

IMPERIAL COLLEGE LONDON

DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING

CENTRE FOR ENVIRONMENTAL CONTROL AND WASTE
MANAGEMENT

**QUANTIFYING THE AGRONOMIC VALUE OF
BIOSOLIDS AND BIOWASTES**

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ABSTRACT

Predicting N release in agricultural soils amended with organic residuals is essential to ensure there are sufficient nutrients for crops, and minimal losses to the environment. Factors such as moisture, temperature, soil type and organic residuals type may affect the amount of mineralised nutrients. Information is required to describe microbial N immobilisation in biosolids-amended soil, which may vary between soil types influencing extent and rate of nutrient release. Industrial biowastes are increasingly being used as soil amendments as a diversion from landfill disposal; these materials result from a diverse range of processes and vary greatly in physical and chemical characteristics. There is little published or advisory information regarding their agronomic benefit, therefore research is required to quantify their fertiliser value. The aims of this research were to quantify mineralisation of N, and investigate other agronomic benefits of biosolids and biowastes, and to investigate microbial biomass N (MBN) dynamics, with the aim of improving fertiliser guidelines. A field trial was established at the Imperial College field station in Wye, Kent, in spring 2005, to investigate N transformations in contrasting soil types amended with conventional and enhanced treated biosolids. Analysis of MBN in biosolids-amended soil indicated that there were differences in N immobilisation processes in soils of differing fertility status, with greater immobilisation observed in the lower fertility soil in some cases. Despite initial differences in rate of mineralisation and nitrification, overall extent of N release was similar in both soils. A programme of field trials was established at Imperial College Silwood Park campus in 2006-2007 to quantify the agronomic value of a range of industrial biowastes. Biowastes from the vegetable, meat and dairy industries and from aerobic and anaerobic digestion plants were investigated. Yield response and N offtake of perennial ryegrass to biowastes, at five rates of application, in comparison to mineral N fertiliser, was used to calculate the replacement N fertiliser value. The results of a laboratory incubation experiment, to investigate MBN and mineral N in biowastes-amended soil, demonstrated lower recoveries of N in fine textured soil with low stability waste. Denitrification was suspected as the potential mechanism for this observation. Interactions between soil type and biowaste type on N availability, and the implications for gaseous N losses to the environment from biowastes-amended soils require further research.

DECLARATION OF OWN WORK

I declare that this thesis: 'Quantifying the Agronomic Value of Biosolids and Biowastes', is my own work and that the work of others is fully cited and referenced, and/or with appropriate acknowledgement given.

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1 INTRODUCTION AND AIMS

1.1 Background

An estimated 103 million t (fresh weight) of biodegradable wastes are recycled to agricultural land each year in the UK (Gendebien *et al.*, 2001), these are also referred to as organic residuals. Relative quantities of the different types of biodegradable wastes applied to farmland are shown in Table 1.1; approximately 88 % is animal manure, 4% is biosolids from wastewater treatment, 1 % is source segregated compost and 7 % is industrial biowastes. Organic residuals are a valuable resource to farmers in terms of their nutrient and organic matter content, and relying on nutrients from biodegradable waste, rather than chemical fertilisers, represents a sustainable approach to meeting crop requirements (Green Alliance, 2007). The practice of landspreading organic residuals recovers resources, which in the case of industrial wastes and municipal solid wastes used as a feedstock for composting, would have been disposed of in landfill, and is economically advantageous to the waste producer.

Following the banning of disposal of sewage sludge at sea under the EC Urban Waste Water Directive (CEC, 1998), there has been increasing reliance on the agricultural outlet as a management strategy for treated sewage sludge (biosolids). The introduction of the Safe Sludge Matrix (ADAS, 2001), a voluntary agreement between the UK Water Industry and the British Retail Consortium (BRC), has further increased acceptance of recycling biosolids to agricultural land.

Table 1.1 Estimates of quantities of organic residuals recycled to agricultural land annually in the UK.

Type	Fresh weight (x 10 ⁶ t)	Dry solids (x 10 ⁶ t)	Source
Animal manures	90.7	15.7	Gendebien <i>et al.</i> , 2001
Biosolids	4.0	0.9	Defra, 2006
Compost [†]	1.0		Nikitas <i>et al.</i> , 2008
Industrial wastes* (paper production)	7.3 (0.7)		Gendebien <i>et al.</i> , 2001 Gibbs <i>et al.</i> , 2005
Total	103		

[†]Includes source segregated household, municipal non-household and commercial composted waste

*Excludes composted waste

The term 'biowastes', in this thesis, is used to refer to organic residuals from industrial and commercial processes, excluding agriculturally-derived wastes and wastewater treatment sludges. However, 'biowastes' may also be used to refer to biodegradable household and green wastes (WRAP, 2007). Land application of biowastes is regarded as the main potential alternative management route to landfill disposal (Gendebien *et al.*, 2001; Defra, 2007). The diversion of organic residuals from landfill serves to reduce greenhouse gas emissions and is necessary to meet the requirements of the Landfill Directive (CEC, 1999), to achieve a 65 % reduction by 2016 (2020 in the UK) from 1995 levels, in the quantity of biodegradable waste sent to landfill.

The total nutrient concentration in organic fertiliser sources is not a reflection of the actual nutrient availability to crops. Nutrients are in organic, as well as mineral forms, some of which will not be readily mineralisable. The Nitrates Directive (CEC, 1991) places restrictions on the total quantity of N from organic wastes that can be applied in Nitrate Vulnerable Zones (NVZs), and, in addition, the available N supplied must not exceed crop requirements. It is therefore necessary to accurately predict the availability of N from organic residuals, to prevent over application and excess N, which may leach causing environmental damage. Precise applications of N in organic residuals are also important to achieve maximum economic benefit in terms of reduced chemical fertiliser costs and improved crop yields.

The fertiliser value of animal manures and slurries is well understood and explicit guidelines exist for their use in agriculture (MAFF, 2001). The use of biosolids as agricultural soil amendments is also well researched (Hall, 1983a;b; Serna and Pomares, 1991a; Serna and Pomares, 1991b; Hernández *et al.*, 2002; Cogger *et al.*, 1999; Smith and Bellett-Travers, 2001; Smith *et al.*, 2002b; Smith *et al.*, 2003; Breedon *et al.*, 2003; Morris *et al.*, 2003.; Corrêa *et al.*, 2004; Cogger *et al.*, 2004; Tarrasón *et al.*, 2007), and fertiliser guidelines (MAFF, 2000) are currently being updated to take account of the results from recent research. Field trials have demonstrated that the new types of enhanced treated biosolids, introduced by the Safe Sludge Matrix, have different nutrient release characteristics to conventional biosolids products (Cogger *et al.*, 1999; Smith and Bellett-Travers, 2001; Smith *et al.*, 2002b; Morris *et al.*, 2003).

Laboratory studies have shown that soil type influences the rate and degree of mineralisation from conventional and enhanced treated biosolids (Smith *et al.*, 1998b; Breedon *et al.*, 2003), with a more rapid rate of mineralisation and more N mineralised

from biosolids in soils of a higher fertility status. A suggested mechanism for this observation is greater microbial retention of N in soils with lower fertility and a less active microbial population. Therefore, investigation into MBN dynamics in biosolids-amended soils is required for different soil types to test this hypothesis under field conditions, to ascertain whether fertiliser recommendations for biosolids should take into consideration any fundamental biological effects of soil type on N release.

Industrial biowastes are currently spread on agricultural land to divert biodegradable waste from landfill disposal and to gain benefit from recycling of nutrients and organic matter. Para 7A of the Waste Management Licensing Regulations (WMLR) (SI, 2005a) requires that biowastes to be spread on farmland must be of agricultural or ecological benefit. In addition, under the Nitrates Directive (CEC, 1991), the supply of N to crops from fertilisers and organic sources must not exceed crop requirements. However, there is little quantitative research on the properties or agronomic characteristics of biowastes, and the availability of N from these organic sources. As with biosolids it is likely that there are complex interactions between waste type, soil type and environmental conditions which influence the nutrient release characteristics of biowastes. Factors such as pre-treatment, storage and method and timing of application are also important as an additional source of variation when predicting the fertiliser value. In addition, microbial immobilisation of nutrients may restrict availability for crop uptake and influence the extent and rate of mineralisation. It is important to elucidate these interactions to provide reliable advice for the application of biowastes to land to gain maximum agronomic benefit and economic value, and to prevent losses of nutrients to the environment.

1.2 Aims and Objectives

To address the issues identified above the objectives of the research described in this thesis were as follows:

1. To investigate the effects of biosolids type on nutrient availability in amended soil in relation to livestock wastes, which have been extensively investigated;
2. To quantify the N release properties of industrial biowastes relative to sewage sludge and mineral fertiliser;
3. To examine nutrient transfers, including P, K, Mg and S, from biowastes to crops, and to define the characteristics of biowastes conferring agronomic benefit;
4. To investigate the interactions between organic residuals type and soil type on N dynamics under field and laboratory conditions;
5. To characterise the total and mineral nutrient concentrations in a selected range of industrial biowastes;
6. To recommend an approach for investigating agronomic value of biowastes, and to develop a strategic research programme for the further examination of the agronomic benefit of industrial biowastes;
7. To study partitioning within soil microbial biomass for different soil types amended with biosolids and the subsequent influence on N release to crops from biosolids in contrasting fertility systems;
8. To develop preliminary N fertiliser value recommendations for the range of industrial biowastes tested.

2 LITERATURE REVIEW

2.1 Sewage Sludge

Sewage sludge is the residual organic material from urban or domestic wastewater treatment, approximately 1.4 million t dry solids (DS) is produced annually (Defra, 2006a). Sludges are a combination of 'settled sludge' from primary water treatment, 'activated sludge' from a secondary biological treatment process and also a tertiary sludge resulting from further N and P removal processes if these are operated at the treatment works. A high proportion of primary sludge is human faecal matter (Bruce and Evans, 2002). In addition, much of the organic matter in sludge, 25-40 % DS, is microbial biomass that was produced in the treatment plant during biological treatment. Sewage may undergo tertiary treatment processes such as removal of P by dosing with $\text{Ca}(\text{OH})_2$, Al_2SO_4 or FeCl_3 or biological methods, which will result in increased concentrations of P in the sludge.

2.1.1 Management Options

Following implementation of the EC Urban Waste Water Treatment Directive (CEC, 1998), sewage sludge is no longer disposed of at sea, and the various management options in the UK now in place are shown in Figure 2.1 (Defra, 2002; Defra, 2006a).

The Landfill Directive (CEC, 1999) places restrictions on the amount of biodegradable waste such as sewage sludges that can be sent to landfill sites. Consequently, landfill disposal is practised only to a limited extent in the UK, where 1 % of biosolids are disposed of by this route (Figure 2.1).

There are currently 10 sewage sludge incinerators operating in the UK (Gunn, 2004), 19.4 % of sludge is managed by this route. Incineration is one of the most expensive methods of sludge disposal, and 35-40 % of the initial sludge DS remain as non-combustible mineral ash which requires disposal by landfilling. This may become increasingly difficult and expensive if the ash was to be classified as biodegradable waste in the future. However, ash has been shown to be suitable for the manufacture of lightweight aggregates in building products, and this is an area under current research (Chiou *et al.*, 2006; Huang *et al.*, 2007). Although incineration may be beneficial on a local level, it does not necessarily represent the best option on a national level. The total primary energy available in all UK biosolids produced in a year

has been estimated to be only 0.3 % of the national annual consumption (Bruce and Evans, 2002); furthermore, incineration means that the value of biosolids as N and P fertiliser replacements is lost. However, under some circumstances it may be economically feasible to recover up to 75 % of waste water treatment plant inflow P, reducing the quantities in sewage sludge ash (Jeanmaire and Evans, 2001).

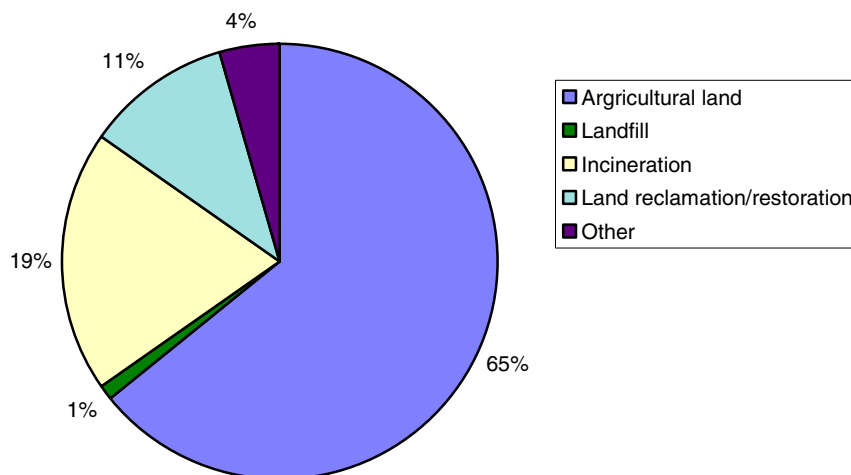


Figure 2.1 UK Sewage sludge management outlets 2004. Data taken from E-digest of Environmental Statistics (Defra, 2006a)

Sewage sludge can be used to improve soil structure, supply organic matter and restore vegetative cover on derelict land (Coker *et al.*, 1982; Walter *et al.*, 2006), and 11 % of sludge is recycled by this method in the UK (Figure 2.1). The 4 % of 'other' outlets may include energy recovery by gasification and aggregate production.

Currently 65 % of sludge is recycled to agricultural land in the UK (Figure 2.1); this is regarded by UK Government as the Best Practicable Environmental Option (BPEO) for management of these materials (Defra, 2007) and is often the most convenient and economically viable option for the water utility. The rationale behind land application of sewage sludge is to treat the waste and to recycle valuable resources. There are, however, potential disadvantages such as odours when landspreading wastes; detrimental effects on soil structure from equipment trafficking; the risk of contamination of soil from potentially toxic elements (PTEs) and organic compounds (e.g. PCBs, dioxins and PAHs) as well as pathogen inputs, representing a potential risk to human and animal health and ecosystem damage (DoE, 1996). Potentially toxic

elements have been reduced in recent years by isolating and regulating the source of the PTEs, and some European countries have set standards for organic contaminants in sewage sludge (Bruce and Evans, 2002). The average concentrations of heavy metals in sludge used in agriculture in the EU are well below the threshold limits set in the European Council Directive on the use of sewage sludge in agriculture (CEC, 1986), and there is a general trend towards a gradual decrease in concentration (COM, 2006).

To address the risk of transfer of pathogens from sludge to crops for human or animal consumption, amongst other measures, the application of raw sewage sludge on agricultural land was phased out under the 'Safe Sludge Matrix' (ADAS, 2001), a voluntary agreement between the UK Water Industry and British Retail Consortium (BRC), and ended altogether in 2001 (Section 2.2.2.1).

There is variable use of biosolids in agriculture within the EU; in a 2006 report to the Council and the European Parliament regarding implementation of Community Waste Legislation for the period 2001-2003 (COM, 2006), seven member states (Belgium-Wallonia, Denmark, Spain, France, Ireland, UK and Hungary) reported that 50 % or more of biosolids produced were applied to land. However, Finland, Sweden and Slovenia spread less than 17 % and Greece, the Netherlands, Belgium, Slovakia and the Czech Republic spread very little or no sludge on agricultural land.

2.1.2 Stabilisation and Dewatering

It is necessary to stabilise and dewater sewage sludge to produce products that are more acceptable for recycling. Dewatering results in sludges that are less bulky, reducing the cost of transport from the treatment plant to the point of disposal or reuse. Stabilisation is necessary to reduce offensive odour and pathogen content (Reed *et al.*, 1995; DoE, 1996) and treated sludges are commonly referred to as 'biosolids'; the term was introduced to present a better image and improve public acceptance of use in agriculture (Bruce and Evans, 2002). Stabilisation may be by biological processes, such as anaerobic or aerobic digestion or composting, chemical processes, such as lime treatment, or physical processes such as pasteurisation or thermal drying (CEC, 2001). The Safe Sludge Matrix (ADAS, 2001) introduced a variety of 'enhanced' treatment processes, such as lime treatment or heating or drying at high temperatures to eliminate pathogens, and reduce risk of transfer of pathogens to crops when biosolids are used in agriculture. Under the Safe Sludge Matrix 'enhanced' treatment

means that biosolids must undergo a 6 log reduction in pathogen content, which is equivalent to background numbers in soil, whereas 'conventionally' treated biosolids are required to have undergone a 2 log reduction. Conventionally treated biosolids are acceptable for land application when there is a barrier such as crop processing, ploughing in or a 'die-off' period to allow the natural attenuation of pathogens in the soil through waiting periods and cropping and harvesting restrictions. The nutritional characteristics of various biosolids types are described in more detail in Section 2.8.3, and frequently used stabilisation processes are described below.

2.1.2.1 Anaerobic Digestion

Sewage sludge treatment is conventionally by mesophilic anaerobic digestion (MAD), which reduces the odour, grease and fibre content of sludge (Chaussod *et al.*, 1985), followed by dewatering to produce a solid cake. Mesophilic anaerobic digestion is the most common treatment process used in the UK (Evans, 2001), and can achieve the 2 log reduction in pathogen content required to meet conventional treatment standards (ADAS, 2001). Anaerobic digestion is the bacterial conversion of organic matter to biogas containing methane, which represents a renewable energy source. The biogas is frequently used at sewage treatment works to generate electric energy, can be fed back into the national grid and is also used to maintain digester temperatures in the plant. Anaerobic digestion takes place in the absence of oxygen (O_2) and produces biogas consisting of approximately 55-80 % methane (CH_4) and 30-35 % carbon dioxide (CO_2), 2-3 % hydrogen sulphide (HS) and small amounts of nitrogen (N_2), carbon monoxide (CO) and hydrogen (H_2) (Torrey, 1979). The mean retention time is a primary digestion period of at least 12 days at a temperature of approximately 35 °C or at least 20 days at 25 °C. This is followed, in both cases, by a secondary batch operated stage, which is not heated, to further reduce pathogens and allow residual gas collection and some consolidation (DoE, 1996). Digested sludge may be dewatered by a variety of methods, such as filter pressing or centrifugation to produce cake (CEC, 2001). This typically increases the dry solids (DS) content from approximately 4 % to 25 %.

2.1.2.2 Aerobic Digestion

Aerobic digestion is biological digestion of sludge in the presence of O_2 , energy is required to aerate the sludge until destruction of organic matter has occurred, but the process is autothermic due to heat generation from the metabolic activity of

microorganisms (CEC, 2001). The process is usually operated thermophilically at a minimum temperature of 55 °C for at least 4 hours, with a mean retention time of 7 days (DoE, 1996). Aerobic digestion produces a less stable product than anaerobic digestion. Aerobic digestion of sewage sludge is not used in the UK but is employed in other European countries such as France, Finland, Denmark and Belgium (CEC, 2001; Evans, 2001).

2.1.2.3 Composting

Composting is aerobic degradation of bulky organic matter to produce a stabilised and dewatered product. Raw sludge can be used as a feed material, and blended with an appropriate bulking agent. Bulking agents such as wood chips, sawdust, animal manure, bark, leaves, paper and straw are generally required to adjust the moisture content to between 50-60% (Tester *et al.*, 1977; CEC, 2001). Requirements for the process are DS contents between 12-50 %, O₂ at 10-15 %, C:N ratio between 26:1 and 30:1, volatile solids (VS) over 30 % and pH 6-11 (Reed *et al.*, 1995). The compost must be maintained at 40 °C for at least 5 days, and within this period it must be held at a minimum of 55 °C for 4 hours, followed by a maturation period (DoE, 1996). Compost systems may be:

- Windrow: material placed in long rows is periodically turned and mixed to ensure it remains aerated and does not overheat.
- Static pile: air is blown or drawn through the pile of material to be composted.
- Enclosed reactors: these are self-contained reactor units or partially enclosed static-pile or windrow operations. These systems have the advantage of reduced odour and greater process control, and more efficient pathogen removal (Reed *et al.*, 1995; DoE, 1996).

2.1.2.4 Lime Treatment

Lime, calcium oxide (CaO) or calcium hydroxide (Ca(OH)₂), is frequently used as a conditioner prior to dewatering of digested sludge, and may also be used on undigested sludge. It raises the pH to 11-12 and reduces odour and pathogen content (Chaussod *et al.*, 1985). The pH should be maintained at 12 or above for a period of at least 2 hours for effective treatment (DoE, 1996). Addition of sludge increases the DS content, it is recommended to add at least 30 % lime to the DS content of the sludge

(CEC, 2001). The time for installation of lime treatment facilities is rapid and the capital cost is low, although operational costs may be high (Evans, 2001).

2.1.2.5 Enhanced Treatment Processes

The Safe Sludge Matrix (ADAS, 2001), introduced a new tier of sewage sludge treatment in which pathogens are eliminated through the use of enhanced methods, involving heating or drying at high temperatures or chemical manipulation. If the adequate temperature and reaction time criteria are met composting can also produce an enhanced biosolids product, achieving a 6 log reduction in pathogens. Lime treatment can also attain enhanced standards if used effectively. Thermal drying also may also be used to treat raw or digested sewage sludge; thermally dried biosolids are 2-4 mm granules, typically 95 % DS, and are an odourless inoffensive product suitable for landspreading (Evans, 2001).

A pre-pasteurisation step may be used, which may involve heating at 70 °C for 30 minutes, or 4 hours at 55 °C to sterilise the biosolids, followed by a stabilisation process such as MAD (DoE, 1996; CEC, 2001). Thermal hydrolysis involves dewatering raw feed material to 14 % DS and heating at 160 °C for 30 minutes, this sterilises the sludge and disrupts cells. This results in improved digestion when the liquid is fed to MAD, producing 40 % more biogas (Evans, 2001). Autothermal aerobic digestion may also be used without additional heating, or with back-up heating, this increases the DS content, improves gas yield and reduces the heat required for MAD (Evans, 2001).

2.2 Legislation and Guidelines Influencing the Use of Biosolids and Industrial Biowastes in Agriculture

2.2.1 The Nitrates Directive

Land application of organic residuals must be operated in compliance with the Nitrates Directive (CEC, 1991). The Directive was established in 1991 and requires Member States to introduce controls on agricultural sources of nitrate (NO_3^-) in areas where concentrations in groundwater exceed or are at risk of exceeding 50 mg l⁻¹, these areas are designated Nitrate Vulnerable Zones (NVZs). In addition, voluntary codes of good agricultural practice must be established, and Action Programmes of measures to

tackle nitrate losses from agriculture should be set-up either within NVZs or throughout the country.

In 1996, 66 NVZs, covering 8% of England, were designated, a further 47 % of England was designated a NVZ in October 2002. The NVZs proposed for designation in 2008 cover approximately 70 % of England (Figure 2.2).

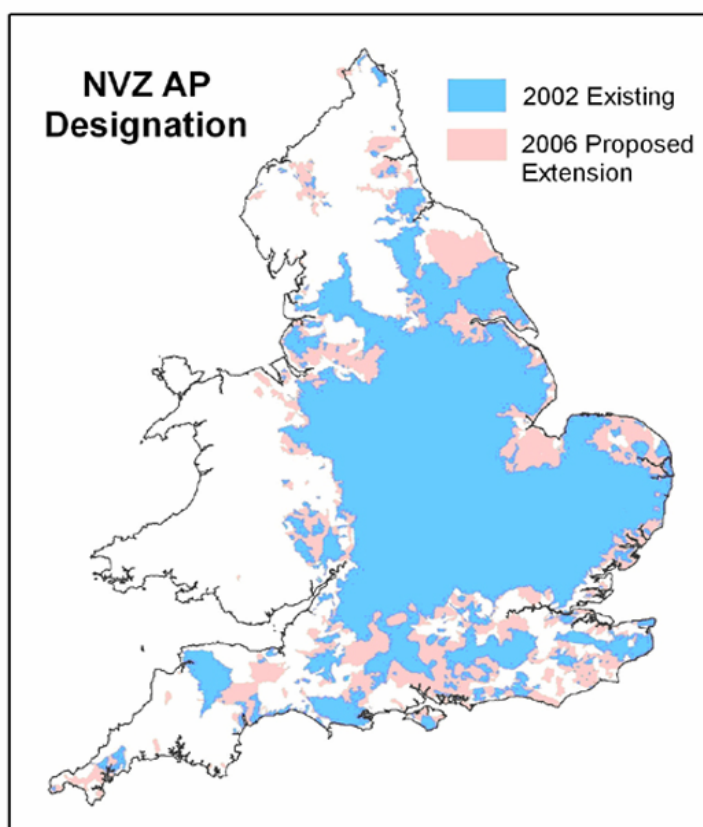


Figure 2.2 Map of existing NVZs in England and extension proposed in 2006 for designation in 2008 (Defra, 2008).

Within these NVZs there are limits on amounts of total N that can be applied in organic residuals. On 19 December 2006 a farm-based limit of 170 kg N ha⁻¹ was introduced on arable land, and a limit of 250 kg N ha⁻¹ on grassland. The maximum field-based limit is 250 kg N ha⁻¹ in any 12 months. In addition, the available N from organic manures must not exceed crop requirement, therefore, care must be taken with high availability sludge types such as liquid digested sludge. In the case of sewage sludges and livestock manures there are detailed published guidelines on available N (MAFF, 2000) (Section 2.8.1), but there are no guidelines for industrial biowastes. Therefore, limits for meeting crop requirements are based on total N contents of industrial

biowastes, plus any additional fertiliser N sources. There are closed periods during which application of slurry, poultry manures and liquid digested sludge is banned in shallow or sandy soils due to increased risk of nitrate leaching; these are between 1 September and 1 November on grassland or autumn sown crop and between 1 August and 1 November where there is no grassland or autumn sown crop (Defra, 2008). Outside NVZs, practices on organic residuals management are recommended in the Code of Good Agricultural Practice for the Protection of Water (Defra, 1998). The recommended annual limit of total N applied in sewage sludge is 250 kg N ha⁻¹. When cakes contain little plant available N, application rates of up to 500 kg ha⁻¹ of total N every two years are acceptable.

2.2.2 Land Application of Sewage Sludge

2.2.2.1 EU and UK

- Council Directive on the protection of the environment and in particular of the soil, when sewage sludge is used in agriculture (CEC, 1986). The Directive aimed to regulate the use of sludge in agriculture to prevent harmful effects to soil, vegetation, animals and man, and set limits for maximum annual quantities of heavy metals which may be introduced into the soil in sludge.
- The Council Directive was implemented in the UK by The Sludge (Use in Agriculture) regulations 1989 (SI, 1989), which were amended in 1990 (SI, 1990). The regulations placed duties upon the sludge producer, operator and land occupier, and introduced regulations for cropping and grazing times and record keeping, preventing over supply of nutrients to crops, sludge and soil testing. This was to control rate of accumulation of potentially toxic elements (PTEs) in soil, and to protect groundwater and protect human and animal health.
- The Urban Waste Water Council Directive (CEC, 1991), as amended by Council Directive (CEC, 1998), banned the dumping of sewage sludges at sea by the end of 1998, increasing pressure on other routes of disposal and resource recovery.

In addition to statutory regulations other guidelines exist:

- The Code of Practice for Agricultural Use of Sewage Sludge was first published by DoE in 1989. A revised Code (second edition) was issued (DoE, 1996) to

take account of the report of the Independent Scientific Committee (MAFF/DoE, 1993) on the soil fertility impacts of particular toxic elements when sewage sludge is applied to soil. It provides more guidance on PTEs, and sludge treatment processes, that are not covered by the statutory regulations.

- The Safe Sludge Matrix (ADAS, 2001) is a voluntary agreement which exists between the British Retail Consortium (BRC) and the UK Water Industry to ensure that certain sludge types are only applied to certain crops and vegetation; it was first introduced in 1999. This agreement prevents the use of untreated sewage sludge on land used for food production, and requires sludges to be treated to predetermined microbiological standards. According to the Matrix, specified time periods are required between sludge application and harvesting of particular categories of crop types.

2.2.2.2 US

The US Environmental Protection Agency (USEPA) Part 503 regulations for the use and disposal of sewage sludge (USEPA, 1993) deal with the landspreading of sewage sludge and mixtures of industrial waste and sewage sludge, but not industrial waste alone. Exceptional Quality (EQ) Biosolids, have (USEPA) Class A pathogen reduction standards and may be used as any other fertiliser product without additional control or regulation (USEPA, 1993). The US Environmental Protection Agency suggest that some of the specifications in the regulations may be relevant when landspreading industrial wastes and composts. USEPA have also produced a 'Guide for Industrial Waste Management', which includes a chapter on best practice when designing a land application program (USEPA, 2007).

2.2.3 European Waste Strategy

The key objectives of European waste policy are primarily to reduce waste production, and secondly, waste that is produced should be reused, recycled or materials recovered, with as little as possible disposed of in landfill. In May 2003 the European Commission proposed a Communication, "Towards a thematic strategy on the prevention and recycling of waste" (COM, 2003). The Communication included an assessment of existing waste policy, in terms of waste minimisation and recycling, and aimed to promote more sustainable waste management. Following this, the Commission proposed a new Communication, 'Taking sustainable use of resources forward: A Thematic Strategy on the prevention and recycling of waste' (COM, 2005).

The outcomes of the Thematic Strategy were that current European waste policy has the ability to achieve the key objectives, and suggestions were provided for ways in which policy should be implemented to meet the overall aim of the EU becoming a recycling society that avoids waste and uses it as a resource. In terms of management of biowastes, the Communication proposed that full implementation of the Landfill Directive (CEC, 1999), which requires Member States to reduce the quantity of biodegradable waste sent to landfill to 75 % of 1995 levels by 2006, 50 % by 2009 and 35% by 2016, would make a significant impact on reducing the emission of greenhouse gases from biowastes. It was suggested that there was no one best option for management of biowastes, but that Member States should apply life-cycle thinking on a local basis to determine the best strategy. Legislation currently in place, that is applicable when landspreading biowastes and biosolids, includes the Directive on the protection of the environment (CEC, 1986), with particular emphasis on the protection of soils, when sewage sludge is used in agriculture. The Thematic Strategy (COM, 2005) also proposed that the Integrated Pollution Prevention and Control Directive (IPPC) (CEC, 1996) as amended (CEC, 2003) should be implemented to achieve a coordinated approach to waste management by reduction of waste and using Best Available Technique Reference documents (BREFS) developed under the Directive to achieve best waste management practice.

It was also proposed that the 1975 Waste Framework Directive (CEC, 1975), which was amended in 1991 (CEC, 1991a) needed to be revised in order to clarify and modernise legislation, to set recycling standards and to oblige Member States to develop national waste prevention programmes. Article 4 of the Directive is relevant to landspreading of wastes and requires Member States to ensure that waste disposal or recovery does not:

- cause a risk to water, air, soil and plants and animals;
- cause a nuisance through noise or odours;
- adversely affect the countryside or places of special interest.

Proposed amendments included clarifying when a waste ceases to be a waste and has been adequately treated to be considered a product. The Thematic Strategy also proposed developing 'life cycle thinking' guidelines for EU biowastes management. The new Waste Framework Directive is now in place (CEC, 2006).

A European wide survey of the types of biodegradable organic waste that member states treat by landspreading was conducted in 2001 (Gendebien *et al.*, 2001); more

than 90 % of wastes spread to land in the EU are farm wastes, of the remainder the most important are food production wastes, dredgings from waterways and paper production waste (Gendebien *et al.*, 2001). There are variable reporting requirements in different countries and landspreading is accepted practice in some Member States but not others, such as Luxembourg and Austria. In Austria, food solid waste is mainly converted into compost and liquid effluents are treated in municipal treatment works.

2.2.4 UK Waste Legislation

The Government's objectives for sustainable waste management are set out in 'Waste Strategy for England 2007' (Defra, 2007). The key objectives include: meeting the Landfill Directive diversion targets for biodegradable municipal waste in 2010, 2013 and 2020, increasing diversion of non-municipal waste from landfill and increasing recycling of resources and recovery of energy. The diversion target dates for the UK are postponed by 4 years as they started from a point where 80 % or more of their municipal waste was landfilled (CEC, 1999).

The Waste Management Licensing Regulations (WMLR) 1994 (SI, 1994), amended 2005 (SI, 2005), apply to those who keep, produce, carry, treat, recover or dispose of waste (excluding householders) under a Duty of Care provision as set out in Section 34 of the Environmental Protection Act (1990). Waste management licenses are issued by the Environment Agency in England and Wales, and in Scotland the responsible authority is the Scottish Environmental Protection Agency (SEPA). To encourage low risk waste recovery operations, license exemptions are given to certain waste recovery activities, these activities are listed under Schedule 3 of the WMLR. Paragraph 7A of Schedule 3 relates to landspreading of wastes. Certain wastes can be used for land treatment if they can be demonstrated to provide agricultural benefit or ecological improvement. Guidelines issued to the Environment Agency (Defra, 2005), define agricultural benefit as:

- Replacement of mineral fertilisers by providing nutrients such as N and P;
- Addition of organic matter, improving the water holding capacity or soil porosity, stability, tilth and workability;
- Addition of moisture in liquid wastes when water content of soil is too low to support growth of crops at time of application;
- Leveling of uneven land by spreading of waste soil.

Ecological improvement is defined as:

- The maintenance of habitats and their biodiversity when they would otherwise deteriorate;
- The provision of new habitats for wildlife;
- Development or restoration of existing habitats to give greater biodiversity.

Additional advice on defining agricultural benefit is outlined in a WRc report for EA/Defra (Davis and Rudd, 1997), which contains guidance on the landspreading of industrial wastes and recommends that the Codes of Good Agricultural Practice for the Protection of Air (MAFF, 1992), Soil (MAFF, 1993) and Water (MAFF, 1998), should be adhered to. Limits on application of total N apply, as described in Section 2.2.1 of this review.

The waste types which may be registered as exempt wastes for landspreading, are listed in Table 2A(A) of Para 7 of the WMLR (Table 2.1). Any of the wastes listed in Parts 1 and 2 may be used to treat agricultural land, the wastes in Part 1 may also be used to enhance the ecological value of additional land types. It is permissible to store 1250 t of the waste which will be used to treat land for up to a year, in a location where it will not cause nuisance or pollution, provided that it is stored a certain distance away from water courses, springs, wells and boreholes. The total limit of any listed waste to be landspread is 1500 t ha⁻¹ of sugar beet spoil, 5000 t ha⁻¹ of dredging spoil and 250 t ha⁻¹ of any other waste. The landspreading activity must also comply with the European Council Regulation laying down health rules concerning animal by-products not intended for human consumption (CEC, 2002) which is enforced in the UK by the Animal By-Products Regulations 2005 (SI, 2005b) and governs the handling and disposal of products of animal origin not intended for human consumption. The legislation categorises animal wastes according to pathogen risk; low-risk (category 3) animal wastes that may be treated by composting or anaerobic digestion are required to meet certain standards. The EU treatment standards require category 3 wastes to pass through a pasteurisation step of 70 °C for 1 h with a maximum particle size of 12 mm. Application of digestive tract contents and milk to pasture land are less tightly controlled, but livestock are not permitted to graze for fixed periods after application. Prior to landspreading, an analysis of the waste and a notification form must be submitted to the Environment Agency. This includes information on the type of waste, quantity to be spread, storage method, status of the land, such as whether it is within a Nitrate Vulnerable Zone (NVZ), the crop, rate and method of application and whether

there have been any previous applications. For regular applications of biowastes, these details must be re-submitted to the Agency every 6 months, or when the characteristics of the materials change. Under Schedule 4, Para 13 of WMLR, the Environment Agency is then required to make periodic checks of the exempted activities (SI, 2005a).

Table 2.1 Waste Management Licensing Regulations 2005 (SI, 2005a) Para 7A. Types of waste which may be landspread (Table 2 A(A)).

Source of Waste	Kind of Waste
Part 1	
Wastes from forestry, aquaculture, horticulture and fishing	Plant-tissue waste
Wastes from sugar processing	Soil from cleaning and washing beet
Wastes from wood processing and the production of panels and furniture	Waste bark and cork Sawdust shavings, cuttings, wood and particle board
Wastes from pulp, paper and cardboard production and processing	Waste bark and wood, pulp from virgin timber
Soil (excluding excavated soil from contaminated sites), stones and dredging spoil	Soil and stones
Wastes from aerobic treatment of solid wastes	Compost of biodegradable garden and park waste
Garden and park wastes (including cemetery waste)	Biodegradable waste Soil and stones
Part 2	
Wastes from the preparation and processing of meat, fish and other foods of animal origin	Blood and gut contents from abattoirs, poultry preparation plants or fish preparation plants Wash waters and sludges (with or without treatment) from abattoirs, poultry preparation plants or fish preparation plants Shells from shellfish processing
Wastes from fruit, vegetables, cereals, edible oils, cocoa, coffee, tea and tobacco preparation and processing; conserve production; yeast and yeast extract production, molasses preparation and fermentation	All wastes derived from the processing of such materials
Wastes from sugar processing	All wastes derived from the processing of sugar
Wastes from the dairy products industry	Wastes derived from the processing of dairy products
Wastes from the baking and confectionery industry	All wastes derived from the processing of raw materials used in the baking and confectionery industry
Wastes from the production of alcoholic and non-alcoholic beverages (except coffee, tea and cocoa)	All wastes derived from the processing of the raw materials used in the production of such beverages

Table 2.1 Cont.

Wastes from pulp, paper and cardboard production and processing	De-inked paper sludge and de-inked paper pulp from paper recycling Lime mud waste
Wastes from the leather and fur industry	Sludges from on-site effluent treatment free of chromium
Wastes from the textile industry	Organic matter from natural products Wastes from finishing other than those containing organic solvents Sludges from on-site effluent treatment Wastes from textile fibres
Wastes from the manufacture of cement, lime and plaster and articles and products made from them	Wastes from calcinations and hydration of lime Gypsum
Wastes from power stations and other combustion plants	Gypsum
Soil (including excavated soil from contaminated sites), stones and dredging spoil	Dredging spoil (other than those containing dangerous substances)
Wastes from aerobic treatment of waste	Compost derived from source segregated biodegradable waste Liquor from aerobic treatment of source segregated biodegradable waste Digestate from aerobic treatment of source segregated biodegradable waste
Wastes from anaerobic treatment of waste	Compost derived from source segregated biodegradable waste Liquor from anaerobic treatment of source segregated biodegradable waste Digestate from anaerobic treatment of source segregated biodegradable waste
Wastes from the preparation of water intended for human consumption or water for industrial use	Sludges from water
Wastes from the preparation and processing of meat, fish and other foods of animal origin	Blood and gut contents from abattoirs, poultry preparation plants or fish preparation plants Wash waters and sludges (with or without treatment) from abattoirs, poultry preparation plants or fish preparation plants Shells from shellfish processing

2.3 The Agricultural Outlet for Biowastes Management in the UK

The Environment Agency commercial and industrial waste survey 2002/3 indicated that the total industrial and commercial waste produced in England in this year was 68×10^6 t (Defra, 2006b). Of this 9 % was of animal and plant origin (Figure 2.3), which represents a minimum 6.1×10^6 t of industrial biowastes in England alone, that have the potential to be recycled to agricultural land.

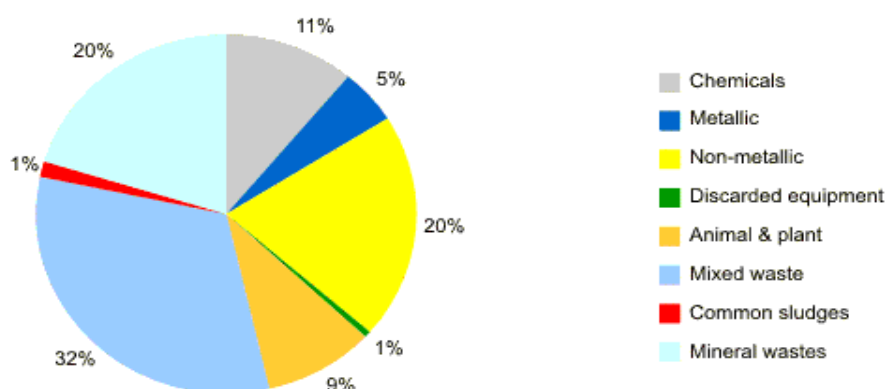


Figure 2.3 Commercial and industrial waste arisings in England, Environment Agency, commercial and industrial waste survey 2002/2003 (Defra, 2006b).

A European wide survey of industrial biowastes conducted by Gendebien *et al.* (2001), estimated that 7.3×10^6 t of industrial biowastes are recycled to agricultural land annually in the UK, further detail of quantities of different industrial biowaste types are given in Table 2.2. The majority of the waste recycled to agricultural land, 6.6×10^6 t, was wastes from food and drink preparation. More recently, a direct telephone survey was conducted (Ellis *et al.*, 2007) to produce estimates of tonnages of waste inputs and capacities of waste facilities in England in Wales, for WMLR exempt waste activities, including those covered by Para 7A. The survey indicated that the 4.7×10^6 t of waste registered for Part 1 of Para 7A, and 2.6×10^5 t were registered for Part 2 activities; this represents a total of 4.9×10^6 t of Para 7A exempt wastes spread to land in England and Wales. The majority of these biowastes were destined for application for agricultural as opposed to ecological improvement.

Recently, a MSc project was conducted (Payne, 2006) to collect data from waste exemption forms held by the Environment Agency offices in the Thames Region on the range of physical and chemical properties of biowaste types being utilised in

agriculture, which demonstrates how the exemption system under the WMLR operates in practice. Exemptions for eleven wastes types were applied for in the Thames Region, representing a total of 2400 t DS for solid and semi-solid wastes and 2482 m³ of liquid wastes at a rate of 221.1 t ha⁻¹. The solid wastes were a variety of textures and included dewatered cakes from water treatment plants, papermill waste, green waste such as leaves, twigs and grass cuttings and mulch from composting facilities. The semi-solids were spoils from construction and demolition, silt from pond dredging and sludge from on-site treatment plants. In the liquid waste group, there were plant effluents, animal slurry, wash waters from meat vegetable processing and site 'run-off'. The average area of land treated for each application was 34.4 ha. The majority of the exemptions, 91.6 %, were for use of biowastes for agricultural rather than ecological benefit, and in most cases, land only received a single application in one year. Further details of the nutritional properties of these wastes are discussed in Section 2.8.4

Table 2.2 Estimates of quantities of different industrial biowastes recycled to agricultural land annually in the UK (Gendebien *et al.*, 2001).

Industrial waste description	Fresh weight (x 10 ³ t)
Food & drink preparation: including vegetable and fruit processing, sugar beet processing, meat and fish processing, abattoir waste, soft drinks and brewery wastes.	6600
Textile	3.5
Leather and tannery	9
Biological processes: biological sludge from fermentation processes in the pharmaceutical industry and other chemical industries	8
Chemical: liquid ammonia from chemical industry	3
Paper production and recycling [†]	700

[†] Estimate of quantity of paper waste landspread from Gibbs *et al.* (2005)

2.4 Methods of Storage, Transport and Application of Organic Residuals

Various methods of storage and application exist for organic residuals, which will have considerable effect on the cost, uniformity of spread, odour and gaseous losses of N. Length of storage also has an impact on the physical and chemical characteristics, and hence, implications for the fertiliser value, which is considered in Section 2.9.6. Organic residuals may be stored in pits, skips or on waterproof platforms for solid sludges (CEC, 2001) and tanks, open-topped or closed lagoons for liquids; they may be stored at the source or on the land to be treated. In a survey of biowastes landspread in the Thames Region, UK, Payne (2006) found that 59.1 % were stored for at least 1 month before spreading.

Methods of sewage sludge application were summarised by Davis (1983) and, at that time, included conventional surface broadcasting using splash-plates (Plate 2.1a), and newly developed sub-soil injection methods. Since then shallow- or deep- injection methods have become more widely used along with 'trailing shoe', dribble-bars (Plate 2.1b) and umbilical delivery systems (Davis and Rudd, 1997; Smith *et al.*, 2000; CEC, 2001), which spread sludge close to the soil surface and achieve a more uniform spread than conventional surface broadcasting. Sludge injection also avoids odour and disease transmission, and reduces gaseous losses of N (Davis and Rudd, 1997). Dried sludges may be spread by using the same equipment as for solid mineral fertilisers (CEC, 2001). Payne (2006) found that the most common method for spreading biowastes in the Thames Region was surface spreading, 55 %, followed by surface spreading and ploughing in, 22.5 % and sub-surface injection, 18.3 %.

(a)

(b)



Plate 2.1 Slurry application equipment: (a) traditional 'splash-plate' (b) 'dribble-bar'.

Sludge may be spread to land direct from a road tanker from the water utility, which is the traditional method, this allows operational flexibility and is generally cost effective. Application by field tanker or tracker drawn trailer is more expensive but may be necessary on wet soils; travelling irrigators are a relatively cheap application method, with the advantage that they are light and avoid soil damage (Davis, 1983). High levels of variability in texture of organic residuals, such as dusty, oily or greasy wastes may cause problems in handleability. Greasy wastes may block spreading equipment or leave residues on the soil surface, so it is necessary to choose an appropriate application method (Davis and Rudd, 1997).

2.5 Environmental Considerations

Excess N and P in the soil may result in losses of these nutrients by leaching of NO_3^- into groundwater (Hansen *et al.*, 2007; Surampalli *et al.*, 2008) and run-off of N and P (King and Torbert, 2007; Otabong *et al.*, 2007; Zeng *et al.*, 2007). This may cause enrichment of water bodies in the surrounding area leading to eutrophication, and also potentially detrimental effects to potable ground water (NRA, 1992). The effects of eutrophication include algal blooms, excessive weed growth and poor water clarity resulting in fish death and loss of diversity (Chambers *et al.*, 2006; Spatharis *et al.*, 2007). There are many sources of nitrates in groundwater, such as atmospheric deposition, leaking residential septic tanks and airfield runway devices; however, the major source is applications of manures and fertilisers to agricultural land (Addiscott *et al.*, 1991; NRA, 1992; Chambers *et al.*, 2006). Factors influencing leaching are discussed in Section 2.6.1.4. Chronic soil enrichment with N and P may also have detrimental affects on soil ecology (Frey *et al.*, 2004). Excessively high levels of NH_3 have been found to inhibit nitrifying bacteria activity (Fdz-Polanco *et al.*, 1994; Kim *et al.*, 2006).

Gaseous emissions of ammonia, mainly from surface applied manures and slurries and other organic wastes, are a contributing factor to acid rain. Ammonia (NH_3) in the atmosphere reacts with sulphuric acid to form ammonium bisulphate (NH_4HSO_4) and ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$). These compounds are hygroscopic and wash out readily during precipitation. Ammonia also reacts with hydroxyl radicals from other atmospheric N species (NO_x), which then contribute to increase the acidity of the rain (Galbally and Roy, 1983). Ammonia deposition on plants, soil and water can cause damage to plants and wildlife and ecological disruption in nutrient poor habitats (Roem *et al.*, 2002; Smarta *et al.*, 2005). For example, increase in N in lowland heaths and Scottish moors gives grass a competitive advantage over native plants.

In addition to emissions from fossil fuel combustion, agricultural activity is a major source of the greenhouse gases, nitrous oxide (N_2O), and nitrogen oxides (NO_x), to the atmosphere (Day *et al.*, 1978; Galbally and Roy, 1983). Nitrous oxide is 296 times more effective than CO_2 as a greenhouse gas, and is also involved in the depletion of the ozone layer (IPPC, 2001). Nitrogen fertiliser application may increase emissions N_2O and NO_x from the soil through denitrification processes (Burford and Bremnar, 1975; Lampe *et al.*, 2006), which are described in Section 2.6.1.4. Factors influencing

denitrification, and other N transformation processes, in soils amended with organic residuals, are discussed further in Section 2.9.

2.6 Soil Processes

2.6.1 Nitrogen

2.6.1.1 Background

Nitrogen has a greater effect on crop growth than any other nutrient, it is generally the nutrient that limits productivity in UK soils (Cooke, 1982), and has previously been considered the nutrient of most agricultural value in organic fertiliser sources (Hall, 1983a). However, it is important to manage N inputs correctly, as excess N in the soil may prove detrimental to crop quality or yield (Wilhelm *et al.*, 1999; Schulte auf'm Erley *et al.*, 2005, Mohr *et al.*, 2007), and cause environmental problems as discussed in Section 2.5. In addition, as a consequence of the Nitrates Directive (CEC, 1999), limits on rates of application of organic residuals in the UK are determined by their total N content. For these reasons, it is of particular concern to understand soil N dynamics when applied in biosolids and biowastes, so, in addition to P (Section 2.6.2) it is N which has been given particular attention in this review. Figure 2.4 shows a general view of the N cycle, including soil inputs, outputs and transformation processes.

