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Measurement and Control of Odorous and Polluting Gases from Wastes

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Manoharan Kulasegarampillai

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Abstract

Management of odorous and polluting gases from wastes is a world-wide challenge. Gaseous losses of nitrogen and sulphur from stored manure and sewage biosolids can be considerable, and these gaseous are offensive and undesirable. Hence, it is necessary to quantify these gas emissions from waste to determine the impact on air quality as well as to find out the efficient and effective control measures.

A field observation indicated that amendment of dairy manure with natural materials, such as soil and wood shavings can reduce gaseous emission. To understand the mechanism for reduction of gaseous emissions and to select an optimum natural medium, laboratory incubation studies were conducted to measure the gaseous loss of ammonia (NH_3) and hydrogen sulfide (H_2S) from stored manure and biosolids under aerobic and anaerobic conditions for a period of about 7 weeks. Natural materials such as soil, untreated pine bark, sawdust and wood savings, were evaluated for their potential to reduce these gaseous emissions.

Ammonia emission rate was typically peak within two days of the experiment and declined rapidly under aerobic and anaerobic condition from stored manure and sewage biosolids. NH_3 emission was higher during aerobic than anaerobic incubation but in the case of biosolids the difference was very small. The total nitrogen loss due to NH_3 emission was very low. It was around 1.23% from manure and 1.87% from biosolids under aerobic incubation. Around 49 mg NH_3 was emitted from a kg of cattle manure during aerobic incubation and it was 1155 mg from biosolids.

H_2S emissions were higher during anaerobic than aerobic incubation from manure and biosolids. Around 9.2 mg H_2S was emitted from a kg of manure and it was around 150.7 mg from biosolids under anaerobic incubation.

All materials tested were found to have an effect on the NH_3 and H_2S emission. However, pine bark and top soil amendment reduced the emission efficiently. NH_3 emission was reduced by 78% under anaerobic condition when 20g bark was amended

with 100g manure and it was around 56% in biosolids. Soil amendment reduced the NH_3 emission by 50% in manure and 46% in biosolids.

Pine bark reduced the H_2S emission by 80% from manure and by 83.5% from biosolids. Top soil amendment reduced the H_2S emission by 50% from manure and 79% from biosolids.

Therefore, the addition of natural materials, such as pine bark and soil, as amendments to manure and biosolids during storage offers potential for reducing emissions of NH_3 and H_2S .

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Chapter 1 Introduction

1.1 The issue

Emission of odorous and polluting gases from wastes is a world-wide problem as it causes nuisance to public and impacts air quality. The gaseous emissions from wastes can also cause environmental health problems (e.g., ammonia and hydrogen sulphide) and also are implicated in global warming (e.g., methane) and the depletion of the stratosphere ozone layer (e.g., nitrous oxide).

In New Zealand, large quantities of wastes are produced from the agricultural industries (e.g., dairy shed waste) and sewage treatment plants (e.g., biosolids) each year. New Zealand's 4.5 million dairy cows and 4.7 millions beef cattle (Statistics New Zealand, 2002) excrete about 130 million kg of dung and 92 million litres of urine. New Zealand's agriculture is dominated by pastoral livestock systems, and pastures are generally grazed year-round. The return of N to the soil in the form of extremely concentrated animal dung and urine patches can lead to losses of N through nitrate leaching and gaseous emissions (Haynes and Williams, 1993; Luo *et al.*, 1999; Bolan *et al.*, 2004a), thereby causing environmental degradation and reduction in N use efficiency (Ledgard *et al.*, 2003). Nitrogen leaching and gaseous emissions from animal excreta are likely to be highest during wet winter period compared to those in other seasons (Luo *et al.*, 2000; de Klein *et al.*, 2001). To reduce this problem improved winter management practices, including the use of stand-off pads have been introduced. Under this system excreta are collected, stored and returned to pasture as manure. It is likely that excreta would be stored for extended periods prior to field application. During storage, the turnover of organics and nutrients may change the excreta composition significantly, and the loss of dry matter, due to conversion of C, N and S compounds into gaseous forms, may be considerable (de Klein and Ledgard, 2001).

Biosolids is a nutrient rich organic material resulting from the treatment of sewage sludge. Biosolids production has increased in recent years. New Zealand currently produces around 77,000 dry tonnes per annum (NZWWA, 2003) and this amount will be increased by at least another 10,000 tonnes in 2011 (Speir *et al.*, 2003).

Therefore, intensive animal operations, including dairies and cattle stand-off pads, and sewage waste management systems are likely to produce emissions of odorous gases, such as NH_3 , H_2S , volatile organic compounds (VOCs), and “greenhouse” gases including nitrous oxides, carbon dioxide and methane. Studies of these emissions are important, not only to assess the degree of odour nuisance, but also because some components are known to have detrimental effects on animals and humans.

1.2 Odour release and measurement

The human olfactory sense organ is highly sensitive and capable of distinguishing about 10,000 different odours, some at extremely low concentrations (Amore *et al.*, 1964). Odour is perceived by our brains in response to chemicals present in the air we breathe. Humans have a sensitive sense of smell and can detect odour even when chemicals are present in very low concentrations. Most odours are a mixture of many chemicals that interact to produce what we detect as an odour (Stuetz *et al.*, 2001).

When chemical contaminants discharged to air from either natural or man-made sources are detected by the olfactory senses then the individual is said to have perceived an odour. Because the olfactory nerve cells are directly connected to the brain, an exposed individual can often have a strong and immediate response.

The lowest concentration of a substance that can be detected by 50% of the population is termed its odour threshold (Bernd and Koster, 1998). This is not an absolute value but is statistically calculated from a sample of individual responses. Published odour thresholds vary due to differing measurement techniques and improvements in measurement technology. Threshold values of some common odorous substances are given in Table 1.1.

When the odour level exceeds the threshold level, nuisance is said to be occurring. Agricultural and industrial processes involving organic materials can be responsible for many odour complaints. Historically, activities likely to cause nuisance odour have been situated away from populated areas. However, urban spread means that previously isolated activities gain access to neighbours whose quality of life can be affected by unpleasant odour. Therefore, many agricultural and waste treatment industries face the challenge of odour management.

Table 1.1 Odour threshold and quality of some common odorous substances (Haug, 1980).

Compound	Threshold ($\mu\text{g l}^{-1}$)	Quality
Acetaldehyde	4	Pungent, fruity
Allyl mercaptan	0.05	Strong garlic, coffee
Ammonia	37	Sharp, pungent
Crotyl mercaptan	0.029	Skunk like
Dibutylamine	16	Fishy
Dimethyl sulphide	1	Decaying vegetables
Hydrogen sulphide	0.47	Rotten eggs
Skatole	1.2	Faecal

Clean air is an important part of a healthy, sustainable environment. It is also protecting people from offensive smells that can affect their daily activities and well being. New Zealand will continue its initiative in protecting its environment from the harmful effects of contaminants including air pollutants and will place increasing importance on whole ecosystem biological criteria to maintain bio diversity. So minimisation of odour emission from sewage treatment works and the agricultural industry, thereby protecting the air quality is one of the most significant challenges for New Zealand in future.

Gaseous emission processes from wastes and the factors affecting such emissions have not been fully studied. Understanding the gas emission processes and quantification are necessary to develop best management practices (BMP) and techniques to reduce such emissions as well as evaluating the efficiency of abatement technologies. General approaches to estimate the strength or intensity of odours include:

- a. Sensory methods that involve collecting and presenting odour samples to human panelists (diluted or undiluted) under controlled conditions, e.g., dynamic olfactometers.
- b. Measurement of concentrations of specific odorous gases (directly or indirectly).

1.3 Odour management and control

New Zealand regulations on discharges to air were covered by the Clean Air Act, 1972. The second schedule of this act defined activities that required 'Clean Air Licences'. These licences were based on 'best practicable means' of control and administered by

the Department of Health. Municipal waste treatment processes did not require a license under this act (MfE, 1995).

The Resource Management Act (RMA) introduced in 1991, established a set of principles and guidelines for issuing resource consents for any activity, which were based on the effect of the activity on the environment. Regional authorities are responsible for administering the RMA and produce a 'Regional Air Plan'. According to RMA (1991) contaminants include any substance or energy or heat that either by itself or in combination with the same, similar or other substance or energy or heat when discharged onto to into land or into air, changes or likely to change the physical, chemical or biological constitution of the land or air onto or into which it is discharged. While the RMA provided temporary relief (control) for existing discharges, municipal waste treatment plants also have a duty to 'avoid, remedy or mitigate adverse effects' (MfE, 1995).

Some odour can be reduced by optimising control of reticulation and treatment processes and good treatment design, but technologies are required to effectively control odour emissions. Amendments of natural materials have become a popular method for treating odours because they are relatively inexpensive, and do not involve handling hazardous chemicals. Odorous compounds such as H_2S , mercaptans and NH_3 are adsorbed to the medium and then oxidised biologically to harmless compounds such as carbon dioxide, water, mineral salts and biomass. Common media used as amendments include soil, sand, peat, compost, bark, activated charcoal and combinations of these (Luo *et al.*, 2004).

1.4 Research objectives

The overall objective of the study is to quantify the gaseous emissions of NH_3 and H_2S from organic by-products and examine the potential value of natural materials in mitigating gaseous emissions. The specific objectives of this study include:

- Carry out a field study using natural materials to observe the ability to control gas emission from a cattle manure bunker.
- Determine the NH_3 and H_2S emission from biosolids and cattle manure.
- Understand the process for gaseous emission and aeration affect on gaseous emissions from biosolids and cattle manure.

- Evaluate the effect of amendment of biosolids or cattle manure with natural materials on the NH_3 and H_2S emissions.

1.5 Thesis layout

This thesis consists of six chapters. In Chapter 1, the environmental and health issues relating to gaseous emissions from organic wastes such as manures and biosolids are discussed. In Chapter 2, the literature relating to odour, its environmental effect and treatment is reviewed, with particular emphasis on measurement techniques and control measures. A field observation study was conducted to monitor gaseous emissions from manure bunkers, which indicated that the amendment of dairy manure with natural materials, such as soil and wood shavings can reduce gaseous emissions. The results from this study are described in Chapter 3. To understand the mechanism for the reduction of gaseous emissions and to select an optimum natural medium, laboratory incubation experiments were conducted to measure gaseous loss of NH_3 and H_2S from stored manure and biosolids under aerobic and anaerobic conditions. The suitability of natural materials such as soil, untreated pine bark, sawdust and wood shavings for treating NH_3 and H_2S were investigated in this study. Chapter 4 describes the materials and methods used in this laboratory investigation. In Chapter 5, the results of these investigations are presented and discussed. Chapter 6 gives the major conclusions from this study and the future research directions.

Chapter 2 Literature review

2.1 Cattle manure and biosolids

2.1.1 Production and disposal of cattle manure and biosolids

New Zealand's agriculture is dominated by pastoral livestock systems, and pastures are generally grazed year-round. Most of the previous research on nitrogen cycling in grazed pastures demonstrated the importance of the grazing animal in returning nitrogen (N) ingested in the herbage to the soil in the forms of urine and dung (reviewed by Ball and Tillman, 1994). However, the return of N to the soil in the form of extremely concentrated animal dung and urine patches can lead to N losses through nitrate leaching and gaseous emissions (Haynes and Williams, 1993; Luo *et al.*, 1999; Bolan *et al.*, 2004a), thereby reducing the N use efficiency (Ledgard *et al.*, 2003). Nitrogen leaching and gaseous emissions from animal excreta are likely to be highest during the wet winter period (Luo *et al.*, 2000; de Klein *et al.*, 2001). An improved winter management practice, involving the use of stand-off pads is likely to reduce the amount of excretal deposition directly on to pasture soil during the wet winter season, thereby mitigating the environmental effects of N leaching and gaseous emissions (de Klein and Ledgard, 2001; Ledgard *et al.*, 2003), as the excreta are collected, stored and re-utilized as manure. Excreta could be stored for extended periods prior to field application.

Biosolids are nutrient rich organic materials resulting from the treatment of sewage sludge that meet specific quality criteria, and which can be recycled for agricultural use as a nutrient source, land reclamation and composting. They are chemically and biologically complex materials consisting of processed biomass, nutrients and contaminants produced during wastewater treatment. Wastewater residuals contain substantial amounts of plant nutrients and traces of heavy metals. Table.2.1 shows the characteristics of biosolids samples from several New Zealand sewage treatment plants.

Table.2.1 Physical and chemical characteristics of biosolids in dry weight basis
(Longhurst *et al.*, 2003).

Source	Moisture (%)	Total N (%)	NH ₄ -N (%)	Carbon (%)	Copper (mg kg ⁻¹)	Zinc (mg kg ⁻¹)
North Shore	82.9	6.2	0.74	41.9	640	850
Hamilton	74.1	4.8	0.60	43.4	420	550
Taupo	80.2	5.1	0.31	40.8	460	780

Biosolids production has increased in recent years. New Zealand currently produces around 77,000 dry tonnes per annum (NZWWA, 2003) and this amount will increase by at least another 10000 tonnes in 2011 when the Auckland plant is fully commissioned (Speir *et al.*, 2003).

Traditionally, most biosolids are disposed of by land-filling. It is not a good option as it leads to odour, pest attraction, ground water contamination from leachates and green house gas production. Biosolids disposal into the sea and other water bodies is no longer environmentally acceptable (Edwards and Burdon, 2003). Polluted gas emissions from biosolids cause environmental health problems and are also implicated in global warming and the depletion of the stratosphere ozone layer. Odours are offensive and sometimes unhealthy. RMA (1991) requires discharges of contaminants into air including odours to be controlled. Hence, municipal waste treatment plants also have a duty to ‘avoid, remedy or mitigate adverse effects’ (MfE, 1995).

Nowadays society has gradually been moving from non-sustainable “disposal” to a “beneficial use” philosophy. Beneficial use of >95% of all biosolids produced by 2007 is a target of “The New Zealand Waste Strategy” (MfE, 2002). Hence alternative methods of disposal are constantly being sought, and one becoming more popular is land application. Recycling biosolids back to the land to improve soil structure and fertility stands to be a far more sustainable beneficial use than any other management alternatives currently available. However, odour emission could be one of the main limiting factors for the land application of biosolids.

2.1.2 Odour emission from cattle manure and biosolids

Cattle manure is stored and often applied at high rates near intensive livestock operations. Because of this stored and land-applied manure, the area surrounding feedlots may be affected by offensive odours. Odours from livestock slurry are due to a complex mixture of volatile compounds arising from anaerobic degradation of plant fibre and protein (Hammond *et al.*, 1989). During storage, the turnover of organics and nutrients may change the excreta composition significantly, and the loss of dry matter, due to conversion of C, N and S compounds into gaseous forms, may be considerable (de Klein and Ledgard, 2001). The most environmentally significant odorous compounds emitted from livestock manure include H_2S and NH_3 , either because of their high concentrations and/or their low odour thresholds (O'Neill and Phillips, 1992). Depending on the storage conditions, up to 50% of the N in freshly excreted manure can be lost through NH_3 volatilisation to the atmosphere (Bussink and Oenema, 1998; Phillips *et al.*, 1999).

Ammonia is released from the natural decomposition of organic material including manure as well as dead animals and plants. Livestock operations are prominent sources of atmospheric NH_3 (Isermann, 1994). Typically, livestock use less than 30% of N contained in their feed, with 50% to 80% of the remainder excreted in urine and 20% to 50% excreted in the faeces (McCrory and Hobbs, 2001). Storage of livestock slurry has been recognised as a major source of NH_3 emission (Hartung and Phillips, 1994) with reported N losses ranging from 3% to 60% of initial total N (Dewes *et al.*, 1990). The majority of the N intake is excreted in the urine, normally in the range 8-15 g N L^{-1} (Whitehead, 1970). Urea is the major nitrogenous compound in urine, accounting for up to 97% of urinary N. Among other nutrients, N is present in manure in inorganic and organic forms. The inorganic N is largely present as ammonium ions and can be lost to the atmosphere as NH_3 gas.

Sewage biosolids contain an abundant source of food for micro-organisms including fats, proteins and carbohydrates. These organic compounds are degraded by the micro-organisms, and odorous compounds are formed, mostly under anaerobic conditions (Walker, 1991; Higgins *et al.*, 2002; Novak *et al.*, 2002). It is generally believed that fermentation is one of the major processes responsible for the formation of odorous compounds in biosolids (Vincent, 2001). Odours can be produced during biosolids

thickening, digestion, dewatering, transport, storage, truck loading, air drying, composting, heat drying, alkaline stabilization, and/or incineration (Bonnin *et al.*, 1990).

In biosolids, depletion of dissolved oxygen occurs very rapidly because of large number of micro-organisms and the high levels of C substrate. Under increasing anaerobic conditions, fermentation of fats, proteins and carbohydrates leads to the production of volatile fatty acids, alcohols, aldehydes, ketones, NH_3 , amines, mercaptan, dimethyl sulphides, methyl disulphide and H_2S . Most of these compounds are volatile and odorous, and have been identified in the air emissions during biosolids treatment, storage, and reuse processes (e.g., Banwart and Bremner, 1976; Rosenfeld and Henry, 2000).

2.1.3 Odorous compounds from cattle manure and biosolids

There are many odour compounds identified from cattle manure by various researchers. These emissions are the result of microbiological, physical and chemical processes and influenced by a multitude of different factors. Peters and Blackwood (1977) listed 31 odorants identified at cattle feedlots. Chemical analysis has identified approximately 170 volatile compounds (O'Neill and Phillips, 1992). Some odorous compounds emitted from cattle manure are given in Table 2.2.

Table 2.2 Selected references on odorous compounds in cattle manure.

Odorous compounds	References
Ammonia and amines	Hutchinson <i>et al.</i> , 1982; Peters and Blackwood, 1977.
Hydrogen sulphide, methane, organic acids, aldehydes, ketones, volatile fatty acids, alcohols, mercaptans and organic sulphides	Miner, 1975b; Barth <i>et al.</i> , 1984.
Methane	Safley <i>et al.</i> , 1992.

Karlsson and Jeppsson (1995) found that storage of deep litter manure from beef cattle leads to N losses mainly caused by NH_3 volatilisation. The losses were 19-34 % of total N content. Most of the losses occurred during the first weeks of storage.

Table.2.3 Selected references on odorous compounds in biosolids.

Biosolids source	Odorous compounds detected	References
Anoka sludge (digested anaerobically)	dimethyl disulphide, carbon disulphide, Methyl mercaptan, dimethyl sulphide, carbonyl sulphide.	Banwart and Bremner, 1976
Hastings sludge (digested anaerobically)	dimethyl disulphide, carbon disulphide, Methyl mercaptan, dimethyl sulphide.	Banwart and Bremner, 1976
Orono sludge (digested aerobically)	dimethyl disulphide, carbon disulphide, Methyl mercaptan, dimethyl sulphide, carbonyl sulphide.	Banwart and Bremner, 1976
Metro sludge (waste activated but not digested)	dimethyl disulphide, dimethyl sulphide, Methyl mercaptan.	Banwart and Bremner, 1976
Biosolids (anaerobic digestion)	hydrogen sulphide.	Bonnin <i>et al.</i> , 1990
Biosolids (alkaline stabilization)	ammonia, trimethyl amine, methyl amine, ethyl amine, and diethyl amine.	Murthy <i>et al.</i> , 2002 Novak <i>et al.</i> , 2002
Biosolids (lime stabilized)	dimethyl disulphide and trimethyl amine.	Novak <i>et al.</i> , 2002

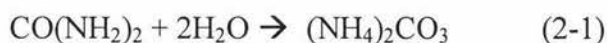
Many of the odorous compounds produced from sewage and biosolids have odour detection thresholds in micro gram per litre ($\mu\text{g}/\text{dm}^3$) concentration ranges (Ruth, 1986). Reduced S compounds, such as H_2S , can be detectable and perceived at greater distances from biosolids sources than NH_3 because they have very low odour detection

thresholds. Some examples of biosolids and their associated odorous compounds are given in Table 2.3.

The reduction of sulphates with the production of H_2S is the other important odour generating process in sewage and sewage biosolids (Hvitved-Jacobsen *et al.*, 2000). Biosolids contain high concentrations of N and S which cause NH_3 and H_2S emission to atmosphere. Both of these gases are odorous and polluting the atmosphere.

Ammonia emission process

Mackie *et al.* (1998) suggested that NH_3 may arise in livestock waste simply from urea hydrolysis, or it may be generated as a product of protein metabolism. Urea is hydrolysed by the enzyme urease, found in the faeces, to ammonium (NH_4^+) and bicarbonate ions [Eq. (2-1), (2-2) and (2-3)], thereby resulting in a high pH close to the site of hydrolysis. Urea hydrolysis occurs rapidly, with complete conversion of urea-N to NH_4^+ possible within a matter of hours, depending on environmental conditions (Muck and Richards, 1980).



Due to this urea hydrolysis, large amounts of NH_4^+ ions accumulate in the soil. High concentrations of NH_4^+ (500 to 1000 mg N kg^{-1}) have been observed in surface soils of urine patches soon after animal urination (Valis *et al.*, 1982).

Faecal N typically consists of 50% of protein and 50% NH_4^+ . Mineralization of faecal protein N mainly occurs through the activity of proteolytic and deaminative bacteria, initially hydrolysing proteins to peptides and amino acids and finally by deamination to NH_4^+ . This process occurs at a far slower rate than hydrolysis of urea and is thought to be a relatively unimportant source of NH_4^+ where livestock is stored for a short period of time (Muck and Steenhuis, 1982). However, where livestock slurry is stored for long periods, especially at higher temperatures it becomes the dominant pathway for NH_4^+ production (Patni and Jui, 1991). Deamination of amino acids is also a primary pathway

for NH_3 production. Lesser quantities of NH_3 may result from bacterially mediated inorganic transformations, including reduction of nitrate.

The conversion of NH_4^+ ions to NH_3 [Eq. (2-4)] and subsequent NH_3 volatilisation is the major process regulating the potential loss of NH_3 from soils. A supply of free NH_3 is necessary at the soil surface before NH_3 volatilisation will occur.



The equilibrium between NH_4^+ and NH_3 is affected by many factors, but generally the supply of NH_3 is favoured by high soil pH and high temperatures (Haynes and Sherlock, 1986).

The process of NH_3 volatilisation may be represented by the following equation (Freney *et al.*, 1981).



The driving force for NH_3 volatilisation is considered to be the difference in partial pressure between NH_3 in equilibrium with the liquid phase and that in the ambient atmosphere. In the absence of other ionic species, this is predominantly influenced by the NH_4^+ concentration, pH and temperature, although any displacement of the equilibrium will affect the NH_3 emission.

Ammonia emission from biosolids comes from the biological degradation of proteins and amino acids. Mineralization of protein N in the biosolids mainly occurs through the activity of proteolytic and deaminative bacteria initially hydrolysing proteins to peptides and amino acids and finally by deamination to NH_4^+ . Volatilisation of N from land applied biosolids reduces the amount of applied N that is available for plant uptake or leaching to ground water. Robinson and Polglase (2000) found that the majority of the NH_4^+ -N found in biosolids was lost within the first three weeks after application. Robinson and Roper (2003) determined that, despite climatic conditions apparently not suited to volatilisation, 44-55% of the NH_4^+ -N applied in biosolids was volatilised. The majority of the losses were within about one day of the application and 95% of the

losses occurred within five days. The rate of volatilisation is dependant on the surface area of the material. Therefore, at high application rates where biosolids are applied thickly there is a low rate of volatile loss due to less surface area available for volatilisation (Robinson and Polglase, 2000).

