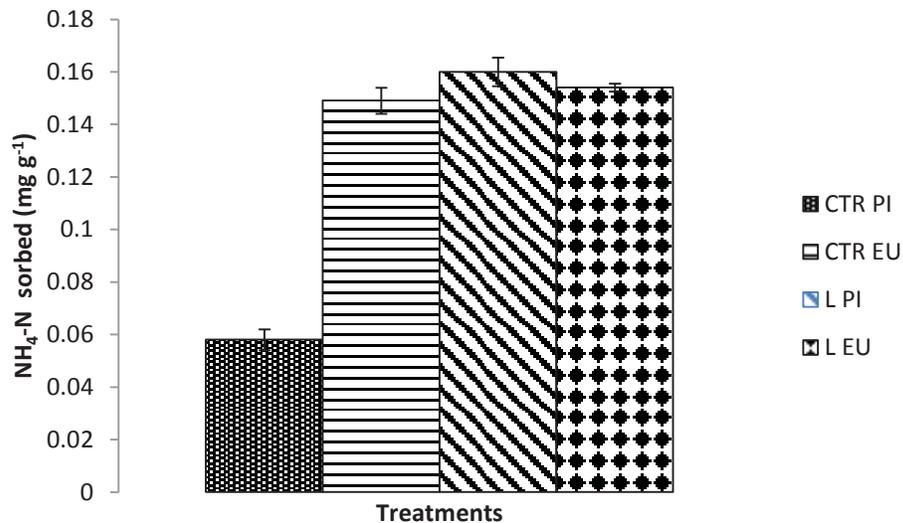


Figure 6.2 NH₄⁺-N sorption from FD-A wastewater in batch sorption study where Ctr PI=control pine biochar, L PI=liquid tannery waste pre-treated biochar, Ctr EU=control Eucalyptus biochar, L EU=liquid tannery waste pre-treated biochar

Flow through or Column NH₄⁺-N sorption experiments

The sorption of NH₄⁺-N from dairy wastewater by column experiments was assessed at two different flow rates: 1 and 0.16 mL min⁻¹. At the higher flow rate (1 mL min⁻¹), the L PI biochar showed highest sorption of 1.32 mg NH₄⁺-N g⁻¹, followed by Ctr Eu=L EU (1.13-1.15 mg g⁻¹) then Ctr PI (0.71 mg g⁻¹). The pine biochar showed significantly increased NH₄⁺-N sorption capacity with chemical activation as compared to Eucalyptus (Fig. 6.3). In case of the slower flow rate (0.16 mL min⁻¹), the sorption trend was as follows: L PI> L EU> Ctr EU> Ctr PI. The maximum sorption recorded was 1.67 mg g⁻¹ for the L PI biochar (Fig. 6.4).

The slower flow rate (0.16 mL min⁻¹), or the longer residence time, and higher solution NH₄⁺-N concentration resulted in more sorption (1.67 mg g⁻¹) in L PI than for the faster flow rate of 1 mL/min (1.32 mg g⁻¹) (Fig. 6.3 and 6.4). This could be due to increased contact time between the wastewater with biochar particles made possible by the longer residence duration. The different experiments done in this chapter were not meant to be compared on the basis of their different influent concentrations or contact times. Almost all the biochars gradually lost their effectiveness as they become saturated with NH₄⁺-N. However, this did not occur until the eluted volume reached 67 mL of wastewater at the 0.16 mL min⁻¹ flow rate (80 µg mL⁻¹ NH₄⁺-N) study and 165 mL at the 1 mL min⁻¹ flow rate of 20 µg mL⁻¹ NH₄⁺-N wastewater

study for L PI biochar (Fig. 6.3, 6.4). Activation of EU biochar did not give any significant differences in sorption efficiency as compared to its control EU biochar, thereby only L PI was carried forward for further investigation.

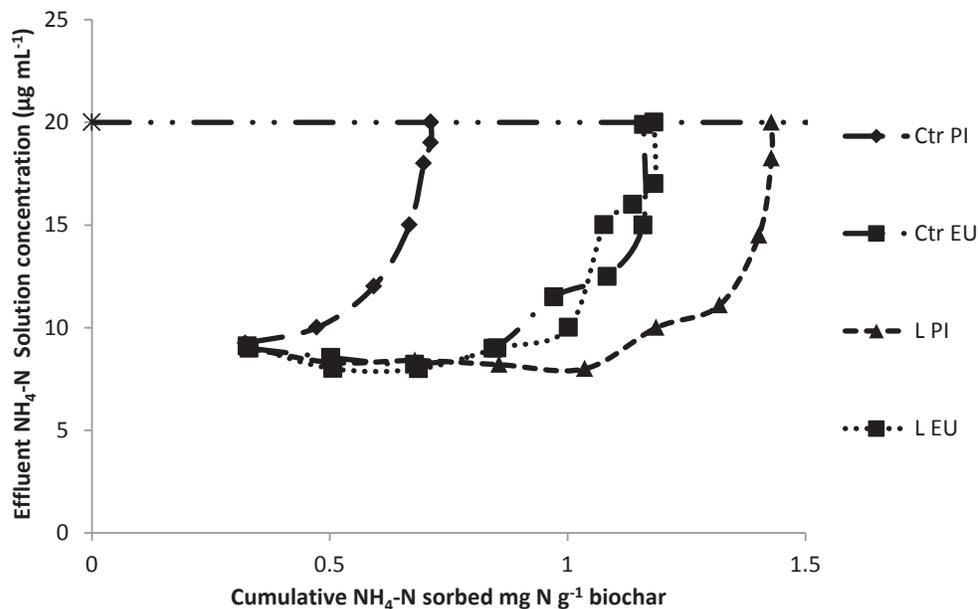


Figure 6.3 Cumulative NH_4^+ -N sorbed from dairy wastewater @ 1 mL/min (column, 11-15 mm diameter) (Column study A).

where Ctr PI=control pine biochar, L PI=liquid tannery waste pre-treated biochar, Ctr EU=control Eucalyptus biochar, L EU=liquid tannery waste pre-treated biochar

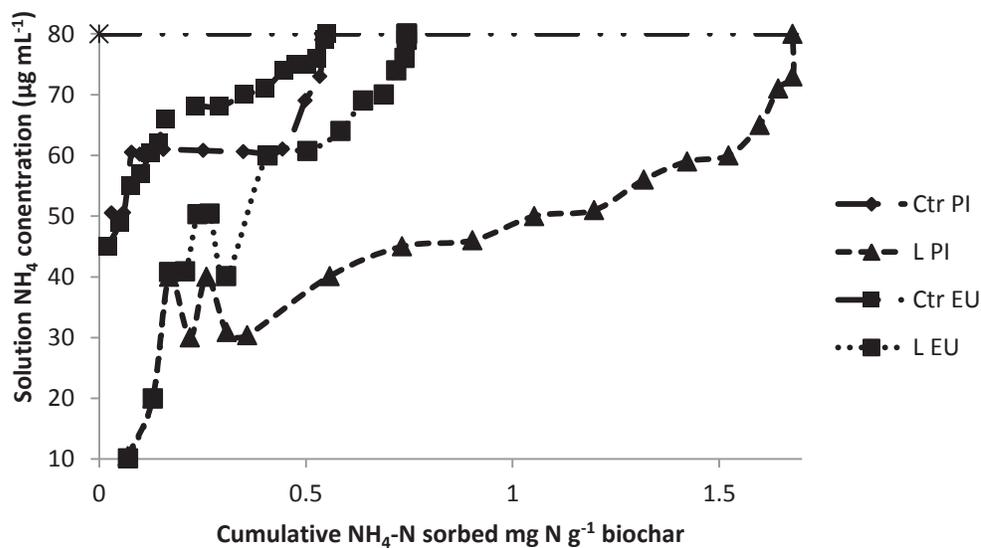


Figure 6.4 Cumulative NH_4^+ -N sorbed from dairy wastewater @ 0.16 mL/min (column, 11-15 mm diameter); (Column study A).

where Ctr PI=control pine biochar, L PI=liquid tannery waste pre-treated biochar, Ctr EU=control Eucalyptus biochar, L EU=liquid tannery waste pre-treated biochar

The $\text{NH}_4^+\text{-N}$ sorbed on biochar under the slower flow rate (0.16 mL min^{-1}) was subjected to desorption by 1M KCl (Fig. 6.5). Maximum desorption was observed from EU biochars (Ctr EU= 0.26 mg g^{-1} , 47 % of sorbed $\text{NH}_4^+\text{-N}$) followed by PI biochars (L PI= 0.22 mg g^{-1} , 13 % of sorbed $\text{NH}_4^+\text{-N}$). The reason for the higher desorption by EU biochar could be due to its finer particle size. Overall, the desorption of $\text{NH}_4^+\text{-N}$ was low (% range) compared to its sorption, thereby, CEC was not the contributing sorption mechanism of ammonium on biochar. So clearly, some other mechanisms like chemical reaction with sulphonate groups developed from tannery waste activation or some sorption in micropores playing a role in increased retention of $\text{NH}_4^+\text{-N}$ on biochar. Toosi et al. (2011) also reported relatively low recovery of adsorbed NH_3 from biochars by KCl extraction. This could be attributed to an increase in coulombic forces that prevented a fast desorption. However, other mechanisms could also be involved in $\text{NH}_4^+\text{-N}$ retention, such as chemisorption-ammonia fixation (Stevenson 1982) or the role of S-functional groups (Petit et al. 2010).

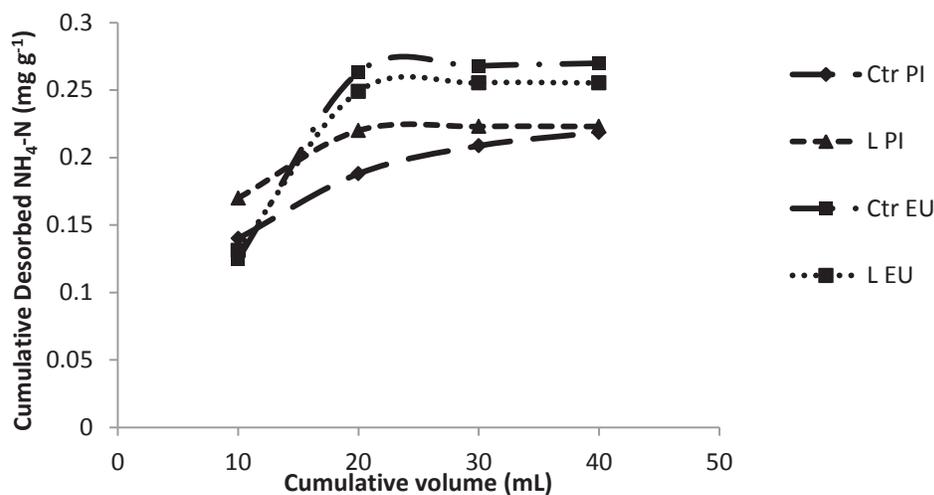


Figure 6.5 Desorption of $\text{NH}_4^+\text{-N}$ by KCl from different biochars (Column study A). where Ctr PI=control pine biochar, L PI=liquid tannery waste pre-treated biochar, Ctr EU=control Eucalyptus biochar, L EU=liquid tannery waste pre-treated biochar.

In Column study B, the $\text{NH}_4^+\text{-N}$ sorption from sewage treatment plant wastewater was assessed for the L PI biochar (Fig. 6.6). The % $\text{NH}_4^+\text{-N}$ sorption was lower with the $11.87 \mu\text{g N mL}^{-1}$ influent concentration (58 % removal), compared with the $5.38 \mu\text{g N mL}^{-1}$ (62 %) solution. However, using the $11.87 \mu\text{g N mL}^{-1}$ influent solution, the total $\text{NH}_4^+\text{-N}$ sorption by the L PI biochar was 1.99 mg g^{-1} as compared to 1.30 mg g^{-1} with the lower concentration solution.

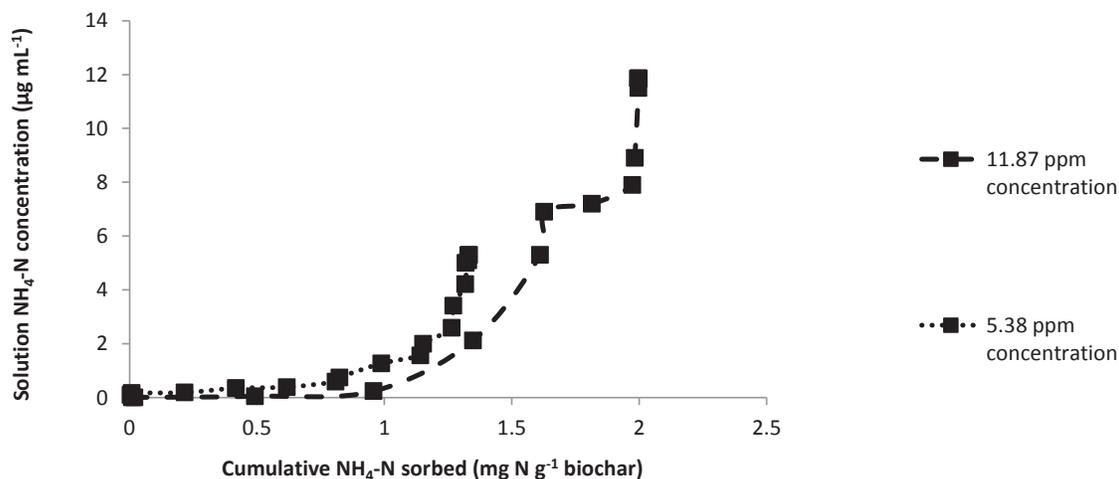


Figure 6.6 Ammonium-N sorption on L PI biochar with urban wastewater under two concentrations @ 0.16 mL min^{-1} (columns, 29 mm diameter) (Column study B).

In Column study B, the L PI biochar removed 2.40 mg N g^{-1} biochar from the synthetic $35 \text{ } \mu\text{g N mL}^{-1}$ synthetic $\text{NH}_4^+\text{-N}$ solution (Fig. 6.7). This was the highest level of $\text{NH}_4^+\text{-N}$ sorbed in this series of column studies as compared to previous column studies with wastewaters, which might be due to the increased competition for the $\text{NH}_4^+\text{-N}$ sorption sites from other cations in wastewaters (Nguyen and Tanner, 1998) compared with synthetic solutions. It can also be due to presence of dissolved organic matter in wastewaters that may engage the sorption sites on the biochar, thereby reducing the sorption capacity.

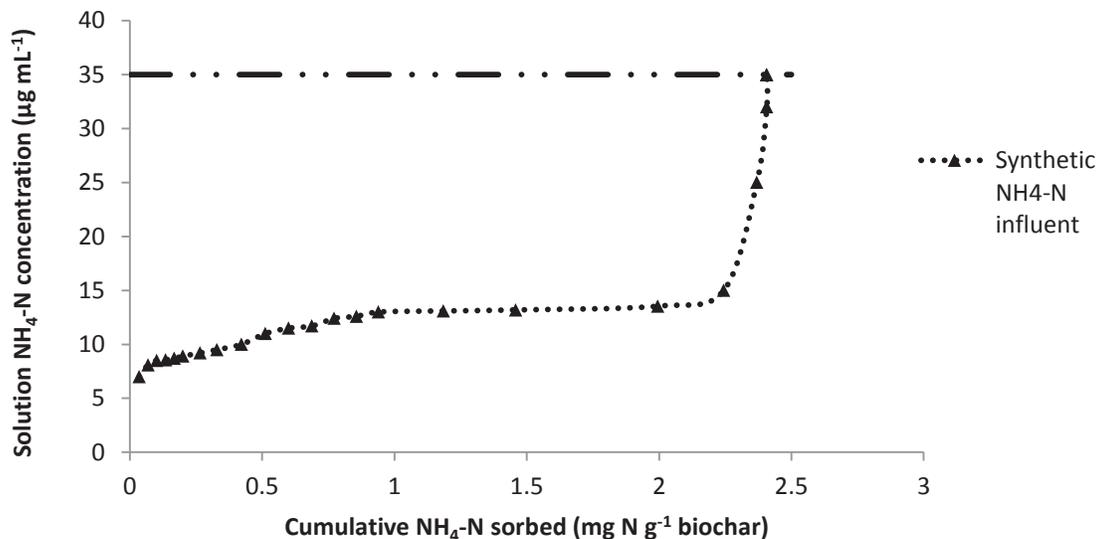


Figure 6.7 Ammonium ($\text{NH}_4^+\text{-N}$) sorption on L PI biochar from synthetic $\text{NH}_4\text{-N}$ water solution (Column study B, 0.16 mL min^{-1} flow rate, 35 ppm influent solution and 4 g biochar).

The bigger columns (80 mm diameter) with only L PI biochar (column study: C) @ 0.8 mL min^{-1} flow rate gave total sorption of $2.17 \text{ mg g}^{-1} \text{ NH}_4^+\text{-N}$ sorbed with urban wastewater (Fig. 6.8). Sorption was lower in this study with wastewater than that in the synthetic influent column study (2.40 mg g^{-1}), which was the expected result from previous studies. The particle size of the biochar used in this study was slightly coarser (2-3 mm) than the previous studies in order to handle the biochar in bigger columns with no sand at the bottom.

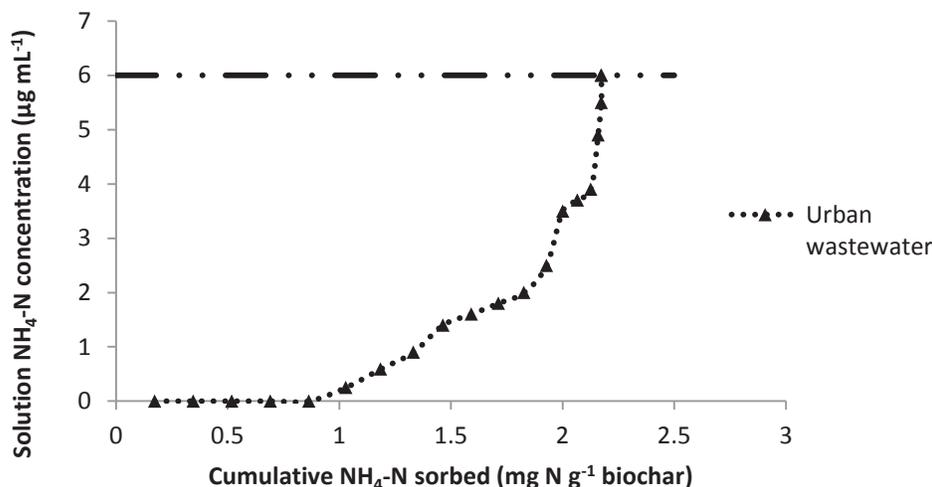


Figure 6.8 Ammonium-N sorption on L PI biochar in 80 mm diameter columns using urban wastewater with a NH_4^+ -N (Column study C, Influent concentration = 6 ppm, Biochar=40 g, Flow rate= 0.8 mL min^{-1}).

6.4 Conclusion

The results from this chapter confirmed the results from previous chapter that biochar sorbs NH_4^+ -N and sorption increases with activation of biochar but the scale of increase did not significantly increase activated biochar's potential for wastewater treatment. The NH_4^+ -N removal of biochars in batch and column studies were found to be dependent on the flow rate, influent concentration, competing cations and contact time between wastewater and biochar particles. Removal efficiency decreased as usual with the increase in influent concentration. Activated EU biochar did not give promising increase in sorption capacity so was not selected for use in later studies. L PI proved best sorbent for NH_4^+ -N and had considerable potential for removing NH_4^+ -N from wastewaters than other biochars and was selected for further study.

The comparison of removal of NH_4^+ -N by biochars from wastewater and ammonium salt solutions showed a little interference from competing cations and anions in the wastewater, therefore the ammonium salt solutions provided appropriate models for sorbent development. Only a small percentage of the sorbed N can be desorbed from all the N loaded biochars indicating that land application may provide the most appropriate use of the N loaded biochar. Based on the Column study C, in which the L PI biochar sorbed $2.17 \text{ mg g}^{-1} \text{ NH}_4^+$ -N from urban wastewater which is equivalent to $2.17 \text{ kg N tonne}^{-1}$ of biochar. For a town with

population of 3000 people producing 1000 m³/day of wastewater from two pond treatment system, the amount of NH₄⁺-N discharged will be 6 kg NH₄⁺-N/ day. Therefore, we need almost 3 tonnes/day of L PI biochar to sorb 6 kg NH₄⁺-N/day. This will remove 70-80% of NH₄⁺-N from wastewater. The acquisition of 3 tonnes/day (approximately 15 m³ /day) is not currently a cost effective NH₄⁺-N removal system for practical wastewater treatment in towns. Further research is required either to increase NH₄⁺-N sorption in biochar or show that the N loaded biochar has a recoverable value as a fertiliser.

References

- Blakemore LC, Searle PL, Daly BK (1987) Methods for chemical analysis for soils. *NZ Soil Bureau Scientific report*. 80, 78–79.
- Bolan N, Wong L, Adriano D (2004) Nutrient removal from farm effluents. *Bioresource technology*. 94(3), 251-260.
- Cao X, Ma L, Gao B, Harris W (2009) Dairy-manure derived biochar effectively sorbs lead and atrazine. *Environmental Science and Technology*. 43, 3285-3291.
- Chang WS, Hong SW, Park J (2002) Effect of zeolite media for the treatment of textile wastewater in a biological aerated filter. *Process Biochemistry*. 37(7), 693-698.
- Chen B, Chen Z (2009) Sorption of naphthalene and 1-naphthol by biochars of orange peels with different pyrolytic temperatures. *Chemosphere*. 76, 127-133.
- Chen B, Chen Z, Lv S (2011) A novel magnetic biochar efficiently sorbs organic pollutants and phosphate. *Bioresource Technology*. 102, 716-723.
- Chen B, Zhou D, Zhu L (2008) Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures. *Environmental Science and Technology*. 42, 5137–5143.
- Cooney E, Booker N, Shallcross D, Stevens G (1999) Ammonia removal from wastewaters using natural Australian zeolite. II. Pilot-scale study using continuous packed column process. *Separation Science and Technology*. 34(14), 2741-2760
- Houlbrooke DJ (2008) Best practice management of farm dairy effluent in the Manawatu-Wanganui region. Report prepared for Horizons Regional Council (February 2008).
- Houlbrooke DJ, Horne DJ, Hedley MJ, Hanly JA, Scotter DR, Snow VO (2004) Minimising surface water pollution resulting from farm-dairy effluent application to mole-pipe drained soils. I. An evaluation of the deferred irrigation system for sustainable land treatment in the Manawatu. *New Zealand Journal of Agricultural Research* 47, 405-415.
- Longhurst RD, Roberts AHC, O'Connor MB (2000) Farm dairy effluent: a review of published data on chemical and physical characteristics in New Zealand. *New Zealand Journal of Agricultural Research*. 43, 7-14.