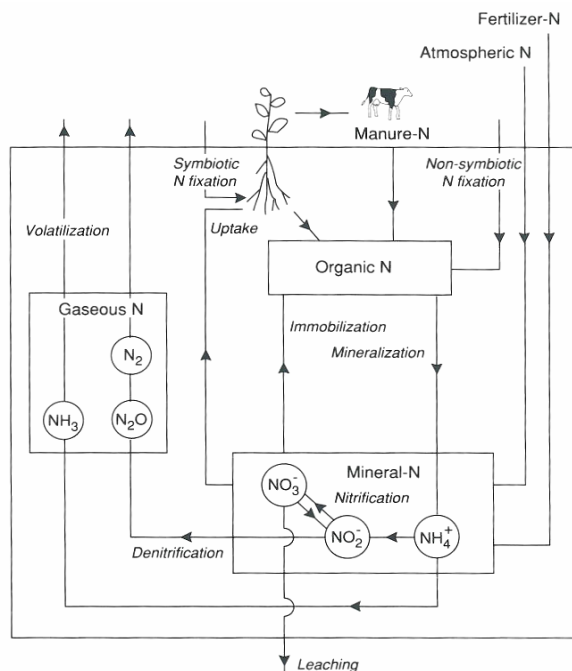
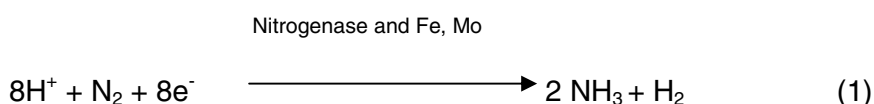


Figure 2.4 The nitrogen cycle, diagram taken from Rowell (1994).

2.6.1.2 Inputs

Soil N is gained through nitrogen gas (N₂) fixation in plants, soil and by lightning. Rainwater containing dissolved ammonium (NH₄⁺) and nitrate (NO₃⁻), mineral and organic fertilisers, animal excreta and plant residues are also sources of N (Figure 2.4). In certain 'nitrate retentive' agricultural soils, such as medium textured silty soils, residues of mineral N may remain in the soil following harvest and remain available for crop uptake in the following crop (Webb *et al.*, 1997; Mendoza *et al.*, 2002).

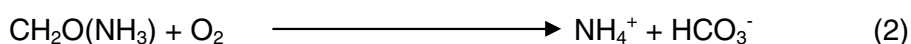
Nitrogen in soil air is inert, before it can be made available for soil organisms it must first be fixed. Nitrogen is fixed from atmospheric N₂ gas to ammonia, NH₃, by microorganisms with the enzyme nitrogenase (equation 1) (Sprent, 1987). Nitrogen fixing bacteria in soil are either free-living, such *Azobacter spp.* and *Clostridium spp.* or in symbiotic associations with plants or other organisms such as termites and protozoa.



Plant-bacteria symbiosis occurs mainly in the legumes (e.g. beans, peas and clover). In temperate regions *Rhizobium spp.* are found in the root nodules of most legumes. Growing a legume in association with grass crop, is advantageous for the grass in addition to the legume and therefore provides a better diet for livestock (Whitehead, 1995).

2.6.1.3 Transformation Processes

Mineralisation: Nitrogen inputs in organic residuals may be in inorganic (eg. as NH₄⁺ in digested materials) as well as organic forms. Mineral N will be immediately available for plants, organic N must first undergo a process of mineralisation, or ammonification, before it becomes available (Figure 2.4). Organic N, from soil humus or organic fertiliser sources, is decomposed or mineralised by microorganisms in the soil, by hydrolysis of proteins and conversion to ammonia (equation 2) (Schwedt, 1996).



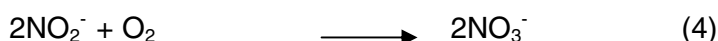
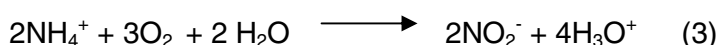
Mineralisation tends to increase in warm moist conditions (Miller, 1974; Stanford and Epstein, 1974; Terry *et al.*, 1979). Soil pH may affect mineralisation; for example, Pietri

and Brookes (2008) found that mineralisation of arginine applied to a silty clay loam was greatest at pH 3.8 and 4.4 in comparison to pH 6.1 and 7.8. Kemmitt *et al.* (2006) also found that soil microbial activity decreased with increasing acidity following addition of urea and amino acids, however glucose mineralisation did not respond to pH.

Immobilisation: Added N may be immobilised into the microbial biomass N (MBN) (Recous and Mary, 1990), or mineralised and converted to $\text{NH}_4\text{-N}$ (Figure 2.4). Mineralisation rate is determined by the stability of the organic matter and its N content. Thus, organic residual treatment processes designed to stabilise the putrescible fraction in the biowaste or sludge, such as composting or anaerobic digestion, influence the mineralisable N content of the product and the overall N fertiliser value (Smith *et al.*, 1998b;c;d; Morris *et al.*, 2003; Cogger *et al.*, 2004; Corrêa, 2004). It is well established that the C:N ratio of organic soil inputs influences the amount of mineralised N (Sabey *et al.*, 1975; Nicolardot *et al.*, 2001; Vinten, 2002; Pansu *et al.*, 2003). In general, if the organic fertiliser source has a high C:N ratio, greater than 20:1, organic N tends to be immobilised by the bacterial community, whereas when the C:N ratio is less than 20:1 organic N tends to be mineralised (Parker and Sommers, 1983).

Nitrification: Nitrifying bacteria oxidise $\text{NH}_4\text{-N}$ to $\text{NO}_3\text{-N}$ (Figure 2.4), which is a two stage process. The bacteria responsible for the process are gram-negative ‘chemoautotrophs’ that can utilise CO_2 as a carbon source. Nitrification requires O_2 and is optimal at approximately 30 °C and a slightly alkaline pH (Day *et al.*, 1978).

In the first stage, ammonia-oxidising bacteria, such as *Nitrosomas spp.* convert NH_3 to nitrite (NO_2^-) (equation 3), which is subsequently converted to NO_3^- by NO_2^- -oxidising bacteria such as *Nitrobacter spp.*, as in equation (4) (Schwedt, 1996). Nitrite is toxic and may have adverse effects on plant root growth, if the pH is greater than 9 NO_2^- may accumulate in the soil (Day *et al.*, 1978). $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ are both available for crop uptake and conversion into plant biomass.



The optimum soil pH for many ammonium oxidisers is between 7 and 9 and for nitrite oxidisers between 7 and 8 (Tester *et al.*, 1977; Pietri and Brookes, 2008).

Ammonium fixation: Ammonium has a positive charge and may become fixed in the soil by forming strong bonds with negatively charged soil particles, this occurs to a greater extent in soils with a high clay content (Trehan, 1996; Tester *et al.*, 1977). This can act as a mechanism for conserving soil N (Shen *et al.* 1997; Steffens and Sparks, 1997).

2.6.1.4 Losses

Leaching, runoff and erosion: Leaching of NO_3^- to groundwater is a major route of N loss from agricultural systems (Figure 2.4) with important consequences for the quality of potable resources (Shankar and Usha, 2007). Leaching through the soil to the groundwater is variable according to rainfall, soil type, depth of the aquifer and geology.

In the UK losses of N by leaching are greater during the winter when there is high rainfall (Addiscott *et al.*, 1991). Thus, autumn applications of manure N, which are followed by periods of high precipitation, lead to high rates of NO_3^- leaching (Beckwith *et al.*, 1998).

Leaching occurs most readily in light sandy soil types, some shallow soils with a high stone content and fissured rocks, such as limestone (Webb *et al.*, 1997; Koo and O'Connell, 2006). Deep clay and silt soils are more retentive (Conry, 1997; Webb *et al.*, 1997) and underlying rocks such as sandstone and chalk are composed of a finer matrix limiting water movement. Areas of the UK at highest risk of poor groundwater quality due to increasing concentrations of nitrates are in the south, east and midlands (NRA, 1992) where intensive agricultural regions overlie vulnerable underlying rock types. Lower rainfall in these areas also increases NO_3^- concentration in the groundwater in comparison to higher rainfall areas in western parts of the country.

Soils with a greater organic matter content, and hence greater water holding capacity, reduce NO_3^- losses (Addiscott *et al.*, 1991). Crop cover also reduces rates of NO_3^- leaching (Addiscott *et al.*, 1991; Beckwith *et al.*, 1998; Hansen *et al.*, 2007). Grass is a perennial crop, with a dense mat of roots, and can lead to lower levels of leaching in comparison to growing arable crops (Addiscott *et al.*, 1991; Christian and Richie,

1998). However, ploughing of grassland can cause peaks in nitrate leaching (NRA, 1991).

Ammonia is less mobile than NO_3^- and not easily lost by leaching, as it forms exchangeable associations with negatively charged ions in the soil (Tester *et al.*, 1977; Shen *et al.* 1997; Steffens and Sparks, 1997), whereas most soils have a low capacity to retain anions (Rowell *et al.*, 1994). However, both NH_3 and NO_3^- may also be lost by erosion of soil or run-off of surface waters (Smith *et al.*, 2001; Ojeda *et al.*, 2006); Factors such as amount of rainfall and gradient of the land will affect the degree of erosion and run-off (Smith *et al.*, 2001a; Arnaez *et al.*, 2007).

Denitrification: Gaseous emissions of N may occur through denitrification (Figure 2.4), a microbially mediated anaerobic process, which tends to occur in moist soils. Denitrification is the reduction of NO_3^- or NO_2^- to nitrogen gas, N_2 , mediated by chemoautotrophic bacteria, with intermediate stages that result in the production of NO or N_2O , equations 5-8 (Schwedt, 1996).



Nitrogen gas is inert, but NO and N_2O are greenhouse gases, and emissions from agriculture contribute to climate change and depletion of the ozone layer. Typical rates of denitrification in the field are approximately $3 \text{ kg N ha}^{-1} \text{ day}^{-1}$ (Addiscott *et al.*, 1991); emissions of N_2O from arable soils may be between 0.2-2.8 % of applied fertiliser N (Webb *et al.*, 2004). Factors increasing denitrification rates are supply of N, increased C availability, low cation exchange capacity (CEC), oxygen deficient conditions, high concentrations of ammonia and high pH (Mendoza *et al.*, 2006), the optimum pH is 7-8 (Sprenst, 1987). At acidic pH values, greater than 3.5, the main product of denitrification is N_2O (Sprenst, 1987) (equation 7). Increased emissions of N_2O have been reported when there is a greater water filled pore space (WFPS), which reduces the capacity for oxygen to diffuse through the soil (Webb *et al.*, 2004).

Volatilisation: Nitrogen may also be lost by NH_3 volatilisation (Figure 2.4), which is increased by surface application of sludges and manures without incorporation (Beauchamp *et al.*, 1978; Sutton *et al.*, 1982; Robinson and Polglase, 2000). Drying

weather conditions, increased temperature and windspeed, low *CEC* and alkaline soil pH are factors which increase volatilisation (Freney *et al.*, 1983; Simpson and Steele, 1983; Sprent, 1987; Rowell, 1994).

Harvesting: Removal of crops also accounts for the removal of N from soil systems in above ground plant biomass, N may also be recovered in stubble or roots. Approximately 55 % of applied N may be recovered in grass or harvested winter wheat (Addiscott *et al.*, 1991). The amount of N contained in the annual production of plant material in intensively managed grassland, including N recovered in grass or roots is generally between 300–700 kg N ha⁻¹ (Whitehead, 1995). Webb *et al.* (2004) reported crop N offtake to be in the range of 45 kg N ha⁻¹ for linseed to 245 kg N ha⁻¹ for winter wheat with N fertiliser additions of between 0-267 kg N ha⁻¹

2.6.2 Phosphorus

2.6.2.1 Background

The global supply of P is finite, additions to the cycle come from rock and soil weathering, plant decomposition and small amounts from the atmosphere (Figure 2.5), therefore P in organic residuals represents a valuable resource. At current rates of extraction, the world's economic resources of P are estimated at only 100 years (Driver *et al.*, 1999). In UK soils, low responses to fertiliser P additions have been reported (Christie *et al.*, 1987 cited in Smith *et al.*, 1998a) and the recommendation is that most crops only require addition of P and other nutrients to replace crop offtake at harvest (MAFF, 2002). However, there is a risk of potential oversupply of mineral fertilisers due to over-conservative estimates of P, availability in organic wastes (Smith *et al.*, 1998a). It is important to accurately predict P availabilities to gain maximum benefit from supply in organic wastes (Williams and Coker, 1980), and prevent depletion of the finite supply of P. As a result of improved methods of removal of P during tertiary wastewater treatment, by ferric chloride dosing or biological methods there is a high amount of P present in biosolids (Kuile *et al.*, 1983; Jardin and Pöpel, 1994; Kyle and McClintock, 1995, Smith *et al.*, 2003). Increased concentrations of P in sludge means there is growing concern regarding the potential oversupply of phosphates to agricultural land.

2.6.2.2 Transformation Processes

Figure 2.5 shows the soil P cycle, including inputs and transformation processes. Bioavailable P is introduced to soils through inputs of inorganic fertiliser and decomposition of organic fertiliser and soil humus (Hayman, 1975). A small fraction of P will be available in soil solution, mainly as phosphate ions, PO_4^{3-} , and a proportion will be present as labile or moderately labile inorganic or organic P in bound form (Hayman, 1975). In the same way that organic N is mineralised, organic P is converted to PO_4^{3-} , which is readily available for crop uptake, and some P will become immobilised in the bacterial biomass (Brookes *et al.*, 1981). A significant fraction of soil P becomes fixed as chemically and physically protected organic P in soil humus and is not available; soil rich in Al-, Fe- or Ca- compounds, for example, will bind to and immobilise plant available P in the soil (Withers and Sharpley, 1995). Aluminium and Fe are the main binding elements in acid soils, and Ca in slightly acidic to alkaline soils (Hayman, 1975).

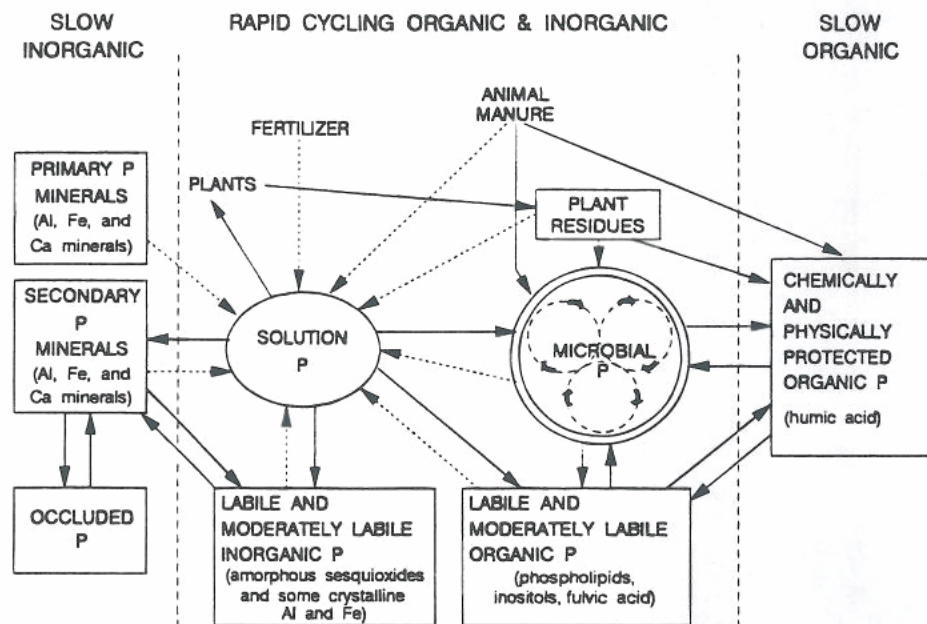


Figure 2.5 The phosphorus cycle, diagram taken from Withers and Sharpley (1995).

2.6.2.3 Losses

Phosphorus is not mobile in the soil but may be lost by removal of plant material, run-off or erosion of insoluble particulate P in surface waters, and subsurface movement of colloidal particles (Sharpley *et al.*, 1994; Smith *et al.*, 2001b).

2.6.3 Organic Matter

Organic matter is an important component of soil, and is composed of living organisms, including root biomass and microorganisms, dead cells and humus. Humus is stable organic material that arises from plant and animal residues that have been decomposed by soil microorganisms (Rowell, 1994). Soil organic matter content is variable and typically between 1.5–6 % ds (Batey 1988), and tends to be greater in soils with high clay content; this is because clay particles physically and chemically protect organic matter (Rowell, 1994). Organic matter coats clay particles, improving structure by increasing adhesion between soil particles (Addiscott *et al.*, 1991). Soil rich in organic matter will become less susceptible to erosion (Ojeda *et al.*, 2003; Ojeda *et al.*, 2006).

Soil organic matter acts as a store of nutrients such as N, S, and P (Paul and Clark, 1996); for example, cultivated soils may contain 2-3 t of N ha⁻¹, in the top 25 cm, mostly in organic forms (Addiscott *et al.*, 1991). Soil organic N may be as little as 0.017 % in a sandy soil (Webb *et al.*, 2000); as much as 0.5 % organic N may be present in cultivated soils with a greater clay content, but this is only very slowly mineralised (Rowell, 1994). Greater soil organic C significantly decreases bulk density, increasing porosity and water holding capacity (Li *et al.*, 2007). Additions of organic wastes to soils may therefore improve soil structure and fertility, by addition of a substrate for microbial biomass, this is discussed further in Sections 2.8.2-2.8.4.

2.6.3.1 Soil Microbial Biomass

Microbial biomass constitutes a small fraction of soil organic matter, 0.1-5 % organic C in the soil (Jenkinson and Powlson, 1975; Banerjee *et al.*, 1997), but has a rapid turnover compared to other soil fractions. The soil microbial biomass is responsible for cycling plant nutrient elements and is closely linked to soil fertility. Microbial biomass N (MBN) is therefore an important fraction of total soil N and may account for approximately 2-6 % N (Brookes *et al.*, 1985b). When organic matter or nutrients are added to the soil, nutrients may become immobilised in the soil biomass, therefore becoming temporarily unavailable for crop uptake, but this represents a labile source of nutrients for crops. The size of the soil microbial biomass is dependent on substrate availability (Zak *et al.*, 1990) and may be related to soil C:N ratio (Trehan, 1996; Templer *et al.*, 2003).

The C:N ratio of microorganisms is variable, fungi have wide C:N ratios of 14:1 to 4.5:1, bacteria have greater N contents and the C:N ratios are usually in the range of 3:1 to 5:1 (Paul and Clark, 1996). Additions of nutrients to soils may change microbial community composition and influence diversity. Frey *et al.* (2004) found that active fungal biomass was reduced by up to 69 % in soils receiving mineral N and ectomycorrhizal fungal community diversity was reduced; bacterial biomass remained relatively unchanged, but the pattern of microbial substrate use was also affected in fertilised soils. It has been suggested that protozoa and nematodes may be of particular importance in turnover of N in the soil by grazing upon the soil microbial biomass (Operman *et al.*, 1989; Ekelund and Rønn, 1994; Bonkowski, 2004; Bjørnlund *et al.*, 2000). Factors influencing the extent and rate of microbial immobilisation in organic residuals-amended soil are discussed in Section 2.9.5.

2.7 Plant Nutrient Requirements

2.7.1 Nutrient Uptake and Transport

Plant mineral uptake is by absorption through roots by bulk flow or diffusion (Hewitt, 1975). Bulk flow depends on the amount of soil water flowing towards the plant, nutrient levels and transpiration rates from the plant. The site of most active absorption is 1-2 mm behind the root apex, but older parts of the root are also capable of active salt absorption (Hewitt, 1975). Water and mineral nutrients are then transported within the plant through the xylem (Scherer *et al.*, 2001). Plant nutrient requirements may depend on species and stage of maturity, and the distribution and partitioning of nutrients varies throughout a plant as they are directed to areas that they are needed in appropriate quantities (Whitehead *et al.*, 1995).

2.7.2 Nitrogen

Nitrogen is the mineral nutrient that plants require in greatest quantities and it is an essential component of chlorophyll, RNA, DNA, amino acids and proteins, therefore a constituent of many plant cell components (Hewitt, 1975). Aside from soil N availability, concentration in plants depends on variety or species, stage of maturity and weather conditions. The concentration of N in roots is usually less than in shoots and leaves (Whitehead, 1995). The typical concentration of N in plant tissue for ryegrass is 2-3.5 % DM at the leafy stage of growth, for clover the concentration is 2.5-5.2 % DM at the leafy stage of growth (Whitehead, 1995).

Nitrogen fertilisation of crops may increase yield and improve quality (Cooke, 1982; Addiscott *et al.*, 1991). Correct timing is essential to ensure crops make best use of N supplied; the quantity required is dependent on crop type and should be applied at the start of periods of rapid crop growth and N uptake. In the UK, N requirement is low during the autumn and winter and fertiliser recommendations suggest that it can normally be met by soil reserves (MAFF, 2000). Grass has a long growing season and is harvested as vegetative growth; it therefore has a greater response to fertiliser N than most other crops as it is more efficient at capturing available N (Addiscott *et al.*, 1991; Christian and Richie, 1998). Variation in N content between different grass species is very small, differences occur in the spring when flowering dates vary. As plants mature there is a decline in N content as a result of an increase in cell wall material and decrease in cytoplasm (Whitehead, 1995).

Nitrogen deficiency has a significant effect on plant growth, there is decreased cell division and expansion, delayed swelling of buds and all parts, especially leaves and fruits, will be reduced in size. Chlorophyll production will be limited therefore leaves will show yellow pigment, chlorosis, and in severe cases the leaves senesce (Hewitt, 1975). An excess of N is also undesirable, it can reduce yield and contribute to problems such as foliar diseases, poor silage fermentation, poor quality grain and lodging of cereals stems (Addiscott *et al.*, 1991; Mantovi *et al.*, 2005).

2.7.3 Other Mineral Nutrient Requirements

Other plant essential mineral nutrients include Phosphorus (P), Potassium (K), Sulphur (S), Magnesium (Mg) and Sodium (Na) and trace elements such as boron (B), Copper (Cu), Iron (Fe) and Manganese (Mn) (Whitehead, 1995).

Phosphorus is mostly taken up in the form of orthophosphate ions, H_2PO_4^- (Hayman, 1975). Phosphate is an essential component of macromolecules such DNA and RNA. It is also part of ATP and has an important role in plant metabolism. Deficiency suppresses lateral bud development and prolongs bud dormancy, and may result in thin and erect growth and purple tinting (Hewitt, 1975).

Potassium is vital in the transfer of carbohydrates from point of production to where they are used in other parts of the plant, and is essential in osmotic and electrical balance of cell solutions (Addiscott *et al.*, 1991).

Sulphur is an essential component of some amino-acids (Hewitt, 1975) and is required in similar quantities to P. Crop S requirements have previously been met from atmospheric deposition, which has fallen in recent years, increasing the risk of S deficiency. Sulphur deficiency causes paling of young leaves and stunted growth; oilseed rape and grass grown for silage are particularly sensitive (MAFF, 2000; Scherer *et al.*, 2001).

Magnesium is required for chlorophyll function (Addiscott *et al.*, 1981) and affects C partitioning in sugar beet (Hermans *et al.*, 2004). Potatoes and sugar beet are susceptible to Mg deficiency, and fertiliser recommendations suggest that they may show small yield responses to applications of Mg fertiliser (MAFF, 2000). However, recent experiments in the UK suggest that use of Mg fertiliser had no increase on total tuber yield, despite increasing concentrations in leaves and stems (Allison *et al.*, 2001).

2.8 Agronomic Value of Organic Residuals

2.8.1 Current Fertiliser Value Recommendations for Organic Residuals

As mentioned previously, nutrients in organic residuals are present in both mineral and organic forms and not all the organic forms will be available for crop uptake. It is important to accurately predict availability of nutrients to prevent over-supply to reduce environmental damage and gain maximum economic benefit.

The most recent edition of RB209, the government's fertiliser recommendations for agricultural and horticultural crops, was published in 2000 (MAFF, 2000). It provides national recommendations for lime and fertiliser use on the major crops and grassland crops in England and Wales and includes guidelines for the nutrients available from organic manures and sewage sludge. Much of the early UK research into the fertiliser value of sewage sludge was conducted by Water Research Centre (WRc) through a series of trials on grassland throughout the UK and these results form the basis of the guidelines in RB209 (Hall, 1983a;b; Hall and Franklin, 1984; Coker and Carlton Smith, 1986; Coker *et al.*, 1987a;b). However, there are currently no guidelines for industrial biowastes, and sewage sludge guidelines need updating to include newly available information of the fertiliser value of biosolids including the sludge types produced by recently developed 'enhanced' treatment technologies. Recent biosolids research is discussed in Section 2.8.3.

In addition to RB209, fertiliser recommendations and advice for use of livestock manures on arable land is available in information booklets from Defra (Chambers *et al.*, 2001a;b), and prediction software, 'MANNER' (MANure Nitrogen Evaluation Routine), is available from ADAS (Chambers *et al.*, 1999). This predicts fertiliser N value of field applied manures, taking into account manure type, N analysis data, soil type, application timing and technique, ammonia and nitrate losses and organic N mineralisation.

2.8.2 Livestock Manures and Slurries

Farmyard manures (FYM), slurries and poultry manures are the main type of organic residual materials applied to agricultural soil (Table 1.1). They supply organic matter, and useful quantities of N, P, K, S and Mg, improving soil structure and condition. Typical nutrient contents and availabilities in livestock manures and slurries are given in Table 2.3

Table 2.3 Typical Nutrient Content and Availability in Livestock Manures and Slurries (Defra, 2001b).

Manure Type	DS (%)	Typical Total Nutrient Content (% DS/mg kg ⁻¹ FW)				
		N	P	K	S	Mg
Cattle FYM*	25	2.4	0.610	2.66	0.288	0.169
Pig FYM*	25	2.8	1.22	1.66	0.288	0.169
Poultry layer manure*	30	5.3	1.89	2.49	0.507	0.442
Poultry litter*	60	5.0	1.81	2.49	0.553	0.442
Cattle slurry [†]	6	2.3	0.523	2.24	0.32	0.442
Pig slurry [†]	4	4.0	0.872	2.08	0.28	0.241

*Nutrient contents in % DS

[†]Nutrient contents in mg kg⁻¹ FW

Current UK fertiliser recommendations are based on extensive research into N and P availability in manures and slurries and the effect of timing, soil type and methods of application and includes laboratory investigations, field investigations and investigations using field-scale equipment (Smith *et al.*, 1984; Nicholson *et al.*, 1996; Jackson and Smith, 1997; Nicholson *et al.*, 1999) to better understand true availability of N to crops. Current recommendations consider the fertiliser value of slurries to be equivalent to their NH₄-N content, which is 40–60 % of total N. For FYM the fertiliser value is considered to be equivalent to their NH₄-N content, which is 10-25 % of total N.

In addition, mineralisable organic N, which is assumed to be 10 % total N, is considered to be available for the second crop following application (MAFF, 2000).

Fertiliser recommendations take into account manure type, dry matter content, application timing, soil type and method of application. It is recommended that 50-60% of crop N requirement is met by supply from organic manures (Defra, 2001b), this is of economic benefit and also means that there is no risk of incurring yield deficit by variable manure N supply. When crops are newly sown, additional mineral fertiliser may improve crop utilisation of nutrients from biosolids, because high availability of nutrients will stimulate root growth and establishment (Krogstad *et al.*, 2003; Mendoza *et al.*, 2006).

Typical total N content in FYM is 2.4 % DS (Table 2.3), and for cattle slurry with a DS content of 6%, typical N content is 6 mg kg⁻¹ FW. Field investigation into first year N availabilities from farmyard manure and cattle slurry in relation to mineral N, have found first year N fertiliser replacement values of 31 % for FYM and 51-53 % for soil injected undigested cattle slurry (Schröder *et al.*, 2007). Laboratory incubation studies have found mineralisable N values of 12 % organic N from sheep manure (Sørensen *et al.* 2001) within the first week of application, similar figures of 6-13 % of N mineralised from cow manure has been reported (Chae and Tabatabai, 1986; Chadwick *et al.*, 2000).

Poultry manures contain higher concentrations of available N, Ca and P than other manures (Chae and Tabatabai, 1986; Sims, 1986; Bitzer *et al.*, 1988; Nicholson *et al.*, 1996; Chadwick *et al.*, 2000; Nicholson *et al.*, 2002). Typical total N contents are 5.0 % and 5.3 % DS for poultry litter and poultry manure respectively (Table 2.3). In field investigations, N fertiliser replacement values of poultry litter was between 33–36 %, and was dependent on crop type and timing (Nicholson *et al.*, 2002). The organic fraction is more stabilised in manures from ruminant animals compared to non-ruminants, and poultry manures may contain a high proportion of labile organic matter; mineralisable N contents of between 25-40 % (Sims, 1986) and up to 67 % (Chae and Tabatabai, 1986; Bitzer *et al.*, 1988; Chadwick *et al.*, 2000) have been reported in laboratory incubation studies. The low C:N ratio of poultry litter (<10:1) means that organic N is readily mineralised (Bitzer *et al.*, 1988). It is a mixture of faeces, bedding material, feathers and uneaten food and is therefore dry and collectable and a useful fertiliser source (Stephenson *et al.*, 1990).

Typical P contents from FYM are 0.61-1.22 % DS (Table 2.3). Current fertiliser recommendations suggest P from livestock manures is 60 % available (MAFF, 2000). In the short-term, P availabilities from manures is less than for inorganic fertiliser P, but in the long-term, availability is equivalent (Smith *et al.*, 1998a). In light of this information, Smith *et al.*, (1998a) suggested that applications of manure at maximum N loading rates would result in soil P enrichment, therefore additional inorganic P additions should be carefully managed to prevent over application.

2.8.3 Biosolids

2.8.3.1 General Characteristics

Biosolids are valuable sources of the organic matter and the major plant nutrient elements, N and P, and provide inputs of S, Mg, Na and Ca and trace elements such as Cu, Zn and B (Chambers *et al.*, 2003). Domestic inputs are a source of a wide range of trace elements such as Cu from plumbing and Zn from cosmetics and galvanising (Bruce and Evans, 2002). However, sludges are not significant sources of K; this is because, during the wastewater treatment process, sludge is elutriated, which is washing of fine particles from the sludge to condition it prior to further treatment and disposal (Vesilind, 1974). Most of the K in the sludge is in mineral forms so it is lost from the sludge during elutriation. Tables 2.4 and 2.5 give the mean and range of physical and chemical properties of dewatered raw, conventional and enhanced treated biosolids, measured by Imperial College (Smith and Bellett-Travers, 2001; Smith *et al.*, 2002b; Smith *et al.*, 2003; Breedon *et al.*, 2003; Morris *et al.*, 2003.; Cass *et al.*, 2005, Perez-Viana *et al.*, 2005; Rigby and Smith, 2005). Table 2.5 shows that typical K content in dewatered digested biosolids (DMAD) may be in the range of 0.9-2.8 g kg⁻¹ DS, a poor source of K in comparison to FYM, which is typically 17-27 g kg⁻¹ DS (Table 2.3). The physical and chemical properties are discussed further for each of the biosolids treatment types in Sections 2.8.3.2–2.8.3.7.

However, as with FYM and livestock slurries, total N and P concentrations do not accurately reflect availability, as, in addition to inorganic N and P that are available in biosolids-treated soil, the majority of N and P contained in biosolids will be in organic forms. The agronomic value of biosolids is dependent on the treatment process, and in particular total N and N availability is affected; this is discussed in more detail for each treatment type. As crop response to fertiliser additions in the UK is primarily determined by the N fertiliser value (Cooke, 1982), this is the nutrient that has received

Table 2.4 Properties of liquid biosolids (fresh weight basis)

Biosolids type	Liquid MAD		Liquid thermophillic aerobic MAD	Liquid thermal hydrolysis MAD
	Mean (range)	n	Value (n=1)	Value (n=1)
DS (%FW)	1.74 (1.62-1.81)	4	3.26	2.34
VS (% FW)	1.06 (1.00-1.11)	4	1.64	1.38
Total N (% FW)	0.16 (0.12-0.20)	4	0.22	0.17
NO ₃ -N (mg kg ⁻¹ FW)	<0.1	2	<0.01	<0.01
NH ₄ -N (mg kg ⁻¹ FW)	914 (714-1166)	4	975.0	556.0
Mineral N (mg kg ⁻¹ FW)	914 (712-1166)	4	975.0	556.0
Mineral N (% TN)	59.1 (41.9-90.7)	4	43.7	32.7
Organic N (% FW)	0.071 (0.010-0.099)	4	0.13	0.11
Organic N (% TN)	40.9 (9.29-58.1)	4	56.1	67.1
Total P (% FW)	0.039 (0.025-0.051)	4	0.07	0.06
Extractable P (mg kg FW)	142.3	1	38.2	131.7
Extractable P (%Total P)	32.1	1	5.52	20.3
K (mg kg ⁻¹ FW)	167.5 (91.9-243)	2	215.0	57.9
Mg (mg kg ⁻¹ FW)	70.7 (66.9-74.4)	2	161.0	63.4
Ca (% FW)	0.089 (0.04-0.094)	3	0.09	0.15
S (mg kg ⁻¹ FW)	153.5 (119-188.0)	2	246.0	324.0

Table 2.5 Properties of dewatered biosolids (dry solids basis)

Biosolids type	DRAW		DMAD	
	Mean (range)	n	Mean (range)	n
DS (%)	20.9 (17-24.5)	3	25.3 (21.2-30.6)	18
VS (% DS)	75.0 (73-76.2)	3	61.0 (53-65.9)	18
pH	-	-	7.1 (6.7-7.9)	8
Total N (% DS)	5.42 (4.06-6.16)	3	5.25 (2.06-6.51)	18
NO ₃ -N (mg kg ⁻¹ DS)	1.74 (0.65-2.82)	3	<0.7 (<0.01-<10)	16
NH ₄ -N (mg kg ⁻¹ DS)	10898 (1916-15600)	3	7297.1 (3397-13986)	18
Mineral N (mg kg ⁻¹ DS)	10899.2 (1918.8-15600.7)	3	7297.1 (3397-13986)	18
Mineral N (% TN)	22.1 (3.17-38.4)	3	14.8 (7.19-44.7)	18
Organic N (% DS)	4.33 (2.50-5.86)	3	4.52 (1.14-5.47)	18
Organic N (% TN)	77.9 (61.6-96.8)	3	85.2 (55.3-92.8)	18
Total P (% DS)	2.7 (2.57-2.79)	3	3.27 (2.27-6.45)	18
Extractable P (mg kg ⁻¹ ds)	-	-	766.6 (338-1259.9)	9
Extractable P (% TP)	-	-	2.32 (1.11-5.05)	9
K (mg kg ⁻¹ DS)	4235 (3440-5030)	2	1807.1 (900-2829)	15
Mg (mg kg ⁻¹ DS)	2530(2230-2830)	2	3235.5 (1690-4640)	15
Ca (% DS)	-	-	6.14 (4.87-7.92)	12
S (g kg ⁻¹ ds)	4.70 (4.11-5.29)	2	10.98 (8.55-1.39)	15

Table 2.5 Cont.

Biosolids type	Compost		Lime Raw		Thermally dried Raw	
	Mean	n	Mean	n	Mean	n
DS (%)	62.2 (56.5-67.7)	5	38.0 (35.1-41.6)	9	93.6 (89.2-96.7)	5
VS (% DS)	39.5 (26.9-59.6)	5	52.1 (37.1-60.6)	9	72.5 (69.8-74.0)	5
pH	8	1	11.2 (9.6-12.3)	5	6.7	1
Total N (% DS)	1.92 (1.47-3.61)	5	2.06 (1.13-2.59)	9	4.49 (4.28-4.58)	5
NO ₃ -N (mg kg ⁻¹ DS)	596.1(0.32-1443)	5	17.5 (<0.01-51.1)	8	7.35 (<0.01-10.7)	4
NH ₄ -N (mg kg ⁻¹ DS)	342.9 (8.44-1030)	5	861 (280-2171)	9	270.6 (144-326)	5
Mineral N (mg kg ⁻¹ DS)	938.9 (196.5-1451.4)	5	876.5 (331.1-2214)	9	276.5 (144-326)	5
Mineral N (% TN)	5.48 (1.28-9.87)	5	4.29 (1.34-9.07)	9	0.62 (0.31-0.76)	5
Organic N (% DS)	1.41 (1.32-1.52)	5	1.98 (1.12-2.56)	9	4.46 (4.25-4.57)	5
Organic N (% TN)	82.8 (38.8-98.7)	5	96.1 (90.9-99.1)	9	99.4 (99.1-99.7)	5
Total P (% DS)	1.38 (0.61-4.2)	5	1.10 (0.45-2.22)	9	2.14 (1.81-2.65)	5
Extractable P (mg kg ⁻¹ ds)	298.9 (227.5-414)	4	828.2 (103.9-1623)	4	111.7 (48.4-202)	3
Extractable P (% total P)	5.32 (4-6.47)	4	14.6 (1.76-36.1)	4	0.56 (0.18-1.12)	3
K (mg kg ⁻¹ DS)	6105.8 (4963-7200)	4	970.8 (600-1330)	5	1992.5 (1300-2380)	4
Mg (mg kg ⁻¹ DS)	4501.2 (3707-5930)	4	1655.8 (1530-1900)	5	2649.3(1500-3130)	4
Ca (% DS)	3.19 (2.82-3.66)	4	19.7 (15.3-25.5)	6	2.69 (2.08-2.89)	5
S (g kg ⁻¹ ds)	5.17 (4.70-5.68)	4	4.04 (2.22-5.83)	5	6.85 (5.20-7.86)	4

Table 2.5 Cont.

Biosolids type	Thermally dried MAD		Thermophilic aerobic DMAD		Thermal hydrolysis DMAD	
	Mean (range)	n	Mean (range)	n	Mean (range)	n
DS (%)	93.2 (89.1-98.5)	10	27.5 (26.6-28.3)	2	27.3 (26.2-28.4)	2
VS (% DS)	59.2 (48.1-66.4)	10	50 (47.7-52.3)	2	56.6 (55.1-58.1)	2
Total N (% DS)	4.31 (3.43-5.11)	10	4.05 (3.89-4.2)	2	5.14 (4.88-5.39)	2
NO ₃ -N (mg kg ⁻¹ DS)	0.92 (<0.01-6.85)	9	<0.01	2	<0.01	2
NH ₄ -N (mg kg ⁻¹ DS)	1245 (333-3100)	10	5637 (4591-6683)	2	8578 (8368-8788)	2
Mineral N (mg kg ⁻¹ DS)	1245.8 (333-2101.4)	10	5637 (4591-6683)	2	8578 (8368-8788)	2
Mineral N (% TN)	2.93 (0.79-8.25)	10	14.1 (10.9-17.2)	2	16.8 (15.5-18)	2
Organic N (% DS)	4.19 (3.37-4.98)	10	3.48 (3.22-3.74)	2	4.28 (4-4.55)	2
Organic N (% TN)	97.0 (91.8-99.2)	10	85.9 (82.8-89.0)	2	83.2 (82.0-84.4)	2
Total P (% DS)	2.82 (1.52-3.77)	10	3.2 (3.05-3.43)	2	5.61 (3.11-8.1)	2
Extractable P (mg kg ⁻¹ ds)	451.9 (232.5-664)	6	94.4 (61.8-127)	2	74.6 (47.2-102)	2
Extractable P (% TP)	1.64 (0.79-2.62)	6	0.30 (0.18-0.42)	2	0.19 (0.058-0.33)	2
K (mg kg ⁻¹ DS)	2709.6 (1740-4290)	7	3835 (2400-5270)	2	2140 (1900-2380)	2
Mg (mg kg ⁻¹ DS)	5689.3 (4200-8070)	7	4945 (4200-5690)	2	5140 (5000-5280)	2
Ca (% DS)	6.17 (4.95-6.8)	8	2.79 (2.78-2.8)	2	3.17 (3.04-3.3)	2
S (g kg ⁻¹ DS)	9.49 (6.58-11.0)	7	10.5 (10.3-10.6)	2	1.61 (1.55-1.67)	2

Table 2.6 Dry solids (DS) contents and total and available (mineral + mineralisable) N and P for a range of conventional and enhanced treated sludge types, a comparison of recent findings and current fertiliser recommendations.

Sludge type	DS (%)	Total N (% DS)	Available N (% total N)	Total P (%DS)	Available P (% total P)	Source
Mesophilic anaerobically digested cake	28.8	5.87	32.1	2.5	50	(Morris <i>et al.</i> , 2003; Smith <i>et al.</i> , 2003)
Mesophilic anaerobically digested cake	25	3	20 [†]	1.57	50	(MAFF, 2000)
Thermally dried mesophilic anaerobically digested cake	98.5	4.32	36.3	2.4	95	(Morris, <i>et al.</i> 2003; Smith, <i>et al.</i> , 2003)
Thermally dried Mesophilic anaerobically digested	95	3.68	15 [†]	2.07	50	(MAFF, 2000)
Lime treated (Raw)	41.6	1.71	37.0	0.45	95	(Morris, <i>et al.</i> 2003; Smith, <i>et al.</i> , 2003)
Lime treated	40	1.5	15 [†]	0.87	50	(MAFF, 2000)
Mesophilic anaerobically digested liquid	1.62	1.7	46.0	2.73	30.6	(Smith <i>et al.</i> , 2003)
Mesophilic anaerobically digested liquid	4	5	55 [†] -65*	1.64	50	(MAFF, 2000)
Compost sludge with greenwaste	64	1.51	21	0.64	Not reported	(Morris, <i>et al.</i> 2003; Smith, <i>et al.</i> , 2003)

[†] N availabilities are for a spring application for all soil types and take into account losses due to volatilisation.

* N availability is for a spring application for all soil types, when the biosolids are deep injected into the soil (25-30 cm)

N.B. Guidelines for Autumn/Winter applications and different methods of incorporation are given in RB209 (MAFF, 2000).

the most attention in this research. The introduction of enhanced methods of sludge treatment, such as a pasteurisation step, thermal drying, lime treatment or composting to eliminate pathogens, has required assessment of the fertiliser value and nutrient release characteristics of these new products under differing conditions (Cogger *et al.*, 1999; Smith and Bellett-Travers, 2001; Smith *et al.*, 2002b; Smith *et al.*, 2003; Breedon *et al.*, 2003; Morris *et al.*, 2003.; Corrêa, 2004; Cogger *et al.*, 2004; Tarrasón *et al.*, 2007). A programme of field trials at the Imperial College field station at Silwood Park, Ascot, between 2001-2003, developed fertiliser advice for enhanced treated and conventional biosolids (Smith and Bellett-Travers, 2001; Smith, *et al.*, 2002b; Morris, *et al.*, 2003). Table 2.6 compares these recent findings, of the total and available (mineral and mineralisable) N and P contents of a selection of conventional and enhanced treated biosolids, to long-standing current recommendations and in recently reported field investigations.

It has been difficult to define the P fertiliser value of biosolids, as agricultural soils in the UK tend to be rich in P from mineral fertiliser applications. Smith and Bellett-Travers (2001) found the yield performance of ryegrass in biosolids-amended soil was independent of P addition and related solely to N release. In general, if sludges are applied according to the N requirements of the crop, there will be sufficient P for the requirements of the crop rotation (Hall, 1983b). Sludges have previously been considered to be rich in total P and the available P is reported to be in the range of 50-60 % relative to superphosphate fertiliser (Hall, 1983a; Coker and Carlton Smith, 1986). This is reflected in the P value of sludges given in the current UK fertiliser recommendations (MAFF, 2000), which is 50 % available P regardless of sludge treatment type (Table 2.6). Recent field trials have shown that this estimate of 50 % P availability stands for dewatered digested biosolids, but that liquid sludges had much greater P availabilities with P release 2-3 times greater than mineral fertiliser (Smith *et al.*, 2003). Since the most recent edition of RB209 (MAFF, 2000) there have been advances in P removal during wastewater treatment, with subsequent effects on P content and availability in sewage sludge. The effects of biological P removal, and chemical dosing methods on P availability in dewatered digested biosolids are discussed in Section 2.8.3.4, and the effects of thermal drying are discussed in Section 2.8.3.7.

In addition to their value as mineral fertiliser replacements, biosolids are a source of organic matter that improves the physical characteristics of the soil. Organic matter content of raw sludge is 70-80 % DS and digested sludge contains 50-60 %, compared

to 75 % in FYM (Hall, 1983b). Improvements to water infiltration rates through the topsoil and porosity have been detected in biosolids-amended soils (Chambers *et al.*, 2003), which reduces surface runoff and erosion and increases plant available water and aeration. The protective effect of a coating of sludge on the soil surface, and the promotion of crop cover also stabilises the soil surface preventing soil erosion (Ojeda *et al.*, 2003). Improvements to soil water holding capacity with biosolids additions of 30-120 t DS ha⁻¹ have been found (Joshua *et al.*, 1997). Significant decreases in bulk density were measured by Hall and Coker (1981) after application of undigested sludge cake on sandy, silt and clay loams at rates of 27 t DS ha⁻¹. Hall and Coker (1981) also found that digested biosolids decreased the bulk density of a calcareous loam and increased its water holding capacity. Large applications of sludge over long periods of time are required to gain a continued significant increase in soil organic matter, as rates of decay of organic matter range between 50-60 % in the first year following application (CEC, 1992). Soil permeability, aggregate stability and bulk density have been found with sludge application rates of 10 t DS ha⁻¹ (CEC, 1992). Cumulative effects of sludge application have increased soil total organic carbon (TOC), and cation exchange capacity (CEC) and decreased pH (Antolín *et al.*, 2005), possibly due to increased rates of nitrification; in alkaline soils this effect may be an advantage. The soil microbial biomass content is increased with biosolids additions to soil, which is associated with improvements in soil fertility (Jedidi *et al.*, 2004; Antolín *et al.*, 2005).

Biosolids additions are of significant value in nutrient depleted soils. For example, Corrêa *et al.* (2004; 2005) reported a higher crop response relative to mineral fertilisers with biosolids application in low fertility soils. In a low fertility Spodosol, with high permeability, low water retention and high aluminium content, stripped of its 10 cm top layer, ryegrass yield showed an improved response to additions of fresh, composted, irradiated, heat dried and lime biosolids types compared to mineral fertiliser (Corrêa *et al.*, 2005).

2.8.3.2 Raw Sludge

Most of the N in raw sewage sludge, 77.9 % total N, is in organic forms (Table 2.5). Mineralisation of N from raw sludge is greater than from anaerobically digested sludge as it is not a stabilised product. Raw sludges have high concentrations of amino acids and there is a high proportion of rapidly mineralisable organic matter, around 25 % of the organic N is mineralised on addition to soil (Parker and Sommers, 1983). Nitrogen availability values between 20-40 % relative to mineral N fertiliser have been reported

for liquid undigested sludge in laboratory and field investigations (Hall, 1983a; Coker *et al.*, 1987; Reed, 1995; Smith *et al.*, 1998b). Coker *et al.* (1987) found 20 % total N in liquid undigested sludge was available in the first year, and a further 40 % total N was available in subsequent years.

Dewatering raw sludge does not significantly affect its fertiliser value, as the principle component of N is in the organic fraction. Bacterial immobilisation on initial addition of untreated sludge to soil has been reported (Smith *et al.*, 1998b; Smith and Tibbett, 2004). This is attributed to the high C:N ratio of undigested sludge, resulting in a rapid increase in microbial activity as organic material is degraded. An increase in N availability will follow as N is mineralised from the organic matter. The use of raw sludge for agricultural production of food crops ended in December 1999 and all agricultural use ended in December 2005 as a result of the implementation of the Safe Sludge Matrix (ADAS, 2001), due to concerns regarding its pathogen content.

2.8.3.3 Digested Sludge

Anaerobic digestion of sludge reduces the amount of organic matter converting a significant fraction of the organic N to ammonia. Therefore, there is a high proportion of mineral N in liquid digested sludge, typically equivalent to 60 % of the total N content (Table 2.4) in liquid mesophilic anaerobic digestate (Liquid MAD). Recent measurements of total N content (Table 2.4) showed a mean total N content of 0.16 % in liquid digested sludge, similar to the value of 0.2 % given in RB209 (MAFF, 2000). Mineral N is the principle source of N fertilisation in this sludge type making it a predictable form of N application, similar to inorganic fertilisers (Coker, 1966; Coker *et al.*, 1987). The relative fertiliser values are generally higher than the proportion of $\text{NH}_4\text{-N}$, due to the contribution from organic N. For example, 15 % of the organic N in digested sludge was mineralised in the year of application (Hall, 1983a).

Current fertiliser recommendations (MAFF, 2000) suggest that 55 % of total N is available (Table 2.6), for a spring application, with the biosolids incorporated into the soil 6 hours after application, and 65 % when liquid biosolids are deep injected, due to reduced volatilisation losses from sludge. Smith *et al.* (1998b) found 80-90 % total N in liquid digested biosolids was available during soil incubation, and most of this was converted to NO_3^- within 20 days of incubation at 25 °C. Coker (1966), in field trials with grass-clover pastures, found a mean relative recovery of N in the crop of 84 % compared to mineral fertiliser. Hall (1983a) reported relative fertiliser values,

summarising results of Water Research Centre (WRc) investigations, of between 35-80 % relative to mineral N, the large degree of variation was related to the variation in $\text{NH}_4\text{-N}$ content in the sludge, which was in the range 30-60 % of total N. Field investigations into tall fescue (*Festuca arundinacea*) growth conducted by Kiemnec *et al.* (1987) found that the relative fertiliser values of liquid digested sludges, measured as dry matter yield, were in the range 36-50%, with $\text{NH}_4\text{-N}$ content in the sludge providing a good predictor of the fertiliser value.