Hydrogen Sulphide (H_2S)

Hydrogen sulphide is a product of the degradation of protein by anaerobic micro-organisms. Cattle manure and biosolids contain proteins, amino acids and carbohydrates which are a plentiful energy source for bacteria such as clostridia, lactobacilli and streptococci which transfer oxygen from S compounds to a hydrogen acceptor under anaerobic conditions. Due to this reduction of S compounds and desulphurisation, H_2S can be formed and emitted to atmosphere. Acidic conditions enhance H_2S formation. Hydrogen sulphide is considered the most important odorous compound in wastewater treatment plants (Van Langenhove *et al.*, 1986).

Environmental effects of gas emission

Battye *et al.* (1994) reported that NH_3 in the atmosphere can have a significant effect on oxidation and deposition rates of acidic compounds. The net result to soil is an increase in acidity. Ammonia volatilisation causes not only the nuisance issue of odour, but also acid precipitation (Sutton *et al.*, 1999). Ammonia deposited to land can damage vegetation (van der Eerden, 1982; van der Eerden *et al.*, 1998) and reduce plant biodiversity in natural ecosystems (Sutton *et al.*, 1995).

Some of the gaseous compounds such as carbon dioxide, methane and nitrous oxide, emitted from cattle manure and biosolids to the atmosphere are deleterious to the ozone layer and are implicated in the greenhouse effect (Clements and Ahlgrimm, 2001). These compounds may also pose environmental and health hazards due to their odorous nature and possible toxicity at high concentrations (Busca and Pistarino, 2003).

2.1.4 Factors affecting odour emission from cattle manure and biosolids

Major factors affecting NH_3 volatilisation rates from manures include manure pH, N content of the manure, temperature, air removal rate, storage condition and air NH_3 concentration (McCrory and Hobbs, 2001). The loss from surface applied manure is influenced by soil pH, soil cation exchange capacity (CEC), soil organic matter content

and soil texture. When the pH changes from 6 to 7, 8 and 9, the relative concentration of NH_3 increases from 0.1% to 1%, 10% and 50% respectively (Freney *et al.*, 1983). Svensson (1991) found that storage of slurry leads to lower NH_3 losses compared with solid manure and amounts to about 10%. Karlsson (1996) measured losses that did not exceed 3% during winter from stored cattle and pig slurry.

Several factors affect biochemical processes of odour production from biosolids, including temperature, pH value, redox potential, concentrations of substrate and nutrients, and the composition of the biosolids (Higgins *et al.*, 2002). Odour production could also be affected by the type of biosolids and the method of treatment processing. For example:

- Anaerobic digestion of biosolids mostly forms H_2S and other S-containing gases (Bonnin *et al.*, 1990).
- Alkaline stabilization of biosolids mostly produces NH_3 and other N-containing compounds, such as trimethyl amine, methyl amine, ethyl amine, and diethyl amine (Murthy *et al.*, 2002; Novak *et al.*, 2002). As the pH of the biosolids increases, more NH_3 is released.
- Autothermal thermophilic aerobic digestion of biosolids mostly produces NH_3 , dimethyl sulphide, dimethyl trisulphide and numerous mixed alkanes (Hepner *et al.*, 2002).
- Addition of dewatering cationic polymers for conditioning of digested biosolids results in a higher production of S compounds (Novak *et al.*, 2002).
- The volatile fatty acids are most likely to be involved in odorous emissions when vegetative matter is present in biosolids (Hepner *et al.*, 2002).
- Hydrogen sulphide was not found to volatilise following biosolids application to soil in aerobic conditions (Banwart and Bremner, 1976; Rosenfeld and Henry, 2000), as the reduced S compounds, like H_2S , is not stable in an aerobic environment and often oxidize to dimethyl disulphide in land applied biosolids. Banwart and Bremner (1975) found that dimethyl disulphide accounted for 55% to 98% of total S evolved from biosolids applied to soil in aerobic conditions.

- Ammonia volatilisation could be a significant N emission pathway from land-applied biosolids, and the emission depends on the type of biosolids and application technique (Quemada *et al.*, 1998; Robinson and Polglase, 2000).

Storage of sewage biosolids also changes odour character (Lambert *et al.*, 2000; Winter and Duckham, 2000; Higgins *et al.*, 2002). Lambert *et al.* (2000) found that the odour of 240 day old dewatered biosolids cake was substantially more putrescent in character and more unpleasant than odours of other biosolids that had been stored for a shorter term. It is suggested that the formation of anaerobic conditions within a biologically unstable sludge may be responsible for the odours arising from the long-term storage of biosolids (Lambert *et al.*, 2000).

Odorous compounds have an impact on the environment only when they are released to the atmosphere. Factors affecting the release of odours to the atmosphere include the solubility of the odorous gases, the concentration of the odorous compounds in the gas and liquid phases, the mass-transfer coefficients, temperature, pH value and surrounding wind conditions (Vincent, 2001). A large amounts of volatile NH_3 losses have been demonstrated from biosolids with a pH of just 7.1 (>25%, Stewart *et al.*, 1975) and 7.2 (>45%, Ryan *et al.*, 1973).

2.1.5 Odour prevention and control

There are many technologies available to control odorous emissions from manure and biosolids. Following two basic approaches are involved in these technologies:

- Capture and treatment of emitted gases
- Manure or biosolids treatment

Capture and treatment of emitted gases

The odorous component can be captured or treated to reduce its effect in many ways. The choice depends on the nature of the contaminants to be removed, available space, degree of treatment required and economic considerations (Devinny *et al.*, 1999). Biofiltration is one of the most popular odour treatment techniques.

Biofiltration

A biofilter system consists of a gas distribution system and a biologically active filter medium, through which odorous gases pass and odours are removed. Biofiltration is most suitable for treating large quantities of air with low contaminant concentrations. Within the past decade, there has been increased use of odour-control biofilter technology due to potentially lower capital and operating costs (Goldstein and Steuteville, 1995; Luo and van Oostrom, 1999).

Two basic odour removal mechanisms are believed to occur simultaneously in a biofilter: adsorption/absorption and biooxidation (Williams and Miller, 1992). As the gas stream passes through the biofilter medium, odorous compounds are adsorbed onto the surface of the medium particles and/or are absorbed into the moisture film surrounding the particles. Most gaseous compounds sorbed in the biofilter are then removed biologically by micro-organisms, which use them for C and energy sources. These micro-organisms are present in a slime or bio-layer on the surface of medium particles (Ottengraf and van den Oever, 1983), and it is here that the biodegradable organic and inorganic compounds are oxidised. It is believed that this biooxidation continuously regenerates the biofilter's ability to sorb and remove more odorous compounds.

Manure treatment

Manure treatment methods for odour control include maintaining aerobic conditions during storage, aerobic treatment (aerated lagoons or composting), anaerobic digestion or biochemical treatment and suitable amendments.

Amendments to control gas emissions

An amendment can be defined as a substance that is applied to a waste with the intention of alleviating the odour emissions. Numerous types of amendments have been investigated over the last three decades including bacterial-enzymatic preparations, plant extracts, oxidizing agents, disinfectants, urease inhibitors, masking agents and adsorbents. However, the effectiveness of additives, particularly commercially available products, has been the major subject of debate (Pain *et al.*, 1987; Ritter, 1989; Zhu *et al.*, 1997a).

Digestive amendments (in the digestive tract or with the manure)

These additives consist of selected microbial strains and/or enzymes that enhance the biodegradation of livestock waste. It can be assumed these additives enhance the degradation of odours volatile compounds or reduce their production. A review in this area has attempted to identify many of the bacteria and the pathways that produce odours, and identified *Eubacterium* and *Clostridium* as the most important genera for odour production (Zhu and Jacobson, 1999).

Disinfectants

Disinfecting additives are indiscriminate in their mode of action, reducing the formation of odorants by attempting to eliminate all microbial mediated processes occurring in livestock slurry. Chlorine was effective in reducing odours but expensive (Warburton *et al.*, 1980). These chemicals are often toxic therefore impractical as well as uneconomic.

Oxidizing agent

Oxidizing agents decrease odorant concentration in livestock slurry and also disinfect to inhibit the formation of odorants by micro-organisms. The most widely investigated oxidising agents are potassium permanganate, hydrogen peroxide and ozone (McCrory and Hobbs, 2001). Ulrich and Ford (1975) reported potassium permanganate to be the most economical and in completely suppressing odour emission from a cattle feedlot. Due to their large volumes of organic matter, livestock wastes require large quantities of reagents for complete oxidation.

Acidifying additives

The pH of the livestock slurry controls the equilibrium between NH_3 and NH_4^+ in solution. Molloy and Tunney (1983) found that NH_3 volatilisation effectively stopped at pH 4.0 for cattle slurry. Various acids have been proven to be consistently effective such as sulphuric (Pain *et al.*, 1990), nitric (Kroodsma and Ogink, 1997), phosphoric (Safley *et al.*, 1983) and lactic acid (Berg and Hornig, 1997). Sulphuric, hydrochloric and nitric acids are cheaper but are hazardous to use and corrosive. Subair (1995) used several different sucrose concentrations to reduce the pH of livestock slurry. For example, 11% sucrose solution reduced the slurry pH to 3.5 and NH_3 volatilisation by 98%. Although this type of additive is uneconomical, it would offer an effective and safe means to prevent NH_3 volatilisation.

Adsorbents

Reduction of malodour emanating from livestock slurry and manure has been claimed for products containing the alumino silicate mineral group, zeolites and the clay minerals bentonite. Their adsorptive capacities are very high (Pain *et al.*, 1987), but limited success has been reported in the literature. Mumpton and Fishman (1977) reported several instances where zeolites have been used to control odours from both poultry and pig manure. Miner and Stroh (1976) found zeolites ineffective in reducing odour intensity from a cattle feedlot. Generally, application directly to the waste appears to be more effective in reducing NH_3 emissions. It is non hazardous and act as a good soil conditioner when spread with slurry.

Urease inhibitors

Additives that inhibit the urease enzyme have been developed in order to reduce NH_3 emission from soils after the application of urea fertilizers (Pain *et al.*, 1987). Since the majority of NH_4^+ in livestock slurry originates from urea hydrolysis (Patini and Jui, 1991), Varel *et al.* (1997) investigated the urease inhibitors phenyl phosphorodiamide (PPD), cyclohexylphosphoric triamide (CHPT), and N-(n-butyl)thiophosphoric triamide (NBPT) in reducing NH_3 emissions from cattle feedlot slurry. All were very effective but required frequent applications. NBPT is marketed in the United States in admixture with urea under the trade name of Agrotain (Bolan *et al.*, 2003). Urease inhibitors are expensive and too easily broken down or inactivated.

Reduction of gaseous emissions from livestock manure has been shown to be possible, particularly with acidifying and adsorbent additives, and the potential exists to develop practical and cost-effective control technologies. For example, incorporation of bedding materials with manure has been proposed for reducing gaseous emissions (Mahimairaja *et al.*, 1994). The bedding materials could include C-rich materials such as straw, sawdust, woodchips and tree bark (Kirchmann and Witter, 1989) and adsorbents with a large surface area such as zeolite and soil (Mahimairaja *et al.*, 1994). Gaseous losses can be reduced possibly due to immobilization of the mineralized N and S from the manure by these C-rich materials or absorption of gaseous compounds of N and S by zeolite, tree bark or soil particle surfaces.

Biosolids treatment during processing

There are a number of methods available for prevention of odorous emissions from biosolids during processing. These include biofilters, bioscrubbers, biotrickling filters, activated sludge basins, activated carbons, wet chemical scrubbers and thermal oxidizers (Bowker, 1999; van Langenhove and de Heyder, 2001). Using amendments also proves to be an effective means to control odorous emissions. For example, using lime during processing prevents the release of H_2S and other odorous gases by controlling the pH (Horan and Catala, 1998), or using iron salts, which prevent the production of H_2S through precipitation and the volatilisation of NH_3 through transformation of NH_3 into nitrate (Allan, 1996).

Other technologies available are oxidation (using oxygen, nitrate, peroxide, potassium permanganate or ozone), bacteriological dosing, nutrient dosing, odour neutralisation and dispersion of residual odours (Williams, 1995; Einarsen *et al.*, 2000; Lambert and McGrath, 2000; Vella, 2002) or minimizing the time of storage of biosolids under anaerobic conditions (Vincent, 2001).

Land application

Physical, chemical and biological processes are often employed to improve the biosolids handling characteristics and increase the economic viability of land application. Some of these processes could reduce potential odour nuisance problems associated with land application practices. For examples, biosolids stabilization before land application can reduce the biological activity for generating odours either by decreasing the level of volatile organic compounds and the availability of nutrients in the biosolids, or changing the physical and chemical characteristics of the biosolids in a way that inhibits microbial growth. The success of odour reduction depends on the degree of stabilization achieved in the biosolids before it leaves the treatment facility and the preservation of stability until used. There are several methods to stabilize biosolids, including:

- Alkaline stabilization. Alkaline stabilization through the addition of alkaline (e.g., lime) to biosolids raises pH and temporarily decreases biological activity, so production of odours, particularly H_2S , can be controlled. However, raising

the pH will induce the emission of NH_3 and amines, especially at the time of treatment (Murthy *et al.*, 2002; Novak *et al.*, 2002).

- Aerobic digestion. Aerobic digestion reduces the biodegradable content of biosolids by conversion to soluble material, and therefore reduces the potential for formation of volatile organic compounds (Hepner *et al.*, 2002).
- Compositing. Composting stabilizes biosolids and reduces the biodegradable content and accordingly, lowers the odour production rate at land application sites (Titko *et al.*, 1996).
- Heat drying. Heat drying kills micro-organisms in biosolids and lowers biological activity for odour formation.
- Natural materials incorporation with biosolids. Natural materials such as soil, tree bark and wood ash reduce odour emissions from biosolids through adsorption or immobilization (Carpenter and Beecher, 1997; Rosenfeld and Henry, 2000).

Biosolids, even when properly treated, may still have odours. Odour production or nuisance effects can further be reduced by adequate biosolids storage, application method, and site selection (Evanylo, 1999).

Biosolids storage can occur at the sewage treatment plant, the site of land application, or a temporary facility. Storage at the treatment plant (if isolated from the public) is a preferred method. Off-site storage requires proper site selection and management to minimize the potential for odour problems. At storage sites, prevention of re-growth of microbes is a means of controlling odours. Microbial decomposition is likely to occur if the pH of lime stabilized biosolids drops, or deficient oxygen conditions occur within the biosolids, or the dried biosolids materials are re-wetted.

The selection of the land application site is important to the success of the operation. The site should ideally be located away from residential areas. Weather conditions (i.e., temperature, relative humidity, wind) will affect odour severity when biosolids are surface-applied. Immediate soil incorporation or direct soil injection of biosolids will reduce the potential for odour problems.

2.2 Odour measurement

Studies on odours includes identifying the origins, mechanisms, and parameters for odour production, odour treatment efficiencies, and measuring odour in the ambient air surrounding land application sites. All these studies need standard odour sampling and quantification methods. However, the science and technology for accurately collecting and analysing odour emissions are not fully established (Gostelow *et al.*, 2001). Various techniques are considered for the measurement of emissions from field trial plots, large-scale field experiments, manure stores, animal housing buildings and directly from the animals themselves. The choice of technique depends to a large extent on cost, level of accuracy required, and the scale and design of the experiments to be undertaken. The following sections give a brief outline of several current methods for odour sample collection and analysis.

2.2.1 Collection of odorous samples

The proper collection of an air sample containing odorous compounds is essential for accurate analysis of the source of the odour. At a waste application site and its surrounding neighbourhoods, ambient air would typically be the source for sample collection. Flux chambers have been developed for sampling odorous emissions, and odour samples can be collected in canisters, tedlar bags, and adsorbent tubes (Jiang and Kaye, 2001).

2.2.2 Measurement techniques

The two basic approaches often used to measure an odour involve either chemical technique using sensors to isolate and quantify the various chemical components of an odour, and/or statistical analysis of responses of human subjects sniffing the odour under controlled conditions. The latter technique is called olfactometry (NZWWA, 2000). Odour can be assessed by two criteria; strength which is measured as concentration or intensity and offensiveness. Based on olfactory measurements the problem of odour nuisance can be tackled by reducing either the perceived strength or offensiveness (O'Neill and Phillips, 1992).

2.2.3 Instrumental analysis.

Gas chromatography (GC)

This technique involves separating odorous air into its components by passing it through a column containing a porous substance with differing affinities for the different components. The air then passes through a detector which responds to the presence of the various components by producing peaks in its output, known as a chromatogram. Gas chromatography can be very sensitive. When used in conjunction with mass spectrometry it can help identify compounds present in a given sample. However, no information is obtained about the contribution, if any, of each compound to the overall odour.

After being separated in the column, the sample air stream can be split into two, with one part going to the conventional detector and the other part to a sniffing port (Veijanen *et al.*, 1983; Luo and Van Oostrom, 1999). The chromatogram peaks can then be correlated with a description of the odour detected at the sniffing port by a human subject. The analyst can then determine which of the many peaks on the chromatogram are contributing to the odour.

Mass spectrometer (MS)

A Mass spectrometer, often combined with a GC, is used to identify compounds by ionizing a compound and comparing (via computer) the resulting mass spectra to a database of known compounds.

Portable monitors

Several portable monitors are available for detecting toxic and odorous gases. This enables the user to measure gas concentrations in real time at the source of emissions. Most can be fitted with alternate sensors depending on the compound of interest. A common detector type uses photo-detection of a chemical colour change, which is proportional to the concentration of the compound. Another common type relies on changes in resistance caused by electrochemical reactions. The Jerome Analyser (Arizona Instruments) selectively adsorbs H_2S onto a gold film micro sensor. The gold sulphide formed causes an increase in sensor resistance proportional to the concentration of H_2S present. Measurement of H_2S *in situ* using either a gold film or a lead acetate tape type detector is easy and rapid, and sampling or pre-concentration are

not necessary (Gostelow *et al.*, 2001). Monitors that can measure down to odour threshold levels are expensive, typically tens of thousands of dollars.

Gas detection tubes

Contaminated air is drawn through these calibrated glass tubes filled with a chemical reagent. The chemical reagent changes colour and the length of the colour change along the tube are proportional to the concentration of the contaminant. These tubes are simple to use and relatively inexpensive but cannot measure low concentrations close to common odour threshold levels.

Electronic nose technology

Electronic nose systems are a relatively recent technology and could be used for measuring odours (Stuetz *et al.*, 1999). The nose is made up of an array of electrically conducting polymer or metal oxide sensors. Volatile odour compounds present in air samples that are passed over the sensor surface change the sensors' electrical resistance. Different sensors within the array react differently to the substance, yielding a variety of changes in resistance that a computer can quantify into an "odour map". This "odour map" is thought to be analogous to the human olfactory system. The potential future use of electronic nose systems should discriminate odours from various sources in the field and help determine the efficiency of odour treatment systems.

2.2.4 Olfactometry

Since the mid 1970s, olfactometry with human subjects has been used to assess environmental odours. Several techniques have been used including: odour test rooms where people enter a room where odorous gas has been released and determine whether they can detect the odour (Whisman *et al.*, 1978); sniffing of flasks (Smith and Hochstettler, 1969); and squeeze bottles containing odorous gas (Amore, 1992). An olfactometer with an odour panel is often used to conduct a sensory analysis of odorous air samples (Sneath, 2001).

The most commonly-used technique is dynamic dilution olfactometry. A sample of odorous air is taken back to a laboratory, diluted and presented to a panel of selected individuals through a sniffing port (NZWWA, 2000). The odour threshold is determined by presenting the panel with a range of dilutions covering the range from where all of

the panel are expected to be able to detect the odour to the level where none can. The dilution level where 50% of the panel can detect the odour is considered to be the odour threshold.

Dynamic dilution olfactometry can be either yes/no type or the forced-choice type. In the former, the panellist has one sniffing port and indicates if an odour is present. In the latter, the panellist has three ports, with one being assigned the odorous air. The panellist is forced to choose which port has the odour. The advantage of this method is that odour measurements are comparable between different experiments. It is generally accepted that the most sensitive method for assessing odour quality is olfactometry.

The disadvantages of olfactometry are that the method is time consuming, labour intensive, has to be carried out in a specially designed laboratory often remote from the sampling site, and on-line measurements are not possible.

2.3 Health effects due to odour

Odour emission is a nuisance to humans and animals and complains are increasing from the public in recent years (Goldstein, 2001; MfE, 2002). Schiffman *et al.* (2000) listed a number of symptoms related to adverse human health effects associated with odours from livestock manure. Hobbs *et al.* (1999) also reported that odours can cause respiratory stress in livestock.

Sulphurous odorants may present a health hazard whilst phenols and indoles are known to inhibit plant growth and cause respiratory stress in livestock (Hobbs *et al.*, 1999). Health complaints associated with odorous emissions from animal facilities include eye, nose, and throat irritation, headache, nausea, diarrhoea, hoarseness, sore throat, cough, chest tightness, nasal congestion, palpitations, shortness of breath, stress, drowsiness, alterations in mood, frustration, annoyance, depression, stress, tearfulness and reduced appetite (Schiffman *et al.*, 2000).

Symptoms are caused by known toxic effects of H_2S , NH_3 , or other emissions, on cellular biochemistry. For example, H_2S at elevated concentrations inhibits the enzyme cytochrome oxidase which is required for cellular respiration. It also has a multitude of

effects on most organ systems (Reiffenstein *et al.*, 1992). Potential health effects may be due to a single component in the emissions (e.g., H₂S) or to the combined load of the total emissions. As well as direct health related problems, odour emissions can affect “quality of life” (Brennan, 1993), which, in turn, can lead to indirect problems such as psychological stress (Wilson *et al.*, 1980).

2.3.1 Health effects of ammonia

The effects of NH₃, with increasing concentration, on humans are given in Table 2.4. At low concentrations, inhaled NH₃ dissolves in the mucous lining of the upper respiratory tract (WHO, 1986). Blood urea nitrogen (BUN) has been reported to be significantly elevated by an eight hour exposure to 20 mg/dm³ of NH₃ (Kustov, 1967). In the housed environment, NH₃ emissions can adversely affect the health, performance and welfare of both animals and human attendants (Donham, 1990; Donham and Gustafason, 1982).

Table 2.4 Health effects of ammonia (NH₃) at various concentrations.

Ammonia concentration (mg/dm ³)	Health effect	Reference
0.7 – 3.8	Odour detection threshold	WHO, 1986
25	Mild irritation to tissue	WHO, 1986
31 – 50	Dryness in the nose	WHO, 1986
140	Exposure is not tolerated	Verberk, 1977
400	Immediate throat irritation	WHO, 1986
500	Increased air intake into lungs	Silverman <i>et al.</i> , 1949

2.3.2 Health effects of hydrogen sulphide

The World Health Organization (WHO) recommends that H₂S concentrations not exceed 5 µg/dm³ for ½-hour to avoid health effects (WHO, 1987; Jaakkola *et al.*, 1990). The effects of H₂S, with increasing concentration, on humans are given in Table 2.5. The scientific literature on H₂S suggests that health symptoms can occur at H₂S concentrations far below the levels at which irritation or toxicity occur (Campagna *et al.*, 2000). Jaakkola *et al.* (1990) indicated that residents of both the severely (6 µg/dm³ H₂S) and moderately (1 µg/dm³ H₂S) polluted communities experienced more eye and nasal symptoms than unpolluted communities. Fatal cases of H₂S poisoning have

occurred during processing of manure which released 500 to 1000 mg/dm³ of H₂S (USEPA, 1992).

Table 2.5 Health effect of hydrogen sulphide (H₂S) at various concentrations.

