Biochar for the mitigation of nitrate leaching from soil amended with biosolids

A dissertation
submitted in partial fulfilment
of the requirements for the degree of
Bachelor of Agricultural Science (Hon.)

at
Lincoln University
by

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Lincoln University

2010

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Abstract

Biosolids are generated in large quantities around the world and as governing bodies move to protect the environment by regulating the disposal practices, environmentally sound strategies of waste disposal are being sought. One disposal practice is applying biosolids to land which in New Zealand is restricted by the amount of nitrogen (N) being applied, as N can have significant adverse effects on groundwater quality and eutrophication of waterways.

The incorporation of pyrolysed biomass known as biochar into soil has been supported as a management tool, in the use of organic fertilisers like biosolids, being applied to land. Biochar has the potential of influencing the soil N cycle by interfering with nitrification and adosorption of NH_3 and NH_4^+. Biochar has also shown signs of enhancing plant nutrient uptake and consequently resulting in biofortification of trace elements. Biochar can be incorporated into soil during renovation of land that is used for a number of practices (forestry, livestock farming, market gardening and mine rehabilitation). Biosolids managed land however, enhances nutrient leaching and can lead to contamination from heavy metals, organics and significantly alter pH.

I hypothesised that biochar additions will improve nutrient availability from biosolids additions changing biomass elemental compositions and that nutrients in leachate such as nitrates will decrease. A field laboratory study was carried out to examine the effect of biochar incorporation into soil (102 kg ha^{-1}) on NO_3^--N fluxes, changes in elemental plant concentrations such as zinc (Zn), leachate composition and the effect leachate composition may have on leached trace elements following the combined application of biosolids at two different rates (600 kg N ha^{-1} and 1200 kg N ha^{-1}). Treatments included controls (soil only), two soil types (Ashley Dene and

Templeton silt loams), and 4 combinations of treatments (soil plus biosolids and soil plus biosolids plus-biochar both at two different levels).

Fluxes of NO_3^- from biochar plus biosolids treatments were generally lower than from biosolids alone during the length of the trial period, with the Ashley Dene soil type demonstrating biochar significantly ($P < 0.001$) reducing NO_3^- leachate concentrations by approximately 31% below control levels. Changes in cumulative NO_3^- leachate concentrations were observed after 21days and with an average of 64 mm of drainage The organic carbon flux in leachate increased with biosolids and biosolids plus biochar treatments with no significant difference of one treatment leaching more than the other; however, it appeared there was a strong relationship between K, Fe, Mg, Ca, As and Al and TOC with the soils amended with both of these treatments. Plant dry matter Zn concentrations were enhanced by biosolids and biosolids plus biochar treatments with the latter soil amendment decreasing plant uptake on average by 17%; similar effects were also observed with Cd plant concentrations. My results indicate that biochar addition to soil may reduce nitrate leaching from other systems, such as intensive dairy farming, and for this reason, should be the focus of future research.

Keywords: *Biosolids, Biochar,* NO_3^-*-N, Nitrate, Heavy Metals, Trace elements, organic carbon*

Acknowledgements

This research has been motivated by the need for developing pathways and places for the disposal of wastes such as biosolids, that are rich in nutrients but pose some potential environmental and ecological issues; and wanting to discover whether products such as biochar are capable of encouraging the use of biosolids in an agricultural setting. This dissertation is the result of a year's work where I have been assisted by many people; therefore I wish to thank the following for their support and assistance with this research:

First and foremost, I would like to thank Environmental Science and Research (ESR) and Foundation for Research, Science and Technology (FRST), for their funding on this project of 'Closing the loop – rebuilding our soils with biowastes', it was a pleasure to take part in this trial and I hope the results presented justify the financial aid you have supplied.

Dr. Brett Robinson for his wonderful supervision during the trial period and write up, and without his overwhelming enthusiasm during the last few weeks, I do not think I would have finished on time. It has been a privilege to work with such keen and budding scientist, who has a wealth of knowledge that is willing to be passed on to people like myself.

Lynne Clucas, and all her assistance, as without Lynne I would be up a creek without a paddle.

Associate Professor Rob Sherlock for obtaining my placement and having faith in me to attempt and complete honours. This year has been a challenge but one that I would not pass up.

James Ross for the invaluable statistical help during the analysis of the results.

Roger McLenaghan for the opportunity to tutor in Soil Science papers, where I was able to reinforce prior learning, by having the opportunity to aid and teach others. Additionally I would like to thank past lectures for their input in educating me and getting me to where I am today.

I would also like to thank the flatmates I have had over my time at Lincoln University, as they have had to put up with my incessant procrastination throughout the semesters.

Finally I would like to thank my Mother, Father, and sisters as they provided the foundations to get me to where I am today, and were the people who shaped me into the person I am. Thanks also for the support you gave me as it would have been a miserable four years without it.

Table of Contents

List of Tables

List of Figures

List of Plates

Chapter 1 – Introduction

1.1 Biosolids - the environmental problem

The use of biosolids or sewage sludge, as it was referred to in history, as a nutrient source dates back to ancient times; however, ever since the treatment of sewage started in the 1880s (Swanson *et al.*, 2004) the process of disposal has always been an issue. More currently, biosolids and similar by-products, produced from the treatment of municipal wastewater occurs world wide, with quantities ranging from 100s of thousands to 10s of billions of tonnes annually (Table 1.1), with an estimated annual output in New Zealand of 234,112 tonnes dry wt yr^{-1} equating to a rate of 53 kg $year^{-1}$ per person (Bradley, 2008). This however, is dependent on the development of wastewater treatment and the population the treatment plants serve (Swanson *et al.*, 2004). As the relationship between population size and wastewater production are directly proportional with extent (number of treatment plants) and development of treatment (efficiency of treatment plants) also influencing biosolids production. The reason for processing this wastewater is to minimise the impact of human civilisation on the environment, by reducing the amount of untreated waste being dumped into the sea or put in landfills. Therefore the greater the proportion of waste processed through wastewater treatment plants the less uncontrolled pollution there will be in the environment (Düring & Gäth, 2002).

Table 1.1: Volumes of biosolids produced by some countries of the world (Bradley, 2008).

Country	Biosolids produced	Biosolids produced per person
New Zealand	234,112 t yr^{-1}	53 kg yr^{-1}
United States	6,514,000 t yr^{-1}	21 kg yr^{-1}
Japan	2,200,000 t yr^{-1}	17 kg yr^{-1}
United Kingdom	1,509,000 t yr^{-1}	24 kg yr^{-1}

Biosolids require treatment to decrease volume, presence of heavy metals, hazardous organics and extreme pH (highly acidic or alkaline), as they consist of waste discharged from urban, commercial and industrial sources. More recently however, studies have found that organic pollutants and heavy metal concentrations have been declining in biosolids due to the regulations being implemented in biosolids treatment (Chaney, 1990).

Land application of biosolids in parts of the world is not only essential due to the economics of reducing the costs of nutrient inputs, but is also necessary for the management of soil, to avoid degradation and erosion, for these reasons, biosolids can be a source of water and a nutrient resource. It is obvious that all over the world the use of mineral fertilisers alone will not ensure adequate sustainable agricultural production and that land application of biosolids will be a necessity (Obi & Ebo, 1995). However to equal the production of mineral fertiliser, biosolids have to be applied at significantly high rates which in turn equals impacts that traditional practices had. Biosolids applications are currently restricted by regional regulations in New Zealand and are based on the amount of Nitrogen (N) being applied to the soil ("Guidelines for the safe application of biosolids to land in New Zealand," 2003). In order to increase nutrient use efficiency, techniques must be developed to keep applied nutrients in the topsoil and therefore in the main root zone of the crop. There are two approaches to reducing nutrient leaching, one is applying slow release nutrient forms the other is increasing the adsorption sites enabling a greater nutrient retention capability. Applications of organic matter (OM) as a form of slow release nutrient input may be a feasible way to create sustainably fertile soils, and an additional option to OM could be the application of biochar to soil (Lehmann *et al.*, 2003). An extensive literature review on the environmental effects of biosolids additions to soil is given in Appendix A.

1.2 Biochar – a potential solution to nitrate leaching

Biochar is a form of black carbon (BC) that can occur both naturally and artificially in the environment from forest fires (DeLuca *et al.*, 2006) and anthropogenic processes such as slash-and-burn (Steiner *et al.*, 2007), burning crop residues or as a by-product of bioenergy (Lehmann *et al.*, 2002). Anthropogenic additions of biochar to soil dates back millennia, in soils called *terra preta* or Amazonian Dark Earths in the Amazon basin, South America formed from the intervention of ancient indigenous practices (Lehmann & Joseph, 2009; Rondon *et al.,* 2007). In the Amazon, biochar was created from clearing forests and burning off old crops and later incorporated into soil (Lehmann *et al.*, 2002). However, more recently biochar has been a focus of research, as there is an increasing volume being produced from bioenergy production through the processes of pyrolysis (Lehmann, 2007b; Winsley, 2007), and its use or disposal to land is in question (Wardle *et al.*, 2008).

Pyrolysis produced biochar is made in an oxygen (O_2) deprived environment, thats rapidly heated to temperatures less than 700^{o}C (Lehmann & Joseph, 2009) for both an extended and short period depending on the purpose of pyrolysis. The residual product following pyrolysis, termed biochar, has a number of beneficial properties which make it a potential soil conditioner (Lehmann *et al.*, 2002) and in returning biochar to soil has an added benefit of reducing impacts of global warming and greenhouse gas emissions (Clough & Condron, 2010; Gaunt & Lehmann, 2008; Laird, 2008; Lehmann *et al.*, 2006; Rondon *et al.*, 2005).

Biochar additions in combination with nutrient applications containing available N in the form of bovine urine, swine manure and greenwaste compost has interfered with the N cycle (Beesley *et al.*, 2010; Clough *et al.*, 2010; Laird *et al.*, 2010a). The N cycle was altered through amending the soils physical, chemical and biological conditions. Biochar mitigated concerns brought on from applying organic fertilisers such as biosolids transform the following soil properties, improved porosity (Steiner *et al.*, 2007; Yanai *et al.*, 2007), surface area (Laird *et al.*, 2010a; Laird *et al.*, 2010b), and structure (Chan *et al.*, 2007). While chemically, biochar may mitigate contaminants of biosolids through increased cation and anion exchange capacity (CEC & AEC) (Liang *et al.*, 2006; Singh *et al.*, 2010), as well as improving pH levels (Cheng *et al.*, 2006).Improvements to plants (Lehmann *et al.*, 2003; Rondon *et al.*, 2007) and microbes (Warnock *et al.*, 2007) may also benefit from applications of biochar. However, biochar has also been found to contain and adsorb toxic molecules, for instance polycyclic aromatic hydrocarbons (PAHs) (Beesley & Dickinson, 2010; Beesley *et al.*, 2010), which can kill microbes and therefore reverse the benefits it brings to the soil environment such as refugin.

Therefore I hypothesised that biochar additions will improve nutrient availability from biosolids additions and anionic species in leachate, such as nitrates will decrease. Consequently the aim of this project was to determine the effect of biochar additions on the leaching and plant uptake of nutrients and heavy metals from biosolids amended soils. This trial was carried out using two biosolids application rates (600 kg N ha^{-1} and 1200 kg N ha^{-1}) and two different soil types. An extensive literature review on the environmental effects of biochar additions to soil is given in Appendix B.

Chapter 2 – Materials and Methods

2.1 Site description and preparation

The twenty four undisturbed soil monolith lysimeters were collected from a pasture soil (Templeton silt loam) and a former forestry plantation soil (Ashley Dene silt loam) on the Lincoln University Dairy Farm (43°38′40.89″S 172°26′24.01″E) and Ashley Dene Sheep Farm (43°39′05.82″S 172°19′41.47″E) respectively. Each lysimeter was 50cm in diameter and 70 cm deep. The design of the lysimeter casings and the method of sampling the soils have been outlined in detail by Cameron *et al.* (1992). The lysimeters were installed at the Field Service Centre, Lincoln University in a field situation that enabled collection of drainage leachate from each sample (Plate 2.1 & Figure). Average daily temperature, rainfall and applied irrigation were recorded and are presented in the results in Figures 2.1.

Plate 2.1: The lysimeter trench facility in the field laboratory.

2.2 Lysimeter Sampling

Two contrasting pasture soils were sampled for this study. The soils were a Templeton silt loam, and an Ashley Dene silt loam. Properties of the soils are shown in Table 2.2. The areas chosen to create the monoliths for the lysimeters were selected at random on land that best represented the Templeton and Ashley Dene silt loam classification. The 70 cm long cylindrical steal casing was slowly dropped over the monolith as the soil was dug out around it, until the soil monolith reached the top of the steal casing. The 70 cm deep monolith was separated at the base from the lower soil horizons and inverted, with 50 mm of soil taken from the base of the lysimeter and replaced with gravel (Gap 20) to create a change in water gradient assisting drainage and easing leachate collection. A base plate with a hole in the middle was then attached to the bottom of the casing and a rubber tube inserted and sealed into the hole. The lysimeters were placed in position along the field trench facility, with the top of the lysimeter level with the surrounding ground, and sitting on top of a 0.2m diameter pipe which the rubber tube ran through and out into a metal box where the other end of the tube was inserted into a 20 L collection container. The soil that was dug out and around the lysimeters was then replaced and compacted around the lysimeters.

2.3 Experimental Design

The experimental design consisted of a complete randomised design (Appendix C). This design was made up of three treatments, i) soil type, ii) biosolids and iii) biosolids with biochar, which were applied to the top 0.1 m of each lysimeter. Eight combinations of the three treatments were applied as shown in Table 2.1. Each treatment was replicated three times giving a total of 24 lysimeters.

Table 2.1: Treatment applications and number of replicates of each treatment.

Treatment	Templeton	Ashley Dene
Control (no biosolids or biochar)	3	3
Biosolids applied at 600 kg N/ha (1.8 kg/plot)	3	3
Biosolids applied at 600 kg N/ ha & biochar applied at 102 t/ha	3	3
Biosolids applied at 1200 kg N/ha (3.6 kg/plot)	3	0
Biosolids applied at 1200 kg N/ha & biochar applied at 102 t/ha	3	0

2.4 Soil Fertility

Soil samples were taken on the 5 May 2010 from the top 0.1 m of soil, prior to and post mixing with biosolids and biochar, so as the soil analysis could also take into account the amendments. Soils were dried for 3 days at 105^{o}C, 105^{o}C until a constant weight was obtained. Large aggregates were broken up using a mortar and pestle and the soil passed through a 2mm Nylon sieve. Soil pH was measured at a water:soil ratio of 2.5:1 with DI water using a Metler Toledo pH meter. Total soil C and N were analysed using 0.5 g of soil through an Elementar Vario MAX CN analyser. The total elemental analysis (Al, As, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Zn) (Table 2.2) was carried out using microwave digestion in 8 ml of Aristar™ nitric acid (± 69%), filtered using Whatman™ 52 filter paper, and diluted with milliQ water to a volume of 25 ml, followed by analysis by inductively coupled plasma optical emission spectrometry (ICP-OES).

Table 2.2: Soil chemical properties (pH and total elemental composition) for both the Templeton and Ashley Dene silt loams.

Properties	Soils	
	Templeton	Ashley Dene
pH	5.57	5.56
C	14.9 t ha^{-1}	18.4 t ha^{-1}
N	1389.2 t ha^{-1}	2138.9 t ha^{-1}
P	517.95	783.87
Fe	14366	10085.66
Al	13148	10554.46
Ca	3005.3	3037.622
Mg	855.69	802.2859
K	1401.5	1438.266
Na	136.26	113.2894
Mn	324.87	193.1
Cd	0.4282	0.185
Cr	11.858	8.457
Cu	4.452	5.732
Ni	9.3118	8.597
Pb	11.958	7.721
Zn	43.4152	35.09

2.5 Soil amendments

2.5.1 Biosolids

Partially treated biosolids were obtained from a storage pile at the Kaikoura Regional treatment works. The biosolids went through an initial treatment of sedimentation and anaerobic digestion in settlement ponds and was then stored in a mound, where the biosolids used for this experiment were obtained. Some 160 kg of biosolids were sampled from the sewage treatment plant storage pile with sampling occurring at eight locations across the pile to obtain a representative sample. An analysis of a sample of the biosolids was carried out including pH, C and N percentage, and elemental components and can be seen in Table 2.3. The Biosolids will be incorporated into the top 0.1 m of soil and at a rate of 600 kg N ha^{-1} and 1200 kg ha^{-}1.

Table 2.3: Chemical properties of biosolids and biochar amendments used in trial

Constituents	Amendments			
	Biosolids		Biochar	
CEC			0.8	cmol/kg
P retention			3.4	%
K			1.8	cmol$_c$/kg
Ca			0.7	cmol$_c$/kg
Mg			0.2	cmol$_c$/kg
Cd	2.8	mg/kg	0.1	mg/kg
Cu	561.2	mg/kg	13.9	mg/kg
P	4682.9	mg/kg	491.2	mg/kg
S	6971.9	mg/kg	287.6	mg/kg
Zn	877.9	mg/kg	16.4	mg/kg
Hg	2.5	mg/kg		
N	2.7	%	2	g/kg
C	29.0	%	706	g/kg
C/N Ratio	10.86		353	

2.5.2 *Biochar*

The biochar was manufactured from Pine (*Pinus radiate* D.Don) at a temperature of 600^{o}C, and was freshly made and unweathered. An analysis of the biochar was carried out and displayed in Table 2.3. The biochar was crushed to a maximum diameter of 1 cm before combining with the soil and biosolids amendments. The biochar was incorporated into the soil at the same time as the biosolids and applied at a rate of 102 t ha^{-1}.

2.6 Treatment applications

Each treatment had the top 0.1 m of soil removed from the lysimeter. The soil collected from the equivalent sites was then incorporated with each treatment amendment in a cement mixer for approximately 2 minutes to create a ‘homogenous’ treatment application imitating the agricultural practice of conventional tillage. The control treatments, only received soil to replace the top 0.1 m of the lysimeter, where the low biosolids treatment received 1.8 kg biosolids and 20 kg of soil per lysimeter treatment. The high biosolids treatment application for the Templeton soil consisted of 3.6 kg biosolids and 20 kg of soil. The biosolids – biochar treatments, received both the above application rates of biosolids and 2 kg of char equating to a 50:50 mixture of biosolids to biochar by volume. All treatments were applied on the 5 May 2010 to all of the lysimeters.

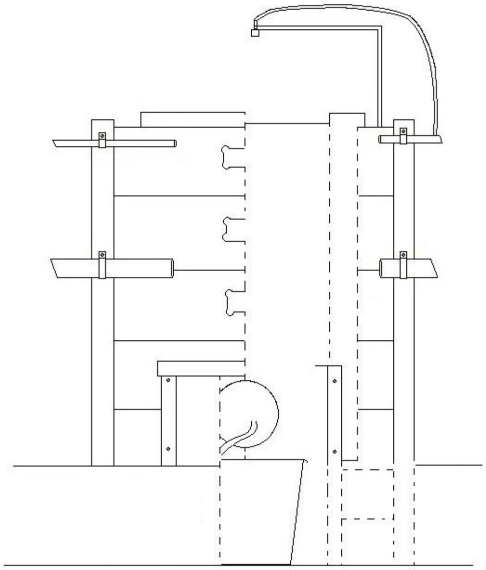

Figure 2.1: A schematic diagram of a lysimeter setup in the field laboratory.

Immediately after the application of each treatment, ryegrass (*Lolium perenne* Bronsyn) treated with AR1 endophyte was broadcast over each lysimeter. A small amount of each treatment – kept back from application – was then applied over the top of the seed and lightly pressed down by hand, imitating farm practices such as, harrowing and Cambridge rolling. As the seed was sown so late in the season some seed was retained to broadcast on areas that were bare as seed did not germinate when the growing season started in early spring (early August).

2.7 Irrigation

The lysimeters were irrigated to simulate a wet year (1 standard deviation above the average of 666 mm) for the Canterbury region in New Zealand. Irrigation was applied when required and intermittently to reduce evapotransperation (ET) loses. The irrigation system was controlled through a remote computerised irrigation program, with an example of the physical irrigation unit seen in Plate 2.2 and Figure 2.1.

Plate 2.2: The irrigation system supplying automated water to each lysimeter.

2.8 Measurements

2.8.1 Leachate collection and analysis

Drainage leachate was collected from the base of each lysimeter on a fortnightly basis or more frequently if a high rainfall event caused significant drainage to occur. The volume of leachate was measured (± 50 ml) and recorded during each sampling prior to any analysis, with a 100 ml sample taken mid flow for analysis. The pH of each leachate sample was measured using a Metler Toledo pH meter, and occurred within 24 hours of sampling then stored in a fridge. Each sample was vacuum filtered with a water aspiration apparatus through 0.45 μm cellulose acetate filter membrane. Once filtered major cations (Ca, K, Mg, Na,), and less abundant cations and metals (Al, As, Cd, Cr, Cu, Fe, Mo, Ni, Pb, Zn) were analysed by ICP-OES, and other major anions and cations (Cl^-, NO_3^--N, NO_2-N, Br^-, SO_4^{2-}-S) by ion chromatography. Organic and inorganic C was analysed using a Shimadzu TOC 5000A organic carbon analyser.

2.8.2 Pasture collection and analysis

The timing of harvesting pasture was determined by a physiological growth stage of ryegrass, which was the emergence and full development of the 3rd leaf. The pasture quality is at its peak at the 3rd leaf growth stage of a ryegrass tiller, with minimal to no leaf death and fully developed leaves (Plate 2.3, A). As each treatment reached this stage at different times due to the various treatment applications, all the pasture from each lysimeter was harvested when the first lysimeter reached this stage to keep growth relative among each lysimeter (Plate 2.3, B). The pasture was harvested to a height of < 2 cm above the soil level (Plate 2.3, C).

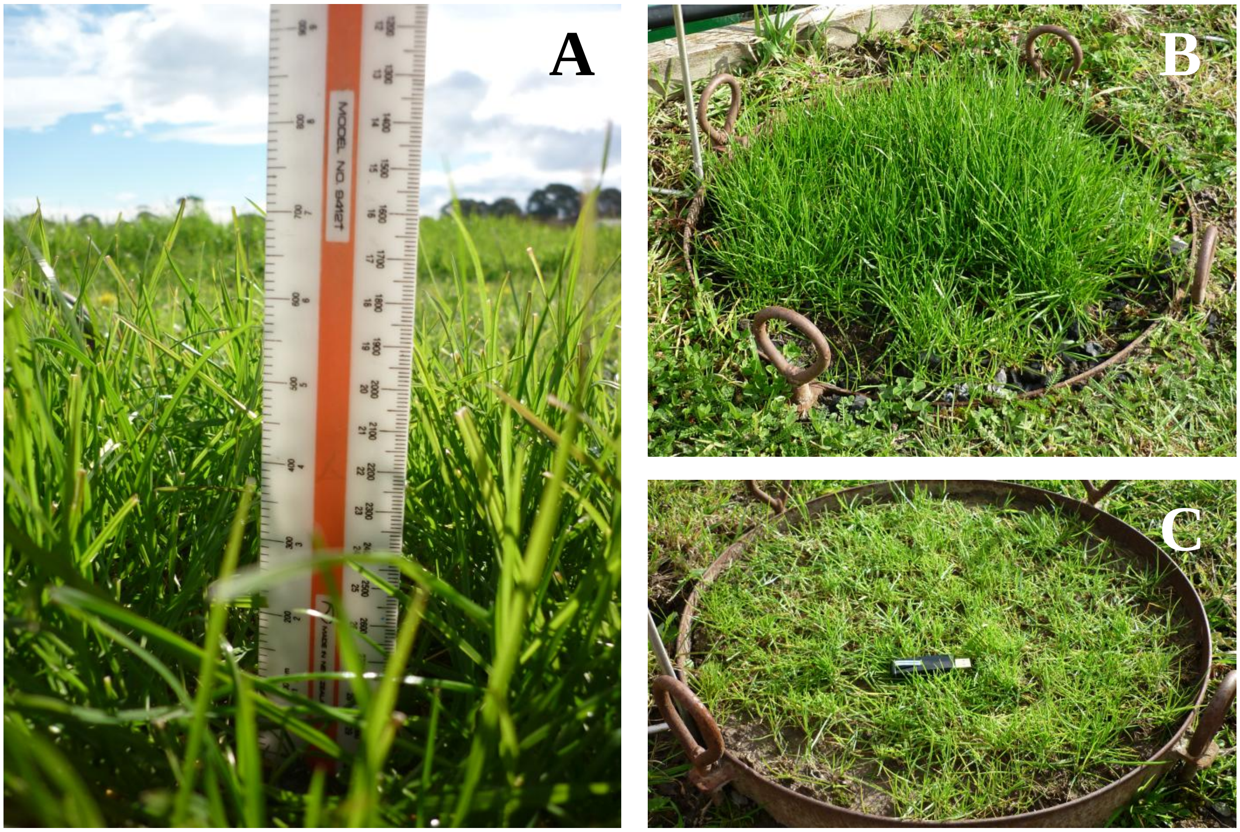

Plate 2.3: (A) Height of grass prior to harvest, (B) Grass growth prior to harvest and (C) grass post harvest.

Once the pasture was harvested it was dried at 105°C for at least 3 days and weighed, followed by grinding a ± 4 gram subsample and stored in an air tight vial. Each subsample was then measured for C and N percentage, and elemental components. The C and N content was determined using 0.2 g of dried ground pasture through an Elementar Vario MAX CN analyser. The elemental components of the grass were established by microwave digestion with CEM MARSXpress of a ground pasture sample in 8 ml of Aristar™ nitric acid (± 69%), and filtered through Whatman™ 52 paper, diluted with milliQ water to a volume of 25 ml, and finally analysed by ICP-OES.

2.9 Statistical analysis

All data sets were statistically analysed to test for treatment effects with respect to time as determined by and conducting a linear mixed model using restricted maximum likelihood (REML) analysis and produced least significant differences (LSD) at a 5% level with the statistical computer program Genstat 12.

Chapter 3 - Results

3.1 Water inputs and drainage

The 2010 autumn and winter in the Canterbury region were abnormally wet, with two severe rainfall events occurring in May and August (Figure 3.1). During the period of this trial the experienced rainfall lead to irrigation only being applied during the initial two weeks and thereafter no irrigation was applied. Total water inputs during the trial period were equivalent to 574 mm over six months (Figure 3.2). This comprised of 547 mm of natural rainfall and 27 mm of irrigation.

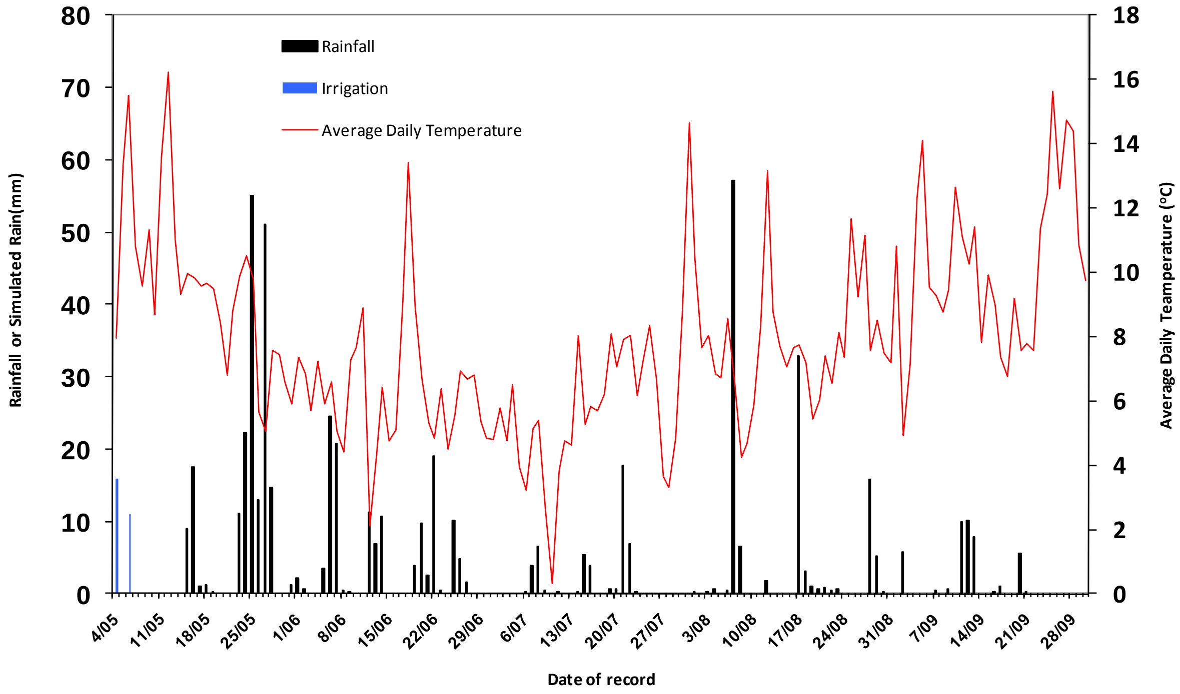

Figure 3.1: Rainfall (■) applied irrigation (🟦) (mm) and average daily temperature (—) for the period of the trial.