It has been demonstrated that aerobically digested biosolids have a greater pool of mineralisable N than biosolids digested anaerobically (Hall, 1983; Serna and Pomares, 1991a; Serna and Pomares, 1991b; Hernández *et al.*, 2002). A review of the literature by Hall (1983b) reports N availabilities for aerobic sludges from pot and field trials of 30-55 %. Magdoff and Amadon (1980) found a first year mineralisation of 55 % organic-N in aerobically treated sludge applied to corn and hay.

2.8.3.4 Dewatered Digested Sludge

Recent findings suggest the mean total N content in dewatered anaerobically digested biosolids (DMAD) is 5.3 % DS (Table 2.4). This is similar to total N contents in anaerobically digested dewatered caked measured by Cogger *et al.* (1999) in the US, which were between 4.1-4.3 % DS, Cogger *et al.* (2004) found values of 5.0-6.7 DS. These recent findings are greater than the value of 3 % total N given in RB209 (MAFF, 2000). Dewatered digested sludges have lower N availabilities than liquid sludges, reflecting their lower $\text{NH}_4\text{-N}$ content, which is typically approximately 15 % of the total N contained in anaerobically digested biosolids (DMAD) (Table 2.5).

Current fertiliser recommendations for spring application of anaerobically digested cake, incorporated into the soil, give an N availability value of 20 % total N (MAFF, 2000). However, results of recent investigations (Smith *et al.*, 1998b; Smith and Bellett-Travers, 2001; Smith *et al.*, 2002b; Breedon *et al.*, 2003; Morris *et al.*, 2003; Patersen *et al.*, 2003) have found higher N availabilities. This, and the higher total N contents reported recently, may be because existing fertiliser recommendations were based on early work with air-dried digested biosolids (Bunting, 1963, cited in Coker, 1966; Hall, 1983a; Hall, 1984), which had a lower N content than mechanically dewatered product due to volatilisation of NH_3 , and were considered a slow release source of N. In trials with air-dried anaerobically digested sludge, first year availabilities of 10.2 % in sandy soils and 13 % in clay soils were reported (Hall, 1983).

Smith *et al.* (1998b) found a similarly low N availability in air-dried digested biosolids, 7 % of N was converted to NO_3^- after 73 days of incubation at 25 °C, whereas 20-40 % N was available from mechanically dewatered digested biosolids. Research has shown that anaerobically digested sludge consists of different pools of organic matter with varying resistance to decomposition (Terry *et al.*, 1979; Smith *et al.*, 1998b), including a rapidly mineralisable fraction. Parker and Sommers (1983) found a mineralisable N content of 15 % organic N in anaerobically digested sludge. Subsequent investigations have shown that although dewatered cakes have a lower mineral N content than liquid digested sludge it is still appreciable (15 % total N), and they have a mineralisable organic N content of approximately 15 % of the organic N, resulting in a fertiliser value of approximately 30 % of their total N content (Breedon *et al.*, 2003; Morris *et al.*, 2003; Smith *et al.*, 2002b; Smith and Bellett-Travers, 2001). Patersen *et al.* (2003) found a similar relative fertiliser value of 32 % in a crop trial with oats (*Avena sativa* L.). In a pot trial with anaerobically digested and composted sewage sludges, in which willow was grown in amended soil for a period of 36 weeks at 25 °C, Adegbidi *et al.* (2003) reported available N contents of 30 % and 57 % for digested sludges in different soil types; the higher value was attributed to the sludge being fresher at time of spreading. Mendoza *et al.* (2006) determined the mineralisable fraction of organic N in an anaerobically digested cake to be 90 % in a moderately alkaline, calcareous desert soil. The explained this high value may be a result rapid nitrification rates in soil that had been previously air-dried for the incubation study.

Typical total P content in DMAD is 2.3–6.5 % DS (Table 2.5), this is similar to findings of O'Connor *et al.* (2004) for DMAD, 2.8-3.1 % DS, but greater than the value of 1.6 % DS given in RB209 (MAFF, 2000). This may be due to recent methods of improving P removal during wastewater treatment which lead to greater P concentrations in the sludge (Smith *et al.*, 2003; O'Connor *et al.*, 2004). Phosphorus in digested sludge has been found to be 50 % (Smith *et al.*, 2003) and 60 % (Coker and Carton-Smith, 1986) as available as a mineral P fertiliser, consistent with current guidelines of 50 % availability (MAFF, 2000). There have been recent developments in biological and chemical P removal methods from wastewater. Recent findings show that biological methods of removing P from wastewater more than double the P availability in dewatered digested sludge, so that P availability is equivalent to fertiliser P (Smith *et al.*, 2003; O'Connor *et al.*, 2004). Therefore, management considerations are especially important for these biosolids types, care needs to be taken to ensure that P is not added in excessive quantities.

Dosing with Fe- or Al- salts to remove P during wastewater treatment may reduce P availability when sludges are applied to soil; O'Connor *et al.* (2004) found relative P availability was reduced in biosolids with more than 10-30 kg⁻¹ of combined Fe and Al, Smith *et al.* (2002a) also found a reduction in P availability from these sludge types. These findings agree with earlier work (De Haan, 1980), which demonstrated that P availability from sewage sludges containing Fe- or Al- salts was 17-54 % in comparison with mineral fertiliser P, compared to 36-90 % availability in sewage sludge without addition Fe- or Al- salts. Smith *et al.* (2003) found that Fe dosing of sludge had no effect on P availability, despite elevated P concentrations in the sludge, which may indicate that increased Fe concentration had a counteracting affect on increased P contents by reducing P availability.

A reduction in soil bulk density has been demonstrated in soil treated with anaerobically and aerobically digested sludge in comparison to unamended control plots with a subsequent two fold increase in water holding capacity in sludge treated soil (Harding *et al.*, 1985).

2.8.3.5 Lime Treated Sludge

Lime treatment reduces the total N content of sludge by increasing the release of NH₃ as a result of the high pH, and by reducing the ratio of N in relation to the CaO content of the sludge (Evans, 2001). Lime sludge has a mean total N content of 2.0 % compared to over 5.0 % typically in DMAD (Table 2.5), due to dilution as a result of lime addition. The total nutrient contents may vary depending on the relative quantities of lime used for treatment; Corrêa (2004) found biosolids treated with 30 % CaO had a total N content of 4 %. Cogger *et al.* (2004) found values of 3.9 % and 5.4 % for lime treated anaerobically digested cake compared to 5.0-6.7 % for dewatered anaerobically digested sludge.

The relative N fertiliser value of undigested limed sludge has been reported as 16 %, half that of digested limed sludge (Hall, 1983a). Current fertiliser guidelines suggest total N in lime treated sludge is 1.5 % DS, and 15 % of total N in lime treated sludge is available, although they do not distinguish between limed undigested or limed digested. Recent trials have suggested higher N availabilities in lime treated raw sludge of 37 % total N relative to mineral fertiliser N (Table 2.6) (Smith and Bellett-Travers, 2001; Smith *et al.*, 2002b; Smith *et al.*, 2003; Breedon *et al.*, 2003; Morris *et al.*, 2003).

Recently measured mean total P content in limed cake was 1.1 % DS compared to 3.3 % in DMAD (Table 2.5), again this is a dilution effect, following lime addition, and is similar to the value of 0.9 % DS in current fertiliser guidelines (MAFF, 2000). Land reclamation experiments by Coker *et al.* (1982) found fresh limed cake had a P availability of 30-40%, and stacked limed cake was 55-80% available as fertiliser P. Smith *et al.* (2003) found that lime stabilised raw sludge had an equivalent P availability to triple superphosphate fertiliser. The increased availability may be a result of decreased P fixation by Al- and Fe-compounds, which is greater at acidic pH values (Hayman, 1975).

Lime addition may have other benefits, for example it has been found to reduce the rate of decay of organic matter. Mineralisation of organic N may be delayed for several weeks after application to the soil until the pH has fallen to 8.5 (CEC, 1992). Lime has been traditionally added to soil as a pH amendment and lime treated sludge can be used as an effective liming material in acidic soils. Lime treated sludges may have increased K contents, as some alkaline additions contain K, which is beneficial as biosolids are a poor source of K in comparison to livestock manures and slurries (Evans, 2001).

2.8.3.6 Composted Sludge

Composting sewage sludge produces a high stability source of organic matter with low nutrient availability with total N contents typically in the range of 0.9-2.0 % (Table 2.5). Similar values were also reported by Mantovi *et al.* (2005) who found total N in sewage sludge compost was 2.95 % DS compared to 4.25 % DS in dewatered cake, and Corrêa *et al.* (2004), who reported a total N content of 1.59 % in composted biosolids. The low total N content is a result of volatilisation of NH₃ during the composting process and the addition of bulking materials with a low total N content. Variability in total N contents is introduced by the type and quantity of bulking material used. Mineralisable N values of 6 % (Tester *et al.*, 1977), 7 % (Epstein *et al.*, 1978), 8 % (Parker and Sommers, 1983), 10 % (Smith *et al.*, 1998d) 12 % (Adegbidi *et al.*, 2003) and 16.7 % (Morris *et al.*, 2003) have been found. Immobilisation of N has been reported in biosolids-compost amended soil (Tester *et al.*, 1982; Sims *et al.*, 1990; Tester *et al.*, 2003), as a result of high C:N ratios, which may be influenced by the materials used for co-composting the sludge. When applied to soil, composted biosolids may improve soil structure and fertility. Tester *et al.* (1982) found that nutrient concentrations in fescue grown in soil amended with sludge compost were equally

distributed between roots and leaves, whereas fescue roots in soil treated with mineral fertilisers contained about one-fourth of the total N; the authors suggested that compost stimulated root growth.

2.8.3.7 Thermally-Dried, Thermal Hydrolysis and Thermophilic Aerobic Biosolids

Thermally-dried biosolids have a high DS content, approximately 95 % (Table 2.5). Ammoniacal-N is lost by volatilisation during the thermal drying process, so total N content is reduced. Whereas mean total N in DMAD was measured at 5.3 %, a mean total N content of 4.3 % DS in thermally dried MAD, has recently been found (Table 2.5). This is similar to the value of 3.7 % DS given in RB209 (MAFF, 2000), and other recently published values of 4.2-6.8 % DS (Cogger *et al.*, 1999; O'Connor *et al.*, 2004; Cogger *et al.*, 2004; Corrêa *et al.*, 2004). It has been suggested that thermally dried biosolids provide a slow release source of N (Whipps and Whorton, 1997). However, subsequent studies have shown that, despite the lower mineral N content compared to mechanically dewatered cakes, thermally dried biosolids provide rapidly available and similar inputs of available N as conventionally digested counterparts (Cogger *et al.*, 1999; Smith and Durham, 2002; Tarrasón *et al.*, 2007). Cogger *et al.* (1999) estimated relative fertiliser values between 22-38 % for heat-dried and thermophilically digested-dewatered biosolids. In a laboratory incubation experiment, Smith and Durham (2002) showed that 30-60% of the total N content in thermally dried biosolids was available, as opposed to 30-40% available N in dewatered digested sludge. Immediate increases in the NH_4^+ content of soil amended with thermally dried sludge have also been found (Breedon *et al.*, 2003). In field investigations, Morris *et al.* (2003) found relative fertiliser values for TDMAD of 37.8 % compared to 30.5 % for DMAD, these are greater availabilities than recommended in current guidelines (MAFF, 2000), which suggest that less than 15 % total N is available from thermally dried biosolids.

Thermal drying may cause fundamental changes to the organic matter composition of the sludge resulting in larger and more rapidly mineralisable pools of N in comparison to conventionally treated sludges. Lowe *et al.* (1996) found that thermally dried sludge has a lower bulk density than digested cake, it is possible that differences in physical structure affect the degradability of the organic matter. Breedon *et al.* (2003) suggested that thermally dried biosolids may contain elevated concentrations of simple organic N compounds such as urea that may be rapidly hydrolysed to NH_4^+ by extracellular soil enzymes on incorporation into the soil.

Recent measurements suggest that total P in thermally dried biosolids is typically 2.8 % DS (Table 2.5) similar to the value given in RB209 (MAFF, 2000) of 2.1 %, and values of 2.7 % reported by O'Connor *et al.* (2004). However Corrêa *et al.* (2004), found a total P content of 7.3 % in heat dried biosolids. Thermal drying of digested biosolids may increase P availability so that it is equivalent to mineral fertiliser (Smith *et al.*, 2003). However, Smith *et al.* (2002a) had previously found a reduction in relative P availability following thermal drying due to formation of insoluble Ca-P minerals; O'Connor *et al.* (2004) also found heat drying reduced relative P availability by approximately 20 %.

Dewatered thermophilic hydrolysed MAD and dewatered thermophilic aerobic digested MAD contain similar total and mineral N contents to DMAD (Table 2.5). Thermal hydrolysis does not alter N availability, however the thermophilic aerobic pasteurisation step has been found to increase the mineralisable N content from approximately 15 % organic N to 27.8 % organic N (Morris *et al.*, 2003). Thermophilic aerobic MAD therefore may have a similar available N content to thermally dried biosolids of 37.8 % total N (Morris *et al.*, 2003).

2.8.4 Industrial Biowastes

2.8.4.1 General Characteristics

Organic residuals applied to agricultural land may include materials such as brewery waste (Mbagwu, 1990; Erdem and Sozudogru Ok, 2002), paper-mill residues (Beyer *et al.*, 1997; Madejón *et al.*, 2003), rice mill waste (Schulz *et al.*, 2003), almond residue (Pedreño *et al.*, 1995), oily food waste (Rashid and Voroney, 2005), wool waste (Zheljazkov, 2005) and dairy factory effluent (Ghani *et al.*, 2005). If they meet the appropriate criteria, many of these wastes may be spread directly on land, or they may receive some pre-treatment prior to spreading such as dewatering, digestion or composting. Waste ashes, from incineration of biodegradable waste, such as food scrap ash and horticultural waste ash (Zhang *et al.*, 2002), may also be landspread. With the exception of paper-mill sludges (King *et al.*, 1984; Mbagwu, 1990; Beyer *et al.*, 1997; Aitken *et al.*, 1998; Pathak *et al.*, 1999; Foley and Cooperband, 2002; Madejón *et al.*, 2003; Douglas *et al.*, 2003; Kütük *et al.*, 2003; Levy and Taylor., 2003; Burgos *et al.*, 2006; Cordovil *et al.* 2007), there has been relatively little quantitative research on the agronomic characteristics of industrial biowastes when applied to land in the UK, despite the strategic importance of this outlet for managing these highly

variable materials, as an alternative to landfill disposal. However, evidence exists to show that some of these materials can increase soil nutrient contents and improve crop growth. Douglas *et al.* (2003) investigated ryegrass yield and nitrogen availability in a 3 year experiment in Ayreshire, Scotland, with five biowastes: composted green waste, abattoir blood and guts, distillery pot ale, and dairy salt whey. Apart from this experiment, data on these, and a variety of other wastes that come under Para 7A of the WMLR (SI, 2005a), is lacking.

A survey of data from waste exemption applications held by the EA in the Thames region (Payne, 2006) found a wide range in nutritional characteristics in the waste types spread to land, except for pH. In the survey the range in pH values was found to be small and tended to be neutral. Range and median N and P concentrations are shown in Figures 2.6 and 2.7 and total nutrient element contents (% DS) and pH are given in Table 2.7. More than 75 % of the biowastes had concentrations of N lower than 2.5 % DS, however N concentrations were as high as 10 % DS (Figure 2.6). Phosphorus concentrations were in the range of <0.001-9.6 % DS (Figure 2.7), K was between <0.001-2.4 % DS, Mg was between 0.02-3.4 % DS, Ca was between 0.3-25 % DS and S concentrations were between <0.001 and 32.4 % DS (Payne, 2006). Research into the nutrient availability of biowastes is necessary to support their increasing use on farmland and facilitate the continued reduction of biodegradable waste sent to landfill sites. Complex interactions between soil type, soil environmental conditions and biowaste type are to be expected in a similar way to biosolids, these are discussed in Section 2.9. However, biowaste materials may be a more complex situation because of the extent of the potential variability in characteristics of these waste types compared to biosolids.

2.8.4.2 Paper Industry

Large quantities of water are consumed in paper production, so types of waste produced by the paper industry may include primary or secondary sludge from wastewater treatment (Gibbs *et al.*, 2005).

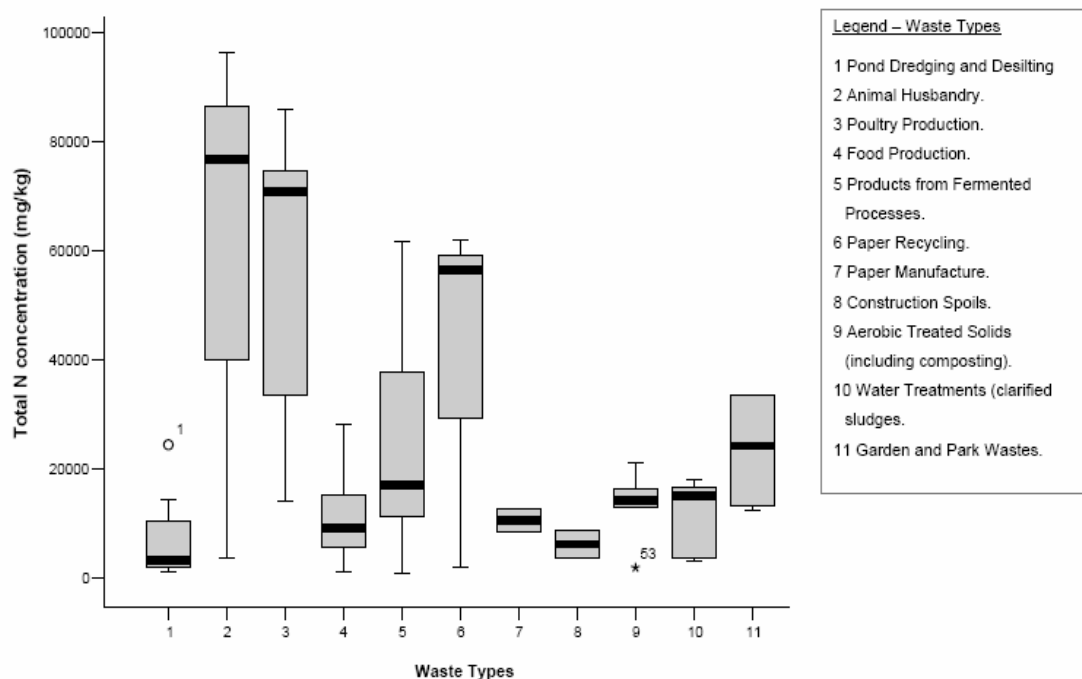


Figure 2.6 Box plots showing the median and interquartile ranges of total N concentration from a survey of exempted biowaste types in the Thames region. Figure taken from Payne (2006).

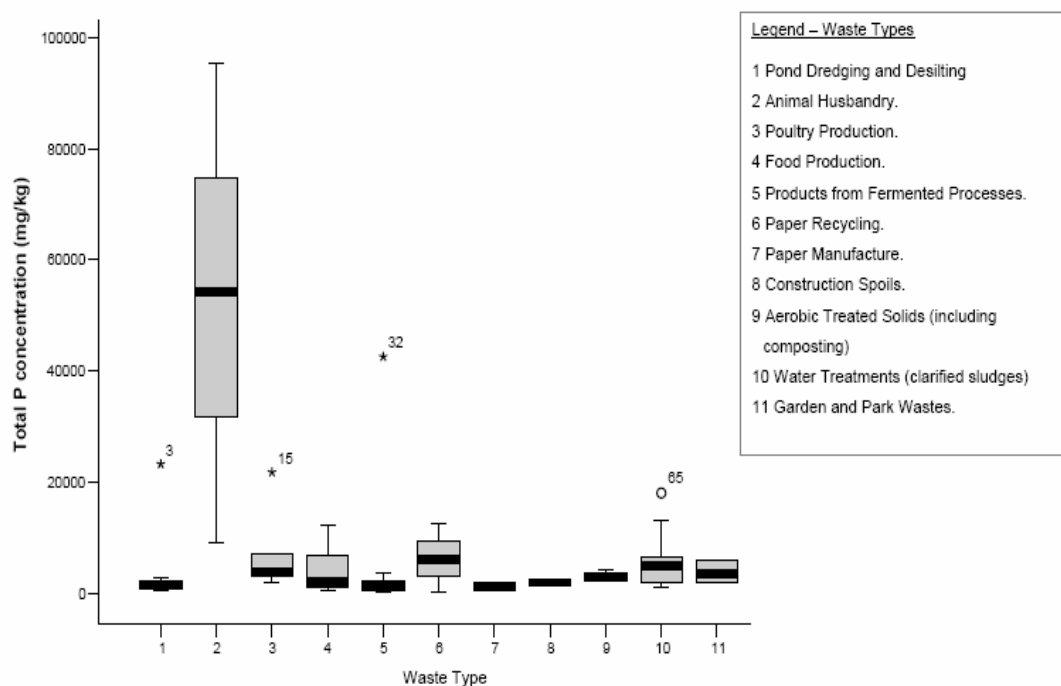


Figure 2.7 Box plots showing the median and interquartile ranges of total P concentration from a survey of exempted biowaste types in the Thames region. Figure taken from Payne (2006).

Table 2.7 Mean total nutrient element content (% DS) and pH of different exempt biowaste types in the Thames Region (Payne, 2006).

Source of waste (extracted from exempt waste notification form)	n	N	P	K	S	Ca	Mg	pH
Animal husbandry (agriculture)	3	5.88	5.30	1.10	0.98	2.39	0.30	7.1
Pond dredging and desilting	8	0.70	0.41	0.48 ^(a)	4.38	1.78 ^(b)	1.23 ^(c)	7.3
Poultry production and processing (including shed washing)	5	5.57	0.75	0.94	0.61	3.37 ^(d)	0.15	6.4
Food production and processing including coffee, fruit, vegetable, frozen meals, and animal feed	9	1.18	0.34	0.28	0.37	3.21 ^(e)	0.18 ^(f)	5.8
Wastes from fermentation processes (brewery, alcoholic drink production, drink recycling and baking processes)	15	2.29	0.41	0.39	0.59	0.29 ^(g)	0.12	4.5
Sludges and pulp from paper recycling processes	3	4.01	0.63	0.44	0.45	24.9 ^(h)	0.27	5.8
Paper manufacturing solid wastes	2	1.05	0.12	0.03	0.07 ⁽ⁱ⁾	NR	0.02	7.1
Construction and demolition dredging spoils	2	0.61	0.19	0.01	NR	NR	NR	7.4
Aerobic treated solid waste including compost	6	1.34	0.3	0.94	1.47	4.74	0.35	7.6
Clarified water treatment sludge (for supply to domestic and industry customers)	12	1.18	0.59	NR	NR	NR	NR	7.5
Municipal and civic amenity green waste (parks and gardens)	7	2.33	0.28	0.85	0.17	3.15	0.23	7.3

(a) n=6 (b) n=3 (c) n=3 (d) n=1 (e) n=7 (f) n=8 (g) n=1 (h) n=1 (i) n=1

NR=no values reported

In addition, liquid effluent and sludge containing lignin and cellulose is produced from the use of virgin wood fibre in paper production. Sludge is also produced from reusing fibre for recycled paper, this may contain colour and chemical and bleaching residues. Findings from a survey of Environment Agency area offices data, paper mills data and contractor data found that spreading to agricultural land is the main management route of paper waste in England and Wales, an estimated 7.12×10^5 t FW is spread to land annually (Gibbs *et al.*, 2005).

Paper wastes generally have low N concentrations; mean total N concentration of paper manufacture wastes in the Thames region was 1.1 % DS (Table 2.8) (Payne, 2006). Similarly, in an EU survey, mean total N concentration in paper sludges was 1.3 % (Gendebien *et al.*, 2001), and Davis and Rudd (1997) found that the mean total N content was 0.42 %, and the maximum was 0.69 %. Total N contents from paper recycling waste to be landspread in the Thames region were more variable than paper manufacture wastes (Figure 2.6) and had a high mean N content of 4.0 % DS (Table 2.7) (Payne, 2006). The maximum N content measured by Gendebien *et al.* (2001) was also high at 5 %. In a survey of paper wastes spread on agricultural land, Gibbs *et al.* (2005) found that wastes that had undergone biological treatment had greater nutrient contents as a result of bacterial biomass. For example, primary treated paper wastes and secondary, chemically or physically treated, biowastes had mean total N contents of 0.25 and 0.18 % respectively compared to 0.75 % for paper wastes that had secondary biological treatment. Therefore, the high N contents observed in some cases for paper recycling wastes in the Thames region, may result from sludge that has had secondary biological treatment. Paper effluent sludges have a wide range of pH values; land-applied paper sludges in the Thames region had a pH range of 2.8-8 (Payne, 2006). Calcium content was only available for one sample in the Thames data (Table 2.7), however the content was very high at 24.9 %, this is due to CaCO_3 additions during the de-inking process (Gendebien *et al.*, 2001). The added CaCO_3 , gives liming value to the paper wastes, pH may rise by 0.1-0.7 units per 100 t FW applied (Gibbs *et al.*, 2005).

Without the addition of sufficient additional fertiliser N, additions of paper wastes to soil may result in initial net N immobilisation, due to the high C:N ratio (King, 1984; Aitken *et al.*, 1998; Douglas *et al.*, 2003; Levy and Taylor, 2003; Burgos *et al.*, 2006). Aitken *et al.* (1998) found 2 kg N ha⁻¹ was immobilised per t DS of de-inked paper mill waste. However, the immobilised N may become slowly available after two years (Aitken *et al.*, 1998; Douglas *et al.*, 2003). The composition of paper wastes is variable and stabilisation treatment may affect N release properties, in a pot trial Cordovil *et al.* (2007) found net mineralisation of 5 % organic N from composted paper waste. Moderate applications of paper mill sludge (Madejón *et al.*, 2003) have had positive effects on crop yield. Biowastes may improve the organic matter content of amended soil (Kütük *et al.*, 2003, Mbagwu, 1990, Pathak *et al.*, 1999), and additions of composted papermill wastes may increase plant available water (Foley and Cooperband, 2002). However, the effect of paper-mill residue on soil organic matter content has been found to disappear within a year (Beyer *et al.*, 1997).

2.8.4.3 Meat and Fish Industry

Waste from abattoirs includes: blood, bones, feathers, stomach and bowel contents manure and wash waters. Wastewaters may be treated by dissolved air flotation (DAF) to separate out solids, and this process generates sludge (Gendebien *et al.*, 2001). Much of the waste is re-used in other industries, such as hoof parts and bone meal (80-90%), but 5-10 % is landspread, this is mainly washwater and gut contents (Gendebien *et al.*, 2001). Abattoir wastes contain high concentrations of N, P and K. In a survey of wastes spread to land in the Thames region, wastes from animal husbandry and poultry production contained the highest concentrations of N and P (Figures 2.6 and 2.7). However, this group of wastes included animal manures and slurries. The findings of an EU survey (Gendebien *et al.*, 2001) found blood waste had total N contents in the range of 0.6-34 % DS; total P was <0.001-4.7 % DS and total K was <0.001-4.8 % DS. Stomach contents had a total N content of 0.2-25 % DS; total P content was <0.001-1.48 % and total K content of <0.001-0.83 % DS.

Nitrogen availability from abattoir wastes may be high; Douglas *et al.* (2003) found that yield of ryegrass grown on blood and gut contents from beef cattle, applied at 250 kg N ha⁻¹, was equivalent to yield from mineral fertiliser N applied at the same rate. In a study into N mineralisation from materials such as hoof, dried blood and crab shell meal, which have a history of being used as horticultural soil amendments, Bremner and Shaw (1957) found the protein in these materials was a rapidly mineralisable source of N, 71 % total N in hoof was mineralised within 40 days incubation in a sandy loam at 25 °C, greater than the amount of total N mineralised from dried blood, which was 60 %. Dried blood and feathermeal (Smith and Hadley, 1992; Smith and Hadley, 1998) have been demonstrated to be an effective fertiliser source for summer cabbage. When base dressings of the organic N sources were applied, the N content was rapidly mineralised to produce yields comparable with mineral fertiliser N.

2.8.4.4 Fruit, Vegetable and Grain Industries

Wastewaters produced by food processing industries result from washing of soil, pulp, peelings, skins, stalks and leaves from fruit and vegetables, dehydration, or cleaning of equipment. For example, the preserves industry uses 10-50 m³ of water per t of material (Gendebien *et al.*, 2001). Raw wastewaters are often spread directly as a land treatment or, alternatively, sludge from wastewater treatment may be landspread. Landspreading is a major outlet for sugar beet waste (Gendebien *et al.*, 2001).

Estimates of sludge fresh weight (FW) produced from sugar beet processing in Europe are 25×10^6 t produced of which 8×10^6 t are recycled to land; the figures for the UK are 9×10^6 t fresh weight produced and 2×10^6 t spread to land. This includes sludge from wastewater treatment and lime sludge generated during the clarifying of sugar juice (Gendebien *et al.*, 2001). Lime sludge generally has a pH greater than 7.5 (Davis and Rudd, 1997), and is therefore of beneficial value on acidic soils. Olive oil processing also relies on landspreading as a management strategy for waste materials. Of the 11×10^6 t FW of waste generated from olive oil processing in Europe, more than 3×10^6 t is recycled to land. There is an estimated 30×10^6 t FW other fruit and vegetable processing waste generated in Europe, with more than 3×10^6 t recycled to land. The UK figures are 3×10^6 t FW produced and 0.15×10^6 t spread to land (Gendebien *et al.*, 2001).

Nitrogen, P and K are found in relatively high proportions in vegetable matter, generally in organic forms. Parnaudeau *et al.* (2006) investigated C and N mineralisation from a wide range of wastewaters from the food processing industries, including a sugar refinery, starch factory and a vegetable cannery. They found N mineralisation rates were generally low, there was high variability in C mineralisation rates under controlled conditions, some were very high and the authors concluded that the wastes could be considered as an efficient land treatment. Rice mill waste applications of 10-15 t DS ha⁻¹ (Schulz *et al.*, 2003) showed positive effects on crop yield.

However, net immobilisation has been observed with application of some crop residues (Chae and Tabatabai, 1986). Applications of crop residues such as liquorice root refuse at rates of up to 30 t ha⁻¹ may have beneficial impacts on bacterial and fungal populations in soil (Sameni and Tajabadi, 2001).

2.8.4.5 Leather and Tanneries

Tannery sludge has significant fertiliser value in terms of N, P, Mg, S, Ca, and Na content, and mineralisable organic N contents between 18-20 % have been measured (Wickliff *et al.*, 1982; Wiseman and Zibilske, 1988,). Irrigation of soil with tanneries wastewater from a leather processing plant in Mexico, over a period of 25 years, was found to double organic C, total N and microbial biomass content of soil (Alvarez-Bernal *et al.*, 2006). However, tannery wastes contain high chromium (Cr) contents, 2-4 % (Wickliff *et al.* 1982; Wiseman and Zibilske, 1988; Alvarez-Bernal *et al.*, 2006), which limit application to land. Alvarez-Bernal *et al.* (2006) found that Cr concentration

in tannery wastewater irrigated soil was 4 times greater than in control soil and Cu concentrations were 2 times greater. Nitrite concentrations were also elevated indicating inhibition of NO_2^- oxidation, which suggested there may be some adverse effects on soil functioning.

2.8.4.6 Dairy Industry

Increased concentrations of microbial biomass have been reported in soil following amendment with dairy effluent (Ghani *et al.*, 2005), due the addition of high concentrations of soluble C compounds such as lactose. Poor fertiliser value of dairy factory effluent has been reported as a result of bacterial immobilisation of soil N (Ghani *et al.*, 2005; Cameron *et al.*, 2002) and S (Ghani *et al.*, 2005), due to the high C content and availability of this material.

Salty whey is produced during cheese manufacture. Large concentrations of N, P, K and Na may be found in this materials, which can be used as plant nutrients; However, excessive salt addition to soil may result in a reduction in availability of water and toxic effects. Application under dry conditions can result in high soil electrical conductivity (Davis and Rudd, 1997). Douglas *et al.* (2003) reported reduced ryegrass yields in comparison to unamended control soil in the first year following soil amendment of salt whey, and less than 10 % of total applied N was recovered in the crop.

2.8.4.7 Drinks Industry

Soft drinks manufacturers produce waste water with low solids content and high levels of soluble sugars. They can become very acidic on storage and normally require neutralising prior to landspreading. Treatment by aerobic or anaerobic digestion to reduce their high biological oxygen demand (BOD) may also be necessary (Davis and Rudd, 1997).

The alcoholic drinks industry is a source of biowastes. Wastes from fermentation processes spread to land in the Thames area (Payne, 2006), which may include processes other than brewing, such as baking, had a mean N content of 2.3 % DS and mean P content of 0.41 % DS (Table 2.7). Types of waste from beer production include waste beer and wash water, spent grain, spent yeast and kieselguhr. Kieselguhr is a siliceous material used to filter organic contaminants from the beer, and is not strictly a 'biowaste', but it is included in this project as a related material. Spent

grain and yeast are commonly used as animal feed but the high content of plant nutrients and organic matter means that they also have value as agricultural soil amendments. Waste beer and wash water contain carbohydrates in solution, the low solids content means that this material will normally have a low nutrient content. Increases in crop yield have been found with applications of brewery waste to soil (Mbagwu, 1990; Erdem and Sozudogru Ok, 2002; Kütük *et al.*, 2003), with application rates of 10 t ha⁻¹ recommended to obtain maximum yields (Kütük *et al.*, 2003). In a field investigation with anaerobically digested sewage sludges and brewery sludges (Hall and Franklin, 1983), total N recovery in grass grown on plots treated with brewery sludge was 1.42 times that in grass treated with biosolids, which was attributed to the larger proportion of mineralisable organic N in brewery sludge compared to sewage sludge.

Wine production wastes, such as grape skin, seeds and extracts, have significant nutrient concentrations and potential value in agriculture. There is a limited amount of research available into the fertiliser value of composted grape waste (Arvanitoyannis *et al.*, 2006).

Distilleries produce large quantities of wash water, 13 l of waste water may be produced per l of ethanol. This liquid contains 0.5-1.0 % soluble C, and is high in K, with concentrations of around 0.91-1.53 kg m⁻³, and concentrations of N in the range 0.25-0.35 kg m⁻³ (De Resende *et al.*, 2006). Increased crop yields have been found with distillery waste, which can be an effective source of available N and P (Pathak *et al.*, 1999; Douglas *et al.*, 2003; Rezende *et al.*, 2004). An incubation study (Rezende *et al.*, 2004) showed that applications of 1 % distillery yeast to soil increased microbial biomass by 3 times and also increased available P and N concentrations in soil. Field experiments in north east Brazil (De Resende *et al.*, 2006), showed that over a 16 year period, applications of distillery waste of 80 m³ ha⁻¹ increased mean sugar cane yields by 12-13%, but there was no significant increase of soil C reserves, as the added organic matter was rapidly mineralised in warm climates. In contrast to these findings, Kaushik *et al.* (2005) found that a salt affected soil in India, with low organic C, increased in soil C, N, K and P, following 10 years of irrigation with distillery waste.

Bentonite is a clay used to remove proteins during winemaking, it may increase soil N, K and P content, CEC and microbial biomass, and it may have liming value as a pH amendment to acidic soils (Arias-Estévez *et al.*, 2007).

2.8.4.8 Pharmaceuticals

The pharmaceutical industry generates biowastes directly from the production process in addition to primary and secondary sludges from wastewater treatment. Production of antibiotics produces fermentation residues such as spent mycelium, and other cell debris, tars and by-products from synthesis of chemicals (Parks, 2006). These materials may have significant value as soil amendments, however concerns over PTEs and pathogens mean they may require pre-treatment instead of landspreading directly.

2.8.4.9 Processed Biowastes

Biowastes may be treated by processes such as composting, anaerobic or aerobic digestion, or dewatering prior to landspreading. These treatments are routinely applied for treatment of sewage sludges and are described in Section 2.1.2. Pre-treatment will incur costs but may prove economically viable if, for example, the process results in a less bulky biowaste, which is easier to transport (Davis and Rudd, 1997). In the case of anaerobic digestion, revenue is also generated through renewable energy production. Pre-treatment will affect the properties of the wastes and may make them more consistent fertiliser materials, by stabilisation of the organic matter content. The nutritional characteristics and agronomic benefit of biosolids treated by these methods are described in Section 2.8.3.3-2.8.3.7, and may have relevance to biowastes treated by these processes, although further research is required in this area.

Composting is frequently practiced as an alternative to landfilling for the biodegradable fraction of municipal solid waste, sewage sludge and other organic wastes. The availability of nutrients in composted wastes such as olive cake, grape waste, hedge trimmings and herbaceous residuals and municipal solid waste, has received more attention than untreated biowastes (Garcia-Gomez *et al.*, 2002; Douglas *et al.*, 2003; Wolkowski *et al.*, 2003; Al-Widyan, *et al.*, 2005; Luxhøi *et al.* 2007). However, whilst supplying valuable organic matter to the soil, which improves soil structure and stability, composts have low and relatively predictable nutrient availabilities as a result of their stable organic matter content. Applications of municipal solid waste (MSW) compost up to rates of 90 Mg ha⁻¹ have been found to have little effect on nutrient concentrations in plant tissue (Douglas *et al.*, 2003; Wolkowski *et al.*, 2003). In a laboratory incubation study, Luxhøi *et al.* (2007) found that anaerobically digested MSW was 10 times more degradable than composted MSW, both types of treated

waste resulted in initial net N immobilisation followed by mineralisation. Sullivan *et al.* (2002) found N availabilities of between 2.0–5.2 % total N in the second and third year following application of food waste compost.

Waste ashes from the incineration of biodegradable waste, such as horticultural waste ash, MSW ash, food scrap ash and animal waste ash, have been supplied as soil amendments, primarily due to their neutralisation capacity of 10-30 % of CaO. Ashes also contain plant nutrient elements, with P contents in the range of 10-29 g kg⁻¹ and K contents in the range of 14-63 g kg⁻¹ (Zhang *et al.*, 2002). However they also contain appreciable concentrations of heavy metals which limit the rate of application.

2.9 Factors Influencing N Transformation Processes in Soils Amended With Organic Residuals

2.9.1 Temperature

Soil temperature has been reported as a major factor influencing sewage sludge decomposition; temperature increases in the range 5-30 °C, may result in concurrent increases in the mineralisation rate (Miller, 1974; Stanford and Epstein, 1974; Terry *et al.*, 1979; Honeycutt *et al.*, 1991; Smith *et al.*, 1998b;c;d; Agehara and Warncke, 2005). In a survey of 15 laboratory incubation studies, in which soil was amended with crop residues, papermill sludges and inorganic fertiliser sources, highly significant relationships were found between NO₃-N formation and thermal time units. Factors such as soil type, pH and climate affected the NO₃⁻ x thermal time relationship (Honeycutt *et al.*, 1991). The effects of soil temperature on mineralisation is dependent on the source of organic N, for example, Agehara and Warncke (2005) found that increasing temperature increased mineralisation from chicken manure, blood meal and alfalfa pellets but did not affect net N release from urea. Presumably this is because urea is a simple organic compound, which is rapidly mineralised. Cookson *et al.* (2003) investigated the effects of winter soil temperatures, between 0-15 °C, on mineralisation of N in soil amended with clover residues. Mineralisation of N increased with increasing temperature; however, significant amounts of N were mineralised at 2 °C, which suggested that soils amended with organic residues over winter continued to be at risk of losses of N by leaching by winter rainfall. Other interesting effects observed were that, in amended soil incubated at 2 or 5 °C, there was an initial accumulation of NH₄-N, but after a period of 56 days, concentrations of NO₃-N increased, indicating a lag phase for the nitrifying bacteria to adjust to the incubation temperature. Opperman

et al. (1989) also observed mineralisation and nitrification in slurry amended and non-amended soil incubated at 5 °C. However, increasing the temperature to 23 °C increased the nitrification rates. Higher temperatures may increase volatilisation rates, Opperman *et al.* (1989) observed a net decline of mineral N in a laboratory incubation study with animal slurries, which was greater at higher temperatures 23 °C.

2.9.2 Moisture

It has been established that, when temperature is above 5 °C, mineralisation of soil organic matter increases with soil moisture status up to field capacity (Stanford and Epstein, 1974). An incubation experiment (Agehara and Warncke, 2005) to investigate the effect of increasing soil moisture from 50-90 % Water Holding Capacity (WHC) on mineralisation of N from various organic sources, demonstrated that different N sources had differing N release patterns depending on the soil moisture status. Mineralisation of soil organic N increased with increasing moisture, reaching a maximum at 90 % WHC. Mineralisation from alfalfa pellets and chicken manure increased with increasing moisture at the late phase of incubation, whereas initial high soil moisture resulted in an increase in mineralisation from blood meal amended soil. Mineralisation has been reported as reaching a maximum at soil moisture contents of 0.3-bar at temperatures between 15-30 °C (Cassman and Munns, 1980). Interactions between soil moisture and temperature have been found to affect soil N mineralisation; additive effects on mineralisation were observed with increases in temperature and moisture (Cassman and Munns, 1980). In contrast, Hsieh *et al.* (1981) found no significant effect of moisture levels of 0.06 bar and 0.33 bar on N mineralisation rate of digested sewage sludge. However, in a field investigation into N mineralisation and immobilisation rates in a deciduous forest soil, Bengtson *et al.* (2005) found that these processes were more dependent on moisture and temperature than available N and C.

2.9.3 Soil pH

Nitrification may be inhibited in organic residual-amended soil with a low pH, as the optimal pH for many soil oxidisers is between 7 and 9. Inhibition of nitrification has been reported in biosolids compost-amended soil with a pH of 5-6 (Tester *et al.*, 1977), and a reduction of ryegrass yield was measured on sewage sludge treated soils with a pH less than 5.5 (Sanders *et al.* 1986), due to increased toxicity of heavy metals at low pH values. Soil pH values between 5.3 and 7.5 have been found to have no significant effect on the decomposition rate of sludge in a silt loam soil (Terry *et al.*, 1979). High

soil pH and high *CEC* may enhance dissociation of rapidly mineralised compounds such as urea (Mendoza *et al.*, 2006).

2.9.4 Soil Type

Tester *et al.* (1977) reported significant variations in N mineralisation from sewage sludge composts in different soil types. Greater amounts of N were mineralised in a loamy sand soil than in a silty clay soil and a silty loam, and this was attributed to NH_4^+ fixation by the high vermiculate clay fractions in the silty loam. They suggested that, as the kaolinitic clay in the silty clay soil is not normally associated with NH_4^+ fixation, the lower NO_3^- recovery in this soil may have been due to bacterial immobilisation. Slower rates of biosolids C decomposition have been found in organic soil types as opposed to mineral soils, despite similar rates of organic matter decomposition overall (Terry *et al.*, 1979).

Sewage sludge crop response trials conducted by WRc throughout the UK (Hall, 1983b) showed significant soil type effects, the greatest response to application of liquid undigested sludge was found on a sandy loam and the lowest on a clay loam following spring applications. A possible explanation may be reduced N availability by $\text{NH}_4\text{-N}$ fixation, which occurs to a greater extent in clay soils (Tester *et al.*, 1977). For lagoon-matured digested sludges, higher responses were also found on a sandy loam and lowest on a calcareous loam after spring application (Hall, 1983b). Hernandez *et al.* (2002) also reported greater amounts of N mineralised in a light textured sandy-loam soil as opposed to a clayey-loam, which they attributed to better aeration in the light soil. In a laboratory investigation Smith *et al.* (1998b) found that although soil type affected nitrate production in biosolids amended soil, of more importance were biosolids type and temperature.

However, mineralisation and nitrification rates may be positively correlated to soil organic matter content, with soils with a greater organic matter content containing a more active microbial population (Zagal, 1993; Jha, 1996; Silva *et al.*, 2005). Lower N availability has been observed in less fertile soils (Smith *et al.*, 1998b; Breedon *et al.*, 2003). Smith *et al.* (1998b) observed lower availability of N in a loamy sand soil with low fertility amended with undigested biosolids in comparison to a high fertility clay loam. A potential mechanism for this observation is immobilisation of N by transfer to microbial biomass, which is discussed below.

2.9.5 Microbial Immobilisation of N

The rate of mineralisation of substrates with a high C:N ratio is determined by availability of soil N. Thus, Recous *et al.* (1995) found C mineralisation and depletion of the inorganic N pool occurred at the same time in soil with low N availability. Rates of mineralisation of maize residue in the N limited soil were half those in soil which had an excess supply of N. As discussed for individual waste types, high concentrations of easily degradable C may promote microbial immobilisation of nutrients in the soil (Recous and Mary, 1990). Therefore, wastes with high C:N ratios, that are not stabilised by a microbial treatment process such as anaerobic digestion or composting, or only partially stabilised may reduce N availability following application to soil. Bernal *et al.* (1998) noted this effect for 3 sewage sludge-cotton waste composts at different stages of maturity, where the least stabilised compost caused initial deficiency of N in plants. Similarly, Calbrix *et al.* (2007) found that less stabilised organic amendments were a greater stimulus for soil microbial communities; significant relationships were determined between the proportion of mineralisable organic matter and lignin content and microbial activity.

Observations by Smith *et al.* (1998b) during incubation of soil with raw sludge indicated that the extent of apparent immobilisation of N was affected by the soil type. Immobilisation appeared to be greater in a loamy sand with a low organic matter content compared to a clay soil with a high organic matter content. Breedon *et al.* (2003) found that more N was released in high fertility soils compared to soil of lower fertility status. Dewatered digested cakes released approximately 60 % of total N in a high fertility soil compared to 45 % in less fertile soil, but the mechanisms responsible for this behaviour, were not elucidated. It may be because the microbial populations in more fertile soils are better adapted to utilise a complex range of organic compounds than those in less fertile soils with lower organic matter content. Alternatively, the biomass may be better adapted to retain N in N starved systems. Although, the microbial biomass N (MBN) component has been investigated in biosolids amended soil (Petersen *et al.*, 2003), there is a lack of information on the relationship between MBN, soil type and biosolids amendment. Petersen *et al.* (2003) found as much as 27 % of total N applied in anaerobically digested sludge in the microbial biomass, a reduction in MBN was accompanied by an accumulation of N in plant biomass. These findings suggest that MBN constitutes an appreciable fraction of soil N in biosolids-amended soil, and a labile source of N for crop uptake. Therefore MBN should be

taken into account when investigating soil type effects on N availability from organic amendments.

2.9.6 Storage Methods and Method and Timing of Application

The timing of spreading and methods of application of organic residuals, which influence losses of N from the soil by volatilisation and leaching, are important factors to be taken into consideration when estimating N availability to crops from biosolids and biowastes in practice. For example, the value of sludges or slurries, in the first year of application, relative to fertiliser-N is 50-70 % when applied in spring and rotivated into soil, whereas in early winter its relative efficiency may be reduced to 20-30 % due to the variable extent of N losses due to leaching by winter rainfall (Hall and Williams, 1985).

Materials providing a slow release source of nutrients may need to be spread several months in advance of a crop's requirement for nutrients. For example, Kütük *et al.* (2003) recommended application of beer factory sludge six or seven months in advance of crop requirements due to the large proportion of slowly mineralisable N contained in this material. Wool and hair waste have also been found to act as a slow release source of S, N, P and K (Zheljazkov, 2005). As discussed, mineralisation increases with increasing temperature, therefore it will be greatest in late summer, so the availability of organic residual N to crops will be affected by the growing season of the crop. Availability of organic residual N to cereals has been found to be approximately half that of grass. However, crops with a longer growing season such as sugar beet will benefit more from mineralised N (Hall, 1983b).

The longer a liquid organic waste is stored the greater the potential for losses of N by NH_3 volatilisation, continued mineralisation, and increased stability of the organic fraction. Dewes *et al.* (1990) found a highly significant correlation between storage time and N losses from cattle and pig slurries, after 35 days storage, between 17.1 %-53.6 % total N was lost by volatilisation. The mineralisable N content from liquid digested sewage sludge has been found to decrease from 15 % to 9 % after a year of storage (Coker *et al.*, 1987).

Spreading organic N sources in waterlogged, frozen or sloping soils increases the risk of surface run-off and is banned in NVZs (CEC, 1991). Surface spreading of slurries, on sloping sites, at rates exceeding $50 \text{ m}^3 \text{ ha}^{-1}$, increases surface runoff of N and P in

comparison to unamended soil or inorganic fertiliser (Smith *et al.*, 2001b;c). In addition, surface spreading of organic wastes may result in losses of N by NH_3 volatilisation. Ammonia volatilisation has been found to result in losses of up to 50 % when sewage sludges are surface spread under dry, windy conditions (Hall, 1986a). Beauchamp *et al.* (1978) observed up to 60 % of ammoniacal N in surface applied anaerobically digested liquid sewage sludge may be lost within a week. Slightly greater values have been found for dewatered biosolids, 68 % and 81 % of $\text{NH}_3\text{-N}$ for anaerobically digested sludge and 74 % for aerobically digested sludge may be lost by NH_3 volatilisation in the first week following spreading (Robinson and Polglase, 2000). Coker *et al.* (1987a) found that 50-75 % of $\text{NH}_4\text{-N}$ was lost when lagoon matured sludge with a pH greater than 7.5 was applied in autumn to short grass. This practice would not be permitted for grazing under the Safe Sludge Matrix (2001). This was not observed with liquid digested sludge, however, and Coker *et al.* (1987a) suggested that the higher viscosity of lagoon matured sludge, which has a DS content of about 10 %, means that the sludge did not penetrate the soil as easily compared to liquid digested sludge, increasing the risk of volatilisation. Donovan and Logan (1983) conducted a laboratory study to investigate the factors influencing N volatilisation from sewage sludge and found that incorporation of sludge into soil greatly reduced losses by volatilisation. For sludge incorporated at 0.25 h, 1 h and 3 h after application 3, 4 and 6%, respectively, of the $\text{NH}_3\text{-N}$ applied was lost in the first 24 h. For sludge incorporated after 24 hours, 26 % of the $\text{NH}_4\text{-N}$ was lost. Spreading to moist soil or soil with crop cover reduces volatilisation losses, and risk of runoff (Ojeda *et al.*, 2006) and immediate incorporation of the organic fertiliser may eliminate losses. Injection of sewage sludges (Hall, 1983b) and of animal slurries (Sutton *et al.*, 1982) result in greater crop yields and nutrient recovery compared to surface spreading organic fertilisers.

