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**Lignite Amendment of Livestock Manure:
Mechanisms for Nitrogen Retention and Effects on Composting
and Nitrogen Release Dynamics**

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Abstract

Intensive livestock production systems, such as cattle feedlots, play an important role in meeting the increasing global demand for animal products, driven by a growing population and increasing affluence. These intensive systems account for a significant proportion (~39%) of global atmospheric ammonia (NH_3), which is released from the large amounts of manure generated. In cattle feedlots, the loss of NH_3 represents about 75% of the excreted nitrogen (N) in the manure and this has important implications for environmental pollution. Consideration of management strategies to reduce this loss provides potential to obtain N enriched manures that can be used as fertilizer.

A number of mitigation techniques have been shown to reduce NH_3 loss from manure. These include: acidifying agents and urease inhibitors (both requiring frequent reapplication), dietary manipulation (can affect animal productivity) and manure compaction and covering (only applicable to stockpiled manure). Lignite (brown coal) has a demonstrated capacity to suppress NH_3 emission from manure by 30-66% and is seen as a more effective, practical and potentially long lasting option.

Lignite's ability to effectively reduce the loss of NH_3 from manure has been credited to its pH, cation exchange capacity (CEC), pH buffer capacity and labile carbon (C) content. However, we do not fully understand what the actual capacity for N retention by lignite is, or the main mechanisms by which lignite retains N, and how these are influenced by the properties of the lignite and changes in the environmental conditions when lignite is mixed with other materials (such as manure). Also, the impact of lignite on the quality of the manure during deposition, storage, processing (such as composting) and land application, has not been studied.

The objectives of this study were to: (i) characterize different lignite materials for their capacity for nitrogen retention, and to understand the mechanisms of N retention; (ii) determine how lignite amendment of manure affects the composting process under both field and laboratory conditions by monitoring changes in biochemical parameters and gaseous emissions that occur during composting, and (iii) determine the C and N mineralization from non composted and composted manure applied to soil and how this is influenced by lignite.

The capacity for N retention by lignite, and the mechanisms of N retention were determined by characterizing five lignites sourced from Victorian brown coal deposits. The chemical properties that were examined for each lignite (e.g. pH, total and labile C, forms of C, pH buffering capacity, CEC, etc.) were related to its ammonium (NH_4^+) adsorption capacity as a function of pH and also to the biological immobilization of N in the lignite. The properties of the lignites, their capacity for NH_4^+ adsorption and the immobilization of N, were determined through a series of laboratory experiments involving SEM, ^{13}C NMR spectroscopy, sample digestion and extraction, batch adsorption isotherms techniques, and controlled environment incubations. Lignite's impact on composting of manure was assessed under field (windrow) conditions to determine the benefits under typical industry scale management processes. The mechanisms by which lignite affected composting of manure was determined under laboratory (in-vessel) conditions. Changes in biochemical parameters (e.g. N forms, organic matter and pH), emissions of NH_3 and greenhouse gases (GHG), as well as compost maturity indices, were monitored. Lignite's effect on C and N mineralization from manure (non-composted and composted) when applied to soil, was determined through a laboratory incubation experiment which monitored CO_2 evolution (as a measure of C mineralized) and changes in NH_4^+ and NO_3^- concentration in soil (as a measure of N mineralized) over a period of 40 days.

The mechanism by which lignite retains N was found to be mainly through pH dependent adsorption of NH_4^+ on exchange sites of deprotonated carboxyl groups. The maximum NH_4^+

adsorption capacity ($Q_{\max}$) increased up to 3 fold when pH was increased from 3.6 to ~7. Biological immobilization of N was insignificant (e.g. maximum of 0.1 mg N g⁻¹ lignite) compared to NH₄⁺ adsorption on exchange sites (e.g. highest $Q_{\max}$ of 25.6 mg NH₄⁺-N g⁻¹ lignite at pH ~7). These findings suggest lignite's ability to suppresses NH₃ from manure occurs by i) initially favouring the formation of NH₄⁺ over NH₃ due to the acidic pH of the lignite, and ii) deprotonation of more carboxyl groups with continuous deposition of alkaline manure leading to increased CEC of the lignite and increased retention of NH₄⁺.

Amending manure with lignite did not inhibit the composting of manure. The addition of lignite suppressed the emission of NH₃ from manure during both field windrow (by 45%) and laboratory in-vessel (by 35-54%) composting. Lignite addition reduced the emissions of GHGs (12-23% for CO₂, 58-72% for N₂O and 52-59% for CH₄) during in-vessel composting. However, during windrow composting, addition of lignite caused the emissions of GHGs to increase (41% for CO₂, 136% for N₂O, and from -5.0 mg kg⁻¹ initial dry matter (DMi) day⁻¹ in the manure only to 9.8 mg kg⁻¹ DMi day⁻¹ for CH₄). The higher emissions of CH₄ and N₂O were presumed to be due to anaerobic pockets that developed within the lignite treated windrow resulting from the small particle size of the lignite, and facilitated by the largely passive aeration method (unlike the forced aeration for in-vessel composting) used during the windrow composting. For the in-vessel composting, lignite addition to manure increased the organic matter (OM) and N contents of the final compost by 10-19 and 28-38% respectively, and also the germination index, a measure of compost maturity, (from 71% to 90-113%). These changes were not observed under windrow composting conditions likely due to the passive aeration method used.

In addition, the effect of lignite in the windrow compost may have differed to that in the in-vessel systems because i) the mode of manure collection using large scale field equipment meant that the lignite content of the manure was estimated based upon that applied but could

have been less due to some being left on the pen surface, and ii) the source of soil used in the cattle pens was quite alkaline (pH 8.8) which may have reduced the lignite pH effect.

Lignite addition to the manure suppressed microbial activity (soil respiration) which reduced the mineralization of C from the manure when applied to soil, more noticeably when the manure was composted. Over a 40-day incubation period, with non-composted manure application rates of 30 and 60 t ha⁻¹ soil, the C mineralized was 26.4 to 27.8% for manure only, and with lignite amendment it was 16.3 to 21.4%. The corresponding C mineralized in the composted manure was 12.4 to 14.1% and 3.5 to 6.5%. The addition of lignite had a mixed effect on N mineralized from manure when applied to soil. The N mineralized was significantly higher in the non-composted manure amended with Loy Yang lignite (10.4 to 13.5% for 30 and 60 t ha⁻¹) than with Bacchus Marsh lignite (4.1 to 9.8%) and non-composted manure only (3.2 to 8.7%). For composted manure, there was no significant difference between N mineralized in the manure only (4.8 to 6.7%) and the lignite treatments (2.5 to 7.8%). Results presented in this study, for the first time, show the dominant N retention mechanism by lignite in manure, its influence on biochemical changes and gaseous emissions during manure composting under both laboratory and field conditions, and finally how the lignite impacts nutrient mineralization from non-composted and composted manure when applied to soil.

In conclusion, this study shows lignite's capacity to mitigate the emissions of both NH₃ and GHGs from manure under optimum composting conditions. Hence, in intensive livestock production systems, lignite has the ability to improve the agronomic value of the large volumes of manure generated and reduce the environmental pollution associated with livestock production and manure management. Lignite addition to manure, especially when composted, has the potential to increase soil OM and improve long term soil health due to the inhibitory effect of lignite on C mineralization from manure. The findings of this study provide the option

for the use of lignite as a tool for sustainable livestock production in intensive livestock industry.

Keywords:

Lignite, Brown coal, Livestock manure, Ammonia emission, Greenhouse gas emissions, Ammonium adsorption, Gaseous emissions, Characterization, Nitrogen mineralization, Carbon mineralization, In-vessel composting, Windrow composting, Soil incubation.

Declaration

This is to certify that:

- i. This thesis comprises only my original work except where indicated in the preface.
- ii. All other materials used has been acknowledged.
- iii. This thesis contains less than 80, 000 words, exclusive of tables, figures, bibliography and appendices.

Signed: Robert Impraim

Date: 16th May, 2020

Preface

This thesis comprised of seven chapters. The first chapter is the introduction, followed by the literature review chapter which discussed literature relevant to this study including current research questions and knowledge gaps, four research chapters, and finally the general discussion and conclusions chapter which highlights the key findings of this thesis. Among the four research chapters, only the chapter four includes data (i.e. the gaseous emission component) collected by other researchers in the course of the field experiment. This was to enable a complete discussion of lignite's impact on manure composting. All other aspects of the research presented in chapter four was carried out by Robert Impraim, who identified the research gaps, designed the experiment, collected and analysed the data, and wrote the chapter.

The following are the four research chapters of this thesis:

Chapter 3:

Characterization of Victorian lignites – mechanisms and capacity for nitrogen retention.

Chapter 4:

Effect of lignite on biochemical processes and gaseous emissions during composting of cattle manure under field conditions.

Chapter 5:

The mechanisms causing lignite's effect on composting of cattle manure – a controlled environment study.

Chapter 6:

Effect of lignite amendment on carbon and nitrogen mineralization from non-composted and composted manure during incubation with soil.

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CHAPTER 1: General Introduction

1.1 Research background

Increasing global demand for animal products – as a result of growing population and urbanization – and the desire for efficient animal production systems have stimulated the expansion of intensive livestock production systems, such as cattle feedlots (Bradford 1999; Makkar 2016). These intensive systems are characteristic by the generation and accumulation of large volumes of manure (Bernal et al. 2009; Arriaga et al. 2017). Although the manure could be a valuable source of plant nutrients, it also accounts for a significant proportion (~39%) of global atmospheric ammonia (NH_3) (Ni 1999; Clarisse et al. 2009). In cattle feedlots, the emission of NH_3 to the atmosphere could represent upward of 60% of dietary N intake or about of 75% of the excreted N (e.g. 73 kg N head⁻¹ year⁻¹ in manure) (Watts et al. 2011). Most of the NH_3 loss happens within the animal pen but additional losses occur during the subsequent stages of manure management, such as stockpiling or composting. The main driver of NH_3 volatilization from manure is the urease catalysed hydrolysis of urinary urea to ammonical N (NH_4^+ and $\text{NH}_{3\text{aq}}$) and the subsequent loss as NH_3 , facilitated by the alkaline pH of the manure (Reddy et al. 1979; Sommer & Husted 1995).

The loss of NH_3 from manure leads to both environmental damage (e.g. formation of particulate matter - $\text{PM}_{2.5}$, eutrophication, soil acidification, indirect greenhouse gas emissions, and in extreme cases plant toxicity through subsequent deposition of the NH_3) as well as economic loss (e.g. reduction in the agronomic value of the manure, mitigation of acidification) (Van der Stelt et al. 2007; Sutton et al. 2008; Wu et al. 2016).

Various NH_3 emission mitigation techniques have been employed to abate N loss from manure. Examples are the use of urease inhibitors (Parker et al. 2005; Singh et al. 2009), manure compaction and covering (Chadwick 2005), dietary crude protein manipulation (Cole

et al. 2005; Le et al. 2009), and acidifying additives (Shi et al. 2001). However, the application of the aforementioned techniques are confronted with challenges: urease inhibitors require frequent reapplication for continued suppression of NH_3 emission (Parker et al. 2005). Acidifying additives, in addition to the need for frequent reapplication, may require complex application systems due to their hazardous and corrosive nature. The frequent reapplication and the need for complex application systems make these mitigation options expensive and less practical to the farmer (McCrory & Hobbs 2001). Manure compaction and covering, on the other hand, are limited to manure collected from the pen and this does not address the significant losses of N that occur prior to the manure collection. Up to 67 % of excreted N can be lost in the pen (Bierman et al. 1999). Reduction in dietary crude protein to levels that affect animal performance may lead to losses in production and an increase in NH_3 emission in the long run as animals will require more days on feed to reach market value (Cole et al. 2005; Hristov et al. 2011).

Lignite (brown coal), with extensive reserves in Victoria, Australia, is seen as a more effective, practical and potentially long lasting alternative for mitigating N loss from cattle manure (Chen et al. 2015). Its application to the surface of feedlot cattle pens reduced NH_3 volatilization from manure by 30 to 66 %, relative to manure in untreated pens (Chen et al. 2015; Sun et al. 2016). Dana and Ardeshtir (2018) reported a 47 to 91% reduction in NH_3 loss from broiler litter following the application of 10 to 30% lignite. A similar observation was made by Berg and Samer (2010) where the application of pulverized lignite to liquid manure resulted in a 70% reduction in NH_3 emission. Hao et al. (2007) fed cattle with lignite extract amended feed and reported a 36 to 60% reduction in NH_3 volatilization from manure.

The ability of lignite to suppress NH_3 loss from manure has been attributed, in the above papers, to the pH buffering capacity and low pH of the lignite which shifts the $\text{NH}_3/\text{NH}_4^+$ equilibrium ratio towards non-volatile NH_4^+ . In addition, it has been suggested that NH_4^+

adsorption owing to the high cation exchange capacity (CEC), biological immobilisation of N due to labile C, and inhibition of urease activity due to the humic acid content of the lignite leads to the reduction in NH_3 volatilization (Chen et al. 2015; Sun et al. 2016). Though lignite was effective in reducing NH_3 loss and the reduction ascribed variously to a number of properties of the lignite, the actual mechanisms, as well as the relative importance of these properties, to N retention, and any interaction between them, are not well understood. Also, the implications of amending manure with lignite on the subsequent management of the manure, after it has been collected from the pen, has not been well studied.

Composting is increasingly being considered as a viable management option for recycling the large volumes of manure generated in intensive livestock production system (Bernal et al. 2009). The quality of the composting process is affected by a number of factors, a key of which is the characteristics of the initial feedstock (Bernal et al. 2017). The application of lignite to alter the characteristics of the manure so as to reduce the release of NH_3 is therefore expected to influence the composting process of the manure. To date, there is a dearth of literature detailing how lignite affects the composting process of manure and it remains unknown whether or not the lignite will continue to retain the N in the manure during the composting process. Addressing these research gaps is critical. In addition, it is important to assess the fertilizer value of the lignite amended manure, both non-compost and composted.

In order to obtain maximum benefit from application of manure to soil, and minimize the environmental risk, the rate and timing of the application should be based on the expected nutrient mineralization rate of the manure, a microbial mediated process also affected by the characteristics of the manure (Hartz et al. 2000; Egghball et al. 2002; Qian & Schoenau 2002). The effect of lignite on mineralization of manure (non-composted and composted) following application to soil has not been reported.

1.2 Research questions and research framework

This research determined the mechanism by which lignite influences N retention in manures, its impact on manure composting, and subsequent nutrient release when applied to soil. The main objectives were to: (i) characterize different lignite materials for their capacity and mechanisms for nitrogen retention and how these are influenced by the lignites' properties; (ii) determine how lignite amendment of manure affects the physicochemical parameters and gaseous emissions during composting of manure under both field and laboratory conditions, and (iii) determine the C and N mineralization patterns of non composted and composted lignite amended manure during incubation with soil. The respective research questions for the three objectives above were: (i) which lignite property or properties are the key drivers of N retention capacity?; (ii) how will the addition of lignite to cattle manure influence the physicochemical processes, gaseous emissions and maturity indices during composting of the lignite amended manure and will this differ under field and laboratory conditions?; and (iii) will the amendment of manure with lignite alter the manure's C and N mineralization patterns during incubation with soil?

The first objective was addressed by determining the basic chemical characteristics of five lignites sourced from Victorian brown coal deposits and relating this to their NH_4^+ adsorption capacity as a function of pH and also the biological immobilization of N in the lignites, through experiments involving material characterization, ^{13}C NMR spectroscopy, adsorption isotherms and laboratory incubations.

The second objective was achieved by monitoring changes in the biochemical parameters (e.g. N transformations, organic matter loss), and gaseous (CO_2 , CO, NH_3 , N_2O and CH_4) emissions during composting of the lignite amended manure under a) field conditions – large scale windrow composting system and b) laboratory conditions – in-vessel composting system.

Preceding the laboratory scale composting was the construction and validation of a comprehensive in-vessel composting system.

To achieve the third objective, the C and N mineralization of non composted and composted lignite amended manures were determined during incubation with soil under controlled temperature and moisture conditions. Carbon mineralization was determined as CO₂ evolved during the incubation whilst N mineralization was determined as the proportion of the applied organic N mineralized (NH₄⁺ and NO₃⁻).

1.3 Thesis structure

This thesis begins with an Introductory Chapter and addresses the research background, conceptual framework, research objectives and questions, and the relevance of this research to the application of lignite in manure management. Chapter 2 reviews literature relevant to this study. This includes nitrogen loss from cattle manure and its implications, ammonia emission mitigation techniques with a focus on the use of lignite. Also discussed are the properties of lignite relevant to its capacity and mechanisms for N retention, the impact of lignite on composting, and the possible effects of lignite on C and N mineralization from manure. A summary of the existing knowledge gaps are presented. Chapters 3 to 6 present a systematic evaluation of the manure/lignite system:

- i. Chapter 3: Characterization of Victorian lignites – mechanisms and capacity for nitrogen retention.
- ii. Chapter 4: Effects of lignite on biochemical process and gaseous emissions during Composting of cattle manure under field conditions.
- iii. Chapter 5: The mechanism causing lignite's effects on composting of cattle manure – a controlled environment study.

- iv. Chapter 6: Effect of lignite on Carbon and nitrogen mineralization from non-composted and composted manure during incubation with soil.

The thesis concludes, with Chapter 7, by discussing and summarizing the key findings of the study with respect to objectives presented above. The section also discusses the overall implications of lignite application to manure management in intensive livestock production systems, the potential agronomic value of the lignite amended manure (non composted and composted) and finally, the implications for future research.

1.4 Relevance of the study

A knowledge of the key mechanisms and capacity for N retention by lignite will enable screening of lignite materials for prescriptive use in minimizing N loss from manure to improve its nutrient value and reduce environmental impacts. The findings of this research on how lignite affects the composting process of manure as well as its effects on the C and N mineralization potential of manure (non-composted and composted) will enable the better use of lignite in recycling manure and also its use as soil amendment for improved soil health. Overall, the findings of this research will provide new information relevant to the adoption of lignite as an NH_3 emission mitigation strategy in intensive livestock production systems and the use of lignite for the recycling of manure for agricultural application.

CHAPTER 2: Literature Review

Increasing global population (expected to reach ~10 billion by 2050) and urbanization (~60% of population by 2050) accompanied by a transition in dietary patterns have resulted in higher demand for animal products (FAO 2017). This, coupled with the desire for efficient and improved animal production systems, has stimulated the expansion of intensive livestock production systems (Bradford 1999; Makkar 2016; FAO 2017). A common feature of these intensive systems is the generation of large volumes of manure. This review focuses on cattle manure but the principles of management apply to all animal manures.

In cattle feedlots, manure can contain up to 85% of the dietary N intake of the cattle (Watts et al. 2011). Hence the manure represents a valuable source of plant nutrients which could be recycled (e.g. by composting) for agricultural application (Bernal et al. 2009; Watts et al. 2011; Arriaga et al. 2017). However between 50 and 75% of the excreted N in manure is lost mainly as NH_3 , leading to both environmental damage and economic loss (Bierman et al. 1999; Watts et al. 2011). Among the various NH_3 emission mitigation techniques for stemming N loss from manure, is the application of lignite to the surface of feedlot cattle pens with a demonstrated capacity to suppress NH_3 emission by around 30-66 % (Chen et al. 2015; Sun et al. 2016). Here, a review of relevant available literature, including the current knowledge gaps, is provided on the following areas: i) mitigation techniques to reduce N loss from animal manures, with a focus on lignite, both during deposition and through subsequent management processes, ii) the impact of lignite on manure composting, and iii) the impact of lignite on nutrient mineralization from manure.

2.1 Cattle feedlot, manure generation and management

2.1.1 Australian cattle feedlots

A cattle feedlot is a confined facility, with watering and feeding systems, where weaned cattle are kept in open pens and fed a prepared ration, mechanically or manually, until they reach a specified market weight (Watts et al. 2011; MLA 2012). In Australia, between 2 and 3% of the total cattle population (corresponding to ~ 1.5 million animals) are held in the 400 accredited feedlots, the majority of which are located in the states of Queensland and New South Wales (60 and 30% respectively) (ALFA 2020). Within a typical Australian cattle feedlot, depending on the target market, the weight of cattle entering the feedlot ranges from 250 to 450 kg, and the exit weight between 400 and 700 kg after 60 to 300 days on feed (Watts et al. 2011). The stocking density in a feedlot is 10 to 20 m² pen area per head (Watts et al. 2011). The major components or facilities within an Australian feedlot include pens, feed and water systems, drainage systems, manure stockpiles and composting pads, and effluent management ponds (MLA 2012).

2.1.2 Amount of manure generated in cattle feedlot

The generation and accumulation of large volumes of manure, often exceeding the fertilization requirement of nearby agricultural fields, is a major characteristic of an intensive animal production system such as a feedlot (Bernal et al. 2009). In Australia, the quantity of manure harvested from feedlot pens per standard cattle unit (SCU, animal weight of 600 kg) ranges from 400-2000 kg total solid (TS)/SCU/year (Watts et al. 2011; Tucker et al. 2015). The quantity of manure harvested is influenced by factors such as diet or feeding regime (e.g. roughage to concentrate ratio), pen scraping method (whether a manure interface layer is maintained or not), and dry matter decomposition losses (higher in summer than in winter) (Watts et al. 2011; Tucker et al. 2015).

2.1.3 Manure management options in cattle feedlots

Depending on the feedlot design, weather, labour and management, manure cleaned from cattle pens may be stockpiled and/or composted or applied directly to nearby fields as fertilizer (Watts et al. 2011).

2.1.3.1 Direct application

Manure collected from the cattle pen may be applied or incorporated into the soil without any form of processing (e.g. composting) in order to minimize NH_3 emission from the manure (Parkinson et al. 2004). However, the direct application of the manure is limited to nearby fields as its high moisture content ($> 70\%$) makes haulage over long distance uneconomical (Larney et al. 2006). In addition, the direct application of manure is associated with the spread of weed seeds and pathogens, as well as the inhibition of seed germination and generation of odour (Hao & Benke 2008; Bernal et al. 2017).

2.1.3.2 Stockpiling

In feedlots, the volume of manure generated often exceeds the fertilization requirement of nearby agricultural fields (Bernal et al. 2009; Arriaga et al. 2017). Thus, stockpiling as a means of temporary storage whilst the manure awaits haulage for field application or composting is a common practice, especially in large feedlots (Larney et al. 2006). The stockpile site is often away from the pen, with controlled drainage and impermeable base (MLA 2012; Tucker et al. 2015). Some level of composting is likely to occur in stockpiled manure but this is usually anaerobic (MLA 2012).

2.1.3.3 Composting

Composting is considered a viable management option for recycling the manure into a stabilized and sanitized product, as well as reducing its volume and moisture content, thus,

facilitating the haulage and off-site application of the manure (Bernal et al. 2009; Arriaga et al. 2017). For land application, the composting of manure is important to eliminate the spread of pathogens and weed seeds, as well as odour, and seed germination inhibitory water soluble compounds associated with raw manure (Eghball & Power 1999; Larney et al. 2006; Bernal et al. 2009). The major composting system employed in feedlots for manure management is the turned windrow, where the manure is formed into a long rectangular pile perpendicular to the slope of the composting pad (to promote drainage) with a trapezoidal or triangular cross section (Tucker et al. 2015). However, the cost of compost production and the loss of N, mainly through NH_3 emission, are major limitations to manure composting. Hence, it has been suggested that composting is limited to manure that requires partial sterilization or when the quality of the compost can offset its production cost (Parkinson et al. 2004; Bernal et al. 2009). A detailed review of the literature on composting processes and systems, as well as the physicochemical changes that characterize the composting process, is provided in section 2.4 below.

The extent of N loss from manure is significantly influenced by the manure management strategy, with the loss lower in stockpiled manure compared to composted manure. For example, Larney et al. (2006) reported an average of 23 and 46% loss of N for stockpiled and composted manures respectively. Luebbe et al. (2011) reported 14-24% N loss from stockpiled manure and 34-44% N loss during composting. Similarly, a loss of 35% and 46% of N for stockpiled and composted manure respectively has been reported by Shah et al. (2010). Generally, it is thought that between 20-40% of initial manure N can be lost during composting (Eghball & Power 1999). Nitrogen loss during composting is influenced by factors such as feedstock and management strategy (discussed under section 2.4.2.3). However, following field application, the loss of N from stockpiled or composted manure is expected to be lower (due to the losses that already occurred during onsite management) than the N loss from the

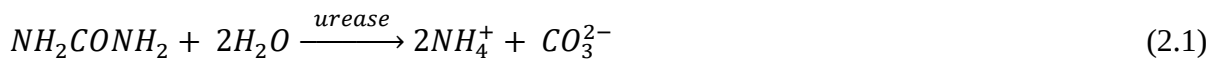
direct application of manure from pen. McGinn and Sommer (2007) found that stockpiled manure lost 27% less NH₃ compared to manure collected directly from the pen.

2.2 Nitrogen loss from cattle manure: implications and mitigation

2.2.1 Nitrogen excretion and loss from manure

Cattle excrete up to 85% of their dietary N intake through manure (urine and faeces), equivalent to about 75 kg N head⁻¹ year⁻¹ (Varel et al. 1999; Watts et al. 2011). Of the total N excreted, 60-80% is present in the urine with the remainder in the faeces (Varel et al. 2007). Up to 97% of the urinary N exists as urea with the rest as peptides and amino acids (Fraser et al. 1994; Mackie et al. 1998).

The urease catalysed hydrolysis of the urinary urea (NH₂CONH₂) to NH₄⁺/NH₃ (equations 2.1 and 2.2) and its subsequent volatilization as NH₃ is the main pathway for the loss of manure N (Reddy et al. 1979). The alkaline pH of the manure (pH >7) drives equation 2.2 to the right, facilitating the volatilization of NH₃ which is affected by the concentration gradient of NH₃ between the manure surface and the atmosphere (Reddy et al. 1979).



Aside from NH₃ volatilization, N loss from manure occurs mainly through N₂O emission and in runoff, and the magnitude of loss depends on factors such as diet, pen management and climatic conditions (Rotz 2004; Watts et al. 2011). Depending on the dietary composition and pen management techniques (e.g. pen cleaning frequency and use of amendments), between 57 and 75% of the excreted N in the manure is lost as NH₃ from the pen surface (Bierman et al. 1999; Watts et al. 2011). The loss of excreted N due to runoff has been found to range between 1.8% for winter conditions to 2.7% for summer conditions (Kissinger et al. 2006). Similarly,

Watts et al. (2011) estimated that N loss from cattle pens owing to runoff accounts for about 1.5% of excreted N, though this could vary between 4.6 and 19.4% depending on the volume of runoff water (Bierman et al. 1999). Nitrous oxide (N_2O) emissions from the pen surface have been found to account for 1-4% of excreted N, and N lost owing to both dust and leaching is considered to be minimal (Watts et al. 2011).

2.2.2 Implications of nitrogen loss from manure

Nitrogen loss from manure has economic, environmental and health implications. The loss of N from manure reduces the fertilizer value of the manure and therefore represents an economic loss as the N lost will have to be replaced using other N sources (e.g. inorganic fertilizer) (Varel 1997; Bernal et al. 2009; Bernal et al. 2017). Aside from the economic loss, N loss as volatilized NH_3 could serve as a precursor to the formation of particulate matter ($\text{PM}_{2.5}$) by reacting with sulphuric and nitric acids to produce ammonium salts such as ammonium sulphate, ammonium bisulphate and ammonium nitrate (Gong et al. 2011). This particulate matter can have adverse impacts on human health, climate patterns and atmospheric visibility (Sutton et al. 2008; Gong et al. 2011; Wu et al. 2016). The deposition of the volatilized NH_3 (as ammonium salt) may lead to soil acidification, eutrophication and in extreme cases plant toxicity (Pearson & Stewart 1993). Considering the global warming potential (GWP) of N_2O being 265 times the GWP of CO_2 , over a 100-year period (Myhre et al. 2013), N loss as N_2O could have a significant impact on the environment (Sherlock et al. 2002).

2.2.3 Mitigating nitrogen loss from manure

A number of mitigation techniques have been applied to minimise the loss of manure N by targeting at least one of the factors driving NH_3 loss from manure (equations 2.1 and 2.2). These include inhibiting ureolytic enzyme activity, lowering pH, reducing urinary N excretion

and enhancing microbial immobilization of NH_4^+ . The key findings of studies applying these mitigation techniques are provided in Table 2.1.

2.2.3.1 Urease inhibitors

Urease inhibitors, such as phenyl phosphorodiamidate (PPDA), N-(n-butyl) thiophosphoric triamide (NBPT) and cyclohexylphosphoric triamide (CHPT), act by inhibiting the ureolytic enzyme responsible for urea hydrolysis to $\text{NH}_4^+/\text{NH}_3$ (equations 2.1 and 2.2) thus decreasing the loss of N as NH_3 (Varel et al. 1999; Parker et al. 2005). The application of NBPT at a rate of 1-2kg/ha reduced NH_3 emission from manure by up to 69% (Parker et al. 2005). Application of CHPT and NBPT at 20mg/kg manure led to longer retention of urea (up to 9 days), however the inhibitor effect was temporary (Varel et al. 1999) (Table 2.1). Urease inhibitors are only effective in the short term (4-11 days), and therefore require frequent reapplication, as they are rapidly broken down (e.g. through microbial activity), making the cost associated with their use prohibitive and also their application impractical to farmers (McCrory & Hobbs 2001; Shi et al. 2001). Encapsulation and chemical modification of urease inhibitors in order to minimize their microbial degradation and also to prolong their effect on ureolytic enzymes has been suggested (Varel 2002), but this is expected to add to the cost of the use of urease inhibitor as an NH_3 emission mitigation technique.

2.2.3.2 Dietary crude protein manipulation

Dietary manipulation aims to improve the N use efficiency of the cattle by reducing dietary N intake (through reduction in dietary N content, precision and phase feedings) and also by shifting the route of N excretion from urine (more susceptible to loss) to faeces (Cowley et al. 2019). A number of studies have investigated the use of dietary manipulation, and also in combination with pen cleaning frequency, to suppress N loss from manure (Table 2.1). Angelidis et al. (2019) reported that, more digestible diets with less N and fibre contents that

produce more metabolisable energy may reduce N excretion. Decreasing dietary crude protein from 14.5 to 13% resulted in a reduction in the proportion of urinary N in the form of urea, from 79 to 68% (Koenig 2013). Misselbrook et al. (2005) observed a 30% reduction in excreted N and a 45% reduction in urinary N when dietary crude protein was reduced from 19 to 14%. Reduction in dietary crude protein has to be balanced with the risk of lost productivity and the potential effect on animal health (Hristov et al. 2011; Angelidis et al. 2019). Reducing dietary protein content to levels that affect animal performance could lead to an increase in NH_3 emission in the long run as animals will require more days on feed to reach market value (Cole et al. 2005).

2.2.3.3 Acidifying agents

Ammonia emission from cattle manure can be reduced by creating an acidic manure pH using acidifying agents such as sulfuric acid (H_2SO_4), acetic acid ($\text{C}_2\text{H}_4\text{O}_2$), hydrochloric acid (HCl), calcium chloride (CaCl_2) and alum ($\text{Al}_2(\text{SO}_4)_3$) (Shi et al. 2001; Gay & Knowlton 2005; Regueiro et al. 2016). For example, the hydrolysis of CaCl_2 and $\text{Al}_2(\text{SO}_4)_3$ generates Ca^{2+} or Al^{3+} which frees up 2 or 3 H^+ , through cation exchange, leading to a reduction in pH (Shi et al. 2001). At acidic pH, the concentration of ammoniacal N in the form of NH_3 is minimized relative to the ionic form (NH_4^+) and thus inhibits NH_3 volatilization (Reddy et al. 1979; Fangueiro et al. 2015). The use of acidifying agent (e.g. H_2SO_4 and HCl) may require complex application systems due to their hazardous and corrosive nature and therefore add to the cost of manure treatment (McCrory & Hobbs 2001). In addition, frequent reapplication of the acidifying agent may become necessary as the pH of the manure increases again within 2-3 weeks of application (Regueiro et al. 2016).

2.2.3.4 Manure covering and compaction

Compaction decreases air-filled pore space within the manure (increases the bulk density) and thus impedes gas exchange which leads to reduction in NH_3 emission by up to 90% in the short-term (Table 2.1) (Dewes 1996; Williams et al. 2008). According to Chadwick (2005), compaction may inhibit the production of NO_3^- in the manure and therefore reduce the generation of N_2O produced from denitrification. However, this could also create anaerobic pockets leading to denitrification of NO_3^- already present in the manure. The compaction and covering of manure is only applicable to manure collected from the pens and thus does not address the significant losses of N that occur in the pen (i.e. up to 67 % of excreted N) (Bierman et al. 1999).

2.2.3.5 Zeolite

The suppression of NH_3 emission by zeolite (clinoptilolite) has been attributed to its ability to adsorb NH_4^+ on its exchange site, decreasing the dissolved ammoniacal N available for volatilization (Lefcourt & Meisinger 2001; McCrory & Hobbs 2001). The addition of 2.5 and 6.3% zeolite to manure slurry reduced NH_3 emissions by 22 and 47%, compared to untreated manure, respectively (Lefcourt & Meisinger 2001). Waldrup et al. (2015) reported an 18-42% reduction in NH_3 emissions following the application of zeolite to simulated cattle pens at a rate of 0.5-5% of manure dry mass. However, feeding cattle with zeolite amended feed did not affect N loss from manure (Table 2.1) (Sherwood et al. 2005).

2.2.3.6 Lignite

Lignite has been suggested as a more effective, practical and longer lasting approach to mitigating N loss from manure compared to other approaches (e.g. urease inhibitors and acidifying agents) (Chen et al. 2015). Lignite application has been found to effectively reduce NH_3 volatilization from cattle manure by 30 to 66 % in a number of studies (Hao et al. 2007;

Chen et al. 2015; Sun et al. 2016). As lignite is the focus of this research, further details on lignite (e.g. its formation, reserves in Australia and agricultural utilization) as well as its effectiveness to mitigate N loss from manure and its application in composting are covered in sections 2.3 and 2.4.

In summary, various NH_3 emission mitigation options in the management of manure have been reported in the literature (Table 2.1). Use of inhibitors and acidifying agents are effective, but only in the short term, and therefore under conditions of continuous manure depositions, such as occur in cattle feedlots, a requirement for frequent reapplication may increase their cost to farmers. Amending manure with zeolite, or dietary manipulation to reduce crude protein both suppress NH_3 emission from manure, however the large scale application of zeolite (especially in the modified or synthetic form) may not be cost effective, and the reduction in crude protein may negatively impact animal health and productivity. Compared to the above mitigation options, lignite has been suggested as a more practical, effective and also with a longer lasting effect on reducing NH_3 emission from manure (Chen et al. 2015).

Table 2.1 Mitigation techniques to reduce N loss from manure

Mitigation option	Summary of treatment	Key findings	Reference
Urease inhibitor (NBPT)	Application rate of 0, 1 and 2 kg/ha of NBPT at frequencies of 8, 16 and 32 days. The NBPT was applied to a simulated beef cattle feedyard manure surface.	NBPT was most effective applied at 8 day intervals. NH ₃ emission was reduced by 49-69% at 1 and 2 kg NBPT / ha respectively when applied every 8 days.	(Parker et al. 2005)
Urease inhibitors (NBPT and CHPT)	Study 1: A single topical application rate of NBPT or CHPT at 20 mg/kg manure. Study 2: Weekly application of NBPT for 6 weeks.	No urea was found in untreated pens. CHPT treated pens had 2 g urea/kg dry manure at day 4 but this disappeared by day 11. NBPT conserved 3 and 3.5 g urea/kg dry manure by day 4 and 9 respectively but this disappeared by day 14. Weekly application of NBPT conserved 17 g urea/kg dry manure by day 30 but urea concentration decreased once application stopped.	(Varel et al. 1999)
Compaction and covering of manure heaps	Manure was compacted in a layer of 30 cm depth and covered with plastic sheeting.	Compaction and covering reduced NH ₃ volatilization by 90% during the first summer storage. NH ₃ emissions were small over the subsequent storage period.	(Chadwick 2005)
Dietary crude protein concentration and source	Three dietary crude protein levels (11.5, 13 and 14.5 %) and three urea: cottonseed ratios (100:0, 50:50 and 0:100) were fed to steers.	Increasing protein concentration from 11.5 to 13% increased the quantity of urinary N excreted and also increased NH ₃ emission by 60 to 200%.	(Cole et al. 2005)
Diet digestibility and pen cleaning frequency	Two diets – control (typical feeding regime) and bran. Pen cleaning was done monthly at the end of the feeding period (166 days).	At a monthly pen cleaning interval, N loss was 45.1 and 25.2% in the control and bran diets respectively. At a pen cleaning interval of 166 days, N loss was 39.8 and 47.9% in the control and bran diets respectively.	(Farran et al. 2005)

Mitigation option	Summary of treatment	Key findings	Reference
Acidifying agents, urease inhibitor and humates	Two rates of alum and calcium chloride (4500 and 9000 kg/ha); 9000 kg/ha brown and black humate; and two rates of NBPT (1 and 2 kg/ha) applied to a simulated cattle feedlot.	Cumulative NH ₃ emission, as percent of the control, after 21 days were: 1.7 to 8.5% for alum, 23 to 25% for calcium chloride, 32% for brown humate, 40% for black humate and 34 to 36% for NBPT.	(Shi et al. 2001)
Acidifying agents	Five acidifying agents (alum, acetic, citric, lactic, and sulfuric acids) applied to dairy slurry to target pHs of 3.5 and 5.5.	NH ₃ loss was negligible (<2 mg NH ₃ kg ⁻¹) over 60 days of storage when slurry was acidified to pH 3.5. At pH 5.5 the greatest decreases in NH ₃ loss were obtained with sulfuric acid (81%) and alum (87%).	(Regueiro et al. 2016)
Clinoptilolite zeolite clay	Steers were fed with a diet containing 1.2% of clinoptilolite zeolite clay over a period of 168 days.	Addition of zeolite did not affect NH ₃ volatilization.	(Sherwood et al. 2005)
Raw lignite application to pen surface	Lignite was applied at 4.5 kg/m ² to a cattle pen surface. The control pens had no lignite.	Lignite resulted in 66% reduction in daily NH ₃ emission relative to the control over 40 days. Pen manure treated with lignite had more N (2.4%) compared to control (1.7% N).	(Chen et al. 2015)
Raw lignite application to pen surface	Lignite was applied at 3 and 6 kg/m ² to a cattle pen surface. The control pen had no lignite	Lignite resulted in 30% reduction in NH ₃ emissions compared to the control over 30-40 days. Lignite caused 40-57% increase in N ₂ O emissions but this was offset by lower indirect N ₂ O emissions due to the reduction in NH ₃ emission. The decrease in N content during stockpiling of lignite amended manure over 64 days was 15% compared to 33% in the control.	(Sun et al. 2016)

2.3 Lignite

2.3.1 Lignite formation and basic properties

Coal is an organic sedimentary rock formed from accumulated partially decomposing plant remains buried under anaerobic conditions and subject to high pressure and temperature over periods of several million years (O'Keefe et al. 2013). The progressive stages of coal formation are: peat; lignite; sub-bituminous; bituminous and; anthracite (low to high grade coal). Compared to the higher rank coals, lignite has high moisture content, high oxygen-containing functional groups, low carbon content and low calorific value (Závodská & Lesný 2006).

Because lignite is formed at the early stage of coalification, its properties are significantly influenced by the source of parent material as well as the environmental and geological conditions (Tran et al. 2015). Hence, there is a wide variation in the properties of lignite (Table 2.2). Lignite deposits are mainly used for power generation, usually close to the mines due to its high water content and low calorific value (World Energy Council, 2016). Lignite is also utilized for other reasons, including agriculture (discussed under section 2.3.3).

Table 2.2 Properties of lignites sourced from global deposits¹

Parameter	Range	References
Total carbon (%)	40-68	Fei et al. (2007); Sakaguchi et al. (2008); Scheffe et al. (2008b)
Labile carbon (%)	15-20	Sakaguchi et al. (2008); Sun et al. (2016)
pH _{water}	3.6-5.0	Scheffe et al. (2008b); Chen et al. (2015); Paramashivam et al. (2016)
Humic acids (%)	14-63	Woskoboenko et al. (1991); Dong et al. (2006)
CEC (cmol _c kg ⁻¹)	15-97	Whiteley and Pettit (1994a); Scheffe et al. (2008b); (Chen et al. 2015)
Porosity (%)	20-50	Küçükbayrak et al. (2001)
Surface area (m ² g ⁻¹)	207-229	Hulston et al. (2005)

¹ Australia, New Zealand, Turkey, United Kingdom, China

Parameter	Range	References
Ash (%)	0.6-5.0	Závodská and Lesný (2006); Fei et al. (2007)
Total Nitrogen (%)	0.1-0.7	Závodská and Lesný (2006); Fei et al. (2007)
Total Phosphorus (mg kg ⁻¹)	<0.5-478.3	Scheffe et al. (2008a); Paramashivam et al. (2016)
Total Potassium (mg kg ⁻¹)	31-219	Paramashivam et al. (2016)
Total Sulphur (mg kg ⁻¹)	6,539-13,799	Simmler et al. (2013); Paramashivam et al. (2016)
Total Calcium (mg kg ⁻¹)	400-4,900	Fei et al. (2007)
Total Manganese (mg kg ⁻¹)	1.5-280	Simmler et al. (2013); Paramashivam et al. (2016)
Total Cadmium (mg kg ⁻¹)	0.04-0.1	Simmler et al. (2013); Paramashivam et al. (2016)
Total iron (mg kg ⁻¹)	500-5,700	Fei et al. (2007)
Total copper (mg kg ⁻¹)	1.9-2.9	Simmler et al. (2013); Paramashivam et al. (2016)
Total Zinc (mg kg ⁻¹)	9.0-35.5	Simmler et al. (2013); Paramashivam et al. (2016)
Total Arsenic (mg kg ⁻¹)	1.8-3.6	Clark et al. (1980); Mar et al. (2013)

2.3.2 Australian lignite reserves

Of the global lignite reserves (320 gigaton) identified in 2017, the majority (over one quarter) were located in Russia (29% of global reserves), followed by Australia (24%), Germany (11%) and USA (10%) (Britt et al. 2017; BGR 2019). The world's leading countries based on lignite reserves in 2017 are presented in Figure 2.1. Australia's 2017 economically recoverable lignite reserve (i.e. part of the total reserve that can be recovered under the present time's technological and economic conditions (Hook et al. 2008)) was estimated at 76,508 million tons, and nearly all of it is located in the state of Victoria with more than 93% in the Gippsland Basin's Latrobe Valley (Britt et al. 2017, 2019). Apart from Victoria, other Australian states with lignite deposits are South Australia, Western Australia, Queensland and Tasmania (Figure 2.2) (Gloe 1991). The Australian lignite reserve is estimated to support over 100 years of production based on the 2016 extraction rates (Britt et al. 2017). Apart from lignite

mined at the Maddingley open cut (Otway basin) that is used for agricultural purposes (soil conditioners and fertilizers), lignite mined in Victoria is used almost exclusively for domestic power generation. Note: whilst there are many brown coal deposits across southern Australia only those in Victoria are considered economic and are being mined, as indicated by (★) in Figure 2.2.

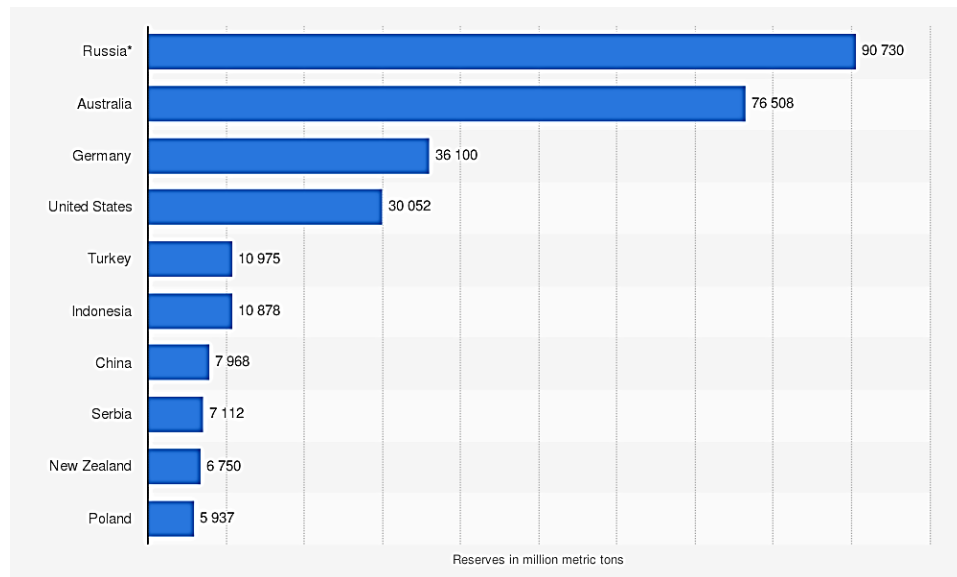


Figure 2.1 Leading countries based on lignite reserves in 2017 (Federal Institute for Geosciences and Natural Resources, BGR, 2017).