- McArthur K, Clark M (2007) Nitrogen and phosphorus loads to rivers in the Manawatu-Wanganui Region: An analysis of low flow state: Technical Report to support Policy Development. New Horizons Regional Council. Report No: 2007/EXT/793, pp.14-77.
- Nguyen M, Tanner C (1998) Ammonium removal from wastewaters using natural New Zealand zeolites. *New Zealand Journal of Agricultural Research*. 41, 427-446.
- Oledzka M (2007) Substrate selection for Constructed Wetlands. Thesis presented for MSc. Faculty of Bioengineering. Universiteit Gent, pp. 4-61.
- Petit C, Kante K, Bandosz TJ (2010) The role of sulphur-containing groups in ammonia retention on activated carbons. *Carbon*. 48, 654-667.
- Stevenson FJ (1982) Ammonia reactions. In: 'Humus Chemistry. Genesis Composition; Reactions'. (Wiley Interscience publication, New York). pp. 101-105.
- Strezov V, Evans TJ, Hayman C (2008) Thermal conversion of elephant grass (*Pennisetum Purpureum Schum*) to bio-gas, bio-oil and charcoal. *Bioresource Technology*. 99, 8394–8399.
- Singh B., Singh BP, Cowie AL (2010) Characterisation and evaluation of biochars for their application as a soil amendment. *Australian Journal of Soil Research*. 48(7), 516-525.
- Taghizadeh-Toosi A, Clough TJ, Sherlock RR, Condon LM (2011) Biochar adsorbed ammonia is bioavailable. *Plant and Soil*. pp. 1-13.
- Ucar S, Ozkan AR (2008) Characterization of products from the pyrolysis of rapeseed oil cake. *Bioresource Technology*. 99, 8771–8776.
- Zhang H, Xiao R, Huang H, Xiao G (2009) Comparison of non-catalytic and catalytic fast pyrolysis of corncob in a fluidized bed reactor. *Bioresource Technology*. 100, 1428–1434.

Chapter 7

Ammonium and phosphorus removal from wastewater using weathered volcanic tephra and biochar combinations

7.1 Introduction

Surface waters receiving high inputs of the nutrients nitrogen (N) and phosphorus (P) are prone to eutrophication (Baker et al. 1998), which can cause degradation in environmental quality. As discussed in previous chapters, pollution of rivers, particularly in the Manawatu region, New Zealand, is currently a problem with point discharges of sewage treatment plant wastewater from towns contributing to the river's N and P loads. These discharges contribute to elevated ammonium (NH_4^+) and dissolved reactive phosphorus (DRP) levels, particularly during low river flow conditions. For example, about half of the sites sampled in the Manawatu River exceeded the council's recommended levels of DRP when the river was at MALF (mean annual low flow) (McArthur and Clark, 2007).

Various studies have been conducted using different P adsorbing materials to remove P from wastewaters; this included the use of iron and aluminium oxy-hydroxides (Baker et al. 1998) and volcanic tephra containing allophane (Hanly et al. 2008). Tephra is a term for all the fine fragmental material erupted explosively from a volcano. As a soil forming material, pedogenic processes can create short-range order weathering products from the tephra, such as amorphous aluminium-silicates (allophane). Allophane has a high positively charged specific surface area that provides tephra with a high P-adsorbing capacity (Ryden and Syers, 1975), possibly by specific adsorption of H_2PO_4^- . Passing dairy and urban effluent through tephra columns have been shown to be an effective technique for P removal (Hanly et al. 2008, Liesch, 2010). Further work is being conducted to identify high P sorbing tephra and to test the practical feasibility of using large tephra filters (pilot studies) for cleaning up urban wastewater (J.A.Hanly pers.com.)

In Chapter 6, it was demonstrated that NH_4^+ can be removed from dairy and urban wastewaters by passing the effluents through biochars made from pine and eucalyptus. In order to remove both NH_4^+ and DRP from wastewaters, it has been proposed that a dual

active filter system containing biochar, for NH_4^+ removal, and tephra, for DRP removal, could be used. In the study described in the current chapter, the two materials are combined to investigate whether combinations of biochar and tephra can be used to simultaneously remove NH_4^+ and DRP from wastewaters.

The objectives of this study were:

- 1) To develop a biochar-tephra filtration system for urban wastewater treatment and assess its feasibility with special attention to the removal of NH_4^+ and DRP from wastewaters.
- 2) To assess the nature of P retained on the filters by chemical fractionation and x-ray diffraction analyses.

7.2 Materials and Methods

7.2.1 Materials

The wastewaters (Table 7.1) used in the experiment was collected from the Ashhurst treatment plant (North Island, New Zealand) and a coarse screen was used to remove the majority of the algae and particulates. The sorbent materials used were Okato tephra (T) and washed pine biochar treated with alkaline tannery waste prior to pyrolysis at 550 °C, as described in Chapter 5 of thesis, and is denoted L PI biochar. Both materials were passed through a 2 mm sieve prior to their use in columns. Their chemical compositions of the tephra and biochar are reported in Tables 7.2 and 7.3, respectively. The Okato tephra was moderately weathered andesitic tephra subsoil collected from the North West Taranaki region (North Island, New Zealand). The location was the corner of Dover Rd and Carrington Rd (39° 13' 28.04' S; 173° 58' 01.05' E). It was sampled from the 0.5-1.5 m soil depth from a road-side cutting. Acid washed fine sand (Ajax Fine chem. Pty Ltd.) was also used in one column treatment.

7.2.2 Methods

Tephra column study design

Syringes (29 mm diameter and 13 cm height; 60 mL internal volume) were used as columns (Fig. 7.1). The following treatments were studied in duplicate:

- 1) Tephra + biochar mixture (25 mL of each, which corresponds to 7 g biochar and 20g tephra, respectively; mixed manually) filled 50 mL of the column (TE/BC-Mix)
- 2) Tephra was added first, filling the bottom 25 mL, then biochar was added, filling the top 25 mL (BC-TE)
- 3) Tephra was added first, filling the bottom 25 mL, then sand was added, filling the top 25 mL (Sand-TE)
- 4) Biochar was added first, filling the bottom 25 mL, then the tephra was added, filling the top 25 mL (TE-BC)

The order in which the tephra and biochar were packed into the columns was alternated for the different treatments to test whether order influenced retention of nutrients, or, whether there were interactions between effluent from one material with the retention of nutrients on the other. For example, when leached it was expected that the biochars would discharge a higher pH effluent, which could influence P sorption on the tephra.

Cotton wool was placed at the top of columns to aid wastewater distribution on the top of the filters. Columns were first leached with deionized water for 1 hour to pass through two pore volumes of water, and electrical conductivity (EC) was monitored in the leachates (data not shown). Thereafter, columns (Fig. 7.1) were pumped continually with wastewater and leachates were collected at 0, 2, 6, 24 hours, and then after every 2 days. Wastewater was sampled at the time of leachate collection. The wastewater flow rate into each column was 0.6 mL min^{-1} . The wastewater samples and leachates were analysed for NH_4^+ and DRP (dissolved reactive phosphate). Retention on the columns was calculated from the flow rate and the difference in the wastewater influent and effluent concentrations. Same volume of influent solution was passed from different columns. The word sorption is used in this study to describe retention of NH_4^+ and DRP in the columns. The experiment was run continually until the columns were saturated (influent concentration becomes equal to effluent) with NH_4^+ and DRP on sorption sites. The analysis of wastewaters is shown in Table 7.1.

Table 7.1 Ashhurst Urban wastewaters analysis.

Cations	8 April, 2011	14 April, 2011	20 April, 2011	1 May, 2011
	$\mu\text{g mL}^{-1}$			
Na	17.0	15.1	10.01	49.1
Ca	13.3	10.2	15.2	26.7
Mg	6.1	7.3	8.9	5.4
K	30.0	37.2	29.5	112.3
$\text{NH}_4^+\text{-N}$	19.0	18.5	19.1	20.0
DRP*	5.0	6.08	2.1	118.2

*Where DRP is dissolved reactive phosphate

**Figure 7.1** Column study setup

Phosphorus analysis of the wastewater and column leachates was conducted using the method described by Murphy and Riley (1962). For this, 5 mL solution was taken into a 50 mL volume-flask and 10 mL of Murphy and Riley reagent was added. The volume was made up to 50 mL and mixed thoroughly. Then the absorbance was read in a UV visible spectrophotometer autoanalyser. This assay measures all soluble phosphorus that reacts with the very acidic reagent and is referred to as dissolved reactive P (DRP). Ammonium analysis was carried out using an auto analyser (Blakemore et al. 1987).

The wastewater treated materials obtained from this column study, excluding the TE/BC-Mix columns, were removed and combined to make two homogenised samples; one of tephra and the other of biochar. Subsamples of these materials were taken for total N and P analysis prior to use in the bioassay trial conducted in Chapter 8. The detailed methodology of the physical and chemical analysis of biochars and soils are given in Chapters 5 and 8, with exception of total P analysis of biochar, which was determined after Kjeldahl's digestion (McKenzie and Wallace, 1954).

Phosphorus fractionation determination

Phosphorus fractionation of the tephra and biochar, before and after wastewater treatment, was carried out to determine the amount of P that was likely to be bioavailable in the short-term (Chapter 8). The first two steps of a common P fractionation method (Hedley et al. 1982), which measures the relatively available forms of P, were used. For this method, either 0.5 g of air dried tephra or 0.25 g of biochar (with particle size of < 2 mm for both sorbents) was weighed into centrifugation tubes and subjected to following steps:

i. Resin -P:

A regenerated anion exchange resin strip (AER) (HCO_3^- form) and a cation exchange resin strip (CER) (Na^+ form) were simultaneously added into the centrifuge tube with 30 mL deionised water and shaken for 16 hours in an end-over-end shaker. The resin strips were placed into a new centrifugation tube to which 30 mL (15 mL for biochar) of 0.5 M NaCl was added, and shaken for 30 minutes to elute the exchangeable resin-P. After elution, P concentration was measured using the method described by Murphy and Riley (1962) previously described. This fraction represents readily available P.

ii. Bicarbonate extractable inorganic P:

0.5 M Sodium bicarbonate (NaHCO_3) (pH 8.5) (30 mL for tephra, 15 mL for biochar) was added to the centrifugation tube containing either tephra or biochar (from previous extraction),

shaken for 16 hours, centrifuged and the supernatant collected. For this, 5 mL of the filtered (0.45 μm pore size) supernatant was analysed using the Murphy and Riley (1962) method previously described. This fraction is assumed to represent a labile pool of P that is well correlated to plant available P (Colwell, 1963).

iii. Bicarbonate extractable organic P:

Bicarbonate extractable organic P was estimated by difference between bicarbonate extractable total P and bicarbonate extractable inorganic P. Bicarbonate extractable total P was determined by taking a 10 mL aliquot of the supernatant extractant solution (5 mL for biochar) into 50 mL digestion tube. About 5 mL concentrated H_2SO_4 was added and digested as in the previous step. The P was measured by Murphy and Riley method (1962).

iv. X-Ray Diffraction (XRD) Analysis

Phosphate mineral forms, in biochars and tephra, crystalline to amorphous (Figs. 7.6, 7.7) were identified using a EMMA diffractometer (GBC, Australia). This was operated at 35 Kv and 20 Ma using monochromatic $\text{Co K}\alpha$ radiation. The samples were powdered finely to be analysed on XRD. Observed XRD patterns were compared with standards compiled by Brown, 1961.

7.2.3 Statistical Analysis

Analysis of variance (General linear model) and Tukey's test was used to test for treatment effects, using SAS 9.2 (2010) statistical software.

7.3 Results and Discussion

Hydraulic conductivity

The column treatments with tephra at the base (Sand-TE and BC-TE) presented flow issues and had to be regularly monitored because the fine texture of tephra had low hydraulic conductivity, which caused some over flowing of the wastewater from the top of the columns. The tephra and biochar mix treatment (TE/BC-Mix) had less flow problems, which was likely to be due to the biochar's coarser texture providing larger flow pathways through the tephra, thus, improving hydraulic conductivity.

Phosphate-P sorption

During the initial stage of the experiment, all the column treatments achieved a high level of P removal efficiency, decreasing from 99 to 75% average removals during the first 60 mg P added per column (Fig. 7.2). The DRP concentrations of leachates initially exiting the columns were $< 0.04 \text{ mg P L}^{-1}$, which were close to the recommended threshold DRP concentration of 0.01 mg P L^{-1} limit (threshold concentrations; ANZECC and ARMCANZ 2000) considered to stimulate periphyton and algal growth in receiving waters. Therefore, very little dilution would be required to reduce the treated wastewater P concentrations to levels below this threshold.

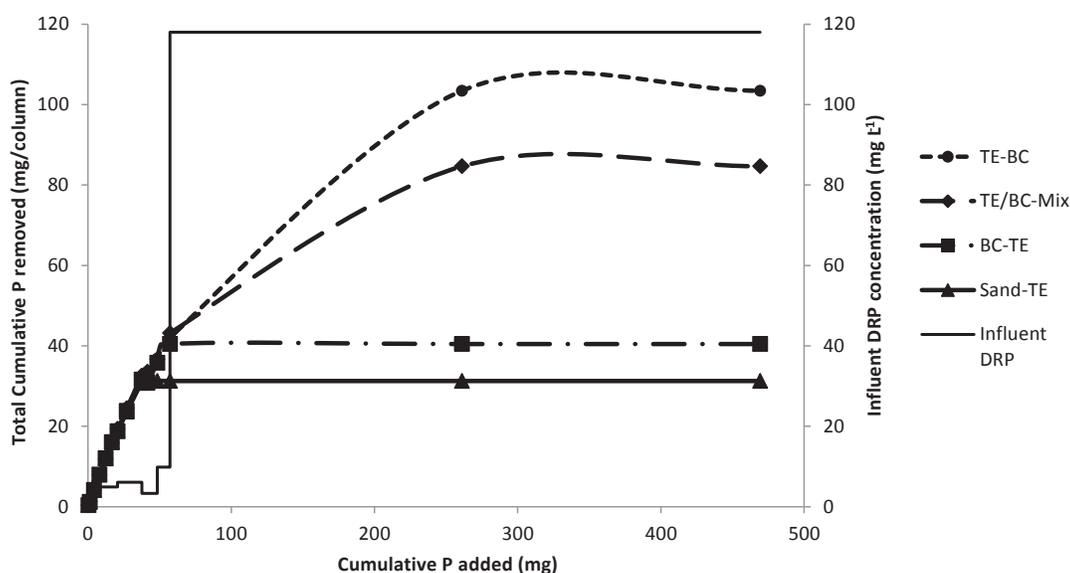


Figure 7.2 Cumulative P removed (mg per column) from urban wastewater by different arrangements of biochar and tephra in leaching columns.

where TE/BC-Mix= tephra/biochar mix, BC-TE= biochar top + tephra bottom, Sand-TE= sand top + tephra bottom, TE-BC= tephra top + biochar bottom.

Removal efficiency declined markedly after approximately 60 mg of P had been added to each column. A key factor influencing this rapid decline was the large increase in the P concentration of the wastewater. In the initial stage of the experiment, the wastewater DRP concentrations ranged from ($2\text{-}9.8 \text{ mg P L}^{-1}$). However, after about 60 mg P had been added, the concentration unexpectedly spiked up to 118 mg P L^{-1} (Table 7.1). This was caused by a new supply of wastewater (1 May, 2011 sample) with an abnormally high DRP concentration, which was about 6 times higher than the upper end of the range (up to $\sim 20 \text{ mg P L}^{-1}$) of the 3 previous sewage wastewater samples. The soluble K ($112 \text{ }\mu\text{g mL}^{-1}$) and Na ($49 \text{ }\mu\text{g mL}^{-1}$)

were also significantly elevated in the 1 May, 2011 wastewater sample (Table 7.1). This had a large influence on the results of the last two sampling times, and therefore, the amounts of P estimated to have been sorbed during this stage of the study and, therefore, needs to be interpreted in light of this large change in wastewater DRP concentration.

By the end of the experiment a total of 469 mg P had been added per column. The highest level of P removal was achieved by the TE-BC treatment, which is estimated to have sorbed 103 mg P per column (Fig. 7.3), or about 24% of the P added. The TE/BC-Mix achieved the second highest level of P sorbed of 84.5 mg P per column. The amounts of P removed by the TE-BC and TE/BC-Mix treatments were significantly ($p < 0.05$) higher than the values achieved by the other two treatments. The BC-TE and Sand-TE treatments are estimated to have sorbed 40 mg and 31 mg P per column, respectively.

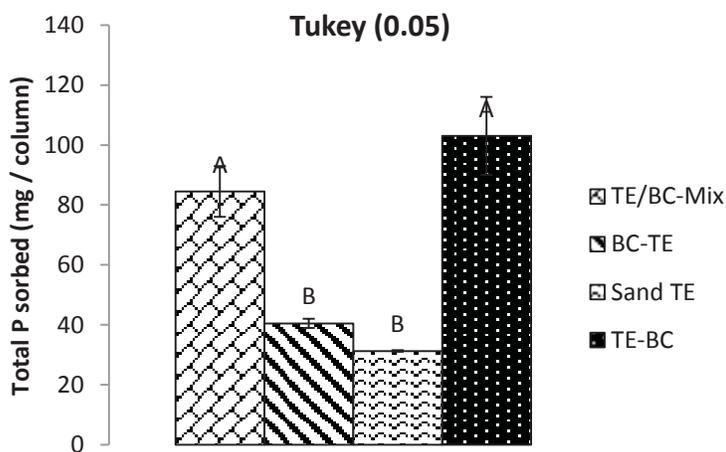


Figure 7.3 Total P sorbed (mg P /column) in the different treatments (calculated as product of leached volume and the difference in influent and effluent DRP)

where TE/BC-Mix= tephra/biochar mix, BC-TE= biochar top + tephra bottom, Sand-TE= sand top + tephra bottom, TE-BC= tephra top + biochar bottom.

The tephra was added to the columns as the primary P sorbent. The levels of P sorbed by the Sand-TE treatment (the only treatment without biochar) were low (31 mg P per column, equating to 1.55 mg g^{-1} tephra) compared to other column studies using Okato Tephra. For example, Liesch (2010) estimated P removal by Okato Tephra being 8 mg P g^{-1} tephra. There are several possible reasons for the lower P removal measured in the current study by the Sand-TE treatment. Liesch (2010) used a synthetic P solution containing 20 mg P L^{-1} , rather than real wastewater. The synthetic solution would not have contained any other anions or

dissolved organic components with potential to compete with P for adsorption sites on the tephra. The Liesch (2010) study had a longer solution residence time within the columns of ~ 180 minutes, compared to only ~ 45 minutes in the current study, which would could have also have contributed the higher P removal in the former study.

Combining biochar to the tephra increased DRP removal, compared to the Sand-TE particularly for the TE-BC and TE/BC-Mix treatments. However, when biochar was placed on top of the tephra (BC-TE treatment), there was significantly lower sorption than when biochar was below the tephra in the column (TE-BC treatment). The lower performance of the BC-TE treatment could be due to the solution pH experienced by the tephra being higher, when the biochar is placed on top of the tephra, compared to vice versa. The pH of the leachate coming out of the treatment when biochar was at the bottom of the column (TE-BC treatment), which ranged from 8.2 to 7.6 over the duration of the study, provides an indication of the solution pH experienced by the tephra, when the biochar placed on top (Fig. 7.4). The P sorption maxima of allophane is at pH 5-7 (depending on the cause/salt responsible for pH rise) when the surface is maximally positively charged (Bolan et al. 1988).

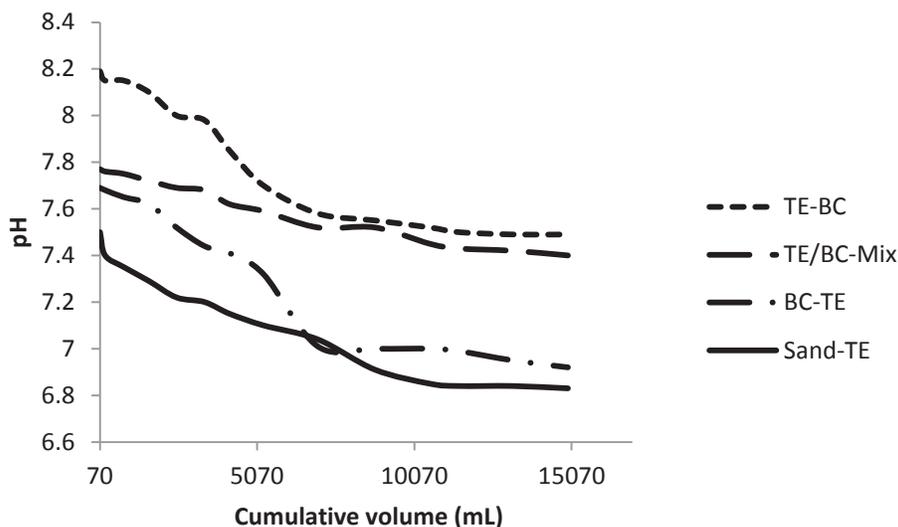


Figure 7.4 pH of the effluents from the column study at different cumulative volumes of wastewater

where TE/BC-Mix= tephra/biochar mix, BC-TE= biochar top + tephra bottom, Sand-TE= sand top + tephra bottom, TE-BC= tephra top + biochar bottom.

The additional contribution of the biochar, in the column treatments, to the removal of P from solution was assumed as being the difference between the P removed by the biochar and tephra combined treatments and the P removed by the Sand-TE treatment. For example, the TE-BC treatment removed 103 mg P per column and the Sand-TE treatment removed 31 mg

P per column. Therefore, the contribution of the biochar was to increase P removal by 72 mg P. One possible cause of P retention on the biochar could be precipitation of Ca and Mg phosphates due to the alkaline conditions (pH 8.2 to 6.9, Fig. 7.4). This possibility was investigated with XRD studies later in this chapter.

Ammonium-N sorption

The range of NH_4^+ -N in the wastewaters was 18-20 mg N L^{-1} . The maximum amount of NH_4^+ -N sorbed (10.8 mg N per column, 17 % of N added in wastewater) was achieved by the TE/BC-Mix treatment (Fig. 7.5), which was significantly higher ($p < 0.05$) than the other treatments. The TE-BC treatment removed the second highest quantity of biochar, of 6.4 mg N per column, followed by the BC-TE treatment with 4.8 mg N. The Sand-TE treatment, which contained no biochar, removed negligible quantities of NH_4^+ -N (0.13 mg N column) from the wastewater (Fig. 7.5). This result shows that biochar was the primary sorbent of NH_4^+ from the wastewater.