Incorporation of biosolids into the soil may, under some circumstances result in denitrification. For example, Mendoza *et al.* (2006) did not fully recover the available N applied in anaerobically digested cake and concluded that deep placement and rapid mineralisation of the biosolids promoted denitrification.

Where surface applications of waste have been made, crops are at risk of being smothered. Sludges with higher dry solids contents are at risk of sticking to grass and the soil surface and yield responses have been found to decrease in relation to the proportion of mineral N (Hall, 1983b). This may be a result of smothering, or could reflect increased losses of N through NH_3 volatilisation. Particle size, texture and

density of organic waste may also affect the risk of runoff. Materials such as thermally-dried and composted sludge may be more prone to transport than compact fresh sludge (Ojeda *et al.*, 2006).

2.9.7 Effects of Repeated Applications and Residual Value

When calculating appropriate rates of application of organic manures, to avoid oversupply, it is important to take into account the residual value of previous applications. Boyle and Paul (1989) found that 3 years after application of anaerobically digested cake there was still a mineralisable N pool remaining. However, this was following 8 years of repeated applications at high applications rates, between 11.3 and 45 t DS ha⁻¹. Soon *et al.* (1978) found that there were high concentrations of NO₃-N in soil to 90 cm depth 3 years after application of anaerobically digested sewage sludge at rates of 800 kg N ha⁻¹, but not 400 kg N ha⁻¹. The effects of previous waste application on mineralisation from freshly applied waste may also need to be considered, although Lindemann *et al.* (1988) found that mineralisation rates from freshly applied sewage sludge were the same in unamended soil and soil that had previously been amended. Harding *et al.* (1985) showed that although potentially mineralisable N remained in soil previously treated with rates of between 6.3–25.2 t ha⁻¹, mineralised N present as mineral N in the soil at the time of planting was a more important predictor of N availability for crops. Similarly, Antolín *et al.* (2005) found that soil treated with sewage sludge at a rate of 15 t ha⁻¹ in October mineralised sufficient N to have a positive effect on crop yield the following year, however, the effect was short lived. The residual value of most treated biosolids reported by Smith *et al.* (2002b) was low, however, with less than 5 % mineralisation of total N at typical rates of application in the field in the second year. It was suggested that, on this basis, second year mineralisation can be largely ignored, although mineral N from initial applications if unused by the crop in the first year may be ‘carried over’ and remain in the soil in the second year and should be taken into account when providing fertiliser guidelines to subsequent crops.

2.10 Methods of Investigation, Predictive Equations and Calculating Availabilities

The environmental, economic and agronomic conditions described above require the accurate prediction of organic nutrient release from biosolids and biowastes that will be

converted to mineral forms to meet crop needs without an excess in the soil that may potentially lead to wastage and pollution of the environment.

Soil incubation studies (Terry *et al.*, 1979; Hsieh *et al.*, 1981; Griffin and Laine, 1983; Parker and Sommers, 1983), with amended soils maintained in controlled conditions, have frequently been used as a tool to assess the concentration of mineralisable N in manures and biosolids, and to study the effects of variables such as application rate, temperature and moisture. Parker and Sommers (1983) compared two different, commonly used, procedures for estimating mineralisable N in laboratory conditions; a leaching procedures involving periodic removal of inorganic N from incubated soils with a vacuum and dilute salt solution, and the alternative method involved periodically removing soil to determine the inorganic N content. The authors found that the non-leached procedure gave higher estimates of sludge mineralisation, due to losses of a proportion of soluble organic N (SON) during the leaching procedure. Therefore, the nonleached procedure may provide a better estimate of potentially mineralisable N.

Nitrogen availability from organic amendments can also be monitored by measuring uptake and growth of plants in pot trials and growth chamber experiments (Serna and Pomares, 1992b; Stockdale and Rees, 1995; Bowden and Hann, 1997). Soil is amended with a known amount of organic fertiliser and control soils are included with no organic amendment and with a mineral fertiliser source for a comparison. The plants are maintained under controlled conditions and harvested for analysis after a growth period (Serna and Pomares, 1992b).

Chemical methods for investigating N availability in biosolids have been used, such as measuring the amount of $\text{NH}_4\text{-N}$ mineralised after autoclaving with CaCl_2 at 121 °C (Smith and Stanford, 1971, Stark and Clapp, 1980, Magdoff and Amadon, 1980, O'Keefe *et al.*, 1986, Serna and Pomares, 1992a). Magdoff and Amadon (1980) found that the autoclaving method was well correlated with N mineralised during laboratory incubation of soil with aerobically digested sludge and both these methods were positively correlated with the recovery of N in corn in a field experiment. Acid permanganate (KMnO_4) oxidation (Stanford and Smith, 1978, O'Keefe *et al.*, 1986, Serna and Pomares, 1992a, Serna and Pomares, 1992b), Walkely-Black acid dichromate digest (Douglas and Magdoff, 1991), an HCl method and a pepsin method (Serna and Pomares, 1992b) have also been used. Serna and Pomares (1992b) found a high correlation with pepsin and HCl extractions, and N availability determined by soil incubation and growth chamber experiments, and therefore recommended these

methods as rapid tests. O'Keefe *et al.* (1986) found that N mineralised during aerobic incubation was better correlated to N uptake by maize or soybeans than mineralisable N determined by chemical tests, whereas Stark and Clapp (1980) found the autoclave test as reliable as laboratory incubation methods.

To perform a realistic assessment of N availability in organic residuals amended soil, as affected by environmental conditions, it is necessary to monitor N transformations under field conditions (Bitzer *et al.*, 1988; Jackson and Smith, 1997; Beckwith *et al.*, 1998; Cogger *et al.*, 1999; Smith *et al.*, 2002b; Morris *et al.*, 2003; Gilmour *et al.*, 2003; Cogger *et al.*, 2004). Field trials also provide the opportunity to examine residual nutrient availability in the years following soil amendment and the effects of repeated applications (Soon *et al.*, 1978; Lindemann *et al.*, 1988; Boyle and Paul, 1989; Smith *et al.*, 2002b; Antolín, 2005). Field trials to define the agronomic quality of organic residuals are designed with replicated randomised plots, which include unamended control and mineral nutrient treatments as a reference comparison. Monitoring may take the form of regular sampling of amended plots for soil analysis of mineral N concentration or crop response trials, in which yields are measured and harvested crops may be analysed for total N and P concentration. In most field experiments, plots treated with different rates of fertiliser are arranged in a random order in order to account for background effects of variation in soil fertility across a field site. Systematic arrangements of fertiliser experiments have also been developed (Cleaver *et al.*, 1970, Smith and Hadley, 1988), in which treatment levels are arranged in a systematic gradient. This removes the need for wide guard rows between each plot which are normally there to prevent the edge effects which may result from a high level plot adjacent to a low level plot. The elimination of guard rows means that there is a greater ratio of harvested to non-harvested area, reducing levels of experimental error. Systematic experiments with smaller plots and fewer guard rows can facilitate more levels of fertiliser application, thereby increasing sensitivity to finding the optimal rate of application. The disadvantage of systematic designs is that effects of fertiliser treatments may be masked by natural fertility trends. Variation due to natural fertility trends can be detected by arranging plots as three blocks containing replicate treatments, and error can also be reduced by randomising the direction of the fertiliser gradient in the systematic plots (Cleaver *et al.*, 1970).

Nitrogen transformations in soil amended with organic residuals are complex as a consequence of the presence of different pools of N; a stable organic pool that is resistant to degradation, a degradable organic pool, and a pool of inorganic N. The

mobility of NO_3^- and microbial immobilisation of N add to this complexity. Models of N availability, taking into account temperature and N losses have been developed to produce predictive tools for the use of organic residuals in agriculture (Stanford and Smith, 1972; Stark and Clapp, 1980; Hsieh *et al.*, 1981; Parker and Sommers, 1983; Smith *et al.*, 1998b; Smith *et al.*, 1998c; Bellett-Travers *et al.*, 2002; Bellett-Travers *et al.*, 2003). Stanford and Smith (1972), Stark and Clapp (1980) and Parker and Sommers (1983), assumed an approximate linear relationship between cumulative N mineralisation and time. However, as mentioned above, the organic N in manures and biosolids varies in its resistance to degradation, there being a rapidly mineralised pool and a recalcitrant pool (O'Keefe *et al.*, 1986). To improve predictions of the rate and extent of degradation, models often consider the degradable organic N as two or more separate pools with different degradation and release rate constants (Deans, 1986, Lindemann, 1988, Smith *et al.*, 1998b). An exponential equation is fitted to the data, where recalcitrant and labile organic N are split into two pools (Bowden and Hann, 1997, Smith *et al.*, 1998d).

The Biosolids-Nitrogen-Release-Model (BNRM), developed by The Centre for Environmental Control and Waste Management at Imperial College London, predicts net mineralisation of organic N accounting for continuous variation in temperature and contains a term for removal of mineral N by microbial lock-up (Bellett-Travers *et al.*, 2002, Bellett-Travers *et al.*, 2003). It used the model of Bradbury *et al.* (1993) to convert $\text{NH}_4\text{-N}$ to $\text{NO}_3\text{-N}$. The model was incorporated into a grass yield prediction model and successfully predicted yield of perennial ryegrass in the field following application of dewatered mesophilic anaerobically digested (DMAD) biosolids. It has also been tested comparing predicted crop yields with crop dry matter yields of perennial ryegrass in a sandy loam soil amended with enhanced treated biosolids in field experiments (Smith and Bellett-Travers, 2001; Smith *et al.* 2002b; Morris *et al.*, 2003) and the predicted yields were found to be a close fit to the experimental data.

2.11 Summary

The UK currently produces approximately 1.4 million tonnes of sewage sludge dry DS per year, which is the solid organic residual material that remains after municipal waste water treatment. The banning of sludge disposal at sea in 1998, under the EU Urban Wastewater Treatment Directive (CEC, 1998) increased pressure on the remaining principal methods of sludge management, including landfill disposal, incineration, and agricultural recycling. Treated sewage sludges, known as biosolids, are a valuable

alternative to mineral fertilisers, are effective soil conditioners, and use as an agricultural soil amendment is regarded as the BPEO. Research into the fertiliser value of the biosolids, development of new treatment methods to eliminate pathogens, the success of the Safe Sludge Matrix (2001) in the UK, and the economic advantages to farmers and water utilities has increased the use of biosolids in agriculture, so that now only 1 % of sludge is sent to landfill and 65 % is recycled to agricultural land.

Biowastes are also a valuable resource to farmers, however, it is more challenging to characterise the nutritional value of these waste types compared to biosolids, to provide guidelines for agricultural utilisation due to the extensive range of processes that produce these wastes streams and the high variability in physical and chemical composition. Landspreading of biowastes is practised to a variable extent in the EU, but in the UK 7 million t is spread annually. This is in compliance with the Landfill Directive (CEC, 1999) to restrict the quantities of biodegradable waste sent to landfill, and is in line with the objectives of the EU Waste Strategy to increase recovery of materials from waste. In the UK, those wishing to landspread biowastes on agricultural land must apply for a WMLR exemption, and prove that the waste is of agricultural benefit.

Organic residuals vary in texture and handleability and various application methods exist which are suited to different waste types. Length and method of storage is also a source of variation in nutrient composition and availability.

Environmental considerations when organic residuals are used in agriculture include potential for loss of N by leaching, and N and P by runoff, into surrounding water bodies resulting in eutrophication and detrimental effects on drinking water quality. Gaseous emissions of NH_3 , N_2O and NO_x are also a risk. The Nitrates Directive (CEC, 1991) restricts the amount of total N which can be applied in organic residuals and for arable land an annual farm-based limit of 170 kg N ha^{-1} applies within NVZs.

It is of vital importance to understand the impact of soil and plant nutrient processes when determining the fertiliser value of organic residuals. Nitrogen and P transformations in soil are complex and total added nutrients will not be available for plant uptake as a result of losses from the soil, microbial immobilisation and chemical fixation. The microbial biomass is fundamental to soil fertility and responsible for cycling of nutrients and organic matter. Essential plant nutrients include N, P, K, S, Mg, Na, B, Ca, Fe and Mn. Soil organic matter is also important in crop requirements.

Nitrogen is the main element which limits crop growth in UK soils, and requirement varies between crop types and inputs are necessary at periods rapid vegetative growth. Grass has a greater response to N than arable crops and uses it more efficiently.

Organic residuals are an effective source of nutrients and organic matter, however as the nutrients are present in mineral and organic forms, the total nutrient content does not reflect availability, and it is necessary to define their fertiliser value. Guidelines for the use of manures and biosolids in agriculture are provided in RB209: 'Fertiliser Recommendations for Agricultural and Horticultural Crops' (MAFF, 2000). Manures have a long history of use in agriculture and additional guidelines such as computer models and extensive research means that nutrient availability in these materials can be predicted reasonably well. The advice for biosolids in RB209 is based on long-standing recommendations and requires updating, however, especially due to the emergence of new treatment technologies which affect the nutritional characteristics of the materials.

Phosphorus availability in biosolids is generally considered to be 50 %, but recent research has shown it to be more or less available in different treatment types, especially following the introduction of tertiary methods such as Fe dosing or biological methods to remove excess P from wastewater. Nitrogen availabilities are highly dependent on sludge treatment method used. The fertiliser value of liquid digested biosolids is primarily dependent on the amount of mineral N present, but there is also some contribution from readily mineralisable organic N. Dewatered digested biosolids (DMAD) have a lower fertiliser value overall compared to liquid forms as a result of loss of mineral N, however, in recent investigations DMAD has been found to have a mineralisable N fraction of approximately 15 % organic N, resulting in relative fertiliser values greater than 30 %. (Smith and Bellett-Travers, 2001; Smith *et al.*, 2002b; Breedon *et al.*, 2003; Morris *et al.*, 2003; Patersen *et al.*, 2003).

Lime treated sludge has the additional benefit of being a useful product to increase pH when used in acidic soils. Composting sludge produces high stability products with low nutrient availabilities, generally less than 10 % N (Tester *et al.*, 1977; Epstein *et al.*, 1978; Parker and Sommers, 1983; Smith *et al.*, 1998d). Thermally dried digested biosolids (TDMAD), despite their low mineral N content, contain a rapidly mineralisable organic N fraction, resulting in N availabilities comparable to that of DMAD (Cogger *et al.*, 1999; Smith and Bellett-Travers, 2001; Smith and Durham, 2002; Smith *et al.*, 2002b; Breedon *et al.*, 2003; Morris *et al.*, 2003; Patersen *et al.*, 2003).

With the exception of paper-mill sludges, there has been little research to quantify the nutritional value of industrial biowastes in the UK. They have a wide range of physical and chemical characteristics including appreciable quantities of plant nutrients in many cases. Abattoir wastes contain the greatest concentrations of N and P, much of which is likely to be present in readily available forms. A wide range of wastes are produced from the fruit, vegetable and grain industries such as washings of soil, pulp, peelings, skins and leaves. Investigations into the use of vegetable residues in agriculture have found beneficial impacts on crops, although nutrient concentrations may be low. Tannery sludges are useful as soil amendments, but contain high concentrations of Cr, which may have detrimental effects in soil. Biowastes from the dairy industry include wash-waters and salt whey from cheese manufacture. These materials may contain beneficial concentrations of N, P, K and Na but some negative effects have been reported. The drinks industry produces a wide range of wastes from brewing, distilling and grape residues from wine production, materials such as yeast and spent grain may be particularly rich in nutrients. Spent mycelium and other cell debris resulting from the pharmaceutical industry may be beneficial soil amendments. Biowastes may be spread directly on land or receive pre-treatment which will affect nutritional characteristics. The nutritional value of composted wastes in agricultural soil has been researched, they are a stable source of organic matter and composts have low nutrient availability.

Nutrient availability in soil amended with organic residuals is affected by temperature, moisture, pH, soil type and microbial immobilisation. In general mineralisation and nitrification rates increase with increasing temperature, optimal pH values may be between 5.3 and 7.5. Mineralisation tends to increase with increasing moisture and has been reported as reaching a maximum rate at water potentials of 0.3 bar. Immobilisation of nutrients in microbial biomass occurs when waste types have high C:N ratio, and a high concentration of readily degradable C. Greater recoveries of N in soils with a high fertility status with high organic matter content in comparison to low fertility soils has led to the suggestion that microbial immobilisation of N may be greater in low fertility soils (Smith *et al.*, 1998b; Breedon *et al.*, 2003).

Storage methods, and method and timing of application impacts on nutrient availabilities. Storage times reduce nutrient availabilities in liquid organic wastes, by reducing the relative proportion of mineral N through volatilisation of NH_3 . In addition, surface spreading results in losses by volatilisation, which vary under different weather

conditions. Applications should be carefully timed to avoid losses by leaching due to winter rainfall and to match the growing season of the crop for most efficient use of N as it becomes available.

When determining appropriate rates of application it is necessary to take into account the residual value of slowly mineralisable organic N. After repeated applications at high rates, residual value may be high, but recent investigations have found that for a range of biosolids types at applications of 10 t DS ha⁻¹ there may not be significant residual value in the second year.

Methods of investigation for calculating N availabilities include soil incubation studies and chemical tests, however field investigations are necessary to elucidate the interacting effects of soil type, organic residual type and varying environmental conditions. Fertiliser value is often defined as a relative availability from the organic fertiliser source compared to an inorganic fertiliser treatment. Models have been developed to predict the amount of available N from biosolids, a two-pool model which takes into account a readily mineralisable N fraction in addition to a recalcitrant pool has been found to be a good fit to experimental data.

3 GENERAL MATERIALS AND METHODS

3.1 Introduction

General materials and methods will be presented in this chapter; methods specific to individual experiments will be given in the relevant chapters. Three field trials were conducted. The first was established on two different experimental areas at the Imperial College Farm in Wye, Kent, in spring 2005, to investigate N transformations in soil amended with biosolids and livestock wastes, including the microbial biomass N (MBN) component in biosolids-amended soil. Further site and soil details are given in Section 3.2 and this experiment is described in full in Chapter 4. The other two trials were based at Silwood Park, the Imperial College Campus near Ascot in Berkshire, see Section 3.2 for the site and soil description, the results are presented in Chapters 5 and 6. The Silwood Park trials formed part of a programme of experiments to investigate the agronomic benefit of biowastes from industrial processes and quantify the N availability, by comparing crop responses to mineral fertilisers. Perennial ryegrass was used as an indicator crop as it is efficient at capturing most of the plant available N (Addiscott *et al.*, 1991; Christian and Richie, 1998), and should therefore account for most of the available N additions. A laboratory incubation experiment was also carried out to investigate N dynamics, including MBN, in biowastes-amended soil under controlled temperature and moisture conditions, the results are presented in Chapter 7.

3.2 Site Locations and Soil Properties

3.2.1 Imperial College Farm, Wye, Kent

The experimental areas were both located on arable fields managed according to conventional intensive agronomic practice. Two soil types with contrasting physicochemical characteristics were chosen, Brices Field (Ordnance Survey Reference 60500, 146500) and North Sidelands (Ordnance Survey Reference 606600,146500) (Figure 3.1). The 2005 biosolids and livestock wastes field trial was established with experimental plots at both sites and is described in further detail in Chapter 4. Brices Field was flat, but the higher altitude site, North Sidelands, was sloping and the experimental site was situated on a gradient increasing from block C–A. Prior to establishing the field experiment (mid-March, 2005), the *in situ* cereal crop was destroyed by herbicide application (paraquat). The herbicide treatment was

effective and very little crop debris was visible on the plots. All other agrochemical inputs had been excluded from the areas. Soils were also sampled from North Sidelands and Brices Field for the laboratory incubation experiment, the results of which are presented in Chapter 7.



Figure 3.1 Location of the two experimental areas on Imperial College Farm, Wye. 1: Brices Field (altitude 50 m, O.S. grid ref. 605800, 146500); 2: North Sidelands (altitude 90 m, O.S. grid ref. 606600, 146900).

3.2.2 Silwood Park, Berkshire

The crop response field trials with biosolids and biowastes in 2006 and 2007 (Chapters 5 and 6) were located in 'Hill Field' at Silwood Park, the Imperial College campus near Ascot in Berkshire (Ordnance Survey reference 606600, 146900); the location is shown in Figure 3.2. The first trial was situated on a slope with a gradient of less than 20 degrees; the direction of which was an increasing gradient from block A-C. Figures 5.1 and 6.1 in Chapters 5 and 6 show the layout of the experimental plots. The second trial was positioned beneath the first trial on a flatter area of Hill Field.

The field had been treated with herbicide several years previously and is cultivated annually during late winter/early spring. In 2006 and 2007 the site had been ploughed several weeks prior to establishment of the trials and was largely weed free.



Figure 3.2 Location of field trials at Silwood Park Buckhurst Road (X), Ascot, Berkshire (Altitude 60 m, O.S. Grid ref.: 494500,168500).

3.2.3 Soil Characteristics

The soils at each site had contrasting physical and chemical properties which are given in Tables 3.1-3.3. They differed in texture and cation exchange capacity (*CEC*) (Table 3.1); North Sidelands soil was a moderately alkaline silty clay, pH 7.8-8.2, and Brices Field was a moderately acidic sandy silt loam with pH 6.2-6.8. The soil at the Silwood Park site was a light, acidic, sandy loam, pH 5.7–6.9. North Sidelands had the greatest *CEC* of the 3 experimental soils (13.0-20.0 meq 100 g⁻¹), reflecting the higher organic matter and clay content of the soil, Brices was intermediate and Silwood Park had the lowest. There was also considerable difference in organic matter content (Table 3.1); North Sidelands was the most fertile soil with high organic matter content of between 4-4.5 % ds, Brices was a low fertility soil with low organic matter content (1.9-2.2 %), approximately half that of North Sidelands and at Silwood Park it was slightly greater than Brices (2.1–3.2 %).

Nutrient concentrations (P, K, Mg, S) are given in Table 3.2. North Sidelands had an adequate P index, but low K and Mg. Brices had a good P status and adequate K and Mg indices, and Silwood Park had an adequate P and Mg status and low to adequate K status with an index of 1 to 2- (116-135 mg kg ds⁻¹). North Sidelands had the greatest S concentration, greater than 20 mg kg⁻¹ ds, S concentration in Silwood and Brices were slightly lower. Nitrogen concentrations are given in Table 3.3.

Table 3.1 General physical and chemical characteristics of soil (dry soil basis) at Brices Field, North Sidelands, and Silwood Park.

Soil	Sample	Depth (cm)	pH	Dry Matter (%)	OM [†] (% ds)	Sand (% ds)	Silt (% ds)	Clay (% ds)	Texture	CEC (meq 100 g ⁻¹ ds)
Brices Field	2005 Biosolids Trial	0-10	6.8	82.6	2.2	39	44	17	Sandy Silt Loam	15.7
	2005 Biosolids Trial	10-20	6.8	81.2	1.9	35	46	19	Clay Loam	16.6
	2007 Lab Incubation	0-15	6.2	82.0	1.9	41	41	18	Sandy Silt Loam	12.0
North Sidelands	2005 Biosolids Trial	0-10	8.2	76.5	4.5	16	46	38	Silty Clay	18.4
	2005 Biosolids Trial	10-20	8.2	75.5	4.6	15	51	34	Silty Clay Loam	20.0
	2007 Lab Incubation	0-15	7.8	74.6	4.0	29	34	34	Clay	13.0
Silwood Park	2006 Biowastes Trial	0-15	6.9	87.6	3.2	78	14	8	Loamy Sand	10.7
	2007 Biowastes Trial	0-15	5.7	86.2	2.5	75	16	9	Sandy Loam	7.3
	2007 Lab Incubation	0-15	5.9	82.0	2.1	80	13	7	Loamy Sand	5.7

[†]Organic matter determined by wet oxidation.

Table 3.2 Nutrient concentrations in soil (dry soil basis) at North Sidelands, Brices Field and Silwood Park.

			Index			Available (mg kg ⁻¹ ds)			
Soil	Experiment	Depth (cm)	P	K	Mg	P	K	Mg	S [†]
Brices Field	2005 Biosolids Trial	0-10	4	2-	2	68.0	173.0	82.0	14.7
	2005 Biosolids Trial	10-20	4	2+	2	69.8	186.4	88.9	17.0
	2007 Lab Incubation	0-15	4	2-	2	60.0	163.0	92.0	18.9
North Sidelands	2005 Biosolids Trial	0-10	2	1	1	19.6	114.3	27.7	22.9
	2005 Biosolids Trial	10-20	2	1	1	20.9	117.8	27.6	20.4
	2007 Lab Incubation	0-15	3	1	1	37.4	75.0	28.0	22.2
Silwood Park	2006 Biowastes Trial	0-15	2	1	2	20.0	118.0	57.0	16.9
	2007 Biowastes Trial	0-15	2	2-	1	24.6	135.2	46.1	13.2
	2007 Lab Incubation	0-15	2	1	2	21.0	116.0	76.0	15.1

[†]Phosphate buffer soluble

Table 3.3 Background N concentrations in soil (dry soil basis) at Brices Field, North Sidelands and Silwood Park.

Soil	Experiment	Depth (cm)	Total N (% ds)	NH ₄ -N (mg kg ⁻¹ ds)	NO ₃ -N (mg kg ⁻¹ ds)	Available N (mg kg ⁻¹ ds)
Brices Field	2005 Biosolids Trial	0-10	-	0.66	21.9	22.5
	2005 Biosolids Trial	0-20	-	0.64	9.74	10.4
	2007 Lab Incubation	0-15	0.12	0.25	6.05	6.3
North Sidelands	2005 Biosolids Trial	0-10	-	0.60	27.8	28.4
	2005 Biosolids Trial	0-20	-	0.58	28.5	29.1
	2007 Lab Incubation	0-15	0.25	0.41	10.6	11.0
Silwood Park	2006 Biowastes Trial	0-15	-	3.04	11.2	14.3
	2007 Biowastes Trial	0-15	0.13	0.33	14.8	15.2
	2007 Lab Incubation	0-15	0.11	0.80	10.8	11.6

- not measured

North Sidelands had the greatest total N content, which is to be expected from its higher organic matter status. Total N was approximately double that of Silwood and Brices, 0.25 % compared to approximately 0.12 % in the other soils. North Sidelands generally had the higher available N content. Heavy metals concentrations also differed between the soils but were within the normal ranges for arable soils and are available in Appendix A1.

3.3 Soil Sampling and Analysis

3.3.1 Sampling and Characterisation

For characterisation of soils for the 2005 biosolids and livestock wastes field experiment at Wye (Chapter 4), a representative soil sample of approximately 2 kg of each soil type, was taken at 2 depths, 0-10 cm and 10-20 cm and submitted to a NAMAS accredited laboratory (NRM Laboratories, Bracknell, Berkshire) for physicochemical analysis. The soil was sieved using a stainless steel sieve to pass 5.6 mm to remove stones and plant debris, placed in a labelled sealed bag and sent by courier to the external laboratory in a polystyrene box with freezer packs.

For each of the other experiments the sample was taken from 0-15 cm. These samples, and those collected for mineral and microbial biomass nitrogen (MBN) analysis for the field experiment at Wye, were collected with a gouge auger. For soil characterisation, approximately 15 soil cores were collected from each experimental site and bulked together to provide a representative composite sample. When sampling the field experiment, five soil cores were collected from each experimental plot and bulked together for mineral N and MBN determinations. Bulk soil samples for the incubation experiment (Chapter 7) were collected using a stainless steel spade to avoid contamination by trace elements.

3.3.2 Transport and Storage

Soil samples from the 2005 biosolids and livestock wastes field trial at Wye (Chapter 4) and for the laboratory incubation study (Chapter 7) were placed in folded polythene samples bags, or black plastic sacks for larger quantities, and were transported to the laboratory in cooler boxes containing frozen ice-packs. At the laboratory, the soils were placed in the dark in a cold-room set at 4 °C. Soils collected for mineral N analyses were frozen at -19 °C. This is a standard soil storage technique in N

transformation studies, and minimises changes in $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ (Gasser, 1958, cited in Smith *et al.*, 1998b).

3.3.3 Gravimetric Moisture Content

Sub-samples of soil (10 g) were dried overnight at 105 °C in a forced air oven, to a constant mass, to determine the gravimetric water content by loss in mass of the soil (MAFF, 1986). Samples were placed in a desiccator to cool before weighing to prevent absorption of atmospheric moisture. The gravimetric moisture content was calculated as:

Gravimetric moisture content (%) = [(mass of fresh soil – mass of oven dry soil) / mass of fresh soil] x100

3.3.4 Mineral N Determination

Concentrations of $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and $\text{NO}_2\text{-N}$ in soils were determined following a standard procedure (MAFF, 1986). Subsamples of 40 g of sieved, fresh soil were shaken with 200 ml of 2 M KCl for 2 hours (LS5 Laboshake, Gerhardt, Bonn, Germany). For the laboratory experiment, these amounts were modified to 20 g of fresh soil and 100 ml of 2 M KCl, to maintain the same soil:extractant ratio. The soil extracts were filtered through Whatman no. 1 filter papers (150 mm). The filtrate was analysed by an automated colorimetric technique (APHA, 1980; Petts and Belcher, 1980) using a multichannel segmented flow analyser (Skalar SAN^{plus} Segmented Flow Analyser, Skalar, Breda, The Netherlands) at absorbencies of 540 nm for $\text{NO}_2\text{-N}$ and $\text{NO}_3\text{-N}$ and 660 nm for $\text{NH}_4\text{-N}$. Stock solutions containing 100 mg l⁻¹ $\text{NO}_2\text{-N}$ and 1000 mg l⁻¹ $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ were prepared in deionised water with sodium nitrite, sodium nitrate and ammonium chloride respectively (Fisher Scientific UK Chemicals, Leicestershire). Working standards were prepared on a daily basis in 2 M KCl from the stock solutions, and a calibration curve was run with each batch of samples in the range of 0-1 mg l⁻¹ for $\text{NO}_2\text{-N}$, 0-5 mg l⁻¹ or 5-50 mg l⁻¹ for $\text{NH}_4\text{-N}$ and 0-10 mg l⁻¹ or 0-50 mg l⁻¹ for $\text{NO}_3\text{-N}$, as appropriate. A moisture content correction to allow for moisture from the soil was made in the calculation of the concentrations of the nutrients. A blank sample of 2 M KCl was included in each batch of samples. In addition, 2 samples were spiked with a known concentration of $\text{NO}_2\text{-N}$, $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ to check for full recovery, and 5 % of the samples were replicated.

3.3.5 Chloroform Fumigation-Extraction Procedure for Determination of Microbial Biomass C and N

A chloroform (CHCl_3)-fumigation, direct extraction (CFE) protocol based on the methods of Vance *et al.* (1987a;b), Brookes *et al.* (1982; 1985a;b) and Saggar *et al.* (1981) was used for measurement of microbial biomass C (MBC) and MBN concentrations in soil. This method has several advantages as it is rapid, it applies to acid soils (Vance *et al.*, 1987b) and soils recently amended with substrates (Harden *et al.*, 1993). The basic principle of the CFE method is that microbial cells are destroyed by CHCl_3 fumigation, releasing soluble extractable components, which can then be measured as an indication of total microbial biomass.

Duplicate 10 g samples of fresh, sieved, amended and control soils were weighed into 50 ml Pyrex beakers or 250 ml plastic bottles. A desiccator was lined with moist paper towels to maintain the humidity of the atmosphere during the fumigation to avoid surface desiccation of the soil samples. Approximately 50 ml of amylene stabilized CHCl_3 (Fisher Scientific UK Chemicals, Leicestershire) together with anti-bumping granules were placed in a Pyrex beaker in the middle of the desiccator along with the soil samples in beakers. The fumigation chamber was closed and evacuated until the CHCl_3 boiled vigorously. The valve was closed and the desiccator was maintained in the dark for 24 h at 25 °C. After incubation, the vacuum was released, the paper towels were removed, and the fumigation chamber was evacuated under vacuum 5 times to remove residual CHCl_3 . Each evacuation was for 2 minutes and air was allowed into the fumigation chamber after each evacuation to remove residual chloroform. Labile C was extracted from the fumigated samples by shaking in 250 ml plastic bottles for 1 h at 180 rpm (LS5 Laboshake, Gerhardt, Bonn, Germany) with 50 ml 0.5 M K_2SO_4 to give a 5:1 ratio of liquid to soil (Horwath *et al.*, 1994). Non-fumigated samples were extracted at the same time the fumigation commenced, following the same procedure. A blank sample of 50 ml K_2SO_4 was included with each batch. After shaking, samples were filtered into 60 ml plastic bottles using Whatman filter papers, No. 1 (150 mm).

3.3.5.1 Microbial Biomass C Determination

The filtered soil extracts were kept at 4 °C until analysis for dissolved total organic carbon (TOC) using a Shimadzu TOC-5000 analyser (Shimadzu, Kyoto, Japan). Total OC analysis was completed within 2 weeks. If longer storage was required samples were frozen at -19 °C. Standards of dissolved carbon were prepared from dry

potassium hydrogen phthalate (Fisher Scientific UK, Leicestershire). The analysis of the TOC was based on wet chemical oxidation, using the NPOC (non-purgeable organic carbon) method, this method is recommended for soil analysis because it is prone to less error than the alternative TC-IC (Total Carbon-Inorganic Carbon) method (Dahlén *et al.*, 2000; Shimadzu, 2003). Samples prepared for analysis were placed in 40 ml glass vials, covered with parafilm to prevent atmospheric C contamination, and were placed in the automatic rack for analysis. A standard sample in the appropriate concentration range was analysed after every 12 samples to ensure accuracy of the analysis.

The MBC concentration was calculated according to the following equation:

$$\text{Microbial biomass C } (\mu\text{g C g}^{-1} \text{ ds}) = E_C / K_{EC};$$

where E_C is the soluble organic C extracted from fumigated soils minus that extracted from non-fumigated soil and K_{EC} is the extractable part of MBC after fumigation (Joergensen *et al.*, 1995). A correction factor is applied because not all the MBC is solubilised by this method. The K_{EC} value used to transform the difference between the extractable OC into MBC was 0.45 (Vance *et al.*, 1987).

3.3.5.2 Microbial Biomass N Determination

The filtered K_2SO_4 soil extracts were frozen at -19°C prior to analysis for MBN, samples were kept at 4°C overnight to defrost prior to analysis. Determination of MBN followed the Kjeldahl procedure adapted from Brookes *et al.* (1985a). Here, 10 ml of each K_2SO_4 extract was digested with 5 ml of concentrated H_2SO_4 , anti-bumping granules and a $CuSO_4$ catalyst in 300 ml digestion tubes on a 20 tube digestion block (Gerhardt, Bonn, Germany). A 10 ml 0.5 M K_2SO_4 blank was included with each batch of samples. Spiked samples, with nicotinic acid, were also digested to determine the recovery of organic N. The temperature was set to 180°C , and over 45 minutes gradually increased to 290°C , and was held at this level for 30 minutes. This allowed water to evaporate from the sample without losses due to spitting. The temperature was raised to 365°C and the samples were refluxed for 2 h. A 40 tube digestion block (Gerhardt, Bonn, Germany) was used, with 100 ml digestion tubes, for the laboratory incubation experiment (Chapter 7) to increase sample processing efficiency. With this higher tube density digestion block, it was necessary to reduce the initial temperature to 140°C , and gradually increase the temperature to 365°C over 2 h in order to prevent sample spitting. The samples were left to cool before diluting to 100 ml in

volumetric flasks, subsamples were stored in plastic tubes at 4 °C prior to analysis. An automated colorimetric technique (Krom, 1980; APHA, 1985; Markus *et al.*, 1985; SCA, 1986) using a multichannel segmented flow analyser (Skalar SAN^{plus} Segmented Flow Analyser, Skalar, Breda, The Netherlands) was used to simultaneously determine total N and P in the digested solution, at absorbencies of 660 nm and 880 nm respectively.

The difference between total N in the fumigated and non-fumigated samples is the chloroform-labile N pool and is proportional to MBN:

$$\text{Microbial biomass N } (\mu\text{g N g}^{-1} \text{ ds}) = E_N/K_{EN};$$

where E_N is the soluble N extracted from CHCl_3 -fumigated – non-fumigated samples, and K_{EN} is the extractable part of MBN after fumigation with CHCl_3 . A K_{EN} of 0.54 was used to transform the difference between the extractable soluble N into MBN (Brookes *et al.*, 1985; Joergensen and Mueller, 1996).

3.4 Biosolids, Livestock Wastes and Biowastes

3.4.1 Selection of Materials

For the 2005 biosolids and livestock wastes field trial at Wye (Chapter 4) representative types of conventional and enhanced treated biosolids currently applied to farmland in the UK were selected in addition to dewatered raw sludge and also representative livestock slurries (cattle and pig), and cattle manure.

Biowastes for the 2006/7 crop response trials (Chapters 5 and 6) included examples of liquid and solid waste materials from the vegetable, meat and dairy processing industries and processed industrial biowastes from aerobic and anaerobic digestion plants. The processes wastes were also investigated in a laboratory incubation study (Chapter 7). A dewatered mesophilic anaerobically digested sewage sludge (DMAD) was included as a reference material in each of the biowastes crop response trials and the laboratory incubation study, as the N fertiliser value is well established and has been demonstrated to be consistent (Terry *et al.*, 1979; Parker and Sommers, 1983; Smith *et al.*, 1998a;b;c; Smith and Bellett-Travers, 2001; Smith *et al.*, 2002a; Breedon *et al.*, 2003; Morris *et al.*, 2003; Petersen *et al.*, 2003).

Biowastes spread on agricultural land are a diverse range of materials and the first step was to identify a representative selection of representative biowastes for the investigation. This task required initial communication with Environment Agency

offices, which issue the exemptions to facilitate spreading the wastes. Contacts at the Environment Agency were able to supply details of landspreading operations. Contacts at ADAS, at biological digestion facilities and speculative enquiries to landspreading operators or waste producers were additional methods used to identify possible materials for investigation. From this point it was necessary to make contact with the waste producer to ascertain further details of the types of waste being spread to land, and whether they were willing to provide samples for the experiment and arrange collection.

3.4.2 General Description and Collection

The range of collected waste types used in the field and laboratory experimental programme is presented in Tables 3.4-3.13. Tables 3.4 and 3.5 give the abbreviations used to describe the different waste types tested in the thesis, and the sources of the biosolids and biowastes are also provided.

Fresh samples of biosolids and biowastes were collected for each experiment. For the field experiments, with the exception of LC, which was delivered by Anglian Water and AD fresh and AD stored which were delivered from the plant in Holsworthy, Devon, the other biowastes and biosolids were personally collected. The biosolids for the trial in Wye were collected on 11 April 2005, the livestock wastes were available at the College farm and were collected on 18 April. The biowastes and biosolids for the first crop response trial at Silwood Park were collected between 26-28 April 2006 and in 2007 the wastes were collected between 18-19 April. Biowastes for the incubation experiment were sampled by the staff at each plant and posted to Imperial College London. The biosolids and biowastes for the laboratory incubation were delivered to Imperial College between 24 and 31 January 2007.

Care was taken to collect samples which were representative of the waste properties, for example when the waste was a solid, which was stored in a pile or in a skip the sample was taken from below the top layer and from several locations.

For each experiment fresh subsamples were taken and sent to a NAMAS accredited laboratory (NRM Laboratories, Bracknell, Berkshire) for physicochemical analysis. Approximately 1 kg was taken for solid samples and 1 l for liquids. Biosolids and biowastes collected for the field trials were kept in a cool, dark storage shed at Silwood Park and used within 3-4 days of collection. Biosolids and biowaste samples for the laboratory experiment were stored at 3-5 °C before use for approximately 1 week. The

dry solids (DS) contents of the solid materials was determined by drying overnight at 105 °C in a forced air oven, the DS content of the livestock wastes were determined by Imperial College farm staff. Solid biowaste and biosolids samples for field application were weighed into the required portions in black plastic sacks the day prior to application and stored overnight in the shed.

Table 3.4 Biosolids and livestock wastes applied in 2005 field investigation at Wye.

Waste description	Source	Abbreviation
Farmyard manure	Imperial College Farm (Wye)	FYM
Pig slurry	Imperial College Farm (Wye)	PIG
Cow slurry	Imperial College Farm (Wye)	COW
Dewatered raw biosolids	Thames Water (Reading)	DRAW
Liquid mesophilic anaerobically digested biosolids	Thames Water (Mogden/Perry Oaks)	LMAD
Dewatered mesophilic anaerobically digested biosolids	Southern Water (Ashford)	DMAD
Thermally dried mesophilic anaerobically digested biosolids	Anglian Water (Fords Farm)	TDMAD
Lime-treated cake	Anglian Water (Fords Farm)	LC

Table 3.5 Biosolids and biowastes applied in the industrial biowastes crop response trials at Silwood Park (2006/7) and laboratory incubation study.

Waste description	Source	Abbreviation	Experiment		
			2006 Biowastes Trial	2007 Biowastes Trial	Laboratory Incubation
Dewatered mesophilic anaerobic digested biosolids	Southern Water, Ashford	DMAD	•	•	•
Abattoir wash water	A&G Barber, Chelmsford	Abattoir	•		
Trout farm waste (uneaten food/faeces), old	UK trout farm	Trout old	•		
Trout farm waste (uneaten food/faeces), fresh	UK trout farm	Trout fresh	•		
Potato processing sludge	FenMarc, March	Potato sludge	•		
Potato processing wash water	FenMarc, March	Potato wash	•		
Chopped vegetable waste (broccoli/carrots/onions/potatoes/parsnips)	FenMarc, Elm	Vegetable		•	
Waste ice-cream mix	Unilever, Gloucester	Ice-cream	•		
Fatty ice-cream waste from dissolved air flotation	Unilever, Gloucester	Ice-cream DAF	•		
Stilton production waste (salty whey)	Tuxford & Tebbutt Ltd., Melton Mowbray	Salt whey		•	
Brewery waste (kieselguhr)	UK brewery	KG	•		
Brewery waste (live yeast and beer)	Fullers, Chiswick	Yeast		•	
Anaerobic co-digestate (food waste/abattoir/farm) pre-storage	Summerleaze, Holsworthy	AD fresh	•	•	•
Anaerobic co-digestate (food waste/abattoir/farm) post-storage	Summerleaze, Holsworthy	AD stored	•	•	•
Thermophilic aerobic digestate (vegetable/bread/cooked meat)	Central Bottling International Ltd., Doncaster	TAD	•	•	•
Anaerobic digestate (municipal solid waste)	Biffa, Wanlip, Leicester	ADMSW	•	•	•

Table 3.6 Selected physical and chemical properties of biosolids cakes and solid livestock wastes (dry solids basis), investigated in the 2005 field trial at Wye, industrial biowaste crop response trials at Silwood Park (2006/7) and the laboratory incubation study.

Biosolids	Experiment	DS (%)	OM (%)	pH	Total P (g kg ⁻¹)	Total K (g kg ⁻¹)	Total Mg (g kg ⁻¹)	Total S (g kg ⁻¹)
DRAW	2005 Field Trial	21.3	73.0	6.3	25.7	3.44	2.23	5.29
DMAD	2005 Field Trial	23.5	62.7	7.0	25.0	1.28	3.38	11.2
	2006 Field Trial	30.8	58.2	7.0	29.3	0.90	1.7	9.3
	2007 Field Trial	27.8	60.5	6.7	30.2	1.58	2.67	10.3
	Laboratory Incubation	28.9	60.1	7.2	28.0	1.94	2.98	11.5
TDMAD	2005 Field Trial	94.9	48.1	7.1	15.2	1.74	5.39	6.58
LC	2005 Field Trial	38.3	56.2	11.6	14.2	0.60	1.64	5.83
FYM	2005 Field Trial	24.1	67.8	7.7	12.4	34.2	8.35	6.74

Table 3.7 Selected physical and chemical properties of liquid biosolids and livestock wastes (fresh weight basis), investigated in the 2005 biosolids and livestock wastes field trial at Wye.

Biosolids	DS (%)	OM (%)	pH	Total P (g m ⁻³)	Total K (g m ⁻³)	Total Mg (g m ⁻³)	Total S (g m ⁻³)
LMAD	1.77	1.08	7.7	246	92.9	66.9	119
PIG	0.72	0.35	7.2	22.3	1093	17.9	21.6
COW	3.08	1.37	7.1	108	2489	152	97.1

Table 3.8 Selected physical and chemical properties of solid biowastes (dry solids basis), investigated in the crop response field trials at Silwood Park (2006/7), and the laboratory incubation study.

Biowaste	Experiment	DS (%)	OM (%)	pH	Total P (g kg⁻¹)	Total K (g kg⁻¹)	Total Mg (g kg⁻¹)	Total S (g kg⁻¹)
Trout old	2006 Field Trial	40.9	16.2	7.2	4.15	1.57	2.16	3.69
Trout fresh	2006 Field Trial	36.9	16.5	7.2	5.47	1.15	1.87	3.38
Vegetable	2007 Field Trial	8.32	89.3	5.2	3.99	38.3	1.64	5.62
TAD	2006 Field Trial	20.3	95.6	3.6	1.74	6.72	0.61	1.65
	2007 Field Trial	26.7	95.1	3.8	2.72	3.18	0.69	1.24
	Laboratory Incubation	17.1	86.0	4.4	3.81	5.44	2.38	3.22
ADMSW	2006 Field Trial	37.2	56.6	7.3	2.60	2.93	3.99	5.02
	2007 Field Trial	34.0	52.3	7.6	4.29	5.36	6.28	7.42
	Laboratory Incubation	28.9	42.3	8.8	4.43	5.06	7.99	7.97

Table 3.9 Selected physical and chemical properties of liquid biowastes (fresh weight basis), investigated in the crop response trials at Silwood Park (2006/7), and the laboratory incubation study.

Biowaste	Experiment	DS (%)	OM (%)	pH	Total P (g m⁻³)	Total K (g m⁻³)	Total Mg (g m⁻³)	Total S (g m⁻³)
Abattoir	2006 Field Trial	0.13	0.07	7.7	<0.01	103	16.3	4.40
Potato sludge	2006 Field Trial	2.14	1.26	3.9	<0.01	2031	90.5	54.9
Potato wash	2006 Field Trial	0.60	0.31	5.3	<0.01	153	17.5	153
Ice-cream	2006 Field Trial	35.2	3.39	4.4	664	1771	150	239
Ice-cream DAF	2006 Field Trial	9.17	8.84	3.5	74.9	151	20.1	170
Salt whey	2007 Field Trial	4.64	2.13	4.3	1064	2019	221	224
KG	2006 Field Trial	5.46	0.58	3.9	<0.01	50.4	9.48	24.2
Yeast	2007 Field Trial	10.2	9.31	6.1	182	2087	116	353
AD fresh	2006 Field Trial	5.14	3.45	8.3	287	2102	256	274
	2007 Field Trial	5.03	3.63	8.3	362	2751	412	246
AD stored	2006 Field Trial	5.70	3.94	8.1	343	1765	342	237
	2007 Field Trial	4.95	3.60	8.3	178	1536	127	218
	Laboratory Incubation	5.25	3.79	8.2	340	1975	348	334

Table 3.10 Nitrogen content of biosolids cakes and solid livestock wastes (dry solids basis), investigated in the 2005 field trial at Wye; the industrial biowastes crop response trials at Silwood Park (2006/7) and the laboratory incubation study.

Biosolids	Experiment	Total N (% DS)	NH ₄ -N (mg kg ⁻¹ DS)	NO ₃ -N (mg kg ⁻¹ DS)	NO ₂ -N (mg kg ⁻¹ DS)	Organic N (% DS)	Mineral N (% total N)	C:N ratio ⁽¹⁾
DRAW	2005 Field Trial	6.05	1916	2.82	-	5.86	3.17	7:1
DMAD	2005 Field Trial	6.03	9236	<0.1	-	5.11	15.3	6:1
	2006 Field Trial	4.70	4853	<0.1	<0.1	4.21	10.3	7:1
	2007 Field Trial	4.67	5800	<10.0	<0.1	4.09	12.4	7.5:1
	Laboratory Incubation	4.64	3397	<0.1	82.1	4.22	9.09	7.5:1
TDMAD	2005 Field Trial	3.43	517	6.85	-	3.38	1.5	8:1
LC	2005 Field Trial	2.44	2171	43.0	-	2.22	9.1	13:1
FYM	2005 Field Trial	2.84	384	1063	-	2.70	5.10	14:1

⁽¹⁾ C Content estimated from OM content using conversion factor of 1.73 (MAFF, 1986)

Table 3.11 Nitrogen content of liquid biosolids and livestock wastes (fresh weight basis), investigated in the 2005 field trial at Wye.