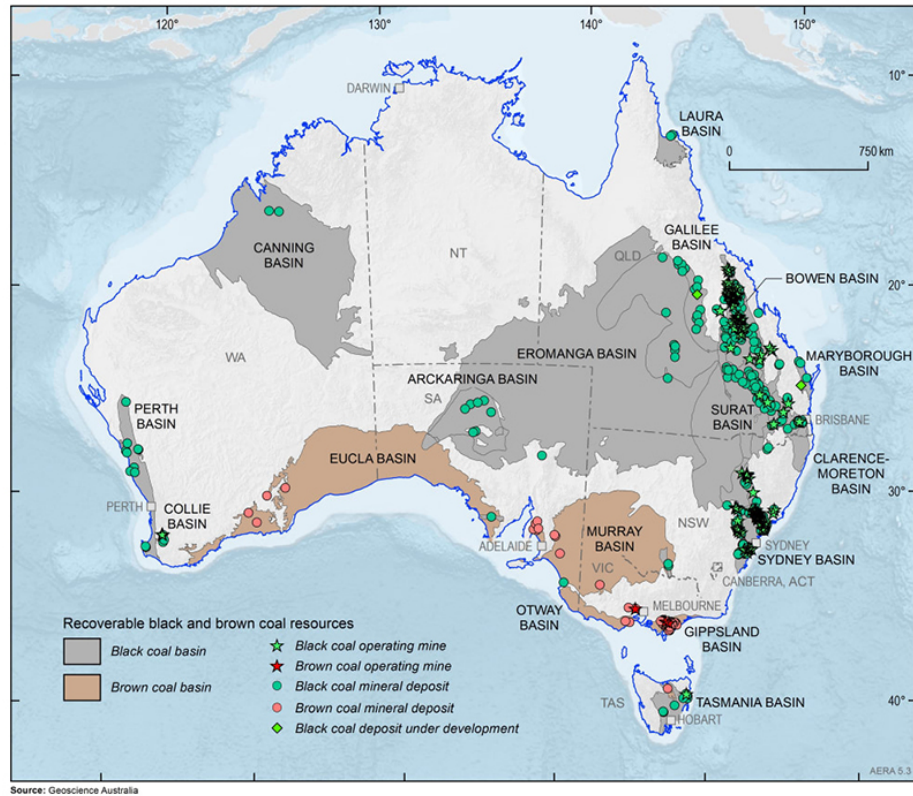


Figure 2.2 Coal deposits and mines in Australia (Geoscience Australia, 2017).

2.3.3 Uses of lignite

Lignite has been utilized in other areas aside from power generation due to its properties such as humic acids content, ion exchange, acidity, surface area and elemental composition (Table 2.2). This includes its use to: adsorb metal ion from acid mine drainage and wastewater (Mohan & Chander 2006; Havelcova et al. 2009), produce of synthetic natural gas through thermo-chemical processes (Kopyscinski et al. 2010), produce montan wax through solvent extraction (Wei et al. 2014), improve soil properties and plant biomass (Pusz 2007; Rao et al. 2013; Simmler et al. 2013), and to mitigate NH_3 loss from livestock manure (Chen et al. 2015; Sun et al. 2016; Dana & Ardeshtir 2018).

2.3.3.1 Lignite use in mitigating N loss from manure

The application of lignite (as-mined, sourced from Gippsland basin, Figure 2.2), at a rate of 4.5 kg m^{-2} (equivalent to $45 \text{ ton dry lignite ha}^{-1}$), to a feedlot cattle pen surface (prior to the introduction of cattle) reduced NH_3 volatilization from manure by 66%, relative to manure in pens with no lignite application, over a period of 40 days (Chen et al. 2015). In a similar study, Sun et al. (2016) reported a 30% reduction in NH_3 emission following the application of lignite to a cattle pen surface at $3\text{-}6 \text{ kg m}^{-2}$. Hao et al. (2007) found a 36 to 60% reduction in NH_3 emission from manure excreted by cattle when lignite extract was added to their diets, though this effect diminished after 53 days. Dana and Ardeshir (2018) reported a 47-91% reduction in NH_3 loss from broiler litter following the application of 10-30% lignite. A similar observation was made by Berg and Samer (2010) where the application of pulverized lignite to liquid swine manure resulted in a 70% reduction in NH_3 emission.

The capacity of lignite to suppress NH_3 emission or retain N has been suggested to be by different mechanisms related to different properties such as its; low pH/acidity which shifts the $\text{NH}_3/\text{NH}_4^+$ equilibrium ratio towards NH_4^+ with NH_4^+ retained in the manure (Sun et al. 2016); high CEC which enables the lignite to retain NH_4^+ on its adsorption sites (Chen et al. 2015); high labile C which enhances microbial immobilization of N (Chen et al. 2015); humic acid content which leads to inhibition of urease catalysed hydrolysis of urea (Dong et al. 2008; Chen et al. 2015); and pore structure which enables the lignite to retain molecules of $\text{NH}_3/\text{NH}_4^+$ (Tu et al. 2019).

In summary, lignite is effective in reducing NH_3 loss and this has been attributed variously to pH, labile C and CEC. However, the actual N retention capacity, and the main mechanism of the retention are unknown. It is unclear which property of lignite, and hence mechanism, is the key determinant of its N retention capacity. Knowledge on these will enable screening of lignites for prescriptive use as an NH_3 emission mitigation option in manure management.

2.3.3.2 Other agricultural uses of lignite

In addition to the use of lignite to reduce NH_3 loss from animal manures, lignite has also been used as a source of humic acid for agriculture (Tahir et al. 2011), as a soil conditioner to reduce heavy metal toxicity and improve nutrient use efficiency, as well as an amendment to improve composting (Table 2.3). Lignite was able to reduce heavy metal phytotoxicity by reducing metal mobility in soil and uptake by plant. Lignite has mixed effect on N use efficiency and suppression N_2O emission when applied to soil, with both stimulatory and inhibitory effects being reported in the literature. Similarly, its effect on plant yield or dry matter production was inconsistent. The application of lignite to soil or lignite humic acid to organic material both resulted in the reduction in microbial respiration, thus reducing CO_2 emission. Its application as odour adsorbing agent, during composting, has also been reported. In summary, though a number of studies have reported on the agricultural application of lignite, further research may be required to address gaps such as factors influencing lignite effect on N transformation and N use efficiency in soil, plant growth as well as other biochemical parameters (other than odour emission) of the manure composting process that are affected by lignite addition.

Table 2.3 Agricultural application of lignite and lignite derived products (other than for NH₃ control)

Research aim	Summary of treatment	Key findings	Reference
Lignite as soil amendment: Effect on plant growth and cadmium (Cd) uptake.	Pot experiment with ryegrass. Lignite rate: 0 - 7.1% w/w of soil/biosolid media.	Lignite reduced extractable Cd levels and uptake by ryegrass by up to 52%. Lignite effect on soluble Cd was more effective in soil with low pH. Lignite rate at 1.0-3.4% had no significant effect on ryegrass yield whilst at 7.1%, yield decreased by 10-20%, compared to control.	(Simmler et al. 2013)
Lignite as soil amendment: Reduce phytotoxicity in soil contaminated with heavy metals (Cd, Cu, Pb and Zn).	Pot experiment with mixed grasses (ryegrass, red fescue and meadow grass). Lignite rate: 0 -105 t ha ⁻¹ .	Lignite decreased solubility / mobility of heavy metals in soil and their uptake by plants, especially at higher lignite rates, and also resulted in increased dry matter production.	(Pusz 2007)
Lignite-urea blend to improve N use efficiency and plant yield.	Pot experiment with silver beet.	Lignite-urea blend resulted in a 23-27% increase in plant yield compared to urea only. The blend increased N uptake, and suppressed N ₂ O emission by 13-29%.	(Saha et al. 2016)
Lignite as soil amendment: Effect on N availability and microbial community.	Experiment 1: Microcosm incubation. Effect of lignite on microbial community structure, enzyme activity and N dynamics. Lignite rate: 10 t ha ⁻¹ . Experiment 2: effect of lignite on respiration and N dynamics in unfertilized soil.	Lignite had a minor and inconsistent effect on N concentration in soil but reduced total CO ₂ emissions. Lignite's effect on microbial biomass was negligible but resulted in a shift in microbial community.	(Tran et al. 2015)

Research aim	Summary of treatment	Key findings	Reference
Lignite as soil amendment: Effect on N and heavy metal mobility in soil (with or without biosolid).	Lysimeter experiment with perennial ryegrass. Lignite rate: 20 t ha ⁻¹ .	Lignite reduced pasture growth and nutrient uptake compared to biosolid or urea alone. There was a 90% increase in N ₂ O emissions when lignite was added to soil receiving urea. Lignite reduced NO ₃ ⁻ leaching, though non significantly.	(Paramashivam et al. 2016)
Effect of lignite humic acid on wheat straw decomposition during incubation.	Lignite mixed with wheat straw at a ratio of 1:1 and incubated for 4 weeks at 22 °C.	Lignite inhibited microbial consumption of O ₂ by 30%. Lignite increased the total alkaline extractable organic fraction but reduced the water soluble fulvic fraction remaining in the straw at the end of incubation.	(Whiteley & Pettit 1994b)
Lignite as odour and moisture absorbent in composting swine manure.	Swine manure mixed with lignite at 1:1 v/v with or without rice peel and ginned cotton residue.	Odour was eliminated in the 1:1 lignite: feedstock mixing ratio. Lignite, mixed with ginned cotton and rice peel residues, improved the composting process.	(Georgacakis et al. 1996)

2.4 Composting of manure

Composting is a spontaneous biological decomposition of organic materials under predominantly aerobic conditions into a stabilized, mature and sanitized product (Bernal et al. 2009; Qian et al. 2014). The composting process is characterized by the mineralization of organic matter, generating CO_2 , CH_4 , $\text{NH}_4^+/\text{NH}_3$, N_2O and heat, as well as the transformation of organic matter into a more stable form, by microorganisms leading to a reduction in mass and volume of the initial feedstock (Bernal et al. 2009; Arriaga et al. 2017). The management of the process, as well as the composting system, is critical to producing a compost with a desired agronomic value (Bernal et al. 2017). The characteristics of the initial feedstock influence the biochemical and physical parameters (e.g. temperature, porosity, pH, nutrient availability and transformation, moisture content, microbial activity, and organic matter decomposition rate) during the composting process (Fraser & Lau 2000; Himanen & Hänninen 2011; Bernal et al. 2017; Barthod et al. 2018).

2.4.1 Composting systems

Diaz et al. (2011) grouped composting systems into two broad categories: windrow system (accumulation of substrate into piles) and in-vessel systems (substrate is composted in a reactor). Bernal et al. (2017) on the other hand classified composting system as either open or closed depending on the aeration system, temperature control and moisture removal methods.

In open systems, the material to be composted is piled or placed in a trapezoidal windrow and then aeration (O_2 supply) is accomplished through i) passive aeration (static pile or windrow with natural ventilation through convection), ii) forced aeration by sucking or blowing air through the composting material with the aid of a compressor and perforated pipes, and iii) turning, where the pile or windrow is mechanically turned, combined with passive aeration

(Hassouneh et al. 1999; Bernal et al. 2017). Compared to forced aeration, turning of the composting material is less effective in providing O₂ though it ensures mixing of the material (Michel 1996).

In a closed system, the material to be composted is kept in a reactor or vessel and aeration is accomplished by forcing air (either continuously or intermittently) through the composting material. The closed composting system enables greater control over the composting process compared to the open system, as O₂ supply, temperature and moisture can be adjusted based on microbial activity (Bernal et al. 2017).

2.4.2 Monitoring the biochemical and physical processes during composting

The main parameters reflecting the biochemical and physical changes that occur during the composting process are summarized in the sections below.

2.4.2.1 Temperature

A typical variation in temperature, with time, during composting is presented in Figure 2.3. The beginning of the composting process is characterized by the rise in temperature due to the onset of breakdown of the simple labile compounds and nitrogenous materials such as sugars, amino acids and proteins, by microorganisms (Brito et al. 2008). This is the mesophilic phase and usually lasts for a period of 1-3 days with temperatures < 40 °C (Bernal et al. 2009). The next phase, thermophilic, is characterized by maximum degradation of organic matter and temperatures in excess of 40 °C leading to destruction of pathogens. During this phase, there is microbial degradation of fats, cellulose and hemicellulose (Bernal et al. 2009; Diaz et al. 2011). At the later stage of the composting period (cooling/ curing phase), the temperature begins to drop due to depletion of degradable organic material leading to a reduction in thermophilic microbial activity, as well as recolonization of the composting material by mesophilic microorganisms (Bernal et al. 2009). The optimum temperature for composting is reported as

40-65 °C with temperatures > 55 °C required to kill pathogenic microorganisms (de Bertoldi et al. 1983).

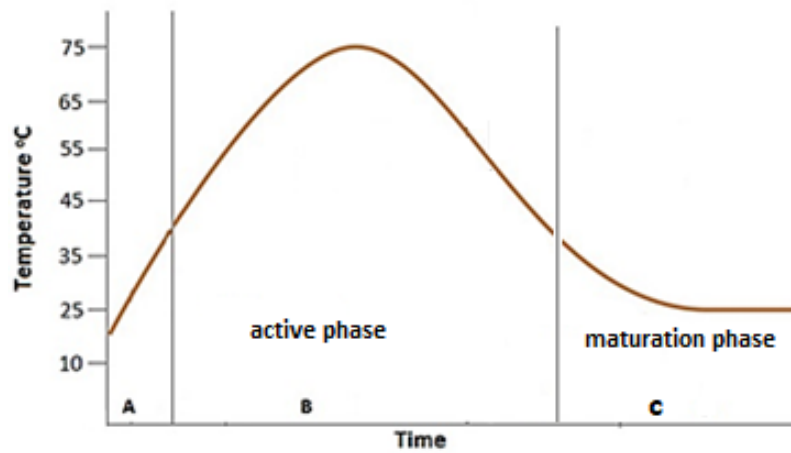


Figure 2.3 Typical variation in temperature and the phases, of the composting process: A = mesophilic; B = thermophilic; C = mesophilic. *Adapted from Cooperband (2002).*

2.4.2.2 pH

The three main acid-base systems that influence the pH of the composting feedstock are carbonic, $\text{NH}_4^+/\text{NH}_3$ and organic acids (Sundberg 2005). The mineralization of organic acids and release of NH_4^+ within the composting material causes pH to increase (Gao et al. 2010). Decrease in pH during composting has been attributed to the production of organic acid from the microbial breakdown of sugars and fats and also the incomplete oxidation of organic matter (Liu et al. 2011; Awasthi et al. 2015). The combination of low pH (< 6) and high temperature (≥ 46 °C) has been reported to inhibit the transition from mesophilic to thermophilic phase during the initial stages of composting due to sensitivity of microorganisms to the combined acidic and high temperature conditions (Sundberg et al. 2004). In terms of microbial activity, a pH range of 6.7-9.0 is favourable for composting. However, at pH > 7.5, especially during the thermophilic phase, leads to the loss of N through NH_3 volatilization (Bernal et al. 2009).

2.4.2.3 N transformations

Nitrogen dynamics during composting are influenced by a number of factors such as temperature, pH, C:N ratio, initial N content, type of feedstock and the composting management strategy (Bernal et al. 2009; Maeda et al. 2011). During composting, organic N is mineralized to NH_4^+ which corresponds with the peak of CO_2 emission from the compost heap (Sundberg 2005). At the early thermophilic phase of composting, NH_4^+ is the dominant form of N in the compost. The NH_4^+ is transformed into other forms of N (NO_3^- , N_2O and N_2) by a number of nitrifiers and denitrifiers as the composting progresses leading to a reduction in NH_4^+ and the accumulation of NO_3^- and can also be lost as NH_3 at alkaline pH (Figure 2.4) (Sundberg 2005; Bernal et al. 2009; Maeda et al. 2011). The nitrification and accumulation of NO_3^- occurs under predominantly mesophilic temperatures ($< 40^\circ\text{C}$) as the microorganisms responsible are inhibited at thermophilic temperatures (Bernal et al. 2009; Caceres et al. 2018). Hence the accumulation of NO_3^- in excess of NH_4^+ has been used as a compost maturity index (e.g. $\text{NH}_4^+/\text{NO}_3^-$ ratio of < 0.16) (Bernal et al. 1998a). Usually, due to the loss of organic matter (mass), the concentration of total N increases during the composting process, provided N loss from the compost is minimized (Bernal et al. 2009). The pathways for N loss during composting are the emissions of NH_3 (main pathway, 11-92% of total N loss Table 2.4), N_2O and N_2 and the leaching of NO_3^- and NH_4^+ (Figure 2.4) (Eghball et al. 1997; Larney et al. 2008b; Caceres et al. 2018). The loss of N is a major challenge for manure composting with the extent of loss dependent on factors such as feedstock characteristics, composting method and management strategy (Table 2.4). In previous studies, total N loss from the windrow method ranges from 12 to 42%, whilst for closed systems (with forced aeration and shorter composting period), N loss ranges from 6 to 25%. The addition of a bulking agent, such as sawdust, straw and woodchip (Michel Jr et al. 2004; Larney et al. 2008b), is a common practice

in cattle manure composting, and this tends to reduce N loss. For example, addition of a bulking agent reduced N loss from 12-42% to 7-36% using a windrow method (Table 2.4).

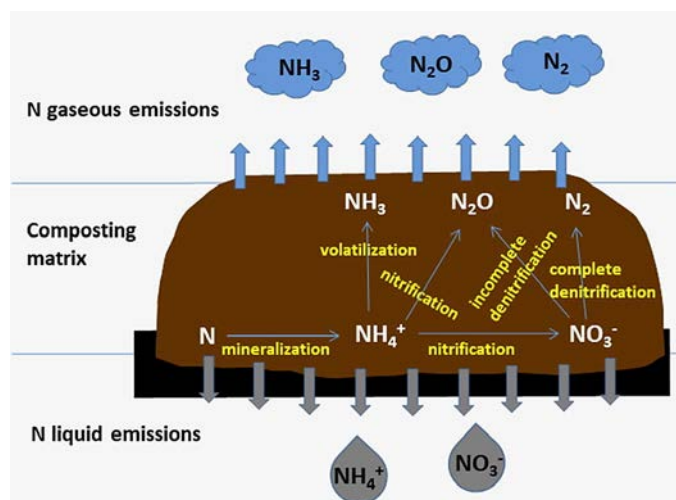


Figure 2.4 Nitrogen transformations during composting (Caceres et al. 2018).

2.4.2.4 C:N ratio

At the start of the composting process, a C:N ratio of 25:1-35:1 is considered optimum, with higher C:N ratio prolonging the composting process due to excess biodegradable substrate whilst lower C:N ratio results in the loss of excess N (Bernal et al. 2009; Bernal et al. 2017). The low C:N ratio of animal manure (e.g. between 15 and 22 for cattle manure, depending on the presence and type of bedding material (Larney et al. 2008a)) is one of the chemical properties that inhibits the efficiency of the manure composting process (Bernal et al. 2009). The incorporation of substrates high in C, such as sawdust or wood shavings, in the manure can improve the manure's C:N ratio, and in turn, its composting (Tucker et al. 2015). During composting, the loss of dry matter occurs faster than the loss of N and results in a decrease in the C:N ratio (Awasthi et al. 2015). Amendments added to the feedstock that are able to retain N during composting may also contribute to the decrease in C:N ratio during composting, and also increase the N content of the final compost (Barthod et al. 2018).

Table 2.4 Nitrogen loss during composting of cattle manure

Feedstock ²	Composting method	Management strategy	TN loss (% of initial N)	Measured forms of N loss (% of TN loss)	References
Beef feedlot manure	Windrow (W x L x H = 3 m x 10m x 1 m) in open concrete area	Turned at 7-10 days interval over a period of 72-107 days.	19-42	NH ₃ = > 92 NO ₃ +NH ₄ = < 2	Eghball et al. (1997)
Dairy manure deep litter	Windrow (W x L x H = 1.9m x 3.7 m x 1.3 m)	Compacted or covered with porous tarpaulin. No turning (132 days).	12-28	NH ₃ = 80 N ₂ O = <0.3	Sommer (2001)
Free stall dairy manure from sawdust and straw bedded pen	Windrow (W x L x H = 3.2 m x 11-28 m x 1.2 m) on concrete pad	Turned at varying intervals (17 times over a period of 110-155 days).	7-38	-	Michel Jr et al. (2004)
Beef manure from wood chip or barley straw bedded pen	Windrow (W x L x H = 2.5 m x 10-11 m x 2 m)	Turned at varying intervals (8-16 times over a period of 124 days).	19-36	-	Larney et al. (2008b)
Dairy manure+ molasses, paper, mono and dibasic sodium phosphates	Closed system (170 L); 0.9 m deep and 0.5 m diameter	Forced aeration throughout the composting period (15 days).	12-25	NH ₃ = 60-99	Liang et al. (2006)
Dairy slurry + Barley straw (1:1)	Laboratory scale: closed system (10 L)	Forced aeration (low and high flows) throughout the composting period (31 days).	6-22	NH ₃ = 14-52 N ₂ O = 0.8-1.6	Chowdhury et al. (2014)
Dairy manure from straw bedded pen	Heap in enclosed cell (area: 3.5 m ² , volume: 8 m ³)	No turning or turned 2 times over a period of 46 days.	7-26	NH ₃ = 51 N ₂ O = 7	El Kader et al. (2007)
Manure from wheat straw bedded pen	Heap/ stack (10-12 m ³)	No turning or turned 1-3 times over a period of 112-133 days.	25-37	NH ₃ = 11-51	Parkinson et al. (2004)

² Feedstock: manure alone or manure + bulking agent.

2.4.2.5 Organic matter degradation

Mineralization and humification are the major process causing the transformation of organic matter during composting (An et al. 2012). The aerobic oxidation of organic carbon by microorganisms, produces CO₂, NH₃, water, organic acids and heat and leads to organic matter loss (loss in mass of initial feedstock) as the composting progresses, with the greatest loss at the thermophilic stage (Tiquia et al. 2002; Bernal et al. 2009). Feedstocks containing resistant organic substrates such as lignin (compared to cellulose and hemicellulose which are relatively easy to degrade) are less likely to lose organic matter (An et al. 2012). The rate of organic matter loss decreases with composting time due to a reduction in the labile organic fraction and the synthesis of new complex and polymerized organic compounds (Bernal et al. 2009). During composting, the loss of C is compensated by the stabilization of the remaining organic compounds and increase in the mineral elements concentrations (Bernal et al. 2009).

2.4.2.6 Microbial activity

Organic matter decomposition is carried out by a succession of diverse microorganisms with varied optimum temperature requirements. Mesophiles require temperatures in the range of 25 - 40 °C whilst thermophiles require temperatures > 45 °C (Sundberg 2005). Bacteria are dominant during the early stages of composting. Fungi are present throughout the whole composting process and become dominant when the moisture content gets below 35% w/w. However, their activity is reduced at temperatures greater than 60 °C. During the final (mesophilic) phase (Figure 2.3), actinomycetes predominate and degrade, together with fungi, recalcitrant substrate (Bernal et al. 2009). Key factors influencing microbial activity during composting are temperature, oxygen, moisture, pH and substrate composition (Sundberg 2005).

2.4.2.7 Gaseous emissions

The composting process is characterized by the generation of gases, mainly CO₂, CH₄, NH₃ and N₂O, during the mineralization or degradation of organic matter (Bernal et al. 2009).

Carbon dioxide evolution usually correlates directly with microbial activity or respiration and thus, emission levels are higher during the thermophilic phase of composting (Bernal et al. 2009). The evolution rate of CO₂ has been used as a compost maturity index with a rate of between 7.3 and 8.1 mg CO₂/g OM/day (or 2.0 and 2.2 mg CO₂-C/g OM/day) suggested for stable and mature compost (Seal et al. 2012; Nakhshiniev et al. 2014).

Formation of CH₄ occurs through reduction of CO₂ by methanogens in anaerobic pockets within the compost (Boldrin et al. 2009; Yang et al. 2013). The possible oxidation of CH₄ to CO₂ as it moves towards the compost surface with higher O₂ concentration has been reported (Hao et al. 2001; Szanto et al. 2007).

Ammonia volatilization during composting is favoured by high temperature, and also pH, which increases the ratio of NH₃ to NH₄⁺ (Bernal et al. 2017; Wang et al. 2018). During the initial stages of composting, the pH and C/N of the feedstock are the main factors impacting NH₃ volatilization (Ekinci et al. 2000; Bernal et al. 2017). The release of gaseous NH₃ from internal void spaces during turning/aeration of the composting material also enhances the NH₃ emission (Ogunwande et al. 2008). Ammonia emission is the main form of N loss during composting, occurring at a much higher rate than N₂O emission, and can account for up to 70% of initial manure N (Hao & Benke 2008).

The formation of N₂O during composting is a result of incomplete nitrification or denitrification of NO₃⁻ to N₂O and is usually facilitated by anaerobic conditions within the compost heap (Yang et al. 2013; Barthod et al. 2018). Nitrous oxide generation from the denitrification of

NO_3^- is unlikely to occur during the thermophilic phase of composting because autotrophic nitrifier activity (which generates NO_3^-) ceases at $> 40^\circ\text{C}$ (Fukumoto et al. 2003; Thompson et al. 2004).

2.4.3 Compost stability and maturity

Compost stability relates to the degree of microbial activity and is assessed by respirometric (O_2 consumption or CO_2 evolution) measurements, whilst compost maturity refers to the extent of completeness of composting or absence of phytotoxic organic compounds (Gomez-Brandon et al. 2008; Bernal et al. 2017). Immature compost contains organic matter that has not been sufficiently degraded, and contains phytotoxic compounds. These phytotoxic compounds include low molecular weight organic acids and phenols. Therefore application of immature compost to soil may lead to inhibition of seed germination and plant growth as well as a reduction in oxygen and N because the readily degradable OM in the immature compost continues to decompose (Ofosu-Budu et al. 2010; Selim et al. 2012). There are several indices, usually grouped under physical (e.g. temperature, particle size and colour), chemical (e.g. $\text{NH}_4^+/\text{NO}_3^-$ ratio, C/N ratio and NH_4^+ concentration) and biological (e.g. CO_2 evolution, germination index and microbial biomass) criteria, for assessing the stability and maturity of composts (Bernal et al. 2009; Oviedo-Ocaña et al. 2015).

An ammonium to nitrate ratio of <1 is the upper reported limit for indicating compost maturity, with values ranging from 0.04 to <1.0 and generally a value of <0.16 considered a good indicator (Bernal et al. 1998a) Sánchez-Monedero et al. (2001) Ko et al. (2008)). Other chemical indices used as indicators for mature compost are NH_4^+ of $< 400 \text{ mg kg}^{-1}$ and C/N ratio of < 12 (Bernal et al. 1998a).

Germination index (GI) is a measure of the combined seed germination and relative root elongation in a compost extract relative to a control (water) and reflects phytotoxicity and extent

of compost maturity (Ko et al. 2008; Tian et al. 2012). The germination index increases with composting time due to the reduction in $\text{NH}_4^+/\text{NH}_3$ concentration and the decomposition of low molecular weight short chain fatty acids such as acetic acid (Guo et al. 2012; Yang et al. 2013). Aside from the presence of phytotoxic compounds in the compost, the GI is also influenced by the type of seed and extract preparation method (e.g. dilutions) (Gariglio et al. 2002). As a result, a wide range of GI values (> 50-110%) have been reported in the literature as an indicator of compost maturity (Tiquia et al. 1996; Bernal et al. 1998a; Tian et al. 2012; Tambone et al. 2015).

The degree of CO_2 production (or O_2 consumption) is indicative of compost stability and maturity. Compared to mature compost, immature compost has high CO_2 production as a result of intense microbial degradation of labile organic matter (Hue & Liu 1995; Bernal et al. 2009). A CO_2 -C evolution rate of 2.0-2.2 $\text{mg g}^{-1} \text{OM day}^{-1}$ indicates a stabilized compost (Seal et al. 2012; Nakhshiniev et al. 2014). Other compost stability indices include the Dewar self-heating test based on temperature increase in a Dewar vessel, the specific oxygen uptake rate (SOUR) test with values between 1.5 and 2.5 $\text{mg O}_2 \text{ g}^{-1}$ volatile solid as stability threshold, and the Solvita test based on CO_2 and NH_3 emissions (Wichuk & McCartney 2010; AS-4454 2012).

2.4.4 Lignite use in composting

There are very limited studies reporting the use of lignite, or its derivatives, in composting with manure or other organic materials. Therefore findings from previous laboratory incubation studies have been used to predict the behaviour of lignite in compost. During the incubation (at 22 °C for 4 weeks) of wheat straw, Whiteley and Pettit (1994a) observed a significant increase in microbial stability with the addition of lignite humic acid. The lignite inhibited microbial respiratory activities leading to a reduction in cumulative O_2 consumption by 30%. Physical protection and substrate adsorption (likely due to the high porosity and CEC of the lignite), as well

as the release of microbial toxins and enzyme inactivation were assigned by the authors as possible means by which the lignite suppressed respiratory activities. Tran et al. (2015) attributed lignite's ability to suppress microbial respiratory activities (during a soil incubation study) to the release of toxic substances, such as phenols, poly-aromatic hydrocarbons and benzenes, by the lignite. Though the microbial inhibitory capability of lignite has been reported under incubation conditions, it remains unknown whether or not this effect will be observed under composting conditions. Georgacakis et al. (1996) reported that, feedstocks containing wet and malodorous swine manure were composted successfully when mixed with lignite, due to the moisture and odour absorbing properties of the lignite. The authors, however, did not discuss how the presence of lignite affected physicochemical parameters (e.g. pH, temperature, and C and N transformations) during the composting process.

Based on the biochemical and physical changes that occur during the composting process and the properties of lignite (Table 2.3), the possible effects of lignite on temperature, organic matter degradation and N transformation are discussed below.

Temperature and organic matter degradation: The combination of low pH (< 6) and high temperature (≥ 46 °C) have been reported to inhibit the transition from the mesophilic to thermophilic phase during the initial stages of composting (Sundberg et al. 2004). This phenomenon might be observed during composting of lignite amended manure if the lignite is able to significantly reduce the pH of the manure. However, this pH effect of lignite (if it occurs) is expected to reduce over the course of the composting process. The possible inhibition of microbial activity by lignite might result in less organic matter loss/degradation during the composting of manure. Also, amending manure with lignite will provide an additional C source, thus increase the C/N ratio of the manure, due to the high C content of lignite (40-68%, Table 2.3).

Nitrogen loss and transformations: The low pH of lignite is however expected to reduce the extent of N loss by inhibiting NH_3 volatilization, which is enhanced at pH above 7.5 (Bernal et al. 2009). Sun et al. (2016) reported of gradual neutralization of the acidity of lignite after 3 weeks of pen application and that the lignite was effective at reducing NH_3 volatilization when pH was less than 6.5. It is however unclear whether the lignite creates an acidic condition in the manure, leading to a reduction in NH_3 emission during composting. The ability of lignite to inhibit NH_3 volatilization from manure, when applied to the surface of cattle pen, has also been attributed to its high CEC which enables the lignite to retain NH_4^+ on its exchange site (Chen et al. 2015). However, it is unknown if this mechanism of N retention by lignite will persist under composting conditions.

In a summary, the effects of lignite on the biochemical and physical changes during composting of manure, as well as on the quality of the resultant compost, remains unclear and research addressing these gaps is required. Composting is a major recycling option in the management of manure generated in intensive animal production systems (Larney & Hao 2007; Bernal et al. 2009). As lignite has been shown to have beneficial effects in the pen, it is important to assess the impact of lignite on the composting process. Nitrogen initially retained in manure, owing to the application of mitigation techniques during the initial stages of manure management, is often lost during the later stages of manure management (Gerber et al. 2013). Determining if the N retention by the lignite that occurs during the initial stage of manure management persists during the composting process will provide knowledge to optimise manure management.

2.4.5 Carbon and nitrogen mineralization from manure

Animal manure (composted or non-composted) collected from feedlots is usually applied directly to soil to increase soil organic matter levels, reclaim degraded soil and as source of N and

essential nutrients for plants (Bernal et al. 1998c; Eghball & Power 1999; Kaleem et al. 2007). Over application of manure can lead to nutrient loss and contamination of surface and groundwater, whilst under application can affect crop yield (Van Kessel & Reeves 2002). In order to obtain maximum benefit from manure application to soil, and minimize potential pollution, such as leaching of NO_3^- , the rate and timing of the application should be based on the expected N mineralization from the manure (Hartz et al. 2000; Qian & Schoenau 2002).

Following the application of manure to soil, the mineralization of nutrients (e.g. carbon and nitrogen) occurs through microbially mediated processes, which are affected by temperature, soil properties and the manure characteristics (Eghball et al. 2002; Qiu et al. 2008; Azeez & Van Averbek 2010). Aulakh et al. (2000) reported that mineralization of manure N is inversely related to the C:N ratio and directly related to N content. Chadwick et al. (2000) reported that the C:organic N ratio of manure accounted for 40% of the variation in the N mineralized in contrasting manure types. In addition, composting alters manure characteristics and thereby influences the pattern and rate of nutrient mineralization (Eghball et al. 2002). Usually, composted manure has slower C and net N mineralization rates than non-composted manure due to the conversion of labile N to inorganic N as well as the loss of labile forms of C as CO_2 and the stabilization of organic matter during the composting process (Hartz et al. 2000; Eghball et al. 2002; Bernal et al. 2009).

It is expected that the addition of lignite to manure, to minimize N loss, will alter the physicochemical characteristics (e.g. pH, C and N contents) of the manure, and in turn, the nutrient mineralization dynamics.

2.5 Key knowledge gaps

Though the application of lignite to animal manure as an NH_3 emission mitigation technique has been demonstrated, there are key knowledge gaps in our understanding of;

- i. The capacity for N retention by lignite, and the mechanism by which the retention occurs, how the properties of lignite (e.g. CEC, pH, forms of C, pH buffering capacity and labile C) affect these, and how they are affected by changes in the lignite's environment such as changes in pH resulting from continuous deposition of manure in a cattle pen;
- ii. How lignite changes the biochemical and physical processes, including gaseous emissions, that occur during the composting of manure, as well as the characteristics of the final compost; and
- iii. How lignite affects the dynamics of nutrient mineralization from manure (non-composted and composted) following its application to soil.

The respective hypotheses for the three knowledge gaps were that;

- i. The N retention capacity of lignite will be driven mainly by its CEC, pH and labile C, and the N retention capacity will vary with the origin of the lignite.
- ii. Lignite will continue to retain N in the manure due to the lignite's low pH and the high CEC, serve as additional C source for microbes but due to the low pH of lignite, it will delay the transition between mesophilic and thermophilic phases of composting.
- iii. Due to lignite's ability to suppress microbial activity, amending manure with lignite will reduce both C and N mineralization from the manure when applied to soil.

CHAPTER 3: Characterization of Victorian Lignites – Mechanisms and Capacity for Nitrogen Retention

3.1 Introduction

The capacity of lignite to suppress NH_3 emission from animal manure has been demonstrated by a number of studies. For instance the application of 3-6 kg lignite m^{-2} to the surface of a cattle pen resulted in a 30-66% reduction in NH_3 volatilization from manure compared to manure without lignite (Chen et al. 2015; Sun et al. 2016). Also, Dana and Ardeshir (2018) reported a 47-91% reduction in NH_3 loss from broiler litter following the application of 10-30% lignite on weight basis. Lignite's capacity to mitigate NH_3 emission has been attributed to its various properties – such pH, CEC, pH buffer capacity and labile carbon content. Detailed discussions on the formation of lignite, its properties and application to mitigate NH_3 emission from manure are provided under section 2.3 of Chapter 2. Whilst lignite is effective in reducing NH_3 emission from manure, and certain properties are considered important for this, the mechanism of, and capacity for retention, and the relative importance of the different properties to these are not well known. In addition the properties of lignite are significantly dependent on the source of the parent material as well as the environmental and geological conditions (Tran et al. 2015).

The objectives of this work were to determine; i) the characteristics of five different lignites sourced from Victorian deposits, ii) the capacity for N retention of the lignites, and the mechanisms by which retention is achieved, iii) how the lignites' properties, such as CEC, forms of C, pH, pH buffer capacity and labile C, affect their N retention capacity and the mechanisms of N retention. The effect of lignite properties on N retention was assessed under increasing pH condition to simulate the increasing pH of the manure-lignite system due to the continuous deposition of manure (alkaline pH) onto the lignite (acidic pH).

3.2 Materials and methods

3.2.1 Source of lignite materials

Five lignites (Bacchus Marsh, Yallourn, Latrobe, Morwell and Loy Yang) were sourced from energy generation and coal technology firms operating in open cut mines in Victoria, Australia. Representative samples were taken from stockpiles of crushed lignite (recently excavated with no treatment of any sort). The Bacchus Marsh lignite was obtained from the Maddingley mine, the Yallourn and Latrobe lignites were sourced from the Yallourn mine, the Morwell lignite was obtained from the Morwell M1 seam at Hazelwood, and the Loy Yang lignite was sourced from the Loy Yang mine. With the exception of Bacchus Marsh lignite, which was sourced from the Otway Basin, the lignites were sourced from the Gippsland Basin's Latrobe Valley (Gloe 1991) (Figure 3.1).



Figure 3. 1 A map showing the sites where the lignites were sourced from (purple colour represents sub-basin): Bacchus Marsh lignite (green square, in the Otway Basin), Yallourn, Latrobe, Morwell and Loy Yang (red square, in the Gippsland Basin) all in the State of Victoria (indicated with a black arrow on the map of Australia).

3.2.2 Characterization of lignites: chemical properties, surface morphology, and carbon functional groups

Prior to characterization, the lignites were oven dried at 40 °C to constant weight, ground and sieved to < 2 mm. Electrical conductivity (EC) (in water) and pH in water and 0.01M CaCl₂ were determined at a lignite: extract ratio of 1:5 w/v using a pH/EC meter (TPS, smartCHEM-LAB) after shaking end over end for 1 hour. Labile C (potassium permanganate (KMnO₄) oxidisable C) was determined as described in method 6E1 of Rayment and Lyons (2011). Briefly, 0.1 g of lignite (ground to < 0.5 mm) was placed in a 50 mL centrifuge tube and then shaken in 25 mL of 0.033 M KMnO₄ and 0.1 mL CaCl₂ for 2 min and allowed to stand for 5 min. Extracts were diluted with MilliQ water (1:50) and absorbance was determined with a spectrophotometer (Novaspec II) at a wavelength of 550 nm. The concentration of KMnO₄ left in the solution (equivalent to oxidized C) was determined using a previously developed standard curve from five different 0.033 M KMnO₄ concentrations, including a blank. The labile C was calculated from the difference of reacted and unreacted (original concentration) KMnO₄. The pH buffering capacity of the lignites was determined using a modified method of Aitken and Moody (1994). In brief, incremental amounts of 0.04 or 0.08 M NaOH were added to 4 g of dry lignite (<2 mm) suspended in 0.01 M CaCl₂ (volume of CaCl₂ depends on the volume of NaOH to be added) in a 50 mL centrifuge tube such that the final volume after the NaOH addition was 20 mL. Chloroform (0.15 mL) was then added to each tube to suppress microbial activity and the samples were shaken end over end for 1h and left to equilibrate for 6 days. The pH buffer capacity was calculated from the reciprocal of the slope of the linear portion of the buffer curve (pH versus OH⁻ (mmol kg⁻¹ lignite) added). Total C and N were analyzed using a LECO Trumac CN Analyzer. The element concentrations were determined using modified methods of Paramashivam et al. (2016) and Simmler et al. (2013) as follows; Dry lignite (0.5 g) was digested with 5 mL concentrated HNO₃ and 3 mL 30% H₂O₂ at

60 °C for 0.5 h and then at 120 °C until the digest became clear, after which they were diluted to 50 mL, filtered and analyzed with ICP-OES (Perkin Elmer Optima 8300 DV-radial view). The base cation exchange capacity (CEC_B) was determined from the sum of exchangeable bases (Ca^{2+} , Mg^{2+} , Na^+ and K^+), using a modified version of the methods described by Ross and Ketterings (1995) and Rayment and Lyons (2011). Effective CEC (CEC_E), was determined from the sum of CEC_B and the exchange acidity (H^+ plus Al^{3+}). Procedures for the determination of the exchangeable bases, and exchange acidity are described in methods 15E1, 15F1/F2 and 15G1 respectively of Rayment and Lyons (2011). Images of the surface morphology of air dry lignites were obtained using a scanning electron microscope (FEI Quanta FEG 200 ESEM, equipped with an Oxford 10 mm SDD Inca X-act X-ray detector and operated at 10 kV).

Solid state ^{13}C NMR spectra, which determines the allocation of organic C to the different C functional groups present in the lignites, were acquired on a 200 Avance spectrometer (Bruker Corporation, Billerica, MA, USA) equipped with a 4.7 T, wide-bore superconducting magnet operating at a resonance frequency of 50.33 MHz. Dry, finely ground lignite samples (245-260 mg) were packed into 7 mm diameter zirconia rotors with a Kel-F[®] end caps and spun at 5 kHz. Chemical shifts were calibrated to the methyl resonance of glycine. Cross-polarization (CP) and direct-polarization (DP) ^{13}C NMR analyses were completed for all lignite samples. For CP ^{13}C NMR analysis, a 90° pulse of 3.2 μs and 195 watts, a contact time of 1ms and a recycle delay of 1 s were used and 10,000 scans were acquired for each sample. For DP ^{13}C NMR analysis, a 90° pulse of 4 μs and 180 W and a recycle delay of 90 s were used and 488-500 scans were acquired for each sample. The acquired spectra were processed using the Bruker TopSpin 3 software. Absolute signal intensities were acquired for all lignite samples and the signal associated with an empty rotor was subtracted after correcting for differences in the number of scans acquired for each sample. The signal intensity within the resultant spectra was integrated over a range of

chemical shifts limits using the methods presented by Baldock et al. (2013). In these calculations, the signal intensities in spinning side bands were allocated to their parent resonances (Baldock & Smernik 2002).

3.2.3 Ammonium adsorption isotherm as a function of pH

The NH_4^+ adsorption capacity of the lignites, and the influence of pH on this, was determined using a modified batch isotherm technique described by Liu et al. (2008). The batch adsorption isotherm has been used to assess ion adsorption capacity of lignite (Pehlivan & Arslan 2007; Nazari et al. 2018). Lignites with EC greater than $300 \mu\text{S cm}^{-1}$ (Bacchus Marsh, Morwell and Loy Yang) were pre-treated to remove soluble salts using 60% of aqueous ethanol and 20% glycerol (as per method 15A2 from Rayment and Lyons (2011)). This step removes the possible effects of the salts competing with NH_4^+ for exchange sites. The adsorption capacity was determined as a function of the solution pH. Varying concentrations of OH^- (0 to 0.319 M), applied as KOH, were used to create five incremental lignite/solution pH treatments, with a maximum pH of between 7 and 8 (the minimum pH was the original pH of the lignite). For each lignite, the concentrations of OH^- used depended on its pH buffering capacity. Following the OH^- addition, the pH of the lignite was allowed to equilibrate for 6 days and adjusted with additional OH^- if required. Briefly, the adsorption isotherm was determined as follows; 30 mL of NH_4Cl solution at concentrations between 25 and 2500 mg $\text{NH}_4^+\text{-N L}^{-1}$ was added to 1 g of lignite in 50 mL centrifuge tubes after which chloroform (0.15 mL) was added to each tube to eliminate microbial immobilization of the added NH_4^+ . The tubes were then shaken end over end for 16 h at 25 °C, centrifuged at 3000 rpm for 10 mins and filtered through Whatman No. 42 filter paper. Afterwards, the final concentration of $\text{NH}_4^+\text{-N}$ in the solution (supernatant) at equilibrium was determined using a colourimetric method (Skalar SAN++ segmented flow analyzer). The amount of $\text{NH}_4^+\text{-N}$ adsorbed per unit mass

of lignite at equilibrium (Q_e) ($\text{mg NH}_4^+\text{-N g}^{-1}$) was calculated using equation 1 (Baskaralingam et al. 2006; Bhatt et al. 2012),

$$Q_e = \frac{(C_o - C_e)V}{m} \quad (3.1)$$

where C_o is the initial concentration of $\text{NH}_4^+\text{-N}$ in solution (mg L^{-1}), C_e is the final concentration of $\text{NH}_4^+\text{-N}$ in solution at equilibrium (mg L^{-1}), m is the mass of lignite used (g) and V is the volume of $\text{NH}_4^+\text{-N}$ solution (L). A plot of Q_e vs. C_e gives the adsorption isotherm.

The adsorption isotherms were fitted to the Langmuir isotherm model (equation 3.2),

$$Q_e = \frac{Q_{max}K_L C_e}{1 + K_L C_e} \quad (3.2)$$

where Q_{max} is the maximum adsorption capacity ($\text{mg NH}_4^+\text{-N g}^{-1}$) and K_L is the Langmuir adsorption constant (L mg^{-1}), indicating the affinity of the exchange sites to NH_4^+ and Q_e , C_o and C_e are as defined in equation 3.1.

A linearized form of equation 3.2 was used to derive Q_{max} , (equation 3.3)

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max}} C_e + \frac{1}{K_L Q_{max}} \quad (3.3)$$

3.2.4 Biological immobilization of N by lignites

To determine the contribution of the lignite labile C to its N retention capacity, biological immobilization of N was measured using the method of Recous et al. (1990). Dry lignite (25 g) was weighed into a 250 mL plastic vial, adjusted to 55% water holding capacity (WHC) and pre-incubated in the dark at 25 °C for 6 days. After the pre-incubation, each vial received 20 mg N as $(^{15}\text{NH}_4)_2\text{SO}_4$ (50.15 atom% enriched) dissolved in 1 mL MilliQ water. Each treatment was replicated three times. After N addition, three vials from each lignite treatment were sampled

immediately (0.5 h) by sequential extraction with 2M KCl to determine non-biological NH_4^+ retention, and the remaining vials were capped and incubated in the dark at 25 °C for a further 6 days. The incubation period was limited to 6 days to avoid remineralization of immobilized NH_4^+ -N (Barraclough 1995). To keep the samples aerated, the vials were uncapped twice during the incubation period and the headspace volume was replaced with fresh air, and then recapped. To determine the applied N immobilized by lignite at days 0 (0.5 h) and 6, the inorganic N was completely removed from the samples through sequential extraction with 2M KCl (1:5 solid: extract ratio) by shaking end over end for 1 h, three times. After extraction, the lignite samples were oven dried at 80 °C for 48h after which the total N and its isotopic composition were analyzed with an isotope ratio mass spectrometer (IRMS, Sercon Hydra 20-20). The N immobilized was determined according to equation 4 (Zogg et al. 2000; Malhi et al. 2004),

Immobilized N (%) =

$$\frac{[\%N \text{ in } L \times L(g) \times \text{atom}\%^{15}N \text{ excess of TN in } L]_{t=6} - [\%N \text{ in } L \times L(g) \times \text{atom}\%^{15}N \text{ excess of TN in } L]_{t=0.5}}{N \text{ applied to } L(g) \times \text{atom}\%^{15}N \text{ excess of TN applied}} \quad (3.4)$$

Where L = lignite; %N in L is the TN content of the lignite, $L(g)$ is the weight of lignite, $\text{atom}\%^{15}N$ excess of total N (TN) in lignite = $\text{atom}\%^{15}N$ abundance of TN in lignite minus $\text{atom}\%^{15}N$ at natural abundance (0.3663%); $t=6$ and $t=0.5$ = sampling days 6 and 0 respectively; and $\text{atom}\%^{15}N$ excess of TN applied = the $\text{atom}\%^{15}N$ abundance of TN applied minus $\text{atom}\%^{15}N$ at natural abundance (0.3663%). The applied N not recovered on day 0 (0.5h after NH_4^+ addition) was assumed to be NH_4^+ fixed in the lignite by mechanisms other than biological immobilization, e.g. in pore spaces (Tu et al. 2019).