At the start of the experiment the NH_4^+ -N concentration in the leachates exiting was reduced to 0.04 mg N L^{-1} , which is close to recommended threshold NH_4^+ -N concentration (0.02 g m^{-3} ; ANZECC and ARMCANZ 2000), above which is considered to stimulate periphyton and algal growth in receiving waters. However, the removal efficacy of NH_4^+ -N quickly decreased after 24 hours as the experiment progressed. The amount of NH_4^+ -N sorbed in this study was less than that reported in previous chapter (Chapter 6). This might be due to the shorter retention time of solution in the columns used in the present study, as the flow rate here was 0.6 mL min^{-1} , compared to that of 0.16 mL/min (using the same column volume) in Chapter 6.

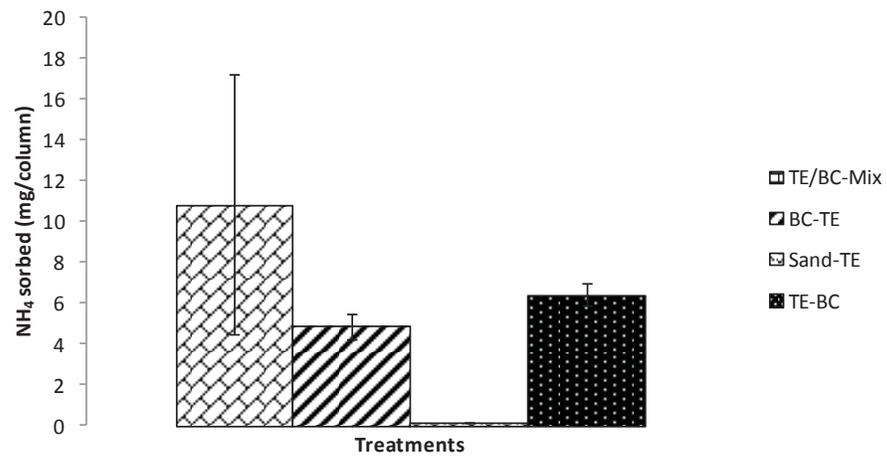


Figure 7.5 Sorption of NH₄⁺-N in the different treatments.

where TE/BC-Mix= tephra/biochar mix, BC-TE= biochar top + tephra bottom , Sand-TE= sand top + tephra bottom, TE-BC= tephra top + biochar bottom.

Characterisation of wastewater treated tephra and biochar

The wastewater treated tephra (WT-T) and biochar (WT-L PI) samples (tephra sample combined from three columns; biochar sample combined from two columns) contained higher concentrations of cations, total N and total P, compared to the respective untreated materials (Tables 7.2 and 7.3), which reflected the nutrient additions from the wastewater. The largest increase in cation concentration on the treated tephra was in Ca ($25.3 \text{ cmol}_c \text{ kg}^{-1}$) and the minimum was Na ($1.13 \text{ cmol}_c \text{ kg}^{-1}$). The wastewater treatment leached significant amounts of SO_4^- reducing the quantity on the tephra from 589 to $43 \mu\text{g g}^{-1}$ in WT-T (Table 7.2), which was due to P from wastewater displacing native SO_4^- from tephra sorption sites. In case of biochar (L PI), it contained significant K and Na (3.3 and $4.5 \text{ cmol}_c \text{ kg}^{-1}$, respectively), probably due to the tannery waste treatment used to pre-treat the biochar. After wastewater treatment the largest increase in exchangeable cations was in Ca. Both tephra and biochar showed increases in total N content after wastewater treatment from 1.13 to 1.29 % and 1.5 to 2.3 %, respectively.

The tephra and biochar also showed an increase in total P after wastewater treatment from 1.1 to 2.45 and 1.3 to 2.1 g kg^{-1} , respectively. When the quantity of P estimated to have been sorbed onto the tephra and biochar samples are compared with the total P analysed on the materials (Tables 7.2 and 7.3), there were difference between the two measures. If it is assumed that the tephra accounted for 31 mg P per column (i.e. based on P removal by the column treatment without biochar; Sand-TE), then the biochar from the TE-BC and BC-TE columns need to account for $[(103-31) + (40-31)]/2 = 40.5 \text{ mg P per column}$. The 31 mg P per column sorbed by the Sand-TE treatment equates to 1.55 mg P g^{-1} tephra, which agrees well with the increase in total P on the wastewater treated tephra of 1.35 mg P g^{-1} tephra. However, the 40.5 mg P per column attributed to the biochar equates to 5.79 mg P g^{-1} , which is many times higher than the increase in total P analysed on the wastewater treated biochar of 0.8 mg P g^{-1} . Moreover, this increased P removal with biochar and tephra combined columns TE-BC and TE/BC-Mix could be due to the interaction (physical or chemical) between the two sorbents and not an additive effect of the biochar.

It is not possible to explain with certainty the cause of the discrepancy between the amounts of P estimated to have been sorbed by the columns and the quantities of total P measured in the materials. One possible contributor to the sorbed P being accounted for could be algal

growth observed on the cotton wool used on top of the columns. An assessment of the P sorption properties of the cotton wool alone demonstrated its ability to retain P was minimal (<0.2 mg P per column). However, the quantity of P uptake by algae was not assessed and so remains unknown. Future studies should assess the uptake of nutrients by algae or ensure the experiment is conducted under conditions that prevent algal growth.

Table 7.2 Chemical analysis of tephra before (T) and recovered after the wastewater treatment (WT-T) (combined from all column treatments except TE/BC-Mix).

Sample	pH	Total P g P kg ⁻¹	SO ₄ -S (µg g ⁻¹)	Exchangeable cations							
				K cmol _c kg ⁻¹	Ca cmol _c kg ⁻¹	Mg cmol _c kg ⁻¹	Na cmol _c kg ⁻¹	CEC cmol _c kg ⁻¹	Bulk Density g cm ⁻³	N g kg ⁻¹	C g kg ⁻¹
T*	-	1.1(0.1)	589.0(8.81)	0.06(0.003)	0.1(0.03)	0.06(0.002)	0.17(0.04)	5(0.08)	0.76(0.018)	1.5(0.15)	28.8(1.10)
WT-T*	-	2.45(0.15)	43.0(1.45)	3.13(0.05)	25.3(1.01)	3.81(0.07)	1.13(0.09)	-	0.86(0.02)	2.3(0.14)	27.4(1.51)

*Where T=Control tephra and WT-T=wastewater treated tephra, Values in brackets show standard error.

Table 7.3 Chemical analysis of biochars before (L PI) and recovered after the wastewater treatment (WT-L PI) (combined from all column treatments except TE/BC-Mix).

Sample	pH	Total P gP kg ⁻¹	Ash %	Exchangeable cations							
				K cmol _c kg ⁻¹	Ca cmol _c kg ⁻¹	Mg cmol _c kg ⁻¹	Na cmol _c kg ⁻¹	CEC cmol _c kg ⁻¹	BET (m ² g ⁻¹)	N g kg ⁻¹	C g kg ⁻¹
L PI	10.31(2.9)	1.3(0.075)	8.67(1.04)	3.30	0.20	0.27	4.55	24.89(0.55)	3.3	11.3(0.06)	784(10.7)
WT-L PI	9.01(0.06)	2.1(0.02)	n.a*	3.36	4.21	0.73	5.30	-	n.a*	12.9(2.9)	734(1.5)

*Not available; where L PI=liquid tannery waste activated biochar, WT-L PI=wastewater treated liquid tannery waste activated biochar. CEC was analysed by SrCl₂ method as described in Chapter 8. Values in brackets show standard error.

Characterisation of P retained on tephra and biochar.

Biochar and tephra samples that were either untreated or treated with wastewater (combined samples from column study) were subjected to XRD analysis. The purpose of the XRD analysis was to confirm if any crystalline phosphates were evident in wastewater treated materials. The samples were also assessed using a P fractionation analysis to determine the proportion of the increase in total P on the materials, caused by the wastewater treatment, was in forms that are like to be plant available in the short-term.

The XRD analysis of the activated biochar showed the presence of peaks at 2.83 and 2.52 Å⁰ (Fig. 7.6) depicting the presence of apatite after wastewater treatment (Brown, 1961), which means that biochar had P retained by precipitation with Ca salts and could be source of P alongwith N if used in wastewater treatment. This also confirmed the precipitation of P with Ca on biochar as was hypothesized earlier. However, there was no evidence of crystalline forms of P on WT-T (Fig. 7.7; XRD analysis), thereby, confirming P presence in amorphous forms that are readily available in soil. Yao et al. (2011) also found that digested sugar beet-tailing biochar (pH 9.95) was able to sorb 73% P out of 20 ppm synthetic P solution. They reported nano-sized peri-clase (MgO) particles to be responsible for P sorption from aqueous solution and reported the presence of the two strong peaks at 43.2° and 62.2° (by XRD analysis), identified as periclase (MgO), suggesting that the colloidal and nano-sized magnesium crystals were present as well as showed presence of calcite. They reported anaerobic digestion to be responsible for the phosphate sorption on biochar.

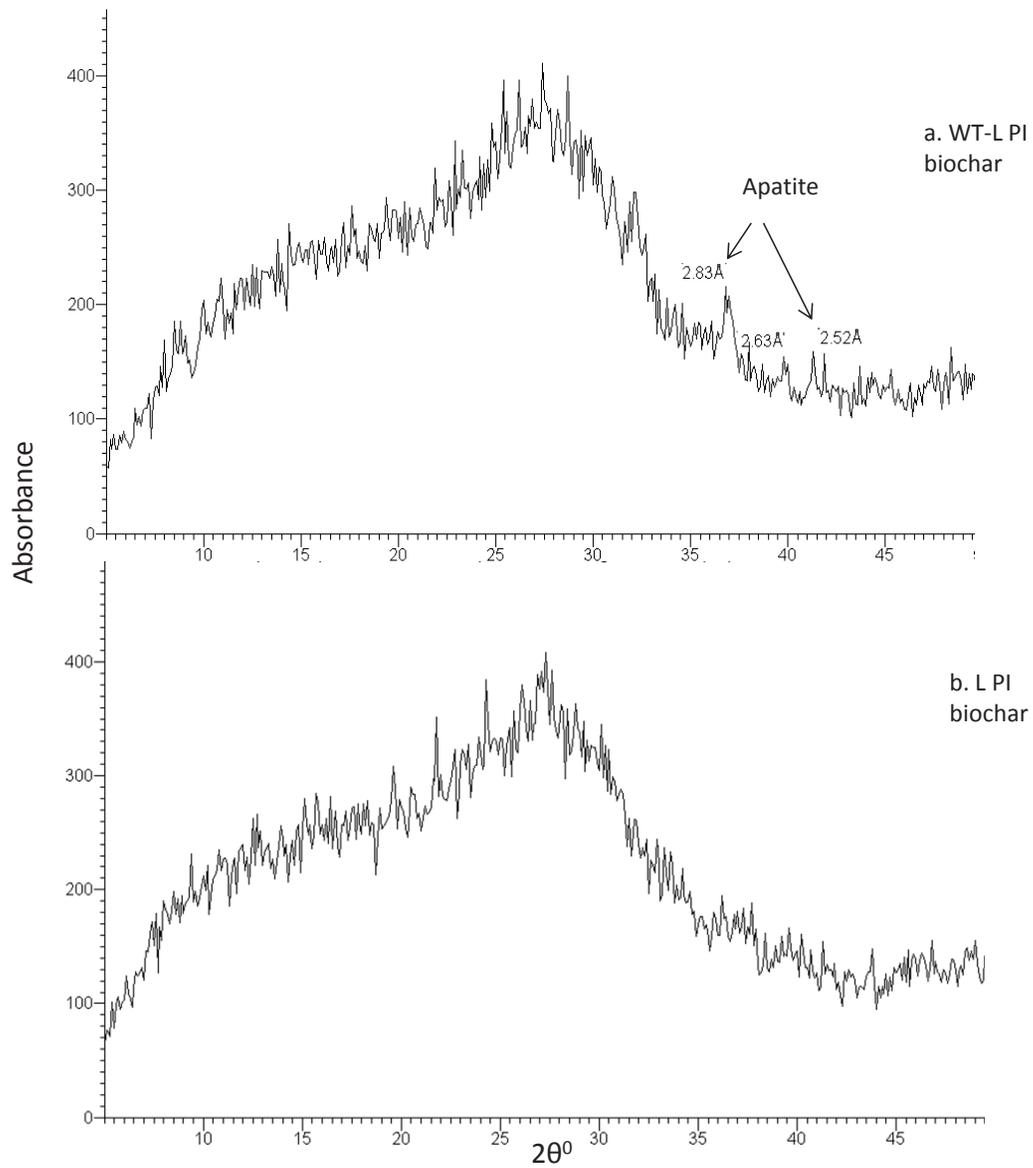


Figure 7.6 XRD spectra of a). WT-L PI (wastewater treated L PI) biochar and b). L PI (liquid tannery waste treated biochar).

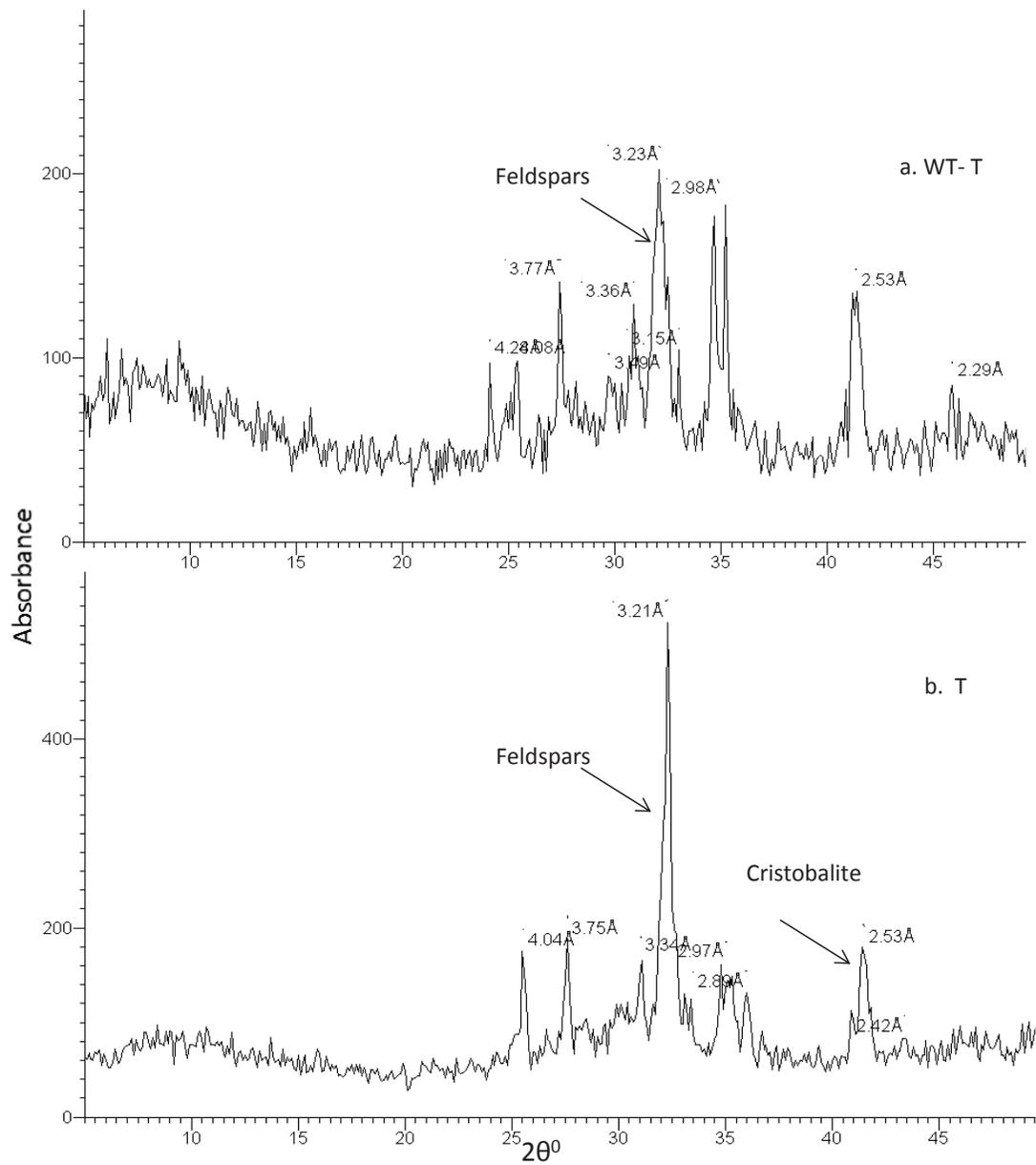


Figure 7.7 XRD spectra of a). WT-T (wastewater treated tephra) and b). T (tephra).

The P-fractionation of tephra and biochar samples was conducted to estimate the availability of the P sorbed by tephra and biochar, using two steps (resin P and sodium bicarbonate extractable P) of the Hedley P fractionation (Hedley et al. 1982). The resin and bicarbonate P fractions of Hedley's P fractionation method represent the most weakly sorbed P fractions, which are, therefore, more likely to be available for plant growth. Phosphorus fractions were grouped into inorganic/organic fractions to understand the type of P interactions with tephra under the experimental conditions of this study.

The wastewater treatment of tephra (WT-T) and biochar (WT-L PI) caused a small decrease in the organic fraction of NaHCO₃ extractable P, but a marked increase in the inorganic fraction in WT-T (Table 7.4). After the wastewater treatment, resin-extractable Pi (134 and 79.5 µg P g⁻¹ in tephra and biochar, respectively) and bicarbonate-Pi (385 and 77.5 µg P g⁻¹ in tephra and biochar, respectively) fractions increased, providing a total NaHCO₃ Pi + Po of 414 and 85 µg P g⁻¹ in tephra (WT-T) and biochar (WT-L PI), respectively (Table 7.4). Significantly more labile P (resin Pi plus NaHCO₃ extractable Pi) was retained on the tephra (WT-T) compared to the WT-L PI biochar.

After wastewater treatment, the total P concentration of wastewater treated tephra and biochar increased by 1350 and 900 µg g⁻¹ (Tables 7.2, 7.3), respectively. The increase in resin-extractable Pi and bicarbonate extractable Pi represented 9.4 and 26.5 % (35.6% combined) of the increase in total P in the wastewater treated tephra. For the biochar, only 2.16 and 5.05 % (7.21 % combined) of the increase in total P from wastewater treatment was attributed to resin-extractable Pi and bicarbonate-Pi fractions, respectively (Table 7.4). Therefore, a greater proportion of the sorbed P on the tephra is likely to be plant available compared to the P retained on the biochar.

Table 7.4 Fractionation of P in tephra and biochar at time 0 and after wastewater treatment.

	Resin P ($\mu\text{gP g}^{-1}$) Inorganic (Pi)	Sodium bicarbonate (NaHCO_3) Extractable P ($\mu\text{gP g}^{-1}$)			Resin P as % of total ¹ P increase	NaHCO_3 Pi + Po as % of total ¹ P increase
		Inorganic (Pi)	Organic (Po)	Total		
Untreated tephra (T)	7.5(2.01)	26(2.8)	34(17.01)	60(14.2)	-	-
Wastewater treated tephra (WT- T)	134(9.00)	385(14.2)	29(2.1)	414(14.0)	9.4	26.2
Untreated biochar (L PI)	60(3.42)	17.5(3.4)	23(9.14)	40(5.71)	-	-
Wastewater treated biochar (WT-L PI)	79.5(0.57)	77.5(3.3)	8(2.28)	85.5(5.01)	2.16	5.05

¹Total P increase was the increase in TP attributed to the wastewater treatment (Tables 7.2 and 7.3). Values in brackets show standard error.

The study showed that tephra is a good sorbent of P and if it is combined by mixing with alkaline activated biochar or added on top of alkaline activated biochar, the net efficiency of P removal from wastewater can be enhanced. Tephra did not sorb NH_4^+ , but L PI biochar showed increased sorption of N when mixed thoroughly with tephra (TE/BC-Mix). The TE/BC-Mix column was considered the most promising treatment to address the flow issues as well as removal of NH_4^+ and the second highest for DRP removal from wastewaters.

Feasibility of tephra and biochar filters

To assess the potential of using tephra and biochar filters to treat town wastewater, it is useful to scale up the results of the study to assess whether the filters will be feasible. For a town with population of 3000 people producing 1000 m^3 /day of wastewater (DRP concentration of 4 mg L^{-1}), the amount of P discharged from two-pond treatment system will be 4 kg P/day. Based on the TE/BC-Mix column removing 84.5 mg P per column (containing 20 g tephra and 7 g biochar), then a total 0.95 tonnes of tephra and 0.33 tonnes of biochar per day to remove 4 kg DRP/day. This equates to 347 tonnes of tephra and 120 tonnes of biochar per year to remove DRP from wastewater. While the quality of tephra required may be feasible due to its low cost (\$ 10-15/tonne plus transport), the cost of the biochar (>\$550/tonne; Bishop et al. 2012) would make it use restrictive. Moreover, if the amount of NH_4^+ -N discharged from two pond system is 20 kg N/ day and the TE/BC-Mix column is capable of removing 10.8 mg N per column, then 12.9 tonnes of biochar per day, 4745 tonnes per year,

is required to treat wastewater for N removal. Therefore, large increases in NH_4^+ removal capability of biochar, and/or ways to increase the value of the final product, will be needed before it can be considered a practical option for wastewater treatment.

7.4 Conclusion

The column study successfully developed a tephra-biochar filtration system for the removal of nutrients from wastewater, although some arrangements of tephra and biochar created reduced flow through the columns. Tephra at the base in columns posed problems regarding inadequate hydraulic conductivity. To address the flow issues, a mixed tephra and biochar treatment (TE/BC-Mix treatment) achieved adequate hydraulic conductivity in relation to the flow rate used in the study. Maximum P sorption was evident in TE-BC treatment column followed by TE/BC-Mix > BC-TE > Sand-TE. About 36% of the increase in total P measured on the wastewater treated tephra was assessed as being in a readily available form, while this value was only 7% for biochar. XRD analysis showed presence of apatite in wastewater treated biochar, but no crystalline forms of P were observed in wastewater treated tephra so only amorphous P was considered in it.

Maximum NH_4^+ -N sorption was observed in the TE/BC-Mix treatment indicating the better loading efficiency of mixed tephra and biochar treatment followed by TE-BC > BC-TE > Sand-TE treatments. Tephra showed negligible NH_4^+ sorption capacity, so cannot be considered for N removal. Activated pine biochar appeared to influence both P along with N to remove from wastewater, which was not evaluated in previous chapters. Although combinations of tephra and biochar have been shown to be effective at removing P and N from wastewater, the large quantities of biochar required for a full-scale filter for a town, and the relatively high cost of biochar production, would be cost prohibitive. The cost issue may be partially off-set if other uses of the used sorbents could be demonstrated, such as the use of slow release fertilisers. In Chapter 8, tephra and biochar with sorbed N and P are evaluated in soil media to assess their fertiliser value.