Biosolids	Total N (% FW)	NH ₄ -N (mg kg ⁻¹ FW)	NO ₃ -N (mg kg ⁻¹ FW)	Organic N (% Total N)	Mineral N (% total N)	C:N ratio ⁽¹⁾
LMAD	0.199	1166	<0.1	41.4	58.6	3:1
PIG	0.177	1671	<0.1	5.59	94.4	1:1
COW	0.202	999	<0.1	50.5	49.5	4:1

⁽¹⁾ C Content estimated from OM content using conversion factor of 1.73 (MAFF, 1986)

Table 3.12 Nitrogen content of solid biowastes (dry solids basis), investigated in the crop response trials at Silwood Park (2006/2007), and the laboratory incubation study.

Biowaste	Experiment	Total N (% DS)	NH ₄ -N (mg kg ⁻¹ DS)	NO ₃ -N (mg kg ⁻¹ DS)	NO ₂ -N (mg kg ⁻¹ DS)	Organic N (% DS)	Mineral N (% total N)	C to N ratio ⁽¹⁾
Trout old	2006 Field Trial	1.00	227	146	<0.1	0.96	3.73	9:1
Trout fresh	2006 Field Trial	0.92	315	9.49	<0.1	0.89	3.52	10:1
ADMSW	2006 Field Trial	1.71	3105	2.69	<0.1	1.40	18.2	19:1
	2007 Field Trial	1.50	2069	691	749	1.22	18.4	20:1
	Laboratory Incubation	2.32	3359	<0.1	191	1.96	15.3	11:1
TAD	2007 Field Trial	4.04	5689	<10	<0.1	3.47	14.1	14:1
	2006 Field Trial	3.43	2783	<0.1	<0.1	3.15	8.12	16:1
	Laboratory Incubation	3.50	2804	<0.1	0.19	3.22	8.01	14:1
Vegetable	2007 Field Trial	2.42	2004	<10	<0.1	2.22	8.28	21:1

⁽¹⁾ C Content estimated from OM content using conversion factor of 1.73 (MAFF, 1986)

Table 3.13 Nitrogen content of liquid biowastes (fresh weight basis), investigated in the crop response trials at Silwood Park (2006/2007), and the laboratory incubation study.

Liquid waste	Experiment	Total N (kg m ⁻³)	NH ₄ -N (g m ⁻³)	NO ₃ -N (g m ⁻³)	Organic N (kg m ⁻³)	Mineral N (% total N)	C to N ratio ⁽¹⁾
Potato sludge	2006 Field Trial	1.24	236	25.4	0.98	21.1	6:1
Potato wash	2006 Field Trial	0.15	22.8	<0.1	0.13	15.2	12:1
Ice-cream	2006 Field Trial	5.35	56.6	<0.1	5.29	1.06	4:1
Ice-cream DAF	2006 Field Trial	1.66	21.3	<0.1	1.64	1.28	31:1
Salt whey	2007 Field Trial	0.95	61	<10	0.89	6.4	13:1
KG	2006 Field Trial	0.75	37.6	<0.1	0.71	5.01	4 :1
Yeast	2007 Field Trial	6.85	105	<10	6.75	1.5	8:1
Abattoir	2006 Field Trial	0.73	479	<0.1	0.25	65.0	0.6:1
AD fresh	2006 Field Trial	7.21	2835	<0.1	4.38	39.3	3:1
	2007 Field Trial	6.73	3576	<10	3.15	53.1	4:1
AD stored	2006 Field Trial	6.19	2882	<0.1	3.31	46.6	4:1
	2007 Field Trial	5.46	3918	<10	1.54	71.8	3:1
	Laboratory Incubation	5.91	2756	<0.1	3.15	46.6	4:1

⁽¹⁾ C Content estimated from OM content using conversion factor of 1.73 (MAFF, 1986)

3.4.3 Physical and Chemical Properties

The dry solids (DS), organic matter (OM), pH and nutrient contents (except N) of solid biosolids and livestock wastes are shown in Table 3.6. The cakes had typical DS contents, of approximately 20-30 %, with the exception of LC and TDMAD. Lime Cake had an intermediate DS content, equivalent to 38.3 %, reflecting its admixture with calcium oxide. The DS content of TDMAD was high, 94.9 %, and was in the expected range for this sludge type (Cogger *et al.*, 1999; Smith and Durham, 2002; Tarrasón *et al.*, 2007). The cakes are a source of OM; the untreated materials, DRAW and FYM have the greatest OM contents of 73.0 % and 67.8 % respectively. The OM of the treated biosolids had been digested, which is reflected in the lower contents of approximately 60 % for DMAD, 48.1 % for TDMAD and 56.2 % for LC. The pH of the cakes was near neutral, with the exception of LC, which, as expected, had an alkaline pH of 11.6.

Dewatered raw sludge (DRAW) and DMAD had slightly higher P concentrations than the other cakes, approximately 25–30 g kg⁻¹ DS, compared to approximately 15 g kg⁻¹ DS for LC and TDMAD; FYM had the lowest P concentration at 12.4 g kg⁻¹ DS. The concentration of K in the cakes was generally low and ranged between 6 g kg⁻¹ DS (LC)–3.44 g kg⁻¹ DS (DRAW), with the exception of the livestock waste (FYM) which was a good source of K, containing 34.2 g kg⁻¹ DS. This was as expected for biosolids, which have a low K content due to elutriation during the wastewater treatment process (Hall, 1983b). The cakes were also a source of Mg and S. DMAD, in particular, was a good source of S, with an approximate concentration of 10 g kg⁻¹ ds.

Table 3.7 shows the physical and chemical characteristics of liquid biosolids and livestock wastes. They had low DS contents, in particular PIG had a very low solids content of less than 1 %. The OM contents were 50 % or greater of the dry solids contents, and they had approximately neutral pH values. The liquid biosolids and livestock slurries were sources of P, K, Mg and S. The livestock slurries were a good source of K, but, as expected for biosolids, the LMAD has a low K content of less than 100 g m⁻³. Pig slurry had the lowest P, Mg and S concentration, which is a reflection of the low dry solids content.

Physical and chemical properties of solid biowastes are presented in Table 3.8. Vegetable waste had the lowest DS content, of less than 10 %, it was a mixture of chopped potato, carrots, onions, broccoli and parsnips and was relatively fresh so this

was to be expected. The OM content was greater than DMAD, approximately 90%, as this material had not been biologically treated. The trout wastes, a mixture of uneaten food and faeces had been discharged into a settlement pit, which was open to the atmosphere, and had a relatively high DS content; this reflects reduction of moisture content by evaporation and leaching. The older waste had a greater DS content, as would be expected, 40.9 % compared to 36.9 %. The trout wastes were mixed with sediment from the settlement lagoon, which is reflected in relatively low OM contents, less than half that of ADMSW for example. The thermophilic aerobic digestate (TAD) was a liquid (Plate 3.1a), but was considered with the solid materials on account of its high DS content (17.1–26.7 %). The variation between samples in the DS content of TAD may reflect differences in input materials, which were vegetables, cooked meat and bread. It had a high OM content of between 86.0–95.6 % on a DS basis. There was also variation between samples in the DS content of ADMSW; this may reflect differences in storage time of ADMSW, which was stored in a stockpile. The relatively high and variable DS content of this material may also represent the contamination of the digestate with non-organic materials such as plastic refuse bags, which are visible in Plate 3.1b. This is reflected in the OM content of ADMSW which was lower and more variable than DMAD (60 % DS), in the range of between 42.3–56.6 % DS. The pH of ADMSW and the trout wastes was approximately neutral, whereas TAD was acidic with a pH in the range of 3.6–4.4. This was a result of the high content of fruit and vegetable acids in the input material, and the vegetable waste was also acidic with a pH of 4.4. The P contents of the solid biowastes was lower than the biosolids, the highest P content was ADMSW, 2.6–4.43 g kg⁻¹ DS, whereas DMAD had a content of 25.0–30.2 g kg⁻¹ DS. The concentration of K in DMAD was low, as expected for biosolids, and ranged between 0.9 and 1.24 g kg⁻¹ DS. With the exception of the trout wastes the biowastes were a better source of K than the biosolids, especially vegetable waste, which contained 38.3 g kg⁻¹ DS. The biowastes were also a significant source of the plant nutrient elements Mg and S.

Selected physical and chemical properties of liquid biowastes are presented in Table 3.9. The DS contents of AD fresh, AD stored, Salt whey and KG were all approximately 5 %. The abattoir wash water had been stored in an open-topped lagoon so was subject to dilution by rainwater, which may partially account for its low DS content of 0.13 %. The potato wash water was a starchy liquid and soil washings from potato processing and also had a low DS content of 0.6 %; potato sludge contained peel and chopped potato pieces, was of a 'porridge'-consistency, and had a greater DS content of 2.14 %. The yeast waste was a thick consistency containing yeast biomass

and waste beer and had a high DS content of 10.2 %. The ice-cream wastes also had high DS contents, especially the waste ice-cream mix (35.2 %), which was a mixture of ice-cream that did not meet quality control criteria. The organic matter contents were in most cases between 50–90 % of the DS content, with the exception of Ice-cream and KG. The OM content of KG was approximately 11 % DS; it is a siliceous material used to filter organic contaminants from beer, so, although it contains organic material, it is primarily a mineral waste.

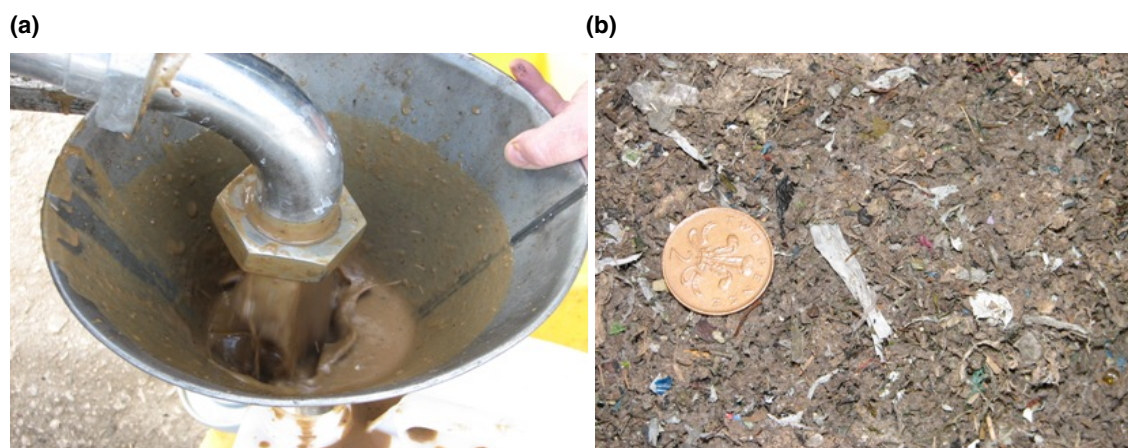


Plate 3.1 Digested biowastes: (a) thermophilic aerobic digestate of mixed food waste (TAD); (b) anaerobic digestate of mechanically separated MSW (ADMSW).

The pH of Abattoir was approximately neutral, and AD stored and fresh were moderately alkaline. The pH of Yeast was moderately acidic at 6.1; KG had an acidic pH, 3.9, this is likely to be a result of weak organic acids resulting from the oxidation of alcohol residues. As with the solid vegetable wastes, the potato sludges were acidic, pH 3.9-5.3. The ice-cream wastes, pH 3.5-4.4, and Salt whey, pH 4.3, were also acidic, which may be a result of high fatty acid content. The salinity of Salt whey was determined, and, as expected, it had a high salinity of $6430 \mu\text{S cm}^{-1}$ (not shown in Table 3.9), as a result of addition of salt during the cheese making process. The liquid biowastes were a source of the plant nutrients P, K, Mg and S, with the exception of Abattoir, Potato sludge/wash and KG which did not contain a detectable amount of P, probably due to the fact they were very dilute. Salt whey was a particularly good source of P, containing 1064 g m^{-3} . Potato sludge, Ice-cream, Yeast and AD fresh and stored were high in K, in the case of AD fresh and stored this is likely to be due to the high proportion of animal slurry in the co-digestate.

The N contents of biosolids cakes are presented in Table 3.10. The largest total N contents were in DMAD and DRAW, equivalent to 4.64-6.03 % DS for DMAD,

approximately twice that in LC and TDMAD. The low total N content of LC was expected and was due to the release of NH_3 due to the high pH and the dilution effect of lime addition to the raw cake (CEC, 2001). The mineral N fraction in both the digested biosolids contained little $\text{NO}_3\text{-N}$ and was mainly $\text{NH}_4\text{-N}$. Lime cake (LC) and DMAD contained mineral N fractions equivalent to approximately 10-15 % of their total N contents, whereas TDMAD contained about 1.5 % of the total N as mineral forms, due to the volatilisation of NH_3 during the thermal drying process (Smith and Durham, 2002). This may also account for the smaller total N content of TDMAD in comparison to DMAD. The mineral N fraction of DRAW was also low, 3.2 % total N, and it had a high C:N ratio, which was expected for undigested sludge (Smith *et al.*, 1998b; Smith and Tibbett, 2004), similarly the mineral N fraction of the untreated FYM was low at 5 % total N. The C:N ratio of LC was high (13:1) compared to the other biosolids, which is a reflection of its admixture with calcium oxide. The N contents of liquid liquid livestock wastes are given in Table 3.11. The liquid biosolids and livestock wastes were good sources of total N, with high mineral N contents of 50 % total N or greater; pig slurry had an especially high mineral N content of approximately 95 %, which was present as $\text{NH}_4\text{-N}$.

The N contents of solid biowastes are presented in Table 3.12. The trout wastes had relatively low total N contents of approximately 1 % DS, this is a result of their mixture with sediment and soil in the settlement lagoon, their mineral N content was also relatively low at approximately 3.5 % total N. Total N content of ADMSW ranged between 1.5–2.32 % DS, which was less than 50 % of the total N content of DMAD, however, mineral N was 15.3–18.4 % of the total N. Total N in TAD was between 3.43 – 4.04 % DS, comparable to the amounts available in the biosolids, available N was approximately 10 % total N, similar to that of DMAD. This was a liquid biowaste that was considered with the solid materials due to its high DS content; the proportion of mineral N was less than the liquid digested biosolids, indicating that the aerobic digestion method does not degrade the organic material to the same extent as anaerobic digestion.

Vegetable waste was a relatively high source of total N, 2.42 % DS and mineral N, equivalent to 8.3 % of the total N content. The total and available N contents of the liquid biowastes are given in Table 3.13. The potato sludges, Salt whey, KG and Abattoir had a low total N content, reflecting their low DS content. However, whereas the mineral N content of Salt whey and KG was less than 10 % total N, most of the total N in Abattoir was in mineral forms, 65 % total N. The co-digestates, AD fresh and AD

stored, had a high total N content as did Yeast and Ice-cream. However, whereas AD fresh and AD stored had high mineral N contents similar to the liquid digested biosolids, between 40–72 %, in Ice-Cream and Yeast the mineral N content was only 1 % and 1.5 % of total N respectively.

The livestock wastes, biosolids and biowastes were also analysed for heavy metal concentrations and the data is available in Appendix A2.

3.5 Grass

3.5.1 Yield Measurements

Fresh weights of samples taken from plots sown with ryegrass in the 2005 biosolids and livestock wastes trial (Chapter 4), and the 2006/7 crop response field trials at Silwood Park (Chapters 5 and 6) were measured, and sub-samples of approximately 150 g fresh material were dried to a constant mass at 80 °C in a forced-air oven to determine dry matter yield. Oven dried grass was ground to <1 mm using a hammer mill grinder (Glen Creston, model 16-151, London) and retained for nutrient element analysis.

3.5.2 Total N and P Analysis

Dried ground grass was analysed for total N and P content using a standard Kjeldahl digestion method (SCA, 1986). A 0.5 g sample of ground grass was weighed into a 100 ml digestion tube, with 10 ml concentrated H₂SO₄, anti-bumping granules and a CuSO₄ catalyst tablet. The samples were heated on a 40 tube digestion unit (Gerhardt, Bonn, Germany) at 140 °C until they were no longer frothing, approximately 1 hour, and then refluxed at 365 °C for 3 hours. After cooling the samples were carefully mixed with approximately 40 ml deionised water, left to cool again and then diluted to 250 ml in volumetric flasks. Sub-samples were stored in plastic containers at 4 °C prior to analysis. An automated colorimetric technique (Krom, 1980; APHA, 1985; Markus *et al.*, 1985; SCA, 1986) using a multichannel segmented flow analyser (Skalar SAN^{plus} Segmented Flow Analyser, Skalar, Breda, The Netherlands) was used to simultaneously determine total N and P in the digested solution, at absorbencies of 660 nm and 880 nm respectively.

Two blanks, containing 10 ml concentrated H₂SO₄, anti-bumping granules and a CuSO₄ catalyst tablet were included in each batch. In addition, spiked samples containing a known concentration of Nicotinic Acid were digested on a regular basis to check efficiency of the procedure, and 5 % of the samples were replicated.

3.6 Experimental Approach for Field Experiments

3.6.1 Design of Field Trials

Systematic arrangements of fertiliser experiments have been developed (Cleaver *et al.*, 1970; Greenwood *et al.*, 1980a;b; Smith and Hadley, 1988), in which treatment levels are arranged in a systematic gradient. This removes the need for wide guard rows between each plot, which are normally there to prevent edge effects that may result from a high rate plot adjacent to a low rate plot. The elimination of guard rows increased the ratio of harvested to non-harvested area, reducing potential for experimental error. Smaller plots and fewer guard rows facilitate more rates of fertiliser application, thereby increasing sensitivity to finding the optimal rate of application. The disadvantage of systematic designs is that the effects of fertiliser treatments may be masked by natural fertility trends. Variation due to natural fertility trends can be detected by arranging plots as three blocks containing replicate treatments, and error can also be reduced by randomising the direction of the fertiliser gradient in the systematic plots.

Nitrogen availability in organic residuals may be expressed as Plant Available Nitrogen (PAN) or as a percentage of total N applied (Cogger *et al.*, 2001; Sripanomtanakorn and Polprasert, 2002; Cogger *et al.*, 2004; Evanylo, 2003; Gilmour *et al.*, 2003). Alternatively, N availability may be expressed in relation to the amount of mineral N available in a mineral fertiliser N reference treatment (Kiemnec *et al.* 1987; Jackson *et al.*, 1997; Nicholson *et al.*, 1999; Smith and Bellett-Travers, 2001; Smith *et al.*, 2002b; Morris *et al.*, 2003; Nicholson *et al.*, 2003; Schröder *et al.*, 2007). This relative N fertiliser value is referred to as an N equivalency value or Nitrogen Fertiliser Replacement Value (NFRV) (Schröder *et al.*, 2007).

A programme of field experiments established at Imperial College, Silwood Park, between 2001-2003 (Smith and Bellett-Travers 2001; Smith *et al.*, 2002b; Morris *et al.*, 2003) to investigate the fertiliser value of biosolids successfully utilised a systematic design to determine optimum application rates; therefore, this was the design

considered appropriate for the crop response trials with biowastes in this investigation. This approach was particularly suitable as it increases the sensitivity of the experiment to finding the optimum application rates for this diverse range of materials. Biowastes were incorporated into the soil to minimise losses of N by gaseous emissions, and perennial ryegrass was used as an indicator crop as it is efficient at capturing most of the plant available N (Whitehead, 1995; Hansen *et al.*, 2007), and should therefore account for most of the N additions. Previously, ryegrass was used in the biosolids experiments at Silwood Park, so this allowed direct comparisons to be drawn between the trials. Mineral N fertiliser controls were included, so that N equivalency values could be calculated, using the statistical methods described in Section 3.7.2. The soil incorporation and choice of indicator crop permitted an absolute N equivalency value to be determined from which the fertiliser value of the material under different application regimes can be predicted.

Field trials can also be used to measure residual fertiliser value, if organic residuals are to be reapplied to land, it is necessary to take into account the residual effects of previous applications to ensure that crop nutrient requirements are not exceeded (Soon *et al.*, 1978; Boyle and Paul 1989; Smith *et al.*, 2002b). In this experiment, mineral N fertiliser gradients were reapplied to the mineral N control plots in the second year so that residual value of biowastes could be investigated. Further specific details of the experimental establishment are described in Chapters 5 and 6.

3.6.2 Site Management

Weeds were removed from the Wye trial with a hoe or by hand when they emerged. At Silwood Park, there was not much weed competition during 2006, but, due to low light and slow growing conditions in 2007 there was some competition from common agricultural weeds. To allow an even ryegrass ley to establish, weeds were removed from the plots by hand, but care was taken not to disrupt the root system. After the first grass harvest there was little recurring weed growth. Necessary precautions were taken to prevent damage to the experimental plots by grazing wild animals. In 2007, a fence was erected to exclude rabbits.

3.6.3 Environmental Data Collection

Remote data loggers were used to continuously collect soil temperature data (Tiny Tag Transit Temperature range H TG-0050, Omni Instruments), 3 temperature loggers

were positioned at a depth of 5 cm in randomly chosen plots. For the 2005 biosolids and livestock wastes field trial (Chapter 4), gravimetric soil moisture content was measured from individual samples, and remote data loggers (e+ loggers, Eijkelkamp, Giesbeek, Netherlands) were used to continuously collect moisture data at 1 h intervals. For the 2006/7 industrial biowastes crop response field trials (Chapters 5 and 6), a pooled soil sample, 0-15 cm, was taken using a gouge auger every 1-2 weeks for gravimetric measurement of soil moisture content. Weather data, including rainfall and air temperature were collected at the sites daily and these data are available in Appendix A2.

3.7 Statistical Analysis and Calculations

3.7.1 Biosolids and Livestock Wastes Field Experiment and Laboratory Incubation

3.7.1.1 Nitrogen Recoveries

Concentration of N (TON, $\text{NH}_4\text{-N}$ and MBN) in kg N ha^{-1} (field experiment) or $\text{mg kg}^{-1} \text{ ds}$ (laboratory experiment) in unamended control soil was subtracted from the amended soil concentration. This value was expressed as a percentage of the total N added in each biosolids or biowastes treatment.

3.7.1.2 Mineralisable N

The mineralisable fraction of the organic N in the organic residuals was calculated by the following formula (Smith and Durham, 2002):

$$N_{\min} (\%) = \frac{(N_s - N_i)}{N_{\text{org}}} \times 100$$

Where:

$N_{\min} (\%)$ = the mineralisable fraction of organic N in the organic residuals;

N_s = the mineral N concentration in organic residuals-amended soil at the end of the experiment ($\text{kg N ha}^{-1}/\text{mg kg}^{-1} \text{ ds}$);

N_i = the amount of inorganic N ($\text{NH}_4\text{-N} + \text{TON}$) supplied to the soil in the organic residuals ($\text{kg N ha}^{-1}/\text{mg kg}^{-1} \text{ ds}$);

N_{org} = the amount of organic N added to the soil in the organic residuals ($\text{kg N ha}^{-1}/\text{mg kg}^{-1} \text{ ds}$).

N_s was calculated using the formula:

$$N_s = (N_s - N_c) \quad (2)$$

Where:

N_c = the mineral N concentration in unamended control soil ($\text{kg N ha}^{-1}/\text{mg kg}^{-1} \text{ ds}$).

3.7.1.3 Analysis of Variance

The statistical approach taken by Smith *et al.* (1998b) was used. Analysis of variance (ANOVA) was used to determine whether soil type and organic residual type (mean for all sampling dates), and soil and sampling date (mean for all organic residuals), had a significant effect on recovered N as MBN or mineral-N. For the 2005 biosolids and livestock waste field trial (Chapter 4) TON recoveries used were the total recoveries in the 0-20 cm profile. Post-hoc tests were performed to further examine the effects of organic residuals types, and sampling date on MBN. When a Levene's test showed that differences between variances were significant at $P=0.05$ the post-hoc test used was a Tamhane's T2 test (Tamhane, 1979), otherwise Tukey's tests were used. All ANOVA tests were carried out using SPSS software (SPSS 15.0 for Windows).

3.7.2 Industrial Biowastes Crop Response Field Experiments

Cumulative fresh and dry weight yields and N offtake in relation to total N applied and biowastes were statistically analysed by linear regression analysis and compared to yields from mineral N calibration plots. Linear models of the form $y = a + bx$ were fitted to the data where y is the yield or N offtake (t ha^{-1} fresh or dry matter or kg N ha^{-1}). Where the linear regression was significant according to ANOVA analysis, the slopes of the regression equations for each biowastes treatment were compared to the slope obtained for mineral N to obtain N equivalency values (Kiemec *et al.*, 1987; Smith and Bellett-Travers, 2001; Smith *et al.*, 2002b; Morris *et al.*, 2003). Where the crop response was curvi-linear at top rates of application, quadratic equations ($y = a + bx + cx^2$) were fitted to the data, if the relationship was significant, the data point for the top rate was removed and the quadratic equation was re-fitted, so that only the approximately linear portion of the yield response pattern was considered. If there was no significant quadratic relationship a linear model was fitted to the remaining data points, and the yield response relative to mineral N was calculated by comparing the

linear regression coefficients. Only in a minority of cases was it necessary to follow this procedure. In general the quadratic term (x^2) in the crop response models was not significant at $P \leq 0.05$, and the yield pattern therefore approximated to a linear function of N application. Yield response to manure N is considered to be linear between applications of 0-300 kg N ha⁻¹ (Whitehead, 1995), as this is within the range of standard rates of application of fertiliser N, it was appropriate to only consider the linear response. A mean N equivalency value was calculated from each of the indicators of crop response to N (fresh yield; dry yield and N offtake) to each biowastes treatment. Using this method it was possible to obtain relative values for the most responsive part of the yield to compare overall response to biowastes and mineral N, rather than individual points and values.

When calculating N equivalencies from sources of organic N, a frequently taken approach, is to compare individual yields produced by known concentrations of total N to a yield response curve for a mineral N control to obtain a fertiliser N equivalency value (George, 1994; Jackson *et al.*, 1997; Nicholson *et al.*, 1999; Nicholson *et al.*, 2003; Schröder *et al.*, 2007). Fertiliser equivalencies were also calculated by this method as a comparison. An asymptotic equation of the form $y = a + b * \exp(-cx)$ (George, 1994) was fitted to the yield data for the different rates of application of mineral N, where y = total yield (t ha⁻¹) or N offtake (kg N ha⁻¹); x = rate of N application (kg N ha⁻¹); and a and b and c are regression coefficients, estimated using the constrained non-linear curve estimation procedure in SPSS (SPSS 15.0 for Windows). Each yield or N offtake value for the biosolids and biowastes was substituted into the equation to calculate the N input from mineral fertiliser N required to give an equivalent yield or N offtake. This was expressed as a percentage of total N applied in the organic N source, to give N equivalency values.

4 A FIELD INVESTIGATION INTO NITROGEN TRANSFORMATION PROCESSES AND MICROBIAL BIOMASS N DYNAMICS IN BIOSOLIDS- AND LIVESTOCK WASTES-AMENDED AGRICULTURAL SOILS WITH CONTRASTING PROPERTIES

4.1 Introduction

4.1.1 Background

The preferred route for managing biosolids from urban wastewater treatment is land application for use as agricultural fertilisers (Defra, 2007); this enables the nutrients and organic matter contained in the material to be recycled.

In addition to mineral forms of N ($\text{NO}_2\text{-N}$, $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$), the majority of N in biosolids is present in organic forms. Organic N is mineralised and converted to NH_4^+ by microorganisms in the soil. Nitrifying bacteria convert $\text{NH}_4\text{-N}$ to $\text{NO}_3\text{-N}$, both of which are available for crop uptake. It is important to be able to predict the amount of organic N from sludge that will be converted to mineral N to ensure that there will be sufficient N available for crops, and that there are not excessive quantities of NO_3^- in the soil, which may leach causing environmental problems. The amount of mineralised N may be influenced by moisture, pH, temperature, soil type and sludge type (Section 2.9). Another important factor is microbial immobilisation of N, which may vary under differing soil and sludge application conditions (Section 2.9.5).

Explicit guidelines exist as to which types of sewage sludge may be applied to certain crop types. Conventionally treated biosolids may only be applied to animal feed and combinable crops, but the Safe Sludge Matrix (ADAS, 2001) approves the use of enhanced treated biosolids on a wider range of crops (Section 2.2.2.1). Enhanced methods of sludge treatment, to eliminate microbial pathogens, involve processing sludge under extreme conditions such as chemical manipulation or heating or drying at high temperatures (Section 2.1.2.5). These treatments may cause fundamental changes to the physicochemical and biological properties of the biosolids, with implications to the fertiliser value, and to N transformations and soil interactions in soil amended with these products. For example, thermal drying involves heating sludge to at least 100 °C, is effective at destroying pathogens (Wantanabe *et al.*, 1997; Oropeza *et al.*, 2001), and, in addition, improves the physical characteristics of biosolids

products. The majority of N in thermally dried biosolids products is in organic forms; however, laboratory incubations have demonstrated that the mineralisable portion may be larger than in conventionally treated biosolids (Cogger *et al.*, 1999; Smith and Durham, 2002; Breedon, 2003). Field trials (Smith and Bellett-Travers, 2001; Smith *et al.*, 2002b; Morris *et al.*, 2003) have also found increased mineralisation of N from thermally dried biosolids in comparison to conventional sludge types in a light, moderately acidic, loamy sand soil of low organic matter content. Consequently, further research is required to define the fertiliser value of enhanced treated biosolids, under field conditions, and to understand the influence of soil type on N availability in soils amended with these forms of biosolids.

The net amount of N mineralised from organic matter is a balance between total mineralisation and immobilisation; the extent of immobilisation is largely dependent on the C:N ratio and structure of the organic matter (Sabey *et al.*, 1975; Nicolardot, 2001; Vinten, 2002; Pansu *et al.*, 2003). Microbial biomass dynamics have previously been investigated in biosolids-amended soil, but have primarily concentrated on microbial biomass C (MBC) (Franco-Hernández *et al.*, 2003, Sánchez-Monedero *et al.*, 2004; Calbrix *et al.*, 2007). There has been some investigation into microbial biomass N (MBN) in biosolids-amended soil in laboratory investigations (Jedidi *et al.*, 2004). In addition, MBN has been measured in field investigations with a single soil and sludge type (Banerjee *et al.*, 1997; Fernandes *et al.*, 2005), but there is limited information under field conditions into the effects of soil and biosolids type on the MBN component in biosolids-amended soil. Partitioning of N in microbial biomass in biosolids-amended soil may be important in understanding N release kinetics and could be responsible for lower N availability observed in less fertile soils (Smith *et al.*, 1998b; Breedon *et al.*, 2003). Nitrogen mineralised from biosolids may be immobilised by transfer to microbial biomass where it will not be available to crops. For example, Smith *et al.* (1998b) observed reduced N availability in a loamy sand soil with low fertility amended with undigested biosolids in comparison to a high fertility clay loam and concluded that this behaviour may be explained by the increased microbial immobilisation of N in low fertility systems.

The results presented in this chapter are from a field trial to investigate N mineralisation processes and microbial immobilisation in livestock wastes and biosolids-amended agricultural soil. The experiment was part of a larger programme of investigations funded by the water industry into enteric pathogen inactivation and ecological interactions in biosolids-amended soil; therefore, the sampling regime included

collection of soil for enteric microbial analysis in addition to determination of nutrient concentrations. The trial included two sites with contrasting soil types, a high fertility silty clay and a lower fertility sandy silt loam. Selected soil amendments included thermally dried digested biosolids (TDMAD) and lime-treated raw cake (LC), as examples of biosolids treated to enhanced status, in addition to liquid, and mechanically dewatered, mesophilic anaerobically digested biosolids (LMAD and DMAD). This was to allow a comparison of enhanced and conventional biosolids types currently spread to agricultural land. Nitrogen mineralisation from animal manures is well understood, so farm and livestock wastes were included as reference materials. Unamended control and biosolids-amended plots sown with perennial ryegrass, to allow analysis of crop uptake of N, were also set up. In addition, mineral N treatments, an ammonium salt and a nitrate salt, were included as a reference for nitrification rate and nitrate mobility in the different soil types.

4.1.2 Aims

The key objective of the investigation was to conduct fundamental research into the mechanisms influencing N availability in contrasting soil types from different biosolids, to improve understanding of microbial and mineral N dynamics in biosolids-amended soil and to develop appropriate fertiliser guidance. The specific aims were:

- To investigate the effects of biosolids type and livestock wastes on nutrient availability in amended soil;
- To investigate the interactions between biosolids or livestock wastes, and soil type on nutrient dynamics under field conditions;
- To quantify a mass flow balance for N species following soil amendment with biosolids;
- To study partitioning of N within the soil microbial biomass for different soil types amended with biosolids and the subsequent influence on N release to crops in contrasting fertility systems;

4.2 Materials and Methods

General materials and methods relating to site locations, soil sampling and analysis are presented in Chapter 3, methods specific to the 2005 biosolids and livestock wastes trial are presented here.

4.2.1 Experimental Establishment

The field trial was located at the Imperial College farm in Wye, Kent, and was established on 19 April 2005. Two soils types with contrasting physicochemical properties were chosen, a silty clay (North Sidelands) and a sandy silt loam (Brices Field), as shown in Plate 5.1. Details of the site locations are given in Section 3.2.1 and soil properties are described in Section 3.2.3.

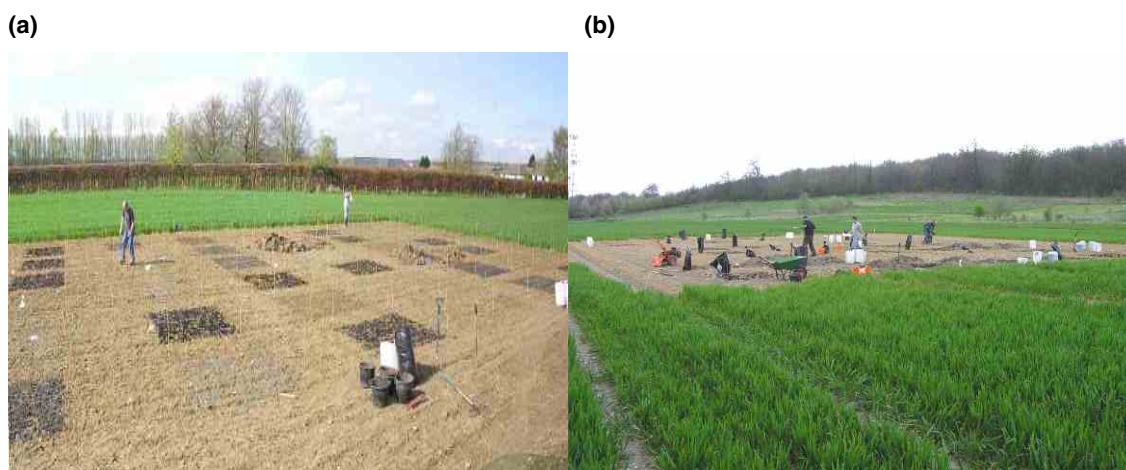


Plate 4.1 Imperial College farm in Wye, Kent: (a) North Sidelands (silty clay); (b) Brices Field (sandy silt loam).

The field experiment was arranged as three randomised blocks with 16, 4 m² (2 x 2 m) treatment plots, an example of the arrangement of the plots is given in Figure 4.1. There were 16 treatments in total; a list of the biosolids and livestock wastes and abbreviations used in this thesis is provided in Table 3.4 in Chapter 3. In addition to control plots with no amendments, the treatments included five representative types of conventional and enhanced treated biosolids, livestock slurries (pig and cow) and farm yard manure (FYM) (Table 3.4). Additional dewatered mesophilic anaerobically digested biosolids (DMAD) amended and unamended control plots were sown with perennial ryegrass (*Lolium perenne*) cv. Lasso, at a rate equivalent to 37 g m⁻². Two inorganic N treatments were set up as controls, sodium nitrate (NaNO₃) to provide a tracer for mineral N movement and ammonium chloride (NH₄Cl) as a basis for

measuring nitrification kinetics. A protozoa inhibition investigation was set up, which included unamended control soil and DMAD amended soil treated with thiram, to inhibit the soil protozoa population, applied at a rate equivalent to 10 g m^{-2} . These treatments were primarily for the purpose of ecological investigations that were conducted alongside the nutrient investigations; however, they were also sampled for nutrient analysis, to investigate the effects of removal of protozoa grazing on the microbially mediated N transformation processes. The remaining treatment was set up solely for investigation of enteric pathogen decay and was not sampled for nutrient analysis. Details of selection, collection and description of physical and chemical properties of the biosolids and livestock wastes are given in Section 3.4.

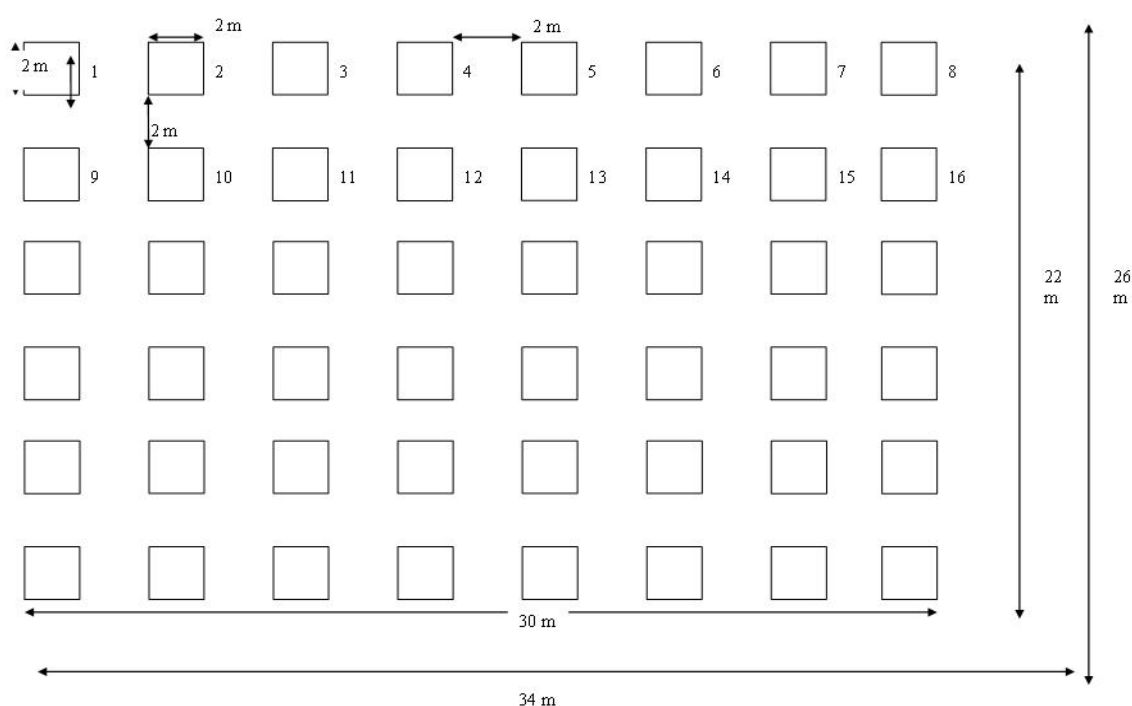


Figure 4.1 Example of arrangement, dimensions and spacing of experimental plots.
Note: treatments were randomly assigned to plot number.

The liquid materials were applied at a rate equivalent to $100 \text{ m}^3 \text{ ha}^{-1}$ and the solids at 10 t DS ha^{-1} . The rates were selected on the basis that, at a N content of approximately 5 % DS, the application rate of total N would be 500 kg N ha^{-1} , the maximum recommended rate outside NVZs (Defra, 1998). Each of the mineral N controls was applied at a rate equivalent to 200 kg N ha^{-1} . Solid sludges, cattle manure and inorganic fertilisers were applied uniformly to the plots by hand and the liquids were manually spread by bucket. The sludges were applied to the soil surface and incorporated immediately using a pedestrian operated rotary cultivator, set to a cultivation depth of 10 cm. Unamended areas of soil were marked out adjacent to the

experiment sites for collection of bulk density samples. Site management is described in Section 3.6.2. Weather data for the duration of the experiment is available in Appendix A3.

4.2.2 Soil Temperature and Moisture

Environmental data collection is described in Section 3.6.3, and Figure 4.2 shows soil temperature and gravimetric moisture content from April 20–19 July 2005 (days 0-90) at the field sites. Moisture content of the soil was, in general, approximately 4 % greater at North Sideland compared to Brices Field, consistent with its greater OM content (Table 3.1) and hence higher water holding capacity (WHC). Moisture content was in the approximate range of 16-25 % at North Sideland and 13-21 % at Brices. Soil temperature was generally 1-7 °C higher at Brices than at North Sideland. Brices had a lower OM content, and therefore less pore space, which may explain the higher temperature. Soil temperature showed a gradual increase from April–July, from approximately 13 °C on day 0 to maximum mean values of 25 °C at North Sideland and 31 °C at Brices, on day 60.

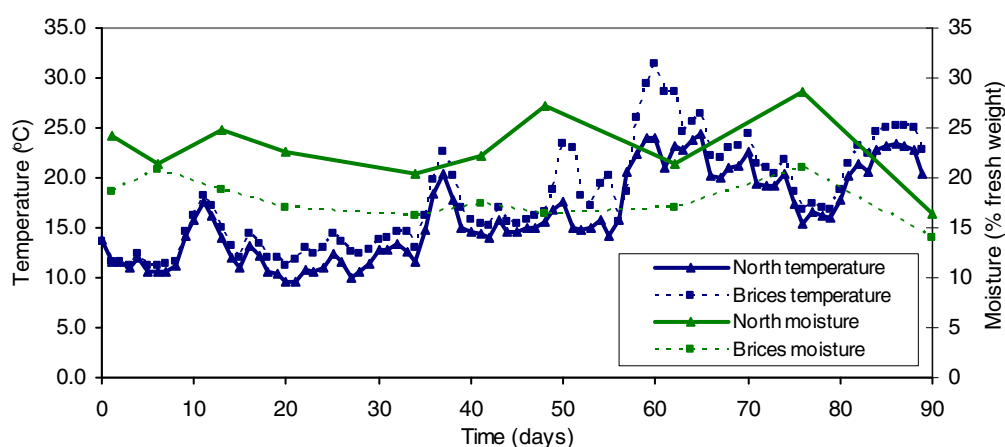


Figure 4.2 Soil temperature and moisture content (0-10 cm) at the field sites, 20 April-19 July 2005 (days 0-90). Temperature is given as a daily mean of remote logger data; moisture is the mean of gravimetric measurements made at approximately weekly intervals at each field.

4.2.3 Sampling and Analysis

4.2.3.1 Sampling

The first samples were collected on 20 April and sampling continued at approximately weekly intervals. The experiment was completed on 19 July 2005, after 90 days of monitoring. In addition to samples collected to a depth of 10 cm, deeper cores were taken at a depth of 10-20 cm to monitor mineral-N mobility. Sampling of the 10-20 cm profile began after 1 week, as it was assumed that losses of $\text{NO}_3\text{-N}$ would be insignificant immediately following soil amendment, because mineral N in the biosolids and livestock wastes was mainly present as $\text{NH}_4\text{-N}$.

Details of soil sampling and characterisation are given in Section 3.3.1; transport and storage methods are described in Section 3.3.2. Collected soil samples were routinely mixed and sieved to <4 mm to remove stones and plant debris. Gravimetric moisture content (Section 3.3.3) and mineral N concentrations ($\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and $\text{NO}_2\text{-N}$) (Section 3.3.4) were determined in 0-10 cm and 10-20 cm samples. Microbial biomass C (MBC) and N (MBN) concentrations were determined in selected treatments in the 0-10 cm samples (Section 3.3.5). The treatments analysed for MBC and MBN were: unamended control; DMAD; TDMAD; RAW and LC. These treatments were selected to provide examples of conventional (DMAD) and enhanced treated (TDMAD and LC) biosolids, and stabilised (DMAD, TDMAD) organic matter as a comparison with unstabilised, or partially stabilised organic matter (RAW, LC).

The ryegrass crop on unamended and DMAD amended plots was harvested on 31 May, 21 June and 18 July. A 1 m² area was randomly selected with a quadrat and the grass cut to 2 cm above ground level using shears. Fresh weights of each sample were measured and dry weights and N and P concentrations were measured as described in Section 3.5.

4.2.3.2 Bulk density

Triplicate samples for bulk density measurements were taken from each experimental site on a weekly basis until measurements were constant. A cylinder of known dimensions was hammered into the soil and carefully removed to collect the whole sample for bulk density measurements. The fresh mass of each sample was taken and

the sample was dried to a constant mass at 105 °C to obtain the dry weight. Dry bulk density of each soil type was calculated as follows:

Bulk density (g cm^{-3}) = total dry mass of the sample (g) / volume of cylinder (cm^3).

4.2.3.3 Calculations and Statistical Tests

Nitrite-N was not detected in Brices Field and was very low in North Sidelands. Therefore, combined values of $\text{NO}_3 + \text{NO}_2\text{-N}$ are presented as Total Oxidised Nitrogen (TON). Mineral N and microbial biomass C and N concentrations, measured as mg N kg^{-1} ds, were adjusted according to the dry bulk density of each soil type and expressed as kg N ha^{-1} . The proportion of added N that was recovered as $\text{NH}_4\text{-N}$, TON, and MBN in selected treatments, at 0-10 cm and TON at 10-20 cm was calculated in each biosolids, livestock wastes or fertiliser amendment (See Section 3.7.1.1). The proportion of organic N from each amendment that was mineralised during the experiment was also calculated (See Section 3.7.1.2). The statistical tests used are described in Section 3.7.1.3.

4.3 Results and Discussion

4.3.1 Ammonium-N and TON Dynamics, 0-10 cm Depth

Figures 4.3-4.13 show the changes in $\text{NH}_4\text{-N}$ and TON concentration in amended soil in comparison to unamended control soils at 0-10 cm depth. General patterns in $\text{NH}_4\text{-N}$ and TON concentrations in the amended soils are described and discussed in this section, N recoveries are discussed in Section 4.3.4.

The nitrate mobility control, NaNO_3 amended soil, demonstrated a gradual decline from initial concentration between days 20 and 90, indicating that a proportion of mineral N moved below the surface layer (Figure 4.3).

In both soil types, there was an initial increase in the $\text{NH}_4\text{-N}$ concentration in soil upon application of NH_4Cl , DRAW, LMAD, DMAD, TDMAD, LC, COW and PIG in comparison to unamended control soil and an increase in TON concentration in NaNO_3 amended soil, whereas FYM had no effect on the initial mineral N status of the soils. Table 3.10 (Chapter 3) gives the total and mineral N contents of the biosolids cakes and solid livestock wastes. In the majority of the materials a proportion of total N was

present as mineral N, in the case of the liquid biosolids and livestock slurries this was a high percentage. It was mainly present as $\text{NH}_4\text{-N}$, so an increase in $\text{NH}_4\text{-N}$ was expected. The mineral N concentration of FYM was low, 5.1 % total N, and there was no increase in $\text{NH}_4\text{-N}$ concentration following application to soil (Figure 4.7). However, despite the low mineral N contents of DRAW and TDMAD, 3.17 and 1.5 % respectively, there were increases in $\text{NH}_4\text{-N}$ on addition to soil, indicating rapidly mineralisable organic N (Figures 4.8 and 4.12). In most cases, the initial increase of $\text{NH}_4\text{-N}$ in the biosolids-amended soil was smaller at Brices (silty clay) than for North Sidelands (sandy silt loam), following sludge and livestock wastes application.

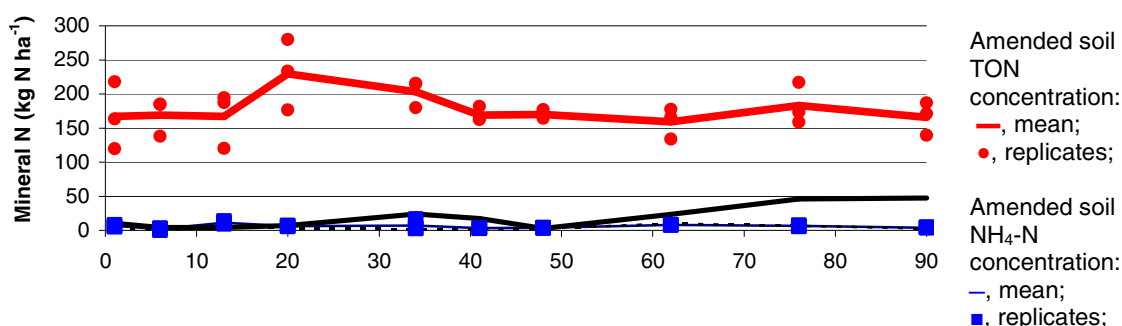
Different nitrification rates at the two field sites were demonstrated by the NH_4Cl treatment plots. Between days 0-6 in the nitrification control, NH_4Cl amended soil, there was a decrease in $\text{NH}_4\text{-N}$ concentration at North Sidelands, and a corresponding increase in TON (Figure 4.4). By day 34, the TON concentration measured in NH_4Cl control plots had attained values comparable with the initial mineral N concentration. Conversely, at Brices Field, $\text{NH}_4\text{-N}$ concentrations increased from day 0-6 and remained greater than $\text{NO}_3\text{-N}$ until day 20. There was an approximate 50 % reduction in $\text{NH}_4\text{-N}$ concentration at Brices Field, between days 0-34, whereas at North Sidelands the majority of added $\text{NH}_4\text{-N}$ had been transformed to TON during this period. This indicated a more rapid nitrification rate at North Sidelands (silty clay). The increase in TON concentration between days 0 and 34 was equivalent to a mean nitrification rate of $4.44 \text{ kg N ha}^{-1} \text{ day}^{-1}$ at North Sidelands, more than double the rate of $2.02 \text{ kg N ha}^{-1} \text{ day}^{-1}$ at Brices. After this initial period of rapid nitrification at North Sidelands, $\text{NH}_4\text{-N}$ concentrations remained at approximately unamended control values until day 90. In Brices, the process was slower and the $\text{NH}_4\text{-N}$ concentration in the NH_4Cl -amended soil remained greater than the unamended control until day 90. Between days 34 and 90 of the trial, TON at North Sidelands remained high, but there was a net decrease, which may be a result of movement of $\text{NO}_3\text{-N}$ below the surface layer. There was a net increase in TON at Brices Field between days 34 and 90 and concentrations reached values comparable with North Sidelands by the end of the field experiment.

