

NATIONAL UNIVERSITY OF IRELAND GALWAY

**TREATMENT OPTIONS FOR THE SEPARATED
SOLID FRACTION OF PIG MANURE**

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The National University of Ireland requires the signatures of all persons using or photocopying this thesis. Please sign below, and give the address and date.

For my parents, sisters and Catherine.

‘The aim of life is self-development. To realise one's nature perfectly - that is what each of us is here for.’

Oscar Wilde.

ABSTRACT

Landspreading of pig manure in quantities greater than that required by plants can result in pollution of ground and surface water bodies. Recent regulations have placed restrictions on the application of manure to land, while further more stringent restrictions will come into force in the coming years. To comply with these regulations, it is estimated that pig farmers will require approximately 50% more spreadlands for manure application in 2017 than is the case in 2012. This will increase the cost of landspreading pig manure and, therefore, alternative viable on-farm treatment options for pig manure are urgently required. Composting and pyrolysis of the separated solid fraction of pig manure may be a solution to this problem.

A composting experiment was designed to identify the most effective readily available bulking agents to produce stable and mature compost from the separated solid fraction of pig manure. Of the bulking agents investigated, sawdust was found to be the best, due to its large surface area and small particle size. A second composting experiment was then designed to investigate the required ratio of sawdust addition to pig manure. Two ratios of separated pig manure solids-to-sawdust (w/w) were examined: 4:1 and 3:2. It was found that the lower ratio of sawdust addition produced stable compost, while the decreased sawdust requirement also reduced costs. An economic analysis, conducted to determine the viability of separation and composting of pig manure in Ireland, suggested that pig manure composting is not currently viable due to the high cost of separation, but may become viable in the future if a cheaper method of separation is used, and if oil prices continue to rise.

A pyrolysis experiment was designed to produce and characterise biochar, bio-liquid and gas from pig manure, and to examine the impact of the addition of different rates of sawdust on the energy yield. Increasing the sawdust content in the wood/manure mixture increased the resultant biochar and gas heating values, but reduced bio-liquid heating values. The nutrient concentrations of the biochar were reduced with increasing sawdust content in the wood/manure mixture. The effect of composting the feedstock before pyrolysis was also examined. An energy balance was conducted on the processes of separation, composting and pyrolysis of pig manure. A positive net

energy yield was produced from these technologies with the addition of sawdust to the manure. Composting the feedstock before pyrolysis reduced the net energy yield.

The effect of amending soil with two types of biochar, produced from pig manure and wood, on nutrient leaching, soil properties and greenhouse gas emissions, was also examined. Both types of biochar affected the nitrogen (N) cycling process within the soil, which, in turn, reduced nitrate (NO_3^-) leaching and increased nitrous oxide (N_2O) emissions. Emissions of carbon dioxide (CO_2) were higher in the biochar-amended soils due to a higher rate of mineralization. The soil water, organic matter, carbon (C) and N contents were impacted when both types of biochar were added. The biochar produced from pig manure released phosphorus (P), and resulted in higher P contents both in the soil and in the leachate.

This study showed that composting and pyrolysis can be used as alternatives to landspreading of pig manure. However, at present, neither of these treatment methods is currently viable for on-farm implementation. Composting is a proven technology and can be quickly implemented at farm-scale, but using the techniques of this study, the cost of slurry separation with a decanter centrifuge would be prohibitively expensive. However, composting of pig manure following a cheaper method of separation should be investigated, and may be economically viable. Pyrolysis of separated pig manure may be an alternative to landspreading in the future. However, farm-scale studies would be first required to investigate whether the laboratory results of the present study can be replicated on a larger scale. The current method of landspreading pig manure remains the most feasible manure treatment option at the current time. This study showed that the application of biochar to soil can reduce nutrient leaching, and may be an effective method of reducing surface and ground water contamination after landspreading of pig manure. However, further studies are required to examine different soil types, biochar types and application rates.

DECLARATION

This dissertation is the result of my own work, except where explicit reference is made to the work of others, and has not been submitted for another qualification to this or any other university.

Shane Troy

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ABREVIATIONS

ABC	Acid binding capacity
AD	Anaerobic digestion
Al	Aluminium
BET	Brunauer-Emmet-Teller surface area
BNF	Biological nitrogen fixation
BOD ₅	Five-day biological oxygen demand
BUF	Buffering capacity
C:N	Carbon-to-nitrogen ratio
Ca	Calcium
CEC	Cation exchange capacity
CH ₄	Methane
CHP	Combined heat and power
CO	Carbon monoxide
CO ₂	Carbon dioxide
COD	Chemical oxygen demand
CP	Pyrolysis feedstocks which have been composted
Cu	Copper
CWs	Constructed wetlands
db	Dry basis
DM	Dry matter
DRP	Dissolved reactive phosphorus
DTG	Derivative of thermogravimetric analysis
DUP	Dissolved unreactive phosphorus
EC	European Commission
EPA	Environmental Protection Agency
FAS	Free air space
FC	Fixed carbon
GHG	Greenhouse gas
GI	Germination Index
H:C	Hydrogen-to-carbon ratio
HHV	Higher heating value

K	Potassium
Ktoe	Kilo-tonne oil-equivalent
MAC	Maximum allowable concentration
Mg	Magnesium
Mn	Manganese
MO	Manure-only pyrolysis feedstock
N	Nitrogen
N ₂ O	Nitrous oxide
NACP	Nutra ammonium citrate soluble phosphorus
NH ₃	Ammonia
NH ₄ ⁺	Ammonium
NO ₂ ⁻	Nitrite
NO ₃ ⁻	Nitrate
NREAP	National Renewable Energy Action Plan
OM	Organic matter
OM ₀	Organic matter at Day 0 of composting
OM ₅₆	Organic matter at Day 56 of composting
OM _{LOSS}	Loss of organic matter during composting
OUR	Oxygen uptake rate
P	Phosphorus
PAM	Polyacrylamide
PM600	Soil amended with pig manure biochar produced at 600°C
POM	Programme of measures
PP	Particulate phosphorus
RES-E	Energy from renewable sources - Electricity
RES-T	Energy from renewable sources - Transport
RES-H	Energy from renewable sources - Heat
S	Sulphur
SADPM	Separated solids of anaerobically digested pig manure
SAS	Statistical Analysis System
SEM	Scanning electron microscope
SPM	Separated solids of pig manure
SS	Suspended solids

STP	Soil test phosphorus
T1	Compost trial 1
T2	Compost trial 2
TCC	Thermo-chemical conversion
TDP	Total dissolved phosphorus
T _f	Final temperature of primary devolatilisation
TGA	Thermogravimetric analysis
TIC	Total inorganic carbon
T _{max}	Onset temperature of primary devolatilisation
TOC	Total organic carbon
TON	Total oxidised nitrogen
T _{on}	Onset temperature of primary devolatilisation
TP	Total phosphorus
TS	Total solids
T _r	Range of primary devolatilisation temperatures
TV	Threshold value
VS	Volatile solids
VM	Volatile matter
W600	Soil amended with wood biochar produced at 600°C
WC	Water content
WEP	Water extractable phosphorus
WFD	Water Framework Directive
WFPS	Water filled pore space
WSOC	Water soluble organic carbon
Zn	Zinc
+PM	Soil which has been amended with pig manure

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1 INTRODUCTION

Overview

In June 2011, the total number of pigs in Ireland was approximately 1,555,100 (CSO, 2011), with almost 3 million tonnes of liquid pig manure produced on a yearly basis. These pigs are concentrated in specific regions, with 52% of the national sow herd located in counties Cavan, Cork and Tipperary (Teagasc, 2008). The most pig-dense region in the country is County Cavan, which has a pig density of 3.5 ha per sow and her progeny (Teagasc, 2008). Currently, most of the pig manure produced in Ireland is landspread. However, pig farmers rarely have sufficient land on which to spread all of the manure produced, and rely on neighbouring farmers, especially tillage farmers, to landspread the manure on their farms. However, the application of manure to farmland, in quantities greater than plant nutrient requirements, may lead to pollution of surface and ground waters (Carpenter et al., 1998; McGarrigle et al., 2010a).

Recent European legislation, such as the Water Framework Directive (2000/60/EC; EC, 2000) and the Nitrates Directive (91/676/EEC; EEC, 1991), aims to protect water bodies from pollution from agriculture and other sources. As a consequence of these Directives, the European Communities (Good Agricultural Practice for Protection of Waters) Regulations 2006 (S.I. 378 of 2006), and its amendment (S.I. 610 of 2010), were adopted in Ireland. These Regulations place restrictions on the application of manure to land. It is estimated that pig farmers will require approximately 50% more spreadlands for manure application in 2017 than is the case in 2012 (Nolan et al., 2012). As a result of these restrictions and increasing transport costs due to rising energy prices, the cost of landspreading pig manure is set to increase dramatically. Therefore, it is essential that practical and economical on-farm pig manure treatment strategies be investigated.

The most important factor in controlling cost of manure transportation is dry matter (DM) content (Treanor, 2008). One way of increasing DM content of manure is through separation. The separation of manure produces a solid fraction and a liquid fraction. The solid fraction can be applied to fields as a fertiliser (Burton, 2007),

composted (Bernal et al., 2009), or used as a feedstock for pyrolysis (Ro et al., 2010). However, before composting or pyrolysis of pig manure can be considered as a viable alternative to landspreading in Ireland, there is a need for an extensive study of their use.

Therefore, the aims of this study are to:

1. Review existing literature on alternative treatment options for the solid fraction of pig manure to select suitable technologies for further study, and to identify knowledge gaps which need to be addressed to allow for the implementation of these technologies at farm-scale.
2. Develop experimental procedures to determine the most viable bulking agents for composting of separated solids of pig manure, and to identify the optimum ratio of bulking agent addition. Examine compost stability using a recently developed Oxitop Oxygen Update Rate test.
3. Establish the economic feasibility of pig manure separation and composting in Ireland.
4. Characterise the biochar, bio-liquid and gas produced from the pyrolysis of separated pig manure, and to examine the effects of composting the feedstock before pyrolysis and the addition of different amounts of sawdust on the products of pyrolysis. The effect of composting a feedstock before pyrolysis has never been examined.
5. Determine the future viability of using separation, composting and pyrolysis as a treatment option for pig manure by undertaking an energy balance study. The application of these three technologies in unison is a novel approach to pig manure management.
6. Determine the effects of using the biochar produced from pyrolysis as a soil additive and to examine the effects on nutrient leaching, soil properties and greenhouse gas emissions using a novel soil column experiment.

1.1 Procedure

A literature review of treatment options for the separated solid fraction of pig manure was undertaken. Composting and pyrolysis of pig manure solids were chosen for further investigation as (1) composting offered the most feasible treatment option for the solid fraction of separated pig manure, which could be implemented reasonably quickly on Irish farms, and (2) pyrolysis has the ability to be a viable treatment option in the longer-term. However, current knowledge of manure pyrolysis is insufficient. Several knowledge gaps were identified, especially in the area of pig manure pyrolysis and land application of biochar. Although knowledge of manure composting was more extensive, it was important to investigate compost technologies using Irish pig manure and climatic conditions. Experiments were designed to acquire robust, practical knowledge to allow for the implementation on-farm composting, and to further develop knowledge of pig manure pyrolysis and biochar amendment of soil. Following the literature review, the body of experimental work was split into three different studies: (1) separation and composting, (2) pyrolysis and (3) land application of biochar.

1.1.1 Composting Procedure

Insulated compost tumblers were used to produce compost over a 56-day composting period. Compost physico-chemical properties, maturity and stability analyses were used to assess compost quality. The compost procedure was broken down into two experiments. In the first composting experiment, the aim was to determine the most effective, readily available, bulking agent for composting the separated solid fraction of pig manure. Woodchip, chopped straw, shredded greenwaste, sawdust, and sawdust and woodchip combined, were examined to find the most suitable bulking agents. Sawdust addition resulted in the best quality compost due to its small particle size and large surface area. The second composting experiment investigated composting of both separated raw and anaerobically digested pig manure using different rates of sawdust addition. Reducing the quantity of bulking agent required would reduce costs for farmers. Once the practical experiments were concluded, it was critical to determine the feasibility of on-farm composting in Ireland. This was achieved by conducting an economic analysis of separation and composting of pig manure.

1.1.2 Pyrolysis Procedure

A laboratory-scale pyrolysis reactor was used to produce biochar, bio-liquid and gas from separated solids of pig manure. The aim of this experiment was to examine the effect of (1) composting the feedstock and (2) adding different amounts of sawdust to the manure, on the properties of the pyrolysis products. It was also critical to determine the balance of energy used during the separation, composting, drying and pyrolysis processes to determine whether using these technologies to treat pig manure resulted in a positive net energy yield. To establish this, an energy balance was conducted using experimental data from the pyrolysis and composting experiments, combined with data from literature. The energy balance examined the effects of (1) sawdust addition (2) composting the feedstock, on net energy production.

1.1.3 Biochar Application to Soil Procedure

Soil columns were amended with biochar from both pig manure and wood, and subjected to leaching under simulated rainfall over a 30-week incubation experiment. The aim of this study was to determine the effect of the application of these biochars to soil on nutrient leaching and soil properties. Pig manure was also added to the soil columns after 10 weeks of leaching. Greenhouse gas emissions from the soils were collected and analysed for 4 weeks following the application of pig manure to determine the effect of biochar on gaseous emissions.

1.2 Structure of Dissertation

Chapter 2 reviews the characteristics of pig manure produced in Ireland, Ireland's water quality status, the impact of agriculture on water quality, and current and future regulations governing landspreading. Alternative treatment options for pig manure are examined, particularly separation, composting, pyrolysis and biochar application to soil. Chapter 3 describes the results of experiments investigating the most effective bulking agents for pig manure composting, while Chapter 4 examines the impact of the addition of various ratios of sawdust to pig manure on compost quality. Chapter 5 describes the economics of pig manure separation and composting in Ireland. Chapter

6 details the results from the pyrolysis experiments, and the energy balance for separation, composting and pyrolysis of pig manure. Chapter 7 details the leaching and soil properties results from the biochar-to-soil experiments, while Chapter 8 details the impact of biochar addition to soil on greenhouse gas emissions. Finally, in Chapter 9, conclusions from the study are presented and recommendations for future research are made.

To date, four international peer review papers have been published from this work:

Troy S.M., Nolan T., Kwapinski, W., Leahy, J., Healy, M. and Lawlor, P., 2012. Affect of sawdust addition on composting of separated raw and anaerobically digested pig manure. *Journal of Environmental Management*, 111: 70-77.

Troy, S.M., Nolan, T., Leahy, J.J., Lawlor, P.G., Healy, M.G. and Kwapinski, W., 2012. Effect of sawdust addition and composting of feedstock on renewable energy and biochar production from pyrolysis of anaerobically digested pig manure. Accepted for publication in *Biomass and Bioenergy*.

Nolan, T., Troy, S.M., Healy, M.G., Kwapinski, W., Leahy, J.J., Lawlor, P.G., 2011. Characterization of compost produced from separated pig manure and a variety of bulking agents at low initial C/N ratios. *Bioresource Technology*, 102: 7131-7138.

Nolan, T., Troy, S.M., Gilkinson, S., Frost. P., Xie, S., Zhan, X., Harrington, C., Healy, M.G., Lawlor, P.G., 2012. Economic analyses of pig manure treatment options in Ireland. *Bioresource Technology*, 105: 15-23.

A full list of outputs from this work, including international and national conference papers and manuscripts submitted to international journals, is tabulated in Appendix A.

2 LITERATURE REVIEW

Overview

This chapter reviews published literature relating to the quantity and characteristics of pig manure generated in Ireland, and the potential environmental effect arising from the landspreading of this manure. Recent and upcoming legislation relating to manure application to soil is reviewed and alternative options to landspreading are explored, with a focus on composting and pyrolysis.

2.1 Quality and Composition of Pig Manure

2.1.1 Manure Production

Pig farming in the EU is concentrated in certain areas. Thirty percent of sows in the EU are located in a major pig production basin which stretches from Denmark, through north western Germany and the Netherlands to Vlaams Gewest in northern Belgium (Marquer, 2010). Other important regions include Cataluna and Murcia in Spain, Lombardia in Italy, and Bretagne in France. In the Republic of Ireland, 50% of the national sow herd is concentrated in Longford, Tipperary South, Cork and Cavan (Boyle, 2010). In June 2011, the total Irish pig numbers were approximately 1,555,100 (CSO, 2011) and comprised 156,800 breeding pigs and 1,398,300 other pigs. However, according the Food Harvest 2020 report, the aim is to increase the national sow herd to 200,000 by 2020 (Department of Agriculture, Fisheries and Food, 2010). High densities of pig farms results in a surplus of pig manure in these areas. The highest pig density in Ireland is in County Cavan, with a pig density of 3.5 ha per sow (Teagasc, 2008). Pig manure in these pig-dense areas must be transported to less dense areas for landspreading.

2.1.2 Composition of Pig Manure

The quantity on manure produced by each pig per year is the equivalent to 6% of its body weight (Kruger et al., 1995). The principle constituents of pig manure are faeces

and urine. It also contains: spilled feed, undigested dietary components, endogenous end products, and indigenous bacteria from the lower gastrointestinal tract (Sutton et al., 1999; Kornegay and Versteegen, 2001). In Ireland, pigs are generally housed on slatted floors. Therefore, pig manure generally takes the form of liquid manure, and this accounts for over 80% of total pig manure produced in this country (Menzi, 2002). This is also the case with most of Europe and the United States. Only in the UK, Norway and some Eastern European countries does solid manure make up more than 40% of the total pig manure produced (Menzi, 2002). Studies have shown that there is a wide variation in the nutrient concentration, composition and DM content of pig slurry in Ireland (Table 2.1). Table 2.2 shows the results of a Europe-wide survey on the DM content and nutrient concentrations of liquid pig manure (Menzi, 2002), indicating that the variability of pig manure is not just an Irish problem.

Table 2.1 Dry matter content and nutrient concentrations of pig manure in Ireland

	O’Bric et al. (1992)		Tunney and Molloy (1975)		McCutcheon (1997)	
	Mean	Range	Mean	Range	Mean	Range
Dry Matter, %	3.2	1.0 – 10.0	8.0	1.0 – 21.0	5.8	0.4 – 13.1
Nitrogen, kg m ⁻³	4.6	1.5 – 9.5	4.3	1.2 – 7.0	6.6	1.2 – 12.3
Potassium, kg m ⁻³	2.6	0.7 - 5.2	2.0	0.6 – 3.4	2.7	0.4 – 6.1
Phosphorus, kg m ⁻³	0.9	0.1 – 3.2	1.8	1.0 – 4.5	1.6	0.1 – 4.6

Table 2.2 Dry matter content and nutrient concentrations of pig manure in Europe (Menzi, 2002)

	<u>Mean</u>	<u>Range</u>
Dry Matter, %	5.2	1.5 – 9.2
Nitrogen, kg m ⁻³	4.8	1.2 – 8.2
Potassium, kg m ⁻³	3.2	0.6 – 8.0
Phosphorus, kg m ⁻³	2.1	0.3 – 5.0

The variability of pig manure in Ireland makes it difficult for farmers to quantify the amount of nutrients which are being spread on their farms without the use of expensive manure tests (Hackett, 2007). In order to ensure that their pig manure is a

sought after product for arable farmers, pig farmers must ensure the composition of pig manure is as consistent as possible for both nutrient concentrations and DM content. There is generally a good relationship between the DM content of pig manure and its N and P content (Hackett, 2007). Increasing the DM content of the pig manure tends to increase the N and P content (Figure 2.1).

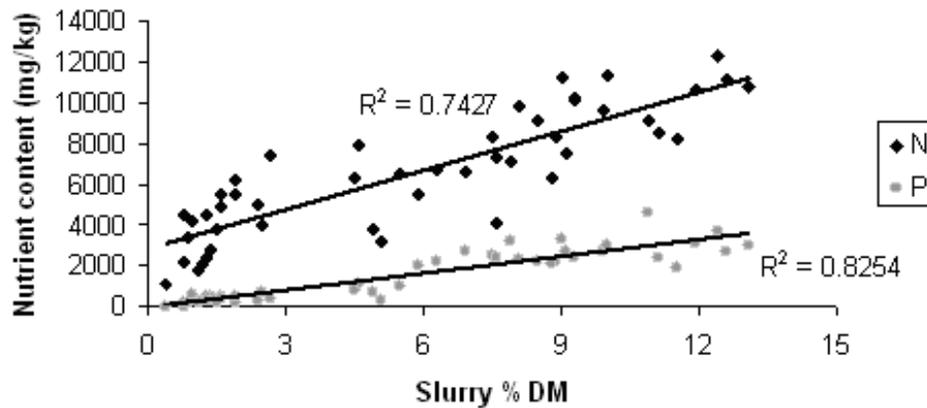


Figure 2.1 Relationship between dry matter content of pig manure and the N and P content (McCutcheon, 1997)

2.1.3 Factors Affecting Slurry Composition

The composition of pig manure may be affected by (O’Connell-Motherway, 1997): (1) category of pig (2) water consumption (3) house temperature (4) diet composition and (5) management of water supplies. The quality and amount of feed, feeding regime, animal size and building environment also impact upon the nutrient content and output volume of pig manure (Smith et al., 2000).

The main reason for the wide range in DM content of pig manure is dilution with water from spillages, washings and drainage. Much research has compared the effect of the systems used to provide drinking water to the pigs on water usage. Pederson (1994) showed that 30% less water was used when bowls were used in place of bite action drinkers. Bite action drinkers release water when a spring-loaded valve is opened by a biting action. The washing of pig houses also accounts for a large amount of water in the slurry system. To counteract this dilution, Roelofs et al. (1993) found

that soaking and the use of a turbo nozzle power washer reduced water usage during washing. Rainwater from gulleys and gutters, if allowed to flow into the slurry system, would have a significant effect on DM content. Good management of storage tanks and building equipment is crucial. Clean roof water should be diverted to a soak hole or open drain away from any source of pollution, rather than into manure tanks.

There is significant difference in the composition of pig slurry from different categories of pig. The DM content of slurry produced by sows is significantly lower than that produced by weaners and finishers (McCutcheon, 1997). The N, P and potassium (K) concentrations are all typically lower in sow-produced slurry (McCutcheon, 1997).

The amount of water consumed by the pig will affect the amount of urine produced and hence the DM of the manure. O'Connell-Motherway (1997) showed that by reducing the water-to-meal ratio from 4:1 to 2:1, there was a 50% reduction in the volume of manure produced by fattening pigs. The DM of the slurry produced was also over 50% higher when the water-to-meal ratio was reduced from 4:1 to 2:1. This was achieved without any apparent effect on feed performance.

There is an increase in the DM composition of manure when the pigs are housed at higher temperatures. This is due to the fact that the pigs lose more water as they sweat. O'Connell-Motherway et al. (1998) found that there was a significant reduction in slurry volume and an increase in slurry DM when pigs were kept at 28 to 30 °C than at 20 to 22 °C. Nitrogen excretion was also higher at the lower housing temperatures, which may be due to the reduced availability of energy for protein deposition. However, increasing house temperatures in this way would considerably increase heating bills.

A pig's diet affects the quality of manure that the pig produces (Velthof et al., 2005). Honeyman (1993) found that the faeces excreted by the pig are dependent on four aspects of the diet: (1) the amount of feed consumed (2) the proportions of each ingredient in the feed (3) their respective nutrient content and digestibility and (4) feed processing. O'Connell-Motherway et al. (1997) found that the N produced from pigs could be reduced by reducing the protein in the pig's diet. Nitrogen content in

manure was also lower in pigs fed with enzyme-supplemented feed. Animal nutritionists in Ireland and worldwide have made huge strides in reducing nutrient excretion in manure by formulating diets which meet, but not grossly exceed the animals' requirements, and by using enzymes (e.g. phytase to release P from plant bound phytate). Furthermore, meat and bone meal is no longer fed in Ireland and this alone has caused a reduction in the P content in pig manure.

2.2 Agriculture and the Environment

2.2.1 Water Quality in Ireland

The quality of surface and subsurface water in Ireland is governed by numerous European Directives. Arguably the most significant of these are the Water Framework Directive (WFD; 2000/60/EC; EC, 2000) and the Nitrates Directive (91/676/EEC; EEC, 1991). The WFD aims to achieve 'at least' good ecological status for all water bodies in all member states by 2015. The Nitrates Directive aims to reduce surface and groundwater pollution caused or induced by nitrates from agricultural sources, with the primary emphasis being on the management of livestock manures and other fertilizers. In order to comply with these Directives, member states must implement Programmes of Measures (POM). The European Communities (Good Agricultural Practice for Protection of Waters) Regulations 2006 (S.I. 378 of 2006) and its amendment (S.I. 610 of 2010) were adopted in Ireland as the POM to satisfy both Directives. The WFD requires that 3-year water catchment testing is undertaken to calculate the response to the POM. The Environmental Protection Agency (EPA) is responsible for the testing of water quality in Ireland. In their latest report, *Water Quality in Ireland, 2007 – 2009* (McGarrigle et al., 2010a), the EPA classified the water quality of groundwater, river water and lake water based on testing carried out between 2007 and 2009. Traditionally in Ireland, *water quality* has been determined using physico-chemical and biological parameters to assess pollution and eutrophication. However, to satisfy the criteria of the WFD, a new programme of measurements is required to determine *water status*. This programme of measurement includes biological, physico-chemical, morphological and chemical quality elements and the resulting *water status* often differs from the traditional *water quality* results

(McGarrigle et al., 2010a). The main findings of the Water Quality in Ireland, 2007 – 2009 study and other studies for groundwater and surface water now follow.

2.2.1.1 Groundwater

In Ireland, approximately 26% of drinking water supply is taken from groundwater sources (Lucey, 2009). In certain parts of the country, this value is much greater. In Roscommon, for example, 75% of drinking water is provided by groundwater (Lucey, 2009). The quality standards used for groundwater in Ireland are a combination of standards set by the EU and "threshold values". These threshold values (TVs) are locally derived standards established and maintained by the EPA to account for the natural characteristics of groundwater in Ireland. If the average concentration of pollutants exceeds the TV and evidence confirms the presence of an impact that compromises the achievement of WFD status objectives, then that groundwater body is classified as poor status (Craig et al., 2010). The Water Quality in Ireland, 2007 – 2009 study found 15.3% of the 211 groundwater sites monitored were of poor status. The greatest proportion (13.3%) of this pollution was attributed to the input of phosphates, most likely from agricultural activities, while only 0.3% was attributed to nitrates (Craig et al., 2010).

The TV for NO_3^- is $37.5 \text{ mg NO}_3^- \text{ L}^{-1}$. The average NO_3^- concentrations exceeded this value at 4.7% of sample locations. The WFD sets the recommended NO_3^- levels for drinking water concentration to 25 mg L^{-1} with the maximum concentration (MAC) being $50 \text{ mg NO}_3^- \text{ L}^{-1}$. The Water Quality in Ireland, 2007 – 2009 study found that 0.9% of sample locations had an average NO_3^- concentration which exceeded the MAC of $50 \text{ mg L}^{-1} \text{ NO}_3^-$ (Craig et al., 2010). The TV for ammonium (NH_4^+) is $0.065 \text{ mg N L}^{-1}$. Eighty one percent of locations achieved an average NH_4^+ concentration below this limit. The Drinking Water MAC is 0.23 mg N L^{-1} and the average NH_4^+ concentration exceeded this value at 6 of the 211 sampling locations (Craig et al., 2010). The average mean concentration of phosphate exceeded the TV of $0.035 \text{ mg P L}^{-1}$ in 7.6% of sample locations, while 3.8% exceeded 0.05 mg P L^{-1} (Craig et al., 2010).

Nutrient pressures from agricultural activities (including livestock farming, arable activities and intensive enterprises) and usage of dangerous substances, e.g. agrochemicals, are the most widespread and nationally significant anthropogenic pressure on groundwater (Craig et al., 2010). However, there has been an improvement in groundwater quality since the previous testing period, 2004 – 2006 (Clabby et al., 2008). Upgrading of slurry storage facilities, reduction in organic fertiliser usage, the implementation of landspreading regulations and higher than average rainfall have been credited with this improvement (Craig et al., 2010).

2.2.1.2 River and Lake Water

More than 30% of the annual flow of river water in Ireland is derived from groundwater. This percentage can increase to greater the 90% during periods of low flow (McGarrigle et al., 2010b). Therefore, any change in the quality of groundwater has a knock-on effect on the quality of river water. The Water Quality in Ireland, 2007 - 2009 study found that 10.4% of the 13,188 km of river network tested was moderately or seriously polluted (McGarrigle et al., 2010b). Twenty one percent of rivers were found to be slightly polluted, while 69% achieved unpolluted status (Figure 2.2). Agriculture was found to be the likely cause of pollution in 47% of the sites which were classified as polluted or of a less than good status. In 2007, 27 river sites were classified as severely polluted. By 2009 this figure had reduced to 20, three of which were caused by agricultural discharges (McGarrigle et al., 2010b).

Over the period 2007 – 2009, there were 72 reported fish kills in Irish rivers (McGarrigle et al., 2010b). Of these, 17% were likely to have been caused by agriculture. There were no incidences of agriculture-caused fish kills in 2009. This is a huge improvement on previous years. For example, for the period 1986 -1988, there were approximately 150 occurrences of fish kills which were attributed to agriculture (McGarrigle et al., 2010b).

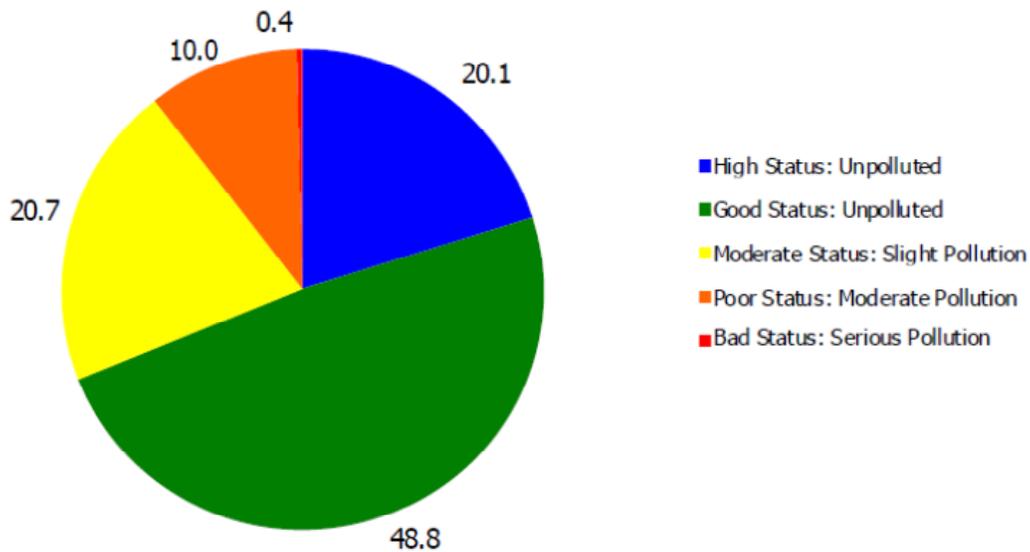


Figure 2.2 River biological status 2007 -2009 (McGarrigle et al., 2010b)

The Water Quality in Ireland, 2007 – 2009 study tested 222 lakes representing 988 km² of lake water. The WFD classification for lake water is based in both the physico-chemical status (total ammonia, dissolved oxygen concentration and pH) of the water and the biological status (aquatic flora, phytoplankton and fish) of the lake. The final ecological status is based on the lowest status quality element. The Water Quality in Ireland, 2007 – 2009 study found that 47% of the lakes achieved high or good, 41% achieved moderate status, while 11% were poor or bad status (Tierney et al., 2010). There are no criteria yet set for NO₃⁻ for lake water as part of the WFD. However, the study found that most samples were below 2 mg L⁻¹ NO₃⁻. There are also no criteria yet set for total P (TP) for lake water as part of the WFD. Clabby et al. (2008) found that significant deterioration is seen in river ecosystems in Ireland once median phosphate concentrations exceed 30 P µg L⁻¹. The TV for TP is 20 P µg L⁻¹. Fifty eight percent of lakes were below this threshold. However, 34% of lakes had a TP value greater than 50 µg P L⁻¹ (Tierney et al., 2010). In general, the incidence of environmentally significant concentrations of metal is low in Irish waters (McGarrigle et al., 2010b).

2.3 Landspreading of Pig Manure

2.3.1 Landspreading Regulations

In order to achieve the aims of the Nitrates Directive, member states must place restrictions on agricultural practices where these contribute to nitrate pollution and identify waters affected by nitrate pollution (EEC, 1991). This Directive was implemented in Ireland with the publication of the European Communities (Good Agricultural Practice for Protection of Waters) Regulations 2006 (S.I. 378 of 2006). The latest review of these Regulations occurred in 2010 (S.I. 610 of 2010).

Measures implemented on farms to reduce the nitrate pollution include: (1) periods during which neither organic nor chemical fertilisers may be applied to the soil (2) buffer zones around water bodies inside which spreading and storage of organic fertilisers is prohibited (3) the requirement of every farm to have sufficient capacity to store manure during times when spreading is prohibited (4) the requirement for application of fertilizers to be based on a balance between the nitrogen requirement of the crops and their supply from soil and fertilization and (5) the requirement for the application of a general land spreading limit of 170 kg N ha⁻¹ year⁻¹ from livestock manure. The limit of application of P to land is dependent on land use and Soil P Index. The Soil P Index is used to categorise soils in Ireland based on the Soil Test P (STP), measured as Morgan's P, in the soil (Table 2.3). Soils with a P index of 1 and 2 are said to be deficient and low in STP, respectively; a P Index of 3 denotes optimum STP concentrations, while soils with a P index of 4 have excessive STP and have a higher risk of P loss in runoff (Schulte et al., 2010).

Table 2.3 Phosphorus index system (S.I. 610 of 2010)

Soil phosphorus Index	Soil phosphorus ranges (mg L ⁻¹)	
	Grassland	Other crops
1	0.0 – 3.0	0.0 – 3.0
2	3.1 – 5.0	3.1 – 6.0
3	5.1 – 8.0	6.1 – 10.0
4	> 8.0	> 10.0

According to this legislation, a sow (including its progeny to slaughter) produces between 16.2 and 25.1 tonnes of liquid manure annually, based on the water-to-meal ratio. This manure is estimated to contain 4.2 kg N t^{-1} and 0.8 kg P t^{-1} (S.I. 610 of 2010). Most of this manure is landspread. However, pig farmers rarely have sufficient land to spread all of the manure being produced on their farms and rely on neighbouring farmers, especially tillage farmers, to landspread the manure on their farms. To date, many pig farmers only had to comply with the landspreading limit of 170 kg ha^{-1} year $^{-1}$ for organic N. Landspreading limits for P could be exceeded (1) when spreading spent mushroom compost, poultry manure, or pig slurry (2) if the size of a holding has not increased since 1st August 2006 and (3) if the N application limit is not exceeded (S.I. 610 of 2010). However, the land available for landspreading of pig manure will further be restricted, starting in 2013, and culminating in 2017, when the transitional period allowing for landspreading of pig manure exceeding the crop's P requirements for growth will expire (S.I. 610 of 2010) (Table 2.4). From 2017 onwards, the application of organic phosphorus to grassland and most tillage soils at soil P index 4 ($\text{P} > 8.0 \text{ mg L}^{-1}$) will be prohibited. Many grassland soils which have previously been used as spreadlands for pig manure are likely to be at P index 4, thereby preventing further manure application (Hackett, 2007). The implication of this will be that pig farmers will require an additional ~50% spreadlands than is the case in 2012. Fealy et al. (2012) attempted to quantify the required distance that pig manure will have to be transported to the nearest available tillage land, assuming that grasslands which were previously used will be exempt in 2017 when soil P requirements are considered. They found that the average journey distance in Ireland will be 21 km (Fealy et al., 2012). This is below the limit of 30 km whereby the cost of landspreading exceeds the fertiliser value of the pig manure (McCutcheon and Lynch, 2008). However, pig-dense counties, such as Longford and Cavan, will have to travel an average distance of 63 and 56 km, respectively (Fealy et al., 2012).

The resulting increase in manure transport costs for farmers in pig-dense regions, along with the potential of surface and groundwater pollution from the landspreading of manure, has resulted in the need for practical and economical on-farm solutions for swine wastewater treatment.

Table 2.4 Phosphorus excess limits (S.I. 610 of 2010)

Date	Amount by which Regulations can be exceeded (kg P ha ⁻¹)
To January 1, 2013 ^a	Not limited
January 1, 2013 - January 1, 2015	5
January 1, 2015 - January 1, 2017	3
January 1, 2017 onwards	0

^aUp to 1 January 2013, the regulation limits can be exceeded when spreading spent mushroom compost, poultry manure, or pig slurry only if the activities which produce this on a holding have not increased in scale since 1 August 2006, and the N application limit is not exceeded.

2.3.2 Manure Application to Soil

The growth of plants is limited by the amount of nutrients that are present in the soil. This growth is limited by the nutrient which is present in the least quantity relative to plant demands. It has been shown that inorganic N and P are the two nutrients that limit the growth of plants (Schlesinger, 1991; Vitousek and Howarth, 1991). Intensive agriculture causes the loss of organic matter (OM) and nutrients, leading to soil degradation (Anderson, 2003). In intensive livestock production areas, land application remains the foremost method of nutrient recycling of manure and slurries. This has resulted in a build-up of major nutrients (such as N, P, and K) and micro-nutrients (such as copper (Cu) and zinc (Zn)) in the soil profiles (Coppinet et al., 1993; Leinweber et al., 1997).

2.3.2.1 Nitrogen

Nitrogen in freshly excreted pig manure is primarily in the form of organic N and NH₄⁺. The organic N must be broken down by soil microbes before it becomes available to plants and, therefore, it is a slow release form of nitrogen. The percentage of total N (TN) present as NH₄⁺ in pig manure is typically between 60-70% (Hackett, 2007) (Figure 2.3). The organic N can be converted to NH₄⁺ through mineralization after soil application or during storage. Mineralisation occurs readily in warm, moist, well-aerated soils. Ammonium is readily available to plants when applied to the soil and is easily adsorbed to soil particles and, therefore, it generally does not leach from

the root zone. Organic N can also be converted to ammonia gas (NH_3) and may be lost to the atmosphere through ammonia volatilisation. Manures which are landspread and not incorporated into the soil are most at risk of volatilisation.

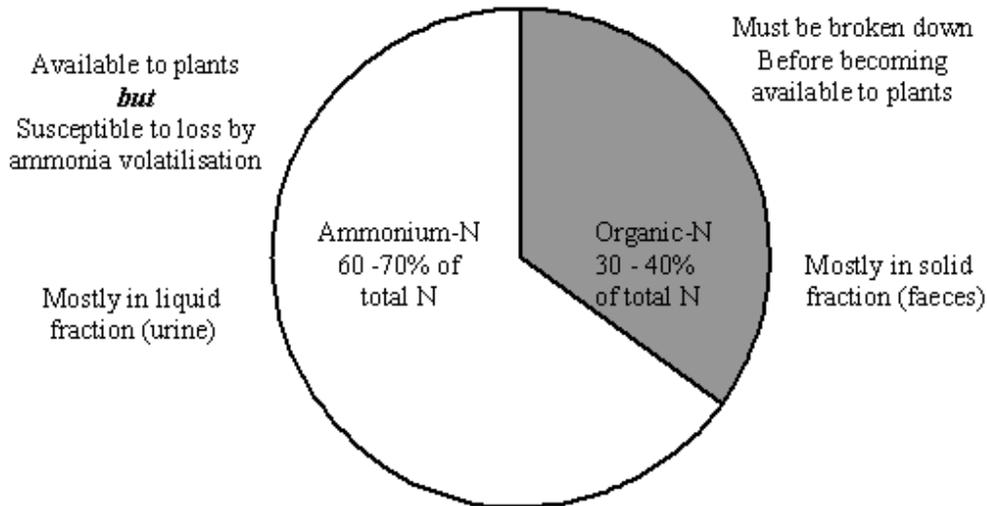


Figure 2.3 Forms of N in pig manure (Hackett, 2007)

Micro-organisms within the soil convert NH_4^+ through nitrite (NO_2^-) to NO_3^- in order to obtain energy. This nitrification process occurs best in moist, well-aerated soils. Nitrate N is also a readily plant-available form of N. However, NO_3^- cannot be retained well by soil particles due to its negative charge. It is also highly soluble and can move easily with the soil water, making it very susceptible to downward leaching to groundwater. In waterlogged soils, NO_3^- may be converted to NO_2^- and eventually to N_2 or N_2O as a result of denitrification. During this process, bacteria use NO_3^- instead of oxygen in their metabolic processes due to the absence of oxygen in the wet soil. When the N supply is limited in a soil, microbes compete with plants for NO_3^- and NH_4^+ in a process called immobilization. Figure 2.4 details the nitrogen cycle in soil.

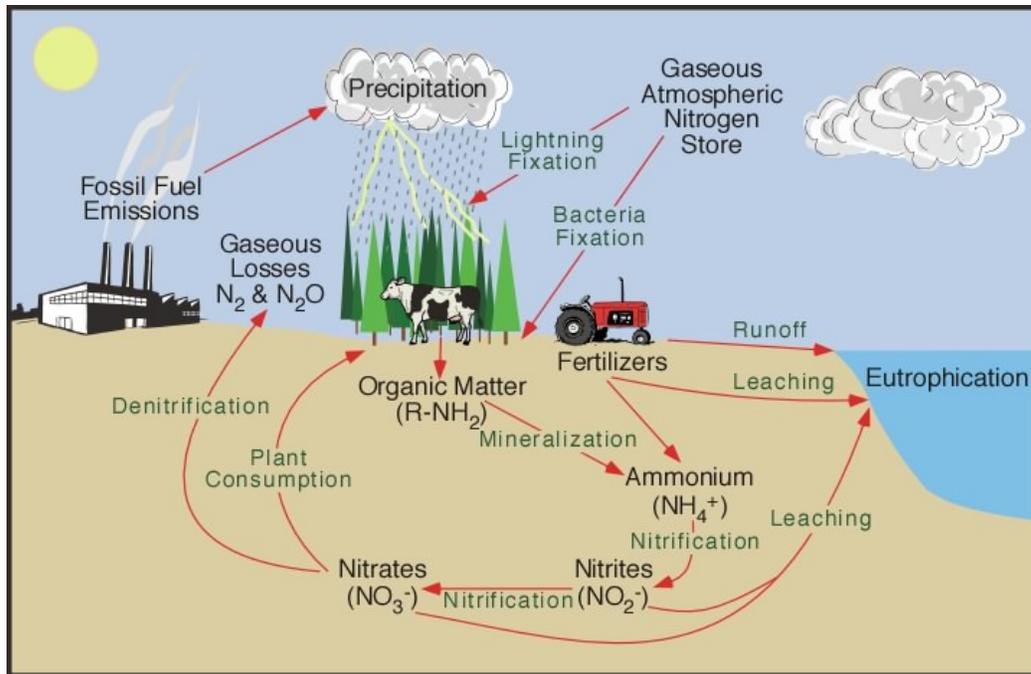


Figure 2.4 The nitrogen cycle in soils (Pidwirny, 2006)

When N applied to a soil is in excess of the requirements from plants, the surplus N can behave in four ways. It may: (1) accumulate in the soil, where it may be used by the plants in the future, (2) leach downwards through the soil and into the groundwater, (3) flow by surface runoff into nearby water bodies, or (4) enter the atmosphere via ammonia volatilization (Vitousek et al., 1997; Carpenter et al., 1998). Smith et al. (2001) compared surface runoff and subsurface flow from farmyard manure, cattle slurry and inorganic fertiliser application to silt clay loam soil over four years. Losses through surface flow were significantly higher than those through subsurface flow. Ammonium concentrations in surface water flow increased after cattle slurry application. Ammonium concentrations also increased with increasing slurry application rate and increasing solids application rate, indicating that sealing of the soil surface may have been the mechanism for through which pollution of the surface water occurs.

Most of N leached from soil is in the form of NO₃⁻ as this does not absorb to soil particles. Olson et al. (2009) investigated manure application to both coarse and medium textured soils in an 8-year field experiment. The treatments investigated were

inorganic fertiliser applied at a rate of 180 kg N ha⁻¹year⁻¹ and cattle manure applied at 20, 40, 60 and 120 tonne ha⁻¹year⁻¹. Olson et al. (2009) found that for every tonne of TN added from manure, the NO₃⁻ concentrations in the top 1.5m of soil increased by 50 kg ha⁻¹ in the coarse textured soil and by 100 kg ha⁻¹ in the medium textured soil. It was also found that groundwater NO₃⁻ concentrations in the medium textured soil were unaffected. However, the addition of the inorganic fertiliser and the addition of the highest rate of manure application significantly increased the groundwater NO₃⁻ concentrations in the coarse textured soil.

Mantovi et al. (2006) studied NO₃⁻ leaching following pig slurry application, over six years, in a nitrate vulnerable zone in Northern Italy. It was recommended that manure application in summer on arable land, which will remain bare in winter, be avoided. This will limit N accumulation in the surface layer of these soils and prevent leaching into groundwater during winter rainy periods. Guerrero et al. (2006) found that the use of composted solids of pig slurry is preferable to non-composted slurry solids in order to avoid excessive inorganic N production and groundwater contamination.

2.3.2.2 Phosphorus

The input of P from agricultural activities is the main cause of groundwater pollution in Ireland (Craig et al., 2010). The N:P ratio in manure, at approximately 4:1, is lower than N:P ratio of 8:1 taken up by major grain and hay crops (SI 610 of 2010). Manure nutrient management for cropland in Europe and North America has traditionally been based on crop N requirements, resulting in increases in soil P levels in excess of crop requirements (Sharpley et al., 1998; Sims, 2000). This excess P in the soil may be lost through surface runoff to surface water bodies (Regan et al., 2010) or through downward leaching to groundwater bodies (Vadas, 2006).

2.3.2.2.1 Surface Runoff

Surface runoff is the predominant P transport pathway from soils to water bodies. Surface runoff of P from soil may be classed as (1) incidental or (2) chronic. Incidental P runoff occurs when a rainfall event takes place shortly after a slurry application and before the slurry can infiltrate into the soil. Using intact soil columns

to a depth of 15 cm, Vadas (2006) found that after 96 hours from time of surface application of swine slurry at a rate of 100 kg P ha⁻¹, 20% of suspended solids (SS) and 65% of TP had infiltrated below the soil surface. This resulted in significantly increased water extractable P (WEP) and Mehlich-3 P concentrations in the top 1 cm of soil, 24 hours and 96 hours after slurry application. However, they found that only minimal amounts of slurry P infiltrated below 1 cm into the soil after 96 hours.

Brennan et al. (2011) compared nutrient and sediment release following the landspreading of dairy cattle slurry, at an application rate of 26 kg TP ha⁻¹, to a poorly-drained, sandy-loam soil. Incidental runoff was measured after three one-hour rainfall simulations, each at an intensity of 10.5 mm hour⁻¹. The authors reported that incidental dissolved reactive P (DRP) and TP concentrations on the runoff water were 5 and 14 times greater from the slurry amended soil, while the SS were 18 times greater. In a similar study, O'Flynn et al. (2012) measured P runoff following the application of pig manure at a rate of 19 kg TP ha⁻¹ to a grassland soil. Incidental runoff was measured after three half-hour rainfall simulations, each at an intensity of 10.3 mm hour⁻¹. The DRP and TP concentrations in the runoff water increased by 2.5 and 3.5 times following the application of pig manure.

Chronic P runoff is a long-term loss of P from soil as a result of a build-up in STP caused by applications of inorganic and organic fertilizer (Haygarth et al., 1998; Buda et al., 2009; Schulte et al., 2010). Soils at soil P Index 4 are considered to have excessive STP, with no yield response to P additions. These soils are at the greatest risk of transferring this excess P via surface runoff to water bodies (Tunney, 2000; Regan et al., 2010). Daly et al. (2001) investigated the P sorption and desorption dynamics of 11 major agricultural grassland soils in Ireland. They found that the mineral soils investigated were heavily saturated with P, indicating P fertilisation in excess of crop requirements was occurring. The P sorption capacity decreased with increasing OM content in soils. Peat soils had a very limited capacity for P sorption and storage, and any P input in excess of crop demand may be lost as surface runoff. Regan et al. (2010) compared nutrient and sediment release in five Irish tillage soils using rainfall simulation studies at an intensity of 30 mm hour⁻¹ and found that tillage soils produce surface runoff with DRP concentrations in excess of 30 µg L⁻¹ (the value above which eutrophication of rivers is likely to occur and the MAC of DRP in rivers

under the WFD (Clabby et al., 2008)) if their Morgan's P, Mehlich-3 P, and WEP concentrations exceed 9.5 mg L^{-1} , 67.2 mg kg^{-1} , and 4.4 mg kg^{-1} , respectively.