The volume of drainage was equivalent to 426 mm (85183 L) and 412 mm (82404 L) for the Templeton and Ashley Dene controls respectively (Figure 3.2). Drainage from the lysimeters with amendments showed varied volumes from their respective controls, however, with no significant variation.

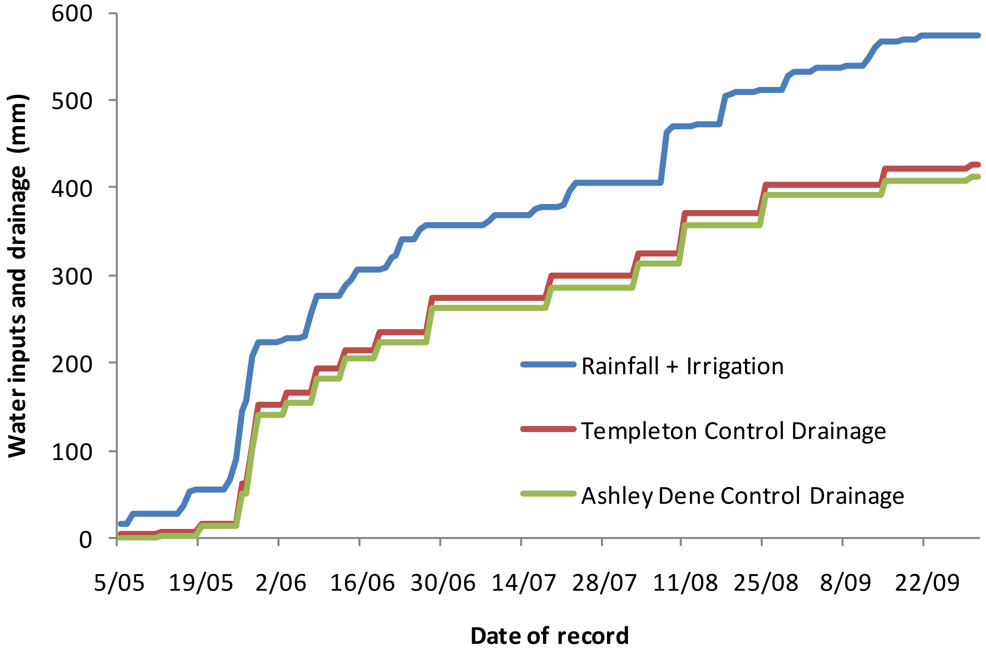

Figure 3.2: Cumulative average water inputs (rainfall + Irrigation) and drainage (mm) from both the control lysimeters during the period of the trial.

There was no significant variation in treatments for the volume of drainage percolating through the lysimeters, and therefore no significant difference in treatments. The Templeton silt loam amended with a low application of biosolids-biochar on average drained the lowest (405.1 mm) volume and the high rate of biosolids-biochar amendment on Templeton soil drained the most with 440.4 mm. This could have been caused by variations in evapotranspiration (ET) rates as the treatments that drained the least had the greatest ET and the lysimeters that drained the most lost the least amount of water accounted for through ET (Table 3.1).

Table 3.1: Average cumulative drainage and ET from each treatment and the average among treatments.

	Total cumulative drainage (mm)	**Total ET** (mm)
Ashley Dene Control	412.0	162.1
1.8 kg biosolids	414.5	159.6
1.8 kg biosolids + biochar	428.6	145.5
Templeton Control	425.9	148.2
1.8 kg biosolids	430.5	143.6
1.8 kg biosolids + biochar	405.1	169.1
3.6 kg biosolids	409.6	169.1
3.6 kg biosolids + biochar	440.4	133.7
Average	420.8 (SED 195.1)	153.3

3.2 Nitrate losses

The N leached from the lysimeters was predominantly in the form nitrate (NO_3^-) with little or no nitrite (NO_2^-) detected in the leachate. No variation in NO_3^--N concentration response was observed from all the treatments within the first 75mm (15 L) of leachate percolating through the lysimeters. Nitrate concentrations from the control of the Ashley Dene and Ashley Dene amended with both biosolids and biochar were lower than the Ashley Dene amended with biosolids (Figure 3.3), however it was only the biochar amended treatments that were significantly different (P <0.001).

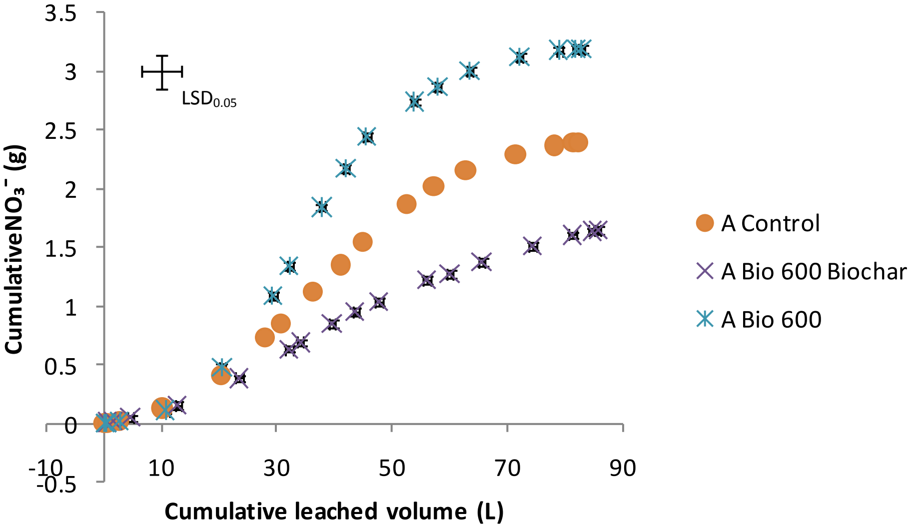

Figure 3.3: NO_3^--N concentrations (SED) in the leached volumes (SED) from the Ashley Dene lysimeters as treated with biosolids and biochar.

The Ashley Dene silt loam treatments also experienced the greatest concentration of NO_3^--N occurring in leachate, with the 600 kg N ha^{-1} biosolids, peaking at a significantly (P <0.001) higher level than all other treatments, with an average of 0.069 g N L^{-1} when 147 mm of cumulative leachate had drained through the biosolids treated lysimeter. A second NO_3^--N concentration peak (0.089 g N L^{-1}) occurred after 189 mm of drainage. The biosolids-biochar amended Ashley Dene lysimeters experienced a similar trend, with peaks occurring 24 and 54 days after application of amendments, and draining 160 and 208 mm of cumulative leachate. The biochar amendment on the Ashley Dene silt loam caused an initial drop (3.9 mg N) in concentration of NO$_3^-$-N in leachate from background levels, however, this effect did not persist after the first collection post the soil amendments.

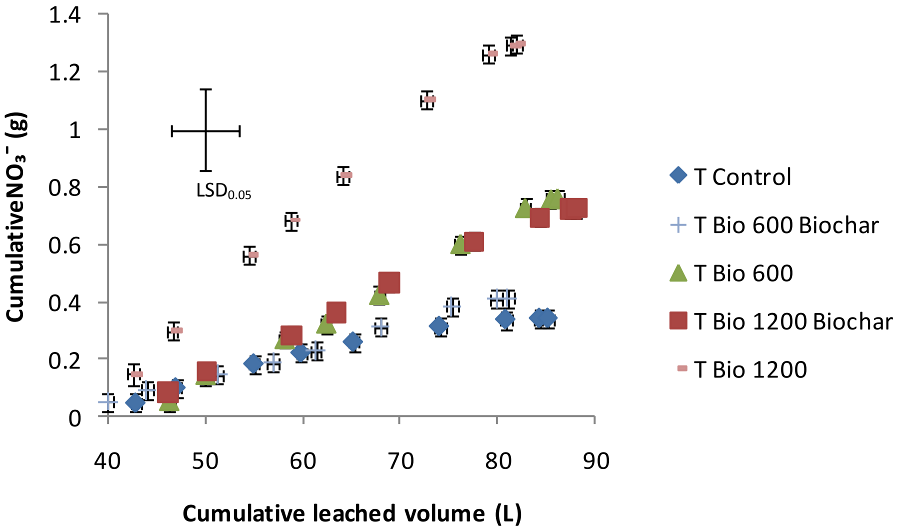

Figure 3.4: NO$_3^-$-N concentrations (SED) in the leached volumes (SED) from the Templeton lysimeters as treated with biosolids and biochar.

The Templeton silt loam control lysimeters appeared to have been contaminated with some form of N, therefore the results in Figure 3.4 for the Templeton soil type lysimeters, have been presented from a period (39 days after the trial started) at which the initial contaminated N, had been flushed through the controls. The application of 600 kg N ha^{-1} biosolids on the Templeton silt loam produced the first greatest NO$_3^-$-N response in leachate, 7 days following amendment. The 1200 kg N ha^{-1} biosolids treatment on Templeton silt loam was the single most significant amendment applied, as can be seen in Figure 3.4. The Templeton control, unlike the Ashley Dene control recorded the lowest NO$_3^-$-N concentrations in leachate. During the latter part of this trial a flush of NO$_3^-$-N was leached with the 1200 kg N ha^{-1} biosolids treatments peaking the greatest with 0.031 g N L^{-1} occurring in leachate compared to 0.006 g N L^{-1} in the control plots.

The total amount of NO$_3^-$-N leached from the soil over the six month trial period was found to be extremely high (2.22 - 9.58 kg N ha^{-1}); including the control plots. A reduction of 31% in NO$_3^-$-N was measured between the control plot and biosolids-biochar Ashley Dene lysimeters, although this was not statistically significant (Figure 3.5). The Ashley Dene lysimeters amended with 600 kg N ha^{-1} biosolids did not significantly increase from the controls, however, the difference between the biosolids and biosolids-biochar plots (4.64 kg N ha^{-1}) was significant (P <0.001), with the greatest reduction of NO_3^--N in leachate by 48%, measured between all treatments.

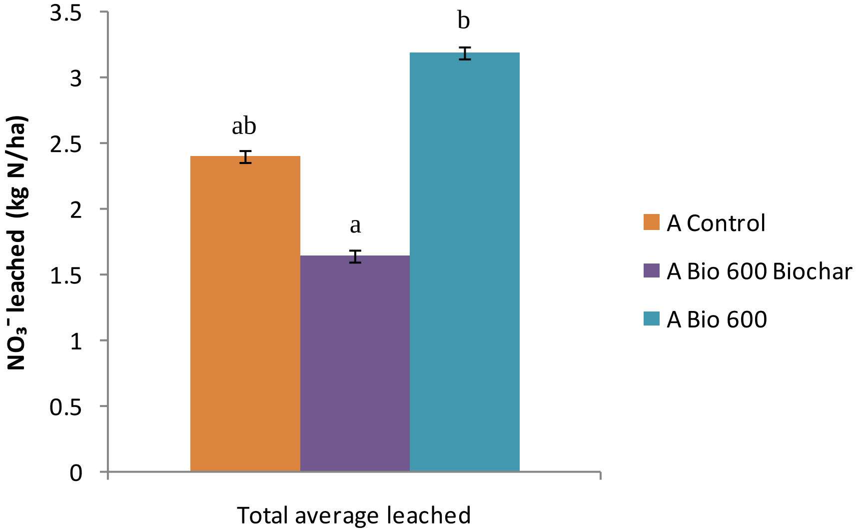

Figure 3.5: Total average NO_3^--N leaching losses (kg N ha^{-1}) from Ashley Dene lysimeter treatments. Error bars indicate SED of the means. Letters above bars indicate significance based on an $LSD_{0.05}$ test.

The application of 1200 kg N ha^{-1} of biosolids to the Templeton silt loam filled lysimeters, caused a significant (P <0.001) increase of 3.69 kg N ha^{-1} (Figure 3.6) in total NO_3^--N, in leachate compared to the control. However, with the application of biochar to the high rate of biosolids, the total NO_3^--N loss was significantly (P <0.001) reduced to 4.15 kg N ha^{-1}. Representing a highly significant, 42% reduction in NO_3^--N loses, although this was not found to significantly differ from the control or other Templeton lysimeters amended with lower rates of biosolids, and biosolids-biochar amendments.

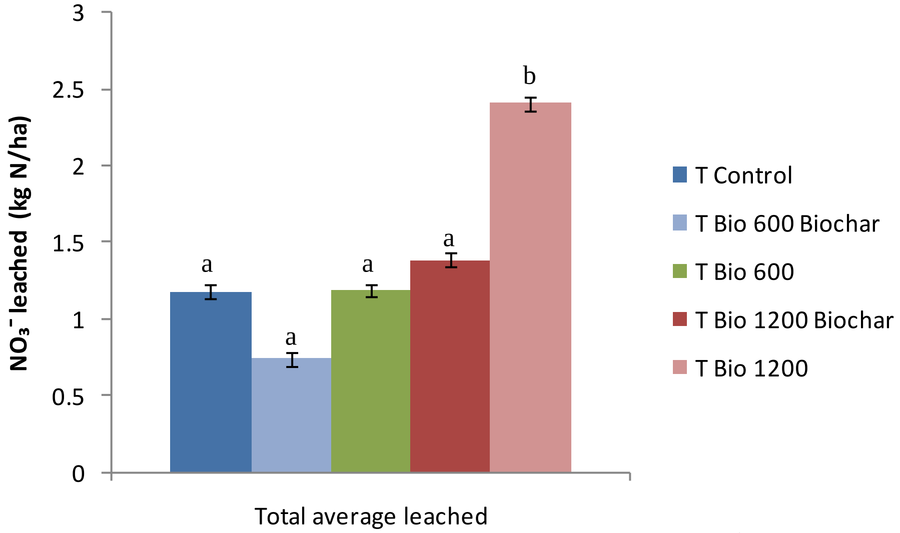

Figure 3.6: Total average NO_3^--N leaching losses (kg N ha^{-1}) from Templeton lysimeter treatments. Error bars indicate SED of the means. Letters above bars indicate significance based on an $LSD_{0.05}$ test.

Furthermore Nitrite (NO_2) was measured in the leachate during the trial period however; the concentrations typically occurred below detection limits but when it occurred at a high concentration it was < 0.287 mg NO_2 L^{-1}.

A mass balance of N in the soil (Table 3.2) showed a loss of 130 kg N ha^{-1} from the Ashley Dene control lysimeters, with the greatest change of N in the soil system among all the soil treatments occurring on the Ashley Dene soil, amended with biosolids. A smaller amount of N was both leached and taken up by plants, on the Ashley Dene soil amended with biosolids plus biochar when compared to the control and biosolids treatments.

Table 3.2: Mass balance of N in the soil system on Ashley Dene soil during the period of the trial.

		Control	**Low Biosolids+Biochar**	**Low Biosolids**
Initial	(t ha^{-1})	2138.86	2491.50	2550.81
Leached	(kg ha^{-1})	122	84	163
Plant Uptake	(kg ha^{-1})	18	16	23
Change	(kg ha^{-1})	140	100	186
Final	(t ha^{-1})	2138.72	2491.40	2550.63

The N accounted for on the Templeton soil lysimeters (Table 3.3 experienced similar outcomes as the Ashley Dene soil treatments, except on the Templeton lysimeters amended with a low rate of biosolids plus biochar, the plant uptake was greater than what occurred in the control treatments. The loss of N from the control of the Templeton soil lysimeters was 79 kg ha^{-1}. The other treatments differed from the control, in the order of, high biosolids > high biosolids+biochar > low biosolids > *x* > low biosolids+biochar with a change of 101, 29, 14 and -20% respectively.

Table 3.3: Mass balance of N in the soil system on Templeton soil during the period of the trial.

	Control	Low Biosolids+Biochar	Low Biosolids	High Biosolids+Biochar	High Biosolids
Initial (t ha^{-1})	1389.15	3359.46	2984.37	4431.48	3599.53
Leached (kg ha^{-1})	60	38	60	71	123
Plant Uptake (kg ha^{-1})	19	25	30	31	36
Change (kg ha^{-1})	79	63	90	102	159
Final (t ha^{-1})	1389.07	3359.39	2984.28	4431.37	3599.37

3.3 Leaching of other elements

The concentration of potassium (K) occurring in leachate had a significant ($P < 0.005$) time by treatment interaction, and as seen in Figure 3.7 cumulative K concentrations had a positive linear correlation (R^2 values ranging from 0.9694 -0.9946) with cumulative drainage. No significant differences occurred between the control, biosolids and biosolids plus biochar amendments on the Ashley Dene lysimeters.

Conversely, the Templeton silt loam, demonstrated that both biosolids and biosolids plus biochar treatments can have a significant ($P <0.005$) effect on K levels in leachate, with the high rate of biosolids plus biochar having less of an effect than other treatments. The point at which most treatments (apart from the one previously mentioned) significantly reduced K concentrations was after 29 days and an average of 170 mm of drainage had passed through the lysimeters. The greatest reduction of K in leachate was by 353%, from the Templeton soil treated at the low rate with biosolids plus biochar; however, this only differed from the low rate biosolids amendment by 62%.

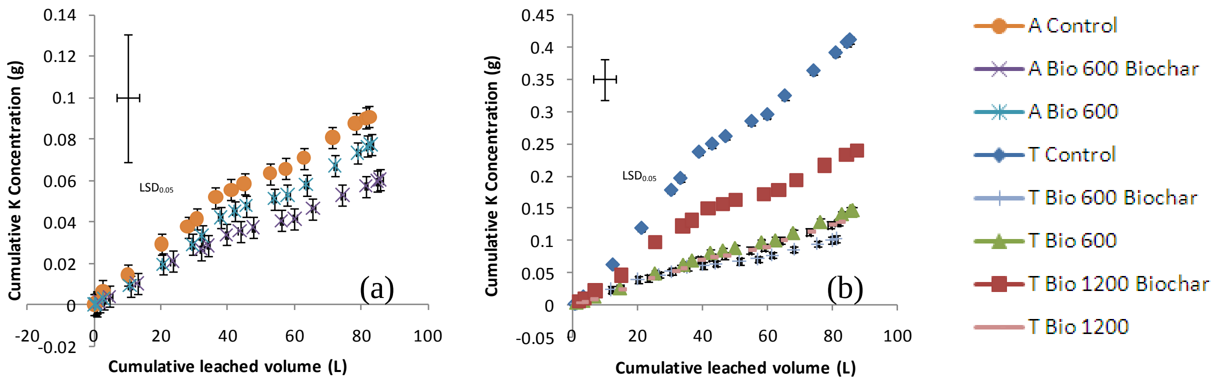

Figure 3.7: Cumulative K concentrations (g K L^{-1}) (SED) in the leachate relative to drainage volume as affected by biosolids and biochar on (a) Ashley Dene and (b) Templeton soil types.

Table 3.4: Total average leachate concentrations from Ashley Dene soil lysimeters of As, Cr, Mg, Cu, Fe, Na, Ni, Pb, Cl^{-}, Br^{-} and SO_4^{2-}.

Element	Control	Low biosolids	Low biosolids+biochar	SED	LSD
As (mg)	0.711	0.719	0.754	0.002	***
Cr (mg)	11.884	18.58	14.141	0.001	***
Mg (g)	0.579	0.698	0.506	0.006	***
Cu (mg)	11.208	6.254	8.138	0.133	***
Fe (g)	0.001	0.002	0.001	0.028	*
Na (g)	1.972	0.608	1.333	0.022	***
Ni (mg)	0.170	0.199	0.127	0.004	***
Pb (mg)	0.983	0.849	0.106	0.006	*
Cl^{-} (g)	2.482	2.735	1.938	0.027	***
Br^{-} (mg)	2.979	2.488	2.238	0.051	***
SO_4^{2-} (g)	0.283	1.303	0.687	0.017	***

Sulphate (SO_4^{2-}) occurrence in leachate had a significant ($P < 0.001$) treatment, time and time by treatment interaction. Sulphate increased cumulatively with respect to time, in a positive linear relationship and variation occurred between treatments. However, there was no significant variation between the Ashley Dene soil treatments and the control (Table 3.4). In contrast the high rate of biosolids and biosolids plus biochar Templeton soil amendments demonstrated a significant ($P < 0.001$) increase from the control by on average 0.05 and 0.06 g respectively, per leachate collection (Table 3.5) Which lead to a cumulative difference of 0.909 and 0.967 g respectively, from the control by the end of the trial.

Once again there was a significant interaction as well as significance with time and treatments with magnesium (Mg) in leachate. Similarly to SO_4^{2-} there was no significant variation between Ashley Dene treatments and the control (Table 3.4), but there was among the Templeton soil treatments (Table 3.5). Further similarity occurred with the Mg concentrations in leachate with the high amendment rate of biosolids and biosolids plus biochar. The high application rate of biosolids increased Mg concentrations in leachate by 46% when compared to the control. The biochar had an inconclusive effect on Mg occurring in leachate, where Mg decreased on Ashley Dene lysimeters and at the high rate of biosolids application on the Templeton but increased Mg concentrations on the low rate Templeton lysimeters.

Table 3.5: Total average leachate concentrations from Templeton soil lysimeters of As, Cr, Mg, Cu, Fe, Na, Ni, Pb, Cl^-, Br^- and SO_4^{2-}.

Element	Control	Low biosolids	Low biosolids+biochar	High biosolids	High biosolids+biochar	SED	LSD
As (mg)	1.076	0.759	0.797	0.749	1.407	0.002	***
Cr (mg)	0.046	0.016	0.017	0.019	0.033	0.001	***
Mg (g)	0.359	0.338	0.421	0.616	0.526	0.006	***
Cu (mg)	14.773	12.019	2.805	6.446	12.377	0.133	***
Fe (g)	0.051	0.013	0.073	0.003	0.058	0.028	*
Na (g)	1.912	1.458	1.452	0.884	2.984	0.022	***
Ni (mg)	0.309	0.307	0.253	0.255	0.358	0.004	***
Pb (mg)	0.329	0.119	0.111	0.084	0.233	0.006	*
Cl^- (g)	0.992	1.153	1.166	1.189	1.274	0.027	***
Br^- (mg)	3.119	3.571	5.137	2.353	3.89	0.051	***
SO_4^{2-} (g)	0.579	0.421	0.682	1.488	1.546	0.017	***

Concentrations of calcium (Ca) in leachate were highly significant ($P < 0.001$) in terms of date, treatment and treatment by time interactions. The addition of biochar to the biosolids amendment on the Ashley Dene soil type reduced Ca concentrations by 0.178 g per collection, which is back to the controls Ca leaching concentration (Figure 3.8). A peak in leached Ca concentrations of 43.29 kg Ca ha^{-1} occurred in leachate from the Ashley Dene treatment amended with biosolids, 24 days after commencement of the trial, at which point 160 mm on average, had drained through the lysimeters.

With respect to the Templeton soil type lysimeters, the only significant difference ($LSD_{0.05}$) that occurred among treatments was with the high rate of biosolids (Figure 3.8 (b)). The high amendment rate of biosolids to Templeton silt loam increased Ca concentrations in the average collected leachate, by 0.13 g Ca from the biosolids-biochar amended soil at the equivalent high rate.

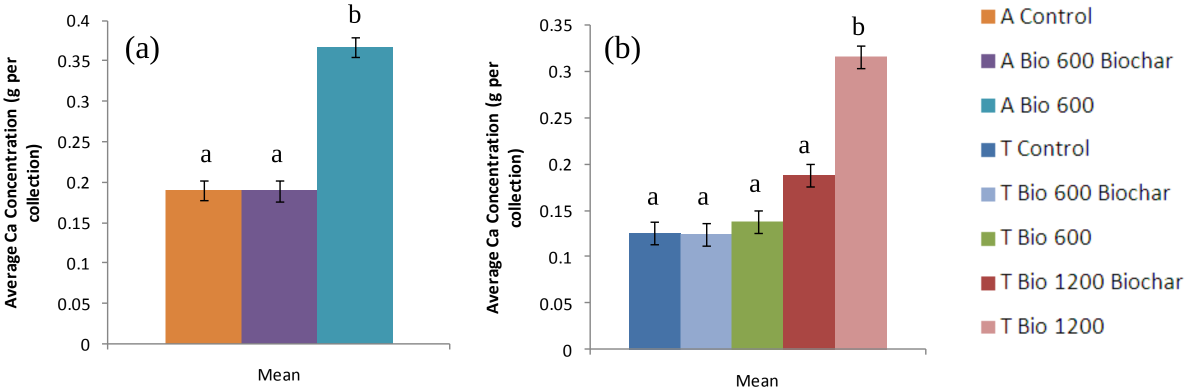

Figure 3.8: Comparison Ca concentrations (g per collection) among Ashley Dene (a) and Templeton (b) lysimeters, in leachate from each treatment. Letters above bars indicate significance based on an $LSD_{0.05}$ test.

Variations in copper (Cu) concentrations occurring in leachate from the response of biosolids and biosolids plus biochar soil amendments was not observed until 21 mm of water on average, had drained through the lysimeters. Tables 3.4 & 3.5 demonstrate the significance ($P < 0.001$) in the effect both time and treatment had on Cu concentrations in leachate, and additionally the Cu leached from both types of soil. The Cu leached from the lysimeters did not significantly differ ($LSD_{0.05}$) from one another, until 21 and 45 days after the Templeton and Ashley Dene soils were amended with biosolids and biochar. By the end of the trial the Templeton Control had leached the greatest cumulative concentration of Cu (14.77 mg Cu); while the low application rate of biosolids amended Templeton silt loam leached the least with 2.8 mg Cu (Table 3.5). The high rate of biosolids and low rate of biosolids plus biochar treatments on Templeton silt loam caused a significant difference. The Cu concentration in leachate from biosolids amendments on Ashley Dene soil were significantly different ($LSD_{0.05}$) once 269 mm of drainage had passed through the lysimeter (Table 3.4).

The concentration of zinc (Zn) in leachate was found to have a significant ($P < 0.05$) time by treatment interaction. Although this occurred there was no significant difference ($LSD_{0.05}$) observed in Zn concentrations in leachate from Ashley Dene lysimeters (Figure 3.9 (a)). There was however, a significant difference ($LSD_{0.05}$) between treatments in the cumulative Zn leachate concentrations on the Templeton silt loam lysimeters, and was in the order of low biosolids > control > high biosolids-biochar > high biosolids > low biosolids-biochar (Figure 3.9 (b)). The greatest differences occurred with the high biosolids and low biosolids plus biochar amendments on the Templeton silt loam lysimeters, leaching a total Zn concentration of 8.3 and 5.16 mg Zn compared to the control experiencing a total of 18.37 mg Zn leached.

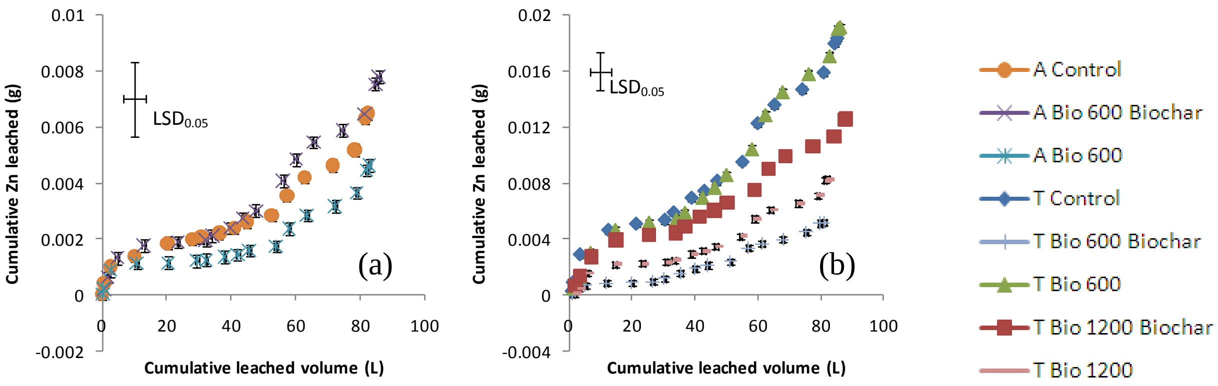

Figure 3.9: Cumulative Zn concentrations (g Zn L^{-1}) (a) and (b) in the leachate relative to drainage volume as affected by biosolids and biochar on Ashley Dene and Templeton soil types (reading left to right) with SED bars.