H ₂ S concentration	Health effect	Reference
2 mg/dm ³	Headache and increased airway resistance	Jappinen <i>et al.</i> , 1990
2.5 to 5 mg/dm ³	Coughing and throat irritation	Bhambhani and Singh, 1985; Collins and Lewis, 2000
5 µg/dm ³	Elevated health symptoms (related to the central nervous system)	Legator <i>et al.</i> , 2001
6.4 mg/dm ³	Complaints of eye pain	Vanhoorne <i>et al.</i> , 1991
10 µg/dm ³	Eye and nasal symptoms and cough for the previous year	Jaakkola <i>et al.</i> , 1990
10 µg/dm ³	Neurophysiological abnormalities in reaction time, colour discrimination and mood	Kilburn and Warshaw, 1995
10 mg/dm ³	Threshold Limit Value (TLV) for H ₂ S.	Milby, 1962; Reiffenstein <i>et al.</i> , 1992; Roth, 1993
10 to 50 mg/dm ³	Eye irritation	
30 mg/dm ³	Induced nasal lesions in olfactory mucosa	Brenneman <i>et al.</i> , 2000
30 mg/dm ³ and above	Neurotoxicity leading to olfactory “paralysis” which can prevent detection of odour	Collins and Lewis, 2000; Reiffenstein <i>et al.</i> , 1992
200-700 mg/dm ³	Dyspnoea, pulmonary oedema and possibly fatal asphyxia.	Beauchamp <i>et al.</i> , 1984
1000 mg/dm ³	Immediate respiratory arrest and death	ACGIH, 1991

Chapter 3 Field observation of cattle manure bunker

3.1 Objectives

Management of cattle manure from feedlots is a growing problem, particularly in areas where high densities of sizeable dairy operations exist. This *in-situ* observation study was carried out to monitor the changes in moisture content, nutrient level and gaseous emission from the manure bunkers with time, and to evaluate different natural materials on their ability to absorb moisture, capture nutrients and control odour emissions from manure.

3.2 Background

A standoff shelter (also known as 'Herd Homes') was constructed to provide covered feedlot facilities for dairy cows (Fig. 3.1) during inclement weather. The structure is comprised of two sheds where the animals are housed. The sheds are roofed with a clear plastic to allow light to enter the building. Animal wastes were dropped through the slotted floor (Fig. 3.2) into the manure bunkers underneath (Fig. 3.3). Each manure bunker was divided down the middle so that there were, in effect, two separate bunkers per shed each with a surface area of 180 m² (Fig. 3.4).

One of the aims of the field observation in the herd home system was to examine the reduction of gaseous emissions from animal wastes. Different materials were placed in each bunker and evaluated on their ability to absorb moisture, capture nutrients and control odour emissions from manure. This chapter outlines the information gathered during a study on the Herd Home operation. The materials used were around 30.6 m³ of top soil (Waipu clay), around 23.4 m³ of wood shavings and a mixture of both (12.6 m³ top soil and 16.2 m³ wood shavings). One manure bunker was left as a control.

The physical and chemical characteristics of the raw manure, wood shavings and top soil are given in Tables 3.1 and 3.2. The raw manure initially had moisture content of 85%, however, as the cows started milking this figure increased to 90% - 92%.



Fig. 3.1 Photo of a Herd Home shed.



Fig. 3.2 Photo of a Herd Home shed.



Fig. 3.3 Photo of a Herd Home shed bunker (inside).



Fig. 3.4 Photo of a Herd Home shed bunker.

Table 3.1 Physical characteristics of raw manure, wood shavings and topsoil.

Materials	Moisture %	Bulk Density t/m ³	Particle size distribution %	
			< 4mm	> 4mm
Raw manure	85	1.01	n/a	n/a
Wood shavings	30	0.14	42	58
Topsoil	33	0.94	51	49

n/a = not applicable

Table 3.2 Chemical characteristics of raw manure, wood shavings and topsoil.

	Carbon %DW	Nitrogen %DW	C/N Ratio	Phosphorus %DW	Potassium %DW
Raw manure	5.8	0.51	11	0.12	0.52
Wood shavings	51.0	0.12	425	0.05	0.10
Topsoil	4.6	0.32	14	0.005	0.001

%DW = % dry weight

3.3 Observation

The average manure volume collected per cow per day was 15 litres but during milking period it was 30-35 litres per cow.

Moisture content

Changes over time in the moisture content of the materials in the four bunkers were monitored during nine months on four occasions. The soil bunker experienced the greatest reduction in moisture content, followed by the soil/wood shavings combination. The manure bunker showed the least reduction in moisture content closely followed by the wood shavings bunker.

Nutrient concentrations

The nutrient content of the bunkers were monitored on four occasions. The depth of the bunker material was recorded on each occasion. The summary of the main findings from three replicated samples is presented, on a dry weight basis in Table 3.3. Nitrogen (N) content of the raw manure declined with time from 2.9% at 6 weeks down to 1.6% at 9 months, while the N in the soil bunker showed a steady increase from 0.5% to 0.8%. Phosphorous (P) concentrations in the soil bunker doubled during the same sampling period whereas P increases in the other materials were minimal. Potassium

(K) concentrations were increased in all bunkers, doubling in the soil bunker and greatly enhanced in the wood shavings bunker. Sulphur (S) levels were enhanced in all bunkers except the soil/wood shavings combinations. The C/N ratio for the soil bunker was similar to that for the raw manure bunker (Table 3.3). The wood shavings bunker had the highest C/N ratio while that of the soil/wood shavings combination was intermediate to the soil bunker C/N ratio.

Table 3.3 Total depth of bunker profile (manure with bedding materials), moisture content (%) and nutrient concentrations (% in DM) in each manure bunker over time.

Bedding	Depth (mm)	Moisture (%)	N	P	K	S	C	C/N Ratio
<u>6 weeks</u>								
Raw manure	80	85	2.88	0.66	2.95	0.29	32.7	11
Soil	170	80	0.53	0.14	0.30	0.08	6.6	12
50%Soil+50% WS	250	77	0.67	0.21	0.48	0.11	14.2	21
Wood shavings	130	83	1.88	0.43	1.56	0.25	57.5	31
<u>3 months</u>								
Raw manure	120	76	2.20	0.56	1.50	0.29	31.4	14
Soil	220	50	0.63	0.19	0.41	0.10	8.0	13
50%Soil+50% WS	270	53	0.79	0.21	0.78	0.13	9.8	12
Wood shavings	185	74	2.08	0.43	1.95	0.26	35.3	17
<u>6 months</u>								
Raw manure	105	77	2.02	0.72	2.83	0.40	26.7	13
Soil	235	40	0.62	0.12	0.72	0.12	7.4	12
50%Soil+50% WS	255	50	0.71	0.25	0.8	0.15	27.0	38
Wood shavings	220	65	0.70	0.22	1.75	0.22	44.4	64
<u>9 months</u>								
Raw manure	55	68	1.59	0.72	3.78	0.47	21.0	13
Soil	170	26	0.82	0.29	0.62	0.15	9.2	11
50%Soil+50% WS	230	39	0.57	0.17	0.54	0.11	13.3	24
Wood shavings	170	52	1.73	0.50	2.79	0.41	42.8	25

Preliminary investigation on the chemical content of the raw manure found that ammonical-N ($\text{NH}_4^+\text{-N}$) contributed about 12% and 3% of the total N of cow urine and dung, respectively. Chemical analysis at nine months showed that $\text{NH}_4^+\text{-N}$ was still present in the raw manure, while this has been converted to nitrate-N ($\text{NO}_3^-\text{-N}$) in the other bedding materials, probably because of nitrification activity in these media. Organic N accounted for 85-89% of the total N in the bunker materials compared to 95% of the raw manure.

Nutrient balances

There was a similar trend in changes in nutrient contents over time in all bunkers. The raw manure bunker showed steady nutrient declines of N (70%) and S (33%) with time (Table 3.4). The soil bunker showed the most promise for nutrient conservation by having the least decline (10-34%) in amounts over time (Table 3.5). The decline in the amounts of nutrients in the wood shavings (42-67%) and the soil /wood shavings combinations (59-67%) were much greater than for the soil (Tables 3.6 and 3.7). These nutrients declines can be partly explained by gaseous losses.

Table 3.4 Amount of nutrients (kg) in the raw manure bunker (180m² surface area).

Nutrients	After 3 months	After 6 months	After 9 months
Nitrogen	115.0	63.0	34.8
Sulphur	15.3	12.4	10.3

Table 3.5 Amount of nutrients (kg) in the soil amended bunker (180m² surface area).

Nutrients	After 3 months	After 6 months	After 9 months
Nitrogen	148.0	117.0	98.2
Sulphur	20.0	21.0	18.0

Table 3.6 Amount of nutrients (kg) in the wood shavings amended bunker(180m² surface area).

Nutrients	After 3 months	After 6 months	After 9 months
Nitrogen	194.0	39.0	64.0
Sulphur	26.0	12.3	15.4

Table 3.7 Amount of nutrients (kg) in the wood shavings and soil amended bunker (180m² surface area).

Nutrients	After 3 months	After 6 months	After 9 months
Nitrogen	235.0	84.0	78.0
Sulphur	34.4	18.0	14.3

Gaseous losses

The effect of different bedding materials on reduction of the emissions from stirred manure in each bunker was compared by using ammonia (NH₃) and hydrogen sulphide (H₂S) meters. It appeared that soil was the most effective bedding material with regard to the reduction of emissions of NH₃ (Fig. 3.5) and H₂S (Fig. 3.6) gases from the manure. The greatest reduction in NH₃ gas emission was obtained in the soil bunker. The same effect with respect to the emission of H₂S and retention of S was also obtained by the addition of soil. Measurements from the manure bunkers also have shown that there was no significant green house gas emission released from the treated manure bunkers.

Advantages

Animals are subject to less stress and healthier environment which resulted to an improved animal welfare and an increase in production. Herd Home owner, Mr Tom Pow has indicated that a significant increase in milk production of 20% since the introduction of the housing system. Moisture of the manure was reduced which resulted the reduction of volume and enriched with nutrients. Ammonia, H₂S and green house gas emissions were reduced. Gas emission reduction was increased by the addition of natural materials.

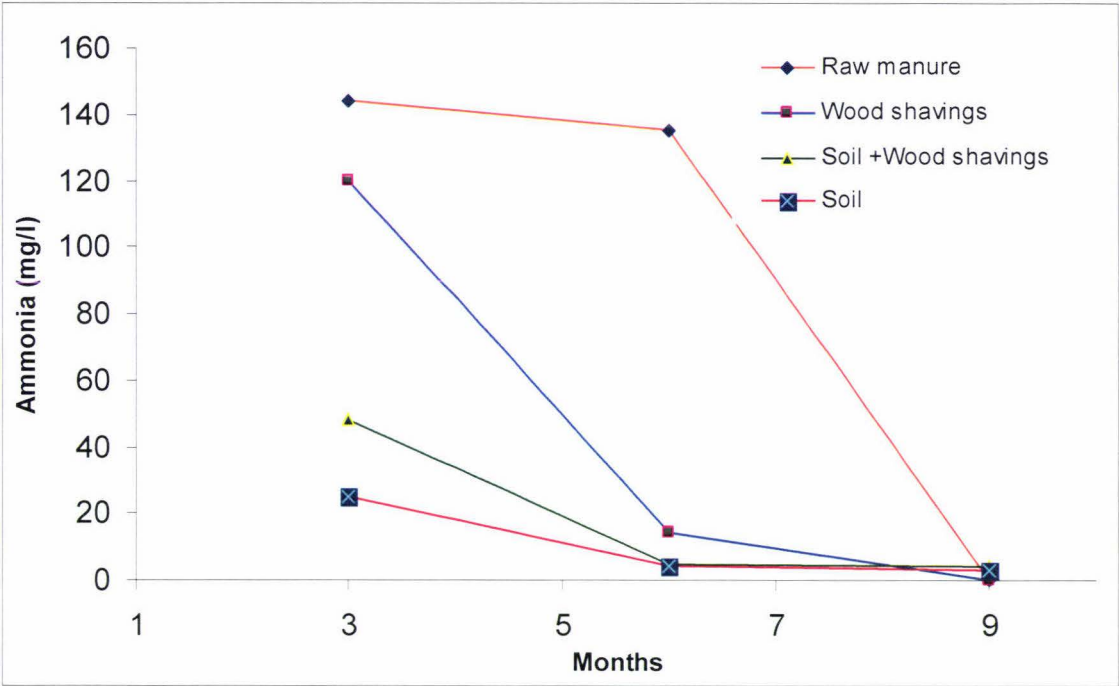


Fig. 3.5 Ammonia (NH_3) emissions (by volume) from manure bunkers.

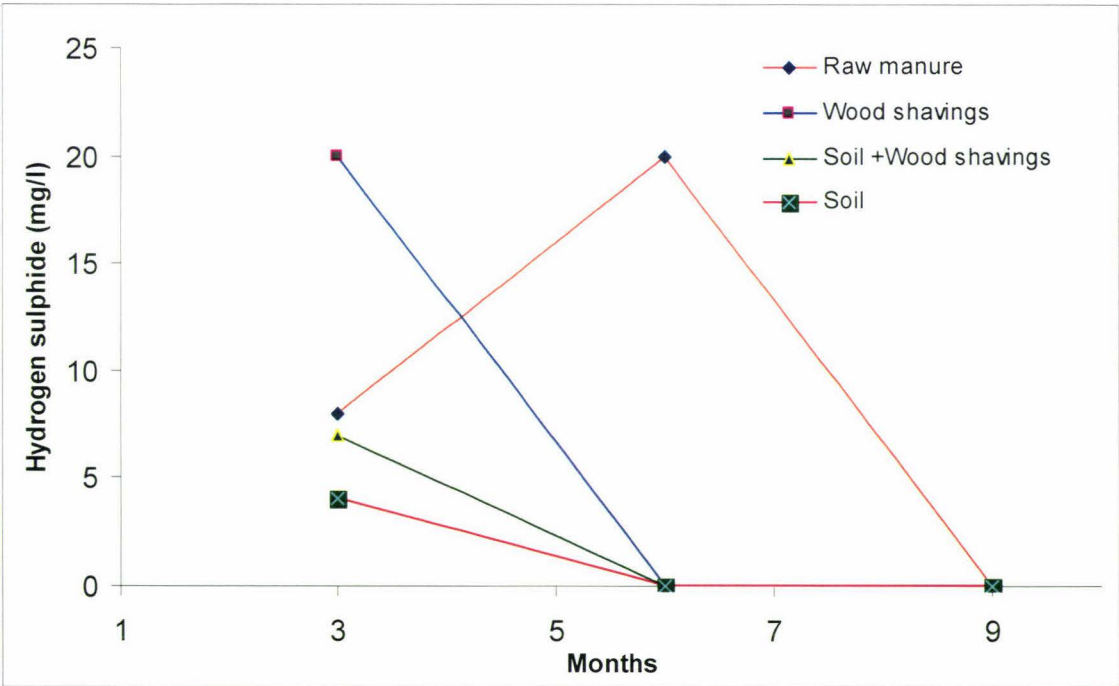


Fig. 3.6 Hydrogen sulphide (H_2S) emissions (by volume) from manure bunkers.

3.4 Conclusion

It was shown that the natural materials used were effective at capturing nutrients from the manure and reducing the gaseous emissions. This resulted in a greater nutrient enrichment of the final product for land application. The top soil for bunker bedding appears to be a viable option and most cost effective.

A series of laboratory experiments was carried out following the observations made in this field study. This laboratory research was aiming to utilise the observations made in the field study, but focussing on the measurement of NH_3 and H_2S gas emissions and the evaluation of the natural materials for their ability to control these gas emissions. A continuous method of measuring the gas emission from the manure under controlled condition was used.

Chapter 4 Materials and methods

4.1 Materials

4.1.1 Cattle manure and biosolids

Cattle dung and urine samples used in this study were collected from the Ruakura dairy farm and were immediately brought to the laboratory and stored at 4°C. Fresh manure and urine samples were mixed (50g dung and 50g urine) and sub-samples were analysed for its physical and chemical properties.

De-watered anaerobically digested biosolids samples were collected from wastewater treatment plants in Hamilton and North Shore cities. Sub-samples were analysed for physical and chemical properties.

4.1.2 Incubation system

The incubation system consists of Schott glass bottles to incubate the samples and Dreschel bottles to trap the gases.

- Schott glass bottle: Glass bottles with an internal diameter of 70mm and a capacity of 0.5 dm³, were used as incubation bottles for this experiment. The inside of the bottle lid is PTFE (Teflon) sealed to avoid the gas leak and the side of the bottle was modified by connecting two mini-nert[®] valves. These valves permit the introduction of two syringe needles, one for the inlet of air and the other one for exhaust gases. (Fig. 4.1).
- Dreschel bottle: Tall glass bottles with a special stopper, designed to allow a gas to pass through the liquid in the bottle (Fig. 4.2). The stopper accommodates both inlet and outlet tubes (500 cm³, Bibby Sterilin Ltd, Stone, England).

4.1.3 Nitrogen and air

Oxygen-free nitrogen gas was used for anaerobic incubation using commercial gas cylinders (Gas code 152, BOC Gases Ltd, Wellington, NZ) and laboratory compressed air supply was used for aerobic incubation.

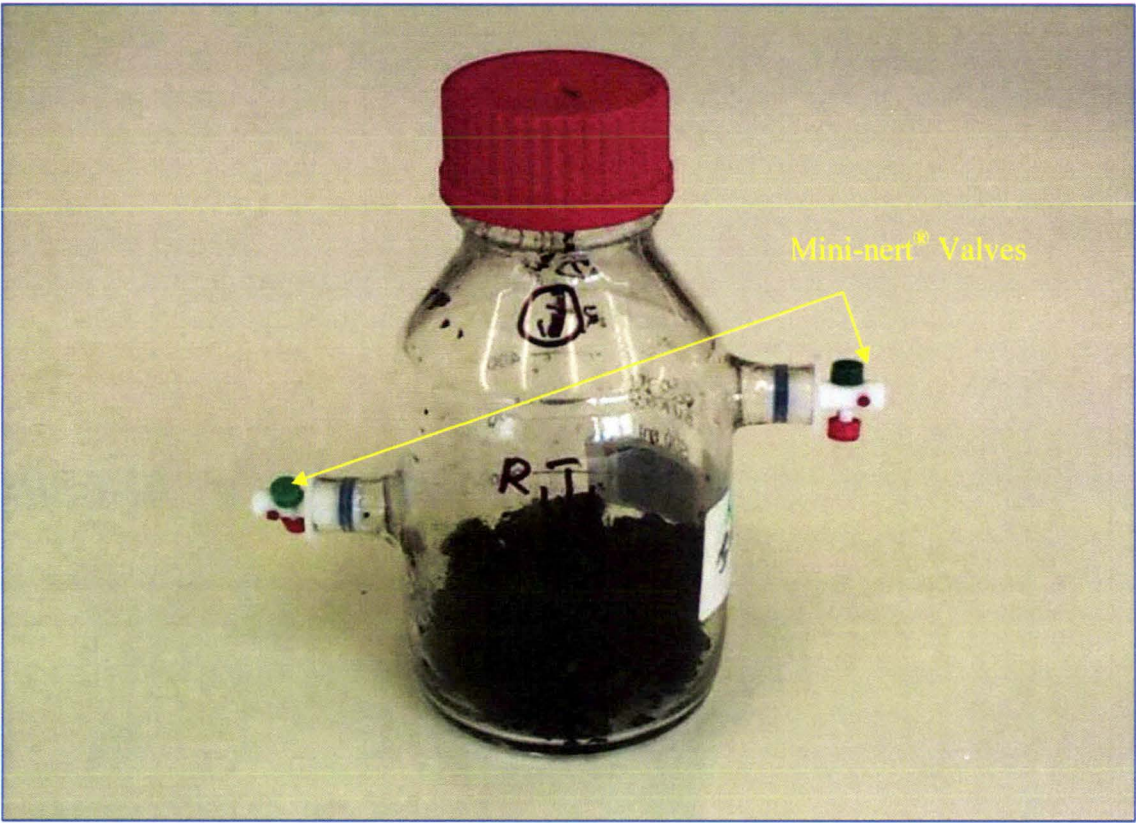


Figure 4.1 Modified schott glass bottle.

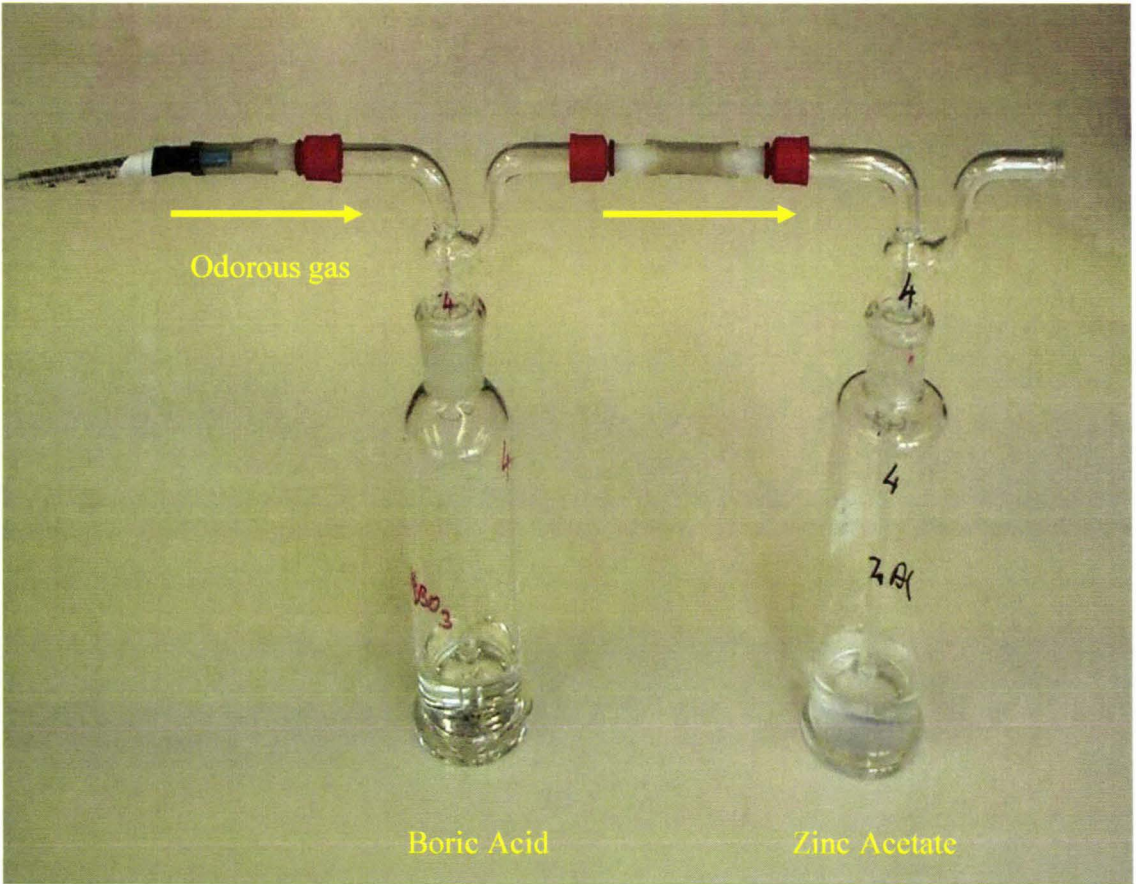


Figure 4.2 Dreschel bottle.