3.2.5 Statistical analysis

One-way analysis of variance (ANOVA) test was performed with GenStat 16 (VSN International UK). Tukey's honestly significant difference (HSD) test was used to assess

significant differences between treatment means at 5% probability level. Pearson correlation coefficients, r , were obtained using R software, version 3.4.0.

3.3 Results and Discussion

3.3.1 Surface morphology of lignites

The SEM images showed that all lignites had a similar structure apart from the Latrobe lignite that showed a flatter surface (Figure 3.2a-e). The lignites appeared as loosely compressed aggregates, with no regular pattern or shape, and several pore spaces. These pore spaces can serve as retention sites for small molecules such as $\text{NH}_4^+/\text{NH}_3$ (Tu et al. 2019), however, physical retention of $\text{NH}_4^+/\text{NH}_3$ in the pore spaces in the lignites was not determined in this study. At 100x magnification (focusing on several lignite particles at the same time), silicates were clearly observed in the Loy Yang lignite (Figure 3.2f), but were less obvious in the other lignites (Figure 3.2 a-e). The obvious presence of silicates in the Loy Yang is supported by the high concentration of total Al (presumably existing as aluminium silicate), ($3,584 \text{ mg kg}^{-1}$) compared to the other lignites ($133\text{-}685 \text{ mg kg}^{-1}$).

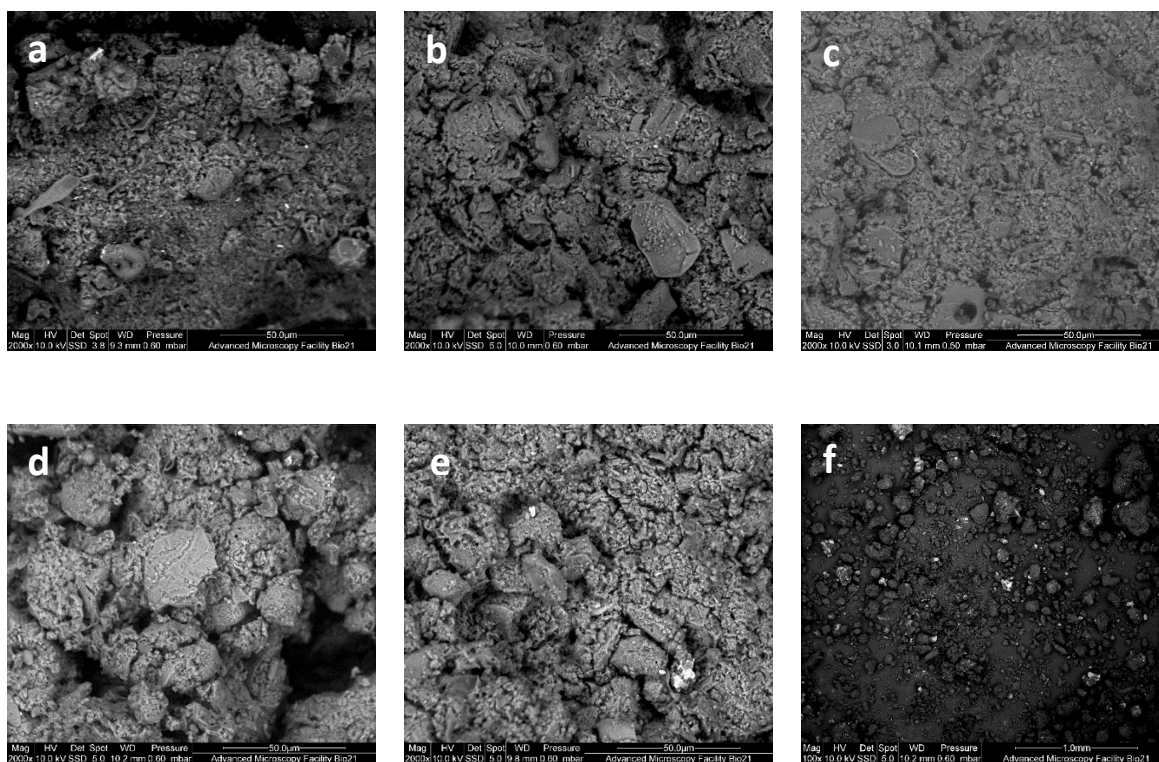


Figure 3. 2 Scanning electron microscopy (SEM) images of lignites (a-e: x2000). (a) Bacchus Marsh; (b) Yallourn; (c) La Trobe; (d) Morwell; (e) Loy Yang; (f) Loy Yang (x100) showing the presence of silicates (white reflective spots).

3.3.2 Chemical properties of lignites

The chemical properties varied with lignite source (Table 3.1). All but the Bacchus Marsh lignite, which was sourced from the Otway Basin, were from the Gippsland Basin's Latrobe Valley. Hence most of the chemical properties of the Gippsland Basin lignites were similar, and different (often higher) to those of the Bacchus Marsh lignite.

All lignites were acidic with $\text{pH}_{\text{H}_2\text{O}}$ between 3.33 (Loy Yang) and 5.76 (Bacchus Marsh), similar to values reported elsewhere; $\text{pH}_{(\text{H}_2\text{O})}$ 3.4 to 6.5 (Woskoboenko et al. 1991; Scheffe et al. 2008a; Simmler et al. 2013; Paramashivam et al. 2016). Carboxylic and phenolic acid groups in the lignite are responsible for the low pH (Schafer 1991; Woskoboenko et al. 1991). The higher

pH of the Bacchus Marsh lignite can be attributed to its higher concentration of exchangeable Mg^{2+} and Ca^{2+} which are likely to exist as carboxylates (i.e. forming salt with deprotonated carboxyl groups) (Önal & Ceylan 1995). Woskoboenko et al. (1991) reported that, the pH of lignites increases as their carboxylate content increases. One of the key drivers of N loss from manure is its high pH (usually > 7) which shifts the $\text{NH}_4^+/\text{NH}_3$ equilibrium ratio toward NH_3 and leads to volatilization (Reddy et al. 1979; Sun et al. 2016). The low pH of the lignites can therefore reduce NH_3 emission from manure by making the environment more acidic, favouring a shift towards NH_4^+ . However, as manure is continuously deposited on the lignite, this pH effect is expected to diminish due to the neutralization by the alkaline manure, and also the accumulation of NH_4^+ in the manure-lignite mix which eventually saturates the exchange sites of the lignite. Sun et al. (2016) reported that, lignite was more effective when the pH of the manure-lignite mix was below 6.5 (reducing NH_3 emission from manure by over 50%). The rate of pH increase in the manure-lignite mix will be influenced by the pH buffer capacity of the lignite. The pH buffer capacity of the lignites was 357, 152, 240, 174 and 183 $\text{mmol kg}^{-1} \text{ pH unit}^{-1}$ for the Bacchus Marsh, Yallourn, Latrobe, Morwell and Loy Yang respectively (Table 3.1). This means that, when applied to animal pen, the Bacchus Marsh lignite, is likely to be the most effective in suppressing the increase in pH of the manure-lignite mix. However, it should be noted that the Bacchus Marsh also had the highest pH ($\text{pH}_{\text{CaCl}_2}$ 5.42) compared to the rest of the lignites ($\text{pH}_{\text{CaCl}_2}$ 3.00-3.89) and so the total amount of manure required to neutralize or increase its pH to that of the manure (about pH 7) is likely to be similar or less than lignites such as Loy Yang ($\text{pH}_{\text{CaCl}_2}$ 3.00) and Latrobe ($\text{pH}_{\text{CaCl}_2}$ 3.38).

The Bacchus Marsh and Loy Yang lignites were characterized by higher EC (1,034 and 1,516 $\mu\text{S cm}^{-1}$ respectively) compared to the other lignites (249 to 321 $\mu\text{S cm}^{-1}$). The Latrobe lignite had higher total N (0.57%) compared to the other lignites (0.49-0.51%) but all were similar to levels reported in the literature (Fei et al. 2007; Sakaguchi et al. 2008; Simmler et al. 2013). Though the

Latrobe lignite had the highest total C (63.2%) compared to the rest of the lignites (54.8 to 61.6%), only 2.4% of the total C fraction was present in the labile form (or 15.3 g labile C kg⁻¹ lignite). The rest of the lignites had between 8.3 and 14.3% of their total C present as labile C (or 45.7 and 88.4 g labile C kg⁻¹ lignite). Labile C enhances the biological immobilization of N and through this mechanism can suppress NH₃ emission (McCalley & Sparks 2008; Chen et al. 2015).

With the exception of the Loy Yang lignite (51%), over 68% of the lignite exchange sites were occupied by base cations (Table 3.1). The Bacchus Marsh lignite had the highest concentration of all the base cations leading to the highest base cation exchange capacity (CEC_B) of 73.8 cmol_c kg⁻¹ compared to the rest of the lignites (8.9-28.1 cmol_c kg⁻¹). The higher CEC_B of the Bacchus Marsh indicates higher capacity for NH₄⁺ adsorption. Apart from the Loy Yang lignite where exchangeable Al³⁺ accounted for 62% of the exchange acidity, most of the exchange acidity (> 86 %) in the lignites was due to exchangeable H⁺.

The element concentration, with the exception of Al, Zn and Cu, was higher in the Bacchus Marsh lignite compared to those from the Latrobe Valley (Table 3.1). Coal from Maddingley (Bacchus Marsh) has been reported to have higher ash yields, than coals from the Latrobe Valley (Gloe 1991). This explains the higher element concentrations in the Bacchus Marsh lignite. It is not known whether this differences in element concentration affect N retention by the lignite, but they would influence the quality of the final product as a plant nutrient source.

Sulfates can contribute to NH₄⁺ retention through the reaction of one mole of SO₄²⁻ with two moles of NH₄⁺ to form (NH₄)₂SO₄ (Petit et al. 2009; Petit et al. 2010). Sulfur in lignite can be present in the form of pyrite, sulfate or organic sulfur (Brockway et al. 1991). Analysis by Smith and Batts (1974) of thirteen Australian lignite seams showed that 54 to 97% of the total sulfur present in lignite (total sulfur content between 0.4 and 2.9% has been reported for Victorian

(Brockway et al. 1991; Barton et al. 1993)) exists in the organic form. In their analysis, the lignites with high organic sulfur contents had 2-25% of their total sulfur present as sulfates whilst the lignites with low organic sulfur content had 0-5% of their total sulfur as sulfates (one out of the thirteen samples had 36% sulfate content). The Bacchus Marsh lignite had a sulfur content 5 to 10 fold that of the lignites from the Latrobe Valley. Hence the role of sulfur in NH_4^+ retention is expected to be greatest in the Bacchus Marsh lignite. Estimates of the contribution of sulfur to NH_4^+ retention in the different lignites is provided under section 3.3.3 below.

Table 3. 1 Chemical properties of five Victorian lignites. Values represent means of analytical triplicates.

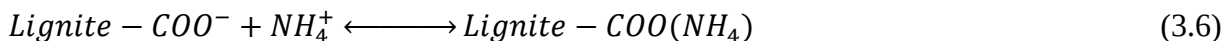
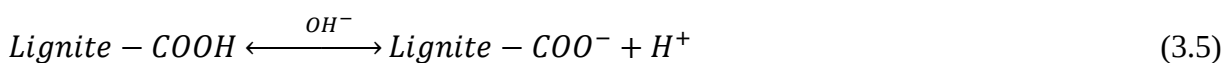
	Bacchus Marsh	Yallourn	Latrobe	Morwell	Loy Yang
pH _(1:5 0.01M CaCl2)	5.42	3.31	3.38	3.89	3.00
pH _(1:5 H2O)	5.76	4.13	4.08	4.55	3.33
EC, $\mu\text{S cm}^{-1}$	1,516	249	278	321	1,034
pH buffer capacity, $\text{mmol kg}^{-1} \text{ pH unit}^{-1}$	357.0	152.3	240.0	174.4	183.0
Total C, %	54.8	60.4	63.2	61.6	56.2
Total N, %	0.49	0.49	0.57	0.51	0.51
Labile C, g kg^{-1}	45.7	76.0	15.3	88.4	71.8
Labile C, % of Total C	8.3	13.5	2.4	14.3	11.9
CEC _E ^{††} , $\text{cmol}_c \text{ kg}^{-1}$	73.8	19.9	8.9	28.1	15.3
Exchange acidity, $\text{cmol}_c \text{ kg}^{-1}$	0.14	2.90	2.69	0.68	7.65
Exchangeable Al, $\text{cmol}_c \text{ kg}^{-1}$	< 0.05	0.20	0.17	0.09	4.78
Exchangeable H, $\text{cmol}_c \text{ kg}^{-1}$	0.14	2.70	2.52	0.59	2.87
Base saturation, %	99.8	85.9	67.9	97.8	51.1
CEC _B [†] $\text{cmol}_c \text{ kg}^{-1}$	73.7	17.1	6.2	27.4	8.0
Exchangeable bases, $\text{cmol}_c \text{ kg}^{-1}$					
Mg	34.61	11.27	2.05	13.26	4.90

	Bacchus Marsh	Yallourn	Latrobe	Morwell	Loy Yang
Na	9.50	2.44	1.43	2.48	1.77
K	0.23	0.08	0.02	0.08	0.04
Ca	29.34	3.28	2.74	11.48	1.28
Element concentration, mg kg ⁻¹					
Al	196.8	133.5	685.3	274.4	3,584
Fe	5,201	3,726	720	2,314	1,335
Mg	5,946	1,424.1	808.8	1,672.3	625.6
Na	2,636	607.9	526.1	606.3	436.3
K	123.9	45.7	32.7	50.0	100.3
Ca	10,880	718.8	1,260	2,698	333.2
P	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
S	19,499	1,989	2,464	2,295	4,023
Zn	6.1	3.7	4.9	4.2	7.0
Mn	188.4	42.0	15.9	48.4	5.8
Cu	< 0.1	< 0.1	< 0.1	< 0.1	2.0

Results are on oven dried basis. [†]CEC_B: Cation exchange capacity from the sum of exchangeable bases. ^{††}CEC_E: Effective CEC, the sum of CEC_B and exchange acidity.

3.3.3 Distribution and role of carbon-functional groups in lignites

A range of C forms was detected with the ^{13}C NMR in the lignites and the pattern of distribution was similar among the lignites (Figure 3.3, Table 3.2). The non-reactive C forms constituted between 81 and 86% of C forms, with the reactive groups (carboxyl/amide and O-aryl C) accounting for 14-19%. Carboxyl and phenolic groups, identified in the carboxyl/amide and O-aryl regions, have been reported as being responsible for the CEC of lignite (Pehlivan & Arslan 2006; Skodras et al. 2014). For the phenolic groups, their deprotonation and participation in ion exchange starts at $\text{pH} > 8$ (Schafer 1991; Simmler et al. 2013). Hence, under the pH range examined in this study (3.38 to 8.15), the carboxyl groups are the most likely groups contributing to the CEC of the lignites as these groups are almost completely deprotonated at pH higher than 4 (Pehlivan & Arslan 2006; Skodras et al. 2014). Equations 3.5 and 3.6 illustrates the deprotonation, in the presence of OH^- , of a carboxyl group attached to lignite and the subsequent adsorption of NH_4^+ on the negative site generated in this process (adapted from Skodras et al. (2014)).



The ^{13}C NMR spectra provides an indication of the combined carboxyl / amide group, so further assessment is required to separate these, and this was achieved by determining the moles of OH^- required to titrate the lignite to $\text{pH} \sim 7$, which ranged from 0.40 to 0.64 $\text{mmol OH}^- \text{g}^{-1}$ lignite, and given that only carboxyl groups will deprotonate at this pH, and that one mole of OH^- will deprotonate one mole of COOH (equation 3.5). The mass of COOH (18.01 to 28.81 mg g^{-1} lignite) was then calculated from the moles of OH^- required and this showed that between 2.8 to 5.3% of the lignite C existed as carboxyl groups. Hence, the carboxyl/amide C identified on the NMR

spectra is mostly carboxyl C. In addition to the non-reactive C forms (alkyl and ketones), other functional groups such as nitrogen and sulfur groups are present in lignite. However, these groups, compared to the oxygen containing functional groups, are very low in lignite (< 0.6-0.8%) and play insignificant role in ion exchange (Schafer 1991).

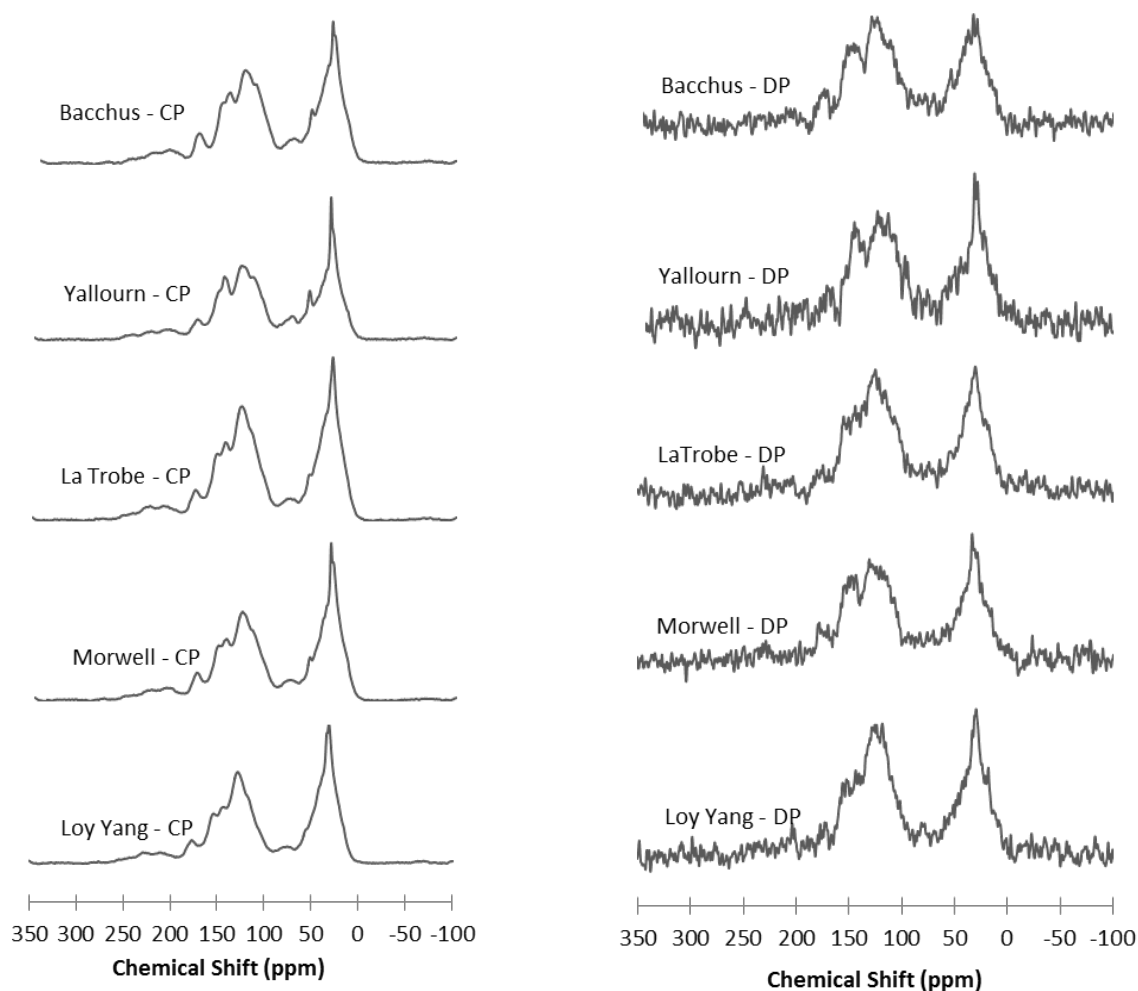


Figure 3. 3 Cross-polarization (CP) and direct-polarization (DP) spectra of five lignites.

Table 3. 2 Relative abundance (%) of C forms present in the lignites obtained from direct-polarization (DP) ^{13}C NMR

Forms of carbon	Chemical shift region (ppm)	Bacchus Marsh	Yallourn	La Trobe	Morwell	Loy Yang
Alkyl C	0 - 45	23.9	25.3	26.7	26.7	27.4
N-Alkyl/Methoxyl C	45 - 60	7.0	5.4	5.6	5.7	6.0
O-Alkyl C	60 - 95	8.4	7.3	7.6	7.7	6.7
Di-O-Alkyl C	95 - 110	6.7	8.0	8.3	6.1	6.9
Aryl C	110 - 145	34.0	32.4	36.6	34.7	36.6
O-Aryl C	145 - 165	13.0	13.9	11.0	13.1	10.1
Carboxyl/Amide C	165 - 190	5.2	4.8	3.2	5.2	3.7
Ketone C	190 - 215	1.8	2.9	1.1	0.8	2.6
<i>Total %</i>	--	<i>100</i>	<i>100</i>	<i>100</i>	<i>100</i>	<i>100</i>

3.3.4 Ammonium adsorption as a function of pH

All lignites exhibited increasing NH_4^+ adsorption with increasing solution pH (Figures 3.4a-e). Pooled data ($n = 24$) of maximum NH_4^+ adsorption capacity ($Q_{\max}$) against pH, shows the slope of $Q_{\max}$ increases sharply as pH increases above 5.0 and the relationship between $Q_{\max}$ and pH was $Q_{\max} = 2.81e^{0.275\text{pH}}$ with $R^2 = 0.73$ (Figure 3.4f). There was a positive correlation ($R^2 = 0.91$) between the initial pH and $Q_{\max}$ of the lignite materials (Figure 3.5a). A similar relationship was observed between CEC and $Q_{\max}$ ($R^2 = 0.88$) (Figure 3.5b). The effect of the increase in pH on NH_4^+ adsorption was more evident in the lignites sourced from the Latrobe Valley than the Bacchus Marsh lignite (Table 3.3). In these lignites, a 2.4-3.2 pH unit increase resulted in a 2-3

fold increase in $Q_{\max}$ (Table 3.3). In the Bacchus Marsh lignite, a 2.4 pH unit increase resulted in 1.2 fold increase in $Q_{\max}$. At the initial pH, the $Q_{\max}$ for the different lignites was 19.23 (Bacchus Marsh, pH 5.74), 14.41 (Morwell, pH 4.59), 8.58 (Yallourn, pH 3.38), 8.24 (Loy Yang, pH 3.65) and 7.86 (Latrobe, pH 4.09) $\text{mg NH}_4^+\text{-N g}^{-1}$. This correlated ($R^2 = 0.83$) with the carboxyl groups determined from the titration method (see above), indicating that the carboxyl groups play a major role in NH_4^+ adsorption.

The increase in $Q_{\max}$ with pH is considered to be due to deprotonation of the carboxyl groups, which has been reported to be the most important site for ion exchange in lignites (Lafferty & Hobday 1990). The deprotonation of these carboxylic groups creates available exchange sites on the lignite leading to increase in the lignite's capacity to adsorb ion (CEC) as pH increases (Skodras et al. 2014). Hence, the higher $Q_{\max}$ of the Bacchus Marsh lignite at the original pH was most likely due to its higher initial pH. In agreement with this Nazari (2017) observed a low NH_4^+ adsorption capacity ($\sim 0.06 \text{ mg g}^{-1}$) of Loy Yang brown coal when the pH was between 2 and 4 but this increased with increasing pH (to 0.5 mg g^{-1} at pH 12). The authors, however, reported that, the increased adsorption capacity at $\text{pH} > 8.3$ could also be due to the loss of NH_4^+ as NH_3 gas. It is important to note that the reported NH_4^+ adsorption capacity, as a function of pH, by Nazari (2017) was determined using a fixed initial $\text{NH}_4^+\text{-N}$ concentration of 25 mg L^{-1} , unlike in this study where the $\text{NH}_4^+\text{-N}$ concentration was varied ($25\text{-}2,500 \text{ mg L}^{-1}$), to enable the determination of $Q_{\max}$, for each pH point. In the study of cation (Zn^{2+} and Cd^{2+}) adsorption capacity of lignites as a function of pH, Pehlivan and Arslan (2006) reported that the adsorption of the cations was negligible at $\text{pH} < 2.5$ but increased as pH increased to 4.5-5.7.

Sulfonic functional groups in lignite can also contribute to its ion exchange characteristics (Eligwe et al. 1999). Smith and Batts (1974) reported that a maximum of 25% of the total S in lignite exists as sulfate. Using this value, and based on the S content of the lignites (Table 3.1), the

maximum potential contribution of S (as sulfate) to NH_4^+ adsorption is estimated at 0.2-0.4mg $\text{NH}_4^+ \text{ g}^{-1}$ for the Latrobe Valley lignites and 1.8 mg $\text{NH}_4^+ \text{ g}^{-1}$ for the Bacchus Marsh lignite. This is small compared to the NH_4^+ adsorption attributed to the carboxyl group (Table 3.3). The physical retention of NH_4^+ in the pores of lignite could also contribute to its N retention capacity (Tu et al. 2019). However, the amount of NH_4^+ retain in the pores is unlikely to increase with increasing pH. Hence, adsorption on carboxyl group exchange sites is likely the dominant mechanism of NH_4^+ retention in lignites.

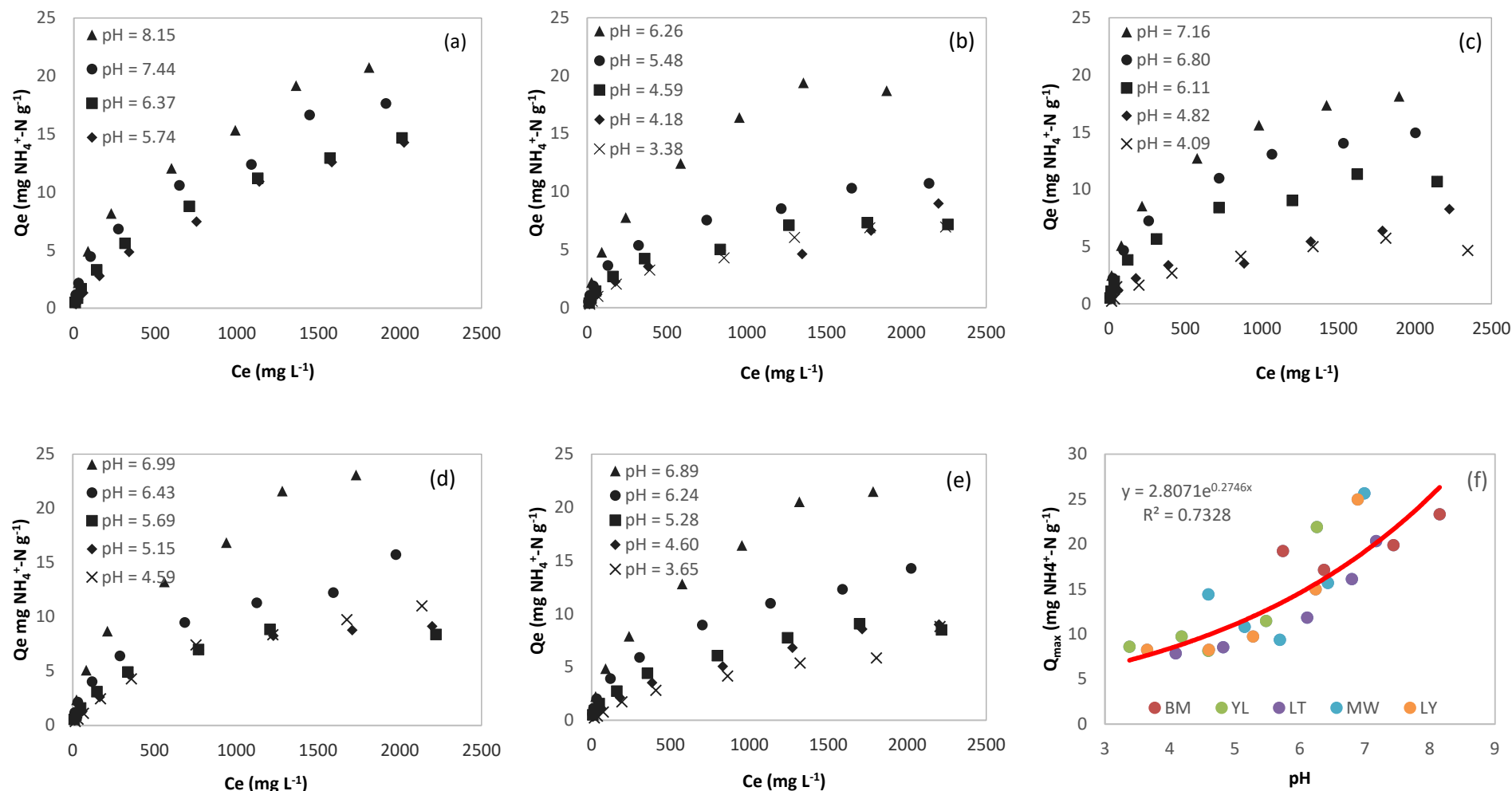


Figure 3.4 NH_4^+ adsorption isotherm of the five lignites as a function of pH. (a) = Bacchus Marsh (BM); (b) = Yallourn (YL); (c) = Latrobe (LT); (d) = Morwell (MW); (e) = Loy Yang (LY). (f) Relationship between pH and maximum adsorption capacity (Q_{max}) across all lignites.

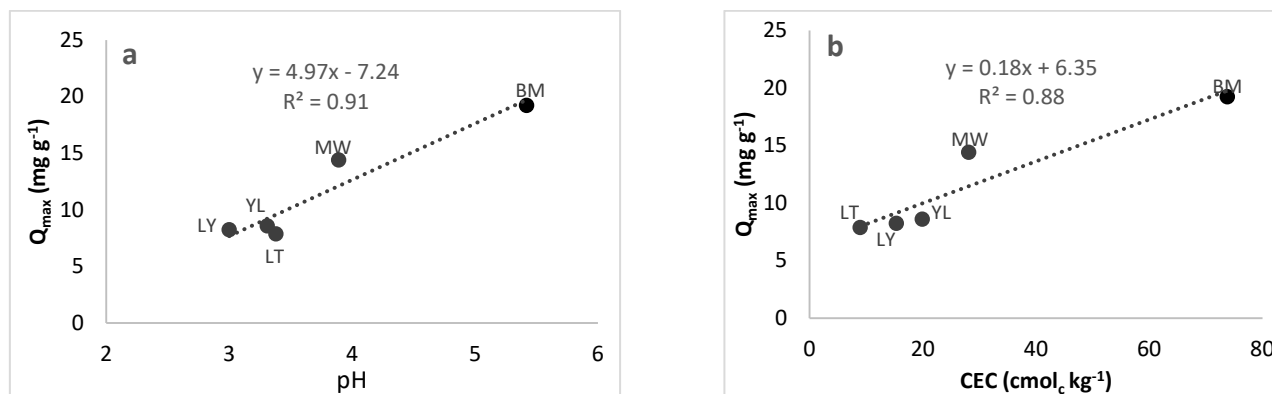


Figure 3. 5 Correlation between maximum adsorption capacity ($Q_{\max}$) determined at the original pH of the lignite and (a) original lignite pH and (b) original lignite CEC. BM = Bacchus Marsh; MW = Morwell; YL = Yallourn; LT = La Trobe; LY = Loy Yang.

Table 3. 3 Langmuir isotherm constant (K_L) for maximum NH_4^+ adsorption ($Q_{\max}$) by lignites at different pHs after addition of OH^- to the lignites (the value in the first column for each lignite is the original pH). R^2 = correlation coefficient for the Langmuir isotherm model prediction.

	Bacchus Marsh					Yallourn					Latrobe				
	5.74	6.37	7.44	8.15		3.38	4.18	4.59	5.48	6.26	4.09	4.82	6.11	6.80	7.17
$Q_{\max}$ (mg g ⁻¹)	19.23	17.12	19.88	23.31		8.58	9.74	8.14	11.45	21.88	7.86	8.53	11.82	16.10	20.33
$K_L \times 10^{-3}$ (L mg ⁻¹)	1.175	2.022	3.083	2.853		1.807	1.855	3.597	3.991	3.318	1.613	2.333	4.406	4.596	3.804
R^2	0.952	0.966	0.962	0.969		0.976	0.936	0.984	0.981	0.981	0.976	0.936	0.984	0.981	0.981

	Morwell					Loy Yang				
	4.59	5.15	5.69	6.43	6.99	3.65	4.60	5.28	6.24	6.89
$Q_{\max}$ (mg g ⁻¹)	14.41	10.80	9.35	15.67	25.64	8.24	8.26	9.74	14.97	24.94
K_L (L mg ⁻¹) $\times 10^{-3}$	1.306	2.457	4.683	3.508	3.191	1.327	2.486	3.348	3.377	2.710
R^2	0.983	0.993	0.988	0.951	0.959	0.995	0.917	0.977	0.966	0.969

3.3.5 Biological immobilization of N in lignite

For the Bacchus Marsh, Latrobe and Loy Yang lignites, between 2.31 and 11.08% (0.26 and 2.74 mg N g⁻¹ labile C) of the applied N was recovered in the lignite after 6 days of incubation (Table 3.4). Although a higher amount of the applied N was recovered in the Bacchus Marsh lignite (11.08%) compared to Latrobe lignite (5.24%), the recovered N per gram of labile C was higher in the Latrobe lignite (2.74 mg g⁻¹ compared to 1.94 mg g⁻¹ for Bacchus Marsh). For the Yallourn and Morwell lignites, the amount of N recovered in the lignites after 6 days of incubation was less than what was recovered in the lignite on day 0 (0.5 h after N addition) indicating N immobilization. This could be due to the release of the NH₄⁺ fixed/ immobilized on day 0. The Yallourn and Morwell lignites had higher labile C (76.0-88.4g kg⁻¹ or 13.5-14.3% of total C) compared to the rest of the lignites (ranges between 15.3 and 71.8 g kg⁻¹ or 2.4 and 11.9% of total C).

Compared to the maximum NH₄⁺ adsorption capacity (7.86 - 19.23 mg NH₄⁺-N g⁻¹ lignite), the amount of applied N immobilized (-0.03 to 0.09 mg N g⁻¹) (equation 3.4, Table 3.4) during the incubation period was negligible. Tran et al. (2015) observed a negative relationship between the rate of application of acidic (pH 4.9) lignite from Morwell to soil and microbial biomass N. The authors also observed a reduced respiration rate during the first three days after lignite application indicating a suppression of microbial activity by the lignite. Whiteley and Pettit (1994a) reported a significantly reduced rate of O₂ consumption and CO₂ evolution from mixing lignite humic acid with straw during 4 weeks of incubation indicating an inhibitory effect of lignite on microbial activity. Hence, although lignite contains labile C (up to 88 g kg⁻¹), its ability to suppress biological activity is likely to limit its impact on N retention through biological immobilization. There was a positive correlation ($r = 0.74$) between pH and N retention in lignite (%N recovery) (Table 3.5). The acidic pH (pH_{CaCl2} 3.00 – 5.42) of the

lignites examined is likely to have inhibited the biological immobilization of NH_4^+ . Pietri et al. (2008) attributed the reduction in microbial biomass and activity at low pH to Al toxicity due to the increase in extractable Al at low pH. In the animal pen, the continuous deposition of alkaline manure on the lignite will lead to an increase in pH of the manure-lignite system and hence the negative effect of lignite on biological immobilization of N, in the animal pen, is expected to reduce over time.

Table 3. 4 Total N applied immobilized in lignites after six days of incubation. Values represent mean ($n = 3$) $\pm$ standard error of mean. Values within the same column followed by different letter are significantly different (Tukey's HSD, $p < 0.05$).

Lignites	Total N applied immobilized, %	N recovered per labile C, mg g^{-1}	N recovered per lignite, mg g^{-1}
Bacchus Marsh	11.08 ± 0.44 d	1.94 ± 0.07 b	0.089 ± 0.004 c
Yallourn	-3.08 ± 0.53 a	-0.39 ± 0.53 a	-0.030 ± 0.001 a
Latrobe	5.24 ± 0.91 c	2.74 ± 0.48 b	0.042 ± 0.007 b
Morwell	-0.24 ± 0.42 b	-0.02 ± 0.04 a	-0.002 ± 0.003 a
Loy Yang	2.31 ± 0.18 bc	0.26 ± 0.02 a	0.018 ± 0.001 b

3.3.6 Lignite properties and N retention - summary

The correlation coefficients between the lignite properties, and between N retention and the lignite properties are presented in Table 3.5. There was a strong correlation between Q_{max} (determined at the original pHs of the lignites) and CEC ($r = 0.94$), and pH ($r = 0.95$) indicating that CEC and pH are key lignite properties driving the retention of N. There was also a strong correlation ($r = 0.91$) between Q_{max} and carboxyl, indicating the importance of carboxyl groups in NH_4^+ adsorption. In addition, there was a correlation between pH and carboxyl group ($r =$

0.75). The extent of increase in $Q_{\max}$ (with increasing pH to 7-8) is likely to be a function of the amount of carboxyl groups present in the lignite. There was a strong correlation between pH buffer and % N recovery ($r = 0.97$) however, the reason for the correlation, and also that between EC and total C ($r = 0.94$), is unclear. There were weak and statistically non-significant relationships between the other lignite properties and $Q_{\max}$. As indicated earlier % N recovered (biological immobilization) in the lignite was negatively correlated with labile C content of the lignite (Table 3.5).

Table 3. 5 Pearson's correlation coefficients, r ; among lignite properties ($n = 5$).

	* $Q_{\max}$	pH _{CaCl2}	Carboxyl ⁺	pH buffer	Labile C	Total C	%N _{recov} ^Δ	EC
CEC	0.94	0.97	0.77	0.81	-0.02	-0.67	0.68	0.76
$Q_{\max}$		0.95	0.91	0.71	0.09	-0.49	0.59	0.61
pH _{CaCl2}			0.75	0.86	-0.17	-0.49	0.74	0.65
Carboxyl ⁺				0.46	0.48	-0.42	0.25	0.44
pH buffer					-0.59	-0.51	0.97	0.74
Labile C						-0.15	-0.65	-0.10
Total C							-0.51	-0.94
%N _{recov} ^Δ								0.76

* $Q_{\max}$ determined at original pH of lignite, ⁺Carboxyl estimated from titration method, ^Δapplied N recovered (biological immobilization) in lignite after 6 days of incubation.

3.4 Conclusions

In this work, all lignites had the potential to adsorb considerable amounts of NH_4^+ (up to 25.6 mg g^{-1} at $\text{pH} \sim 7$). The main mechanism of NH_4^+ retention by the lignite, irrespective of the origin, was through adsorption on exchange sites with retention of NH_4^+ owing to biological immobilization being insignificant. The pH of the lignite was the main driver of its NH_4^+ adsorption capacity through its effect on the deprotonation of the carboxyl groups (as pH increases) which in turn influenced the CEC of the lignite.

Based on the above, it would appear that lignite suppresses NH_3 loss in two ways. First the low pH causes formation of NH_4^+ over NH_3 , then with continued deposition of alkaline manure ($\text{pH} > 7$), the increasing pH of the lignite environment causes increased CEC and hence increased NH_4^+ retention. Although labile carbon did not play a substantial role in NH_4^+ retention in the lignite, due to inhibition of immobilisation at low pH, in the animal pen, the continuous deposition of alkaline manure, containing labile C, would enhance the biological immobilization of NH_4^+ by the lignite. The adsorption of NH_4^+ on exchange sites of lignite is, however, expected to remain the dominant mechanism for N retention by lignite.

CHAPTER 4: Effect of Lignite on biochemical Process and Gaseous Emissions during Composting of Cattle Manure under Field Conditions

4.1 Introduction

Studies have shown that the application of lignite to the surface of a cattle pen is able to suppress NH_3 emission from cattle manure by 30-66% (Chen et al. 2015; Sun et al. 2016). One benefit of this is that the manure is then nitrogen enriched and can be utilized as a nutrient source, typically following a composting process, representing a major recycling option for manure generated in intensive animal production systems. However it remains unclear whether the lignite added to the manure will affect the composting process (Bernal et al. 2009). This is because, to date, there is very little literature on the use of lignite in composting with no information on how the lignite affects changes in the physicochemical parameters during the composting process. Reviews on lignite, composting and the application of lignite in composting are provided under sections 2.3 and 2.4 of Chapter 2.

In this study, the objective was to determine the effect of lignite amendment of cattle manure on the physicochemical changes and gaseous emissions that occur during large scale windrow composting of the manure under field conditions. It was hypothesized that i) the lignite will continue to retain N in the manure due to the lignite's low pH and the high CEC, ii) the low pH of lignite will delay the transition between the mesophilic and thermophilic phases of the composting, and iii) the labile fraction of the high C content of the lignite will serve as an additional source of energy for microbes and thus increase the rate of decomposition.

4.2 Materials and methods

4.2.1 Lignite application to cattle pen – generation of lignite amended manure for composting

This work was carried out at the Charlton Feedlot, a commercial beef cattle feedlot located 220 km northwest of Melbourne, Australia (36°21'18.4"S 143°25'28.2"E). Two resurfaced pens with area 1450 m² (29 m x 50 m) each, were selected for the generation of the lignite amended manure. The resurfacing of the pen surface is a standard practice in the feedlot following the scraping of manure from the pen after cattle are removed and before the introduction of a new batch of cattle (Figure 4.1a). The resurfacing usually involves spreading soil over the pen surface to a depth of 10 cm and then leveling with a soil compactor. The pens were resurfaced with an alkaline clay soil (pH_{H2O} 8.8) sourced from the same farm. After resurfacing, one of the pens had 16.2 tons of pulverized as-mined lignite (~60% moisture content), equivalent to 45 t ha⁻¹ dry lignite (this rate was based on a previous study conducted by Chen et al. (2015)), spread on its surface whilst the other served as the control (no lignite applied). The thickness of the lignite layer on the pen surface was between 2 and 6 cm (Figure 4.1b). The lignite used was Bacchus Marsh lignite (properties provided in Table 3.1 in Chapter 3) which was sourced from the Maddingley open cut mine in Victoria, Australia. Following the lignite application, 135 Angus beef steers (with an average live weight of ~460 kg) were moved into each of the pens on 15 November, 2017 (Figure 4.1c).



Figure 4. 1 Generation of lignite amended manure: a) cleaned and resurfaced pen; b) pen with lignite; c) two pens (lignite amended (left) and control (right) pens) with cattle.

4.2.2 Manure sampling from pens after lignite application

To assess how the chemical properties of the manure in the pen changed over time as a result of the lignite application (this was likely to provide some information on how the composting process of the manure is affected by the lignite), manure samples were collected three times, at monthly intervals, from the two pens following the introduction of cattle. The cattle were temporarily removed from the pen during sample collection. The sampling method involved partitioning each pen into 5 segments (yellow lines, Figure 4.2) and taking 20 samples from each segment which were then composited to provide one sample per segment, i.e. 5 replicate composited samples per pen made from 100 samples collected. At each sampling point, a pickaxe was used to dig out the manure down to the soil level. The samples were stored under ice during transit to the laboratory and then stored at -20 °C for subsequent processing and analysis.

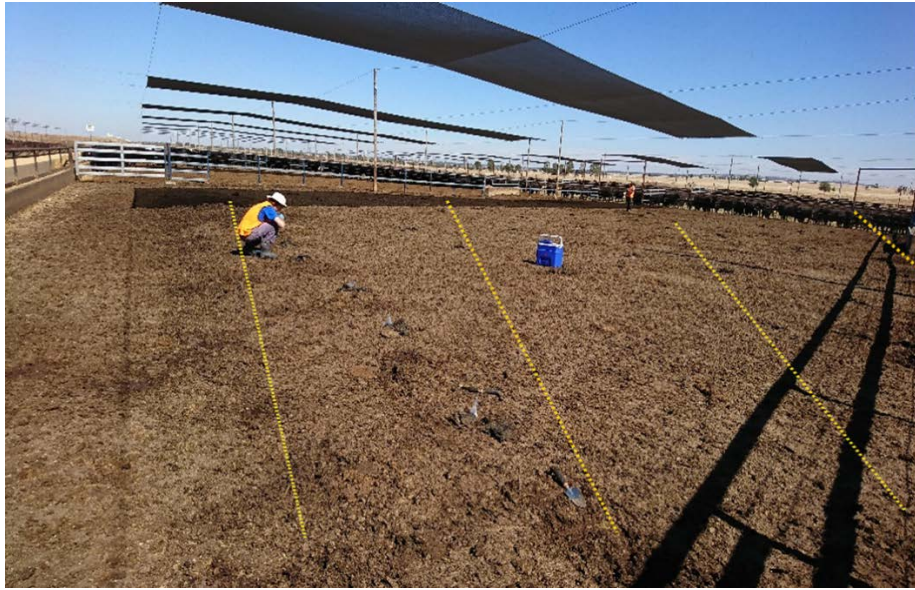


Figure 4. 2 Sampling of manure across the surface of cattle pen.