References

- ANZECC and ARMCANZ 2000: Australian and New Zealand guidelines for fresh and marine water quality. Volume 1. The guidelines. Canberra, Australia, Australia and New Zealand Environment and Conservation Council and Agriculture. *Resource Management Council of Australia and New Zealand*.
- Baker MJ, Blowes DW, Ptacek CJ (1998) Laboratory development of permeable reactive mixtures for the removal of phosphorus from online wastewater disposal systems. *Environmental Science Technology*. 32, 2308-2316.
- Bishop P, Hedley M, Knox C, Rikihana P, Jones J (2012) Practical aspects on the production of biochar and its delivery to soil. *Biochar Workshop*, (9-10 February). Massey University, Palmerston North, NZ.
- Blakemore LC, Searle PL, Daly BK (1987) Methods for chemical analysis for soils. *NZ Soil Bureau Scientific report*. 80, 78-79
- Bolan NS, Syers JK, Tillman RW (1988) Effect of pH on the adsorption of phosphate and potassium in batch and in column experiments. *Australian Journal of Soil Research*. 26, 165-70.
- Brown G (1961) The X-ray identification and crystal structures of clay minerals. Mineralogical Society (Clay Minerals Group), London. pp. 473-486.
- Colwell JD (1963) The estimation of phosphorus fertilizer requirement of wheat in southern New South, Wales. *Australian Journal of Experimental Agriculture and Animal Husbandry*. 3, 190-197.
- Hanly JA, Hedley MJ, Horne DJ (2008) Evaluation of tephra for removing phosphorus from dairy farm drainage waters. *Australian Journal of Soil Research*. 46, 542-551.
- Hedley MJ, Stewart JWB, Chauhan BS (1982). Changes in inorganic and organic soil phosphorus fractions induced by cultivation practices and laboratory incubations. *Soil Science Society of America Journal*. 46, 970-976.
- Liesch AM (2010). Wastewater phosphorus removal by two different types of Andesitic Volcanic Tephra. *Journal of Natural Resources and Life Sciences Education*. 39, 40-44.
- McArthur K, Clark M (2007) Nitrogen and phosphorus loads to rivers in the Manawatu-Wanganui Region: An analysis of low flow state. Technical report to support Policy development. *New Horizons Regional Council*. pp. 6-20
- Mckenzie HA, Wallace HS (1954) The Kjeldahl determination of Nitrogen: A critical study

of digestion conditions, temperature, Catalyst and oxidizing agents. *Australian Journal of Chemistry*. 7, 55-70.

Murphy J, Riley JP (1962) A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta*. 27, 31-36.

Olsen SR, Cole CV, Watanabe FS, Dean LA (1954) Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA.

Ryden JC, Syers JK (1975). Use of tephra for the removal of dissolved inorganic phosphate from sewage effluent. *New Zealand Journal of Science*. 18, 3-16.

Yao Y, Gao B, Inyang M, Zimmerman AR, Cao X, Pullammanappallil P, Yang L (2011) Biochar derived from anaerobically digested sugar beet tailings: Characterization and phosphate removal potential. *Bioresource technology*. 102, 6273-8.

Chapter 8

Assessment of N and P bioavailability from biochar and volcanic tephra treated with urban wastewater

8.1 Introduction

The biochar and tephra sorbents used in column sorption studies in Chapter 7, for the removal of ammonium (NH_4^+) and dissolved reactive phosphorus (DRP) from wastewater, are evaluated as potential fertiliser materials in this chapter.

In Chapter 3, the ability of non-activated pine biochar and activated pine biochar to remove NH_4^+ from an influent NH_4^+ -enriched solution was evaluated. The chemically-activated biochar was able to retain ~ 22 % more NH_4^+ from the influent solution than the non-activated form. Activated biochars (pine) showed, however, a lesser ability to retain phosphate (P) from wastewater compared with volcanic tephra (Chapter 7).

Biochar enriched with NH_4^+ after treating wastewater may have the potential to be used as N fertiliser for pasture and crop plants. If biochar is combined with materials that have P sorption capabilities then the final mixture may have the potential to be used as both a P and N fertiliser. Taghizadeh-Toosi et al. (2011) exposed biochars to ^{15}N enriched ammonia (NH_3) and obtained a final ^{15}N enrichment of 5.36 atom%. These authors reported that when NH_3 gas was absorbed on biochar (produced from *Pinus radiata* using microwave pyrolysis with maximum temperatures of 300, 350 and 500 °C), a considerable fraction of it remained bioavailable. Bioavailability was assessed using 2 M KCl extraction and plant growth. Extraction with 2 M KCl indicated that following exposure to the NH_3 gas the biochars (made at 300, 350 and 500 °C) contained on average 400-760 $\mu\text{g NH}_4^+\text{-N g}^{-1}$ biochar. When incorporated in soils, 26 to 11 % of the added N was recovered in leaf tissues and 6.8 % in roots.

The objective of the present study was to test the bioavailability of NH_4^+ and P retained on tannery waste activated biochar and volcanic tephra, respectively following their addition (either separately or together) to two soils (Kiwitea silt loam and Manawatu sandy loam) using the “Stanford and Dement (1957)” using exhaustive bioassay technique. Additional treatments included the amendment of the same soils with a non-activated pine biochar and

tannery waste-activated pine biochar, which had not been used to treat wastewater, as well as non-amended soils as controls. The bioassays were conducted in two stages: (i) *Experiment 1* tested the bioavailability of N and P when rates of biochar application to soil simulated C amendments of topsoils (10 and 20 t biochar ha⁻¹); and (ii) *Experiment 2* involved the use of high rates of biochar application (i.e. 40 and 100 t biochar ha⁻¹) to simulate doses of biochar “disposal” to soil.

8.2 Materials and Methods

8.2.1 Materials

Pine residues were chipped with a commercial chipper to a final particle size of 3-11 mm. The feedstocks were oven-dried at 65 °C prior to their use. Chemical activation treatments were carried out through impregnation of the feedstocks with alkaline tannery slurry, previously diluted with distilled water to a 1:3 ratio (volume basis) following the method described in Chapter 5. Triplicate samples of untreated and treated pine residues (200g per replicate) were pyrolysed at an average heating rate of 25 °C min⁻¹, to a final temperature of 550 °C in a gas-fired, 5 L stainless steel rotating drum kiln. Then the three replicates of each treatment were pooled into a single sample thereafter. The biochar without pre-treatment was referred to as Ctr PI biochar and the pre-treated biochar was referred to as L PI biochar. Subsamples of the different biochars were washed repeatedly with deionized water and only rinsed samples were used. The dominant particle-size of the biochars used in this study was ≤ 2 mm.

The Okato tephra used in this experiment was moderately weathered andesitic tephra subsoil collected from the North West Taranaki region (39° 13' 28.04' S; 173° 58' 01.05' E). The tephra was sampled from a soil depth of about 0.5-1.5 m from a road-side cutting. The main physicochemical properties are reported in Table 7.2, 7.3, 8.1.

Soil sampling and Preparation

Kiwitea silt loam soil (Typic Orthic Melanic soils; New Zealand Soil Classification system) and Manawatu fine sandy loam soil (Weathered Fluvial Recent Soils; New Zealand Soil Classification system) were used as the soil mediums for the Stanford and Dement study. The Kiwitea soil was collected (0-10 cm depth) from permanent sheep grazed pasture (40° 06' 54.02' S; 175° 42' 27.82' E). The Manawatu soil was collected (0-10 cm soil depth) from grazed pasture (40° 23' 04.42' S; 175° 36' 14.63' E) at Massey University No. 1 Dairy Farm.

Soils were air-dried soon after sampling, and then passed through a 2 mm sieve. Plant stem and thick root material was removed in the sieving process. These soils were used in both experiments. Soils were incubated (aerobic incubation) with the biochar and tephra treatments prior to the bioassay trial and one set of Kiwitea soil incubations was analysed for mineralisable N and pH.

Aerobic incubations

The method used for aerobic incubations and analysing NH_4^+ and NO_3^- in this study was adapted from the method described by Keeney and Bremner (1967). This method involved weighing 10 g air dry soil (< 2mm sieved) and mixing with different biochars (Ctr PI, L PI, WT-L PI, WT-T) and tephra at 0, 1%, 2%, 4% and 10% of soil dry weight (approximately equivalent to 0, 10, 20, 40 and 100 t ha⁻¹ at 10cm depth). The contents of the flask were stirred and distilled water was added to 70 % of field capacity. The flask was then capped with aluminium foil. The sample in the flask was incubated at 30 °C for 10 days. At the end of the incubation period, pH, NH_4^+ and NO_3^- content was analysed. The N (NH_4^+ and NO_3^-) content was determined by 2 M KCl extraction followed by shaking for 1 hour, and centrifugation.

8.2.2 Establishment of the “Stanford and Dement (1957)” Bioassay

Experiment 1: Preparation of soils.

Control pine biochar (Ctr PI), activated pine biochar (L PI), urban wastewater treated activated biochar (WT-L PI), wastewater-treated activated biochar-tephra mixtures, referred to as WT(T+L PI) and wastewater-treated tephra (WT-T) were mixed with 70 g (dry weight) Kiwitea and Manawatu soils at rates equivalent to 10 and 20 t ha⁻¹ (1 and 2% by weight) and added to pots (5.5 cm height×8-9.5 cm diameter; similar size to that of Stanford and Dement upper pots). A total of 11 treatments (including a soil only control) were replicated in triplicate for each of the two soil types, which make a total of 66 pots with controls. The soils and mixtures were incubated in the laboratory at a temperature of 30 °C for 10 days at 70 % field capacity.

This is an exhaustive technique with the aim of depleting nutrients from a small volume of soil. The double pot technique quickly produces a root mat rhizosphere, which is then placed in contact with the soils and amendments to be studied (Fig. 8.1). The trial commenced in

mid of March 2011. Manawatu river fine-sand was collected and washed three times with dilute HCl and then with deionised until the pH returned to pH 5.7.

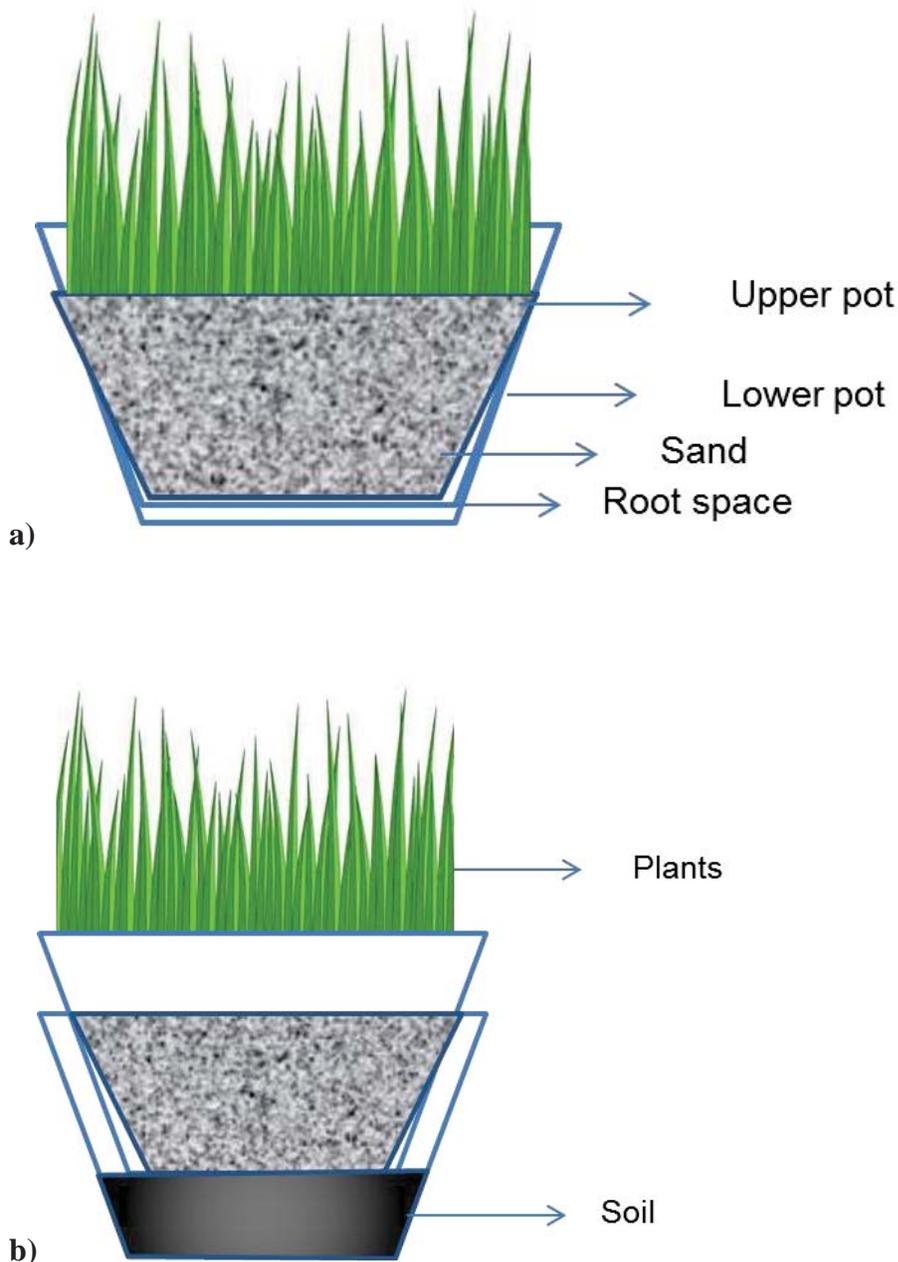


Figure 8.1 The arrangement of pots for the Stanford and Dement technique **a)** At establishment of test plants, the upper pot containing sand with no soil present, and **b)** after the addition of the upper pot with ryegrass to the lower pot with the soil treatments.

Acid washed and air-dried sand (232 g pot^{-1}) was placed in small false bottom pots. The sand was moistened with deionised water and 30 seeds of ryegrass added per pot. After

germination, pots were moved to a glasshouse and a nutrient solution containing 5 mg N and 0.70 mg P pot⁻¹ per week was applied in order to grow approximately 1 g plant dry weight/pot. After six weeks, plants were cut at 5 cm above the top of the pot. After harvest, pots were supplied with water only; plants were re-grown under nutrient stress and cut again after two weeks. Then the sand pots were placed on top of the pre-incubated soil treatments without nutrient solution and maintained at 70% field capacity through daily watering to weight. Plants were allowed to grow for 25 days until deficiency symptoms occurred. Then plants were harvested by cutting at 5 cm height and soil was removed along with roots.

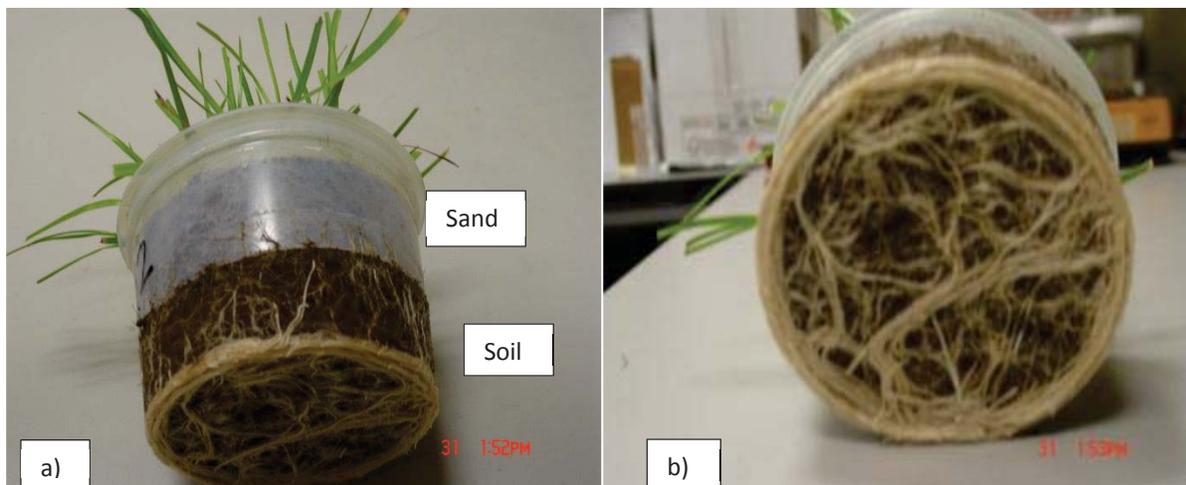


Figure 8.2 a). “Stanford and Dement” pots at the 4th week after placing the top pot on the soil treatments, b). A thick rhizosphere root mat has formed in the small volume of soil at the bottom of the pot.

Experiment 2

Control pine biochar (Ctr PI), activated pine biochar (L PI), urban wastewater-treated activated biochar (WT-L PI) and both wastewater treated activated biochars and tephra WT(T+L PI) biochars were mixed with Kiwitea (70 g dry soil) and Manawatu soils (70 g dry soil) at rates equivalent to 0, 40 and 100 t ha⁻¹ (4 and 10% by weight). The soils and mixtures were incubated as above. Plants already established in “upper pots” of sand from the previous trial were re-supplied with nutrient solution (with macro and micro nutrients) grown on for 7 days and then grown without nutrient solution for 14 days before their harvest to 5cm in height. After harvest, the upper pots were then placed on the amended soils that had been pre-incubated, and incubated as described above.

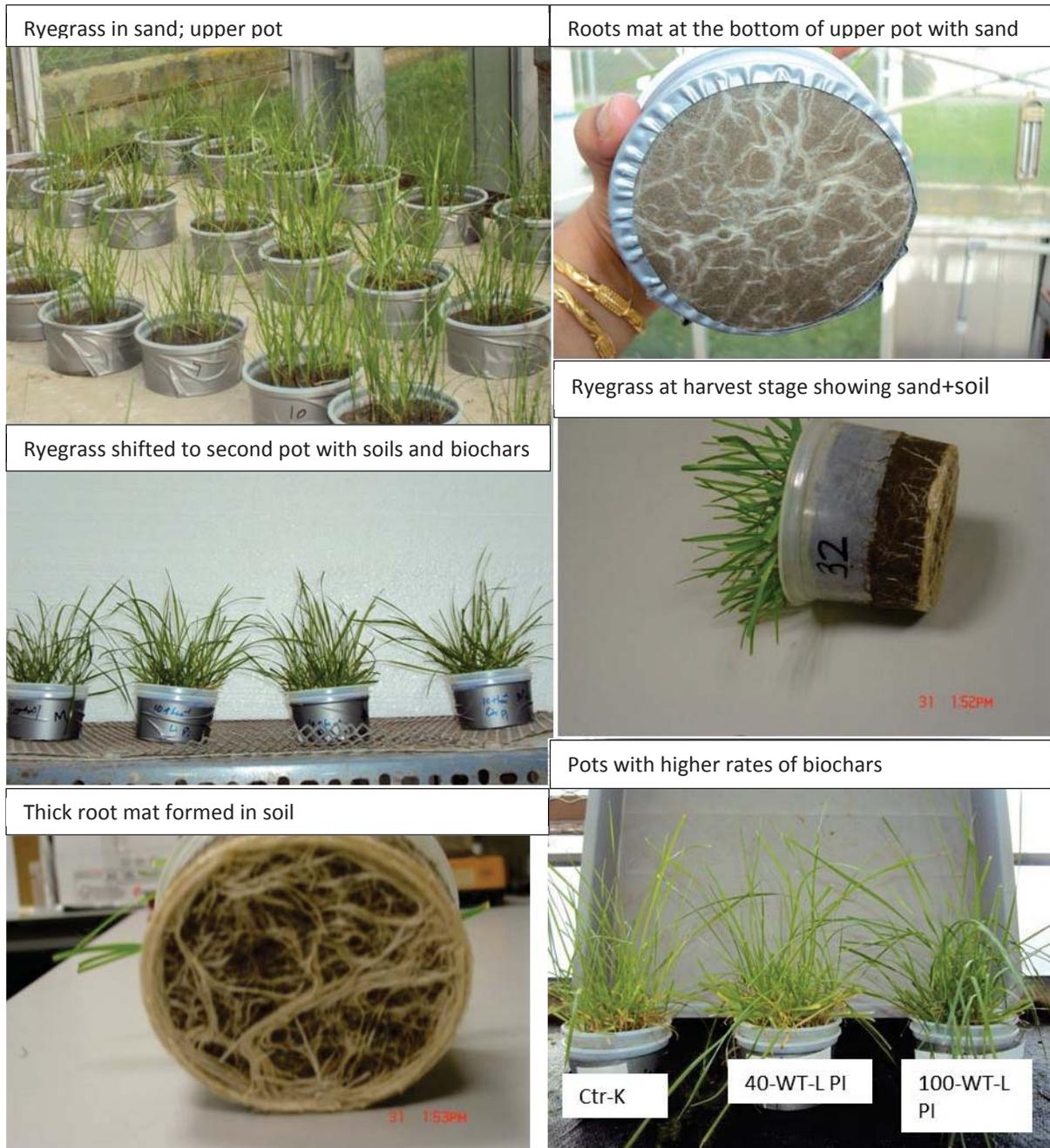


Figure 8.3 Different stages of plant bioassay (Stanford and Dement Bioassay).

8.2.3 Chemical Analyses of Soils, Tephra and Biochars

Soil and tephra pH was determined in water using 10 g air dry soil in a beaker stirred with 25 mL water. The mixture was kept overnight and then analysed with a pH electrode following the method of Blakemore et al. (1987). Biochar pH was measured using the methodology of Ahmedna et al. (1997), which involved a 1 % (wt/wt) suspension of biochar in deionised water. The suspension was heated in a water bath to about 90 °C and stirred for 20 min to allow the dissolution of highly water-soluble biochar components. After cooling to room temperature, the pH of the biochar suspension was measured. Plant available P in soil and tephra was defined as that extracted by the method of Olsen et al. (1954), in which 0.5 M NaHCO₃ is used as extracting agent with pH adjustments. Extracts were analysed for reactive P by the method of Murphy and Riley (1962). Extractable SO₄²⁻ was obtained using a 0.4 M Ca(H₂PO₄)₂ solution (Searle, 1979) and determined in a Technicon Autoanalyser using an automated Johnson and Nishita (1952) technique.