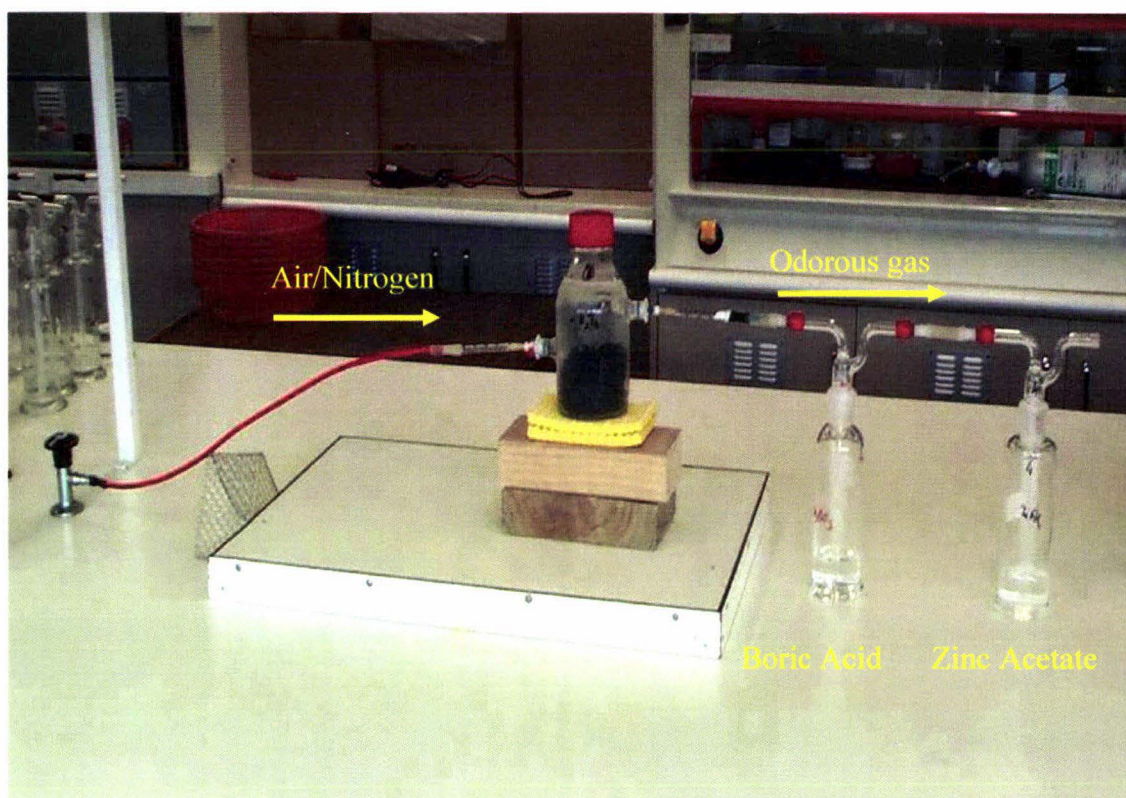


Figure 4.3 A single unit of the incubation set up.

4.1.4 Media

Pine bark, saw dust, wood shaving and top soil were used as amendments to mitigate gaseous emissions. Screened pine bark with a nominal size range of 9-15 mm (No.3 ‘Mini Chip’) was purchased from Daltons Ltd (Matamata, New Zealand). This costs \$3600 per 100m³. Untreated saw dust and wood shaving were collected from the Ruakura Carpentry work-shop and the saw dust was passed through a 2-mm screen to remove the coarse particles. Top soil was collected from the top 10 cm of an area of Te Kowhai silt loam (Typic Ochraqualf), which is a typical orthic gley (Soil survey staff, 1990). The soil was gently crushed and passed through a 4-mm screen to remove stones. Screened top soil can be purchased locally for \$1500 per 100m³.

4.1.5 Incubation system set-up

The incubation system consists of a Schott glass bottle for incubation, air or nitrogen gas supply to flush the emitted gases and chemical traps to capture NH₃ and H₂S emission. Fresh cattle manure (mixture of 50% dung and 50% urine) or biosolids were taken in the Schott glass bottle. Air from the laboratory compressed air supply or nitrogen gas from the cylinder was allowed to pass through water first in order to

remove any NH_3 and also to avoid drying of the manure and biosolids samples in the incubation bottle. A constant flow rate was maintained ($0.8 \text{ dm}^3/\text{min}$). The air/nitrogen coming through the outlet of the incubation bottle was passed through a “dreschel” bottle containing 1% H_2SO_4 solution or 2% boric acid solution to trap NH_3 and again through 0.1M zinc acetate solution to trap H_2S . A single set-up of the experiment using Schott glass bottles for incubation and Dreschel bottles to trap the emitted gases is shown in Figure 4.3. The room temperature was maintained at $20 \pm 1^\circ\text{C}$. Appropriate amounts of natural materials were mixed with manure or biosolids and the gaseous emission was monitored as explained above in order to evaluate their ability to mitigate emissions.

Since H_2S is highly toxic, a Safecheck 100 gas monitor (Quest Technologies, Oconomowoc, USA) was used daily to check the approximate H_2S concentration of air coming through the outlet of the bottle. The meter had an alarm function and was left in the room throughout the study to detect any H_2S leaks.

4.2 Analytical methods

Elemental analysis of cattle manure, biosolids and natural materials

A commercial laboratory performed most of these analyses. Total nitrogen content of cattle manure, biosolids and natural materials was analysed by Kjeldahl digestion followed by titration. Ammonium content of cattle manure and biosolids was analysed by water extraction followed by colorimetric determination. Fresh cattle manure samples were digested in a hydrochloric/nitric acid mixture. The digest was then analysed for potassium, magnesium and calcium using Atomic Absorption Spectroscopy (AAS) and sulphur by Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES). The digest was also analysed for phosphorus by Murphy and Riley (1962) colorimetric method.

Organic carbon

Samples of cattle manure, biosolids and natural materials were dried at 105°C and ground in a mortar and pestle then analysed by combustion and infra-red spectroscopy using a TOC-5000A carbon analyser with a SSM-5000A solid sample module (Shimadzu Corporation, Kyoto, Japan).

Water content

Samples of cattle manure, biosolids and natural materials were weighed in ceramic dishes then dried overnight at 105°C. The dishes were weighed to a constant weight and the weight of the lost water was calculated.

pH

Ten grams samples of cattle manure, biosolids and natural materials were weighed in a 100 cm³ beaker and 50 cm³ of deionised water was added. This was left for 30 minutes, occasionally being stirred with a glass rod. The pH value was then read using an Orion Model 370 pH meter fitted with an Orion Model 9202 electrode (Orion Research Inc., Beverly, USA). All the pH analyses were carried out in duplicate.

Water holding capacity, porosity factor and bulk density of natural material

A measuring cylinder was weighed (M_1), then filled to 100 cm³ with fresh material (soil or pine bark). Water was then added up to 100 cm³ level. As water soaked in to the material, the water level decreased. When the level stopped decreasing (approx 30 min), the water was topped up to the 100 cm³ level and the total volume of water added to reach the 100 cm³ was recorded (V_1). The measuring cylinder was then inverted for 2 hours and the water allowed to drain out. The measuring cylinder containing saturated material was weighed (M_2) then dried overnight at 105°C. It was then cooled and reweighed to a constant weight (M_3). These analyses were carried out in duplicate.

$$\text{Water holding capacity (\%)} = [(M_2 - M_3) / (M_2 - M_1)] \times 100\%$$

$$\text{Porosity factor} = (V_1 / 100)$$

$$\text{Bulk density (g cm}^{-3}\text{)} = (M_3 - M_1) / 100$$

Particle size

Approximately 100 g of fresh natural material was placed in the top of a stack of sieves with 10, 5.6, 2.8 and 1.0 mm mesh size. The sieves were gently agitated for 30 seconds. Each fraction was weighed, recorded (S_1 : > 10 mm; S_2 : 10 – 5.6 mm; S_3 : 5.6 – 2.8 mm; S_4 : 2.8 – 1.0 mm; and S_5 : < 1.0 mm) and expressed as a percentage of the total weight.

4.2.1 Analysis of gas emission

Ammonia analysis

The H_3BO_3 and H_2SO_4 acid solutions were collected periodically during incubation. An auto titrator (Mettler DL 25) was used to analyse the H_3BO_3 solution for ammonical nitrogen (NH_4^+ -N) concentration by titration with standard 0.5 M H_2SO_4 . Absorption of NH_3 by the H_3BO_3 acid results in the formation of NH_4^+ and H_2BO_3^- ions, thereby increasing the pH of the H_3BO_3 acid (Eq. 4-1). The borate formed is determined by titration with standard 0.5 M H_2SO_4 (Eq. 4-2).

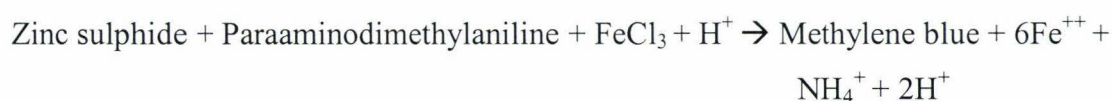


Phenol/hypochlorite colorimetry method (APHA, 1995) was used when the NH_3 was trapped using 1% H_2SO_4 solution.

Hydrogen Sulphide analysis

Zinc acetate (ZnAc) solutions were collected periodically during incubation. The H_2S reacts with ZnAc and form zinc sulphide precipitate. This suspension was analysed periodically to give the H_2S concentration.

A 7.5 cm^3 aliquot (contains zinc sulphide precipitate) of the ZnAc trap solution (or an aliquot of the solution diluted to give a concentration in the range 0–1 mg dm^{-3}) was pipetted to a test-tube. Amine-sulphuric acid reagent (0.5 cm^3 dimethyl -P-phenylenediamine), ferric chloride (0.15 cm^3) and 1.6 cm^3 di-ammonium hydrogen orthophosphate (to remove the ferric chloride colour) were added and the absorbance of the methylene blue produced was measured using a CE292 spectrophotometer (Cecil Instruments, Cambridge, England) set at 664 nm wave length (Eaton *et al.*, 1995). This method is suitable for measuring sulphide concentration ranging from 0.1 to 2.0 mg dm^{-3} .



Effect of different types of amendments under anaerobic conditions

The amendments used were untreated pine bark, wood shavings and saw dust as carbon-rich materials and soil as an absorbent. Cattle manure and biosolids materials were mixed thoroughly with these amendment substrates in the proportion of 10 g substrate to 100 g materials.

Effect of the amount of amendment materials under anaerobic conditions

Pine bark and soil were used to examine the effect of varying the proportion of amendment on gaseous emission. The amendments were mixed with cattle manure as follows: (i) no amendment (control), (ii) 20 g amendment to 100 g manure and (iii) 40 g amendment to 100 g manure.

4.3 Data analysis

Daily rates of NH_3 and H_2S emissions were calculated based on their measured concentrations in the H_3BO_3 acid solution and ZnAc solution, respectively, and the mean rates of emissions were calculated from three replicates. Total emission losses were calculated by integrating the daily rates over the incubation times. An analysis of variance was performed using the Genstat statistical package and least significant differences (LSDs) or least significant ratios (LSRs) were calculated to show the differences in the emission rates and total emission losses among various treatments. LSRs were used where data was log-transformed for analysis.

Chapter 5 Results and discussion

5.1 Results

5.1.1 Characteristics of manure, biosolids and natural materials

Manure

The properties of cattle manure (1:1 w/w mixture of urine and dung) was analysed before and after each experiment. The composition of cattle manure varied considerably with time. The N concentration of cattle manure varied from 0.37% to 0.48% (Table 5.1). More than 50% of the N content was in organic form. The mean percentage values of P, K, Ca and Mg contents in the manure were 0.033, 0.538, 0.066 and 0.022, respectively (Table 5.1).

Biosolids

The properties of biosolids also varied considerably with time. The average N content was about 1.16% (Table 5.2). Around 80% of N content was in organic form. Organic C content is very low. The average C/N ratio was around 4.0.

Natural materials

Nitrogen content was very low and C content was high in all materials except soils (Table 5.3). The pH of the materials was also around 4 except soil which was around 6.

5.1.2 Properties of the selected medium

Data on some important physical and chemical properties of pine bark and soil used in this experiment (Table 5.4) indicate that they were able to hold sufficient water to maintain optimum conditions for control gaseous emission (40-60%) (Bohn, 1992). The water contents of pine bark was in the recommended range but the soil's water content was slightly below the recommended range, which is likely to affect the performance of the soil. Porosity of both media was in the recommended range of 0.4-0.8 (Devinny *et al.*, 1999). The bulk density of the soil was higher than the bark. The bulk density of the materials affects the area required for storage. Using bark as a control medium requires more storage area than using soil. The pH of soil and bark were all initially acidic.

Available N ($\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$) and P concentrations of 0.4% and 0.15%, respectively, are considered sufficient for control gaseous emission (Devinny *et al.*, 1999). However, both media were deficient in available N, whilst the bark was deficient in P (Table 5.4).

Particle size

The particle size distributions varied between the media (Table 5.5). Soil had a higher proportion of smaller particles than bark. The soil was screened through a 4-mm screen to remove roots and stones so it had mainly smaller particles and contained no particles larger than 5.6 mm. The bark had been graded between 9-15 mm and only 3% had a particle size less than 5.6 mm.

Table 5.1 Characteristics of cattle manure in wet basis (1:1 w/w mixture of urine and dung) (n=5).

	Minimum	Maximum	Average
Total N (%)	0.374	0.480	0.414
Total P (%)	0.029	0.040	0.033
Organic C (%)	1.70	2.06	1.89
Total S (%)	0.031	0.060	0.048
$\text{NH}_4\text{-N}$ (%)	0.142	0.198	0.177
Potassium (%)	0.436	0.634	0.538
Calcium (%)	0.046	0.09	0.066
Magnesium (%)	0.021	0.023	0.022
pH	8.0	8.4	8.2
C/N	4.32	5.13	4.60
Moisture (%)	94.6	95.6	95.1

Table 5.2 Characteristics of biosolids (wet basis) (n=3).

	Minimum	Maximum	Average
Total N (%)	1.073	1.279	1.161
NH ₄ -N (%)	0.161	0.128	0.145
Total P (%)	0.267	0.657	0.462
Organic C (%)	1.18	10.60	4.65
Total S (%)	0.192	0.253	0.218
pH	6.6	7.1	6.9
C/N	1.10	9.38	4.01

Table 5.3 Characteristics of amendment materials in wet basis (Numbers in brackets are standard errors of the mean, n=3).

	Pine bark	Soil	Sawdust	Wood shavings
Total N (%)	0.23(0.02)	0.39(0.02)	0.19(0.01)	0.19(0.01)
Total C (%)	53.6(1.15)	3.87(0.11)	50.1(1.21)	48.9(0.80)
pH	4.0(0.06)	6.5(0.13)	4.1(0.19)	4.6(0.12)
C/N	233	10	264	257

Table 5.4 Physical and chemical characteristics of bark and soil.

Characteristics	Medium	
	Bark	Soil
Water content (% wet weight)	53	31
Water holding capacity (% wet weight)	47	52
Porosity factor	0.60	0.78
Bulk density (kg dm ⁻³)	0.17	0.58
Total P (% of dry weight)	0.02	0.16
Total S (% of dry weight)	0.04	0.13

Table 5.5 Particle size distribution of bark and soil (%).

Medium	Particle size				
	< 1.0 mm	1.0-2.8 mm	2.8-5.6 mm	5.6-10 mm	>10 mm
Bark	0	0	3	41	56
Soil	22	37	41	0	0

5.1.3 Aerobic and anaerobic incubations

Manure

Around 70% of the manure N was recovered in the NH_4^+ form after the 7 weeks incubation both under aerobic and anaerobic conditions (Table 5.6). Manure pH was significantly higher ($P<0.05$) after aerobic incubation than anaerobic incubation (Table 5.6).

Ammonia emission rate reached the peak value within two days of the experiment and declined rapidly under both aerobic and anaerobic incubation conditions (Fig. 5.1). Cumulative volatilisation losses of NH_3 during the 7 weeks incubation of cow manure are presented in Fig. 5.2. There were about 2 fold differences in NH_3 loss between aerobic and anaerobic incubation by the end of the incubation period. Total losses of N from the manure, through NH_3 volatilisation during the 7 weeks incubation, were 49.5 mg and 20.5 mg $\text{NH}_3\text{-N kg}^{-1}$ manure under aerobic and anaerobic incubations, respectively. The initial manure N was 3.92 g kg^{-1} , so these NH_3 volatilisation losses amounted to only 1.2% and 0.52% of the initial N content in the manure.

In contrast to NH_3 emissions, emissions of H_2S were significantly higher from anaerobic incubation than aerobic incubation (Fig. 5.3). The total S loss through H_2S emissions was 9.3 mg $\text{H}_2\text{S-S kg}^{-1}$ manure, amounting to 1.8% of the initial manure S under anaerobic incubation, with most of the emissions occurring during the initial 25 days incubation. The loss of S was insignificant under aerobic conditions. More ($P<0.05$) total manure S was recovered in the aerobic manure than in the anaerobic manure at the end of the incubation (Table 5.6).

Biosolids

Biosolids pH was increased after the 8 weeks of incubation both under aerobic and anaerobic conditions (Table 5.7).

Ammonia emission rate reached the peak value within two days of the experiment and declined rapidly under both aerobic and anaerobic incubation conditions (Fig. 5.4). Cumulative volatilisation losses of NH_3 during the 8 weeks incubation of biosolids are presented in Fig. 5.5. There was no difference ($P < 0.05$) in the total NH_3 loss between aerobic and anaerobic incubation by the end of the incubation period. Total losses of N from the biosolids, through NH_3 volatilisation during the 8 weeks incubation, were 1155.8 mg and 1056.6 mg $\text{NH}_3\text{-N kg}^{-1}$ biosolids under aerobic and anaerobic incubations, respectively. The initial biosolids N was 61.7 g kg^{-1} (Table 5.7), so these NH_3 volatilisation losses amounted to 1.87% and 1.71% of the initial N content in the biosolids under aerobic and anaerobic incubations, respectively.

But the emissions of H_2S were significantly higher from anaerobic incubation than aerobic incubation (Fig. 5.6). The total S loss through H_2S emissions was 150.7 mg and 6.1 mg $\text{H}_2\text{S-S kg}^{-1}$ biosolids under anaerobic and aerobic incubation, respectively. The initial biosolids S was 1.92 g kg^{-1} (Table 5.7), so these H_2S volatilisation losses amounted to 7.8% and 0.3% of the initial S content of the biosolids under anaerobic and aerobic incubation.

5.1.4 Effect of natural amendments on gaseous emission

Manure

The effect of the four natural materials tested on NH_3 volatilisation loss under anaerobic incubation is presented in Fig. 5.7. At the end of 8 weeks incubation the cumulative NH_3 volatilisation losses were significantly less ($P < 0.05$) from the manure amended with each of the natural materials than from the unamended manure. Amongst the natural materials examined, pine bark was found to be the most efficient in reducing NH_3 loss, achieving reduction of 58% compared with unamended manure, followed by soil (30%), wood shavings (25%) and sawdust (24%). The temporal pattern of cumulative NH_3 volatilisation loss was also affected by the addition of amendments. The 2nd day of the incubation, pine bark and soil amendments had demonstrated a significant ($P < 0.05$) decrease in the amount of NH_3 volatilisation, and at the 29th day

sawdust and wood shavings started to show significantly ($P<0.05$) different results from the unamended control. There were no significant differences ($P<0.05$) in the NH_3 volatilisation between treatments of soil, sawdust and wood shavings after 29th day of the incubation.

Biosolids

The effect of amendment with the four natural materials on NH_3 volatilisation loss under anaerobic incubation is presented in Fig. 5.8. At the end of 6 weeks incubation the cumulative NH_3 volatilisation losses from biosolids were reduced by the amended natural materials. Amongst the natural materials examined, pine bark was found to be the most efficient in reducing NH_3 loss, achieving reduction of 56% compared with unamended biosolids, followed by soil (46%), wood shavings (41.5%) and sawdust (36%).

Hydrogen sulphide emission also was reduced by the amendment of natural material (Fig. 5.9). At the end of 6 weeks incubation the cumulative H_2S emission losses were significantly ($P<0.05$) less from the biosolids amended with each of the natural materials than biosolids without amendment. Amongst the natural materials amended with biosolids, pine bark reduced the H_2S emission by 83%, followed by soil (79%), wood shavings (72%) and sawdust (57%).

Table 5.6 Effects of aeration status on cattle manure properties after 7 weeks of incubation in wet basis (Numbers in brackets are standard errors of the mean, n=3).

Properties	Total N (%)	NH ₄ -N (%)	Total S (%)	Org C (%)	pH
Before incubation	0.391	0.142	0.05	1.7	8.4
After aerobic incubation	0.343(0.010)	0.238(0.010)	0.062(0.001)	1.283	8.8(0.25)
After anaerobic incubation	0.373(0.003)	0.278(0.007)	0.054(0.002)	1.572	8.3(0.20)

Table 5.7 Effects of aeration status on biosolids properties after 7 weeks of incubation in wet basis (Numbers in brackets are standard errors of the mean, n=8).

Properties	Total N (%) (dry basis)	NH ₄ -N (%)	Total S (%)	pH
Before incubation	6.17	0.128	0.192	7.1
After aerobic incubation	5.15(0.138)	0.1(0.014)	0.29(0.042)	8.25(0.098)
After anaerobic incubation	5.69(0.167)	0.13(0.003)	0.21(0.019)	8.89(0.030)

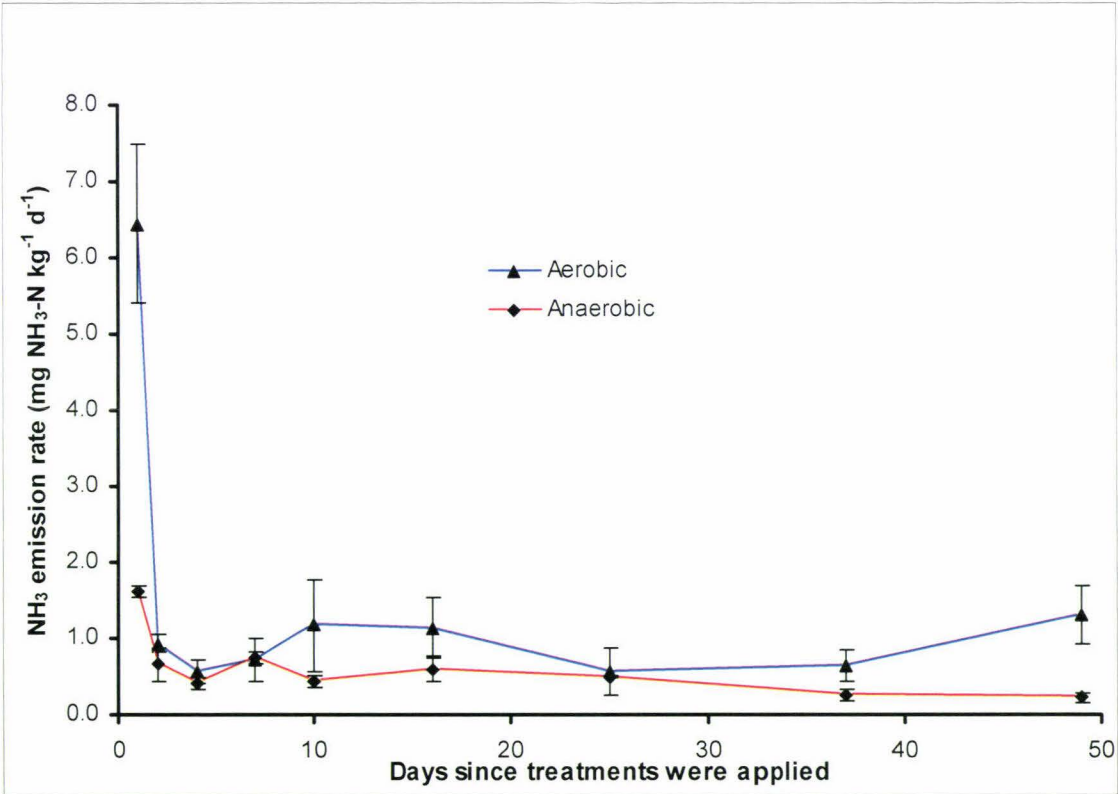


Fig. 5.1 Specific ammonia (NH₃) emission rate of cattle manure in incubation bottles under aerobic vs. anaerobic conditions at 20°C.