4.2.3 Cleaning and collection of manure from pens for composting

Both the control and lignite pens were cleaned on 15 February 2018, three months after the cattle were moved into the pens, in keeping with standard feedlot procedure. The cleaning was done by scraping the manure from the surface of the pen into heaps using an excavator, after which the manure was loaded into a truck (after taking samples for moisture content determination), weighed and transported to a site for composting (Figure 4.3). Due to the size of the equipment used in removing the manure from the pens, there were some inconsistencies in the depth of the excavation as the operator attempted to minimize the amount of soil removed during the manure scraping process. This resulted in obtaining different amounts of manures from the two pens (44 tons, equivalent to 32 tons dry matter from the control pen and 25 tons, equivalent to 17 tons dry matter from the lignite treated pen). Based on the amount of manure collected from the control pen and the amount of dry mass of lignite added to the pen, the proportion of lignite in the manure-lignite mixture was estimated at 17%. The movement of the cattle in the pen leads to a thorough mixing of the manure and lignite and therefore the

amount of manure collected from the pen was assumed to contain the same proportion of lignite as the manure left in the pen.



Figure 4. 3 Cleaning and removal of manure from cattle pens: excavator (yellow equipment) used for scraping and loading manure into truck.

4.2.4 Composting of the manure collected from control and lignite treated cattle pens

4.2.4.1 Windrow formation, management and monitoring

Manure collected from the control and lignite pens were windrowed separately, 30 m apart in a north-south orientation to allow concurrent measurements of gaseous emissions during periods of westerly winds (to exclude emissions from the feedlot located to the east of the composting site) (Figure 4.4). Windrow (formed with a truck, Figure 4.5a) dimensions for manure from the control pen were 20m long x 4.3m wide x 1.2m high whilst the dimensions of the manure + lignite windrow were 14m long x 4.3m wide x 1.2m high. The difference in windrow lengths was due to the different amount of manure collected from the pens. The moisture content of both windrows was adjusted to about 50% (w/w) with the aid of a water truck. In order to improve aeration and oxygen levels within the windrows, both windrows were turned weekly (12 times during the entire composting period) using a windrow turner

(Komptech, Topturn X55) (Figure 4.5b). The turning was also necessary in order to subject the manure at the outer parts of the windrow to conditions at the center of the windrow where composting is expected to be optimum. Three temperature probes and loggers (TainData Tierra), with sensors at 10 cm interval, were kept in each windrow for recording temperature at 1-hour intervals (Figure 4.5.c). The probes and loggers were temporarily removed during periods of windrow turning.

4.2.4.2 Gas emissions measurements

The gas emissions measurement technique employed in this study is similar to that described by (Bai et al. 2019). In brief, carbon dioxide (CO_2), methane (CH_4), ammonia (NH_3) and nitrous oxide (N_2O) from both the windrows were measured using an open-path Fourier transform infrared spectrometer (OP-FTIR) (Matrix-M IRcube, Bruker Optics). The spectrometer measured gas concentrations from three 80 m paths (one path for background and two paths for the compost windrows), marked by three retro reflectors on the south, north and west of the windrows (Figure 4.4), with the aid of a motorized aiming system. A 2.5 min aiming sequence was performed for each of the three paths (1.5 min of spectrum collection, 20 s of spectrum analysis and data logging and then 40 s for moving the FTIR from one path to the other). The gas concentrations were only measured during periods of westerly wind directions and thus not on every day of the composting period. The gas measurement periods covered the various phases of the composting process (initial mesophilic (Day 1 to 17 (17 days)), thermophilic (days 37 to 47 and days 56 to 62 (18 days)) and cooling (days 74 to 77 (4 days)) phases). No gas measurements were done outside the days indicated. The concentration measurement precisions were: 2 ppb for CH_4 , 0.4 ppb for NH_3 , 0.3 ppb for N_2O , and 1 ppm for CO_2 at a 100 m path length. A three dimensional sonic anemometer (CAT-3, Campbell Scientific) measured wind data (3 dimensional speed and direction) necessary for the calculations of gas emissions.

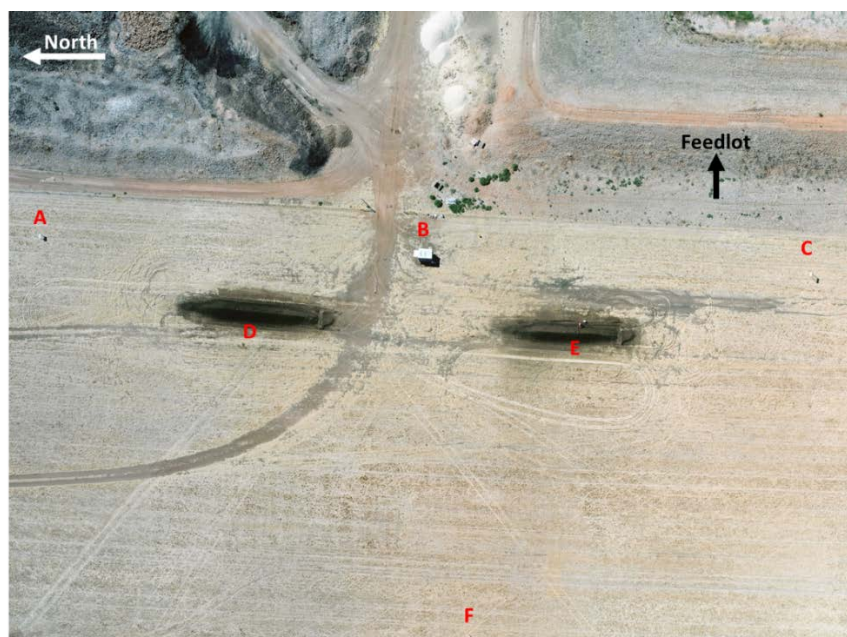


Figure 4. 4 Image showing the layout of the composting site, west of the feedlot: A and C are retro reflectors 80 m each from B (open path FTIR). A third retro reflector was positioned 80 m at the west side of the FTIR (F); D and E are compost windrows (manure and manure plus lignite respectively), 30 m apart.



a.



b.



c.



d.

Figure 4. 5 Composting of manure in windrows: a) windrowing of manure; b) turning of windrow; c) windrow with temperature probes/loggers; d) sampling from windrow

4.2.4.3 Collection of samples from windrows

The first manure samples were collected just after formation of windrows (day 0, to obtain baseline data). Subsequently, sampling of manure from the windrows was done immediately after each turning, at weekly intervals, to ensure homogeneity of samples. Twenty sub-samples were collected, using a corer (100 cm long and 3 cm internal diameter (Figure 4.5d), along the length of each windrow (5 locations at about 4 m intervals along the windrow length x 4 samples per location, i.e. 2 samples each from the east and west sides of the windrow). The 4 samples from each location of the windrow were bulked into one replicate, such that there were 5 samples collected per windrow per sampling time, and kept under ice during transport to the laboratory, after which they were stored at -20 °C before processing and analyses.

4.2.5 Analysis of samples

For total and mineral N analyses, the manure samples, collected from the cattle pens and the windrows, were acidified to $\text{pH} \leq 5$ with H_2SO_4 before oven drying at 60 °C for 48 hours to minimize N loss through NH_3 volatilization (Van Vliet et al. 2006; An et al. 2012). All other analyses were conducted on unacidified samples. Manure samples were ground to < 2mm prior to analysis. The electrical conductivity (EC) and pH were measured in a manure: extract ratio of 1:5 w/v using pH/EC meter (TPS, smartCHEM-LAB) after shaking end over end for 1 hour. Total C and total N were determined using LECO Trumac CN Elemental Analyzer. Mineral N (NH_4^+ -N and NO_3 -N) was determined using Skalar SAN++ segmented flow analyser following extraction of the samples with 2M KCl at a sample to extract ratio of 1:60 (Wolf et al. 2003) and shaking end over end for 1 hour.

4.2.6 Data analysis

To compensate for a lack of windrow replication, measurements and composite samples taken along the length of each windrow served as replicates (Eghball & Lesoing 2000; Tirado et al. 2010). Daily average temperature and gas emissions (based on the days when emissions were measured) were determined from data collected at 1 hour and 15 min respectively. Data obtained from manure samples taken from the windrows were expressed in either percent or per kg of sample whilst daily gas emissions were expressed as g per kg initial dry matter (DMi). This addresses the difference in the quantity of manure collected from the two pens. Student's t test was performed with GenStat 18 (VSN International UK) to evaluate difference between the two treatments at 5% probability level.

4.3 Results and discussion

4.3.1 Chemical properties of manure sampled from pens

The chemical properties of the manure sampled, over three months, from the control and lignite treated pens are presented in Table 4.1. The pH of the manure in the control pen was significantly lower than the manure from the lignite treated pen one month (15th December 2017) and two months (16th January 2018) after lignite application, likely due to higher NH_3 volatilization, from the control pen compared to the lignite treated pen. Lignite's capacity to reduce NH_3 loss from manure in cattle pens has been reported by Chen et al. (2015) and Sun et al. (2016). It was expected that the addition of lignite (pH_{water} 5.76) would have decreased the pH of the manure in the pens, however this was not observed. This was likely due to the time to the first sampling being one month after cattle were introduced to the pen, by which time the amount of manure deposited on the lignite had neutralized the acidity and pH buffer capacity of the lignite. This may have also been facilitated by the high pH (8.8) of the soil used in resurfacing the pen. The high pH of the soil may have affected the lignite's capacity to retain

NH_4^+ , especially at the initial stages following the lignite application. Based on the findings on the N retention mechanism of lignite (discussed in Chapter 3), the alkaline pH of the soil could facilitate the deprotonation of carboxyl groups in the lignite, and thus increased its N retention capacity. However, at such a high pH (8.8), N loss through NH_3 emission is facilitated. There was no difference in the NH_4^+ concentration between the manures from the two pens for the first two months but it was significantly higher in the lignite treated pen on the final sampling likely due to continuous retention of NH_4^+ by the lignite.

The total N concentration of the manure in both pens increased gradually over the 3 months sampling period with the manure in the lignite treated pen having significantly higher N compared to manure from the control pen at all sampling times. The higher N concentration in the lignite treated pen, especially at the initial sampling time (15th December 2017), can be attributed to lignite's ability to retain N in the manure (Chen et al. 2015; Sun et al. 2016). At the initial stages, following the lignite application to the pen, the lignite retained N in the manure most likely due to its low pH (by favouring the formation of NH_4^+ over NH_3) and then as more manure was deposited on the lignite, there was increase in the lignite's CEC leading to more retention of NH_4^+ (discussed in Chapter 3). It was expected the application of lignite to the pen will result in initial reduction (dilution) of N content in the manure, due to the relatively low N in the lignite compared to the manure, before increasing over time as more manure was deposited. However, the one month interval between lignite application and first sampling was probably too long to observe the expected N dilution effect of the lignite. At the first and second sampling times, the total C content was lower in the manure from the control pen compared to the lignite amended pen, and this could be attributed to the labile fraction of the higher C content of the lignite. After three months the extra C from the lignite was masked with increasing manure deposition, resulting in similar C content in both pens. The reason for the marked increase in C, between the second and third samplings is unclear. The EC of the

manure from the control pen was significantly higher than the manure in the lignite treated pen at all sampling times and this could be due to a diluting effects of the lignite (1.5 mS cm^{-1} compared to average manure EC of 12.5 mS cm^{-1} recorded over the sampling period) and the higher moisture content of the manure in the lignite treated pen (Table 4.1). In the lignite treated pen, salt concentration due to water loss or evaporation was less. Though the lignite effect was overridden by the continued manure deposition (leading to increase in EC of the lignite treated pen over time), the EC did not reach the level of the manure only.

Table 4. 1 Chemical properties of manure sampled from control (no lignite application) and lignite treated pens over a three month period. Values represent mean (n = 5) $\pm$ standard error of the mean.

	15th December 2017 (one month after cattle moved into pen)		16th January 2018		14th February 2018	
	Control	Lignite	Control	Lignite	Control	Lignite
pH _{water}	7.5 $\pm$ 0.03a	7.7 $\pm$ 0.05b	7.4 $\pm$ 0.01a	7.6 $\pm$ 0.04b	7.6 $\pm$ 0.03a	7.6 $\pm$ 0.04a
pH _{CaCl2}	7.4 $\pm$ 0.02a	7.6 $\pm$ 0.05b	7.4 $\pm$ 0.01a	7.5 $\pm$ 0.06b	7.5 $\pm$ 0.01a	7.4 $\pm$ 0.04b
NH ₄ ⁺ -N (mg kg ⁻¹)	6,567 $\pm$ 403a	5,385 $\pm$ 561a	6,671 $\pm$ 375a	6,383 $\pm$ 544a	6,432 $\pm$ 314a	7,533 $\pm$ 188b
Total N (%)	1.54 $\pm$ 0.11a	2.17 $\pm$ 0.07b	1.67 $\pm$ 0.05a	2.18 $\pm$ 0.08b	2.24 $\pm$ 0.03a	2.48 $\pm$ 0.03b
Total C (%)	17.6 $\pm$ 0.84a	22.2 $\pm$ 0.89b	18.4 $\pm$ 0.59a	22.6 $\pm$ 1.18b	29.0 $\pm$ 0.65a	29.9 $\pm$ 0.19a
EC (mS cm ⁻¹)	12.2 $\pm$ 0.29b	8.3 $\pm$ 0.54a	12.4 $\pm$ 0.41b	9.1 $\pm$ 0.44a	13.0 $\pm$ 0.18b	11.5 $\pm$ 0.18a
Moisture (%)	21.2 $\pm$ 1.3a	33.9 $\pm$ 1.4b	21.1 $\pm$ 1.5a	27.8 $\pm$ 2.0b	26.6 $\pm$ 0.8a	31.1 $\pm$ 1.8a

Values with the same letter in each row are not significantly different

4.3.2 Properties of the windrowed manures

Manure samples were taken from the windrows at the start of the composting process (day 0) to establish the baseline properties for composting. This ensured any changes in the manure properties that occurred during manure collection, transport and management prior to the windrow establishment were accounted for. The sampling was done after both windrows were homogenized by turning with the windrow turner and the moisture contents were adjusted to 50%. Hence, at the start of the composting, the properties of the manure only windrow were $\text{pH}_{\text{H}_2\text{O}}$ of 7.33, EC of 13.65 mS cm^{-1} , total C of 26.96%, total N of 2.45%, and NH_4^+ of $8,189 \text{ mg kg}^{-1}$. For the manure + lignite windrow, the properties were $\text{pH}_{\text{H}_2\text{O}}$ of 7.35, EC of 12.59 mS cm^{-1} , total C of 29.30%, total N of 2.26%, and NH_4^+ of $6,512 \text{ mg kg}^{-1}$.

4.3.3 Temperature profile during composting

The temperature profiles for the manure windrow and the manure + lignite windrow followed a similar pattern during the composting period with both treatments attaining thermophilic temperatures, $> 40^\circ\text{C}$ (Bernal et al. 2009; Czekala et al. 2016), by day 3 of composting (Figure 4.6). The microbial degradation of readily available compounds such as sugars and proteins leads to an increase in temperature at the onset of the composting process (Brito et al. 2008; An et al. 2012). The highest temperature recorded in the manure windrow was 61°C on day 12 whilst that recorded in the manure + lignite was 59°C on day 7. From day 41 to 85, the manure + lignite generally had a higher temperature than the manure alone. This could be due to the manure C being depleted faster than the lignite C, expected to be less bioavailable (Yoon et al. 2016), and thus able to sustain microbial activity over a longer period (Figure 4.6). Changes in temperature during composting reflect the intensity of the microbial activity and also the progress of the composting process (An et al. 2012). Based on the temperature profile, the presence of lignite did not stimulate or inhibit the windrow composting

of cattle manure. In addition, compared to the manure alone, the lignite did not distinctly alter the pattern of changes in temperature during the composting period, except extending the thermophilic phase for about 5 days (due to the lower bioavailability of the lignite).

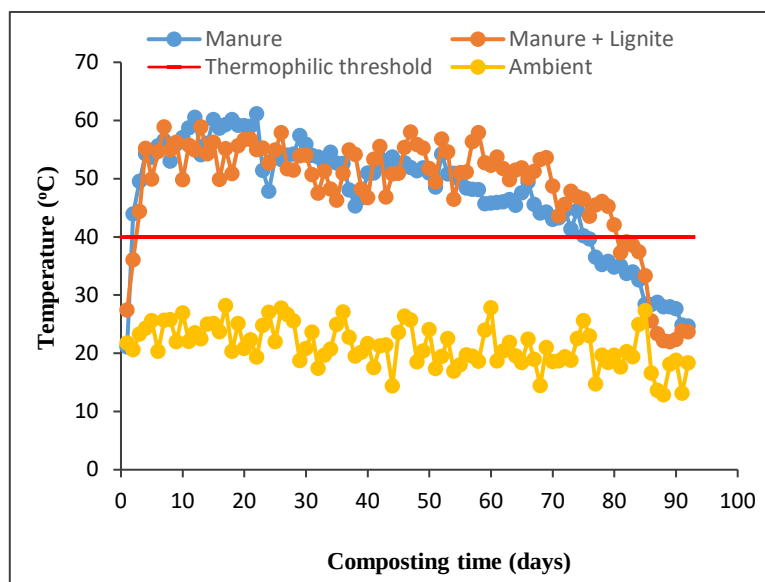


Figure 4. 6 Temperature profiles during composting of manure and manure + lignite

4.3.4 Changes in pH during composting

In both treatments, the pH increased markedly between day 0 and 7, remained fairly stable till day 49, then increased again (Figure 4.7). During composting, increases in pH have been attributed to ammonification or release of volatile NH_3 within the compost heap and proteolysis (Caceres et al. 2006; Gigliotti et al. 2012; Jia et al. 2016). Decreases in pH on the other hand have been attributed to the formation of organic acids, secondary metabolites, loss of NH_3 from the compost, and nitrification, (Beck Friis 2001; An et al. 2012; Li et al. 2019a). The marked increase in pH by day 7 coincided with an increase in NH_4^+ -N concentration in this period (Figure 4.7). The presence of lignite did not alter the pattern of pH change with composting time, though the pH of the manure remained significantly higher than the pH of the manure + lignite throughout the composting period except for days 0, 56 and 70. The lower pH of the manure + lignite could be a result of the lignite buffering increases in pH compared to the

manure only. At the end of the composting period, the pH of the manure and the manure + lignite increased by 0.62 and 0.53 units respectively.

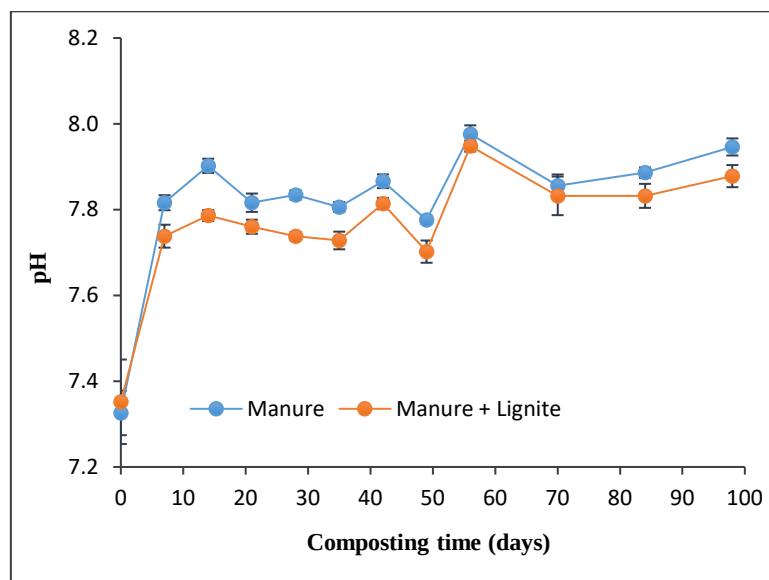


Figure 4. 7 pH during composting of manure and manure + lignite. Bars indicate standard error of mean (n=5)

4.3.5 Electrical conductivity

The concentration of salt resulting from organic matter mineralization usually leads to an increase in EC during composting (Gigliotti et al. 2012). A reduction in EC during composting has been attributed to microbial immobilization of nutrient electrolytes such as NH_4^+ salt (Khan et al. 2016; Li et al. 2019a). In this study, changes in the EC in both the manure and manure + lignite did not follow a consistent trend with composting time though the EC of the former increased for most parts of the composting period (Figure 4.8). The EC of the manure remained higher than that of the manure + lignite over the entire composting period, with the difference more pronounced after day 14. Compared to the manure, microbial activity was higher in the manure + lignite (reflected in higher CO_2 emission, Figure 4.14) which likely resulted in the immobilization of soluble salt, and thus relatively low EC. The immobilized salt, however, could be released at the later stages of the composting period, causing EC to decrease. In

addition, the lower EC of the lignite (1.5 mS cm^{-1}) compared to the manure (13.65 mS cm^{-1} at the start of composting) could also result from a dilution effect. At the end of the composting period, the EC of the manure was 15.1 mS cm^{-1} whilst that of the manure + lignite was 11.4 mS cm^{-1} .

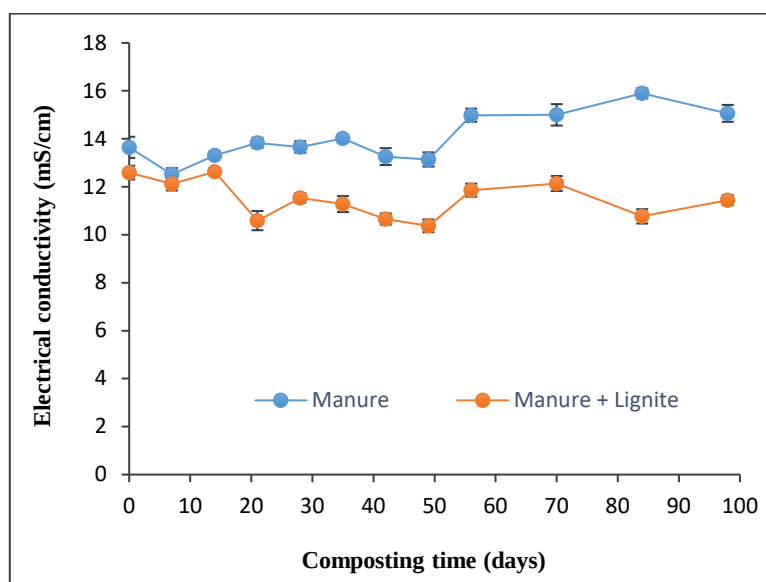


Figure 4. 8 EC of manure and manure + lignite during composting. Error bars represent standard error of means ($n = 5$).

4.3.6 Total nitrogen

Total N increased in both the manure alone and manure + lignite windrows by day 7 of composting and then decreased gradually for the rest of the composting period (Figure 4.9). Increases in total N during composting have been observed and reported to be due to a concentration effect resulting from the loss of organic matter (mass), at a faster rate than the loss of N (Bernal et al. 2009). In this study, the decrease in N with composting, especially during the initial thermophilic phase (day 7-21), in both treatments could be due to faster N losses from the windrows compared to the rate of organic matter loss. The high N loss between day 7 and 21 coincided with high NH_3 emission (Figure 4.13). Ammonia volatilization is highest during the thermophilic phase of composting due to high temperature and high pH (Bernal et al. 2009). Throughout the composting period, the manure + lignite had lower total

N concentration than the manure. It was expected that the manure + lignite will have higher total N concentration due to the ability of lignite to retain N as reported by Chen et al. (2015) and Sun et al. (2016). However, in both these studies, the lignite's capacity to retain N was assessed under ambient conditions which are different to the conditions (e.g. high temperature, high microbial activity) that prevail under composting conditions. The lower total N in the manure + lignite could be due to increased anaerobic conditions within the windrow, as composting progresses, due to the physical characteristics of the lignite (visually, the manure + lignite had less pore spaces due to the fine lignite particles) likely leading to denitrification and loss of N as dinitrogen (N_2). The manure + lignite had higher CH_4 and N_2O emissions (Figures 4. and 4. respectively), indicating anaerobic conditions (Hao et al. 2001; Bernal et al. 2009). The windrows were turned at weekly intervals and so aeration of the windrows was passive for most of the composting period and influenced by the porosity of the composting feedstock which appeared higher in the manure windrow than in the manure + lignite.

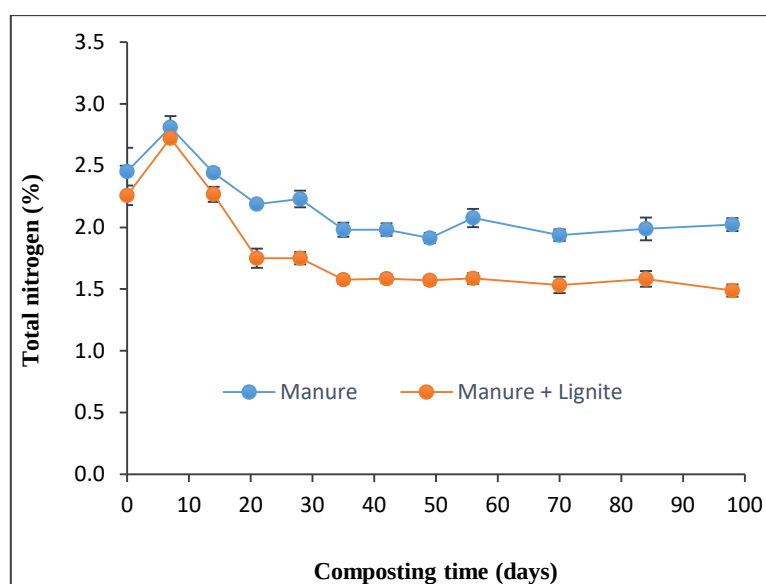


Figure 4. 9 Total N concentration in manure and manure + lignite during composting. Error bars represent standard error of means (n = 5).

4.3.7 Mineral N: NH_4^+ -N and NO_3^- -N

The changes in NH_4^+ -N concentration with composting time followed a similar pattern as the total N (Figure 4.10). In both the manure and the manure + lignite, the NH_4^+ -N increased by day 7 and then reduced gradually for the rest of the composting period, reaching 5,388 and 3,570 mg N kg^{-1} in the manure and manure + lignite respectively. The lignite did not have a significant effect on the change in NH_4^+ -N, relative to the initial concentration, at the end of the composting period: 2,801 and 2,942 mg N kg^{-1} for the manure and manure + lignite respectively. As composting progresses, especially the post thermophilic phase, the oxidation of NH_4^+ -N to NO_3^- leads to reduction in NH_4^+ -N concentration with corresponding increase in NO_3^- concentration (Bernal et al. 2009; Caceres et al. 2018). In this study, relative to the reduction in NH_4^+ -N concentration, the increase in NO_3^- concentration (Figure 4.10) was insignificant and therefore could not be the main mechanism accounting for the reduction in NH_4^+ -N during composting. Other processes leading to a reduction in NH_4^+ -N during composting are biological immobilization, NH_3 emission, especially during the thermophilic phase, and denitrification under predominantly anaerobic conditions (Bernal et al. 2009). Ammonia emission during the composting process was higher in the manure than in the manure + lignite (discussed under section 4.3.9.1). Hence, nitrification and denitrification of NH_4^+ to N_2 could be a major pathway or mechanism accounting for the lower NH_4^+ concentration in the manure + lignite caused by more anaerobic conditions due to the higher bulk density, and hence lower porosity, of the material due to the small particle size of the lignite.

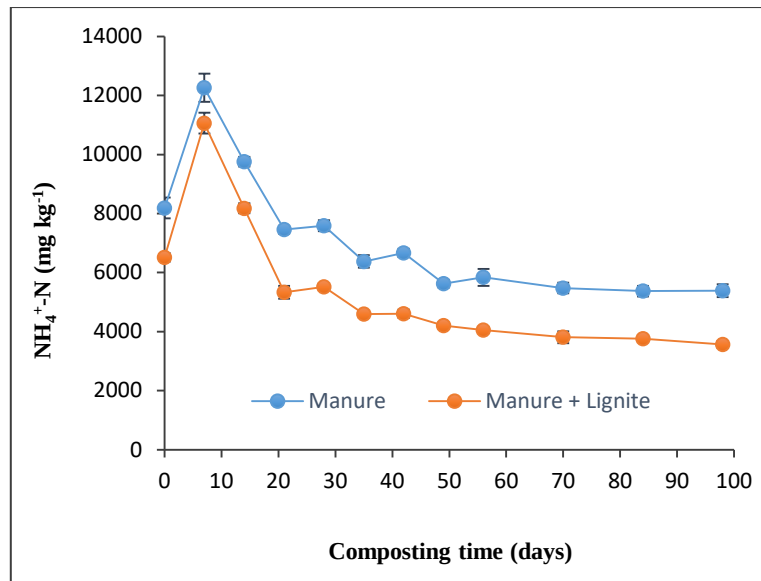


Figure 4. 10 Ammonium ($\text{NH}_4^+\text{-N}$) concentration in manure and manure + lignite during composting. Error bars represent standard error of means ($n = 5$).

Nitrate concentration remained low ($< 25 \text{ mg kg}^{-1}$), with no nitrate detected between days 28 and 49, in both the manure alone and manure + lignite throughout the composting period (Figure 4.11). Changes in NO_3^- concentration followed a similar pattern in both treatments except between days 84 and 98 where the concentration decreased in the manure + lignite. The later stages of the composting process are often characterized by nitrification of NH_4^+ leading to the accumulation of NO_3^- (Caceres et al. 2018). In this study, in both treatments, the levels of NO_3^- concentrations recorded was negligible relative to the reduction in NH_4^+ concentration.

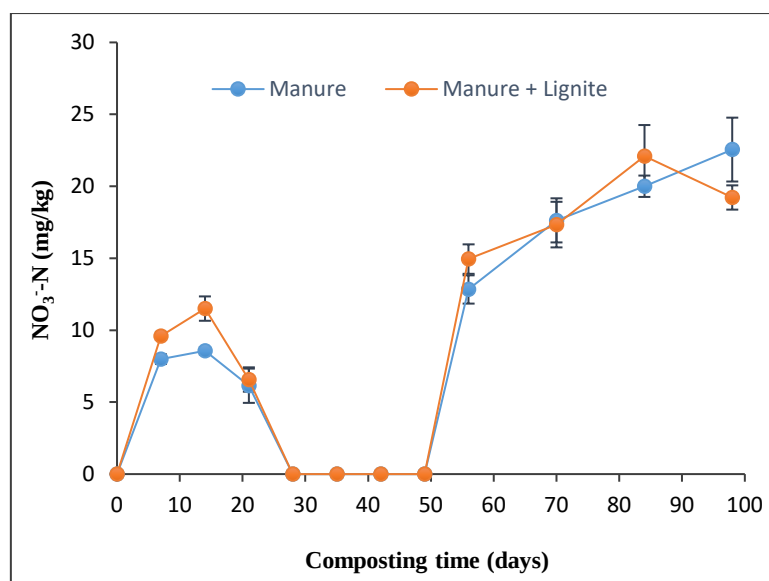


Figure 4. 11 Nitrate ($\text{NO}_3\text{-N}$) concentration in manure and manure + lignite during composting. Error bars represent standard error of means ($n = 5$).

4.3.8 Total carbon

The reduction in total C concentration during composting is a result of the mineralization of organic matter to CO_2 (Bernal et al. 2009). Under anaerobic conditions, the loss of C as CH_4 could be significant (De Guardia et al. 2010b). Changes in C concentration with composting time followed a downward trend in both the manure and the manure + lignite (Figure 4.12). Up to day 7 of composting, the manure + lignite had a higher, though non significant, total C than that of the manure after which the C in the manure remained significantly higher for the rest of the composting period. The lower C in the manure + lignite, especially the steep reduction between day 7 and day 21, could be attributed to the lignite enhancing microbial activity and thus leading to higher C loss mainly through CO_2 emission (Figure 4.14) and to a lesser extent through CH_4 emission (Figure 4.15). At the end of the composting period, the C concentration was 23.4 and 16.7% in the manure and manure + lignite respectively. The change in C:N ratio from start to end of composting for the manure was 11.0:1.0 to 11.4:1.0 (due to lower C loss compared to N loss) whilst for the manure + lignite, the change was from 13.0:1.0 to 11.2:1.0.

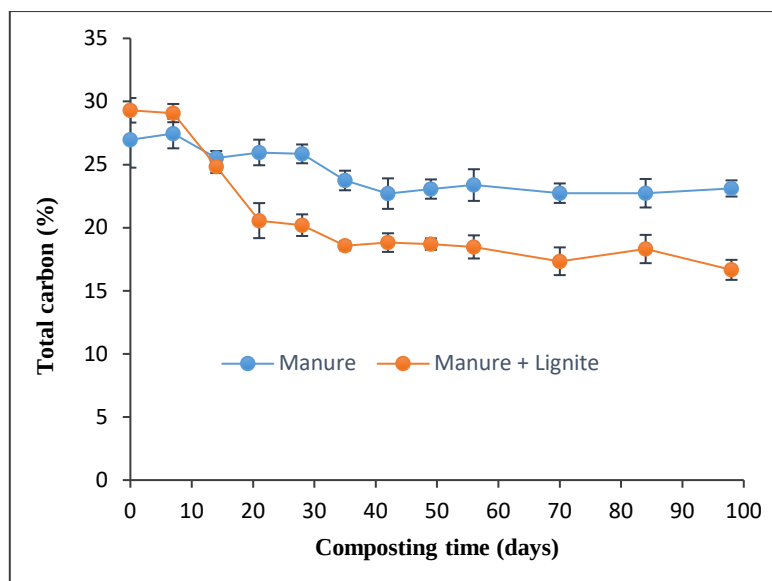


Figure 4. 12 Total carbon concentration in manure and manure + lignite during composting. Error bars represent standard error of means (n = 5).

4.3.9 Gaseous emissions

A manuscript, with the title “Lignite effects on NH_3 , N_2O , CO_2 and CH_4 emissions during composting”, has been submitted for publication in the Journal of Environmental Management (Ref: JEMA-D-19-06999), and it is currently under review [this has now been published and attached in the appendix]. As indicated in the methodology, the gas emissions were only measured during periods of westerly winds and therefore there are gaps in the data (e.g. from day 18 to 36).

4.3.9.1 Ammonia emissions

Ammonia emissions followed a downward trend with composting time in both treatments (Figure 4.13). The capacity of lignite to suppress NH_3 emission was only seen during the initial stages (at least up to day 17) of the composting period where emission levels were high, after which there was little difference between the treatments. Lignite’s capacity to suppress NH_3 emissions could be attributed to the high CEC of the lignite, especially at higher pH due to deprotonation of carboxyl group (discussed in Chapter 3), leading to retention of NH_4^+ on

exchange sites and thus reduced the proportion of NH_4^+ available for conversion to NH_3 (Jones et al. 2007). In addition, the higher C from the lignite likely favoured the immobilization of mineral N, leading to reduction in NH_3 emission (Paillat et al. 2005). Relative to the manure alone, the addition of lignite reduced the average daily NH_3 emission by 45 % (from 81.92 to 45.18 mg kg^{-1} DMI). Ammonia loss is a major concern when it comes to composting, leading to a reduction in compost quality as well as posing health and environmental problems (Bernal et al. 2009), and the use of lignite shows clear benefits for reducing NH_3 loss.

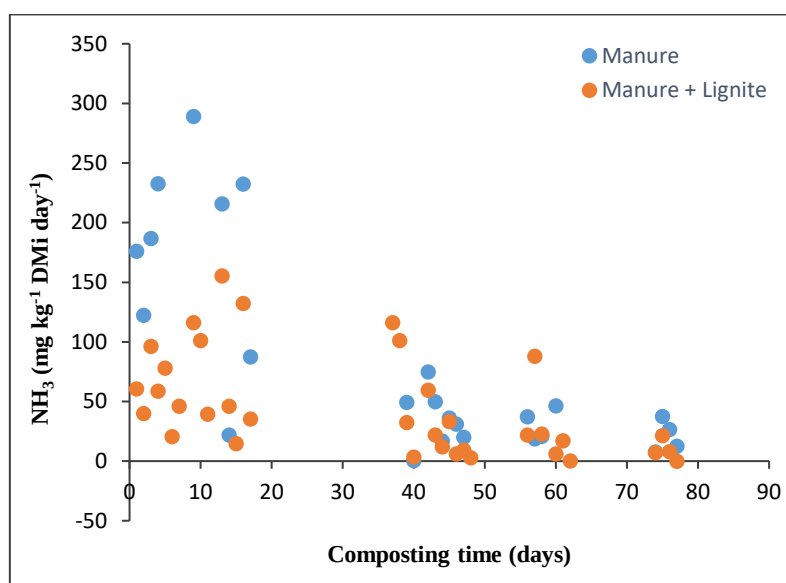


Figure 4. 13 Daily NH_3 flux from manure and manure + lignite during composting

4.3.9.2 Carbon dioxide emissions

Carbon dioxide (CO_2) emissions were higher in the manure + lignite than the manure alone throughout the composting period (particularly at the later stages) (Figure 4.14). Whiteley and Pettit (1994a), reported, from an incubation study, the ability of lignite to inhibit microbial respiration leading to a reduction in CO_2 evolution during the decomposition of wheat straw. However, this inhibitory effect of lignite was not observed under the condition of windrow composting of cattle manure. Under this condition, the lignite appears to have served as an additional C source for microbial activity resulting in higher CO_2 evolution, compared to the manure. The CO_2 emission from the manure followed a downward trend with composting time

whilst from the manure + lignite, the pattern of emission exhibited more fluctuations. The fluctuations in the CO₂ emissions coincided with the windrow turning times, likely due to redistribution of C during the turning process. The higher fairly stable CO₂ emission (from day 56) from the manure + lignite was likely caused by the more resistant C in the lignite sustaining microbial activity for a longer period. The daily average CO₂ evolved (based on the days the gas measurements were taken) was 6.97 and 9.84 g kg⁻¹ DMi for the manure and the manure + lignite respectively. This corresponds to the manure + lignite emitting 41% more CO₂ relative to the manure.

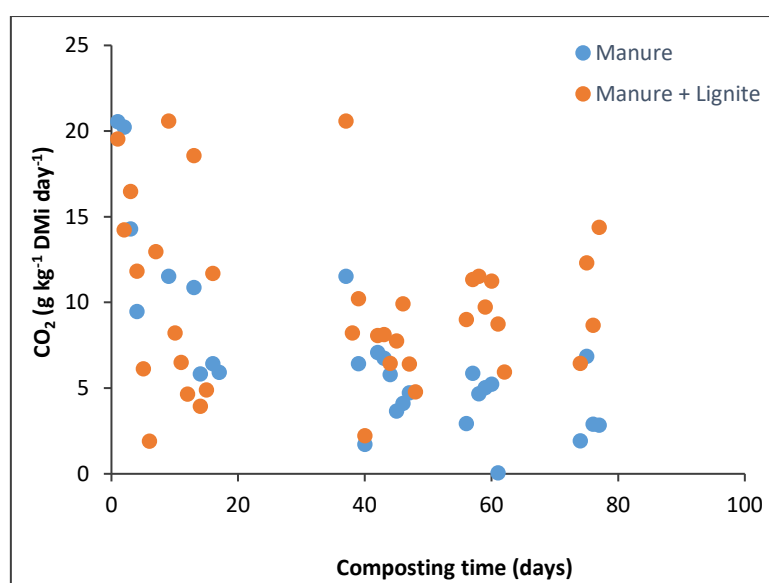


Figure 4. 14 Daily CO₂ flux from manure and manure + lignite during composting.

4.3.9.3 Methane emissions

The daily average CH₄ emissions (-0.0050 and 0.0098 g kg⁻¹ DMi for manure and manure + lignite respectively) were much lower than the CO₂ emission (6.8 and 9.8 g kg⁻¹ DMi for manure and manure + lignite respectively). Hence, compared to the CO₂, CH₄ emission had little impact on the loss of total C during the composting process.

Methane emissions did not follow any consistent pattern during the composting period for either treatment (Figure 4.15). Formation of CH₄ occurs through reduction of CO₂ by methanogens in anaerobic pockets within the compost (Boldrin et al. 2009; Yang et al. 2013).

The manure + lignite had higher CH₄ emissions than the manure alone. This could be attributed to more anaerobic pockets in the manure + lignite windrow created by the smaller particle size of the lignite and facilitated by the passive aeration system employed in this study. Negative CH₄ fluxes were recorded in both treatments but more so in the manure where most of the fluxes were negative. Methanotrophs represent a distinct group of bacteria which use CH₄ as their sole source of C and energy and are the largest biological sink for CH₄ (Halet et al. 2006). Methanogens on the other hand are organisms that utilize compounds such as acetate, dihydrogen and CO₂ for CH₄ production (Sharma et al. 2011). Net emission of CH₄ is the balance of its production from anaerobic methanogenesis and oxidation aerobic/anaerobic methanotrophy (Chen et al. 2014). The conditions within the manure windrow, compared to the manure + lignite, is likely to favour the activities of methanotrophs which oxidized the methane produced within the windrow. According to Sharma et al. (2011), the reduction in CH₄ emission during the composting of cattle manure could be attributed to the increasing aerobic methanotrophs, rather than decreasing anaerobic methanogens. The average daily CH₄ flux during the composting period was -5.01 and 9.77 mg kg⁻¹ DMi day⁻¹ for the manure and the manure + lignite respectively. The emission of CH₄ from the manure + lignite remained fairly stable due to sustained microbial activity under presumably anaerobic condition.

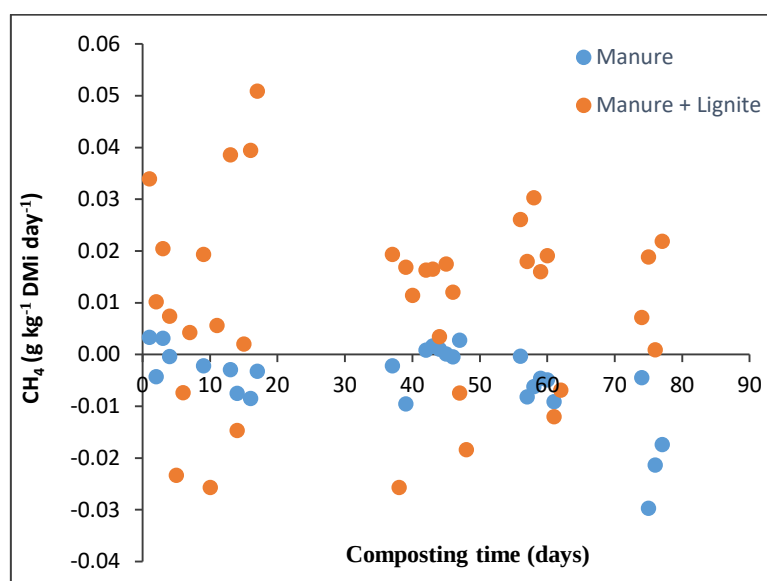


Figure 4. 15 Daily CH₄ flux from manure and manure + lignite during composting.

4.3.9.4 Nitrous oxide emissions

Nitrous oxide emissions during composting were higher in the manure + lignite than the manure alone (Figure 4.16). In both treatments, negative fluxes were recorded at certain times of the composting period. In the manure alone, the negative N₂O fluxes were recorded at the later stages of the composting period whilst in the manure + lignite, most of the negative fluxes occurred at the initial stages of composting. There was a net positive average daily N₂O flux in both treatments, with the flux more than two-fold in the manure + lignite compared to the manure alone: 3.28 mg kg⁻¹ DMi and 1.43 mg kg⁻¹ DMi respectively. The higher N₂O fluxes in the manure + lignite was likely as a result of more anaerobic conditions created by the fine particles of the lignites. During composting, the development of anaerobic pockets within the material leads to the emission of N₂O through denitrification (Bernal et al. 2009; Caceres et al. 2018), and when lignite is used in field-based windrows, the conditions appear to be more conducive to this N loss pathway. This was consistent with the higher CH₄ emission in the manure + lignite compared to the manure only (Figure 4.15).

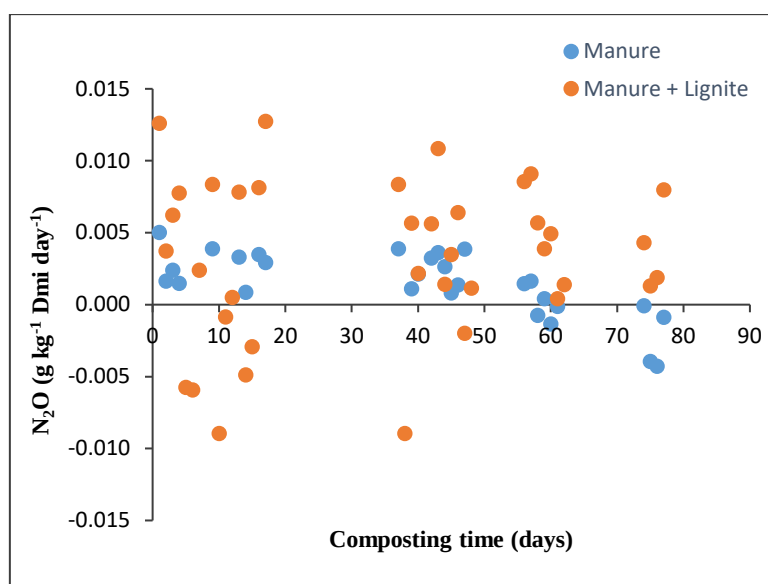


Figure 4. 16 Daily N₂O flux from manure and manure + lignite during composting.

4.4 Conclusions

Lignite application to the cattle pen caused an increased retention of N in manure after a three-month period of continuous manure deposition (Table 4.1). However when the manures were windrowed, the control and lignite amended manure had similar N content (Figure 4.9) on day 0. This is likely due to i) heterogeneity in N deposition across the cattle pen which was not accounted for despite the comprehensive pen manure sampling strategy (a total of 100 samples per pen from 5 segments), and ii) inconsistencies in scraping the manure from the pens. The lignite was able to retain N in the pen and also suppressed NH_3 loss during the composting process most likely through increased retention on the cation exchange sites associated with deprotonation of the carboxyl groups at the alkaline pH, but N loss, likely through other pathways such as N_2O and possibly N_2 , led to a lower concentration of total N in the lignite amended manure compost. Higher emissions of CH_4 observed in the lignite treatment during the composting process could be attributed to the finer particles of lignite increasing the bulk density (and decreasing the porosity and aeration) of the manure + lignite (by visual observation, the lignite treatment appeared less porous) compared to the manure alone. Overall, the presence of lignite in manure did not prolong or delay the duration of the windrow composting process. In addition, the lignite did not negatively affect the manure composting process.