Exchangeable cations (K⁺, Mg²⁺, Ca²⁺, Na⁺) in soil and tephra were measured using the ammonium acetate extraction method (Blakemore et al. 1987) followed by atomic adsorption spectroscopy (AAS) analysis. All base cations plus an estimate of the acidity equivalents (by pH) in the extract were added to estimate the cation exchange capacity (CEC). Determination of exchangeable cations of biochars was carried out following the method of Matsue and Wada (1985). For this, a 0.2 g sample was taken in small columns filled with sand and leached with 0.01 M and 0.001 M SrCl₂ followed by 0.5 M HCl (up to 45 minutes in each leaching) to desorb the strontium (Sr) from exchange sites. The first leachate was analysed for exchangeable cations and third Sr to enable CEC determination. The total C and N content of oven dried soils, tephra and biochars were determined using a TruSpec CHNS analyser (Leco FP 2000 Analyser).

Acid hydrolysis of the biochars was conducted by modifying the method of Pansu and Gautheyrou (2006), as described in Wang et al. 2012, to estimate available N. Briefly, ~ 0.5 g of biochar was weighed into a 50 mL Pyrex® cation digestion tube. Then 25 mL of acid mixtures (6 M HCl and 0.1% phenol and drops of octylic alcohol) were added. The tubes were sonicated for 5-10 min, covered with a 10 mL volumetric flask and placed on an aluminium digestion block for 24 hrs at 105°C. Thereafter, the hydrolysates were passed through a pre-weighed dry Whatman® 542 filter paper and diluted to 100 mL; the non-

hydrolysable residues were washed and oven-dried at 60°C. Nitrogen gas adsorption analyses (BET) for specific surface area measurements (Brunauer et al., 1938) were performed on the chemical activated biochar and the control biochar using a Micromeritics Tristar 3000 volumetric adsorption system (Micromeritics; Georgia, US). Laboratory available N (NH_4 and NO_3) was extracted in the WT- L PI biochar using 10 mL of 2 M KCl synthetic solution per 1 g of biochar. The desorption of NH_4^+ -N from WT- L PI biochar was conducted in centrifugation tubes and shaken for 6 hours leading to centrifugation and filtration of solution.

Plant Analysis

Kjeldahl digestion of herbage for total N and P was carried out following the method of McKenzie and Wallace (1954). For this, 0.1 g ground herbage was placed in a 100 mL Pyrex tube along with the 4 mL of digestion mixture ($\text{K}_2\text{SO}_4 + \text{H}_2\text{SO}_4 + \text{selenium powder}$ to heat until clear). The tubes were heated in an aluminium block at 350 °C for 4 hours. After cooling the tubes, the digestion mixture was diluted to 50 mL with deionised water and mixed on a vortex mixture. After settling, the supernatant was analysed for P and NH_4^+ using a Technicon II autoanalyser.

Yield Measurement

All pots from the two trials were harvested when plant growth stopped (treatment's nutrient source exhausted) and showed deficiency symptoms. Plant growth duration was 25 and 45 days for *Experiment 1* and 2, respectively from the placement of the upper pot on the incubated soils until harvest.

8.2.4 Statistical analysis

Analysis of variance (general linear model) and Tukey's test was used to test the effect of soil type, biochar addition with or without wastewater treatment and tephra amendment using SAS (2010) statistical software.

8.3 Results

Soil Characterisation

Initial pH values of Kiwitea and Manawatu soils were mildly acidic (Table 8.1) and optimal for ryegrass growth. However, plant available P was low (Cornforth, 1998), as indicated by their low Olsen P values (8-9 $\mu\text{g g}^{-1}$). The CEC of the Kiwitea soil (23 $\text{cmol}_c \text{kg}^{-1}$) was higher than the Manawatu soil (14 $\text{cmol}_c \text{kg}^{-1}$), possibly due to the finer texture and higher organic

matter content of the former soil. Soil bulk densities were identical (0.95 g cm^{-3}), which avoided problems with soil weight and volume differences among pots. Total N content was higher in the Kiwitea soil (0.4%) than in the Manawatu soil (0.3%).

Tephra and Biochar Characterisation

The original tephra sample was low in Olsen extractable P, total P and exchangeable cations but high in extractable SO_4^- for a soil material (Table 7.2, 8.1). After the wastewater treatment, exchangeable K, Ca, Mg and Na increased, but SO_4^- was displaced by H_2PO_4^- and leached out. Olsen extractable P concentration increased from 2.8 in the untreated tephra to $339.3 \mu\text{g g}^{-1}$ in wastewater treated tephra, while TP increased from 1.1 to 2.45 mg P g^{-1} ($1350 \mu\text{g P g}^{-1}$). This represented a 25% recovery of the increase in total P as Olsen extractable P. Nitrogen content of the wastewater treated tephra increased by 0.8 mg N g^{-1} .

The original L PI biochar sample was low in Olsen extractable P, total P and exchangeable Ca and Mg, but contained significant amounts of exchangeable cations, K and Na (Table 8.2). After the wastewater treatment, exchangeable Ca, Mg and Na increased. Total P concentration increased from 1.3 mg g^{-1} in the untreated L PI to 2.1 mg g^{-1} ($800 \mu\text{g P g}^{-1}$) in wastewater treated (WT L PI) biochar.

The N content of the L PI biochar after wastewater treatment increased from 1.13% to 1.29% (11.3 to 12.9 mg N g^{-1} , L PI vs. WT-L PI; Table 8.2). Mineral N (KCl extractable) was below the detection limit in all biochars and tephtras, except the WT-L PI, where $\text{NH}_4^+\text{-N}$ was 0.03 mg g^{-1} and $\text{NO}_3^-\text{-N}$ 0.92 mg g^{-1} (Table 8.3). Hydrolysable N in biochars increased with wastewater treatment (Table 8.3).

Table 8.1 Chemical analysis of soils and tephra before (T) and after wastewater treatment (WT-T).

Sample	pH	Olsen P ($\mu\text{g g}^{-1}$)	Total P (mg g^{-1})	SO ₄ -S ($\mu\text{g g}^{-1}$)	K cmol _c kg ⁻¹	Ca cmol _c kg ⁻¹	Mg cmol _c kg ⁻¹	Na cmol _c kg ⁻¹	CEC cmol _c kg ⁻¹	Bulk density g cm ⁻³	N g kg ⁻¹	C g kg ⁻¹
T	-	2.8	1.10	589.0	0.06	0.1	0.06	0.17	5	0.76	1.5	28.8
WT-T	-	339.3	2.45	43.0	3.13	25.3	3.81	1.13	n.a.*	0.86	2.3	27.4
Kiwitea soil	5.8	9.0	-	8.5	0.50	8.8	2.07	0.66	23	0.95	4.1	36.0
Manawatu Soil	5.8	8.1	-	6.5	0.27	5.8	2.05	0.11	14	0.95	3.0	25.0

* n.a. = not available; where T and WT-T is non-treated tephra and wastewater-treated tephra, respectively.

Table 8.2 Chemical analysis of biochars (WT-L PI=wastewater treated activated pine biochar, L PI= activated pine biochar, Ctr PI= non activated pine biochar).

Treatment	C %	N %	P g kg ⁻¹	pH	Ash %	BET (m ² g ⁻¹)	K Cmol _c kg ⁻¹	Ca Cmol _c kg ⁻¹	Mg Cmol _c kg ⁻¹	Na Cmol _c kg ⁻¹	CEC (cmol _c kg ⁻¹)
Ctr PI	77.7	0.61	0.5	9.30	4.81	235	3.17	0.42	0.32	4.22	17.60
L PI	78.4	1.13	1.3	10.31	8.67	3.3	3.30	0.20	0.27	4.55	24.89
WT-L PI	73.4	1.29	2.1	9.0	n.a.*	n.a.*	3.36	4.21	0.73	5.30	-

*n.a.=not available.

Table 8.3 Total N and mineral N content of different sorbents.

Sample	Total N (mg g ⁻¹)	2 M KCl extractable NH ₄ ⁺ (mg g ⁻¹)	2 M KCl extractable NO ₃ ⁻ (mg g ⁻¹)	% Hydrolysable N of total N
WT-L PI biochar	13.1	0.03	0.92	10.01
L PI biochar	11.3	-		6.22
Ctr PI biochar	6.1	-		9.01
WT-T	2.3	-		-
T	1.5	-		-

where WT-L PI=waste water treated activated pine biochar, L PI= activated pine biochar, Ctr PI= non activated pine biochar, WT-T= waste water treated tephra, T= tephra with no waste water treatment.

Analysis of Incubated Kiwitea soil

The objectives of the 10-day incubation of chars and tephra with soils was to ensure time for amendment/soil interactions to take place prior to assessment of nutrient bioavailability and in addition allow soil measurements to be made that may assist in interpretation of the results from the Stanford and Dement bioassay. The soils were taken out at the end of incubation and analysed. After incubation for 10 days, the Ctr PI biochar amended Kiwitea soil showed no significant change in KCl extractable NH₄⁺-N, especially at 20 and 40 t ha⁻¹ rates of application. However, extractable NO₃⁻-N increased with rate of Ctr PI biochar addition (Fig. 8.4). The L PI biochar amended Kiwitea soil, however, showed significant reduction in KCl extractable NH₄⁺-N, with a significant increase in extractable NO₃⁻-N as the rate of L PI biochar addition increased.

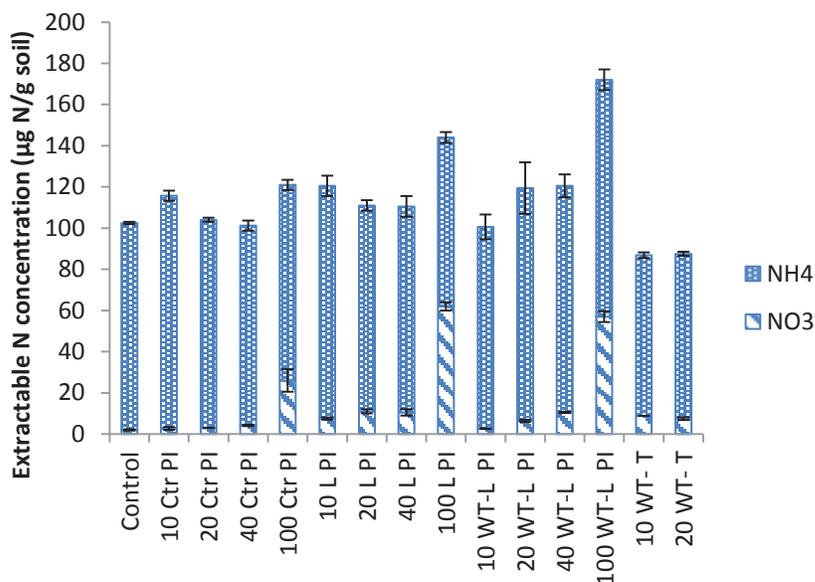


Figure 8.4 KCl extractable NH_4^+ -N and NO_3^- -N in Kiwitea soil after 10 day incubation with different treatments; non-activated pine biochar (Ctr PI), activated biochar (L PI), wastewater treated tephra (WT-T) and activated biochar (WT-L PI) (Application rates equivalent to 0, 10, 20, 40 and 100 t ha^{-1})

After the 10 days incubation, the pH of the soil amended with different biochars was in a range suitable but not excessive for grass growth (pH 6 – 8) and gradually increased as Ctr PI and L PI biochars were added at increasing rates of application. The pH was significantly different in all the treatments ($p < 0.05$) with maximum values in L PI biochar treatments (Fig. 8.5). But pH tended to be lower in soils amended with WT-L PI and at the highest rate (100 t ha^{-1}) of L PI, partly due to nitrification (Fig. 8.4).

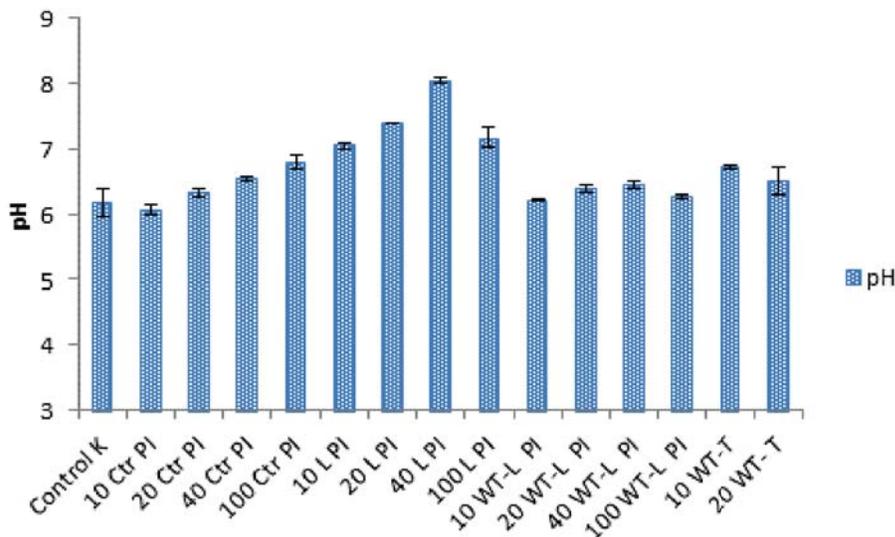


Figure 8.5 pH of Kiwitea soil after 10 day incubation with different treatments ($p < 0.05$);

soil alone (Control), non-activated pine biochar (Ctr PI), activated biochar (L PI), wastewater treated tephra (WT-T), wastewater treated (WT) activated biochar (WT-L PI) (Application rates equivalent to 0, 10, 20, 40 and 100 t ha⁻¹)

Experiment 1 (Biochar applied at 10 and 20 t ha⁻¹ rates)

Shoot Dry Matter

Mean values of above-ground dry matter (DM) yield grown on soil alone (Ctr) (0.33 g DM pot⁻¹, Kiwitea; 0.32 g DM pot⁻¹, Manawatu) were higher than those of soils amended with non-activated biochar. Soils amended with activated biochar and wastewater-treated activated biochar (WT-L PI) grew yields equal to or greater than the soil alone (Ctr). The exception was the unexplainable low yield for the Manawatu soil amended with 20 t ha⁻¹ of L PI (Fig. 8.6). Mean yields of tephra-amended (WT-T) and tephra plus biochar amended WT(T+L PI) soils were above the yields of the control soils, except for the Manawatu soil amended with 20 t ha⁻¹ of WT-T. The highest yield was observed in the 20 t ha⁻¹ WT(T+L PI) treatment in both soils, with values 0.43 and 0.44 g DM pot⁻¹ in Manawatu and Kiwitea soils, respectively. The variation in yield within treatments was large and the differences in shoot dry matter were non-significant ($p < 0.05$) between the two soils.

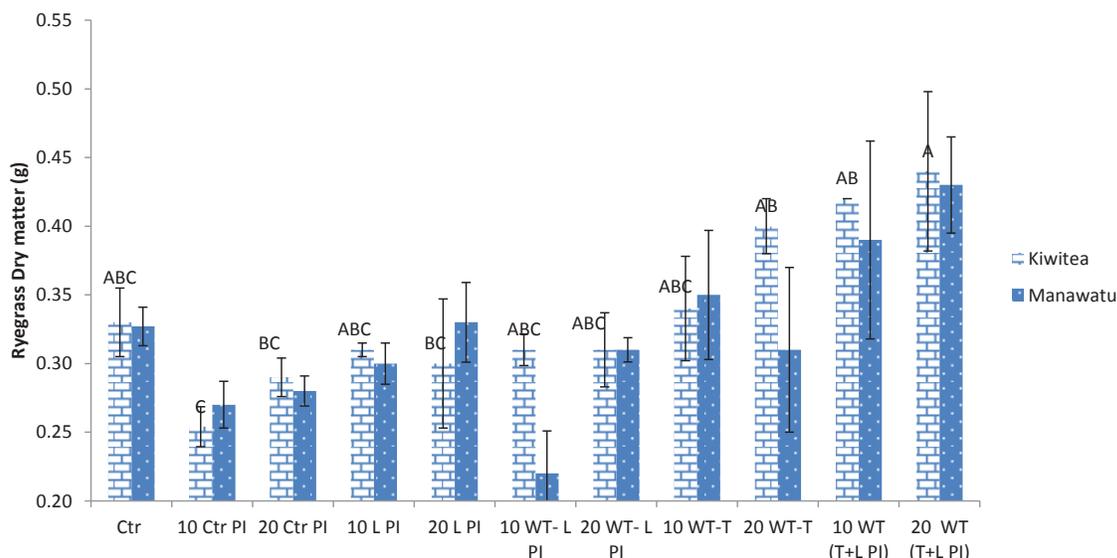


Figure 8.6 Dry matter yield per pot of ryegrass grown on Kiwitea and Manawatu soils (Ctr) amended with biochars and tephra;

namely soil alone (Ctr), non-activated pine biochar (Ctr PI), activated biochar (L PI), wastewater-treated activated biochar (WT-L PI), wastewater-treated tephra (WT-T) and wastewater-treated tephra and activated biochar mixture WT(T+L PI). Application rates were equivalent to 0, 10 and 20 t ha⁻¹. Treatments with different alphabets are statistically different (at $p < 0.05$; Tukey lettering) in Kiwitea soil while Manawatu soil is non-significantly different.

Root biomass

Mean values of air-dried root biomass (Fig. 8.7) recovered from soils amended with all biochars, were either lower or equal to the root biomass recovered from the soils only controls. Tephra addition with or without biochar caused a considerable increase in root biomass, with a maximum root weight (0.63 and 0.97 g DM pot⁻¹) in the WT(T+L PI) treatment at 20 t ha⁻¹ of Manawatu and Kiwitea soils, respectively. There were non-significant differences in root biomass ($p < 0.05$) between the two soils.

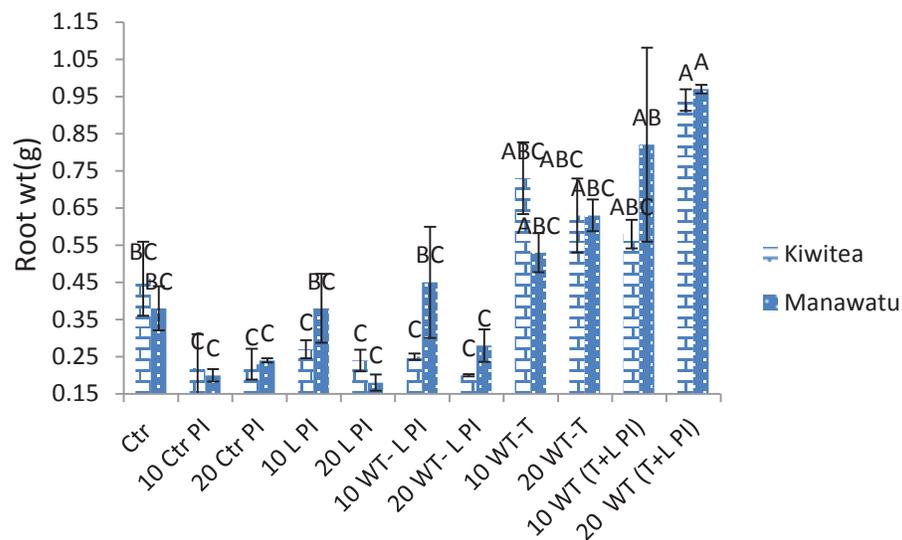


Figure 8.7 Weight of air dried roots per pot of ryegrass in control soils (Ctr) and soils amended with biochars and tephra (with Tukey lettering);

namely soil alone (Ctr), non-activated pine biochar (Ctr PI), activated biochar (L PI), wastewater treated activated biochar (WT-L PI), wastewater treated tephra (WT-T) and, tephra and activated biochar mixture WT(T+L PI). Application rates equivalent to 0, 10 and 20 t ha⁻¹.

Phosphorus in shoots

The phosphorus concentration in shoot biomass was higher when wastewater-treated material [either biochar or tephra; WT-L PI, WT-T and WT(T+L PI) treatments] was added to soils (concentrations > 0.3%) compared with the non-wastewater treated amendments (concentrations < 0.3%; Fig. 8.8). These differences were significant at $P < 0.05$ in Manawatu soil. The herbage P concentration in the treatments without wastewater pre-treated amendments (< 0.3 %) was in the range limiting ryegrass growth (Cornforth, 1998).

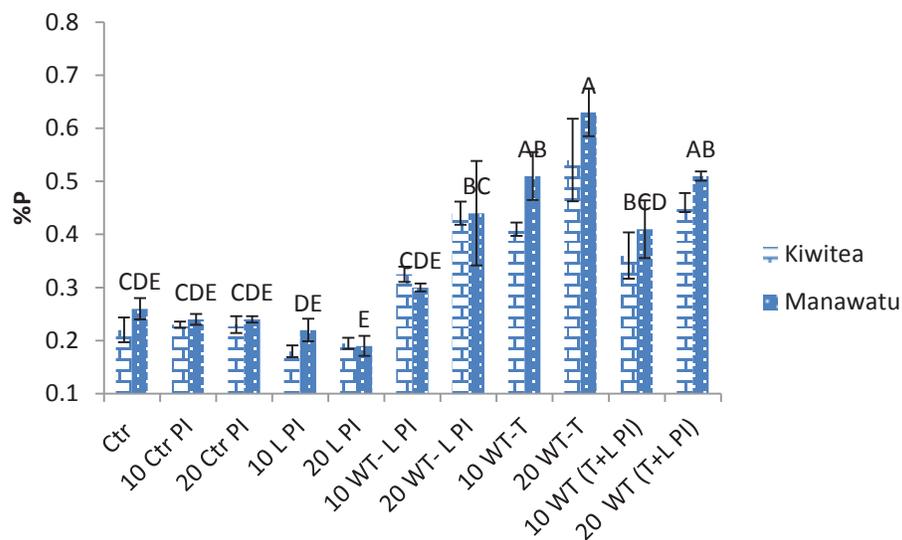


Figure 8.8 The percentage P in ryegrass shoots in control soils (Ctr) and soils amended with biochars and tephra (with Tukey lettering);

namely soil alone (Ctr), non-activated pine biochar (Ctr PI), activated biochar (L PI), wastewater-treated activated biochar (WT-L PI), wastewater treated tephra (WT-T) and tephra and activated biochar WT(T+L PI) mixture. Application rates were equivalent to 0, 10 and 20 t ha⁻¹.

When total P taken up by plants (Fig. 8.9) was compared among treatments, the same trends as for % P concentrations (Fig. 8.8) were observed. The amount of P recovered in shoot (product of shoot mass and % P content) from soils amended with all non-activated and activated biochars were either lower or equal to the P recovered from the soils only controls. Only when wastewater treated biochars and tephra were added to the soils, was there a significant increase in the amounts of P recovered.