2.3.2.2.2 *Leaching*

Accumulated P may be lost from the soil through downward leaching to groundwater, either by slow leaching through the soil profile or preferential flow through macropores (Sims et al., 1998). The sorption capacities of the soil, the potential for P release from the soil, and the pathways for preferential flow within the soil structure are the most important factors which may contribute to P leaching loss from soil receiving P fertilisation (Djodjic et al., 2004). Preferential flow is the main transport mechanism for P leaching in fine-textured soils (Djodjic et al., 2004; van Es et al., 2004), while P sorption capacity is generally the most important factor for P leaching in slow-draining soils (Djodjic et al., 2004). When P sorption capacity of a soil becomes filled, the risks P leaching to groundwater increases (Sims et al., 1998). The application of manures to soil has been shown to significantly decrease the P sorption maxima of the soil (Siddique and Robinson, 2003).

The form in which P is applied to the soil may also affect the way in which P is leached through the soil. A long-term (40 years) manure application study undertaken in a corn field in western Nebraska showed that P from manure application moved deeper into the soil than P from artificial fertilisers. The P from the manure may travel further due to it being in organic form, or due to increased solubility (Eghball et al., 1995).

Phosphorus can become fixed in soil; therefore leaching is generally thought to be of little concern when compared to surface runoff (Haygarth et al., 1998; Algoazany et al., 2007). However, it may also be a significant pathway to surface waters sensitive to eutrophication, as concentrations as low as $30 \text{ }\mu\text{gL}^{-1}$ P can cause significant deterioration in river ecosystems (Clabby et al., 2008). Long-term applications of animal manures can lead to leaching of P into groundwater, especially in areas with a high water tables or coarse soils (Eghball et al., 1995; Novak et al., 2000). In Ireland, more than 30% of the annual flow of river water is derived from groundwater, with this value increasing to greater than 90% during periods of low flow (McGarrigle et

al., 2010b). Therefore, excess soil P leaching to groundwater has the potential to reach surface water bodies where it may lead to eutrophication.

2.4 Alternatives to Landspreading of Pig Manure

2.4.1 Introduction

Traditionally in Ireland, the treatment of pig manure involves landspreading. However, as described in Section 2.3, landspreading of pig manure can have negative effects on the environment and the legislation governing its use has made it more expensive for pig farmers to use this method of manure treatment. Therefore, pig manure treatment strategies other than the direct application to land spreading need to be considered and exploited if applicable.

Anaerobic digestion (AD) is a technology which can use manure as a feedstock to produce energy to use on the pig farm or to export to the electrical grid. However, AD does little to reduce the nutrient content of pig manure, which still needs to be recycled in the same way as undigested manure. Slurry separation can be used to produce a solid fraction and a liquid fraction. The solid fraction after separation can be exported at a lower cost than unseparated manure due to its high DM content. Alternatively, the solid fraction can be composted or used as a feedstock for pyrolysis to produce renewable energy and biochar. The liquid fraction can be used to irrigate land nearby the pig farm, or alternatively be further treated using woodchip bio-filters or integrated constructed wetlands.

2.4.2 Anaerobic Digestion

Anaerobic digestion uses micro-organisms to convert organic wastes (such as manures or sludge) and biomass (such as wood or crop residues) into a bio-gas which can be used for electricity and/or heat generation. When compared with landspreading pig manure, AD has a number of additional benefits: (1) production of renewable energy which can be exported as an additional income source for farmers (2) improvement in the fertiliser value of the manure (3) reduction in pathogens and foul odours and (4) reduction in pollution potential (Xie et al., 2012). However, AD does

not reduce the overall nutrient concentrations in the manure. Additionally, as pig manure is generally co-digested with other feedstocks, the N and P content of the digestate may be even higher than that of the raw manure. Therefore, the problem of manure treatment is only replaced with that of digestate treatment.

Anaerobic digestion of manures is already a widely used technology on mainland Europe, especially in Germany, Denmark, Austria and Sweden (Holm-Nielsen et al., 2009). There are two models used for AD of manure in these countries: farm-scale units and centralised plants (Holm-Nielsen et al., 2009). In Germany, there are more than 4000 on-farm AD units (Wilkinson, 2011). The German government intends to increase this number to between 10,000 and 12,000 by 2020 to meet renewable energy targets (Wilkinson, 2011). In Denmark, there are 21 large-scale centralised AD systems and 60 farm-scale plants. These treat 5% of all manure produced in Denmark. The centralised plants are mostly owned by groups of farmers or co-operatives of farmers and heat consumers. Recent increases in Danish Government incentives are expected to increase the number of centralised plants by around 50, tripling the amount of biogas production by 2025. They aim to process 50% of all animal manures using AD by 2020 (Holm-Nielsen, 2009).

Pig manure is a good feedstock for AD as it has a high OM content, a high buffering capacity and plentiful nutrients to allow for bacterial growth (Cuestos et al., 2011). However, pig manure has a relatively high N content, which may inhibit digestion due to the production of high levels of ammonia if digested individually (Hansen et al., 1998). For this reason, manures should be co-digested with high C wastes, such as crop residues to improve the carbon: nitrogen (C:N) ratio of the feedstock (Mata-Alvarez et al., 2000). Cuestos et al. (2011) found a major increase in the amount of biogas produced daily when crop residues were digested with pig manure, in comparison to pig manure digestion alone. Xie et al (2011) investigated AD of pig manure and grass silage under different ratios of pig manure-to-grass silage on a volatile solids (VS) basis. They found that applying a pig manure-to-grass silage VS ratio of 1:1 was best due to the high specific methane yield and short lag phase.

Nolan et al. (2012) performed an economic analysis on the co-digestion of pig manure and grass silage using a volatile solids ratio of 1:1. They found that the viability of an

anaerobic digester in Ireland depended on the size of the farm, the import infrastructure and the tariff paid for electricity exported to the grid. Anyone exporting electricity to the national grid is responsible for the costs associated with grid connection. If the farmer already has a large import infrastructure, his grid connection agreement may only require ‘metering infrastructure’ at a small cost (< €10,000). However, a much larger investment of up to €250,000+ will be required if cables, transformer upgrades etc. are required (Nolan et al., 2012). In Ireland, new support tariffs for biomass technologies (REFIT 3) which received clearance from the European Commission in October 2011, were approved by Government in December 2011 and were opened for new applications in January 2012 (Department of Communications, Energy and Natural Resources, 2012). Electricity exported to the national grid is paid at €0.15 kWh⁻¹ from a combined heat and power (CHP) plant smaller than 500 kW and €0.13 kWh⁻¹ for a CHP plant greater than 500 kW. In Germany, the equivalent price is €0.26 kWh⁻¹ (Blokhina et al., 2011). Nolan et al. (2012) found that under the current renewable energy feed-in tariffs, co-digestion of pig manure and grass silage for a 500-sow unit is not a financially feasible treatment option. Feed-in tariffs as high as €0.27 and €0.18 kWh⁻¹ would be required to reach break-even point for a 500 and 2000 sow unit, respectively.

Therefore, at the present time, with current feed-in tariffs, co-digestion with grass silage is not a feasible treatment option for pig manure in Ireland. However, with rising oil prices increasing the cost of landspreading and heating for pig farmers, and with pig farm sizes increasing, it is feasible that AD of pig manure will be an attractive technology in the future, especially if the farm has good import infrastructure.

2.4.3 Slurry Separation

As described in Section 2.3.1, recent landspreading legislation will result in pig farmers requiring an additional ~50% spreadlands for manure application by 2017, than is the case in 2010. Therefore, the distance that manure will need to be transported is likely to increase, which will result in increased transportation costs. Treanor (2008) modelled manure handling costs and concluded that the single most important factor in controlling cost of manure transportation is DM content. For liquid

pig manure with a DM of 4% and 2%, for example, the maximum economical haulage distance by tractor and vacuum tanker was 18 and 7 km, respectively (Treanor, 2008). One way of increasing DM content of manure is through separation.

The separation of manure produces a solid fraction and a liquid fraction. The solid fraction can be applied to fields as a fertiliser, composted, or used as a fuel. The liquid fraction may be irrigated, or it could be treated further using constructed wetlands (CWs) or woodchip bio-filters. There are many methods of slurry separation. These include: (1) sedimentation (2) filtration and (3) mechanical methods. Efficient separation usually requires the use of chemical additives to the slurry to encourage the binding of smaller particles before separation begins.

2.4.3.1 Use of Chemical Additives

Most of the organic nutrients and odour-generating compounds in swine manure are contained in very fine (<0.3 mm in size) suspended particles that are not separated by mechanical separators (Zhang and Westerman, 1997; Vanotti et al., 2002). Separation efficiency of swine manure is greatly improved by the addition of chemical additives before separation. The chemical additives act to bind together the fine particles into larger, more easily separated particles. These chemical additives include metal salts (ferric chloride and aluminium sulphate (alum)) and organic polymers. Metal salts are effective in coagulating suspended particles in the manure to form flocs which enhance the settling rate (Zhang and Lei, 1998). Polyacrylamide (PAM) polymers effectively flocculate the manure particles into large, rapidly settling flocs. This enhances the separation efficiency (Walker and Kelley, 2003; Vanotti et al., 2005). Linear cationic PAM polymers are more effective for the flocculation of animal slurries than branched or anionic types (Vanotti and Hunt; 1999; Rodriguez et al., 2005).

2.4.3.2 Sedimentation

During sedimentation, the manure is placed in a settling basin. The solids in the manure settle to the bottom of the basin over time, resulting in a solids layer at the bottom with a liquid layer on the top. Sedimentation can be made to work more

efficiently by adding organic polymers or metal salts to the liquid manure as it enters the settling basin (Sievers et al., 1994; Zhang and Lei, 1998). Walker and Kelley (2003) evaluated four different concentrations of PAM on gravity settling of swine manure. They found that an optimal PAM concentration for the removal of SS, total solids (TS) and chemical oxygen demand (COD) was between 62.5 and 125 mg L⁻¹, and for N and P reduction, the optimal concentration is between 375 and 750 mg L⁻¹.

Worley and Das (2000) used a settling basin and skimmer to remove solids from liquid swine waste with and without the addition of alum. A 240 m³ capacity settling basin was used with an average depth of 0.6 m. The basin was filled and allowed to settle for 15 minutes before draining began. The initial TS concentration of the swine manure was 15.2 kg m⁻³. Without alum, this was reduced by 58% after sedimentation. They also reported 38% and 18% reductions in P and N, respectively. With alum addition at a rate of 2900mg alum L⁻¹ of liquid waste, TS removal efficiency increased to 72%, while P and N reduction efficiencies rose to 75% and 25%, respectively. Moore et al. (1975) measured settling efficiency of liquid swine manure over time. They reported that 52% of TS were removed in the first minute of settling, while 62% of TS settled after 10 minutes and 66% of TS were removed at 100 minutes.

2.4.3.3 Filtration

Filtration involves passing the swine manure through natural (e.g. sand or crop residues) or man-made (e.g. porous membrane) filter media. The solid particles in the manure become trapped by the filters while the liquid fraction passes through. Zhang and Lorimor (2000) filtered swine manure using readily available crop residues as filter media (oat straw, soybean stubble, corn stover and corn cobs). Swine manure with a DM of 4% was applied to a 25-cm-diameter x 58-cm-tall PVC cylinder containing the filter media. This process was repeated until the filter clogged. They found that oat straw, corn stover and soybean were effective as filter media with average DM removal efficiencies from 24.5 to 42.2%. Removal efficiencies and filtration times increased with each additional unit of manure applied.

Sand filtration of swine manure with the addition of PAM is also efficient in removing DM and nutrients from pig manure (Vanotti et al., 2005). This study found that polymer flocculation improved drainage characteristics of sand filter beds and prevented clogging and surface sealing with repeated applications by increasing the particle size of manure. The sand bed consisted of 45 cm of washed stone on the bottom, a 15 cm pea gravel middle layer and 15 cm of coarse gravel on the top. The optimum flow rate was found to be 490 L min⁻¹ while the optimum PAM application was 348 mg L⁻¹. The process removed 97% of SS, 85% of 5-day biochemical oxygen demand (BOD₅), 83% of COD, 61% of total Kjeldahl N and 72% TP.

Membrane separation also works on the principle of filtration. Membranes can be grouped according to pore size; micro filtration (100 to 2000 nm), ultra filtration (10 to 100nm), nano-filtration (1 to 10 nm) and reverse osmosis (<1 nm) (Burton, 2007). Unlike other forms of separation, membrane separation can be highly efficient in removing N. However, this technology is still too expensive to be used at a farm level. Membrane separation is currently the only option for the removal of the finest particles and dissolved matter. However, because they are only suitable for very dilute effluents due to its very fine pore size, pre-treatment of the liquid pig manure is needed. The membrane separation step is often included as the last step in a complete treatment process (Pieters et al., 1999; Zhang et al., 2002). In a laboratory scale treatment system where membrane separation was used as the last step after anaerobic digestion and sand filtration, the recovery of TN and TP was 84 and 100%, respectively (Zhang et al., 2002).

2.4.3.4 Mechanical

2.4.3.4.1 Screen Separators

Screen separators also use filtration to remove solids from swine manure. Slurry flows over a metal screen and the liquid fraction passes down through the screen while the solids are held. Screen separators may be stationary, tilted, brushed, vibrating or rotating. Vibrating screen separators have a screen that vibrates rapidly, avoiding clogging, while rotating screen separators have a screen that turns continuously, allowing liquid to pass through the screen and solids to move across the screen.

Presses work on the principle of mechanical pressure where the liquid is squeezed out and the solids remain on a screen (roller press) or perforated belt (belt press). In a screw press, a screw-type conveyor forces the manure through a tube and past a cylindrical screen. Solids retained on the screen are pressed to the end and discharged.

Moller et al. (2000) separated pig slurry using five different mechanical screen separators (tilted plane screen, 2-stage separator, belt press separator and two different screw presses). They reported DM separation efficiencies of 22-43%. However, the efficiency for TP was almost zero in three of the treatments and almost no TN was separated in four of the treatments. Separation by screening alone is quite ineffective. However, screen separation efficiency can be increased substantially by flocculating the flushed swine manure with a cationic polymer (Zhang and Lei; 1998; Vanotti et al., 2002). Vanotti et al. (2002) flocculated flushed swine manure with various rates of PAM polymer (0 to 140 mg L⁻¹) before passing it through a stationary screen. Using the highest rate of PAM addition (140 mg L⁻¹), a TS separation rate of 95% was achieved. Removal rates of 69% and 59% were achieved for COD and BOD₅, respectively.

2.4.3.4.2 *Decanting Centrifuges*

Centrifugation uses centrifugal forces to increase the settling velocity of suspended particles. Decanter centrifuges have an auger that turns at a slightly higher speed than the cylinder in which it is contained. This force causes the heavier solids to move to the outside wall of the cylinder where they are removed. Gilkinson and Frost (2007) used a decanting centrifuge to separate swine manure with and without chemical additives. Without chemicals, they removed 53%, 21% and 79% of TS, TN and TP from the solid stream. They tested separation efficiency using different quantities of alum (0.16%, 0.24% and 0.38% of slurry volume) and PAM (diluted to 0.4% by volume and then added to the slurry at 17% of slurry volume). The addition of these chemicals increased the removal rate to an average of 71%, 34% and 93%, respectively, for TS, TN and TP. The separation efficiency for NH₄⁺ and K was poor with and without the added chemicals. Moller et al. (2002) compared the separation efficiency of a decanter centrifuge and a screw press separator using liquid pig manure with a DM of 5.3%. They found that the decanter centrifuge separation

efficiency was much higher (60.5% for TS, 62.3% for TP and 29.3% for TN) than screw press separation efficiency (27.3% for DM, 7.1% for TP and 6.6% for TN). The removal percentage of DM and TN in the decanter centrifuge was related to the amount of TS in the input liquid manure.

2.4.4 Liquid fraction

The separation of manure produces a solid fraction and a liquid fraction. The liquid fraction can be applied to nearby land around the pig farm. It has an increased N:P ratio which results in a more balanced fertiliser for crops (Worley and Das, 2000; Vanotti et al., 2002), and has greatly reduced levels of insoluble OM, P and heavy metals. If land is not readily available nearby to spread the liquid fraction after separation, then other treatment options such as CWs or woodchip bio-filters are available.

2.4.4.1 Constructed Wetlands

There are over 140 CWs in use in Ireland (Babatunde et al. 2008). Most of these CWs are designed for the treatment of municipal or domestic wastewater (Healy and O'Flynn, 2011). However, some of these CWs treat influent from agricultural sources, especially dairy yard runoff (Healy and O'Flynn, 2011). There are two types of CW: free water surface flow CWs and sub-surface flow CWs. In free water surface flow CWs, wastewater flows in a shallow water layer over a soil substrate. In sub-surface CWs, the wastewater flows through a sand or gravel below the surface. Constructed wetlands may be planted with a mixture of submerged, emergent and, in the case of free water surface flow CWs, floating vegetation (Healy et al., 2007; Healy and O'Flynn, 2011).

Integrated Constructed Wetlands (ICWs) have also become popular in Ireland. This is essentially a traditional CW, but it takes economic, social, environmental, and landscape aesthetic aspects into consideration in their design, construction and operation (Harrington and Scholz, 2011). Integrated Constructed Wetlands promote nature conservation and an integrated management of land, water and living resources (Harrington and McInnes, 2009). Harrington and Scholz (2011) investigated the

treatment of the separated liquid fraction of anaerobically digested pig manure in meso-scale ICWs. They found that the ICWs were effective in removing total organic N, NH_4^+ , and NO_3^- and DRP. In a related study using the same meso-scale ICWs, McCarthy et al. (2011b) found that coliform, yeast and mould and spore-forming bacteria counts were reduced by flow through the ICWs. However, in an economic analysis, Nolan et al. (2012) found that the treatment of the separated liquid fraction of pig manure by ICWs, added a cost of €4.60 m^3 manure, in addition to separation costs, and was not cost-effective.

2.4.4.2 Woodchip Bio-filters

Woodchip bio-filters can be used to treated dilute waste waters such as dairy soiled water or the liquid fraction of separated pig manure. Effluent passes through the woodchip bio-filters and is treated by the physical, chemical and biological processes that occur within the filter (Carney et al., 2011). The idea of treating manure using woodchip bio-filters originates from the use of out-wintering woodchip pads. These pads originated in New Zealand but have become popular in Ireland and Scotland as an environmentally beneficial means of over-wintering cattle (McDonald et al., 2008). Ruane et al. (2011) studied the removal of OM, SS and nutrients from dairy soiled water using 100 m^2 by 1 m deep farm-scale aerobic woodchip filter. The study found that the average reduction in COD, SS and TN, over the 11 month duration of the study was 66, 86 and 57%, respectively, in the filters.

2.4.5 Solid fraction

The solid fraction of separated pig manure has a much higher P concentration than that of the unseparated manure. Gilkinson and Frost (2007) reported that 93% of the TP in pig slurry was partitioned into the solid fraction after separation with a decanter centrifuge, when chemical additives were used. However, only 34 and 41% of K and NH_3 , respectively, were partitioned into the solid fraction. The weight of separated solids produced after separation is dependent on the DM content of the input manure (Gilkinson and Frost, 2007). Dry matter content is the single most important factor in controlling cost of manure transportation (Treanor, 2008). Therefore, the separated solid fraction of pig manure may be exported more cheaply than unseparated manure.

Further options for the treatment of the solid fraction are to use it to produce compost or to use it as a feedstock for pyrolysis to produce renewable energy and biochar. Both of these options may be a way of diversifying farm income using a farmyard waste as a resource. These options are explored in more detail in Sections 2.5 and 2.6.

2.5 Composting

Composting is an aerobic process of decomposition of OM that occurs under controlled temperature, moisture, and oxygen and nutrient conditions. The biodegradable OM in the manure is converted to oxidised end products, primarily CO₂ and water (Sweeten and Auvermann, 2008). Stabilization of the OM is necessary to eliminate the risk of putrefaction, the adverse health effects associated with pathogens and to prevent the production of metabolites which are toxic to plants. There are many advantages associated with composting of manures. The process destroys pathogens and weed seeds found in untreated manures. This gives it an advantage over the direct application of untreated manure (Larney and Hao, 2007). Composting of the solid fraction of manure has the potential to stabilise the organic N fraction. This may allow for higher application rates than with uncomposted manure due to the slow release nature of the N (Sims, 1994; Sequi, 1996). These advantages work to maintain soil quality and fertility which, in turn, increases plant growth. Composting also reduces the volume and moisture of the manure and reduces the odours coming from it. This makes the product easier to transport, store and use than uncomposted manure solids (Bernal et al., 2009).

2.5.1 Phases of the Process

The composting process can be divided into two main phases: (1) the bio-oxidative phase and (2) the maturing phase (Chen and Inbar, 1993; Bernal et al., 1996). The first stage is characterised by high oxygen uptake rates (OURs), thermophilic temperatures, high biodegradable volatile solids reductions, and higher odour potential. The maturing phase is characterised by lower temperatures, reduced OURs and lower odour production potential (Haug, 1993). A temperature profile is normally used to indicate the different phases of the composting process.

2.5.1.1 The Biooxidative Phase

The biooxidative phase can be broken into three steps: an initial mesophilic stage, a thermophilic stage and a cooling stage (Keener et al., 2000). In the initial mesophilic phase, simple compounds, such as sugars, amino acids and proteins are quickly degraded by mesophilic bacteria. The accumulation of this heat raises the temperature of the compost mass. Once sufficient temperature is achieved in the compost pile, the thermophilic phase begins. Thermophilic bacteria degrade organic compounds such as fats, cellulose, hemi cellulose and some lignin, producing CO₂, NH₃, H₂O, organic acids and heat (Haug, 1993; Hao et al., 2004; Bernal et al., 2009). This causes a high aeration demand and an increase in pH. The pile weight is reduced, OM degradation is at its maximum and the C:N ratio decreases. The ideal thermophilic temperature is 55-65 °C, the temperature at which pathogens are destroyed. The cooling phase is characterized by the drop in the temperature of the compost pile. This indicates that thermophilic bacterial activity has decreased due the reduction in degradable organic compounds remaining in the compost pile. Mesophilic bacteria recolonise the compost and degrade any remaining organic compounds (Bernal et al., 2009).

Nitrogen losses through composting can occur by NH₃ volatilisation, leaching and denitrification. The losses through NH₃ volatilisation can be particularly significant during the thermophilic phase, when temperatures are at their highest, pH is above 7.5 and nitrification does not occur. Nitrification, detected by the formation of NO₃⁻, occurs when the temperature falls below thermophilic values (Martins and Dewes, 1992; Tiquia, 2002). Nitrous oxide emissions start when the NH₃ emissions and the temperature of the composting material start to decline (Fukumoto et al., 2003).

2.5.1.2 The Curing/Maturing Phase

Bernal et al. (1998) described the attainment of maturity as the stabilisation of the OM content and the elimination of pathogens and phytotoxic compounds. During the curing phase, stabilisation and humification of the OM occurs (Bernal et al., 2009). Most of the nitrification occurs during maturation, leading to a low NH₄:NO₃ ratio in mature compost.

Insufficiently mature compost has an abundance of easily biodegradable compounds in the raw materials. If this is applied to soils, it maintains high decomposition activity. This causes a strong demand for O₂ and high CO₂ production rates, due to intense development of microorganisms, which may retard plant growth (Hue and Liu, 1995).

2.5.2 Limiting factors

The stabilisation of the OM in the composting materials determines the effectiveness of the composting process. The rate and efficiency of this stabilisation is reliant on the factors that determine the optimal conditions for microbial development and OM degradation. For stabilisation to occur, key factors, such as temperature, aeration, water content, pH, structure and C:N ratio, must be at an optimum level both initially and throughout the composting process (Haug, 1993; Das and Keener, 1997; Richard et al., 2002; Sweeten and Auvermann, 2008).

2.5.2.1 Temperature

Temperature is the most important indicator of the efficiency of the composting process (Lau et al., 1992). The rise in temperature in a composting pile indicates that microbial activity is occurring. Aerobic composting begins when the temperature reaches 45 °C (Sweeten and Auvermann, 2008). Table 2.5 shows the optimum temperature range for optimising the composting process as given in various studies.

Table 2.5 Optimum temperature range for composting

	Optimum temperature (°C)
Stentiford, 1996	45 - 55
McKinley and Vestal, 1984	50 - 55
Miller, 1992	52 - 60
De Bertoldi et al., 1983	40 - 65

Temperatures in excess of 58 °C for at least 12 hours are considered essential for pasteurisation and the elimination of pathogens to be complete (Szmidt, 1997;

Epstein, 1997). Stentiford (1996) recommended that a maximum temperature of 55-65 °C is necessary to destroy pathogens. However, if temperatures increase beyond this, microbial activity declines rapidly. At temperatures exceeding 63 °C, microbial activity begins to slow, while if temperatures reach 72 °C, microbial activity reaches low values as the optimum for various thermophiles has been surpassed (Miller, 1992). Sweeten and Auvermann (2008) found that if temperatures of 85 °C are reached, it may indicate that a dangerous conversion from biological to chemical oxidation is taking place, which could result in a spontaneous compost fire. The primary method of regulating compost temperature is through aeration; increasing the air flow through the compost pile, or increasing the turning frequency of the pile, results in lower temperatures in the compost.

2.5.2.2 Aeration

Composting is the aerobic decomposition of biodegradable solid OM. Therefore, maintaining aerobic conditions in the compost is essential for the process to progress. Proper aeration controls the temperature of the compost (heat removal demand), provides O₂ for the biological processes (stoichiometric demand) and removes water from wet substances (drying demand). The heat removal and drying demands generally far outweigh the requirements for the biological process (Haug, 1993). The optimum O₂ concentration is between 15% and 20% (Miller, 1992).

There are many different ways of aerating the compost. The method chosen will depend on the amount of oxygen needed and the type of compost pile in operation. Intensive composting systems include forced aeration and turning in windrows. Forced aeration uses fans or compressors to blow or drag air through the compost pile, while windrows are long rows of compost which are turned using specialised machinery. Passive aeration may also be used to compost pig manure in a static pile. Intensive systems result in shorter compost times. However, they will lead to higher NH₃ emissions (Mahimairaja et al., 1994). Elwell et al. (2001) found a 50% reduction in NH₃ emissions was achieved with a 75% reduction in airflow. Passive aeration gives a significant reduction in NH₃ emissions, but may lead to higher methane (CH₄) emissions due to the prevalence of anaerobic regions (Lopez-Real and Baptista, 1996; Szanto et al., 2007). The aeration rate required by separated pig manure is quite low in

comparison to cattle and poultry manure. Lo et al. (1992) recommended aeration rates of 0.04 to 0.08 l min⁻¹ kg⁻¹ VM and an intermittent mode of aeration for the composting of separated swine manure.

2.5.2.3 Water Content

The water content (WC) of the substrates to be composted is also a factor in the efficiency of the composting process. The WC of a compost pile is generally recommended to be between 50 and 60% (Epstein, 1997). For manure compost, Sweeten and Auvermann (2008) recommended this range to be between 40 and 60%. When the WC exceeds this 60% limit, O₂ movement is inhibited in the compost pile resulting in zones which become anaerobic (Das and Keener, 1997). Values below the limit of 40% may result in inhibited bacterial activity and excess temperatures. During composting, a large amount of water can evaporate from the pile. Water may need to be applied to the pile in this case to maintain the WC within the correct range. Studies have found that the solid fraction from mechanically-separated pig manure is too wet to be composted alone and, therefore, requires the use of low-moisture bulking agents (Georgacakis et al., 1996).

Tiquia et al. (1996) studied composting of spend pig litter (sawdust and manure) at WCs of 50, 60 and 70%. They showed that the pile which had a WC of 70% decomposed at a slower rate than those at 50 and 60% WC. At 70% WC, the microbial activity during the thermophilic phase was lower and there was also a delay in reaching peak values of temperature. High WC can result in a cooling effect and can also influence gaseous exchange by limiting diffusion and thus restricting oxygen utilization by the microbial mass (Tiquia et al., 1996). Successful composting has been achieved on a larger scale with WC of greater than 60%. Liao et al. (1993) found that as long as there is enough air in the compost to satisfy the oxygen needs of the microbes, then composting may be feasible with an initial WC above 65%.

2.5.2.4 pH

The pH of the compost is another factor influencing the composting process as the rate growth of bacterial populations will depend on the pH of their living conditions.

Elwell et al. (2001) found a pH of 6.0 to be a critical boundary. Below this level, the growth of bacterial populations was found to be slow. Above pH 6.0, rapid heating indicated increased growth in bacterial populations. This finding is in agreement with values found by Sweeten and Auvermann (2008), who found that the initial compost pH should be 6.5 to 7.2 for best composting results. Nitrogen losses through ammonia volatilization can increase at higher pH values, particularly at a pH greater than 7.5.

2.5.2.5 Structure

The structure of the compost pile is also an important factor. If the porosity is too low, aeration is inhibited, decomposition is reduced, and anaerobic conditions may occur, leading to CH₄ and odour emissions. High porosities may lead to decreased temperatures, inhibiting the growth of thermophilic bacteria, and the killing of pathogens (Veeken et al., 2002). Smaller particle sizes provide increased surface area for growth of microorganisms. Distribution of larger particles throughout the pile is important to maintain enough free air space (FAS) for aeration. A compromise must be reached between the need for large surface areas and the need to keep the pile adequately aerated. The optimum FAS of a composting pile is 30% (Haug, 1993). This allows sufficient airflow for the supply of oxygen, the removal of CO₂ and excess moisture, and the prevention of excess heat accumulation (Iqbal et al., 2010). Veeken et al. (2002) studied the effect of the density of straw-rich pig manure compost beds and achieved best compost results with a bed density of 700 kg m⁻³, while Szanto et al. (2007) found that a density of 820 kg m⁻³ provided a suitable permeability for passive aerated composting of straw-rich pig manure.

2.5.2.6 C:N ratio

The microorganisms required for composting need organic C as an energy source and N for reproduction and development through protein synthesis. The C:N ratio is one of the most important factors affecting the effectiveness of the composting process (Michel et al., 1996; Zhu, 2007). If the C:N ratio is too high, the microorganisms responsible for decomposition will have excess degradable substrate (Bernal et al., 2009). They will have insufficient N to achieve maximum development, resulting in a slower process as they will need to recycle the N through many generations of

bacteria. If the C:N ratio is too low, excess N will be lost through ammonia volatilization or leaching. Sweeten and Auvermann (2008) recommend a C:N ratio of 20-30, while Rynk (1992) recommended 25-30. Since the C:N ratio of the separated solid fraction of pig manure is reported to be 11.3 (Huang et al., 2006), the addition of C-rich bulking agents is required to provide optimum C:N conditions.

Research has been undertaken to compare lower C:N ratios to the ideal range to investigate if adding less bulking agents could produce similar compost. Huang et al. (2004) compared initial C:N ratios of 30 and 15 on the composting process of pig manure with sawdust as a bulking agent. The compost with the initial C:N ratio of 30 reached maturity after 49 days, while the compost with the initial C:N ratio of 15 failed to reach maturity after 63 days. Composting at the lower initial C:N of 15 also affected the germination index (GI) value, which remained lower than 50%, compared with 85% for the higher C:N ratio. Electrical conductivity within the pile was found to be higher at the lower C:N ratio. Zhu (2007) compared the effect of initial C:N ratios of 25 and 20 on the composting of pig manure and rice straw. The compost with the lower initial C:N value showed a higher N loss, shorter thermophilic phase, and a longer maturity. Lower initial C:N ratios have also been found to result in a longer time to achieve thermophilic conditions (Elwell et al., 2001; Huang et al., 2004).

The C:N ratio of the compost pile decreases during the composting process due to CO₂ loss and an relative increase in N concentrations due to mass loss. Huang et al. (2006) and Zhu (2007) found that the solid C:N ratios decreased rapidly during the biooxidative phase of manure composting. Huang et al. (2006) also reported a rapid decrease in the soluble C:N ratio during the biooxidative phase, which then became constant, indicating that compost maturity had been reached. When the initial C:N ratio value is within the ideal range of between 25 and 30, then the final value should be around or below 20 (Hiria et al., 1983; Mayer and Hofer, 1987).

2.5.3 Bulking Agents

Bulking agents generally have low WCs and high organic C contents (Bernal et al., 2009) and, when added to manure before composting, act to increase the C:N ratio, decrease WC, and improve the structure, porosity and FAS of the composting mix.

The composting of manure with a bulking agent results in an accelerated and odour-free process. This is due to the absorption of excess moisture by the bulking agent (Georgacakis et al., 1996).

Many different types of bulking agents have been used in the literature including straw, sawdust, peat, peanut shells, rice hull, and chicken litter. Bhamidimarri and Pandey (1996) reported that sawdust was an ideal bulking agent for composting pigs manure due to its ability to absorb moisture and its structure, which provides adequate porosity in the compost heap. However, the addition of sawdust or other bulking agents adds an extra cost to the composting process.

2.5.4 Greenhouse Gas Emissions

During the composting of manure, aerobic decomposition converts biodegradable OM in the manure to oxidised end products, primarily CO₂ and water (Sweeten and Auvermann, 2008). However, CO₂ and water vapour are not the only two gases emitted from a composting bed. Ammonia is one of the principal exhaust gases from the animal manure composting process. Studies have shown that NH₃ emissions are at their maximum during the thermophilic phase of composting when the composting material is at a high temperature. During this phase, nitrification barely occurs, pH is high, and mineralisation of the organic N results in the formation of NH₄⁺ (Elwell et al., 2001; Fukumoto et al., 2003; Hong and Park, 2004). Nitrous oxide is released through nitrification or denitrification. These processes generally begin in the cooling and maturing phases as the temperature and NH₃ emissions begin to drop (Fukumoto et al., 2003). The amount of N₂O released depends on the quantity of NH₄⁺ available to the nitrifying bacteria (Tiquia, 2002). If anaerobic conditions develop due to poor aeration or porosity, then CH₄ will be produced (Szanto et al., 2007).

Ammonia and greenhouse gas (GHG) emissions should be kept to a minimum during the composting process. Factors which can affect these gaseous emissions include (1) the type of composting system used (2) initial C:N ratio of the compost pile (3) pile size and (4) the addition of nitrite-oxidizing bacteria. Szanto et al. (2007) reported that when composting straw-rich pig manure, NH₃ emissions were 61% higher in turned piles compared to static piles. However, CH₄ emissions were higher in the static pile,

possibly due to the occurrence of anaerobic zones. Elwell et al. (2001) reported a 50% reduction in NH_3 emissions when the airflow to the compost pile was reduced by 75%. Parkinson et al. (2004) reported a 64% increase in NH_3 losses, during cattle manure composting when the number of pile turns was increased from 1 to 3.

The C:N ratio of the compost pile can also affect NH_3 emissions. At lower C:N ratios, higher NH_3 emissions can occur if the amount of N in the compost is greater than that needed for microbial growth. Ekinici et al. (2000) found that NH_3 loss depends on both initial pH and initial C:N ratio. They found that by increasing the initial C:N ratio from 18 to 30, NH_3 losses were reduced by 50%. The addition of bulking agents to manure increases the C:N ratio, and can result in lower NH_3 emissions. Martin and Dewes (1992) also reported 54% reductions in NH_3 emissions when pig manure was composted with straw.

Fukumoto et al. (2003) found sharp peaks of CH_4 emissions were detected immediately after two piles of pig manure and sawdust were set up. The two piles were identical except for their sizes - large (780 kg) and small (320 kg) - and it was found that the high CH_4 emissions level continued after the first turn only in the large-scale pile. In the same experiment, Fukumoto et al. (2003) reported that N_2O emissions begin around the middle stage of composting as the temperature and NH_3 emissions begin to drop. Fukumoto et al. (2006) added nitrite-oxidizing bacteria during pig manure composting to inhibit NO_2^- accumulation into the compost and consequently N_2O emissions. The pattern of NO_2^- in the compost agreed with that of N_2O emissions. As a result, N_2O emissions ceased rapidly when the nitrite-oxidizing bacteria were added.

2.5.5 Compost Quality

Compost stability and compost maturity are often used interchangeably. However, they refer to different properties of compost quality. *Compost stability* relates to microbiological activity. Insufficiently stable compost contains an abundance of easily biodegradable compounds. This leads to the intense development of microorganisms, which produce high levels of CO_2 and cause a strong O_2 demand (Hue and Liu, 1995). This strong demand for oxygen leads to a decreased oxygen

supply for plants, which may have a negative effect on plant growth. *Compost maturity* is associated with plant-growth potential or phytotoxicity (Iannotti et al., 1993). However, both maturity and stability are related, since the phytotoxicity in immature compost is caused by the microbial activity in unstable composts (Bernal et al., 2009). Other physical criteria such as odour, colour, temperature, particle size and inert material, as well as chemical criteria, such as nutrient content, ammonia, pH, soluble salts and pollutants, also determine compost quality (Bernal et al., 2009).

There are many different methods used to test compost quality including: GI (Tiquia, 2005; Zhu, 2007), OUR, CO₂ production rate (Wang et al., 2004), final C:N ratio (Bernal et al., 1998), water soluble organic C: total organic N ratio (Hue and Liu, 1995; Bernal et al., 1998) and degree of OM humification (Hue and Liu, 1995). Bernal et al. (2009) reviewed a wide range of manure compost quality parameters and highlighted the need for a harmonization of such criteria internationally if the development of a market for manure compost materials, which supports and promotes a waste composting strategy, is to be achieved. There are currently no European standards for compost and growing media (Baumgarten, 2011). However, this may not be the case in the future as the European Peat Media Association has called for standards to be developed (Baumgarten, 2011). These standards would likely be based on CEN test methods including, “Determination of plant response (cress seed germination test) (EN 106086-2)” and, “Determination of the aerobic biological activity (OUR test) (EN 10087-1)” (Baumgarten, 2011). Industry-led quality standards for biodegradable material-derived compost are currently being developed for Ireland by the EPA (Prasad and Foster, 2009). As part of these standards, an OUR test has been recommended for measuring compost stability. They recommended a value equal to or below 13 mmol O₂ kg OM⁻¹ hour⁻¹ as the limit for good quality compost. This compares favourably to the upper limit of 15 mmol O₂ kg OM⁻¹ hour⁻¹ used in the Netherlands and Belgium.

Germination Index is a combination of the germination rate and root elongation of the seeds used to detect the degree of toxicity present in a compost sample (Tiquia, 2010). Zucconi et al. (1981) reported that GI values below 50% indicated the presence of phytotoxic compounds in the compost. Jodice (1989) reported that a GI of 50 – 70% indicated low levels of phytotoxins present, while Tiquia and Tam (1998) used GI

values above 80% to indicate phytotoxic free compost. Other studies have followed this threshold (Huang et al., 2004, 2006; Tiquia, 2005).

2.6 Renewable Energy Generation through Pyrolysis

2.6.1 Ireland's Renewable Energy Targets

Global mean surface temperatures have risen by 0.74 ± 0.18 °C over the last century (1906-2005) with the rate of warming in the last 50 years twice that of the preceding 50 years (IPCC, 2007a). Emissions of GHG increased by about 70% (from 28.7 to 49.0 Gt CO₂ equivalent) from 1970–2004. Carbon dioxide emissions have risen 80%. These increases, primarily from the combustion of coal, oil and gas, ensure that CO₂ is the largest source of GHG. Methane emissions grew by about 40%, with agriculture being the largest source. Nitrous oxide emissions rose by about 50%, primarily caused by increased fertilizer usage and the growth of agriculture (IPCC, 2007b). Ongoing plans focusing on replacing energy produced from fossil fuels with energy from renewable sources have been shown to reduce emissions, but will not reverse climate change (Lehmann, 2007).

In a time where global warming, climate change, rising energy prices and depleted reserves of fossil fuels are receiving more attention than ever, there is ever-increasing interest in renewable energy as a means of reducing greenhouse gases and delivering reliable energy. The Copenhagen Accord aims to limit the increase in global temperatures to 2 °C above pre-industrial level (IEA, 2010). In their 'New Policy Scenario', the International Energy Agency has investigated the effects that the policy commitment and plans of countries around the world will have on the world energy supply in 2035 (IEA, 2010). They have suggested, based on the implementation of these policies, that by 2035, energy production from renewable sources will have risen three-fold. Renewable sources will account for 33% of total electricity supply and 16% of total heat production of the global energy supply could be provided by renewable sources.

The European Commission Directive 2009/28/EC (EC, 2009) for the promotion of energy from renewable sources aims to achieve an overall target of 20% for the overall share of energy from renewable sources (RES) within the European Community by 2020. There is also a target of 10% for RES in transport for all Member States (EC, 2009). As part of this overall aim, Ireland has received a target of 16% for the overall share of RES by 2020. This includes renewable energy from transport (RES-T), electricity (RES-E), and heating and cooling (RES-H). In 2005, Ireland's percentage share of renewable energy stood at 3.1%. This indicates the large change to renewable energy which is required in order to meet the targets set down by the European Commission. Each Member State was required to adopt a national action plan and report their progress to the European Commission every 2 years (EC, 2009).

The National Renewable Energy Action Plan (NREAP) was submitted to the European Commission in July, 2010. The NREAP has set the yearly targets for RES for electricity, transport and heating until 2020 to allow Ireland to achieve the target of 16% RES by 2020 (Table 2.6). The targets for 2020 are for 42.5% RES-E, 10% RES-T and 12% RES-H (Department of Communications, Energy and Natural Resources, 2010). Energy consumption is expected to be 14,142 Ktoe (Kilo-tonne oil-equivalent) by 2020, of which 2,269 Ktoe will be provided by RES. The first progress report for Ireland was submitted in January 2012 and detailed energy consumption in the years 2009 and 2010 (Department of Communications, Energy and Natural Resources, 2012). The share of energy from renewable sources for electricity, transport and heating and cooling is given in Table 2.6. The overall share of energy from renewable sources had risen to 5.5% by 2010.

Table 2.6: The sectoral and overall shares of energy from renewable sources (RES) in 2009 and 2020, and the targets for 2020 (Department of Communications, Energy and Natural Resources, 2012)

	2009	2010	2020 target
Heating and Cooling (%)	4.3	4.4	12
Electricity (%)	13.7	14.8	42.5
Transport (%)	1.8	2.4	10
Overall RES share (%)	5.0	5.5	16

In 2010, of the 1467 MW RES-E generation capacity in Ireland, only 3% (47 MW) could be generated from biomass. The majority of RES-E generation capacity comes from wind power (1421 MW) with the other significant portion from hydro-generation (234 MW). The use of wind generated electricity is the primary strategy for achieving 42.5% RES-E by 2020. However, biomass technologies are expected to make the second largest contribution. It is planned to have 274 MW RES-E generation capacity from biomass technologies by 2020. Of the 229 Ktoe RES-H consumed in 2010, 221 Ktoe came from biomass technologies. It is planned that 591 Ktoe RES-H will be consumed in 2020, of which 486 will be RES-H from biomass technologies. In order to provide for this increase in RES-E and RES-H from biomass technologies, new plants will be required to be set up in the coming years. This will be promoted by a new support tariff for biomass technologies (REFIT 3), which opened for new applications in February 2012 (Department of Communications, Energy and Natural Resources, 2012). Electricity exported to the national grid will be paid at €0.14 kWh⁻¹ from a biomass CHP plant smaller than 1500 kW and €12 kWh⁻¹ for a biomass CHP plant greater than 1500 kW.

Pyrolysis of biomass is one renewable energy technology which may help to reach these renewable energy targets.

2.6.2 The Pyrolysis Process

Pyrolysis is a thermochemical conversion (TCC) process whereby a biomass feedstock is thermally degraded at high temperatures in an oxygen-free atmosphere. Other TCC technologies include gasification, liquefaction and combustion. The type of TCC process used will often depends on the type of feedstock and the products required after TCC. There are many advantages of using a TCC process over biological treatment processes (for example AD or composting) for the treatment of animal manures (Cantrell et al., 2007): (1) thermochemical reactors are smaller (2) conversion occurs in a number of minutes rather than days, weeks or months (3) pathogens are destroyed by the high temperatures (4) the process can use a variety of blended crop residues and animal manure feedstocks (5) there are no fugitive gas emissions and (6) more efficient nutrient recovery is achievable.

The use of biomass technologies, such as pyrolysis, to produce energy reduces GHG emissions by reducing our dependence on fossil fuels. The use of biomass for energy generation completes the carbon cycle: plants take CO₂ from the air during the growing process, the plant material is pyrolysed to produce char, pyrolysis oil and gas, and these can be burned releasing CO₂ back into the air.

There are three subclasses of pyrolysis, based on the temperature of the reactor and the operating time: (1) slow pyrolysis (2) fast pyrolysis and (3) flash pyrolysis (Maschio et al., 1992). Many different wastes, crop residues and wood by-products can be used as feedstocks for the pyrolysis process. These include:

- Residues from the forestry and timber processing industries
- Straw and other crop residues such as nut shells and rice hulls
- Food waste
- Domestic wastes
- Separated animal slurries and chicken litter
- Anaerobic digestate

During the pyrolysis process, the organic portion of these feedstocks is converted to char and volatile gases. The volatile gases contain condensable tars and incondensable gases. The tars when condensed form combustible pyrolysis oil. The incondensable gases contain a mixture of H₂, CO₂, CO, N₂, and hydrocarbon gases (Bridgewater and Peacocke, 2000; Cantrell et al., 2007). The char produced through pyrolysis may also be used as a fuel; as a feedstock in coal powered power stations, for example. Char may also be activated using steam or other chemicals to produce activated carbon (Ro et al., 2009). This form of processing produces a form of carbon, which is very porous with an extremely large surface area. Activated carbon can be used for water and gas treatments, material recovery, catalysts and gas storage applications (Zanzi et al., 2001). However, char may also be applied to soil as a soil conditioner, where it has been shown to result in carbon sequestration and altered soil properties. When char is produced with intent to use as a soil conditioner, it is known as biochar.

Many modern systems use the gas produced by the pyrolysis process to provide all the energy needs of the pyrolysis reactor. It can also be easily converted to electrical energy. The pyrolysis oil produced can be burned directly to generate heat. However, pyrolysis oil produced from manures tends to be unstable, have low pH and viscosity, and high water and oxygen contents which give rise to low heating values (Mante and Agblevor, 2010). It is possible to extract valuable platform chemicals from pyrolysis oils; they can be a source of food flavorings, agri-chemicals, fertilizers, resins, and emissions control agents. Certain pyrolysis oils can be refined to a petroleum-like product. This refinement can be achieved through physical and chemical methods. This involves filtration of the pyrolysis oil and solvent addition or hydrogenation.

The percentage of gases, pyrolysis oil and char produced during pyrolysis is dependent on the heating rate, the reactor temperature and the residence time of the pyrolysis reactor (Briens et al., 2008; Melligen et al., 2011). The yields of pyrolysis oil obtained through pyrolysis is maximised by having a low operating temperature, a high heating rate, and a short gas residence time. Gas yields are maximised with a high operating temperature, a low heating rate and long gas residence time. A low operating temperature and a low heating rate give maximum yields of char (Kwapinski et al., 2010). The pyrolysis conditions and the biomass feedstock characteristics will also affect the chemical and physical characteristics of the products formed. For example, raising the pyrolysis temperature results in decreased char yield and volatile compounds, but increased ash and C contents, macronutrient (P, K, calcium (Ca), magnesium (Mg)) and micronutrient concentrations, and surface area (Gaskin et al., 2008; Abdullah and Wu, 2009). Char produced from woody feedstock generally contains lower proportions (< 1% by weight) of ash when compared with char produced from biomass with high mineral contents such as grass, and straw. The mineral content of the feedstock is retained in the resultant char, and is often more concentrated than that feedstock due to the loss of C, H and oxygen (O) during the pyrolysis process (Demirbas, 2004).