Tables 3.4 & 3.5 shows the treatment effect of biosolids and biochar amendments to Templeton and Ashley Dene soil types, on the average arsenic (As) concentration in leachate samples, collected on 17 different occasions. This demonstrates the significant effect of the treatments, of which there was also, a significant time and time by treatment effect. The only treatment that created a significant difference was the high rate of biosolids plus biochar on Templeton lysimeters. This treatment on average increased As occurrence in leachate by 3.867 and 1.948 µg compared with the high rate of biosolids treatment and control on Templeton silt loam.

Similarly to As, chromium (Cr) and lead (Pb) concentrations in leachate were found to have a significant ($P < 0.001$) treatment effect, however, the only significant variation among treatments for Cr was between the Templeton control (2.69 µg Cr per collection) and Ashley Dene control (0.70 µg Cr per collection). The significant difference occurring on average in Pb concentrations from leachate collections was between the Templeton control, at 19.33 µg Pb, and the high application rate of biosolids on the Templeton lysimeters (4.93 µg Pb). Additionally, on average there was a significant difference of 13.23 µg Pb per leachate collection, between all Ashley Dene treatments and the Templeton control.

The variation among nickel (Ni) treatments was highly significant ($P < 0.001$) with a significant difference ($LSD_{0.05}$) occurring in Ni concentrations in the average leachate collections among all treatments (Tables 3.4 & 3.5). On the Ashley Dene soil packed lysimeters, the biosolids plus biochar treatment significantly reduced (36%) the occurrence of Ni in leachate. While the Templeton lysimeters experienced a similar effect with the low rate of biosolids and biosolids plus biochar amendments – a reduction of 18% – the opposite appeared to occur on the high rate of biosolids amendments. The high application rates of biosolids significantly reduced Ni occurring in leachate from the control by 18% and produced a difference of 6.06 µg Ni in leachate from the high rate of biosolids-biochar amended Templeton silt loam.

3.4 Effect of biosolids and biochar on leachate composition

Not all collection samples were tested for total organic carbon (TOC) due to time restraints, however, the first twelve collected samples were analysed for TOC. All treatments had the same occurrence of organic carbon (OC) in leachate, with both a significant ($P < 0.001$) time and treatment effect as well as an interaction of both time by treatment. All treatments built up to a peak concentration occurring 23 days after amendment and occurred with 100-127 mm of drainage. The 1200 kg N ha^{-1} biosolids plus biochar amendment on the Templeton silt loam lysimeters experienced the greatest peak of OC measured in leachate at 0.39 g C L^{-1}. This is compared to 18 and 0.15 g C L^{-1} for the Templeton and Ashley Dene control lysimeters respectively.

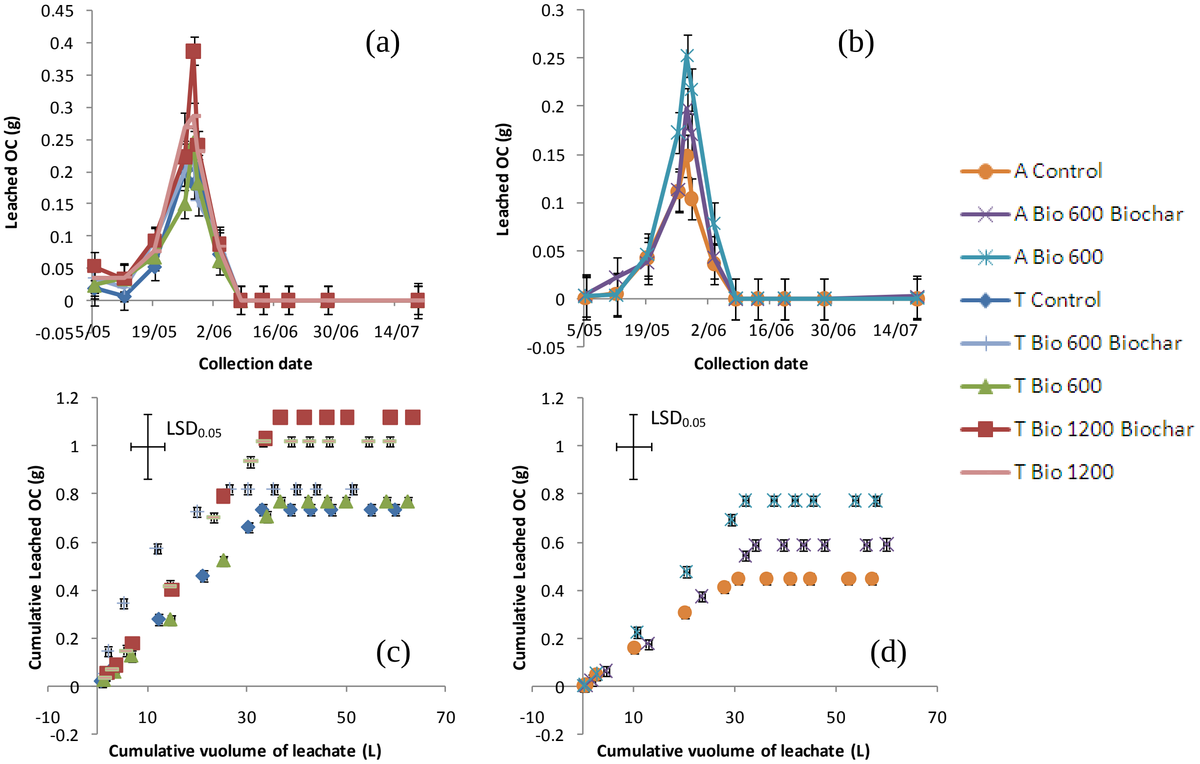

Figure 3.10: Organic C concentrations (g C) (SED) in the leachate as affected by biosolids and biochar on (a) Templeton lysimeters and (b) Ashley Dene lysimeters and cumulative C concentrations (g C L^{-1}) (SED) in leachate relative to drainage volume on (c) Templeton lysimeters and (d) Ashley Dene soil.

There was no significance in the mass of OC occurring in leachate during the span of this trial. However, there were noticeably different concentrations of OC in drainage between the two types of soil, with both controls leaching the least. The biosolids plus biochar and biosolids treatments on the Ashley Dene lysimeters increased the occurrence of OC leached by 32 and 73% respectively (Figure 3.10). While on the Templeton soil type lysimeters, the low rate of biosolids plus biochar and biosolids treatments raised OC by 12 and 4%, respectively, and at the high rate of biosolids-biochar and biosolids amendments by 52 and 39 % respectively from the control.

3.5 Pasture biomass

Pasture harvested from each lysimeter showed a significant (P< 0.001) treatment effect, with biosolids amendments on Ashley Dene lysimeters, decreasing plant biomass on average by 13%

and the biosolids plus biochar treatment increasing 31% (Table 3.6). However, the differences between harvests within treatments growing on Ashley Dene soil was in the order of control > low biosolids > low biosolids plus biochar with increases of 36, 24 and 8 % respectively.

Table 3.6: Pasture mass (t ha^{-1}) harvested 105 days after emergence from the Ashley Dene Lysimeters.

Harvest	Control	Low biosolids	Low biosolids+biochar
1 (t ha^{-1})	0.535	0.488	0.795
2 (t ha^{-1})	0.725	0.606	0.862
Average (t ha^{-1})	0.630	0.546	0.828

The highest mass (1.191 t ha^{-1}) of pasture harvested occurred on Templeton soil amended with a high rate of biosolids plus biochar (Table 3.7). The low rate of biosolids on Templeton silt loam lysimeters increased pasture biomass by < 1% and by 56% on the high biosolids plus biochar treatments. The difference between biomass harvested on the two different dates within treatments saw the lowest (6%) experienced on the low biosolids treatment and the greatest on the low biosolids plus biochar Templeton soil treatment.

Table 3.7: Pasture mass (t ha^{-1}) harvested 105 dyas after emergence from the Templeton Lysimeters.

Harvest	Control	Low biosolids	Low biosolids+biochar	High biosolids	High biosolids+biochar
1 (t ha¯1)	0.660	0.523	0.807	0.754	0.962
2 (t ha¯1)	0.719	0.865	1.033	1.037	1.191
Average (t ha¯1)	0.690	0.694	0.920	0.895	1.077

3.6 Elemental pasture composition

All soil amendments caused similar effects on K concentrations in pasture DM as previous elemental analysis with a significant ($P < 0.001$) effect. The additions of biosolids to soil lead to an increase in K accumulating in the pasture, and with the addition of biochar to the amendment the level of concentration was reduced, with a single treatment significantly dropping below the control (Figures 3.11 (a) & (b)). The biosolids plus biochar amended Ashley Dene lysimeters caused a significant (P<0.001) reduction of 3.70 mg K concentration in pasture DM compared, to the biosolids amended soil as seen in Figure 3.11 (a).

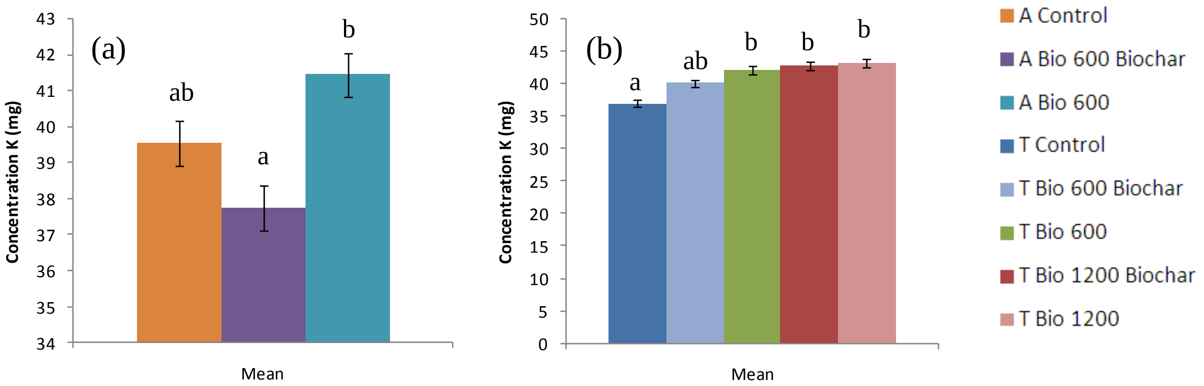

Figure 3.11: Average K concentrations in harvested pasture on (a) Ashley Dene and (b) Templeton lysimeters. Error bars indicate SED of the means. Letters above bars indicate significance based on an $LSD_{0.05}$ test.

The concentration of molybdenum (Mo) significantly (P <0.001) increased with the amendment of biosolids and biosolids plus biochar from the control, on both soil types (Tables 3.8 & 3.9) indicating a treatment effect. Pasture Mo concentrations significantly (P <0.001) increased by 2.10 and 3.08 µg Mo, with the addition of biochar to both low and high levels of biosolids treatments, on the Templeton soil lysimeters. The Mo level also increased (0.328 µg Mo) with the addition of biochar to biosolids applied to the Ashley Dene lysimeters, although this was not significantly different.

Cadmium (Cd) was found to have a significant (P <0.01) treatment effect, with all biosolids and biosolids-biochar amendments causing an obvious increase in pasture DM Cd concentrations from control plots. However again, these were not proven to be significantly different (Figures 3.12 (a) & (b)). The Templeton soil type lysimeters saw an increase from the control 310 and 411% in Cd concentrations in pasture DM, from low and high biosolids treatments respectively, and a reduction (66 and 25%) from these values when biosolids treatments were applied concomitantly with biochar. In relation to the Ashley Dene lysimeters the biochar

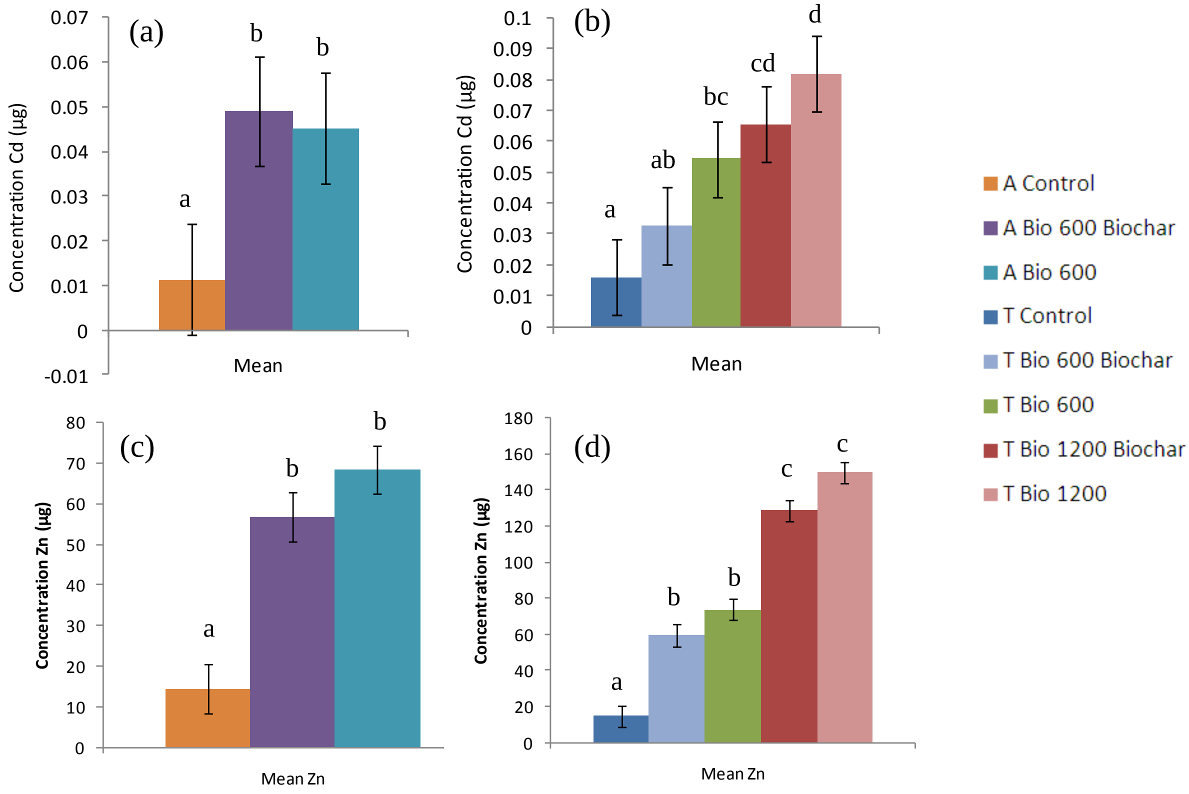

Figure 3.12: HM concentrations (µg) of Cd (a) and (b) and Zn (c) and (d) among Templeton lysimeters, in pasture harvested (SED) from each treatment. Letters above bars indicate significance based on an LSD$_{0.05}$ test.

The element Zn was significantly ($P < 0.001$) increased by both the biosolids and biosolids-biochar amendments on both soil types shown in Figures 3.12 (c) & (d). On the Ashley Dene treatments the biosolids amendment increased Zn levels in pasture DM by 0.05 mg Zn from the control. The biosolids-biochar treatments limited the Zn plant uptake by 0.01 mg Zn from biosolids amended soils which was still significantly ($P < 0.001$) higher than the concentrations reached by pasture on the controls lysimeters. The Templeton soil types demonstrated a similar result, with the higher rate if biosolids and biosolids plus biochar amendments increasing the uptake of Zn by the pasture further still. The biosolids and biosolids plus biochar treatments improved Zn uptake of pasture by 922 and 778% respectively, from the control; however, they were not significantly different as were the lower biosolids rate for both soil types.

Table 3.8: Element concentrations (µg g^{-1}) in pasture harvested from Ashley Dene soil lysimeters.

Element	Control	Low biosolids	Low biosolids+biochar	SED	LSD
Ca	5465	5863	6666	189	***
Cr	16.2	18.898	5.598	3.471	*
K	39532	41439	37740	620.5	***
Mg	2740.6	2940.949	3335.799	54.95	*
Mn	163.8	195.4	76.4	6.071	*
Mo	1.114	5.559	5.887	0.1627	***
Na	932	603	1221	48.48	***
P	4555	4572	4108	122.9	***
S	2703	3586	3143	99.34	***

The concentration of phosphorus (P) in pasture DM did not appear to significantly differ from the application of biosolids and biochar with respect to the controls (Tables 3.8 & 3.9), although treatment effect was calculated with a significance of $P < 0.001$. However, as was the case for K, the addition of biosolids to soil leads to an increase in P concentrations in pasture DM with biochar limiting the effect. Additionally, biosolids plus biochar amendments on the Ashley Dene lysimeters caused a reduction in P levels below the control.

Table 3.9: Element concentrations (µg g^{-1}) in pasture harvested from Templeton soil lysimeters.

Element	Control	Low biosolids	Low biosolids+biochar	High biosolids	High biosolids+biochar	SED	LSD
Ca	9358	6406	6297	7578	6999	189	***
Cr	8.431	10.219	5.41	9.544	4.401	3.471	*
K	37035	42075	40082	43198	42814	620.5	***
Mg	4683.216	3208.11	3151.205	3793.772	3501.701	54.95	*
Mn	198.3	132.8	87.6	144.9	111.7	6.071	*
Mo	0.789	3.086	5.189	3.399	6.481	0.1627	***
Na	2705	1554	1520	1742	1351	48.48	***
P	4101	4459	4396	4755	4655	122.9	***
S	3258	3678	3293	4281	3819	99.34	***

Magnesium accumulation in harvested pasture showed a significant ($P < 0.05$) time by treatment interaction. The concentration of Mg accumulating in leaves was reduced between harvests, when comparing the control (0.08 mg Mg) and biosolids (0.13 mg Mg) treatments (Table 3.8), with additions of biochar to Ashley Dene soil. Similar effects appeared to occur to the Templeton soil type lysimeters with the low rate of biosolids with regards to Mg. However, at the higher rate of biosolids the addition of biochar appeared to increase Mg concentrations in leaf dry matter (DM) for both harvest dates (11% and 5% respectively).

Across all the treatments Manganese (Mn) and Mg concentration increased from the first harvest to the second indicating accumulation. When 600 kg N ha^{-1} of biosolids was applied without biochar, to Ashley Dene silt loam in May, an increase (0.083 mg Mn) in Mn concentration occurred, in the harvested pasture (Table 3.8). However, when biochar was added to the biosolids amendment, the increase in Mn concentration between harvests was limited to 0.029 mg Mn, as well as restricting the initial Mn concentration to 0.062 mg Mn, which was lower than the control (0.134 mg Mn). Similar effects of biosolids and biochar amendments were observed on the Templeton silt loam treatments. Although the Templeton control lysimeters had a higher initial concentration (176 mg Mn) of Mn accumulating in harvested pasture. The effect of the biochar on biosolids amendments to the Templeton silt loam caused a reduction of 22 and 12% at the low and high applications rates of biosolids respectively.

Similarly to cadmium (Cd), Cr did not show any significant variance between treatments, however, the effect of the treatments still caused fluctuations to occur above and below the controls as shown in Tables 3.8 & 3.9 indicating a treatments effect ($P < 0.05$). Across both soil types the addition of biosolids caused Cr concentrations to elevate in pasture DM when compared to the controls. The biochar amendments lead to decreases in Cr levels in pasture from the biosolids amended treatments. The greatest reduction in Cr concentrations in pasture DM was on the Ashley Dene soil lysimeters from 0.019 mg Cr amended with biosolids to 0.006 mg Cr amended with a biosolids-biochar mix.

Chapter 4 – Discussion

4.1 Nitrate leaching

Results from this study show that the treatment of soil with 102 t ha^{-1} of biochar was effective in reducing NO_3^--N leaching from soils treated with biosolids applications. A 48% reduction ($P < 0.001$) in the total NO_3^--N leachate represents a substantial reduction in N losses. This conflicts with previous studies that showed minimal variation in NO_3^--N soil concentrations after treatment with organic fertiliser and organic fertiliser plus biochar, which elevated NO_3^--N concentrations in the leachate (Lehmann *et al.*, 2002). In this study, the total NO_3^--N leachate losses from biosolids without biochar (Figures 3.3 & 3.4) ranged from 60 – 163 kg N ha^{-1}, which was 54.0 – 148.5 times greater than losses found in an earlier study conducted using mineral fertiliser and mineral fertiliser plus biochar in Amazonian soils (Lehmann *et al.*, 2003).

The two treatments that leached the least NO_3^--N were from the low biosolids plus biochar treatments applied to both the Ashley Dene and Templeton soils (1647 & 740 mg NO_3^--N). However, this was higher compared to a bovine urine application (397 mg NO_3^--N) in a previous 55 day N mitigation study on a Wakanui silt loam soil (Clough *et al.*, 2010). Clough *et al*. (2010) found that the amendment of biochar in combination with bovine urine increased concentrations of NO_3^--N (242 mg NO_3^--N) in leachate compared with a bovine urine treatment, rather than reduce concentrations of NO_3^--N. Laird *et al*. (2010a) also established biochar applications (43 t ha^{-1}) can significantly increase NO_3^--N concentrations in leachate (26%) in comparison to a control. The different outcomes of NO_3^--N concentrations in leachate, may have resulted from N forms in bovine urine being more readily available to denitrification than the N forms in biosolids; which are well known to require a significant amount of decomposition and mineralisation before large amounts of N are available, and vulnerable to denitrification (Singh & Agrawal, 2008). The extent of N in biosolids requiring mineralisation – before being susceptible to the nitrification – can be explained by Tables 3.2 & 3.3, where biosolids and biochar amendments raised total N concentrations in the soil by 16-219%, however, after 148 days the majority (>99%) of added N was still able to be accounted for. In spite of the mass balance of N in the soil, the results may be in question, as it does not take into account losses through volatilisation, nitrification or concentrations of N in below ground biomass.

Consequently in regards to biosolids gradually releasing N into the soil, the properties of biochar, such as the carboxylic functional groups on the particle surfaces, can easily attract and retain large quantities of the slowly released available N, reducing NO_3^--N concentrations in leachate (Cheng *et al.*, 2006). Clough *et al.* (2010) however, explained their result through increases in the total N pool in the soil, which may have caused larger concentrations of other forms of N to be present in the soil causing lower NO_3^--N concentrations in leachate to occur.

When the results of the current trial are compared with a study involving an application of 30 kg N ha^{-1} of mineral fertiliser (Lehmann *et al.*, 2003), this trial produced a greater total leaching loss (by ~ 89 kg N ha^{-1}) over a longer time period (110 days). Although it may appear that, this could be explained by the longer period of this trial, the concentration of NO_3^--N leached from this trial at the equivalent time period (55 days) was still significantly larger. This was unusual, as the equivalent water inputs (2500 mm vs. 1400 mm $year^{-1}$) were also significantly higher from their study; however the equivalent N inputs in this trial were also considerably greater, ranging from 600 – 1200 kg N ha^{-1}. Therefore the ratio of the average treatment of N applied to the average NO_3^--N concentration leached was in turn significantly lower, with a ratio of 13.3 compared to 27.5, indicating that in this trial, a larger amount of NO_3^--N was retained by the soil in relation to the total concentration of N applied i.e. a greater nutrient use efficiency.

Mechanisms that may have contributed to the reduction in NO_3^--N concentrations occurring in leachate from the present trial are displayed in Figure 4.1. To begin with, concentrations of NO_3^--N in leachate may have decreased due to increased immobilisation of other forms of N, due to these N forms not being given enough time to mineralise and therefore lead to nitrification (Chaney, 1990; McLaren & Cameron, 1996). Increased immobilisation may have occurred through the change in C:N ratio, on addition of biochar to soil (Lehmann *et al.*, 2003). As there was an increase in C:N ratio on the Ashley Dene soil lysimeters, from 8.77 on the control to 35.21 on the biosolids plus biochar treatment, a 300% increase. This is supported by

Lehmann *et* al. (2004) who demonstrated that with a high C:N ratio microbial biomass may decrease the availability of nitrogen through immobilization. Similarly Ogunwande *et al*. (2008) who measured N concentrations leached from composting, noted that additions of sawdust which increased the C:N ratio to 25, significant decreased N losses.

Another factor possibly contributing to immobilisation of N in soil, and leading to the reduction of NO_3^--N concentrations in leachate is the oxidation of biochar surfaces over the study period. Oxidation of biochar surfaces increases with age and the interaction of biotic and abiotic process with the soil, and subsequently leading to increase CEC (Cheng *et al.*, 2006; Liang *et al.*, 2006). Therefore the oxidation of biochar potentially increasing sorptive properties over time may explain the results in Figures 3.3 & 3.4 where concentration of NO_3^--N typically decreased over the 5 month trial period. Singh *et al*. (2010) also proposed this as a potential reason for the 73% reduction in N_2O emission from soils amended with wood and poultry manure sourced biochar.

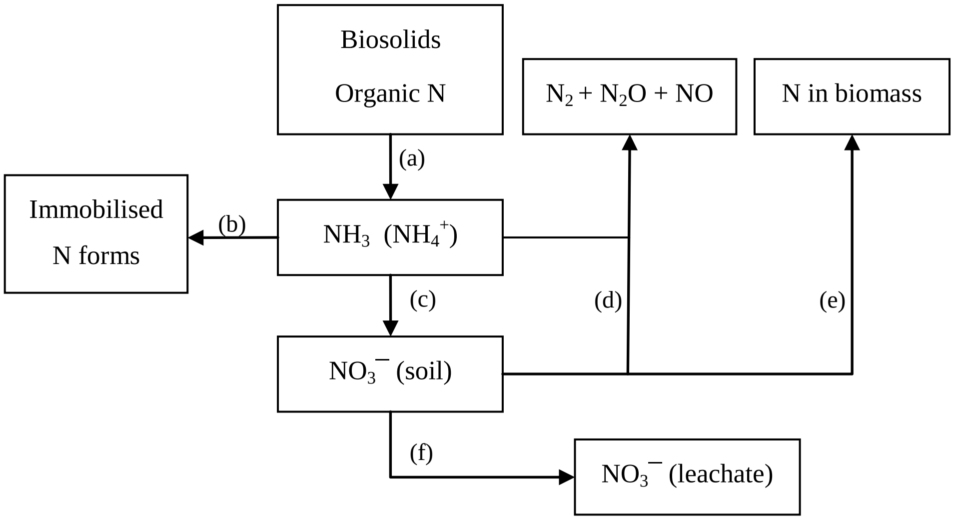

Figure 4.1: Mechanisms changing the form of biosolids applied N (a) in soil, immobilisation (b), nitrification (c), denitrification and volatilisation (d) plant uptake (e) and leachate mobilisation (f).

The NO_3^--N flux from biosolids applications may have also decreased from increased anaerobic conditions in the soil environment, as a result of rainfall exceeding evapotranspiration (Figure 3.2) (McLaren & Cameron, 1996) during the period of the trial. The oxygen deprived soil environment, may have then lead to denitrification (decreasing NO^-_3 levels in the soil) through biological interactions resulting in the production of nitrogen gases such as N_2, N_2O and NO. This process would then decrease the concentrations of NO_3^--N in the soil and the possibility of the now denitrified NO_3^--N being leached. This mechanism is good in theory however, it has been proven inconclusive with Clough *et al*. (2010) finding increases in N_2O emissions from biochar and bovine urine soil treatments, while Singh *et al*. (2010) found significant reductions in N_2O emission from soil amended with biochar sourced from various feedstocks.

Pasture biomass (Tables 3.6 & 3.7) significantly increased with the soil amendments in this trial, and as a result would be expected to have a greater uptake of nutrients. Nutrients such as nitrogen, which is essential for plant growth, would then be extracted from the soil by the plant and utilised decreasing concentrations in the soil. However, the mass balance of N in Tables 3.2 & 3.3 indicates that some biochar applications may decrease (1.33 kg N ha^{-1}) the concentration of N in the plant rather than increase the N concentration. Major *et al*. (2010b) found that N plant uptake increased from 1-50 kg N ha^{-1} with increasing amendments of biochar applied at 8 and 20 t ha^{-1}. Therefore with any changes caused to the N cycle at any of the points – (a) through (f) – in Figure 4.1 the concentration of NO_3^--N in leachate should alter.

4.2 Leaching of other elements

The effect of biosolids and biochar amendments on elemental concentrations occurring in leachate was in conclusive when combining the effects on both the soil types examined in the current trial, however, on individual soil types specific patterns appeared to occur. The Ashley Dene soil type (being the poorer of the two in soil quality) amended with biosolids plus biochar overall leached less nutrients when compared to the control and biosolids treated lysimeters. The elements that increased with biochar additions were As and Cr. Sulphate was also found to increase from the control with the treatment of biosolids plus biochar. However, the increases in concentrations were limited to 43 µg As, 2.3 mg Cr and 4 g SO_4^{2-}. The decrease in elemental concentrations in leachate may have been the result of improved sorptive capacity in the soil from the biosolids plus biochar amendment. Soil sorptive capacity is thought to increase from enhanced CEC and specific surface area (SSA) on additions of biochar to soil (Laird *et al.*, 2010b). Laird *et al*. (2010b) measured the CEC and SSA in soil amended with biochar and biochar plus swine manure, and found that after an application of biochar at 43 t ha^{-1}, the SSA increased by 23 m^2 g^{-1} of soil and CEC increased by 4-30%. Just as NO_3^--N was possibly affected by the oxidation of fresh biochar, other nutrients such as the cations listed in Tables 3.8 & 3.9 may have also had a significant effect on the adsorption of nutrients, as they to show a reduction in concentration leached per litre over time. As stated by Cheng *et al*. (2006) fresh biochar may have relatively low CEC, but as mineralisation occurs when incorporated into the soil environment, the CEC increases due to oxidation of the biochar surfaces.