This study provided an understanding of industry-scale issues in management of animal manures, and the potential for lignite to improve this under feedlot conditions. However we were not able to study the mechanisms driving lignite's effect on the composting of manure (for instance gas emissions could only be measured during periods of westerly wind direction, and the alkaline soil used in resurfacing may have affected the initial N content of the lignite amended manure by influencing lignite's ability to acidify the manure and reduce NH_3 loss) and could only deduce the mechanisms based on our previous characterization of the lignite

(Chapter 3). Therefore a controlled environment is required to better understand these mechanisms. In Chapter 5, the impact of lignite on composting of manure in an in-vessel composting system under a controlled environment is presented. Two different lignite materials were used in the generation of the lignite amended manure under simulated pen conditions (including the same material used in this field experiment), and these were then composted using a comprehensive laboratory scale in-vessel composting system which allowed for online measurements of gaseous emissions over the entire duration of the composting process.

CHAPTER 5: The Mechanisms causing Lignite's Effect on Composting of Cattle Manure – a Controlled Environment Study

5.1 Introduction

This laboratory scale in-vessel composting experiment was carried out to understand the mechanisms controlling the impact of lignite on composting of cattle manure (discussed under in Chapter 4). The use of the in-vessel composting system allowed for the assessment of the mechanisms in a controlled environment. Two lignites with differing properties (e.g. pH, C, EC and CEC), the Bacchus Marsh lignite used in the field study (Chapter 4) and a lignite from Loy Yang, were used in this study to generate lignite amended manure.

The objective of this study was to assess the effect of lignite amendment on the process of composting of cattle manure by comparing the i) changes in physicochemical parameters of the manure during composting, such as organic matter degradation and N transformations, ii) greenhouse gas and ammonia emissions, and iii) compost maturity indices between non-amended and lignite amended composting manure.

5.2 Materials and methods

5.2.1 Raw materials (manure and lignite) and preparation of feedstocks for composting

The manure used in this study was collected from the cattle feedlot where the field study was carried out (Chapter 4). Sample was collected from different spots of heaped manure (to obtain representative sample) in cattle pen using shovel into plastic containers. The Bacchus Marsh (BM) lignite and Loy Yang (LY) lignite were respectively sourced from the Maddingley and Loy Yang open cut mines located in Victoria (refer to 3.2.1 of Chapter 3 for details). Representative samples were taken from stockpiles of crushed lignite (recently excavated with no treatment of any sort). It should be noted that the lignites used for the composting study, were from a separate sample collection (collected in 2018) than that used for the

characterization study reported in Chapter 3 (collected in 2016). Lignite amended feedstocks were prepared by mixing separate samples of manure with the as-mined BM lignite (manure + BM) and the LY lignite (manure + LY) so that the proportion of dry lignite in the dry manure-lignite mix was 20% w/w. This was identified as a suitable ratio for N retention based on previous studies with cattle manure by Chen et al. (2015) and Sun et al. (2016). A third composting feedstock, made up of manure alone (from the same batch used in preparing the lignite treatments), served as the control. Care was taken to ensure that feedstocks were prepared in a manner to simulate the generation of manure in a cattle pen with and without lignite. In a typical feedlot, it is estimated that up to 67% of excreted N in cattle manure could be lost through NH_3 volatilization from the pen surface (Bierman et al. 1999). To replenish the N lost prior to the manure collection, in order to assess N retention capacity of the lignite (similar to what would occur in a lignite treated cattle pen), urea solution was added, at 2-day intervals for a period of 10 days, to all feedstocks after spreading them on impervious mats (0.8 m x 4 m) (Figure 5.1). The amount of urea added (a total of $\sim 60 \text{ g kg}^{-1}$ dry manure) was based on the difference between the expected N ($\sim 5\%$ of total solids) in freshly excreted manure (Watts et al. 2011) and the N content (2.13%) of the manure prior to the urea addition. The feedstock was mixed after each addition of urea to ensure uniform distribution of the added urea, and was collected 4 days following the final urea addition and stored under ambient conditions prior to composting.



Figure 5. 1 Preparation of feedstocks for composting: manure and manure + lignite on mats to which urea solution was added at 2 day intervals.

5.2.2 In-vessel composting system

The in-vessel composting system consisted of six 60 L vessels, 60 cm in depth and 40 cm in diameter. Each vessel had a perforated plate, 12 cm from the base of the vessel, for even distribution of air and two type-T thermocouples, one at the centre of the vessel and the other inside the wall of the vessel, for temperature measurements. Temperature was controlled within each vessel with a heating cable coiled around the outside of the vessel and covered with a 0.5 cm thick foam insulation layer. The heating cable served to maintain compost temperature and was automatically activated by a CR23x Micrologger (Campbell Scientific Inc. Logan, Utah USA) when the vessel wall temperature was cooler than the compost temperature. The top and bottom of each vessel were capped with polystyrene to reduce heat loss. Humidified air was continuously supplied to all vessels through a manifold using a diaphragm vacuum pump (KNF Neuberger, N840.3FT.18) at a constant rate of $0.21 \text{ L min}^{-1} \text{ kg}^{-1}$ initial feedstock dry matter (DMi). The moisture in the air exiting the vessels was removed (to prevent damage to the gas analyser and also to minimize its interference with gas spectra analysis (Griffith et al. 2012)) by connecting each air stream to a dehumidifier (Kelk, DH-209C) and collecting the condensate on a daily basis in 500 mL plastic containers with the aid

of peristaltic condensate pumps (Buhler technologies, CP double). Collected condensate was frozen prior to analysis for $\text{NH}_4^+\text{-N}$. Dehumidified air exiting the condensers, as well as the background air (for calibration), was passed through a Valco 8-port gas sampling valve (Valco Instruments Co. Inc., Houston, TX, USA) set to a 30 min switching interval with background air collected after every second sample (1 hr intervals) (4.5 hr interval per vessel), and then to a closed path Fourier Transform Infrared Spectrometer (FTIR) (Spectronus, Ecotech Group, Knoxfield, VIC, Australia) for gaseous (CO_2 , CH_4 , N_2O and CO) measurements (Griffith et al. (2012)). Each of the 30-min switching intervals comprised 5 min of flushing and evacuation of the FTIR sample cylinder (previous gas); 4 mins for filling the cylinder with the gas sample; 3 mins for settling of gas in the cylinder; 15 mins for collection and analysis of spectra and finally 3 mins delay before switching to the next vessel or background.

Ammonia concentration was measured in exhaust air drawn from a second port on the vessel by bubbling the air, at 0.5 L min^{-1} , through a flask containing 150 mL of 0.3M H_3PO_4 . The acid was replaced at 24 h intervals and samples were frozen prior to analysis. Ammonia flux was calculated according to Woodley et al. (2018). The oxygen level of the exhaust air was monitored with an O_2 sensor (SO-210, Apogee Instruments, Inc. Logan, Utah, USA) at 2 min intervals. A schematic diagram and photograph of the composting system are shown in Figures 5.2 and 5.3 respectively.

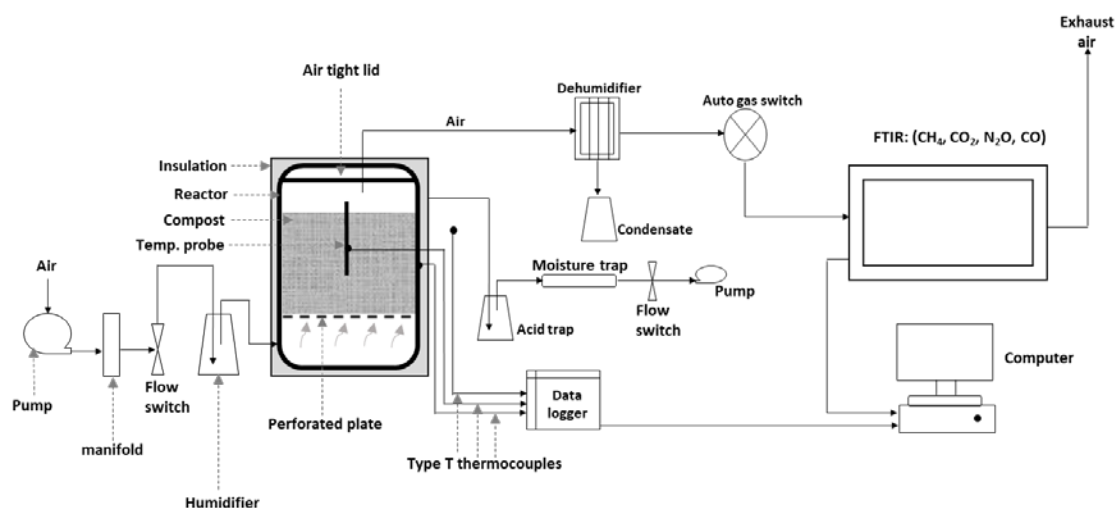


Figure 5. 2 Schematic diagram of the in-vessel composting system.

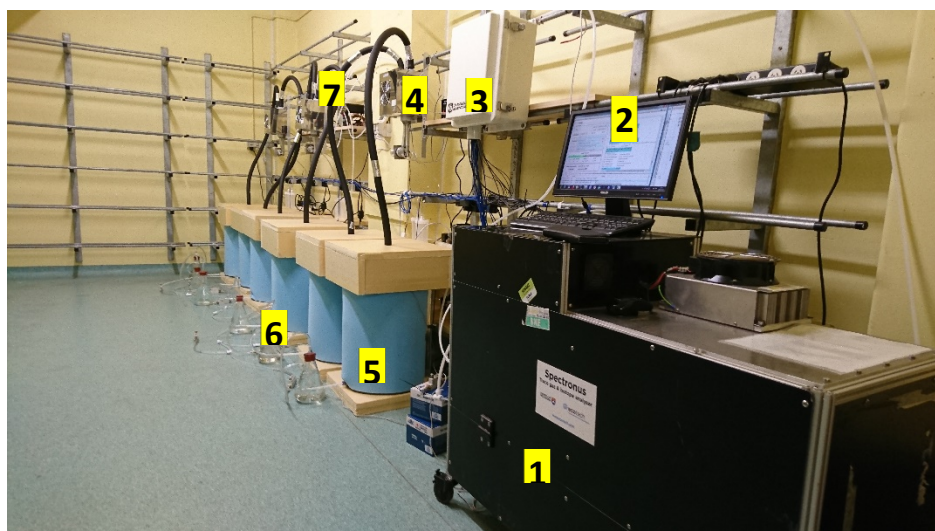


Figure 5. 3 Photograph showing the components of the in-vessel composting system: 1. Closed path Fourier Transfer Infrared spectroscopy (FTIR) for gas measurement; 2. Computer with FTIR operating program; 3. Data logger for storing temperature data and for controlling heating cable; 4. Dehumidifier for stripping moisture from air exiting the vessels; 5. Insulated composting vessel with polystyrene sheets at both ends; 6. Humidifier to minimize moisture loss from compost; 7. Insulated tubes carrying gas from vessels to FTIR.

5.2.3 Composting and sampling procedure

To enable sufficient replication (4 reps), due to the restricted capacity of the in-vessel composting systems (six composting vessels), the three treatments were put through the composting vessels in two batches with two replicates of each treatment per batch. Results reported are averages of the four replicates. To ensure continuity of the physicochemical properties between batches and prevent composting from occurring, the second batch of feedstocks was maintained at $\leq 20\%$ w/w moisture content and stored in closed plastic containers at room temperature (maximum of $\sim 20^\circ\text{C}$).

Prior to a composting run, the moisture content of each feedstock (manure, manure + BM and manure + LY) was adjusted to 55% w/w, before loading into each composting vessel at a rate of 7 kg DM per vessel. During the composting period, the vessels were opened at 3-day intervals for compost sampling. At each sampling time, the contents of the vessels were thoroughly mixed with a trowel to ensure homogeneity after which 4 grab samples were taken with the trowel for a combined sample of ~ 70 g fresh weight (~ 30 g DM). Moisture content was adjusted if required (based on moisture content of the sample collected). Collected samples were immediately frozen at -20°C for subsequent analyses. Collected acid trap samples were analysed colourimetrically for $\text{NH}_4^+\text{-N}$ using a Skalar SAN++ segmented flow analyser. No difference was observed in the composting process of the first and second batches of feedstock, both lasting for 21 days.

5.2.4 Physicochemical analyses of raw materials, feedstocks and compost samples

Raw materials (excluding lignites due to their already acidic pH), feedstocks and compost samples were acidified (as described in section 4.2.4.3 of Chapter 4) for analysis of total and mineral N to minimize N loss through NH_3 volatilization (Van Vliet et al. 2006; An et al. 2012). All other analyses were conducted on unacidified samples. The electrical conductivity (EC),

pH, total and mineral N and total C in the samples were measured as described in section 4.2.4.3 of Chapter 4. The moisture and organic matter contents in the samples were determined after drying the samples at 105 °C for 24h in an oven and ashing at 550 °C for a further 24 h in a muffle furnace respectively (Awasthi et al. 2015). Total element concentrations were determined after digestion of oven dried samples in concentrated HNO₃/30% H₂O₂ and analysed by ICP-OES (Perkin Elmer Optima 8300 DV-radial view) (Wolf et al. 2003).

5.2.5 Calculations

The flux of CO₂, CH₄, CO, N₂O was determined using equation 5.1. For the intake (background) and exhaust (from composting vessels) air, the FTIR gas reading (ppm) was converted to flux (g min⁻¹) by determining the moles (n) of the gas (e.g. CO₂) using the ideal gas law and then multiplying the number of moles by the molar mass (g mol⁻¹) of the gas and the airflow rate (m³ min⁻¹) during composting according to;

$$\text{Gas flux (g min}^{-1}\text{)} = \frac{\left(\frac{[\text{Gas}]}{1000000}\right) \times P \times \text{airflow rate} \times \text{molar mass of gas}}{RT} \quad (5.1)$$

where $\left(\frac{[\text{Gas}]}{1000000}\right)$ is the concentration of the gas (ppm) divided by 1 million to obtain the amount of gas (volume, m³), P is the pressure (HPa), R is the ideal gas constant (m³ HPa mol⁻¹ K⁻¹) and T is the temperature (°K). The flux for the vessel is the difference between the intake and exhaust air.

Organic matter, total N and total C losses, as well as the final dry matter at the end of the composting period were calculated according to the equations (Larney et al. 2005; Bernal et al. 2009);

$$\text{Organic matter (g)} = \text{Dry matter (g)} - \text{ash content (g)} \quad (5.2)$$

$$\text{Organic matter loss (\%)} = 100 - 100 \times \left(\frac{X_1(100-X_2)}{X_2(100-X_1)}\right) \quad (5.3)$$

$$Total\ N\ or\ Total\ C\ loss\ (\%) = 100 - 100 \times \left(\frac{X_1 Y_2}{X_2 Y_1} \right) \quad (5.4)$$

$$Final\ dry\ matter\ (g) = initial\ dry\ matter \times \frac{X_1}{X_2} \quad (5.5)$$

where X_1 and X_2 are the initial and final ash contents (%) respectively of the compost ; Y_1 and Y_2 are the initial and final total N or total C concentrations respectively.

5.2.6 Germination index

The germination index (GI), which estimates the degree of compost maturity based on tests for phytotoxicity (Bernal et al. 2009), was one of the indices (others were CO₂ evolution rate and change in temperature) used in monitoring the maturity of the compost and was determined using a modified method of Tiquia (2010). Extracts from compost samples were prepared by shaking compost samples with distilled water at 1:10 w/v ratio end-over-end for 1h, followed by centrifuging and filtering with Whatman number 42 filter paper. Ten cress (*Lepidium sativum* L.) seeds were placed in a petri dish (9 cm diameter) lined with Whatman number 42 filter paper and containing 3 mL of the filtered compost extract. Distilled water was used as the control. The Petri dishes were covered with Parafilm to minimize moisture loss whilst allowing air exchange (Wu et al. 2000) and kept in the dark in an incubator at 25°C for 48 hours. The number of germinated seeds were counted and the length of the primary root measured in both the compost extract (extract) and control (water). Seeds with radicle length of > 2mm were considered germinated (Marcu et al. 2013). The GI was calculated from the relative seed germination (RSG) and the relative root growth (RRG) as follows;

$$RSG\ (\%) = \frac{\text{seeds germinated in extract}}{\text{seeds germinated in water}} \times 100 \quad (5.6)$$

$$RRG\ (\%) = \frac{\text{root length in extract}}{\text{root length in water}} \times 100 \quad (5.7)$$

$$GI = \frac{RSG \times RRG}{100} \quad (5.8)$$

5.2.7 Statistical analysis

One-way analysis of variance (ANOVA) test was carried out using GenStat 16 (VSN International UK). Gas and temperature data obtained from the FTIR and Datalogger were processed using SAS software 9.4 (SAS Inc., Cary, NC, USA). Tukey HSD test was used to assess significant differences between treatment means at 5% probability level.

5.3 Results and discussion

5.3.1 Characteristics of raw materials and feedstocks

The main properties of the raw materials, feedstocks and composts are presented in Table 5.1. For the raw materials, both lignites were acidic (pH_{water} 4.57-4.96) while the manure was alkaline (pH_{water} 7.48). The EC, total and ammonium-N, and the total elemental concentration, with the exception of iron (Fe) and sulfur (S) was higher in the manure than the lignites. The BM lignite was more saline, and contained higher amounts of N and all elements (except total C and aluminium) than the LY lignite.

The pH_{water} of the feedstocks was alkaline: 7.26, 7.36 and 7.21 for manure, manure + BM, and manure + LY respectively. The presence of lignite in the manure-lignite mix did not create acidic pH in the mix likely due to the pH buffer capacity of the lignite being neutralized by the manure (lignite constituted 20% w/w of the lignite-manure mix). The lignite amended manure feedstocks had higher total C (36.1% for manure + BM and 35.3% for manure + LY) compared to 26.8% of the manure alone and this was attributed to the higher total C of the lignites (57-62%). Similar observation was made with respect to the organic matter (OM) content of the feedstocks. Owing to lignite's ability to retain N in manure (Chen et al. 2015; Sun et al. 2016), the lignite amended manures had higher total and ammonium-N than the manure alone (Table 5.1). Nitrate was not detected in any of the tested materials.

Table 5. 1 Properties of the lignites, manure, and feedstock (after addition of urea) and mature compost. Values represent mean (n = 3 for raw materials and feedstocks and n = 4 for final compost) $\pm$ standard error of mean.

	Raw materials			Feedstocks			Final composts		
	Manure	BM	LY	Manure alone	Manure + BM	Manure + LY	Manure alone	Manure + BM	Manure + LY
pH _{H2O}	7.48 $\pm$ 0.01	4.96 $\pm$ 0.03	4.63 $\pm$ 0.04	7.26 $\pm$ 0.02	7.36 $\pm$ 0.03	7.21 $\pm$ 0.03	8.16 $\pm$ 0.10	7.86 $\pm$ 0.13	7.79 $\pm$ 0.14
EC (mS cm ⁻¹)	13.06 $\pm$ 0.15	2.09 $\pm$ 0.11	0.18 $\pm$ 0.01	13.31 $\pm$ 0.26	11.05 $\pm$ 0.28	9.18 $\pm$ 0.31	12.28 $\pm$ 0.39	10.05 $\pm$ 0.30	9.30 $\pm$ 0.31
TC (%)	29.66 $\pm$ 0.26	57.14 $\pm$ 0.37	62.19 $\pm$ 1.66	26.8 $\pm$ 0.88	36.1 $\pm$ 0.81	35.3 $\pm$ 0.52	24.39 $\pm$ 1.21	34.30 $\pm$ 1.10	33.57 $\pm$ 0.45
OM (%)	65.75 $\pm$ 1.60	93.2 $\pm$ 0.22	89.6 $\pm$ 1.1	63.0 $\pm$ 0.45	69.2 $\pm$ 0.43	68.7 $\pm$ 0.15	51.3 $\pm$ 0.33	61.77 $\pm$ 0.61	63.19 $\pm$ 0.16
TN (%)	2.15 $\pm$ 0.09	0.61 $\pm$ 0.01	0.60 $\pm$ 0.02	2.34 $\pm$ 0.06	2.52 $\pm$ 0.10	2.52 $\pm$ 0.03	2.56 $\pm$ 0.01	2.66 $\pm$ 0.07	2.73 $\pm$ 0.03
CN ratio	13.30 $\pm$ 0.12	94.0 $\pm$ 0.44	103.5 $\pm$ 0.35	11.5 $\pm$ 0.12	14.7 $\pm$ 0.08	14.0 $\pm$ 0.18	9.51 $\pm$ 0.43	12.88 $\pm$ 0.49	12.29 $\pm$ 0.07
NH ₄ ⁺ -N (mg kg ⁻¹)	2,737 $\pm$ 27	<0.2	<0.2	3,118 $\pm$ 60	5,786 $\pm$ 69	5,252 $\pm$ 139	3,004 $\pm$ 62	4,308 $\pm$ 141	4,479 $\pm$ 325
<i>Total element concentration, mg kg⁻¹</i>									
Al	9,770 $\pm$ 192	506 $\pm$ 14	3,278 $\pm$ 34	10,653 $\pm$ 169	9,076 $\pm$ 426	9,235 $\pm$ 376	13,649 $\pm$ 215	8,583 $\pm$ 344	11,182 $\pm$ 179
Fe	4,755 $\pm$ 226	5,452 $\pm$ 109	418 $\pm$ 81	5,412 $\pm$ 153	5,154 $\pm$ 213	5,219 $\pm$ 418	6,514 $\pm$ 55	6,124 $\pm$ 306	5,357 $\pm$ 66
Mg	7,200 $\pm$ 133	5,489 $\pm$ 39	418 $\pm$ 26	6,528 $\pm$ 81	5,450 $\pm$ 27	5,173 $\pm$ 85	9,431 $\pm$ 77	8,105 $\pm$ 135	6,752 $\pm$ 190
Na	12,802 $\pm$ 80	2,036 $\pm$ 24	346 $\pm$ 11	13,274 $\pm$ 66	10,702 $\pm$ 147	10,658 $\pm$ 63	15,163 $\pm$ 109	13,884 $\pm$ 96	12,239 $\pm$ 137
K	13,796 $\pm$ 29	104 $\pm$ 8.4	20 $\pm$ 1.6	14,485 $\pm$ 100	11,480 $\pm$ 178	11,458 $\pm$ 98	16,711 $\pm$ 117	14,011 $\pm$ 168	13,357 $\pm$ 97
Ca	1,5484 $\pm$ 213	11,767 $\pm$ 409	145 $\pm$ 23	16,291 $\pm$ 38	11,568 $\pm$ 134	1,1032 $\pm$ 161	20,433 $\pm$ 407	17,046 $\pm$ 417	14,619 $\pm$ 424
P	6,780 $\pm$ 80	<0.1	14.14 $\pm$ 1.0	7,086 $\pm$ 17	4,824 $\pm$ 102	4,488 $\pm$ 86	8,867 $\pm$ 188	5,591 $\pm$ 143	5,690 $\pm$ 274
S	5,015 $\pm$ 22	18,101 $\pm$ 270	2,834 $\pm$ 15	5,136 $\pm$ 26	6,799 $\pm$ 112	4,764 $\pm$ 27	6,094 $\pm$ 103	10,453 $\pm$ 116	5,357 $\pm$ 103
Zn	166.7 $\pm$ 0.8	6.94 $\pm$ 0.3	5.51 $\pm$ 2.8	171.6 $\pm$ 0.1	126.6 $\pm$ 4.8	119.21 $\pm$ 4.3	213.6 $\pm$ 6.9	142.2 $\pm$ 1.9	149.4 $\pm$ 5.7
Mn	164.4 $\pm$ 0.5	129.34 $\pm$ 6.4	3.99 $\pm$ 0.7	170.6 $\pm$ 2.6	123.6 $\pm$ 3.0	116.93 $\pm$ 1.9	207.8 $\pm$ 5.4	171.9 $\pm$ 1.4	147.4 $\pm$ 3.4
Cu	30.1 $\pm$ 0.4	<0.1	<0.1	32.1 $\pm$ 0.2	24.7 $\pm$ 1.1	22.67 $\pm$ 0.5	37.9 $\pm$ 1.4	27.0 $\pm$ 0.5	27.8 $\pm$ 0.7
B	37.2 $\pm$ 2.4	89.91 $\pm$ 5.41	21.07 $\pm$ 3.59	64.6 $\pm$ 6.6	45.5 $\pm$ 2.9	38.49 $\pm$ 4.7	82.5 $\pm$ 21.1	96.2 $\pm$ 6.3	69.8 $\pm$ 15.6

BM = Bacchus Marsh lignite; LY = Loy Yang lignite

5.3.2 Temperature profile during composting

Though the changes in compost temperature followed a similar pattern for all treatments, lignite amendments delayed both the onset of the thermophilic phase, $> 40^{\circ}\text{C}$ (Bernal et al. 2009; Czekala et al. 2016), and the time taken to attain maximum temperature (Figure 5.4). The onset of thermophilic temperatures in the manure only treatment began around 2 days (1.8 days) from the start of the composting process (Figure 5.4), compared to almost 4 days (3.7 days) for manure + BM and almost 5 days (4.6 days) for manure + LY. Likewise, the maximum temperature for the manure (56°C), occurred 5 days from the start of composting compared to 9 days for manure + BM (56°C) and 7 days for manure + LY (51°C). The rise in temperature at the beginning of composting marks the onset of rapid breakdown of the labile fraction of organic matter and nitrogenous materials by microorganisms (Brito et al. 2008). Temperature patterns reflect the extent of microbial activity as well as the progress of the composting process (An et al. 2012). The delay in the attainment of thermophilic and maximum temperatures in the lignite amended manures is likely due to a temporary inhibition of microbial activity by the lignite. This is supported by previous work by Tran et al. (2015) who observed a significantly lower respiration rate in lignite amended soils during the first three days of incubation, and Whiteley and Pettit (1994a) who reported a significant increase in microbial stability (size of microbial biomass), leading to a reduction in microbial O_2 consumption and CO_2 evolution, during the decomposition of wheat straw in the presence of lignite humic acid. At the later stages of the composting period, the temperature approached ambient due to a reduction in microbial activity (reduction in CO_2 evolution) as the labile fraction of OM became depleted (Bernal et al. 2009). In all treatments the end of the thermophilic phase occurred around day 14, after which the temperature steadily declined following a similar trend for all treatments.

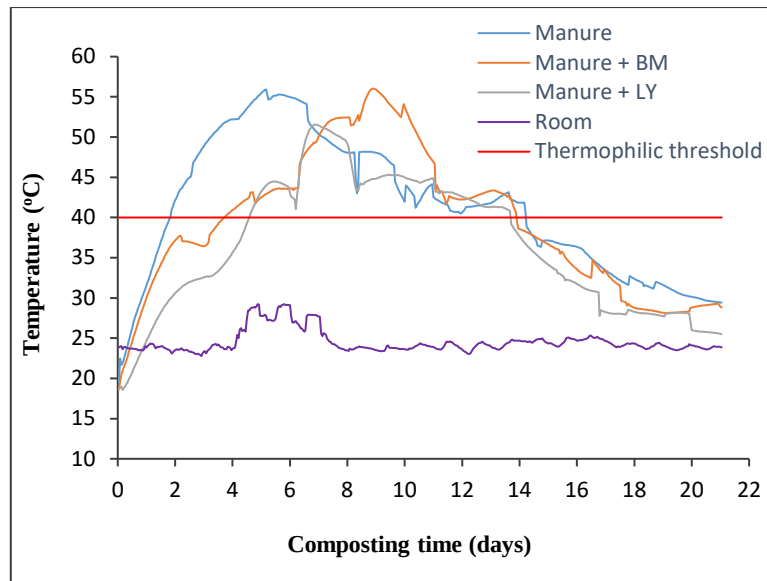


Figure 5. 4 Temperature recorded during composting, showing the thermophilic phase threshold. BM = Bacchus Marsh lignite; LY = Loy Yang lignite

5.3.3 Organic matter

Organic matter (OM) decreased in all treatments during composting (Figure 5.5). The mineralization of organic carbon, especially at the thermophilic phase of composting, by microorganisms, producing CO₂, NH₃, water, organic acids and heat, leads to OM loss (Bernal et al. 2009; Awasthi et al. 2015). Compared to the manure alone, lignite inhibited the decrease in OM during composting. The delay in the onset of the thermophilic phase in the lignite treatments (Figure 5.4) explains the initial smaller drop in OM in these treatments compared to the manure alone. The smaller OM reduction in the lignite treatments could be due to the lignite inhibiting the microbial activity, at the start of the composting period (Whiteley & Pettit 1994a; Tran et al. 2015) as discussed under section 5.3.2 above, and also providing a more recalcitrant organic fraction compared to the manure alone (Chabbi et al. 2006; Yoon et al. 2016). Composting feedstocks higher in recalcitrant organic fractions, such as those containing lignite, usually have a smaller OM and dry matter loss (Bernal et al. 2009; An et al. 2012). At the end

of the composting period the OM content had decreased by 38.2% (from 63.0% to 51.3%), 28.2% (from 69.2% to 61.8%), and 21.7% (from 68.7% to 63.2%) in the manure, manure + BM and manure + LY respectively (Table 5.2).

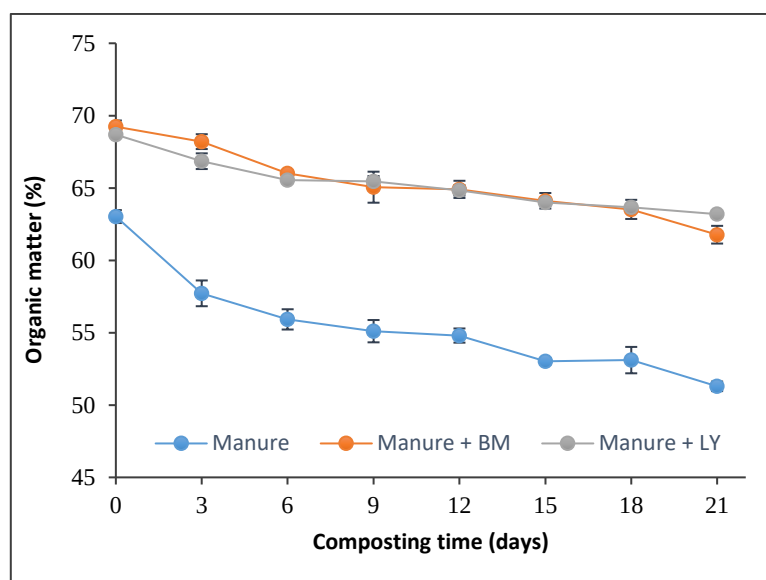


Figure 5. 5 Organic matter content of manure and lignite amended manure during composting. Bars represent standard error of means (n = 4).

Table 5. 2 Summary of dry matter, organic matter, total carbon and total nitrogen as well as their losses over the composting period. Values represent mean (n = 4) $\pm$ standard error of mean.

	Manure	Manure + BM	Manure + LY
Dry matter			
Initial ³ dry matter (g)	7,000	7,000	7,000
Final ⁴ dry matter (g)	5,314 $\pm$ 145	5,633 $\pm$ 115	5,955 $\pm$ 42
Loss of DM (% of initial)	24.1	19.5	14.9
Organic Matter			
Initial concentration (%)	63.0 $\pm$ 0.4	69.2 $\pm$ 0.4	68.7 $\pm$ 0.2
Initial amount (g)	4,412 $\pm$ 313	4,847 $\pm$ 299	4,808 $\pm$ 107

³ per vessel at the start of composting

⁴ per vessel at the end of composting

	Manure	Manure + BM	Manure + LY
Final concentration (%)	51.3 ± 0.3	61.8 ± 0.6	63.2 ± 0.2
Final amount (g)	2,726 ± 175	3,480 ± 344	3,763 ± 97
<i>Loss of OM (% of initial)</i>	38.2	28.2	21.7
Total Carbon			
Initial concentration (%)	26.8 ± 0.9	36.1 ± 0.8	35.3 ± 0.5
Initial amount (g)	1,876 ± 62	2,528 ± 56	2,472 ± 37
Final concentration (%)	24.4 ± 0.6	34.2 ± 1.1	33.6 ± 0.5
Final amount (g)	1,268 ± 32	1,932 ± 61	1,986 ± 27
<i>Loss of total C (% of initial)</i>	32.42	23.55	19.67
Total Nitrogen			
Initial concentration (%)	2.34 ± 0.06	2.52 ± 0.10	2.52 ± 0.05
Initial amount (g)	163.7 ± 4.7	176.3 ± 8.1	176.7 ± 2.3
Final concentration (%)	2.56 ± 0.04	2.66 ± 0.07	2.73 ± 0.03
Final amount (g)	136.3 ± 5.2	150.0 ± 3.7	162.7 ± 1.7
<i>Loss of total N (% of initial)</i>	16.77	14.92	7.94

5.3.4 Changes in total C content during composting

Total C (%) decreased during the composting period in all treatments (Figure 5.6). The loss of C during composting is a result of the mineralization of organic matter and release of CO₂ (Said et al. 2007). The C content of the lignite amended manures remained significantly higher than the manure alone throughout the composting period due to the high C content of the lignite (Table 5.1). Manure + BM had a higher initial C content than the manure + LY treatment but there was no significant difference at the end of the composting period. At the end of the composting, the C in the manure alone, manure + BM and manure + LY was 24.39, 34.30 and 33.57% respectively with the lignite amended manures recording less change, relative to the initial value, than in the manure alone. After accounting for dry matter loss, the loss of TC at

the end of the composting period was 32.4, 23.6 and 19.7% of the initial TC for manure, manure + BM and manure + LY respectively. These losses are lower than values previously reported for TC losses during the composting of cattle manure: 42-62% (Eghball et al. 1997); 39-67% (Larney et al. 2006); 53% (Hao et al. 2004); 39-49 (Larney et al. 2008b) and 44-65% (Lim et al. 2017). Most of these studies however used manure feedstocks with an initial C:N ratio (17-48) higher than that of the feedstocks used in this study (12-15). In this study, the urea solution added during the feedstock preparation (section 5.2.1) contributed to the lower C:N ratio.

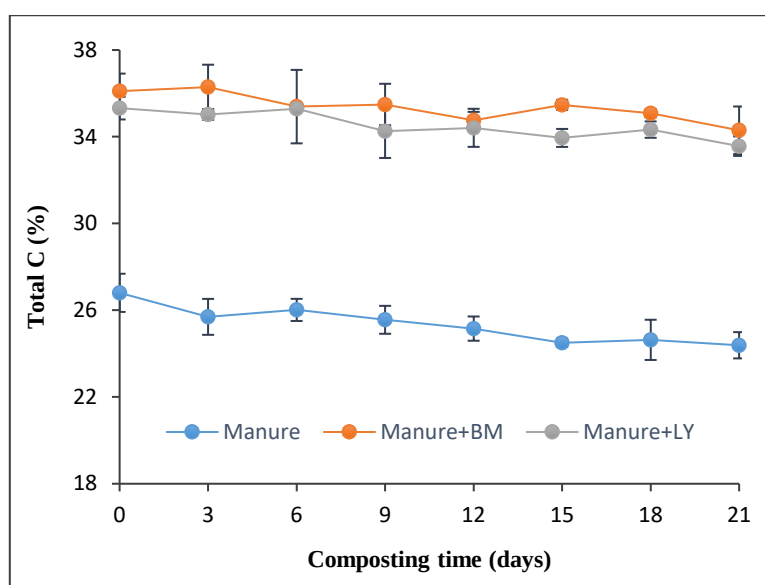


Figure 5. 6 Total carbon content of manure and lignite amended manure during composting. Bars indicate standard error of mean (n=4)

5.3.5 Total N and NH_4^+

A decrease in the concentration of total N during composting has been attributed mainly to NH_3 volatilization (Awasthi et al. 2015). An increase in concentration, on the other hand, is as a result of OM loss (through mineralization and release of CO_2), reducing the compost mass and increasing the concentration of N (Sánchez-Monedero et al. 2001; Zhu 2007). In all treatments, there was a decrease in TN between day 0 and 3 (Figure 5.7a). In the manure, this coincided with an increase in NH_3 emission (Figure 5.10). There was an increase in total N in

all treatments by day 6 due to rapid OM loss at the thermophilic phase of composting (see temperature profile, Figure 5.4). From day 9 (apart from manure + LY where the increase started from day 12), changes in total N generally followed an increasing trend with composting time, although in the manure + BM the total N increased till day 15 and then decreased for the rest of the composting period. Total N in the lignite treatments remained significantly higher than the manure alone throughout the composting period due to the higher total N in lignite treatments at the start of composting, as well as suppression of NH_3 loss (see section 5.3.8.5 below). After accounting for DM loss, the loss of the initial total N at the end of the composting period was 16.8, 14.9 and 7.9 % in the manure, manure + BM and manure + LY respectively (Table 5.2).

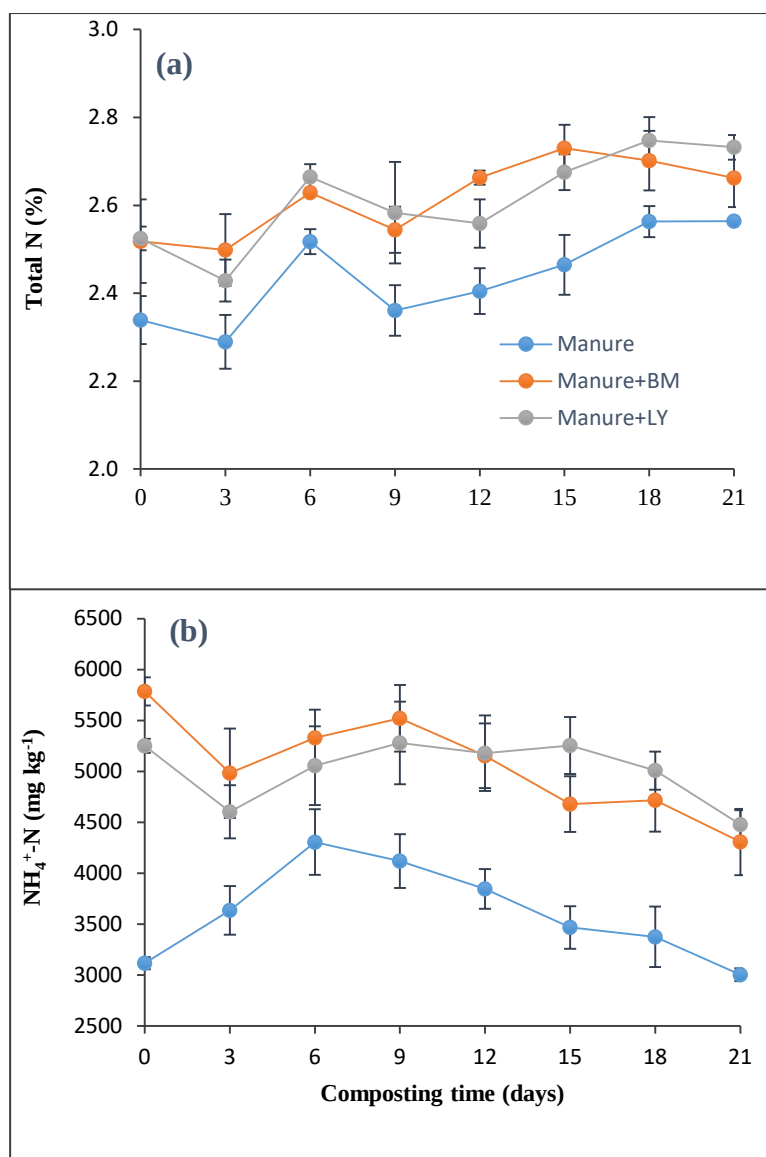


Figure 5. 7 Total N (a) and NH₄⁺-N (b) of manure and lignite amended manure during composting. Bars indicate standard error of mean (n=4)

The NH₄⁺ in the manure alone increased at the initial stage of composting (to day 6) and then decreased with composting time to reach the similar level as observed on day 0 (Figure 5.7b). In both lignite amended manures, the NH₄⁺ concentration initially decreased to day 3, then increased between days 3 and 6, and then decreased with composting time. An increase in NH₄⁺ concentration during composting, especially during the thermophilic phase, has been attributed to organic matter mineralization (Gao et al. 2010). Therefore the delay in the increase in NH₄⁺ in the lignite treatments could be explained by the delay in the onset of the thermophilic

phase (1.8 days for manure, 3.7 days for manure + BM and 4.6 days for manure + LY, Figure 5.4). Other processes that can result in a reduction in NH_4^+ concentration during composting include NH_3 volatilization, nitrification of NH_4^+ to NO_3^- , biological immobilization of NH_4^+ into organic N, and nitrification-denitrification of NH_4^+ to N_2 or N_2O (Bernal et al. 2009; De Guardia et al. 2010a). The cumulative N_2O loss recorded (0.004-0.008 g kg^{-1} DMi, see section 5.3.7.2 below) over the composting period was much lower than the cumulative NH_3 loss (1.93-4.19 g kg^{-1} initial DM, see section 5.3.7.1 below). Hence, the reduction in NH_4^+ concentration with composting time was largely as a result of NH_3 volatilization.

During composting nitrification occurs only after the thermophilic phase has passed as the activities of the ammonia-oxidizing bacteria or archaea (AOB/AOA) are inhibited at temperatures in excess of 40 °C (Bernal et al. 2009; Caceres et al. 2018). The presence of free NH_3 , favoured by high concentrations of NH_4^+ -N and high pH, over the long time period of composting, could also inhibit AOB/AOA and thus the formation of NO_3^- (AlJabi et al. 2008; Caceres et al. 2018). It has been suggested that a moisture content of $\geq 70\%$ (w/w) and a high biological O_2 demand can lead to the formation of aerobic-anoxic pockets within the compost, a condition favourable to both biological nitrification and denitrification (Caceres et al. 2018). Under this condition, characterized by the simultaneous occurrence of N_2O and CH_4 during the thermophilic phase, NO_3^- is unlikely to be detected in the feedstock or final compost as the NO_3^- produced is simultaneously denitrified to N_2O and N_2 (Chowdhury et al. 2014; Caceres et al. 2018). This likely explains the absence of NO_3^- detected in all treatments in this study. The moisture content used in this study (55%, w/w) was lower than the 70% stated above but anaerobic pockets could still exist in this condition. Also, the high concentration of NH_4^+ in the composting materials, even at the post-thermophilic phase, inhibited the nitrification rate. De Guardia et al. (2010a) reported that no NO_3^- was detected in composts produced from feedstocks with high initial $\text{NH}_4^+/\text{NH}_3$ (1,000-12,000 mg kg^{-1} DM).

5.3.6 pH and Electrical conductivity

In all treatments, pH increased by day 3 (Figure 5.8a). During composting, a number of processes occur that can lead to pH increases. At the onset of composting rapid degradation of acids, proteolysis and ammonification lead to an increase in pH (Caceres et al. 2006; Li et al. 2019a). The increase in pH was greater in the manure alone compared to the lignite-amended manures, which likely results from the delayed onset of rapid organic matter degradation, which is also reflected in the slower rise in temperature compared to the manure (Figure 5.4) as well as the ability of lignite to buffer changes in pH. The manure and manure + BM treatment followed a similar pH trend during composting, where pH increased to day 3, then decreased between day 3 and 9 before increasing again to day 18. As composting progresses, especially during the thermophilic phase, the formation of organic acids and secondary acid metabolites as well as the dissolution of CO₂ within the compost lead to a drop in pH (An et al. 2012; Li et al. 2019b). The subsequent decomposition of these organic acids and secondary acid metabolites leads to a rise in pH during composting (Bernal et al. 2017). The pH of the manure + LY increased throughout the composting process except on days 15 and 18 where a slight decrease was recorded. The manure generally had a higher pH throughout the composting process. In addition, the extent of fluctuations in pH as the composting progressed was less in the lignite treatments and is likely due to the higher pH buffer capacity associated with lignites. There was increase in the pH of all treatments over the composting period, from 7.26 to 8.16 for manure; 7.36 to 7.97 for manure + BM, and 7.21 to 7.86 for manure + LY. Though the pH of the manure was significantly higher than the lignite treatments from day 15 to 18, there was no significant difference among the treatments at the end of composting period.