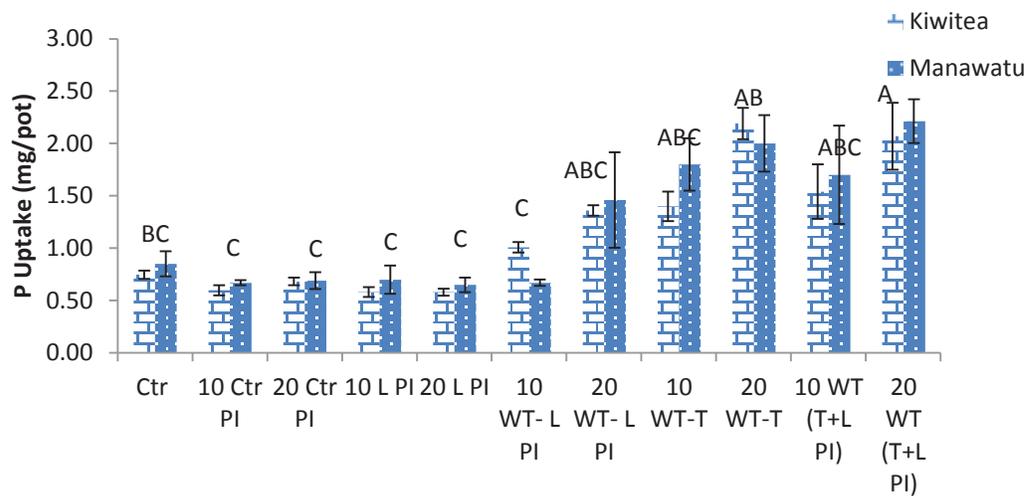


Figure 8.9 P uptake (mg P pot^{-1}) in herbage in control soils (Ctr) and soils amended with biochars and tephra (with Tukey lettering); namely soil alone (Ctr), non-activated pine biochar (Ctr PI), activated biochar (L PI), wastewater treated (WT-T) activated biochar (WT-L PI), wastewater treated tephra (WT-T) and tephra and activated biochar WT(T+L PI) mixture. Application rates were equivalent to 0, 10 and 20 t ha^{-1} .

Nitrogen in shoots

The concentration of N in the shoot biomass ranged from 1.7 to 2.5 % (Fig. 8.10), indicating the plants were below the optimal range for ryegrass growth ($>3\%$) (Cornforth, 1998). There were no significant differences ($p < 0.05$) among treatments, although some trends could be observed (Fig. 8.10). The addition of non-wastewater treated biochar (Ctr PI and L PI) to the Kiwitea and Manawatu soil induced a decrease in N concentration of the above-ground biomass, compared with the Ctr soil. Addition of wastewater-treated amendments to the Kiwitea soil [WT-L PI and WT-T and WT(T+L PI) treatments] increased N content in all treatments, while the effect in the Manawatu soil tended to be the opposite (Fig. 8.10), except for the WT(T+L PI) treatment at the high dose.

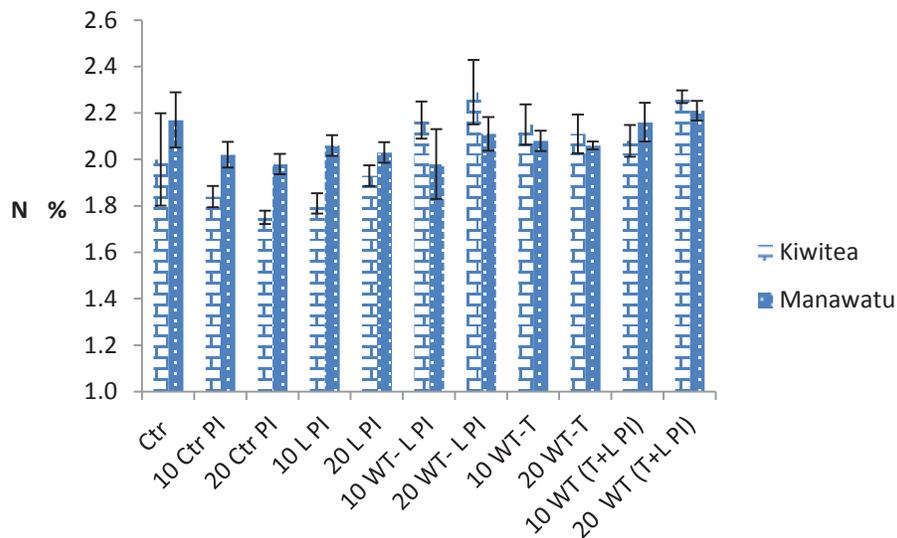


Figure 8.10 The percentage N in herbage in control soils (Ctr) and soils amended with biochars and tephra (Tukey, 0.05);

namely soil alone (Ctr), non-activated pine biochar (Ctr PI), activated biochar (L PI), wastewater treated activated biochar (WT-L PI), wastewater-treated tephra (WT-T) and tephra and activated biochar WT(T+L PI) mixture. Application rates were equivalent to 0, 10 and 20 t ha⁻¹. (No significant differences ($P < 0.05$) among treatments were observed)

Total N taken up by plants showed a similar pattern to N concentration in tissue, but differences among treatments were more accentuated (Fig. 8.11). Addition of non-wastewater treated biochar decreased N uptake from the Kiwitea soil compared with the non-amended soil, although the effect was only significant ($p < 0.05$) for the Ctr PI treatment. In the Manawatu soil, a decline was evident in the Ctr PI biochar and the low dose of L PI biochar, but was not significant ($p < 0.05$). Adding either the WT-L PI biochar at the two doses or the low dose of the WT-T tephra did not show any effect on N uptake. Adding the high dose of the WT-T and both doses of WT(T+L PI) increased N uptake in the Kiwitea soil, compared with the control soil; however, differences were only significant ($p < 0.05$) for the 20 t ha⁻¹ of WT(T+L PI) treatment. Maximum N uptake (10 mg pot⁻¹) was observed in 20 t ha⁻¹ of WT(T+L PI) for the Kiwitea soil (Fig. 8.11).

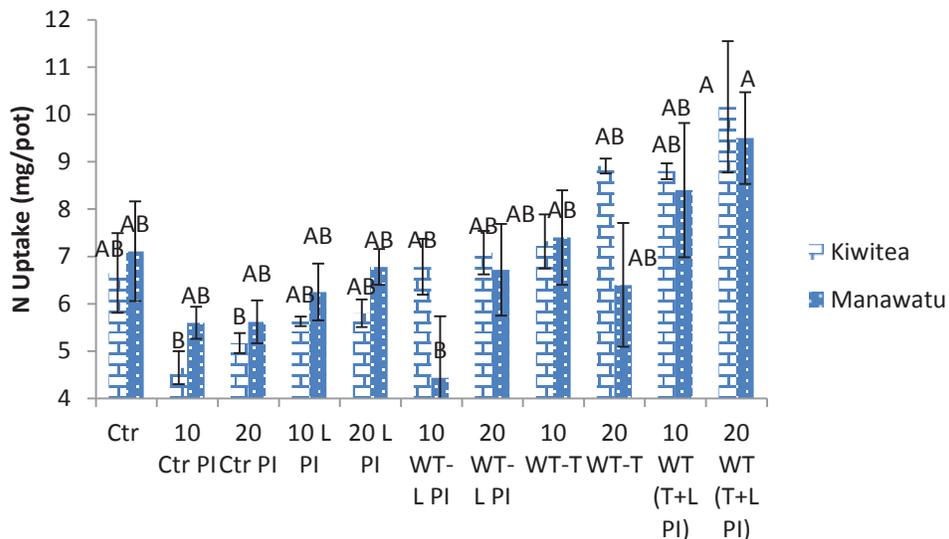


Figure 8.11 N Uptake in herbage in control soils (Ctr) and soils amended with biochars and tephra (Tukey, 0.05);

namely soil alone (Ctr), non-activated pine biochar (Ctr PI), activated biochar (L PI), wastewater treated (WT-T) activated biochar (WT-L PI), wastewater treated tephra (WT-T) and tephra and activated biochar WT(T+L PI) mixture. Application rates were equivalent to 0, 10 and 20 t ha⁻¹.

Experiment 2 (Biochar applied at disposal rates of 40 and 100 t ha⁻¹)

The biochar applications evaluated at lower rates in Experiment 1 are re-tested for the nutrients bioavailability in soils at higher ‘disposal’ rates (40 and 100 t ha⁻¹) of application in Experiment 2.

Dry Matter

When high disposal doses of non-activated pine biochar (Ctr PI) and activated biochar (L PI) were applied to both Kiwitea and Manawatu soils, ryegrass yields tended to be equal to or higher than yields on the un-amended (Ctr) soils (Fig. 8.12). Notably, application of 40 and 100 t ha⁻¹ of activated biochar (L PI) to the Manawatu soil produced lower yields than the same weights of non-activated pine biochar (Ctr PI). This did not occur with Kiwitea soil. When increasing rates of wastewater-treated biochar were added to the Kiwitea soil, there was an increasing trend in plant growth, although this was only significant for the WT-L PI at the dose of 100 t ha⁻¹ (yield 0.47 g).

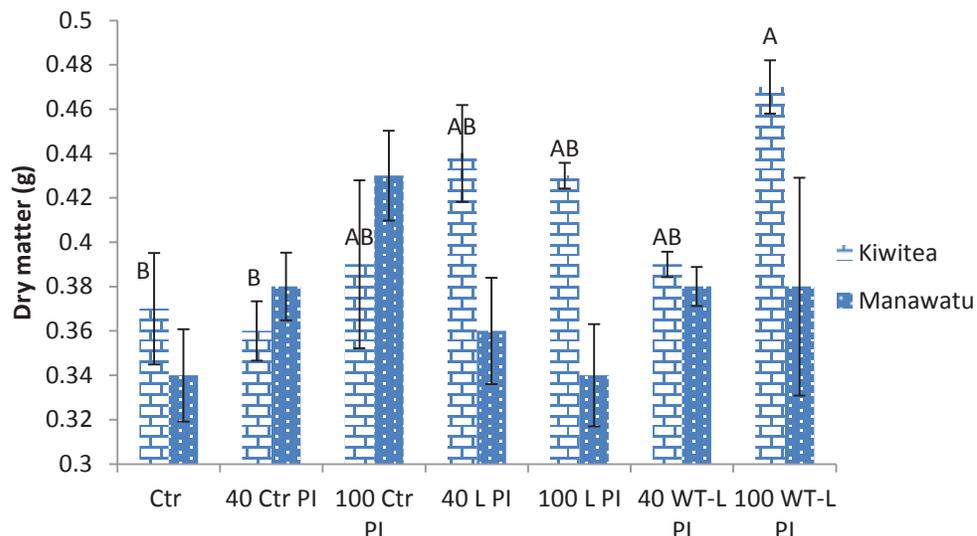


Figure 8.12 Dry matter yield of ryegrass grown on Kiwitea and Manawatu soils treated with higher levels of biochars (Tukey, 0.05);

namely soil alone (Ctr), non-activated pine biochar (Ctr PI), activated biochar (L PI), wastewater-treated (WT) activated biochar (WT-L PI) (Application rates equivalent to 0, 40 and 100 t ha⁻¹)

Roots Biomass

All treatments significantly decreased ($p < 0.05$) root biomass of the Manawatu soil compared with the corresponding Ctr soil (Fig. 8.13). The same trend was observed in the Kiwitea soil, but differences were not statistically significant at $p < 0.05$.

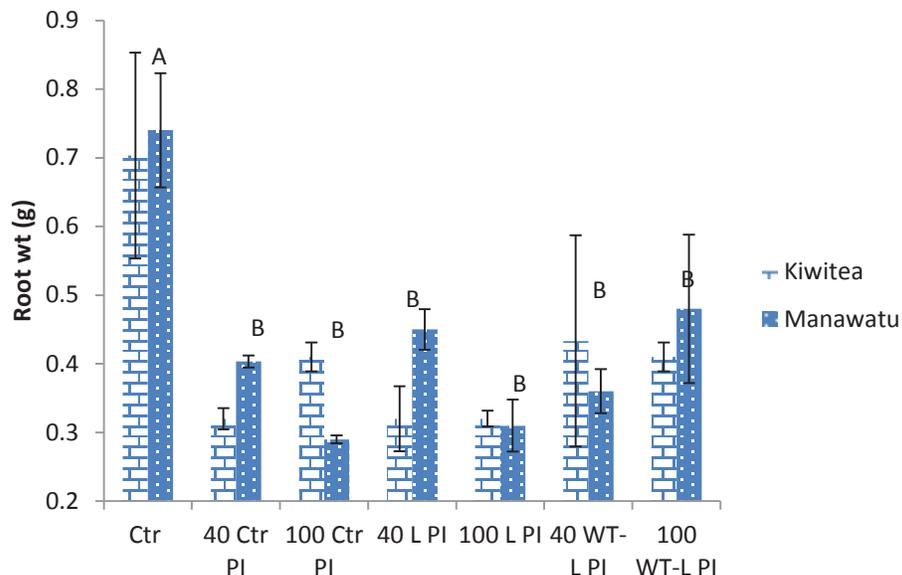


Figure 8.13 Root weights grown on Kiwitea and Manawatu soils treated with higher biochar rates (Tukey, 0.05);

namely soil alone (Ctr), non-activated pine biochar (Ctr PI), activated biochar (L PI), wastewater treated (WT) activated biochar (WT-L PI) (Application rates equivalent to 0, 40 and 100 t ha⁻¹). (Non-significant differences were observed between treatments)

P content in herbage (Shoot drymatter P)

No significant differences ($P < 0.05$) were observed either in % P content or in P uptake by ryegrass from the different treatments studied, with the exception of the P uptake (1.28 mg/pot) in the Kiwitea soil amended with 100 t ha⁻¹ of WT-L PI (Fig. 8.14 and 8.15).

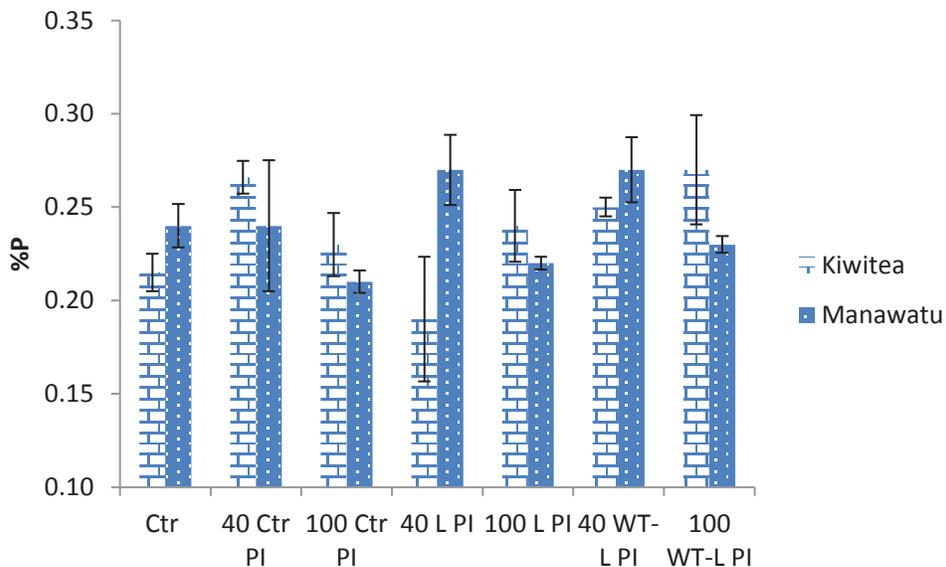


Figure 8.14 The percentage P in ryegrass herbage grown on Kiwitea and Manawatu soils treated with higher biochar rates;

namely soil alone (Ctr), non-activated pine biochar (Ctr PI), activated biochar (L PI), wastewater treated (WT) activated biochar (WT-L PI) (Application rates equivalent to 0, 40 and 100 t ha⁻¹). No significant differences ($P < 0.05$) were observed.

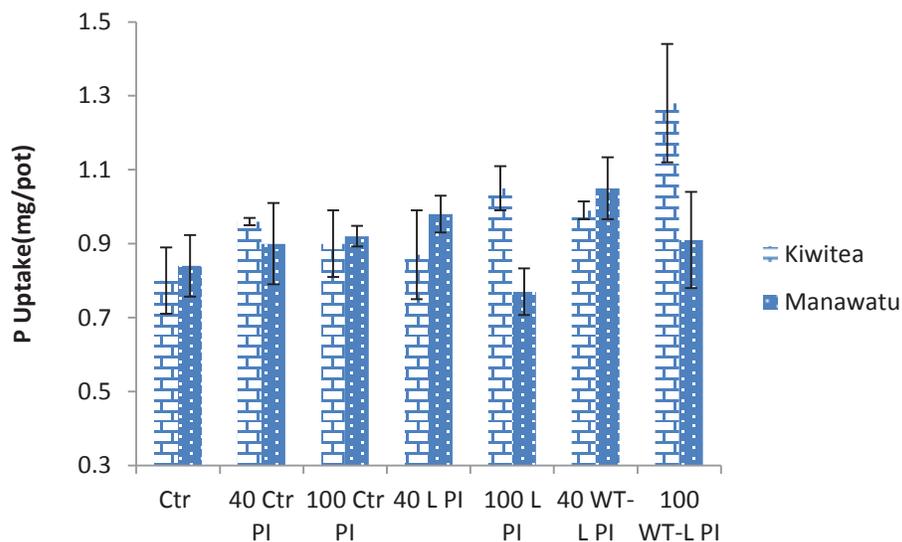


Figure 8.15 P Uptake in ryegrass herbage grown on Kiwitea and Manawatu soils treated with higher biochar rates;

namely soil alone (Ctr), non-activated pine biochar (Ctr PI), activated biochar (L PI), wastewater treated (WT) activated biochar (WT-L PI) (Application rates equivalent to 0, 40 and 100 t ha⁻¹). No significant differences ($P < 0.05$) were observed.

N content in herbage

All soil amendments increased ryegrass N concentration and N uptake compared with the unamended Ctr soil, although differences were only significant for the Kiwitea soil amended with L PI biochar at 40 t ha⁻¹ and with the WT-L PI biochar at 100 t ha⁻¹ (Fig. 8.16 and 8. 17). The latter had the highest N concentration and uptake, with values 2.5 % and 12.25 mg pot⁻¹, respectively. The WT-L PI showed lower N content than the L PI at 40 t ha⁻¹, which could be due to the liming effect of high pH of L PI leading to higher rate of nitrification in soil. The WT-L PI showed increase in % N at highest rate of application, probably due to the increased concentration of sorbed NH₄⁺-N. In spite of the high doses of biochar added, concentrations of N (1.8-2.6 %) in biomass were still in the growth limiting range for ryegrass growth (Cornforth, 1998).

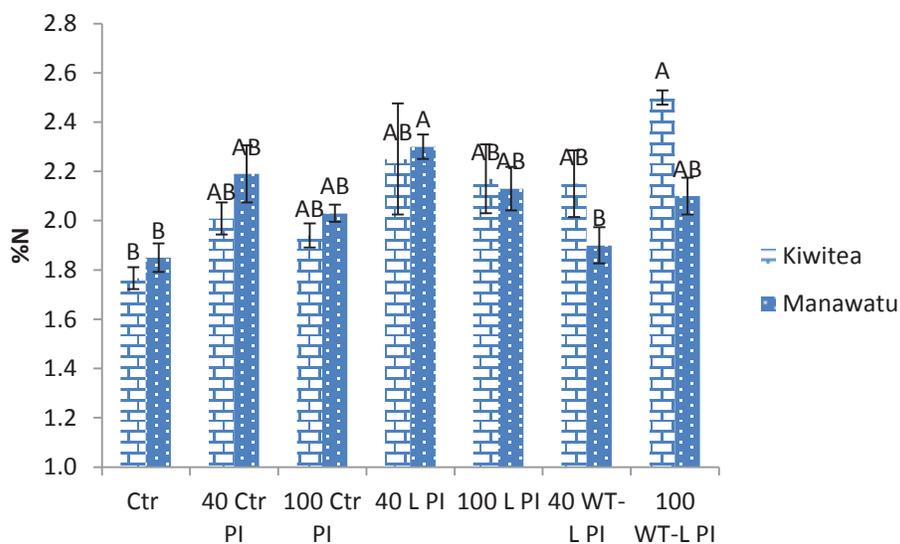


Figure 8.16 The percentage N in herbage grown on Kiwitea and Manawatu soils treated with higher biochar rates (Tukey, 0.05);

namely soil alone (Ctr), non-activated pine biochar (Ctr PI), activated biochar (L PI), wastewater treated (WT) activated biochar (WT-L PI) (Application rates equivalent to 0, 40 and 100 t ha⁻¹)

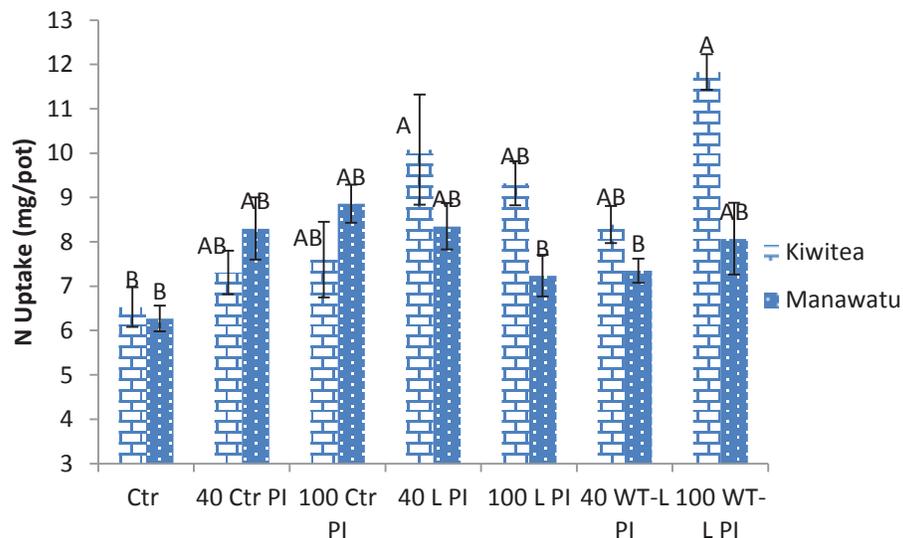


Figure 8.17 N content in herbage grown on Kiwitea and Manawatu soils treated with higher biochar rates (Tukey, 0.05);

namely soil alone (Ctr), non-activated pine biochar (Ctr PI), activated biochar (L PI), wastewater treated (WT) activated biochar (WT-L PI) (Application rates equivalent to 0, 40 and 100 t ha⁻¹)

8.4 Discussion

General plant and root growth

The objective of this study was to test the bioavailability of the NH₄⁺ and P that had been loaded onto activated biochar and volcanic tephra by treatment with wastewater. This was assessed with the exhaustive extraction of N and P (product of shoot dry matter and N and P content) from the soil amendment mixtures, however, the two experiments have produced an interesting trend in shoot and root growth. In both Experiment 1 and 2, the shoot and root masses (Figs. 8.6, 8.12 and 8.13), grown during the period of nutrient uptake, were of similar magnitude. Notably only high rates of biochar application (40 t ha⁻¹ and 100 t ha⁻¹) and wastewater treated tephra application caused notable increases in shoot mass in both experiments. Only wastewater treated tephra caused increases in root biomass (Fig. 8.7). Biochar treatments either treated with wastewater or non-treated did not stimulate root growth. The large loading of P on the tephra could be the cause of root growth stimulation as it has been widely reported that increased P availability stimulated primary root growth (Linkohr et al. 2002, Williamson et al. 2001). Unfortunately, the significance of treatment effects on root biomass differences in a Stanford and Dement experiment are unclear because the roots were constrained to such a small volume of soil.