The Templeton silt loam soil type had varied results in the concentrations of elements in the leachate from all the amended soils when compared to the control. The high rate of biosolids plus biochar treatments showed an increase in most elements in leachate compared to the Templeton control. The elements that decreased for the high rate of biosolids plus biochar also decreased for the low rates which were Cr, Cu, Pb and Ca when compared to the control. While the concentrations of As, Mg, Fe, Cl^-, Br^-, and SO_4^{2-} increased in leachate from the Templeton soil lysimeters amended with the low rate of biosolids plus biochar compared to the control. Laird *et al*. (2010b) found that the addition of biochar plus swine manure increased Ca, Cu, K, Mg, Sulphur and Zn concentrations in leachate from control lysimeters, which is similar (except Ca and Cu) to the effect the high biosolids plus biochar treatment from the Templeton soil type, had on elemental composition in leachate in the current study.

The concentrations of anions (Cl^-, Br^-, and SO_4^{2-}) measured in the leachate decreased with the low rate of biosolids plus biochar treatments on both soil types, which is plausible with the properties biochar brings to the soil environment. The surface of biochar is typically similar to soil having a net negative charge (Singh *et al.*, 2010), however, in the soil environment biochar can be highly variable due to interactions with the soil and soil solution and, mineralisation of biochar. The soil can adhere to the exterior, encapsulating the biochar particle changing the exterior biochar properties that interact with nutrients (Major *et al.*, 2009). While in other cases it has also been known that through the process of oxidation of biochar, functional groups develop (Cheng *et al.*, 2006) on the surface as well as polar functional groups (Sarmah *et al.*, 2010) and are therefore able to interact with anionic molecules, and compounds such as hydrophobic organic pollutants.

4.3 Role of organic carbon

Ashworth & Alloway (Ashworth & Alloway, 2004) stated that while the solid organic matrix in biosolids immobilises trace elements, dissolved organic matter (DOM), which leaches from biosolids as they age, may increase trace element solubility. DOM and organic C (OC) have been shown to increase trace element mobility in contaminated soil (Kalbitz & Wennrich, 1998; Karathanasis *et al.*, 2005). The current trial may have observed this relationship, with leachate concentrations of K, Fe, Al (at high rates) Mg, Ca and As (Table 3.8 & 3.9) increasing at a similar rate, as the amount of OC occurring in the leachate (Figure 3.10). Liu *et al*., (2007) proposed that the dissolved organic matter released from biosolids should be considered in the course of regulating the safe application rates of sewage sludge to soil.

Beesley and Dickinson *et al*. (2010) found Cu and As were strongly correlated with DOC suggesting the mechanisms co-mobilisation were exhibited. However, Kalbitz and Wennrich (1998) found that highly protonated DOM was inept to binding positively charged elements leading to a greater proportion of nutrients in soil solution.

Another potential path of C lost in soil, is translocation, with fine biochar particles smaller than 200 μm, which may represent a large portion (20-85%) of the biochar amendment (Figure 3.10) to move through the soil profile, and can act as agents of facilitated transport of nutrients. (Major *et al.*, 2009). Nguyen *et al*. (2008) also measured C loses from soil post biochar amendments and found biochar-derived C losses from the top 0.1 m over 100 years were estimated at 6 t ha^{-1}.

The addition of biochar to soil has been suggested as a means to sequester carbon thereby reducing the effects of human-induced climate change caused by carbon dioxide emissions (Lehmann, 2007b). Biochar improves soil fertility by increasing the soil’s capacity to absorb water and nutrients (Novak, 2009). Recently, Cao *et al*. (Cao *et al.*, 2009) showed that biochar strongly absorbs contaminating lead and atrazine in soil.

The role of organic The association of nutrients to organic matter OM has been a controversial topic for decades and whether the associated nutrients are transported through the soil profile while being attached to the OM or

4.4 Pasture quality and quantity

Increases in soil fertility attributable to biochar are known from naturally occurring fires (DeLuca *et al.*, 2006). Additions of bio-char to soil have shown definite increases in the availability of major cations and phosphorus as well as in total nitrogen concentrations (Glaser *et al.*, 2002; Lehmann *et al.*, 2003). Both CEC and pH are also frequently increased through such applications (Cheng *et al.*, 2006; Steiner *et al.*, 2007). Higher nutrient availability for plants is the result of both the direct nutrient additions by the biochar and greater nutrient retention (Lehmann *et al.*, 2003) but it can also be an effect of changes in soil microbial communities (Warnock *et al.*, 2007).

Yield increases have frequently been reported that are directly attributable to the addition of biochar over a control without biochar (Lehmann *et al.*, 2003). However, growth depressions have been found in some instances (Steiner *et al.*, 2007; Warnock *et al.*, 2007). The immediate beneficial effects of biochar additions for nutrient availability are largely due to higher potassium, phosphorus, and zinc availability, and to a lesser extent, calcium and copper (Lehmann *et al.*, 2003). Longer-term benefits for nutrient availability include a greater stabilisation of organic matter (Nguyen *et al.*, 2008), and concomitant reductions in nutrient release from added organic matter (OM) such as biosolids (Accardi-Dey & Gschwend, 2002), and better retention of all cations due to a greater cation exchange capacity (Laird *et al.*, 2010a).

The effect of biochar on the pasture growth in the current trial was generally positive with increases in total above ground DM production ranging from 20 – 52% (Tables 3.6 & 3.7). Although the current trial did not use varying biochar applications progressive growth improvements have been seen with comparatively low levels of biochar; and have been achieved at very low application rates of 0.4 to 8 t C ha^{-1}, significant improvements in productivity have also been observed ranging from 20 to 220% (biomass production equal to 120 to 320% of the control in many cases). Lehmann *et al.*(2003)again found that N limitation will be the reason for declining yields at high application rates, as N availability decreases through immobilization by microbial biomass at high C:N ratios, although other growth-limiting factors may be responsible as well. With increasing rates of application, plant response at a given site is positive until some maximum is reached, above which growth response is negative, as shown for beans when biochar applications exceeded 78 t ha^{-1} (Rondon *et al.*, 2007). Although this appeared to be the case with the previous bean trial there did not appear to be any negative effects to plant growth or yield, in the current trial with an application of 102 t biochar ha^{-1}, with all biosolids plus biochar treatments obtaining higher yields than solely biosolids amendments.

There also appeared to be a relationship between soil type and the extent to which the elemental concentrations in the plants were effected (Figure 3.8 & 3.9). As indicated on the Ashley Dene lysimeters with more than one element, for instance K was taken up by pasture in significantly (P <0.001) larger concentrations from the addition of biochar to the biosolids amendment than on the Templeton soil type. However, this also with Mo on the Templeton soil type with increases of 210% between the low biosolids and biosolids plus biochar treatment and 308% between the high biosolids and biosolids plus biochar treatment.

The Zn concentration in the harvested pasture not only decreased over time from one harvest to the next and but biochar also decreased the concentration of Zn taken up by plants (Figure 3.12 (a) & (b)). Zinc concentration on the low biosolids amendments increased in pasture by 375 and 402% from the controls on Ashley Dene and Templeton soils respectively, with biochar decreasing this by 16 and 19 %. The high rate also significantly enhanced Zn concentrations in pasture by a 9.2 fold increase and the high biosolids plus biochar treatment reducing this increase by 14%. With these increases in pasture Zn concentrations, biofortification may be possible added benefit to a combined biosolids and biochar soil amendments (Zhao & McGrath, 2009).The reduction in Zn concentration in plant biomass was also exhibited by Namgay *et al*. (2010), with approximately a 17% reduction with the addition of 6.5 t biochar ha^{-1}.

4.5 Field application and practicality

Biosolids have been identified as a source of nutrients that can be easily leached, especially under a winter pastoral setting. This trial was performed in a near field situation that would take into account natural variations such as weather. Therefore the results presented here should be similar if not the same if applied in a system such as an intensive dairy farm. The data collected from the trial can then be integrated into a farm, forestry or market garden scale system.

Even though this trial was conducted in Canterbury, the data can be transferred to a setting that experiences up to 1415 mm of rainfall per year, and moderate leaching, this is due to the volume of water inputs being similar to regions that receive higher rainfall than Canterbury, such as Northland, New Zealand. Therefore, larger scale situations can be based on average management systems for regions that are wetter on average than Canterbury conditions.

In order to calculate the concentration of NO_3^--N lost on a field scale, a mass balance of N could be calculated with the N inputs being applied, added to the initial N concentration in the soil, and NO_3^--N losses subtracted from the total N. The effectiveness of the biochar at the field scale can then be calculated and recommendations made alongside best management practices (BMPs) for users of biochar such as farmers to use in order to reduce NO_3^--N leaching losses. The mass balance of N in the soil system could then be added to a computer modeller or program such as OVERSEER® to make the use of biosolids easier for people in industries such as agriculture, horticulture and silviculture.

4.6 Future value of using biosolids and biochar

Firstly, reducing NO_3^--N concentration in leachate from fertilised soil with the use of biochar provides environmental benefits such as reducing NO_3^- contamination of ground and surface waterways. This is may be due to biochar interfering with the conversion of NH_4^+ to NO_3^--N through immobilisation, nitrification, denitrification, volatilisation and plant uptake keeping N in the NH_4^+ form for longer or rapidly converting NO_3^--N into other forms that are not so susceptible to leaching. This would result in less NO_3^--N diffusing into waterways, reducing eutrophication and mitigating adverse effects to water quality. Furthermore, the potential use of biochar in the agricultural industry may reduce the amount of greenhouse gas emissions, with particular reference to N_2O, reducing the effects of global warming (Clough *et al.*, 2010).

The application of biochar to pasture in an agricultural system would potentially allow farmers to continue farming sustainably while farming at a higher stocking rate. Farm profitability could therefore be improved, as a greater number of animals are able to be stocked for the same environmental impact and increasing production at the farm gate. The economics and rationale of applying biochar to soil in an agricultural system is becoming more apparent with the ever increasing cost in urea fertilisers (> $700/t) due to increasing costs of energy, therefore farmers are looking at ways to minimise costs. Where farmers' maybe able to reduce inputs of N fertiliser through improving N use efficiency multiple benefits (economical, ecological and environmental) could be achieved. The use of biochar on a large scale is however in question as it will require significant processing before incorporation it into the soil or combining it with another product such as biosolids. The additional processing may cause extra environmental issues with air pollution and possible C enrichment of neighbouring waterways.

As sustainability becomes the 'topic of the day', regional councils may target practices that lead to enrichment of waterways from and restrict productivity to reduce the effects of nutrient leaching. Therefore using biochar could allow practices such as intensive dairy farming to continue running current stocking rates while reducing NO_3^--N leaching into the environment.

Chapter 5- Conclusions

This trial has clearly identified that nitrate losses are not only a concern with the application of biosolids to land, but are also a concern in terms of the associated trace elements that make up their content. Over the late autumn-winter-spring period, nitrate leaching and nutrient loss are potentially at their greatest due to the presence of cool/moist weather and environmental conditions, producing drainage and aerobic soil conditions. Results from this study clearly indicate great potential for the use of biochar in combination with biosolids, with significant ($P<0.001$) reductions in NO_3^--N by 48%, with the application of biochar at 102 kg ha^{-1} on biosolids (600 kg N ha^{-1}) amended in May. This trial has also shown that biochar has the potential of mitigating the N issue that is limiting biosolids application rates and therefore have the possibility of being used in lieu of mineral fertiliser as a source of nutrients. Sole biochar applications could also be a valuable tool for the management of agroecosystems such as intensive dairy farms to mitigate current N issues.

The effect of biosolids and biochar varies among soil types therefore soil properties and in particular physical, chemical and biological properties effecting the additions of biosolids and biochar, should be accounted for, and taken into consideration when deciding on, whether the soil is appropriate for the amendment.

In the future, biosolids may become the preferred source of land applied nutrient, due to the cost of mineral fertilisers increasing, and as sustainability becomes the ‘hot issue’, where biosolids not only close the loop on nutrient cycling but with the addition of biochar may be achieved with minimal detrimental effects on the environment. Therefore, the use of biosolids-biochar soil amendments in regards to the current trial could be beneficial to future farmers, silviculturists and mine site rehabilitation; and as biochar may increase nutrient use efficiencies, costs may decrease making the use of biosolids as a source of nutrient, more favourable over mineral fertilisers nearer in the future.

Recommendations for further biosolids and biochar research:

- Longer-term studies with biochar applications are needed to evaluate their effects on sustained soil fertility and nutrient dynamics as it is not clear from this study as to if or when biochar becomes inundated with nutrients and is no longer a site for potential adsorption.

- The effect of biochar as a soil amendment should also be analysed by itself as the effect of biochar in this study, has shown that NO_3^--N can be reduced through possible N-immobilisation in the soil therefore increasing the efficiency of the available N.

- Further research is required on the possible effects of aged versus fresh biochar, as there has been some speculation here from other studies and as this trial used fresh biochar, the adsorption ability of the biochar may not have been at its optimum, as it may have been if aged/activated biochar was used.

- Various application methods should be tested along with the appropriate aggregate size of biochar as this could potentially have an effect on the ability of adsorbing nutrients not only in the short-term but also the long-term.

- Interaction effects of individual nutrients should be studied as these may affect the mobility and immobilisation of nutrients and contaminants in the soil.

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Appendices

Appendix A – Literature Review

7.1 Biosolids

7.1.1 Treatment and Characteristics

Biosolids are essentially the solid by-product of wastewater treatment plants. Therefore the constituents of the wastewater will determine the characteristics of the end product – biosolids. Typical origins of waste that enter into wastewater systems originate from urban, commercial and industrial points sources. Urban waste may include storm water runoff and sewage, while commercial and industrial wastes may contain processing chemicals including solvents and surfactants, or wastes such as blood and bone from meat processing plants. Consequently, countries that still allow industrial and commercial waste to be disposed of in their wastewater systems, which are typically toxic, end up in the biosolids. However, recently regulations have been implemented in developed countries limiting or fully stopping this practice, decreasing the amount of harmful substances in the biosolids. For example the U.S. Environmental Protection Agency (EPA) in 1993 established the 40 CFR 'Part 503' rules for standards in the use and disposal of biosolids (Krogmann *et al.*, 1999; Oleszkiewicz & Mavinic, 2002).

Table 7.1: Typical characteristics of biosolids over 2007 in New Zealand (Bradley, 2008).

Characteristic	Quantity	
Average solids	92 %	
OM	67.8 %	
Zinc	510 – 620	mg/kg dry wt
Copper	170 – 240	mg/kg dry wt
Nickel	30 – 55 mg/kg dry wt	
Mercury	1 - 2	mg/kg dry wt
Cadmium	< 1	mg/kg dry wt
Lead	30 – 40 mg/kg dry wt	
Nitrogen	6 %	
Phosphorus	3.25 %	
Potassium	0.14 %	
Size: 2-4 mm	80 – 90 (% Wt/Wt)	

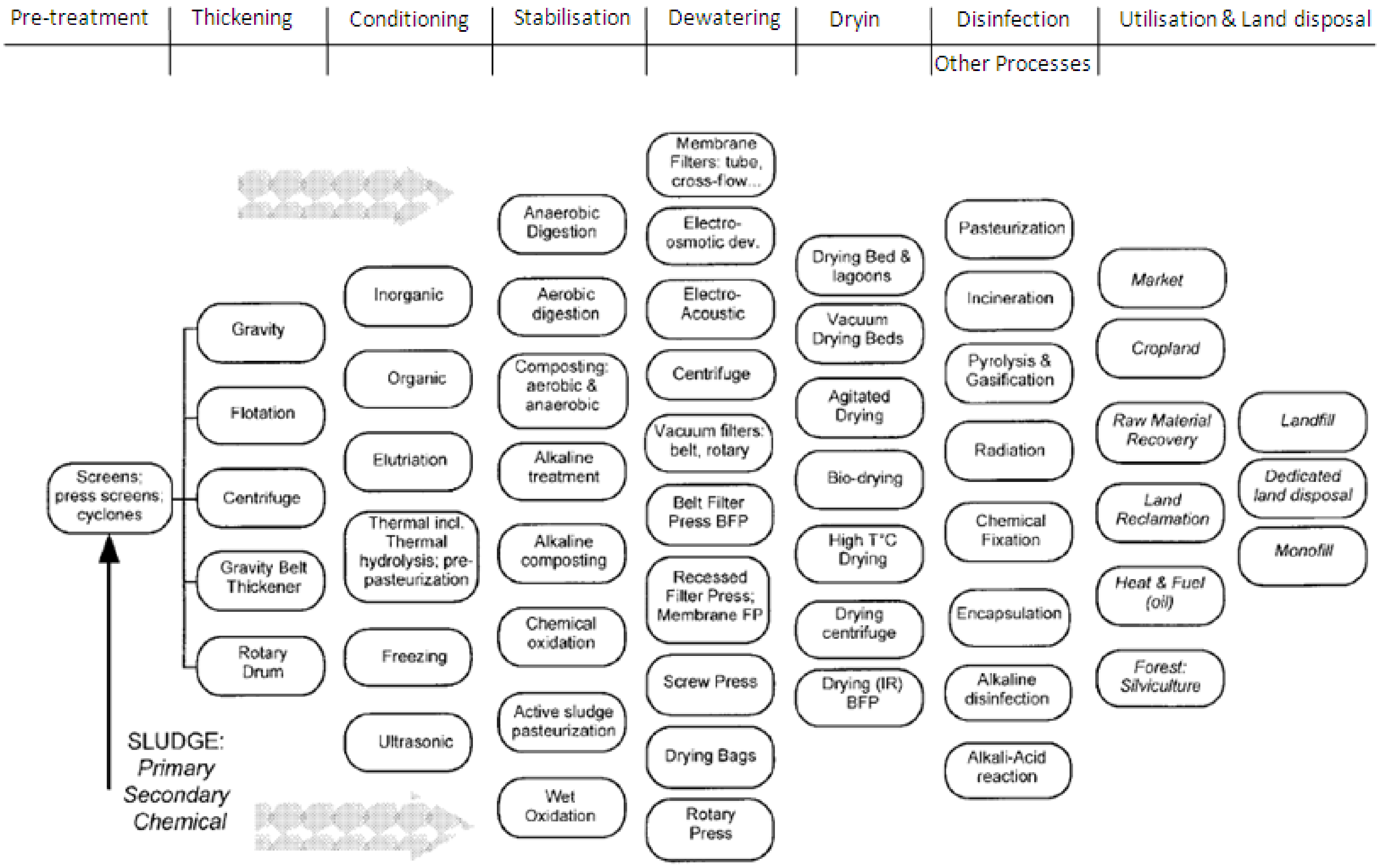


Figure 7.1: Some of the many unit processes available for biosolids treatment from Oleszkiewicz & Mavinic (2002).

Biosolids are a heterogeneous material, which varies between seasons and treatment plants which have general characteristics comprising of (Table 7.1) a high carbon content indicated by a high proportion of organic matter (OM), a high concentration of organic acids - humic

and fluvic acids (HA & FAs) demonstrated by a high acidity, and also a high concentration of macro and micro-nutrients, organic compounds – pesticides, herbicides, surfactants, and populations of pathogens – helminths, bacteria, viruses and fungi (Krogmann *et al.*, 1999; Singh & Agrawal, 2008).

Table 7.2: A summary of stabilisation processes that produce biosolids modified adapted from Epstein (2003).

	Stabilisation Process	**Uses**
Alkaline Stabilisation	Use of lime or other alkaline materials, such as cement kiln dust, lime kiln dust, Portland cement and fly ash. Increase of pH to reduce pathogens and achieve vector attraction reduction.	Agricultural, reclamation, slope stabilisation, structural fill and municipal solid waste (MSW) landfills.
Anaerobic Digestion	Biologically stabilising biosolids in a closed vessel to reduce the organic content, mass, odour, and pathogens. Mesophillic (35°C) and thermophillic (55°C) temperatures are used.	Agricultural and forestry.
Aerobic Digestion	Utilises oxygen or air to biologically stabilise biosolids in an open or closed vessel or lagoon. OM is converted to CO_2, water and N. Pathogens and odours are reduced. High thermophillic temperatures are now being used	The principal use is for agriculture.
Composting	The biological decomposition of the OM. Generally biosolids composting is done at thermophillic (>55°C) temperatures in order to destroy pathogens. Odorous compounds are reduced.	Horticultural including landscaping, nursery operations, turf, lawn and sod production, agricultural, public works department projects, highway beautification and reclamation.
Heat Drying & Pelletizing	Active or passive dryers are used to remove water from biosolids. Pathogens are destroyed and water removed, reducing the volume of material. In some cases heat dried products are formed into pellets.	Its primary use is in agriculture. Other sues are in turf and sod production and golf courses. Pellets are also blended with other N, P and K chemicals to produce fertilisers.

The characteristics of biosolids, as stated above, are primarily functions of their source with the extent of treatment, process modes and methods of stabilisation being subsequent determinants of their final properties and ultimately their use or disposal. Types of processes used to treat biosolids are outlined in Figure 7.2 from thickening to drying and disinfecting (Clapp *et al.*, 1994; Oleszkiewicz & Mavinic, 2002).

The type of treatments described in Table 7.2 have an effect on speciation, solubility and mobility of constituents and compounds attributed to biosolids composition (Epstein, 2003). The varying treatments that wastewater goes through to produce biosolids may also be determined by the biosolids end use. For instance biosolids used for agricultural purposes as a source of nutrient input for plants, requires a higher standard of processing than biosolids disposed of in a landfill. This is due to biosolids used in a agricultural system having the potential to come in contact with plants and livestock which humans later consume necessitating the greater degree of treatment to reduce or eliminate contaminant concentrations and pathogen populations (Clapp *et al.*, 1994).

Treatment and processing of biosolids may include but are not limited to pre-treatment, thickening, conditioning, stabilisation, dewatering, drying, disinfection and utilisation, Figure 7.1. Pre-treatment is the initial screening of wastewater at a treatment plant, which is followed by thickening which is the initial step in reducing the wastewaters volume causing thickening. The conditioning process changes biosolids physico-chemical properties in preparation of mechanical dewatering. Stabilisation processes are used to digest, pasteurise, oxidise, compost or chemically treat biosolids. Dewatering normally refers to the mechanical dewatering of biosolids and disinfection in order to further reduce volume and pathogen populations respectively (Oleszkiewicz & Mavinic, 2002).

7.1.2 Regulations and Planning

Planning in relation to the disposal or use of biosolids is normally associated with the use of biosolids as a nutrient source for example as a fertiliser or conditioner in an agricultural system. Planning is essential in risk assessment and limiting the potential adverse effects of biosolids on the environment, animals and humans.

As of 1993, the regulations for the use and risk management of biosolids were tightened and officially outlined by the US, with Europe and other significant countries soon following. These regulations were set to protect the public and the environment from potential contaminants and pathogens being introduced or from the occurrence of excessive accumulation of organic pollutants and HMs. The requirement for the introduction of official regulations resulted from research and public opposition to past practices such as abyssal ocean disposal having uncertain costs on the environment, landfill disposal becoming increasingly expensive and the use of biosolids on agricultural land being seen as a beneficial use for disposal ("Guidelines for the safe application of biosolids to land in New Zealand," 2003; Krogmann *et al.*, 1999). Chaney (1990) stated from a review of the industry in 1990, that the exclusion of industrial waste and pre-treatment of biosolids from wastewater treatment plants significantly decreased the amount of contaminants allowing the application of biosolids to agricultural land to become an acceptable process of disposal.

Table 7.3: Pathways for risk assessment for potential transfer of sludge-applied contaminants (Chaney, 1990).

	Pathway	**Most exposed Individual**
1	Biosolids → Soil → Plant → Human	General food chain; 2.5% of food.
1F	Biosolids → Soil → Plant → Human	Home garden after 5 yrs; 60% leaf veg.
2F	Biosolids → Soil → Human	Residential Soil, 5 yrs; 200 mg soil/d
2-D&M	Biosolids → Human	Biosolids product; 200 mg biosolids/d
3	Biosolids → Soil → Plant →Animal → Human	Farms; 40% of meat
4-Surface	Biosolids →Animal → Human	Farms; 40% of meat
4-Mixed	Biosolids → Soil → Animal → Human	Farms; 40% of meat
5	Biosolids → Soil → Plant →Animal	Livestock feeds; 100% on treated land
6	Biosolids → Soil → Animal	Grazing livestock; 1.5% biosolids in diet
7	Biosolids → Soil → Plant	‘Crops’; strongly acidic treated soil
8	Biosolids → Soil → Soil biota	Earthworms, slugs in treated soils
9	Biosolids → Soil → Soil biota → Predator	Birds; 33% diet affected by biosolids
10	Biosolids → Soil → Airborne dust → Human	Tractor operator
11	Biosolids → Soil → Surface water → Human	Water quality criteria
12	Biosolids → Soil → Air → Human	Farm households
12W	Biosolids → Soil → Groundwater → Human	Well water on farms; 100% of supply

The situation currently in New Zealand involves guidelines for the wastewater industry, central and local governments and other associated bodies in the production and use of biosolids, so the risks associated with the land application of biosolids is managed with quality control and best management practices being implemented ("Guidelines for the safe application of biosolids to land in New Zealand," 2003). For instance in Table 7.9 in a later section, lists standards for maximum populations of pathogens and concentrations of heavy metals (HMs) in biosolids so as to limit the contamination and accumulation of adverse properties associated with biosolids.

However, as stated in an earlier section the degree of treatment for biosolids will depend on the planned end use. This is because there are differing regulations for the use of biosolids in an agricultural system than biosolids disposed of in a landfill. This is due to risks associated to biosolids in each situation as determined by possible exposure pathways to the adverse components of biosolids (Table 7.3). For instance the disposal of biosolids to landfill has far fewer possible exposure pathways than the use of biosolids in an agricultural system (Chaney, 1990; Clapp *et al.*, 1994). Therefore, classes of biosolids have been introduced where a high class (treated to a high degree) of biosolids is required when planned for use in an agricultural system, but a lower class can be used when biosolids are planned to be disposed of in a landfill (Epstein, 2003).

7.1.3 Alternative Uses

There are many uses of biosolids for land application, and when treated to the correct degree can come in several different forms. The different forms or products of biosolids are liquid, dewatered, air-dried, alkaline-treated, and composted and heat dried, with both the dewatered and air-dried products having the potential to be anaerobically processed. The end uses of each of theses products are fertiliser or soil conditioner for pasture, crops, forests or reclamation, in agriculture, horticulture, landscaping and nurseries. The alkaline-treated biosolids are usually used as agricultural lime and artificial soil for landfill cover and the heat dried biosolids are typically used at low rates as a nutrient source or carrier for inorganic fertilisers. Advantages for each product may range from most economical to produce, to high public acceptance for use, but may also include a low rate of nutrient release, ease of handling and storing, low transport costs, higher concentrations of nutrients and potential to harness energy during processing.

Disadvantages towards each end product may include malodour, site restrictions, high transport or production costs, high lime content and problematical processing concerns (Clapp *et al.*, 1994).

Additionally however, there have also been many alternative uses typically methods for disposal of biosolids in the past. Current favoured forms of disposal and use are land filling, incineration but abyssal ocean dumping and discharge to waterways still occurs, with each method having both positives and negatives in terms of economic, environmental and social repercussions but all typically having a lower public acceptance when compared with the application of biosolids to land (Cameron *et al.*, 1997; Krogmann *et al.*, 1999).

Currently in New Zealand end uses and disposal of biosolids include land reclamation (116,380t), landfill (79,440t), other beneficial uses (36,817t), ponding (875t) and forest application (600t) (Bradley, 2008).