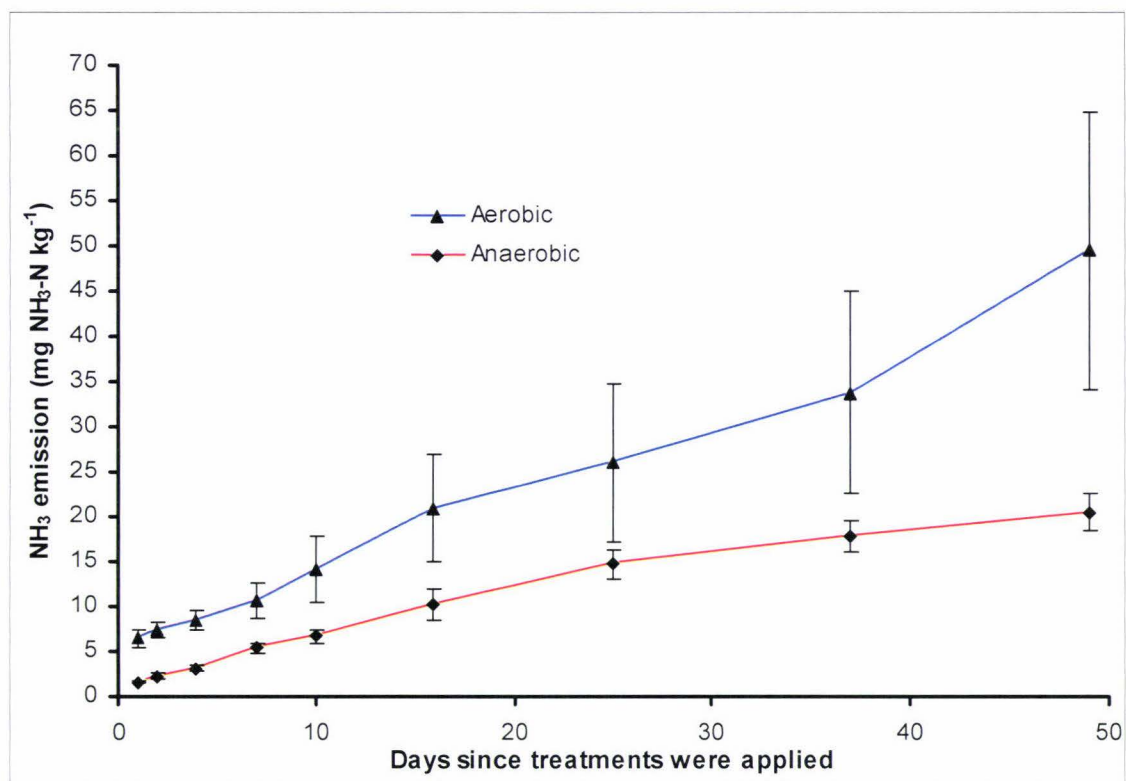


Fig. 5.2 Cumulative ammonia (NH_3) loss from cattle manure in incubation bottles under aerobic vs. anaerobic conditions at 20°C.

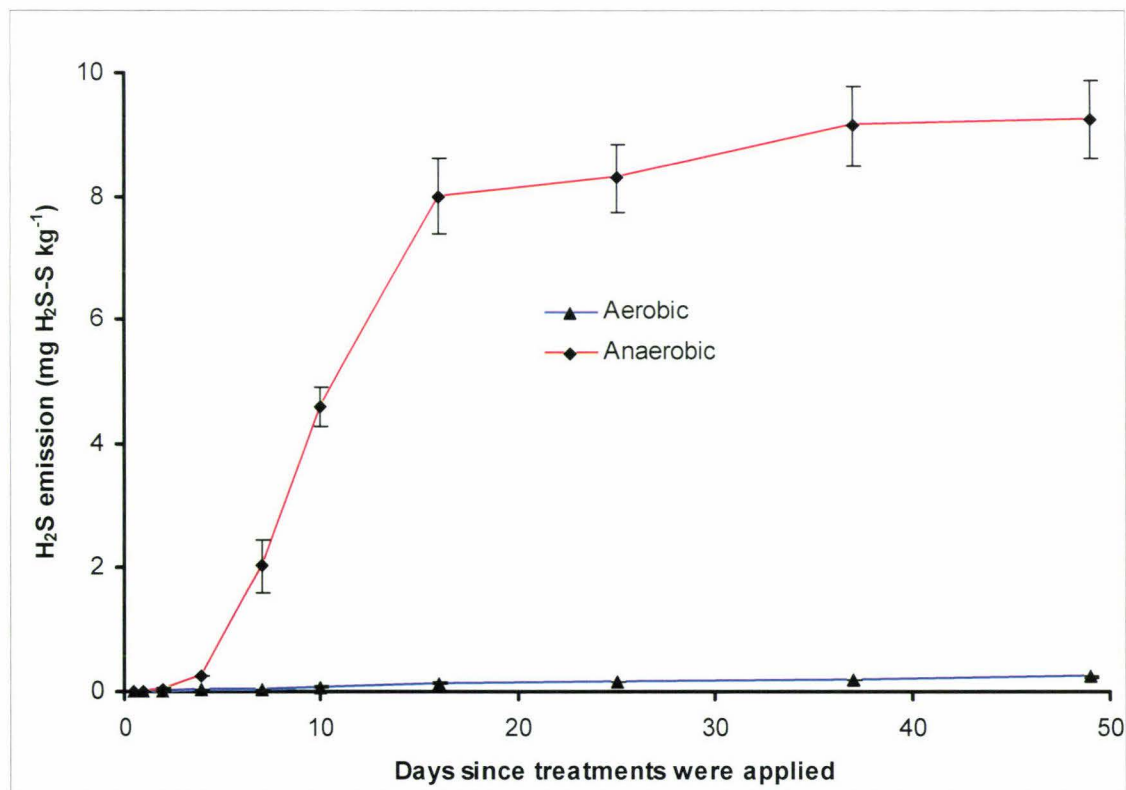


Fig. 5.3 Cumulative hydrogen sulphide (H_2S) loss from cattle manure in incubation bottles under aerobic vs. anaerobic conditions at 20°C.

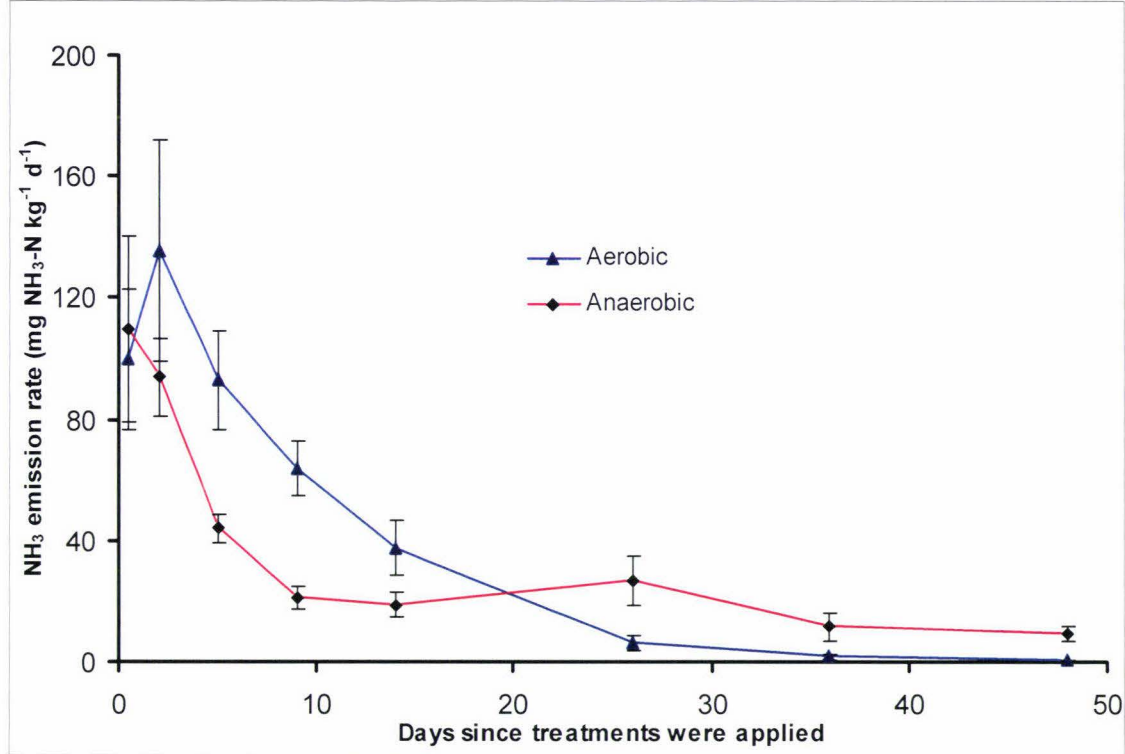


Fig. 5.4 Specific ammonia (NH₃) emission rate of biosolids in incubation bottles under aerobic vs. anaerobic conditions at 20°C.

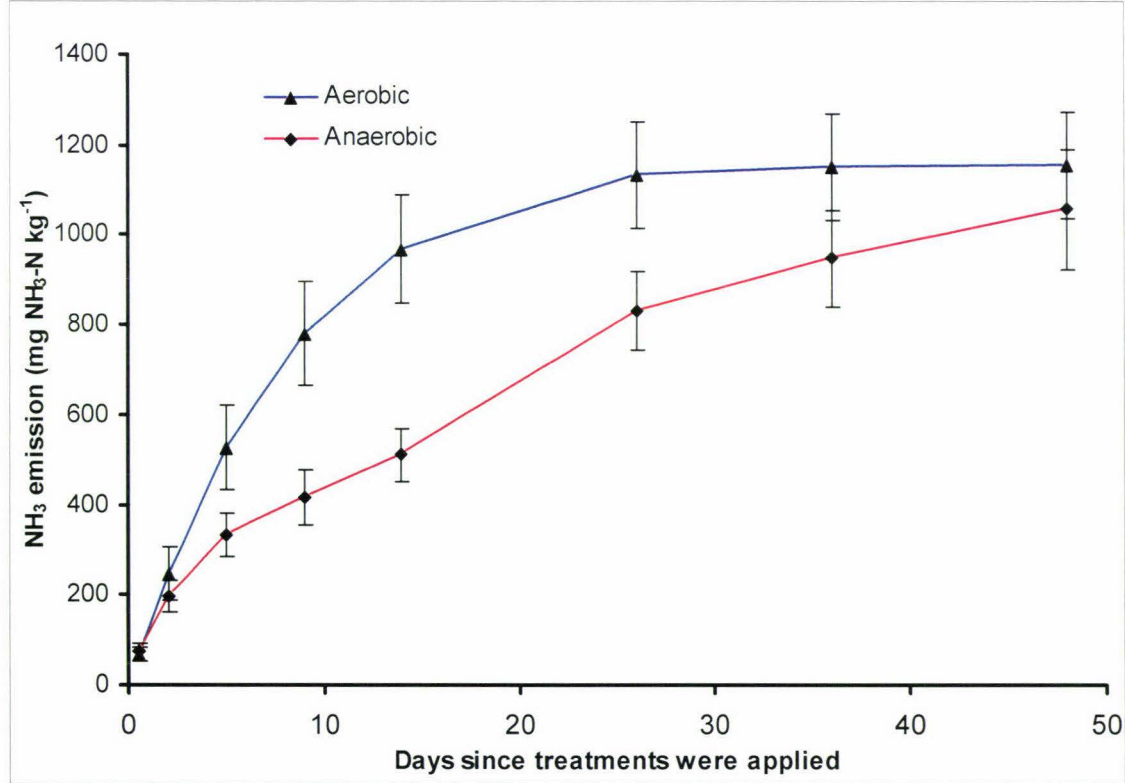


Fig. 5.5 Cumulative ammonia (NH₃) loss from biosolids in incubation bottles under aerobic vs. anaerobic conditions at 20°C.

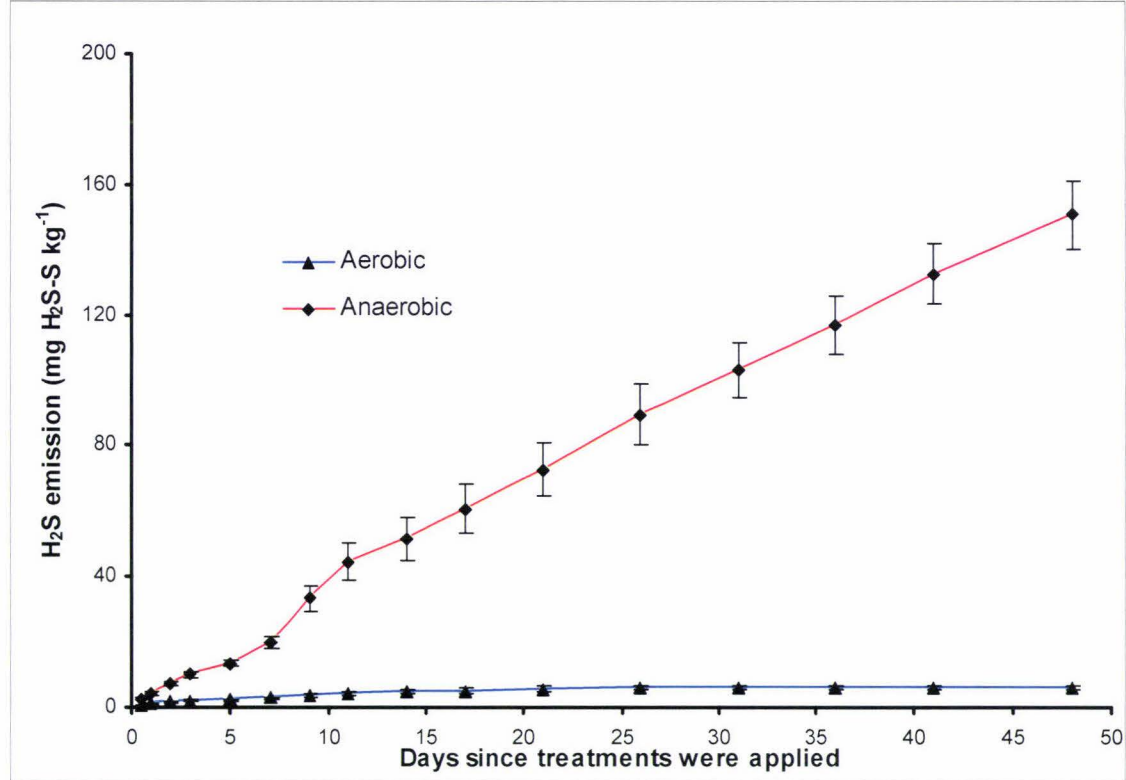


Fig. 5.6 Cumulative hydrogen sulphide (H₂S) loss from biosolids in incubation bottles under aerobic vs. anaerobic conditions at 20°C.

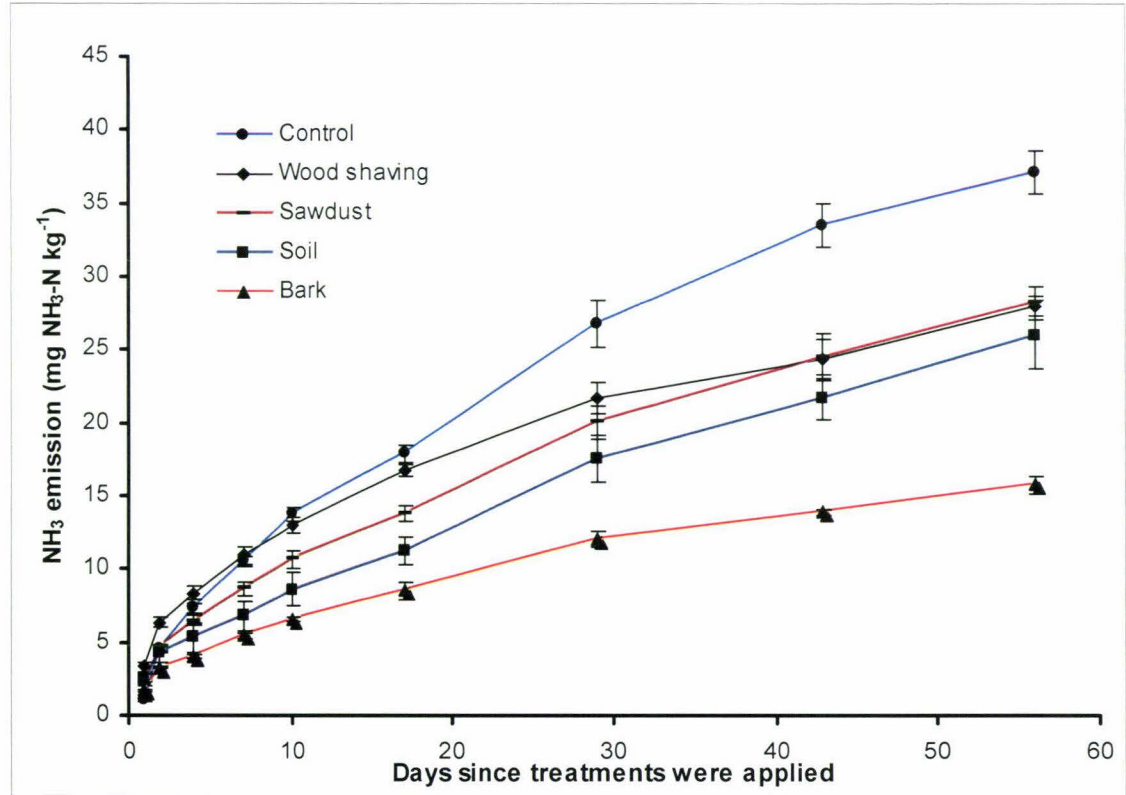


Fig. 5.7 Effect of natural amendments on cumulative ammonia (NH₃) loss from cattle manure under anaerobic incubation.

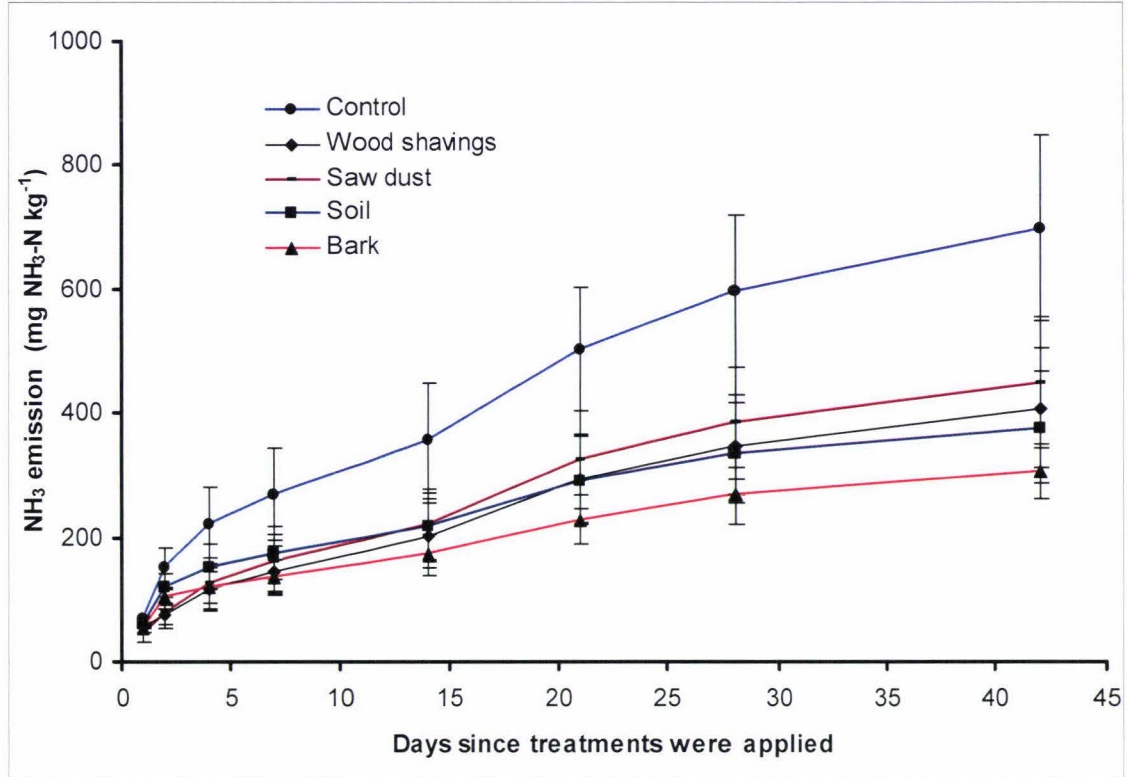


Fig. 5.8 Effect of natural amendments on cumulative ammonia (NH_3) loss from biosolids under anaerobic incubation.

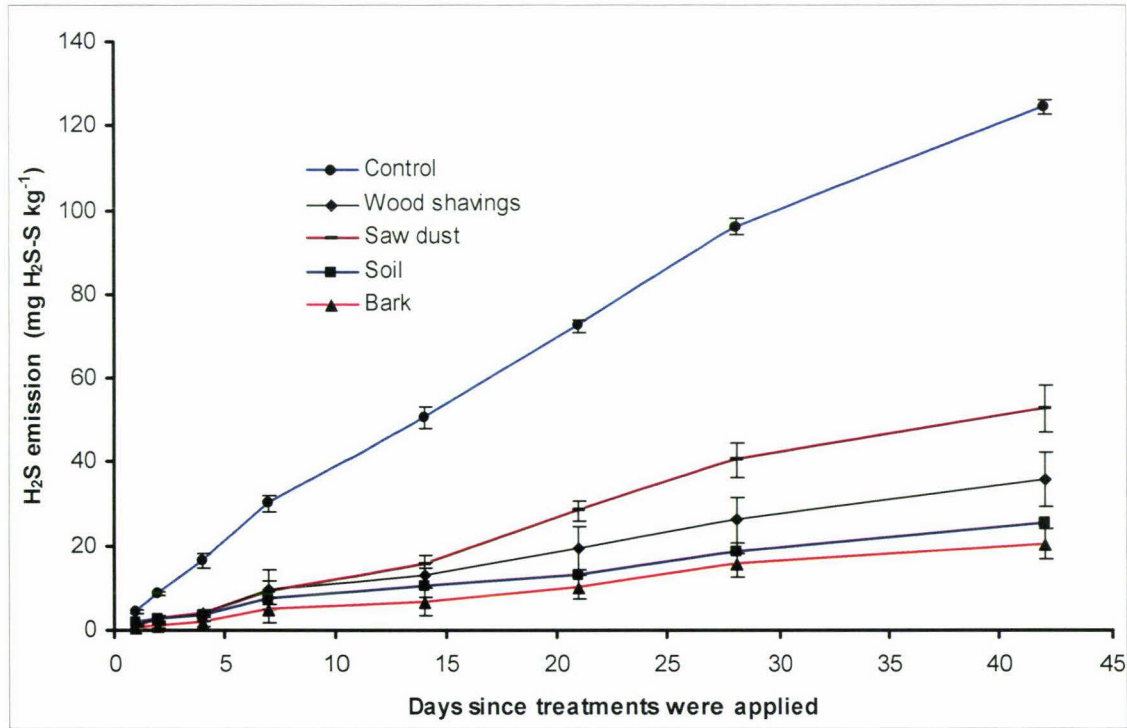


Fig. 5.9 Effect of natural amendments on cumulative hydrogen sulphide (H_2S) loss from biosolids under anaerobic condition.