Pyrolysis may be a suitable technology for use on a smaller farm scale as well as on a larger industrial scale. Pyrolysis reactors may be scaled from small to large to suit the local needs. This minimises the requirement to transport bulky biomass over long distances, thus reducing cost (Badger and Fransham, 2006). On a farm scale, the

production of biochar and energy from wastes such as manure, wood residues and straw may reduce waste disposal costs and provide cost effective energy at a relatively fixed price to be used by agriculture industries (Marris, 2006). The process has the potential to be the lowest cost biomass to electrical energy conversion systems (Bridgewater and Peacocke, 2000). However, there is a paucity of data concerning biochar from feedstocks other than wood, and future research needs to focus on char production from crop residues, manures, sewage and green wastes (Verheijen et al., 2010).

2.7 Biochar Application to Soil

2.7.1 Introduction

The production of biochar through the pyrolysis of biomass, and the application of that biochar to soil results in four beneficial effects: (1) long-term carbon sequestration (2) renewable energy generation (3) biochar as a soil amendment and (4) biomass waste management (Roberts et al., 2010). Using the biochar produced through pyrolysis as an amendment to soil, rather than as a fuel, can further decrease the GHG emissions. Gaunt and Lehmann (2008) found that the avoided GHG emissions are between 2 and 5 times greater when biochar is applied to agricultural land than when it is burned to offset fossil fuel usage. These reductions are primarily (41 - 64%) due to the retention of C in biochar, with other reductions caused by savings in fertiliser requirement, reductions in fossil fuel usage and reductions in soil emissions (Gaunt and Lehmann, 2008).

2.7.2 Carbon Sequestration

In the sequestration of C through the application of biochar to soils, atmospheric CO₂ is fixed from the atmosphere by plants through photosynthesis. The plant material is then pyrolysed to produce biochar. The C within the biochar is much more recalcitrant than the C from the original plant material and, therefore, its residence time in the soil is much longer than that of the plant-derived C. In a study comparing soil amended with wheat straw and soil amended with biochar produced from the slow pyrolysis of

wheat straw, Bruun et al. (2012) found that 2.9% of the biochar C was lost as CO₂ in the 65 days of soil incubation, while 53% of wheat straw C was lost. Carbon dioxide release is reduced as the C is stored in the soil, thereby reducing CO₂ concentrations in the atmosphere and mitigating the effects of global warming (Lehmann et al., 2006).

Biochar is composed of a range of different forms of carbon, from recalcitrant aromatic ring structures, which are known to persist in soil for millennia, to more easily degradable aliphatic and oxidised carbon structures, which will mineralise more rapidly (Schmidt and Noack, 2000). The proportion of aromatic biochar increases as the temperature of production increases (Demirbas, 2004). The application of biochar to soil leads to a much higher percentage of sequestered carbon (~50%, Lehmann et al., 2006) compared to other forms of OM such as manures and compost, which are quickly mineralised and released to the atmosphere as CO₂ (Steiner et al., 2007). Biochar is mineralised to CO₂ through degradation by biotic and abiotic oxidation, however, at a much slower rate than other forms of OM (Cheng et al., 2006; Liang et al., 2008). In a two year study on an Oxisol, Major et al. (2010a) found that only 3% of applied biochar was lost by CO₂. They found that 75% of the biochar mineralisation occurred in the first year and they expected that losses by mineralisation would decrease further with time. The stability and resistance of the biochar against oxidation is known to vary depending on the feedstock and pyrolysis procedures and temperatures (Schmidt and Noack, 2000; Liang et al., 2008). Woody feedstocks results in more resistant biochars, while biochars produced from manures and crop residues are more readily degradable (Collison et al., 2009). Biochar is also lost from soil through erosion and leaching, and this can be a bigger loss of C than through mineralisation (Major et al., 2010a).

The long-term effects of biochar can be seen in fertile Anthrosols found around the Amazonian basin. These soils have very high biochar contents due to the charring of the forest wood by the indigenous people thousands of years ago (Lehmann et al., 2003). The high OM and fertility of these soils have remained and this vastly contrasts the low fertility of the adjacent acid soils. Liang et al. (2008) found that the Anthrosols had a higher proportion of carbon within organic-mineral fractions than biochar-poor soils in surrounding areas.

When assessing the climate change potential of biochar, Roberts et al. (2010) found negative values for the net GHG emissions from the pyrolysis and soil application of biochar from corn stover and yard waste (-864 and -885 kg CO₂ equivalent emissions reduction per tonne dry feedstock, respectively). The effect of sequestering the C within the soil accounted for between 62 and 66% of the total reduction in GHG emissions. Lehmann et al. (2006) estimated the global potential of C sequestration from biochar produced from current forestry, agricultural wastes and urban wastes to be 0.16 Gt year⁻¹. However, the long-term carbon sequestration effect of biochar is largely hypothesised (Verheijen et al., 2010).

2.7.3 Response of Soils and Plants to Biochar Addition

The response of soils and plants to the addition of biochar is dependent on the properties of the specific biochar (Tyron, 1948), the properties of the soil, further additions of nutrients and OM, and the plant species (Lehmann and Rondon, 2006). The feedstock used to produce the biochar and the pyrolysis conditions used in its production can have a large impact on the effects of the biochar when applied to soils (Atkinson et al., 2010). Differences in feedstock nutrient concentrations have been seen to persist after pyrolysis (DeLuca et al., 2009), while pyrolysis temperature can also affect the concentrations of these nutrients (Gaskin et al., 2008). Chan et al. (2008) found differences in electrical conductivity, pH, and P and N concentrations in biochars produced from chicken manure at different pyrolysis temperatures.

Biochar has been shown to influence the soil physico-chemical properties, such as pH, porosity, bulk density, pore-size distribution and water holding capacity (Glaser et al., 2002; Chan et al., 2007; Laird et al., 2010b). Increased pH helps to reduce the acidifying conditions of N fertilisers. Biochar has greater surface area and porosity, and a lower density than mineral soils. Therefore, its application to soil may increase soil surface area, density, drainage, root penetration and aeration (Chan et al., 2007; Laird, 2008; Downie et al., 2009). Laird et al. (2010b) found that the water retention value for Midwestern agricultural soil amended with biochar was up to 15% greater than that of soil which contained no biochar. Major et al. (2009) suggested that percolation patterns, residence times and flow paths of water in soil could be altered due to the changes in soil pore-size distribution caused by biochar addition.

Studies have shown increased biomass yield and plant growth using biochar additions in conjunction with another nutrient source such as manure or inorganic fertilisers (Lehmann et al., 2003; Rondon et al. 2007; Chan et al., 2007; Steiner et al., 2007, 2008a; Asai et al., 2009, Major et al., 2010b) (Table 2.7). The rate of biochar addition may also have an effect the plant response. Rondon et al. (2007) reported positive yield effects in common beans with biochar application rates up to 50 tonne C ha⁻¹. However, there was no increase in yield at 60 tonne C ha⁻¹ and a negative yield effect at 150 tonne C ha⁻¹.

Table 2.7 Effect of biochar (BC) addition to soil on biomass yield when applied with another nutrient source

Soil type, location	Plant type	BC type, amount	Fertiliser added	Yield Response*	Reference
Ferrasol, Amazon	Rice	Wood, 10% w/w	Inorganic	+32% shoot biomass	Lehmann et al., 2003
Ferrasol, Amazon	Rice	Wood, 10% w/w	Chicken manure	+84% shoot biomass	Lehmann et al., 2003
Ferrasol, Brazil	Rice	Wood, 11 t ha ⁻¹	Inorganic	+29% stover yield +73% grain yield	Steiner et al., 2007
Ferrasol, Brazil	Sorghum	Wood, 11 t ha ⁻¹	Inorganic	+34-44% crop residue [#] , +50-100% grain yield [#]	Steiner et al., 2008a
Oxisol, Columbia	Maize	Wood, 20 t ha ⁻¹	Inorganic + urea	+28, 30 & 140% grain yield in years 2, 3 & 4	Major et al., 2010b
Anthrosol, China	Rice	Wheat straw, 10 & 40t ha ⁻¹	Urea	+8.8 & 12.1% grain yields for 10 & 40 t BC ha ⁻¹	Zhang et al., 2010

*Yield response compared to the addition of fertiliser alone, [#]Over two harvest events

The addition of biochar without any other form of fertiliser has shown mixed results (Table 2.8). Chan et al. (2007) found no significant increases in yield of radish when biochar was added to an Australian Alfisol at a rate of 10, 50 and 100 tonne ha⁻¹

without additional nitrogen fertiliser. The recalcitrant nature of biochar leads to low C losses; however, it also results in slow nutrient release by mineralisation. For this reason, and also because of its low nutrient content, Steiner et al. (2007) found that biochar alone is unlikely to be a balanced fertiliser. However, when using biochar from poultry litter at addition rates of 10 and 50 tonne ha⁻¹, Chan et al. (2008) found an increase in N availability and increases in yields of radish by adding biochar alone. These yield increases were mostly attributed to the ability of the poultry litter biochars to release available N once applied in the soil *via* mineralization and increased mineralization of native soil N due to the application of the biochar. Biochar from manures have been shown to mineralise quicker than those from woody feedstocks (Collison et al., 2009). Due to its higher N, P and K concentrations, biochar from manures can have many benefits to plant growth when used in conjunction with additional organic or inorganic forms of fertiliser. The P and K content of the manure are almost completely recovered in the biochar leading to higher concentrations in the biochar than in the original manure (Ro et al., 2010). It can be used to alleviate the problems of N leaching from soils, which is a characteristic of the use of manures as fertilisers (Lehmann, 2007).

Table 2.8 Effect of biochar (BC) addition to soil on biomass yield when applied without any other nutrient source

Soil type, location	Plant type	BC Type, amount	Yield Response	Reference
Ferrasol, Amazon	Rice	Wood, 10% w/w	+43% shoot biomass	Lehmann et al., 2003
Alfisol, Australia	Radish	Greenwaste, 10,50 & 100t ha ⁻¹	No significant increases in radish yield	Chan et al., 2007
Ferrasol, Brazil	Rice	Wood, 11t ha ⁻¹	Minor effects on stover and grain yield	Steiner et al., 2007
Alfisol, Australia	Radish	Poultry litter, 10 & 50t ha ⁻¹	+42 & 96% TDM of radish yield for 10 & 50t BC	Chan et al., 2008
Anthrosol, China	Rice	Wheat straw, 10 & 40t ha ⁻¹	+11.6 & +14% grain yields for 10 & 40t BC	Zhang et al., 2010

TDM = total dry matter

There have been many reasons given for the increased plant growth rates and crop yields attributed to the addition of biochar to soil. Increased plant growth may also be a result of higher nutrient availability caused by nutrient additions from the biochar and from greater nutrient retention (Lehmann et al., 2003). Steiner et al. (2008a) found increased N retention and increased N recovery in soil, crop residues, and grains with the addition of biochar to soil, in comparison with inorganic fertiliser only plots. Soil K, manganese (Mn), Cu, Ca and Mg have also been shown to be increased with the addition of biochar to soil (Lehmann et al., 2003; Topoliantz et al., 2005; Novak et al., 2009, Major et al., 2010b), while availability of Zn, aluminium (Al) and sulphur (S) has been shown to decrease (Topoliantz et al., 2005; Novak et al., 2009). High Al concentrations in soil can reduce crop production dramatically (Sierra et al., 2003). The high absorptive capacity of biochar not only prevents leaching of nutrients from soil, but also pesticides used to prevent plant disease.

Most of the studies detailed here were carried out in tropical regions. These soils often suffer from weathering, poor physical properties and low OM contents caused by accelerated mineralisation of OM due to the hot humid climates (Busscher et al., 2010). This results in low long-term efficiency of organic fertilisers. Biochar addition to these soils not only increases the organic C content (Novak et al., 2009), but also improves physical characteristics by reducing soil strength, thereby increasing root penetration and improving water holding capacity (Busscher et al., 2010). However, there is a scarcity of research on the effect of biochar application to soils outside the tropical and subtropical regions (Verheijen et al., 2010). Even in relatively fertile soils with higher OM contents, biochar may be used to increase the efficiency of fertilisers, thus reducing fertiliser applications (Blackwell et al., 2009).

2.7.4 The Effect of Biochar Addition on Soil Nutrient Retention

Organic fertilisers such as compost, mulch or manure, retain nutrients and release them in a gradual manner which may lead to reduced leaching compared to inorganic fertilisers (Burger and Jackson, 2003). However, because of its absorptive capacity, biochar has a superior ability to retain nutrients in comparison to other forms of OM (Lehmann, 2007). Lehmann et al. (2003) found that the application of biochar reduced the leaching of applied mineral fertilisers and when applied with biochar. This can be

seen in the fertile Amazonian Anthrosols where nutrient leaching is minimal despite their high nutrient content. The retention of nutrients in the soil leads to greater nutrient availability, greater plant uptake and causes reduced leaching of these nutrients to surface and ground waters. Increased water retention through biochar addition to soil also reduces leaching of mobile nutrients such as nitrates. Longer nutrient retention times and higher nutrient efficiencies also reduce the fertiliser requirements for crop growth in future harvests.

Novak et al. (2009) found decreased concentrations of Ca, P, Mn and Zn in the leachate from a South-Eastern coastal plain soil. They attributed these reductions to the higher sorption capacity of biochar for selected nutrients. In a column study using a fine-loamy Midwestern agricultural soil, Laird et al. (2010a) studied nutrient leaching from swine manure with the addition of 0, 5, 10 and 20 g-hardwood biochar kg⁻¹-soil. This study found substantially reduced leaching of N, P, Mg and silicon (Si) as the rates of biochar addition increased. In a companion paper, Laird et al. (2010b) found significantly increased N, organic C, P, K, Mg and Ca concentrations after leaching, in the soil that been amended with biochar. Biochar has been shown to maintain the improvements due to the application of mineral fertiliser over a longer period of time than that achieved by fertiliser alone (Steiner et al., 2007).

2.7.4.1 Cation Exchange Capacity

One of the reasons for biochars effect on nutrient leaching and improved nutrient retention capabilities of soil amended with biochar due to greater cation exchange capacity (CEC) (Liang et al., 2006). Cation exchange capacity is a measure of how well cations are bound to the soil. Biochars are highly porous, usually alkaline and exhibit large specific surface area (Downie et al., 2009; Lima et al., 2009; Novak et al., 2009). Nevertheless, the CEC of fresh biochar has been shown to be low (Lehmann, 2007; Busscher et al., 2009; Clough et al., 2010). It is only aged or weathered biochar which has being shown to have a high CEC due to oxidation and adsorption of other OM in the soil over time (Liang et al., 2006). Aged biochar has a greater ability to absorb nutrients than other soil OM, due to its greater surface area for cation adsorption per unit mass, and its higher negative charge density per unit of surface area, allowing greater binding of cations to its surfaces (Liang et al. 2006;

Chan and Xu, 2009; Atkinson et al., 2010). The CEC of biochar depends on the temperature of the pyrolysis process, with higher temperatures resulting in higher CEC (Lehmann, 2007). Increased soil pH also allows for increased CEC and nutrient retention. Cation exchange capacity is typically low or even zero, at low pH, with a pH of greater than 5.5 required for an increase in CEC with OM addition (Steiner et al., 2007). Oxidation of the edges of the aromatic backbone of the char and adsorption of other OM is responsible for the increased CEC (Liang et al., 2006), which suggests the addition to soils of biochar consisting of primarily single ring aromatic C will provide the greatest increase in soil CEC.

2.7.4.2 Microbial Growth Rates

The ability of biochar to retain nutrients in soil may also be due to the increased growth rate of microorganisms, including mycorrhizal fungi (Ishii and Kadoya, 1994; Steiner et al., 2008b). Steiner et al. (2004) showed that even small additions of biochar (7.9 tonne C ha⁻¹) can significantly enhance microbial growth rates when nutrients were supplied by fertiliser. Enhanced microbial growth rates in soils amended with biochar result from increased C availability, increased pH, porosity, and air and water retention provided by the biochar (Ogawa, 1994). The micro-pores found in biochar are an excellent habitat for small soil organisms, such as beneficial mycorrhizal fungi, due to lower competition from saprophytes (Saito and Marumoto, 2002). A study by Mori and Marjenah (1994) showed that colonisation rates of mycorrhizal fungi on the roots of host plants increased significantly in biochar amended soil. Mycorrhizae have a symbiotic relationship with plant roots.

The increased colonisation rate of these fungi, caused by biochar addition to soil, enhances the absorption of minerals that would otherwise potentially be lost to leachate (Allen, 2007). This may result in increased plant growth rates. Nishio (1996) reported that biochar was ineffective at stimulating alfalfa growth when added to sterilised soil. However, alfalfa growth was increased by almost 80% when biochar was added to unsterilised soil containing native mycorrhizal fungi.

2.7.4.3 Nitrogen and Phosphorus Retention

Studies have shown that the addition of biochar to soil affects the N cycling process within the soil (Berglund et al., 2004; DeLuca et al., 2009; Steiner et al., 2008a; Busscher et al., 2009; Clough et al., 2010; Singh et al., 2010; Laird et al., 2010a).

Studies have suggested that biochar has the ability to (1) retain N within soils by enhanced NH_4^+ and NH_3 retention (2) reduce N_2O and NO_3^- leaching fluxes and (3) enhance biological N fixation and beneficially influence soil microbial communities (Clough and Condon, 2010). Many reasons have been given for the ability of biochar to affect the cycle of N in soil. Changes in the N cycling process may be a result of (1) enhanced adsorption of NH_4^+ and soluble organic compounds within the soil due to a higher CEC (Singh et al., 2010; Laird et al., 2010a) (2) reduced nitrification due to the presence of nitrification inhibitors of unweathered biochar (Clough et al., 2010) (3) increased soil pH which can increase soil nitrification (DeLuca et al., 2009; Major et al., 2010b) (4) changes to soil aeration which can influence nitrification and denitrification rates through increased oxygen availability (Yania et al., 2007) or (5) greater C availability due to the high C:N ratio of biochar stimulating microbial growth, resulting in greater N demand, which promotes the immobilisation and recycling of NO_3^- (Burger and Jackson, 2003).

Singh et al. (2010) investigated the effect of different types of biochar addition on N leaching over three wetting-drying cycles. Nitrate leaching was increased in the soil amended with poultry litter biochar in the first leaching event, while the wood biochar did not affect NO_3^- leaching in any leaching event. Ammonium leaching was unaffected by biochar addition in the first leaching event; however, biochar addition significantly decreased NH_4^+ leaching in subsequent leaching events. Singh et al. (2010) attributed this reduction in leaching over time to increased sorption capacity of biochar through oxidative reactions on the biochar surfaces with aging. Laird et al. (2010a) reported reduced NO_3^- leaching from biochar-amended soil after 23 weeks of incubation. They attributed this to biochar adsorption of NH_4^+ and soluble organic compounds with the soil. Consequently, mineralisation of organic N and/or nitrification of NH_4^+ were inhibited.

In an incubation study using freshly made biochar, Clough et al. (2010) reported soil NH_4^+ concentrations were higher in biochar-amended soil after urine application, compared to soil amended with urine only. They attributed this increase to a reduced rate of NH_4^+ depletion due to the inhibition of nitrification. Unweathered biochar has been shown to contain microbially toxic compounds, which may inhibit the *Nitrosomonas* bacteria responsible for nitrification (Kim et al., 2003; Clough and Condron, 2010). The residence time of the biochar in the soil is important when considering the effect of biochar on the N cycling process (Clough and Condron, 2010), as weathering of the biochar may decrease the presence of nitrification-inhibiting compounds (Clough et al., 2010).

Biochar addition to soil has been shown to increase extractable phosphate concentrations within the soil (Gundale and DeLuca, 2006). Changes in soil pH have a large impact on the availability of P, with availability increasing in more alkaline soils. The pyrolysis process also increases the availability of P relative to biochar C, as C volatilises at relatively low temperatures (100°C), compared to P (700°C) (DeLuca et al., 2009). Biochar has been shown to be able to absorb P through its anion exchange capacity or by influencing activity or availability of the cations that interact with P (DeLuca et al., 2009). However, more research is needed to understand biochar's role in influencing the anion exchange capacity of soils (Verheijen et al., 2010).

2.7.5 N fixation

Rhizobia have a symbiotic relationship with many legume species. These organisms can fix atmospheric nitrogen and convert it to organic N through a series of enzymatic reactions (Giller, 2001). The addition of biochar to soil has been shown to result in increased biological nitrogen fixation (BNF) by legumes (Nishio, 1996; Rondon et al., 2007). The reason for this enhanced BNF is most likely related to nutrient availability in the soil (Lehmann et al., 2003a) and increased rates of root infection by arbuscular mycorrhizae (Nishio and Okano, 1991).

Rondon et al. (2007) found enhanced BNF and a 30 – 40% increase in biomass production by common beans with the addition of up to 50 g kg^{-1} biochar to the soil,

while N uptake from soil was found to be significantly reduced. The main reason for this increase in BNF was the increased availability of nutrients such as boron and molybdenum. Molybdenum fertilisation has proved to be an effective way of increasing nitrogen fixation (Campo and Lantmann, 1998). To a lesser extent, increased availability of K, Ca and P, combined with a higher pH, decreased availability of N and decreased saturation of Al may also have had a positive effect (Rondon et al., 2007). The higher C:N ratio of biochar causes the limited N availability in the soil which stimulates the legumes to increase nitrogen fixation.

Biochar-amended soil may also provide an excellent support material for the propagation of useful symbiotic microorganisms (Ogawa, 1994). Nishio and Okano (1991) found that root infection by arbuscular Mycorrhizae increased significantly in alfalfa plants when the soil was amended with biochar. The same study showed significantly increased BNF in these plants with the addition of biochar to the soil. Lal and Mishra (1998) suggested that biochar provides an excellent habitat for the Rhizobia, which may also be a reason for the increase in nitrogen fixation.

2.7.6 Greenhouse Gas Emissions

The application of biochar to soil can affect the emission of GHG from the soil. Studies have shown reduced N₂O emissions after the inclusion of biochar into the soil. Singh et al (2010) investigated the effect of biochar addition at a rate of 10 tonne ha⁻¹ to a depth of 10 cm on N₂O emissions over three wetting-drying cycles. They found significantly reduced N₂O emissions in the biochar-amended soils in the second and third wetting events. They attributed this reduction to increased sorption capacity of biochar through oxidative reactions on the biochar surfaces with aging. Yanai et al. (2007) found that variations in the soil water filled pore space (WFPS) caused biochar additions to the soil to either increase or suppress N₂O emissions due to its effect on soil aeration, since denitrification and therefore N₂O production is aeration dependent. They found an 89% suppression of N₂O emissions at 73-78% WFPS and a 51% increase at 83% WFPS. Rondon et al. (2005) recorded reductions in N₂O emissions of 50% in soybean plantations and 80% in grass stands when biochar was incorporated into the soil. They attributed the reduced N₂O emissions to slower N cycling, possibly due to a higher C:N ratio. Taghizadeh-Toosi et al. (2011) found that the incorporation

of 30 tonne ha⁻¹ biochar into soil reduced N₂O emissions ruminant urine patches by 70%. Zhang et al. (2010) investigated N₂O emissions from a rice paddy amended with biochar at rates of 10 tonne ha⁻¹ and 40 tonne ha⁻¹ both with and without N fertilization. They found that total N₂O emissions were decreased by 40–51% in biochar amended soils with N fertilization and by 21–28% in biochar amended soils without N fertilization. However, Clough et al. (2010) found no changes in the cumulative N₂O flux when biochar was incorporated into soil under the application of bovine urine.

Methane emissions have been reported to both increase and decrease due to biochar addition to soil. In a greenhouse pot experiment, Rondon et al. (2005) measured the CH₄ emissions from a low-fertility Oxisol after grass had been planted. They reported a near complete suppression of methane upon biochar addition at an application rate of 20 g kg⁻¹ to soil. The explanation given for this suppression of CH₄ emissions was due to a reduction in the frequency and extent of anaerobic conditions within the soil due to increased soil aeration. However, in a field experiment in a rice paddy, Zhang et al (2010) found that soil CH₄ emissions increased where soil was amended with biochar at a rate of 40 tonne ha⁻¹. The addition of biochar amendment to the soil caused emissions to increase by 34% when N fertiliser was applied and by 41% without N fertilization, when compared to unamended soils.

2.8 Summary

This chapter reviewed the quantity and composition (Table 2.1) of pig manure produced on a yearly basis in Ireland and the effect that landspreading of this pig manure can have on surface and ground water quality. The current status of groundwater, and river and lake water in Ireland was examined, and a review of the current and future water quality regulations and landspreading regulations was undertaken. It is apparent that landspreading of pig manure will be restricted in the coming years and viable alternatives to landspreading are required.

Alternatives options to landspreading of pig manure were reviewed. One such alternative was AD to produce bio-gas for renewable energy generation (Xie et al.,

2012). However, AD does little to reduce the overall nutrient concentration of pig manure, which still needs to be recycled in the same way as undigested manure. Slurry separation can be used to produce a solid fraction and a liquid fraction from raw or anaerobically digested manure. The solid fraction after separation can be exported at a lower cost than unseparated manure due to its high DM content (Treanor, 2008). Alternatively, the solid fraction can be composted (Bernal et al., 2009) or used as a feedstock for pyrolysis to produce renewable energy and biochar (Ro et al., 2010). The liquid fraction can be used to irrigate land nearby the pig farm, or alternatively, further treated using woodchip bio-filters (Carney et al., 2011) or integrated constructed wetlands (Harrington and Scholz, 2011).

Composting is an aerobic process where stabilisation of the organic fraction of the manure occurs. The rate and efficiency of this stabilisation is reliant on key factors that determine the optimal conditions for microbial development and OM degradation; temperature, aeration, water content, pH, structure and C:N ratio, must be at an optimum level both initially and throughout the composting process (Haug, 1993; Das and Keener, 1997; Richard et al., 2002; Sweeten and Auvermann, 2008). In order to achieve these optimal conditions it is essential to mix the separated solid fraction of the manure with a low-moisture, high-carbon bulking agent such as wood or crop residues. However, the use of bulking agents adds an expense to the composting process. Therefore, the addition rate must be kept to a minimum to keep costs low.

Pyrolysis is a thermochemical conversion process whereby a biomass feedstock such as manure or wood or crop residues, is thermally degraded at high temperatures in an oxygen-free atmosphere. During the pyrolysis process, the organic portion of these feedstocks is converted to char, gases and bio-liquid. The yield and characteristics of each product is dependent on the pyrolysis conditions and the feedstock characteristics (Briens et al., 2008; Melligen et al., 2011). The gas and bio-liquid produced are generally combusted to generate heat and electricity. The char produced may also be used as a fuel or used as a soil additive. Pyrolysis of manure and other agricultural wastes to produce renewable energy has the potential to be a viable alternative to landspreading and also a means of diversifying farm income (Bridgewater and Peacocke, 2000; Marris, 2006). However, pyrolysis is a relatively

new technology and most studies are focused on pyrolysis of wood feedstocks. There is a paucity of data concerning biochar from manure or crop residues (Verheijen et al., 2010), and a great deal of research is required before pyrolysis could be recommended for implementation on a farm-scale in Ireland.

When biochar is applied to soil as a soil conditioner, it has been shown to result in carbon sequestration and altered soil properties, such as pH, porosity, bulk density, pore-size distribution and water holding capacity (Glaser et al., 2002; Chan et al., 2007; Laird et al., 2010b). Studies have shown increased biomass yield and plant growth using biochar additions in conjunction with a nutrient source such as manure or inorganic fertilisers (Lehmann et al., 2003; Rondon et al., 2007; Chan et al., 2007; Steiner et al., 2007, 2008a; Asai et al., 2009, Major et al., 2010b) (Table 2.7). Increased plant growth may be a result of greater nutrient retention in soils with added biochar (Lehmann et al., 2003). This may be due to increased soil cation exchange capacity (Liang et al., 2006), enhance microbial growth rates (Steiner et al., 2008b) or alterations to the N cycling process within the soil (DeLuca et al., 2009; Steiner et al., 2008a; Laird et al., 2010a; Singh et al., 2010). The application of biochar to soil has also been shown to alter the greenhouse gas emissions from soil (Rondon et al., 2005; Singh et al., 2010; Zhang et al., 2010). However, most research on biochar application to soil has occurred on highly weathered soils lacking in organic matter in tropical and subtropical regions and there is a scarcity of research in temperate regions (Verheijen et al., 2010). The effect of biochar addition to relatively fertile soils in temperate climates needs to be examined further.

3 CHARACTERIZATION OF COMPOST FROM SEPARATED PIG MANURE AND A VARIETY OF BULKING AGENTS AT LOW INITIAL C:N RATIOS

Overview

This chapter details two experiments investigating the quality of compost produced from the solid fraction of separated pig manure, with and without the addition of a variety of bulking agents, at low initial C:N ratios. The method of separation and composting used in this study are detailed. The physico-chemical, stability and maturity analyses undertaken on the compost before, during and after the composting process are also described. Experimental data from these analyses are presented. Compost stability was investigated using an oxygen uptake rate test and compost maturity was investigated using a germination index test.

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3.1 Introduction

The stabilisation of the OM in the composting materials determines the effectiveness of the composting process. Stabilization of the OM is necessary to eliminate the risk of putrefaction and to prevent the production of metabolites, which are toxic to plants (Bernal et al., 2009). The stabilization and maturity of the compost is dependent on careful material preparation and optimization of initial conditions such as water content, structure and C:N ratio (Haug, 1993; Das and Keener, 1997; Richard et al., 2002; Sweeten and Auvermann, 2008).

The initial C:N ratio of the material is of great importance. Sweeten and Auvermann (2008) recommend a C:N ratio of 20-30 for manure composting. The C:N ratio of the separated solid fraction of pig manure is reported to be 11.3 (Huang et al., 2006), therefore, the addition of C-rich bulking agents is required to provide optimum C:N conditions. The WC of the composting pile is also of utmost importance. For manure

compost, Sweeten and Auvermann (2008) recommended that the WC be between 40 and 60% throughout the composting process. Values below 40% may result in excess temperatures. High WCs can result in a cooling effect and can influence gaseous exchange by restricting oxygen utilization by the microbial mass (Tiquia et al., 1996). The solid fraction from mechanically-separated pig manure is too wet to be composted alone and, therefore, requires the use of low-moisture bulking agents (Georgacakis et al., 1996).

Bulking agents generally have low water contents and high organic C contents (Bernal et al., 2009) and, when added to manure before composting, act to increase the C:N ratio, decrease the water content, and improve the structure, porosity and FAS of the composting mix. Many different types of bulking agents have been used for pig manure composting including straw (Zhu, 2007), sawdust (Huang et al., 2004), peat (Vuorinen and Saharinen, 1999), cotton residues (Georgacakis et al., 1996), rice hull (Georgacakis et al., 1996), and leaves (Huang et al., 2001). The addition of bulking agents adds an extra cost to the composting process; a low initial C:N ratio will reduce the amount of bulking agents needed and consequently the cost (Zhu, 2007). To ensure that a low initial C:N ratio does not impair the compost process, it is essential to examine the stability and maturity of the final compost.

The objective of this study was to investigate the physico-chemical parameters of compost mixtures comprising the solid fraction of separated pig manure with and without a variety of bulking agents (sawdust, shredded greenwaste, chopped straw and woodchip) at low initial C:N ratios.

3.2 Materials and Methods

3.2.1 Trial Site and Manure Separation Process

This experiment comprised two trials, Trial 1 (T1) and Trial 2 (T2). In both trials, raw pig manure was collected from an overground aerated manure storage tank at Teagasc, Pig Development Department, Fermoy, Co. Cork, Ireland, and was a mixture of pig manure that came from all stages of production.

A decanter centrifuge (GEA Westfallia Separator UCD 205, GEA WestfaliaSurge GmbH, Bönen, Germany) (Figure 3.1) was used to perform the mechanical separation of the liquid manure. Alum - in liquid form - and water soluble PAM flocculent were used to increase the efficiency of separation. Alum was applied at approximately 3 L m⁻³ of slurry. PAM was diluted with water to 0.4% by volume and added at approximately 17% by volume. For both trials, the separation process was replicated each day for 4 days to achieve 4 replicates.

Average DM (means ± SD) for liquid pig manure before separation, the solid fraction after separation, and the liquid fraction after separation for T1 were 2.4 ± 0.17%, 38.0 ± 3.2% and 0.3 ± 0.07%, respectively. For T2, these values were 2.5 ± 0.98%, 30.6 ± 2.27% and 0.2 ± 0.05%, respectively.



Figure 3.1 Decanter centrifuge used for the separation of pig manure into a solid and liquid fraction

3.2.2 Compost Preparation

In T1, there were 4 treatments each using the solid fraction of separated pig manure (SPM) with and without the addition of bulking agents, to achieve a C:N ratio of 20 or less: (Treatment A) 38 kg of SPM; (Treatment B) 38 kg of SPM + 9.5 kg of sawdust; (Treatment C) 38 kg of SPM + 9.5 kg of shredded green waste and (Treatment D) 38 kg of SPM + 2.8 kg of chopped straw. In T2, there were also 4 treatments: (Treatment A) 38 kg of SPM; (Treatment B) 38 kg of SPM + 9.5 kg of sawdust; (Treatment C) 38 kg of SPM + 9.5 kg of woodchip; and (Treatment D) 38 kg of SRM + 4.75 kg of sawdust + 4.75 kg of woodchip.

The straw (barley) was chopped to a length of 30 to 100 mm. The sawdust was Sitka spruce (*Picea Sitchensis*) and the woodchip was Fir (*Abies*). The shredded green waste was a mixture of leaves, foliage and small twigs, and was collected from a local arboriculture management company. Selected physico-chemical parameters for the SPM for both trials are presented in Table 3.1. Physico-chemical parameters for the bulking agents are presented in Table 3.2.

Table 3.1 Physico-chemical parameters for separated pig manure for Trial 1 and 2 (means \pm SD)

Parameters	Trial 1	Trial 2
pH	8.3 \pm 0.2	8.9 \pm 0.2
DM (%)	38.0 \pm 3.2	30.6 \pm 2.3
Nitrogen (%)	3.3 \pm 0.3	3.1 \pm 0.2
Carbon (%)	39.1 \pm 1.0	38.3 \pm 0.9
C:N ratio	12.0 \pm 1.1	12.5 \pm 0.8
Bulk density (kg m ⁻³)	374 \pm 43.1	498 \pm 75.3
OM (g kg ⁻¹)	750 \pm 13	732 \pm 13

n=4 for pH, bulk density and ash; n=19 for DM Trial 1; n=12 for DM Trial 2; n=4 for N and C contents

Table 3.2 Physico-chemical parameters for bulking agents (means \pm SD)

Parameters	Sawdust	Green Waste	Straw	Woodchip
pH	4.9 \pm 0.1	5.2 \pm 0.1	7.5 \pm 0.1	6.0 \pm 0.2
DM (%)	84.2 \pm 3.0	52.9 \pm 4.6	88.2 \pm 2.3	89.6 \pm 2.5
Nitrogen (%)	0.1 \pm 0.0	0.8 \pm 0.1	0.6 \pm 0.0	0.8 \pm 0.0
Carbon (%)	48.8 \pm 0.3	49.3 \pm 0.0	44.9 \pm 0.4	47.2 \pm 0.1
C:N ratio	467 \pm 59	60.8 \pm 5.1	72.4 \pm 2.6	513 \pm 24
Bulk density (kg m ⁻³)	40.2 \pm 1.7	50.1 \pm 4.1	9.6 \pm 0.8	45.2 \pm 4.3
OM (g kg ⁻¹)	907 \pm 0	967 \pm 5	963 \pm 1	997 \pm 0

n=4 for pH, bulking density and ash; n=8 for DM; n=2 for N and C contents

In both trials, each treatment was replicated four times, with 16 fully insulated compost tumblers (Jora JK270 Composter, Joraform AB, Mjölby, Sweden; built without the internal partition) used to compost the mixtures (Figure 3.2). The SPM and bulking agent were mixed thoroughly to insure uniformity. The temperature of the compost pile was recorded daily with long-stemmed thermometers (Traceable X-long Stem Therm Ultra, Control Company, Texas, USA). Two thermometers were inserted into the middle of the pile at different locations and from different directions. The higher temperature was recorded. Aeration was provided by manually rotating the tumblers twice daily (morning and afternoon) during the first week of the trial and once-a-day for the remainder of the trial. The tumblers were rotated fully around their axis 3 times for each turning event. The addition of water during composting was not required because the WC did not fall below 40% for any treatment at any time during the process. Tumblers were turned after the temperature was recorded.



Figure 3.2 Jora JK270 Composter used in the composting experiments

3.2.3 Compost Sampling

Both trials were undertaken for 56 days and samples were collected from each tumbler on Days 0, 3, 7, 14, 21, 28, 42 and 56 for analyses. Each sample was a composite of 6 sub-samples; 3 sub-samples taken from the top 2 mm of the compost pile and 3 from the bottom 200 mm. Each of the 3 sub-samples was taken at different locations (right, centre and left of the pile).

Fresh samples collected from the compost piles were tested for pH and WC on all sample days. After determination of WC, the dried material was milled and stored in a cold room (*c.* 2 °C) for C and N analyses later. Fresh samples were collected on Days 0 and 56 for bulk density, OM and respiration tests (OUR), and, on Day 56, for the cress seed germination test.

3.2.4 Physico-chemical Analyses

Water content was determined by drying the samples in an oven at 60°C for 24 hours to a constant weight (Hao et al., 2004). Measurement of pH was performed in water solution using a bench top meter (SevenEasy, Mettler-Toledo, Switzerland) at a compost/distilled water ratio of 1:10 (w/v) (Tiquia et al., 2002a). Carbon and N content was determined using a CHNOS Elemental Analyser Vario EL Cube (Elemental Analysensysteme GmbH, Hanau, Germany) at a combustion temperature of 1100 – 1200 °C. Ash content was determined by incinerating pre-dried samples in a furnace at 550 °C for 5 hours (Tiquia, 2005). Organic matter was calculated as the difference between the dried and ash weights. The loss of organic matter (OM_{Loss}) was calculated from the Day 0 (OM_0) and Day 56 (OM_{56}) organic matter contents according to:

$$OM_{Loss} = \frac{OM_0 - OM_{56}}{OM_0 \times (100 - OM_{56})} \times 100 \quad [3.1]$$

Bulk density was performed by suspending a funnel above a 1-litre measuring cylinder. The funnel was filled with the sample and allowed to flow freely into the measuring cylinder. The excess material on top of the measuring cylinder was scraped off. The sample and the cylinder were then weighed and the weight / volume (bulk density) was calculated in kg m⁻³.

3.2.5 Compost Stability and Maturity Analyses

3.2.5.1 Oxygen Uptake Rate

The aerobic biological activity of the compost was measured by calculating the OUR using a pressure transducer system (System OxiTop® Control ^{OC}110, WTW GmbH, Weilheim, Germany) (Figure 3.3). Two grams of OM of each compost sample were mixed with 180 mL of distilled water and 10 mL of a nutrient solution, 10 mL of pH buffer and 2.5 mL of a nitrification inhibitor (Appendix B) in 1000 mL Duran® bottles. The control tests were performed without a compost sample.



Figure 3.3 Oxitop Control System used for measuring the Oxygen Uptake Rate

The bottles were placed, unsealed, on a stirring platform and incubated at $30 \pm 2 \text{ }^\circ\text{C}$ for 4 hours. Pressure transducer heads were then attached to the bottles and the samples returned to the incubator for 5 days. During this period, the rate at which oxygen was consumed by the inherent micro-organisms was estimated by measuring the pressure drop in the headspace above the water phase. Soda lime pellets, placed in a compartment in the headspace, were used to remove the effect of CO_2 production. The oxygen consumption was then calculated according to:

$$O_c = \frac{\Delta P \times 10}{R \times (273.15 + T)} \frac{V_{\text{gas}} \times 10000}{W \times DM \times OM} \quad [3.2]$$

where O_c is the oxygen consumption ($\text{mmol O}_2 \text{ kg}^{-1} \text{ OM hour}^{-1}$); ΔP , the pressure drop in the headspace (kPa); R , a gas constant ($83.14 \text{ L kPa K}^{-1} \text{ mol}^{-1}$); T , the

temperature at which the measurement was performed (°C); W , the initial weight of the sample (kg); DM , the dry matter content of the sample (%-w); OM , the organic matter content of the sample (%-w); and V_{gas} is the volume of the gas phase (mL), calculated according to:

$$V_{gas} = V_{vessel} - \frac{W \times DM \times 10000}{\rho} - V_{liquid} \quad [3.3]$$

where V_{vessel} is the total volume of vessel (mL), V_{liquid} , all added liquids (water, nutrient solution, pH buffer and ATU solution; mL), and ρ is the sample density (kg m⁻³), calculated according to:

$$\rho = \frac{1}{\frac{OM \times W \times DM}{1550} + \frac{(1 - OM) \times W \times DM}{2650}} \quad [3.4]$$

where 1550 is the particle density of OM (g cm⁻³) and 2650 is the particle density of mineral material (g cm⁻³). The OUR (mmol O₂ kg⁻¹ OM hour⁻¹) was then calculated from Eqn. [3.2] and the related time period according to:

$$OUR = \frac{Oc}{\Delta t} \quad [3.5]$$

where Δt is the time (in hours) when $\Delta P = 0$.

3.2.5.2 Germination Index

A cress seed germination test was performed after Prasad et al. (2010) on a mixture of 50% compost and 50% peat moss in a 10 mm square Petri dish to assess the compost maturity (Figure 3.4). The dish was completely filled with the compost and peat mixture. Ten cress seeds were sown per dish. To ensure that there was good contact with the sample material, approximately 0.5 mL of water was added to each seed before incubation.



Figure 3.4 Cress seed germination test in Petri-dishes

The dishes, inclined at a 70 – 80° angle to the horizontal with the seeds on the underside, were incubated at 25 ± 2 °C, in the dark. After 72 hours, the number of germinated seeds was counted and the root length measured. The control test was performed with fertilised peat. Each treatment was performed in triplicate. Germination index was then calculated after Tiquia and Tam (1998):

$$GI = \frac{\text{Mean germination in treatment}}{\text{Mean germination in control}} \times \frac{\text{Mean root length in treatment}}{\text{Mean root length in control}} \times 100 \quad [3.6]$$

3.2.6 Statistical Analysis

Data were analyzed using the Statistical Analyses System (SAS Institute, 2004) with each tumbler as the experimental unit. Water content, pH, bulk density, OM, N, C and H contents, C:N ratio and OUR, were analysed as repeated measures using the MIXED procedure of SAS with Tukey-Kramer adjustment for multiple comparisons. The dependent variables were: WC, pH, bulk density, OM, N, C and H contents, C:N ratio and OUR. For all the above analyses, the fixed effects were: treatment, day and tumbler. Day was the repeated measure and Day 0 was included as a random variable. Comparison of GI at Day 56 was performed using the MIXED procedure in SAS. Germination index was the dependent variable. Treatment was included as a fixed effect and start day included as a random effect. For all analyses, significance was given as p<0.05.

3.3 Results and Discussion

3.3.1 Physico-chemical Analyses

3.3.1.1 Physical Changes

In the first 5 days, all the composts had a malodour and attracted a great amount of flies. During this period, there was also a smell of NH₃ when the tumblers were opened for sampling. After 7-8 days, the presence of flies was greatly reduced and there was no longer a malodour. At the end of the composting period, most of the treatments had a reduced malodour, especially the green waste treatment. However, in the manure-only treatments, the bad odour remained and conglomerates (small spheres) were formed over time during the turning of the tumblers. The manure in the other treatments, however, remained loose, in small particles and well mixed with the bulking agents. The structure of these composts improved with time and, by the end of the composting period, the majority had achieved a peat-like appearance. This was reflected in the results of initial and final bulk density (Table 3.3, p values for Day 0 vs. Day 56 comparison not shown).

Table 3.3 Bulk density for compost treatments (means \pm SD; n=4)

	A	B	C	D	s.e.	p
Trial 1						
Day 0	374 \pm 43 ^A	268 \pm 46 ^B	300 \pm 28 ^{AB}	231 \pm 53 ^B	23.2	<0.01
Day 56	428 \pm 94 ^a	273 \pm 4 ^b	324 \pm 21 ^b	228 \pm 15 ^b	23.2	<0.01
Trial 2						
Day 0	498 \pm 75 ^A	339 \pm 64 ^B	359 \pm 56 ^B	376 \pm 66 ^B	27.2	<0.01
Day 56	582 \pm 54 ^a	330 \pm 46 ^b	341 \pm 30 ^b	362 \pm 18 ^b	27.2	<0.01

^{abc/ABC} Means without the same subscript, in a row, for the same Trial, were significantly different (p<0.05). Trial 1: A = 38 kg manure, B = 38 kg manure + 9.5 kg sawdust, C = 38 kg manure + 9.5 kg greenwaste, D = 38 kg manure + 2.8 kg straw; Trial 2: A = 38 kg manure, B = 38 kg manure + 9.5 kg sawdust, C = 38 kg manure + 9.5 kg woodchip, D = 38 kg manure + 4.75 kg sawdust + 4.75 kg woodchip.

In both T1 and T2, Day 0 and Day 56 bulk density for all the treatments with added bulking agents was the same ($p>0.05$). For T2, the bulk density of Treatment A increased with time ($p<0.01$). The T1, the bulk density increase for Treatment A was not statistically significant ($p=0.57$), most likely because its lower initial WC; 62% - initial WC for T1, 69% initial WC for T2 (Table 3.1). Moreover, in both trials, bulk density at Day 56 for Treatment A was higher than the bulk density of the other treatments (Table 3.3).

3.3.1.2 Temperature

Changes in the temperature of composts for both trials are shown in Figure 3.5. The pattern of temperature change in a pig manure composting pile has been used to monitor the stabilization of the composting process in many studies (Tiquia et al., 1996; Eiland et al., 2001; Cronje et al., 2004; Huang et al., 2004, 2006; Tiquia, 2005; Szanto et al., 2007). The temperature variation during composting in these studies followed the same 3-phase pattern as the one observed in the present study: (1) initial heating phase (2) thermophilic phase and (3) cooling/maturing phase.

In the initial heating phase, the temperature inside the compost piles began to rise immediately, rapidly achieving peak temperatures. In T1, temperatures had reached $>60\text{ }^{\circ}\text{C}$ for all treatments by Day 3. In T2, temperatures had reached $>50\text{ }^{\circ}\text{C}$ for all treatments by Day 1. In this initial heating phase, mesophilic bacteria and fungi metabolized readily degradable compounds such as sugar, fats, starch, amino acids and protein, producing CO_2 , NH_3 , H_2O , organic acids and heat (Bernal et al., 2009). The accumulation of this heat was responsible for the rise in temperature of the compost mass. Although temperatures in both trials followed similar patterns (Figure 3.5) in T2 the temperatures failed to remain as high for as long. The average daily ambient temperature during Trial 2 was lower (min $6.9\text{ }^{\circ}\text{C}$, max $14.2\text{ }^{\circ}\text{C}$) than that during T1 (min $14.6\text{ }^{\circ}\text{C}$, max $21.5\text{ }^{\circ}\text{C}$), which may account for the slightly lower temperatures in the second trial.