7.1.4 Benefits

7.1.4.1 Macro & Micronutrients

Biosolids as stated under characteristics are a great resource of nutrients, an aspect that is generally overlooked and not usually exploited. Typical nutrients in biosolids can be put into and identified as essential, non-essential and toxic for plants and animals groups (Cameron *et al.*, 1997). Many studies have researched this fact and also the benefit of sustainably improving and maintaining productive soils and stimulate plant growth. Singh and Agrawal (2008) found that biosolids were a great source of micro and macronutrients and when applied to soil served as a great source for plant nutrients such as nitrogen (N), phosphorus (P), calcium (Ca) and magnesium (Mg) while organic constituents as in OM act as a soil conditioner . Chaney (1990) also agreed with these effects of biosolids on soil by identifying that twenty years of land application can increase elements such as zinc (Zn) and copper (Cu) on low fertility soils and stated that biosolids were more beneficial than normal commercial or mineral fertilisers. However specific management practices for the use of biosolids was recommended so that N leaching and erosion control are prevented as eutrophication (depletion of dissolved oxygen), increased salinity and groundwater contamination will not occur (Cameron *et al.*, 1997; Chaney, 1990). With N leaching rates, dependant on a number factors such as presence of irrigation and its rate, soil type and management and environmental setting.

On the other hand, the current use of mineral fertilisers can also lead to contamination of waterways and eutrophication occurring if poor management practices are exercised. Where, Loganathan et al. (2003) discussed the issue of Cd and fluorine (F) concentrations being present in mineral fertilisers which can accumulate in animals and plants decreasing quality and risking animal health due to accumulations exceeding the maximum permissible concentration (MPC) set but food authorities, yet they are still used.

Chaney (1983), also found from the introduction of the 'soil-plant barrier' concept of trace elements (TEs) entering the food chain from applied biosolids to agricultural land, that some nutrients find their way into plants with several e.g. molybdenum (Mo), Zn and Cu, having beneficial results and others e.g. Cd not so much. Therefore the potential to capitalise on the beneficial source of nutrients in biosolids for agronomic and horticultural purposes would have a significant effect on eliminating the issue of disposal, improving soil conditions and increasing plant growth.

7.1.4.2 Soil Physical Condition

Overall there has been minimal research carried out on the affects biosolids has on soil physical conditions as these are perceived as insignificant when compared to the potential adverse effects of toxic nutrient accumulation or pathogen survivability. However, research to date and knowledge of individual compounds conditioning effects that are also present in biosolids, have lead to the conclusion, that biosolids benefit the soils physical condition, by improving soil structure with the degree of improvement being dependant on various soil properties (Cameron *et al.*, 1997). The soil properties that may hinder the improvement are soil pH and soil texture. Haynes et al. (2009) reported that inorganic and organic constituents and contaminants of biosolids improved the soils physical properties. Epstein (2003) also stated that soil structure improved from the addition of biosolids through bulk density, porosity, strength and aeration.

7.1.4.3 Plant Growth

Biosolids generally have a positive effect on plant growth however; depending on the situation, biosolids may also have a negative effect on plants (Cameron *et al.*, 1997). The positive effect on plant growth is essentially due to the readily available N found in biosolids, as N is the most limiting nutrient for optimising plant growth (Taiz & Zeiger, 2002). The increase in growth from plants has been reported to cause an overall yield increase and also decrease the time taken to reach physiological growth stages. Quinn and Woods (1978) showed that pasture response to biosolids was greatest in summer and autumn. While Singh and Agrawal (2008) have described the benefits of soil amended with biosolids and reported an increase in crop production and development (Table 7.4) from a variety of plants - Tall fescue (*Fescue arundinaceous Schreb*.), Maize (*Zea Mays L.*) and Barley (*Hordeum vulgare*) – and within their growth stages, such as germination. The increment increase in yield was also noted as being higher than crops grown on recommended mineral fertiliser amended soils. Boswell (1975) also found forage yields of Tall Fescue increased by 30% from the application of biosolids compared to yields obtained using mineral fertilisers.

The application of biosolids was also reported as creating a more robust plant, which in a agricultural pastoral system would be highly beneficial to reduce plants lost to trampling and removal by livestock (Singh & Agrawal, 2008). Increased plant persistence was examined by Döring and Gäth (2002) with composted biosolids recognised as helping control plant disease and reduce crop losses due to competition by introduced beneficial organisms which in turn aided plant growth.

The quality of biosolids and involvement of poor management practices, for instance applying large quantities over a short period were identified as significant functions of plant growth. This was shown by plants experiencing reductions in growth or even plant death due to the types or amounts of nutrients taken up by the plant (Chaney, 1990). Cameron et al. (1997) reported that essential plant nutrients supplied by biosolids were identified as being beneficial in low fertility soils, with high rates of applications being phytotoxic due to elevated levels of HM concentrations. Antolin, et al. (2005) recognised that low cumulative applications of biosolids would increase plant yields when compared to a control stand, with the increase being associated with improved early establishment of seedlings.

Table 7.4: Effect of biosolids amendment on growth, yield and HM accumulation in plants integrated by Singh & Agrawal (2008).

Plant	Biosolids amendment rate	Effect on growth & yield	Accumulation of HM in plants
Fescue	5.6 Mt/ha dry weight.	30% increase from control	Cd, Cr, Cu, Mn, Pb, Zn & P concentration increased
Corn	Applied to supply 50, 100, 150 & 200 kg N/ha/yr.	Increase in yield between soil types.	-
Maize	0, 1.1, 2.3, 4.5, 10, 20, 30, 40 & 50 t/ha dry weight.	Increase in germination, root and shoot lengths, leaf area at 20 t/ha and an increase in yield.	-
Barley	10 t/ha/yr	Plant growth improvement, increase in DM and yield	-
Sunflower	0, 80, 160 & 320 t/ha dry weight.	Increase in average dry weight.	Zn, Cu, Pb & Ni decreased with increase in biosolids doses for acidic, where as Zn & Cu increased in alkaline soil.
Pine (*P. Radiata*)	0, 300 & 600 kg N/ha	Basal area increased by 29 & 40% and stem volume increased by 30 & 41% for each treatment.	-

Although biosolids return valuable nutrients to the soil which in turn enhance vegetative growth, changes in plant species, composition and plant density may occur especially in remediation situations if continuous applications ensue. This could be a result of changes in soil properties such as pH, nutrient availability and microbial activity. Therefore as suggested by Cameron et al. (1997) land application effects should be carefully monitored to ensure that the plant-soil system is not damaged.

7.2 Associated contaminants of biosolids

7.2.1 Heavy metals

Heavy metals are present in a number of waste materials utilised for land application and as they have a long residence time in soil this gives reason for concern for their bioavailability. Biosolids are probably the most significant source of HMs (Table 7.5) with elevated metal concentrations occurring du to land application, for example 1748 mg Zn kg^{-1} dry wt soil (Alloway & Jackson, 1991). Mean HM concentrations are given in Table 7.5 for New Zealand (NZ) biosolids as surveyed from 1992 (*Contaminants and the soil environment in the Australasia-Pacific region*, 1996), and NZ limits for two classes of biosolids which are modelled on the US limits in accordance with the EPA 503 regulations (Epstein, 2003). The concentration of HMs in biosolids can therefore contribute to HM accumulation in soils (Cameron *et al.*, 1997).

As stated in treatment and characteristics, concentrations of HMs can vary depending on a number of factors such as wastewater origin, treatment and the treatment of biosolids. For example the source of wastewater where the primary source includes industrial points, the HM concentration usually increases. However, heavy metal concentrations have decreased in biosolids since the restriction of industrial discharges to wastewater systems over the past twenty years (Chaney, 1990; Epstein, 2003). Chaney (1990) also identified that the pre-treatment of biosolids significantly reduced HM concentrations in biosolids. This can be shown by comparing values from Table 5 and 1 for biosolids produced in NZ from 1991 and 2007.

Additionally the bioavailability of biosolids born HMs to soil can be further influenced, by such soil properties as OM, pH, redox potential (Table 7.11) and concentration of sesquioxides along with application rate. McBride (2004) found from the application of biosolids to agricultural land an increase in elemental concentrations of Cd, chromium (Cr), Cu, vanadium (V), and Ni in relation to alternative farms in the region with a positive correlation occurring between the application rate and loading concentrations. Singh and Agrawal (2008) also identified that excessive applications of biosolids increased bioavailability of HMs in soils but low doses e.g. 80 t/ ha dry wt/ yr did not cause significant increases in concentrations.

Table 7.5: Average New Zealand concentrations and ranges in biosolids and max. concentrations of HMs allowed in soils (mg/kg dry wt) (Alloway & Jackson, 1991; Bradley, 2008; *Contaminants and the soil environment in the Australasia-Pacific region*, 1996; Guidelines for the safe application of biosolids to land in New Zealand," 2003).

Metal	Auckland	Christchurch	Biosolids limits		Typical Range	Soil limit
			Grade A [a]	Grade B		
Silver	-	-	-	-	< 930	
Arsenic	21	11.9	20	30	3 - 30	20
Gold	-	-	-	-	0.25 - 7	
Boron	-	-	-	-	16 - 680	
Barium	-	-	-	-	9 - 1,004	
Cadmium	9.2	6.2	1	10	< 1 - 3,410	1
Cobalt	-	-	-	-	1 - 260	
Chromium	1209	1618	600	1500	8 - 40,600	600
Caesium	-	-	-	-	0.45 - 2.9	
Copper	571	572	100	1250	500 - 8,000	100
Mercury	1.8	5.2	1	7.5	0.1 - 55	1
Lanthanum	-	-	-	-	6.4 - 380	
Manganese	-	-	-	-	60 - 3,900	
Molybdenum	-	-	-	-	1 - 40	
Nickel	179	117	60	135	6 - 5,300	60
Lead	579	443	300	300	29 - 3,500	300
Antimony	-	-	-	-	3 - 44	
Selenium	-	-	-	-	1 - 10	
Tin	-	-	-	-	40 - 700	
Uranium	-	-	-	-	0.8 - 3.3	
Vanadium	-	-	-	-	20 - 400	
Tungsten	-	-	-	-	0.9 - 99.6	
Zinc	1826	1648	300	1500	91 - 4,900	300
Zirconium	-	-	-	-	4.8 - 319	

[a] Class A biosolids limits are for standards applicable from the 31 December 2010

They also reported that the release of HMs in soils treated with biosolids was strongly influenced by pH. Soil pH has been recognised as one of the single most influential soil properties on HM bioavailability. With HMs that typically occur as cations, Cu^{2+} and Pb^{2+} becoming highly bioavailable in acid soils, and decreasing as soil pH increases. Conversely, HMs such as arsenic, (As) and molybdenum (Mo), that usually occur as anions also bioavailably abundant in soils of high pH and less available in acid soils (Cameron *et al.*, 1997; Guidelines for the safe application of biosolids to land in New Zealand," 2003). The redox potential of soil can affect HMs in two ways. One way is the reduction (oxidisation) of HMs such as Iron (Fe), and Manganese (Mn), under waterlogged conditions solubilising and releasing any bound metals into soil solution. The other way is the capability of volatilisation occurring with metalloids such as As and Hg under reducing conditions ("Guidelines for the safe application of biosolids to land in New Zealand," 2003). The last of the soils properties possibly effecting HM availability are sesquioxides. Sesquioxides are able to sorb HMs may later be occluded by further growth into minerals such as silicate clays ("Guidelines for the safe application of biosolids to land in New Zealand," 2003; McLaren & Cameron, 1996). Although it is somewhat contentious, the concept of time decreasing contaminant HMs has strong support from laboratory experiments and is yet to be proven in the field. The increasing time in contact between soil and the added HMs can decrease the metal's subsequent ability to desorb from the soil (Gray *et al.*, 1998; McBride, 1991). This effect can be seen in Cd concentrations of soils in New Zealand (Table 7.6) where older soils that have experienced more weathering, will have a higher content of sesquioxides and therefore has a greater potential to retain HMs increasing the total concentrations in soils.

Table 7.6: Total Cd (mg/kg) in soils in New Zealand (Roberts *et al.*, 1994).

Soil group	Fertilised	Unfertilised
Recent soils	0.16	0.13
Granular Soils	0.49	0.19
Gley Soils	0.42	0.24
Organic soils	0.69	0.22
Brown soils	0.22	0.16
Allophanic soils	0.70	0.23
Pumice soils	0.75	0.31
Pallic soils	0.12	0.13
Mean of 312 fertilised sites and 86 unfertilised sites	0.44 (range 0.04-1.53)	0.20 (range 0.02-0.77)

Further factors determining the bioavailability of HMs in soils are the speciation and mobility of the individual. These factors may prove more important than total concentrations due to their effect on flora and fauna however, is currently debatable, as contradictory research has found (Alloway & Jackson, 1991). For example Krogmann et al. (1999) reported the effects of numerous trace elements (TEs) (arsenic As, Cd, mercury Hg, and Zn) having varied effects on soil and plants due to the solubility and speciation of HMs easing possible pathways increasing their bioavailability. More specifically Cabrera, et al. (1988) and Graham (1981) found a significant correlation between Cu and Cd bioavailability and the activity of free, total trace metal concentrations. However, Weggler-Beaton, et al. (2000) have demonstrated that Chlorine (Cl)-complexed Cd may also be highly bioavailable. Therefore whether complexed species or complexation enhances bioavailability remains to be determined ("Guidelines for the safe application of biosolids to land in New Zealand," 2003).

The effect of non-digested and digested biosolids on the availability of potentially toxic elements (PTE) was investigated. Lavado, et al. (2005) found no differences in Cd concentrations among soils but when plant concentrations were analysed significant increases were shown.

The concentration of metals vertically through soil profiles has failed to produce conclusive evidence through past research. With McBride, *et al.* (1997) observing substantial movement with the redistribution and translocation of certain metals out of the soil surface by physico-chemical or biological processes such as biota selectively bioaccumulating Zn and Cd.

7.2.1.1 Period to threshold

Period to threshold refers to the time period the soil has before it reaches a concentration level in either HMs or organic contaminants, where it is no longer deemed productive or possibly ‘safe’. The following calculations show how the thresholds were obtained, with Eq. 1 and Eq. 2 calculating the weight of the soil. Eq. 3 demonstrates how the maximum allowable application of biosolids to land in Canterbury was calculated, and Eq. 4 the maximum allowable concentration of Cd in soil for New Zealand. Eq. 5 shows the amount of Cd applied from biosolids per hectare per year, and Eq. 6 estimates the time period that the soil has before becoming highly contaminated by Cd.

Weight of soil:

$$\begin{aligned} volume\ of\ soil\ &= 0.01m^{a}\ \times 10{,}000\ m^{2} \\ &= 1{,}000\ m^{3} \end{aligned} \qquad Eq.\ 1$$

$$\begin{aligned} soil\ weight\ &= 1.3^{b}\ \times 1{,}000\ m^{3} \\ &= 1{,}300\ tons\ ha^{-1} \end{aligned} \qquad Eq.\ 2$$

[a] mixing depth of 10 cm

[b] assumed bulk density of 1.3

Maximum allowable application of biosolids:

$$application\ rate\ = \frac{0.2\ tN\ ha^{-1}yr^{-1}}{0.06^{c}} \qquad Eq.\ 3$$

$$= 3.33\ t\ ha^{-1}yr^{-1}$$

[c] kg N/kg biosolids (Bradley, 2008)

Maximum allowable concentration of Cd in soil:

$$\max.concentration\ = \frac{[1\ g\ t^{-1}soil^{d}\ \times 1300\ t\ soil]}{1000} \qquad Eq.\ 4$$

$$= 1.3\ kg\ Cd\ ha^{-1}$$

[d] MPC of Cd is 1g/t soil (Bradley, 2008)

Time taken to reach threshold:

$$Cd\ applied\ from\ biosolids\ = \frac{[1\ g\ t^{-1}biosolids^{e}\ \times 3.33\ t\ ha^{-1}yr^{-1}]}{1000} \qquad Eq.\ 5$$

$$= < 0.003\ kg\ Cd\ ha^{-1}yr^{-1}\ applied$$

[e] MPC of Cd is 1g/t biosolids ("Guidelines for the safe application of biosolids to land in New Zealand," 2003)

$$Period\ to\ threshold\ = \frac{1.3\ kg\ Cd\ ha^{-1}}{0.003\ kg\ Cd\ ha^{-1}yr^{-1}} \qquad Eq.\ 6$$

$$= 390.39\ years$$

The time taken to reach the threshold for other HMs was calculated, with Cu, taking 191 years for biosolids, Cd 391 and 43, Hg 391 and 110, and Pb 391 and 3286 for biosolids and fertiliser respectively and are in Figure 7.2.

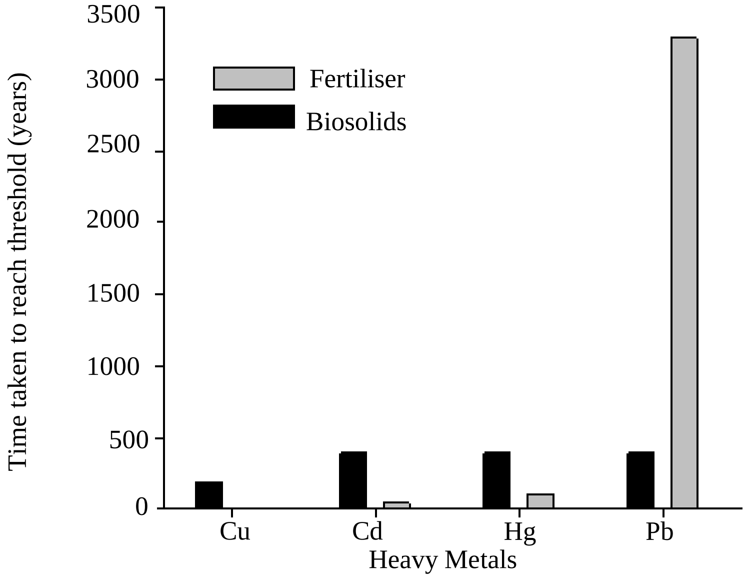


Figure 7.2: Time taken for biosolids and supersulphate fertiliser applications to reach the threshold of the soil (Bradley, 2008; *How much Cadmium is in superphosphate?*, 2007).

7.2.2 Organic contaminants

Organic compounds are chemicals which structures contain carbon (C), and in this case refer to organic contaminants of both synthetic and natural forms that typically have an anthropogenic origin. Organic contaminants may include but are not limited to pesticides (e.g. atrazine) and herbicides, pharmaceutical and personal care products (PPCPs), drugs, surfactants and polychlorinated biphenyls (PCBs) (Table 7.7) (Krogmann *et al.*, 1999; Xia *et al.*, 2010). All of the previously stated organic compounds have the potential to materialise in biosolids. Organics classified as a contaminant were emphasised by Cameron et al. (1997), as having a detrimental effect on plants, grazing animals, humans, soil quality and water from such processes as leaching, runoff, volatilisation, desorption and adsorption. They also identified the extent of contamination was a function of numerous management practices, with bioaccumulation noted as a limited risk.

Cameron et al. (1997) stated that volatilisation; degradation and sorption would dissipate and absorb chemicals in the soil with the significance of each process being a function of the contaminants physico-chemical, biosolids and soil properties and environmental conditions.

Specific treatments such as composting and anaerobic and aerobic digestion of biosolids were identified by Dϋring and Gäth (2002), as degrading organic contaminants during processing, although improvements are still required during processing. The effect of organic compounds on the soil were discussed by Krogmann et al. (1999) with their fate in respect to sorption being dependant on soil pH and OM content. They also found noted that biosolids also degraded organic compounds fumigants and herbicides such as 1,3-dichloropropane. Xia, et al. (2010) also observed from a 30 yr trial varying results of organic compounds breaking down in soil, with polybrominated diphenyl ethers (PBDEs) slowly degrading and triclocarbon (TCC), triclosan (TCS) and 4-nonylphenol (4-NP) rapidly transforming. Volatilisation of organic contaminants was also identified as a process of degradation for instance As, under anaerobic conditions and with the aid of bacteria and fungi has the ability to transform into volatile forms predominately dimethlyarsine and trimethylarsine gases (Cameron *et al.*, 1997; Krogmann *et al.*, 1999; Tamaki & Frankenberger, 1992).

Table 7.7: Typical concentrations (mg/kg) of selected organics found in biosolids (Cameron *et al.*, 1997).

Compound	Concentration	Compound	Concentration
Pesticides		PCB	<1
Aldrin	0.08	Halogenated aliphatics	
Dieldrin	0.1	Chloroform	1.0
DDT/DDE/DDD	0.3	Carbon tetrachloride	0.1
2,4-D	5.0	Tetrachloroethylene	0.4
Heptachlor	0.7	Trichloroethylene	1.0
Lindane	0.1	Vinyl chloride	6.0
Malathion	0.05		
Monocyclic aromatics		PCDD & PCDF	<0.01
Benzene	0.3	Phenols	
Toluene	0.03	Chlorophenol	3.0
Xylene	0.03	Pentachlorophenol	5.0
Ethylbenzene	6.0	Phenol	5.0
PAH		Phthalate esters	
Pyrene	5.0	Diethylexlphthalate	10^2
Fluoranthene	9.0	Surfactants	
Benzo-[a]-pyrene	3.0	LAS	10^4
Benzo-[b]-pyrene	8.0	Nonylphenol	10^3

Certain organic compounds (PCPPs) have been noted to translocate through the soil profile indicating leaching, leading to contamination of groundwater resources. The process of leaching has been attributed to biosolids-derived OM adsorbing organic contaminants that later break away from the solid soil surface and into soil solution (Krogmann *et al.*, 1999). Xia, et al. (2010) reported that although leaching of organic contaminants did occur it was generally limited with elevated levels being significantly constrained to the soil surface.

Also noted was that there were no current regulations on limits of anthropogenic organic compounds for land applied biosolids (Xia *et al.*, 2010). However, with the reassessment of the USEPA 503 certain PCBs and other organics may require restrictions due to new scientific findings, which will consequently lead to other governing bodies to change their regulations (Clapp *et al.*, 1994).

7.2.3 Pathogens

Wastewater often contains a wide variety of pathogenic organisms due to urban sewage inputs. Therefore pathogenic organisms such as bacteria, viruses, protozoa, helminths and fungi (Table 7.8) can end up in biosolids, and if treated or managed incorrectly, humans may become infected leading to illness (e.g. tuberculosis or gastroenteritis) and in some circumstance fatalities (Epstein, 2003).

Table 7.8: Principal pathogens of concern in wastewater and biosolids (Gerba & Smith, 2005).

Bacteria	Viruses	Protozoa	Helminth worms
Salmonella spp.	Poliovirus	*Cryptosporidium*	*Ascaris lumbricoides*
Shigella spp.	Coxsackievirus	*Entamoeba histolytica*	*Ascaris suum*
Yersinia spp.	Echovirus	*Giardia lamblia*	*Trichuris trichiura*
Vibrio cholera	Hepatitis A & E virus	*Balatidium coli*	*Toxocara canis*
Campylobacter jejuni	Rotavirus	*Toxoplasma gondi*	*Taenia sasginata*
Escherichia coli	Human caliciviuses		*Taenia solium*
Mycobacterium tuberc.	Reovirus		*Necator americanus*
	TT hepatitis		*Hymenolepis nana*
	Astroviruses		
	Adenoviruses		

The treatment of biosolids can diminish the populations of pathogenic micro-organisms. Cameron et.al (1997) stated a decrease in faecal coliforms from 600,000/100ml to 8,000/100ml due to the implementation of disinfection treatments. Clapp et al. (1994) observed reductions in pathogenic numbers by ≥90% after primary treatment; with reductions in viruses of up to ≈50%

and slightly greater after secondary treatment (Clapp *et al.*, 1994). Regulations have been set to minimise health risks with biosolids classes standards based on the number of pathogenic and indicator organisms (Table 7.9) after treatment (Cameron *et al.*, 1997)

Table 7.9: Maximum standards for populations of pathogens in biosolids (Bradley, 2008).

Pathogen	Standard limits
E. coli	< 100[a] / g
Campylobacter	< 1 / 25g
Salmonella	< 1 / 25g
Enteric viruses	< 1[b] / 4g
Helminth ova	< 1 / 4g

[a] Most probable number.

[b] Plaque forming unit.

Specific treatment processes are saturating biosolids for an extended period (at least 4 months) in a facultative lagoon system, air-drying for an extended period, composting - with the solids reaching and holding a specific temperature (40ºC) over a period of time (5 days). Other processes may also include treatment in or without the absence of air for a period of time (60 days) at a mean temperature (15 and 20ºC, respectively), or a sufficient amount of lime may be added to the biosolids to raise the pH to 12 for at least 2 hrs of contact (Gerba & Smith, 2005).

The soil environment is the last factor inhibiting pathogen survival. Epstein (2003)discussed survivability of pathogens, and concluded survival was low for viruses, bacteria and fungi, and since parasites such as helminths are larger and heavier, the risk of them readily moving through soil is limited, therefore the potential for groundwater contamination is reduced. However from a more recent study, Horswell et al. (2010) observed pathogen mobility down to 20 cm in depth, which they stated highlighted the importance of treatment requirements. Additionally numerous studies have identified varying durations in survivability between pathogens (Table 7.10), which can be decreased with the implication of good management practices (Clapp *et al.*, 1994; Horswell *et al.*, 2010). For instance infection through plants is low even with the practice of spraying biosolids onto crops as survival periods in direct sunlight and ultraviolet are very short max. 28 days compared to max. 120 days in the soil for *Salmonella typhimurium* (Epstein, 2003). However, the practice spraying biosolids on to land can also result in elevated pathogen populations in runoff (Clapp *et al.*, 1994).

Furthermore, to keep up to date with potential risks from pathogens, ongoing research is going to have to occur, because over the last decade at least one new pathogen has been identified each year (Gerba & Smith, 2005).

Table 7.10: Survival time of pathogens in soil and on plants (Gerba & Smith, 2005).

	Soil		**Plants**	
Pathogen	**Absolute Max.**	**Common Max.**	**Absolute Max.**	**Common Max.**
Bacteria	1 yr	2 mths	6 mths	1 mth
Viruses	6 mths	3 mths	2mths	1 mth
Protozoa	10 days	2 days	5 days	2 days
Helminths	7 yrs	2 yrs	5 mths	1 mth

7.3 Biosolids affect on soil function

7.4.2 Bulk Soil Properties

Dϋring and Gäth (2002) reviewed the generation and environmentally sound strategies for soil applications of biosolids and concluded that the control of biosolids quality was not only suggested but the application rate of biosolids should be adapted to best fit soil properties as in soil pH. Soil properties were also noted as filtering additional nutrients whether essential or non-essential, protecting waterways from possible pollution.

7.4.3 Physical properties

7.3.2.1 Organic carbon

Soil organic carbon (C) levels are typically used to determine the OM content. Although types of OM and content in soils, is mainly due to variations in factors such as climate, soil acidity, drainage conditions, carbon inputs and anthropogenic interactions (McLaren & Cameron, 1996). However it is predominantly the soil microbial population that dictates the OM content of soils as they have a large capacity to degrade the added OM from biosolids. Cameron et al. (1997)

stated that the rate of degradation was dependant on the source of the biosolids, biosolids treatment, method and rate of application as well as the initial factors expressed previously.

Industrial point sources of biosolids may result in a higher pH which naturally leads to organic C being dissolved with soil physical problems such as poorly decomposed OM accumulating (McLaren & Cameron, 1996). If best management practices (BMPs) are exercised then such issues as excessive volatilisation of ammonia (NH_3) will not occur from unnecessary rates of application (Siddarramappa *et al.*, 1994). However, when BMPs are employed, organic carbon levels typically increase. Adani and Tambone (Adani & Tambone, 2005) reported the effects of 10 years of biosolids application to agricultural land (1t DM/ha/yr) and the affect it had on soil organic properties. Chemical parameters such as total organic C, humified and non-humified fractions were determined, with the conclusion that biosolids humic acid (HA) content on treated soil at a low rate of biosolids application will significantly increase the aliphatic and HA fractions. Albiach, Canet, Pomares, and Ingelmo (2001) used two different rates of biosolids application and also found OM and associated humified substances and HAs in the treated soils significantly increased from 0.134 to 0.263 %C for HAs.

Lastly the climate (temperature and moisture) and soil drainage conditions influence the rate of microbial decomposition of OM as they are generally retarded by low and very wet (anaerobic) conditions. Therefore, organic C levels are increased from decomposing factors, not simply as a result of biosolids having a high content of OM (Cameron *et al.*, 1997).

7.3.2.2 Texture

Typically the soil texture refers to the solid inorganic constituents known as the fine earth fraction but may also include larger inorganic particles such as humified OM which is usually used to recognise and qualifying textural terms (McLaren & Cameron, 1996). Therefore due to the pre-treatment (settlement of wastewater) of biosolids minimal fine earth fractions are added to the soil to alter its texture. Therefore, overall soil texture does not.

In addition, bacteria as stated earlier are limited in terms of the degree they can be leached, in relation to viruses. With the influence of physico-chemical properties such as soil texture, the soil can have a significant effect on the soils leaching potential. Therefore pathogens have the greatest potential to leach under saturated flow through soils that have a higher percentage of macropores (Clapp *et al.*, 1994).