5.1.5 Effect of varying level of pine bark amendment on gaseous emission

Manure

Response of NH_3 volatilisation from manure to varying proportions of pine bark was statistically significant ($P < 0.05$) (Fig. 5.10). After 9 weeks incubation, 80% reduction of cumulative NH_3 volatilisation was achieved by amending 20 g of bark with 100 g cow manure, while 85% reduction was achieved by amending with 40 g bark to 100 g cow manure.

Emissions of H_2S from amended manure were significantly different ($P < 0.05$) between the two proportions of bark, with more reduction being achieved when higher level of bark was used after 9 weeks incubation (Fig. 5.11). Cumulative H_2S emissions were reduced by about 86% when 100 g cow manure was amended with 20 g bark and by 94% when 100 g cow manure was amended with 40 g bark.

Analysis of the manure demonstrated that most of the initial manure N was recovered as organic N after incubation of manure with bark (Table 5.8). The pH of the bark-amended manure was also lower than the unamended manure. Significantly higher ($P < 0.05$) amounts of S were recovered in the bark-amended manure than the unamended manure.

Biosolids

Response of NH_3 volatilisation from biosolids to varying proportions of pine bark was also significant ($P < 0.05$) (Fig. 5.12). After 7 weeks incubation, 50% reduction of cumulative NH_3 volatilisation was achieved by amending 20 g of bark with 100 g biosolids, while 57% of reduction was achieved by amending with 40 g bark to 100 g biosolids.

The increased pine bark additions from 20 to 40 g to 100 g biosolids did not significantly ($P < 0.05$) increase the efficiency in reduction of H_2S volatilisation (Fig. 5.13). Cumulative H_2S emissions were reduced by 72% about when 100 g biosolids was amended with 20 g bark and by 76% when 100 g biosolids was amended with 40 g bark.

Most of the initial biosolids N content was recovered as organic N after incubation of biosolids with bark (Table 5.10). The pH of the bark-amended biosolids was also lower ($P<0.05$) than the unamended biosolids after incubation.

5.1.6 Effect of varying level of soil amendment on gaseous emission

Manure

Increasing soil additions from 20 to 40 g to 100 g cow manure did not significantly ($P<0.05$) increase the efficiency in reduction of NH_3 volatilisation (Fig. 5.14) and H_2S emission either (Fig. 5.15). After 7 weeks incubation, amendment of cow manure with soil at both levels reduced the emissions of both gases by about 50%.

Most of the initial manure N was recovered in the NH_4^+ form in all the incubated manures, although less ($P<0.05$) amounts of NH_4^+ -N were measured in the soil-amended manure than in the unamended manure (Table 5.9). The pH of the soil amended manure was also lower ($P<0.05$) than the unamended manure.

Table 5.8 Effects of pine bark amendment on cattle manure properties in wet basis

(Numbers in brackets are standard errors of the mean, $n=3$).

Properties	Before incubation			After 9 weeks incubation		
	Treatment			Treatment		
	Control	20 g bark	40 g bark	Control	20 g bark	40 g bark
Total N (%)	0.374	0.350	0.333	0.367(0.005)	0.334(0.004)	0.319(0.003)
Organic N (%)	nd	nd	nd	0.229	0.246	0.263
NH_4^+ -N (%)	nd	nd	nd	0.138(0.002)	0.088(0.011)	0.056(0.006)
Total S (%)	0.031	nd	nd	0.023(0.001)	0.031(0.001)	0.033(0.001)
pH	8.1	7.4	6.9	8.5(0.15)	8.0(0.16)	7.9(0.35)

*nd = no data

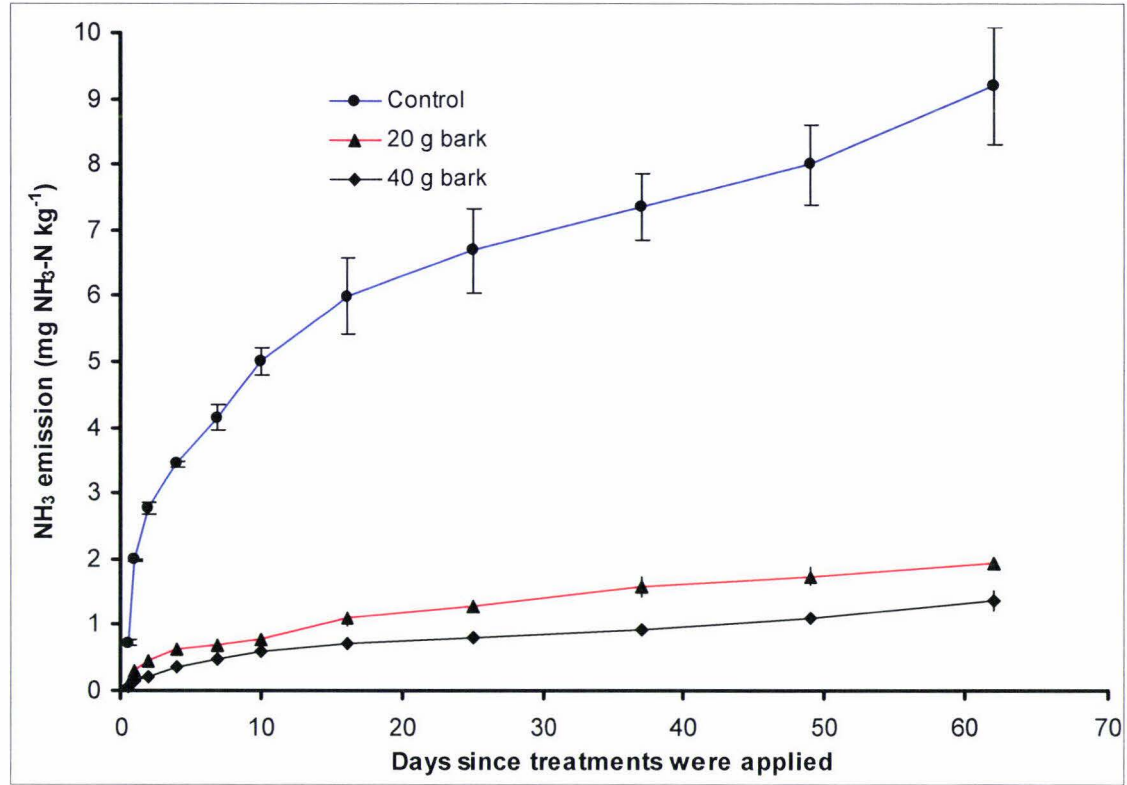


Fig. 5.10 Effect of addition rate of pine bark on cumulative ammonia (NH_3) loss from manure under anaerobic incubation.

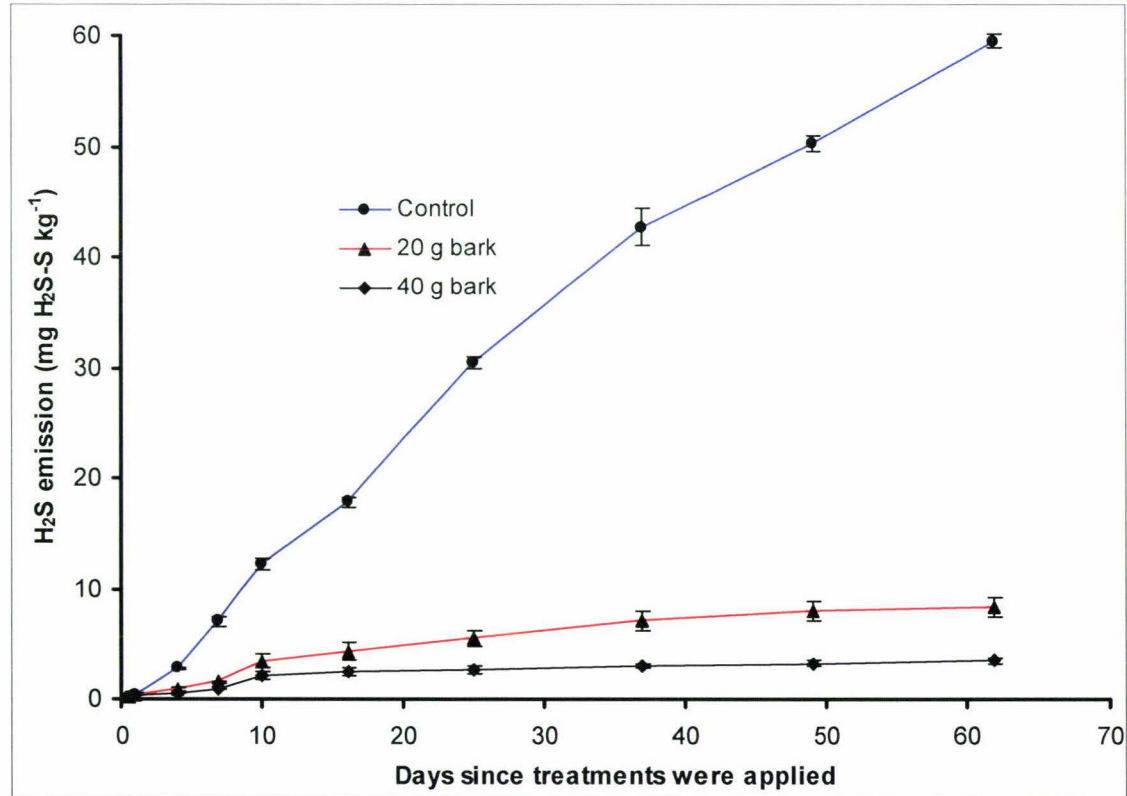


Fig. 5.11 Effect of addition rate of pine bark on cumulative hydrogen sulphide (H_2S) loss from manure under anaerobic incubation.

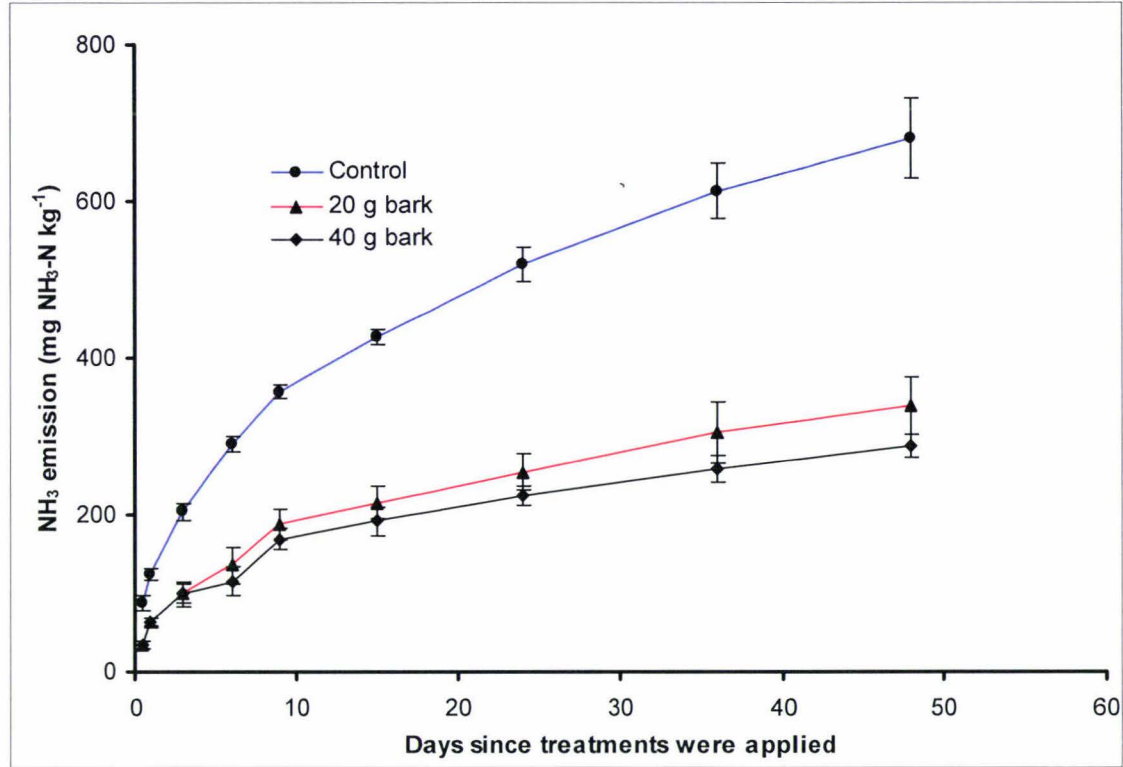


Fig. 5.12 Effect of addition rate of pine bark on cumulative ammonia (NH_3) loss from biosolids under anaerobic incubation.

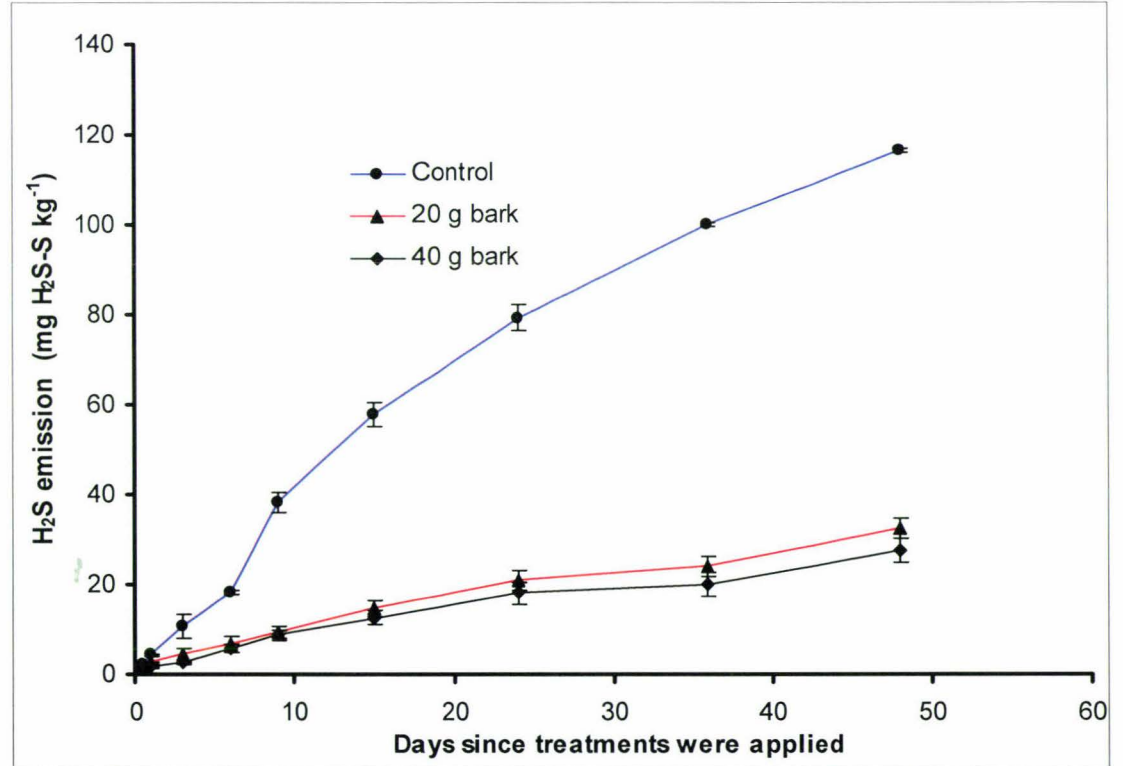


Fig. 5.13 Effect of addition rate of pine bark on cumulative hydrogen sulphide (H_2S) loss from biosolids under anaerobic incubation.

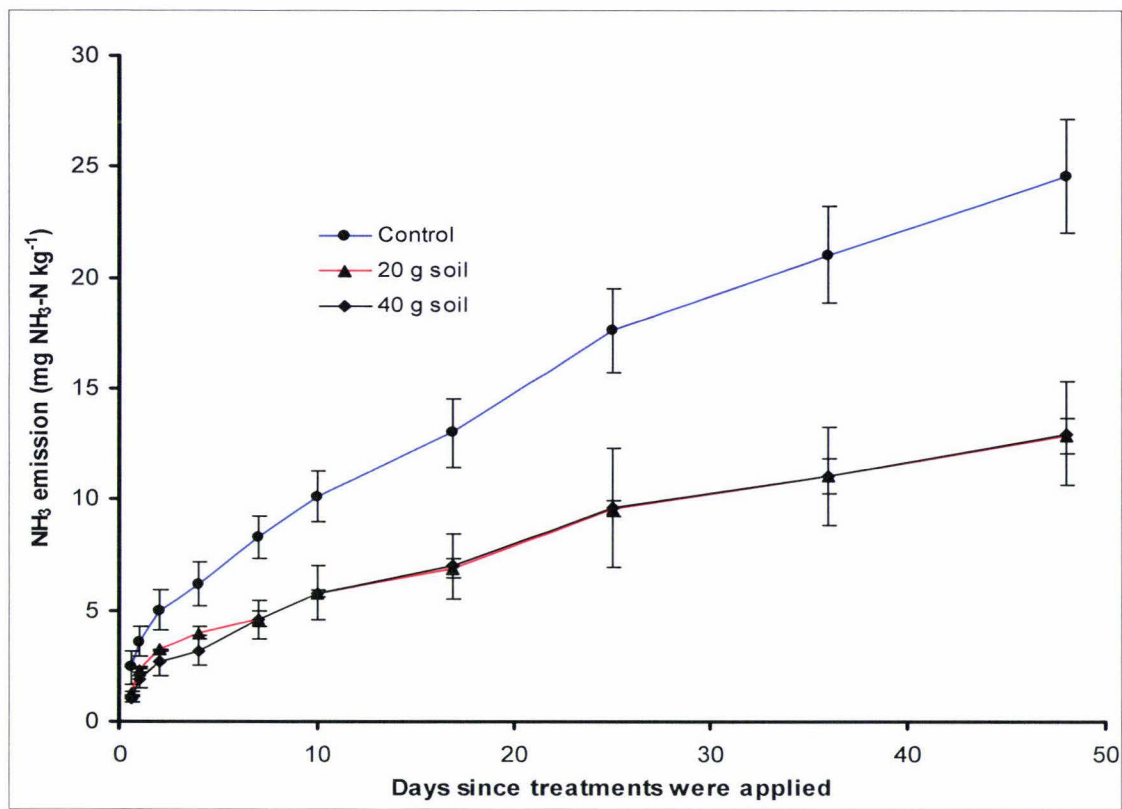


Fig. 5.14 Effect of addition rate of soil on cumulative ammonia (NH_3) loss from manure under anaerobic incubation.

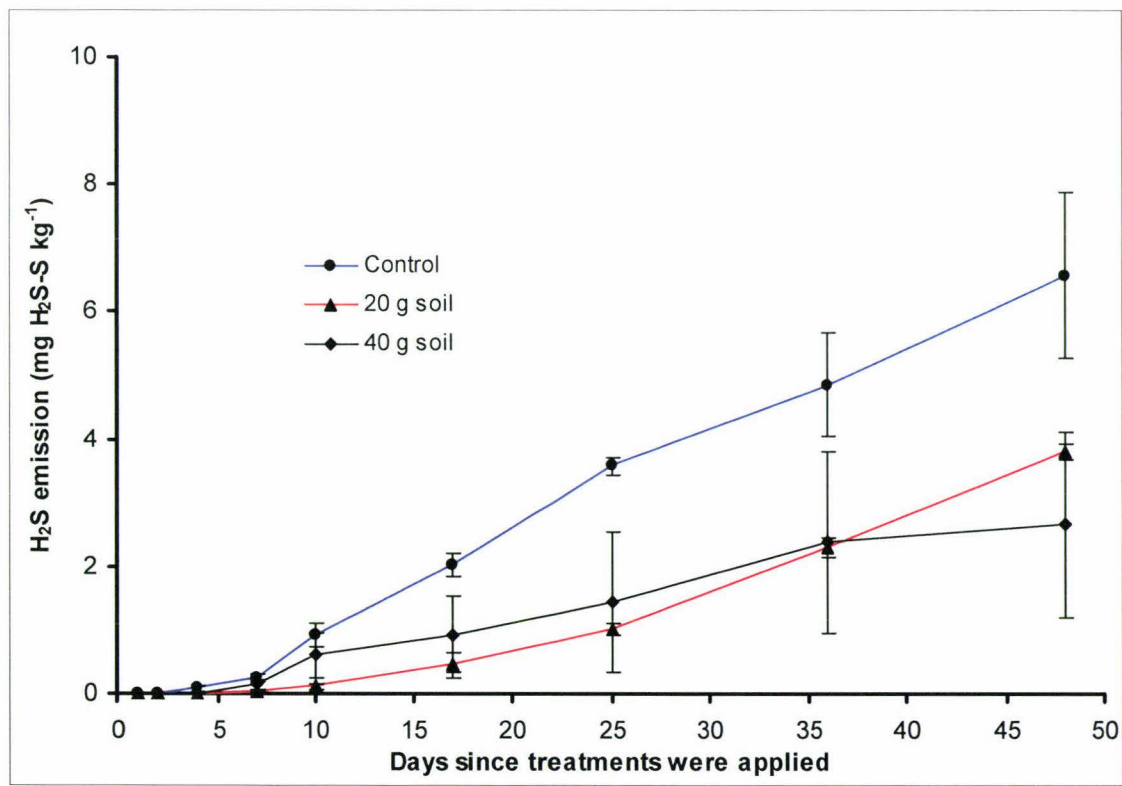


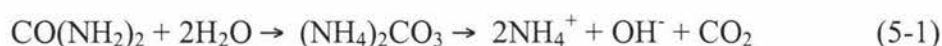
Fig. 5.15 Effect of addition rate of soil on cumulative hydrogen sulphide (H_2S) loss from manure under anaerobic incubation.

5.2 Discussion

5.2.1 The effect of aerobic and anaerobic conditions

Ammonia

The initial high NH_3 volatilisation rates, particularly under aerobic conditions in cow manure (Fig. 5.1), may have been due to rapid hydrolysis of urine in the cow manure. It would be expected that the major proportion of urine N was transformed to mineral NH_4^+ -N. The major N component in urine is urea (Bolan *et al.*, 2004a) and the urea is rapidly (within few hours) hydrolyzed by the enzyme urease (Eq. 5-1).



Hydrolysis of urea results in the release of OH^- ions, which would be expected to increase the pH of the manure. The conversion of NH_4^+ ions to NH_3 (Eq. 5-2), which is favoured under alkaline conditions, is the major process regulating the potential loss of NH_3 from manure. Increases in pH also favour the NH_3 volatilisation losses (Bolan *et al.*, 2004a).



By the end of the 7 week aerobic incubation period the pH of the manure sample also increased from 8.4 to 8.8. Hence, this may be the reason for the increased rate of NH_3 volatilisation during aerobic incubation.

The total N content of the biosolids was higher than the manure, and about 87.5% of the total N in the digested biosolids was in organic form and the balance was NH_4^+ -N (Table 5.2). The initial high rate of NH_3 volatilisation under aerobic conditions (Fig. 5.5) may have been from the inorganic N available in the biosolids because the organic N needs to be mineralized before it becomes volatile.