P and N bioavailability

The assessment of N and P bioavailability has been carried out using the Stanford and Dement procedure, which relies on measuring the difference in N or P uptake pot^{-1} between test plants growing on soil alone and soil amended with biochar or tephra. This difference in nutrient uptake between the soil alone and amended soil can be caused either by the amendment releasing its own nutrients, stimulating the release of soil nutrients or causing the immobilisation of soil nutrients. The latter can be expressed in terms of a decrease in plant N and P uptake.

The recovery of nutrients was calculated from the change in N and P uptake caused by the amendment expressed as the percentage of the N and P added in the amendment (Figs. 8.18, 8.20, 8.21). The change in bioavailability was calculated as the change in N and P uptake caused by the amendment expressed as a percentage of the N and P taken up by the control (Figs. 8.19, 8.22, 8.23).

Recovery of N and P added

In Experiment 1, the greatest amounts of P recovered (2.43 mg pot^{-1}) was in Kiwitea soil treated with 20 t ha^{-1} of wastewater treated tephra (Fig. 8.9, WT-T) or mixed wastewater treated tephra and activated biochar WT(T + L PI). However, there were no significant differences ($p < 0.05$) observed when comparing the two types of soils. Addition of WT-T increased the P recovery by 38-42 % of the total P added in Kiwitea soil at lower rates, while it was 34-57 % of that added in Manawatu soil at 10 and 20 t ha^{-1} (Fig. 8.18). In the wastewater treated activated biochar (WT-L PI) treatment, the recovery of P added by the ryegrass plants was negative or low (-11 to 21%) for both the lower rates (10 and 20 t ha^{-1}) of WT-L PI and 4.2 to 0.45 % for the higher rates (40 and 100 t ha^{-1}) (Fig. 8.20) in both soils. Negative recovery showed the retention or immobilisation of nutrients with biochars. When expressed as a fraction of the labile P (resin plus bicarbonate extractable P (Table 7.4), equivalent to 2.16- 5.05% P of the total P added, as activated biochar, the recovery of labile P from WT-L PI biochar treated soils ranges from 40-43 and 6-34 % at 40 and 100 t ha^{-1} rates in Kiwitea and Manawatu soils, respectively (Chapter 7). These levels of recovery are similar to those expected for the recovery of soluble P from MCP (monocalcium phosphate) amended soils described by Syers et al. (2008) with 38-44 % recovery. Although not a direct comparison, Stout et al. (2003) reported that a Stanford and Dement exhaustive study, removed 82-86 % of resin and bicarbonate P in two soils.

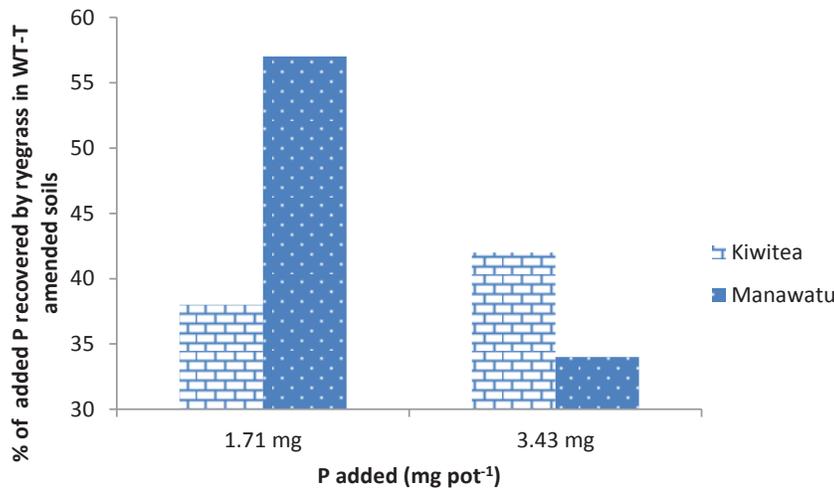


Figure 8.18 The percentage P recovered (of that added) by ryegrass plants grown on Kiwitea and Manawatu soils fertilised with wastewater treated tephra WT-T at two rates of application; 10 and 20 t ha⁻¹

When WT- L PI biochar was added to the pots at lower rates, the recovery of N added in the biochar was very low ranging from 1.4 to 6 % for the Kiwitea soil (on total N basis) (Fig. 8.21), while negative recovery (negative values at lower rates of application) was observed in Manawatu sandy soil. The results are consistent with the low plant availability of N in biochar, as estimated with acid hydrolysis. Yao et al. (2010) observed a restricted N availability (< 1 % of total N) using a modified Soxhlet to determine the nutrient availability of biochar made from biosolids.

Bioavailability index

The results from the present pot trial also provide evidence of the fact that soil N becomes less available to plants when untreated biochar (Ctr PI biochar) and activated biochar (L PI) is added to the soil. This could be attributed to either (i) the sorption of N forms (e.g. NH₄⁺) on the surface of the biochar (Chapter 7) (Steiner et al. 2008) and/or (ii) microbial N immobilisation – as reported by Lehmann et al. (2003) and Steiner et al. (2008). Deenik et al. (2010) investigated the effects of charcoal's volatile content on plant growth and soil N availability. They found that charcoal products with a high volatile matter content reduced plant growth, reduced N uptake, reduced available N content in soils, and increased microbial activity. The N sorbed on the biochar was not recovered in shoot biomass at lower rates

indicating the N immobilisation effect of Ctr PI biochar, which decreased N bioavailability to ryegrass compared to ryegrass grown in soil with no biochar.

Addition of NH_4^+ and P to the soil via wastewater treated (WT-L PI) biochar changed the effect of biochar on available P by increasing its uptake (Figs. 8.9, 8.15), as compared to control soils and other non-wastewater treated biochars. This is consistent with the results of Nelson et al. (2011) who reported that when N was added to the soil, Mehlich-3 P concentrations increased over time in soil with high biochar application relative to the no biochar treatment. Despite the low recovery of P and N from the wastewater treated L PI biochar (Figs. 8.20 and 8.21, the higher rates of application increased the bioavailability of P and N (Figs. 8.22 and 8.23) in the Kiwitea and Manawatu soil.

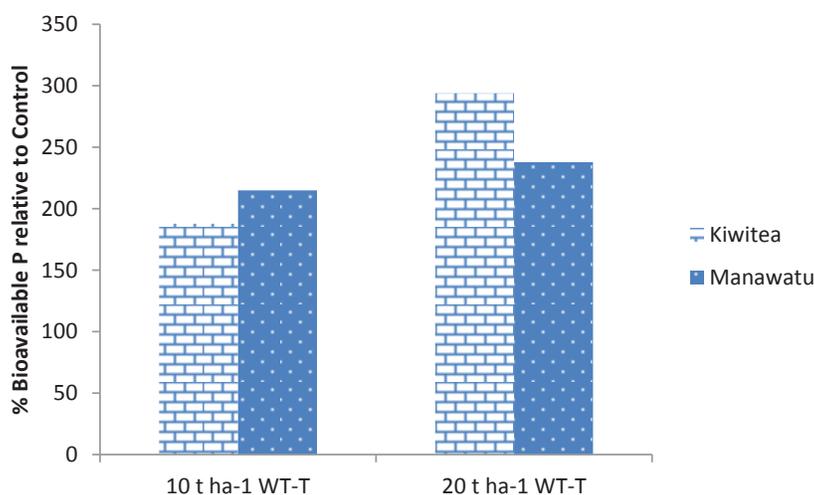


Figure 8.19 Bioavailable P indicated by ryegrass plants grown on Kiwitea and Manawatu soils fertilised with wastewater treated tephra (WT-T @ 10 and 20t ha⁻¹) expressed as percentage of P uptake from unfertilised control

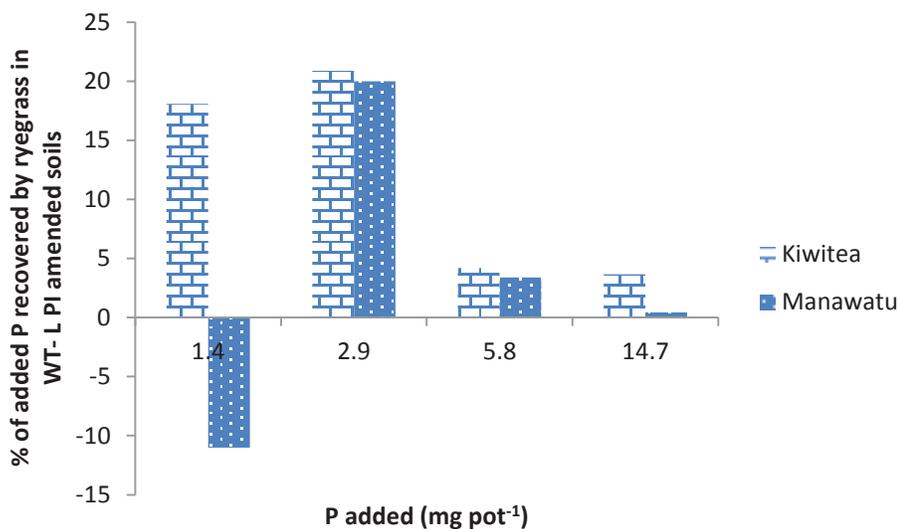


Figure 8.20 The percentage P recovered (of that added) from ryegrass plants grown on Kiwitea and Manawatu soils fertilised with wastewater treated biochar (WT-L PI) at four rates of application; 10, 20, 40 and 100 t ha⁻¹.

The total amount of N recovered from that added as WT- L PI was negative in Manawatu soil at lower rates of application (Fig. 8.21).

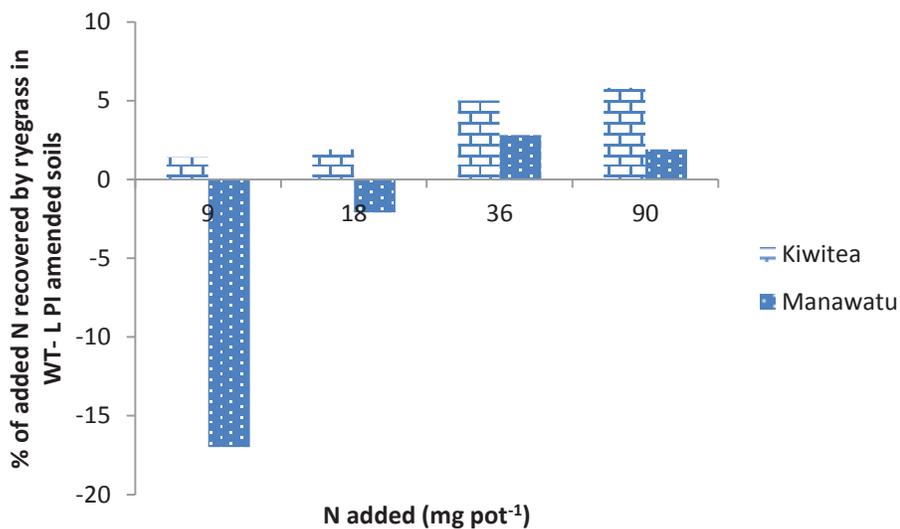


Figure 8.21 The percentage N recovered (of that added) from ryegrass plants grown on Kiwitea and Manawatu soils fertilised with wastewater treated biochar (WT-L PI) at four rates of application; 10, 20, 40 and 100 t ha⁻¹.

The bioavailability of P and N relative to the control (Fig. 8.22, 8.23) was greater in Kiwitea soil than the Manawatu soil treated with WT-L PI biochar. The total amount of N added as WT- L PI biochar was not linearly related to the amount of N recovered in the Manawatu soil but was linearly related to N recovered in the Kiwitea soil (Fig. 8.24). For example, the total amount of N added as different biochars either as total N added (Fig. 8.24 a) or as N added as hydrolysable N pot^{-1} (Fig. 24 b) was poorly related to the amount of N recovered in the Manawatu soil but was linearly related to N recovered in the Kiwitea soil.

There was no relationship between the amount of KCl extractable N (NO_3^- -N plus NH_4^+ -N) in the soil biochar mixtures after 10-day incubation in the Kiwitea soils and the total N uptake by the ryegrass plants (data not shown).

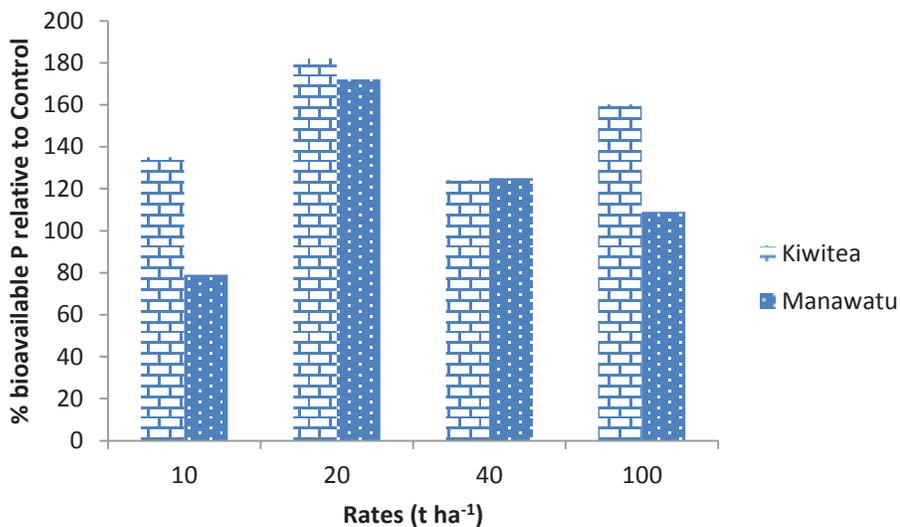


Figure 8.22 The percentage bioavailable P as indicated by ryegrass plants grown on Kiwitea and Manawatu soils fertilised with wastewater treated biochar (WT-L PI) at four rates of application; 10, 20, 40 and 100 t ha^{-1} ; expressed as % of P uptake in unfertilised soil.

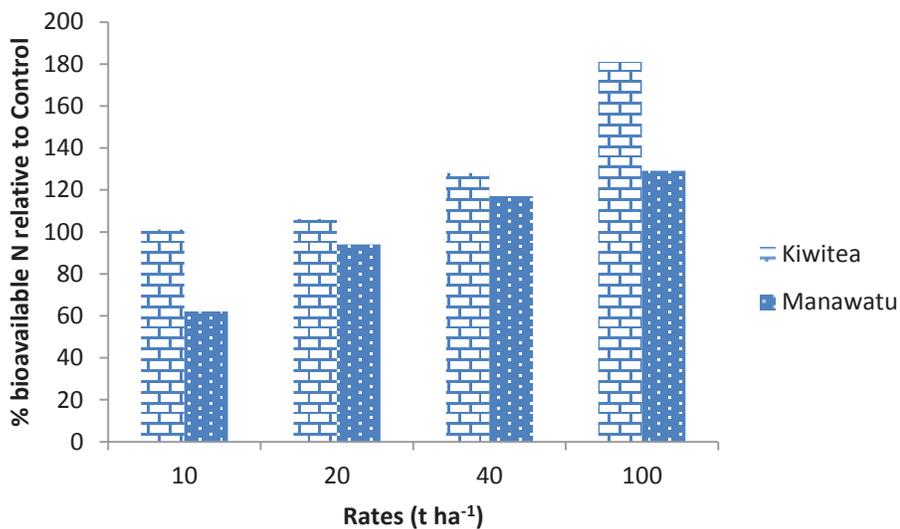
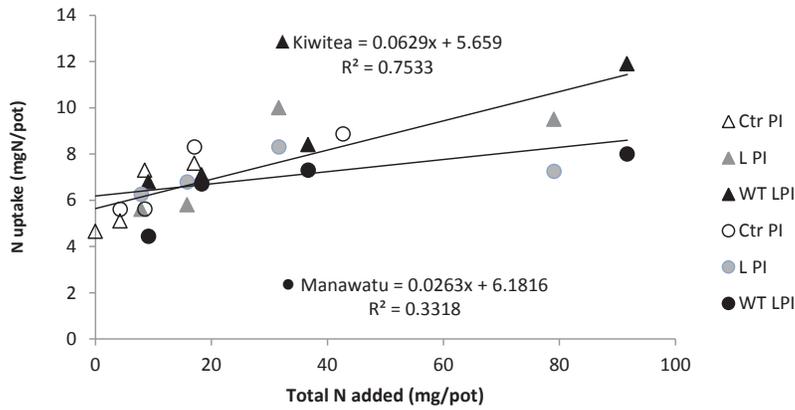


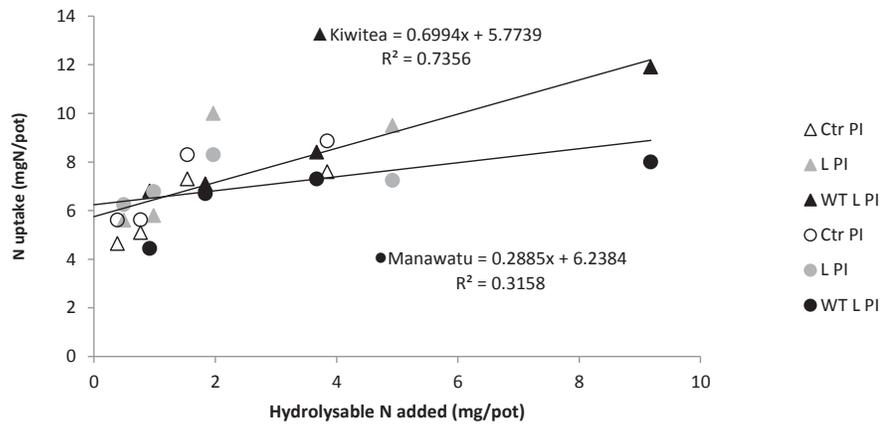
Figure 8.23 The percentage bioavailable N as indicated by ryegrass plants grown on Kiwitea and Manawatu soils fertilised with wastewater treated biochar (WT-L PI) at four rates of application; 10, 20, 40 and 100 t ha⁻¹, expressed as % of N uptake in unfertilised soil.

The hydrolysable N content of the chars has been measured (Table 8.3) and represents less than 10% of total N. In the Kiwitea soil, the general increment in N uptake over the unfertilised control soil is of a similar size to the amount of hydrolysable N added (Fig. 8.24 c). Therefore, hydrolysable N is more representative of the plant available N content of the wastewater treated chars. However, it must be noted that application of the chars at 20 t ha⁻¹ or less created a situation where char and soil N was less available than in the unfertilised soil.

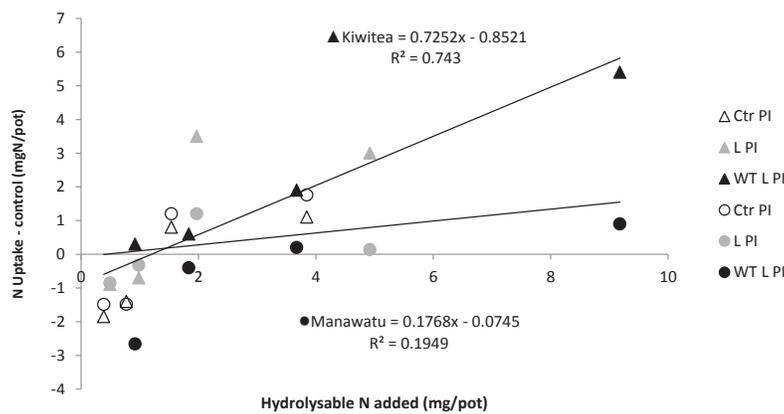
At the higher rates of char application, 40 and 100 t ha⁻¹, the increase in N availability could also result from the liming effect of biochars with more nitrification occurring, as was evident in the Kiwitea soil incubation (Fig. 8.4), thereby leading to the increase in yield. An increase in crop yield due to biochar application has also been reported by Chan et al. (2008), working with radish grown on an Alfisol amended with biochar from poultry litter (produced at 450, 550 °C). Similarly, Chan et al. (2007) reported 130% increase in biomass yield in radish @ 100 t ha⁻¹ of green waste biochar.



a).



b).



c).

Figure 8.24 Graphs showing the relationships between the amount of N taken up by ryegrass and two measures of N added; total N (a) and hydrolysable N (b and c) for biochars (Ctr PI, L PI, WT-L PI) applied to the Kiwitea (triangles) and Manawatu (circles) soils.

8.5 Conclusions

The Stanford and Dement procedure indicated the availability of nutrients, N and P very well. The exhaustive technique showed clearly the differently treated chars, untreated, activated and wastewater treated, contained significantly different amounts of nutrients. Most of the NH_4^+ -N sorbed (90-98 %) on the (WT- L PI) wastewater treated activated biochar was not available to plants, especially in Manawatu soil, thereby not supporting the idea of use of wastewater treated biochar as slow release fertiliser for sandy soils. The bioavailability of N and P from amendments and soil was more pronounced in the Kiwitea soil at higher biochar application rates. However, when low biochar application rates (10 and 20 t ha⁻¹) were used there still seemed to be N immobilisation through microbial growth or sorption of NH_4^+ -N into the biochar micropore lattice.

The P recovery from wastewater treated activated biochar (WT- L PI) and wastewater treated tephra (WT-T) range from -11 to 21 % and 34-58 % of that added, respectively in both soils. These higher rates of P recovery are useful and further studies of wastewater treated tephra and biochar as a P fertiliser could be feasible.

Within the time constraints of this PhD study the Stanford and Dement technique provided a rapid method for assessing the P and N availability in a range of activated, non-activated and wastewater treated biochars, however, it is recommended that other longer-term studies are conducted to confirm these findings that N has a low level of availability when added to the soil as part of or in the presence of biochar. In these short-term studies the amount of hydrolysable N in chars was an approximate indicator of the amount of N they would release for plant uptake.