7.3.2.3 Structure

Soil structure refers to the degree of development of the aggregation of the primary soil particles into formed structural units i.e. peds (McLaren & Cameron, 1996). Therefore soil structure as measured by soil aggregates and aggregate stability was found to be enhanced after biosolids were applied, with the effects remaining constant for up to a year after amendments were made. Sort and Alcaniz (1999) explained this change further by stating OM as the source of the transformation. As OM bound the macro-aggregates and was found to degrade faster than the OM located in micro-aggregates.

The effect of biosolids on structure was discussed by Cameron et al (1997), as a function of soil texture, with potential chemical constituents (hydroxide solutions), that maybe present in some biosolids as having concomitant adverse effects such as increasing pH and decreasing inter-particle bonds. However in general soil aggregate stability was reported to increase by 40% with the addition of biosolids.

7.3.2.4 Soil Water

Soil water content and soils ability to hold water (water holding capacity – WHC) can be increased with the input of OM in the applied biosolids and from improved soil physical conditions. Organic matter assists in the development and maintenance of good soil structure, and a soil with a high OM content has a greater available water capacity than a soil with a low OM content (McLaren & Cameron, 1996).

The effect of biosolids on soil WHC is however inconclusive with conflicting results from various research. Cameron *et al.* (1997) stated that biosolids increased the macroporosity of a sandy loam from 11 to 19% and the saturated hydraulic conductivity (K_{sat}) from 39 to 57 mm

hr^{-1}. Although Reneau, *et al.* (1989) reported reductions in infiltration rate impeded by the dissolution of OM.

7.3.2.5 Bulk density

There have been very few reports on the effects of land applications of biosolids on bulk density; however general conclusions can be established. Moolenaar, Lexmond and vander Zee (1997) suggested the ‘balance approach’ be taken for persistent contaminants and soil amendments on composition which in turn determines soil bulk density. The main constituent effecting soil bulk density from biosolids amendments is OM as this will lower the ratio between soil mass and soil volume. Persistent contaminants that may result in effecting soil bulk density are hydroxides, causing pH to significantly change, and consequently the dissolution of OM potentially causing bulk density to increase.

7.4.4 Chemical properties

7.3.3.1 Hydrogen ion concentration (pH)

Soil pH can either be increased or decreased depending on the type of biosolids applied, or conversely soil pH can affect biosolids chemicals and compounds availability in the soil environment.

Table 7.11: Relative mobility of trace metals as a function of soil redox potential (Eh) and pH (Ross, 1994a).

	Soil condition			
Relative mobility	**Oxidising**	**Acid**	**Neutral-alkaline**	**Reducing**
Very high	-	-	-	-
High	Zn	Zn Cu, Co, Ni, Hg, Ag, Au	-	-
Medium	Cu, Co, Ni, Hg, Ag, Au Cd	Cd	Cd	-
Low	Pb	Pb	Pb	-
Very low to immobile	Fe, Mn, Al, Sn, Pt, Cr, Zr	Al, Sn, Pt, Cr	Al, Sn, Cr	
	-	-	Zn, Cu, Co, Ni, Hg, Ag, Au	Zn, Cu, Co, Ni, Hg, Ag, Au, Cd, Pb

Biosolids treatment at wastewater plants usually changes their pH, for instance lime can be added to biosolids during the dewatering process increasing pH, with some biosolids having enough of a lime contribution to provide cost savings for farmers (Chaney, 1990). Krogmann et al. (1999) reviewed a specific type of anaerobic digection of biosolids treatment identifying a reduction in methanogenic activity by 10%, affecting more ammonia (NH_4^+) rather than NH_3. This signifies that through biosolids treatment, pH maybe altered due to a decrease in available H^+ ions.

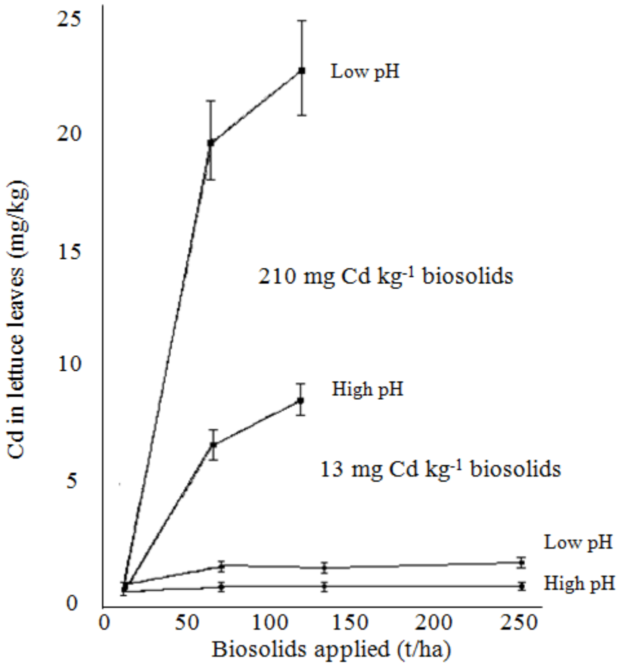


Figure 7.3: Response of a plant, lettuce (*Lactuca sativa*) to Cd applied in two biosolids adapted from Chaney (1990).

The addition of industrial sourced wastes in biosolids was also has the potential to increasing sodium and other salt concentrations causing an increase in soil pH values (Cameron *et al.*, 1997) In addition, Cameron et al. (1997) also stated that the use of coal combustion by-products which are highly alkaline can be used as a substitute for mineral lime fertiliser and applied to land in conjunction with acidified biosolids to neutralise the high acidifying effect this particular type of biosolids has on soil acidity.

Long-term bioavailability and mobility of biosolids constituents were considered in agricultural systems. Alloway and Jackson (1991) recognised heavy metal availability to crops was influenced by a wide range of soil variables (Table 7.11), of which pH is the most important. In particular Chaney (1990) reported that phytotoxicity occurred as a result of applications from biosolids, due to high a presence of metals (salts), that were applied to strongly acidic soils (Figure 7.3). However, the levels in the plants were not high enough to be toxic to grazing animals and the plants died before they could be consumed therefore the food chain was protected (Chaney, 1990).

McBride (2004) observed the effect of pH as significantly altering the plant availability of Mo; therefore concluded the type of pre-treatment processing the biosolids experienced can change the pH value of the soil. This also raised issues with the effect of additional Mo inputs from biosolids when applied to acidic soils concurring with findings from Chaney (1990).

7.3.3.2 Cation Exchange Capacity (CEC)

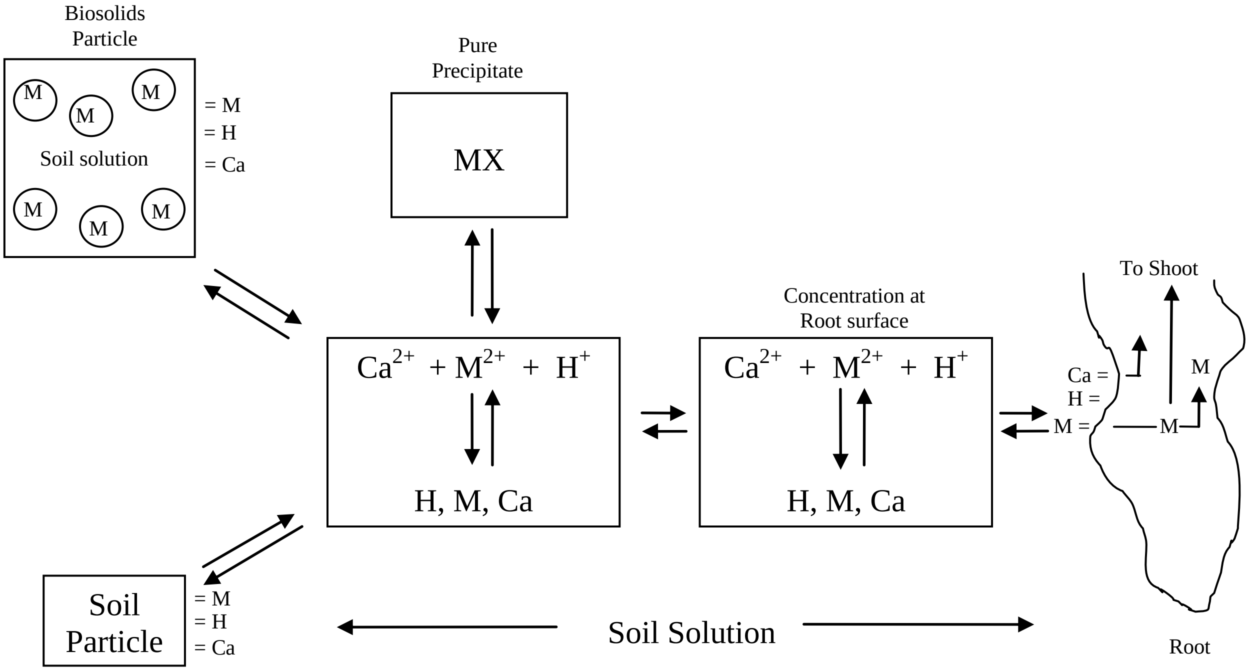


Figure 7.4: Metal reactions in a biosolids-soil-water-plant system. M represents a metal ion, H a hydrogen ion and X a substance that combines with M to form a precipitate (Fujii *et al.*, 1983).

The concomitant effect of increased OM in the soil was said to result in an increase in soil CEC from 17.2 cmol_c/kg to 23.7 cmol_c/kg from the application of 5 t/ha over 7 years according to Stadelmann and Furrer (1985). Along with the previous findings the increase in other exchangeable cations base saturation (BS) may also be improved from the application of biosolids with commercial and industrial sources (Cameron *et al.*, 1997). The application of biosolids simultaneously increases the adsorptive capacity of HM concentrations due to the biosolids matrix (Figure 7.4) (Alloway & Jackson, 1991).

7.4.5 Soil Microbes

The addition of biosolids to soil stimulates microbial activity by increasing nutrient pools and carbon substrates. The extent and effect to which biosolids achieve this is not completely understood but several trials have investigated certain aspects. Singh and Agrawal (2008) found biosolids amendments caused enhancements in enzyme and microbial activities which increased over a 2-3 week period before reaching an optimum level, and was discovered to have a high correlation with C:N ratios. This was in agreement with Haynes et al. (2009) who concluded that the constituents of biosolids would ultimately only have a positive effect on soil microbial activity.

However, the outcome from Cameron et al (1997) discussion was that although the effect was only positive, native populations were said to alter. Concurring with this find was Yeates (1995) who also established that populations of biota under a forest plantation increased for example 1,274,000 to 2,066,000 bacteria feeders/m^{-2} for a specific taxa, while other populations, typically native, decreased.

In contrast Albiach, et al.(2001) found no significant increase in microbial biomass under two different types of biosolids applications. They also measured a high variability in soil microbial activity. Krogmann et al. (1999) conclusions of microbial activity and popultions coincided with this, where the activity of rhizobia (*Rhizobium legumniosarum*) on white clover (*Triflium repens*) was found to be delayed when high concentrations of Zn and Cd were present. Whereas McBride et al. (1997) stated worms as selectively accumulating Cd and Zn over Pb, Cu and Cr. Bacteria was also identified as bio-concentrating HM causing possible mobilisation of other

HMs and bioavailable elements. However, concentrations of metals vertically through soil profiles failed to produce substantial movement from the redistribution and translocation out of the soil surface by biological processes.

7.4 Effect of existing soil constituents on biosolids additions

7.4.1 Organic matter

7.4.1.1 Heavy metals

The potential for a chemical or compound to leach is dependent on the mobility and persistence of the chemical in unsaturated soil. Sorption of the compound by the soil solid phase, specifically OM, reduces the velocity of chemical transport. Organic matter in biosolids therefore may reduce leaching through sorption. Other biosolids constituents such as surfactants and solvents may however, increase mobility by increasing the apparent solubility of hydrophobic compounds. Biosolids have consequently been identified as potential soil conditioners in soil at sites of disturbance for example mine spoils. Biosolids could be used at contaminated soil sites to bind toxic constituents to the soil limiting mobility of these toxins (Chaney, 1990). Brown and Chaney (2003) examined the effects of various biosolids on Pb contaminated soils with a minimum reduction of 6% and a maximum reduction of 37% in Pb concentrations occurring from a control site. Cameron et al. (1997) review concurred with the fact that soil OM adsorbed HMs therefore binding them to the soil as long as other biosolids elements for instance organic salts raising pH did not interfere with this process.

Ashworth and Alloway (2004) found that Zn was released from biosolids to be adsorbed by inorganic soil colloids within soil columns, indicating that biosolids dissolved OM did little to maintain Zn in the soil solution phase. On the contrary, surface applications of biosolids were established as reducing $Ca(NO_3)^2$ extractable Zn in the subsoil from approximately 50 mg kg^{-1}in the control to less than 4 mg kg^{-1} in a treated site (Brown *et al.*, 2003). Therefore the initial trial potentially had a higher concentration of $Ca(NO_3)^2$ extractable Zn causing an increase in easily available Zn. However Ashworth and Alloway (2004) also found dissolved OM as being highly soluble from the point source of biosolids for instance 6.6 mg and 15.4 mg of dissolved organic C for control and treated soil columns respectively. Leaching of Ni from soil columns was also observed and was put down to the propensity of Ni to form complexes with the biosolids-derived OM.

Complexing agent-extracted metals were stated as declining with time as a result of OM applied with biosolids fixing metals over time. High soil pH reduced HM leaching due to the interaction of the metals with OM (Düring & Gäth, 2002). Düring & Gäth (2002) also noted that HMs could be released from OM complexes through the process of OM mineralisation. Cadmium and F were stated as having similar qualities to phosphorus (P) in terms of their immobility within the soil but having high susceptibility to losses from runoff (Loganathan *et al.*, 2003; Ojeda *et al.*, 2003).

McBride, Richards, Steenhuis and Speirs (1999) found a number of HMs with the potential to percolate vertically through soil for example Hg, as facilitated by higher dissolved OM in the leachate, which caused an increase in Hg concentrations in the groundwater. As a result from this research OM was identified as decreasing with depth in the soil profile therefore the ability of the soil to retain mobilised HMs increases, hence the low concentrations in the subsoil. Kalbitz and Wennrich (1998) also found that concentrations of Hg, Cr, Cu and As in soil leachate was positively correlated to DOM, however, it was stated that the importance of metal mobilisation in soil is dependent on pH with low pH (<4.5) soils having less of an effect.

7.4.1.2 Organic contaminants

The intervention from the increase in OM from the application of biosolids increasing the sorption capacity of the soil was suggested by Cameron et al. (1997) as a way to reduce the concentration of organics in soil solution and the affect of volatilisation.

7.5 Plant contaminant uptake from biosolids

7.6.2 Uptake

7.5.1.1 Heavy metals and trace elements

Heavy metals can be divided into two groups, essential elements, (micronutrients) required for growth and development, and non-essential elements. Although micronutrients such as Zn are

required for growth, high concentrations can become toxic. Therefore the critical issue of HMs being plant available is whether adsorbed metals can subsequently become desorbed from solid soil or biosolids surfaces such as clay particles and OM colloids or chelate complexes (McLaren & Cameron, 1996; Ross, 1994a).
leaves (Chaney, 1990).

Table 7.12: Relative sensitivity of crops to biosolids applied TE (Epstein, 2003).

Very Tolerant	Tolerant	Sensitive	Very Sensitive
Corn	Oat	Perennial ryegrass	Alfalfa
Red fescue	Tall fescue	Timothy	White & Sweet clover
Smooth bromgrass	Flat pea	Alfalfa	Alsike & Lidino clover
Sudan grass	Redtop	Zigzag, Red Kura & crimson clover	Crown vetch
	Kentucky bluegrass	Hairy vetch	Weeping & Lehman love grass
	Buffalo grass	Soybean	Chard
	Switchgrass	Colonial & Creeping bent grass	Turnip
		Kale	
		Blue lupine	

Some regions have been recognised as being deficient in micronutrients and were identified as potential benefactors of land applied biosolids (Cameron *et al.*, 1997) for example the central North Island of New Zealand is highly deficient in cobalt (Co). Alloway and Jackson (1991) considered the consequences of biosolids applied in agricultural, horticultural and forestry systems with regards to HMs long-term bioavailability and mobility in soil profiles. They showed various HMs (Zn, Cd, Cu, Mn, Ni, Mo and Pb) having a greater tendency to move from soil to plant, with the elements accumulated being dependant on the plant. This was consistent with Chaney's (1983) 'soil-plant barrier' concept which considered the consequence of potential toxic elements (PTEs) to the food chain. The effect of plant species on trace element (TE) tolerance (Table 7.12) was outlined by Ross (1994b), with mention of legumes having a greater affinity to Mo and Cu than grasses due to legumes ability to fix N so growth is then limited by Mo availability. For instance Red clover (*Trifolium pratense*) showed a high uptake of Mo (up to 34.1 mg Mo kg^{-1}) (McBride *et al.*, 2004). The soil-plant barrier justifies why initially guidelines for applications were based on the phytotoxic effects HMs inflicted (Cameron *et al.*, 1997) as a 25 % yield reduction of most plants occurs when plants have 50 to 100 ppm in their

Singh and Agrawal (2008) found crops grown on soils amended with high rates of biosolids (≥ 320t/ha dry wt) accumulated toxic concentrations of HMs especially in leafy vegetables such as lettuce (*Lactuca sativa*) (Chaney, 1990), and consumption by humans could pose a serious health risk. The effect of non-digested and digested biosolids on the availability of PTEs was investigated by Lavado et al. (2005). They examined the concentrations of PTEs in plant tissue and found maize (*Zea mays L.*) tissue accumulated 0.50 mg Cd kg^{-1} compared to the control of 0.03 mg Cd kg^{-1}.

The increase in elemental concentration of soil, from the application of biosolids, did not result in a higher average forage crop yields. However, elemental concentrations of, sulphur (S), Zn and Mo showed significant increases in forage with the latter element being dependant on the type of biosolids pre-treatment and soil pH which in turn may cause animal health issues such as hypocuprosis (McBride, 2004). McBride et al. (2004) established that as long as soil pH was managed by lime, and the biosolids applied with using BMP at rates no greater than 135 kg Cu/ha, or 125 kg Zn/ha, no obvious long-term metal phytotoxicity will develop in crops.

7.5.1.2 Organic contaminants

As the knowledge and effects of organic contaminants are relatively novel and unclear, few reports have been presented on their effects towards plants and little understood about the effects. Cameron et al.(1997) identified that risks of plant uptake of PAHs, PCBs and chlorinated pesticides were minimal (< 0.01 dry wt) due to plant metabolic potential.

To date the most significant finding was the volatilisation of organics contaminating plant tops and roots rather than dissolving in soil water. Volatilisation of organic contaminants (herbicides, pesticides) will only occur under aerobic conditions (Cameron *et al.*, 1997; Chaney, 1990; Krogmann *et al.*, 1999). Therefore if BMPs are exercised for example direct injection of biosolids rather than surface applications, losses are greatly diminished. Cousins, et al. (1997) calculated the average cumulative loss of 2,2,5-trichlorobiphenyl as 102, 35 and 6.5 $\mu g/m^2$ for surface application (broadcast), surface incorporation (ploughed in) and subsurface injection, respectively.

7.6.3 Risk of biomagnification

The risk assessment of contaminants of biosolids has been reviewed by Chaney (1990) as transferring in the food chain with 12 fundamental pathways identified (Table 7.3) as set out by the USEPA. Although Clapp et al. (1994) stated that with appropriate pretreatment of biosolids humans, animals and plants could not experience adverse effects when >1000 Mg biosolids ha^{-1} are applied. This is because limitations on metal uptake and bioavailability, including the plateau response (Figure 7.3), prevent toxic levels being reached in plants used as food or feed.

Although plants and soil organisms have shown signs of HM accumulation Cameron et al. (1997) stated the ultimate concern with biomagnification, is human accumulation of contaminants; however, this was not identified as a major concern due to reports as stated previously. Conversely Düring and Gäth (2002) firmly stated that the application of biosolids onto pasture should be banned due to obvious contamination of plants and metal uptake by grazing animals with the possibility of contaminated food being passed onto humans, causing detrimental effects on human health.

7.6 Sustainability of biosolids

7.6.1 Environmental

The effects of HMs in the soil and the greater environment have normally been assessed to the point where poor management practices are being implemented but as can be seen in Figure 7.5 even rates of up to 150 t/ha of biosolids will result in a minimal increase in HM concentrations (Cameron *et al.*, 1997).

Alloway and Jackson (1991) considered the consequences of biosolids applied to agricultural soils in regard to long-term bioavailability and mobility of contaminants in soil profiles. Where it was concluded that, the majority of HMs were to remain in the topsoil, with marked reductions in concentration with depth, and soil, vegetation type and climate influencing this process of translocation.

From twenty years of biosolids land application research Chaney (1990) identified that the effect of biosolids organic N contribution to soils was less likely to cause groundwater pollution than chemical N fertilisers. However, as stated by Haynes et al. (2009) the sustainable application rates of biosolids should be based on such requirements as N demand of the crop and potential N mineralisation of biosolids, along with P loadings rates to reduce the impact of applications on the environment.

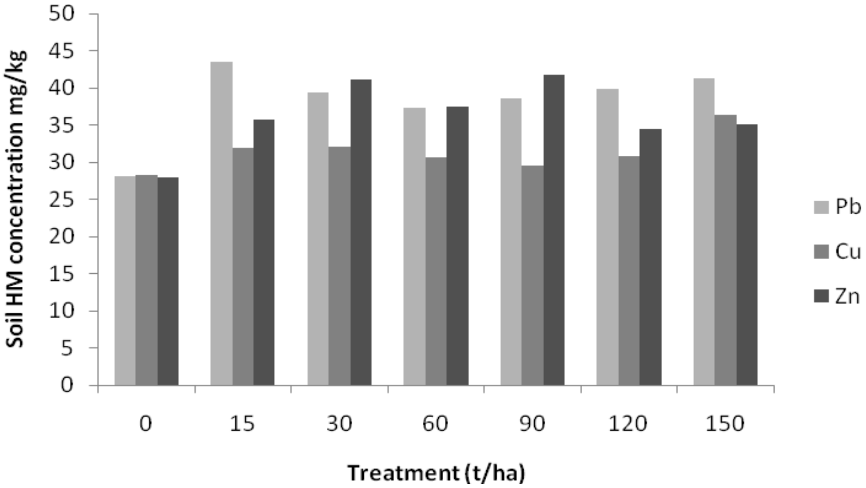


Figure 7.5: Effects of (Chinese) biosolids application on the concentration of HMs in soil mg kg^{-1} with *Poa annua* growing (Xia *et al.*, 2010).

The generation of biosolids and environmentally sound strategies for soil applications were reviewed by Düring and Gäth (2002) summarising that metal bioavailability was yet to be clarified, with organic pollutants showing a strong interaction with OM and certain organic pollutants were identified as being hard to trace in soils indicating leaching and volatilisation. The application of biosolids can therefore be a practical way of recycling organic municipal waste as long as the materials are quality controlled.

7.6.2 Ecological

As HMs have been shown to percolate through the soil with increased concentrations occurring from 1 mg Hg kg^{-1} in the control to 8 mg Hg kg^{-1} in the treated leachate from the application of biosolids, the occurrence of contamination in shallow groundwater ecosystems could exceed standards (McBride *et al.*, 1999), which could also result in significant implications to aquatic ecosystems.

7.6.3 Social & Cultural

When selecting a suitable site for applying biosolids it is important to consider social and cultural issues as well as bio-physical aspects. This is so the potential inconvenience and bother of applying biosolids on a large scale and in large quantities can be limited or properly managed. Potential adverse effects from the use of biosolids to a community may range from an unpleasant odour to exclusion of access to recreational areas following applications, or other factors such as people's reactions, based on the perception of public health risks. Therefore due to the types of issues as stated above, the involvement of the community is essential. This is so public acceptance is gained, alliances are built between such parties as researchers and farmers, regulatory decisions involve all people directly concerned and so that communication channels are improved through public meetings (Clapp *et al.*, 1994; Guidelines for the safe application of biosolids to land in New Zealand," 2003).

Cultural values may also play an influential role in the use and location of biosolids. The Maori in New Zealand for instance, favour the application of biosolids to land rather than discharging them to waterways and polluting natural water resources, as their philosophy believes it is best to return human waste to the land. In saying this other issues arise when cultural relations are taken into account which may include avoiding applications or in the locality of sacred sites (Cameron *et al.*, 1997; Guidelines for the safe application of biosolids to land in New Zealand," 2003).

Therefore once an appropriate treatment is found for the sustainable use of biosolids the main issue will be marketing, so as public acceptance is gained, which will ultimately determine the economic success of the land application or value-added processing of biosolids (Oleszkiewicz & Mavinic, 2002).

Appendix B – Literature review

7.7 Biochar

7.7.1 Treatment and Characteristics

Biochar is a form of black carbon (BC), ubiquitous in form, comprising of a range of materials from polyaromatic to elemental or graphitic carbon, this is in comparison to organic carbon, which forms covalent bonds, with other elements such as (hydrogen) H and (oxygen) O. Biochar is a term reserved for the plant biomass-derived materials contained within the BC continuum. Materials forming the BC continuum, are produced by partially combusting carbonaceous source materials, and have both natural as well as anthropogenic sources. Biochar in the environment is believed to originate largely from, the thermal alteration of various organic precursors e.g. the burning of coal or vegetation (Chun *et al.*, 2004; Warnock *et al.*, 2007)

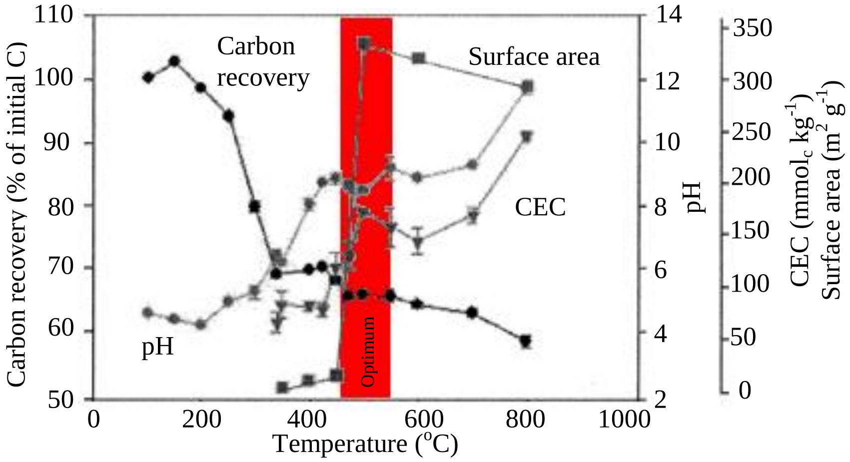


Figure7.6 : The effect of production procedure on biochar properties adpated from Lehmann (2007a).

Pyrolysis converts trees, grasses, crop residues and other biomass into biochar, with a twofold higher C content (Table 7.13) than ordinary biomass. Restricting the oxygen supply (pyrolysis), during combustion can prevent complete combustion (carbon volatilisation and ash production) of the source materials. Depending on the temperature reached during combustion, and the species identity of the source materials, char's chemical and physical properties may vary considerably. In addition, plant species with many large diameter cells in their stem tissues can lead to greater quantities of macropores in biochar particles (Chun *et al.*, 2004; Lehmann, 2007a; Warnock *et al.*, 2007).

The dominating property distinguishing biochar from other forms of OM is the organic portion which has a high C content. The C content consists mainly of aromatic compounds characterised by rings of six C atoms linked together without O or H. However, due to biochar's chemical complexity and variability, more irregular arrangements of C will form containing O and H and, in some cases minerals, depending on the feedstock (Lehmann & Joseph, 2009). Sarmah *et al.* (2010) iterated this by stating that biochar can have an amorphous structure, with aromatic C present which aid sorption of non-polar molecules.

Although manufactured carbon is activated at high temperatures (>400^{o}C), chars formed in the environment formed under partial or complete carbonisation, and depending on charring temperature, may result in biochar possessing a wide range of compositions and surface properties. Temperture during charring can have a significant effect, with high temperatures (>500^{o}C) for pyrolysis, resulting in increased surface functional group density creating a surface that is highly hydrophilic (Chun *et al.*, 2004). Within the suitable temperature range (450-550^{o}C) for producing biochar (Figure 7.6), temperature has a negligible effect on C, while differing feedstocks can change the recovery of the initial C from 39 to 64% (Lehmann *et al.*, 2006). In agreement to this Gaunt and Lehmann (2008) found that slow pyrolysis avoids creating polyaromtic hydrocarbons (PAHs). However Warnock *et al*. (2007) found that coniferous sourced biochar generated at low temps (350^{o}C) can contain larger amounts of available nutrients while having a smaller sorptive capacity for cations. In contrast Major *et al*. (2009) discovered that biochar should be produced at >500^{o}C, if immediate results are to occur from enhanced sorption consequently from increased surface area.