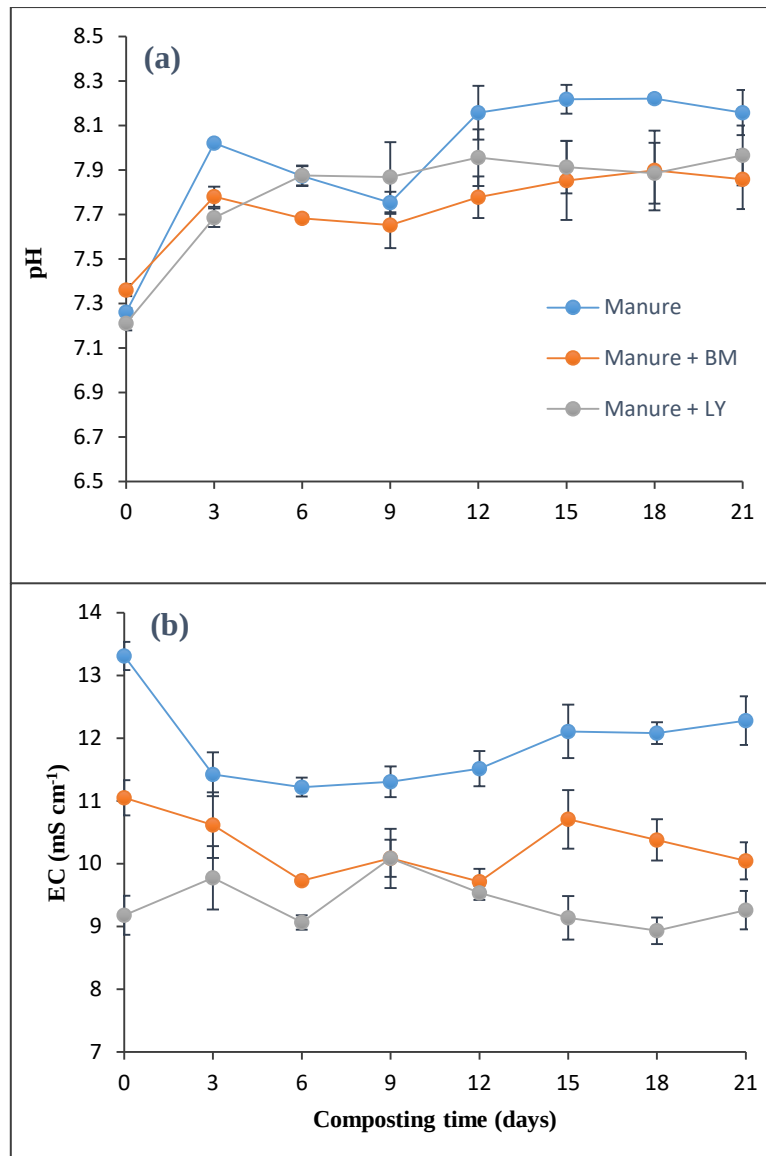


Figure 5. 8 pH (a) and EC (b) of manure and lignite amended manure during composting. Bars indicate standard error of mean (n=4)

Electrical conductivity of compost gives an indication of its possible phytotoxicity to plant growth, especially seed germination (Gao et al. 2010). At the start of the composting process, the EC of the manure was significantly higher than the lignite treatments (Figure 5.8b) and this was as a result of the high EC of the manure (13.1 mS cm^{-1}) compared to the lignites (2.1 mS cm^{-1} for BM and 0.2 mS cm^{-1} for LY). The EC of the manure alone decreased from day 0 to day 6 of composting and then increased gradually for the rest of the composting period. For the lignite treatments, there was no consistent pattern though the manure + LY generally

decreased between day 9 and 21. Increase in EC results from the release of salts (e.g. ammonium, phosphate) from the OM pool during mineralization (Gao et al. 2010; Gigliotti et al. 2012; Li et al. 2012). The EC of the manure alone remained significantly higher than the lignite amended manures throughout the composting period likely due to dilution effect as the lignites had lower EC (Table 1). The lignite also reduced microbial activity, reflected in the cumulative CO₂ emission (discussed in section 5.3.7.3), and this likely minimized the release of salt from OM mineralization. At the end of the composting period, the EC for the manure alone and manure + BM reduced, with respect to the initial EC, by 1.03 and 1.00 mS cm⁻¹ respectively whilst the manure + LY increased slightly (by 0.1 mS cm⁻¹).

5.3.7 Gaseous emissions during composting

5.3.7.1 Ammonia (NH₃) emission

An increase in temperature, and also pH, during composting enhances the loss of NH₃ by increasing the ratio of NH₃ to NH₄⁺ (Bernal et al. 2017). Following a similar pattern as the temperature profile (Figure 5.3), the peak NH₃-N emissions occurred earlier in the manure alone during the composting period than in the lignite treatments (Figure 5.9): 0.63 g kg⁻¹ DMi day⁻¹ on day 6 for manure alone, 0.59 g kg⁻¹ DMi day⁻¹ on day 9 for manure + BM and 0.43 g kg⁻¹ initial DM day⁻¹ on day 8 for manure + LY. The cumulative NH₃-N emitted by the end of the composting period was, 4.19, 2.73 and 1.93 g kg⁻¹ initial DM for manure, manure + BM and manure + LY respectively. This corresponds to the lignite suppressing NH₃ emission from the manure by 35-54%. The lignite suppressed NH₃ emission most likely through the retention of NH₄⁺ on its exchange site due to its high CEC, especially at pHs observed during the composting period (Figure 5.8a). This reduces the NH₄⁺ available for conversion to NH₃ and subsequent volatilization (Jones et al. 2007). Detailed discussion on the mechanisms by which lignite retains N is presented in Chapter 3.

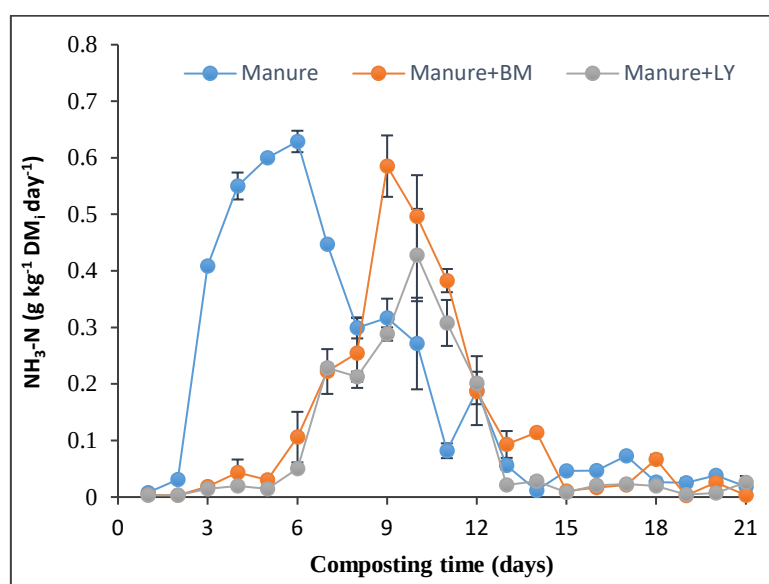


Figure 5. 9 Flux of ammonia emissions during composting of manure and lignite amended manure. Bars indicate standard error of mean (n=4)

5.3.7.2 Nitrous oxide (N₂O) emission

The formation of N₂O during composting is a result of incomplete nitrification, or denitrification which is favoured by anaerobic conditions (Yang et al. 2013; Barthod et al. 2018). Up to day 8 of composting, the pattern of N₂O fluxes followed a similar pattern in all treatments with initially relatively high fluxes at the start of composting, followed by a drop in the flux and a further rise (Figure 5.10 a). The high fluxes seen at the start of composting were likely due to the release of N₂O produced by denitrification from nitrate accumulated prior to the start of composting and stored in anaerobic pockets of the initial feedstock (Yang et al. 2013; Wang et al. 2016). In both manure + BM and manure + LY, the peak N₂O flux was recorded on day 8 (0.21 and 0.09 mg kg⁻¹ DMi day⁻¹ respectively) whilst that of the manure alone (0.34 mg kg⁻¹ DMi day⁻¹) occurred on day 11. Fukumoto et al. (2003) and Thompson et al. (2004) explained that N₂O generation from the denitrification of NO₃⁻ is unlikely to occur during the thermophilic phase because autotrophic nitrifier activity (which generates NO₃⁻) ceases at > 40 °C. However, some studies report that significant N₂O emissions occur during

the thermophilic phase of composting and suggested this could be due to the co-existence of aerobic and anaerobic conditions within the compost (Jarvis et al. 2009; Jiang et al. 2011). Chowdhury et al. (2014) suggested that the varying results on N₂O emission reported could be attributed to varying physicochemical properties of feedstocks, O₂ availability and differences in composting systems and scales. In this study, in all the treatments, a significant proportion and the peak of the N₂O production happened during the thermophilic phase. Oxygen concentration (Figure 5.10 b) throughout the composting period was within the optimum range recommended for composting, 15 to 20% (Bernal et al. 2017). However, it was likely that anaerobic sites existed within the compost mass, as the feedstock began to breakdown and compress soon after mixing/sampling. This was reflected in the trend of increasing CH₄ emission with composting time (Figure 5.13). The period of higher N₂O emission in the manure, with the exception of day1, coincided with the period of higher CH₄ emission. The cumulative N₂O evolved by the end of the composting was 2.29, 0.64 and 0.89 mg kg⁻¹ initial DM for manure, manure + BM and manure + LY respectively. Compared to the manure alone, lignite amendments reduced the cumulative N₂O evolved at the end of the composting period by 58-72%.

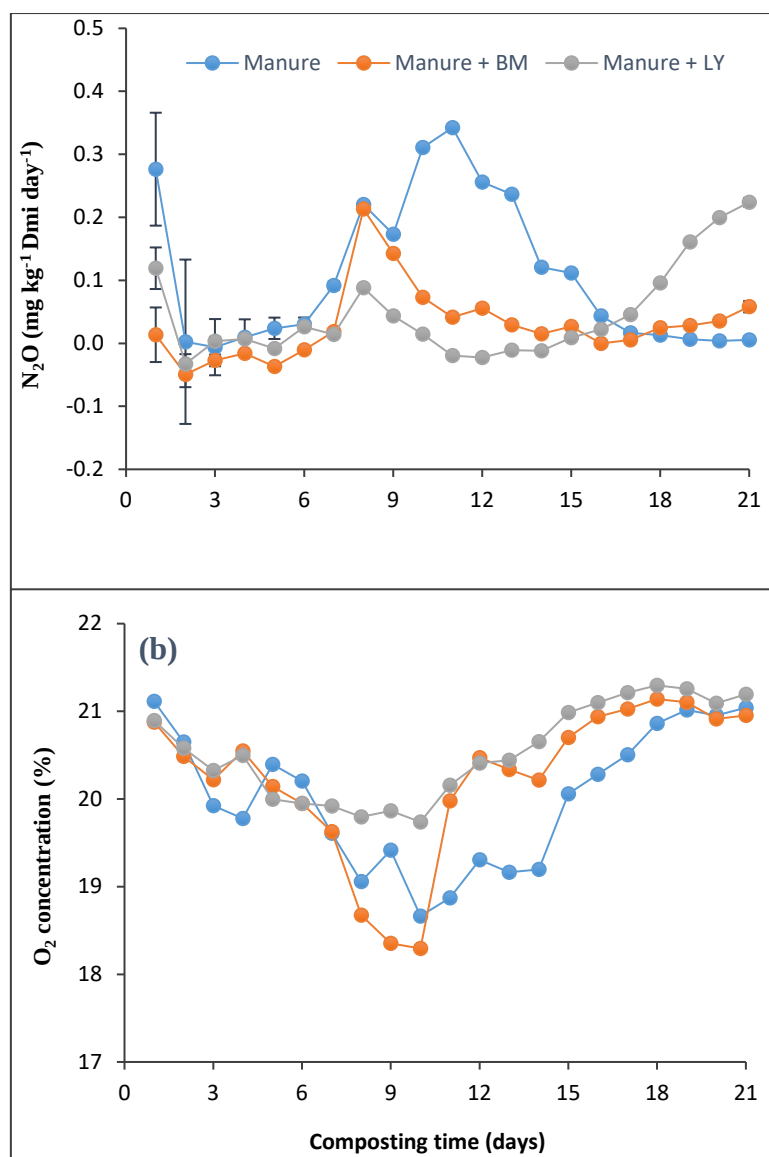


Figure 5. 10 Flux of nitrous oxide emissions (a) and oxygen concentration (b) during composting of manure and lignite amended manure. Bars indicate standard error of mean (n=4).

5.3.7.3 Carbon dioxide (CO_2) emission

The pattern of CO_2 fluxes was similar to the temperature profile for all treatments (Figure 5.4 and Figure 5.11). A similar relationship between CO_2 flux and temperature profile was reported by Sánchez-García et al. (2015) and Czekala et al. (2016) during composting. Changes in temperature and CO_2 emission are the result of microbial activity (Sánchez-García et al. 2015). The CO_2 flux was higher in the manure alone than the lignite amended manures in

the first 4 days and then from 10 to 14 days of composting. The CO₂ fluxes from the lignite amended manures followed a similar pattern but differed to the manure only. The reduction in fluxes in all treatments from day 14 onwards coincides with the end of the thermophilic phase (< 40 °C) (Figure 5.4). Cumulative CO₂ evolved over 21 days of composting was 280.9, 246.3 and 216.6 g kg⁻¹ DMi for manure, manure + BM and manure + LY respectively, with lignite reducing CO₂ emission from the manure by 12-23%. The lower CO₂ loss in the lignite amended manures is likely due to inhibition of microbial activity by the lignite, particularly at the initial stage of composting (onset of the thermophilic phase occurred at 3.7 to 4.6 days in the lignite treatments compared to 1.8 days in the manure). Lignite's ability to inhibit microbial respiration and in turn CO₂ emission has been reported by Tran et al. (2015) and Whiteley and Pettit (1994a). A CO₂-C evolution rate of 0.5-2.2 mg g⁻¹ OM day⁻¹ indicates a stabilized compost for field application (Michel Jr et al. 2004; Nakhshiniev et al. 2014). In this study, the threshold of CO₂-C evolution rates were attained (1.3-2.0 mg g⁻¹ OM day⁻¹) by day 18 of composting, indicating stabilized compost for all treatments by that period. The CO₂-C evolution rates recorded on day 21 were 1.47, 1.57 and 1.03 mg g⁻¹ OM day⁻¹ for manure, manure + BM and manure + LY respectively.

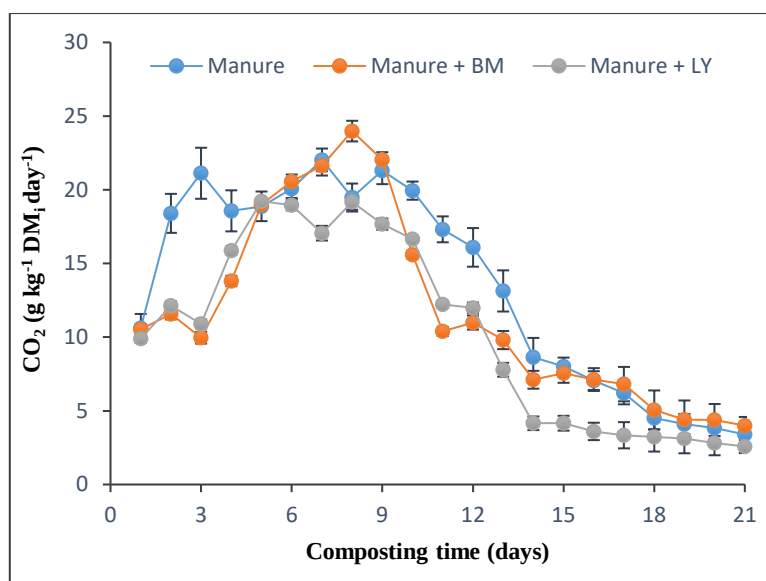


Figure 5. 11 Flux of CO₂ during composting of manure and lignite amended manure. Bars indicate standard error of mean (n=4).

5.3.7.4 Carbon monoxide (CO) emission

Carbon monoxide has a small global warming potential, between 2 and 5 on a 100-year horizon, but can lead to indirect radioactive effects by increasing the lifetime of CH₄ (Myhre et al. 2013; Sánchez et al. 2015). The emission CO during composting is a result of physical-chemical processes and correlates positively with O₂ availability and temperature (Hellebrand & Kalk 2001; Phillip et al. 2011). The lignite resulted in significantly higher CO fluxes compared to the manure alone up to day 11 of composting (Figure 5.12). It was observed during the sampling periods that amending manure with lignite reduces the compaction of the manure as reflected in the CH₄ emissions (Figure 5.13). Under conditions of continuous air supply, this is likely to improve availability of O₂ and hence favour CO emission in the lignite amended manures. The microbial oxidation of CO to CO₂, leading to reduction in CO levels, has been reported by Phillip et al. (2011). In the manure only treatment, the early onset of the thermophilic phase, compared to the lignite amended manures, could also explain its lower CO fluxes, especially in the initial period of composting. The peak CO flux occurred at different times for the various treatments during the composting period: 3.85 mg kg⁻¹ DM_i on day 11 for

manure alone, 9.65 mg kg⁻¹ initial DM on day 8 for manure + BM and 7.32 mg kg⁻¹ initial DM on day 6 for manure + LY. Cumulative CO evolved at the end of 21 days of composting was 37.5, 64.2 and 61.9 mg kg⁻¹ initial DM for manure, manure + BM and manure + LY respectively. This corresponds to lignite increasing CO emission by 64-70% compared to the manure alone. Compared to the cumulative CO₂ loss (217-281 g kg⁻¹ DMi), the CO loss was negligible (0.04 to 0.06 g kg⁻¹ initial DM, i.e. 0.01-0.03% of CO₂). Hence, though the CO emission was higher in the lignite treatments, the lignite, overall, reduced the loss of C from manure during composting. Over the composting period, the total C lost, relative to the initial, was 32.42% (608g), 23.55% (596 g) and 19.67% (486 g) for manure, manure + BM and manure + LY respectively.

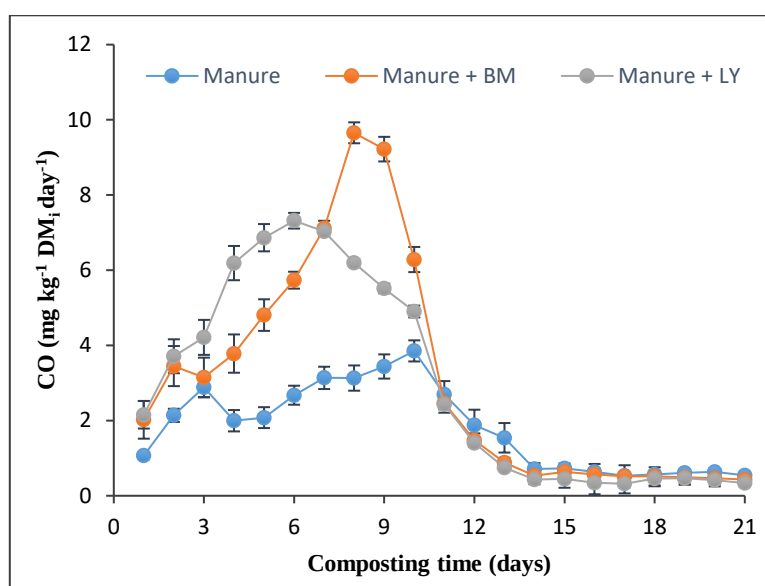


Figure 5.12 Flux of CO during composting of manure and lignite amended manure. Bars indicate standard error of mean (n=4).

5.3.7.5 Methane (CH₄) emission

Formation of CH₄ occurs through reduction of CO₂ by methanogens in anaerobic pockets within the compost (Boldrin et al. 2009; Yang et al. 2013). The oxidation of CH₄ to CO₂ as it moves towards the compost surface with higher O₂ concentration has been reported (Hao et al. 2001; Szanto et al. 2007). In this study, there was no consistent pattern of CH₄ fluxes as

observed for the other gases (Figure 5.13). Between day 5 and 15 of composting, CH₄ emissions from the manure only were generally higher, though not always significantly, than the lignite amended manures. The peak CH₄ emission for the various treatments was 0.06 mg kg⁻¹ DMi on day 15 for the manure alone and the manure + BM and then 0.03 mg kg⁻¹ DMi for the manure + LY on day 4. Cumulative CH₄ emissions for the manure alone, manure + BM and manure + LY were 0.42, 0.20 and 0.17 mg kg⁻¹ DMi respectively. These correspond to the lignite reducing CH₄ emission by 52-59%. Optimum oxygen concentration was maintained throughout the composting period (Figure 10 b) and thus, the overall increasing trend in CH₄ emission over time was likely a result of the breakdown or settling of the feedstocks, leading to oxygen deficient sites, as composting progressed. In this study, cumulative CH₄ emission recorded were lower compared to values previously reported during manure composting and this could be due to the continuous aeration system. Values reported in the literature are: 11.9 g kg⁻¹ DMi (windrow turned 8 times over a 100 day composting period) (Hao et al. 2004); 6.0-7.6 g kg⁻¹ DMi (windrow turned 3 times over a 220 day composting period) (Hao et al. 2011); 1.7 g kg⁻¹ DMi (windrow turned 15 times over a 98 day composting period) (Vergara & Silver 2019). Szanto et al. (2007) reported CH₄ emission of 12.6% of degraded OM in a static composting system compared to only 0.4% of degraded OM in a turned/aerated system.

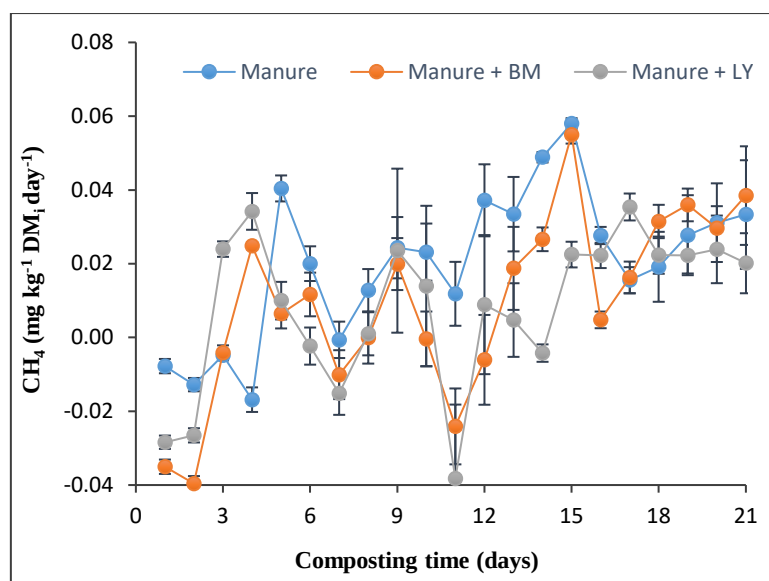


Figure 5. 13 Flux of methane emissions during composting of manure and lignite amended manure. Bars indicate standard error of mean (n=4).

5.3.8 Germination index

The threshold value of GI that indicates compost maturity and non-phytotoxicity varies in the literature, with reported values ranging between 50 and 110% (Tiquia et al. 1996; Tian et al. 2012; Tambone et al. 2015). The wide variation in GI values can be explained by differences in the type of composts and also in the seeds used for the germination test (Komilis & Tziouvaras 2009). The GI increased with composting time in all treatments (Figure 5.14) and this can be attributed to the decomposition of low molecular weight short chain fatty acids such as acetic acid and ammonia (Guo et al. 2012; Yang et al. 2013). The manure had lower GI (71% by day 21), compared to the lignite treatments (90-133% by day 21), throughout the composting period and this can be attributed to its higher EC (Figure 5.8 b). The accumulation of salt in seeds results in an imbalance in the uptake of nutrients and water, as well as a modification in the seed germination process (Masciandaro et al. 2002). An EC of 3.3 mS cm⁻¹ has been suggested for non-phytotoxic compost (Gao et al. 2010). Amending manure with lignite resulted in a significant increase in the GI, even of the initial feedstock, though the EC was > 3 mS cm⁻¹. This could be due to the high humic substances in lignite which are able to

reduce the inhibitory effect of EC on germination by forming Na-humate complexes making Na^+ less available to accumulate in seed (Masciandaro et al. 2002; Ouni et al. 2014). In addition, humic substances have been reported to increase respiration and cell division in seeds (Ouni et al. 2014). Lignite is a rich source of humic substances, and represent 10-80% of the lignite's OM (Woskoboienko et al. 1991; Dong et al. 2006; Nasir et al. 2011). The GI of the raw BM and LY lignites was determined as 116 and 93% respectively. The GI values obtained in this study suggest that for lignite amended cattle manure, a higher GI of at least 90% should be used as an indicator for compost maturity. This GI value coincides with the $\text{CO}_2\text{-C}$ evolution rate for the lignite amended manure compost which was attained by day 18 in this study (discussed in section 5.3.7.3).

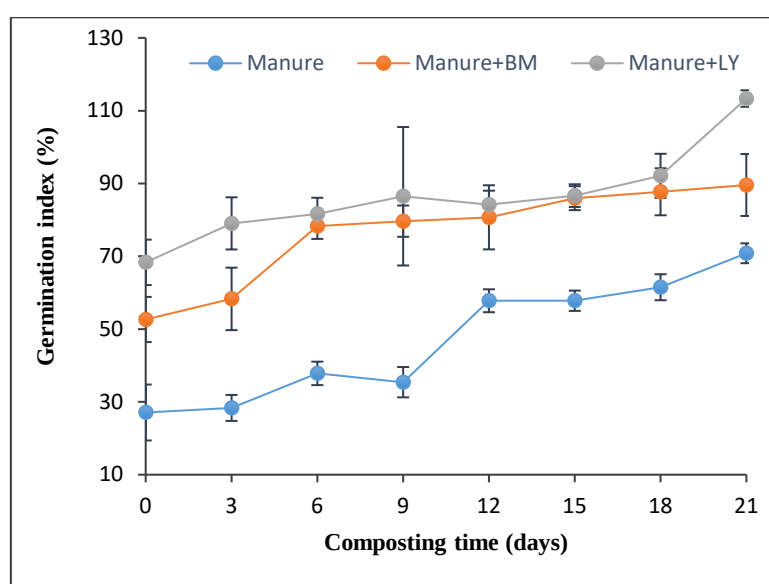


Figure 5. 14 Germination index of manure and lignite amended manure samples collected during composting. Bars indicate standard error of mean (n=4).

5.3.9 Characteristics of final compost

Table 5.1 shows the chemical characteristics of the final compost obtained from the manure alone, manure + BM and manure + LY. The presence of lignite resulted in slightly lower pH (by 0.30-0.37 units) of the compost likely due to the proportion added to the manure, 20% of the manure-lignite mix. The OM and N contents in the lignite amended manures were higher

than in the manure alone due to the lower losses of these parameters during the composting process. Compared to the start of the composting process where the manure + BM and manure + LY contained 7.7 and 7.9% more total N than the manure alone, these lignite treatments respectively contained 10.0 and 19.4% more total N at the end of the composting period. Other properties such as C:N ratio and total element concentration were not significantly altered by the presence of lignite. Compared to the manure alone (GI of 71%), the lignite markedly increased the GI of the compost (90% for manure + BM and 113% for manure + LY).

5.4 Conclusions

This study evaluated the mechanism behind the impact of lignite amendment on the composting of cattle manure. Overall, use of lignite, irrespective of origin, did not delay or shorten the duration of manure composting however, compared to manure alone, the addition of lignite delayed the onset of the thermophilic phase by reducing microbial activity. The capacity of lignite to suppress NH_3 volatilization, mainly through retention of NH_4^+ due to its high CEC, persisted during the composting process with lignite reducing NH_3 emission from the manure by 35-54%. In addition, lignite suppressed N_2O emission from the manure resulting in a final product with higher total N than in the manure only. This is a significant effect of the lignite as often the N retained in the manure through the application of NH_3 emission mitigation techniques is lost during the later stage of the manure management. In this study, a GI of $\geq 80\%$ (threshold often reported for mature compost) was attained in the lignite amended manures by day 6-9, due to high humic substances in the lignite, even though the composting was still in the thermophilic phase and the CO_2 evolution rate indicated unstable compost. Hence, for lignite amended manure, a higher GI of $\geq 90\%$ is recommended as the threshold for mature compost and this has to be used in addition to other parameters such as CO_2 -C evolution rate ($1.3\text{-}2.0 \text{ mg g}^{-1} \text{ OM day}^{-1}$). At the end of the composting period (21 days), amending

manure with lignite resulted in the production of compost with higher total N and OM due to lignite's ability to suppress the loss of total N, OM and gaseous emissions. These finding show that the application of lignite as NH₃ emission mitigation strategy also has the capacity to improve the manure composting process of the manure, and thus reduce the environmental pollution associated with the process.

CHAPTER 6: Effect of Lignite on Carbon and Nitrogen Mineralization from Non-Composted and Composted Manure during Incubation with Soil

6.1 Introduction

Animal manures, non-composted and composted, are a valuable source of organic matter and plant nutrients and therefore their application to improve soil quality and crop yield has remained a common agricultural practice (Bernal et al. 1998c; Risse et al. 2006; Abbasi et al. 2007). In order to obtain optimum effect from manure application to soil to meet the nutrient requirements of a crop, the rate and timing of the application should be based on the expected nutrient mineralization from the manure (Hartz et al. 2000; Eghball et al. 2002; Qian & Schoenau 2002). Mineralization is a microbial mediated process influenced by many factors including the manure characteristics (Eghball et al. 2002; Azeez & Van Averbeké 2010). Compared to non-composted manure, the rate of C and N mineralization from composted manure is often slower due to most of labile organic C being transformed to CO₂, and the labile N fraction to mineral forms during the composting process (Hartz et al. 2000; Eghball et al. 2002). A review of mineralization from manure, when applied to soil, is provided under section 2.4.5 of Chapter 2.

The application of lignite to abate N loss from manure alters the physicochemical properties of both the non-composted and composted manure (organic matter, NH₄⁺, total N and C concentrations, as reported in Chapters 4 and 5), and this is expected to alter the pattern of nutrient mineralization from the manure. Lignite's ability to suppress microbial activity (leading to lower emission of CO₂) was observed during in-vessel composting (Chapter 5). Very few studies have also reported the inhibitory effect of lignite on microbial activity under incubation condition (Whiteley & Pettit 1994a; Tran et al. 2015). Studies on the effect of lignite on nutrient mineralization from cattle manure, when applied to soil, have not been reported in the literature.

The aim of this study was to assess the impact of lignite amendment on the C and N mineralization dynamics of non-composted and composted cattle manure in a laboratory incubation with soil. The hypothesis was that due to lignite's ability to suppress microbial activity, amending manure with lignite will reduce both C and N mineralization from the manure when applied to soil.

6.2 Materials and methods

6.2.1 Soil, lignites, feedstocks and compost properties

The soil (Mottled mesonatric red Sodosol) used for the incubation study was a clay loam and was collected from the top 20cm of a pasture-field in Victoria, Australia. The soil was air dried and sifted with a 2 mm sieve prior to being used for the study. The manure was collected in the summer of 2018 from a commercial feedlot pen located in Victoria, Australia (feedlot described in Chapter 4). Two lignites, Bacchus Marsh (BM) and Loy Yang (LY), were sourced from open cut mines in Victoria. Refer to Table 5.1 in Chapter 5 for the properties of these lignites.

The methodology for the preparation of the non-composted unamended and lignite amended manures and their composting are described under sections 5.21 and 5.23 of Chapter 5 respectively. In this Chapter, the term feedstock is used to represents all non-composted manures, with and without lignite.

6.2.2 Incubation procedure

Twenty grams (20 g) of soil (oven-dry equivalent) was weighed into 250 mL plastic vials and brought to 60% water filled pore space (WFPS) with MilliQ water. The volume of water required to attain 60% WFPS was calculated according to Adviento-Borbe et al. (2006);

$$Volume\ of\ water\ (mL) = \frac{\%WFPS \times (1 - \frac{BD}{2.65}) \times m}{BD} \quad (6.1)$$

where %WFPS is the targeted WFPS (60%), BD is the bulk density of the soil or soil plus amendment (g cm^{-3}), 2.65 is the specific density of the soil (g cm^{-3}), and m is the mass of soil or soil plus amendment (g) to be incubated.

The vials were then pre-incubated in the dark in a temperature controlled incubator at 25 °C for 7 days in order to overcome the “Birch effect” (Plante et al. 2011). This was necessary to avoid increase in microbial activity and nutrient transformations following soil wetting, which may override the treatment effect. At the end of the pre-incubation the soil (20 g) in each vial was mixed with the feedstocks and composts at two rates (258 mg and 516 mg feedstock or compost per vial), equivalent to 30 and 60 t ha^{-1} respectively. The amount of feedstock and compost applied to the soil was based on the bulk density of the soil (1.16 g cm^{-3}) and for a soil depth of 20 cm (equation 6.2). Soil with no feedstock or compost added (unamended soil) served as the control (see Table 6.1 for treatments). The vials were then capped (lids were placed over the vials without tightening), to restrict moisture loss whilst allowing for aeration, and returned to the incubator (Figure 6.1).



Figure 6. 1 Incubation vials with fittings for gas sampling

Throughout the pre-incubation and the incubation period, 60% WFPS in the soil was maintained by replenishing with MilliQ water as required, based on mass loss measurements of the incubated sample, twice per week. A jar of MilliQ water was kept in the incubator to maintain a humid environment to further minimise moisture loss from the incubated soils. The

vials were uncapped and fanned over twice a week in order to maintain aerobic condition. On days 0 (within 30 min of treatment application), 1, 3, 6, 10, 20, 30 and 40 of incubation, four replicates of each treatment were destructively sampled and analysed for mineral N ($\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$). Methodologies for mineral N analysis during the incubation period, as well as for total C, pH, EC, organic matter and element concentration analyses of the feedstocks and composts are described under sections 4.2.5 and 5.2.4 of Chapters 4 and 5 respectively. The soil was analysed in a commercial laboratory.

Table 6. 1 Treatments applied in the incubation study. Manure + lignite treatments include both feedstocks and composts.

Treatment (Feedstocks and Composts)	Application rate	Abbreviation
Soil	-	-
Soil + manure	30 t ha ⁻¹ soil	Soil + M 30
Soil + manure + Bacchus Marsh lignite		Soil + M + BM 30
Soil + manure + Loy Yang lignite		Soil + M + LY 30
Soil + manure	60 t ha ⁻¹ soil	Soil + M 60
Soil + manure + Bacchus Marsh lignite		Soil + M + BM 60
Soil + manure + Loy Yang lignite		Soil + M + LY 60

Carbon mineralization was determined by measuring CO_2 evolution from the samples (Bernal et al. 1998b). Gas samples were collected from the headspace of three sets of incubated vials (per treatment) with the lids fitted with a gas sampling system comprised of a metal port, Teflon tubing, 3-way valve and a needle (Figure 6.1). Gas samples were collected on days 0, 1, 3, 6, 10, 20, 30 and 40, matching the mineral N sampling times. Prior to the gas sampling, the lids of the incubated vials were taken off and then fanned over for 30 s to remove any gas that might have accumulated in the headspace of the vial. During the gas sampling, with the

lids of the vials tightly fitted, 20 mL of headspace was drawn with a 25 mL syringe connected to the gas fittings into a pre-evacuated 12 mL exetainer vial (Garcia-Pausas & Paterson 2011). The headspace gas was homogenised by performing five pumping movements with the syringe before drawing the gas. On each day of sampling, a background gas sample was collected (time zero) and three samples were taken from the vials after capping them, at 1 h intervals to allow for flux calculations. After the gas sampling, the lids of the vials were removed and the vial headspace replaced with background air before the lids were placed over the vials (without tightening) and vials were returned to the incubator. The gas samples were analysed by gas chromatography (GC, Agilent 7890A with thermal conductivity detector (TCD) for CO₂).

6.2.3 Calculations

The amount of feedstock and compost (amendment) added to the 20 g of soil in each vial was calculated as follows;

$$Amendment (g) = \frac{soil\ to\ incubate\ (g) \times amendment\ application\ rate\ (kg/m^2)}{bulk\ density\ of\ soil\ (kg/m^3) \times soil\ depth^5\ (m)} \quad (6.2)$$

At each sampling time, cumulative net nitrification (NO_{3-cum}) and the applied organic N mineralized (N_{org}) were calculated according to Griffin et al. (2005);

$$NO_{3-cum}(mg\ kg^{-1}) = ([NO_3]_t - [NO_3]_{t=0})_{amended\ sample} - ([NO_3]_t - [NO_3]_{t=0})_{unamended\ sample} \quad (6.3)$$

$$N_{org}(mg\ kg^{-1}) = ([N_i]_t - [N_i]_{t=0})_{amended\ sample} - ([N_i]_t - [N_i]_{t=0})_{unamended\ sample} \quad (6.4)$$

where $[NO_3^-]_t$ and $[NO_3^-]_{t=0}$ is the NO_3^- concentration in the sample at a given sampling time (t) and at the start of the incubation period (t=0), *unamended sample* is the soil with no feedstock or compost applied, *amended sample* is the soil with either feedstock or compost applied, and $[N_i]_t$ and $[N_i]_{t=0}$ is the concentration of mineral N (NO_3^- -N + NH_4^+ -N) at a given sampling time (t) and at the start of the incubation period (t=0). The manure (applied) organic

⁵ Equation 6.2, soil depth (plough depth) was taken as 20 cm.

N mineralized (Eqn. 6.4) at each sampling time (t) was expressed as a percentage of the applied organic N at the start of the incubation study (Corrêa et al. 2012).

$$N_{org}(\%) = \frac{N_{org}(mg\ kg^{-1})}{Applied\ organic\ N(mg\ kg^{-1})} \times 100 \quad (6.5)$$

CO₂-C evolved (flux) (mg kg⁻¹ day⁻¹) was calculated according to Pitombo et al. (2018);

$$CO_2 - C\ Flux = \frac{\frac{\Delta gas}{\Delta t} \times no.mols}{mass\ of\ material} \times M\ gas \times \frac{M \times n}{M\ gas} \quad (6.6)$$

where $\frac{\Delta gas}{\Delta t}$ is the slope of the linear regression of the CO₂ concentration (units) versus time (sampling period expressed in day), *no. mols* is the number of moles of CO₂ in the incubated vial, mass of material is the mass of soil 20 (g) or the mass of soil plus mass of amendment for the amended soils, *M gas* is the molar mass of CO₂ (g), *M* is the molar mass of C (g) and *n* is the number of C atoms in CO₂.

The number of moles of CO₂ in the incubated vial was determined using the ideal gas law $PV = nRT$, where, in the context of this incubation, *P* is the pressure (atm), *V* is the volume of the vial headspace (L), *n* is the number of moles of CO₂ in the vial, *R* is the ideal gas constant and *T* (K) is the temperature during incubation.

The percent of applied total C mineralized (% C_{min}) at each sampling time (day) was calculated according to Busby et al. (2007),

$$\%C_{min} = \frac{(CO_2-C)_{amended\ sample} - (CO_2-C)_{unamended\ sample}}{total\ C\ applied} \times 100 \quad (6.7)$$

where CO₂-C is the flux (mg kg⁻¹ day⁻¹) over a given sampling time and *total C applied* is the C (mg kg⁻¹) in the feedstock or compost. To obtain the cumulative total C mineralized in the course of the 40 day incubation period, the area under the curve (a plot of CO₂-C flux against time) was calculated using the trapezoid formula and then summed. The area *A* between two adjacent sampling times, *t*₁ and *t*₂, was calculated according to Duiker and Lal (2000);

$$A_{t_1,t_2} = \frac{(t_1 - t_2) \times (CO_2 - C_{t_1} + CO_2 - C_{t_2})}{2} \quad (6.8)$$

where CO_2-Ct1 and CO_2-Ct2 are the measured flux at sampling times $t1$ and $t2$.

6.2.4 Statistical analysis

Analysis of variance (ANOVA) test was performed with GenStat 16th edition (VSN International UK) to assess main effects (lignite, composting, application rate and time) and also their interactions on the measured parameters. Least significant difference (LSD) was used to separate treatment means when significantly different at 5% level of probability.

6.3 Results and discussion

6.3.1 Characteristics of soil, lignites, feedstocks and composts used for incubation

The chemical properties of the soil as well as the non-composted and composted feedstocks are presented in Table 6.2. The chemical properties of the Bacchus Marsh (BM) and Loy Yang (LY) lignites are presented under section 5.1 of Chapter 5. The soil had acidic pH of 6.4 (in water) and 5.4 (in 0.01M $CaCl_2$) and a clay loam texture. It had low total N of 0.19% and mineral N of 2.3 mg kg^{-1} for NO_3^- -N and 6.3 mg kg^{-1} for NH_4^+ -N and an organic matter content of 4.1%. The total and mineral N values are low and therefore were not expected to mask the N transformation in the applied amendment during the incubation study.

In the feedstocks, the higher total N and NH_4^+ -N concentration in the lignite amended manures, compared to the unamended manure, can be attributed to the ability of lignite to retain N (Chen et al. 2015; Sun et al. 2016). The higher total C in the lignites, compared to the manure, resulted in the lignite amended manures having a higher concentration of total C (Table 6.2). Similarly, in the composted feedstocks, the lignite amended manures had higher total N, NH_4^+ -N and total C than the unamended manure. No NO_3^- -N was detected in any of the feedstocks and composts. With the exception of iron (Fe) and aluminium (Al), the total element concentrations were higher in the feedstocks and composts than the soil owing to the inherently higher concentrations of these elements in the manure and lignites compared to the soil.

Table 6. 2 Properties of soil, feedstocks and composts used for incubation. Values represent mean (n = 3 for feedstocks and n = 4 for compost) $\pm$ standard error of mean. Values followed by the same letter in each row are not significantly different

	*Soil	Feedstocks			Composts		
		Manure	Manure + BM	Manure + LY	Manure	Manure + BM	Manure + LY
pH _{H2O}	6.4	7.59 $\pm$ 0.02a	7.87 $\pm$ 0.01abc	7.92 $\pm$ 0.01bc	8.16 $\pm$ 0.10c	7.86 $\pm$ 0.13ab	7.79 $\pm$ 0.14ab
EC (mS cm ⁻¹)	0.07	13.3 $\pm$ 0.26c	14.2 $\pm$ 0.15d	13.7 $\pm$ 0.37cd	12.28 $\pm$ 0.39b	10.05 $\pm$ 0.30a	9.30 $\pm$ 0.31a
TC (%)	2.5	25.26 $\pm$ 0.3b	34.62 $\pm$ 0.18c	34.75 $\pm$ 0.28c	24.39 $\pm$ 1.21a	34.30 $\pm$ 1.10c	33.57 $\pm$ 0.45c
OM (%)	4.1	64.5 $\pm$ 1.43b	72.77 $\pm$ 0.75e	70.21 $\pm$ 0.2d	51.29 $\pm$ 0.33a	61.77 $\pm$ 0.61b	63.19 $\pm$ 0.16b
TN (%)	0.19	2.55 $\pm$ 0.02a	2.82 $\pm$ 0.01e	2.69 $\pm$ 0.02cd	2.56 $\pm$ 0.01ab	2.66 $\pm$ 0.07bc	2.73 $\pm$ 0.03d
CN ratio	13	11.1 $\pm$ 0.14b	12.3 $\pm$ 0.06c	12.9 $\pm$ 0.18d	9.5 $\pm$ 0.43a	12.9 $\pm$ 0.49d	12.3 $\pm$ 0.07c
NH ₄ ⁺ -N (mg kg ⁻¹)	7.3	4,533 $\pm$ 40b	8,366 $\pm$ 235c	8,004 $\pm$ 104c	3,004 $\pm$ 62a	4,308 $\pm$ 141b	4,479 $\pm$ 325b
NO ₃ ⁻ -N (mg kg ⁻¹)	2.3	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
<i>Total element concentration(mg kg⁻¹)</i>							
Al	13,000	9,770 $\pm$ 124c	7,076 $\pm$ 110a	8,706 $\pm$ 192b	13,649 $\pm$ 215e	8,583 $\pm$ 344b	1,1182 $\pm$ 179c
Fe	10,000	4,755 $\pm$ 88a	4,519 $\pm$ 96a	4,340 $\pm$ 226a	6,514 $\pm$ 55c	6,124 $\pm$ 306c	5,357 $\pm$ 66b
Mg	1,100	7,200 $\pm$ 105c	6,719 $\pm$ 196b	5,268 $\pm$ 133a	9,431 $\pm$ 77e	8,105 $\pm$ 135d	6,752 $\pm$ 190b
Na	53	12,802 $\pm$ 111d	10,563 $\pm$ 94b	9,649 $\pm$ 80a	15,163 $\pm$ 109f	13,884 $\pm$ 96e	12,239 $\pm$ 137c
K	2,500	13,796 $\pm$ 198c	10,741 $\pm$ 124a	10,461 $\pm$ 29a	16,711 $\pm$ 117d	14,011 $\pm$ 168c	13,357 $\pm$ 97b

		Feedstocks			Composts		
Ca	1,500	15,484 ± 253c	14,009 ± 60b	12,022 ± 213a	20,433 ± 407e	17,046 ± 417d	14,619 ± 424bc
P	270	6,780 ± 154c	5,481 ± 53b	4,644 ± 81a	8,867 ± 188d	5,591 ± 143b	5,690 ± 274b
S	200	5,015 ± 103b	7,517 ± 102e	4,314 ± 22a	6,094 ± 103d	1,0453 ± 116f	5,357 ± 103c
Zn	13	166 ± 33.5d	130 ± 14.5ab	123 ± 0.9a	213.6 ± 6.9e	142.2 ± 1.9ab	149.4 ± 5.7c
Mn	180	164 ± 6.8c	142 ± 9.2b	121 ± 0.5a	207.8 ± 5.4d	171.9 ± 1.4c	147.4 ± 3.4b
Cu	5.9	30.1 ± 6.0d	24.8 ± 204ab	22.8 ± 0.4a	37.9 ± 1.4e	27.0 ± 0.5cd	27.8 ± 0.7cd
B	0.64	37.2 ± 8.1a	53.0 ± 6.4ab	40.4 ± 2.4a	82.5 ± 21.1bc	96.2 ± 6.3c	69.8 ± 15.6bc

*representative soil sample was analysed at a commercial soil laboratory (non replicates). BM = Bacchus Marsh lignite; LY = Loy Yang lignite.

6.3.2 Changes in ammonium concentration during incubation

Changes in the concentration of NH_4^+ -N during the incubation of the non-composted and composted feedstocks are presented in Figure 6.2. The concentration of NH_4^+ -N in the soil was significantly ($p < 0.05$) affected by the presence of lignite, composting, incubation time, and the rate of application, as well as all levels of their interaction. Throughout the incubation period, the NH_4^+ -N concentration in the unamended soil (control) remained low, $< 4 \text{ mg kg}^{-1}$. In all the amended soils, the concentration of NH_4^+ -N initially increased to day 1, due to ammonification, and then decreased with incubation period, with the same pattern shown in all samples (Figure 6.2a). The reduction in NH_4^+ -N was most likely due to nitrification of the NH_4^+ to NO_3^- leading to a corresponding increase in the concentration of NO_3^- -N (Figure 6.3). However, other processes such as biological immobilization could also contribute to the reduction in NH_4^+ -N during incubation (Azeez & Van Averbek 2010) as well as NH_3 volatilization under alkaline pH condition (Bernal & Kirchmann 1992) and denitrification, usually favoured under predominantly anaerobic condition (Moreno-Cornejo et al. 2014). In this study, the loss of NH_4^+ through NH_3 volatilization is expected to be insignificant given the acidic pH of the soil ($\text{pH}_{\text{H}_2\text{O}} = 6.4$, $\text{pH}_{\text{CaCl}_2} = 5.4$), the small amount of amendment used relative to the soil (0.26 to 0.52g in 20g of soil), and the static nature of the incubation experiment. The incubation vials were expected to remain predominantly aerobic over the incubation period as the vials were aerated twice a week so NH_4^+ loss through denitrification is expected to be insignificant.