References

- Ahmedna M, Johns MM, Clarke SJ, Marshall WE, Rao RM (1997) Potential of agricultural by-product-based activated carbons for use in raw sugar decolourisation. *Journal of the Science of Food and Agriculture*. 75, 117-124.
- Blakemore LC, Searle PL, Daly BK (1987) Methods for chemical analysis for soils. *NZ Soil Bureau Scientific report*. 80, 78–79
- Brunauer S, Emmett PH, Teller E, (1938) Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society*. 60, 309-319.
- Chan KY, 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, 629-634.
- Chan KY, Van Zwieten L, Meszaros I, Downie A, Joseph S (2008) Using poultry litter biochars as soil amendments. *Australian Journal of Soil Research*. 46,437-444.
- Cornforth IS (1998). *Practical Soil Management*. Lincoln University Press, Lincoln Univ., Canterbury. New Zealand.
- Deenik JL, McClellan T, Uehara G, Antal Jr MJ, Campbell S (2010) Charcoal volatile matter content influences plant growth and soil nitrogen transformations. *Soil Science Society of America Journal*. 74.
- Johnson CM, Nishita H (1952) Microestimation of sulphur in plant material, soil, and irrigation waters. *Analytical Chemistry*. 24, 736-742.
- Keeney DR, Bremner JM (1967) Determination and isotope-ratio analysis of different forms of nitrogen in soils: 6, Mineralizable nitrogen. *Soil Science Society of America Proceedings*. 31, 34-39.
- Lehmann J, da Silva JP, Steiner C, Nehls T, Zech W, Glaser B (2003) Nutrient availability and leaching in an archaeological Anthrosol and a Ferralsol of the Central Amazon basin: fertilizer, manure and charcoal amendments. *Plant and Soil*. 249, 343-357.
- Linkohr BI, Williamson LC, Fitter AH, Leyser H. (2002) Nitrate and phosphate availability and distribution have different effects on root system architecture of Arabidopsis. *The Plant Journal*. 29(6), 751-760.
- Matsue N, Wada K (1985) A new equilibrium method for cation-exchange capacity measurement. *Soil Science Society of America Journal*. 49, 574–578.

- Mckenzie HA, Wallace HS (1954). The kjeldahl determination of nitrogen: A critical study of digestion conditions, temperature, Catalyst and oxidizing agents. *Australian Journal of Chemistry*. 7, 55-70.
- Murphy J, Riley JP (1962) A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta*. 27, 31-36.
- Nelson NO, Sandra C, Wenqiao Yuan A, Gan J (2011) Nitrogen and Phosphorus Availability in Biochar-Amended Soils. *Soil Science*. 176
- Olsen SR, Cole CV, Watanabe FS, Dean LA (1954) Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA.
- Pansu M, Gautheyrou J, (2006). Organic forms of nitrogen, mineralizable nitrogen (and carbon). Chapter 14. In: Pansu, M., Gautheyrou, J. (Eds.). *Handbook of soil analysis: Mineralogical, organic and inorganic methods*. Springer Berlin, Heidelberg, New York. pp. 497-547.
- Ryden JC, Syers JK, Tillman RW (1975). Use of tephra for the removal of dissolved inorganic phosphate from sewage effluent. *New Zealand Journal of Science*. 18, 3-16.
- Searle PL (1979). Measurement of adsorbed sulphate in soils—effects of varying soil: extractant ratios and methods of measurement. *New Zealand journal of Agricultural Research*. 22, 287-290.
- Stanford G, Dement JD (1957) A method for measuring short-term nutrient absorption by plants: I. Phosphorus. *Soil Science society of America Proceedings*. 21, 612-617.
- Steiner C, Das KC, Garcia M, Forster B, Zech W (2008). Charcoal and smoke extract stimulate the soil microbial community in a highly weathered xanthic Ferralsol. *Pedobiologia*. 51, 359-366.
- Stout WL, Sharpley AN, Weaver SR (2003) Effect of amending high phosphorus soils with flue-gas desulfurization gypsum on plant uptake and soil fractions of phosphorus. *Nutrient cycling in agroecosystems*. 67, 21-29.
- Syers JK, Johnston AE, Curtin D (2008) Efficiency of soil and fertiliser phosphorus use. *FAO Fertilizer and plant nutrition Bulletin No. 18*. FAO, UN, Rome, pp 30-34.
- Taghizadeh-Toosi A, Clough TJ, Sherlock RR, Condon L M (2011) Biochar adsorbed ammonia is bioavailable. *Plant and Soil*. 1-13.
- Wang T, Camps Arbestain M, Hedley M, Bishop P (2012) Nitrogen forms and lability of biochars produced from dairy manure and biosolids. *Elsevier*.

- Williamson LC, Ribrioux SPCP, Fitter AH, Leyser HMO (2001) Phosphate availability regulates root system architecture in Arabidopsis. *Plant Physiology*. 126(2), 875-882.
- Yao FX, Camps Arbestain M, Virgel S, Blanco F, Arostegui J, Maciá-Agulló JA, Macías F (2010). Simulated geochemical weathering of a mineral ash-rich biochar in a modified Soxhlet reactor. *Chemosphere*. 80, 724-732.

Chapter 9

Overall Conclusions and Recommendations for future work

9.1 Justification and organisation of work

A review of current literature suggested that adoption of biochar technology is mainly constrained by the cost of manufacture and application to soil exceeding the value of sequestered carbon and any agronomic value biochar may have. The dustiness of biochar during preparation and application and the potential release of poly aromatic hydrocarbons (PAH) during manufacture are also deterrents (Lehmann and Joseph, 2009). Biochar may cost \$NZ 200/m³ biochar to manufacture and apply to soils, depending on feedstock availability. To overcome these constraints, researchers are looking to provide evidence that biochar can provide additional benefits that would increase its value. Most of the research conducted on biochar previously focussed on properties of biochar and its stability in soils as a carbon sink. Associated with this work on biochar as a carbon sink, there has been detailed research into the chemical and physical properties of biochar and its interactions with soils. Specific biochars had been recognized as good sorbents for different kinds of organic and inorganic pollutants removal (Chen et al. 2008, Chen and Chen 2009, Chen et al. 2011). Of particular interest was research demonstrating the cation exchange capacity of biochar. To achieve a higher cation exchange capacity in biochar, there is need of some pre or post treatments (activation) that either oxidise the surface or increase the acidic functional groups, especially carboxyl groups (Glaser et al. 2003).

A parallel review of wastewater treatment revealed that there remains a need to develop active filters to remove the cation NH_4^+ and the anion H_2PO_4^- from dairy and urban wastewaters. In particular the treatment of urban and dairy farm wastewater using a two-pond system remains ineffective for the complete removal of nutrients like N and P. Further treatment, such as passing the effluents through active filters, prior to discharge, needs to be developed. Several other sorbents, such as zeolite (Nguyen and Tanner, 1998; Cooney et al. 1999) and bark (Bolan et al. 2004; Wieczorek, 2008) had been studied for this purpose however, no research work was identified that investigated the role of biochar in wastewater treatment.

The research in this thesis therefore focussed on manufacturing and activating biochars for testing as active filter media for removing NH_4^+ from wastewaters. The research then tested the fertiliser value of the wastewater treated biochars.

The research conducted in this thesis was arranged in four main areas (Fig. 9.1)

1. Optimization of Pyrolysis conditions and Biochar manufacture from a range of pine chip and eucalyptus bark materials (Chapters 3, 4, 5 and 6).
2. Testing and enhancing, by activation (Chapter 3), biochars ability to sorb ammonium in comparison to other sorbents (Chapters 4 and 5) (
3. Testing biochars and biochar /tephra mixtures for wastewater treatment (Chapters 6 and 7).
4. Evaluation of wastewater treated sorbents (biochar and tephra) as slow release fertilisers (Chapter 8).

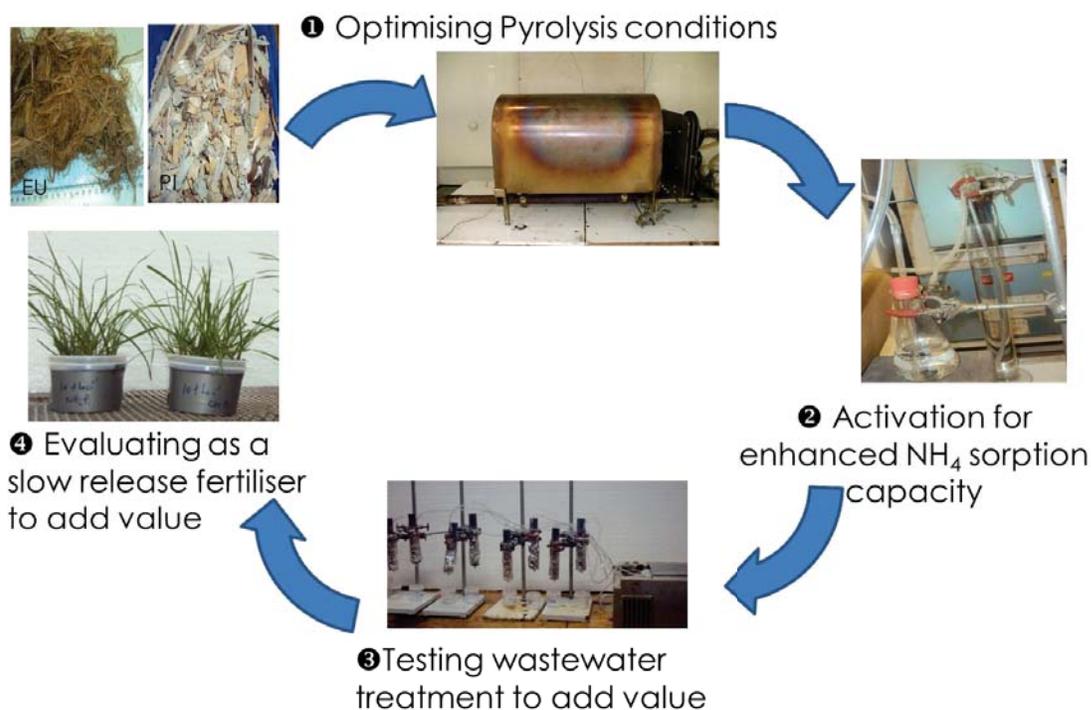


Figure 9.1 Different Key experimental steps of Thesis

9.2 Important findings

Pyrolysis Conditions

All pyrolysis was conducted in a small rotary kiln (5 L) with feed stocks taken to a final temperature of 550 °C. It was found that at this final temperature consistent yields of biochar with high CEC values were obtained. This was consistent with the report of Singh et al. (2010), that higher CEC was achieved when biochars were produced at higher temperatures.

Activation of biochar for enhanced NH_4^+ sorption

A low cost activating agent was needed to enhance the CEC of biochars. An alkaline, high sulphur containing tannery waste was a successful activating agent, used on the feedstock prior to pyrolysis (Chapter 3). Utilising this waste was a lower cost method compared to the use of alkaline salts previously recommended in the literature for the activation of biochar. After activation it was important to wash the soluble alkaline ash from the activated biochars prior to use as NH_4^+ sorbents. This avoided the risk of high pH conditions causing NH_3 volatilisation (Chapter 5). The tannery waste activation did enhance the cation exchange capacity and ammonium sorption capacity of biochars (Chapter 3). For example, chemically-treated biochars (S EU) retained greater NH_4^+ from a 40 mg $\text{NH}_4^+\text{-N L}^{-1}$ synthetic solution than the control biochars (Ctr EU) (e.g. 61 % retention in Ctr EU and 83 % in S EU). Chemical and physical characterisation indicated that the increase in CEC was not caused by changes in specific surface area but through the increase in functional groups such as carboxylic and probably sulphonic acid surface groups (Chapter 3). The high S content of the tannery waste responsible for the formation of the latter during pyrolysis.

Ammonium was more strongly held by the activated than unactivated biochar. Desorption of NH_4^+ ions was lower from tannery waste treated biochars (0.1-2 % desorption) compared to the untreated control biochars (14-27 % desorption). The mechanism of $\text{NH}_4^+\text{-N}$ sorption on biochars was considered to be non-specific (CEC mostly on carboxylic groups and sulphonate groups developed from tannery waste activation). If the retention was solely because of CEC, then it is expected that the majority of the sorbed NH_4^+ would desorb back into solution by KCl extraction. However, it did not happen so there must be other retention reactions. These could be NH_4^+ retention on CEC (sulphonate) groups in small pores. Or it could be that some small pores remain alkaline. Generation of NH_3 in an alkaline

environment in the presence of sulphonate groups on charcoal has been shown to lead to ammonium sulphate and amine formation in the carbon lattice (Petit et al., 2010). The latter conversion to amines may partly explain the irreversibility of NH_4^+ sorption and the low plant availability of biochar N found in Chapter 8.

Despite the enhanced NH_4^+ sorption of activated biochars shown in Chapter 3, it is still evident that some commercial Zeolites will have higher NH_4^+ sorption capacity per unit weight and per unit volume (Chapter 4). However Zeolite of this grade is known to be an expensive material given the cost of \$NZ 600/tonne (Blue Pacific minerals, NZ). This gives a target value for the production of biochars to replace zeolite in some water treatment roles.

Wastewater treatment with biochars

The removal of NH_4^+ by biochars in batch and column studies were found to be dependent on the flow rate, influent concentration, competing cations and contact time between wastewater and biochar particles. These features need to be carefully described when sorbents are being compared for their efficiency of NH_4^+ sorption from waste waters.

The evaluation of the effectiveness of tannery waste activated biochars and non-activated biochars at removing the NH_4^+ from aerobic pond treated farm dairy and town sewage wastewaters was tested under different batch and column studies. The greatest NH_4^+ sorption capacity ($2.17 \text{ mg N g}^{-1} \text{ biochar}$) was achieved by the L PI biochar (pine biochar pre-treated with liquid tannery waste, activated) in a column study with urban wastewater. Based on this sorption capacity, a commercial water treatment model could be designed as shown in Fig. 9.2.

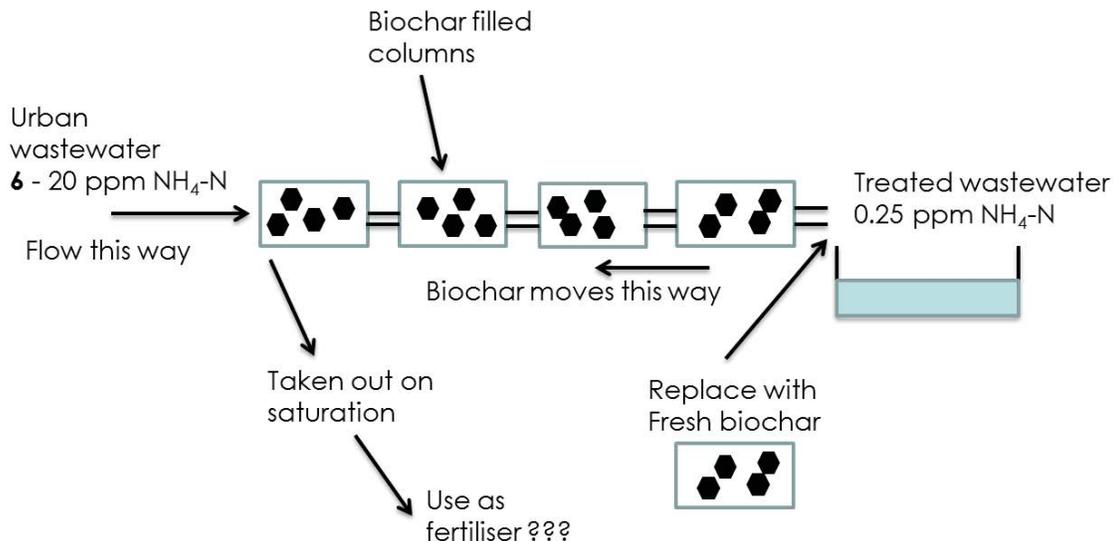


Figure 9.2 Biochar Column Model for wastewater treatment.

Theoretically 1 m^3 Biochar will treat 38 m^3 wastewater based on Column study C in Chapter 6 with influent concentration of $6\text{ ppm NH}_4^+\text{-N}$. Biochar costs about $\$100/\text{m}^3$ to make and $\$100/\text{m}^3$ to supply. If wastewater/capita/year is 110.5 m^3 then 2.9 m^3 biochar/year/capita is required which will cost $\$580$ per year/capita. As this is expensive option, so more research is needed to find other added values of biochars as well as some other activation techniques that may achieve greater increases in the cation exchange capacity of biochars.

In order to develop a filter capable of removing both NH_4^+ and DRP, it was necessary for activated biochar be combined with a material known to have a high P sorption capacity, an andesitic tephra (Okato tephra). This mixture, TE/BC-Mix, was the most promising filter of those assessed (Chapter 7) as it had the best hydraulic conductivity, highest NH_4^+ sorption ($1.54\text{ mg NH}_4^+\text{-N g}^{-1}$) and second highest P sorption (85 mg P/column). The XRD analysis of tephra and biochar before and after wastewater treatment showed the presence of apatite in biochar after wastewater treatment, which confirmed the hypothesis of precipitation of P with Ca at high pH that was one of the causes of P removal by biochar alone. Therefore, columns of biochar alone should be tested in future for both N and P removal from wastewaters.

Evaluation of the fertiliser value of nutrient sorbed biochars

The wastewater treated materials (tephra and biochar) from this study were evaluated for their fertiliser value in soils by using the Stanford and Dement exhaustive technique (1957)

and simulating low (10 and 20 t ha⁻¹) and high (40 and 100 t ha⁻¹) application rates per hectare.

In the wastewater treated activated biochar (WT-L PI) treatment, the recovery of P added with the biochar amendments in plant tissues decreased from -11 to 21% in the lower application rates (10 and 20 t ha⁻¹) of WT-L PI to 4.2 to 0.45 % in the higher rates (40 and 100 t ha⁻¹) in both soils (Manawatu and Kiwitea). The recovery was negative to minimal for N (-17 to 6 %) in both soils for all treatments including wastewater treated activated biochar treatments. With the addition of wastewater treated tephra, P recovery ranged from 38-42 % of the total P added in the Kiwitea soil and was 34-57 % in the Manawatu soil at the lower rates of application (10 and 20 t ha⁻¹).

Based on the relatively low initial N and P content and low to medium plant recovery of N and P from wastewater treated biochars, their large-scale use for wastewater treatment and reuse as N and P fertiliser is still likely to be uneconomic.

9.3 Main Conclusions

This thesis has made a contribution to the literature by showing for the first time that:

1. Biochars made from non-activated pine feedstock sorbed similar amounts of NH₄⁺ from wastewaters as bark media.
2. Zeolite was the best sorbent for NH₄⁺ removal but was costly with no further use to add value.
3. Biochar can be activated for improved NH₄⁺ sorption by using alkaline tannery waste pre-treatment of feedstock prior to pyrolysis. The enhanced NH₄⁺ sorption capacity of activated biochars was confirmed in a small batch sorption study.
4. Alkaline pre-treated activated pine washed biochar can remove more NH₄⁺ from wastewater than non-activated char. Washing of alkaline activated biochars is an important step for use of biochar as an NH₄⁺ sorbent, as it reduced the volatilisation of ammonia from solution as well as enhancing the sorption capacity.
5. Combined tephra and biochar filters can be developed for both N and P removal from wastewaters, but recovery of these nutrients by plants was relatively low when used as a soil amendments. Therefore, the use of these materials as wastewater filters and soil amendments are unlikely to be economic, without further improvements. Moreover,

alkaline activated biochars can also remove P from wastewaters, which was partially explained by precipitation reactions as identified by XRD analysis.

6. The NH_4^+ sorbed by activated and non-activated pine biochar showed less rate of desorption of NH_4^+ by KCl extraction and gave low plant recovery of N from wastewater treated biochars in Stanford and Dement (1957) bioassay study.

9.4 Implications for Future Research

The experimental work reported in this thesis was constrained by the time limit for the PhD programme. There are a number of areas arising from this PhD study that require further research, which include:

1. Tannery waste activation of pine biochar proved to enhance nutrient sorption of pine biochar. However, other activation techniques for biochars should be evaluated with a range of different feedstocks for their potential to sorb nutrients.
2. Chemically activated biochars showed enhanced sorption of NH_4^+ than non-activated biochars but the desorption of NH_4^+ from biochars was minimal by KCl extraction, which needs further work to identify the mechanisms responsible for this as well as ways to trigger the desorption of NH_4^+ in soils.
3. Studies on the ability of biochar to remove organic pollutants from wastewaters are needed.
4. Other added values of biochar should be evaluated apart from wastewater treatment like odour control etc.

References

- Bolan N, Wong L, Adriano D (2004) Nutrient removal from farm effluents. *Bioresource technology*. 94(3), 251-260.
- Cooney E, Booker N, Shallcross D, Stevens G (1999) Ammonia removal from wastewaters using natural Australian zeolite. II. Pilot-scale study using continuous packed column process. *Separation Science and Technology*. 34(14), 2741-2760.
- Chen B, Chen Z (2009) Sorption of naphthalene and 1-naphthol by biochars of orange peels with different pyrolytic temperatures. *Chemosphere*. 76, 127-133.
- Chen B, Chen Z, Lv S (2011) A novel magnetic biochar efficiently sorbs organic pollutants and phosphate. *Bioresource Technology*. 102, 716-723.
- Chen B, Zhou D, Zhu L (2008) Transitional adsorption and partition of non-polar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures. *Environmental Science and Technology*. 42, 5137-5143.
- Glaser B, Guggenberger G, Zech W, Ruivo ML (2003) Soil organic matter stability in Amazonian dark earths. In: Lehmann et al (ed.) Amazonian dark earths: Origin, properties, management. Kluwer Academic Publishers, Dordrecht, The Netherlands. p. 141-158.
- Lehmann J, Joseph S (2009) Biochar for environmental management: an introduction. In: Lehmann J, Joseph S. (Eds.), Biochar for Environmental Management: Science and Technology. Earthscan, London. 1-12.
- Nguyen M, Tanner C (1998) Ammonium removal from wastewaters using natural New Zealand zeolites. *New Zealand Journal of Agricultural Research*. 41, 427-446.
- Petit C, Kante K, Bandosz TJ (2010) The role of S containing groups in ammonia retention on activated carbons. *Carbon*. 48, 654-667.
- Singh B, Singh BP, Cowie AL (2010) Characterisation and evaluation of biochars for their application as a soil amendment. *Australian Journal of Soil Research*. 48(7), 516-525.
- Stanford G, Dement JD (1957) A method for measuring short-term nutrient absorption by plants: I. Phosphorus. *Soil Science society of America Proceedings*. 21, 612-617.
- Wieczorek S (2008) Assessing the Influence of Adsorbent Bed (Tree Bark) Parameters on the Reduction of Ammonia Emissions from Animal Husbandry. *Polish Journal of Environmental Studies*. 17(1), 147-154.