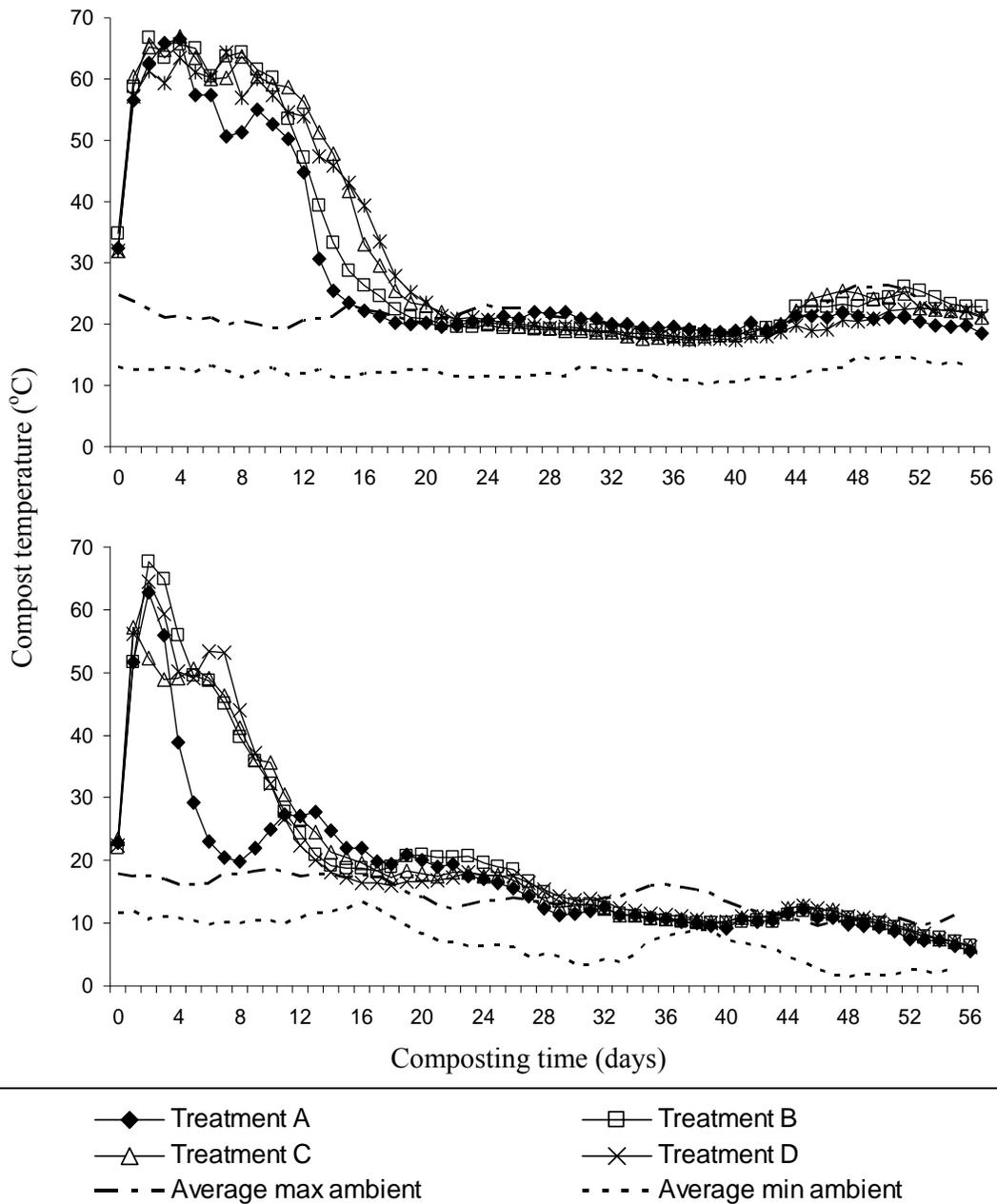


Figure 3.5 Changes in temperature during composting for (top) Trial 1 and (bottom) Trial 2. Trial 1: A = 38 kg manure, B = 38 kg manure + 9.5 kg sawdust, C = 38 kg manure + 9.5 kg greenwaste, B = 38 kg manure + 2.8 kg straw; Trial 2: A = 38 kg manure, B = 38 kg manure + 9.5 kg sawdust, C = 38 kg manure + 9.5 kg woodchip, B = 38 kg manure + 4.75 sawdust + 4.75 woodchip.

Cronje et al. (2004), studying the relationship of stability and temperature in composting of pig manure and straw, reported that the highest rate of bacterial activity occurred at around 60 °C. They concluded that this temperature corresponded with the compost of greatest stability, and therefore, it is the optimum temperature at which a composting mix of pig manure and straw should operate. Bernal et al. (2009) identified an optimum temperature range of 40-65 °C for composting. In the present study, during the second phase of composting, this ideal thermophilic temperature (50-65 °C) was maintained for a period of 1 to 2 weeks. In T1, temperatures remained above 50 °C for a period of *c.* 2 weeks for all 4 treatments. In Trial 2, temperatures remained above 45 °C for a period of 8 or 9 days for Treatments B, C and D. However, temperature for Treatment A dropped below 40 °C on Day 4. The final composting phase was characterized by a drop in temperature, indicating that thermophilic bacterial activity had slowed down.

While temperatures of around 40-65 °C are optimum for composting, temperatures above 55 °C are required to kill pathogenic microorganisms (Bernal et al., 2009). In both trials, all the treatments achieved temperatures above 55 °C.

McCarthy et al. (2011a) conducted microbiological analyses (*Salmonella*, yeasts and moulds, total coliforms, *E. coli*, *Enterococci* and spore-forming bacteria) at different time points on samples from the current study. Analyses results showed that there was no overall treatment by day interactions for either compost trial. Mean Day 0 *E. coli* counts for T1 and T2 were 5.33 and 4.12 log₁₀ cfu g⁻¹, respectively. These counts decreased to below the limit of detection of 2.00 log₁₀ cfu g⁻¹ by Day 14 and were still below the limit of detection by Day 56. Mean Day 0 *Enterococcus* counts for T1 and T2 were 4.26 and 4.89 log₁₀ cfu g⁻¹, respectively. By Day 14, these counts decreased to 2.18 and 2.04 log₁₀ cfu g⁻¹, respectively, and were below the limit of detection by Day 56. In T2, *Salmonella* was detected in one of the Treatment D compost tumblers on Day 0 but it was not detected again in any subsequent time point, indicating that it had been inactivated by the heat generated in the compost. No *Salmonella* was detected in any tumblers in T1. In both trials, the final compost complied with EU regulations (EC/208/2006; EC, 2006), which states that a marketable, processed manure product must be free from *Salmonella*, with *E. coli* or *Enterococcus* counts not exceeding 3.0 log₁₀ cfu g⁻¹.

3.3.1.3 Water Content

The initial WCs for T1 were 64.1, 51.8, 61.0 and 58.2 for Treatments A, B, C and D, respectively. For T2, these values were 69.3, 58.3, 56.9 and 55.9, respectively. In both trials, within each treatment, WC remained the same during the 56 days ($p > 0.05$). The final WCs for T1 were 62.1, 52.0, 59.2 and 57.5 for Treatments A, B, C and D, respectively. For T2, these values were 68.3, 57.7, 52.7 and 56.8, respectively. The reason for the limited change in WC over time is most likely because enclosed vessels (tumblers) were used to carry out the composting in our study. With the rise in temperature, the water which evaporated from the piles could not easily escape the tumblers. Much of the water vapour condensed on the inner walls of the tumbler, replacing the water that was initially lost through evaporation. This phenomenon could be clearly seen when the tumblers were opened for sampling.

The ideal WC of a manure compost pile is between 40 and 60% (Tiquia, 2005; Sweeten and Auvermann, 2008). Results show that the addition of bulking agents to the separated fraction of pig manure reduced WC to adequate levels for composting. In both trials, the WC for the 3 treatments that contained bulking agents remained within the range of 49-61%. Water content for the manure-only treatments remained above 60% in T1 and above 68% in T2. Treatment A lacked the bulking agent to absorb the high initial WC of the SPM. As a result, the WC of these piles had a significant effect on the microbial activity. This was more evident in T2 because of its higher initial WC. With a high initial WC of 69%, O_2 movement within the pile became restricted, resulting in anaerobic conditions (Das and Keener, 1997). Consequently, microbial activity slowed down and the production of heat was diminished. As a result, temperature dropped below 40 °C on Day 4 (Figure 3.5). This also had a detrimental effect on the stability of this treatment (Section 3.3.2.1).

3.3.1.4 pH

Changes in pH for both trials are shown in Figure 3.6. In both trials, the change in pH for the 4 treatments followed a similar pattern. The increase in pH values between Day 0 and Days 3 and 7 coincide with the highest temperatures in the compost (Figure 3.5). Higher temperatures are indicative of higher microbiological activity

(Tiquia, 2005). This higher microbiological activity resulted in a higher NH_3 production due to the mineralization of the organic N (Eklind and Kirchmann, 2000b). Finally, the higher NH_3 production was reflected in the elevated pH. The subsequent decrease in pH was caused by nitrate formation as a result of H^+ released during microbial nitrification (Eklind and Kirchmann, 2000b).

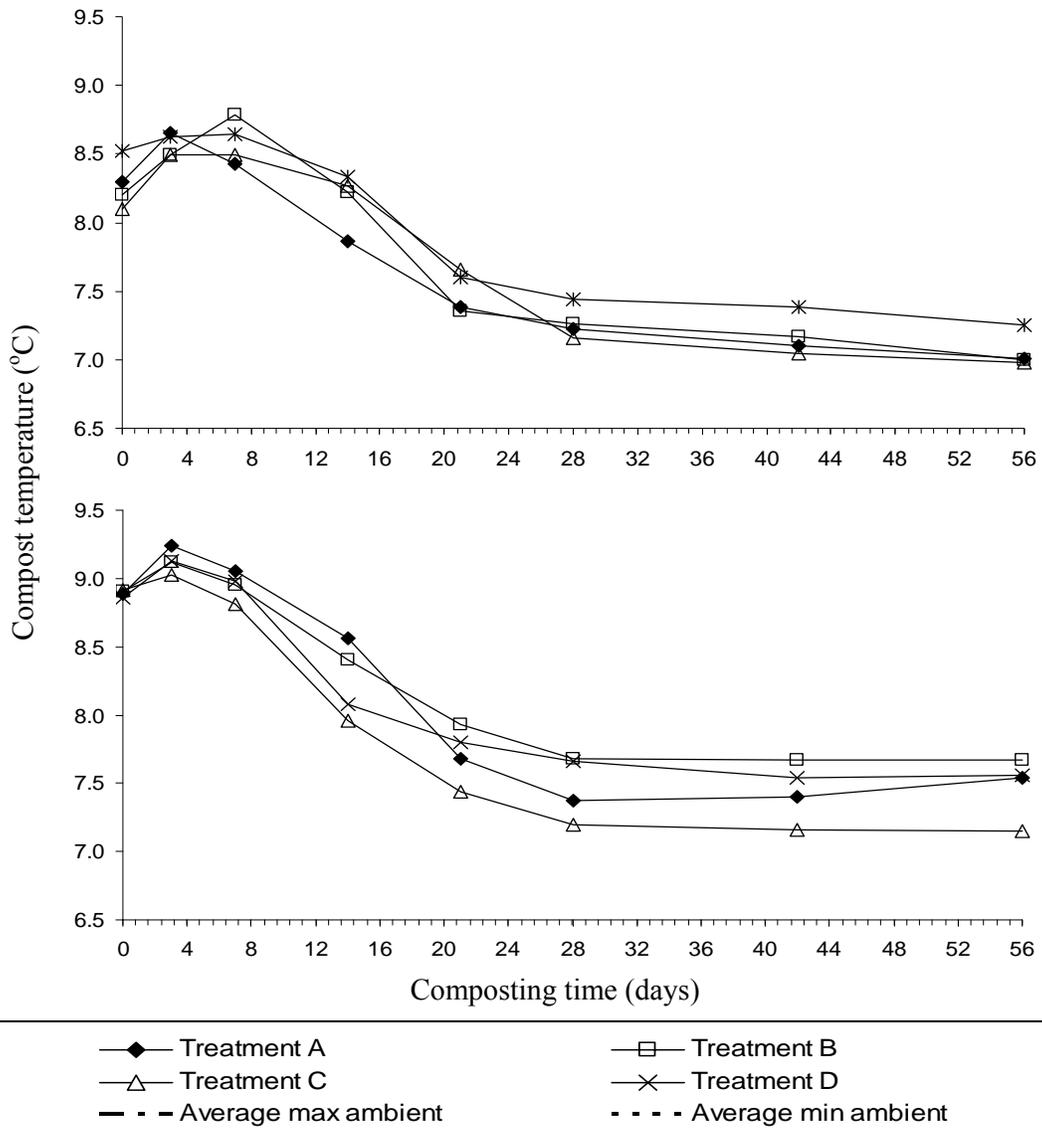


Figure 3.6 Changes in temperature during composting for (top) Trial 1 and (bottom) Trial 2. Trial 1: A = 38 kg manure, B = 38 kg manure + 9.5 kg sawdust, C = 38 kg manure + 9.5 kg greenwaste, B = 38 kg manure + 2.8 kg straw; Trial 2: A = 38 kg manure, B = 38 kg manure + 9.5 kg sawdust, C = 38 kg manure + 9.5 kg woodchip, B = 38 kg manure + 4.75 sawdust + 4.75 woodchip.

3.3.1.5 Organic Matter

Results for OM are shown in Table 3.4. In T1, final OM for Treatments A, C and D were significantly lower than initial OM ($p < 0.001$). However, for Treatment B, initial and final OM was not significantly different ($p = 0.46$). Consequently, average loss of OM for Treatment B (16.6%) was lower than OM loss for Treatments A, C and D (37.0%, 42.9% and 40.0%, respectively). In T2, for Treatment B, C and D, initial and final OM were not significantly different ($p = 0.99, 0.93$ and 1.0 , respectively). Organic matter for Treatment A decreased significantly over time ($p < 0.01$). Consequently, average OM loss for Treatment A (22.1%) was higher than OM loss for Treatments B, C and D (4.9%, -13% and 1.3%, respectively).

Table 3.4 Organic matter for compost treatments (g kg^{-1} , means \pm SD; $n=4$)

	A	B	C	D	s.e.	p
Trial 1						
Day 0	750 \pm 17 ^A	851 \pm 43 ^B	834 \pm 29 ^{BC}	783 \pm 20 ^{AC}	13.1	<0.01
Day 56	654 \pm 14 ^a	830 \pm 37 ^b	740 \pm 21 ^c	684 \pm 9 ^{ac}	13.1	<0.01
Trial 2						
Day 0	732 \pm 12 ^A	843 \pm 29 ^B	812 \pm 21 ^B	835 \pm 41 ^B	12.9	<0.01
Day 56	681 \pm 11 ^a	835 \pm 05 ^b	826 \pm 44 ^b	833 \pm 12 ^b	12.9	<0.01

^{abc/ABC} Means without the same subscript, in a row, for the same Trial, were significantly different ($p < 0.05$). Trial 1: A = 38 kg manure, B = 38 kg manure + 9.5 kg sawdust, C = 38 kg manure + 9.5 kg greenwaste, B = 38 kg manure + 2.8 kg straw; Trial 2: A = 38 kg manure, B = 38 kg manure + 9.5 kg sawdust, C = 38 kg manure + 9.5 kg woodchip, B = 38 kg manure + 4.75 sawdust + 4.75 woodchip.

Szanto et al. (2007) recorded a 57% loss of OM during the composting of straw rich pig manure (initial C:N ratio of 13) in turned piles. The smaller value of OM loss in the present study (40% for Treatment D, T1) can be explained by the methodologies used. In the present study, the OM losses were calculated as the difference in concentration of OM only. The piles were not weighed at the end of the composting process. Therefore, it was not possible to take into account the dry weight reduction of the pile as in Szanto et al. (2007). Huang et al. (2004) did not take into account the

dry weight reduction of the piles and found a comparably small (5%) loss of OM when composting pig manure and sawdust at a C:N ratio of 15.

On one hand, the lower loss of OM in Treatment B (T1) and Treatments B, C and D (T2) when compared to the other treatments in the same trial can be explained by nature of the bulking agents used (sawdust and woodchip). Woody materials have a high content of lignin (Eklind and Kirchmann, 2000a). Lignin is extremely resistant to chemical and enzymatic degradation. During a 150-day compost of sugar beet vinasse, Madejón et al. (2001) did not record any lignin degradation. When composting cattle manure, Hao et al. (2004) and Michel et al. (2004) also found a lower decomposition of the compost substrate when using bulking materials rich in lignin (woodchip and sawdust) compared to composting with straw, which had a lower lignin content. On the other hand, the lower degradability of the woodchip mixture, when compared to the sawdust mixture (T2), was probably associated with its smaller surface area-to-mass ratio.

Prasad and Foster (2009) recommended a 20 g kg⁻¹ minimum OM for Irish compost. In both trials, all treatments exceeded this limit.

3.3.1.6 Elemental Analysis and C:N Ratio

Day 0 and Day 56 C:N ratios and N content are shown in Table 3.5. For all treatments, initial C:N ratio was higher than final C:N ratio, except Treatment C (T2). The lower C:N ratio at the end of the composting process was a result of the degradation of the C fraction of the materials composted, as the N content did not change significantly (Table 3.5). During the compost process, carbonaceous materials such as carbohydrates, fats and amino acids (degraded quickly in the first stage of compost) and also, cellulose, hemicelluloses and lignin (partially degraded at a later stage) are partially mineralised, leading to C losses throughout the process (Bernal et al., 2009).

As discussed earlier, the recalcitrant nature of the lignin present in the woodchip, as well as its lower surface-to-mass ratio area, can help explain the lower degradation that occurred in Treatment C (T2).

Carbon: Nitrogen ratio has been used to assess compost maturity (Hsu and Lo, 1999; Huang et al., 2004, 2006) where a final C:N ratio of 20 or less was indicative of mature compost (when initial C:N ratio was above 20). In the present study, the final C:N ratio was below 20 for all treatments, except Treatment C, T2. However, the initial C:N ratios were already below 20 for most of the treatments (Table 3.5). Analysing the compost produced from pig manure and sawdust, Huang et al. (2004) considered that the C:N ratio cannot be used as an absolute indicator of compost maturation due to the large variation in initial C:N ratio of the starting material. Likewise, in the present study, final C:N ratio should not be used as an indicator of compost maturity.

Table 3.5 Nitrogen and C:N ratio for compost treatments (means \pm SD; n=4)

	A	B	C	D	s.e.	p
Trial 1						
N (%)						
Day 0	3.3 \pm 0.3 ^A	2.3 \pm 0.3 ^B	2.6 \pm 0.2 ^{AB}	2.7 \pm 0.4 ^{AB}	0.08	<0.01
Day 56	3.5 \pm 0.1 ^a	2.3 \pm 0.1 ^c	3.1 \pm 0.2 ^b	3.3 \pm 0.2 ^{ab}	0.04	<0.01
C:N						
Day 0	12.0 \pm 1.1 ^A	18.2 \pm 3.1 ^B	16.0 \pm 1.2 ^{AB}	14.6 \pm 1.9 ^{AB}	0.50	<0.01
Day 56	9.4 \pm 0.4 ^a	16.6 \pm 1.3 ^b	12.4 \pm 0.8 ^c	10.3 \pm 0.4 ^a	0.14	<0.01
Trial 2						
N (%)						
Day 0	3.1 \pm 0.2 ^A	2.2 \pm 0.3 ^B	1.9 \pm 0.4 ^B	2.0 \pm 0.3 ^B	0.14	<0.01
Day 56	3.1 \pm 0.2 ^a	2.2 \pm 0.1 ^b	1.8 \pm 0.1 ^b	2.2 \pm 0.1 ^b	0.08	<0.01
C:N						
Day 0	12.5 \pm 0.8 ^A	18.3 \pm 2.1 ^{AB}	23.3 \pm 5.5 ^B	21.7 \pm 3.8 ^B	1.76	<0.01
Day 56	11.1 \pm 0.8 ^a	17.9 \pm 1.0 ^b	23.4 \pm 1.8 ^c	17.5 \pm 1.1 ^b	0.61	<0.01

^{abc / ABC} Means without the same subscript, in a row, for the same Trial, were significantly different (p<0.05). Trial 1: A = 38 kg manure, B = 38 kg manure + 9.5 kg sawdust, C = 38 kg manure + 9.5 kg greenwaste, D = 38 kg manure + 2.8 kg straw; Trial 2: A = 38 kg manure, B = 38 kg manure + 9.5 kg sawdust, C = 38 kg manure + 9.5 kg woodchip, D = 38 kg manure + 4.75 kg sawdust + 4.75 kg woodchip.

3.3.2 Stability and Maturity Analyses

3.3.2.1 Oxygen Uptake Rate

Figure 3.7 shows Day 0 and Day 56 pressure profile for Treatment B, T1 and for a control sample throughout a 5-day incubation period. Pressure drop (maximum reading minus final reading) for Day 0 (178 hPa) was much higher than the pressure drop on Day 56 (58 hPa), reflecting the higher demand for O₂ in the initial, unstable material. Pressure drop for Day 0 and Day 56 for all the treatments followed the same trend (data not shown). Pressure in the control tests remained virtually unchanged (Figure 3.7).

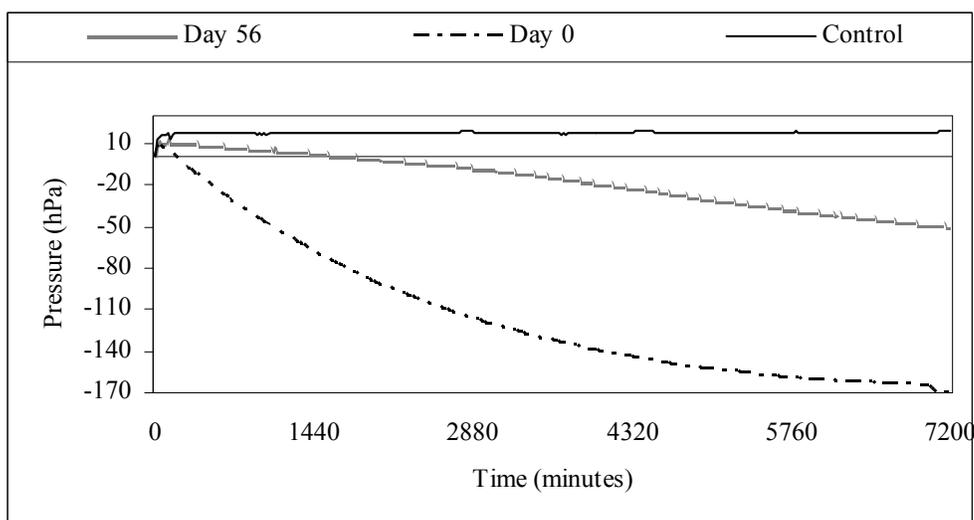


Figure 3.7 Effect of incubation time on pressure drop on Day 0 and Day 56 of Treatment B, Trial 1 (separated pig manure + sawdust) and blank control (no compost sample)

Results for the OUR tests across all trials and treatments are presented in Table 3.6 (p values for Day 0 vs. Day 56 comparison not shown). For all treatments, in both trials, OUR Day 0 was significantly higher ($p < 0.01$) than OUR Day 56, except for Treatment A, T2 ($p = 0.38$). In both trials, with the exception of Treatment A in T2, all treatments achieved OUR values below $14 \text{ mmol O}_2 \text{ kg}^{-1} \text{ OM hour}^{-1}$. The proposed OUR value for stable compost for Irish compost standards is $13 \text{ mmol O}_2 \text{ kg}^{-1} \text{ OM}$

hour⁻¹ (Prasad and Foster, 2009). This value is similar to that used in Belgium and The Netherlands, where values below 15 mmol O₂ kg⁻¹ OM hour⁻¹ are considered stable. Our results show that, with the exception of Treatment A (T2), a good degree of OM stabilization was achieved for all treatments.

In T2, the final OUR value was higher (p<0.01) for Treatment A when compared to Treatments B, C and D. One factor that could have affected the stability of Treatment A was its very low initial C:N ratio (12.5). However, Treatment A in T1 (also a manure-only treatment), had a similar initial low C:N ratio (12.0) and Day 56 OUR value of 13.4 mmol O₂ .kg⁻¹ OM. hour⁻¹. The initial WC of the pig manure used in T1 was not as high as that in the manure used in T2 (62% and 69.4%, respectively). Therefore, the lack of a bulking agent and the initial low C:N ratio did not affect Treatment A in T1 as significantly as it did in T2. The drop in temperature was not as evident in T1 as it was in T2 (Figure 3.5). It appears that the high WC was responsible for the poor stability of the manure-only treatment in T2.

Table 3.6 Oxygen Uptake Rate (mmol O₂ kg⁻¹ OM hour⁻¹) for compost treatments (means ± SD; n=4)

	A	B	C	D	s.e.	p
Trial 1						
Day 0	50.8 ± 11.7	47.4 ± 12.2	43.2 ± 13.1	40.0 ± 9.4	5.91	0.59
Day 56	13.4 ± 1.3 ^a	6.8 ± 2.1 ^b	12.5 ± 2.7 ^a	13.8 ± 3.1 ^a	1.19	<0.01
Trial 2						
Day 0	35.6 ± 11.1	30.2 ± 8.4	35.0 ± 6.6	33.2 ± 4.8	4.16	0.78
Day 56	25.2 ± 4.2 ^a	11.0 ± 1.4 ^b	12.3 ± 1.5 ^b	13.3 ± 2.5 ^b	1.28	<0.01

^{abc / ABC} Means without the same subscript, in a row, for the same Trial, were significantly different (p<0.05). Trial 1: A = 38 kg manure, B = 38 kg manure + 9.5 kg sawdust, C = 38 kg manure + 9.5 kg greenwaste, D = 38 kg manure + 2.8 kg straw; Trial 2: A = 38 kg manure, B = 38 kg manure + 9.5 kg sawdust, C = 38 kg manure + 9.5 kg woodchip, D = 38 kg manure + 4.75 kg sawdust + 4.75 kg woodchip.

These results show that the high initial WC of the separated pig manure used had a negative impact on the composting process. The high initial WC hampered the free passage of air through the empty spaces of the compost mass, resulting in zones of anaerobic conditions (Das and Keener, 1997). As a result, aerobic microbiological activity was impaired and less heat was produced, which was also reflected in the lower compost temperatures achieved with this treatment (Figure 3.5).

Tiquia et al. (1996) studied the effect of different WCs (50, 60 and 70%) on the composting of spent litter (a mixture of partially decomposed sawdust and pig manure). They showed that the decomposition process on the 70% WC pile was slower than that on the piles with 50 and 60% WC. At a WC of 70%, not only the microbial activity during thermophilic phase was lower, but there was also a delay in reaching peak temperatures. They found that high WC resulted in a cooling effect and also influenced gaseous exchange by limiting diffusion and thus restricting oxygen utilization by the microbial mass.

3.3.2.2 Germination Index

Germination indices are shown in Table 3.7. In T1, the GI for Treatments A and D were lower ($p < 0.01$) than that of Treatments B and C. In T2, there was no difference ($p = 0.81$) between the GIs for all treatments.

Table 3.7: Germination index for compost treatments (means \pm SD; n=4)

	A	B	C	D	s.e.	p
Trial 1						
Day 56	78 \pm 6.0 ^a	92 \pm 11.2 ^b	93 \pm 6.0 ^b	76 \pm 12.1 ^a	4.64	<0.01
Trial 2						
Day 56	101 \pm 12.0	99 \pm 2.4	100 \pm 6.9	97 \pm 5.6	3.41	0.81

^{abc} Means without the same subscript, in a row, for the same Trial, were significantly different ($p < 0.05$). Trial 1: A = 38 kg manure, B = 38 kg manure + 9.5 kg sawdust, C = 38 kg manure + 9.5 kg greenwaste, B = 38 kg manure + 2.8 kg straw; Trial 2: A = 38 kg manure, B = 38 kg manure + 9.5 kg sawdust, C = 38 kg manure + 9.5 kg woodchip, B = 38 kg manure + 4.75 sawdust + 4.75 woodchip.

Different studies have proposed different GIs to indicate the disappearance of phytotoxicity compounds in manure composts. Tiquia et al. (1996) propose a GI above 80-85%. Many manure compost studies follow this threshold (Tiquia and Tam, 1998; Huang et al., 2004; Tiquia, 2005). In the present study, 6 out of 8 composts achieved GIs above 90% with the other two (Treatment A and D, T1) being >76%.

The cress seed test and the OUR test were used in this study to measure different parameters of compost quality. On one hand, the cress seed test measures compost maturity and it is indicative of the presence or absence of phytotoxic components in the compost. On the other hand, the OUR test indicates how stable the compost is. However, because phytotoxic compounds are produced by the microorganisms present in unstable composts (Zucconi et al., 1985), it was expected that results from both tests would present some correlation. In T1, the OUR of Treatments A and D were above the recommended $13 \text{ mmol O}_2 \text{ kg}^{-1} \text{ OM hour}^{-1}$. Therefore, their lower GI could be explained by the production of phytotoxic compounds by the microorganisms present in these less stable composts. In T2, all treatments presented the same high GI even though the OUR value for Treatments A was significantly higher when compared to the other treatments.

The results of the present study show that unstable composts will not always inhibit germination. According to Zucconi et al. (1981), toxins are produced only during certain stages of decomposition and tend to be quickly inactivated. Moreover, when the first contact between roots and organic matter is not lethal, the plant shows a capability to recover and thrive in solids enriched with organic matter (Zucconi et al., 1981). This might explain why the unstable compost in the present study did not produce a detrimental effect on seed germination and root elongation.

Compost quality (maturity and stability) is not related to only one compost characteristic and, therefore, it should not be measured by a single parameter. In this study, especially in T2, the GI results, or any other parameter for that matter, should not be analysed on their own. For Treatment A, when including the results of OUR tests, C:N ratios and physical properties into the analyses of compost quality, it can be concluded that even though the GI was 101.6, the compost was not of good quality. Furthermore, for Treatment C, although the OUR value was below $13 \text{ mmol O}_2 \text{ kg}^{-1}$

OM hour⁻¹, the results of C:N ratio and OM degradability indicated that the compost might not have achieved complete maturation.

3.4 Summary

The addition of bulking agents and an initial WC less than 60% were necessary to successfully compost the solid fraction of pig manure at a low initial C:N ratio. Suitable bulking agents were sawdust and shredded green waste. The density of the straw was too low, which resulted in the need for very high volume of straw addition. This would be impractical on a large scale. Woodchip, due to the presence of recalcitrant lignin and its large surface area, was not a suitable bulking agent when used on its own. However, when used with sawdust, it provided good quality compost. Test results for GI, OUR and C:N ratio highlight the need to use parameters that measure maturity and stability simultaneously when assessing compost quality. In this chapter, of the bulking agents tested, sawdust resulted in the most stable compost (the compost with the lowest OUR value) in both Trial 1 and Trial 2. Therefore, it was decided to undertake further experiments using sawdust as a bulking agent. This work is detailed in the next chapter.

4 EFFECT OF SAWDUST ADDITION ON COMPOSTING OF SEPARATED RAW AND ANAEROBICALLY DIGESTED PIG MANURE

Overview

This chapter details two experiments investigating composting of the solid fraction of separated pig manure mixed with sawdust at different mixing ratios. In the first experiment, separated solids from raw pig manure were used, while in the second experiment, separated solids from anaerobically digested pig manure were used. The objective was to investigate the rate of sawdust addition to the solid fraction of separated raw and anaerobically digested pig manure required to produce stable and mature compost.

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4.1 Introduction

As described in Chapter 3, the initial C:N ratio is one of the most important factors influencing the quality of compost produced. Carbon is mainly used as an energy source and for building microbial cells and N is required for microbial development and reproduction through protein synthesis (Sweeten and Auvermann, 2008). The addition of a bulking agent is required to increase the C:N ratio of separated pig manure before composting. However, the addition of bulking agents adds an additional cost to the composting process (Zhu, 2007), and their addition rates should be the minimum amount which can be added without affecting the standard of the compost produced.

Sweeten and Auvermann (2008) recommended a C:N ratio of 20-30 for manure composting, while Rynk (1992) recommended 25-30. However, other studies have examined the use of C:N ratios at or below 20. Eiland et al. (2001) used a mixture of

Miscanthus straw and pig manure with initial C:N ratios of 25 and 16 without any adverse impact on the composting process. Furthermore, Zhu (2007) found that an initial C:N ratio of 20 could successfully produce high quality compost from pig manure mixed with rice straw. However, Zhu (2007) also found increased N loss, a shorter thermophilic phase and a longer maturity in the compost with the initial C:N ratio of 20, when compared to a similar compost with initial C:N ratio of 25. Huang et al. (2004) compared composting of pig manure with sawdust at initial C:N ratios of 15 and 30. The compost with the higher C:N ratio reached maturity after 49 days. However, the low C:N ratio compost was still immature after 63 days composting and had high salinity due to the high amount of pig manure in the mixture.

Recently, AD has become topical as a means of producing energy from farmyard by-products, including pig manure. However, AD does little to reduce the nutrient content of pig manure, which still needs to be recycled in the same way as undigested manure. Composting of pig manure after AD has not been previously investigated. The aim of this study was to investigate the effect of adding different quantities of sawdust as a bulking agent to the solid fraction of separated raw and anaerobically digested pig manures on the physiochemical and growth properties of the compost produced.

4.2 Materials and Methods

4.2.1 Trial Site and Manure Separation Process

Two composting trials were conducted to determine the effect of varying the proportion of sawdust to either separated raw or separated anaerobically digested pig manures. In Trial 1 (T1), raw pig manure was collected from an uncovered over-ground manure storage tank at the Teagasc Pig Development Department, Moorepark, Fermoy, Co. Cork, Ireland, and was a mixture of pig manure from all stages of pig production. In Trial 2 (T2), anaerobically digested pig manure was collected from another pig farm and transferred to the study site before separation. This manure also came from all stages of production and was aerated prior to AD. Since the pig manure

from each trial was taken from different pig farms, with different diets and manure management systems, it was not possible to compare the composts from T1 and T2.

A decanter centrifuge (Figure 3.1) was used to perform the mechanical separation of both the raw pig manure and the anaerobic digestate as described in Section 3.2.1. Approximately 10 m³ of liquid feedstock was separated for each trial. Ten samples for each the liquid pig manure before separation, solid fraction after separation, and liquid fraction after separation were analysed for DM in T1 and T2. The results obtained were 1.5 ± 0.71%, 32.7 ± 2.66% and 0.3 ± 0.14%, respectively, in T1. For T2, the results obtained were 2.3 ± 0.68%, 30.6 ± 3.09% and 0.6 ± 0.07%, respectively. Sitka spruce (*Picea sitchensis*) sawdust was added as a bulking agent to adjust the C:N ratio and to reduce the WC. The sawdust and separated manure were thoroughly mixed to ensure homogeneity. Samples were taken from the raw and anaerobically digested pig manures before separation and the separated solid and liquid fractions after separation. The WC, pH, bulking density, elemental analysis, C:N ratio and OM of the separated solids and of the sawdust were determined before mixing (Table 4.1).

Table 4.1 Physico-chemical parameters for separated pig manure (SPM), separated AD pig manure (SADPM) and sawdust (means ± SD)

Parameters	SPM (Trial 1)	SADPM (Trial 2)	Sawdust
pH	8.03 ± 0.14	8.19 ± 0.22	4.85 ± 0.09
DM (%)	32.7 ± 2.7	30.6 ± 3.1	85.6 ± 2.7
Nitrogen (%)	4.2 ± 0.7	4.1 ± 0.6	0.1 ± 0.01
Carbon (%)	43.8 ± 3.4	41.3 ± 2.7	51.4 ± 0.3
Hydrogen (%)	6.1 ± 0.3	5.7 ± 0.3	5.7 ± 0.01
C:N ratio	10.6 ± 1.4	10.1 ± 0.9	466.5 ± 58.6
Bulk density (kg m ⁻³)	389 ± 53	467 ± 26	40 ± 2
Organic matter (g kg ⁻¹)	752 ± 33	778 ± 10.8	997 ± 0.2

n=5 for pig manure; n=10 for sawdust

4.2.2 Compost Preparation and Sampling

Fifteen insulated tumblers (Figure 3.2) were used to compost the swine manures and sawdust mixtures. Separated raw pig manure was used for T1 and separated AD pig manure (SADPM) was used for T2. Three sawdust rates were added to the manures: Treatment A consisted of 40 kg (fresh weight) of separated manure solids and no sawdust. Treatment B consisted of 40 kg of separated solids and 10 kg of sawdust (to provide an initial C:N ratio of ~16). Treatment C consisted of 30 kg of separated solids and 20 kg of sawdust (to provide an initial C:N ratio of ~ 30). Each treatment was replicated five times except for Treatment A in T2, which consisted of only four replications. One replication of each treatment commenced on each day over 5 days until all 5 replicates were commenced. Aeration of the tumblers, temperature recording and sampling was the same as the previous study (Section 3.2.2).

4.2.3 Physico-chemical Analysis

Physico-chemical analyses undertaken for this study were the same as those described in Chapter 3. Fresh samples taken from the compost piles were tested for pH, WC and bulk density as described in Section 3.2.4. Ash content, OM, C, N, and H contents were determined from dried samples collected on Day 0 and Day 56, as described in Section 3.2.4.

4.2.4 Compost Stability and Maturity Analyses

Compost stability was measured using the OUR test as described in Section 3.2.5. Compost maturity was measured using a cress seed germination test to determine the GI as described in Section 3.2.5.

4.2.5 Statistical Analysis

Data were analyzed using the Statistical Analyses System (SAS Institute, 2004). For comparison of WC, pH, bulk density, OM, N, C and H contents, C:N ratio and OUR, repeated measures ANOVA was used (Mixed procedure) with these parameters as the dependent variables. For all the above analyses, the fixed effects were: treatment, day

and tumbler. Day was the repeated measure and starting day was included as a random variable.

Comparison of GI at Day 56 was performed using the Proc Mixed SAS procedure. Germination index was the dependent variable. Treatment was included as a fixed effect and start day included as a random effect. For all analyses, significance was given as $p < 0.05$.

4.3 Results and Discussion

4.3.1 Physio-chemical Analyses

4.3.1.1 Physical Changes

From Day 0 to approximately Day 7, all treatments in both trials were malodorous. This was particularly noticeable when the tumblers were opened for sampling. However, by Day 14 the pungent odour could no longer be detected. Water was observed to be leaching out of the tumblers in Treatment A for both trials. There was no leaching recorded from Treatments B and C in either trial.

On Day 0, when the tumblers were filled, the separated pig manure had the flaky appearance of peat. However, for both trials, conglomerates (spheres of manure) were formed during the turning of the tumblers in Treatment A. The occurrence of large conglomerates was not evident in Treatments B and C. In these treatments, particle sizes were small, well mixed, and were peat-like in appearance throughout the composting process. The turning of the composting tumblers may influence the formation of conglomerates, which may not occur in a large-scale operation, where windrows and mechanical turning are used.

The bulk densities on Day 0 and Day 56 are given in Table 4.2. For both trials, the mean bulk density for Treatment A increased significantly from Day 0 to Day 56 ($p < 0.01$ for T1, $p < 0.001$ for T2). However, the mean bulk density of Treatments B and C did not change significantly ($p > 0.05$) over time in either trial. For T2, there was a significant decrease ($p < 0.001$) in bulk density as the proportion of sawdust in the

tumblers increased. For T1, there was also a decrease in bulk density; however, this decrease was not significant ($p>0.05$). Decreasing bulk density is linearly proportional to increasing FAS and decreasing WC (Agnew et al., 2003; Iqbal et al., 2010). Bulk density, WC, and FAS all play an important role in achieving the optimum aerobic conditions during the composting process which, in turn, affects the efficiency of the process (Iqbal et al., 2010).

Table 4.2 Bulk density for compost treatments (means \pm SD; n=5)

	A	B	C	s.e.	P
Trial 1					
Day 0	389 \pm 52.8	296 \pm 51.5	226 \pm 17.8	26.0	<0.001
Day 56	460 \pm 66.3	278 \pm 20.7	210 \pm 10.6	26.0	<0.001
Trial 2					
Day 0	467 \pm 26.1 ^A	309 \pm 43.1 ^B	243 \pm 16.7 ^C	7.2	<0.001
Day 56	589 \pm 19.1 ^a	337 \pm 16.4 ^b	231 \pm 10.5 ^c	7.2	<0.001

^{abc / ABC} Means without the same subscript, in a row, for the same Trial, were significantly different ($p<0.05$). Trial 1 = raw manure; Trial 2 = AD manure; Treatment A = 40 kg manure only; Treatment B = 40 kg manure + 10 kg sawdust; Treatment C = 30 kg manure + 20 kg sawdust.

4.3.1.2 Temperature

Temperature is an excellent indicator of the microbial activity in a composting pile (Bernal et al., 2009). Temperatures in the tumblers went through three distinct phases similar to those in Chapter 3 (Figure 3.5): an initial heating phase, a thermophilic phase, and cooling/maturing phase (Figure 4.1). The patterns of compost temperature change have been used to monitor the stabilization of the composting process (Tiquia et al., 1996; Huang et al., 2004; Tiquia, 2005). Temperatures rose very quickly in all reactors during the heating phase, indicating a rapid establishment of microbial activity. During this phase, readily degradable simple organic compounds are broken down (de Bertoldi et al, 1983). Bernal et al. (2009) identified an optimum temperature range of 40-65 °C for composting. Average temperatures of >50 °C were achieved by Day 2 across all treatments, indicating a thermophilic phase. During this phase, more

complex compounds such as fats, cellulose and lignin are degraded by thermophilic microorganisms (Bernal et al., 2009). The thermophilic phase was relatively short, due to the small scale of these composting tumblers, when compared with large-scale windrow composting, for example.

The thermophilic phase for Treatment A for both trials was much shorter than that of Treatments B and C. In T1, Treatment A dropped below 50 °C after Day 6 compared to Days 10 and 8 for Treatments B and C, respectively. For T2, Treatment A dropped below 50 °C after Day 4 compared to Day 11 for both Treatments B and C. The shorter thermophilic phase in Treatment A may be attributed to its lower C:N ratio and higher WC due to the absence of any C-rich bulking agent in this treatment. The insufficient supply of C likely caused unfavourable conditions for the growth and activity of the thermophilic microorganisms (Huang et al., 2004). The higher WC in this treatment caused the formation of conglomerates. Reduced oxygen movement within these wet conglomerates may have given rise to anaerobic conditions (Das and Keener, 1997), further causing a shorter thermophilic phase.

Treatments B and C had similar temperature profiles in both trials. Treatment B had the higher maximum temperature for both T1 and T2 - 68.8 and 70.1 °C, respectively, compared to 64.2 and 66.2 °C, respectively, for Treatment C. This could indicate higher initial microbial activity in Treatment B, or it could also be due to the increased porosity caused by the larger amount of added sawdust in Treatment C. This increased porosity allows for increased air movement that may have reduced the temperatures. However, Treatment C did remain above ambient temperatures for a longer period of time than Treatment B, indicating that elevated microbial activity continued for longer in this treatment. The average daily ambient temperatures are given in Figure 4.1. These show that during T1, average ambient temperatures were lower (min 6 °C, max 16 °C) than that during T2 (min 13 °C, max 23 °C), which may account for the slightly lower composting temperatures and shorter thermophilic phases observed in T1.

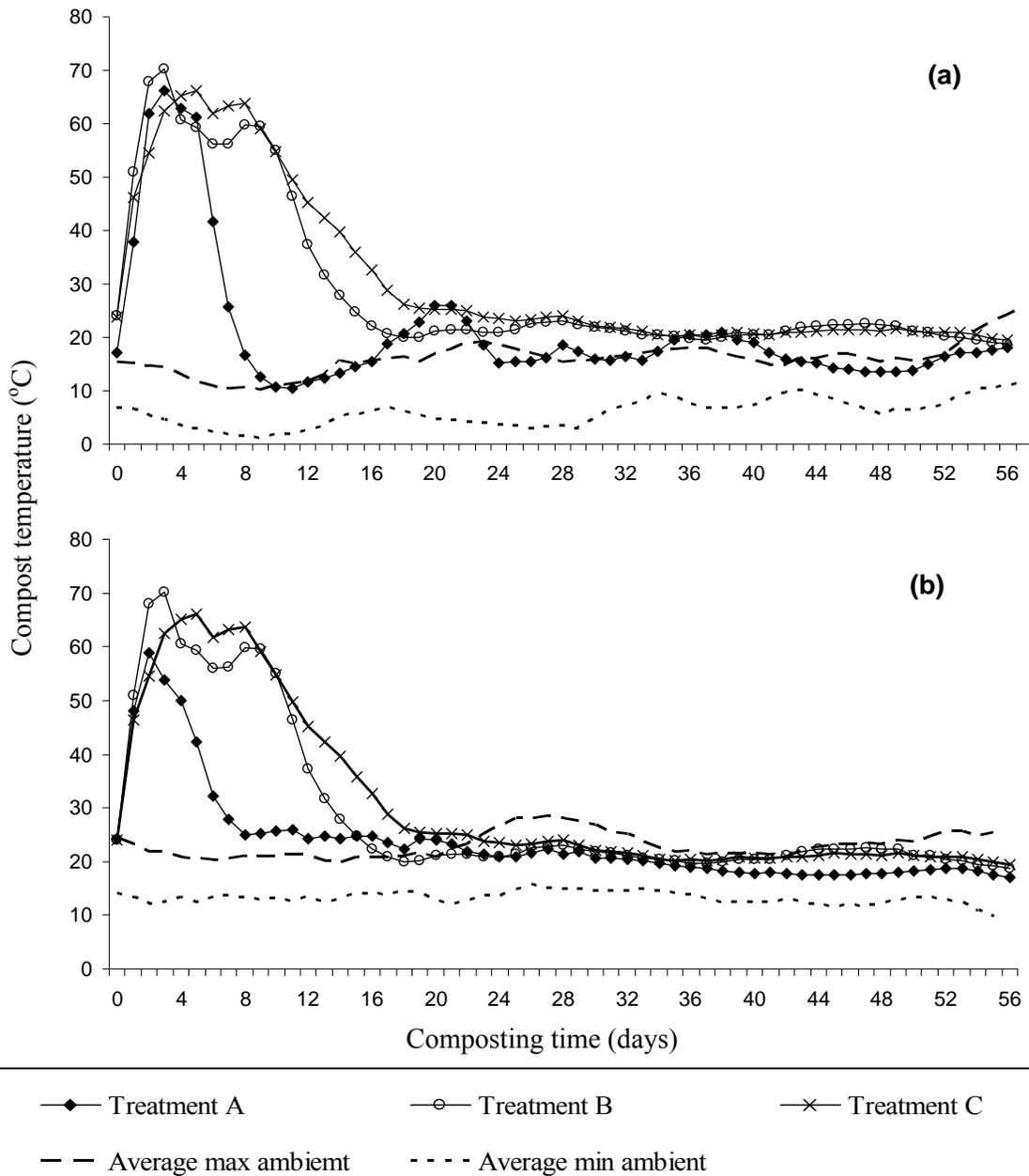


Figure 4.1 Changes in temperature during composting for (a) Trial 1 – raw manure and (b) Trial 2 – AD manure. Treatment A = 40 kg manure only; Treatment B = 40 kg manure + 10 kg sawdust; Treatment C = 30 kg manure + 20 kg sawdust

4.3.1.3 pH

The pH values followed a similar pattern for all treatments (Figure 4.2). Compost pH increased significantly after Day 0 to a maximum value during the thermophilic

phase. There was no significant difference in pH between any treatment on any particular sampling day ($p > 0.05$). For T1, the pH was initially 8.0, 7.9 and 7.6 for Treatments A, B and C, respectively, and increased significantly to reach respective peak values of 8.6, 8.6 and 8.3 ($p < 0.001$), respectively, on Day 21. This was followed by a significant decrease to final values of 7.3, 7.5 and 7.1 ($p < 0.001$), respectively, on Day 56. For T2, the pH was initially 8.2, 8.1 and 7.8 for Treatments A, B and C, respectively. This quickly increased to respective peak values on Day 3 of 8.6, 8.6 and 8.2 ($p < 0.001$), respectively. Unlike T1, there was then a slow decrease in pH until Day 21. This was followed by a significant decrease in pH until the final values of 6.7, 6.6 and 6.6 ($p < 0.001$), respectively, were achieved on Day 56.

The highest pH values occurred during the thermophilic phase when temperatures were at their highest. High temperatures are indicative of higher microbial activity (Tiquia, 2005). This high rate of microbial activity caused increased pH due to the production of NH_3 during ammonification and mineralisation of organic nitrogen (Eklind and Kirchmann, 2000a). At lower C:N ratios, NH_3 emissions can occur if the amount of N in the compost is greater than that needed for microbial growth. Ekinci et al. (2000) found that NH_3 loss depends on both initial pH and initial C:N ratio, and that by increasing the initial C:N ratio from 18 to 30, NH_3 losses were reduced by 50%. This indicates that NH_3 volatilisation may have been higher for Treatment B than Treatment C due to the lower initial C:N ratios. Compost pH fell when the temperature in the compost had decreased during the maturing phase. The decrease in pH likely resulted from NH_3 volatilisation and the release of H^+ during nitrification (Eklind and Kirchmann, 2000a). Some of this decrease may also have been caused by the production of organic acids in the compost (Sweeten and Auvermann, 2008).