At a given application rate (30 or 60 t ha⁻¹), the NH_4^+ -N concentration was higher in the feedstocks than in the composts and this was due to the loss of NH_4^+ , retained in the initial feedstock, during composting process as NH_3 due to high temperature and pH. The concentration of NH_4^+ was higher in the lignite treatments owing to its capacity to retain NH_4^+ -N in the feedstock as well as in the composts. By day 20 of incubation, the NH_4^+ -N

concentration in all amended soils, irrespective of the application rate, had reduced to $\leq 20 \text{ mg kg}^{-1}$ except in the 60 t ha^{-1} non-composted BM treatment which increased to 51 mg kg^{-1} on day 40 from a previous concentration of 6 mg kg^{-1} on day 30. In both feedstocks and compost, the presence of lignite delayed the reduction NH_4^+ of concentration (beyond day 10 and 20 for the lower and higher rates in respectively).

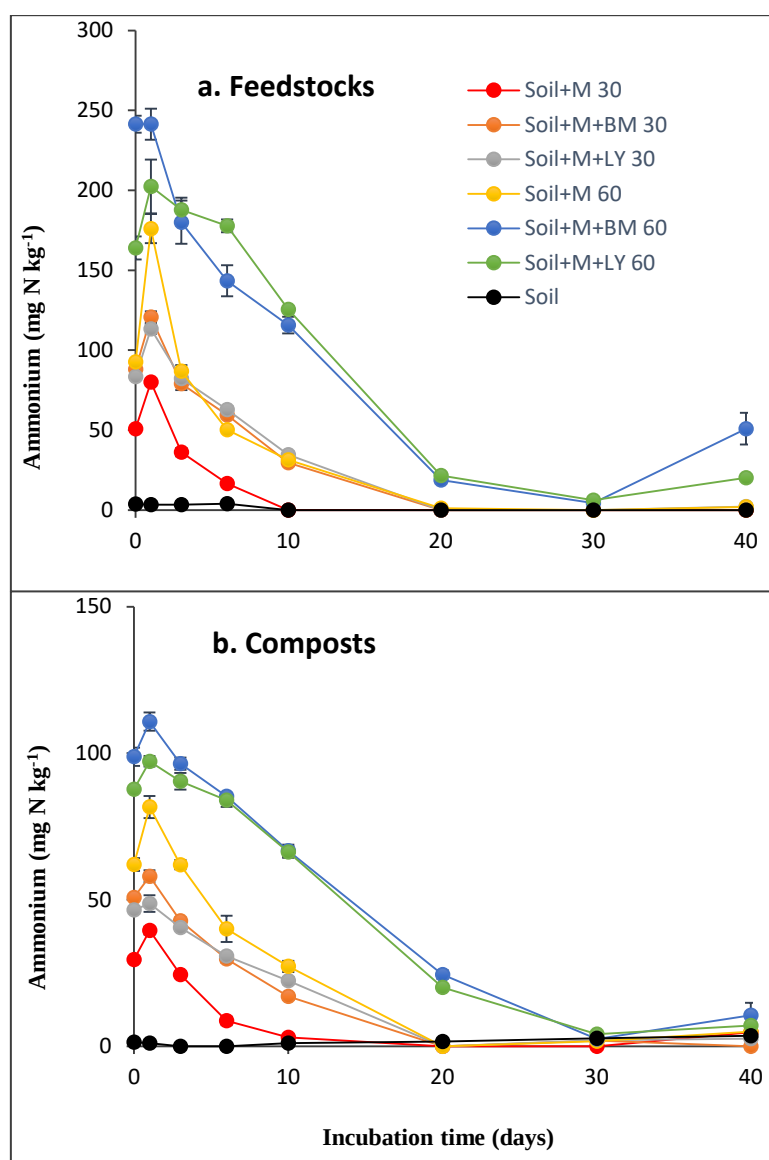


Figure 6.2 Concentration of ammonium (NH_4^+)-N in unamended and lignite amended feedstocks (a) and composts (b), applied to soil at 30 and 60 t ha^{-1} . Bars represent standard error of means ($n = 4$). Note: the scale of the y-axis differs between the two charts.

6.3.3 Changes in nitrate concentration during incubation

There was no nitrate in any of the feedstocks and composts at the start of the incubation (Table 6.1). Owing to nitrification of NH_4^+ , there was an increase of NO_3^- in both the feedstock and compost amended soils over the incubation period (Figure 6.3). This was significantly ($p < 0.05$) affected by the presence of lignite, composting, incubation time and rate of feedstock application. In addition, there were significant effects of their interaction (except for rate and composting and also as interaction among rate, time, lignite and composting) on NO_3^- concentration. In both the feedstocks and composts, the lignite treatments had higher rate of nitrification after day 10 likely due to their higher initial NH_4^+ concentration (Table 6.1), providing more substrate for nitrification. Similar to the reduction in the NH_4^+ -N concentration, in all treatments, most of the nitrification occurred during the first 20 days of incubation.

In the composts, except at the higher rates of application of the composts with lignites, there was a continuous rise in the concentration of NO_3^- between day 20 and 40 (Figure 6.3b) despite the very low NH_4^+ concentration ($< 5 \text{ mg kg}^{-1}$) in these treatments over the same incubation period (Figure 6.2 b). This was likely as a result of simultaneous oxidation of the mineralized N to NO_3^- leading to no changes in the NH_4^+ concentration (Bernal & Kirchmann 1992). This was also observed in the soils with feedstocks. It is important to note that in the soil only (unamended), NO_3^- concentration increased throughout the incubation period, indicating mineralisation of soil organic N, and therefore contributed to the rise in the NO_3^- in the feedstock and compost amended soils. However, the rate of nitrification in the feedstocks and composts was always higher than in the soil.

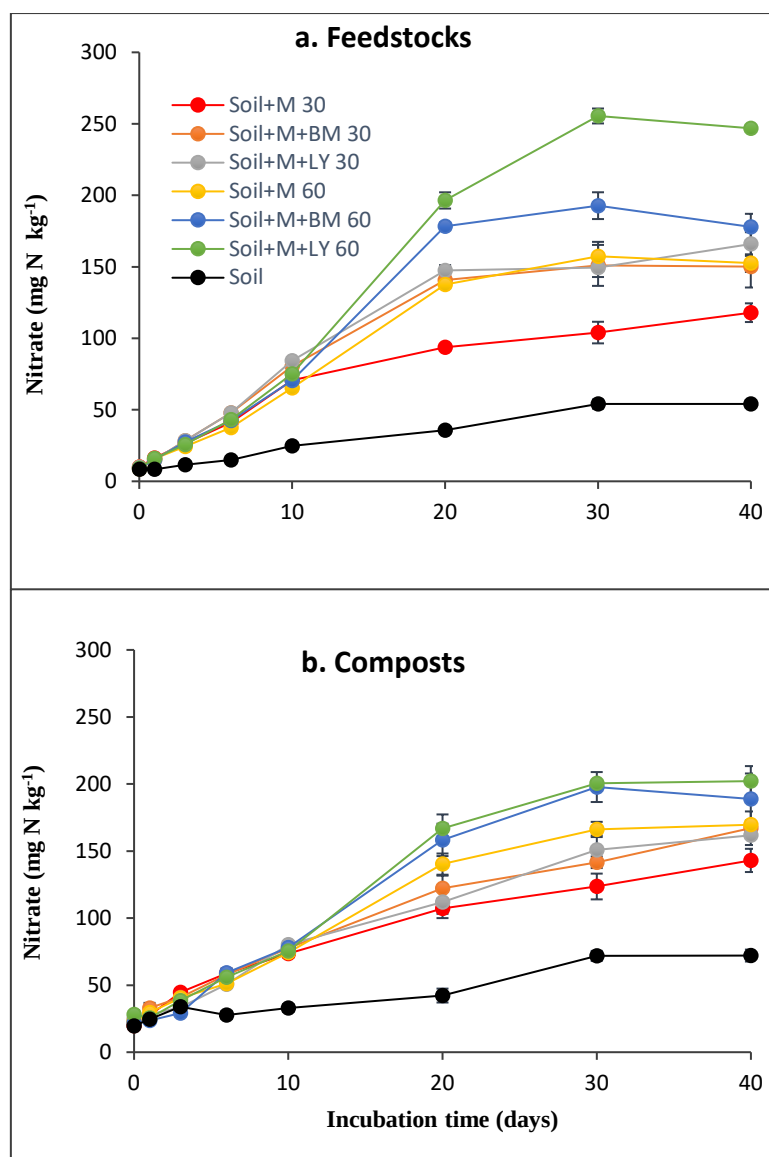


Figure 6. 3 Concentration of NO_3^- -N in unamended and lignite amended feedstocks (a) and composts (b), applied to soil at 30 and 60 t ha^{-1} . Bars represent standard error of means ($n = 4$).

6.3.4 Cumulative net nitrification during incubation

After accounting for NO_3 present in the feedstock and compost amended soils on day 0 and also correcting for the N nitrified in the unamended soil for each sampling point, the cumulative net nitrification (NO_3_{cum}) during incubation of the feedstocks and composts is presented in Figure 6.4. The ANOVA test showed that the cumulative net nitrification was significantly ($p < 0.05$) affected by presence of lignite, composting, incubation time and the rate of application.

Also, their interactions (except for rate, time and lignite; and rate, time, lignite and composting) significantly affected the cumulative net nitrification during the incubation period. There was net nitrification (i.e. accumulation of NO_3^- in excess of the unamended soil) throughout the incubation period in the feedstock amended soils. This was also observed in the composts except at the higher rate (60 t ha^{-1}) of the lignite amended composts where a net negative nitrification was recorded between day 1 and 3 of incubation. The negative NO_3^- values could be indicative of net immobilization of the initial NO_3^- -N inherently present in the soil (Moreno-Cornejo et al. 2014). However, according to Calderón et al. (2004) and Calderon et al. (2005), a negative NO_3^- value is not necessarily equivalent to immobilization as this could also be due to denitrification, capable of occurring in aerobic microcosms. The slope for the cumulative net nitrification in all treatments, both feedstocks and composts, was steeper in the first 20 days of incubation compared to the rest of the incubation period. This pattern reflected the changes in NH_4^+ concentration during the incubation period, with steeper drop in the first 20 days than in the rest of the days. Hence, the relatively stable NO_3^- concentration between day 20 and 40 could be ascribed to the lack of or very low levels of NH_4^+ (substrate) for nitrification over this period.

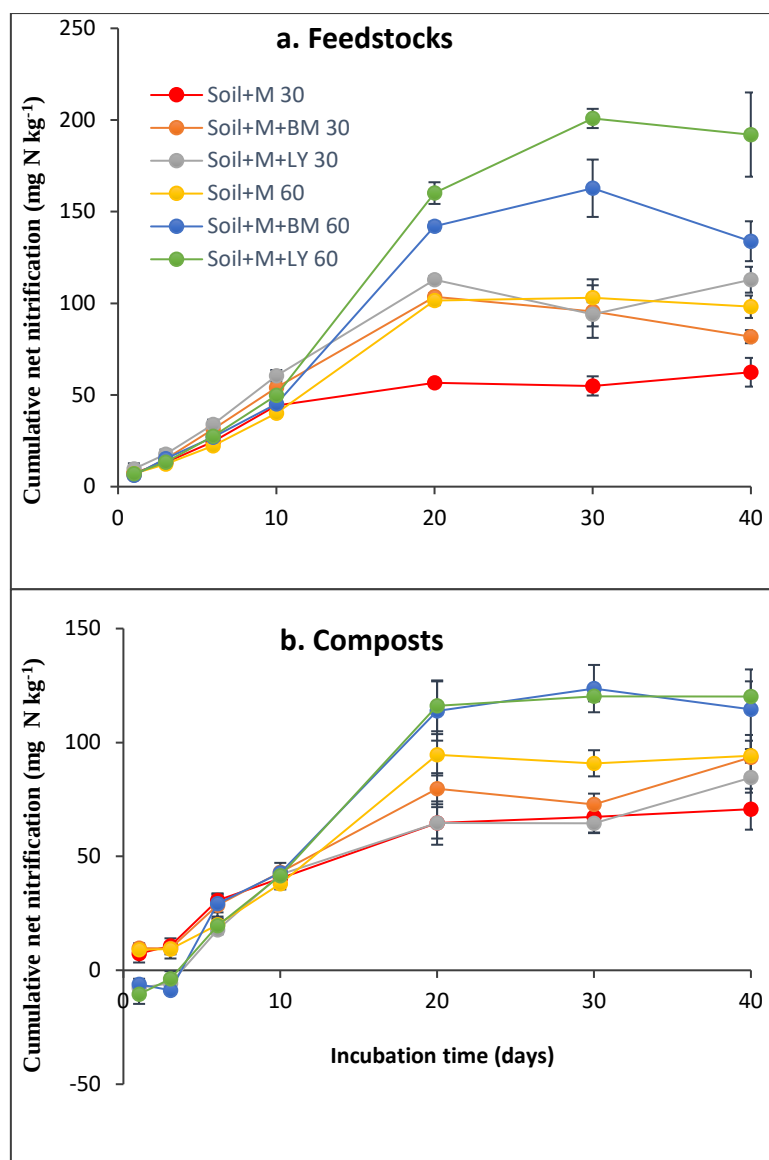


Figure 6. 4 Cumulative net nitrification (NO_3_{cum}) in unamended and lignite amended feedstocks (a) and composts (b), applied to soil at 30 and 60 t ha^{-1} . Bars represent standard error of means ($n = 4$).

6.3.5 Organic N mineralized during incubation

The pattern of applied organic N mineralized (N_{org}), (equation 6.2), varied significantly ($p < 0.05$) with composting, rate of application, lignite and incubation time, as well as their interaction (Figure 6.4). In the feedstocks, the organic N mineralized decreased from day 1 to day 6 or 10 of incubation and then generally increased for the rest of the incubation period (Figure 6.4a). In the lignite amended feedstocks at the 60 t ha^{-1} rate of application, the decrease

in organic N mineralized continued until day 10 and 20 in the BM and LY treatments respectively before increasing for the rest of the incubation period. Also in the feedstocks, the manure (at both application rates) had negative organic N mineralized between day 3 and 10, and this was likely as a result of higher microbial activity (leading to immobilization of mineral N) during this period than in the lignite amended manures, as reflected in the higher CO₂ evolution in the manure on days 3 and 6 than in the in lignite treatments (Figure 6.6 a).

In the composts, the organic N mineralized decreased by day 3 in all treatments except in the LY treatment at the 60 t ha⁻¹ rate of application. Like the feedstocks, the decrease in organic N mineralized corresponded with an increase in microbial activity on day 3 (Figure 6.5b) with the subsequent drop in the CO₂ evolution resulting in increased organic N mineralized. Compared to the CO₂ evolution which consistently decreased from day 3 till the end of the incubation period, the changes in organic N mineralized did not follow a consistent pattern. A decrease or an increase in CO₂ did not always have the same effect on organic N mineralized. Unlike the other treatments, the LY amended compost at 60 t ha⁻¹ rate, the organic N mineralized increased throughout the incubation period (Figure 6.4b).

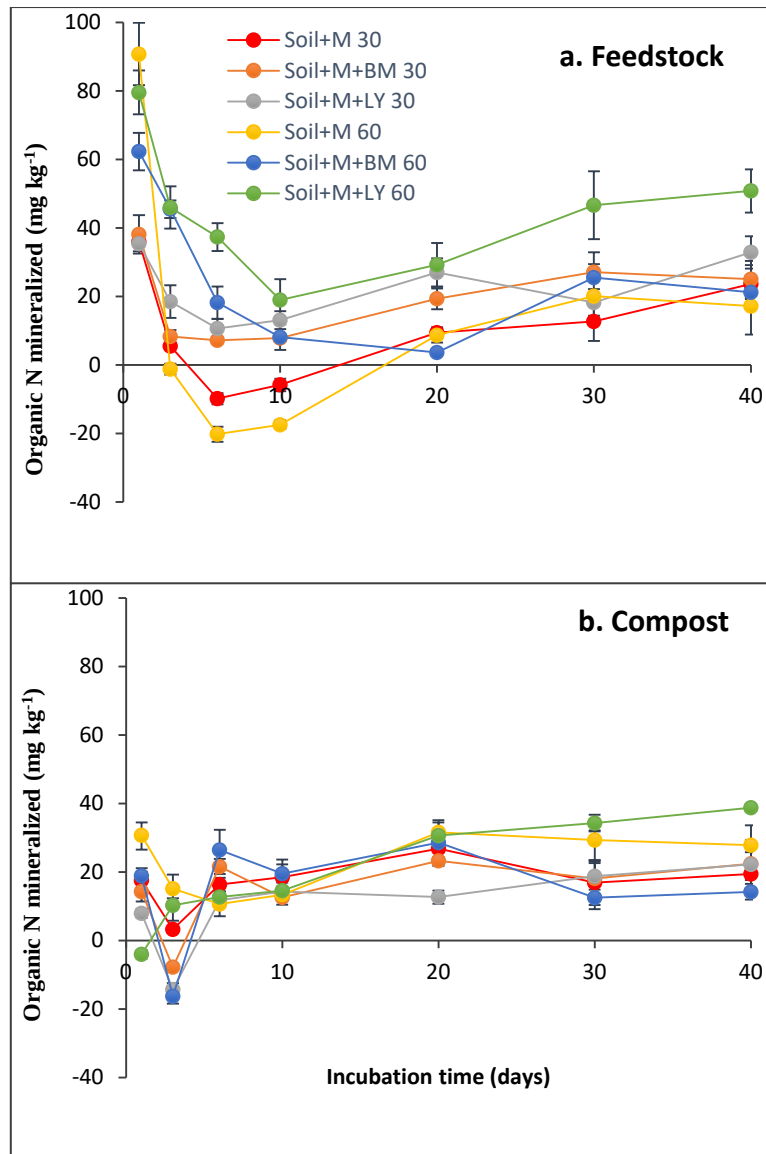


Figure 6. 5 Organic N mineralized (N_{org}) in unamended and lignite amended feedstocks (a) and composts (b), applied to soil at 30 and 60 t ha⁻¹. Bars represent standard error of means (n = 4).

The cumulative organic N mineralized over the 40-day incubation period (there was a net mineralization in all treatments) was expressed as a percentage of the organic N applied at the start of the incubation (Figure 6.6). The percentage of the applied organic N mineralized was higher in the feedstocks than in the composts, and also higher in the lower application rates than in the higher rates. The lower N mineralized in the composts could be attributed to the formation of a more stable form of organic compounds during the composting process (Masunga et al. 2016). Also during this process, easily mineralizable N is transformed into

inorganic forms with the remaining organic N less subject to mineralization (Eghball 2000; Eghball et al. 2002). Hartz et al. (2000), reported that the mineralization of organic N from non composted manure and composted manure was 7 and 1% respectively after 12 weeks of incubation with soil. Eghball (2000) found that over a period of 8 weeks, 21% of applied organic N was mineralized in manure, and 11% in composted manure. Other N mineralization values reported in the literature are: 4-5% in composted cattle manure over 168 days (Antil et al. 2011); -29 (net immobilization) to 55% in dairy manure over 56 days (Van Kessel & Reeves 2002); 21, 19 and 13% in chicken, pig and cattle manure respectively over 161 days (LI & LI 2014). Apart from composting, other factors such as soil properties, manure characteristics and incubation conditions can also influence the extent of organic N mineralization, thus the wide variation usually reported in the literature (Hartz et al. 2000; Abbasi et al. 2007). In this study, the proportion of applied organic N mineralized across all treatments was between 2.5 and 13.5 %, within the range reported in the literature.

The presence of LY lignite in the feedstocks resulted in significantly higher percent of the applied organic N mineralized. This lignite effect however diminished in the composts, especially at the lower rate of application. Note that, the organic N concentration in the manure and lignite treatments (feedstock or compost) were similar: 2.10, 1.98 and 1.89% in the manure feedstock, BM and LY amended feedstocks respectively and also the corresponding concentration in the composts were 2.26, 2.23 and 2.28%.

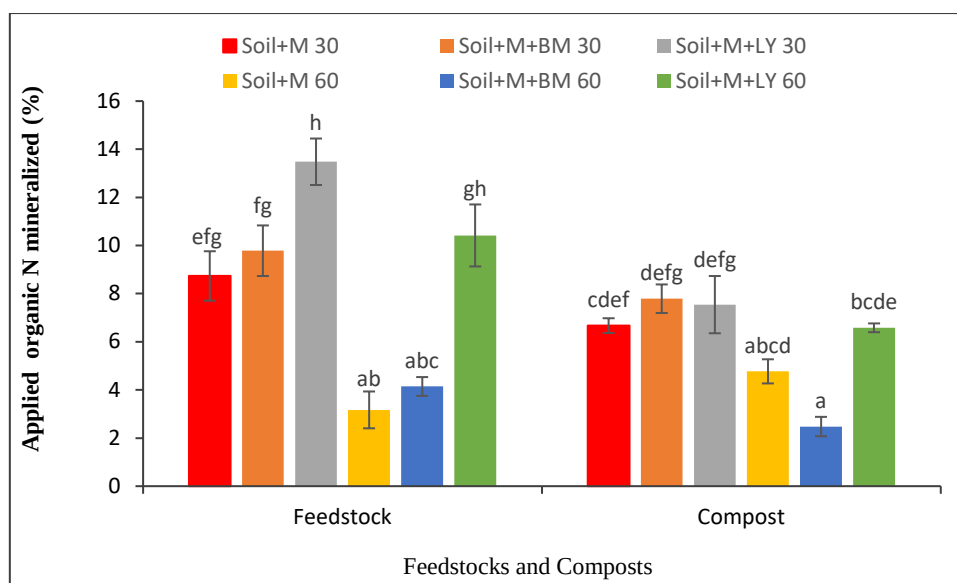


Figure 6. 6 Percentage of applied organic N mineralized over 40 days in unamended and lignite amended feedstocks (a) and composts (b), applied to soil at 30 and 60 t ha⁻¹. The bars indicate standard error of means (n = 4). Columns with the same letter (across all treatments) are not significantly different ($p < 0.05$).

6.3.6 Carbon mineralization during incubation

The pattern of C mineralization rate, measured as CO₂-C evolved, for the feedstocks and composts are shown in Figure 6.7. There was a significant ($p < 0.05$) effect of lignite, application rate, composting and time, as well as their interaction on the C mineralization. In all treatments, there was a decrease in the CO₂ evolution between day 0 (within 30 mins of treatment application) and day 1. The higher CO₂ levels on day 0 was likely due to onset of rapid microbial activity stimulated by the addition of the feedstock or compost and mixing with soil. Between day 1 and 3, there was an increase in C mineralization which then decreased gradually over the incubation period. In all treatments, the highest C mineralization occurred during the first 10 days of the incubation period (64-79% of the mineralized C in the feedstocks and 46-7% in the composts, Figure 6.7). This was likely as a result of the onset of increased microbial growth and activity due the readily degradable C in the feedstocks and composts, at the start of the incubation, and then decreased as the readily degradable C becomes depleted

(Bernal et al. 1998b). This can be seen in the pattern of organic N mineralized (Figure 6.5) where by day 3 in the composts and up to day 6 or 10 in the feedstocks, there was a decline (most likely due to immobilization) in the mineral N.

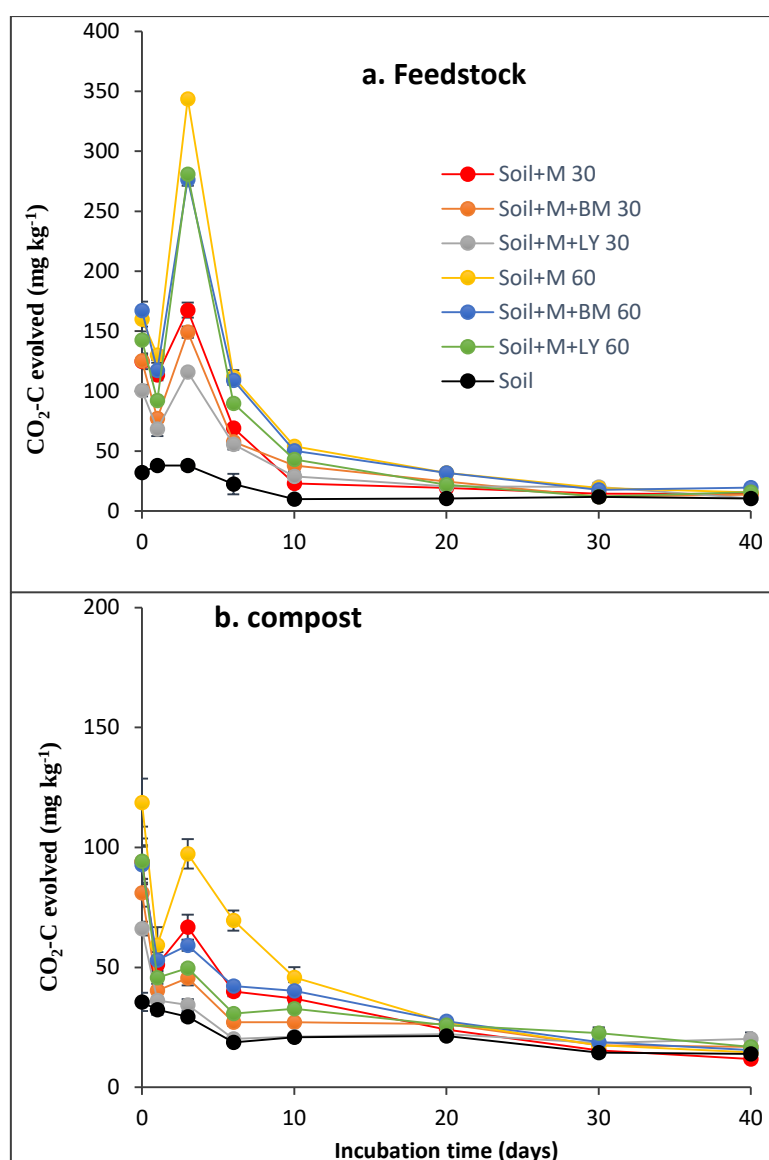


Figure 6. 7 Carbon mineralization rate in unamended and lignite amended feedstocks (a) and composts (b), applied to soil at 30 and 60 t ha⁻¹. Bars represent standard error of means (n = 3). Note different y-axes scales

The cumulative applied C mineralized (% C_{min}) was higher in the feedstocks than in the composts with lower values recorded in the lignite treatments (Figure 6.8). The lower C

mineralization in the feedstocks could be attributed to the reduction in the labile C fraction during the composting process (Hartz et al. 2000; Eghball et al. 2002; Cambardella et al. 2003). Lignite's capacity to reduce C mineralization is consistent with Tran et al. (2015) who reported that lignite inhibited microbial respiration during with soil leading to lower emissions of CO₂. A similar observation was made by Whiteley and Pettit (1994a), in assessing the effect of lignite humic acid on decomposition of wheat straw over a 4-week incubation period, who reported that lignite inhibited both oxygen consumption and CO₂ evolution. Scheffe et al. (2008b) observed a lower CO₂ evolution in soil amended with lignite compared to soil amended with compost. The mechanism of lignite's suppression of C mineralization is unclear though this has been attributed to the lower bioavailability of lignite (Scheffe et al. 2008b; Yoon et al. 2016). The BM and LY lignite had only 8.3-11.9% of their total C (54.8-56.2%) present in the labile form (Table 3.1, Chapter 3). Tran et al. (2015) suggested that a more likely mechanism through which lignite suppresses microbial activity is through the leaching of protons from the lignite in soils with neutral/alkaline pH or the release of inhibitory or toxic compounds (e.g. phenols, benzenes and poly-aromatic hydrocarbons) from the lignite.

Many studies have evaluated the mineralization of applied manure (composted and non-composted) C using soil incubation. Antil et al. (2011) reported 11-16% mineralization of applied composted cattle manure C over a 168-day incubation period. Between 1.6 and 11.4% of C mineralization in poultry, swine and cattle composted manures over a period of 100 days have been reported by Lim et al. (2012). A range of 12-40% of applied organic C from poultry manure was mineralized over a period of 60 days Martín et al. (2012). In a 24-week incubation, Hartz et al. (2000) reported 35% of manure C was mineralized whilst only 14% of composted manure C was mineralized. Over 28 days of incubation, between 1 and 8.2% of total applied C from composted sheep, pig and cattle manure was mineralized in the study by Hebert et al. (Hébert et al. 1991).

In this study, over the 40-day incubation period, the C mineralized in the feedstock at the 30 t ha⁻¹ application rate was 26.4, 21.4 and 17.3% of the applied total C for manure alone, manure + BM and manure + LY respectively whilst the corresponding C mineralized in the composts was 14.1, 6.5 and 3.5%. For the 60 t ha⁻¹ application rate, the C mineralized in the feedstocks was 27.8, 20.4 and 16.3% of the applied total C for manure alone, manure + BM and manure + LY respectively whilst the corresponding C mineralized in the composts was 12.4, 5.9 and 4.9%. For the feedstocks, within a treatment, the rate of application did not significantly influence the percent of applied C mineralized. A similar observation was made in the composts except in the manure + LY where the percent applied C mineralized was higher in the higher rate of application. In both the feedstocks and composts, at both rates of application to soil, the magnitude of cumulative percent of the applied C mineralized was in the order: manure > manure + BM > manure + LY (Figure 6.8).

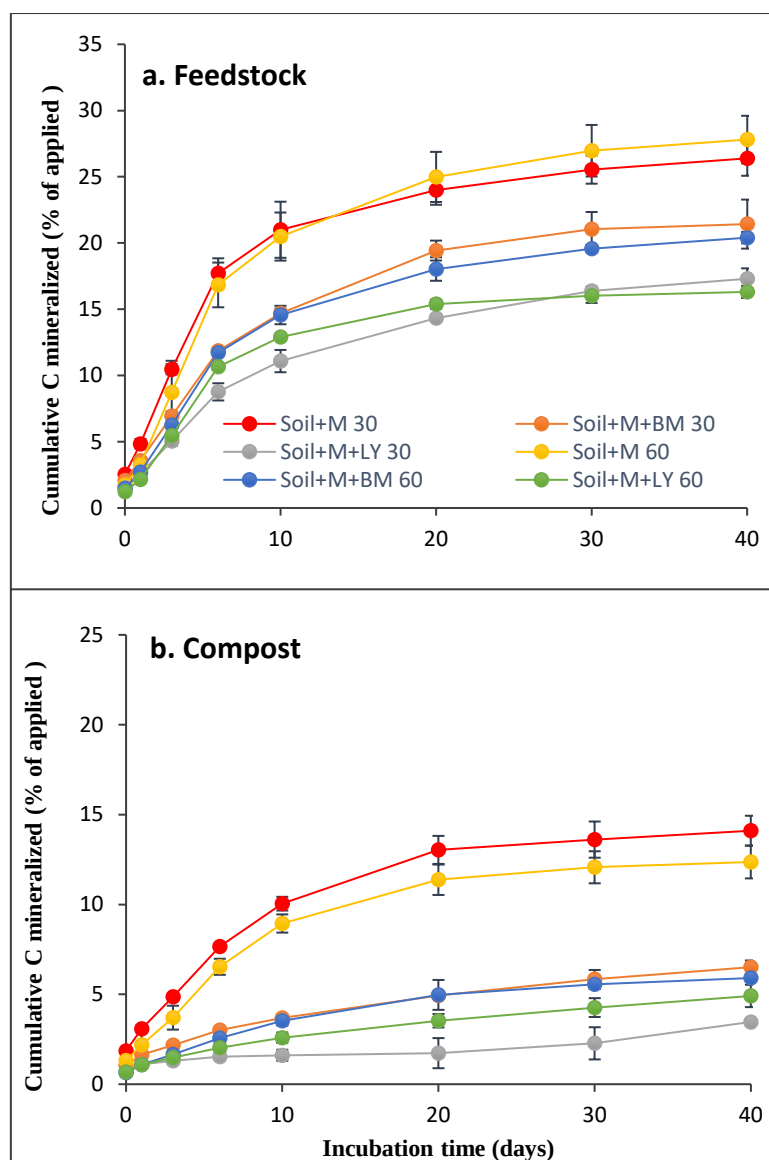


Figure 6. 8 Cumulative carbon mineralized in unamended and lignite amended feedstocks (a) and composts (b), applied to soil at 30 and 60 t ha⁻¹. Bars represent standard error of means (n = 3). Note different scales of the y-axes.

6.4 Conclusions

To utilize animal manure as a source of nutrients for plant growth, understanding the nutrient mineralization pattern in the manures when applied to soil is important to determine optimum application rates and timing. In this study, the cumulative net nitrification in cattle manure, both non-composted and composted, was higher in the lignite treatments owing to their higher initial NH₄⁺ (due to the capacity of lignite to retain NH₄⁺) providing more substrate for

nitrification. Composting of the manures, though necessary for destroying pathogens and improving the handling of the initial material (e.g. haulage and off-site application), reduced its N mineralization, most likely due to the conversion of labile organic matter into a more stabilized form (Hartz et al. 2000; Bernal et al. 2017). This suggests that, for the composts, higher application rates may be required to meet the N demand (especially in the short-term) of the crop (Hartz et al. 2000). However, the net mineralization of 2.5-13.5% of applied organic N (across all treatments) may not be adequate to sustain the productivity of certain crops, and therefore complementing the feedstock or compost application with inorganic N fertilizers may become necessary (Abbasi et al. 2007; Azeez & Van Averbek 2010). Though more manure may be applied to compensate for the lower N mineralization, repeated over application could have negative effect on soil, e.g. increase EC, as well as the loss of P and NO_3^- , through runoff and leaching, into water bodies (Mukhtar et al. 2003; Cabrera et al. 2009). The presence of lignite enhanced the mineralization of the applied organic N in the feedstock whilst its effect on N mineralization in composted manure was non-significant.

The mineralization of applied total C was lower in the composts compared to the feedstocks. The presence of lignite in the feedstocks and composts reduced C mineralization, supporting the hypothesis of the study. Thus, for building up soil organic matter, the application of composts is preferable to feedstocks. This study suggests that, as soil amendment, lignite amended manure (especially when composted) has the potential to improve soil organic matter (due to the relatively stable form of OM as well as the lignite reducing rate of C mineralization) and long term soil health. Further incubation studies (including field studies) comprising the use of different soil types (e.g. different pH, texture and OM), moisture content and extended incubation period is, however, recommended to provide more understanding on the effect of lignite on C and N mineralization in cattle manure under different conditions.

CHAPTER 7: General Discussion and Conclusions

Intensive livestock production systems are major sources of atmospheric NH_3 , released from the manure and enhanced by the alkaline pH of the manure (Reddy et al. 1979; Todd et al. 2008). Lignite has a demonstrated capacity to minimise the environmental release of NH_3 from livestock manure (Chen et al. 2015; Sun et al. 2016), but the mechanisms by which this occurs and the lignite's impact on the quality of the manure through subsequent management steps is unknown. To address these knowledge gaps, the mechanism by which lignite influences i) N retention in manure, ii) composting of manure, and iii) nutrient release from manure when applied to soil were examined in this research project through laboratory and field studies. This chapter addresses major findings of the research. The implications of the findings, as well as recommendations, for future studies and the conclusions from the research are also presented.

7.1 Major findings and general discussions

7.1.1 Lignite retains nitrogen primarily through pH dependent adsorption of NH_4^+ on sites of deprotonated carboxyl groups

Based on the findings of the characterization of five Victorian lignites for their capacity for, and mechanism of, N retention, lignite retains N primarily through pH dependent adsorption of NH_4^+ on exchange sites of deprotonated carboxyl groups (Chapter 3). Hence, lignite's ability to mitigate NH_3 emissions from manure, e.g. when applied to the animal pen, most likely occurs through these two main ways: i) the acidic pH of lignite causes the ammoniacal N in the manure to exist predominantly in the ionic form (NH_4^+), and ii) with continuous deposition of alkaline manure, more carboxyl groups become deprotonated, leading to increased CEC of the lignite and retention of NH_4^+ . Compared to NH_4^+ adsorption on exchange sites (e.g. highest Q_{max} of 25.6 mg $\text{NH}_4^+\text{-N g}^{-1}$ lignite at pH ~7), the N retention capacity of lignite through biological immobilization was insignificant (less than 0.1 mg N g^{-1} lignite). Pearson's correlation

coefficients between $Q_{\max}$ and lignite's properties showed that the CEC and pH are the key properties driving the N retention capacity, with $Q_{\max}$ increased by up to 3 fold when pH was increased from 3.6 to ~7. A study (unpublished) shows that the NH_3 adsorption capacity and biological immobilization of N in the lignite was higher in manure environment.

7.1.2 Lignite addition to manure did not impede the composting process, further mitigated NH_3 emission during compositing and improved the quality of the final compost

Composting enables the transformation of manure, generated in intensive livestock production systems, into a stabilized and sanitized product (with reduced volume and moisture content) for offsite application (Bernal et al. 2009; Arriaga et al. 2017). The addition of lignite to manure did not inhibit the composting of the manure under both field scale windrow and laboratory scale in-vessel composting conditions (Chapters 4 and 5). During the in-vessel composting, the presence of lignite delayed the onset of thermophilic temperatures though this did not prolong the duration (21 days) of the composting process. Amending manure with lignite improved the quality of the final compost: increased total N content by 10-19% and OM by 28-38% relative to manure only. Also, it increased the germination index (GI) of the compost (from 71% to 90-113%). However, these improvements in the quality (total N and OM) of the final compost was not observed during the windrow composting likely due to the largely passive aeration system used. The loss of N via NH_3 emission is a major challenge in composting of manure in terms of the agronomic value of the compost and environmental impact (Bernal et al. 2017). This study found that, lignite's capacity to retain N in manure (mechanism discussed in Chapter 3) persisted under both windrow and in-vessel composting conditions (Chapters 4 and 5). Lignite reduced NH_3 emission by 45% during windrow composting and by 35-54% during in-vessel composting. The effect of lignite on GHG emissions varied with the type of composting system. For windrow composting (aeration was

largely passive), lignite addition increased GHG emissions from manure (41% for CO₂, 136% for N₂O and also increased CH₄ from -5.0 mg kg⁻¹ DMi day⁻¹ in manure only to 9.8 mg kg⁻¹ DMi day⁻¹) (Chapter 4). However, under in-vessel composting (with forced aeration), lignite addition reduced the emissions of GHGs (12-23% for CO₂, 58-72% for N₂O and 52-59% for CH₄) (Chapter 5). The higher emission of GHGs (N₂O and CH₄) from the lignite treated windrow was presumed to be due to a more anaerobic condition within the windrow due to the passive aeration system used, facilitated by the relatively small particle size of the lignite. In addition, the difference in effect of lignite in the windrow compost compared to that in the in-vessel system could be attributed to i) the mode of manure collection using large scale field equipment meant that the lignite content of the manure was estimated and could have been less due to some being left on the pen surface, and ii) the source of soil used in the cattle pens had a pH of 8.8 which would have reduced the lignite pH effect on N retention in the manure.

These findings suggest that lignite has the capacity to mitigate NH₃ and GHG emissions from manure during composting and also improve the quality of the final compost. However, in field scale windrow composting, the amendment of manure with lignite may need to be combined with improved management in order to reduce the GHG emissions. Management strategies, such as improved aeration and sufficient moisture content, are key to creating optimum conditions during composting (Bernal et al. 2009). Overall, lignite has the potential to improve manure recycling through composting, a major manure management option in intensive livestock production system.

7.1.3 Lignite inhibited carbon mineralization from manure when applied to soil, but had mixed effect on nitrogen mineralization

Manure is a valuable source of soil organic matter and plant nutrients, and in order to obtain the optimum benefit when applied to soil, the rate and timing of its application should be based

on the expected nutrient mineralization, a microbial mediated process affected by the characteristics of the manure and the soil (Bernal et al. 1998b; Eghball et al. 2002; Qian & Schoenau 2002). It was found during the 40-day soil incubation experiment that amending manure with lignite inhibited the mineralization of C (leading to lower CO₂ evolution) from the manure, with the inhibition more pronounced when the lignite amended manure is composted (Chapter 6). With non-composted manure at application rates of 30 and 60 t ha⁻¹ soil, the C mineralized was 26.4 to 27.8% for manure only, and with lignite amendment it was 16.3 to 21.4%. The corresponding C mineralized in the composted manure was 12.4 to 14.1% and then 3.5 to 6.5%. Though the main mechanism behind lignite's suppression of microbial activity is unclear, some studies have suggested that this occurs through physical protection or adsorption of substrate, the release of toxic organic compounds from the lignite, or due to its recalcitrant nature (Whiteley & Pettit 1994a; Tran et al. 2015). Lignite had mixed effect on N mineralization from manure where for non-composted manure amended with LY lignite, at application rates of 30 and 60 t ha⁻¹, the N mineralized was significantly higher (10.4 to 13.5%) than with BM lignite (4.1 to 9.8%) and non-composted manure only (3.2 to 8.7%). For composted manure, there was no significant difference between N mineralized in the manure only (4.8 to 6.7%) and the lignite treatments (2.5 to 7.8%). Overall, the lignite amended manure (particularly when composted), could play a very important role as a soil amendment, especially building soil C reserves to promote long term soil health.

7.2 Implications for future study and recommendations

The mechanisms of, and capacity for, N retention by lignite was determined under laboratory conditions, and the correlation between lignite's properties and N retention capacity was obtained using five Victorian lignites. The pH dependent adsorption of NH₄⁺ is expected to remain the main mechanism of N retention in lignites sourced from different locations.

However, studies involving larger sample size is recommended to further understand how lignite properties (especially properties other than pH and CEC) influence its N retention. Though the main mechanism of N retention will most likely persist under field conditions, the capacity for N retention, especially the biological immobilization of N, may differ. In the manure, the alkaline pH (compared to the acidic pH of the lignite) may create a more favourable environment for biological immobilization of N, and thus increase lignite's capacity for N retention. Therefore, future studies should investigate the capacity for N retention by lignite in the presence of animal manure.

Though lignite effectively mitigated NH_3 loss from manure during composting under both laboratory and field conditions, it only effectively mitigated the emissions of GHGs under laboratory condition. The increase in the emissions of GHGs (CH_4 and N_2O) from the lignite amended manure windrow was presumed to be due to anaerobic pockets within the windrow as well as the manure management in the pen, however further studies are recommended to investigate the main factors driving the higher emissions of GHG from lignite amended manure during field scale windrow composting. Parameters such as oxygen concentration, bulk density and porosity of the windrow should be monitored continuously and also higher windrow aeration or turning frequency (though this has the potential to result in higher NH_3 loss (Bernal et al. 2017)) should be considered. Also, in the generation of lignite amended manure in large scale animal pens, manure harvesting techniques that ensure uniformity in manure collection between pens should be used. These studies are important in determining optimum conditions for lignite application in industry scale manure composting.

The effect of lignite on C and N mineralization from manure when applied to soil was determined through laboratory incubation experiments over a period of 40 days and only one soil type was used. Future long term incubation studies (including field studies) that employ

different lignite amended manure application rates, soil types (e.g. different pH, texture, OM and N contents) and moisture contents are recommended to further understand how lignite impact on C and N mineralization is influenced by these factors. Also the continuous or long term application of lignite amended manure on soil properties should be investigated. Further studies on lignite amended manure would benefit from inclusion of microbial analysis (e.g. microbial size and diversity) to elucidate the main mechanism behind the observed inhibitory effect of lignite on microbial respiration (under both incubation and composting conditions). In addition, the assessment of priming effect owing to lignite-manure application to soil and the use of ^{13}C natural abundance to determine the mineralization of lignite C is recommended.

7.3 Conclusions

Results from this study show the application of lignite as an NH_3 emission mitigation technique during manure deposition in intensive livestock production systems has an additional benefit in the subsequent recycling of this manure for agricultural use. During composting, lignite has the capacity to suppress the emissions of both NH_3 and GHGs if the compost is managed effectively. This has important implications in the management of manure in intensive livestock production systems from the standpoints of nutrient management and environmental pollution. Composted lignite amended manure, when applied as a soil amendment, has the potential to build up soil organic matter and improve long term soil health due to the lignite's ability to inhibit C mineralization. In summary, this study provides new information on the mechanisms by which lignite interacts with manure, and can be used to better manage manure to reduce the environmental impact of intensive livestock production systems, and to produce high quality recycled products to improve soil health.

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Appendix



Plate 1 Loy Yang coal mine (Victoria, Australia) – One of the mines from where lignite samples were collected.



Plate 2 Charlton beef feedlot (Victoria, Australia): The site for the field experiment – lignite application to cattle pen and windrow composting (Chapter 4).



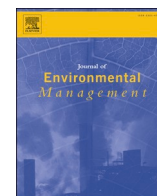
Plate 3 Open path Fourier Transform Infrared Spectroscopy used for measurement of gaseous emissions during field composting (Chapter 4)



Plate 4 In-vessel composting system with a closed path Fourier Transform Infrared Spectroscopy used for the laboratory scale composting (Chapter 5).



Plate 5 Acid trap used for NH_3 emission measurements during laboratory scale composting (Chapter 5).