Figures 4.5-4.13 show that, in biosolids and livestock wastes amendments where an initial increase in $\text{NH}_4\text{-N}$ was observed, there was also an overall decline in $\text{NH}_4\text{-N}$ following initial application. As observed in the nitrification controls, the decrease was more rapid in North Sidelands, where the mean $\text{NH}_4\text{-N}$ concentration had reached approximately control values by day 6 in cow slurry-, pig slurry-, DRAW-, LMAD-, DMAD-, DMAD+grass-, and LC-amended soil; day 13 in TDMAD-amended soil and

day 20 in DMAD+thiram-amended soil, with a corresponding increase in TON. However, between days 0-6, an accumulation of $\text{NH}_4\text{-N}$ was observed at Brices Field; for example, $\text{NH}_4\text{-N}$ concentrations in DMAD-amended soil decreased by approximately 75 % after 6 days in North Sidelands, whereas in Brices there was a mean increase of approximately 50 %, compared to the initial concentration. At Brices field, $\text{NH}_4\text{-N}$ concentrations reached approximately control concentrations by day 13 in cow slurry-, pig slurry- and LC-amended soil; day 20 in DRAW-, LMAD- and TDMAD-amended soil and remained above control concentrations until day 34 in DMAD- and DMAD+grass-amended soil. In soil amended with DMAD+thiram $\text{NH}_4\text{-N}$ concentrations did not reach unamended control values until day 90.

The formation of TON in biosolids- and livestock wastes-amended soil at each of the field sites corresponded to the changes in $\text{NH}_4\text{-N}$ concentrations, and the results were consistent with a slower rate of nitrification observed in Brices soil. Total Oxidised Nitrogen concentrations in amended soil from Brices Field were very low or undetectable until day 13, whereas in North Sidelands TON concentrations had rapidly increased in the treatment plots in comparison to the controls by day 6.

(a) North Sidelands: Nitrate Mobility Control



(b) Brices Field: Nitrate Mobility Control

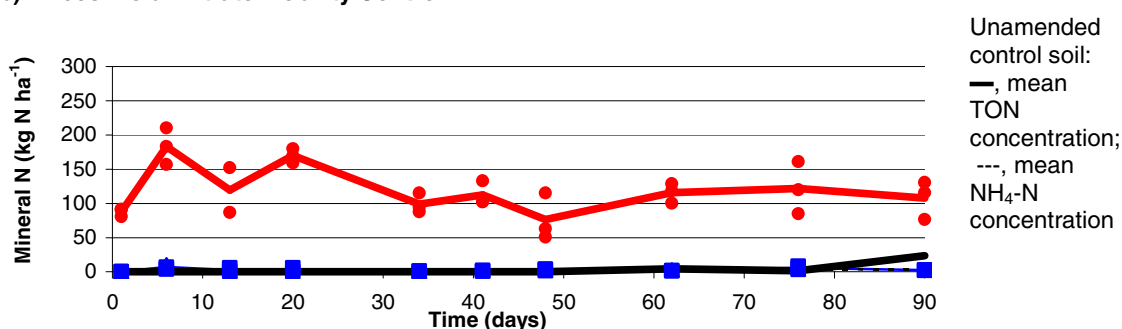
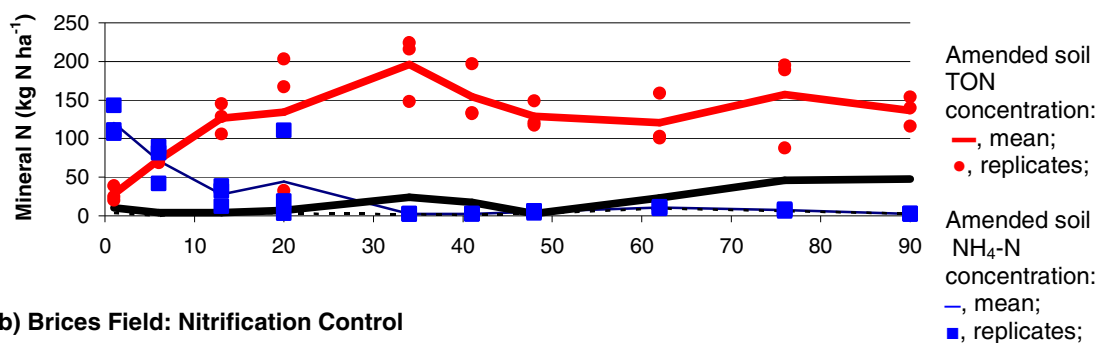


Figure 4.3 Ammonium-N and TON concentrations in relation to time in two soil types (a) North Sidelands (silty clay) and (b) Brices Field (sandy silt loam) in the unamended control, and soil amended with NaNO_3 , incorporated to a depth of 10 cm at a rate equivalent to 200 kg N ha^{-1} .

(a) North Sidelands: Nitrification Control



(b) Brices Field: Nitrification Control

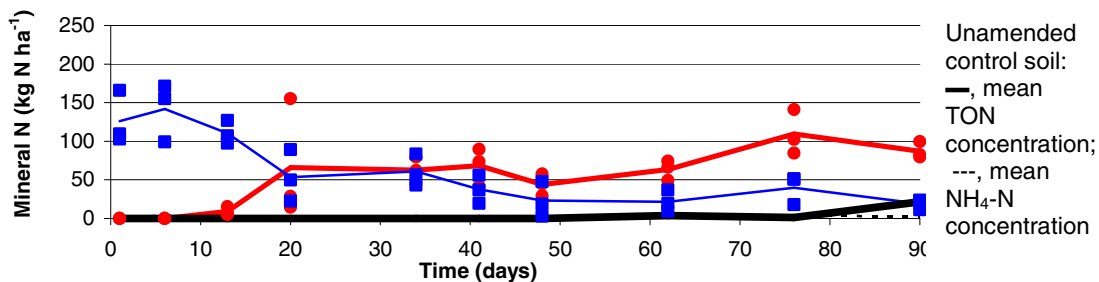
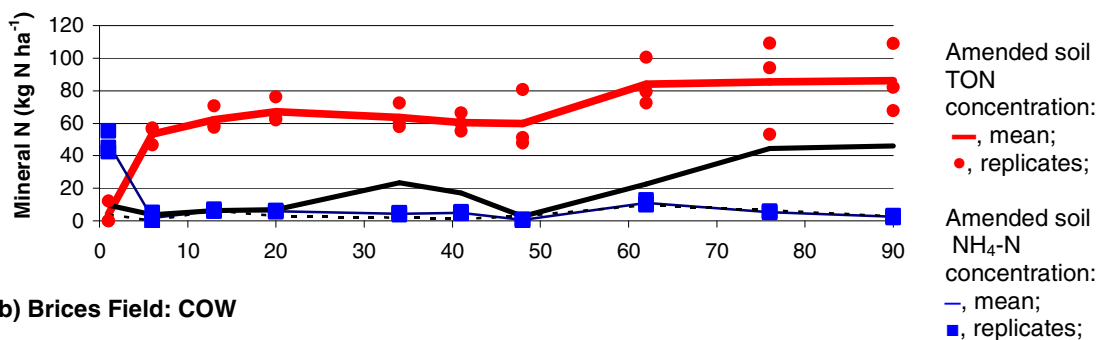


Figure 4.4 Ammonium-N and TON concentrations in relation to time in two soil types (a) North Sidelands (silty clay) and (b) Brices Field (sandy silt loam) in the unamended controls, and soil amended with NH₄Cl incorporated to a depth of 10 cm at a rate equivalent to 200 kg N ha⁻¹.

(a) North Sidelands: COW



(b) Brices Field: COW

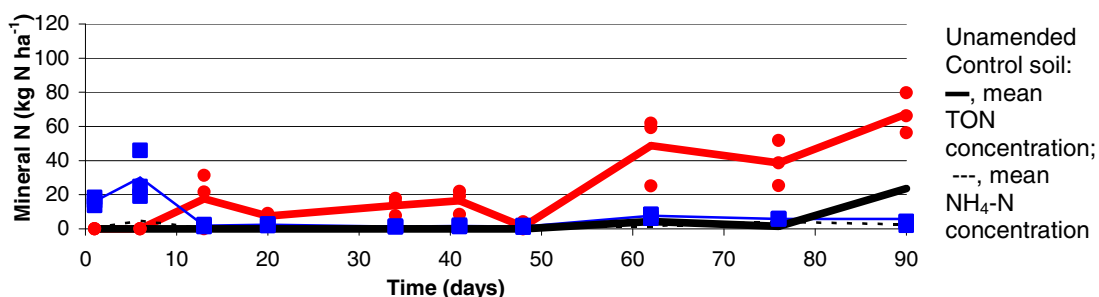
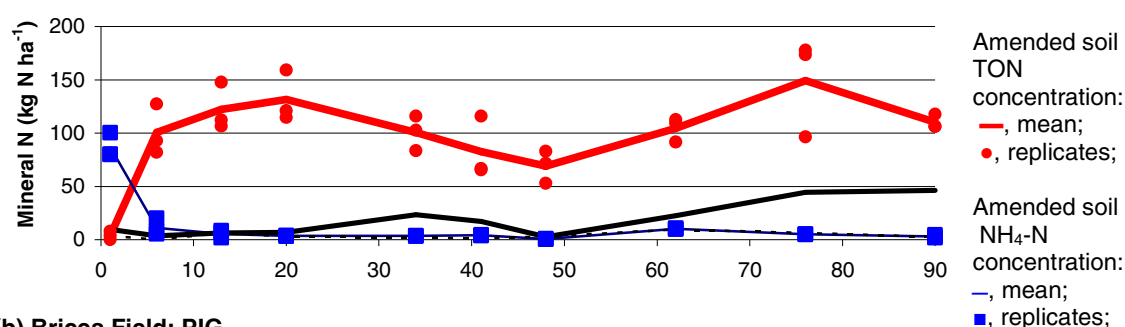


Figure 4.5 Ammonium-N and TON concentrations in relation to time in two soil types (a) North Sideands (silty clay) and (b) Brices Field (sandy silt loam) in the unamended control, and soil amended with cow slurry (COW), incorporated to a depth of 10 cm at a rate equivalent to 100 m³ ha⁻¹.

(a) North Sidelands: PIG



(b) Brices Field: PIG

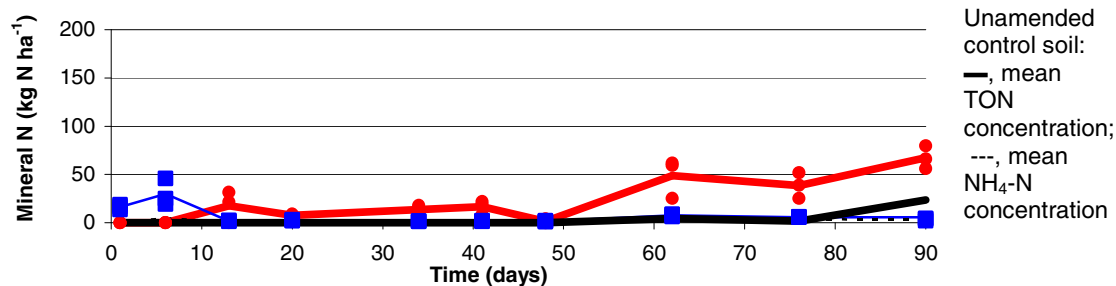
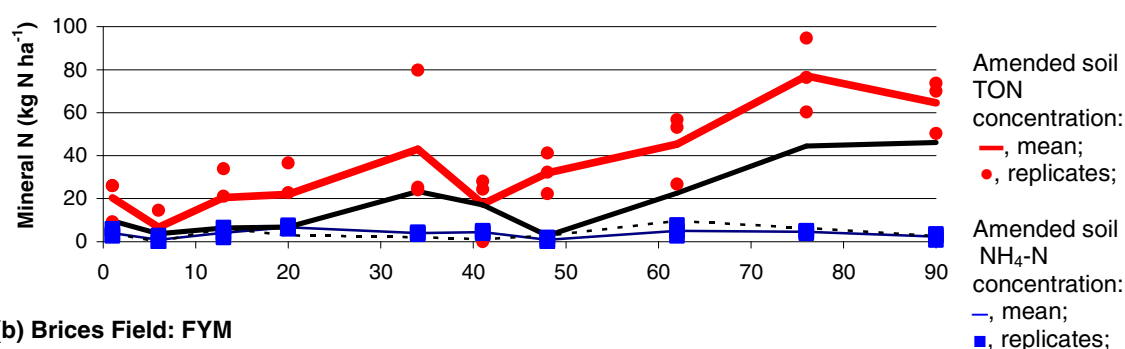


Figure 4.6 Ammonium-N and TON concentrations in relation to time in two soil types (a) North Sidelands (silty clay) and (b) Brices Field (sandy silt loam) in the unamended control, and soil amended with Pig slurry (PIG), incorporated to a depth of 10 cm at a rate equivalent to 100 m³ ha⁻¹.

(a) North Sidelands: FYM



(b) Brices Field: FYM

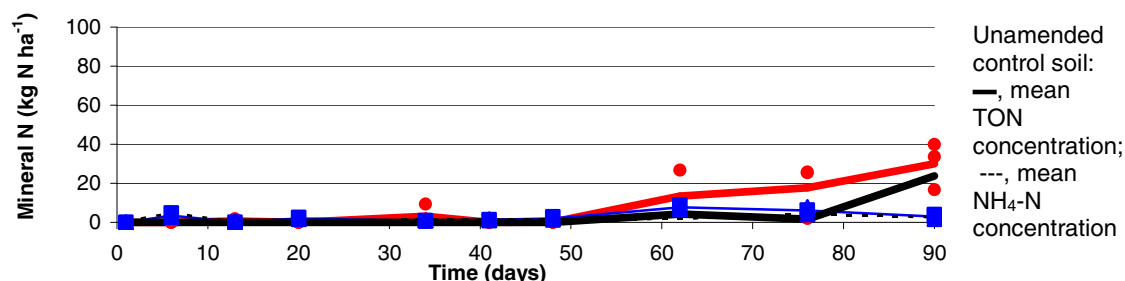
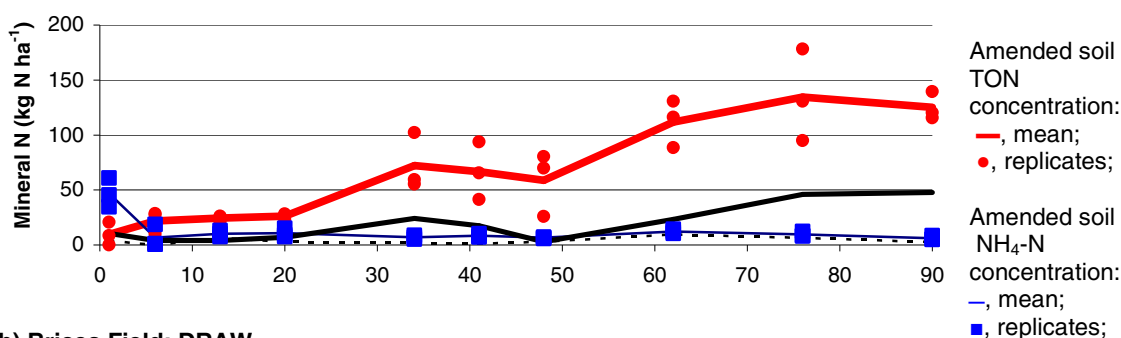


Figure 4.7 Ammonium-N and TON concentrations in relation to time in two soil types (a) North Sidelands (silty clay) and (b) Brices Field (sandy silt loam) in the unamended control, and soil amended with FYM incorporated to a depth of 10 cm at a rate equivalent to 10 t DS ha⁻¹.

(a) North Sidelands: DRAW



(b) Brices Field: DRAW

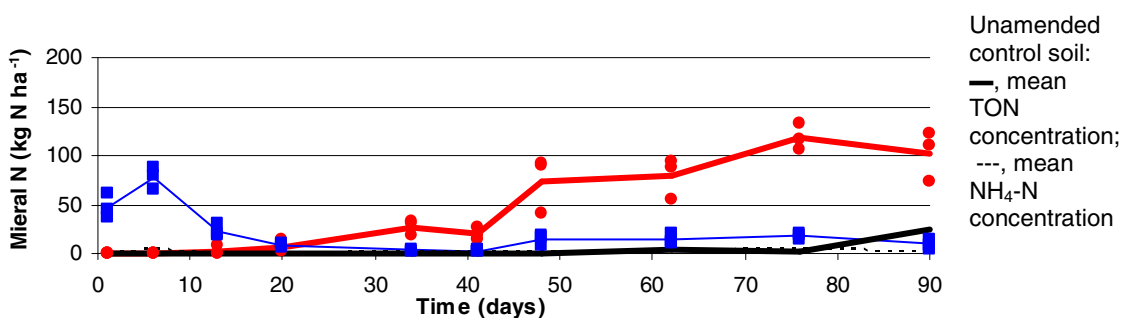
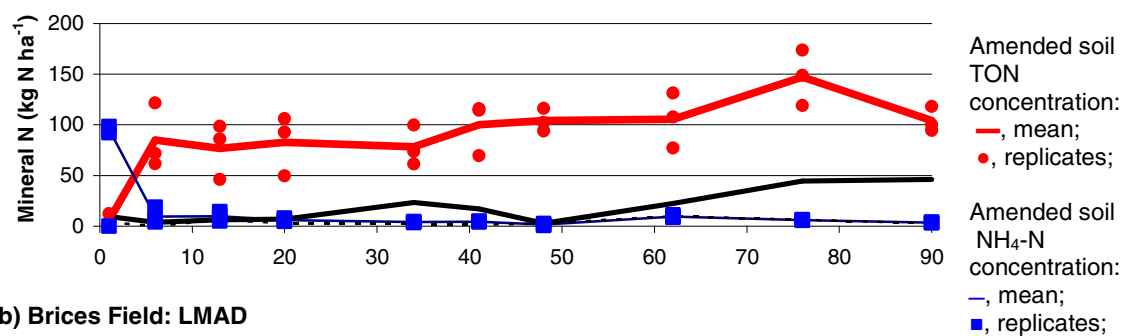


Figure 4.8 Ammonium-N and TON concentrations in relation to time in two soil types (a) North Sidelands (silty clay) and (b) Brices Field (sandy silt loam) in the unamended control, and soil amended with DRAW, incorporated to a depth of 10 cm at a rate equivalent to 10 t DS ha⁻¹.

(a) North Sidelands: LMAD



(b) Brices Field: LMAD

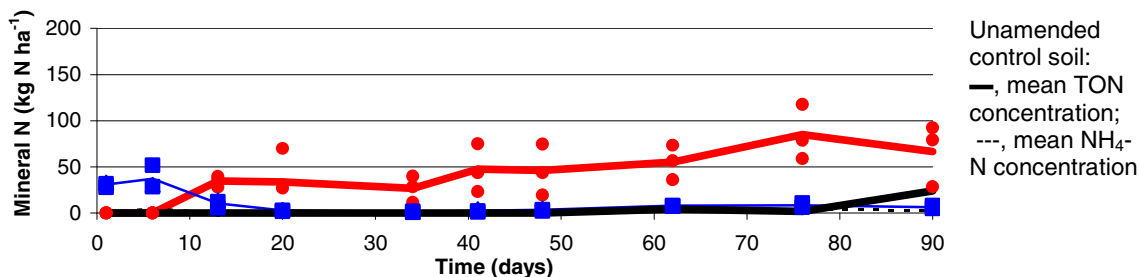
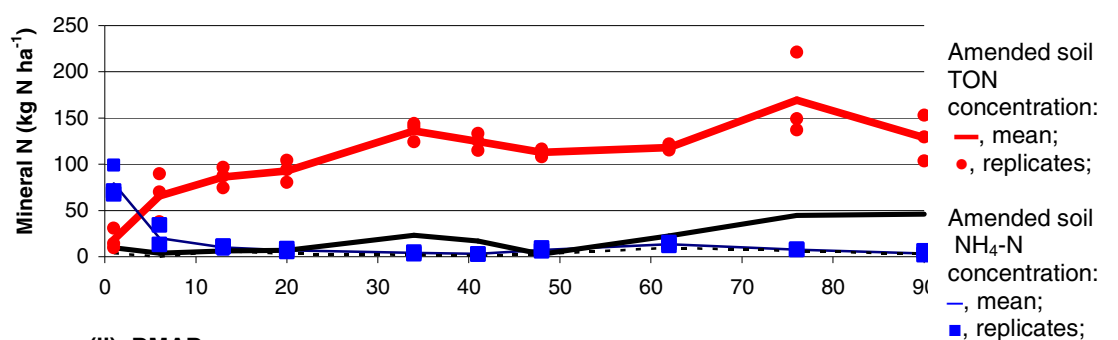


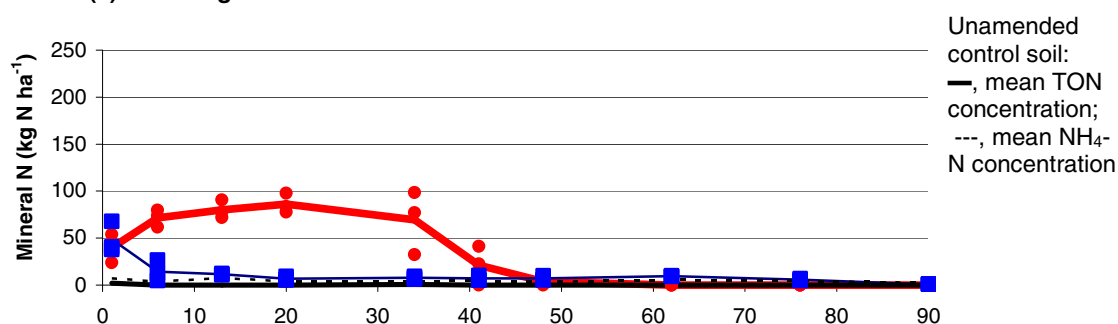
Figure 4.9 Ammonium-N and TON concentrations in relation to time at North Sidelands (silty clay) and Brices Field (sandy silt loam) in unamended control, and soil amended with LMAD, incorporated to a depth of 10cm at a rate equivalent to 10 t DS ha⁻¹.

(a) North Sidelands

(i) DMAD

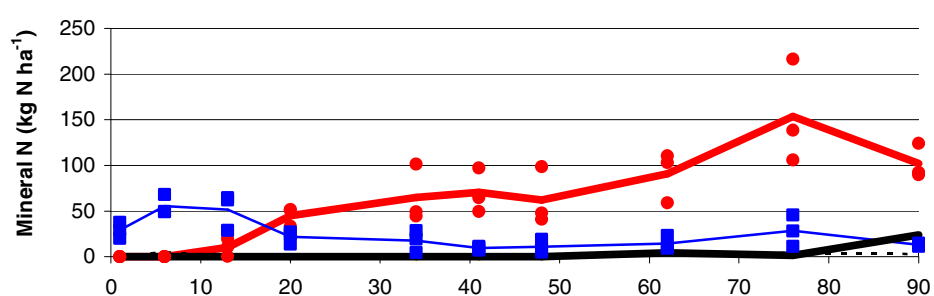


(ii) DMAD+grass



(b) Brices Field

(i) DMAD



(ii) Brices Field: DMAD+grass

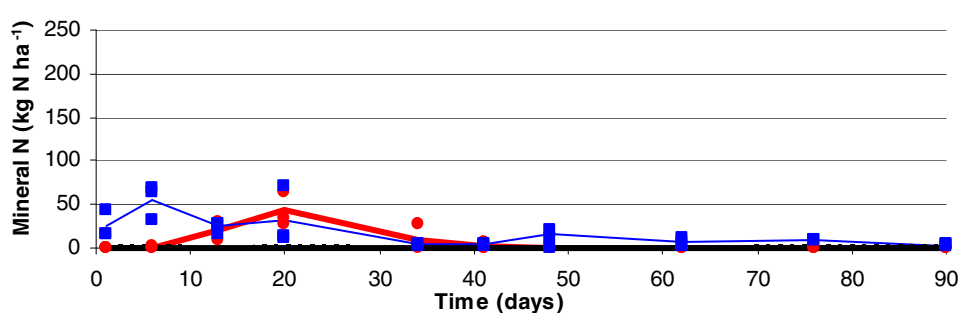
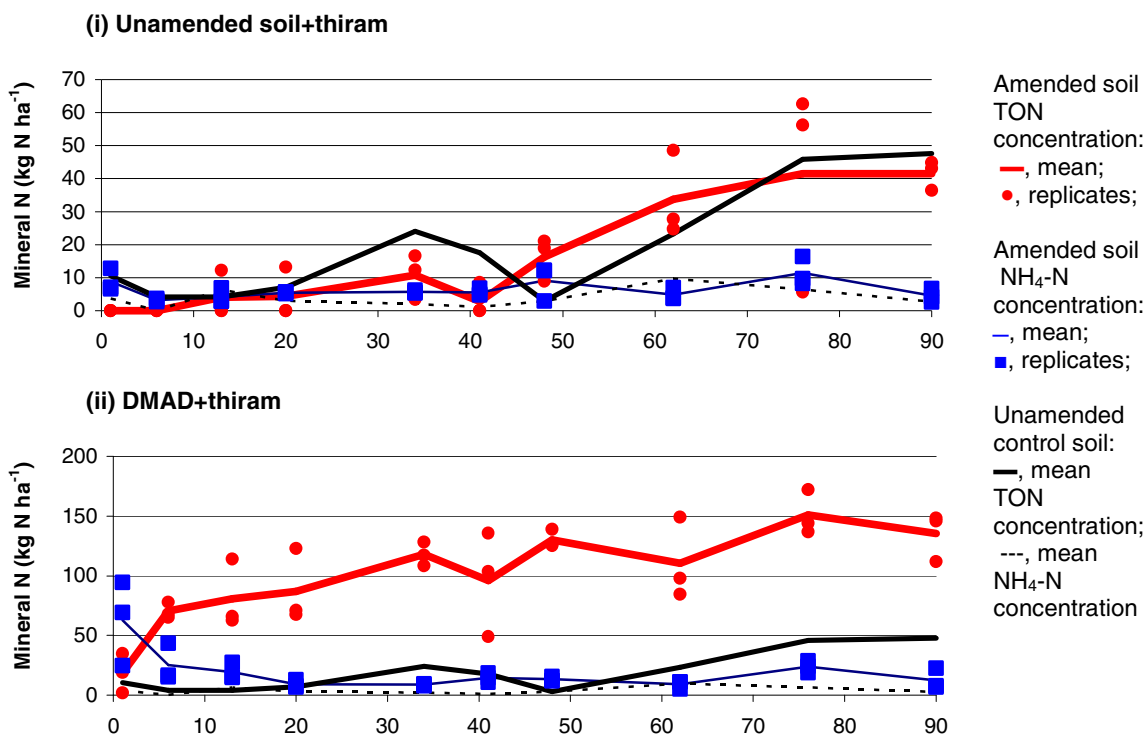


Figure 4.10 Ammonium-N and TON concentrations in relation to time in two soil types (a) North Sidelands (silty clay) and (b) Brices Field (sandy silt loam) in (i) unamended control, and soil amended with DMAD, incorporated to a depth of 10 cm at a rate equivalent to 10 t DS ha⁻¹ and (ii) unamended control+grass and soil amended with DMAD+grass.

(a) North Sidelands



(b) Brices Field

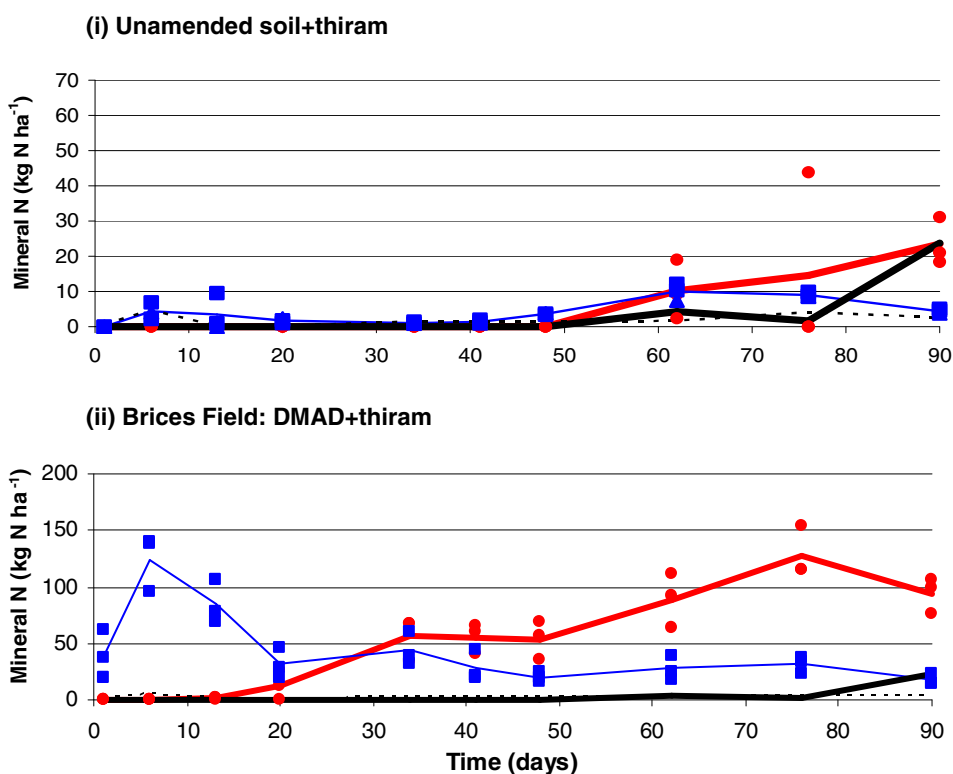
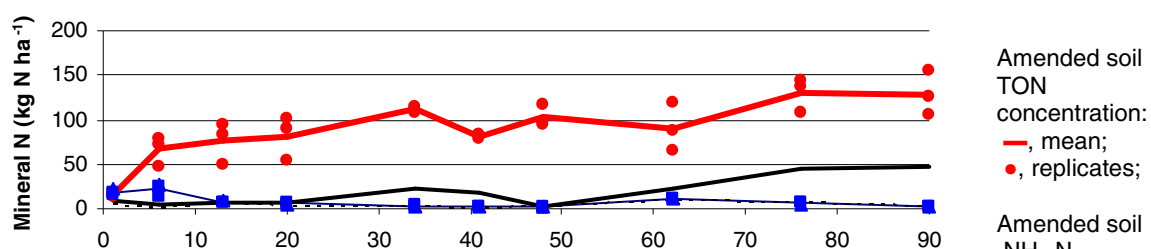


Figure 4.11 Ammonium-N and TON concentrations in relation to time in two soil types (a) North Sidelands (silty clay) and (b) Brices Field (sandy silt loam) in (i) unamended control, and unamended soil treated with thiram (protozoa inhibitor); (ii) unamended control, and DMAD amended soil (10 t DS ha⁻¹; 10 cm incorporation depth) treated with thiram.

(a) North Sidelands: TDMAD



(b) Brices Field: TDMAD

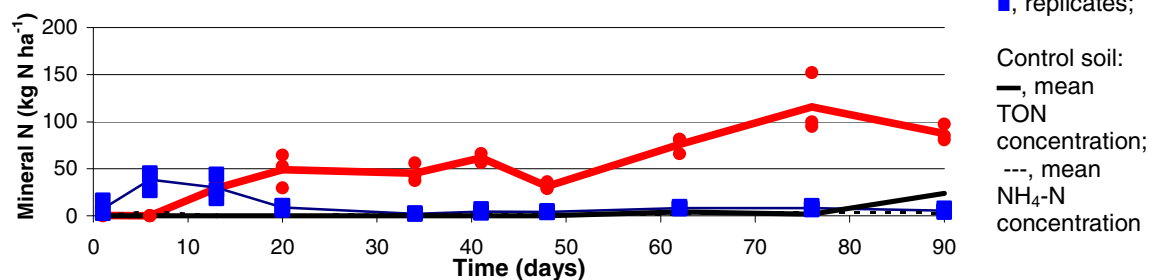
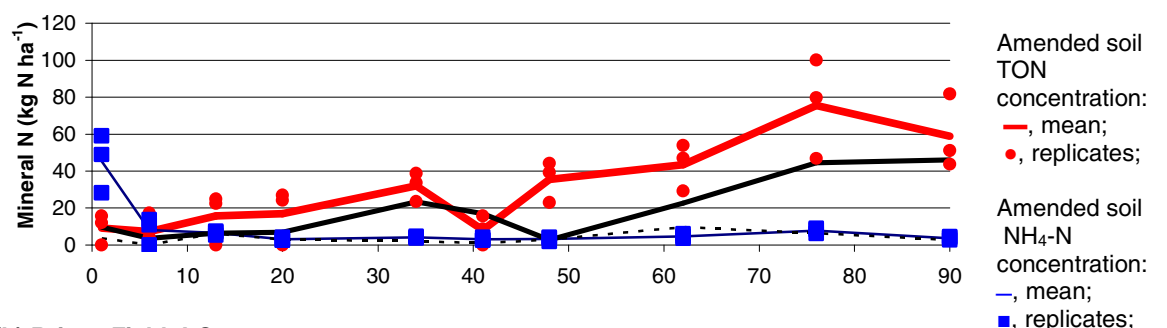


Figure 4.12 NH₄-N and TON concentrations in relation to time in two soil types (a) North Sidelands (silty clay) and (b) Brices Field (sandy silt loam) in unamended control, and soil amended with TDMAD incorporated to a depth of 10 cm at a rate equivalent to 10 t DS ha⁻¹.

(a) North Sidelands: LC



(b) Brices Field: LC

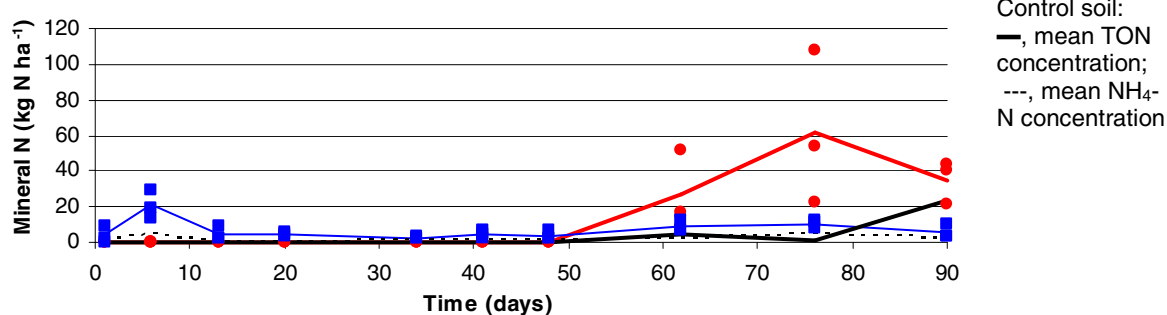


Figure 4.13 NH₄-N and TON concentrations in relation to time in two soil types (a) North Sidelands (silty clay) and (b) Brices Field (sandy silt loam) in unamended control, and soil amended with LC, incorporated to a depth of 10 cm at a rate equivalent to 10 t DS ha⁻¹.

This demonstrated that, in fertile soil, biosolids provide a rapidly available source of TON. For example, by day 34, TON in the DMAD-amended soil at North Sidelands had increased to three times the concentration at Brices in relation to the unamended control plots. Thus, soil at North Sidelands had an appreciably higher capacity for nitrification commensurate with the better fertility status of the soil indicated by the larger organic matter content of this soil (Table 3.1). This is consistent with previous findings (Breedon *et al.*, 2003) and is indicative of the intrinsic fertility of soils performing a central role in N transformations following sludge amendment.

Liquid biosolids and livestock slurries would be expected to have the greatest TON production due to their high mineral N content. Figures 4.5 and 4.6 show that in soil amended with cow slurry and pig slurry, there was a rapid increase in TON in North Sidelands but a slow increase in Brices. The final net accumulation by day 76 was approximately 40-65 kg N ha⁻¹ for cow slurry and approximately 40-100 kg N ha⁻¹ in pig slurry treatments, after which point mineral N concentrations decreased, indicating movement of NO₃-N below the amended surface layer. Although greater than TON accumulation for the solid livestock waste, FYM, these concentrations were less than DMAD, which was 126-176 kg N ha⁻¹. The relatively low net TON production from the liquid livestock wastes may be due to losses by movement of NO₃-N below 0-10 cm, this is discussed in Section 4.3.2. The slow TON accumulation in Brices Field for the livestock wastes may be related to their stability. As they had not been biologically stabilised, these livestock wastes may have a higher proportion of labile C, stimulating microbial activity on addition to the soil, and resulting in microbial immobilisation of N, as has previously been suggested for livestock wastes (Chae and Tabatai, 1986; Sims, 1986; Plaza *et al.* 2005). This may occur to a greater extent in the lower fertility soil, where there is lower organic matter availability. This effect is also observed in FYM-amended soil, with TON concentrations in the low fertility soil not increasing above the unamended control until day 62, and low TON production in both soil types. This organic waste type had the greatest C:N ratio of 14:1 (Table 4.10). Microbial biomass N (MBN) was not measured for livestock wastes-amended soil, but was measured in biosolids-amended soil and is discussed in Section 4.3.3.

Total oxidised nitrogen production in the liquid digested biosolids treatment, LMAD (Figure 4.9) was greater than for cow slurry in North Sidelands and equivalent to pig slurry, despite having a lower mineral N content (Table 3.11); it was greater than for both livestock wastes in Brices Field. This supports the assumption that there may be greater microbial immobilisation following amendment with the unstabilised livestock

wastes. For the biosolids cakes, TON production was greatest for DMAD, followed by DRAW, then TDMAD, and LC on a DS addition basis for both soil types. This is not as expected by their mineral N concentration, which was greatest in DMAD, followed by LC, then DRAW and TDMAD (Table 3.11).

Initial TON accumulation from DRAW was low in both soil types, with concentrations not increasing above the unamended control until day 34 in the low fertility soil (Figure 4.8). This indicated that there may have been microbial immobilisation of N resulting from the greater C:N ratio of the unstabilised, or partially stabilised, waste, this is discussed further in Section 4.3.3. However, the high final production of TON indicated that, as may be expected for unstabilised sludge cake, DRAW contained a proportion of rapidly mineralisable organic N (Parker and Sommers, 1993).

There was rapid production of mineral N in TDMAD amended soil, and accumulation of $\text{NH}_4\text{-N}$ in Brices Field by day 6, which may be related to differences in the balance between mineralisation and nitrification at the two sites. Following this, there was rapid accumulation of TON in both soil types resulting in end production that was lower but comparable to that from the conventionally treated biosolids type, DMAD. Previous data have also shown TON production from DMAD and TDMAD to be high and in a similar range (Breedon *et al.*, 2003, Morris *et al.*, 2003, Smith *et al.* 2002b) despite the loss of mineral N during thermal dehydration treatment processes.

The lowest production of TON in biosolids amended soil was from LC. In Brices, concentrations in LC plots remained undetectable between days 0-48, and reached a maximum of approximately 60 kg N ha^{-1} during the remainder of the trial. Lime cake had the lowest total N content of the three biosolids, approximately 40% of the total N contained in DMAD (Table 3.10). Lime cake also had a much smaller mineral N fraction than DMAD, due to losses of free NH_3 during the treatment process (Evans, 2001) and because the biosolids were not biologically digested. This may have partially contributed to the low initial productivity of TON. Franco-Hernández *et al.* (2003) reported a reduction of C mineralisation in lime treated biosolids in comparison to anaerobically digested biosolids in a neutral soil; however, they did not observe this inhibitory effect in an acidic soil type. They suggested that an increase in soil alkalinity was responsible; however, in their laboratory incubation, biosolids were applied at a rate 5 times greater than in this experiment. Therefore, it is unlikely that reduced mineralisation due to increased soil pH value was a significant factor in this investigation. Franco-Hernández *et al.* (2003) reported that the inhibitory effect of

biosolids alkalinity did not affect N mineralisation of the biosolids, indeed, greater N mineralisation was observed in the neutral soil in comparison to anaerobically digested biosolids. However, the lime treated biosolids used by Franco-Hernández *et al.* (2003) had been anaerobically digested; whereas, in this experiment, raw, unstabilised, sewage sludge was amended with lime, which may explain the differences in N mineralisation.

Mineral N concentrations at 0-10 cm depth in unamended soil and DMAD-amended soil sown with perennial ryegrass, to investigate the effects of a crop establishment on mineralisation processes, are shown in Figure 4.10 (a)(ii) and (b)(ii). In comparison to DMAD-amended soil with no crop cover Figure 4.10 (a)(i) and (b)(i), $\text{NH}_4\text{-N}$ concentration declined more rapidly, and TON concentration, increased until day 20 in both soil types, after which point it decreased, due to crop uptake.

The experiment included unamended soil and DMAD-amended soil treated with thiram to inhibit the soil protozoa population (Figure 4.11). This was primarily for the purpose of the soil ecological investigations that were conducted in conjunction with the soil nutrient study, however, differences were observed in mineral N dynamics. There was a greater accumulation of $\text{NH}_4\text{-N}$ and delay in nitrification in DMAD-amended soil at Brices Field, with the addition of thiram. Protozoa grazing stimulates bacterial activity (Ekelund and Rønn, 1994; Bjørnlund *et al.*, 2000; Bonkowski, 2004); several studies have shown that grazing by protozoa stimulates bacterial processes such as N mineralisation (Ekelund and Rønn, 1994) and nitrification (Griffiths, 1989). These findings suggested that inhibition of the soil protozoa population caused some disruption to the bacteria-mediated processes of mineralisation and nitrification in this investigation. However, thiram may not have been effective in isolating and disrupting the protozoa population and may have disrupted the whole microbial community. Therefore the observations at Brices Field may result from lower resilience in the less fertile soil to thiram addition.

4.3.2 TON Dynamics in Biosolids and Livestock Amended Wastes, 10-20 cm Depth

In addition to samples taken from the amended surface layer at 0-10 cm depth, soil samples were taken from 10-20 cm to examine the mobility of $\text{NO}_3\text{-N}$ from the biosolids and livestock wastes below the incorporation depth. The TON concentration at 10-20 cm depth from days 0-90 for both soil types for biosolids amended soil in comparison to unamended and mineral N controls is shown in Figure 4.14, and for livestock wastes it

is shown in Figure 4.15. As would be expected, in both soil types, the greatest losses of TON below the top 10 cm were observed in the mineral N control soils. The concentration of mineral N in NaNO₃-amended soil in the 10-20 cm profile increased to a maximum of approximately 60 kg N ha⁻¹ greater than the unamended control on day 20 in Brices Field and day 40 in North Sidelands, and then decreased to approximately 35 kg N ha⁻¹ above the unamended control at North Sidelands, and 30 kg N ha⁻¹ above the unamended control at Brices. This indicated that 25 kg N ha⁻¹ at North Sidelands and 30 kg N ha⁻¹ at Brices moved below the top 20 cm. These findings suggest that the sandy silt loam, Brices Field, was more prone to NO₃⁻ movement than the silty clay. This is as would be expected for a soil with a greater sand content and lower organic matter content and hence lower water holding capacity (Addiscott *et al.*, 1991).

The greatest movement of TON below the surface 10 cm in biosolids-amended soils was observed for LMAD, due to its high mineral N content. Maximum TON concentrations at 10-20 cm depth were measured on day 20 in Brices Field, at 40 kg N ha⁻¹ above the unamended control, and day 34 for North Sidelands at approximately 50 kg N ha⁻¹ above the unamended control. After this, TON concentration decreased, indicating possible leaching of N below 0-20 cm. For both soil types, the concentrations of TON at 10-20 cm in unamended control+grass and DMAD+grass treatments were less than unamended control soil. This indicated a reduction in available soil N due to the crop cover. In addition, in LC amended soil, the TON concentration was less than in the unamended control, until day 34 in Brices and day 41 in North Sidelands which indicated that initial microbial immobilisation of mineral N in these treatments reduced movement of TON below the surface layer.

In livestock wastes-amended soil the greatest concentrations at 10-20 cm were observed in soil amended with pig slurry, which is consistent with its high mineral N concentration of approximately 95 % total N. In North Sidelands, TON concentrations in cow slurry-amended soil were also relatively high, reaching a maximum value of 40 kg N ha⁻¹ above the unamended control soil on day 48. However in Brices Field TON in cow slurry-amended soil was below the unamended control, supporting the suggestion that immobilisation of mineral N may have occurred in the less fertile soil type following addition of unstabilised livestock waste. The TON concentration in FYM-amended soil was initially also below the unamended control soil in Brices Field. The MBN component was not measured for livestock wastes but was measured in biosolids-amended soil and is discussed in Section 4.3.3.

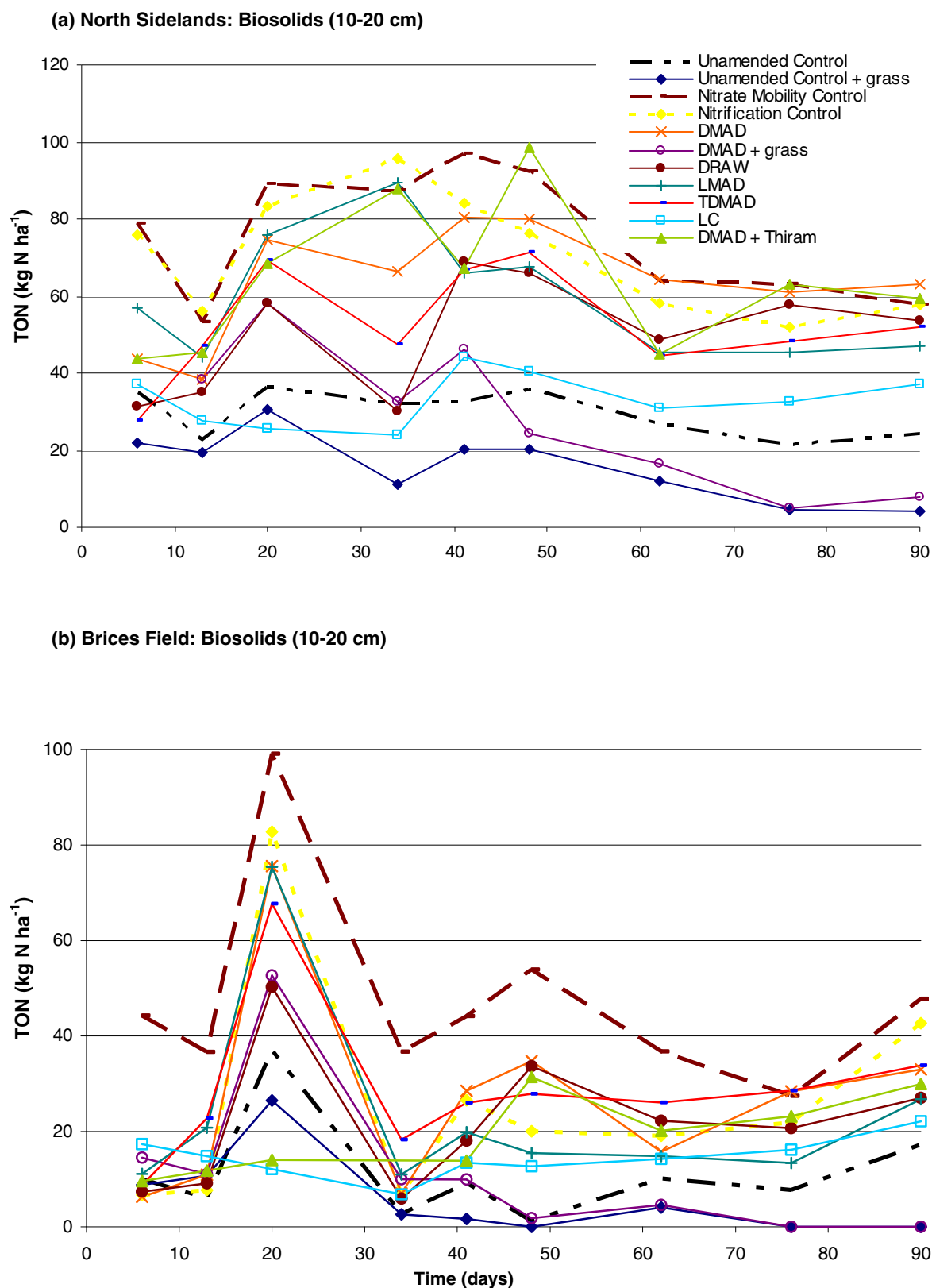
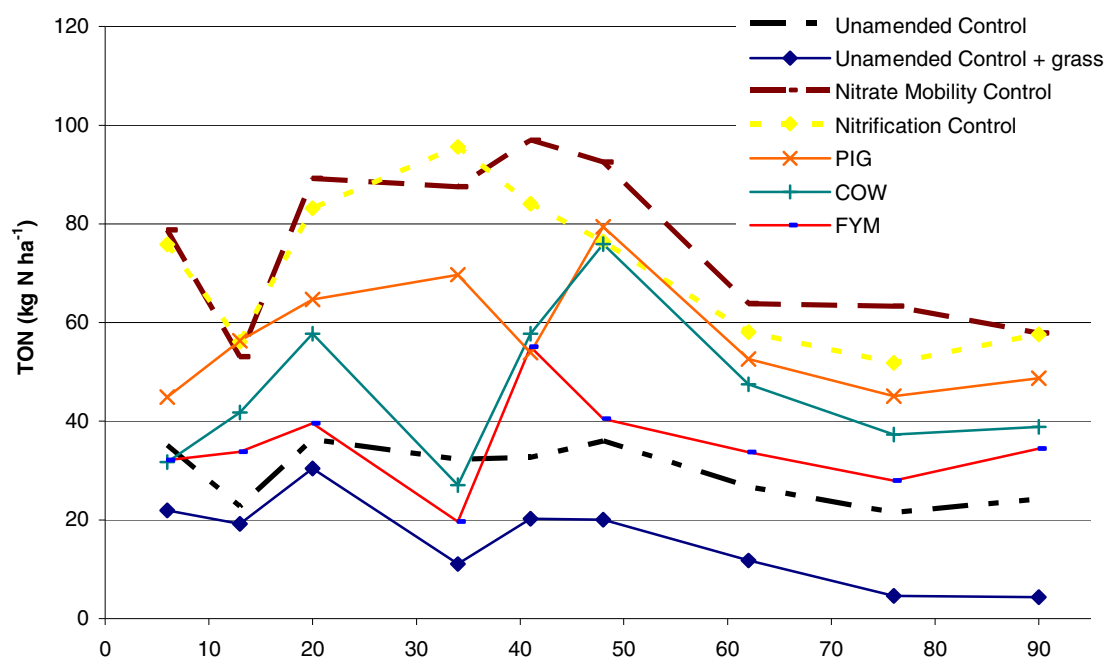


Figure 4.14 Total oxidised N (TON) concentration at 10-20 cm in biosolids amended soil, unamended control soil and mineral N controls in two soil types (a) North Sidelands (silty clay) and (b) Brices Field (sandy silt loam) from days 6-90.