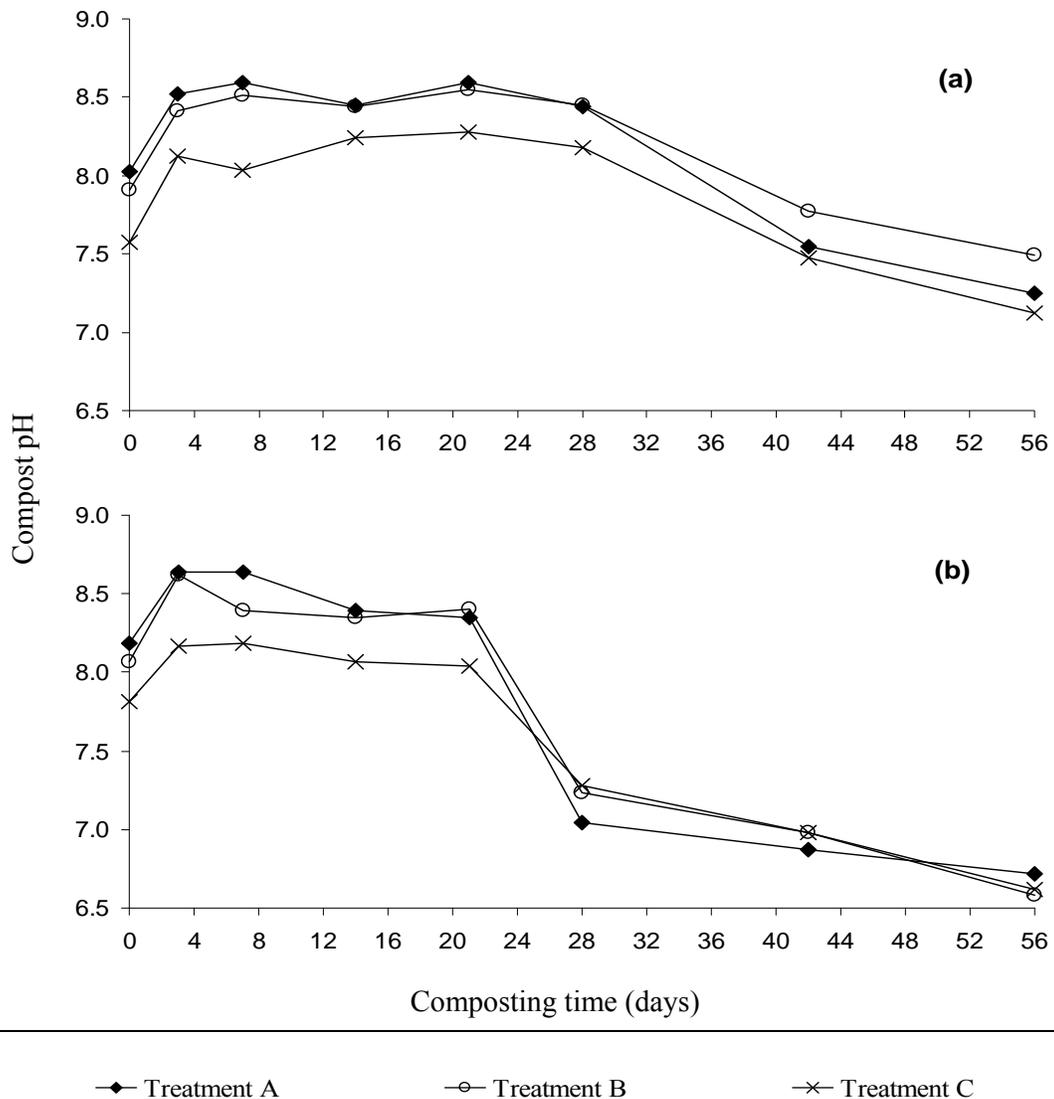


Figure 4.2 Changes in pH during composting for (a) Trial 1 – raw manure and (b) Trial 2 – AD manure. Treatment A = 40 kg manure only; Treatment B = 40 kg manure + 10 kg sawdust; Treatment C = 30 kg manure + 20 kg sawdust.

4.3.1.4 Water Content

The optimum WC for efficient composting is between 40 and 60% (Sweeten and Auvermann, 2008). When the WC exceeds 60%, oxygen movement is inhibited in the compost pile and the process becomes anaerobic (Das and Keener, 1997). Increased WC also results in a decrease in FAS within the composting pile (Iqbal et al., 2010). In both trials, Treatment A was above 60% for the duration of the composting

process, while Treatments B and C were between 40 and 60%. Tiquia et al. (1996) found that a WC of 70% caused premature cooling and decreased microbial activity during composting of pig manure sawdust litter in comparison to WCs of 50% and 60%. These results are reflected in this study where Treatment A - with the higher WC - achieved lower temperatures in both trials (Figure 4.1).

The initial WCs for T1 were 70.7, 60.5 and 48.4 for Treatments A, B and C, respectively. For T2, these values were 68.4, 57.7 and 45.0, respectively. For both trials, Treatment A had a higher WC than Treatment B and C on every sampling day ($p < 0.001$). In both trials, all three treatments showed no decrease in WC over the duration of the trials ($p = 0.93$ for T1, $p = 0.62$ for T2). The final WCs for T1 were 68.4, 59.3 and 47.1 for Treatment A, B and C, respectively. For T2, these values were 69.5, 58.1 and 49.1, respectively. The limited change in WC over time was due to the type of composting process used in these experiments. The enclosed nature of the tumblers caused some of the water vapour lost from the compost through evaporation to condense on the inside of the tumbler walls and drop back into the compost. This caused the WC to remain relatively stable throughout the composting process. This would not have occurred in large-scale windrow composting where the water vapour would have been lost to the atmosphere.

4.3.1.5 Elemental Analysis and C:N Ratio

The elemental analysis and C:N ratios of all treatments on Day 0 and Day 56 are given in Table 4.3 (standard error and p values for changes over time not shown). The C content increased with each incremental addition of sawdust to the manure, and was significant in T1 but not in T2 (Table 4.3). Increasing the sawdust addition significantly decreased N contents in both trials (Table 4.3). All treatments in both trials showed increases in N content, decreases in C and H contents, and reductions in the C:N ratio from the beginning to the end of the composting process, except for Treatment A in T2. Carbon losses are caused by the degradation of carbohydrates, fats and amino acids in the first stage of the composting process and the partial degradation of cellulose, hemicelluloses and lignin during the later stages (Bernal et al., 2009).

Table 4.3 Nitrogen, carbon, hydrogen and C:N ratio for compost treatments (means \pm SD; n=5)

	A	B	C	s.e.	p
Trial 1					
N (%) Day 0	4.2 \pm 0.7 ^a	2.6 \pm 0.4 ^b	1.6 \pm 0.2 ^c	0.27	<0.01
N (%) Day 56	4.3 \pm 0.5 ^a	2.8 \pm 0.2 ^b	1.8 \pm 0.3 ^c	0.27	<0.01
C (%) Day 0	43.8 \pm 3.4 ^a	46.1 \pm 1.2 ^{ab}	47.8 \pm 1.5 ^b	0.94	<0.01
C (%) Day 56	39.3 \pm 3.9 ^a	44.1 \pm 1.5 ^b	45.5 \pm 1.7 ^b	0.94	<0.01
H (%) Day 0	6.1 \pm 0.3	6.2 \pm 0.2	6.3 \pm 0.2	0.18	0.06
H (%) Day 56	5.4 \pm 0.6	5.9 \pm 0.2	5.9 \pm 0.2	0.18	0.06
C:N Day 0	10.4 \pm 1.4 ^a	17.5 \pm 3.3 ^b	29.6 \pm 4.3 ^c	1.76	<0.01
C:N Day 56	9.3 \pm 0.7 ^a	16.0 \pm 0.9 ^b	24.9 \pm 5.0 ^c	1.76	<0.01
Trial 2					
N (%) Day 0	4.1 \pm 0.6 ^a	2.8 \pm 0.4 ^b	1.6 \pm 0.3 ^c	0.23	<0.01
N (%) Day 56	1.8 \pm 0.2 ^A	3.9 \pm 0.6 ^B	2.8 \pm 0.5 ^C	0.23	<0.01
C (%) Day 0	41.3 \pm 2.7	44.3 \pm 0.8	45.4 \pm 1.4	1.27	0.26
C (%) Day 56	43.3 \pm 2.0	38.9 \pm 5.4	41.7 \pm 2.2	1.27	0.26
H (%) Day 0	5.7 \pm 0.3	5.7 \pm 0.1	5.7 \pm 0.2	0.22	0.60
H (%) Day 56	5.3 \pm 0.2	5.1 \pm 0.7	5.4 \pm 0.3	0.22	0.60
C:N Day 0	10.1 \pm 0.9 ^a	16.0 \pm 2.0 ^b	30.3 \pm 6.2 ^c	2.49	<0.01
C:N Day 56	25.0 \pm 3.7 ^A	10.0 \pm 2.1 ^B	15.2 \pm 2.8 ^C	2.49	<0.01

^{abc / ABC} Means without the same subscript, in a row, for the same Trial, were significantly different (p<0.05). Trial 1 = raw manure; Trial 2 = AD manure; Treatment A = 40 kg manure only; Treatment B = 40 kg manure + 10 kg sawdust; Treatment C = 30 kg manure + 20 kg sawdust.

In Treatment A in T2, the C:N ratio increased significantly (p<0.001) from 10.1 to 25.0 from Day 0 to 56. This unexpected increase was caused by the large reduction in the N content of the pile, from 4.1% on Day 0 to 1.8% on Day 56 (Table 4.3). In all other treatments, there was an increase in N content over time due to the loss of CO₂ and also water loss through evaporation. Losses of N during the composting of

manure can occur due to volatilisation of NH_3 (Tiquia and Tam, 2000). Also, when the WC of the compost is high, leaching of NO_3^- may occur (Tiquia et al., 1998). As described in Section 4.3.1.1, there was some leachate lost from this treatment, due to its high WC, which may have resulted in the higher loss of N from this treatment.

In Treatment C, the initial C:N ratios were 29.6 and 30.3 for T1 and T2, respectively. When the initial C:N ratio is between 25 and 30, the final value for a stable compost should be at or below 20 (Hiria et al., 1983). This was the case in T2, where the final C:N ratio decreased significantly ($P < 0.001$) to 15.2. However, the C:N ratio in T1, at 24.9, surpassed this upper limit, indicating that the composting process was more efficient in T2. This result was supported by the longer thermophilic period observed in T2 in comparison to T1, and by the GI and OUR values (discussed in Section 4.3.2), which, for T3, were better in T2 than T1.

The initial C:N ratio of Treatment B was 17.5 and 16.0 in T1 and T2, respectively, while the final C:N ratio was 16.0 and 10.0, respectively. However, it is not appropriate to use final C:N ratio as an indicator of compost maturity when the initial C:N ratio is low (Huang et al., 2004). Therefore, in this case, another method, such as GI, may be used to test the maturity of the compost (Huang et al., 2004).

4.3.1.6 Organic Matter

It has been recommended that the minimum OM content for compost in Ireland be set at 200 g kg^{-1} (Prasad and Foster, 2009). All of the treatments in both trials easily exceeded this, as final OM values for all composts treatments were above 700 g kg^{-1} . The OM content for all treatments is given in Table 4.4. Treatment C had the highest OM in both trials due to the high levels of sawdust added to this treatment, while Treatment A had the lowest OM. In both trials, all three treatments were significantly different from each other (Table 4.4, $p < 0.001$).

The total loss of OM may be used as an indicator of compost biodegradation. However, the dry weight reduction was not measured as part of this experiment; therefore, it was not possible to measure the total loss of OM. The OM losses were calculated as the differences in concentrations of OM only (Huang et al., 2004). The

OM content of the piles decreased from Day 0 to Day 56 for all treatments ($p < 0.001$). This was caused by the degradation of the OM by the microorganisms during composting. For T1, the losses of OM from the beginning to the end of the composting process were 22.5%, 19.2% and 14.8% for Treatments A, B and C, respectively. For T2, these losses were 20.6%, 17.5% and 9.6%, respectively. The loss in OM was greatest in Treatment A, followed by Treatment B and then Treatment C. These reduced rates of change in OM content were due to the addition of lignin-rich sawdust in Treatments B and C. Lignin is extremely resistant to chemical and enzymatic degradation. Michel et al. (2004) also found a lower decomposition in the compost substrate and decreased amounts of organic C lost during the composting process when using lignin-rich bulking agents.

Table 4.4 Organic matter for compost treatments (means \pm SD; $n=5$)

	A	B	C	s.e.	p
Trial 1					
Day 0	75.2 \pm 3.3 ^a	85.2 \pm 2.2 ^b	91.1 \pm 2.1 ^c	0.75	<0.001
Day 56	70.1 \pm 3.2 ^A	82.4 \pm 1.0 ^B	89.8 \pm 0.1 ^C	0.75	<0.001
Trial 2					
Day 0	77.8 \pm 1.1 ^a	86.8 \pm 2.9 ^b	91.8 \pm 0.8 ^c	0.45	<0.001
Day 56	73.6 \pm 1.4 ^A	83.4 \pm 1.0 ^B	91.0 \pm 0.7 ^C	0.45	<0.001

^{abc/ABC} Means without the same subscript, in a row, for the same Trial, were significantly different ($p < 0.05$). Trial 1 = raw manure; Trial 2 = AD manure; Treatment A = 40 kg manure only; Treatment B = 40 kg manure + 10 kg sawdust; Treatment C = 30 kg manure + 20 kg sawdust.

4.3.2 Maturity and Stability Analysis

4.3.2.1 Oxygen Uptake Rate (OUR)

Results for the OUR tests for both trials are shown in Table 4.5 (standard errors and p values for changes over time not shown). For both trials, Day 0 OUR values were significantly higher than those on Day 56 for all treatments ($p < 0.001$). This indicates that the compost was more stable at the end of the process than at the beginning. For

both trials, Day 56 OUR values for Treatment A were higher compared to Treatments B and C ($p < 0.05$) (Table 4.5). This signifies that Treatment A underwent less biological decomposition than Treatment B and C, thereby producing a less stable end-product. This was confirmed by the lower microbial activity and lower temperatures observed for this treatment (Figure 4.1) as a consequence of the treatment's initially high WC and low C:N ratio. Tiquia et al. (1996) studied the effect of WCs (50, 60 and 70%) on the decomposition rate of spent pig litter. They found that the decomposition process was slower for the 70% WC pile, due to the cooling effect of the water and the restriction of oxygen from the microbial mass.

Table 4.5 Oxygen Uptake Rate ($\text{mmol O}_2 \text{ kg}^{-1} \text{ OM hour}^{-1}$) for compost treatments (means \pm SD; $n=5$)

	A	B	C	s.e.	p
Trial 1					
Day 0	53.0 ± 11.5^a	42.6 ± 7.8^b	35.9 ± 4.5^b	1.85	<0.001
Day 56	26.4 ± 8.4^A	12.1 ± 4.5^B	8.0 ± 2.3^B	1.85	<0.001
Trial 2					
Day 0	42.4 ± 8.8^a	28.7 ± 7.4^b	22.9 ± 5.3^b	1.58	<0.001
Day 56	16.2 ± 2.7^A	8.3 ± 2.9^B	8.0 ± 1.3^B	1.58	<0.001

^{abc / ABC} Means without the same subscript, in a row, for the same Trial, were significantly different ($p < 0.05$). Trial 1 = raw manure; Trial 2 = AD manure; Treatment A = 40 kg manure only; Treatment B = 40 kg manure + 10 kg sawdust; Treatment C = 30 kg manure + 20 kg sawdust.

The proposed OUR threshold value in Ireland for stable compost is $13 \text{ mmol O}_2 \text{ kg OM}^{-1} \text{ hour}^{-1}$ (Prasad and Foster, 2009). This value is similar to that used in Belgium and The Netherlands, where this test is commonly used. In these countries, values above $15 \text{ mmol O}_2 \text{ kg OM}^{-1} \text{ hour}^{-1}$ are considered unstable (Prasad and Foster, 2009). Treatments B and C in both trials reached stability values below the recommended Irish threshold by Day 56. However, Treatment A was higher than this value and could not be considered stable at Day 56. There was no difference in Day 56 OUR

values between Treatments B and C in either of the trials ($p=0.94$ for T1, $p=1.00$ for T2).

4.3.2.2 Germination Index

The GI values for T1 and T2 are given in Table 4.6. The GI for Treatment C was significantly higher than Treatment A ($p<0.05$) for both treatments. Zucconi et al. (1981) reported that GI values below 50% indicated the presence of phytotoxic compounds in the compost. Jodice (1989) reported that a GI of 50 - 70% indicated low levels of phytotoxins present, while Tiquia and Tam (1998) suggest that phytotoxic free compost is indicated when GI is above a threshold of 80%. Other studies have followed this latter threshold (Huang et al., 2004, 2006; Tiquia, 2005). Using these results, Treatment C in both trials could be classified as phytotoxin free, while Treatments B and C in both trials had low levels of phytotoxins.

Table 4.6 Germination index for compost treatments (means \pm SD; $n=5$)

	A	B	C	s.e.	p
Trial 1					
Day 56	59 \pm 18.9 ^a	63 \pm 26.5 ^{ab}	83 \pm 15.5 ^b	8.59	<0.05
Trial 2					
Day 56	61 \pm 26.4 ^a	70 \pm 16.3 ^{ab}	95 \pm 8.3 ^b	11.2	<0.05

^{abc} Means without the same subscript, in a row, for the same Trial, were significantly different ($p<0.05$). Trial 1 = raw manure; Trial 2 = AD manure; Treatment A = 40 kg manure only; Treatment B = 40 kg manure + 10 kg sawdust; Treatment C = 30 kg manure + 20 kg sawdust.

Phytotoxins produced by the microorganisms in the less stable composts inhibit growth (Zucconi et al., 1981) and lead to lower GI values. High copper, zinc, organic acids and NH_4^+ concentrations and high electrical conductivity have also been shown to inhibit seed germination in manure-based composts (Tiquia and Tam, 1998; Huang et al., 2004). Sawdust addition to manure will dilute the concentration of these inhibitors and reduce EC in the mixture. The GI values for both trials compared favourably with those from Huang et al. (2004), who studied composting of pig

manure and sawdust at initial C:N ratios of 30 and 15. After 63 days of composting, Huang et al. (2004) reported a GI of 85% for a C:N ratio of 30, and 46% for a C:N ratio of 15. The lower GI was attributed to a higher EC in the treatment which received the lower sawdust inclusion.

There was generally a good correlation between the results of both tests for compost quality. The OUR test was used to test the stability of the compost, while the GI measured the presence of phytotoxicity, which indicates compost maturity. This relationship was expected since the phytotoxins measured in the GI test are produced by the microorganisms present in the unstable compost (Zucconi et al., 1985). In both trials, the treatments with the highest OUR values corresponded to the treatment with the lowest GI values. However, as seen in Chapter 3, this relationship may not always be present, hence the need for the two separate tests to determine compost quality. Other parameters important in determining compost quality are pathogen load and heavy metal (especially Cu and Zn) content, but these were not determined in the current study.

4.4 Summary

The effect of varying the proportion of sawdust to either separated raw or separated anaerobically digested pig manures was analysed in two trials. Composts with manure-to-sawdust ratios of 4:1 and 3:2 (fresh weight) were found to be stable after 56 days of aerobic composting. Both treatments met the proposed stability standard for composts in the Republic of Ireland. No differences between these two treatments were found for the stability test (oxygen uptake rate) and the maturity test (germination index).

It is concluded that co-composting either separated raw or separated anaerobically digested pig manures with sawdust at a manure-to-sawdust ratio of 4:1 (w/w) and a C:N ratio of 18 or 16, respectively, can produce stable compost. Using this lower ratio reduces the quantity of sawdust required and hence the cost to produce stable compost; 60% less sawdust is required to compost at a manure-to-sawdust ratio of 4:1, compared to 3:2. Using this lower ratio may make composting pig manure more

financially attractive to farmers, and persuade them to implement on-farm composting as a means of nutrient recycling. However, an economic analysis is required to analyse the cost-effectiveness of composting pig manure at these lower C:N ratios. This economic analysis is detailed in the next chapter.

5 ECONOMIC ANALYSIS OF SEPARATION AND COMPOSTING OF PIG MANURE IN IRELAND

Overview

An economic analysis was performed on separation and composting of pig manure after AD. This work forms part of a larger study, which included other pig manure treatment options including AD of pig manure mixed with grass silage and the use of ICWs to treat the liquid fraction after separation, and has been published in *Bioresource Technology* (2012; 105, 15 – 23). However, only the analyses dealing with separation and composting which will be the focus of this Chapter.

5.1 Introduction

In Chapter 3, composting of the separated solid fraction of pig manure using various bulking agents was investigated. From the bulking agents examined in that study, sawdust resulted in the most stable compost. In Chapter 4, composting of both raw and anaerobically digested pig manure with sawdust at a low initial C:N ratio was investigated. From that study, it was concluded that stable compost could be produced using an initial C:N ratio lower than the value of 25-30 previously recommended. However, if separation or composting of pig manure is to become a widely used pig manure treatment option on farms, an economic analysis is required to compare this treatment option with the current method of landspreading the manure.

The volume of pig manure (or digestate) is the most important factor influencing transportation costs. Solid–liquid separation by decanting centrifuge produces two fractions: a P-rich solid fraction and a N-rich liquid fraction (Gilkinson and Frost, 2007). The solid fraction, due to its higher DM and P concentration, is cheaper to transport per unit of nutrient and can, for example, be transported relatively long distances for application to tillage land, where there is a requirement for plant available P. The solid fraction may also be used to produce stable compost, again for export to tillage farmers, but also to the horticulture industry, thus, diversifying farm

income. The N-rich liquid fraction can be applied to land in the proximity of the pig farm where the soil P status is likely to be adequate or in excess of crop requirements.

With increasing oil prices and the implementation of P restrictions when landspreading pig manure from 2013 (Section 2.3.1), the cost of landspreading pig manure will increase in the next number of years. The use of pig manure treatment technologies, such as separation and composting, may not be viable at the present time. However, it is important to understand the cost of each technology, so that when the cost of landspreading increases beyond a sustainable level that there will be an option available to pig farmers.

5.2 Material and Methods

5.2.1 Farm Characteristics and Assumptions Used

The economics of any pig manure treatment is greatly dependent on the size of the pig farm as well as the specific characteristics of each technology. Therefore, to assess the costs and benefits of separation and composting of pig manure, the first step was to assemble a comprehensive list of basic assumptions. The assumptions used in this case study are shown in Table 5.1 and are described below.

5.2.1.1 Pig Farm

Costs were calculated based on a case study of a 500 sow integrated pig farm, which is the average size for a pig farm in Ireland. The N and P content of the pig manure is based on S.I. 610 of 2010 (EC, 2000). According to this S.I., in an Irish integrated pig farm, one sow (plus its progeny) produces 87 kg of N and 17 kg of P per year, with 1 m³ of pig manure containing 4.2 kg of N and 0.8 kg of P. Therefore, one sow produces approximately 21 m³ of manure per year. Pig manure DM was based on a recent survey of pig farms in Ireland and was assumed to be 4.8% (Fiszka, 2010).

Table 5.1 Assumptions required to assess the operating costs of separation and composting of pig manure for a 500 sow integrated farm in Ireland.

Parameter	Value	Reference
Pig farm		
Pig farm size	500 sow integrated	M. Martin, pers. comm.
Pig manure production	10,500 m ³ year ⁻¹	S.I. 610 of 2010
N content of manure	4.2 kg m ⁻³	S.I. 610 of 2010
P content of manure	0.8 kg m ⁻³	S.I. 610 of 2010
Dry matter of pig manure	4.8%	Fiszka, 2010
Solid-liquid separation		
Decanter centrifuge flow rate	20 m ³ hour ⁻¹	N/A
Coagulant addition	3.0 L m ⁻³ of manure	Chapter 3, Section 3.2.1
Flocculant addition (0.4% diluted)	17% of manure vol.	Chapter 3, Section 3.2.1
kg of solid fraction / kg manure	0.079	Moller et al., 2002
Solid fraction bulking density	498 kg m ⁻³	Chapter 3, Table 3.1
Separation efficiency for dry matter	70.6%	Gilkinson & Frost, 2007
Separation efficiency for N	34.4%	Gilkinson & Frost, 2007
Decanter electrical consumption	15 kWh	Manufacture
Composting		
Target initial C:N ratio	18.0	Chapter 4, Table 4.3
C content of solid fraction	41.32%	Chapter 4, Table 4.1
N content of solid fraction	5.01%	Calculated
Solid fraction produced per day	3152 kg day ⁻¹	Calculated
Dry matter solid fraction	30.1%	Calculated
Sawdust C content	48.8%	Chapter 4, Table 4.1
Sawdust N content	0.1%	Chapter 4, Table 4.1
Sawdust moisture content	15.8%	Chapter 4, Table 4.1
Sawdust bulk density	40 kg m ⁻³	Chapter 4, Table 4.1
Compost bulk density (Day 0)	339 kg m ⁻³	Chapter 3, Table 3.3
Blower electrical consumption	5.5 kW	Manufacture

5.2.1.2 Anaerobic Digestion

Although an economic evaluation of anaerobic digestion of pig manure is included in this study, it was completed by others (Nolan et al., 2012) and will not be described in detail in this chapter. However, some outputs from an AD study (Xie et al., 2011) are required as they are used as inputs for the solid–liquid separation of the digestate.

Co-digestion of pig manure and grass silage was investigated by Xie et al. (2011) and values for the DM and N content of grass silage were based on this study. Xie et al. (2011) recommended a ratio for commercial application of 1:1 pig manure-to-grass silage on a VS basis. This equates to a daily load, at 7.3% DM, of 33.8 tonne of fresh material (28.8 tonne of pig manure and 5.1 tonne of grass silage).

The daily N load being discharged from the AD plant at 138.2 kg was the sum of the daily N load of the pig manure plus the daily N load of the grass silage, as it was assumed that AD does not affect the amount of N. Therefore, the grass silage contributes to an increase in the N amount of the effluent of 17.4 kg day⁻¹, compared to pig manure (120.8 kg day⁻¹). The N concentration of the digestate (4.1 kg tonne⁻¹) was slightly lower than that of raw pig manure (4.2 kg tonne⁻¹).

It was assumed that the effluent volume was similar to the influent volume. However, effluent DM will be lower than influent DM, as VS are removed in the biogas during the AD process. The effluent DM was calculated to be 4.0%.

5.2.1.3 Solid-liquid Separation of Digestate

For solid-liquid separation of digestate, a decanter centrifuge with a 20 m³ hour⁻¹ capacity was used as described in Section 3.2.1. Working at this capacity, the decanter centrifuge will operate for 3 hours day⁻¹ and 256 day year⁻¹. Electrical consumption was calculated assuming a continuous absorbed power of 15 kW (Peter Fiska, Spomasz, Wrongi, Poland, pers. comm.). The amount of chemicals used during separation (coagulant and flocculant) was based on Section 3.2.1 (Table 5.1). The N load of the digestate (kg day⁻¹) was calculated by adding the N load from the influent

pig manure and the N load from the influent grass silage, as it is assumed that AD will not change the N amount (kg day^{-1}). The efficiency of separation for DM and N was based on the mean separation efficiency of a decanter centrifuge separating pig manure with the addition of chemicals found in Gilkinson and Frost (2007) (Table 5.1). The amount of the solid fraction produced was based on Moller et al. (2002) (Table 5.1).

The size of storage facilities required for the separated fractions (a covered concrete shed for the solids and an open slurry tank for the separated liquid) were calculated based on a storage requirement of 6 months (after S.I 610 of 2010; EC, 2000). The covered concrete shed also acts as the composting facility and compost storage area. For the solids storage capacity, a bulk density of 498 kg m^{-3} was assumed (Chapter 3, Table 3.3).

5.2.1.4 Composting of the Solid Fraction of Pig Manure

The targeted C:N ratio for compost was 18:1 (Chapter 3, Table 3.4). The quantity of sawdust necessary to achieve the target C:N ratio was calculated using an Excel™ Solver spreadsheet with the following set values and constraints:

The daily quantity of solids produced and its DM is the result of calculations described in Section 5.2.1.3. It was assumed that 1 compost pile is formed from solids produced during 7 days of separation. The N content of the separated solid fraction was calculated based on the N load and separation efficiency as described in Section 5.2.1.3. A search of existing literature did not find any data on decanter centrifuge separation efficiency for C, or on the C content of the separated fraction of digested pig manure and grass silage. Therefore, the C content of the grass silage that is added during the AD process is not accounted for here. The C content of the separated fraction of anaerobically digested pig manure only (Chapter 4, Table 4.3) was used instead as an approximation. If the C content of grass silage was included in the calculations, the sawdust required for compost would probably be reduced, making the composting process a bit more affordable. The C, N and moisture content of sawdust was based on values from Chapter 4 (Table 4.1).

The following constraints were applied in the Excel™ programme: the WC of mixture was between 40 and 60%, the C:N ratio was equal to 18 and the sawdust quantity was greater than 1.

Bulk density values for separated manure, sawdust and for the mixture of sawdust and separated pig manure were based on those given in Chapter 3 (Table 3.1 for separated manure, Table 3.2 for sawdust, Table 3.3 for the mixture of manure and sawdust). In the present study, composting was carried out indoors by aerated static piles after Rynk (1992) and aeration was provided via blowers attached to perforated pipes on a 30-minute cycle (10 minutes on and 20 minutes off). Therefore, no mechanical turning of the pile was required. The pile height was assumed to be 3.8 m, and the pile width and spacing between piles was equal to half the height (after Rynk, 1992). It is also assumed that a mechanical bucket loader is available to construct the compost pile. For calculations on the amount of compost produced at the end of the composting period (56 days, similar to Chapters 3 and 4), a weight reduction of 50% was assumed (after Rynk, 1992). The electrical consumption of the blower was based on the manufacture's specifications (Vaccumspares, Cobh, Co. Cork, Ireland).

5.2.2 Transport and Landspreading of Raw Pig Manure

In Ireland, initial pig manure storage is usually under the slatted floor of the pig house, with a tank depth of 0.5 to 2.5 m (average 1.2m), or in an outdoor tank. Above-ground steel tanks (usually without covers) with a total depth of approximately 4 m are commonly used for secondary storage and aeration. In order to be transported and landspread, the manure is usually removed from the tank by a tractor-drawn vacuum tanker of 5 to 12 m³ capacity. The manure is then hauled to the field and spread using a splash plate (usually low-trajectory), or a device such as a band-spreader, which places the manure in narrow rows on the grass, or by trailing shoe, which places the manure along the surface of the soil after parting the grass sward. Less often, the manure may be applied (injected) into narrow slots cut into the ground.

As described in Section 2.3.1, by 2017 pig farmers in Ireland will require an additional ~50% spread lands than is the case in 2012. Therefore, the transport of raw manure for longer distances by truck may become routine. Two manure handling

scenarios (transport and spreading) were analysed in the present study. In the first scenario, a tractor and vacuum tanker is used, while in the second scenario, a truck is used. In both scenarios, it was assumed that the pig farmer delivers and spreads the manure without charge to the customer. This may not always be the case in Ireland, where increasingly costumers are starting to incur the costs of transporting and spreading. In both scenarios, the use of a contractor is employed. Use of a contractor makes the costs more transparent and makes it possible to list each cost component individually and accurately (Ishler et al., 2002).

The following assumptions are made based on observations on manure haulage from the Teagasc Moorepark Pig Unit and discussions with pig producers. For the tractor and vacuum tanker, the following design criteria were used: load size of 11.8 m^3 loading time of 6 minutes; outward travel speed while loaded increases with the distance (for a distance from the pig farm to customer farm of 1 km or less, the speed is 20 km hour^{-1} ; after that, the travel speed increases by one quarter of the distance); return speed is 5 km hour^{-1} more than the outward journey; hire cost for tractor, tanker and operative is $\text{€}40 \text{ hour}^{-1}$ and the unloading time is twice the loading time when landspreading (for manure DM of 4.8%). For the truck, the design criteria were: load size of 27 m^3 ; loading time of 15 minutes; travel speed while loaded increases with distance; return speed is 5 km hour^{-1} more than the outward journey; hire cost for truck and operative is $\text{€}72 \text{ hour}^{-1}$; unloading time (discharged into a store) is equal to loading time and cost of spreading is $\text{€}2 \text{ m}^{-3}$.

5.3 Results and Discussion

The costs for each technology are tabulated separately. However, most of the technologies must be used in combination. For example, composting can only be performed after the pig manure has been separated into its solid and liquid fractions. The solid fraction after separation is used for composting. Consequently, to calculate the full cost of composting, the costs associated with the separation process must also be included. Furthermore, because the initial manure has been separated into its solid and liquid fractions, the liquid fraction must also be handled. The liquid fraction will either be further treated or land spread and the associated costs must be included.

For the calculations of annual costs, described in the sections below, the annual repayment per €1000 borrowed is after Teagasc (2006), assuming an interest rate of 6%.

5.3.1 Solid-liquid Separation

Taking into account the volume of digestate produced daily and the amount of coagulant and flocculant used, the total daily volume to be separated was calculated to be 39.7 tonnes, a 17.3% increase on the volume of the original digestate. This volume increase was primarily caused by the water required to dilute the flocculant. Digestate DM was 4.0%. However, due to the addition of water, the DM of the material to be separated decreased to 3.4%. The N content of the digestate was 138.2 kg day⁻¹ (4.08 kg t⁻¹ and 3.48 kg tonne⁻¹, before and after water addition, respectively). The daily amount of solid and liquid fraction produced was 3,152 and 36,550 kg, respectively, with 30.1 and 1.08% DM, respectively. This compares favourably to the DM of the separated solid fraction of pig manure digestate in Chapter 4 (Table 4.1), which was 30.5. The DM of the liquid fraction after separation of pig manure digestate in Chapter 4 was 0.6%. The N transferred to the solid and liquid fractions were calculated at 47.6 and 90.7 kg, respectively, which were equivalent to 1.4 and 2.5 kg t⁻¹, respectively.

The initial investment costs associated with the solid-liquid separation of the digestate is described in Table 5.2.

Calculations show that a total investment cost of €699,074 was necessary. This includes the capital cost necessary for the separator (€125,000) and construction of storage for the separated liquid (at €40 m⁻³) and separated solid fractions (at €240 m⁻²). Table 5.2 also shows the calculation for annual operating costs. This includes the annual repayment for the decanter centrifuge (over 10 years), liquid storage and solid storage (over 20 years). It also includes an annual maintenance value for the decanter centrifuge of 3% of the investment costs and of 1% for the storage facilities. Labour was calculated at €12 hour⁻¹.

Table 5.2 Annual costs associated with solid-liquid separation

Capital Investment	Required	Unit	Cost/unit (€)	Total (€)
Decanter Centrifuge	1.00	unit	125,000	125,000
Storage for liquid fraction	6670.33	m ³	40.00	266,813
Storage for solid fraction	1155.25	m ²	240.00	277,261
Total capital investment				669,074
Annual costs	Required	Unit	Cost/unit (€)	Total (€)
Repayments (centrifuge)	€137.00	per €1000		17,125
Repayments (liquid storage)	€88.00	per €1000		23,480
Repayments (solid storage)	€88.00	per €1000		24,399
Maintenance (centrifuge)	3.00	%		3,750
Maintenance (liquid storage)	1.00	%		
Maintenance (solid storage)	1.00	%		2,773
Labour	2.00	hours day ⁻¹	12.00	8,760
Flocculant	8400.75	L year ⁻¹	3.87	32,511
Coagulant	37062.14	L year ⁻¹	0.46	17,049
Calculations for energy input:				
Electricity consumed	11520.00	kWh year ⁻¹	0.14	1,613
Total annual costs				134,127
Total costs per m ³				12.77

5.3.2 Composting of the Solid Fraction of Pig Manure

A daily 1,171.9 kg of sawdust was necessary to compost the separated solid fraction of the digestate at a C:N ratio of 18 (solids: sawdust ratio of 2.7, fresh weight) in the present study. As each compost pile comprises 7 days of the manure produced, 8 piles of 89.3 m³ of separated solids and sawdust may be composted at any given time. Pile length was calculated at 12.7 m and shed length is 15.7 m (3 m was added to allow tractor access). The calculated shed area was ~900 m²; therefore, the solids storage facility, described in Section 5.2.1.3, was suitable for the compost process. Although 8 compost piles may be composting at any given time, four blowers should be able to provide the aeration necessary as the blowers work in a 30-minute cycle. Therefore,

with 1 blower providing aeration for 2 piles, each blower may be operational for 960 minutes day⁻¹.

The costs of composting the separated solid fraction are presented in Table 5.3. The capital costs associated with the composting include the blowers and the shed construction. However, because the cost associated with the shed construction was already accounted for in the separation, it was not included here. It was assumed that one blower will have to be replaced every two years (life expectancy of eight years). Therefore, the total annual costs for the composting alone (including pipes, thermometers, sawdust, blowers, electrical consumption and labour) were calculated as €36,883. However, for a complete cost analysis, the cost of the separation process also needs to be included as the manure can only be composted after separation. The total cost was therefore €171,010.

With a 50% weight reduction of the pile (Rynk, 1992), a total of 790 tonnes of compost will be produced annually. In Ireland, municipal waste based compost is available for collection at a cost of approximately €30 t⁻¹. In the present study, assuming that the farmer would be able to charge €10 t⁻¹, yearly revenue of €7,900 can be made from the sale of the compost. This reduces the yearly costs of the compost treatment to €28,983 (or €163,110; including separation costs).

Table 5.3 Annual costs associated with composting

Capital Investment	Required	Unit	Cost / unit (€)	Total cost (€)
Blower	4.0	units	1,950.00	7,800
Shed for compost ^a	891.1	m ²	240.00	N/A
Total capital investment				7,800
Annual costs				
No. of pipes needed for all cells	24.0	6m lengths	23.00	552
Thermometers	2.0	units	250.00	500
Sawdust	406.5	tonnes	35.00	14,227
Blower	0.5	unit	1,950.00	975
Blower consumption (kWh year ⁻¹)	48180	kWh	€0.14	6,745
Labour	3.0	hours day ⁻¹	12.00	13,140
Total annual costs				36,139
Total costs per m ³				3.44
Total annual costs (incl. separation)				170,265
Total costs per m ³ (incl. separation)				16.22
Annual benefits				
Total compost produced per year	779	tonnes	10.00	7,790
Annual net costs				
Net cost per year				28,349
Net cost per m ³				2.70
Net cost per year (incl. separation)				162,475
Net cost per m ³ (incl. separation)				15.47

^a Costs for solid storage after separation is already accounted for under separation costs.

5.3.3 Landspreading of Raw Manure

Annual costs for transporting and spreading raw pig manure by tractor and vacuum tanker or by truck are shown in Table 5.4. For a distance of up to 14 km from the pig farm to the customer's farm, the most cost effective way of transporting and spreading is by tractor and vacuum tanker. To transport and spread the manure a distance of 14

km from the pig farm the cost per m³ of manure was €4.7 if transported by tractor and €4.8 if transported by truck. For distances longer than 15 km (30 km return journey), transporting by truck becomes more cost effective. To transport and spread the manure a distance of 30 km from the pig farm, for example, the cost per m³ of manure was €7.8 if transported by tractor and €6.2 if transported by truck (Table 5.4).

Table 5.4 Annual costs associated with raw pig manure transport and landspreading by tractor and vacuum tankers and by truck for a 500 sow integrated pig farm

Distance to farm (km)	Tractor Outward speed (km hour ⁻¹)	Tractor annual costs (€)	Tractor (€ m ⁻³)	Truck outward speed (km hour ⁻¹)	Truck annual costs (€)	Truck (€ m ⁻³)
1	20.00	13,877	1.32	45.0	36,048	3.43
2	20.50	16,936	1.61	45.0	37,220	3.54
5	21.25	25,824	2.46	45.0	40,736	3.88
10	22.50	39,427	3.75	47.5	46,006	4.38
14	23.50	49,350	4.70	48.5	50,150	4.78
15	23.75	51,711	4.92	48.8	51,161	4.87
20	25.00	62,860	5.99	50.0	56,070	5.34
30	27.50	82,334	7.84	52.5	65,216	6.21
50				57.5	81,213	7.73
75				60.0	101,591	9.68
100				60.0	123,830	11.79
125				60.0	146,068	13.91
150				60.0	168,306	16.03
200				60.0	212,782	20.26
500				60.0	479,641	45.68

In a 2001 study of costs of field application of manure in Europe (Huijsmans et al., 2004), the cost per m³ of manure applied in Ireland (0.5 and 2 km distance from customers' farm) was estimated to be €3.6 – 6.3. The higher costs in Huijsmans et al. (2004) can be attributed to the lower quantities of manure applied (between 946 and

2,247 m³ year⁻¹). In the present study, the cost of application was based on a yearly manure production of 10,500 m³. For comparable yearly manure production of 2,200 m³ and distance to a hypothetical customer's farm of 2 km, the cost for the manure application would be €7.7 m⁻³.

5.4 Summary

The cost analysis shows that the technologies investigated are currently not cost effective in the Republic of Ireland compared to conventional landspreading. However, they may become viable in the future, as transport costs increase with rising oil prices, and restrictions on landspreading increase the distance travelled to spread the manure.

The cost of separation is the most prohibitive cost in this treatment option. The use of a decanter centrifuge is an expensive method of separation. The use of other separation technologies, such as screen separation, should be investigated with a view to increasing the cost effectiveness of the separation process.

6 EFFECT OF SAWDUST ADDITION AND COMPOSTING ON RENEWABLE ENERGY AND BIOCHAR PRODUCTION FROM PYROLYSIS OF PIG MANURE

Overview

This chapter details pyrolysis experiments which were conducted on the separated solid fraction of anaerobically digested pig manure. The feedstocks for this pyrolysis study were taken from Composting Trial 2, outlined in Chapter 4. The aim of these experiments was to investigate the influence of: (1) sawdust addition and (2) composting the feedstock, on the products of pyrolysis and on the net energy yield from the pyrolysis process. The method of pyrolysis used in this study and the methods of analysis used to characterise the gas, bio-liquid and biochar produced from the pyrolysis process are also described in this chapter. Experimental data from these analyses are presented, and an energy balance is conducted using the data from this study and data from the composting analyses detailed in Chapters 3, 4 and 5.

The contents of this chapter have been accepted for publication in *Biomass and Bioenergy*.

6.1 Introduction

Pyrolysis is a thermochemical conversion process whereby a biomass feedstock, such as woodchips, crop residues, manure or digestate, is thermally degraded at high temperatures in an oxygen-free atmosphere. The organic portion of these feedstocks is converted to biochar and volatile gases. The volatile gases contain condensable tars and incondensable gases. The tars, when condensed, form a bio-liquid. The incondensable gases contain a mixture of H₂, CO₂, carbon monoxide (CO), N₂, and hydrocarbon gases (Bridgewater and Peacocke, 2000; Cantrell et al., 2007). The proportion of biochar, bio-liquid and gas produced is dependent on the heating rate, the reactor temperature and the residence time of the reactor (Briens et al., 2008; Melligen et al., 2011). The pyrolysis conditions and the biomass feedstock

characteristics will also affect the chemical and physical characteristics of the products formed. The gases and bio-liquids produced may be used to provide the energy needs for the pyrolysis process, or converted to electricity and heat. The biochar can also be used as a fuel or, alternatively, applied to land as a low-grade fertiliser, soil additive (Lehmann et al., 2003; Steiner et al., 2008a; Steinbeiss et al., 2009, Laird et al., 2010b), or for carbon sequestration (Fowles, 2007; Lehmann, 2007; Kwapinski et al., 2010; Bruun et al., 2011)

The generation of renewable energy through pyrolysis has been shown to result in net reductions in GHG emissions compared to fossil fuel combustion (Gaunt and Lehmann, 2008). On a farm scale, the production of biochar and energy from wastes such as manure, wood residues and straw, may reduce waste disposal costs and provide cost effective energy at a relatively fixed price to be used by agriculture industries (Marris, 2006). However, the net energy generation from the drying and pyrolysis of manure has been shown to be negative due to the high WC of manures (Ro et al., 2010). The addition of sawdust to separated manure reduces the WC and may result in a positive net energy yield. Composting also reduces the WC of the feedstock (Bernal et al., 2009) and may also be incorporated into the treatment process to alter the net energy yield. Some research has been performed on biochar production from manures (Lima et al., 2009; Mante and Agblevor, 2010; Ro et al., 2010); however, no study has yet characterised the biochar and renewable energy production from pig manure after AD. The effect of composting the feedstocks before pyrolysis has also never been previously studied. Therefore, the objectives of this study were to: (1) investigate the effect of sawdust addition on the products of pyrolysis of SADPM previously (2) analyse the effect of composting the feedstocks before pyrolysis, and (3) investigate the effect of composting and sawdust addition to the energy balance.

6.2 Materials and Methods

6.2.1 Feedstock

Anaerobically digested pig manure from all stages of production was separated by decanter centrifuge (GEA Westfallia Separator UCD 205, Bönen, Germany; Figure 3.1) The SADPM had an average dry matter content of 31%. This SADPM was mixed with sawdust (Sitka Spruce) at different rates (4:1 and 3:2) based on their wet weights. These feedstocks were then pyrolysed both before and after composting. The feedstocks were: SADPM only (MO); SADPM and sawdust mixed at a 4:1 ratio (4:1); SADPM and sawdust mixed at a 3:2 ratio (3:2); composted SADPM (MO(CP)); SADPM and sawdust mixed at a 4:1 ratio and composted (4:1(CP)), and SADPM and sawdust mixed at a 3:2 ratio, and composted (3:2(CP)). The composting process consisted of 56-day aerobic composting in small-scale (c. 50 kg) composting tumblers similar to the methods described by in Chapter 4 (Section 4.2.2). All materials were dried at 60 °C for 48 hours and milled before storage in a refrigerator (~4 °C) prior to pyrolysis and analysis.

6.2.2 Pyrolysis

A laboratory-scale pyrolysis reactor, with an internal diameter of 5 cm, was used to produce the biochar, bio-liquid and gases (Figure 6.1). A temperature of 600 ± 10 °C and a residence time of 15 min were used for all feedstocks. Approximately 50 g of feedstock was used for each pyrolysis run. The vapour exhaust end of the pyrolysis reactor was connected to a condensing zone, which was maintained at a temperature of -6 ± 1 °C. A flow of $50 \text{ N cm}^3 \text{ N}_2 \text{ min}^{-1}$ for 15 min before pyrolysis commenced, ensured that the atmosphere inside the reactor was oxygen free. The vapours produced by the pyrolysis process were carried through to the condensing zone, where the condensable fractions were converted to bio-liquid. The bio-liquid was collected in a round-bottomed flask at the end of the condensing zone and the gases were collected in Tedlar gas sampling bags.

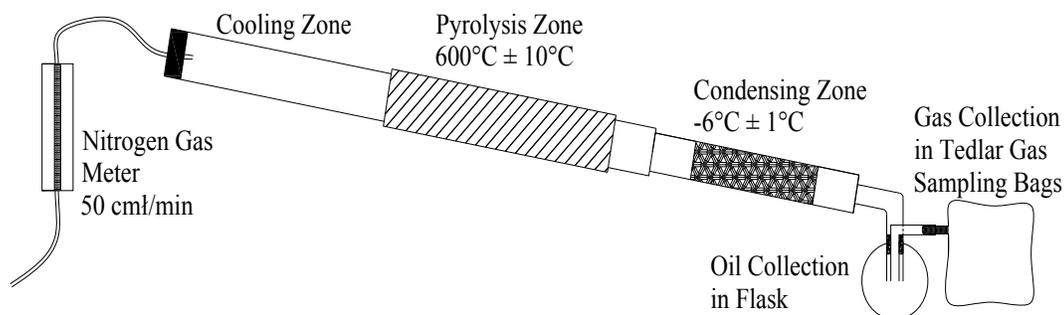


Figure 6.1 Schematic diagram of the laboratory scale pyrolysis reactor.