Another biochar feature that alters greatly, dependant on the production process and feedstock, is surface area. Lehmann *et al*. (2003), found that surface properties of biochar vary greatly depending on OM used and the charring environment such as O_2 supply. This concurred with Singh *et al*. (2010) who stated, biomass source and treatment, dictated the specific surface area (SSA). Low ash content was stated by Sarmah *et al*. (2010) as increasing higher C content, enhancing SSA by 4-5 fold and aromatic condensation which was understood as potentially increasing sorption ability of biochar.

It has been identified that smaller-sized biochar particles have a greater ability to sorb more nutrients than larger particles, suggesting possible effects of surface area. However the small particles (< 5 mm) also released proportionally more nutrients than larger particles. Major *et al*. (2009) ascertained that kinetics of sorption on outer surfaces versus internal pores explain this effect, with small particles that have greater outer surface areas released more nutrients than larger particles, as the latter retained more nutrients inside pores.

The pH of fresh biochar appeared to increase with production temperature (450-550^{o}C) before C yield started decreasing (Figure 7.6) (Lehmann, 2007b). Aitkenhead *et al*. (2009) also identified variability in biochar properties, with variation being a function of temperature influencing CEC and ash content – its liming effect (Table 7.13) – and rate of charring influencing morphology.

Table 7.13: Various feedstocks of biochar and their TOC, TN and pH properties modified from Cayuela *et al* (2010); Namgay *et al*. (2010) and Sarmah *et al*. (2010).

Product	**TOC (%)**	**TN (%)**	**pH**
Greenwaste	86.3	0.3	6.6
Poultry manure	37.0	1.2	10.3
Bluegum (*Eucalyptus saligna*)	80.20	0.12	9.50
Corncob	82.2	1.51	9.5
Pine sawdust	90.9	0.11	9.7

7.7.1.1 Activated/aged biochar

It has been established the CEC of freshly produced biochar is relatively low (Figure 7.6) with only aged biochar showing signs of high cation retention (Lehmann, 2007a). Major *et al*. (2009) concurred with this stating aged biochar has a higher CEC and that this was due to increased surface area as activated biochar has a large portion (>95%) of micropores (<2nm) (Tseng & Tseng, 2006), and that this not only leads to higher potential CEC, but also higher capillary forces, causing increases in nutrient retention. However, activated biochar has been found to possibly attract the formation of polar functional groups on biochar surfaces, to preferentially adsorb water molecules and polar adsorbates, forming water clusters on the surfaces, hindering nonpolar molecules from occupying exchange sites (Chun *et al.*, 2004), which in turn would decrease nutrient retention abilities. Activated biochar can be formed during the pyrolysis process by introducing steam towards the end of production (Singh *et al.*, 2010).

7.7.1.2 Oxidation of biochar

The significance of oxidation of biochar particles is that it leads to mineralisation, but also may create negatively-charged surfaces and surface functional groups, which could lead to greater CEC and nutrient retention (Liang *et al.*, 2006). This is supported by Lehmann (2007a), who established that biochar does not only consist of recalcitrant aromatic ring structures, but also more easily degradable oxidised C and aliphatic structures, with the aliphatic C forms being rapidly mineralised. Nguyen *et al*. (2008) also found that the molecular properties of biochar changed more rapidly on surfaces than in the interior of biochar particles and more rapidly during the initial years. The carbonyl groups increased over the first 10 to 30 years by 192%, indicating oxidation was an important process controlling biochar CEC potential, and overall quality. Additionally Lehmann *et al*. (2006), stated that the decomposition of biochar leads to biochemical changes rather than mass loss, concurring with the following section on the stability of biochar.

Biochar can be oxidised through two processes, abiotic and biotic. Abiotic processes oxides faster than biotic with higher temperatures increasing oxidation with the creation of negatively charged sites (Cheng *et al.*, 2006). Cheng *et al*. (2006) also concluded that abiotic processes were more important for the initial oxidation of fresh biochar. It has also been identified that, abiotic oxidation may have important implications for biochar stability, since further microbial decomposition may be less constrained by the recalcitrance of the PAH structures typical of biochar. Also stated was that biotic oxidation processes can lead to the oxidation of biochar surfaces forming carboxyl, lactonic, carbonyl, phenolic, ketone, pyrone and chromene or quinine C species and forms, changing the amphoteric characteristics (Chun *et al.*, 2004). Singh *et al*. (2010) also found slow oxidation of biochar leads to greater production of functional groups.

7.7.1.3 Recalcitrance of biochar

The recalcitrance of biochar in the soil environment is of particular interest, due to the long-term fate of sorbed toxic HMs and organic contaminants, as well as a potential global warming mitigation tool, through C sequestration (Chan *et al.*, 2007). Over recent years there has been some dispute, however, with the legitimacy of biochar being recalcitrant, and its effect on other C forms in the soil environment. Biochar has been identified as being recalcitrant by many in the past, with biochar being stated as more resilient than OM (Figure 7.7) to microbial decomposition. This fact was determined by the *terra preta* soils in the Amazon with its high persistence, and is the reason for the stability of the SOM in this region (Steiner *et al.*, 2007).

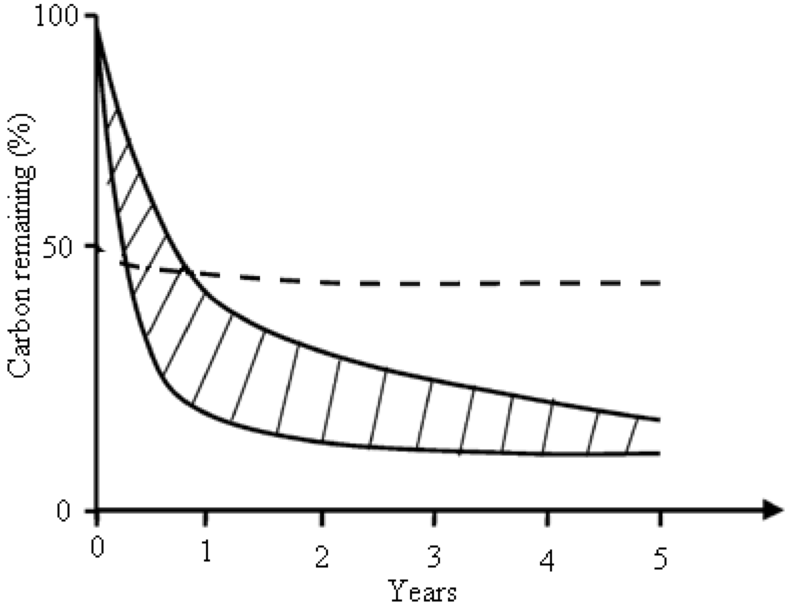


Figure 7.7: Range of biomass C remaining after decomposition of crop residues. Dashed line is decomposition of biochar and hashed area is uncharred biomass decomposition adapted from Jenkinson & Ayanaba (1977) and modified by Lehmann et al. (2006).

The recalcitrance of biochar has been related to the abundance of strong aromatic structures (Singh *et al.*, 2010), and the ability to attract soil particles and become encapsulated through aggregation (Nguyen *et al.*, 2008), decreasing degradation and increasing stability. Lehmann (2007b) established the recalcitrance of biochar was a function of biomass source, and production, such as feedstock used for pyrolysis, the production conditions, soil properties and climate. He also identified that biochar was very resilient to microbial decomposition. This is in agreement to findings by Major *et al*. (2010a) where over a 2 year period, measured a loss of 2.2% of applied biochar to respiration, and calculated a mean residence time of 600 years at 26°C mean annual temperature, or 3264 years at 10°C for biochar. However, Clough *et al*. (2010) stated that although biochar has a high stability in the soil environment, biota have an effect on its decomposition. This was supported by Wardle *et al*. (2008) who established biochar was not biologically recalcitrant, with biomass increased in soil, as a result of increased available C. But alternatively, suggested that the increase in biomass may be a result of the decomposition of native sources of C. Although microbes may have an affect on biochar decomposition, the half life of soil biochar is in excess of 1000 years (Glaser *et al.*, 2002), and from multiple bioenergy by-products that could be used as a soil amendment biochar was found to have the lowest CO_2 loses between 0.5% and 5.8% of the total C added (Cayuela *et al.*, 2010).

7.7.2 Application and Alternative Uses

Table 7.14: Typical product yields on a dry wood basis, obtained by different modes of wood pyrolysis from ("Biomass Pyrolysis," 2007)

Mode	Conditions	Bio-oil	Biochar	Gas
Fast	Moderate temperatures (500°C) for 1 second	75%	12%	13%
Intermediate	Moderate temperatures (500°C) for 10-20 seconds	50%	20%	30%
Slow (carbonisation)	Low temperature, (400°C), very long solids residence time	30%	35%	35%
Gasification	High temperature, (800°C), long vapour residency time	5%	10%	85%

The application of biochar to land is best done when treated like biosolids, therefore fully incorporated into soil; this is to reduce potential effects of runoff. Lehmann (2007a) explained that if biochar was not incorporated into soil, biochar may be prone to erosion, and may even increase net losses of adsorbed nutrients negating the benefits biochar brings to soil. Major *et al*. (2010a), carried out a mass balance for biochar applications, and found that a large flux of C (20-53% of applied Carbon) was not accounted for and was assumed to have occurred by surface runoff during intense rain events due to poor incorporation. Furthermore, in relation to the most appropriate soils for biochar additions, generally most soil types would benefit from the application. However, as the greatest amounts of leached nitrate occur on coarse-textured soil or when hydraulic conductivity (K_{sat}) and infiltration rates are high, biochar should have the greatest value of reducing nutrient leaching in sandy soils (McLaren & Cameron, 1996). Major *et al*. (2009) also noted that biochar would be most effective in reducing leaching losses in regions of high rainfall, therefore regions of the world such as the tropics that experience high annual rainfalls and weathering conditions should significantly benefit from biochar applications to land.

Cayuela *et al*. (2010) stated that in the production of biochar, the production process biomass undergoes will dictate the proportions of either bio-oil, biochar or gas created during the process of pyrolysis (Table 7.14). Winsley (2007) also noted this tradeoff between pyrolysis production of biochar, bio-oil and gas, however, stated that the process can be calibrated to maximise the output of different products, depending on economic factors. Emphasising the importance of biochar production, is that the most effective climate change mitigation strategy involving pyrolysis of biomass, is bioenergy production combined with the application of biochar to soil, which is more beneficial than producing solely bioenergy (Gaunt & Lehmann, 2008).

7.8 Benefits of biochar applications

7.8.1 Soil Physical Condition

7.8.1.1 Aggregation

Biochar effects on soil aggregation will, among others, be linked to its surface charge characteristics, with improved soil aggregation promoting water infiltration; and thus, increase the amount of water percolating through the soil, as opposed to encouraging run off (Major *et al.*, 2009).

7.8.1.2 Soil aeration/porosity

The significance of soil aeration to soil is that it enhances the soil-microbial-plant environment reducing anaerobic soil conditions, increasing microbial biomass and plant yields. In soils that have poor structure and are structureless massive in classification, the addition of biochar as a porous amendment, develops this characteristic in the soil, improving the structure and in turn aeration through aggregation which creates continuous pores through the soil profile. With the improvement of soil aeration through water adsorption a reduction in denitrification may occur.

Yanai *et al*. (2007) found that at 73% water-filled pore space (WFPS) denitrifciation was reduced, while at 83% WFPS, nitrous oxide (N_2O) fluxes were enhanced, and thought to be a result from insignificant improvement in soil aeration. A possible adverse effect of improved aeration is increased dissolved and percolate organic carbon (DOC and POC) as measured by Major *et al*. (2010a), with as greater water flux through the soil due to increased aeration. However, the porous nature of biochar is dependant on a number of factors, charring temperature, anatomical structure of the biological tissues and interactions of biochar with soil (adsorption of OM to biochar can decrease porosity by blocking pores) (Warnock *et al.*, 2007).

7.8.1.3 Surface area

Table 7.15: Proposed biochar characteristics affecting nutrient leaching, related mechanisms and degree of certainty associated with each process adapted from Major, *et al.* (2009).

Mechanism	**Impact on leaching**	**Biochar characteristic**	**Leaching impact mechanism**
Biochar's negative surface charge directly retains positively charged nutrients	Decrease for positively charged ions and domains of nutrient-containing OM	Proven	Strong evidence
Biochar increases the soil's WHC	Decrease (extent will vary with soil texture)	Strong evidence	Not proven
Biochar leads to increased soil aggregation	Increase or decrease	Not proven	Not proven
Biochar increases microbial biomass and nutrient cycling	Increase or decrease	Proven	Strong evidence
Sorbed nutrients are preferentially transported by biochar particles	Increase	Not proven	Not proven
Fresh biochar sorbs nutrients in hydrophobic OM	Decrease	Strong evidence	Not proven

Surface area is one of the most beneficial properties biochar adds to soil (Laird *et al.*, 2010b), as increased surface area leads to potential increases in adsorbed nutrients. Lehmann (2007a) explained that a high surface area allows for a greater negative surface charge and greater charge density, and this high surface area provides the ability to sorb both hydrophobic, and hydrophilic molecules, depending on the available functional groups on the surface of the biochar (Major *et al.*, 2009) (7.15). Although organic hydrophobic nutrients (e.g. N, P and S) can be sorbed onto biochar particles, which may reduce surface area by steric hindrance, and block further adsorption of both organic and inorganic nutrients to biochar particles (Major *et al.*, 2009). Surface area has been found to increase with fresh biochar (Lehmann, 2007a), and appeared to be a function of production temperature (Chun *et al.*, 2004). Additionally, increased surface area has also been found to result in greater water holding capacity (WHC) (Major *et al.*, 2009).

7.8.2 Macro & Micronutrients

7.8.2.1 Increases

Biochar has been shown to be both a source of nutrient, and an excellent site of sorption. To start with biochar contains the majority of the plants nutrients when the biomass was harvested, and has the capacity to slowly release the nutrients to growing plants when decomposed (Laird, 2008). Therefore in relation to biochar being a direct source of nutrient, Chan *et al*. (2007) found an increase in P and K (exchangeable cations) at a biochar application rate >50t/ha, with the biochar used in this experiment being high in both of these nutrients. Warnock *et al*. (2007) also stated biochar itself contains small amounts of nutrients that are available to soil biota and plants. It has also been observed that biological N fixation (BNF) can be enhanced (by 49%, 78% and 30% with 39, 78, and 117 t ha $^{-1}$) by biochar amendments, and was thought to be in response to a combination of factors related to nutrient availability (increased P, K, Mg, Ca, Mo, B with the latter two contributing the most and decreased N from immobilisation) in soil, and stimulation of plant-microbe interactions. Rondon *et al*. (2007) proved Mo fertilisation to be the most effective way of increasing BNF, as its a constituent of the Mo-Fe protein of nitrogenise. Furthermore as Mo increased in non-N fixing plants, with biochar additions, this indicated this affect. Rondon *et al*. (2007) also explained that the differences in micronutrient availability may be the result of the well-known variations in base cation concentrations between biochar feedstocks. This rationalised the observed available K increase in soil by 132% with 39 t ha^{-1} from the control in their trial. Conversely, Steiner *et al*. (2007) found biochar alone could not be used as a fertiliser due to its recalcitrant nature and low nutrient content, but in combination with fertilisers can potentially increase nutrients and nutrient use efficiency.

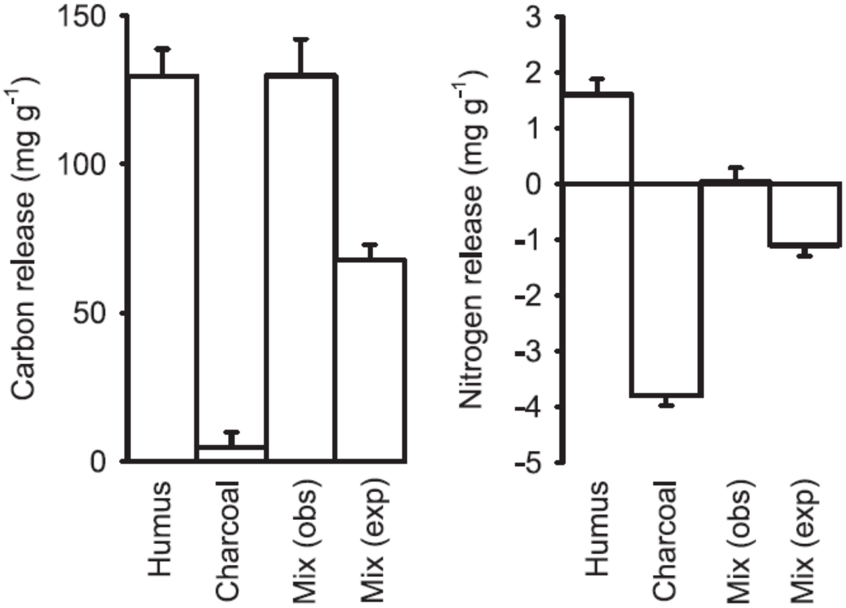


Figure 7.8: Loss of C and N from litter bags (per unit initial mass) over 10 years – with negative values in N release reflecting N gain through immobilisation from Wardle *et al*. (2008)

The mechanism of biochar being a site of sorption, potentially enhancing nutrient efficiency has been identified by numerous studies, with Laird *et al*. (2010b) finding total N increased by 7% and increases in extractable fractions of P, K, Mg and Ca occurring. These and other nutrients such as Cu, Si and Zn have been thought to increase in soils with biochar additions, as leachate concentrations have decreased and plant uptake increased, therefore the ratio of nutrient uptake to leached nutrient increased indicating improved efficiency (Lehmann *et al.*, 2003; Major *et al.*, 2010b; Steiner *et al.*, 2007). Further findings have supported this mechanism, with 70 % of P applied in a trial remaining plant available, as the P was assumed to have precipitated, along with Ca on the alkaline biochar matrix (Major *et al.*, 2009), this was thought to be abnormal as some fractions of P were adsorb as phosphate (PO_4) even though its an anion (Lehmann, 2007a). Laird *et al*. (2010a) measured a decrease in total dissolved N and P (TDN and TDP) by 11 and 69% respectively, with an application of ~43 t/ha. Chan *et al*. (2007) observed increases in N fertiliser use efficiency of plants with an increase in yield by 266% from radishes (*Raphanus satvius*) receiving an application of 100 t ha^{-1} of greenwaste biochar due to an increase in retained N forms as in Figure 7.8 & 7.9 (Major *et al.*, 2009). Lehmann *et al*. (2003) also noted that this mechanism is still not clearly understood, and that another theory has been presented. The other possible mechanism for nutrient retention was through soil water containing nutrients. However, Lehmann *et al*. (2003) found that water percolation was not decreased by biochar applications, therefore increased retention was caused by adsorption to an exchange complex, with such nutrients as Ca, more than doubling in availability on exchange sites.

Biochar has also been found to immobilise N, enhancing the soil environment for greater responses in legume growth. Rondon *et al*. (2007) demonstrated this, by enhancing N_2 fixation of soybean (*Glycine max* L., Merr.) crops, when biochar was applied to highly weathered and acidic soils, at rates of 39-117 t ha^{-1}, and was thought to be the result of biochar as a liming treatment, or soil conditioner. However, mineralisation of N was stated as increasing due to adsorption, and resultant inactivation of secondary plant compounds, which would normally decrease microbial activity (Lehmann, 2007a). Clough *et al*. (2010) found that the inorganic N pool increased in their trial (Figure 7.9), but did not decrease the inorganic N pool for N_2O production.

Furthermore biochar has been found to increase As in pore water, by more than 3 fold in a lysimeter trial (Beesley & Dickinson, 2010). The occurrence of HM availability increasing in soils concurred with findings from Namgay *et al*. (2010), who measured increases in extractable As and Zn but decreases in extractable Pb, and that biochar had no influence on Cu, and inconsistent effects on Cd in soil. They also found that preferential sorption occurred in the sequence of Pb>Cu>Cd>Zn>As once biochar was applied to soil (Namgay *et al.*, 2010).

7.8.2.2 Immobilisation/losses

Chan *et al*. (2007) identified from an increase in pH, exchangeable Al was reduced, which was supported in findings by Rondon *et al*. (2007) and Steiner *et al*. (2007) with decreased Al saturation with the addition of both mineral fertiliser and biochar, compared to mineral fertiliser alone for the latter. Likewise the addition of both biochar and greenwaste, was found to diminish water soluble Cd and Zn in contaminated soil by 76 and 44% respectively, significantly reducing their phytotoxic effect (Beesley *et al.*, 2010). Namgay *et al*. (2010) also examined the effect biochar has on HMs in soil with an outcome of decreased concentrations of AS, Cd and Cu in maize shoots.

Additionally, it has been established that biochar can stimulate net nitrification rates, which is likely a result of biochar mediating and adsorbing inhibitory phenols; however this is thought to be specific to soils with ectomycorrhizal fungi (ECM) trees and or ericaceous fungi (ERM) shrubs with an abundance of phenolic compounds that interfere with nitrifictaion (DeLuca *et al.*, 2006). Further N reductions in plant uptake were significantly impeded at high biochar application rates (equivalent to >122 t ha^{-1}) leading to lower productivity which was thought to be a result of such a high C/N ratio (Lehmann *et al.*, 2003; Rondon *et al.*, 2007).

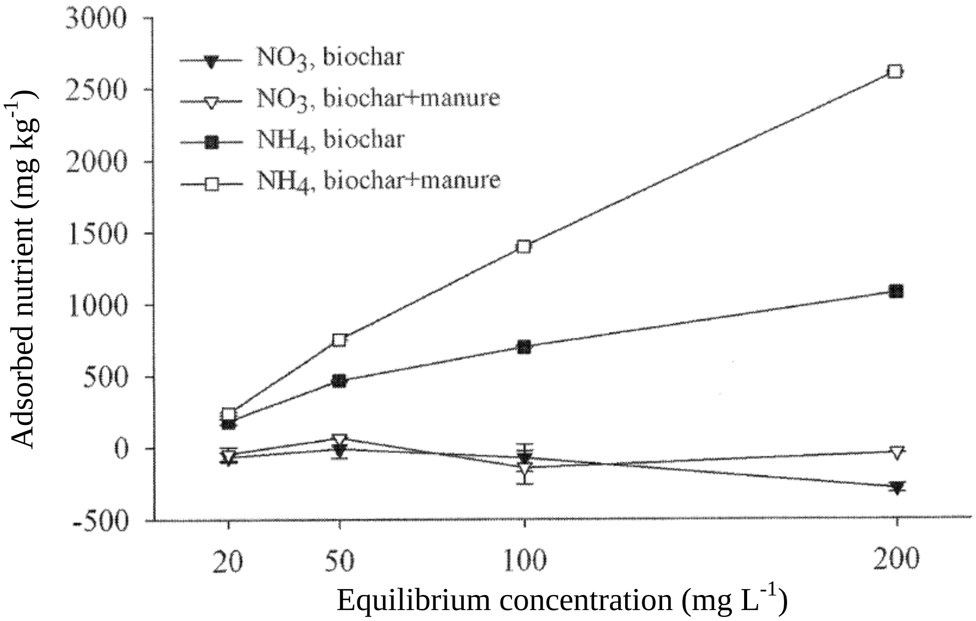


Figure 7.9: Adsorption isotherms for biochar from the tree *Robinia pseudoacacia* L., with and without manure adapted from Major *et al*. (2009), and sourced from Lehmann *et al*. (2002).

7.8.3 Plant Growth

There has been a conclusive outcome of the affect biochar has on plant dry matter production however, there is contradictory reports on the mechanisms involved in aiding plant growth. Chan *et al*. (2007) found that biochar alone did not increase dry matter yield even at a high rate (100 t/ha) of application. Although improved soil conditions rendered it more favourable for root development and growth which increased the plants ability to utilise applied N. Increased pH and reduced exchangeable Al were also thought to have improved the chemical environment in the rhizosphere. They also indicated that at low rates of application, a negative effect on plant production may occur.

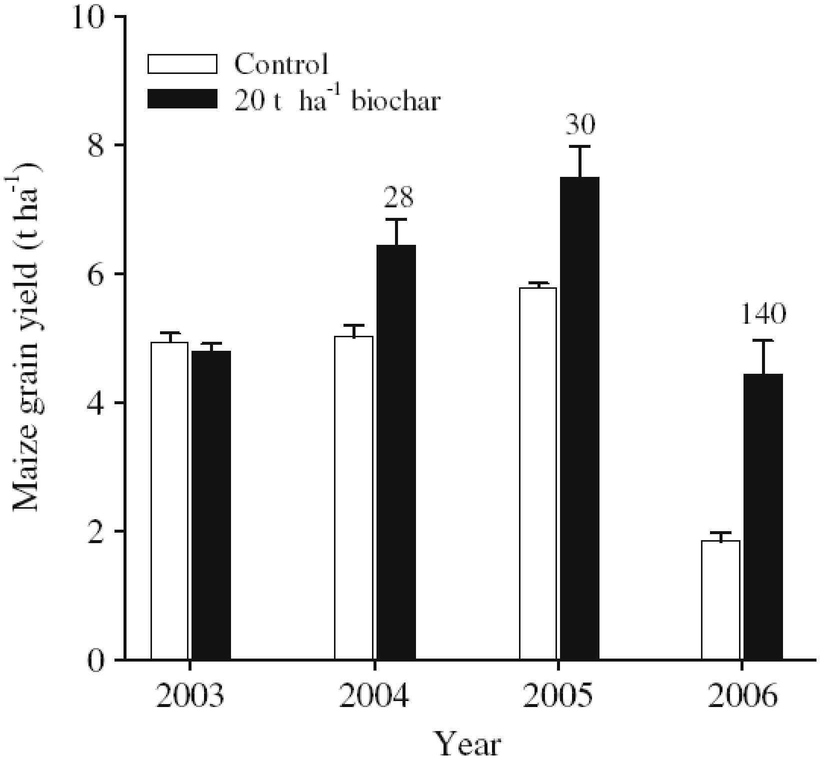


Figure 7.10: Maize grain yield on a biochar amended soil. Numbers above bars are the percent yield increase compared to the optimally managed control, and different letters signify differences between means within each year adapted from (Major *et al.*, 2010b)

Gaunt and Lehmann (2008) also establish that crop yields increased in low-input agriculture and increased crop yield per unit of fertiliser applied in high-input agricultural systems. This concurred with Rondon *et al*. (2007) where legumes were shown to perform better on N-limited soils than grasses after biochar application. However, although this trial showed bean (*Phaseolus vulgaris* L.) yields increased, their biomass production decreased significantly when biochar was applied above 78 t ha^{-1}. Rondon *et al*. (2007) deduced that the decreased productivity at high biochar application rates was caused by a number of factors which included allelopathic effects associated with hydrocarbons and HM toxicity. In another trial biochar and mineral fertiliser was shown to double the cumulative grain yield of rice (*Oryza sativa* L.). Legume production also increased due to decreased soil acidity and exchangeable Al (as Al decreases production severely) and increased Ca and Mg availability (Steiner *et al.*, 2007). In confirming the positive effect biochar has on plant growth Lehmann *et al*. (2003) found plant roots clustered around biochar fragments and even growing into the biochar indicating nutrient availability in pieces of biochar was higher in and around biochar than the surrounding mineral soil and plants could easily access them.

Biochar was shown to increase biomass production by 189% measured 5 months after application, with an increase of 1916% measured for legumes (Major *et al.*, 2010a). With an application rate of 10 t ha^{-1} of biochar radish and wheat (*Triticum* spp.) production increased and was achieved using three times less N fertiliser (Van Zwieten *et al.*, 2009). Major *et al*. (2010b) found maize (*Zea mays* L.) yields increased by 28, 30 and 140% (Figure 7.10), after 2, 3 and 4 years respectively, after an initial application of 20 t ha^{-1} of biochar. They stated the increase in crop yields was attributed to a 77-320% increase in available Ca and Mg. It was further speculated that biochar may enhance crop growth through several mechanisms, improved pH and base cation retention in the rooting zone which would cause improved crop nutrition and would prove highly significant in an environment where acid soil occurs under high rainfall conditions. It was also stated by an agricultural consultant that corn yields could potentially be raised by 20% through biochar use in the field (Renner, 2007). Major *et al*. (2009) also said that increased plant productivity could possibly translate into decreased nutrient leaching through soil profiles.

7.9 Effect of biochar on soil function

7.9.1 Bulk Soil Properties

As changes in soil properties are generally consistent with the characteristics of the biochar used, soil quality typically improves (Clough & Condron, 2010) through various soil chemical, biological and physical properties causing observable increases in crop production (Steiner *et al.*, 2007). Such soil physical characteristics that biochar can alter are percolation patterns, residence times and flow paths by changing pore size distribution (Major *et al.*, 2009). However, it has also been found that at low application rates of biochar, positive changes in soil quality may not be detectable (Chan *et al.*, 2007).