(a) North Sidelands: Livestock wastes (10-20 cm)



(b) Brices Field: Livestock wastes (10-20 cm)

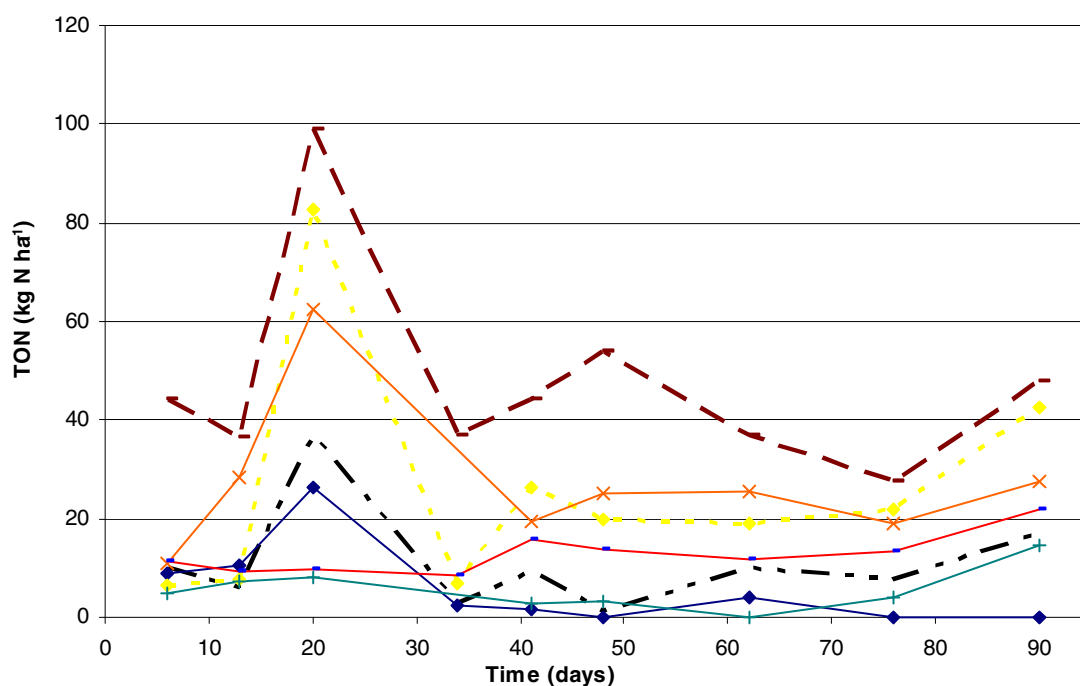


Figure 4.15 Total oxidised N (TON) concentration at 10-20 cm in livestock wastes amended soil, unamended control soil and mineral N controls in two soil types (a) North Sidelands (silty clay) and (b) Brices Field (sandy silt loam) from days 6-90.

4.3.3 Microbial Biomass C and N

Microbial biomass C (MBC) concentrations for DRAW-, DMAD-, TDMAD- and LC-amended soil in comparison to unamended control soils at North Sidelands and Brices Field for days 0 to 90 (Perez-Viana, pers. comm.) are given in Figure 4.16, and MBN concentrations in the two soil types are presented in Figure 4.17. Microbial biomass C and N contents in unamended control soil were approximately 6 times greater at North Sidelands, generally in the range of 300-1200 kg C ha⁻¹ and 100-140 kg N ha⁻¹ in comparison to Brices Field, which was in the range of 80-150 kg C ha⁻¹ and 15-40 kg N kg ha⁻¹ (Figures 5.16-5.17). These results are within normal ranges (Banerjee *et al.*, 1997; Franco-Hernández *et al.*, 2003; Jedidi *et al.*, 2004; Fernandes *et al.*, 2005), and are consistent with the larger microbial biomass expected in the silty clay soil at North Sidelands due to the higher organic matter content of the soil at this site, compared to Brices Field.

Microbial biomass C concentrations increased above unamended control values following addition of DRAW, DMAD, TDMAD and LC in both soil types (Figure 4.16). This is consistent with previous findings (Banerjee *et al.*, 1997; Franco-Hernández *et al.*, 2003; Jedidi *et al.*, 2004; Fernandes *et al.*, 2005) where increases in MBC in comparison to unamended soil were observed following sludge application. Calbrix *et al.* (2007) found no significant increase in MBC following soil amendment with sewage sludge, however, it was applied at a comparatively low rate of 3.7 t DS ha⁻¹. In a laboratory incubation investigation, Franco-Hernández *et al.* (2003) also found that MBC increased when lime-treated, irradiated and pasteurised biosolids were added to an acidic sandy clay loam soil from under pasture but not to a neutral sandy clay loam from under forest. The background MBC concentrations in these soils were in a similar range to North Sidelands, between 400-1500 kg C ha⁻¹.

Thermal drying and lime treatment processes eliminate pathogens, therefore the observed increase in MBC on addition of TDMAD and LC, resulted primarily from stimulation of growth of the soil microbial population through the introduction of organic matter to the soil. Amendment of soil with DRAW and DMAD on the other hand, provided an organic substrate for the indigenous soil microbial population, but also introduced microbial biomass from the sludges. The microbial biomass from DRAW will be from faecal matter and biological sludges from secondary wastewater treatment processes, whereas DMAD will contain biomass derived from the anaerobic digestion

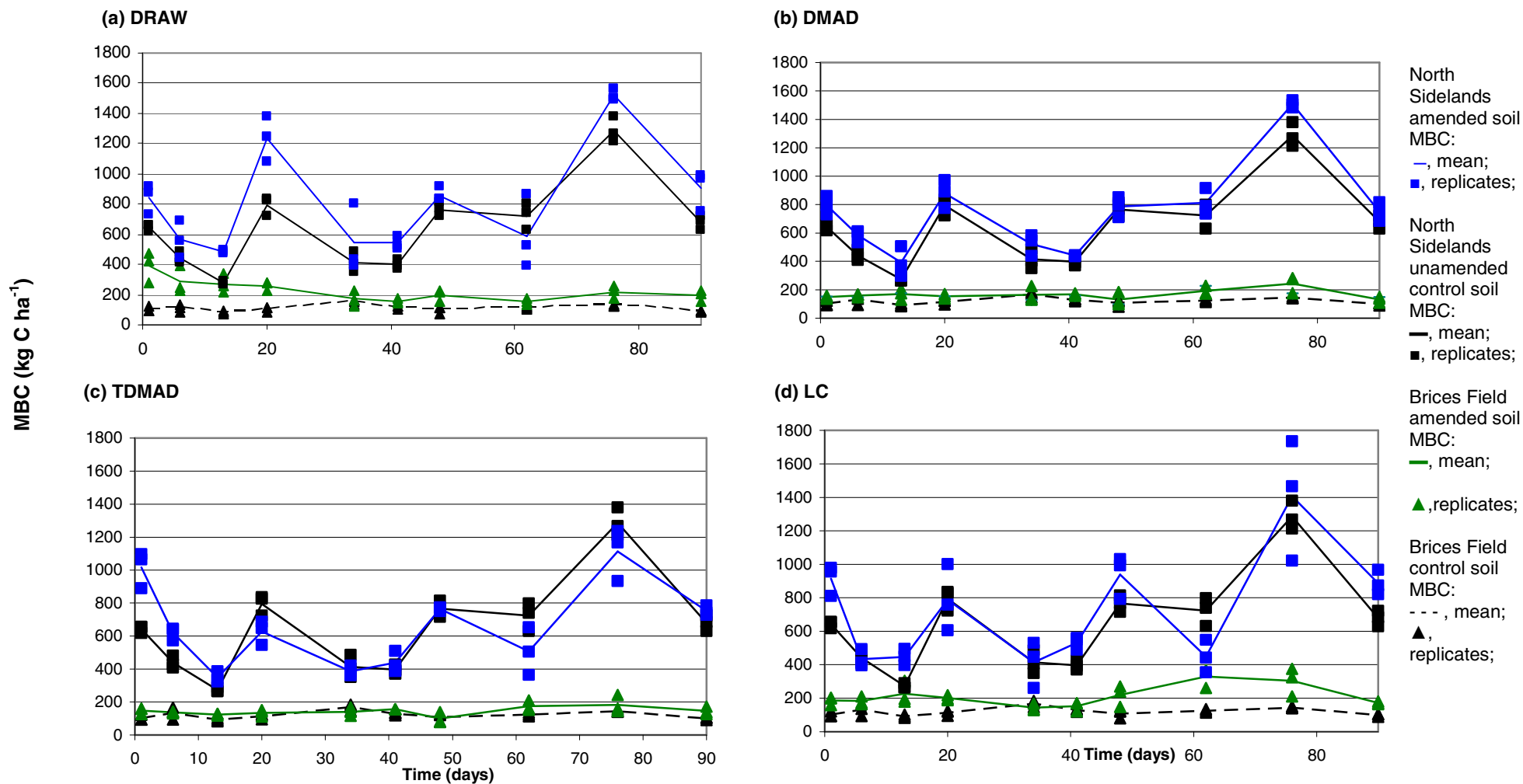
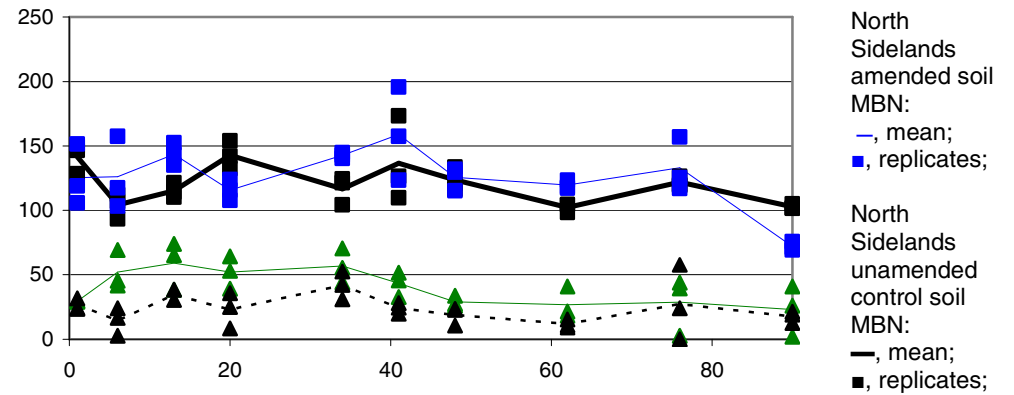


Figure 4.16 Microbial biomass C (MBC) concentrations in relation to time at Brices Field (sandy silt loam) and North Sidelands (silty clay) in the unamended controls, and soil amended with: (a) DRAW; (b) DMAD; (c) TDMAD and (d) LC, at a rate equivalent to 10 t DS ha⁻¹, and incorporation depth of 10 cm.

(b) DMAD



(d) LC

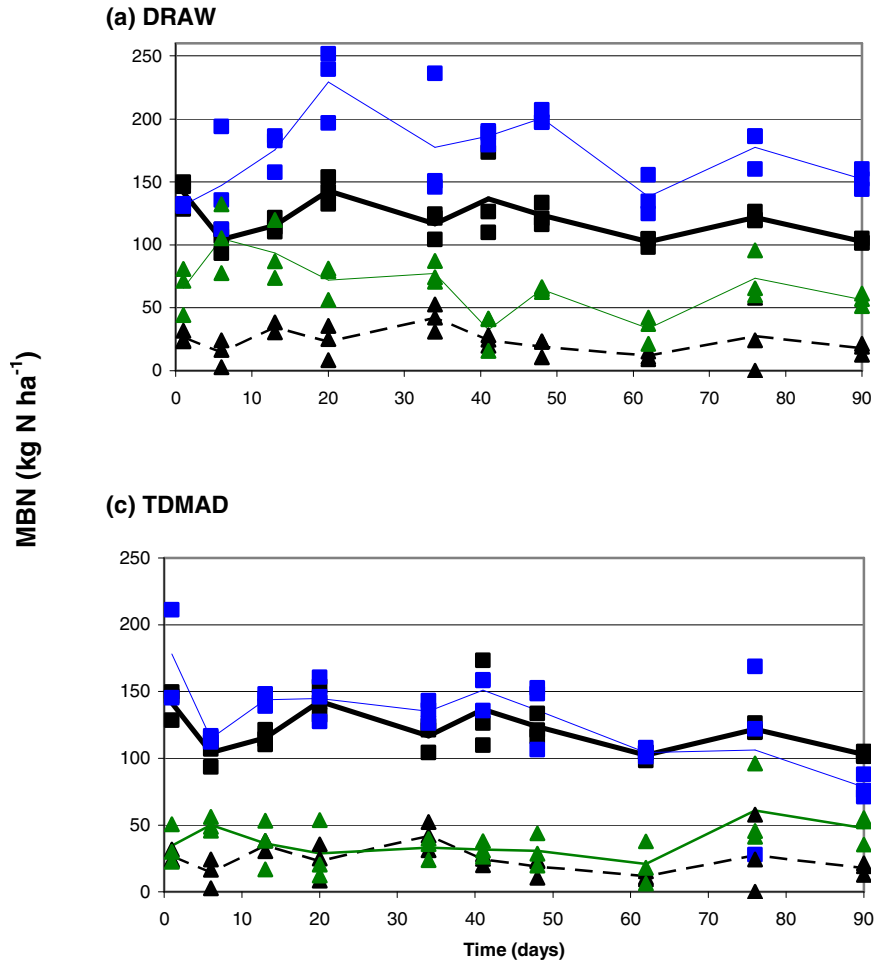
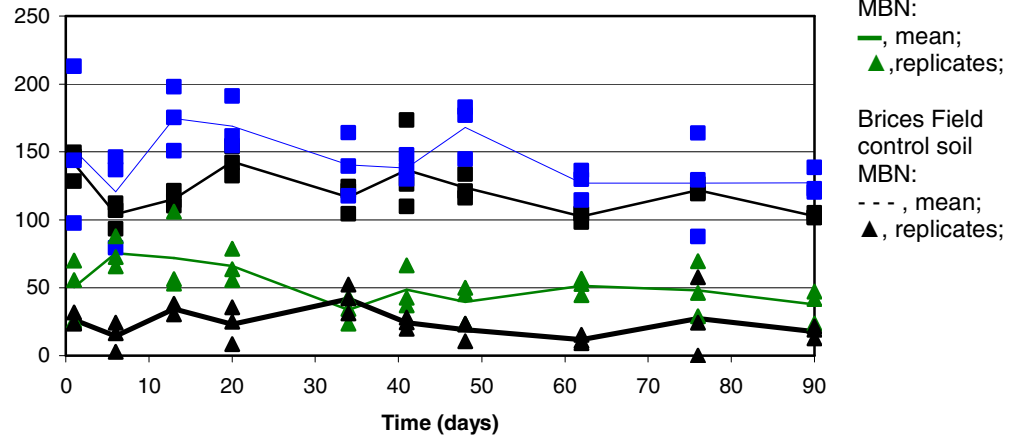


Figure 4.17 Microbial biomass N (MBN) concentrations in relation to time at Brices Field (sandy silt loam) and North Sidelands (silty clay) in the unamended controls, and soil amended with: (a) DRAW; (b) DMAD; (c) TDMAD and (d) Lime Cake, at a rate equivalent to 10 t DS ha⁻¹, and incorporation depth of 10 cm.

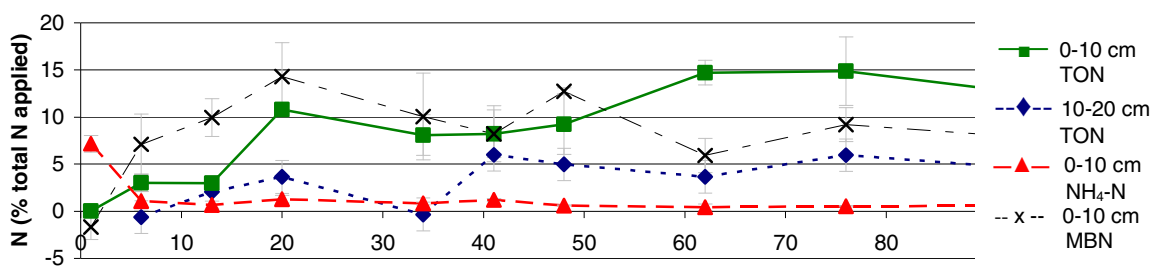
process. In DRAW amended soil the initial increase in MBC, above unamended control concentration, was approximately 200 kg C ha^{-1} in North Sidelands and 300 kg C ha^{-1} in Brices Field. In a field investigation into the effects of raw sludge applied to a clayey soil (Fernandes *et al.*, 2005), at similar rates of application ($8.1\text{-}12 \text{ t DS ha}^{-1}$), observed similar increases of approximately $300\text{-}450 \text{ mg C kg}^{-1}$ greater than unamended soil were observed in amended soil. The concentration decreased to approximately control values in North Sidelands by day 48. In Brices Field, MBC had decreased to 160 kg C ha^{-1} above the unamended control by day 20, but remained larger than control values for the duration of the trial.

In Brices Field, the increase following addition of LC was less than half that observed for DRAW, approximately 80 kg C ha^{-1} , and was also smaller at North Sidelands, equivalent 160 kg C ha^{-1} . This is as expected from the organic matter content of the materials, which was lower in LC, as a result of lime addition, compared to DRAW, 56 % DS and 73 % DS respectively. Following application of DMAD and TDMAD the increase in MBC was also not as great as in DRAW amended soil, as expected due to the stability and lower biomass in digested products compared to unstabilised. Microbial biomass C increased by 45 kg C ha^{-1} in Brices Field after addition of both TDMAD and DMAD; in North Sidelands the increase was approximately 150 kg C ha^{-1} after DMAD addition and 370 kg C ha^{-1} after TDMAD addition, more than twice the increase. In DMAD amended soil, concentrations of MBC remained above those in the unamended control soil for the duration of the experiment, in both soil types. At North Sidelands MBC returned to values approximately equivalent to the unamended control in TDMAD amended soil.

In a field investigation, following land application of sewage sludge and sewage sludge co-composted with cotton waste at varying degrees of stabilisation, Sanchez-Monedero *et al.* (2004) also found that the increase in MBC was dependent on the stability of the organic waste source; the size and activity of the microbial biomass following addition of untreated sewage sludge was twice that of fully matured compost.

The percentage of added N in DRAW, DMAD, TDMAD and LC recovered in the different N fractions measured, including N recovered in the microbial biomass, is shown in Figures 4.18-4.21. Nitrogen recoveries are discussed further in Section 4.3.4. There was no strong evidence for immobilisation of added N immediately following DRAW and biosolids amendment at either field site, although MBN concentrations were greater than in unamended soil in DRAW and LC amended soil at Brices by 40

(a) North Sidelands: DRAW



(b) Brices Field: DRAW

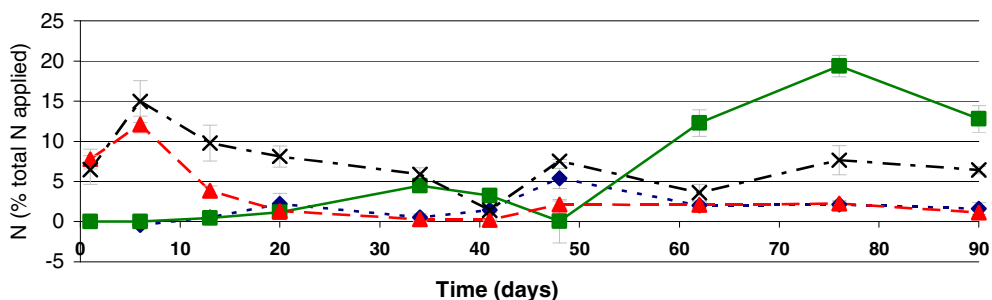
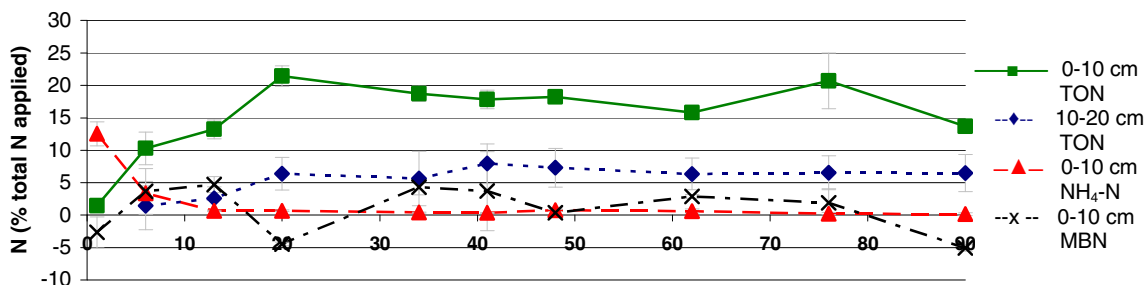


Figure 4.18 Nitrogen dynamics in DRAW-amended soil as % total N applied in (a) North Sidelands: silty clay and (b) Brices Field: sandy silt loam. Error bars are standard errors of the means.

(a) North Sidelands: DMAD



(b) Brices Field: DMAD

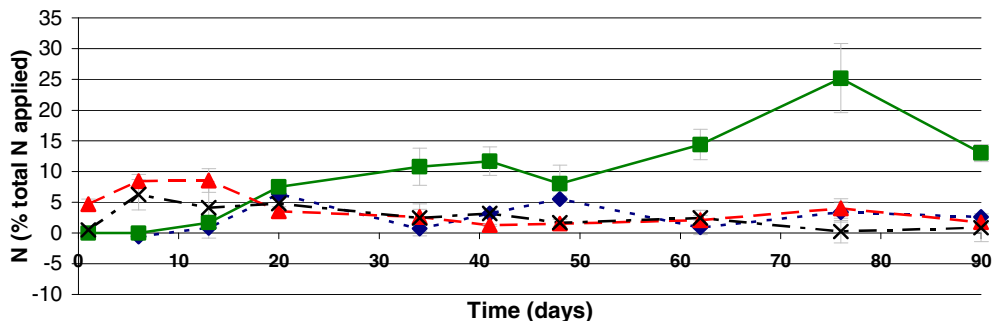
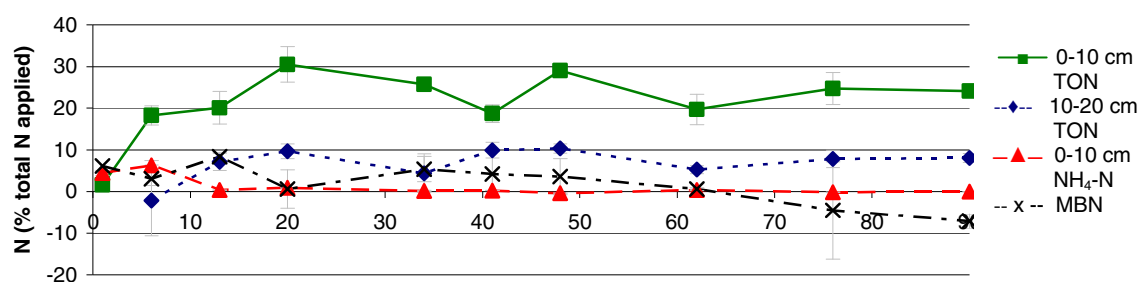


Figure 4.19 Nitrogen dynamics in DMAD-amended soil as % total N applied in (a) North Sidelands: silty clay and (b) Brices Field: sandy silt loam. Error bars are standard errors of the means.

(a) North Sidelands: TDMAD



(b) Brices Field: TDMAD

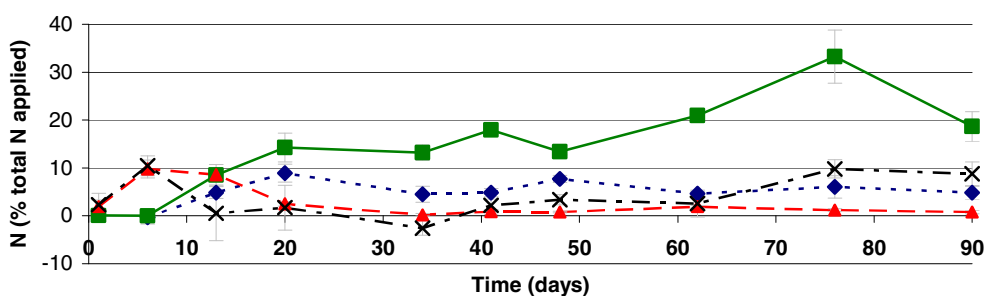
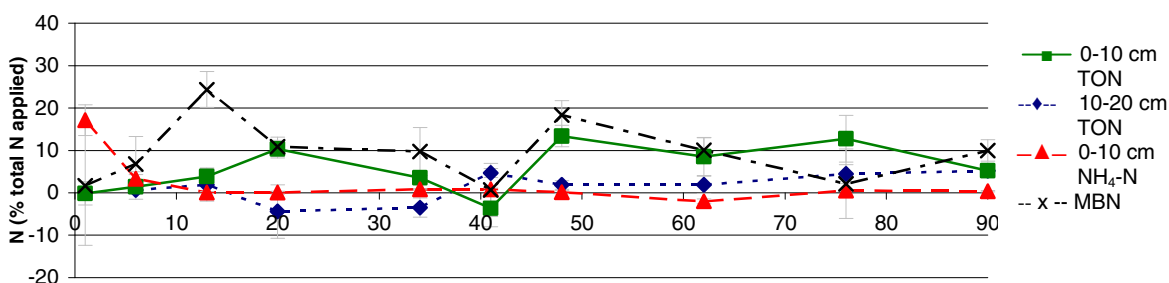


Figure 4.20 Nitrogen dynamics in TDMAD-amended soil as % total N applied in (a) North Sidelands: silty clay and (b) Brices Field: sandy silt loam. Error bars are standard errors of the means.

(a) North Sidelands: LC



(b) Brices Field: LC

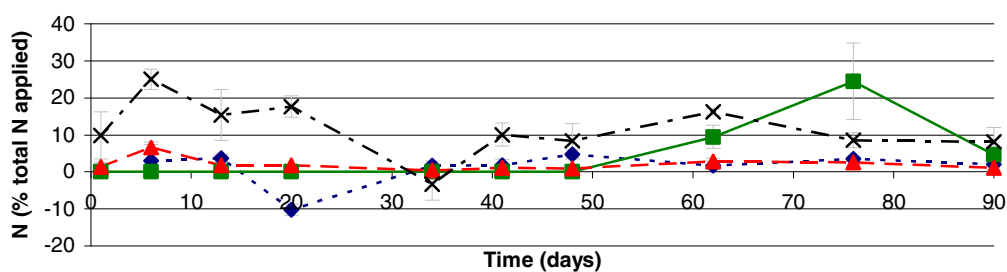


Figure 4.21 Nitrogen dynamics in LC-amended soil as % total N applied in (a) North Sidelands: silty clay and (b) Brices Field: sandy silt loam. Error bars are standard errors of the means.

and 25 kg N ha⁻¹ respectively on day 0 (Figure 4.17), equivalent to 6.5 % and 10 % of the added N (Figures 4.18 and 4.21). Between days 0-6 at Brices Field, there was an increase in MBN (Figure 4.17) in all four treatments relative to the unamended control. The increase in concentration was greatest in DRAW, equivalent to approximately 90 kg N ha⁻¹; followed by LC, approximately 60 kg N ha⁻¹; approximately 40 kg N ha⁻¹ for DMAD and 20 kg N ha⁻¹ for TDMAD amended soil. These observations were as expected; LC had a greater C:N ratio than the other biosolids (Table 3.10), and DRAW, as an unstabilised source of OM contained a high proportion of rapidly degradable C, stimulating microbial activity, as observed in MBC dynamics (Figure 4.16), which explained the observed N immobilisation in these treatments. In Brices Field, with the exception of TDMAD, MBN concentrations were significantly larger than unamended controls for the duration of the experiment. In TDMAD treatments, the MBN concentration in soil was generally greater than the unamended control but decreased below the control on day 34.

In North Sidelands, the greatest increase in MBN relative to the unamended control was in DRAW-amended soil, followed by LC. With the exception of day 0 in North Sidelands, MBN was greater than unamended control values in both these treatments for the duration of the experiment. From day 6–90 MBN was in the range of 35–90 kg N ha⁻¹ greater than control in DRAW amended soil, and 0–60 kg N ha⁻¹ greater than the control in LC-amended soil. This was equivalent to 0-15 % of the added total N recovered as MBN in both treatments (Figure 4.18 and 4.21), which was within the same range of immobilised N observed at Brices Field. The results in this soil type are consistent with those in Brices Field, which suggests that there was most significant microbial immobilisation of N following addition of LC and DRAW, which had the greatest content of unstabilised organic C. At North Sidelands, MBN concentration in TDMAD-amended soil was greater than or equal to the unamended control until day 62, when it decreased below the control. In DMAD-amended soil at North Sidelands, MBN fluctuated at concentrations approximately equal to unamended control soil. This was contrary to findings in Brices soil for this treatment, where MBN was generally greater than in unamended control soil.

Jedidi *et al.* (2004) reported significantly greater MBN in soil amended with raw sewage sludge, compared to other amendments including straw, compost and farmyard manure, and the effects remained after 8 weeks of incubation. This observation was attributed to the biological instability of the applied sewage sludge. A field investigation into the effects of anaerobic digested sludge applied to a clay loam soil (Banerjee *et al.*,

1997) showed that MBN was either not affected, or increased, following sludge application at rates of 50-100 t DS ha⁻¹. Fernandes *et al.* (2005) found that similar rates of application, 8-16 t DS ha⁻¹, of raw sludge increased MBN content, by 42-61 mg kg⁻¹ ds, in a clayey soil, which is consistent with the findings in this investigation for both soil types.

In an incubation study with organic amendments of varying stability, Jedidi *et al.* (2004) reported microbial biomass C:N ratios were between 6.6-31.5. The high degree of variation between different microbial responses was associated with the type of organic amendment. The microbial biomass C:N ratios were calculated for the unamended control and each of the different biosolids treatments; Figure 4.22 shows the microbial biomass C:N ratio in each soil from day 0-90. There was no apparent pattern in C:N ratios according to treatment type in either soil type, however, C:N ratios were slightly greater at North Sidelands, generally between 3.5-6.5, but up to 11.5, in comparison to Brices Field, which had ratios generally between 3-5, but as high as 10.5. In both soil types, there was a general increase in microbial biomass C:N ratio with time in the unamended control and treated soils. Changes in population composition may be related to changes in the soil environmental conditions, since there was an increase in soil temperature and decrease in moisture content during the course of the experiment (Figure 4.1). Fernandes *et al.* (2005), for raw sludge applied at rates between 8-16 t DS ha⁻¹, measured microbial biomass C:N ratios of between 7.5-10.5.

(a) North Sidelands

(b) Brices Field

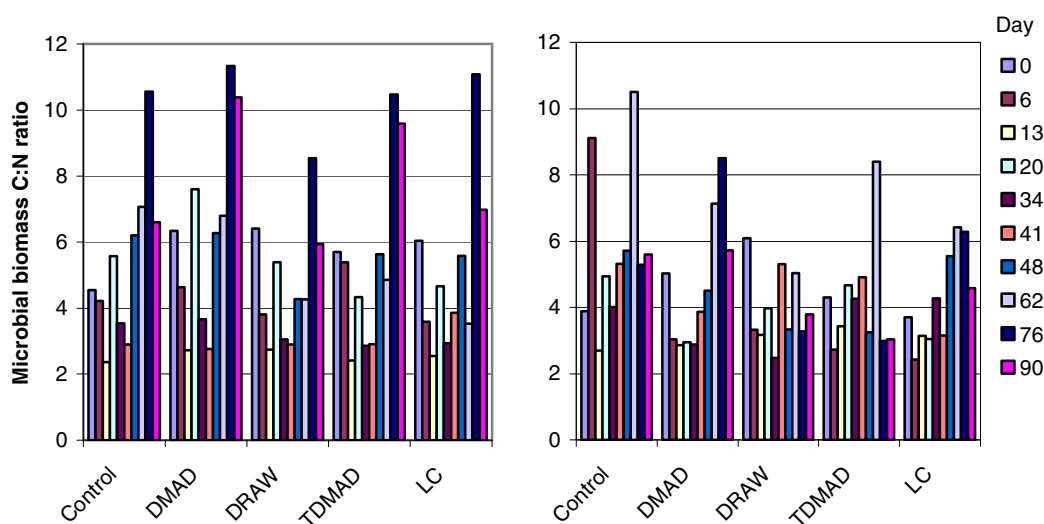


Figure 4.22 Microbial biomass C:N ratio in two soil types (a) North Sidelands (silty clay) and (b) Brices Field (sandy silt loam) in unamended control soil; DMAD; DRAW; TDMAD and LC from days 0-90.

The variation in C:N ratio was not as great as observed here, however, there was not as much variation in the times of sample collection, as collection times were March and October, so there may not have been as much environmental variability. Fernandes *et al.* (2005) found no significant effects of rate or time of application on C:N ratio.

This evidence suggests microbial immobilisation of N is highly dependent on waste stability in both soil types, with greater immobilisation of N, and increases of MBC, occurring with less stable sources of organic matter such as DRAW and LC. There was no microbial N immobilisation in DMAD amended soil in the high fertility soil, but immobilisation of up to 60 mg kg⁻¹ ds in the low fertility soil occurred after 2 weeks. In both soil types there was microbial immobilisation of small concentrations of N in TDMAD amended soil for up to 14 days following application, but after this time concentrations of MBN decreased in both soils although they remained above control concentrations in the lower fertility soil. This indicated that there may be some degree of retention of N in the microbial biomass in this soil type for a relatively short duration. These results support the hypothesis that there are differences in microbial biomass N immobilisation between the two soil types of differing fertility status, although there is no strong evidence for initial differences in immobilisation of N.

4.3.4 Nitrogen Recoveries and Mineralisable Fraction in Biosolids and Livestock Wastes Amended Soils

The initial recoveries of mineral N in biosolids, livestock wastes and mineral N amended soils are shown in Table 4.1. These values were obtained by subtracting mineral N concentrations in unamended control soil from those measured with sludge, livestock wastes and fertiliser amendment. The proportion of added N that was recovered as MBN in DRAW-, DMAD-, TDMAD- and LC-amended soil was also calculated. The recoveries of N as MBN, NH₄-N in the 0-10 cm profile and TON in the 0-10 cm and 10-20 cm profiles, as a percentage of total N added in biosolids treatments (unamended control values subtracted) is shown in Figure 4.18-4.21. Initial recoveries of mineral N were not consistent with expected concentrations of mineral N added to the soil, which were calculated taking into account the mineral N content of the biosolids and rate of application of the sludge or NH₄Cl (Table 4.1). At both sites, in the NH₄Cl plots, the initial recovery of mineral N was approximately 65 % of the expected value. There was also a deficit in the recovery of mineral N in the NaNO₃ treatments. For this inorganic N source 73 % was recovered at North Sidelands and 44 % at Brices Field. This deficit may have been a result of immediate loss of

Table 4.1 Nitrogen additions and initial mineral N recoveries at North Sidelands and Brices Field (0-10 cm).

Treatment	N additions				Day 0 recoveries at North Sidelands (0-10 cm) [†]				Day 0 recoveries at Brices Field (0-10 cm) [†]			
	Total N (kg N ha ⁻¹)	TON (kg N ha ⁻¹)	NH ₄ -N (kg N ha ⁻¹)	Mineral N (% total N)	TON (kg N ha ⁻¹)	NH ₄ -N (kg N ha ⁻¹)	Mineral N (kg N ha ⁻¹)	Mineral N (% total N)	TON (kg N ha ⁻¹)	NH ₄ -N (kg N ha ⁻¹)	Mineral N (kg N ha ⁻¹)	Mineral N (% total N)
NaNO ₃	200	200	0	100	142.3	2.82	145.2	72.6	87.6	-0.69	86.9	43.5
NH ₄ Cl	200	0	200	100	15.9	116.9	132.8	66.4	<0.01	127.8	127.8	63.9
DMAD	603	<0.01	92.4	15.3	8.68	75.7	84.4	14.0	<0.01	28.3	28.3	4.69
DMAD+ grass	603	<0.01	92.4	15.3	37.6	41.7	79.3	13.2	<0.01	21.9	21.9	3.63
DRAW	605	0.03	19.2	3.17	0.10	43.3	43.4	7.18	<0.01	47.1	47.1	7.79
LMAD	199	<0.01	116.6	58.6	-3.43	91.6	88.2	44.3	<0.01	30.0	30.0	15.1
TDMAD	343	0.07	5.17	1.53	5.44	15.3	20.8	6.05	0.31	6.64	6.95	2.03
PIG	177	<0.01	167.1	94.4	-5.70	83.2	77.5	43.8	<0.01	15.5	15.5	8.76
COW	202	<0.01	99.9	49.5	-5.55	44.1	38.5	19.1	<0.01	16.8	16.8	8.33
FYM	284	10.6	3.84	5.10	10.8	0.42	11.2	3.95	<0.01	-0.69	-0.69	-0.24
LC	244	0.43	21.7	8.89	-0.36	41.7	41.4	17.0	<0.01	3.25	3.25	1.33
DMAD+ thiram	603	<0.01	92.4	15.3	8.97	59.1	68.1	11.3	<0.01	39.0	39.0	6.46

[†]Unamended control mineral N concentrations subtracted

mineral N below the surface layer or was perhaps caused by rapid immobilisation by the microbial population, or a combination of these factors. It was assumed that no mineral N was lost as TON below the surface layer at this early stage, especially in Brices Field, where the nitrification rate was slow (Figure 4.4). This is confirmed by the TON concentration in the 10-20 cm profile in the NH_4Cl control on day 6, which is equivalent to unamended control values (Figure 4.14 and 4.15). In each of the mineral N control plots at North Sidelands and the NaNO_3 control at Brices Field on day 6, approximately 40 kg N ha^{-1} was measured in the 10-20 cm profile, equivalent to 20 % of the N additions. It is therefore possible that $\text{NO}_3\text{-N}$ mobility accounted for a fraction of the deficit at Brices Field and in the NaNO_3 amended soil at Brices. It is possible, especially in the low fertility soil at Brices, that the microbial biomass rapidly locked up the mineral N in this N deficient soil, accounting for a proportion of the 35 % unrecovered N in NH_4Cl treatment plots in this soil type. Increases in MBN have previously been observed following addition of NH_4Cl (Zaman *et al.*, 2002).

Loss of ammoniacal N ($\text{NH}_3\text{-N}$) by volatilisation is also a possibility in the short period between spreading the sludge or NH_4Cl and incorporation into the soil. Significant losses of $\text{NH}_3\text{-N}$ by volatilisation from anaerobically digested sludge have been reported (Beauchamp *et al.*, 1978, Robinson and Polglase, 2000). However, these studies were based on sludges which were not incorporated into the soil, whereas here the biosolids and fertilisers were incorporated immediately after spreading to minimise volatilisation losses. Donovan and Logan (1983) conducted a laboratory study to investigate the factors influencing N volatilisation from sewage sludge and found that incorporation of sludge into soil greatly reduced NH_3 volatilisation losses (Donovan and Logan, 1983). For sludge incorporated 0.25 h, 1 h and 3 h after application 3, 4 and 6 %, respectively, of the $\text{NH}_3\text{-N}$ applied was lost in the first 24 h. There was a period of 1 to 2 h between spreading the biosolids and incorporating them into the soil when this field trial was set up. Therefore, for the NH_4Cl and DMAD plots, where larger proportions of total N are in the form of ammoniacal N, volatilisation may have accounted for a relatively small portion of the unrecovered N. Another potential factor that may influence the initial recoveries of mineral N is $\text{NH}_4\text{-N}$ fixation, which is greater for soils with increased clay contents (Kowalenko and Yu, 1996; Trehan, 1996). Trehan (1996) reported that 23 % of $\text{NH}_4\text{-N}$ added to soil with a clay content of 53 % was fixed within 30 mins in laboratory incubations. There was much less fixation in soil with lower clay content of approximately 15 % (Trehan, 1996). Fixation of NH_4^+ may, therefore, account for a proportion of the unrecovered $\text{NH}_4\text{-N}$ at North Sidelands, which had a clay content of 38 % in the top 10 cm, however, the clay content in the top 0-10

cm at Brices was significantly smaller and equivalent to 17 % so this process was less likely to be a significant factor here. There are many variables to control in a field trial of this scale and it may be that the observed differences in initial mineral N recoveries were a result of experimental error in the initial incorporation depth of NH_4Cl . Increasing the depth of cultivation by 2 cm below the intended depth of 10 cm, could account for the deficit, although it is emphasised that the cultivation depth of the tilling equipment was carefully controlled.

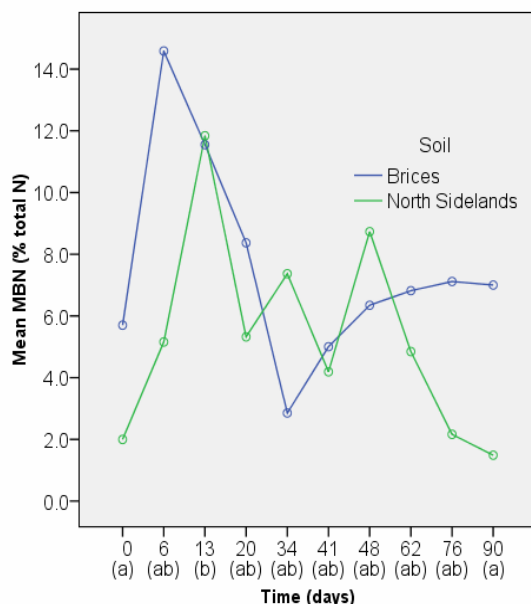
The initial recovery of mineral N in the biosolids-amended plots also showed some deviation from theoretical values, which, again, is potentially a result of experimental variation during application. In DMAD-amended soil at Brices, the mineral N recovery was 5 % total N addition, approximately 30 % of the expected concentration (Table 4.1). However, in DMAD plots at North Sidelands the initial recovery of mineral N was approximately 14 % total N, close to the expected concentration (Table 4.1; Figure 4.16), suggesting that variations in incorporation depth were unlikely to be a major factor controlling N recovery in this case.

In LMAD amended soil at North Sidelands, initial mineral N recovery was 44.3 % total N and in Brices it was 15 % total N compared to an expected 58.6 %. Recoveries of mineral N in pig slurry-amended soil were 43.8 % and 8.8 % total N in North Sidelands and Brices respectively compared to an expected 94.5 % total N. In soil amended with cow slurry, recoveries were 38.5 % and 8.3 % total N for North Sidelands and Brices respectively, compared to an expected 49.6 % (Table 4.1). The 10-20 cm TON concentration in LMAD, cow and pig slurry amended soil on day 6 were close to control concentrations (Figure 4.12) and indicated that there was little initial loss of nitrate below the surface layer, or variation in incorporation depth. Inputs of mineral N to the soils in DRAW, TDMAD and LC were small and may not provide a reliable basis for estimating the mechanisms responsible for the initial recovery of N from these soils.

There was no evidence to suggest that the initial deficit in N recovery in DMAD-amended soil in Brices Field on day 0 was due to microbial immobilisation of N (Figure 4.19). However, immobilisation may occur for this treatment to some extent in this soil type as between day 6-41, 3-6 % of the added N was recovered as MBN, whereas at North Sidelands, although up to 4.5 % of the added N was recovered as MBN during this period, MBN concentrations also fell below the unamended control (Figure 4.19). Figures 4.23 (a) and (b) show the effects of sampling date and soil type (means for all

biosolids) and soil type and biosolids type (means for all sampling dates) on the proportion of N recovered in the microbial biomass.

(a) Sampling date and soil type effects on MBN



(b) Biosolids effects on MBN

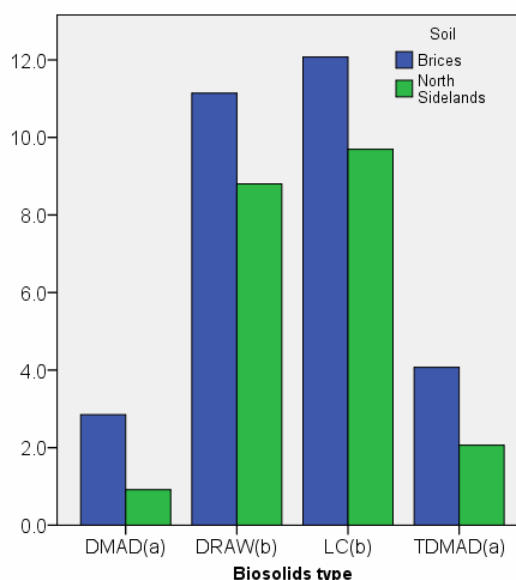


Figure 4.23 Effects of (a) soil type and sampling date (means for all four biosolids) and (b) soil type and biosolids (means for all sampling dates) on MBN (% total N added). Letters in brackets on x axis indicate results of pair-wise comparisons: sampling dates that do not have the same letter (Tukey's test) are significantly different at $P=0.04$; biosolids types that do not have the same letter (Tamhane's T2 test) are significantly different at $P<0.001$.

Analysis of Variance (ANOVA) demonstrated that there was a significant effect of soil type on immobilised N with greater N immobilisation occurring for Brices Field ($P<0.05$). The mean difference between soils in (a) was 2.22 % (Brices>North Sidlands) and was significant at $P=0.03$, according to ANOVA. The mean difference between soils in (b) was 2.17 % (Brices > North Sidlands) and was significant at $P=0.02$, according to ANOVA. There was a significant effect of sampling date on MBN recovered ($P=0.008$) and a significant effect of biosolids type ($P>0.001$). However, there were no significant interactions between soil type and biosolids type, or, in a separate test, with sampling date, on the amount MBN ($P>0.05$).

Mean MBN recoveries in each soil type increased on day 6 and there was a peak in MBN on day 13 (Figure 4.23a). Tukey's pairwise comparisons (Figure 4.23a) showed that MBN on day 0 (mean of both soil types) was significantly less than day 13, and that MBN on day 13 was significantly greater than day 90 ($P=0.04$). This indicated that the greatest quantities of N were immobilised in the week following soil amendment, and that there was a general decrease by day 90. Initial recovery of N in the microbial biomass in DRAW- and LC-amended soil also indicated that the microbial biomass in the lower fertility soil type may be more retentive in terms of N immobilisation, as this fraction initially accounted for 6.5 % of the added N in DRAW and 10 % in LC amended soil in Brices Field, compared to 0 % in North Sidelands (Figures 4.18 and 4.21). Figure 4.23b shows that mean recoveries of N in the microbial biomass in DRAW and LC amended soil were greater than for TDMAD and LC. Tamane's T2 pair-wise comparisons showed that MBN recovered in DMAD and TDMAD amended soils was not significantly different and MBN in LC and DRAW amended soil was also not significantly different. However, there were significant differences between each of the stabilised sources of organic matter (TDMAD and DMAD) compared to the unstabilised materials (DRAW and LC) ($P<0.001$).