After pyrolysis, the biochar was moved to the cooling zone of the pyrolysis reactor and allowed to cool in the N atmosphere before being removed from the reactor. The mass of the biochar and bio-liquid was determined after pyrolysis to allow calculation of the percentage yield of biochar and bio-liquid. Gas yield was calculated from the difference after biochar and bio-liquid yield calculation.

6.2.3 Chemical and Physical Properties of Biochar

Feedstock and biochars were subjected to proximate analysis for WC (B/EN 14774:3:2009), ash content (BS/EN 14775:2009) and volatile matter (VM) content (BS/EN 15148:2009). Duplicate samples of feedstock and the biochars were analysed for total C, N, S and H contents in accordance with CEN/TS 15104:2005. Elemental analysis was undertaken using a “CHNOS Elemental Analyser Vario EL Cube” (Elemental Analysensysteme GmbH, Hanau, Germany) operated at a combustion temperature of 1100 – 1200 °C. All analyses were performed on a dry basis (db). Higher heating value (HHV; MJ kg⁻¹) was calculated from the elemental analyses using (Channiwala and Parikh, 2002):

$$\text{HHV} = 0.3491 \text{ C} + 1.1783 \text{ H} + 0.1005 \text{ S} - 0.1034 \text{ O} - 0.0151 \text{ N} - 0.0211 \text{ Ash} \quad [6.1]$$

Biochar pH measurements were performed in water solution using a bench-top meter (SevenEasy, Mettler-Toledo, Switzerland) at a biochar/distilled water ratio of 1:10 (w/v). Acid binding capacity (ABC) and buffering capacity (BUF) were measured by

adjusting the pH to values of 6.5 and 7 after Lawlor et al. (2005). In this method, 0.5 g of biochar was suspended in 50 cm³ de-ionised water and continuously stirred. Titrations of 0.1 M hydrochloric acid were performed using increments from 0.01 cm³ to 0.1 cm³ until a pH of 6.5 and a pH of 7 were attained. Acid binding capacity was calculated as the amount of acid in milli-equivalents required to reach the target pH. Buffering capacity was calculated by dividing the ABC by the change in pH units. This test was repeated using lime to compare the potential of the biochar as a replacement for lime.

The fertiliser value of the biochar was investigated by determining the concentrations of P and K. The amount of P available to plants is given by the nutra ammonium citrate soluble P (NACP) concentration (Gowariker et al., 2009). This test is used to denote the P content of common fertilisers. Formic acid soluble P relates to less available P (Chien, 1993), and is often found in high concentrations in slow release fertilisers, which are often utilised in forest plantations. Total P was analysed by acid digestion according to Standard Method 4500-P B&E (Eaton et al., 2005). Water soluble P, nutra ammonium citrate soluble P, and formic acid soluble P were determined after Byrne (1979). Potassium concentration was also determined after Byrne (1979). Brunauer-Emmet-Teller (BET) surface area of the biochars was measured by nitrogen gas sorption analysis at 77 K using a surface area analyser (Micromeritics Gemini 2375 V5.01). Samples were pre-treated by degassing at 300 °C for 4 hours in nitrogen gas.

6.2.4 Thermogravimetric Analysis

The six feedstocks were subject to thermogravimetric analysis runs (TGA) using a TGA analyser (Q600 TGA/DTA Thermal Analyser System, TA Instruments). Samples were placed in open-top alumina crucibles and were pyrolysed with N₂ as a carrier gas at a flow rate of 100 cm³ min⁻¹. A temperature ramp of 10 K min⁻¹ from ambient temperature up to 600 °C was used to create a temperature-based mass profile.

6.2.5 Gas and Bio-liquid Analyses

Elemental analyses of duplicate samples of the bio-liquids were performed in accordance with CEN/TS 15104:2005 as described in Section 6.2.3. Samples were analysed on the same day as production to ensure there was no reduction in the quality of the bio-liquids associated with storage. Higher heating values (MJ kg^{-1}) were calculated from the ultimate analyses using (Friedl et al., 2005):

$$\text{HHV} = 3.55 \text{ C}^2 - 232 \text{ C} - 2230 \text{ H} + (51.2 \text{ C} \cdot \text{H}) + 131 \text{ N} + 20600 \quad [6.2]$$

Analysis of the major non-condensable gases produced by pyrolysis was undertaken using a gas chromatograph (Agilent Micro GC, Agilent Technologies). The yields were quantified by calibration with a standard gas mixture consisting of N_2 , H_2 , CO , CO_2 , CH_4 , C_2H_4 , C_2H_6 and C_2H_2 in helium. Higher heating values (MJ Nm^{-3}) were calculated from the gas composition results using (Basu, 2010):

$$\text{HHV} = 39.82 \text{ CH}_4 + 12.63 \text{ CO} + 12.74 \text{ H}_2 + 7.29 \text{ C}_2\text{H}_6 + 63.42 \text{ C}_2\text{H}_4 + 58.06 \text{ C}_2\text{H}_2. \quad [6.3]$$

6.2.6 Energy Balance

The energy required to treat digested manures, through pyrolysis, can be split into four processes: separation, composting, drying, and pyrolysis (Figure 6.2). The separation energy requirements of SADPM using a decanter centrifuge was taken as 7.92 MJ t^{-1} manure input (Moller et al., 2000) and the quantity of manure solids produced per tonne of SADPM input was taken as 0.07 tonne (Moller, 2003). The energy use during composting was estimated to be 18.4 MJ t^{-1} input material (Diaz et al., 1986). The overall mass reduction of the composting pile from the beginning to end of the composting process was taken to be 50% (Tiquia et al., 2002b), including a reduction of 15% in the water content. The drying energy requirement was estimated by adding the heat required to increase the temperature of the wet feedstock from ambient ($10 \text{ }^\circ\text{C}$) to $100 \text{ }^\circ\text{C}$, plus the latent heat required to evaporate the water from the feedstock (Ro et al., 2010). The heat capacity of the wet manure was estimated to be $0.003292 \text{ MJ kg}^{-1} \text{ }^\circ\text{C}^{-1}$ (Bohnhoff and Converse, 1987), while the heat capacity of

sawdust at 12% WC was estimated to be $0.0015 \text{ MJ kg}^{-1} \text{ K}^{-1}$ (Raglands and Aerts, 1991). The efficiency of the drying process was estimated at 80% (Ro et al., 2010). The energy requirement for pyrolysis was the energy required to increase the temperature of the dried feedstock from 100 to 600 °C. The heat capacity of the dried manure was estimated to be $0.00092 \text{ MJ kg}^{-1} \text{ K}^{-1}$ (Bohnhoff and Converse, 1987), while the heat capacity of dry sawdust was estimated to be $0.00251 \text{ MJ kg}^{-1} \text{ K}^{-1}$ (Raglands and Aerts, 1991). The energy loss during pyrolysis is estimated to be 5% (Ro et al., 2010).

There are two output options investigated (Figure 6.2) with regards to the end use of the products (biochar, bio-liquid and gases). For option one, all three pyrolysis products are used as a fuel. Option two uses the bio-liquid and gases as a fuel, while the biochar is used as a soil additive. When calculating the energy production from combustion of the biochar, bio-liquid and gases, a CHP efficiency of 80% was assumed.

6.2.7 Statistical Analysis

Data was analyzed using the Statistical Analyses System (SAS Institute, 2004). Comparison of yield, elemental analyses, proximate analyses and HHV were performed using the Proc Mixed SAS procedure. Treatment was included as a fixed effect. For all analyses, significance was at $p < 0.05$.

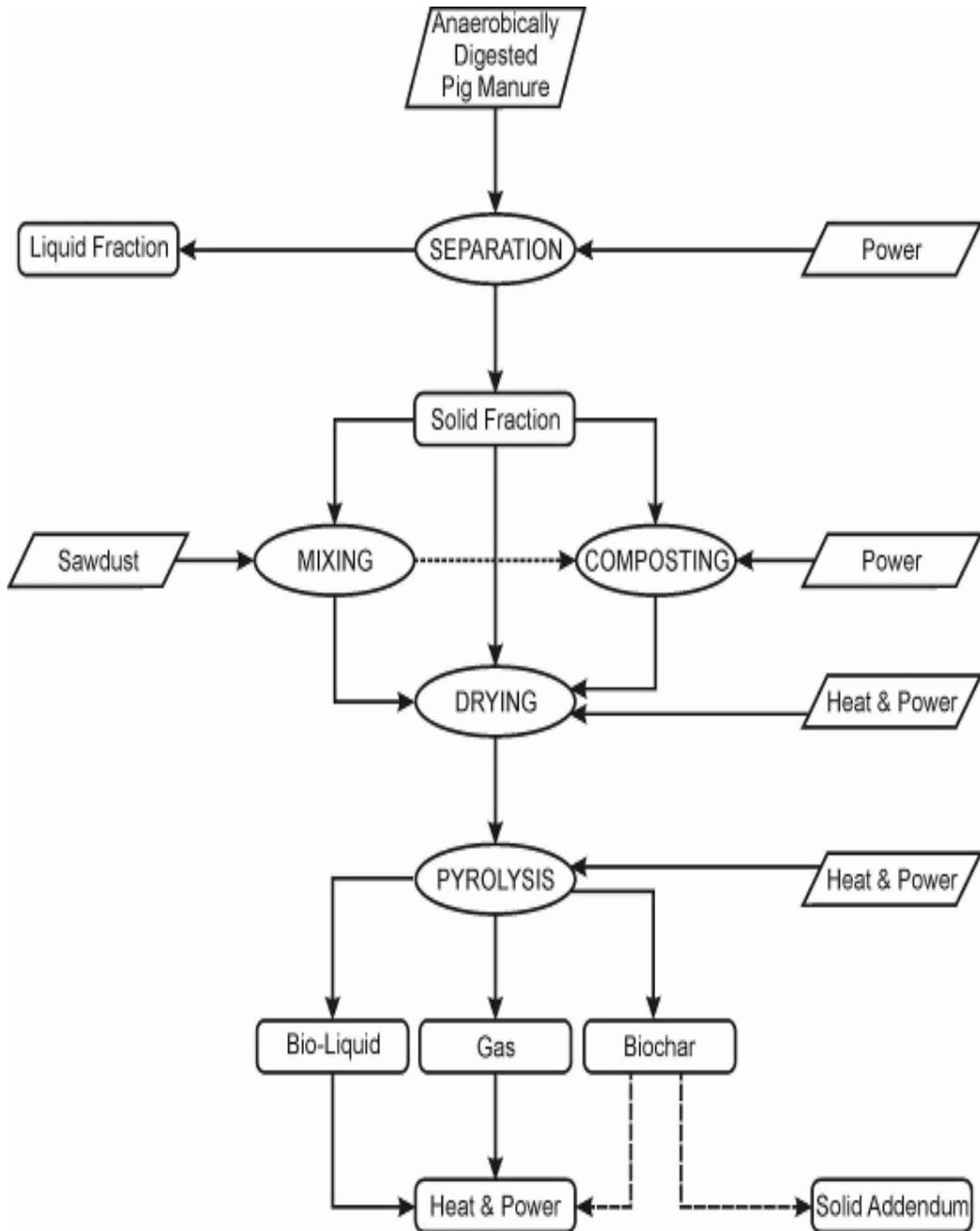


Figure 6.2 Schematic outlining the process, inputs and outputs for the energy balance

6.3 Results and Discussion

6.3.1 Feedstock Characteristics

Proximate and ultimate analyses of the biomass feedstock are given in Table 6.1. The addition of sawdust to the SADPM resulted in higher VM and fixed C (FC) contents ($p < 0.001$ and $p < 0.01$, respectively), while the ash and N contents decreased with sawdust addition ($p < 0.01$ for both). Feedstock MO(CP) was an exception to this, where the N content was unusually low. The low N content was most likely caused by leaching which occurred from this feedstock during the composting process (described in Chapter 4, Section 4.3.1.5). There was an increase in C contents when sawdust was added to the SADPM, although this increase was not significant ($p = 0.26$). There was no significant difference in feedstock HHV with increasing sawdust addition ($p > 0.05$). Composting of the feedstocks resulted in lower VM contents ($p < 0.001$). Ash contents were also higher, although the increase was not significant ($p > 0.05$). Organic matter is decomposed by microorganisms during composting, resulting in higher ash contents, while VM is lost as gases during the composting process (Bernal et al., 2009). There was a reduction in C contents after composting, although the decrease was only significant in the 4:1 treatment ($p < 0.05$). Carbon is lost during the composting process, primarily as CO_2 (Bernal et al., 2009). The decrease in C content and the increase in ash content, following composting, resulted in a decrease in HHV in the composted feedstock ($p < 0.001$).

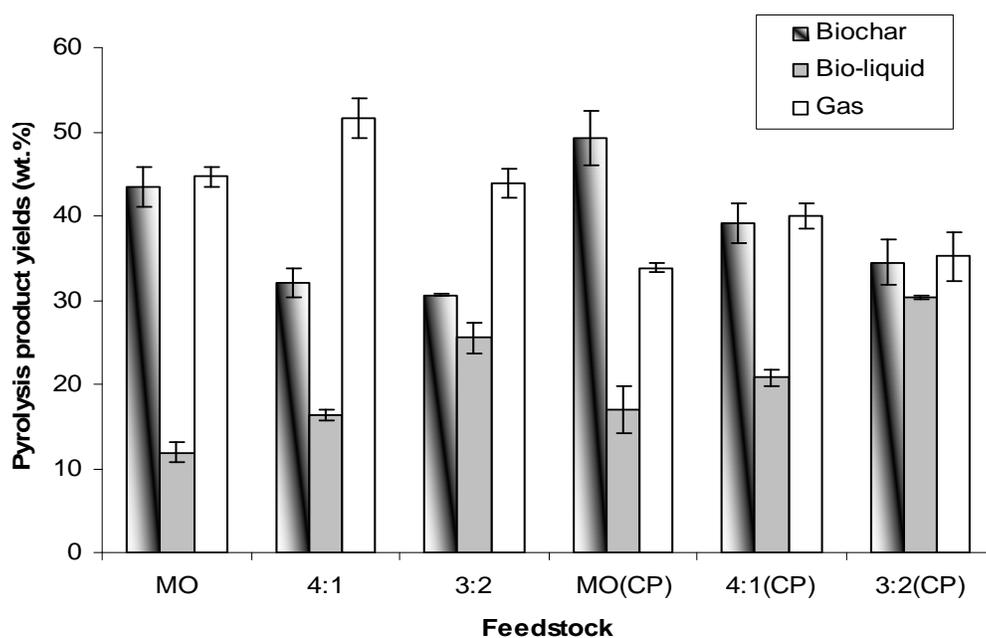
6.3.2 Biochar Characteristics

The biochar yields obtained from the pyrolysis process are shown in Figure 6.3. Biochar yield was influenced by feedstock composition. However, composting of the feedstock had no significant effect on biochar yield ($p > 0.05$). The addition of sawdust to SADPM reduced biochar yield significantly ($p < 0.05$). In a study using poultry manure (Mante and Agblevor, 2010), the increasing addition of wood also resulted in decreasing biochar yield. The higher biochar yield for the manure-only feedstock was due to changes in the high ash content of the manure, which decreased with sawdust addition (Table 6.1). Composting of the feedstock increased the ash content, resulting in higher biochar yields.

Table 6.1 Proximate and ultimate analysis of feedstock before pyrolysis

Parameters	MO	4:1	3:2	MO (CP)	4:1 (CP)	3:2 (CP)
Water content (%)	8.5	7.0	7.4	9.0	6.2	5.8
Volatile matter (% _{db})	69.7	71.8	75.5	62.8	66.3	74.0
Fixed C (% _{db})	8.1	15.0	16.3	10.8	17.1	17.0
Ash (% _{db})	22.2	13.2	8.2	26.4	16.6	9.0
N (% _{db})	4.5	3.0	1.7	1.9	4.2	3.0
C (% _{db})	45.2	47.6	49.0	40.6	41.4	44.2
H (% _{db})	5.1	5.3	5.2	4.7	4.7	5.1
O (% _{db})	21.9	30.1	35.4	25.8	31.9	37.8
H/C	1.37	1.34	1.28	1.39	1.35	1.37
HHV (MJ kg ⁻¹)	19.1	19.5	19.5	16.5	16.4	17.3

db=dry basis; (CP)=composted feedstock; HHV=higher heating value

**Figure 6.3** The yield of biochar, bio-liquid and gas from each treatment

The results of proximate and ultimate analyses of the biochars are shown in Table 6.2.

The C content of the biochar increased as the proportion of sawdust in the feedstock

was increased ($p < 0.01$ for non-composted feedstock and $p < 0.05$ for composted feedstock). This resulted in an increase in HHV and a reduction in the H:C ratio ($p < 0.05$ for both). This was a result of the higher C content and lower ash contents of the feedstocks with added sawdust. The FC was also increased ($p < 0.05$), while ash and N contents decreased with sawdust addition ($p < 0.05$ and $p < 0.001$, respectively). Composting of the feedstock increased VM and N contents in the sawdust amended treatments only ($p < 0.05$ and $p < 0.001$, respectively). In the MO feedstock, there was no significant increase in VM and N contents when the feedstocks were composted ($p = 0.83$ and $p = 0.13$, respectively). Carbon and FC contents in the biochars were not significantly changed when the feedstocks were composted ($p > 0.05$ for both). With composting, biochar HHV was not significantly changed ($p > 0.05$). Biochar surface area increased with sawdust addition to the SADPM, but decreased when the feedstocks were composted.

The MO biochars without sawdust addition had a HHV lower than a low-rank coal (lignite, 16 MJ kg^{-1}). The 3:2 biochars with the higher rate of sawdust addition had a HHV in the range of bituminous coal ($17\text{-}23 \text{ MJ kg}^{-1}$), and above that of peat ($14\text{-}21 \text{ MJ kg}^{-1}$). On the basis of yield and HHVs of the feedstock and biochar, 26-38% of the non-composted feedstocks energy was retained in the biochar. However, when the feedstock was composted, this proportion increased to 35-44%.

The H:C ratios for the feedstocks were greater than 1.28. This decreased to less than 0.50 in the biochars. This reduction indicates an increase in aromaticity in the biochars when compared to the feedstocks. Charring of lignin and cellulose has been reported to cause loss of aliphatic components along with the conversion of ring structures into aromatic compounds (Rutherford et al., 2004). This increase in aromaticity can also be seen in the increased FC contents of the biochars when compared to their feedstock. Increases of 181-243% were shown in the FC contents of biochars from non-composted feedstock, while increases of 117-222% were found in the FC contents of biochars from composted feedstock.

Table 6.2 Biochar yield, chemical analysis, higher heating value and surface area

Parameters	MO	4:1	3:2	MO (CP)	4:1 (CP)	3:2 (CP)
Yield (%)	43.4	32.1	30.6	49.3	39.1	34.5
Water content (%)	5.3	5.5	7.7	3.0	4.8	5.8
Volatile matter (% _{db})	22.6	16.6	17.1	23.0	20.4	19.2
Fixed C (% _{db})	26.2	42.3	56.1	23.3	37.2	54.7
Ash (% _{db})	51.2	41.2	26.8	53.6	42.4	26.1
N (% _{db})	3.8	2.7	2.2	4.0	3.3	2.7
C (% _{db})	33.8	51.6	66.9	33.0	50.1	62.4
H (% _{db})	1.0	1.1	1.1	1.3	1.1	1.3
Total P (% _{db})	3.18	2.34	2.37	3.21	3.02	2.59
Water Soluble P (% _{db})	0.013	0.015	0.015	0.011	0.009	0.009
NACP (% _{db})	3.07	1.96	1.48	2.73	1.51	0.84
Formic Acid Sol. P (% _{db})	1.08	0.75	0.55	0.88	0.59	0.36
K (% _{db})	1.61	1.23	0.90	1.66	1.23	0.86
H/C	0.34	0.26	0.20	0.48	0.26	0.25
HHV (MJ kg ⁻¹)	11.3	18.2	24.0	11.6	17.9	22.1
S _{BET} (m ² g ⁻¹)	17.0	19.4	24.4	14.2	17.4	23.2

db=dry basis; (CP)=composted feedstock; HHV=higher heating value; S_{BET}=BET surface area; NACP= Nutra Ammonium Citrate Soluble P

The concentration of K, TP, and the soluble fractions of P in the biochar are given in Table 6.2. Composting of the feedstock resulted in no major change in K concentrations and small increases in TP concentrations in the biochar. Biochar TP and K decreased with increasing sawdust addition. The amount of P leached from soil is dependent on the amount of water soluble P available (Weaver and Ritchie, 1994). Concentrations of water soluble P are generally very high (15-50%) in superphosphate fertilisers. The water soluble P concentrations in the biochars studied are very low (<0.016%), indicating unsuitability as a fast release fertiliser. However, it also indicates that P leaching from the biochar would probably be very small and that biochars might be suitable as a slow release P fertiliser.

The concentration of NACP decreased when feedstocks were composted and when sawdust was added, reducing the fertiliser value of the biochar. The percentage of TP which is available to plants also decreases when feedstocks are composted and amended with sawdust. Plant-available P decreased from 97% of TP for the MO biochar to 32% of the TP for the 3:2(CP) biochar. Formic acid P accounted for between 14 and 34% of the TP concentration. There was a decrease in formic acid P concentrations with sawdust addition and after composting of the feedstock.

Acid binding capacities and BUF to achieve pH values of 6.5 and 7.0 are given in Table 6.3. The optimum pH for grass, wheat, barley and maize is reported to be 6.5, while a soil pH of 7 is recommended for white clover, beet, beans, peas and oilseed rape (Teagasc, 2010). The biochar from SADPM alone had the highest BUF for both pH 6.5 and 7.0. The addition of sawdust to the SADPM resulted in a lower ABC and BUF in the biochar for both pH values. Composting of the feedstock also reduced ABC and BUF. In comparison, when this test was repeated using lime in place of biochar, values of 161 and 307 were recorded for BUF-6.5 and BUF-7, respectively. This demonstrates that lime has a significantly greater buffering capacity, indicating that while biochars offer some ability to increase soil pH when added to acid soils, they are not an adequate replacement for lime.

Table 6.3 pH, acid binding capacity (ABC) and buffering capacity (BUF) of biochar

Parameters	MO	4:1	3:2	MO (CP)	4:1 (CP)	3:2 (CP)
pH	9.3	9.0	8.9	9.4	9.5	8.7
ABC-6.5	158	90	42	140	72	27
ABC-7.0	95	55	25	94	51	14
BUF-6.5	41	27	13	39	21	8
BUF-7.0	56	36	18	48	24	12

(CP)=composted feedstock

6.3.3 Thermogravimetric Analyses

Figure 6.4 (a) and (b) show the mass (Thermogravimetric (TG)) and derivative of TG curves (DTG) of the feedstocks, respectively. The TG analyses show the loss of mass of the feedstock as the temperature increases from ambient temperature to 600 °C. The primary devolatilisation stage is indicated by the highest peaks on the DTG curve (Figure 6.4b). The temperatures of primary devolatilisation are shown in Table 6.4. The onset temperature (T_{on}) was determined as the point of 5% loss of weight (db). The temperature at maximum devolatilisation (T_{max}) was determined from the peaks on the DTG curves. The final temperature of primary devolatilisation (T_f) was determined from the DTG curve as the temperature corresponding to the intersection of the tangent lines in the primary and secondary devolatilisation stages. The final temperature of primary devolatilisation was similar for all feedstock at 370 ± 6 °C. The temperature range (T_r) of devolatilisation is the difference between T_f and T_{on} . The primary devolatilisation stage is followed by the secondary devolatilisation stage (Figure 6.4b) when heavier chemical structures are degraded (Biagini and Tognotti, 2006).

Table 6.4 Temperatures of primary devolatilisation (°C)

Parameters	MO	4:1	3:2	MO (CP)	4:1 (CP)	3:2 (CP)
T_{on}	191	202	223	124	172	191
T_{max}	323	342	347	331	349	354
T_r	184	167	149	240	202	184

(CP)=composted feedstock; T_{on} =onset temperature; T_{max} =maximum temperature; T_r =temperature range

Similar to the results in Section 6.3.2, sawdust addition and composting of the feedstocks reduced biochar yield. The MO feedstocks had a greater secondary devolatilisation stage, indicating the presence of heavier chemical structures in the manure (Biagini and Tognotti, 2006). This stage was reduced with sawdust addition. The addition of sawdust to SADPM increased T_{on} due to the presence of more complex compounds in the sawdust. Composting of the feedstock caused a reduction in T_{on} . This is due to the degradation of complex compounds into simpler molecules

during the composting process (Bernal et al., 2009). These simpler compounds are more easily volatilised at lower temperatures. The temperature at maximum devolatilisation increased with sawdust addition and with composting of the feedstocks. The temperature range reduced with sawdust addition and increased with composting of the feedstock due to the changes in T_{on} .

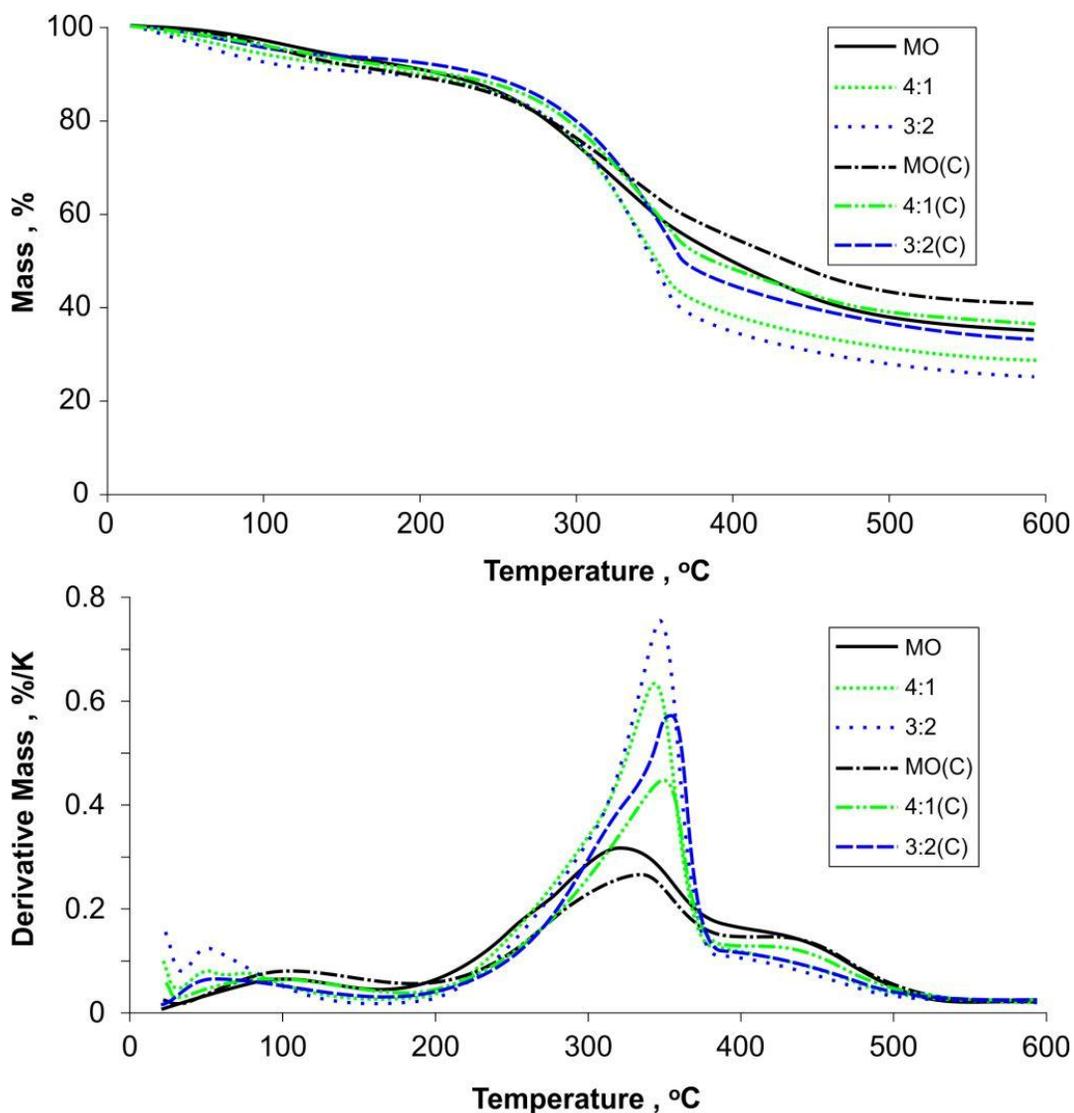


Figure 6.4 (a) Mass (TG) curves and (b) derivative mass (DTG) curves during N pyrolysis: ambient – 600°C, 10K min⁻¹; mass (%) is the percentage of actual weight.

6.3.4 Characteristics of Bio-liquid and Gas

Bio-liquid yield ranged from 11 to 30% (Table 6.5). Sawdust addition to SADPM increased bio-liquid yield ($p < 0.01$), however, composting of the feedstock did not significantly alter the yield ($p > 0.05$). Between 21 and 46% of the volatiles were found to be condensable. Similar to the overall bio-liquid yield, sawdust addition and composting increased the proportion of volatiles which were condensable. Elemental analyses of the bio-liquids are shown in Table 6.5. Carbon contents of the bio-liquids decreased as the proportion of sawdust in the feedstock increased ($p < 0.01$). This results in a decrease in HHV ($p < 0.01$). Mante and Agblevor (2010) also found increased bio-liquid yields, decreased C and N contents and HHV values by adding wood to poultry manure. Composting of the feedstock resulted in increased C and N contents ($p < 0.01$ and $p < 0.05$, respectively) and HHV of the bio-liquids ($p < 0.01$).

Table 6.5 Yield, elemental analysis and higher heating values of the bio-liquids

Parameters	MO	4:1	3:2	MO (CP)	4:1 (CP)	3:2 (CP)
Yield (%)	11.9	16.3	25.5	16.9	20.8	30.3
N (%)	4.5	3.6	2.6	5.6	4.8	3.4
C (%)	38.8	35.8	35.4	43.8	42.1	39.4
H (%)	9.2	9.4	9.4	9.0	8.8	9.5
HHV (MJ kg ⁻¹)	15.3	13.6	13.2	18.1	17.1	15.4

(CP)=composted feedstock; HHV=higher heating value

Gas yield ranged from 34 to 52% (Table 6.6). Yields decreased significantly when the feedstocks were composted ($p < 0.05$). This is because gases, primarily CO₂ and NH₃, but also N₂O and CH₄, are lost during the composting process (Bernal et al., 2009). The compositions of the non-condensable gases are given in Table 6.6. As N₂ was used as a carrier gas during pyrolysis, the proportion found in the produced gas was artificially high. Therefore, the proportion of N₂ in the manure only feedstock was estimated to be 10%, as found by Ro et al. (2010), and this was revised downwards for all other feedstocks based on the proportion of manure to sawdust in the feedstock.

Table 6.6 Yield, composition (% volume) and higher heating value of non-condensable gases

Parameters	MO	4:1	3:2	MO (CP)	4:1 (CP)	3:2 (CP)
Yield (%)	44.7	51.6	43.9	33.8	40.1	35.2
N ₂	10.0	5.6	3.2	10.0	5.6	3.2
CH ₄	6.1	11.3	13.5	6.2	11.5	11.7
CO ₂	43.2	34.8	35.2	47.5	38.7	34.5
CO	19.3	31.0	36.2	14.8	25.6	37.2
H ₂	2.4	3.4	3.5	2.5	3.2	3.3
C ₂ H ₆	0.9	1.5	1.4	1.1	1.3	1.3
C ₂ H ₄	8.9	6.7	5.7	10.0	8.0	6.9
C ₂ H ₂	0.3	0.3	0.3	0.3	0.3	0.2
Other C _x H _y *	8.8	5.4	1.1	7.5	5.9	1.6
HHV (MJ Nm ⁻³)	11.7	14.4	15.1	12.0	14.4	15.2

(CP)=composted feedstock; HHV=higher heating value; *=by difference

The largest component gas in the mixtures was CO₂ (35-48%) followed by CO (15-37%). Carbon dioxide decreases the overall quality of the gas produced, therefore, pyrolysis conditions which reduce the production of CO₂ are desirable (Lima et al., 2009; Mullen et al., 2010). Increasing the rate of sawdust addition to SADPM decreased the CO₂ concentration and increased the CO concentrations in the gas produced, similar to the finding of a similar study by Mante and Agblevor (2010) using poultry manure. The addition of sawdust to the SADPM also increased the concentrations of CH₄ and H₂, while there was a reduction in C₂H₄ concentration. The HHV of the gases increased with sawdust addition. There was little difference in the overall gas composition or HHV when the feedstock was composted.

More than 54% of the original energy in the feedstock remained in the biochar, bio-liquid and gas after pyrolysis. This figure ranged from 54-81% for the non-composted feedstock, increasing as the proportion of sawdust increased. For the composted feedstock, the figure was higher (70-94%) and rose with increasing sawdust addition.

6.3.5 Energy Balance

The inputs required and the outputs obtained from each feedstock are given in Table 6.7. All values are calculated on the basis of one tonne of liquid pig manure after anaerobic digestion.

6.3.5.1 Inputs

There are no differences between feedstocks for the separation energy requirement. However, following separation, different quantities of sawdust were mixed with the separated manure solids to form the various feedstocks (Table 6.7). The addition of sawdust to SADPM increased the energy requirements for composting, drying and pyrolysis, due to the increased mass of the feedstock. The quantity of bio-liquid, gases and biochar produced were increased, resulting in greater energy generation.

The input energy required for the composting process was relatively small in comparison to the other processes. However, the inclusion of a composting step had a large influence on the energy requirements of the drying and pyrolysis processes. The energy required for drying showed a decrease of approximately 58% when a composting stage was included. The energy required for pyrolysis also showed a reduction of between 31 and 43% with the addition of a composting stage. These reductions were due to a mass reduction of 50%, including a 15% decrease in water content, which occurs during the composting process (Tiquia et al., 2002b).

6.3.5.2 Outputs

The amount of biochar, bio-liquids and gases is dependent on whether a composting stage is applied. The quantity of biochar produced decreased by between 20 and 38% when a composting stage was incorporated. Similarly, bio-liquid and gas production decreased by between 36 and 47% with the addition of a composting stage. The severity of these reductions increased with sawdust addition. This resulted in reduced energy generation when a composting step was applied. Therefore, although the inclusion of a composting stage reduced the energy requirements for drying and pyrolysis, there was a decrease in energy production.

6.3.5.2.1 Output 1: Using Biochar as a Fuel

The results of using the biochar produced through pyrolysis as a fuel are shown in Table 6.7. There was a positive net energy yield for all feedstocks, except for the MO treatment. However, the addition of sawdust to SADPM substantially increased the net energy yield. The addition of a composting stage resulted in a reduced net energy yield with the exception of the MO treatment, where the addition of a composting stage changed a negative net energy yield to a positive net energy yield.

6.3.5.2.2 Output 2: Using Biochar as a Soil Additive

The results of using the biochar produced through pyrolysis as a soil additive are shown in Table 6.7. There was a positive net energy yield only when sawdust was added to SADPM. For the MO treatment, the energy generated from the combustion of the bio-liquid and gas was not sufficient to sustain the treatment processes. The addition of sawdust substantially increased the net energy yield. The addition of a composting stage had a positive effect in treatments MO and 4:1, while for 3:2, the addition of a composting stage reduced the net energy yield. Some feedstocks did show a small increase in the biochar nutrient concentrations (Table 6.2) when a composting step was incorporated. However, the nutrient concentration of the biochar produced decreased with sawdust addition to the manure (Table 6.2), decreasing the value of the biochar as a soil additive.

Table 6.7 Inputs and Outputs from each feedstock and process (values per tonne liquid manure)

	MO	4:1	3:2	MO(CP)	4:1(CP)	3:2(CP)
Inputs						
Separation (MJ)	-7.9*	-7.9	-7.9	-7.9	-7.9	-7.9
Composting (MJ)	0.0	0.0	0.0	-1.3	-1.6	-2.1
Drying Heat (MJ)	-168.9	-177.8	-192.7	-72.3	-76.2	-81.3
Pyrolysis (MJ)	-9.5	-29.8	-63.7	-6.6	-18.3	-36.3
Sawdust (t)	0.0	0.0175	0.0467	0.0	0.0175	0.0467
Outputs						
Bio-liquid & gases (t)	0.0112	0.0238	0.0425	0.0069	0.0131	0.0224
CHP Generated (MJ)	86.0	217.6	413.2	63.6	133.8	239.3
Biochar (t)	0.0084	0.0112	0.0188	0.0067	0.0084	0.0117
CHP Generated (MJ)	76.2	163.1	361.1	61.8	119.7	207.6
Output 1: Biochar as a Fuel						
Energy Balance (MJ)	-24.1	165.1	509.9	37.3	149.5	319.2
Output 2: Biochar to Soil						
Energy Balance (MJ)	-100.4	1.9	148.9	-24.5	29.8	111.7

* Positive values indicate an energy generation, while negative values indicate an energy requirement.

6.4 Summary

The influence of (1) the addition Sitka Spruce sawdust and (2) composting of the feedstock on the products of pyrolysis of anaerobically digested pig manure was significant. The proportion of biochar, bio-liquid and gas produced, and the physical and chemical characteristics of these products were influenced by both sawdust addition and feedstock composting. Increasing the sawdust content in the wood/manure mixture decreased the biochar yield and increased the bio-liquid yield. The biochar showed increased heating values, but reduced nutrient concentrations with increasing sawdust addition. The heating value of the gases produced also increased, while that of the bio-liquid was decreased with sawdust addition.

Composting of the feedstock before pyrolysis increased the biochar and bio-liquid yield, but decreased the gas yield. The biochar showed reduced heating values, while the bio-liquid heating values were increased with composting.

The net energy yield from biochar and renewable energy production increased with sawdust addition to the manure digestate. The energy yield also increased when the manure only (without sawdust addition) feedstock was composted before pyrolysis. However, with increasing sawdust addition, composting of the feedstock reduces the net energy yield. If the biochar is used as a fuel, all feedstocks except for the non-composted manure only feedstock, produced a positive net energy yield. Should the biochar be used as a soil additive, then sawdust addition to the manure may be required to produce a positive energy yield.

It is important to investigate the further benefits of using biochar as a soil additive. These are investigated in the soil column study outlined in the next two chapters.

7 IMPACT OF BIOCHAR ADDITION ON NUTRIENT LEACHING AND SOIL PROPERTIES IN TEMPERATE CONDITIONS

Overview

In this chapter, a soil column study investigating the effect of the addition of two types of biochar to soil on nutrient leaching and soil properties is described. The first biochar examined was produced from the separated solid fraction of anaerobically digested pig manure, while the second biochar was produced from Sitka Spruce. The aim of this experiment was to quantify the effect of the addition of biochar to an Irish tillage soil on (1) leaching of carbon, nitrogen and phosphorus and (2) on soil properties, including organic matter content, water content and nutrient concentrations.

7.1 Introduction

Biochar addition to soil has been shown to influence soil physico-chemical properties, such as pH, porosity, bulk density, pore-size distribution, water holding capacity, soil surface area, drainage and aeration (Glaser et al., 2002; Chan et al., 2007; Downie et al., 2009; Laird et al., 2010b). The response of soils to biochar amendment depends on the biochar properties (Tyron, 1948), soil properties, and on further nutrient addition to soil (Lehmann and Rondon, 2006). The feedstock and pyrolysis conditions used to produce the biochar can also have a significant impact on the effects of the biochar when applied to soils: differences in feedstock nutrient concentrations have been seen to persist after pyrolysis (DeLuca et al., 2009), while the pyrolysis temperature can also affect the concentrations of these nutrients (Chan et al., 2008; Gaskin et al., 2008).

Numerous studies have documented reduced leaching from soil amended with biochar (Lehmann et al., 2003, Novak et al., 2009; Laird et al., 2010a; Singh et al., 2010). The retention of nutrients in the soil has been attributed to the higher sorption capacity of

biochar (Novak et al., 2009; Singh et al., 2010), increased water retention, which reduces leaching of mobile nutrients; increased growth rate of microorganisms (Ishii and Kadoya, 1994; Steiner et al., 2008b), and alterations to the N cycling process within the soil (Steiner et al., 2008a; DeLuca et al., 2009; Clough et al., 2010; Laird et al., 2010a). Changes in the N cycling processes due to biochar addition to soil may be caused by: (1) the adsorption of NH_4^+ and soluble organic compounds onto the biochar, which inhibits mineralisation of organic N and/or nitrification of NH_4^+ (Laird et al., 2010a; Singh et al., 2010) (2) nitrification inhibitors found on unweathered biochar, which reduces nitrification of NH_4^+ (Clough et al., 2010), and (3) increased water holding capacity and organic C concentrations, which facilitates increased denitrification (Rivett et al., 2008).

Most of the studies investigating biochar addition to soil have taken place in tropical regions using wood-based biochar. However, there is a dearth of research on the effect of biochar application to soils outside tropical and subtropical regions (Verheijen et al., 2010). Therefore, the objectives of this study were to: (1) investigate the effect of biochar derived from pig manure and wood on nutrient leaching from an Irish tillage soil and (2) analyse the effect of the biochar addition on soil properties.

7.2 Materials and Methods

7.2.1 Soil and Biochar

Surface soil to a depth of 0.2 m was collected from a tillage farm near Fermoy, County Cork. The soil was classified as an Acid Brown Earth (Regan et al., 2010) and had a P Index of 1. A low P Index soil was chosen to alleviate the risk of chronic P leaching from the soil. The texture and characteristics of the soil used in this study were previously studied by Regan et al. (2010). The soil was air dried at 30°C, passed through a 2 mm sieve, and mixed to ensure homogeneity.

Two types of biochar were used for this study: pig manure biochar and wood biochar. Pig manure biochar was produced from the solid fraction of separated pig manure after anaerobic digestion, which was then mixed with Sitka Spruce sawdust (at a 4:1 ratio by wet weight), and subjected to slow pyrolysis in a laboratory pyrolysis reactor

operated at 600 °C. Wood biochar was produced by slow pyrolysis of Sitka Spruce wood in a large-scale pyrolysis reactor at 600 °C. Both biochars were ground to pass through a 2 mm sieve. A scanning electron microscope (SEM) (Hitachi S-4700, Hitachi High Technologies Ireland) was used to take high resolution images of both biochars (Figure 7.1). The characteristics of the biochars are given in Table 7.1.

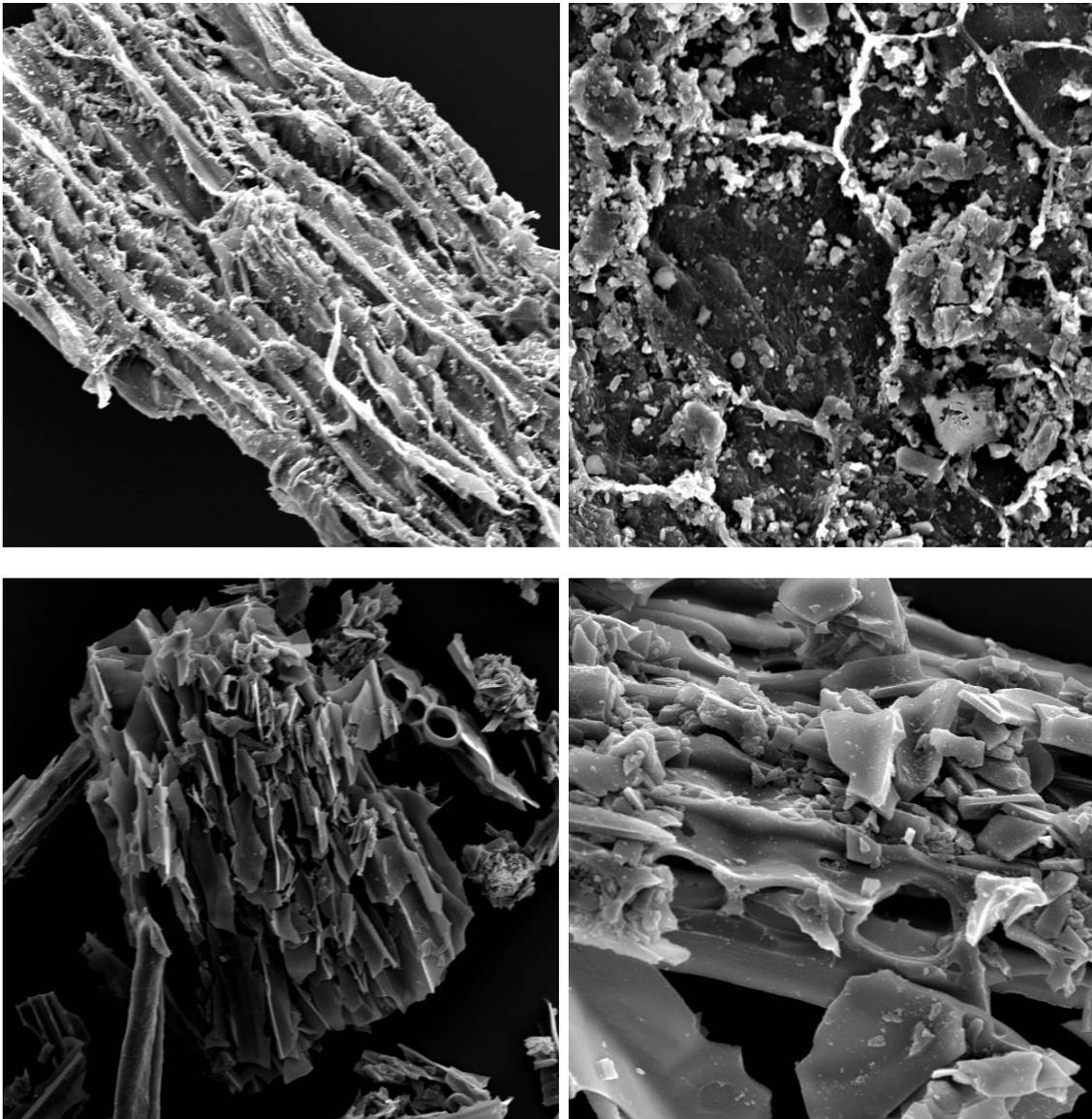


Figure 7.1 Scanning Electron Microscope image of pig manure (top) and wood (bottom) biochar at x250 magnification (left) and x1000 magnification (right)

Table 7.1 Characteristics of the biochars used in the column experiment

	Pig manure biochar	Wood biochar
Water Content (%)	0.39 ± 0.044	0.45 ± 0.039
Organic Matter (g kg^{-1})	725 ± 7.8	970 ± 12.4
Bulk Density (g cm^{-3})	0.19 ± 0.020	0.18 ± 0.016
Total N (%)	2.67 ± 0.042	0.42 ± 0.024
Total C (%)	62.7 ± 1.30	82.0 ± 1.15
Total H (%)	2.60 ± 0.184	1.82 ± 0.165
WEP (mg kg^{-1})	112.8 ± 5.36	3.6 ± 0.20
pH	9.6 ± 0.34	9.3 ± 0.19

WEP, water extractable phosphorus

7.2.2 Preparation of Soil Columns

The experiment was conducted in 0.3 m-deep and 0.104 m-internal diameter PVC columns, which were sealed at the base with perforated PVC end-caps to allow for the outflow of leachate (Figure 7.2). The leachate was collected in plastic containers via funnels connected to the end-cap of each column.



Figure 7.2 PVC columns used to contain soil for the leaching experiment

Three treatments (n=8) were examined over a study duration of 30 weeks: (1) non-amended soil (the study control), (2) soil mixed with pig manure biochar (PM600) and (3) of soil mixed with wood biochar (W600). Batches of air-dried sieved soil (<2 mm) were mixed with sieved biochar (<2 mm) at biochar application rates equivalent to 18 tonne ha⁻¹ to a soil depth of 0.2 m. Prior to placing the soil in the columns, distilled water was added to bring the mixtures to a WC of approximately 26% (the WC of the soil in the field at the time of sampling) and the mixture was thoroughly mixed by hand. Pea gravel, 5 – 10 mm in size, was placed at the base of each column to a depth of 0.05 m, and was overlain by soil mixtures (with a WC of 26% and a dry bulk density of 1.1 g cm⁻¹) to a depth of 0.2 m. The soil was packed in 0.05-m-depth increments to ensure uniform packing of soil. At each depth increment, soil was pressed along the wall of the column to prevent preferential flow (Bhupinder Singh, pers. comm.). The characteristics of the soil and the soil and biochar mixes before leaching are given in Table 7.2.