7.9.2 Physical Properties

7.9.2.1 Organic carbon

Due to dissolved organic matters (DOMs) net negative charge at typical soil pH, it generally moves easily through soils. Stable and soluble complexes have the ability to form on DOM with HMs, which can be maintained in solution and transported in soil. Hydrophilic dissolved organic C (DOC) fractions have been shown to favour the formation of dissolved organo-metallic complexes with sorption of metals described by the SOM for Cu and Pb (Liu *et al.*, 2007). Despite biochars high level of stability, it will ultimately be mineralised to CO_2. The range of C forms in a biochar particle depends, on the C properties of the biomass used, such as cell structure, charring conditions, and the formation process. The proportion of C retained during pyrolysis can vary greatly; with Lehmann (2007b) and Major *et al*. (2009) demonstrating C contents dependence on production and feedstock processes (Figure 7.6). The mineralisation timescale of C in biochar is greater than other forms of OM with, the amount of stored C being limited by soil properties such as texture, mineralogy as is the issue with other OM forms (Lehmann, 2007b).

Echeverria *et al*. (1998) also found the retention of HMs is dependent on the nature of OC. The commented that differences in the behaviour of metals between soils, may be attributed to their OM content. OM forms have the ability to develop complexes on the surface which are more stable for Pb and Cu than for Cd, Ni and Zn. This is due to, Ni having a greater affinity towards organically active sites than inorganic sites, whereas Cd and Zn prefer inorganic sites. The specificity of retention has also been demonstrated with occurrence being higher in soils with high OM content (Echeverria *et al.*, 1998). Beesley and Dickinson *et al*. (2010) found Cu and As were strongly correlated with DOC suggesting the mechanisms co-mobilisation were exhibited. However, Kalbitz and Wennrich (1998) found that highly protonated DOM was inept to binding positively charged elements leading to a greater proportion of nutrients in soil solution.

With OC increasing (69%) from applications of biochar (Laird *et al.*, 2010b) and only being significant when applied at high rates (>50 t ha $^{-1}$) (Chan *et al.*, 2007), C/N ratios have typically increased. The Increase in C/N ratio has been found to alter a number of properties in the soil and its behaviour. Steiner *et al*. (2010) demonstrated that high C content increases C/N ratio which limited NH_3 volatilisation. They explained that this mechanism was achieved by helping immobilise some of the available N. The C from biochar amended soils can also be influenced by other amendments. Such as mineral fertiliser with losses to soil C occurring at 8 and 4% when mineral fertiliser and no mineral fertiliser respectively were applied (Steiner *et al.*, 2007). Wardle *et al*. (2008) recently found that the incorporation of fir-derived charcoal can plausibly stimulate the loss of native soil C as shown in Figure 7.8.

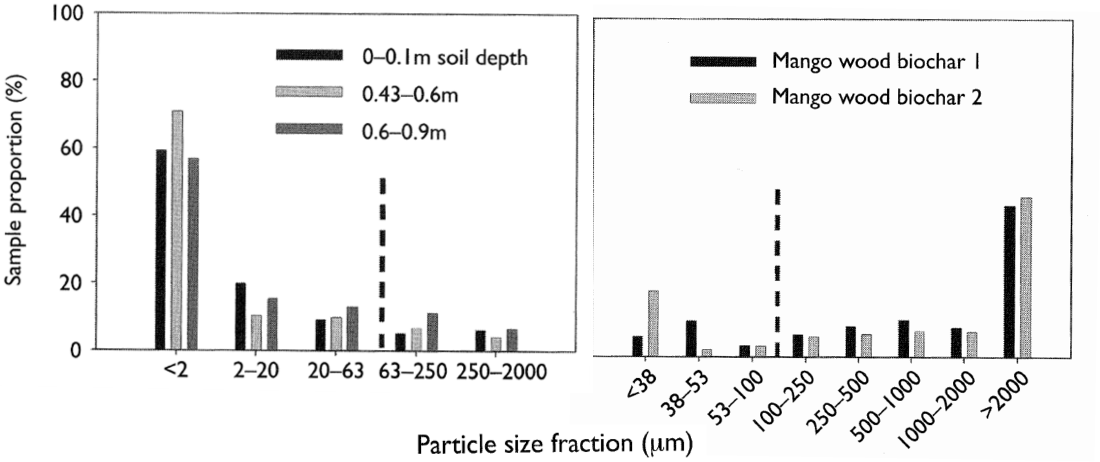


Figure 7.11: Particle size distribution of naturally occurring chars in fertilised intensive crop soil, Germany and hardwood biochar produced traditionally in mounds for soil application, hand ground to pass through a 0.9 mm sieve from Major *et al*. (2009).

Another potential path of C lost in soil, is translocation, with fine biochar particles smaller than 200 μm, which may represent a large portion (20-85%) of the biochar amendment (Figure 7.11) to move through the soil profile, and can act as agents of facilitated transport of nutrients. (Major *et al.*, 2009). Nguyen *et al*. (2008) also measured C loses from soil post biochar amendments and found biochar-derived C losses from the top 0.1 m over 100 years were estimated at 6 t ha^{-1}.

7.9.2.2 Structure

The effect biochar has on soil structure has been varied generally with good direct effects to the soil itself but potentially poor indirect outcomes occurring. Major *et al*. (2010a) confirmed this by observing an improvement to soil structure from additions of biochar while increasing the soil water flux enhancing dissolved and particulate organic C (DOC and POC) to occur in leachate. Chan *et al*. (2007) also found that the tensile strength of a hard setting soil was decreased with an amendment of at least 50 t ha^{-1} was applied.

7.9.2.3 Soil water

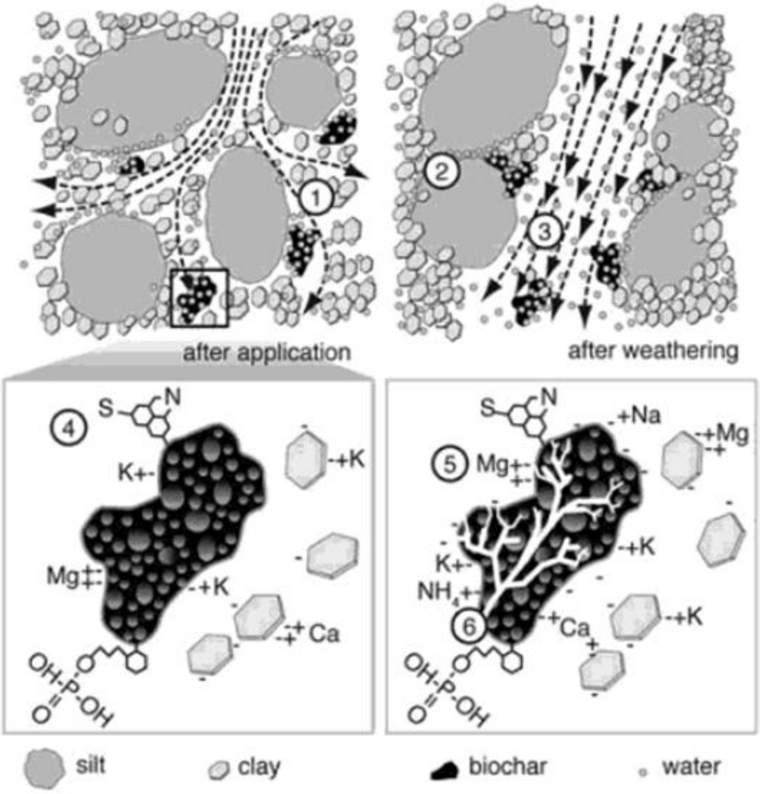


Figure 7.12: A schematic diagram of potential effects of nutrient leaching: (1) Upon biochar application soil, WHC increases because porous biochar particles retain water and reduce its mobility; (2) after watering, soil aggregation is improved as biochar binds to other soil constituents, and preferential flow of water occurs as well as the facilitated transport of biochar particles; (3); (4) at a smaller scale, newly applied biochar sorbs hydrophobic organic forms of nutrients; (5) after weathering, the surface charge of biochar increases, thus improving cation exchange capacity, and soil biota is enhanced from (Major *et al.*, 2009)

Typically two factors of soil water are altered with the addition of biochar to soil one is WHC and the other water percolation. Soil WHC generally increases (Laird *et al.*, 2010b; Warnock *et al.*, 2007), with affects varying depending on soil type, as with sandy soils available moisture is increased, and clayey soils decreased with increasing biochar applications (Steiner *et al.*, 2007). Chan *et al*. (2007) observed that field capacity water content was improved in a hardsetting soil, in unison with improved structure. Major *et al*. (2009) also noted biochar additions to clay soils biochar may indirectly reduce water mobility through increased plant biomass and evaporative surfaces, while in sandy soils this mechanism may be complemented by the direct retention of water by biochar. Biochar in sandy soils may even increase WHC at high matrix potentials acting similarly to clay. The nutrients in the soil solution could then later be made available when they transpire elevating the matrix potential. By and large soil percolation declines from biochar applications when compared to pure soil, and is in accordance with increased crop growth when biochar has been added (Lehmann *et al.*, 2003). Percolating water has also been found to mobilise (1% of applied biochar ~30t ha^{-1}) smaller fractions of biochar through the soil profile with (Major *et al.*, 2010a) (Figure7.12).

7.9.3 Chemical Properties

7.9.3.1 pH

The effect of pH from the application of biochar in soil has had mixed conclusions, from decreasing pH of soil solution to no change in pH and even increasing pH which in turn enhanced other soil properties. The effect biochar has on soil pH occurs as the properties biochar has will contribute to the soils current condition. Therefore as Steiner *et al*. (2007) observed that soil pH did not change from an application of 11 t ha^{-1} of biochar. In another instance pH was found to decrease when in an enhanced weathering environment with pH declining from 5.4 to 5.2 and 3.4 after incubation at 30^{o}C and 70^{o}C respectively (Cheng *et al.*, 2006).

There has however, been numerous reports of biochar having a liming effect when applied to soil (Laird, 2008; Laird *et al.*, 2010b). The pH of soil was increased when applications of greenwaste sourced biochar were applied at rates ≥ 50 t ha^{-1} (Chan *et al.*, 2007). Lehmann *et al*.

(2003) also reported biochar increasing soil pH by 0.36 and 0.75 units with and without fertiliser, respectively, in an acid soil. Therefore Laird (2008) stated that with biochar possessing this conditioning property, acidifying effects from organic and inorganic fertilisers could potentially be offset reducing the need for lime. As biochar is highly persistent in the environment this should require less application than lime, not only keeping costs down for farmers but also decreasing CO_2 emissions from having to applying lime every year or second year.

The effects of biochar increasing pH, on soil properties and constituents have resulted in both positive and negative effects. Rondon *et al*. (2007) found that the increase in pH from biochar applications contributed to a greater biological N fixation (BNF), concurring with similar effects observed in liming trials. Increases in pH were also found to be the mechanism mobilising As causing a 3 fold increase of As in soil pore water (Beesley & Dickinson, 2010). Echeverria *et al*. (1998) observed sorption of Cu, Cd and Zn by some acid soils increased with increasing pH from biochar additions, with Cu being preferentially sorbed over Zn and Cd.

7.9.3.2 CEC

The ability of a soil to retain cations in an exchangeable and plant available from increases in proportion to the amount of biochar inputs. The effect of biochar on the soil chemical property CEC is more often than not positive (Laird *et al.*, 2010b). However, the factors and mechanisms that increase soil CEC from biochar applications can influence this property greatly. Such factors are production processes and biomass source, and potential mechanisms are oxidation and soil interactions. The production in particular charring temperature, of biochar as stated earlier, can have a significant effect on biochar SSA, and in turn increase the capability of biochar to retain nutrients through a greater CEC (Liang *et al.*, 2006). Singh *et al*. (2010) concurred with this finding while also stating that the feedstock of biochar can dictate SSA. Lehmann *et al*. (2003) however, found biochar from both hardwood and softwood increased CEC by up to 50%, but noted that this could also be altered by OM used to create the biochar, and the charring environment such as the temperature and O_2 supply. Lehmann (2007b) indicated that the point at which biochar zero net charge is dependent on production temperature with CEC increasing with increasing temperature, the optimum temperature before C yield starts decreasing is between 450-550°C as seen in Figure 7.6.

Oxidation of biochar influences soil CEC through creating and increasing the number of sites cations can interact with the soil-biochar surface. Oxidation of biochar creates aromatic fractions on the edges of biochar, forming carboxylic (functional) groups which are responsible for both the increased CEC, and the potential for forming organo-mineral complexes (Steiner *et al.*, 2007). Cheng *et al*. (2006) found an increase in CEC was shown by a 53 and 538% increase after incubation at 30 and 70°C respectively, and following titration analysis it was suggested that the formation of carboxylic functional groups was the reason for the enhanced CEC. Furthermore, when soil provides poor environmental conditions, where exposure to microbial activity and abiotic oxidation is low, CEC properties of biochar may not develop making it unsuccessful to apply on such sites (Lehmann, 2007b). Steiner *et al*. (2007) also noted that no increase will be observed with a rate of application of 11 t ha^{-1}. Another mechanism increasing CEC through the application of biochar is inorganic molecules potentially adsorbing onto mineral or OM, which is attached to biochar or precipitate onto surfaces (e.g. Ca-PO$_x$). Therefore Major *et al*. (2009) suggested, that fertiliser dipped biochar would have a greater ability to sorb a larger mass of N, P and K than ‘fresh’ biochar.

7.9.4 Soil Microbes

With the addition of biochar come a higher colonisation rate of host plant roots by arbuscular mycorrhizal fungi (AMF), resulting in enhanced plant performance and elevated tissue nutrient concentrations, as soil nutrient availability increases, and leachate concentrations decrease (Clough *et al.*, 2010; Major *et al.*, 2009; Warnock *et al.*, 2007). Biochar can increase the ability of AMF to assist their host in resisting infection by plant pathogens which may be enhanced by the use of biosolids. Increases in plant root colonisation by ECM fungi have also been discovered (Major *et al.*, 2009). This is supported by Wardle *et al*. (Wardle *et al.*, 2008) as biochar was found to be a foci for biota, which as mentioned previously, can lead to enhanced decomposition rates and mass loss of associated humus. The positive responses are thought to be the result of C in the biochar material being added to the soil, with char being more C-rich than OM. However, there is a thought that the response is not only from biochar being C rich but due to the unique properties of biochar for instance alkalinity, porosity and WHC (Steiner *et al.*, 2007). Additionally pore space, which could serve as a refuge for colonising microbes has been suggested, as the average size of soil bacteria and fungi range from 1 to 4 µm and 2 to 64 µm respectively and as average body-size of a protist and micro-arthropod are 8 to 100 µm and 100µm to 2 mm respectively soil micro-organisms can be accommodated in biochar pores which can be smaller than 16 nm in diameter. Rondon *et al*. (2007) also stated biochar, as being an excellent support material for rhizobium, and in contrast mycorrhizal associations did not appear to change with additions of biochar.

Where an unfavourable nutrient ratio such as increased C/N ratio in soils occurs as a result from biochar additions and a portion of the char is decomposable, immobilisation of N may arise. The immobilisation of N can shift the N/P ratio which can affect AMF colonisation, although many of these alterations occur on a micro-scale, therefore only affecting the hyphae in the immediate vicinity of biochar particles (Warnock *et al.*, 2007). Microbial immobilisation has also been established as an important mechanism to retain N in soil affected by leaching. Steiner *et al*. (2007) observed that greater C availability stimulates microbial activity, increasing N demand, and promoting immobilisation and recycling of NO_3.

Stimulatory signal compounds for microbial growth can be influenced by soil pH, therefore as biochar increases pH, this change alone, can lead to stimulatory effects causing increases in microbial abundance. Biochar particles however, can adsorb stimulatory compounds reducing the effect pH has on microbial abundance, with future research required to find whether these compounds can then be re-dissolved into soil water and made available again when biochar is mineralised (Warnock *et al.*, 2007).

7.10 Sustainability of biochar

7.10.1 Environmental

Recently there has been much interest in biochars driven by two major global issues one of them being climate change and the other the realisation for the need of more sustainable soil management practices (Chan *et al.*, 2007). Biochar is a near-term technology that can meet the requirements of carbon sequestration through long term and substantial net withdrawal of CO_2

from the atmosphere, the potential for accountability, and has low risk of rapid or large scale leakage of CO_2. Therefore biochar offers the chance to turn bioenergy into a carbon-negative industry (Lehmann, 2007a). Biochar creating a C-negative industry is due to CO_2 is assimilation by plants through photosynthesis, which is then pyrolysed, producing energy from captured gases, while the biochar residue is retained and subsequently stored in soil. If new CO_2 is fixed by plants, the biochar burial becomes a net sink of carbon. Using pyrolysis in combination with a land application of biochar residue, carbon sequestration, and renewable energy are not alternatives to one another, but may become a joint strategy. With the use of corn or switchgrass as a feedstock approximately 3-9 kg of C can be yielded from a kg of C invested, and this is with biochar being used as a C sink rather than an energy source. Therefore pyrolysis produces 3-9 times more energy, than is invested in generating the energy, and if the residual product is sequestered in soil this C-negative technology would lead to a net withdrawal of CO_2 from the atmosphere. Furthermore, compared to other climate change advances such as no tillage, biochar as a sink has the ability to be accountable and provides multiple environmental benefits (Lehmann, 2007b).

It is estimated that a total of 9.5 billion tons of C could potentially be stored in soils by the year 2100 using a wide variety of biochar applications (Lehmann *et al.*, 2006). This is due to biochar being one of the most stable (Clough & Condron, 2010) organic amendments with reduced greenhouse gas emissions (Gaunt & Lehmann, 2008) in particular low CO_2 losses, decreasing N_2O emissions below background levels (Cayuela *et al.*, 2010) (Figure 7.8). Singh *et al*. (2010) measured decreases in N_2O emissions by 14-73% from control plots. Rondon *et al*. (2005) also found that methane (CH_4) emissions, were completely suppressed and N_2O emissions were reduced by 50% when biochar was applied at 26 t ha^{-1}, to soybeans, and 80% in grass stands. The reduction in emissions was thought to be the result of enhanced aeration, C stabilisation and decreased N cycling possibly due to a higher C/N ratio. Although N_2O has been found to decrease, increased mineralisation and volatilisation may occur beyond plant requirements as a result of microbial interactions, and if anaerobic conditions prevailing, due to changes in water retention. Biochar however, is not expected to enhance mineralisation immediately as bulk available C is recalcitrant. Major *et al*. (2009) explained that through reduced fertiliser requirements will decrease, due to increased nutrient use efficiency, reducing non-point source pollution concerns but also decrease C emissions from production and transport of synthetic fertilisers. Van Zwieten *et al*. (2009) calculated Nitrogen's (as urea) greenhouse gas footprint to be 4.018 t CO_2 per ton of N, due to its production and N conversion into N_2O in the soil. Additionally, Johannes Lehmann and colleagues found that the potential for biochar sequestration trading will not become economically viable until CO_2 emissions trading reaches US$ 37/t CO_2 (Renner, 2007).

7.10.2 Ecological

Soil amendments of biochar give the possibility to increase crop yields while decreasing environmental pollution by nutrients. Returning C to the soil as biochar reduces the negative effects of biomass removal from land, as this procedure is highly extractive, and can lead to widespread soil degradation, negative effects on habitats and off-site pollution (Gaunt & Lehmann, 2008).

It has been established that biochar has the ability to adsorb ammonium (NH_4^+). Lehmann *et al*. (2003) measured a decrease of NH_4^+ by 60% from leachate, in pots growing rice. Leaching of Ca (~ 20%) and Mg was also reduced during the first week of this trial. Consequently, Ca availability on exchange sites was more than double while concomitantly reducing leaching losses. Alternatively, K was not reduced in leachate with additions of biochar, since the biochar used, contained large amounts of K, however, biochar increased K content in soil while having no detrimental effect on leachate (Lehmann *et al.*, 2003). In addition, P decreased by 70% from sorption but remained plant available with additions of biochar. Irreversible adsorption of P was documented with biochar applications resulting from enhanced P sorption in acid soils. Major *et al*. (2009) stated that bases such as Ca, K and Mg were on occasion more abundant in leachate from pure biochar columns than sand columns and this was due to their high solubility and leachate try to maintain electro-neutrality.

Two ways in which biochar could decrease pollution, is a reduction in the amount of nutrient leached by way of lowering concentrations of soluble nutrients in soil solution (Lehmann, 2007b), and reduced fertiliser requirements as nutrients would be retained (Lehmann, 2007a). Renner (2007) also documented farmers using biochar will decrease fertiliser use, while producing less nutrient rich runoff. Biochar applications alongside labile organic N fractions can lead to increased net rates of nitrification which Pacala and Socolow (2004) thought was most likely caused by sorption of nitrification-inhibiting phenolic compounds. Clough *et al*. (2010) found nitrate-N fluxes was enhanced by approximately 3% of the N applied in bovine urine-biochar treatments, compared with urine-only treatments after 17 days. The mechanism through which biochar is able to sorb anions is with CEC and AEC, however, this is dependant on pH, age and weathering environment of biochar (Cheng *et al.*, 2006).

Major *et al*. emphasised that fresh biochar with low surface oxidation is generally hydrophobic and therefore sorbs hydrophobic molecules, such as organic contaminants. The reduction in
The BC fraction lowers the chemical availability of PAH's by 4-6 times (Accardi-Dey & Gschwend, 2002). Beesley *et al*. (Beesley *et al.*, 2010) also found that bochar and compost decreased PAHs by more than 50%, which is encouraging for the remediation of contaminated soils and for the use in combination with fertiliser that may conatain contaminants or elemtns in high concentrations. However, they also found a 30 fold increase in Cu and As which they associated with significant increases in dissolved OC and pH. Copper, Ni and Pb have also been stated as having a relatively high affinity for organic complexation, and when the OM solubility increases it is likely to result in either, increased concentrations of HMs in soil solution or increased concentrations of organically complexed forms of these metals in soil solution (Ashworth & Alloway, 2008).

Biochar has been found to decrease environmental pollutants (Clough & Condron, 2010), such as benzene, which has been shown to be adsorbed by wood char derived from pyrolysis at 400^{o}C (Chun *et al.*, 2004). Karathanasis *et al*. (2005) also stated that negatively charged colloids had the ability to facilitate the downward migration of metals and organic pollutants through soil. However, with an increased abundance of polar functional groups, soil amended with biochar has exhibited a high sorptive capacity for an excreted bovine hormone typically found in higher concentrations in waterways bordering New Zealand dairy farms. (Sarmah *et al.*, 2010). It has also been found that small amounts (65 t ha^{-1}) of biochar can potentially reduce bioavailability and efficacy of pesticides through inhibition towards biodegradation, but accumulation and ectoxicological impacts are still a potential concern. (Kookana, 2010). Laird

(2008) additionally noted that biochar is a nutrient in its own right and a chemical adsorber, able to reduce environmental contamination from plant nutrients and agrichemicals.

7.10.3 Economical

The economics behind applying biochar is that it will potentially reduce fertiliser use and possible increase in agricultural productivity (Lehmann, 2007a). However, if biochar is used in an agricultural system farmers renting land on a short-term lease will have no incentive to apply biochar as the effects are not experienced immediately and are occur over an extended period.(Laird, 2008)

7.11 Conclusions

- Managing organic wastes such as biosolids pose a significant environmental burden that can lead to pollution of ground and surface waters. These wastes as well as other by-products are usable resources for pyrolysis and can also be managed using biochar to mitigate environmental impacts.

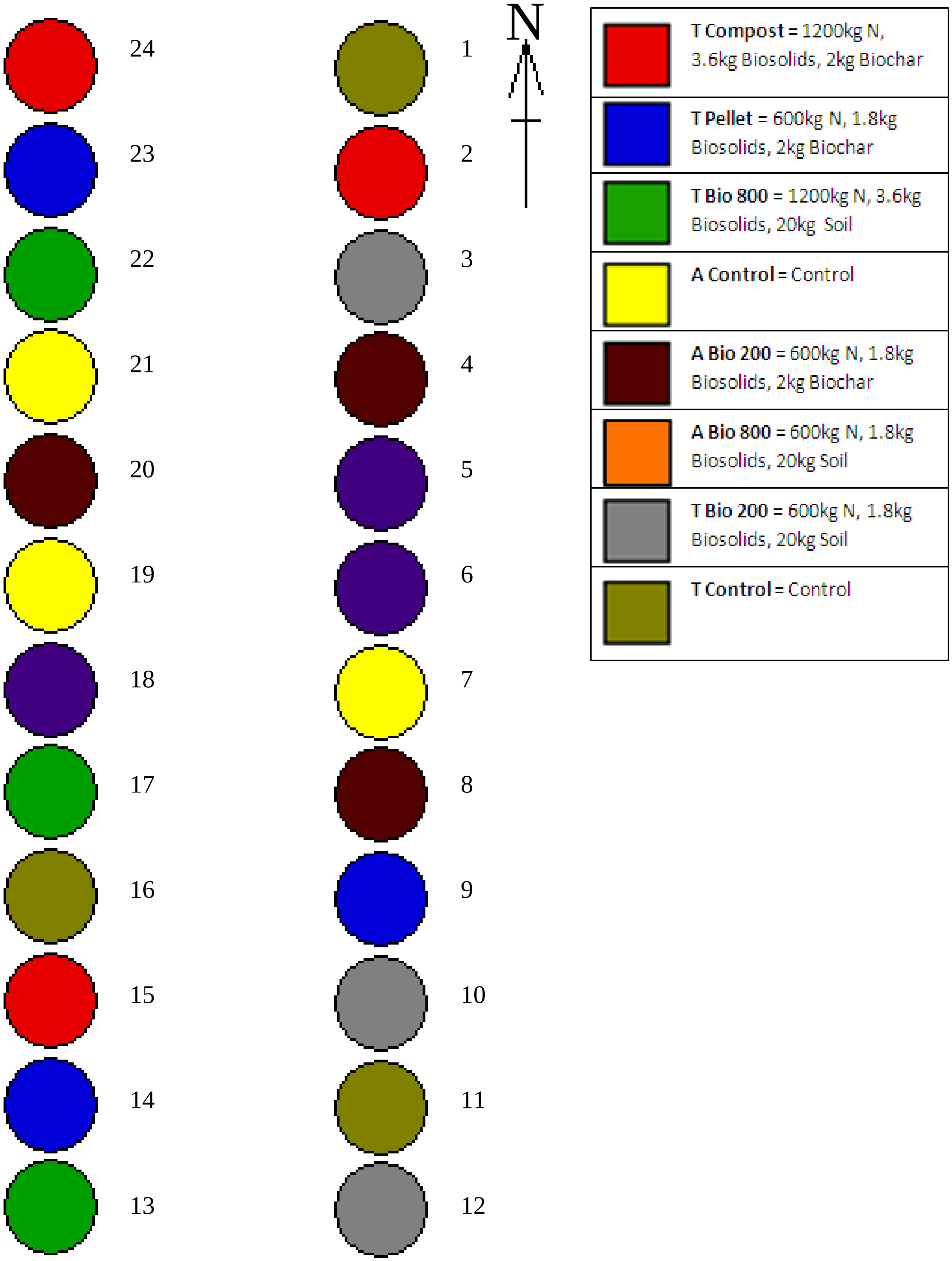
- Biosolids contain a significant concentration of nutrients and, if used with BMPs can indeed serve as a valuable fertiliser, and have the potential to be used in agricultural systems without causing significant adverse effects on the soil or the wider environment.

- The types of soil that would be appropriate for the application of biosolids and biochar are those that are well developed with a considerable depth of quality soil from ground level to groundwater. Soils that are well developed would have a high proportion of soil colloids that will aid the soil in retaining the undesirable components of biosolids while the depth of soil will increase its filtering ability further reducing the implications of the undesirable constituents of biosolids, and aid the benefits biochar adds to soil.

- Biochar soil amendments incorporated into the soil with organic and inorganic fertilisers have shown to increase the total N pool, with limited effects on NO_3^- leaching.

Appendix C – Trial Design

Complete Randomised Design



T Compost = 1200kg N, 3.6kg Biosolids, 2kg Biochar

T Pellet = 600kg N, 1.8kg Biosolids, 2kg Biochar

T Bio 800 = 1200kg N, 3.6kg Biosolids, 20kg Soil

A Control = Control

A Bio 200 = 600kg N, 1.8kg Biosolids, 2kg Biochar

A Bio 800 = 600kg N, 1.8kg Biosolids, 20kg Soil

T Bio 200 = 600kg N, 1.8kg Biosolids, 20kg Soil

T Control = Control