The mineralization occurs through the activity of proteolytic and deaminative bacteria, initially hydrolysing proteins to peptides and amino acids and finally to NH_4^+ . In the later stages NH_3 can be volatilised from organic N source because the mineralization of

organic N is a biological process and occurs at a slower rate (Muck and Steenhuis, 1982). During the 7 weeks incubation period, organic N in the cow manure and biosolids should have been mineralized and volatilised as NH_3 . Around 50 mg of NH_3 -N was released from a kg of cow manure but 1155 mg was released from a kg of biosolids under aerobic incubation. Under anaerobic incubation 20 mg of NH_3 -N was released from a kg of cow manure but 1056 mg was released from a kg of biosolids. High content of total N in the biosolids, processing method used for the biosolids production and the increase in pH may have increased the cumulative amount of NH_3 volatilisation from biosolids.

There was about two fold difference in cumulative NH_3 volatilisation loss from the manure under aerobic compared to anaerobic conditions (Fig. 5.2). These data agreed with results from previous studies with poultry manure rich in urea N (e.g., Kirchmann and Witter, 1989; Mahimairaja *et al.*, 1994), suggesting that NH_3 losses from animal manures are typically higher under aerobic than anaerobic storage conditions. The higher loss in NH_3 volatilisation from the manure under aerobic condition than under anaerobic condition (Fig. 5.2) may have been a consequence of the higher manure pH observed under aerobic conditions (Table 5.6). Previous studies found that the increased NH_3 emission from aerated manure was due to a higher pH as alkaline conditions developed (Mahimairaja *et al.*, 1994). Kirchmann and Witter (1989) suggested that reduced NH_3 emission in the anaerobic animal manures may be caused by acids that were formed due to fermentation of organic C under anaerobic conditions.

The low losses of NH_3 from organic matter rich manure observed in this study could be due to an equilibrium between dissolved and exchangeable NH_4^+ ions, which are held on the exchange sites of the organic matter in cow manure, the latter being unavailable for volatilisation. Kirchmann and Lundvall (1998) also found that only a very small proportion of (0.1% of the total initial) cattle dung N was lost through NH_3 volatilisation under aerobic decomposition conditions and reported no N loss from anaerobic dung during 7 months storage.

Ammonia emission from biosolids was high during the first two weeks of the aerobic incubation and thereafter the rate of NH_3 emission was increased under anaerobic conditions than the aerobic conditions. Hence, the NH_3 emission from biosolids after

two weeks incubation may have come from the organic nitrogen in the biosolids. The biosolids pH was higher after the anaerobic incubation than the aerobic incubation. This may be the reason for the higher rate of NH_3 emission observed under anaerobic incubation after 2 weeks because the rate of NH_3 volatilisation is highly dependant on pH. NH_3/NH_4 ratio increases with pH, thereby increasing the volatilisation (Moore *et al.*, 1995).

Hydrogen sulphide

As expected, emissions of H_2S from cow manure and biosolids were significantly higher under anaerobic than under aerobic conditions (Fig. 5.3 and 5.7). The rapid release of H_2S , under anaerobic conditions may have been due to the reduction of sulphates in the manure in the presence of readily available C sources which acted as a reducing agent. It was also reported that the addition of elemental S to manure samples rich in organic C (e.g., poultry manure) during the preparation of sulphur-compost results in the release of H_2S , especially under anaerobic conditions (Mahimairaja *et al.*, 1994).

Around 9 mg of H_2S -S was released from a kg of cow manure but 150 mg was released from a kg of biosolids under anaerobic incubation. The larger amount of H_2S released from biosolids than manure was probably due to the higher sulphur content in the biosolids than manure (Tables 5.6 and 5.7). Under aerobic incubation 6 mg of H_2S -S was released from a kg of biosolids (Fig. 5.3 and 5.6). The total S loss through H_2S emissions amounted to about 1.8% of the initial manure S under anaerobic conditions but it was around 7.8% from biosolids. The safety of worker's handling stored manures should be seriously considered and protected, as H_2S could be emitted at high concentrations when manure is taken from anaerobic storage and applied to the fields.

5.2.2 Effect of natural amendments on gaseous emission

Manure

The beneficial effect of organic-rich amendment materials in reducing NH_3 volatilisation is attributed to direct absorption of NH_4^+ ions and NH_3 (Witter and Kirchmann, 1989; Al-Kanani *et al.*, 1992), acidification of the manure sample and/or enhanced microbial N immobilization (Kirchmann and Witter, 1989; Phillips *et al.*, 1999). In this study the reduction in NH_3 loss (Fig. 5.4) was probably caused by the

immobilization of NH_4^+ ions by the wood materials due to their high C/N ratios (Table 5.3). For example, recently Bolan *et al.* (2004b) have demonstrated that treatment of farm effluent with pine bark achieves a considerable reduction in the concentration of N, which they attributed to immobilization of N by the carbon rich bark material (C/N ratio 265:1). Net immobilization of N occurs when the manure C/N ratio is ≥ 15 (Castellanos and Pratt, 1981), so immobilization would be expected in this experiment where the initial C/N ratios of all treatments except soil were higher than 15. This can be supported by the lower amounts of NH_4^+ ions that were measured in the bark-amended manure compared to the unamended manure, while the concentrations of total N were similar at the end of the experiment (Table 5.6). Increasing the proportion of pine bark additions to manure resulted in a higher C/N ratio, and the observed decrease in NH_3 volatilisation could be explained by increase in N immobilization (Fig. 5.10).

Crushed pine bark has a large total surface area and cation exchange capacity. NH_4^+ ions and organic N compounds can be readily adsorbed onto surfaces, as demonstrated by the sorption of odorous compounds by pine bark that has been found to be one of the important mechanisms in the removal of odours by biofilter (Luo and van Oostrom, 1997). This study was not designed to specifically determine the relative effectiveness of the amendments to achieve adsorption and immobilization.

The reduction in NH_3 volatilisation observed by addition of soil (Figs. 5.4 and 5.13) is also likely to be due to soil's exchange capacity for NH_4^+ ions. For example, Selvarajah *et al.* (1989) obtained an inverse relationship between the NH_3 volatilisation and CEC of a number of soils, which they attributed to increased retention of NH_4^+ onto the cation exchange sites. Similar amounts of NH_4^+ ions in soil-amended manure and unamended manure after incubation (Table 5.4) would again suggest the adsorption of NH_4^+ ions played an important role in reducing NH_3 volatilisation. The addition of soil decreased the quantity of dissolved NH_4^+ ions, and thus the quantity of equilibrated NH_3 gas available for NH_3 volatilisation.

The pH of treated manure was consistently above 7 and the addition of natural materials decreased manure pH values slightly (Tables 5.8 and 5.9). Reductions of pH may be one of the reasons causing lower NH_3 volatilisation loss in the treated manure than in the unamended control.

Similar to the reduction of NH_3 volatilisation, H_2S losses can also be reduced by immobilization or absorption of the mineralized S from the manure by addition of C-rich materials, such as pine bark (Fig. 5.11) and soil particles (Fig. 5.13). Biofilter containing C-rich pine bark have been used successfully to reduce the emission of gaseous S compounds (Luo, 2001; Luo and Agnew, 2001). Similarly soil has a substantial capacity for sorption of H_2S (Smith *et al.*, 1973), and H_2S produced from decomposing cow manure may also have been converted to metallic sulphides (e.g., FeS) when the manure was amended with soil.

Biosolids

The driving force for the volatilisation of NH_3 from biosolids is the difference in partial pressure of NH_3 between the liquid phase and atmosphere. The partial pressure of NH_3 in the liquid phase is controlled by the pH and NH_4^+ ion concentration (Lauer *et al.*, 1976), and lowering the pH of the biosolids or amount of NH_4^+ ions will reduce the volatilisation of NH_3 . It is understood that the beneficial effect of organic-rich amendment materials in reducing NH_3 volatilisation is attributed to direct absorption of NH_4^+ ions and NH_3 , and acidification of the biosolids resulting from stimulation of microbial activity by the added C and/or enhanced microbial N immobilization (Subair *et al.*, 1999). In this study the pattern of NH_3 volatilisation varied with the treatments (Fig. 5.8). The reduction in NH_3 loss (Fig. 5.8) was probably caused by the immobilization of NH_4^+ ions by the wood materials. Increasing the proportion of pine bark additions to biosolids resulted in a higher C/N ratio, and increase in N immobilization. It could be the reason for further decrease in NH_3 volatilisation.

The pH of treated biosolids was consistently above 7 and the addition of natural materials decreased manure pH values slightly (Table 5.10). Reductions of pH may be one of the reasons causing lower NH_3 volatilisation loss in the treated biosolids than untreated. Similar to the reduction of NH_3 volatilisation, H_2S losses can also be reduced by immobilization or absorption of the mineralized S from the biosolids by addition of C-rich materials, such as pine bark (Fig. 5.15).

As these experiments were conducted under controlled laboratory conditions, appropriate care should be taken while extrapolating the results to natural manure and biosolids storage systems. The technological aspects of the use of natural materials to

manage manure N and S dynamics at an operational scale have not been addressed in this study.

Chapter 6: Conclusions and future directions

6.1 Introduction

The general objective of this study was to quantify the gaseous emissions of NH_3 and H_2S from organic by-products such as cow manure and biosolids and to assess the suitability of pine bark, soil, wood shavings and saw dust (locally available natural materials) as media for mitigating these emissions. The initial study was a field observation to monitor gaseous emissions from manure bunkers. The ability of amendment with natural materials, such as soil and wood shavings, to control gas emission from bunkers also was investigated. Following this, a series of laboratory experiments were carried out focussing on the quantification of NH_3 and H_2S gas emissions and more detailed evaluation of the natural materials for their ability to control the gas emissions. This Chapter summarises the findings of these studies.

6.2 Field observation

Nutrient balances

It was shown that the natural materials used (soil, wood shavings and a combination of soil/wood shavings) were all effective at capturing nutrients (N and S) from the manure in the bunker. The benefit of this amendment is greater nutrient enrichment of the final material, which makes it more useful for subsequent land application. Use of soil for bunker bedding appears to be a viable option and the most cost effective, showing more promise for nutrient conservation than other amendments.

Gaseous losses

It appeared that the soil was the most effective bedding material for reduction of gaseous emissions (NH_3 and H_2S) from the manure. This corroborates with the observation that the soil retained the most manure N and S after nine months in the bunker. Measurements from the manure bunkers also showed that there was less greenhouse gas (e.g., nitrous oxide) emission from the treated manure bunkers.

6.3 Quantification of gaseous emission

The NH_3 emission rate reached the peak value within two days of the experiment and declined rapidly under both aerobic and anaerobic incubation conditions from manure

and biosolids. The initial high rate of NH_3 volatilisation under aerobic conditions may have been due to rapid hydrolysis of urine in the cow manure and from the inorganic N available in the biosolids, because the organic N needs to be mineralized before it becomes volatile. In the later stages, NH_3 can be volatilised as a result of biological processes mineralizing the organic N. The total N losses are presented in Table 6.1.

The emissions of H_2S were significantly higher from anaerobic incubation than aerobic incubation from both wastes. The rapid release of H_2S , under anaerobic conditions may have been due to the reduction of sulphates in the manure and biosolids in the presence of readily available C sources which acted as reducing agents. The total S losses are presented in Table 6.2.

Table 6.1 Total Nitrogen (N) loss through ammonia (NH_3) volatilisation from manure and biosolids during aerobic and anaerobic incubation (mg kg^{-1} waste)

	Aerobic condition		Anaerobic condition	
	Total N loss (mg kg^{-1})	% of the initial N content	Total N loss (mg kg^{-1})	% of the initial N content
Manure	49.5	1.2	20.5	0.52
Biosolids	1156	1.9	1057	1.71

Table 6.2 Total Sulphur (S) loss through hydrogen sulphide (H_2S) volatilisation from manure and biosolids during aerobic and anaerobic incubation (mg kg^{-1} waste)

	Aerobic condition		Anaerobic condition	
	Total S loss (mg kg^{-1})	% of the initial S content	Total S loss (mg kg^{-1})	% of the initial S content
Manure	Insignificant	-	9.3	1.8
Biosolids	6.1	0.3	150.7	7.8

6.4 Medium selection

The second stage of the thesis involved an investigation of amendment of manure and biosolids with four materials (soil, pine bark, sawdust and wood shavings) to control NH_3 and H_2S emission. All four materials had an effect on reduction of the NH_3 and H_2S emission. However, pine bark and top soil amendments were most effective in reducing the emissions. NH_3 emission was reduced by 78% under anaerobic conditions when 100g of manure was amended with 20g of bark. The reduction was around 56% in biosolids. Amendment with top soil reduced the NH_3 emission by 50% in manure and 46% in biosolids.

Pine bark reduced the H_2S emission by 80% from manure and by 83.5% from biosolids under anaerobic condition. Amendment with top soil reduced the H_2S emission by 50% from manure and 79% from biosolids.

6.5 Conclusions

Reduction in gaseous NH_3 losses during storage of cow manure and biosolids can be achieved using anaerobic rather than aerobic storage. However, anaerobic storage significantly increases the emission of H_2S , which is highly toxic to animals and humans. Addition of natural materials to cow manure and biosolids reduced the NH_3 and H_2S volatilisation, which can be an effective means of conserving the N and S in both materials. Although all tested substrates were effective in reducing losses of both NH_3 and H_2S , pine bark was found to be the most effective. The reduction was probably caused by immobilization of mineral N and S and adsorption of N and S compounds by the natural amendments. Therefore, the addition of natural materials, such as pine bark and soil, as amendments to cow manure and biosolids during storage offers potential for reducing emissions of NH_3 and H_2S .

6.6 Future direction

Quantification of gaseous emission

Measurement of gaseous emission in the laboratory is easy and less expensive, and this method can be used to measure gaseous emission from any other waste materials. This method could be modified to measure other gaseous emissions such as methane (CH_4) and nitrous oxide (NO_2) from waste materials. Further research is required to quantify

the gaseous emissions from the amended manure and biosolids following their application to land as their nutrient enrichment may result in increased gaseous emission at this stage.

Medium selection

Selecting an appropriate medium to control gaseous emission is critical. Better understanding of the processes operating during the waste storage is necessary. The medium should have suitable nutrient content, water holding capacity, pH, structure and surface texture. Research is required to demonstrate the suitability of locally available materials and to determine their effectiveness.

Because the physical, chemical and biological processes occurring in a medium are complex, accurate information on design and modelling parameters are not available. In order to design an efficient amendment strategy to meet required performance criteria, information is required about the removal efficiency of a chosen medium treating the contaminant of interest (Devinny *et al.*, 1999). Data from this study will be used to develop practical and cost effective control technologies.

References

- ACGIH (American Conference of Governmental Industrial Hygienists). (1991). Documentation of the Threshold Limit Values, 6th ed., Vol II. ACGIH, Cincinnati, OH: 786-788.
- Al-Kanani, T., E. Akochi, A.F. MacKenzie, I. Alli and S. Barrington. (1992). Organic and inorganic amendments to reduce ammonia losses from liquid hog manure. *Journal of Environmental Quality* 21: 709-715.
- Allan, C.C. (1996). Quality improvement of biosolids by ferrate (VI) oxidation of offensive odour compounds. *Water Science and Technology* 33: 119-130.
- Amore, J.E. (1992). Odour standards in squeeze-bottle kits for matching quality and intensity. *Water Science and Technology* 25: 1-9.
- Amore, J.E., Jr. J.W. Johnston and M. Ruben. (1964). The stereochemical theory of odour. *Scientific American* 21: 42-49.
- APHA. (1995). *Standard Methods for the Examination of Water and Wastewater*, 19th edition, American Public Health Association, Washington, D.C.
- Ball, P.R. and R.W. Tillman. (1994). Efficient use of nutrients in the intensive pastoral farming industry in New Zealand. In: *The efficient use of fertilizer in a changing environment – reconciling productivity with sustainability*. Eds: Carrie, L.D. and P. Loganathan. Pp. 96-117. FLR, Massey University, Palmerston North, New Zealand.
- Banwart, W.L. and J.M. Bremner. (1975). Formation of volatile sulfur compounds by microbial decomposition of sulfur-containing amino acids in soils. *Soil Biology and Biochemistry* 7: 359-364.
- Banwart, W.L. and J.M. Bremner. (1976). Evolution of volatile sulfur compounds from soils treated with sulfur containing organic materials. *Soil Biology and Biochemistry* 8: 439-443.
- Barth, C.L., L.F. Elliot and S.W. Melvin. (1984). Using Odour Control Technology to Support Animal Agriculture. *Transactions of the American Society of Agricultural Engineers* 27 (3): 859-864.
- Battye, R., W. Battye, C. Overcash and S. Fudge. (1994). Development and Selection of Ammonia Emission Factors. Final Report. EC/R Inc., Durham, NC. EPA.

- Contract Report #68-D3-0034, U.S. Environmental Protection Agency, Research Triangle Park, NC. Pp. 111.
- Beauchamp, R.O., Jr. J.S. Bus, J.A. Popp, C.J. Boreiko and D.A. Andjelkovich. (1984). A critical review of the literature on hydrogen sulphide toxicity. *Critical Reviews in Toxicology* 13(1): 25-97.
- Berg, W. and G. Hornig. (1997). Emission reduction by acidification of slurry—Investigations and assessment. Pp. 459–466. In: *Proceedings of the International Symposium on Ammonia and Odour Emissions from Animal Production*, Vinkeloord, the Netherlands. 6–10 Oct. 1997. NVTL, Rosmalen, the Netherlands.
- Bernd, F. F. and W. Koster. (1998). Odour emission capacity of wastewaters – standardization of measurement method and application. *Water Science and Technology* 38(3): 61-69.
- Bhambhani, Y. and M.Singh. (1985). Effects of hydrogen sulphide on selected metabolic and cardio respiratory variables during rest and exercise. Report submitted to Alberta Worker's Health and Safety and Compensation. June, 1985.
- Bohn, H.L. (1992). Consider biofiltration for decontaminating gases. *Chemical Engineering Progress* 4: 34-40.
- Bolan, N.S., L. Wang and D.C. Adriano. (2004b). Nutrient removal from farm effluents. *Bioresource Technology* 94: 251-260.
- Bolan, N.S., S. Saggar, J. Luo, R. Bhandral and J. Singh. (2004a). Gaseous emissions of nitrogen from grazed pastures: processes, measurements and modelling, environmental implications and mitigation. *Advances in Agronomy* 84: 37-120.
- Bolan, N.S., S. Saggar, J. Singh and R. Bhandral. (2003). Gaseous emission of nitrogen from farm effluents: economic and environmental implications. *New Zealand Land Treatment Collective Annual Conference Proceedings*, Wellington, New Zealand, Technical Session No 24: 92-101.
- Bonnin, C., A. Laborie and H. Paillard. (1990). Odour nuisance created by sludge treatment: problems and solutions. *Water Science and Technology* 22: 65-74.
- Bowker, R.P.G. (1999). Activated sludge diffusion; clearing the air on an overlooked odour control technique. *Water Science and Technology* 11: 30-35.
- Brennan, B. (1993). Odour nuisance. *Water Waste Treatment* 36: 30-33.

- Brenneman, K.A., R.A. James, E.A. Gross and D.C. Dorman. (2000). Olfactory neuron loss in adult male CDrats following sub chronic inhalation exposure to hydrogen sulphide. *Toxicologic Pathology* 28(2): 326-333.
- Busca, G. and C. Pistarino. (2003). Technologies for the abatement of sulphide compounds from gaseous streams: A comparative overview. *Journal of Loss Prevention in the Process Industries* 16: 363-371.
- Bussink, D.W. and O. Oenema. (1998). Ammonia volatilisation from dairy farming systems in temperate areas: A review. *Nutrient Cycling in Agroecosystems* 51: 19-33.
- Campagna, D., M.D. Lewin, S.G. Inserra, B.L. Phifer and M.C. White. (2000). Impact of ambient hydrogen sulfide and total reduced sulphur levels on hospital visits for respiratory disease in Dakota City and South Sioux City, Nebraska, during 1998 and 1999; Interim Results. 12th Annual Meeting of the International Society for Environmental Epidemiology Buffalo, New York, USA, August 2000.
- Carperter, A. and N. Beecher. (1997). Wood ash finds niche in biosolids composting. *Biocycle* 38(1): 37-39.
- Castellanos, J.Z. and P.F. Pratt. (1981). Mineralization of manure nitrogen. Correlation with laboratory indexes. *Soil Science Society of American Journal* 45: 354-357.
- Clemens, J. and H.J. Ahlgrimm. (2001). Greenhouse gases from animal husbandry: mitigation options. *Nutrient Cycling in Agroecosystems* 60: 287-300.
- Collins, J. and D.Lewis. (2000). Hydrogen sulphide evaluation of current California air quality standards with respect to protection of children. Prepared for California Air Resources Board, California Office of Environmental Health Hazard Assessment.
- de Klein, C.A.M. and S.F. Ledgard. (2001). An analysis of environmental and economic implications of nil- and restricted-grazing systems designed to reduce nitrate leaching from New Zealand dairy farms. I. Nitrogen losses. *New Zealand Journal of Agricultural Research* 44: 201-215.
- de Klein, C.A.M., R.R. Sherlock, K.C. Cameron and T.J. van der Weerden. (2001). Nitrous oxide emissions from agricultural soils in New Zealand - a review of current knowledge and directions for future research. *Journal of the Royal Society of New Zealand* 31: 543-574.

- Devinny, J.S., M.A. Deshusses and T.S. Webster. (1999). *Biofiltration for air pollution control*. Boca Raton, CRC Press LLC.
- Dewes, T., L. Schmitt, E. Valentin and E. Ahrens. (1990). Nitrogen losses during the storage of liquid livestock manures. *Biological Wastes* 31:241–250.
- Donham, K.J. (1990). Relationships of air quality and productivity in intensive swine housing. *Journal of Agricultural Practice* 10: 15–18.
- Donham, K.J. and K.E. Gustafson. (1982). Human occupational hazards from swine confinement. *Annual American Conference of Governmental Industrial Hygienists* 2: 137-142.
- Eaton, A.D., L.S. Clesceri and A.E. Greenberg. (1995). *Standard Methods for the Examination of Water and Wastewater* (19th edition.) American Public Health Association. Washington DC, USA.
- Edwards, S. and B. Burdon. (2003). Land treatment – managing the risk and achieving sustainable land use. *New Zealand Land Treatment Collective Annual Conference Proceedings*, Wellington, New Zealand, Technical Session No 24, Pp. 127-132.
- Einarsen, A.M., A. Aesoy, A.I. Rasmussen, S. Bungum and M. Sveberg. (2000). Biological prevention and removal of hydrogen sulphide in sludge at Lillehammer wastewater treatment plant. *Water Science and Technology* 41: 175-187.
- Evanylo, G.K. (1999). *Agricultural land application of biosolids in Virginia: risks and concerns*. Virginia Cooperative Extension, publication Pp. 452-304.
- Freney, J.R., J.R. Simpson and O.T. Demmead. (1983). *Gaseous losses of nitrogen from plant – soil systems* (Eds. J.R. Freney and J.R. Simpson). P. 1-12. (Martinus Nijhoff/Dr. W. Junk Publishers: The Hague, The Netherlands).
- Freney, J.R., O.T. Denmead, I. Watanabe and E.T. Craswell. (1981). Ammonia and nitrous oxide losses following applications of ammonia sulphate to flooded rice. *Australian Journal of Agricultural Research* 32: 37–45.
- Goldstein, N. (2001). New frontiers for odour research. *BioCycle* 42 (9): 46-51.
- Goldstein, N. and R. Steuteville. (1995). Biosolids composting maintains steady growth. *BioCycle* 36 (12): 49-60.
- Gostelow, P., S.A. Parsons and R.M. Stuetz. (2001). Odour management for sewage treatment works. *Water Research* 35: 579-597.