7.2.3 Soil Column Incubation and Leaching

The temperature (10 °C) and relative humidity (75%) at which the columns were stored were based on climatic conditions in Ireland (Walsh, 2012). All columns were leached with 160 mL of distilled water, applied twice weekly in two 80-ml increments over two hours, each week for 30 weeks. The rate of water addition was designed to simulate an annual total rainfall of 980 mm per year, which is approximately the average yearly precipitation in Ireland. On week 10 of the study, pig manure, collected from an integrated pig farm in Fermoy Co. Cork, was applied to the surface of four columns of each treatment at a rate equivalent to 170 kg N ha⁻¹ and 36 kg P ha⁻¹. This application rate corresponds with the general land spreading limit of 170 kg N ha⁻¹ yr⁻¹ from livestock manure imposed by S.I. 610 of 2010. The treatments which received pig manure were then known as Control+PM, PM600+PM and W600+PM. The pig manure had a DM content of 3% and TN, NH₄⁺ and TP contents of 2.94, 1.74 and 0.62 kg m⁻³, respectively.

Table 7.2 Characteristics of the soil (Control), and the soil and biochar mixes (PM600 and W600) on Week 0 of the experiment before leaching was applied

	Control	PM600	W600
Water Content (%)	26.8 ± 0.24	25.5 ± 0.58	25.8 ± 0.36
Organic Matter (g kg ⁻¹)	46.2 ± 0.13	54.4 ± 1.94	54.0 ± 2.10
Bulk Density (g cm ⁻³)	1.10 ± 0.010	1.11 ± 0.009	1.11 ± 0.017
Total N (%)	0.21 ± 0.008	0.22 ± 0.002	0.21 ± 0.013
Total C (%)	1.75 ± 0.049	2.18 ± 0.001	2.48 ± 0.170
WEP (mg kg ⁻¹)	0.36 ± 0.037	0.52 ± 0.008	0.39 ± 0.016
Morgan's P (mg L ⁻¹)	4.84 ± 0.269	7.53 ± 0.137	5.04 ± 0.184
WSOC (mg kg ⁻¹)	120 ± 1.9	196 ± 11.8	163 ± 9.4
K (cmol L ⁻¹)	0.36 ± 0.003	0.39 ± 0.000	0.33 ± 0.018
Ca (cmol L ⁻¹)	7.14 ± 0.105	6.74 ± 0.010	7.22 ± 0.154
Mg (cmol L ⁻¹)	0.30 ± 0.004	0.31 ± 0.004	0.31 ± 0.004
Na (cmol L ⁻¹)	0.23 ± 0.006	0.14 ± 0.075	0.11 ± 0.048
CEC (cmol L ⁻¹)	8.03 ± 0.111	7.58 ± 0.079	7.97 ± 0.084
pH	6.9 ± 0.20	6.9 ± 0.18	6.8 ± 0.04

WEP, water extractable phosphorus; WSOC, water soluble organic carbon; CEC, cation exchange capacity.

7.2.4 Leachate Analyses

A sample of leached water was collected from the base of each column once per week for analysis. Unfiltered leachate samples were analysed for total organic C (TOC) and TN using a BioTector TOC TN TP Analyzer (BioTector Analytical Systems Limited, Cork, Ireland). Sub-samples of leachate were passed through a 0.45 µm filter and analysed colorimetrically for total oxidised N (TON), NH₄⁺, NO₂⁻ and DRP using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland). Nitrate was calculated by subtracting NO₂⁻ from TON. Filtered and unfiltered samples were tested for total dissolved P (TDP) and TP using acid persulfate digestion. Particulate P (PP) was calculated by subtracting TDP from TP. Dissolved un-reactive P (DUP) was calculated by subtracting DRP from TDP.

7.2.5 Analysis of Soil and Biochar Properties

Columns (n=4) from each treatment were destructively sampled at time increments of 10, 20 and 30 weeks. Analyses were conducted at depth increments of 0-0.05, 0.05-0.1, and 0.1–0.2 m below the soil surface. The soil from each depth increment was air-dried and sieved to a particle size of 2 mm, or less, before analyses. Soil organic matter content of the soil was determined using the loss on ignition test (B.S.1377-3; BSI, 1990b). Water extractable P was measured by shaking 5 g of soil in 25 mL of distilled water for 30 min, filtering (0.45 µm) the supernatant water and determining P colorimetrically (McDowell and Sharpley, 2001). Morgan's P, the national test used for the determination of plant available P in Ireland, was determined using Morgan's extracting solution (Morgan, 1941). Soil TC and TN were determined by high temperature combustion using a LECO Truspec CN analyser (LECO Corporation, St. Joseph, MI, USA). Water soluble organic C (WSOC) was determined by shaking a 1:10 extract of soil/biochar-to-deionised water (w/v) for 30 min (Yanai et al., 2007), filtering (0.45 µm) the supernatant water and determining TOC using a BioTector TOC TN TP Analyzer (BioTector Analytical Systems Limited, Cork, Ireland).

The ability of the biochar and soil to adsorb P was assessed using adsorption isotherms. In graduated containers, 90 ml of ortho-phosphorus (PO₄-P) solutions, synthesised using dissolved potassium phosphate (KH₂PO₄) in distilled water, ranging in concentration from 3 to 30 mg P L⁻¹, were added to 5 g samples of biochar or soil. The mixtures were shaken using an end-over-end shaker for 24 hours. Sub-samples of the supernatant were passed through 0.45 µm filters and analysed colorimetrically for DRP using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland).

A Langmuir isotherm was used to estimate the mass of P adsorbed per mass of the soil or biochar (Fenton et al., 2009):

$$\frac{C_e}{x/m} = \frac{1}{ab} + \frac{C_e}{b} \quad [7.1]$$

where C_e is the concentration of P in solution at equilibrium (mg L⁻¹), x/m is the mass of P adsorbed per unit dry weight of soil or biochar (g kg⁻¹), a is a constant related to

the binding strength of molecules onto the soil or biochar, and b is the maximum adsorption capacity (g kg^{-1}).

7.2.6 Statistical Analysis

Soil and leachate data were analyzed using the Statistical Analyses System (SAS Institute, 2004) with each column as the experimental unit. For all analyses, significance was given as $p < 0.05$.

Water content, OM, Morgan's P, WEP, N and C contents, and C:N ratio were analysed as repeated measures using the MIXED procedure of SAS with Tukey-Kramer adjustment for multiple comparisons. The dependent variables were: WC, OM, Morgan's P, WEP, N and C contents, and C:N ratio. For all the above analyses, the fixed effects were: treatment, week, depth and column. Week and depth were the repeated measures.

Comparison of cumulative leaching of TN, NO_3^- , NO_2^- , NH_4^+ , TP, TDP, DRP, DUP, TPP, TC, and TOC (between both week 1 and 30, and week 11 and 30) was performed using the MIXED procedure in SAS. The dependent variables were TN, NO_3^- , NO_2^- , NH_4^+ , TP, TDP, DRP, DUP, TPP, TC and TOC. Treatment was included as a fixed effect. Total organic C and NO_3^- were analysed as repeated measures using the MIXED procedure of SAS with Tukey-Kramer adjustment for multiple comparisons. The dependent variables were TOC and NO_3^- . The fixed effects were: treatment, week and column. Week was the repeated measure.

7.3 Results and Discussions

7.3.1 Water Content and Organic Matter

The columns remained freely draining throughout the entire experiment. There was a small amount of ponding, for one hour following water application, on the surface of the soils which had received pig manure. This lasted for approximately 5 weeks following manure application, after which no ponding occurred. No leachate passed through the columns on the first week of leaching. On week 2, the leachate volume

collected was 133 ± 15.7 , 89 ± 9.0 and 75 ± 6.2 mL for Control, PM600 and W600 columns, respectively. From week 5 onwards, except for week 11 when the manure was added, the average leachate volume was greater than 147 mL for all columns. The average leachate volume collected from week 12-30 was 151 ± 2.2 , 152 ± 2.4 and 154 ± 1.8 mL for Control, PM600 and W600, respectively, while the averages were 151 ± 1.6 , 152 ± 1.5 and 153 ± 1.9 for Control+PM, PM600+PM and W600+PM, respectively. Around 5 – 10 mL of water evaporated from each column each week.

The WC of all treatments increased significantly between week 0 and week 10 ($p < 0.01$) (Figure 7.3). The WC on week 0 was between 25.5 and 26.7%, but by week 10, the WC had risen to $>31\%$ for all treatments at all sampling depths. After week 10, there was no further significant increase in WC ($p > 0.05$). There was an increase in WC with sampling depth: soil sampled at 0.1–0.2 m depth had a significantly higher WC than soil at the 0–0.05 m depth for all treatments on every sampling week ($p < 0.0001$). There was an increase in the WC of the biochar-amended treatments when compared with the Control on most sampling weeks. On week 30, the WC of biochar-amended treatments at each sampling depth was 7.2–13.6% greater than that corresponding sampling depth of the Control. Previous studies have shown biochar-amended soil can have a higher water holding capacity than unamended soil (Laird et al., 2010b; Streubel et al., 2011). Soil WC can impact many soil processes, including mineralization, plant uptake, leaching and denitrification (Porporato et al., 2003). The ability of biochar to increase the water retention capacity of the soil may be due to blockages of soil pores by the smallest sized fraction of biochar, increased net surface area with biochar addition, or the increased OM content of biochar-amended soils (Downie et al., 2009; Verheijen et al., 2010). The addition of pig manure had no effect on soil WC ($p > 0.05$).

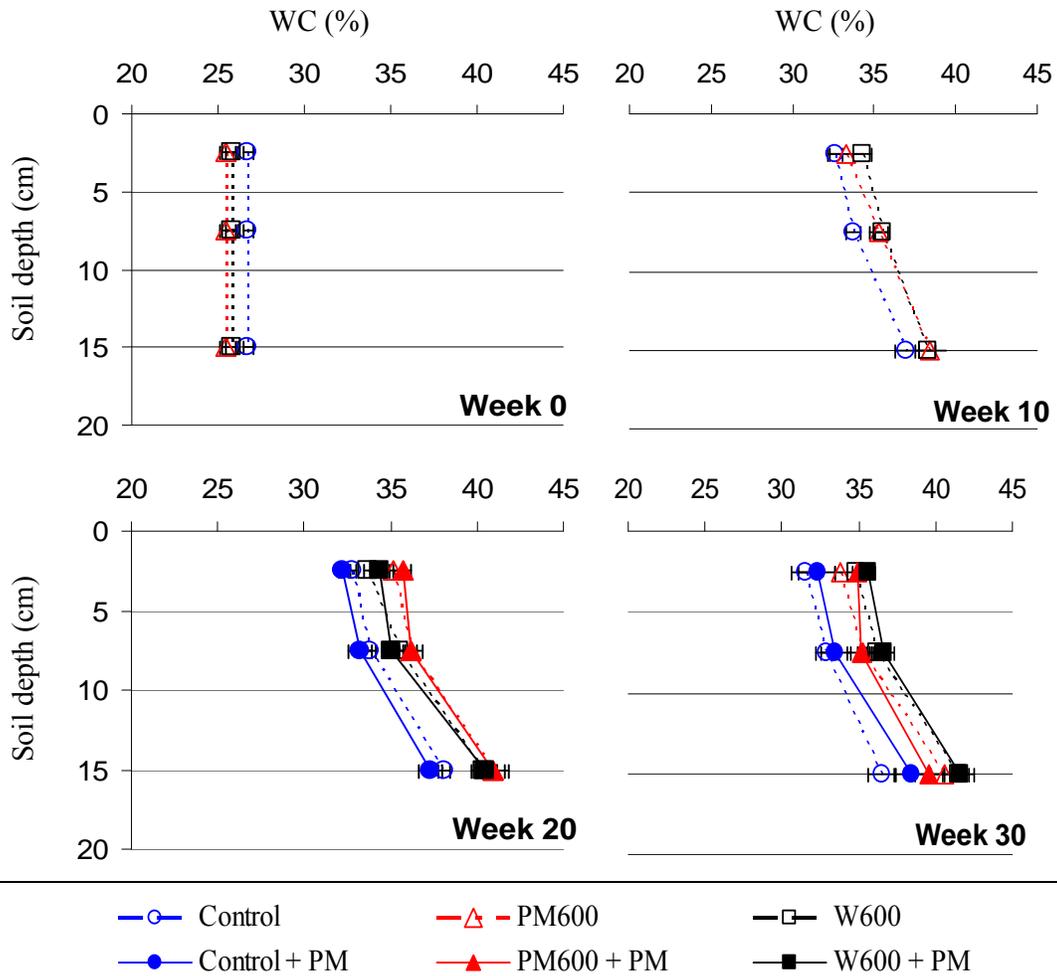


Figure 7.3 Soil water content (WC) at different sampling events, and at different sampling depths. The treatments which were amended with the pig manure between week 10 and 11 are shown with (+PM)

The OM contents of the soils are shown in Figure 7.4. The biochar-amended soils had significantly higher OM contents than the Control on the majority of sampling days and sampling depths ($p < 0.05$). There was no difference in OM content with depth for any treatment on any sampling week ($p > 0.05$). The addition of pig manure to the columns had no effect on the OM content of the soil on week 20 or 30 ($p > 0.05$). In general, there was a decrease in OM content from week 0 to week 30 ($p < 0.05$).

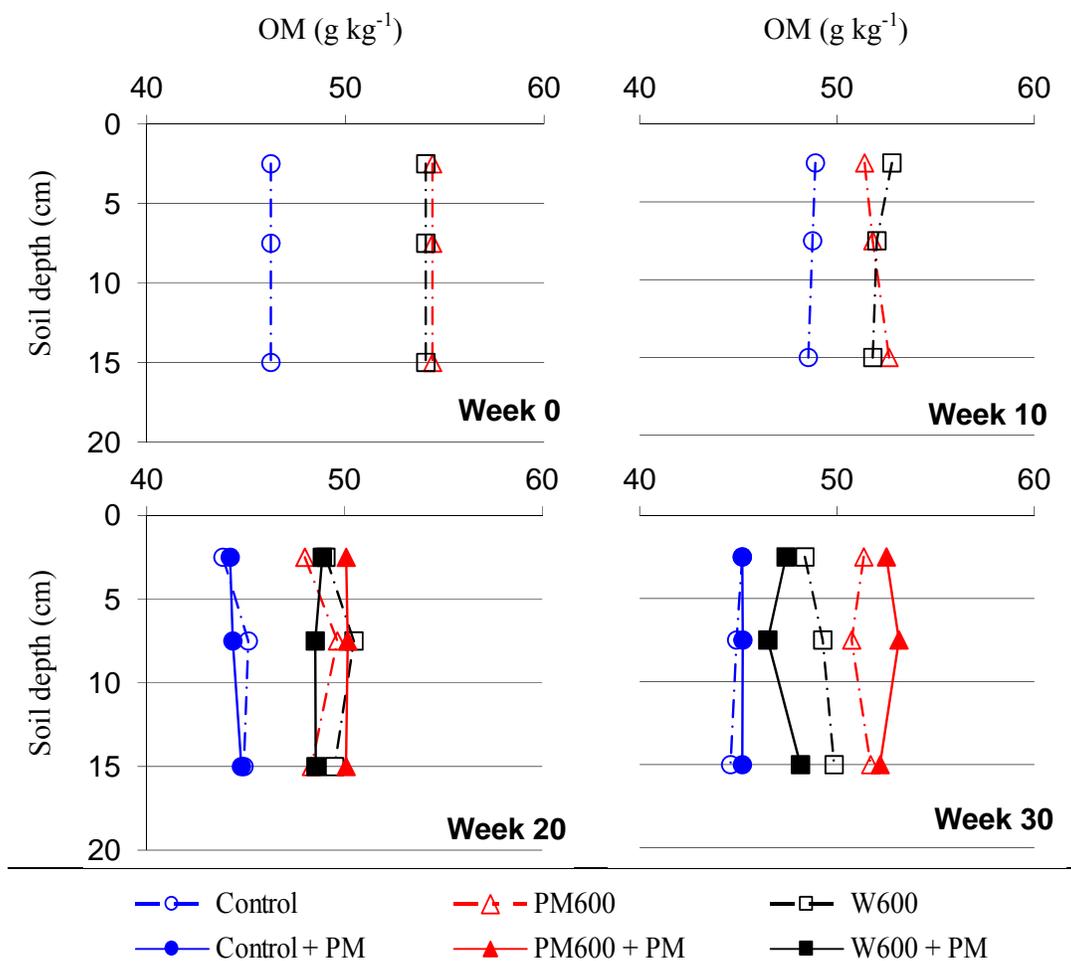


Figure 7.4 Soil organic matter (OM) content at different sampling events, and at different sampling depths. The treatments which were amended with the pig manure between week 10 and 11 are shown with (+PM)

7.3.2 Carbon Leaching and Soil Content

The quantity of TOC leached from the treatments is shown in Figure 7.5. The total amount of TOC leached from PM600 over the 30-week experiment was greater than the Control and W600 ($p < 0.0001$ for both). PM600 had significantly higher TOC leaching on all sampling weeks compared with W600, and on weeks 2 – 26 compared with the Control ($p < 0.05$). The WSOC of PM600 was higher than the Control and W600 (Table 7.2), indicating more mobile C in the pig manure biochar. Biochar from wood has a higher aromaticity than biochar from manures due to the higher lignin and cellulose content of the wood. Biochars produced from manures and crop residues are

more readily degradable (Collison et al., 2009). Therefore, a greater proportion of C in the pig manure biochar is likely to be lost through mineralisation and leaching, compared with the wood biochar. In the previous chapter (Section 6.3.2), it was found that increasing the sawdust content in the blended pig manure and sawdust biochar resulted in elevated fixed C contents, indicating higher C aromaticity, and less C mobility. Gaskin et al. (2008) in a study using biochars from both pine chips and poultry manure, produced at 500 °C, found that leaching of total dissolved C from the manure-based biochar was seven times higher than that leached from the wood-based biochar (0.85 and 0.12 g kg⁻¹, respectively).

There was significantly less TOC being leached from W600, compared with the Control ($p < 0.0001$), on weeks 2-18. This occurred despite the fact that W600 had a higher WSOC content than the Control at the beginning of the experiment (Table 7.2). The reduction in TOC leaching in this study is likely to be due to enhanced mineralisation in the biochar-amended treatments. This higher mineralisation rate results in increased CO₂-C emissions described in the next chapter (Section 8.3.2). Some of the organic C may also be used as an electron donor for denitrification (Section 7.3.3). This reduction in TOC leaching is not seen in the PM600 treatment compared with the Control, due to the very high WSOC of this treatment (Table 7.2). Laird et al. (2010a) also found reduced TOC leaching through the addition of wood-based biochar to soil compared with unamended soil. They suggested that TOC leaching was reduced through the ability of wood biochar to adsorb organic C. However, this was not the case in the current study, as the CEC of the biochar-amended treatments was similar to that of the Control (Table 7.2).

Pig manure addition did not result in increased TOC leaching ($p > 0.05$) in Control+PM and PM600+PM compared with Control and PM600, respectively. However, the cumulative leaching of TOC between weeks 11 and 30 was higher for W600+PM compared with the W600 ($p < 0.05$).

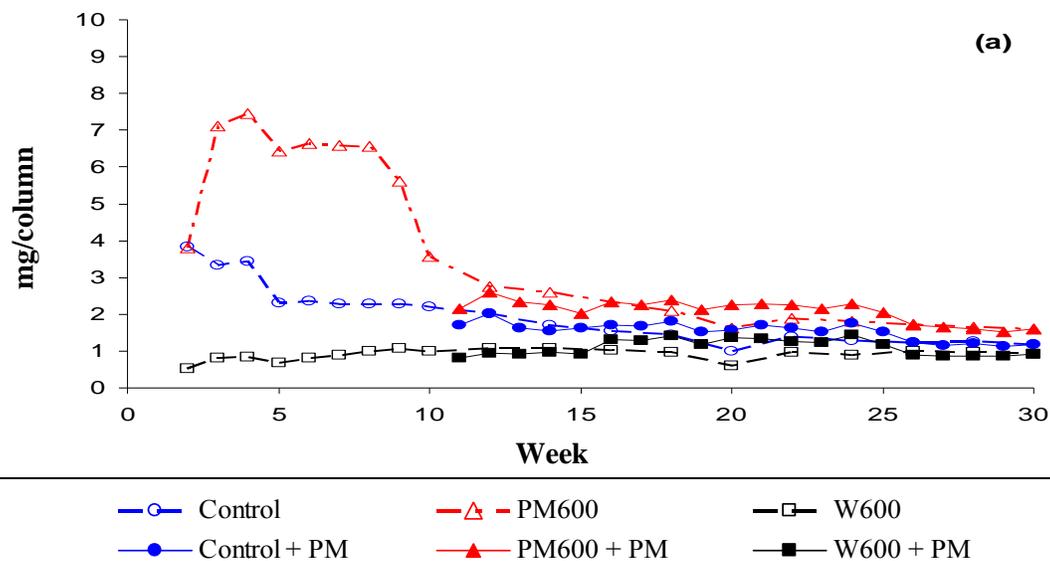


Figure 7.5 Leaching of TOC from soil amended with biochar and leached weekly with 160 mL distilled water. The treatments which were amended with the pig manure between week 10 and 11 are shown with (+PM)

The C content of the biochar-amended soils was higher than the Control soil on every sampling week (Table 7.3). There was no difference in C content between sampling depths for any treatment on any sampling week ($p > 0.05$). The addition of pig manure did not increase the soil C content ($p > 0.05$). The soil C:N ratio in the W600 treatment was greater than that of the Control on all sampling weeks and depths ($p < 0.05$), except for 0-5 cm on week 20 (Table 7.3). The soil C:N ratio of the PM600 soil was also greater than that of the Control on the majority of sampling days and depths. The addition of pig manure did not increase the soil C:N ratio in the manure-amended treatments, except for the 0-5 cm depth in W600+PM on week 20 (Table 7.3).

Table 7.3 Carbon, nitrogen (%) and C:N ratio at 3 sampling depths (cm below surface) over 4 sampling events

Week	Depth				Pig manure added week 10			s.e.	p
		Control	PM600	W600	Control	PM600	W600		
<u>Carbon</u>									
0		1.75 ^a	2.18 ^b	2.48 ^b				0.072	<0.05
10	0-5	1.81 ^a	2.25 ^b	2.42 ^b				0.035	<0.0001
	5-10	1.80 ^a	2.30 ^b	2.45 ^b				0.035	<0.0001
	10-20	1.81 ^a	2.29 ^b	2.39 ^b				0.035	<0.0001
20	0-5	1.67 ^a	2.14 ^b	2.29 ^b	1.79 ^a	2.17 ^b	2.28 ^b	0.039	<0.0001
	5-10	1.72 ^a	2.17 ^b	2.26 ^b	1.66 ^a	2.19 ^b	2.16 ^b	0.039	<0.0001
	10-20	1.71 ^a	2.23 ^b	2.35 ^b	1.70 ^a	2.27 ^b	2.26 ^b	0.039	<0.0001
30	0-5	1.74 ^a	2.25 ^b	2.11 ^b	1.76 ^a	2.22 ^b	2.29 ^b	0.036	<0.0001
	5-10	1.68 ^a	2.19 ^b	2.14 ^b	1.67 ^a	2.25 ^b	2.30 ^b	0.036	<0.0001
	10-20	1.70 ^a	2.23 ^b	2.23 ^b	1.66 ^a	2.13 ^b	2.27 ^b	0.036	<0.0001
<u>Nitrogen</u>									
0		0.214	0.220	0.210				0.0064	0.6176
10	0-5	0.217 ^{ab}	0.227 ^b	0.206 ^a				0.0020	<0.0001
	5-10	0.181 ^a	0.203 ^b	0.176 ^a				0.0020	<0.0001
	10-20	0.172 ^a	0.194 ^b	0.170 ^a				0.0020	<0.0001
20	0-5	0.162 ^a	0.179 ^a	0.204 ^b	0.172 ^a	0.185 ^{ab}	0.174 ^a	0.0029	<0.0001
	5-10	0.203 ^{ab}	0.226 ^b	0.203 ^{ab}	0.197 ^a	0.211 ^{ab}	0.200 ^a	0.0029	<0.0001
	10-20	0.196	0.219	0.208	0.198	0.218	0.207	0.0029	<0.0001
30	0-5	0.204 ^{ab}	0.216 ^b	0.194 ^a	0.211 ^{ab}	0.219 ^b	0.203 ^{ab}	0.0021	<0.0001
	5-10	0.190 ^a	0.218 ^b	0.195 ^a	0.187 ^a	0.216 ^b	0.194 ^a	0.0021	<0.0001
	10-20	0.191 ^a	0.203 ^{ab}	0.196 ^{ab}	0.188 ^a	0.210 ^b	0.196 ^{ab}	0.0021	<0.0001
<u>C:N ratio</u>									
0		8.18 ^a	9.93 ^b	11.84 ^c				0.052	<0.001
10	0-5	8.34 ^a	9.90 ^{ab}	11.75 ^b				0.338	<0.001
	5-10	9.92 ^a	11.31 ^{ab}	13.91 ^b				0.338	<0.001
	10-20	10.52 ^a	11.81 ^b	14.08 ^c				0.338	<0.001
20	0-5	10.34 ^a	11.92 ^{ab}	11.25 ^a	10.40 ^a	11.72 ^{ab}	13.13 ^b	0.233	<0.0001
	5-10	8.48 ^{ab}	9.66 ^{abc}	11.15 ^c	8.43 ^a	10.36 ^{bc}	10.82 ^c	0.233	<0.0001
	10-20	8.71 ^a	10.19 ^b	11.30 ^c	8.58 ^a	10.43 ^{bc}	10.90 ^{bc}	0.233	<0.0001
30	0-5	8.53 ^a	10.43 ^b	10.91 ^b	8.35 ^a	10.12 ^b	11.24 ^b	0.161	<0.0001
	5-10	8.84 ^a	10.06 ^{ab}	10.96 ^{bc}	8.93 ^a	10.43 ^b	11.86 ^c	0.161	<0.0001
	10-20	8.90 ^a	10.04 ^{bc}	11.37 ^{bc}	8.83 ^a	10.11 ^{ab}	11.61 ^c	0.161	<0.0001

^{abc} Means were separated using the Tukey-Kramer adjustment for multiple comparisons. Means without a common superscript, in a row, for the same Trial, differ by p<0.05.

7.3.3 Nitrogen Leaching and Soil Content

Generally, there were no significant differences in soil N content between the treatments on any time of destructive sampling (Table 7.3). The addition of pig manure did not increase the soil N content in the manure-amended treatments ($p>0.05$).

The total amount of N leached from the soil columns over the 30-week experiment is shown in Figure 7.6. Over 90% of the total mass of TN leached from the columns over the entire study duration was in the form of NO_3^- . Immediately after column set-up and pig manure application, the proportion of TN leached as NO_3^- was less than 80%. This may have been due to some organic N being leached when the columns were first set up. There was less TN leached from PM600 and W600 than the Control ($p<0.001$ for both). Following pig manure application, between weeks 10 and 11, there was a significant increase in the total amount of TN leached from the manure-amended columns compared with the other columns ($p<0.0001$ for all three treatments). Of the 144 mg of pig manure TN added, 66-70 mg had leached by week 30, with no significant differences between treatments.

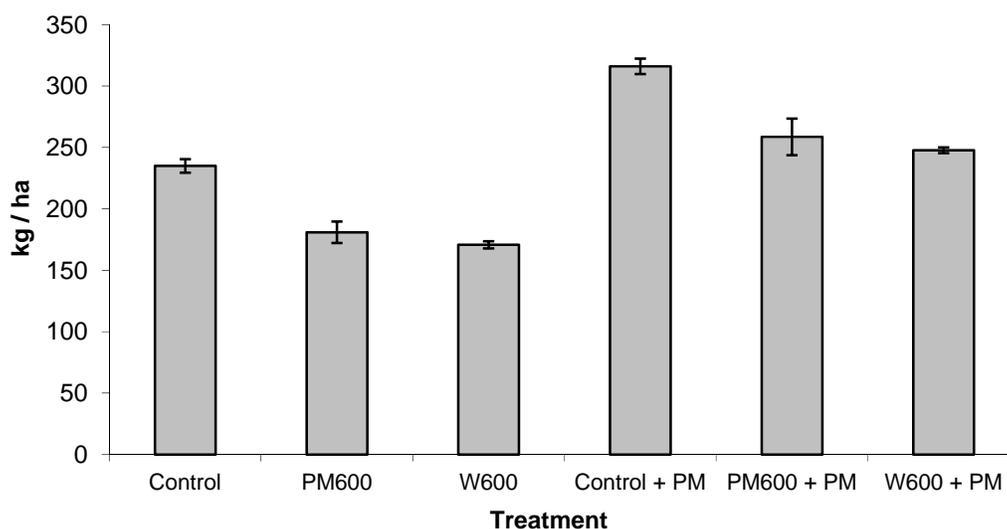


Figure 7.6 Total amount of nitrogen leached over the 30-week leaching experiment. The pig manure amended treatments (+PM) received 49 mL of pig manure between week 10 and 11

The amount of NO_3^- and NO_2^- in the leachate exiting the soil columns each week is shown in Figure 7.7 (a) and (b). Very high concentrations of NO_3^- were leached from all treatments for the first number of weeks, peaking at $>110 \text{ mg L}^{-1}$ for all treatments on week 3. There was a swift decline in the concentration of NO_3^- in the leachate after week 4, and, by week 9, the concentration of NO_3^- in the leachate had decreased to $<35 \text{ mg L}^{-1}$ for all treatments and remained below this value for all the non-manure-amended columns for the duration of the experiment. Drying and re-wetting of soil during the construction of the columns may have caused a burst in microbial activity and a sharp increase in C and N mineralisation (Van Gestel et al., 1991; Bengtsson et al., 2003; Borken and Matzner, 2009). Microorganisms increase concentrations of inner-cellular solutions during drying to counteract the more concentrated soil solution (Stark and Firestone, 1994; Borken and Matzner, 2009). Following rewetting, enhanced mineralisation is caused by organic substrates derived from the microorganisms killed during drying, and from other non-living soil organic matter (Van Gestel et al., 1991). The soil used in this experiment had a low C:N ratio of 8.2. Soil with C:N ratios below 20 can be characterised as having a surplus of available NH_4^+ for nitrification (Bengtsson et al., 2003).

Biochar amendment to the soil reduced the amount of NO_3^- leached from the columns by 24 and 26%, respectively, for PM600 and W600, compared with the Control. The reduction of NO_3^- leached per week from the biochar-amended soils was only significant ($p < 0.05$) in the first 12 weeks of the study. The application of pig manure resulted in a peak in the leaching of NO_3^- (Figure 7.7a), which reached maximum values for all treatments on weeks 17 and 18. For 4 weeks after pig manure application, PM600+PM and W600+PM leached significantly less NO_3^- than the Control+PM. Previous experiments have shown that biochar addition to soil can affect NO_3^- leaching (Busscher et al., 2009; Laird et al., 2010a; Singh et al., 2010).

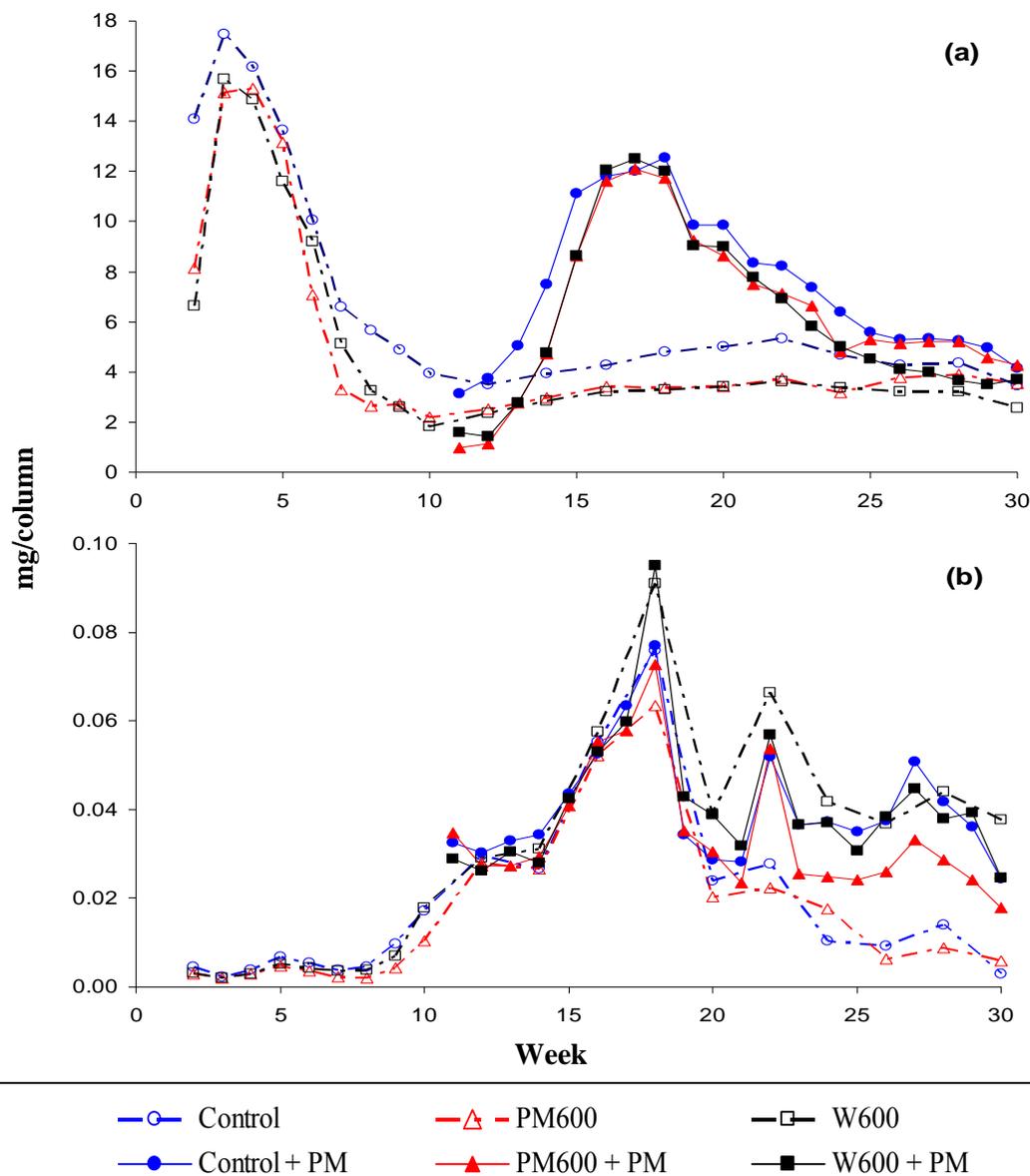


Figure 7.7 Leaching of NO_3^- (a) and NO_2^- (b) from soil amended with biochar and leached weekly with 160 mL distilled water. The treatments which were amended with the pig manure between week 10 and 11 are shown with (+PM)

The reduction in NO_3^- leaching in this study was likely caused by the impact of biochar on the rates of nitrification and denitrification within the soil due to (1) nitrification inhibitors present on unweathered biochar and (2) higher WFPS and organic C contents in the biochar-amended treatments, which created ideal conditions for denitrification.

In an incubation study using freshly made biochar, Clough et al. (2010) measured higher soil NH_4^+ concentrations in biochar-amended soil after the application of urine, compared with soil amended with urine only. This increase was attributed to nitrification inhibitors which slowed the rate of NH_4^+ depletion. Unweathered biochar has been shown to contain microbially toxic compounds (e.g. polyaromatic hydrocarbons), some of which may inhibit the *Nitrosomonas* bacteria responsible for nitrification (Kim et al., 2003; Clough and Condron, 2010). This inhibition of nitrification, due to toxic compounds is likely to be short-term: Clough et al. (2010) found that signs of nitrification inhibition had stopped after 55 days of soil incubation, as weathering of the biochar decreases its ability to inhibit nitrification. Weathering of the biochar and the subsequent increase in nitrification rates may be the reason why there is only a significant difference in NO_3^- leaching between the biochar and Control treatments in the first 12 weeks of testing. For the manure-amended treatments, significant differences in NO_3^- leaching were seen only in the first 4 weeks after manure application (except for W600+PM from week 24 to 29).

In general, the presence of anaerobic conditions and organic C as an electron donor facilitates denitrification (Rivett et al., 2008). The increased WFPS in the biochar-amended columns may have caused the development of anaerobic zones within the soil, reducing nitrification and increasing denitrification. The WFPS measured at the 10-20 cm depth on weeks 20 and 30 was 69-72% for the Control. The WFPS was 78% and 77-79%, respectively, for PM600 and W600. Increasing the WFPS beyond 60% causes anaerobic conditions. This results in reduced aerobic microbial activity and nitrification, and increased denitrification (Linn and Doran, 1983; Brady and Weil, 1996; Porporato et al., 2003). Denitrification, measured by N_2O emissions from soil, has been shown to be sensitive to soil WFPS (Brady and Weil, 1996; Dobbie and Smith, 2001; Bateman and Baggs, 2005; Yanai et al., 2007). In an incubation study, using arable soil fertilised with ammonium nitrate, Dobbie and Smith (2001) found a 30-fold increase in N_2O emissions by increasing the WFPS from 60 to 80%. In the study of Dobbie and Smith (2001), the N_2O emissions were primarily attributed to denitrification and the increase was attributed to the development of anaerobic zones within the soil. In addition to a higher WFPS, the WSOC content of the biochar-amended treatments was higher than that of the Control (Table 7.2), indicating higher

organic C availability for denitrification. Despite this, leaching of TOC was lower in the W600 treatment than the Control, an indication that the organic C may have been used as an electron donor for denitrification. The denitrification pathway for N removal was confirmed by the high (relative to the Control) N₂O emissions from the biochar-amended treatments (Section 8.3.1).

Laird et al. (2010a) also found significantly reduced NO₃⁻ leaching from pig manure-amended soil + biochar treatments than from manure-amended soil-only treatments. They speculated that the biochar adsorbed the NH₄⁺ and soluble organic compounds with the soil, thus inhibiting mineralisation of organic N and/or nitrification of NH₄⁺. However, the reductions in NO₃⁻ leaching were not immediate; only after 23 weeks of biochar weathering was there any reduction in NO₃⁻ leaching (Laird et al., 2010a). The biochar used in this experiment was freshly made and unweathered. The CEC of fresh biochar has been shown to be low (Lehmann, 2007; Busscher et al., 2009; Clough et al., 2010), with only weathered biochar being shown to have a high CEC due to oxidation and adsorption of other OM in the soil over time (Liang et al., 2006). The CEC of the biochar-amended soils in the current study was found to be similar to that of the Control on week 0 (Table 7.2), and therefore, the reduction in NO₃⁻ leaching was unlikely, initially at least, to be caused by NH₄⁺ adsorption. Additionally, there was no difference in NH₄⁺ leaching between treatments. The CEC of the biochar amended treatments may have increased over time. However, biochar oxidation, which results in CEC increases, is temperature dependant (Cheng et al., 2006), and incubation at 10 °C is unlikely to have caused a dramatic increase in biochar CEC. The reduction in NO₃⁻ leaching was also unlikely to be due to the adsorption of the NO₃⁻ anion itself, as the anion exchange capacity of the biochar is very limited and decreases rapidly with oxidation within the soil (Cheng et al., 2008).

The amount of NO₂⁻ leaching was very small when compared with NO₃⁻. The concentration of NO₂⁻ in the leachate was <0.1 mg L⁻¹ from week 2-9. This corresponds with the peak in NO₃⁻ leaching (Figure 7.7a). This low amount of NO₂⁻ leached from all treatment may also be due to the drying and re-wetting effect described earlier. The burst of microbial activity caused by re-wetting may have ensured that almost complete nitrification to NO₃⁻ occurred for the first 9 weeks. The quantity of the NO₂⁻ leached increased significantly from week 9 to week 18 across all

treatments, irrespective of whether soil was amended with biochar or pig manure. This temporary build-up on NO_2^- in the soil may be due to a time lag between NO_3^- reduction and NO_2^- reduction during the denitrification process, due to the preference of denitrifiers to NO_3^- , even when both NO_2^- and NO_3^- are present (Rivett et al., 2008). The addition of manure to the columns resulted in increased NO_2^- leaching in the Control and PM600 columns from week 20 to 30. However, the addition of manure had no effect on NO_2^- leaching from the W600 soil. Nitrite leaching from W600 was higher than from the Control and PM600 columns from week 20 to 30, indicating higher rates of denitrification in the wood biochar-amended soil.

The amount of NH_4^+ leached was very low compared with NO_3^- . This indicates high nitrification across all treatments and good CEC in the soil. Throughout the leaching experiment, the quantity of NH_4^+ leached from each column on most sampling weeks remained between 0.005 and 0.015 mg. There was a small peak (0.017 – 0.024 mg per column) in the NH_4^+ concentration on week 11 in the leachate from the columns which received manure, as some NH_4^+ from the manure passed through the column. There was no significant difference between the amount of NH_4^+ leached from the columns which received manure and those which did not. There was also no difference between amount of NH_4^+ leached from the biochar-amended columns and the Control ($p > 0.05$). This re-iterates the fact the CEC of the soil was not affected by biochar addition.

7.3.4 Phosphorus Leaching and Soil Content

The amount of DRP, DUP and PP leached from the soil columns over the 30-week study period is shown in Figure 7.8. The trend in each treatment is similar with most of the TP leached from the columns being the dissolved fraction; for most of the weeks, the amount of PP leached from the columns was less than 0.004 mg per column. The concentration of P leached from the columns was very low, indicating that the soil was P deficient. The maximum adsorption capacity of the soil was very high at $0.194 \text{ g P kg}^{-1}$, whereas the maximum adsorption capacity of the wood biochar was $0.134 \text{ g P kg}^{-1}$. Therefore, the addition of the wood biochar to the soil was unlikely to impact the P absorbency.

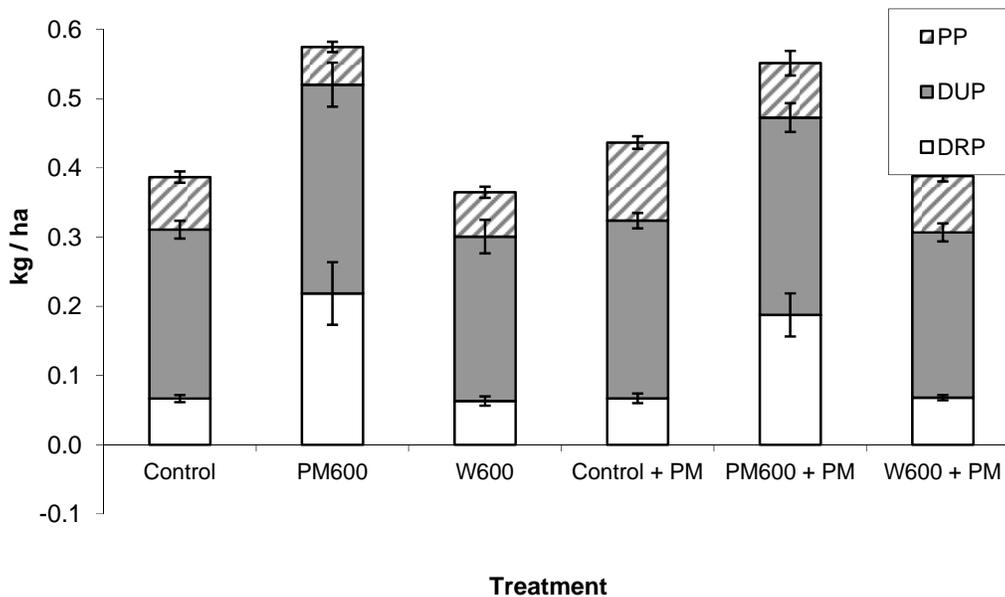


Figure 7.8 Cumulative amounts of dissolved reactive phosphorus (DRP), dissolved unreactive phosphorus (DUP) and particulate phosphorus (PP) leached over the 30-week leaching experiment. The pig manure amended treatments (+PM) received 49 mL of pig manure between week 10 and 11

The pig manure biochar had no capacity to adsorb P (data not shown), and it had a higher WEP than the wood biochar (Table 7.1). Over the 30-week study period, there was significantly more TP ($p < 0.001$) and TDP ($p < 0.0001$) leached from PM600 than the Control or W600. The increase in P leaching from PM600 was primarily due to increased DRP leaching ($p < 0.0001$). This was a result of higher WEP in the PM600 treatments when compared with the Control and W600 treatments on all sampling weeks and depths ($p < 0.001$) (Table 7.4). The PM600 treatments also had significantly higher Morgan's P values when compared with the Control and W600 treatments on all sampling weeks and depths ($p < 0.05$) (Table 7.5). The addition of PM600 caused the soil to change from a P Index 2 soil to a P index 4 soil by week 10. The amount of DRP leached from PM600 was between 0.004 mg and 0.01 mg per column from week 5 to 30. In contrast, the amount of DRP leached from both the Control and W600 peaked at between 0.002 and 0.004 mg per column per week between weeks 4 and 14. From week 14 until the end of the experiment, less than 0.002 mg was leached from the Control and W600 on most sampling weeks.

Table 7.4 Water Extractable Phosphorus (WEP, mg kg⁻¹) contents for each treatment at 3 sampling depths (cm below surface) over 4 sampling events

Week	Depth	Pig manure added week 10						s.e.	p
		Control	PM600	W600	Control	PM600	W600		
0		0.364 ^a	0.524 ^b	0.391 ^a				0.0167	<0.05
10	0-5	0.500 ^a	1.774 ^b	0.533 ^a				0.1861	<0.01
10	5-10	0.506 ^a	1.532 ^b	0.515 ^a				0.1861	<0.01
10	10-20	0.576 ^a	1.131 ^b	0.525 ^a				0.1861	<0.01
20	0-5	0.403 ^a	1.670 ^b	0.284 ^a	0.965 ^{ab}	2.923 ^c	0.682 ^a	0.1371	<0.0001
20	5-10	0.398 ^a	1.682 ^b	0.263 ^a	0.387 ^a	1.974 ^b	0.425 ^a	0.1371	<0.0001
20	10-20	0.413 ^a	1.861 ^b	0.312 ^a	0.440 ^a	1.942 ^b	0.249 ^a	0.1371	<0.0001
30	0-5	0.518 ^a	1.106 ^b	0.482 ^a	0.969 ^b	1.921 ^c	0.881 ^{ab}	0.4708	<0.0001
30	5-10	0.473 ^a	1.213 ^b	0.479 ^a	0.525 ^a	1.333 ^b	0.402 ^a	0.4708	<0.0001
30	10-20	0.520 ^a	1.276 ^b	0.509 ^a	0.458 ^a	1.299 ^b	0.475 ^a	0.4708	<0.0001

^{abc} Means were separated using the Tukey-Kramer adjustment for multiple comparisons. Means without a common superscript, in a row, for the same Trial, differ by $p < 0.05$.

There was a no significant difference between the total quantities of TP leached from W600 compared with the Control ($p=0.84$ for the non-amended columns and $p=0.15$ for the pig manure-amended columns). There was also no difference between the soil WEP (Table 7.4) or Morgan's P (Table 7.5) for the Control and W600 treatments. Laird et al. (2010a) found a large reduction in TDP in the leachate from hardwood biochar-amended columns after pig manure addition, compared with control columns after manure addition. They attributed this effect to adsorption of ortho-phosphate and organic P compound by the biochar. Laird et al. (2010b) found increased available P in the soil from the biochar-amended treatments. However, in the current study, the adsorption capacity of the soil was shown to be higher than that of the wood biochar. Therefore, no increase in P adsorption was expected. There was very little leaching of the P from the pig manure addition after week 10. Approximately 30 mg of P was added with the pig manure and the vast majority of this P remained in the soil; there was no increase in DRP and DUP leaching when manure was added to the treatments ($p > 0.05$). However, there was a 49% increase in PP leached from the Control+PM treatments ($p < 0.01$), compared with the Control. The addition of manure did increase WEP values for PM600+PM on week 20, and Control+PM and PM600+PM on week

30, compared with the treatments which did not receive manure (Table 7.4). The only effect pig manure addition had on Morgan's P was on PM600+PM on week 30 (Table 7.5). However, the addition of pig manure did result in the soil in the 0-5 cm top section of the Control+PM and W600+PM to being classed as P Index 3, compared with P Index 2 in the Control and W600 treatments.