Research article

Lignite effects on NH_3 , N_2O , CO_2 and CH_4 emissions during composting of manureMei Bai^{a,*}, Robert Impraim^a, Trevor Coates^a, Thomas Flesch^b, Raphaël Trouvé^c, Hans van Grinsven^d, Yun Cao^e, Julian Hill^f, Deli Chen^a^a School of Agriculture and Food Sciences, Faculty of Veterinary and Agricultural Sciences, The University of Melbourne, Parkville, Victoria, 3010, Australia^b Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, AB, T6G 2R3, Canada^c School of Ecosystem and Forest Sciences, Faculty of Science, The University of Melbourne, Richmond, Victoria, 3121, Australia^d PBL Netherlands Environmental Assessment Agency, The Hague, the Netherlands^e Circular Agriculture Research Centre, Jiangsu Academy of Agricultural Sciences, NanJing, 210014, China^f Ternes Agricultural consulting Pty Ltd, Upwey, Victoria, 3158, Australia

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ABSTRACT

Production of compost from cattle manure results in ammonia (NH_3) and greenhouse gas emissions, causing the loss of valuable nitrogen (N) and having negative environmental impacts. Lignite addition to cattle pens has been reported to reduce NH_3 emissions from manure by approximately 60%. However, the effect of lignite additions during the manure composting process, in terms of gaseous emissions of NH_3 , nitrous oxide (N_2O), carbon dioxide (CO_2), and methane (CH_4) is not clear. This composting study was conducted at a commercial cattle feedlot in Victoria, Australia. Prior to cattle entering the feedlot, we applied 4.5 kg m^{-2} of dry lignite to a treatment pen, and no lignite to a control pen. After 90 days of occupancy, the cattle were removed and the accumulated manure from each pen was used to form two separate compost windrows (control and treatment). During composting we collected manure samples regularly and quantified gaseous emissions of NH_3 , N_2O , CO_2 , and CH_4 from both windrows with an inverse-dispersion technique using open-path Fourier transform infrared spectroscopy (OP-FTIR). Over the 87-day measurement period, the cumulative gas fluxes of NH_3 , N_2O , CO_2 , and CH_4 were $3.4 (\pm 0.6, \text{ standard error})$, $0.4 (\pm 0.1)$, $932 (\pm 99)$, and $1.2 (\pm 0.3) \text{ g kg}^{-1}$ (initial dry matter (DM)), respectively for the lignite amended windrow, and $7.2 (\pm 1.3)$, $0.1 (\pm 0.03)$, $579 (\pm 50)$ and $-0.5 (\pm 0.1) \text{ g kg}^{-1} \text{ DM}$, respectively for the non-lignite windrow. The addition of lignite reduced NH_3 emissions by 54% during composting, but increased total greenhouse gas (GHG) emissions by 2.6 times. Total N losses as $\text{NH}_3\text{-N}$ and $\text{N}_2\text{O-N}$ were approximately 11 and 25% of initial N for the lignite and non-lignite windrows, respectively. The effectiveness of retaining N was obvious in the first three weeks after windrow formation. A cost-benefit analysis indicated that the benefit of lignite addition to cattle pens by reduced NH_3 emission could justify the trade-off of increased GHG emissions.

1. Introduction

Animal excretion contributes to ammonia (NH_3), nitrous oxide (N_2O), and methane (CH_4) emissions. This has negative impacts on the environment through global warming, air pollution, and water way contamination; on natural ecosystems as threats to species diversity; on human health, including adverse effects on respiratory and cardiovascular systems and visibility (Stokstad, 2014), and causes a financial loss for farmers. Identification of mitigation strategies to lower emissions of NH_3 and the greenhouse gases (GHG) of N_2O and CH_4 from livestock is

an important need, both nationally and internationally.

Feedlot production of cattle has expanded to meet the high demand for meat production. During the finishing period of cattle production, animals are kept in feedlot pens for 50–120 days to increase rates of weight gain and meet market quality requirements. Large feedlots can have more than 15,000 animals, producing large amounts of cattle manure that need to be treated before application to croplands as fertilizer or soil amendment. Approximately 1 million tonnes of manure is produced each year from Australian feedlots (RIRDC, 2012). In the United States, approximately 377 million tonnes of beef cattle manure

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was produced in 2007 (USEPA, 2013). In Canada, 180 million tonnes of manure was produced by livestock in 2006 (Hao and Larney, 2017). In the United Kingdom, 44 million tonnes of solid cattle manure was produced annually from farmyards, accounting for 53% of total cattle manure (Smith and Williams, 2016).

Aerobic composting of organic matter is a well-established method of stabilising and sterilising material before application to agricultural lands. About 16% of Canadian farms use composting to treat manure (Hao and Larney, 2017). In Australia, northern feedlots often store the fresh cattle manure in pens for 6 months before spreading on croplands, while southern feedlots in Victoria compost the manure before land application, combining initial stockpiling and regular-turned windrow composting for 3 months in summer or 6 months in winter seasons. Composting manure decreases the mass, volume and water content of the manure; reduces odour, pathogens, and weed seeds; and turns the animal manure into a more stable source of fertilizer nutrients needed for crop production (Pardo et al., 2015; Stentiford, 1996). However, if the process of compost manure is not managed well, it can also lead to increased emissions of GHG and NH_3 (Bernal et al., 2017; Chadwick et al., 2011; Hao et al., 2001; Hao and Larney, 2017). Appropriate manure management strategies are needed to improve production efficiencies without negative impacts on the environment.

Studies investigating management practices to reduce N losses during manure stockpiling and manure composting, include adding material (straw, wood) (Hao et al., 2004; Sommer et al., 2006); composting at different seasons using passive or active aeration combined with static piling treatments (Amon et al., 2001; Hao et al., 2001; Parkinson et al., 2004); and varying the duration of composting (Chadwick et al., 2011; Zhao et al., 2020). Our previous work in Australia reported on a short-term study (40 days) where lignite was applied at the rate of 3, 4.5 and 6 kg m^{-2} to cattle pen surfaces as a means to reduce NH_3 and N_2O emissions, due to N retention by the lignite (Chen et al., 2015; Sun et al., 2016). Lignite, also known as brown coal, is a by-product of the coal industry in Victoria, Australia that is inexpensive and easy to access. However, there was no further study of the treatment stage of compost at a commercial scale, which takes 3–6 months (depending on the season). In particular it is not clear if the N retained in the lignite amended manure will persist through the composting process. It is also unclear what effect the lignite will have on emissions of NH_3 , N_2O , CO_2 , and CH_4 during composting.

The objectives of this study were to examine the ability of a lignite additive to retain N in composted manure, and the resulting impact on NH_3 and GHG emissions (N_2O , CH_4 , and CO_2) during the windrow composting process. The study was done at a commercial feedlot using compost rows created as part of normal feedlot operations (with and without lignite). A micrometeorological technique was used to measure emissions. This study will help us understand the effectiveness of lignite additions on the continuum of manure management process. Furthermore, we estimated the direct and indirect costs and benefits of adding lignite to the manure, at the farm scale and for society, in terms of the value of manure fertilizer and the societal damage caused by change of NH_3 and GHG emissions. The results of this study can provide important information to inform Australian NH_3 and GHG mitigation strategies, as well as guide sustainable agricultural production that includes increased production efficiencies and profit potential for cattle producers.

2. Materials and methods

2.1. Initial conditions

The study was conducted at a commercial feedlot in Australia (36.28°S, 144.33°E), located ~200 km northeast of Melbourne, Victoria, with measurements taken from 14 February to 12 May 2018.

2.2. Accumulated manure

Prior to admitting the cattle, (29 × 50 m) two side-by-side pens were resurfaced with clay to provide a stable base to collect manure. Following Chen et al. (2015), 4.5 kg m^{-2} of dry lignite was uniformly applied to the treatment pen surface on November 9, 2017. No lignite was applied to the adjacent control pen. The lignite originated from a coal mine in Victoria, and had the following characteristics: moisture 60%, pH 5.76, labile carbon (C) 45.7 g kg^{-1} , and electrical conductivity 1515.7 $\mu\text{S cm}^{-1}$. Each pen was populated with 135 Angus steers having an average body weight of 460 ± 5 kg on 15 November. After 90 days the cattle were removed, and both pens were scraped in keeping with standard feedlot procedures. The accumulated manure from each pen (including the applied lignite) was weighed and transported outside the feedlot to form two windrows (Fig. 1), one from the non-lignite pen (44.0 tonnes) and one from the lignite-treated pen (25.1 tonnes). The initial physical and chemical properties of the manure are shown in Table 1.

2.3. Compost windrows

The composting measurement site was located just west of the feedlot, on a field with crop stubble and residue (harvested in December in the previous year). This environment provided a homogeneous surface suitable for the micrometeorological approach to measure emissions. The two windrows were oriented north-south (30 m apart), with equipment placed to allow concurrent emission measurements during westerly winds (Fig. 1). We target westerly winds for our emission measurements, so that no other emission sources would “contaminate” our site: the feedlot was to the east, and the nearest farms to the west were several kilometres away. The lignite windrow was (14 m long × 4.3 m wide × 1.2 m high) in size, and the non-lignite windrow was (20 m long × 4.3 m wide × 1.2 m high). From windrow formation to the final compost-product as organic fertiliser took 87 days. Both windrows were turned 12 times using a Komptech, Topturn X55 turner, with each turning taking about 10 min. Emission measurements began on 14 February immediately after the compost windrows were formed and ended on 12 May 2018.

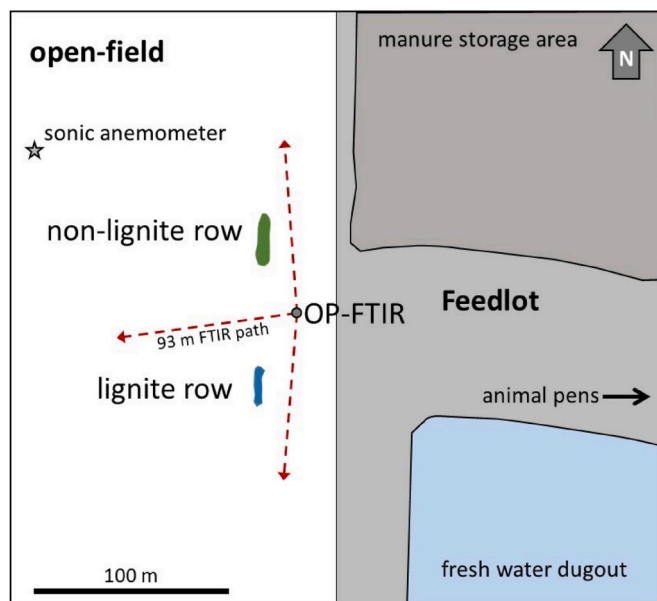


Fig. 1. Configuration of the compost experiment (lignite and non-lignite windrows). Three OP-FTIR pathlengths are denoted by dashed lines. The experiment was conducted at a commercial feedlot in Victoria, Australia from 14 February to 12 May 2018.

Table 1
Initial characteristics of windrow manure in this study.

	Moisture (%)	pH	NH ₄ ⁺ -N (%)	NO ₃ ⁻ -N (%)	TC ^a (%)	TN ^b (%)
Lignite amended manure	31.1	7.4	0.8	0	29.3	2.8
Non-lignite amended manure	28.9	7.3	0.9	0	27.0	2.5

^a total carbon.

^b total nitrogen.

2.4. Manure sampling and analyses

The manure was sampled immediately after each turning event, with samples taken from five windrow locations. Four sub-samples were collected using a core (3 cm diameter, 90 cm long) at each location (two samples from the eastern side, and two samples from the western side of the windrow) and mixed to one sample. Each collected sample (~500 g) was frozen at -20 °C for further processing and analysis. These samples were later oven-dried at 40 °C until the mass was stabilized, and analysed for pH (1:5 H₂O), total carbon (TC), total nitrogen (TN), ammonium-nitrogen (NH₄⁺-N), and nitrate-nitrogen (NO₃⁻-N) (TrACess Soil Node, University of Melbourne). Manure TC and TN were measured from dried manure, which was ground (< 2 mm) and analysed on a LECO Trumac CN Analyzer. Samples (~4 g) were also extracted with 2M KCl (1:20) and manure NH₄⁺-N and NO₃⁻-N were analysed using a Skalar SAN++ segmented flow analyser.

2.5. Gas emission measurements

An open-path Fourier transform infrared spectrometer (OP-FTIR, Matrix-M IRCube, Bruker Optics) measured the line-average concentrations of CH₄, CO₂, N₂O, and NH₃ between the spectrometer and three retroreflectors (three paths, each 93 m from the spectrometer). The path heights were 1.65 m above the ground. Gas concentrations were calculated from the OP-FTIR spectra using a non-linear least squares fitting procedure based on computed spectrum given by the HITRAN database of spectral line parameters (Rothman et al., 2009) using MALT software (Multiple-Atmospheric Layer Transmission) (Griffith, 1996; Paton-Walsh et al., 2014). The measurement precisions were 2 ppb for CH₄, 1 ppm for CO₂, 0.3 ppb for N₂O, and 0.4 ppb for NH₃. A motorised system enabled the spectrometer to automatically aim at the three retro reflectors (Fig. 1). The system used a 2.5-min aiming sequence for each path measurement, which included 1.2 min of spectrum collection, 40 s of turning aiming system, and 15 s of spectrum analysis and data logging. This OP-FTIR configuration was used in a previous study (Bai et al., 2020).

2.6. Gas flux calculation

An inverse-dispersion model (WindTrax, Thunder Beach Scientific) was used to calculate gas emission rates. The principle of this technique has been reported by Flesch et al. (2004), where emissions are calculated from a measurement of the enhancement of concentration downwind of the compost rows (compared to the background gas level). The WindTrax analysis assumes gas is emitted from a ground level area source, taken as the surface area (m²) of the manure windrow measured by GPS. The windrows are not actually surface area sources, but more complex three-dimensional sources. We assume the gas concentration is measured sufficiently far downwind of the manure (minimum distance of 20 m, or >10 compost heights) so that the calculated emission rates are insensitive to this error (a principle discussed in Flesch et al. (2005)). For the westerly and southeasterly winds that are targeted for our calculation, the background concentration corresponds to the

concentration measured from one of the upwind OP-FTIR paths.

A three-dimensional sonic anemometer (CSAT3, Campbell Scientific) was located west of the compost site at a height of 2.8 m above the ground (Fig. 1). Wind and temperature were measured at a frequency of 10 Hz, and the wind and temperature statistics were later processed to give the wind properties needed for a flux calculation: friction velocity (u_*), Obukhov stability length (L), surface roughness (z_0), wind direction, and wind velocity standard deviations ($\sigma_{u,v,w}$). We used SAS software (version 9.4) to process gas concentration and wind data into 15-min average timeseries.

Following Flesch et al. (2014), we excluded atmospheric conditions that are associated with erroneous WindTrax results: surface roughness $z_0 > 0.2$ m, friction velocity $u_* < 0.05$ m s⁻¹, and the percentage of particle touchdowns on the source area < 75%. We also ignored wind directions from 0 to 120°, and from 330 to 360° as these did not allow an emission calculation given the measurement configuration. Furthermore, OP-FTIR concentration measurements were not counted when the spectral signal intensity was less than 0.06 (Spec.max).

2.7. Statistical modelling of daily and cumulative gas emission trends

Statistical modelling of daily and cumulative emission trends for each gas from each windrow followed four steps:

1. We first calculated daily gas emissions on a weight of dry manure (DM) basis (g day⁻¹ kg⁻¹ DM) from the 15-min emission dataset.
2. We then modelled the time-series of daily gas emissions using time-series methods. Since composting is a slowly evolving process and daily fluxes exhibit a certain degree of smoothness (i.e., fluxes measured one day apart are more similar to each other than fluxes measured 10 days apart), it can be aptly modelled using Gaussian Processes (Rasmussen and Williams, 2005; Roberts et al., 2013), which are particularly relevant when data are measured at irregular time intervals. In Gaussian process regression, the degree of similarity (i.e., the covariance or scaled correlation) between any two points in time is a function of the time difference between the measurements. This imposes a certain degree of smoothness (estimated from the day-to-day variation in daily gas emission) to the daily emission curves and also means that the further in time we go from any measured data, the higher the uncertainty in reconstructed gas emissions. For the practical implementation of the method, we used a squared exponential covariance function, the most widely used covariance function (Rasmussen and Williams, 2005), to model the progressive decrease of gas emission autocorrelation with time. The models were fitted individually to each time series of daily gas emission using the "brm" function in the "brms" package in R 3.5.1 (RCoreTeam, 2018) using the Gaussian process terms "gp" with default priors.
3. To propagate uncertainties in daily emissions, we sampled 10,000 parameters from the joint posterior distribution and simulated 10,000 daily emission curves consistent with our data. From these curves, we computed the mean and 95% credible intervals of daily gas emissions. Note that these credible intervals are statements about the smoothed mean value of emission per day, not about individual measurements.
4. For each day, we computed potential cumulative gaseous emission by summing the daily gas emission since the start of the experiment. We propagated the uncertainties by repeating this process 10,000 times (once for each of the 10,000 simulated daily emissions curves) and summarized the result by computing the mean and 95% credible intervals per day. As expected, periods without measurements have higher uncertainties in the mean daily emission, which in turns inflate the uncertainty in the cumulative gas emissions. The cumulative sum on the last day of the experiment (Day 87) represented the estimated losses from manure for the whole experiment period.

2.8. Cost and benefit analysis

To assess the integrated impact of windrow composting subsequent to adding lignite to cattle pens, we applied a simple cost-benefit analysis. We assigned values to the change in environmental impacts as the change in GHG and NH_3 emissions, as well as the economic benefit of N retention in the manure fertilizer. The Australian carbon price of \$24.15 AUD per carbon unit was used to evaluate the costs of GHG emissions (CO_2 equivalent, $\text{CO}_2\text{-e}$) (AGCER, 2012). The fertilizer value of manure was evaluated using a N fertilizer price of \$1.37 AUD kg^{-1} N (CEIC, 2013). We also applied the unit damage cost approach of van Grinsven et al. (2013), who derived a set of marginal damage costs per unit of reactive N emission for all known relevant impacts of nitrogen pollution

in Europe. European values were used to represent the marginal costs of NH_3 emissions as impacts on ecosystem via atmospheric deposition of N ($\text{€}2\text{--}10 \text{ kg}^{-1} \text{ NH}_3\text{-N}$), and on human health via air pollution by NH_3 induced aerosols ($\text{€}10\text{--}20 \text{ kg}^{-1} \text{ NH}_3\text{-N}$) (van Grinsven et al., 2013, 2018).

3. Results and discussions

3.1. Environmental conditions

During the measurement period, the average daily ambient temperatures ranged between 15 and 25 °C (Fig. 2). Temperatures decreased over the period of study, with minimum temperatures

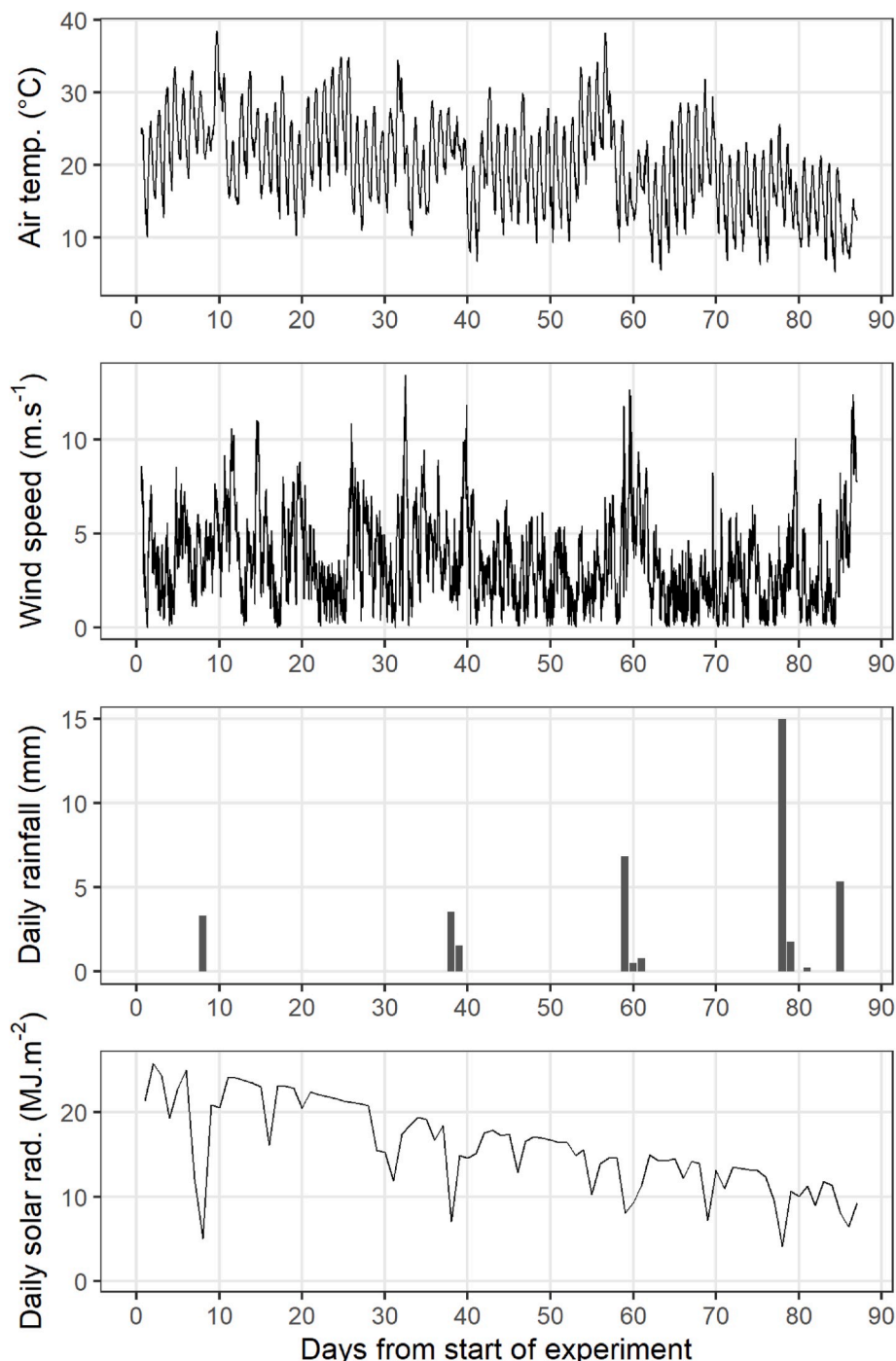


Fig. 2. Climatic conditions (ambient temperature, wind speed, daily rainfall, and daily solar radiation) during the measurement period.

dropping below 8 °C 60 days from the start of the experiment (DOE). The prevailing winds were north or northwest during the study. Wind speeds typically ranged between 1 and 5 m s⁻¹, with the strongest winds recorded on DOE 32 (> 11 m s⁻¹). A total of 10 days with rain were recorded, with three days recording over 5 mm. Maximum daily rainfall was recorded on DOE 78 (~15 mm). Total rainfall for the measurement period was 38.9 mm (Fig. 2). Daily solar radiation decreased over the measurement period and ranged between 4 and 26 kJ m⁻². The lower values were associated with the rainfall events shown in Fig. 2.

3.2. Manure pH, ammonium, nitrate, total nitrogen, and total carbon

The manure pH of both windrows increased in the first few days after DOE, then gradually decreased and remained above 7.8 by the end of the experiment (Fig. 3). The initial rapid increase in pH was attributed to the onset of organic matter mineralization and release of NH₄⁺ or volatile NH₃ (Gigliotti et al., 2012). The gradual reduction in pH after the peak value on DOE 59 could be caused by NH₃ ammonification from the

compost when the NH₃ was volatilized. The lower pH in the lignite compost compared to the non-lignite compost can be attributed to the acidic properties of the added lignite.

The NH₄⁺-N content in both windrows followed a similar pattern: an initial increase to the peak on DOE 9, then a decrease until the end of the measurement (Fig. 3). A similar observation was reported in Hao et al. (2004). In our study, the greater initial NH₄⁺-N content in the lignite windrow could be due to the greater ammonification rate compared to the non-lignite windrow. The decrease in NH₄⁺-N in the later stage of composting could be attributed to its conversion to NH₃ and subsequent volatilization (Hao et al., 2011).

The NO₃⁻-N content in both windrows followed an upward trend over the 87-day study period (Fig. 3). However, the increase in NO₃⁻-N did not correspond to the decrease in NH₄⁺-N. Similar observations were made by Tiquia (2002) who reported that some of the NH₄⁺-N might have been lost through NH₃ volatilization and/or denitrification. In our study, NO₃⁻-N loss through leaching and/or runoff is expected to be insignificant as no heavy rainfalls occurred during the composting period. We also found that NO₃⁻-N content in both windrows was below 0.003%, reflecting a slow nitrification process during composting.

The TN content in both windrows followed a similar trend as the NH₄⁺ change, but the changes were relatively slow in the non-lignite windrow compared to the lignite windrow (Fig. 3). The transformation and transfer of ammoniacal nitrogen has been reported as the main mechanisms for nitrogen removal from material during composting (De Guardia et al., 2010). During our study, more of these transformations occurred without lignite additions to the manure.

The TC content in the lignite and non-lignite windrows decreased over the 87-day study (Fig. 3). Over the first 35 days, 37 and 12% of the initial TC was lost in the lignite and non-lignite windrows, respectively. Thereafter, the total C losses were 1% for the lignite windrow and 4% for the non-lignite windrow. The initial loss of TC in the lignite windrow could be due to enhanced microbial activity as a result of the high labile C fraction of the lignite. The decrease in TC content in the lignite windrow could be attributed to degradation of readily available C forms, which provides an energy source for microorganisms. This also suggests a higher microbial activity and faster degradation rate of organic C in the lignite windrow compared to the non-lignite windrow, particularly in the first 20 days after compost formation.

3.3. Gas fluxes

Over the 87 days of the experiment, 3126 measurements were available in 15-min intervals. Of these, 1598 and 924 met the criteria of useful data for the lignite and non-lignite windrows, respectively, accounting for 51 and 30% of the study period for the lignite and non-lignite windrow, respectively.

3.3.1. NH₃ emission rates

The daily average NH₃ emission rates from the lignite windrow decreased from an initial 0.06 g day⁻¹ kg⁻¹ DM on DOE 1 to near-zero by DOE 86 (Fig. 4). A peak of 0.16 g day⁻¹ kg⁻¹ DM on DOE 14 was observed, probably associated with the turning event on DOE 14. Compared to the lignite windrow, emissions of NH₃ from the non-lignite windrow showed a similar decreasing trend, but with a higher initial emission rate of 0.13 g day⁻¹ kg⁻¹ DM on DOE 2, and a higher peak of 0.30 g day⁻¹ kg⁻¹ DM on DOE 10, nearly double the rate of the lignite windrow peak emission. The lower NH₃ emissions from the lignite windrow compared to the non-lignite windrow could be due to the slightly lower pH of the lignite amended manure. Biological immobilization of NH₄⁺-N, owing to the labile C fraction of the lignite, might contribute to the lower NH₃ emission from the lignite windrow. Furthermore, the absorption of NH₃ by the lignite may play a role in reducing NH₃ emissions.

We observed a diurnal pattern of NH₃ emissions from both windrows: with higher afternoon emissions between 12:00 and 15:00, and

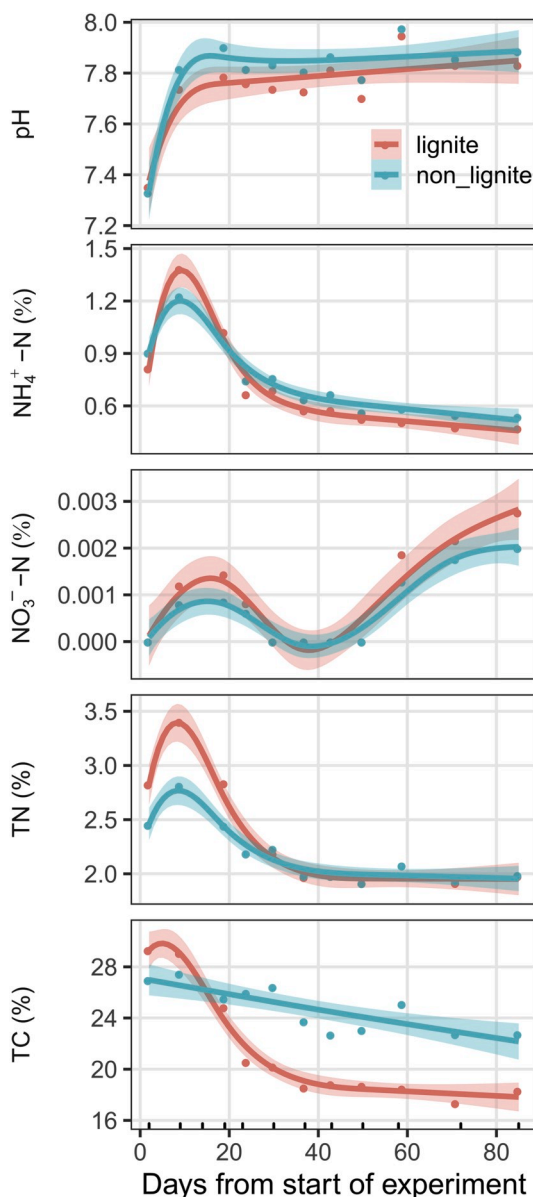


Fig. 3. Changes of pH, NH₄⁺-N, NO₃⁻-N, TN, and TC in lignite and non-lignite windrows during the composting period. The short vertical bars on the x-axis indicate turning events. The shaded areas represent 95% confidence.

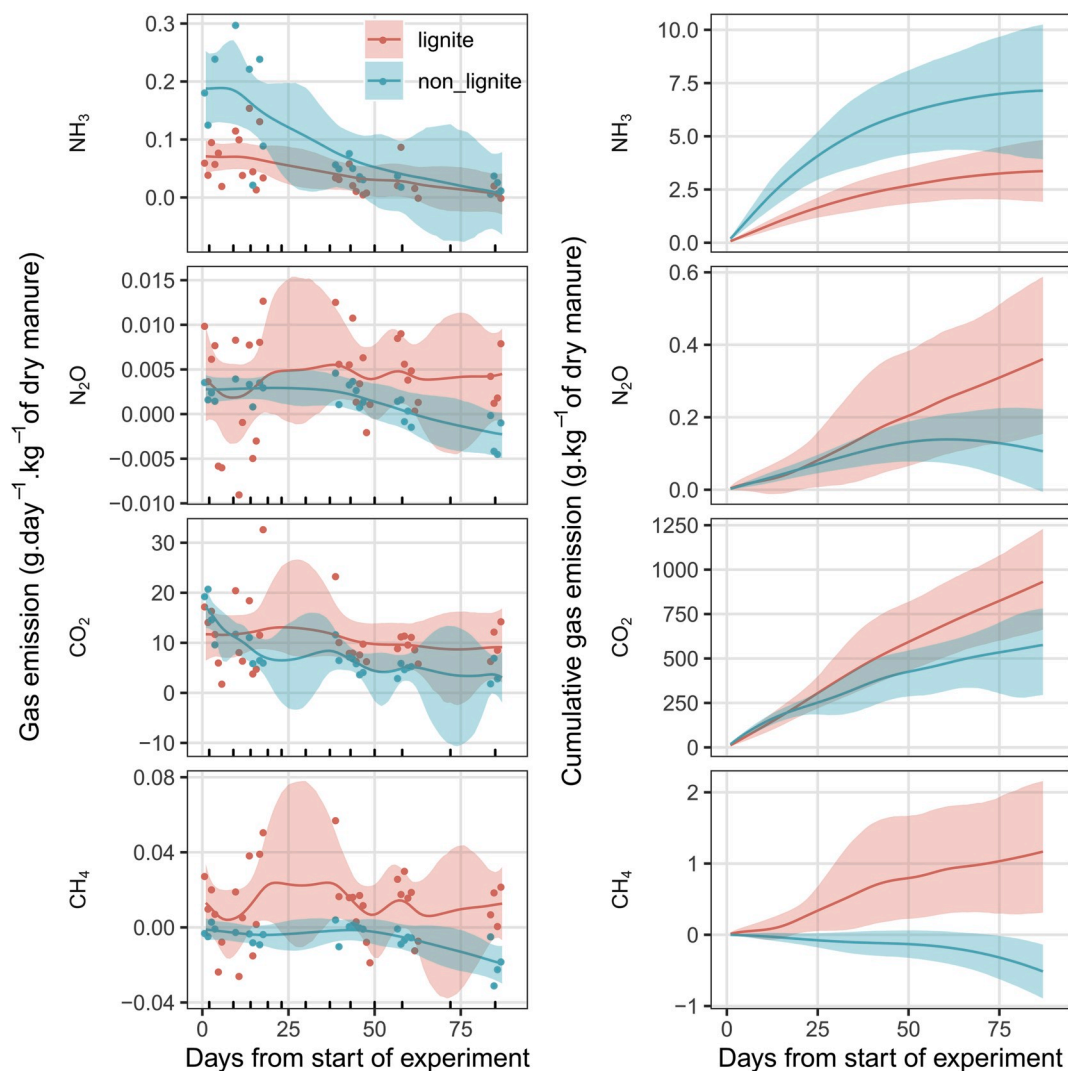


Fig. 4. Daily fluxes of NH_3 , N_2O , CO_2 , and CH_4 (left panels) and cumulative fluxes (right panels) measured from the lignite (red symbols) and non-lignite (green symbols) windrows over the 87-day measurement period. Lines denote fitted statistical trends. The short vertical bars on the x-axis of left panels indicate turning events. Right panels show accumulated fluxes. The shaded areas represent 95% confidence. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

lower emissions at night-time. This pattern can be explained by the positive correlations between NH_3 fluxes and wind speed ($R = 0.44$ and 0.48 ($P < 0.001$), for lignite and non-lignite windrow respectively), and between NH_3 fluxes and air temperature ($R = 0.62$ and 0.64 ($P < 0.001$), for lignite and non-lignite windrow respectively). This pattern was also reported by Sommer et al. (2004).

3.3.2. N_2O emissions

Daily N_2O emissions from the lignite manure windrow started from $0.01 \text{ g day}^{-1} \text{ kg}^{-1} \text{ DM}$ on DOE 1, and then fluctuated gently during the composting process, to remain between 0.01 and $0.008 \text{ g day}^{-1} \text{ kg}^{-1} \text{ DM}$ by the end of the study. The N_2O emissions from the non-lignite manure windrow started from $0.004 \text{ g day}^{-1} \text{ kg}^{-1} \text{ DM}$ on DOE 1, then decreased gradually to near-zero by DOE 60. Thereafter no N_2O emissions were detected. Negative N_2O emissions were also observed from both windrows, but this could be attributed to the fact that the downwind enhancement of N_2O concentrations were close to the FTIR detection limit during these events.

Low N_2O emissions from both windrows were attributed to low $\text{NO}_3^- - \text{N}$ content that reflected the slow nitrification process during composting. The lower N_2O level at the end of the composting process in the non-lignite windrow suggested that denitrification could have

contributed to decreased N_2O emissions near the end of the trial.

3.3.3. CO_2 fluxes

The daily CO_2 flux from the lignite windrow followed a decreasing trend over the composting period. The initial daily CO_2 flux was $14.2 \text{ g day}^{-1} \text{ kg}^{-1} \text{ DM}$, reached a peak flux of $32.8 \text{ g day}^{-1} \text{ kg}^{-1} \text{ DM}$ on DOE 18, and thereafter decreased to a range between 5 and $10 \text{ g day}^{-1} \text{ kg}^{-1} \text{ DM}$ between DOE 40 and DOE 60. Daily CO_2 flux increased from 8.7 to $14.4 \text{ g day}^{-1} \text{ kg}^{-1} \text{ DM}$ due to the last turning on DOE 85. In contrast, the CO_2 fluxes from the non-lignite windrow decreased substantially from the initial $19.4 \text{ g day}^{-1} \text{ kg}^{-1} \text{ DM}$ on DOE 1– $1.9 \text{ g day}^{-1} \text{ kg}^{-1} \text{ DM}$ on DOE 6, then gradually declined. We observed near-zero CO_2 fluxes after DOE 60. Similarly, the response of CO_2 fluxes to turning events decreased with the time. The high CO_2 fluxes from the lignite windrow likely corresponded to the high labile C contents, reflecting stronger microbial activity and faster degradation of labile C.

3.3.4. CH_4 fluxes

The daily average CH_4 flux from the lignite windrow was $0.012 \text{ g day}^{-1} \text{ kg}^{-1} \text{ DM}$ (ranging from near-zero to $0.06 \text{ g day}^{-1} \text{ kg}^{-1} \text{ DM}$), while a range of negative emissions were observed from the non-lignite windrow over the same period. Negative CH_4 emissions could be

attributed to the fact that the downwind enhancement in concentration was close to or lower than the OP-FTIR measurement detection limit. The addition of lignite to the manure may have allowed anaerobic conditions to develop in some areas (due to fewer pores in the mixture) which led to higher CH₄ emissions compared with the non-lignite windrow. However, the effect of lignite on increasing anaerobic conditions in the compost could be a factor of when the windrows were formed with different sizes/mass, or managed differently, i.e. turned a different number of times. There were no correlations between N₂O or CH₄ and climatic conditions (wind speed or air temperature) over the measurement period.

3.4. Cumulative gas fluxes

The cumulative fluxes of NH₃, N₂O, CO₂, and CH₄ from the compost windrows are given in Table 2. Note that the cumulative NH₃ emissions from the non-lignite windrow was more than two times higher than that from the lignite windrow, while the cumulative emissions of N₂O and CH₄ from the lignite windrow were higher than that from the non-lignite windrow. After converting these cumulative fluxes to a percentage of initial N, the N lost as N-NH₃ was 9.7 and 24.0% of the initial N for the lignite and non-lignite windrow, respectively. The N lost as N-N₂O was 0.8 and 0.3% of the initial N for the lignite and non-lignite windrow, respectively. The total N losses as N-NH₃ and N-N₂O were approximately 11 and 25% of the initial N for the lignite and non-lignite windrow, respectively. These results show that the addition of lignite to the manure reduced N losses as NH₃ and N₂O during the composting process.

3.5. GHG emissions and cost-benefit analysis

Following the IPCC protocol (Hartmann et al., 2013), we calculated total GHG emissions based on the global warming potential, which integrates the radiative forcing over a 100-year time equivalent to CO₂ (CO₂-e): 28 and 265 times that of CO₂ for CH₄ and N₂O, respectively (Myhre et al., 2013). We then assume that 1% of N-NH₃ emissions will be deposited downwind the feedlot and then re-emitted as N-N₂O emissions (de Klein et al., 2006). Excluding CO₂, the total GHG

Table 2

Daily mean and cumulative (87-day) emissions of NH₃, N₂O, CO₂, and CH₄ from lignite and non-lignite amended windrows. The N losses and GHG emissions (CO₂ equivalents, CO₂-e, including N₂O^a and CH₄) are estimated.

	NH ₃ ^b	N ₂ O ^b	CO ₂ ^b	CH ₄ ^b
Daily mean flux (g day ⁻¹ kg ⁻¹ DM)				
Lignite windrow	0.04 (0.01)	0.004 (0.001)	10.7 (1.1)	0.01 (0.01)
Non-Lignite windrow	0.08 (0.02)	0.001 (0.001)	6.7 (1.4)	-0.01 (0.001)
Cumulative flux (g kg ⁻¹ DM)				
Lignite windrow	3.35 (0.6)	0.36 (0.09)	931.81 (98.9)	1.16 (0.3)
Non-Lignite windrow	7.15 (1.3)	0.11 (0.03)	578.84 (49.7)	-0.52 (0.1)
N Loss (% of initial N)	N-NH ₃	N-N ₂ O	Total N losses (%)	
Lignite windrow	9.7	0.8	10.6	
Non-Lignite windrow	24.4	0.3	24.6	
GHG emissions (CO ₂ -e) ^c (g kg ⁻¹ DM)	N ₂ O ^a	CH ₄		
Lignite windrow	106.9	32.5		
Non-Lignite windrow	53.7	-14.6		

^a calculation includes 1% emitted NH₃-N is deposited and re-emitted as N₂O-N.

^b Mean (standard error).

^c global warming potential: 28 for CH₄, and 265 for N₂O. CO₂-e, equivalent to CO₂.

emissions (NH₃, N₂O, and CH₄) from the lignite windrow (139.4 g kg⁻¹ DM) were higher than from the non-lignite windrow (53.7 g kg⁻¹ DM), with N₂O being the dominant GHG source in both windrows (Table 2). In the lignite windrow, 76.7% of the total GHG emissions were as N₂O, including 8.2% from re-emitted NH₃, followed by 23.3% from CH₄. In the non-lignite windrow, 45.7% of the total GHG emissions was attributed to re-emitted NH₃ emissions, and there was no contribution from CH₄ emissions over the study period.

The environmental cost of increased GHG emissions can be estimated by applying the C price that is used for emission trading and C-taxes in emission policy reduction schemes as implemented in several countries (\$tonne⁻¹ CO₂-e). Carbon prices vary between countries and over time. Currently, the C price in Sweden is the highest in the world at \$139 US tonne⁻¹ CO₂-e. Australia applied a C price in 2012 of \$23 AUD tonne⁻¹ CO₂-e that increased to \$24.15 AUD tonne⁻¹ CO₂-e in 2013–2014 for power plants and industries (although road transport and agricultural emissions were exempted) (AGCER, 2012). Australia revoked C taxation in July 2014, however, the C price scheme may be resumed in the future, and the C price may be increased. We estimated the cost for the GHG emissions from windrow composting process, using the 2013–2014 Australian price of \$24.15 AUD tonne⁻¹ CO₂-e, at approximately \$4.0 and \$2.0 AUD tonne⁻¹ DM for lignite and non-lignite windrow, respectively. Following Sun et al. (2016), we also calculated the cost of transporting lignite (16.2 tonnes) to the feedlot to be \$1.8 AUD tonne⁻¹ DM, while generating 489.24 kg CO₂ from fossil fuel use. The economic benefit of retaining N in the windrow manure was estimated to be \$4.0 AUD tonne⁻¹ DM (given the N fertilizer price of \$1.37 AUD kg⁻¹ N). Furthermore, we considered the benefits of adding lignite to reduce NH₃ emissions from the cattle pen surface. Although this study did not measure the gas emissions over the period when cattle were kept in the pen, our previous feedlot studies reported that daily NH₃ emissions from cattle pen manure (without lignite addition) were 116 g animal⁻¹ day⁻¹ (Bai et al., 2015), and adding lignite to cattle pen surface reduced NH₃ emissions by 66% (Chen et al., 2015), i.e., the emissions would be 39.4 g animal⁻¹ day⁻¹. We applied those published data to this study and estimated the reduction of NH₃ emissions from the pen surface by adding lignite over the period when cattle were kept in the pen to be 29.8 g kg⁻¹ DM. Therefore, the benefit of retaining N in cattle pen manure was \$34.0 AUD tonne⁻¹ DM, which would result in the total economic benefit of reducing NH₃ losses by applying lignite in this study of \$38.0 AUD tonne⁻¹ DM.

To estimate the total marginal damage cost of NH₃ to human health and ecosystems (i.e., eutrophication, biodiversity), the European damage cost of NH₃ was estimated at €10–30 kg⁻¹ NH₃-N (van Grinsven et al., 2013, 2018). Using these European unit costs, the reduction of NH₃ emissions by lignite addition of 3.9 g kg⁻¹ DM from composting, and 29.8 g kg⁻¹ DM from pen manure would represent an environmental benefit of \$440.0–1,310.0 AUD tonne⁻¹ DM, which would outweigh the environmental cost of increased GHG emission. However, European unit damage costs for effects of NH₃ on human health and ecosystems may not be applicable for Australia. In view of much higher livestock and population densities, the marginal N damage costs in Europe will be higher than in Australia. For example, dose-response-relationships (number of additional premature deaths per kg of additional NH₃ emission) will be different because of different spatial relationships between emissions sources and human receptors, as well as different atmospheric chemistry (van Grinsven et al., 2018).

Emissions of NH₃ and GHG from feedlots pose significant challenges in the evaluation of societal impacts of the beef production chain, especially when considering the strategic role of feedlots in the domestic and international beef markets. Since effective mitigation methods at one stage of the process must be considered for the following stages (Sommer et al., 2009), a whole farm system approach is needed. Although our simple cost benefit analysis indicated beneficial aspects of lignite additions to feedlot pens due to reduced N losses, the agronomic and downstream environmental impacts following the application of

lignite amended manure to cropland will require further study. In addition, possible negative impacts of mitigation strategies on other industry's employment due to the competitive consequence of 'knowledge spillover' (Aldieri and Vinci, 2017, 2018) will require further analyses by economists and policy makers.

4. Summary

We compared the impact of lignite addition on gaseous emissions during the composting of cattle manure. Adding lignite reduced N losses by 54% over the 87-day composting process, but increased CH₄ and N₂O emissions (due to anaerobic conditions), as well as CO₂ emissions (due to additions of labile C). Total GHG emissions (CO₂-e) (N₂O and CH₄ and NH₃ as indirect N₂O) from the lignite amended manure was 2.6 times greater than that of the non-lignite treatment.

While adding lignite to the feedlot pen did reduce N losses during the 87-day composting process, the effectiveness of retaining N was not obvious beyond three weeks after the windrow formation. This suggests a need to optimize the duration of windrow composting or improve the N absorption capacity of lignite. More importantly, our analyses indicate that the environmental benefit of reducing NH₃ emissions by adding lignite could outweigh the environmental cost of increasing the GHG emissions. Our study indicates that a manure management strategy that includes lignite amended windrow composting could be a viable option for feedlots to mitigate emissions of NH₃.

Declaration of competing interest

The authors declare no conflict of interest.

CRediT authorship contribution statement

Mei Bai: Conceptualization, Data curation, Methodology, Formal analysis, Writing - original draft, Writing - review & editing. **Robert Impraim:** Conceptualization, Data curation, Methodology, Formal analysis, Writing - review & editing. **Trevor Coates:** Conceptualization, Data curation. **Thomas Flesch:** Conceptualization, Methodology, Formal analysis, Writing - original draft, Writing - review & editing. **Raphaël Trouvé:** Formal analysis, Writing - original draft, Writing - review & editing. **Hans van Grinsven:** Conceptualization, Formal analysis, Writing - original draft, Writing - review & editing. **Yun Cao:** Formal analysis, Writing - review & editing. **Julian Hill:** Conceptualization, Funding acquisition, Project administration, Writing - review & editing. **Deli Chen:** Conceptualization, Methodology, Formal analysis, Funding acquisition, Investigation, Project administration, Supervision, Writing - review & editing.

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