- Hammond, E.G., C. Heppner and R. Smith. (1989). Odour of swine waste lagoons. *Agriculture, Ecosystems and Environment* 25: 103–110.
- Hartung, J. and V.R. Phillips. (1994). Control of gaseous emissions from livestock buildings and manure stores. *Journal of Agricultural Engineering Research* 57: 173–189.
- Haug, R.T. (1980). *Compost engineering principles and practice*. Lancaster, PA, Technomic Publishing Co.
- Haynes, R.J. and P.H. Williams. (1993). Nutrient cycling and soil fertility in the grazed pasture ecosystem. *Advances in Agronomy* 49: 119-199.
- Haynes, R.J. and R.R. Sherlock. (1986). Gaseous losses of Nitrogen. In: Haynes, R.J. ed. *Mineral Nitrogen in the Plant-Soil System*, Orlando Academic Press: Pp. 242-302.
- Hepner, S., B. Striebig, R. Regan and R. Giani. (2002). Odour generation and control from the autothermal thermophilic aerobic digestion (ATAD) process. *Odours and Toxic Air Emissions proceedings*. Water Environment Federation.
- Higgins, M.J., S.N. Murthy, W.E. Toffey, B. Striebig, S. Hepner, D. Yarosz and S. Yamani. (2002). Factors affecting odour production in Philadelphia Water Department biosolids. *Odours and Toxic Air Emissions proceedings*. Water Environment Federation.
- Hobbs, P.J., T.H. Misselbrook and T.R. Cumby. (1999). Production and emission of odours and gases from ageing pig waste. *Journal of Agricultural Engineering Research* 72: 291-298.
- Horan, N. and M. Catala. (1998). New development in odour control. *Water and Waste Treatment* 41: 28-29.
- Hutchinson, G.L., A.R. Mosier and C. E. Andre. (1982). Ammonia and Amine Emissions from a Large Cattle Feedlot. *Journal of Environmental Quality* 11(2): 288-293.
- Hvitved-Jacobsen, T., J. Vollertsen and N. Tanaka. (2000). An integrated aerobic/anaerobic approach for prediction of sulphide formation in sewers. *Water Science and Technology* 41: 107-115.
- Isermann, K. (1994). Agriculture's share in the emission of trace gases affecting the climate and some cause-oriented proposals for sufficiently reducing this share. *Environmental Pollution* 83: 95-111.

- Jaakkola, J.J., V. Vilkkä, O. Marttila, P. Jappinen and T. Haahtela. (1990). The South Karelia Air Pollution Study. The effects of malodorous sulphur compounds from pulp mills on respiratory and other symptoms. *American Reviews of Respiratory Disease* 142(6 Pt 1): 1344-50.
- Jappinen, P., V. Vilkkä, O. Marttila and T. Haahtela. (1990). Exposure to hydrogen sulphide and respiratory function. *The British Journal of Industrial Medicine* 47(12): 824-8.
- Jiang, J.K. and R. Kaye. (2001). Sampling techniques for odour measurement. In: *Odours in Wastewater Treatment, Measurement, Modelling and control*, Edited by Steutz, R. and Frechen, F. Pp. 95-119.
- Karlsson, S. (1996). Measures to reduce ammonia emissions during storage of animal manure. JTI-rapport 228. Jordbrukstekniska institutet. Uppsala. Sweden.
- Karlsson, S. and K.H. Jeppsson. (1995). Deep litter in livestock buildings and field storages. JTI-rapport 204. Jordbrukstekniska institutet. Uppsala. Sweden.
- Kilburn, K.H. and R.H. Warshaw. (1995). Hydrogen sulphide and reduced-sulphur gases adversely affect neurophysiological functions. *Toxicology and Industrial Health* 11(2): 185-97.
- Kirchmann, H. and A. Lundvall. (1998). Treatment of solid animal manures: identification of low NH_3 emission practices. *Nutrient Cycling in Agroecosystems* 51: 65-75.
- Kirchmann, H. and E. Witter. (1989). Ammonia volatilisation during aerobic and anaerobic manure decomposition. *Plant and Soil* 115: 35-41.
- Kroodsma, W. and N.W.M. Ogink. (1997). Volatile emissions from cow cubicle houses and its reduction by immersion of the slats with acidified slurry. Pp. 475-483. In: *Proceedings of the International Symposium on Ammonia and Odour Emissions from Animal Production*, Vinkeloord, the Netherlands. 6-10 Oct. 1997. NVTL, Rosmalen, the Netherlands.
- Kustov, V.V. (1967). Means of determining the maximum allowable concentration of toxic products of natural human metabolism (from Russian). In: *General Questions of Industrial Toxicology*, Moscow, Pp. 63-65. National Aeronautics and Space Administration technical translation.

- Lambert, S.D. and K.E. McGrath. (2000). Can stored sludge cake be deodorised by chemical or biological treatment? *Water Science and Technology* 41: 133-139.
- Lambert, S.D., A.L. Beaman and P. Winter. (2000). Olfactometric characterisation of sludge odours. *Water Science and Technology* 41: 49-56.
- Lauer, D.A., D.R. Bouldin and S.D. Klausner. (1976). Ammonia volatilization from dairy manure spread on the soil surface. *Journal of Environmental Quality* 5: 134-141.
- Ledgard, S.F., J.D. Finlayson, J. Gavin, M.B. Blackwell, R.A. Carran, M.E. Wedderburn and N.A. Jollands. (2003). Resource use efficiency and environmental emissions from an average Waikato dairy farm, and impacts of intensification using nitrogen fertiliser or maize silage. *Proceedings of the New Zealand Grassland Association* 65: 185-189.
- Legator, M.S., C.R. Singleton, D.L. Morris and D.L. Philips. (2001). Health effects from chronic low-level exposure to hydrogen sulphide. *Archives of Environmental Health* 56: 123-137.
- Longhurst, B., M.Dexter and A. Ghani. (2003). Vermicomposting of biosolids for beneficial reuse. *New Zealand Land Treatment Collective Annual Conference Proceedings*, Wellington, New Zealand, Technical Session No 24: 183-189.
- Luo, J and A.J. Van Oostrom. (1999). Application of biofilter for odour control. In: *Manual for Wastewater Odour Management*, Edited by NZWWA. Pp. B1-B13.
- Luo, J. (2001). A pilot-scale study on biofilters for controlling animal rendering process odours. *Proceedings of IWA International Conference on Odour and VOCs: Measurement and Control Techniques*. Pp. 521-531. The University of New South Wales, Sydney, Australia. Water Science and Technology.
- Luo, J. and A.J. Van Oostrom. (1997). Biofilters for controlling animal rendering odour – a pilot scale study. *Pure and Applied Chemistry* 69: 2403-2410.
- Luo, J. and M.P. Agnew. (2001). Gas characteristics before and after biofiltration treating odorous emissions from animal rendering processes. *Environmental Technology* 22: 1091-1103.
- Luo, J., M. Kulasegarampillai, N.S. Bolan and A. Donnison. (2004). Control of gaseous emissions of ammonia and hydrogen sulphide from cow manure by

- use of natural materials. *New Zealand Journal of Agricultural Research* 47: 545-556.
- Luo, J., R.W. Tillman and P.R. Ball. (1999). Grazing effects on denitrification in a soil under pasture during two contrasting seasons. *Soil Biology and Biochemistry* 31: 903-912.
- Luo, J., R.W. Tillman and P.R. Ball. (2000). Nitrogen loss through denitrification in a soil under pasture in New Zealand. *Soil Biology and Biochemistry* 32: 497-509.
- Mackie, R.T., P.G. Stroot and V.H. Varel. (1998). Biochemical identification and biological origin of key odour components in livestock waste. *Journal of Animal Science* 76: 1331-1342.
- Mahimairaja, S., N.S. Bolan, M.J. Hedley and A.N. Macgregor. (1994). Losses and transformation of nitrogen during composting of poultry manure with different amendments: An incubation experiment. *Bioresource Technology* 47: 265-273.
- McCrory, D.F. and P.J. Hobbs. (2001). Additives to Reduce Ammonia and Odour Emissions from Livestock Wastes A Review. *Journal of Environmental Quality* 30: 345-355.
- MfE. (1995). Odour management under the resource management act. Ministry for the Environment, Wellington, New Zealand.
- MfE. (2002). 'The New Zealand Waste Strategy'. Ministry for the Environment, Wellington, New Zealand.
- Milby, T.H. (1962). Hydrogen sulphide intoxication. *Journal of Occupational and environmental Medicine* 4(8): 431-437.
- Miner, J. R. (1975b). Management of Odours Associated with Livestock Production. Managing Livestock Wastes, *Proceedings of Third International Symposium on Livestock Wastes*. American Society of Agricultural Engineers. St. Joseph, MI. Pp. 378-380.
- Miner, J.R. and R.S. Stroh. (1976). Controlling feedlot surface emission rates by application of commercial products. *Transactions of the American Society of Agricultural Engineers* 19: 533-538.
- Molloy, S.P. and H. Tunney. (1983). A laboratory study of ammonia volatilisation from cattle and pig slurry. *Irish Journal of Agricultural Research* 22: 37-45.

- Moore, Jr. P.A, T.C.Daniel, D.R.Edwards and D.M.Miller. (1995). Effect of chemical amendments on ammonia volatilisation from poultry litter. *Journal of Environmental Quality* 24: 293-300.
- Muck, R.E. and B.K. Richards. (1980). Losses of manurial N in free-stall barns. *Agricultural Manure* 7: 65-93.
- Muck, R.E. and T.S. Steenhuis. (1982). Nitrogen losses from manure storage. *Agricultural wastes* 4: 41-54.
- Mumpton, F.A. and P.H. Fishman. (1977). The application of natural zeolites in animal science and aquaculture. *Journal of Animal Science* 45: 1188-1203.
- Murphy, J. and J.P.Riley (1962). A modified single solution method for the determination of phosphate in natural waters. *Analytica Chemica Acta* 27: 31-36.
- Murthy, S., T. Sadick, L. McConnell, C. Peot, W. Bailey, J. Novak and D. Glindemann. (2002). Mechanisms for odour generation during lime stabilization. *Odours and Toxic Air Emissions proceedings*. Water Environment Federation.
- Novak, J., D. Glindemann, S.Murthy, S. Gerwin and C. Peot. (2002). Mechanisms for generation and control of trimethyl amine and dimethyl disulfide from lime stabilized biosolids. *Odours and Toxic Air Emissions proceedings*. Water Environment Federation.
- NZWWA. (2000). *Manual for wastewater odour management* (2nd edn.). Auckland, New Zealand Water and Wastes Association.
- NZWWA. (2003). *Guidelines for the safe application of biosolids to land in New Zealand*, Volume 1: guidelines. New Zealand Water and Wastes Association.
- O'Neill, D.H. and V.R. Phillips. (1992). A review of the control of odour nuisance from livestock buildings: part 3, properties of the odorous substances which have been identified in livestock wastes or in the air around them. *Journal of Agricultural Engineering Research* 34: 23-50.
- Ottengraf, S.P.P. and A.H.C. van den Oever. (1983). Kinetics of organic compound removal from waste gases with a biological filter. *Biotechnology and Bioengineering* 25: 3089-3102.
- Pain, B.F., V.R. Phillips, C.R. Clarkson, T.H. Misselbrook, Y.J. Rees and J.W. Farrent. (1990). Odour and ammonia emissions following the spreading of aerobically-treated pig slurry on grassland. *Biological Wastes* 34: 149-160.

- Pain, B.F., R.B. Thompson, L.C.N. De La Cremer and L. Ten Holte. (1987). The use of additives in livestock slurries to improve their flow properties, conserve nitrogen and reduce odours. *In: Animal manure on grassland and fodder crops. Fertiliser or waste?* Pp. 229–246. Eds. Van der Meer H.G., Unwin R.J., and Ennik G.C. Goes Dijk T.A. Martinus Nijhoff Publishers, Dordrecht, The Netherlands.
- Patni, N.K. and P.Y. Jui. (1991). Nitrogen concentrations in dairy-cattle slurry stored in farm tanks. *Transactions of the American Society of Agricultural Engineers* 342: 609–615.
- Personal Communication, Tom Pow, Herd Home Owner. (2004).
- Peters, J. A. and T. R. Blackwood. (1977). Source Assessment: Beef Cattle Feedlots. EPA-600/ 2-77-107, U.S. Environmental Protection Agency, Research Triangle Park, NC. June. P 101.
- Phillips, V.R., D.A. Cowell, R.W. Sneath, T.R. Cumby, A.G. Williams, T.G.M. Demmers and D.L. Sandars. (1999). An assessment of ways to abate ammonia emissions from UK livestock buildings and waste stores. Part 1: ranking exercise. *Bioresource Technology* 70: 143-155.
- Quemada, M., B. Lasa, C. Lamsfus and P.M. Aparicio-Tejo. (1998). Ammonia volatilisation from surface or incorporated biosolids by the addition of dicyandiamide. *Journal of Environmental Quality* 27: 980-983.
- Reiffenstein, R.J., W.C. Hulbert and S.H. Roth. (1992). Toxicology of hydrogen sulfide. *Annual Review of Pharmacology and Toxicology* 32: 109-134.
- Ritter, W.F. (1989). Odour control of livestock manure: State-of-the-art in North America. *Journal of Agricultural Engineering Research* 42: 51–62.
- Robinson, M.B. and H.Roper. (2003). Volatilisation of Nitrogen from land applied bio solids. *Australian Journal of Soil Research* 41: 711-716.
- Robinson, M.B. and P.J. Polglase. (2000). Volatilisation of Nitrogen from dewatered bio solids, *Journal of Environmental Quality* 29: 1351-1355.
- Rosenfeld, P.E. and C.L. Henry. (2000). Wood ash control of odour from biosolids application. *Journal of Environmental Quality* 29: 1662-1668.
- Roth, S.H. (1993). Hydrogen sulfide. *In: Handbook of Hazardous Materials*. Academic Press. Pp 387-376.

- Ruth, J. H. (1986). Odour thresholds and irritation levels of several chemical substances: a review. *American Industrial Hygiene Association Journal* 47: A142-A151.
- Ryan, J.A., D.R. Keeney and L.M. Walsh. (1973). Nitrogen transformation and availability of an anaerobically digested sewage sludge in soil. *Journal of environmental quality* 2: 489-492.
- Safley, L. M., M. E. Casada, J. W. Woodbury and K. F. Roos. (1992). Global Emissions from Livestock and Poultry Manure. Report No. EPA 1400/1-91/048. U. S. Environmental Protection Agency, Washing D.C. Pp. 145.
- Safley, L.M., D.W. Nelson and P.W. Westerman. (1983). Conserving manurial nitrogen. *Transactions of the American Society of Agricultural Engineers* 26: 1166-1170.
- Schiffman, S.S., J.M. Walker, P. Dalton, T.S. Lorig, J.H. Raymer, D. Shusterman and C.M. Williams. (2000). Potential health effects of odour from animal operations, wastewater treatment and recycling of by products. *Journal of Agromedicine* 7: 7-81.
- Selvarajah, N., R.R. Sherlock, N.P. Smith and K.C. Cameron. (1989). *Proceedings of the workshop on Nitrogen in New Zealand agriculture and Horticulture*. (L. D. Currie and P. Loganathan, eds), Pp.145-156. Massey University, Palmerston North.
- Silverman, S. D., J.L. Whittenberger and J. Muller. (1949). Physiological response of man to ammonia in low concentrations. *Journal of Industrial Hygiene and Toxicology* 31: 74-78.
- Smith, H.O. and A.D. Hochstettler. (1969). Determination of odour thresholds in air using C¹⁴-labelled compounds to monitor concentrations. *Environmental Science and Technology* 3: 169-170.
- Smith, K.A., J.M. Bremner and M.A. Tabatabai. (1973). Sorption of gaseous atmospheric pollutants by soils. *Soil Science* 116: 313-319.
- Sneath, R.W. (2001). Olfactometry and the CEN standard prEN 17352. In: *Odours in Wastewater Treatment, Measurement, Modelling and control*, Edited by Steutz, R. and Frechen, F. Pp. 130-154.
- Soil Survey Staff, (1990). Keys to soil taxonomy. SMSS Technical Monograph No. 19, Virginia Polytechnic Institute and State University, USA, Pp 422.

- Speir, T., J. Horseywell, J. Baker, K. Stuart, H. Percival, G. Yeates and R. McLaren. (2003). Sewage biosolids – safe, beneficial and acceptable use on land – an overview of ESR's collaborative research programme. *New Zealand Land Treatment Collective Annual Conference Proceedings*, Wellington, New Zealand, Technical Session No 24: 65-72.
- Statistics. (2002). *New Zealand in Profile*. Compiled by Statistics, New Zealand.
- Stewart, N., E.G. Beauchamp, C.T. Corke and L.R. Webber. (1975). Nitrate nitrogen distribution in cornland following application of digested sewage sludge. *Canadian Journal of Soil Science* 55: 287-294.
- Stuetz, R.M., P. Gostelow and J. E. Burgess. (2001). Odour perception. *Odours in Wastewater Treatment, Measurement, Modelling and Control*. Edited by Richard .M.Stuetz and Franz –Bernd Frechen. 2001 IWA Publishing. Pp 3-13.
- Stuetz, R.M., R.A. Fenner and G. Engin. (1999). Assessment of odours from sewage treatment works by an electronic nose, H₂S analysis and olfactometry. *Water Research* 33: 452-461.
- Subair, S. (1995). Reducing ammonia volatilisation from liquid hog manure by using organic amendments. M.Sc. thesis. McGill Univ., Montreal, QC, Canada.
- Subair, S., J.W. Fyles and I.P. O'Halloran. (1999). Ammonia volatilisation from liquid hog manure amended with paper products in the laboratory. *Journal of Environmental Quality* 28: 202-207.
- Sutton, A.L., K.B. Kephart, M.W.A. Verstegen, T.T. Canh and P.J. Hobbs. (1999). Potential for Reduction of Odorous Compounds in Swine Manure through Diet Modification. *Journal of Animal Science* 77: 430-439.
- Sutton, M.A., C.J. Place, M. Eager, D. Fowler and R.I. Smith. (1995). Assessment of the magnitude of ammonia emissions in the United Kingdom. *Atmospheric Environment* 29: 1393–1411.
- Svensson, L., 1991. Emissions of ammonia during storage of cattle and pig manure. JTI-meddelande 433, Jordbrukstekniska institutet, Uppsala. Sweden.
- Titko, S., L.W. Jessop, R.D. Seymour, J.D. Baker, C.K. Blaylock and L.J. Roussel. (1996). Mixing ratios in biosolids composting. *BioCycle* 37 (9): 66-68.
- Ulrich, W.F. and J.P. Ford. (1975). Malodour reduction in beef cattle feedlots. In: *Managing Livestock Manure, Proceeding of the 3rd International Symposium*

- on *Livestock Manure*. 369–371. Publ. PROC-275. American Society of Agricultural Engineering, St. Joseph, MI.
- USEPA. (1992). Anthropogenic Methane Emissions in the U. S. Office of Air and Radiation, U. S. Environmental Protection Agency, Washington D. C.
- Valis, I., L.A. Harper, V.R. Catchpoole and K.L. Weier. (1982). Volatilisation of ammonia from urine patches in a subtropical pasture. *Australian Journal of Agricultural Research* 33: 97-107.
- Van der Eerden, L.J.M. (1982). Toxicity of ammonia to plants. *Agricultural Environment* 7: 223-235.
- Van der Eerden, L.J.M., P.H.B. de Visser and C.J. van Dijk. (1998). Risk of damage to crops in the direct neighbourhood of ammonia sources. *Environmental Pollution* 102: 49-53.
- Van Langenhove, H. and B. de Heyder. (2001). Biotechnological treatment of sewage odours. In: *Odours in Wastewater Treatment, Measurement, Modelling and Control*. Edited by Steutz, R. and Frechen, F. Pp. 396-414.
- Van Langenhove, H., E. Wuyts and N. Schamp. (1986). Elimination of hydrogen sulphide from odorous air by a wood bark biofilter. *Water Research* 20: 1471-1476.
- Vanhorne, M., L. van den Berge, A. Devreese, E. Tijtgat, L. van Poucke and C. van Peteghem. (1991). Survey of chemical exposures in a viscose rayon plant. *Annals of Occupational Hygiene* 35(6): 619-631.
- Varel, V., H. Niesenaber and B. Byrnes. (1997). Urease Inhibitors reduce ammonia emission from cattle manure. *Proceedings of the International Symposium on Ammonia and Odour Emissions from Animal Production*, Vinkeloord, the Netherlands. 6–10 Oct. 1997 Pp. 721–728. NVTL, Rosmalen, the Netherlands.
- Veijanen, A., M. Lahtipera, R. Paukku, H. Kaariainen and J. Paasivirta. (1983). Recent developments in analytical methods for identification of off-flavour compounds. *Water Science and Technology* 15: 161-168.
- Vella, P. (2002). Potassium permanganate for odour and corrosion control: new products for old problems. *Odours and Toxic Air Emissions proceedings*. Water Environment Federation.
- Verberk, M.M. (1977). Effects of ammonia in volunteers. *International Archives of Occupational and Environmental Health* 39(2): 73-81.

- Vincent, A. (2001). Sources of odours in wastewater treatment. In: *Odours in Wastewater Treatment, Measurement, Modelling and control*, Edited by Steutz, R. and Frechen, F. Pp. 69-92.
- Walker, J.M. (1991). Fundamentals of odour control. *Biocycle* 30(9): 50-55.
- Warburton, D.J., J.N. Scarborough, D.L. Day, A.J. Muehling, S.E. Curtis and A.H. Jensen. (1980). Evaluation of commercial products for odour control and solids reduction of liquid swine manure. In: *Livestock waste: A renewable resource*. Pp. 309-313 American Society of Agricultural Engineering, St. Joseph, MI.
- Whisman, M.L., J.W. Goetzinger, F.O. Cotton and D.W. Brinkman. (1978). Odorant evaluation: A study of ethanethiol and tetrahydrothiophene as warning agents in propane. *Environmental Science and Technology* 12: 1285-1288.
- Whitehead, D.C. (1970). Bulletin 48. Commonwealth Agricultural Bureaux, Hurley, Maidenhead.
- Williams, T.O. (1995). Odours and VOC emissions control methods. *BioCycle* 36 (5): 49-56.
- Williams, T.O. and F.C. Miller. (1992). Odour control using biofilters. *BioCycle* 33(10): 72-77.
- Wilson, G.E., Y.C. Huang and W.Schroepfer. (1980). Atmospheric sublayer transport and odour control. *Journal of Environmental Engineering* 106: 389-401.
- Winter, P. and S.C. Duckham. (2000). Analysis of volatile odour compounds in digested sewage sludge and aged sewage sludge cake. *Water Science and Technology* 41: 73-80.
- Witter, E. and H. Kirchmann (1989). Peat, zeolite and basalt as adsorbents of ammoniacal nitrogen during manure decomposition. *Plant and Soil* 115: 43-52.
- World Health Organization (WHO). (1986). Ammonia. Environmental Health Criteria 54, published under the joint sponsorship of the United Nations Environment Programme, the International Labour Organisation, and the World Health Organization. Geneva.
- World Health Organization (WHO). (1987). Air quality guidelines for Europe. WHO regional publications, European series 23. Denmark.

- Zhu, J. and L.D. Jacobson. (1999). Correlating microbes to major odorous compounds in swine manure. *Journal of Environmental Quality* 28: 737–744.
- Zhu, J., D.S. Bundy, L. Xiwei and N. Rashid. (1997a). The hindrance in the development of pit additive products for swine manure odour control. A review. *Journal of Environmental Science and Health A* 32: 2429–2448.