Table 7.5 Morgan's Phosphorus (mg L^{-1}) contents for each treatment at 3 sampling depths (cm below surface) over 4 sampling events

Week	Depth	Pig manure added week 10							
		Control	PM600	W600	Control	PM600	W600	s.e.	p
0		4.84 ^a	7.53 ^b	5.04 ^a				0.143	<0.01
10	0-5	5.66 ^a	10.14 ^b	5.06 ^a				0.183	<0.0001
	5-10	5.68 ^a	10.72 ^b	5.28 ^a				0.183	<0.0001
	10-20	5.73 ^a	11.03 ^b	5.44 ^a				0.183	<0.0001
20	0-5	3.88 ^a	29.18 ^b	4.54 ^a	9.03 ^a	36.20 ^b	8.89 ^a	1.445	<0.0001
	5-10	4.28 ^a	32.20 ^b	5.19 ^a	4.36 ^a	35.00 ^b	5.65 ^a	1.445	<0.0001
	10-20	4.67 ^a	32.50 ^b	5.37 ^a	4.24 ^a	36.73 ^b	4.80 ^a	1.445	<0.0001
30	0-5	5.05 ^a	11.63 ^b	5.47 ^a	7.06 ^a	16.05 ^c	8.61 ^{ab}	0.040	<0.0001
	5-10	5.52 ^a	12.07 ^b	6.08 ^a	5.33 ^a	12.98 ^b	5.89 ^a	0.040	<0.0001
	10-20	5.73 ^a	12.65 ^b	6.38 ^a	5.40 ^a	13.33 ^b	6.16 ^a	0.040	<0.0001

^{abc} Means were separated using the Tukey-Kramer adjustment for multiple comparisons. Means without a common superscript, in a row, for the same Trial, differ by $p < 0.05$.

7.4 Summary

The influence of the addition both pig manure biochar and wood biochar on the soil properties and the nutrient leaching from an Acid Brown Earth were significant. The addition of biochar to the soil increased the WFPS compared with unamended soil. Biochar addition also resulted in higher OM and C contents in these soils. Amendment with pig manure biochar increased Morgan's P and WEP contents in the soil due to higher concentration of easily extractable P in the manure-derived biochar. This also increased P leaching from the columns, compared with the unamended soil and the soil amended with wood biochar.

The addition of both types of biochar reduced NO_3^- leaching from the columns. In the first number of study weeks, this was most likely caused by microbially toxic compounds found on unweathered biochar which inhibit nitrification. However, this inhibition of nitrification is short-term and decreases with weathering of the biochar. The continued reduction in NO_3^- was attributed to the development of anaerobic zones within the biochar-amended columns, brought around by increased WFPS. The increase in denitrification also resulted in reduced organic C leaching from the wood biochar-amended columns as the organic C was used in the denitrification process. Leaching of organic and inorganic C increased with the addition of pig manure biochar due to the higher concentrations of water soluble C in the pig manure biochar.

By altering the N and C cycling processes within the soil, it is likely that biochar addition also changed the gaseous emissions from the soil. Quantifying these emissions is important to better understand the changes in soil processes. The emission of greenhouse gases following pig manure addition to the soil is investigated in the next chapter.

8 IMPACT OF BIOCHAR ADDITION TO SOIL ON GREENHOUSE GAS EMISSIONS FOLLOWING PIG MANURE APPLICATION

Overview

In this chapter, a soil column study investigating the effect of the addition of two types of biochar (derived from pig manure and wood) to soil on greenhouse gas emissions is described. This study follows on from Chapter 7, which investigated the effect of biochar application to soil on nutrient leaching and soil properties over a 30-week duration. Gaseous emissions from these columns were collected and analysed for 28 days following pig manure application. The aim of this study was to quantify the effect of the addition of biochar to an Irish tillage soil on emissions of carbon dioxide, nitrous oxide and methane, with and without applied pig manure.

8.1 Introduction

In 2010, 30.5% of Ireland's GHG emissions were due to agriculture (EPA, 2012). This represents the highest national proportion of GHG emissions within the EU. Ireland has committed to an overall reduction in GHG emissions of 20% by 2020, relative to 1990 levels (EPA, 2012). To achieve this target, GHG emissions from agriculture must be reduced. Using the biochar produced through pyrolysis as a soil amendment can reduce agricultural GHG emissions. Gaunt and Lehmann (2008) found that avoided GHG emissions are 2 to 5 times greater when biochar is applied to land than when it is burned. These reductions are due to the retention of C in biochar, savings in fertiliser requirement, reductions in fossil fuel usage and reductions in soil emissions (Gaunt and Lehmann, 2008).

Biochar addition to soil has been reported to influence GHG emissions (Spokas and Reicosky, 2009; Clough et al., 2010; Singh et al., 2010; Zhang et al., 2010; Rogovska et al., 2011). Emissions of N₂O have been reported to increase (Clough et al., 2010) and decrease (Singh et al., 2010), with biochar application to soil. Singh et al. (2010)

attributed the increased sorption capacity of a soil amended with wood biochar on the significantly reduced N₂O emissions. Clough et al. (2010) attributed higher N₂O emissions from biochar amended soil to greater NO₂⁻ concentrations brought about by nitrification inhibitors on biochar which slowed NO₃⁻ formation.

Many studies have found an increase in CO₂ emissions with biochar addition to soil (Major et al., 2010a; Smith et al., 2010; Rogovska et al., 2011). This has been attributed to increased mineralisation rates in the biochar-amended soil due to mineralisation of applied biochar C and enhanced soil organic C mineralisation. Rogovska et al. (2011) found accelerated soil organic C mineralisation with biochar addition to soil and hypothesised that the increases may be due to (1) increased aerobic microbial activity as a result of higher soil aeration due to the lower bulk density of the biochar-amended soil and (2) enhanced microbial colonisation causing accelerated decomposition of organic compounds. However, this stimulatory effect on mineralisation rates may be short-term. In a two-year experiment, Major et al. (2010a) reported increased CO₂ emissions in biochar-amended soil compared with unamended soil. However, the increase in CO₂ emissions was considerably lower in the second year of the study, suggesting that the stimulatory effects were short-term.

Soil CH₄ emissions have been reported to both increase (Zhang et al., 2010) and decrease (Rondon et al., 2005) with biochar addition. Rondon et al. (2005) credited a near complete suppression of CH₄ upon biochar addition to soil to a reduction in anaerobic conditions and increased aeration. However, in a field experiment in a rice paddy, Zhang et al (2010) found biochar addition to soil biochar increased CH₄ emissions by 34% with N fertilization and by 41% without N fertilization.

8.2 Materials and Methods

8.2.1 Soil Columns for Gas Analysis

Soil columns, described in Chapter 7, were used in this study. Large rubber stoppers, placed on top of each column, sealed the headspace (0.08 m) and allowed gas samples to be collected via rubber septum stoppers located at the side of each column (Figure

8.1). The columns were stored at a constant temperature (10 °C) and relative humidity (75%) for the duration of the study. The characteristics of the biochars used in the experiment are given in Table 7.1 and the characteristics of the soil and soil/biochar mixtures, measured after week 10, are given in Table 8.1.



Figure 8.1 The rubber stopper used to seal the column headspace and the septum through which a gas sample was taken.

Gas analysis began following pig manure application and continued for 4 weeks. One hour before gas analysis began on the first sampling day (10 weeks after the start of the column experiment; hereafter referred to as Day 1 in the context of the GHG study); 49 mL of pig manure (equivalent to an application rate of 170 kg N ha⁻¹ and 36 kg P ha⁻¹) was added to half of the columns in each treatment. The characteristics of the pig manure are given in Table 8.2. Gaseous emissions from columns which did not receive pig manure were also analysed. Each column was leached with 80 mL of distilled water on Days 4, 8, 11, 15, 18, 22 and 25 of the gas analysis. The columns which did not receive pig manure on Day 1, received 49 mL of water. On days when the columns received water, gas samples were taken 1 hour after water application.

Table 8.1 Characteristics of the soil (Control), and the soil and biochar mixes (PM600 and W600) for 3 sampling depths (cm below surface) after 10 weeks of soil incubation and leaching, before pig manure was applied

	Depth	Control	PM600	W600	s.e.	p
WFPS (%)	0-5	61.6 ^a	63.7 ^{ab}	65.6 ^b	0.45	<0.001
	5-10	63.6 ^a	67.5 ^b	67.8 ^b	0.45	<0.001
	10-20	69.9 ^a	73.5 ^a	73.1 ^a	0.45	<0.001
Organic Matter (g kg ⁻¹)	0-5	48.9 ^a	51.4 ^{ab}	52.8 ^b	0.21	<0.001
	5-10	48.8 ^a	51.8 ^b	52.0 ^b	0.21	<0.001
	10-2	48.5 ^a	52.6 ^b	51.8 ^b	0.21	<0.001
Carbon (%)	0-5	1.81 ^a	2.25 ^b	2.42 ^b	0.035	<0.001
	5-10	1.80 ^a	2.30 ^b	2.45 ^b	0.035	<0.001
	10-20	1.81 ^a	2.29 ^b	2.39 ^b	0.035	<0.001
Nitrogen (%)	0-5	0.217 ^{ab}	0.227 ^b	0.206 ^a	0.0020	<0.001
	5-10	0.181 ^a	0.203 ^b	0.176 ^a	0.0020	<0.001
	10-2	0.172 ^a	0.194 ^b	0.170 ^a	0.0020	<0.001
C:N	0-5	8.34 ^a	9.90 ^{ab}	11.75 ^a	0.338	<0.001
	5-10	9.92 ^a	11.31 ^{ab}	13.91 ^a	0.338	<0.001
	10-20	10.52 ^a	11.81 ^b	14.08 ^a	0.338	<0.001
pH	0-5	7.23	7.24	7.11	0.127	0.245
	5-10	7.34	7.33	7.20	0.127	0.245
	10-20	7.42	7.39	7.23	0.127	0.245

C:N, carbon to nitrogen ratio; WFPS, water filled pore space.

Table 8.2 Characteristics of the pig manure added to the soil

	Total applied		
	kg m ⁻³	kg ha ⁻¹	mg column ⁻¹
Dry Matter	21.0 ± 0.98	1214	1030
Total N	2.94 ± 0.156	170	144
NH ₄ ⁺ -N	1.74 ± 0.08	78.2	66.4
Total C	5.86 ± 0.08	340	289

8.2.2 Gas Sampling and Analysis

Gas was sampled after Singh et al. (2010). Ten minutes before sampling, the headspace in the column above the soil was fanned to remove accumulated gases. Then, just before sealing the top of the column with the rubber stopper, the headspace was again fanned gently for 15 seconds and a gas sample (20 ml) was withdrawn from the headspace. This sample represented the zero minute sampling time. Subsequent to sealing the headspace, gas samples were extracted from the enclosed headspace 5, 10 and 20 minutes after the headspace was sealed. These gas samples were immediately injected into pre-evacuated 6 mL Exetainer vials (Labco, Buckinghamshire, UK). This allowed the vials to be over pressurised, removing the possibility of contamination of the samples with external air.

Nitrous oxide and CH₄ were measured in the samples taken at sampling times 0, 10 and 20 minutes using a Shimadzu Gas Chromatograph (GC-2014) (Shimadzu Scientific Instruments, Maryland, USA). Carbon dioxide was measured in the samples taken at sampling times 0, 5 and 10 minutes using a Agilent Gas Chromatograph System (7890A) (Agilent Technologies, California, USA). All GHGs were measured using linear regression. The changes in volumetric concentration were converted to a mass flux using the ideal gas law (Eqn. 8.1):

$$n = PV / RT \quad [8.1]$$

where n = moles of gas; P = standard atmospheric pressure (1014.4 hPa); V = volume of gas; R = Ideal Gas Constant (8.314 J/mol K); T = air temperature (283.15 K)

Each gas was extrapolated over a hectare and is expressed as the following: kg CO₂-C ha⁻¹ h⁻¹, g CH₄-C ha⁻¹ h⁻¹, g N₂O-N ha⁻¹ h⁻¹, similar to Collins et al., 2011 and Zhang et al., 2010. Negative fluxes of gases indicated uptake of gas by soil and positive fluxes indicated net emissions from the soil. Cumulative fluxes were determined by multiplying each gas flux by the interval between sampling days. These cumulative

fluxes were then summed to find the cumulative emissions of each gas over the 28-day sampling period.

8.2.3 Statistical Analysis

Emissions data were analyzed using the Statistical Analyses System (SAS Institute, 2004) with each column as the experimental unit. For all analyses, significance was given as $p < 0.05$. The hourly flux of $\text{N}_2\text{O-N}$, $\text{CO}_2\text{-C}$, and $\text{CH}_4\text{-C}$ were analysed as repeated measures using a repeated measured ANOVA using the MIXED procedure of SAS with Tukey-Kramer adjustment for multiple comparisons. The dependent variables were: $\text{N}_2\text{O-N}$, $\text{CO}_2\text{-C}$, and $\text{CH}_4\text{-C}$. For all the above analyses, the fixed effects were: treatment, sampling day and column. Sampling day was the repeated measure. Comparison of cumulative emissions of $\text{N}_2\text{O-N}$, $\text{CO}_2\text{-C}$, and $\text{CH}_4\text{-C}$ over the 28-day sampling period was performed using the MIXED procedure in SAS. $\text{N}_2\text{O-N}$, $\text{CO}_2\text{-C}$, and $\text{CH}_4\text{-C}$ were the dependent variables. Treatment was included as a fixed effect.

8.3 Results and Discussions

8.3.1 Nitrous Oxide Emissions

The 28-day $\text{N}_2\text{O-N}$ flux, illustrated in Figure 8.2a, remained low from the non-manure-amended treatments through the study (-0.12 to 0.13 g $\text{N}_2\text{O-N}$ ha⁻¹ hour⁻¹). The addition of biochar to these treatments had no effect on $\text{N}_2\text{O-N}$ emissions on any particular sampling day ($p > 0.05$). Similarly, there was no difference between non-manure-amended treatments in their cumulative emissions over 28 days ($p > 0.05$) (Figure 8.3a). The addition of pig manure to the soil influenced $\text{N}_2\text{O-N}$ emissions: one week following pig manure application there was a significant increase in $\text{N}_2\text{O-N}$ emissions from all the manure-amended treatments. The greatest emissions occurred 11 days after manure application (0.89 , 1.02 and 0.99 g $\text{N}_2\text{O-N}$ ha⁻¹ hour⁻¹ for Control+PM, PM600+PM and W600+PM, respectively). The $\text{N}_2\text{O-N}$ emissions from the manure-amended treatments decreased rapidly from their peak on Day 11 and returned to the level of the treatments which did not receive manure by Day 19. From

Day 19 until the study ended, the N₂O-N emissions were similar for all treatments. The patterns of N₂O-N emissions were similar for the three manure-amended treatments. There was no difference between N₂O-N emissions from PM600+PM and W600+PM compared with Control+PM on any sampling day ($p>0.05$). This is due to a high variability between columns in the same treatment. However, over the 28-day sampling period, the cumulative emissions from PM600+PM were significantly higher compared with Control+PM ($p<0.05$), while W600+PM also tended to have higher N₂O-N emissions than Control+PM ($p<0.1$). Cumulative emissions from W600+PM and PM600+PM were similar ($p=1.0$) (Figure 8.3a).

High soil inorganic-N concentrations (especially NO₃⁻), high soil WC, an elevated C:N ratio, and the presence of dissolved organic C in the soil, result in denitrification and N₂O emissions (Rivett et al., 2008). Mineralisation and nitrification of the organic-N in the pig manure resulted in an increase in NO₃⁻ concentrations in the soil after pig manure application. This increase in NO₃⁻ concentrations and the increase in organic C concentration from the manure resulted in the peak in N₂O emissions seen in the manure-amended treatments (Figure 8.2a). Figure 8.4 shows the amount of NO₃⁻ leached from each treatment during the 28 day gas sampling period. The amount of N lost through N₂O-N emissions is low (<10% for the manure-amended treatments, <1% for the non-manure-amended treatments) compared with N lost through NO₃⁻-N leaching. As described in the previous chapter, the quantity of NO₃⁻ leached from the soils amended with biochar was lower than the Control soil. This result, coupled with the higher N₂O emissions, indicated the occurrence of higher denitrification rates in the biochar-amended treatments. The increase in denitrification can be attributed to (1) higher WFPS and (2) greater organic C availability in the biochar-amended soils. Organic C may be used as an electron donor during denitrification, with the oxygen lost during the denitrification process being used to form CO₂ (Rivett et al., 2008). Denitrifying bacteria also obtain their energy from the oxidation of organic C (Rivett et al., 2008). The greater WFPS in the biochar-amended columns may have caused the development of anaerobic zones within the soil, increasing denitrification. Denitrification can occur once the soil WFPS increases beyond 60%, with further increases in WFPS causing higher rates of denitrification (Brady and Weil, 1996; Dobbie and Smith, 2001; Porporato et al., 2003).

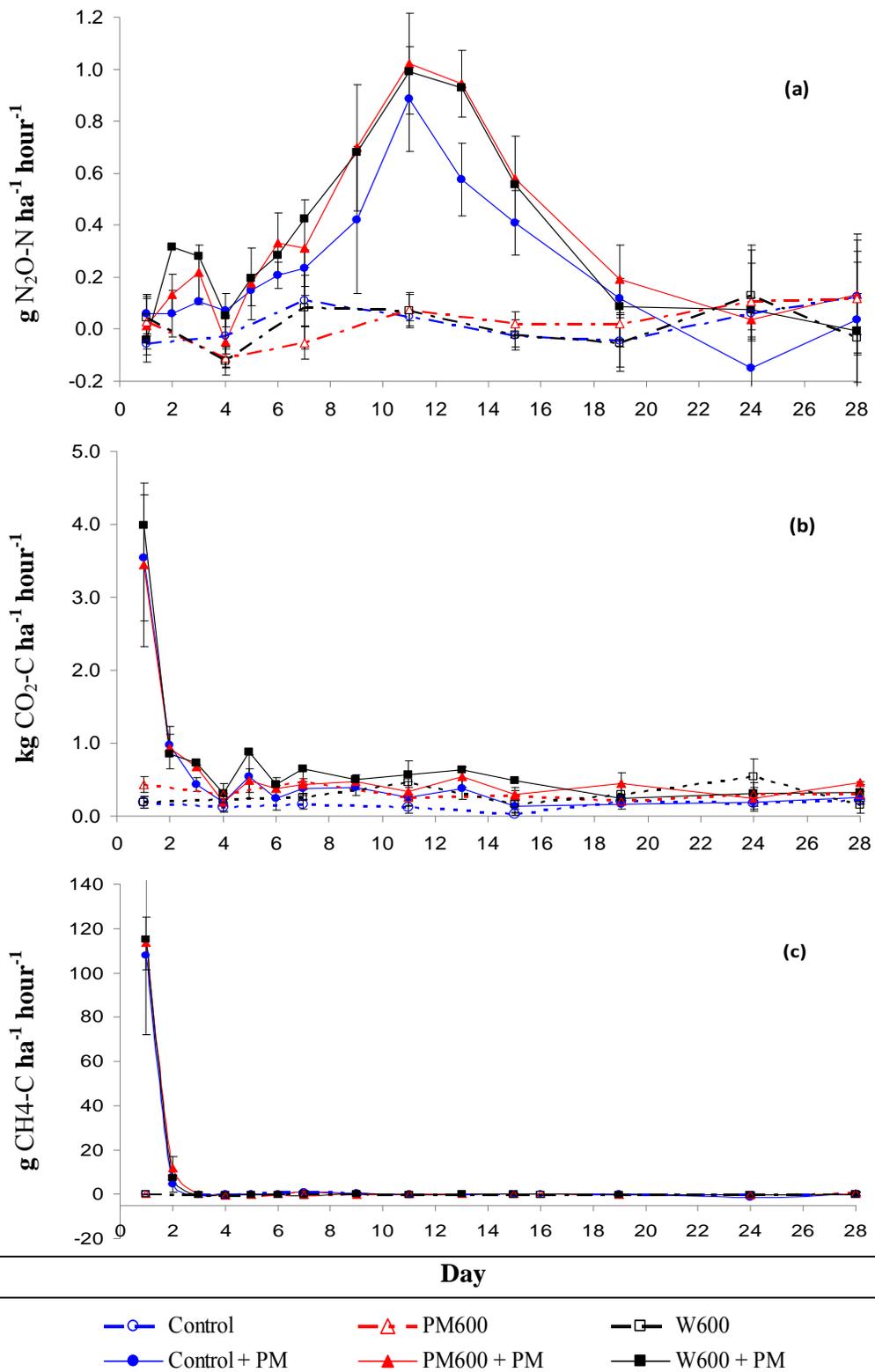


Figure 8.2 Emissions of $\text{N}_2\text{O-N}$ (a) $\text{CO}_2\text{-C}$ (b) and $\text{CH}_4\text{-C}$ (c) from soil amended with biochar. The treatments which were amended with the pig manure on Day 1 are shown with (+PM)

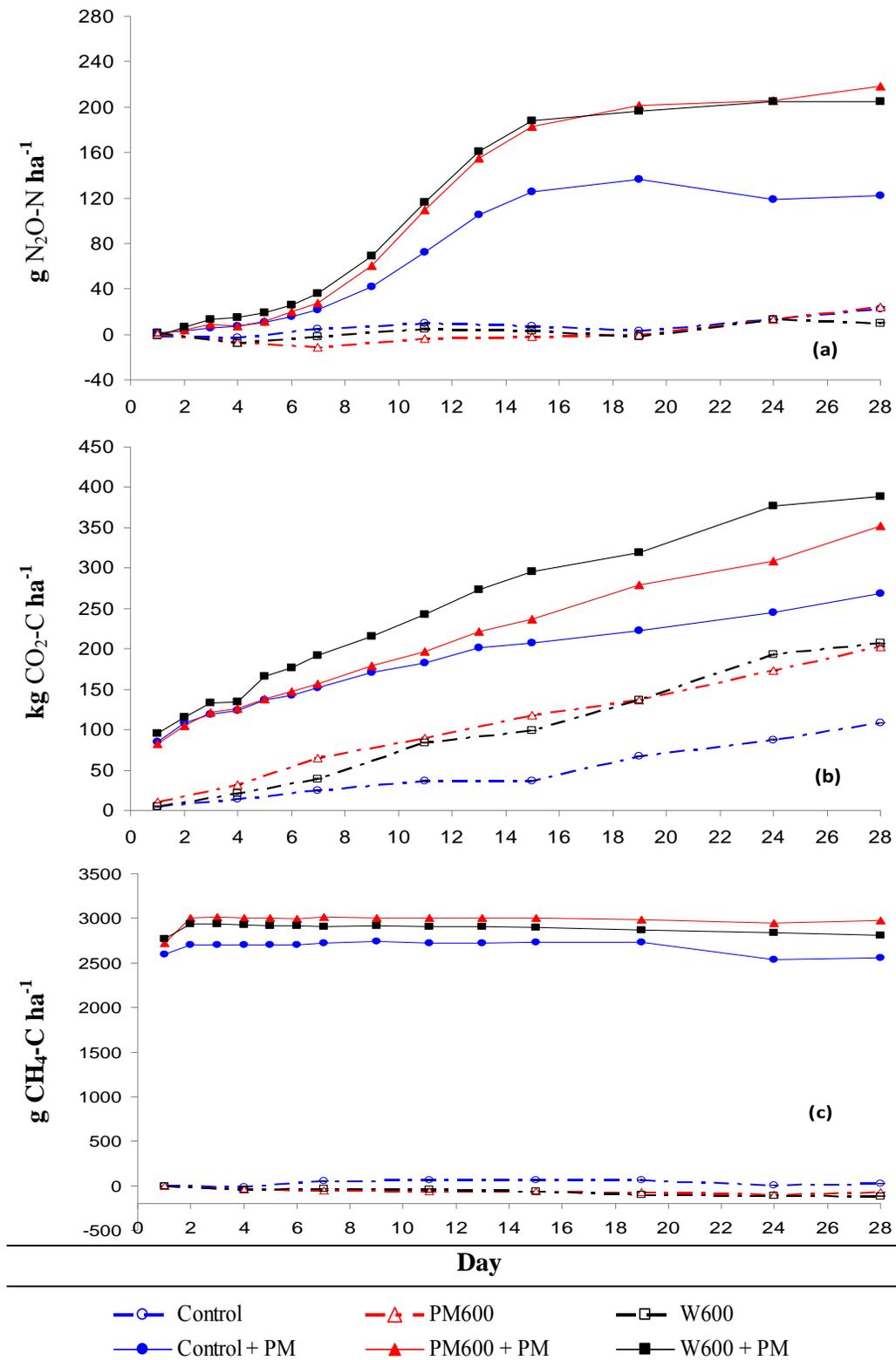


Figure 8.3 Cumulative emissions of $\text{N}_2\text{O-N}$ (a) $\text{CO}_2\text{-C}$ (b) and $\text{CH}_4\text{-C}$ (c) from soil amended with biochar. The treatments which were amended with the pig manure on Day 1 are shown with (+PM)

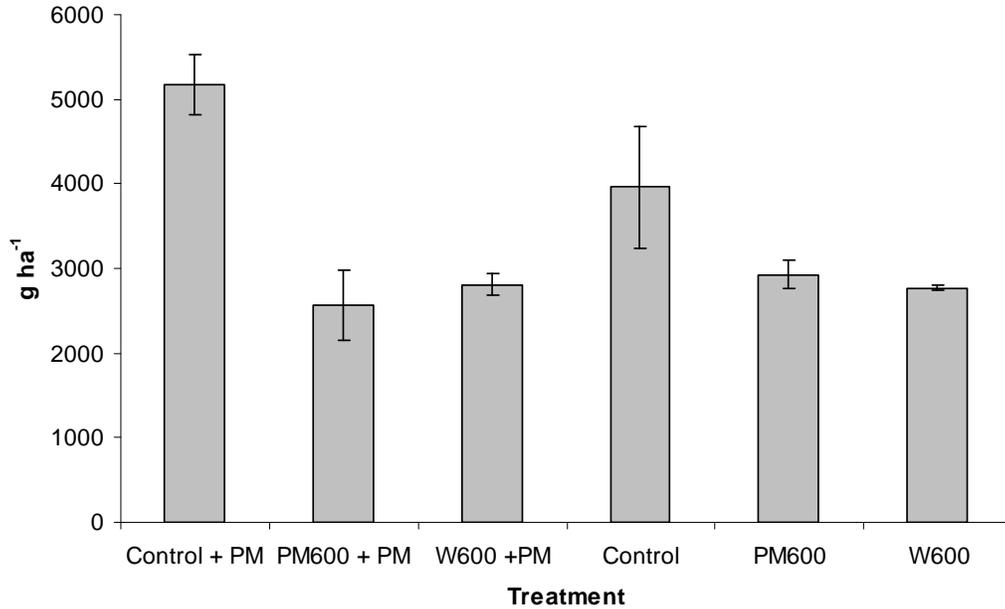


Figure 8.4 Cumulative leaching of NO₃⁻-N during the 4 weeks of gas sampling. Treatments amended with the pig manure are shown with (+PM)

8.3.2 Carbon Dioxide Emissions

The CO₂-C emissions, shown in Figure 8.2b, remained low from the non-manure-amended treatments throughout the study duration (0.03 to 0.54 kg CO₂-C ha⁻¹ hour⁻¹). Soil CO₂-C fluxes from the manure-amended treatments were significantly higher than the non-manure-amended treatments on the day of manure application ($p < 0.001$), and on Day 1 were 3.5, 3.5 and 4.0 kg CO₂-C ha⁻¹ hour⁻¹ for Control+PM, PM600+PM and W600+PM, respectively. However, from Day 4 until the end of the study, there was no significant difference between any treatment ($p < 0.05$). The manure-amended treatments had higher cumulative emissions than the treatments which did not receive manure, largely due to the high CO₂-C emissions on the day of manure application (Figure 8.3b). The addition of manure slurries to soil has been shown to cause a short-lived spike in microbial activity and CO₂-C emissions (Dumale et al., 2009; Collins et al, 2011). The amount of pig manure C mineralised during the sampling period was estimated as the difference between the cumulative CO₂-C emissions from the manure-amended and non-manure-amended treatments (Rogovska et al., 2011). Between 150 and 180 kg ha⁻¹ of the total CO₂-C emissions

were caused by the mineralisation of C in the manure, with no significant difference between treatments. This corresponds to 44 - 54% of the total applied manure C being mineralised in the 28 days after application. In a column study investigating GHG emissions from pig manure, Dendooven et al. (1998) reported that 62% of the C applied in the pig slurry mineralized within 28 days.

The soil CO₂-C emissions from the non-manure-amended treatments show the decomposition of the soil (and biochar) OM and microbial respiration (Collins et al., 2011). The addition of biochar to these non-manure-amended treatments had no effect on CO₂-C emissions on any particular sampling day ($p>0.05$). However, the biochar-amended treatments had higher cumulative emissions over the 28-day sampling period ($p<0.1$) (Figure 8.3b), with 94 and 99 kg ha⁻¹ more CO₂-C emitted from PM600 and W600, respectively, compared with the Control. The addition of biochar to the manure-amended treatments also had no effect on CO₂-C emissions on any particular sampling day ($p>0.05$). However, W600+PM had higher cumulative emissions than Control+PM over the 28-day study period ($p<0.1$). PM600+PM also had numerically higher cumulative emissions than Control+PM. However, but the difference was not significant ($p=0.39$). Cumulative emissions from W600+PM and PM600+PM were similar ($p=0.92$) (Figure 8.3b).

The increase in CO₂-C emissions due to the addition of biochar may be due to mineralisation of available C added with the biochar (Cross and Sohi, 2011) or enhanced mineralisation of the soil organic C (Major et al., 2010a). However, it is not clear how much CO₂-C emissions came from the biochar C mineralisation and how much came from enhanced mineralisation of soil OM. In a field experiment using biochar applied at 23.2 tonne ha⁻¹, Major et al. (2010a) found that increased CO₂ emissions recorded from the biochar-amended soil was mostly caused by increased non-biochar-C respiration. However, Cross and Sohi (2011) found that higher CO₂ mineralisation in biochar amended soils was from the utilisation of the small labile component of the biochar, and not from the loss of the native soil OM. In the current study any increase in CO₂-C emissions corresponding to the increased denitrification rates in the biochar-amended treatments between Days 7 and 19 is small compared with the CO₂-C emitted from mineralisation. The increased CO₂-C emissions from PM600 and W600 compared with the Control represent 0.83 and 0.67%, respectively,

of the total applied biochar C. This compares to 44 - 54% mineralisation of the applied manure C. This shows that the application of biochar C to soil leads to a much higher percentage of sequestered C compared with other forms of OM, such as manure, which are quickly mineralised and released as CO₂. In a study using soil amended with both wheat straw and biochar from the slow pyrolysis of wheat straw, Bruun et al. (2012) found that 2.9% of the biochar C was lost as CO₂ in the 65 days of soil incubation, while 53% of wheat straw C was lost. Major et al. (2010a) found that 2.2% of biochar C was lost by respiration in the first 2 years after soil application. However, the stimulatory effect on CO₂-C emissions, provided by biochar addition, reduced considerably in the second year of the study, suggesting that losses by mineralisation would decrease further with time (Major et al., 2010a). Figure 8.4 shows the amount of TOC leached from each treatment during the 28 day gas sampling period. Leaching of TOC from W600 with and without manure addition was significantly lower than the Control, despite the fact that the WSOC of the W600 soil was higher than that of the Control at the beginning of the leaching experiment (Table 7.2). The reduction in TOC leaching and the increase CO₂-C emissions is attributed to enhanced mineralisation of the organic C in the biochar-amended treatments. It was noted previously that some of the reduction in organic C may also have been caused by the increased denitrification rates in biochar-amended treatments. The reduction in TOC leaching was not observed in the PM600 treatment compared with the Control due to the very high WSOC of this treatment (Table 7.2).

The trend for higher CO₂-C emissions from biochar-amended soils than from non-biochar-amended soils is similar to the results of other studies (Major et al., 2010a; Smith et al., 2010; Rogovska et al., 2011). In a 500-day column incubation study, Rogovska et al. (2011) found that biochar application significantly increased CO₂ emissions on all sampling days compared with the soil which did not receive biochar. The authors attributed the increase in CO₂ emissions to an accelerated rate of soil OM mineralisation caused by (1) increased soil aeration due to the lower bulk density of the biochar-amended soil resulting in higher aerobic microbial activity, and (2) enhanced microbial colonisation causing accelerated decomposition of organic compounds. However, in the current study, the WFPS was higher in the biochar-amended treatments (Table 8.1), suggesting reduced aeration. Therefore, the

acceleration in mineralisation rates in the current study is more likely to have been caused by mineralisation of the biochar C.

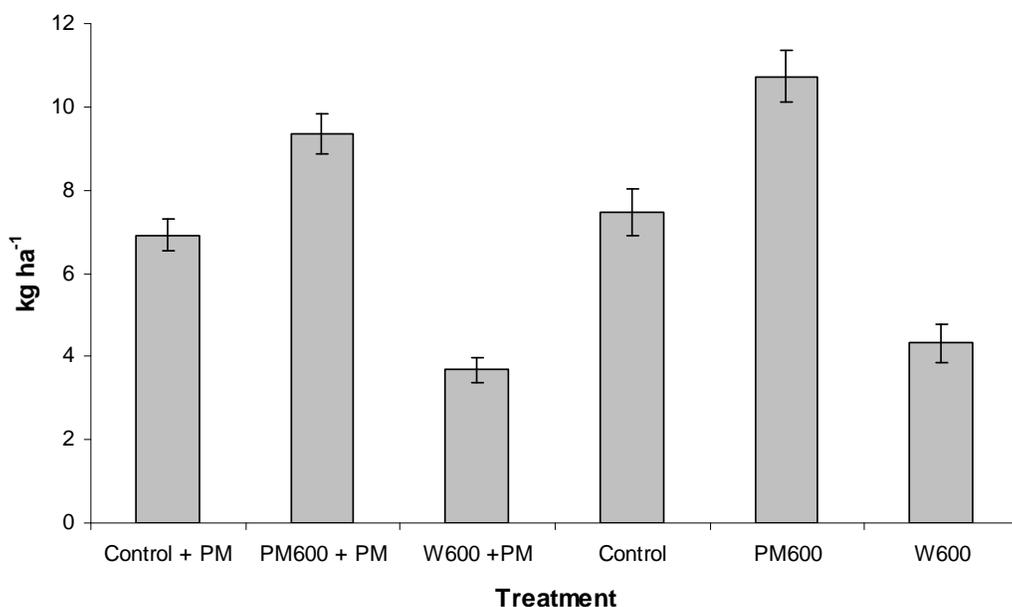


Figure 8.5 Cumulative leaching of TOC during the 4 weeks of gas sampling. Treatments amended with the pig manure are shown with (+PM)

8.3.3 Methane Emissions

Similar to the CO₂-C fluxes, the CH₄-C emissions from the pig manure-amended treatments were high on the day of manure application (108 – 115 g CH₄-C ha⁻¹ hour⁻¹), but quickly reduced to the levels of the non-pig manure-amended treatments (Figure 8.2c). From Day 4 until the end of the study, there was no significant difference between the treatments which received manure and those which did not. Emissions of CH₄-C were low throughout the study, apart from Days 1 and 2 for the manure-amended treatments. Excluding these, the flux of CH₄-C was negligible for every treatment on every sampling day. The pig manure-amended treatments had significantly greater cumulative emissions than the non-pig manure-amended treatments, due to the high CH₄-C emissions on the day of manure application (p<0.0001) (Figure 8.3c). Adding biochar to the soil did not significantly affect daily or cumulative CH₄-C emissions irrespective of whether pig manure was added or not

($p > 0.05$). Elevated CH_4 emissions in the days following the application of slurry to soil has been shown in previous studies (Chadwick et al., 2000; Sistani et al., 2010; Collins et al., 2011). These elevated CH_4 emissions are attributed to the release of dissolved $\text{CH}_4\text{-C}$ produced during storage of the manure prior to application (Collins et al., 2011).

8.4 Summary

The application of pig manure to soil increased GHG emissions. Although the peak effluxes occurred at various times after application (one the day after application for CO_2 and CH_4 emissions, and at 11 days for N_2O emissions), they had reduced to the efflux of the control columns by the end of the study.

The addition of biochar to the soil increased N_2O emissions (only when pig manure was also added) and CO_2 emissions (with and without pig manure addition). Increased N_2O emissions resulted from increased denitrification in the biochar-amended columns, caused by higher WFPS and organic C contents. The increase in CO_2 emissions with biochar addition was attributed to increased rates of C mineralisation in these columns. The increased mineralisation may have been due to mineralisation of the labile C added with the biochar, or through increased mineralisation of the soil organic matter. Amendment of the soil with biochar had no effect of CH_4 emissions.

The greenhouse gas emissions in this study were examined over a short time period of one month following manure application. Longer-term studies would be necessary to give a true picture of the overall effect of biochar addition on soil greenhouse gas emissions.

9 CONCLUSIONS AND RECOMMENDATIONS

Overview

The objective of this study was to identify possible treatment options for the solid fraction of separated pig manure. Experiments were designed and conducted to evaluate the effectiveness and feasibility of composting and pyrolysis as alternatives to landspreading. A further experiment, which examined the effect of biochar application to Irish soil, was also conducted.

The main conclusions and recommendations are now presented.

9.1 Conclusions

1. Composting experiments showed that stable and mature compost could be produced from the separated solids of both raw and anaerobically digested pig manure. However, the addition of a low-moisture, carbon-rich bulking agent is required. Sawdust was the best available bulking agent for pig manure composting, and the addition of the sawdust at a rate of 1 part sawdust to every 4 parts pig manure solids (by weight) was sufficient to produce stable compost.
2. An economic analysis showed that separation and composting of pig manure is not currently a feasible alternative to landspreading, due to the high cost of manure separation when a decanter centrifuge is employed (Table 9.1). However, in the future, the use of a cheaper method of separation, coupled with potentially higher landspreading costs, may make separation and composting economically feasible for farmers in pig-dense areas where there is a scarcity of tillage land. Landspreading will continue to be the most feasible option for pig farmers based in concentrated tillage areas even after landspreading restrictions are fully implemented in 2017.

Table 9.1 Costs associated with solid-liquid separation and composting (per m³ slurry)

Annual costs	Total (€)
Total costs for separation	12.77
Total cost for composting	2.70
Total cost for separation and composting	15.47

3. The yield and the physical and chemical characteristics of biochar, bio-liquid and gas produced from the pyrolysis of pig manure are influenced by amending the manure with sawdust and by composting the feedstock. Increasing the rate of sawdust addition to the pig manure increased heating values, but reduced nutrient concentrations in the resulting biochar. Sawdust addition also increased the heating value of the gases produced, while the heating value of the bio-liquid was decreased. Composting of the feedstock before pyrolysis reduced biochar heating values, while the bio-liquid heating values increased.
4. An energy balance, using energy requirements from the processes of separation, composting and pyrolysis of pig manure and energy generation from the combustion of the pyrolysis products, showed that a positive net energy yield was possible from these processes (Table 9.2). However, in order to produce a positive energy yield, the pig manure must be amended with sawdust. Composting of the feedstock before pyrolysis is not recommended as it reduces the net energy yield.

Table 9.2 Energy balance (MJ per tonne liquid manure)

	Composting stage included					
	MO	4:1 [#]	3:2	MO	4:1	3:2
Biochar as a fuel	-24.1*	165.1*	509.9	37.3	149.5	319.2
Biochar to soil	-100.4	1.9	148.9	-24.5	29.8	111.7

* Positive values indicate an energy generation, while negative values indicate an energy requirement; [#] 4:1 and 3:2 are the mix ratios of separated pig manure solids to sawdust (by weight), MO is the manure only treatment.

5. When biochar, produced from either pig manure or wood, was used as a soil amendment, the N cycling process within the soil was affected, which in turn reduced NO_3^- leaching and increased N_2O emissions. Biochar addition to soil increased CO_2 emissions as a result of higher rates of C mineralization. Soil water, organic matter and C contents increased in biochar-amended soil. The biochar produced from pig manure was shown to release P, resulting in higher P contents both in the soil and in the leachate.

9.2 Recommendations for Future Work

1. On-farm composting using sawdust as a bulking agent could be a viable alternative to landspreading in the coming years, if the cost of manure separation could be reduced. Future work must examine composting following cheaper methods of manure separation, such as gravity belt separators or screen separators. If a viable, less-expensive method of separation was found, then farm-scale windrow composting experiments using sawdust as a bulking agent should be investigated before composting could be recommended to farmers in pig-dense areas as an alternative to landspreading.
2. The pyrolysis experiments were conducted on a laboratory-scale. Large-scale pig manure pyrolysis experiments are required before any on-farm implementation of this technology could be recommended. A farm-scale pyrolysis unit, working in unison with a manure separator and a farm-scale CHP unit, would provide detailed results on the viability of on-farm pyrolysis, and provide sufficient amounts of biochar for field-scale application studies.
3. Field-scale studies on the effect of biochar on soil properties, nutrient leaching, plant growth rates and greenhouse gas emissions over a longer time period are required. It would be important to investigate the effect of biochar on soil under ploughing, tillage and harvesting events. The application of biochar to other common Irish soils, such as sandy and peat soils should be investigated to see if the effect is similar to that of the current study. The application of wood biochar to a P Index 4 soil to investigate if biochar application can reduce P leaching, should

be a priority, given the imminent P application restrictions. Future work must also examine if the reduction in nutrient leaching results in increased plant growth.

9.3 Context and Future Outlook

Ireland has committed to meeting the requirements of the European Union Water Framework Directive (WFD; 2000/60/EC; EC, 2000) to achieve at least ‘good status’ of all surface and groundwater by 2015, and the Nitrates Directive (91/676/EEC; EEC, 1991) to reduce surface and groundwater pollution from agricultural sources. In order to comply with these Directives, the application of organic manure to land has been restricted. Land available for landspreading of pig manure will be further reduced by 2017, when landspreading of pig manure exceeding the crop’s P requirements for growth will be prohibited. Many grassland soils which have previously been used as spreadlands for pig manure are likely to be restricted from further manure application. This will increase the cost of landspreading pig manure, especially in areas with high pig densities and with minimum available tillage land, such as counties Cavan and Longford. Therefore, it is imperative that viable alternatives to landspreading are available for pig farmers, to ensure the continuation of the of the pig industry in these areas. In the future, separation and composting of the pig manure to produce a marketable end-product could be a viable treatment option for pig manure in pig-dense regions. The problem of finding viable land for landspreading would be reduced, while simultaneously diversifying farm income. Pyrolysis of pig manure may also be a viable treatment option in the long-term. However, further research is required before pyrolysis could be implemented on a farm-scale.

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APPENDICES

Appendix A: List of Publications

JOURNAL PAPERS (Accepted)

Nolan, T., Troy, S.M., Healy, M.G., Kwapinski, W., Leahy, J.J., Lawlor, P.G., 2011. Characterization of compost produced from separated pig manure and a variety of bulking agents at low initial C/N ratios. *Bioresource Technology*, 102: 7131-7138.

Troy, S.M., Nolan, T., Kwapinski, W., Leahy, J.J., Healy, M.G., Lawlor, P.G., 2012. Affect of sawdust addition on composting of separated raw and anaerobically digested pig manure. *Journal of Environmental Management*, 111: 70-77.

Nolan, T., Troy, S.M., Gilkinson, S., Frost. P., Xie, S., Zhan, X., Harrington, C., Healy, M.G., Lawlor, P.G., 2012. Economic analyses of pig manure treatment options in Ireland. *Bioresource Technology*, 105: 15-23.

Troy, S.M., Nolan, T., Leahy, J.J., Lawlor, P.G., Healy, M.G., Kwapinski, W., 2012. Effect of sawdust addition and composting of feedstock on renewable energy and biochar production from pyrolysis of anaerobically digested pig manure. Accepted for publication in *Biomass and Bioenergy*.

MANUSCRIPTS SUBMITTED

Troy S.M., O' Flynn, C.J., Lawlor, P. and Healy, M.. Impact of two different biochars on nutrient leaching and soil quality of an acid brown earth in temperate conditions. Submitted September 2012.

Troy S.M., O' Flynn, C.J., Lawlor, P. and Healy, M.. Impact of two different biochars on soil greenhouse gas emissions following pig manure application. Submitted September 2012.

INTERNATIONAL CONFERENCE PRESENTATIONS

Troy, S.M., Nolan, T., Leahy, J.J., Lawlor, P.G., Healy, M.G., Kwapinski, W., 2012. Renewable energy and biochar production from pyrolysis of anaerobically digested pig manure. Biochar as Option for Sustainable Resource Management: A European Perspective, Crete, September, 2012 (*Oral presentation*).

Troy, S.M., Nolan, T., Healy, M.G., Lynch, P.B., Lawlor, P.G., 2011. Characterization of separated pig manure composted with a variety of bulking agents at low initial C/N ratios. ISHS, International Symposium on Growing Media and Substrate Analysis, Barcelona, October, 2011 (*Oral presentation*).

Kwapinski, W., Troy, S.M., Wnetrzak, R., Healy, M.G., Nolan, T., Lawlor, P.G., Leahy, J.J., Hayes, M.H.B., 2010. Pyrolysis of waste organic substances and product applications. EU Workshop: Managing livestock manure for sustainable agriculture. Wageningen, The Netherlands, November, 2010 (*Poster presentation*).

Troy, S.M., Nolan, T., Healy, M.G., Lynch, P.B., Lawlor, P.G., 2010. Composting the solid fraction of separated pig manure with sawdust, chopped straw or shredded green waste. British Society of Animal Science. Belfast, April, 2010 (*Poster presentation*).

NATIONAL CONFERENCE PRESENTATIONS

Troy, S.M., Nolan, T., Leahy, J.J., Lawlor, P.G., Healy, M.G., Kwapinski, W., 2012. Influence of sawdust addition and pre-composting on energy production from the pyrolysis of pig manure. The 22nd Irish Environmental Researchers' Colloquium. Dublin, March, 2012 (*Oral presentation*).

Troy, S.M., Nolan, T., Leahy, J.J., Lawlor, P.G., Healy, M.G., Kwapinski, W., 2011. Influence of the addition of different carbon rich bulking agents and composting on the characteristics of pig manure biochar. The 21st Irish Environmental Researchers' Colloquium. Cork, April, 2011 (*Oral presentation*).

Troy, S.M., Nolan, T., Healy, M.G., Lynch, P.B., Lawlor, P.G., 2011. Effect of manure to sawdust ratio on the composting of separated solids from anaerobically digested pig manure. Irish Agricultural Research Forum. Tullamore, March, 2011 (*Oral presentation*).

Nolan, T., Troy, S.M., Healy, M.G., Lynch, P.B., Lawlor, P.G., 2011. Characterization of separated pig manure composted with a variety of bulking agents at low initial C/N ratios. Irish Agricultural Research Forum. Tullamore, March, 2010 (*Oral presentation*).

Appendix B: Solutions used in the Oxygen Uptake Rate test carried out on compost samples in experiments detailed in Chapters 3 and 4.

Nutrient solution

Add 1ml of micronutrient solution to 1 litre of macronutrient solution:

Macro nutrient solution: NH_4Cl (4.3 g L^{-1}), $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (5.4 g L^{-1}), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (4.3 g L^{-1}) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.03 g L^{-1}).

Micro nutrient solution: EDDHA 6% iron chelate (5.0 g L^{-1}), MnSO_4 (1.4 g L^{-1}), ZnSO_4 (1.1 g L^{-1}), $\text{Na}_2\text{B}_4\text{O}_7$ (4.2 g L^{-1}), CuSO_4 (0.2 g L^{-1}); NaMoO_4 (0.13 g L^{-1}) and HCl (36%; 1 ml L^{-1}).

pH buffer

KH_2PO_4 (86 g L^{-1} of deionised water) and $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ (89 g L^{-1} of deionised water). Mixed ratio of about 1:4 for pH 7.

ATU (nitrification inhibitor)

N-Allylthiourea – $\text{C}_4\text{H}_8\text{N}_2\text{S}$ (4 g L^{-1})