The soil mineral N recoveries at the mid-point of the trial (means of days 34 and 41), as a proportion of total N applied in the biosolids and NH_4Cl , and mineralisable N fractions (calculated according to the method in Section 3.7.1.2) are shown in Tables 4.2 and 4.3. Not all the mineral N applied as NH_4Cl or NaNO_3 was extractable or present in the 0-10 cm sampling depth in either soil type, a fraction of mineral N was recovered at 10-20 cm, so mineral N recoveries and mineralisable N fractions for 0-20 cm depth were also calculated. The majority of the of the applied mineral N was recovered in soil at 0-20 cm depth at North Sidelands amended with NH_4Cl and $\text{NO}_3\text{-N}$, compared to approximately 70 % for both inorganic fertiliser treatments at Brices. The initial N recovery in the NH_4Cl control plots was similar at both sites, indicating that there were fundamental differences in the N transformation processes and biophysicochemical dynamics operating in the two soils. The apparent increase in N recovery between day 0– days 34-41, indicated that the initial deficits were not due to loss below the surface layer or variation in incorporation depth.

Recoveries of mineral N in TDMAD and DMAD plots were greater at North Sidelands than Brices at the mid-point of the trial (Tables 4.2 and 4.3). This is consistent with previous findings that N release from biologically stabilised biosolids is greater in more fertile soil (Smith *et al.*, 1998b; Breedon *et al.*, 2003).

Table 4.2 Mid-point N recoveries at North Sidelands, mean of day 34 and 41 values (0-10 cm and 10-20 cm), mineral N concentrations in unamended control soil are subtracted.

Type	TON recovered, 0-10 cm (kg N ha ⁻¹)	NH ₄ -N recovered, 0-10 cm (kg N ha ⁻¹)	Mineral N recovered, 0-10 (kg N ha ⁻¹)	Mineral N recovered, 0-10 cm (% total N)	TON, 10-20 cm (kg N ha ⁻¹)	TON, 10-20 cm (% total N)	Mineral N recovered, 0-20 cm (% total N)	Mineralisable N, 0-20 cm (% organic N)*
NaNO ₃	160.5	3.65	164.1	82.1	59.8	29.9	111.9	0
NH ₄ Cl	149.9	0.88	150.8	75.4	57.3	28.7	104.1	0
DMAD	110.2	2.11	112.3	18.6	40.8	6.77	25.4	11.9
DMAD + grass	44.9	3.22	48.2	7.99	23.6	3.92	11.9	-4.03
DRAW	49.4	6.08	55.5	9.16	17.1	2.83	12.0	9.11
LMAD	68.9	2.76	71.8	36.1	45.2	22.7	58.8	0.47
TDMAD	76.2	0.71	76.9	22.4	24.6	7.15	29.6	28.5
PIG	71.5	2.23	73.7	41.6	29.3	16.6	58.2	-647.3
COW	41.9	3.09	44.9	22.3	9.90	4.90	27.2	-44.1
FYM	10.1	2.60	12.7	4.46	4.86	1.71	6.17	5.08
LC	-0.11	2.08	1.97	0.81	1.50	0.61	1.42	-8.20
DMAD + Thiram	86.9	10.0	96.9	16.1	73.5	12.2	28.3	15.3

*Calculated according to method given in Section 3.7.1.2.

Table 4.3 Mid-point N recoveries at Brices Field, mean of day 34 and 41 values (0-10 cm and 10-20 cm), mineral N concentrations in unamended control soil are subtracted.

Type	TON recovered, 0-10 cm (kg N ha ⁻¹)	NH ₄ -N recovered, 0-10 cm (kg N ha ⁻¹)	Mineral N recovered, 0-10 (kg N ha ⁻¹)	Mineral N recovered, 0-10 cm (%TN)	TON, 10-20 cm (kg N ha ⁻¹)	TON, 10-20 cm (%TN)	Mineral N recovered, 0-20 cm (% TN)	Mineralisable N, 0-20 cm (% organic N)*
NaNO ₃	105.8	-0.63	105.2	52.6	34.4	17.2	69.8	0
NH ₄ Cl	71.9	52.5	124.4	62.2	10.6	5.32	67.5	0
DMAD	67.8	11.7	79.5	13.2	11.8	1.95	15.1	-2.52
DMAD + grass	6.31	3.47	9.79	1.62	7.84	1.30	2.92	-15.3
DRAW	23.3	1.57	24.9	4.11	5.99	0.99	5.10	1.72
LMAD	36.9	0.19	37.1	18.7	9.42	4.73	23.4	-85.3
TDMAD	53.3	1.76	55.1	16.1	16.1	4.70	20.8	19.0
PIG	15.1	-0.10	15.0	8.45	5.10	2.88	11.3	-1432.8
COW	26.0	0.46	26.5	13.1	3.19	1.58	14.7	-66.1
FYM	1.56	-0.54	1.02	0.36	6.01	2.11	2.48	-2.56
LC	<0.001	1.72	1.72	0.71	4.12	1.69	2.40	-7.91
DMAD + Thiram	55.7	34.9	90.6	15.0	0.94	0.16	15.2	-7.00

*Calculated according to method given in Section 3.7.1.2.

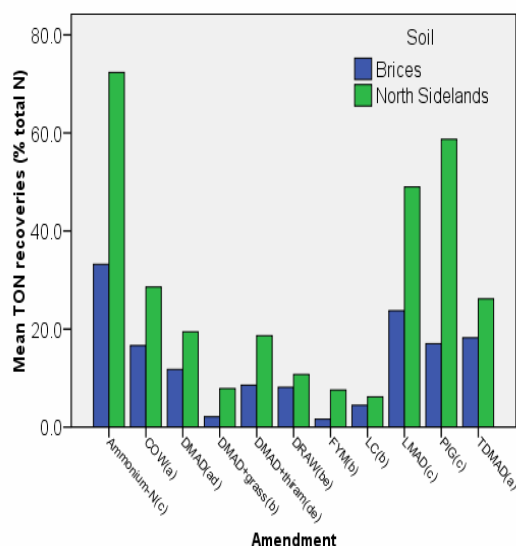
There is no evidence that there were differences between the two soil types in the proportion of N immobilised in the microbial biomass between days 34-41 (Figures 4.16 and 4.17). This demonstrated that mineralisation of N is rapid in more fertile soil and suggests a lag phase in less fertile soil. This lag phase is not due to immobilisation in the biomass, but a delayed response to biosolids amendment in the soil with the less active microbial population, or simply a longer period of time required to turnover the added organic matter.

Mineral N recoveries at Brices in DRAW-, LMAD-, COW-, FYM- and LC-amended soils were approximately 50 % of the mineral N recovered at North Sidelands at the mid-point of the trial (Tables 4.2 and 4.3). In DRAW and LC amended soil, as for DMAD and TDMAD, the differences in recovered N cannot be accounted for by the proportion of N immobilised in the microbial biomass (Figures 4.19 and 4.20). The proportion of added N immobilised in the microbial biomass was between approximately 1-25 % of the N added for both soil types in LC amendments and 0-15 % added N in DRAW regardless of soil type. This indicated that the differences in mineral N recoveries were a result of the slower turnover of added organic N in the less fertile soil rather than greater immobilisation by the biomass. Mineral N recovery in PIG amended soil was much greater at North Sidelands at the mid-point of the trial, 58.2 % compared to 11.3 % total N. In DMAD-amended soils at Brices Field, 15.1 % total N was recovered at 0-20 cm, compared to 25.4 % at North Sidelands. In TDMAD amended soil, approximately 21 % of total N was recovered at Brices compared to 30 % at North Sidelands. The results at this stage of the field experiment suggested that TDMAD was a better source of available N than DMAD in both soil types. This is consistent with findings of Tarrasón *et al.* (2007), who found that, in the first three weeks following incorporation, soil amended with thermally dried biosolids contained more mineral N than soil amended with anaerobically digested sludge, although the difference was not significant. For both of the biosolids cakes examined here more mineral N was released as a proportion of the total N supplied than for FYM, which had availabilities of 2.5 and 6.2 % total N in Brices Field and North Sidelands respectively.

Figure 4.24 shows the effects of soil type, treatment type and sampling date on mean TON recoveries at 0-20 cm. The mean recoveries of N for each soil type show that significantly greater TON was recovered overall at North Sidelands than Brices field, this can be explained by the higher initial recoveries in all the treatments in this soil type, as demonstrated by Figure 4.24b. The mean difference between soils was 14.5 % (Brices<North Sidelands) and was significant at $P<0.001$, according to ANOVA.

There was a significant effect of sampling date ($P<0.001$), and interacting effect of sampling date and soil type ($P=0.009$). This demonstrated the differences in rates of mineralisation and nitrification between the two soil types.

(a) Effects of treatment and soil type



(b) Effects of soil type and sampling date

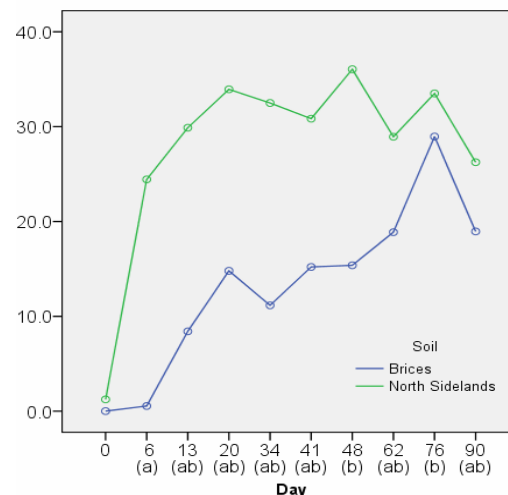


Figure 4.24 Effects of (a) soil type and sampling date (means for all four biosolids) and (b) ammonium-N ($\text{NH}_4\text{-N}$), livestock wastes or biosolids (means for all sampling dates) on TON recovered at 0-20 cm (% total N added). Letters in brackets on x axis indicate results of Tamhane's pair-wise comparisons: sampling dates or treatments that do not have the same letter were significantly different at $P<0.05$.

The mineral N recovery in the two soils at the end of the experiment is given in Tables 4.4 and 4.5. These values were calculated from day 76 concentrations, as Figures 4.3-4.13 demonstrated that after this point there was a net decrease in TON concentration in amended soils, suggesting mineralisation and nitrification had peaked and there was movement of N below the surface layer.

Table 4.4 Final N recoveries at North Sidelands, day 76 (0-10 cm and 10-20 cm), mineral N concentrations in unamended control soil are subtracted.

Type	TON recovered, 0-10 cm (kg N ha ⁻¹)	NH ₄ -N recovered, 0-10 cm (kg N ha ⁻¹)	Mineral N recovered, 0-10 (kg N ha ⁻¹)	Mineral N recovered, 0-10 cm (% total N)	TON, 10-20 cm (kg N ha ⁻¹)	TON, 10-20 cm (% total N)	Mineral N recovered, 0-20 cm (% total N)	Mineralisable N (% organic N)
NaNO ₃	133.0	-0.04	133.0	66.5	41.7	20.9	87.4	0
NH ₄ Cl	108.2	0.92	109.1	54.6	30.3	15.2	69.7	0
DMAD	124.7	1.34	126.1	20.9	39.3	6.52	27.4	14.0
DMAD + grass	<0.001	1.36	1.36	0.23	0.21	0.04	0.26	-18.1
DRAW	90.0	3.24	93.2	15.4	36.0	5.95	21.4	18.2
LMAD	102.7	-0.34	102.3	51.4	23.6	11.9	63.3	11.8
TDMAD	84.9	-0.46	84.4	24.6	26.8	7.82	32.4	31.5
PIG	104.7	-1.40	103.3	58.4	23.6	13.3	71.7	-391.9
COW	41.0	-1.01	40.0	19.8	15.7	7.77	27.6	-42.3
FYM	32.6	-1.78	30.8	10.8	6.38	2.25	13.1	9.08
LC	31.1	1.44	32.5	13.3	10.9	4.46	17.8	9.12
DMAD + Thiram	106.5	17.4	123.9	20.6	58.9	9.77	30.3	14.3

*Calculated according to method given in Section 3.7.1.2

Table 4.5 Final N recoveries at Brices Field, day 76 (0-10 cm and 10-20 cm), mineral N concentrations in unamended control soil are subtracted.

Type	TON recovered, 0-10 cm (kg N ha ⁻¹)	NH ₄ -N recovered, 0-10 cm (kg N ha ⁻¹)	Mineral N recovered, 0-10 (kg N ha ⁻¹)	Mineral N recovered, 0-10 cm (% total N)	TON, 10-20 cm (kg N ha ⁻¹)	TON, 10-20 cm (% total N)	Mineral N recovered, 0-20 cm (% total N)	Mineralisable N (% organic N)
NaNO ₃	120.4	1.39	121.8	60.9	19.7	9.83	70.7	0
NH ₄ Cl	118.7	39.8	158.4	79.2	14.1	7.05	86.3	0
DMAD	151.9	24.2	176.1	29.2	20.6	3.41	32.6	20.4
DMAD + grass	-1.55	7.03	5.48	0.91	<0.01	<0.01	0.91	-17.0
DRAW	117.2	13.6	130.9	21.6	12.9	2.13	23.8	21.3
LMAD	83.6	4.29	87.9	44.2	5.62	2.83	47.0	-28.0
TDMAD	114.1	4.11	118.2	34.5	20.8	6.05	40.5	39.6
PIG	37.0	1.61	38.6	21.8	11.4	6.42	28.2	-1183.2
COW	65.0	1.47	66.5	32.9	5.36	2.65	35.6	-27.5
FYM	16.1	1.90	18.0	6.34	5.62	1.98	8.32	3.40
LC	59.8	6.11	65.9	27.0	8.40	3.44	30.4	23.7
DMAD + Thiram	113.6	27.7	141.3	23.4	15.4	2.55	26.0	12.6

*Calculated according to method given in Section 3.7.1.2

Final mineral N recoveries at North Sidelands were approximately 87 % and 70 % in NaNO₃- and NH₄Cl-amended soils respectively (Table 4.4) and 71 % and 85 % in NaNO₃ and NH₄Cl amended soils, respectively, at Brices Field (Table 4.5). This suggested that there had been some NO₃-N leaching below the 0-20 cm profile. The order of greatest final mineral N recovery for biosolids and livestock wastes (day 76) in 0-20 cm in North Sidelands as a proportion of total N added was:

PIG > LMAD > TDMAD > DMAD+thiram > DMAD > COW > DRAW > LC > FYM > DMAD+grass

In Brices Field the order was:

LMAD > TDMAD > COW > DMAD > PIG > LC > DMAD+thiram > DRAW > FYM > DMAD+grass

For North Sidelands, the greatest recovery of mineral N was in pig slurry-amended soil. In this case, 72 % of the total applied N was recovered as mineral N (Table 4.4); this is to be expected from its high mineral N content equivalent to 95 %. However, by contrast, in Brices Field, there was 28% recovery in PIG amended soil. It is possible that in this soil type with a lower water holding capacity, there were greater movement of NO₃⁻ below the top 20 cm; however, this was not observed in the NO₃⁻ mobility control. Plaza *et al.* (2005) reported similar large recoveries of N, 50-60 % total N, in a laboratory incubation study for soil amended with pig slurry with a mineral N content of 65 % of total N.

Large recoveries of mineral N were also measured in LMAD-amended soil for both soil types, equivalent to 63 and 47 % for North Sidelands and Brices Field, respectively, which is also to be expected from the high mineral N content of the material. The current fertiliser recommendations for N availability for a spring application of LMAD, incorporated into the soil are 55 % total N (MAFF, 2000), which is intermediate to the availabilities determined in this field trial. Smith *et al.* (1998b) found that for LMAD with an approximate NH₄-N content of 50 % of total N, 80-90 % of total N was available in laboratory incubation study, therefore, there was no potential for leaching of NO₃-N, which may account for the higher value. In a field investigation with a sandy loam soil, Smith *et al.* (2002b) found relative availabilities of 50-60 % total N, consistent with current recommendations and the findings of this investigation. Despite a mineral N

content of approximately 50 %, mineral N recoveries for soil amended with cow slurry (COW) were 28 % of added total N in North Sidelands and 36 % in Brices Field. It is possible that in this unstabilised material the unrecovered N may have been accounted for by microbial immobilisation. Microbial biomass C (MBC) and MBN were not measured in the livestock slurries and FYM in this investigation, however the greater recoveries of N in the microbial biomass observed in the soils amended with unstabilised sources of organic C, LC and DRAW, supports this assumption. It has previously been suggested (Chae and Tabatai, 1986; Sims, 1986; Plaza *et al.* 2005) that unrecovered N in soils amended with untreated animal slurries and manures may be accounted for in the microbial biomass.

The greatest N recoveries from the solid material types tested were from TDMAD in both soils, 41 % total N in Brices and 32 % in North Sidelands. This demonstrated that, despite a low mineral N content of 1.5 %, TDMAD provided a significant and readily available source of N for crop growth, largely independent of soil type in this case. Final mineral N recovery in DMAD and DMAD+thiram amended soil was similar in both soil types, between 26-33 %, this is consistent with recent findings of 20-40 % N availability (Smith *et al.*, 1998b) and approximately 30 % availability (Morris *et al.*, 2003). The final recoveries measured in DMAD-amended soils were similar in both soil types, which demonstrated that, despite an initial period of slower mineralisation and nitrification rates in the less fertile soil type, overall TON production from the biosolids was equivalent in both soil types.

The LC material tested here was produced from raw sludge cake and, consequently, had a higher C to N ratio than the other biosolids examined (Table 3.10), which may explain the initial reduced N mineralisation and lower recovery of mineral N observed for this sludge type (Tester *et al.*, 1977; Rowell *et al.*, 2001). However, end-recoveries of N demonstrated that LC was an adequate source of available N with final recoveries of 18 % in North Sidelands and 31 % in Brices Field. Field and laboratory investigations conducted to develop USEPA fertiliser guidelines (Gilmour *et al.*, 2003) with a range of biosolids types, including dewatered anaerobically digested biosolids, lime-treated digested biosolids and thermally dried biosolids found mean available N, in laboratory incubation of 30 % total N, and from field trials with perennial grass, a mean value of 37 % was found. With the exception of composted or biosolids that had had an extensive storage period, there was no significant effect of treatment type on available N release; the results were, therefore, consistent with the findings of this investigation that DMAD and TDMAD produced comparable amounts of mineral N.

Imperial College field trials with perennial ryegrass into N availability in conventional and enhanced-treated biosolids, also found no significant effect of biosolids treatment type (Morris, 2006).

Recovery of mineral N in FYM amended soils was low in both soil types, 13.1 % total N at North Sidelands and 8.32 % total N at Brices Field. This unstabilised or partially stabilised material had a mineral N content of 5.1 % total N and the greatest C:N ratio of 14:1 (Table 3.10), it is therefore possible that there was microbial immobilisation of N in FYM treatments, as has previously been reported for undigested animal slurries and manures (Chae and Tabatai, 1986; Sims, 1986; Plaza *et al.*, 2005). Alternatively, low overall recovery may have been due to increased stability of FYM, due to incidental composting and NH₃ volatilisation during storage.

Figure 4.25 shows the proportion of N from DMAD amendment recovered in the ryegrass crop; concentrations of N recovered in ryegrass grown on unamended control soil were subtracted. The lowest recovery of mineral N at 0-20 cm was in the DMAD+grass treatments. Evidently ryegrass was effective at removal and acted as a sink for soil N released from the biosolids. In contrast to the soil analysis results, there was greater initial recovery of applied N at Brices Field in ryegrass in comparison to North Sidelands; approximately 3.2 % total N addition in comparison to 3.9 % on day 41.

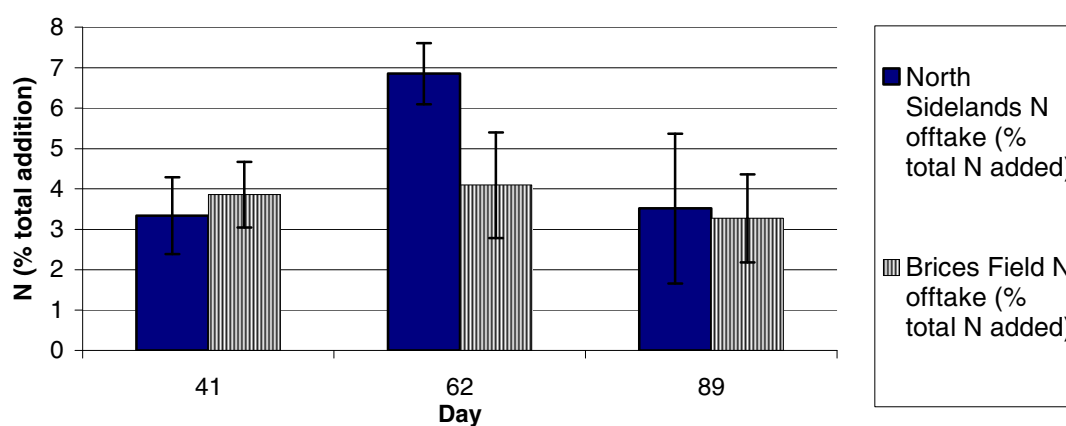


Figure 4.25 N offtakes in ryegrass on DMAD amended soil, in North Sidelands and Brices Field (% total N additions in the biosolids). Offtakes in ryegrass grown on unamended control soil are subtracted. Error bars are S.E. of the mean.

This may have been due to differences in establishment of the crop as on day 62, N recoveries were greater at North Sidelands equivalent to 6.9 % of the added N, compared to 4.1 %. Cumulative N offtake in ryegrass was greatest at North Sidelands,

13.2 % of total N compared to 11.2 % at Brices. This is less than half the N recovered in soil in the bare DMAD plots based on soil analysis. As no TON was recovered in soil in DMAD+grass plots on day 76, the remaining unrecovered N was probably accounted for as N in the root system.

There was also a significant effect of amendment ($P<0.001$) and an interacting effect between amendment and soil type ($P<0.001$) on the amount of N recovered as TON, when calculated as mean TON recovery for all sampling dates. Mean TON recoveries for both soil types (mean for all sampling dates) (Figure 4.24a) showed that quantities of recovered N as TON at 0-20 cm for NH_4Cl , pig slurry (PIG) and LMAD were significantly greater than the recoveries from the other amendments, as demonstrated by Tamhane's T2 tests ($P<0.05$). This confirms that liquid livestock manures and liquid digested biosolids can act as comparable fertiliser sources to mineral N fertiliser. No statistically significant differences in the amounts of total N were recovered as TON from TDMAD, DMAD, consistent with findings of Gilmour *et al.* (2003); cow slurry (COW) could also be placed in this 'N availability' group in terms of TON recoveries. Recoveries of TON in this group of treatments were significantly greater than for DRAW, FYM and LC, and TDMAD and COW were significantly greater than DMAD+thiram. DRAW, FYM and LC were in a group with the lowest mean recoveries, and DMAD+grass had significantly less TON at 0-20 cm than the other treatments.

The results were entirely consistent with the findings of Smith *et al.* (1998), who found NO_3^- production was greatest in $\text{LMAD}>\text{DMAD}>\text{DRAW}$. Smith *et al.* (1998b) categorised conventional and enhanced treated biosolids according to their NO_3^- production in incubated soil. According to their classification, liquid digested biosolids came under category 1, producing the highest concentration of NO_3^- , as a result of the large $\text{NH}_4\text{-N}$ content; dewatered digested biosolids came under category 2, with intermediate NO_3^- production potential; dewatered undigested biosolids came under category 3.

Mineralisable N contents of the different biosolids types in the 0-20 cm profile are also presented in Tables 4.2-4.5. Negative values indicate that less mineral N was recovered than was added in the biosolids or livestock wastes. The mean values for days 34-41 showed that at this point in North Sidelands soil there had been net mineralisation in DMAD-, DMAD+thiram-, DRAW-, TDMAD- and FYM-amended soils. In Brices Field there was net mineralisation in DRAW- and TDMAD-amended soils only. These results demonstrate lower rates of mineralisation in the less fertile soil.

There was a high proportion of rapidly mineralisable organic N from TDMAD, which was greater than for DMAD, equivalent to 3 times the value for DMAD in North Sidelands. Breedon *et al.* (2003) reported that in 2 out of 3 soil types tested in laboratory incubations TDMAD was also found to contain a larger pool of mineralisable organic N than DMAD.

The final (day 76) mineralisable N for DMAD, present in the 0-20 cm profile, was calculated as 14 % at North Sidelands and 20 % at Brices Field, this is consistent with recent estimates of 15-17 % mineralisable N (Parker and Sommers, 1983; Smith and Bellett-Travers, 2001; Smith *et al.*, 2002b; Breedon *et al.*, 2003; Morris *et al.*, 2003). Mineralisable N in DMAD+thiram treatments was in the same range.

Final mineralisable N values for TDMAD were 32 % at North Sidelands and 40 % at Brices (Tables 4.4 and 4.5). Previously, mineralisable N in a crop response trial in a sandy loam amended with thermally dried biosolids was calculated as 33.6 % organic N (Morris *et al.*, 2003).

It appears that in this experiment the mineralisable N pool in TDMAD was rapidly released and that it reached values comparable to those in previous trials. Cogger *et al.* (1999) also reported heat-dried biosolids to be a fast-release source of N. It is possible that the smaller particle size of TDMAD could be responsible for the increased amount of N recovered from this material, however, Cogger *et al.* (1999) found that heat-dried dust, <0.1 mm diameter, had similar fertiliser value to pellets with a diameter of 1-4 mm. Ambus and Jensen (1997) reported that decomposition of ground plant residues had no effect on N dynamics, in comparison to residues that were not ground prior to soil amendment. Previous experiments have found N mineralisation from biosolids is not directly related to decomposition of the whole material, but decomposition of one or more labile pools, each having different rates of mineralisation (Rowell *et al.*, 2001, Tester *et al.*, 1977). It appears that, although thermal drying processes reduce the total N content and remove the mineral N fraction, in comparison to conventional mechanically dewatered digested sludge, heat treatment conditions the sludge so that the organic fraction is more rapidly and extensively mineralised. Consequently, mineral N is present in comparable quantities to soil amended with DMAD.

The mineralisable N fraction calculated for DRAW amended soil was approximately 20 % in both soil types, this demonstrated that despite the low mineral N content of

approximately 5 %, DRAW had a high proportion of rapidly mineralisable organic matter. Parker and Sommers (1983) found a mineralisable N fraction of 25 % organic N. Mineralisable N from LMAD was calculated as 12 % in North Sidelands, this supported findings of other investigations that have indicated that the fertiliser N value of liquid digested biosolids is greater than the mineral N content alone. Mineralisable N has previously been calculated as 15 % (Hall, 1983a). However, mineral N recoveries in Brices Field were less than the proportion of added mineral N, possibly due to leaching of NO_3^- .

Mineralisable N in LC amended soil was calculated as 9 % in North Sidelands and 24 % in Brices. These values are lower than mineralisable N calculated by Morris *et al.* (2003) of 34.1 %; based on the mean value of 3 years of crop response trials. Production of TON in LC amended soils was slower than for the other biosolids treatments and it may be that the greater value obtained by Morris *et al.* (2003) is a result of a more slowly released pool of organic N, or by remineralisation of N immobilised in microbial biomass.

Mineralisable N in FYM was calculated as 3.4 % organic N in Brices Field and 9.1 % organic N in North Sidelands, current fertiliser recommendations suggested that approximately 10 % of the organic N fraction is available (MAFF, 2000). Chae and Tabatai reported 13 % total N in cow manure was mineralised. Farmyard manure is a potentially highly variable source of organic N due to types and amounts of bedding materials used and varying degrees of stabilisation. These findings indicate that N availability from FYM is difficult to predict in different soil types. No mineralised N was detected in soils amended with PIG and COW, this may be a result of losses of N through leaching or denitrification; Plaza *et al.* (2005) also reported no net mineralisation in a laboratory incubation with pig slurry amended soil.

4.4 Summary

The field trial was established to investigate the effects of biosolids type and livestock wastes, and interactions with soil type, on N availability in amended soil. Partitioning of N in microbial biomass in biosolids-amended soil may be important in understanding N release kinetics and could be responsible for lower N availability observed in less fertile soils (Smith *et al.*, 1998b; Breedon *et al.*, 2003). Therefore, MBN dynamics in biosolids-amended soil were measured, to study partitioning of N within the soil

microbial biomass for different soil types and the subsequent influence on N release to crops in contrasting fertility systems.

Microbial biomass C and N concentrations were greatest in the silty clay with the higher OM content, North Sidelands, demonstrating its higher fertility status. Higher rates of mineralisation and nitrification were measured in the more fertile soil, demonstrated by NH_4Cl control. Concentrations of TON in biosolids- and livestock wastes-amended soil also increased more rapidly in the higher fertility soil, and mineral N recoveries at the mid-point of the trial showed greater recoveries in the higher fertility soil type, consistent with higher rates of mineralisation and nitrification. The interacting effects of soil type and sampling date on the amount of TON recovered were significant.

Recoveries of TON at 10-20 cm suggested that there had not been significant movement below the top 10 cm on day 6 from the biosolids and livestock wastes in either soil type. Subsequently, higher concentrations of TON were measured in Brices, the sandy silt loam, at 10-20 cm indicating that this soil may have been more prone to NO_3^- mobility and to leaching. Higher concentrations of TON in 10-20 cm samples were observed primarily with liquid biosolids and biowastes types. Recoveries of mineral N from control plots at the mid-point of the trial also indicated greater movement of mineral N in Brices Field. However, final recoveries at 0-20 cm demonstrated movement of between 15-30 % mineral N from control plots independent of soil type. Lower concentrations of mineral N in DMAD+grass plots at 0-20 cm in both soil types in comparison to unamended controls indicated that the ryegrass crop was effective at capturing the available N mineralised in amended soil.

Initial recoveries of mineral N were smaller than expected for the biosolids-amended soil at Brices Field (sandy silt loam). This may have been due to a combination of immediate differences in mineralisation and nitrification activity at the two sites, $\text{NH}_4\text{-N}$ fixation, or losses of TON below the surface layer. However, there was no strong evidence to suggest that initial differences were a result of microbial immobilisation. Applications of DRAW, DMAD, TDMAD and LC resulted in initial increases in MBC in both soil types. Greater increases were observed following addition of lower stability carbon sources, DRAW and LC. The results therefore indicated that applications of biosolids to agricultural soil may improve soil fertility. Microbial biomass N contents of soil receiving different biosolids amendments suggested that there were differences in N immobilisation processes in soils of differing fertility status, with a greater retention of N in the microbial biomass amended with biosolids in the lower fertility soil in some

cases. The greatest increases in MBN also occurred with the addition of unstabilised or less stabilised biosolids, DRAW and LC, consistent with previous findings. The DMAD-amended soil treated with a protozoa inhibitor showed delayed nitrification rates in Brices Field. This may have demonstrated the importance of protozoa grazing on stimulating microbial activity, and showed that the higher fertility soil was generally resilient to disruption to soil ecology.

The patterns and rates of N recovery dynamics were dependent on biosolids or livestock waste type, and initially on soil type. However, the final overall release of N was similar in both soil types. The results indicated that, despite subtle differences in N immobilisation in DMAD-amended soil between soil types, differences in net production of TON are primarily due to a more active bacterial population in the high fertility soil type.

The greatest recovery of N from biosolids and livestock wastes in North Sidelands (silty clay) was from pig slurry, this is predictable from its high mineral N content. However, recoveries were lower in Brices Field (sandy silt loam), which were assumed be a result of immobilisation through addition of an unstabilised C source or increased NO_3^- mobility in the sandy silt loam soil. Whereas net mineralisation was measured in liquid digested biosolids amended soil at North Sidelands, no net mineralisation was measured from liquid livestock wastes, again, indicating the importance of the biological stability of the organic matter. Microbial biomass C and MBN were not measured in livestock wastes amended soil, however findings for unstabilised biosolids types supported this assumption.

With the exception of DMAD+grass treatments, the lowest recovery of N in both soil types was from FYM. Recovery of N was lower in Brices Field, suggesting potentially greater N immobilisation in this soil type. The greatest recovery of N from biosolids was in liquid digested biosolids in both soil types, equivalent to 47-63 % of the applied total N, this can be explained by its high stability and mineral N content. In both soil types for the biosolids cakes the order of recovery of N was TDMAD>DMAD>LC. In TDMAD-amended soil, 32-41 % total N was recovered at 0-20 cm, 26-33 % total N was recovered in DMAD-amended soil and 18–31 % in LC amended soil. Although TDMAD had less total and mineral N than DMAD, it had a larger mineralisable pool of N and is an effective rapid release N source for crop production.

5 FIELD INVESTIGATION OF THE NITROGEN VALUE AND OTHER AGRONOMIC BENEFITS OF INDUSTRIAL BIOWASTES - 2006

5.1 Introduction

5.1.1 Background

Biowastes are a diverse range of materials in terms of their physical and chemical properties and, although approximately 7 million tonnes are spread to land annually in the UK (Gendebien *et al.*, 2001), there has been little quantitative research into their agronomic and fertiliser value. To improve the efficiency of use of nutrients from the materials and provide guidelines for best practice it is necessary to develop appropriate methods for investigating industrial biowastes under field conditions. Addressing the lack of information on the agronomic value of the industrial biowastes will enable farmers to gain the maximum economic benefit, maximise recycling opportunities closing nutrient loops (Green Alliance, 2007) and increase the use of biowastes in agriculture as a diversion of biodegradable materials from landfill in compliance with the Landfill Directive (CEC, 1999).

A programme of field experiments was established at Silwood Park, the Imperial College campus near Ascot, Berkshire, in spring 2006, on a low nutrient status sandy loam soil. A range of biowastes from industrial and commercial processes were investigated, including examples from the meat, vegetable and dairy processing industries. Processed biowastes from anaerobic and aerobic digestion plants were also selected to investigate the influence of pre-treatment on fertiliser value. An example of an anaerobic digestate fresh from the digestion plant and after a period of storage in a lagoon, and fish farm wastes, which varied in the period of storage in a settlement pit, were included to investigate the effects of storage on agronomic value. The majority of biowastes materials identified for the field experiment are currently spread on land for agricultural benefit (SI, 2005a). Mineral N fertiliser controls and dewatered mesophilic anaerobically digested biosolids (DMAD) from wastewater treatment were included so that the N release properties of the biowastes relative to these well characterised fertiliser sources could be assessed.

A systematic design was used (Cleaver *et al.*, 1970; Greenwood *et al.*, 1980a;b; Smith and Hadley, 1988) that included smaller plots and fewer guard rows than are

necessary for conventional field experimental methods. This allowed testing of more levels of more fertiliser application rates, thereby increasing sensitivity of the experimental approach to defining the optimal rate of application, which was of particular importance with this diverse range of materials. The biowastes were incorporated into the soil to minimise losses of N by gaseous emissions. Perennial ryegrass was used as an indicator crop as it is efficient at capturing most of the plant available N (Addiscott *et al.*, 1991; Whitehead, 1995; Christian and Richie, 1998), and should therefore account for most of the released N additions. This approach permits an absolute N equivalency value, relative to mineral fertiliser N, to be determined from which the fertiliser value of the material under different application regimes can be predicted. Perennial ryegrass was used in a previous programme of experiments at Silwood Park to quantify the agronomic benefit of different biosolids (Smith and Bellett-Travers, 2001; Smith *et al.*, 2002b; Morris *et al.*, 2003), this allowed direct comparisons to be drawn between the trials. The experimental design also allowed examination of the residual value of the materials, by re-application of mineral N fertiliser to control plots and observation of second year growth on biowastes-amended plots.

5.1.2 Aims

This experiment was amongst the first to be established to provide quantitative information on N availability from industrial biowastes. The overall aim was to develop fertiliser guidelines, in order to optimise the use of biowastes in agriculture and prevent excessive fertiliser applications that could lead to nutrient losses and damage the environment. The specific objectives of this experiment were to:

- Characterise the total and mineral nutrient concentrations in a selected range of industrial biowastes;
- Quantify the N release properties of industrial biowastes relative to sewage sludge and mineral fertiliser;
- Examine nutrient transfers, including P, K, Mg and S, from biowastes to crops;
- Develop a strategic approach for investigating agronomic value of biowastes.

5.2 Materials and Methods

General materials and methods relating to experimental design and sampling and analysis of biosolids, biowastes, soil and plant material are presented in Chapter 3; methods specific to the 2006 Biowastes Fertiliser Response trial are presented here.

5.2.1 Field Establishment

The field experiment was established during 3-5 May 2006, the biowastes investigated in the experiment, and abbreviations used in this thesis are listed in Table 3.5. Selection, collection and physical and chemical properties of the biowastes are described in Sections 3.4.1-3.4.3. A systematic design was used with 14 treatments arranged as three replicate blocks, each with 1.2 m x 10.5 m main-plots. A diagram of the 2006 experiment is given in Figure 5.1; the main plots were divided into 5 subplots, each 2.52 m². The solid materials were applied at rates of 0 (control), 2.5, 5, 7.5 and 10 t DS ha⁻¹ and liquid materials were applied at rates of 20, 50, 75 and 100 m³ ha⁻¹. The thermophilic aerobic digestate (TAD) was applied on a DS basis due to its high solids content (Table 3.8). Mineral N calibration plots were established with inorganic fertiliser, using prilled ammonium nitrate (NH₄NO₃), applied at rates of 0, 60, 120, 180 and 240 kg N ha⁻¹. In the case of biowastes treatments where a low N content was expected, treatments 3 and 4 (Figure 5.1), a base dressing of N was applied at a rate of 120 kg N ha⁻¹. Following N analysis of the waste materials it was considered appropriate to apply a top dressing of ammonium nitrate at a rate of 120 kg N ha⁻¹ to further biowastes treatments with a low total N content, treatments 7-11 (Figure 5.1), this was applied on 7 June 2006. This was to ensure that the crop was not N limited, so that other benefits of biowaste amendment could be detected.

The biosolids, biowastes and mineral fertiliser treatments were uniformly applied by hand to the soil surface, and the liquid biowastes were applied by bucket, and incorporated immediately using a pedestrian operated rotary cultivator set to a cultivation depth of 10 cm (Plate 5.1). The ground was raked to flatten the soil following rotation. Perennial ryegrass (*Lolium perenne*) cv Guilford was sown at a rate of 260 kg ha⁻¹ across the plots and the guard areas.

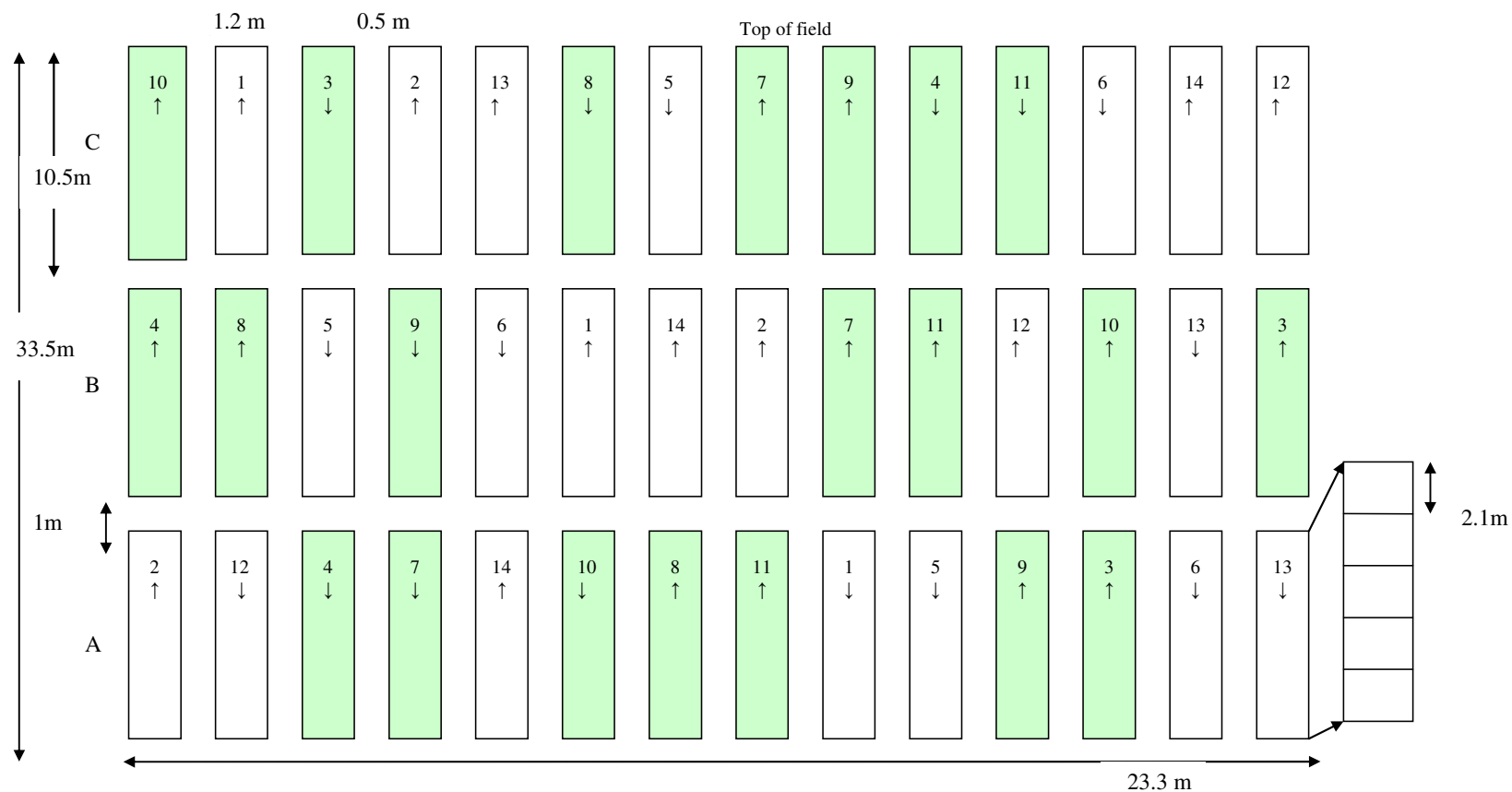


Figure 5.1 Experimental design for 2006 trial, showing arrangement, dimensions and subdivision of plots. Shaded plots are treatments which received a dressing of mineral N at 120 kg N ha⁻¹. Direction of arrow indicates gradient of application, low to high. Each plot is labelled with randomised treatment number: 1, DMAD; 2, Abattoir; 3, Potato sludge; 4, Potato wash; 5, TAD; 6, ADMSW; 7, Trout old; 8, Trout fresh; 9, Ice-cream; 10, Ice-cream DAF; 11, KG; 12, AD fresh; 13, AD stored; 14, mineral N control (Key to abbreviations given in Table 3.5).

(a)



(b)



Plate 5.1 Field trial establishment: (a) applying biowastes uniformly to the soil surface; (b) incorporation to a depth of 10 cm using a pedestrian operated rotary cultivator.

The soil was then raked and trampled to set the seeds into the ground. Large stones were removed from the plots to allow even sward growth. After establishment, the pathways around the plots were mown approximately every 2 weeks. It was not necessary to irrigate the site after sowing grass in 2006 as there was a period of rainfall which allowed the seed to germinate. Site management and environmental data collection are described in Sections 3.6.2 and 3.6.3. Weather data for the period of the experiment are presented in Appendix A3.

5.2.2 Harvesting

The longitudinal pathways between plots and horizontal guard areas between sub-plots were mown and the grass was discarded. Plant material was harvested using a pedestrian operated reciprocating blade mower at a height of 2 cm above the soil surface, a 1.28 m² (0.8 x 1.6 m) area at the centre of each subplot was harvested. The cut grass was raked and bagged (Plate 5.2). The longitudinal guard areas were then mown and discarded. Four harvests were taken during 2006 on 13 June, 25 July, 19 September and 20 November. Material from treatments 7-11 was not harvested on 13 June, due to insufficient growth. Yield measurements of the harvested grass and total

N and P analysis are described in Section 3.5. In addition, sub-samples of grass from the first harvest, from the top rates of application for each plot and subsamples from randomly selected control plots from each block, were analysed using ICP-AES to determine full elemental content, see Section 5.2.5.

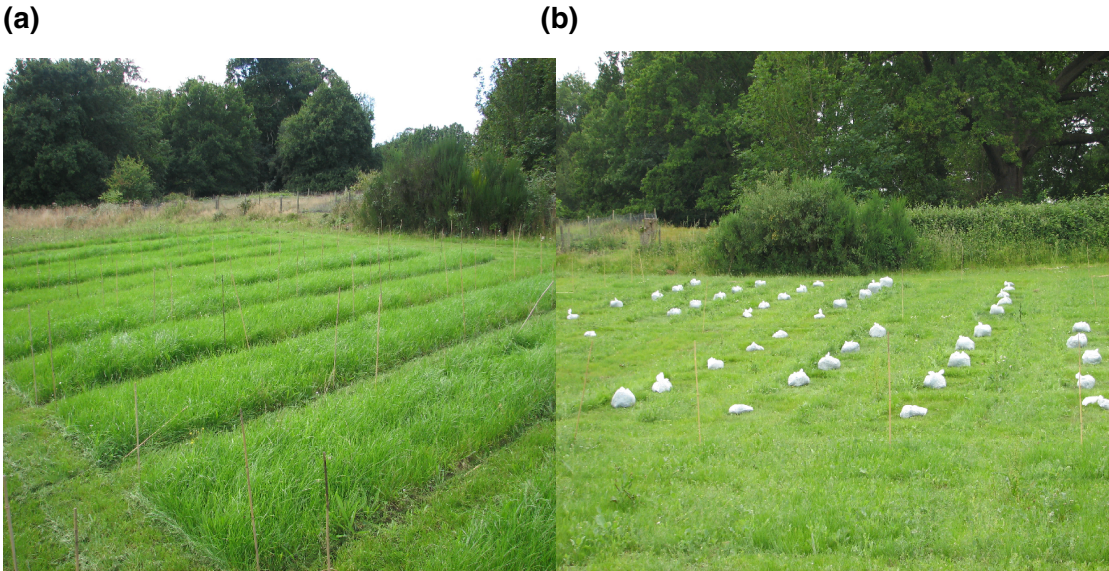


Plate 5.2 Biowastes crop response trial 2006: (a) gradient of crop response; (b) grass from each sub-plot (central 1.28 m²) was mown, raked and bagged.

5.2.3 Soil Conditions

Soil temperature and gravimetric moisture content in the 2006 trial are presented in Figure 5.2.

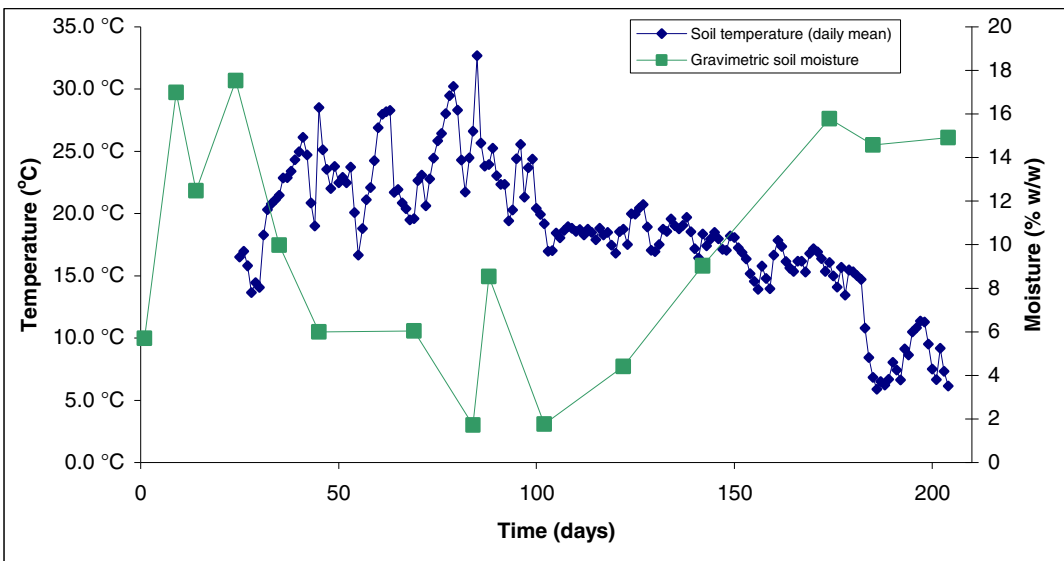


Figure 5.2 Gravimetric soil moisture (% w/w) and temperature (°C), 3 May - 22 November 2006 (days 0-203).

At the start of the experiment in May, there was a period of rainfall, resulting in peaks in soil moisture content of approximately 17 % (day 9 and day 24). Soil moisture decreased during the summer months to a minimum of approximately 2 % (day 100) and increased again between days 100-200, to approximately 15 % when the experiment was completed at the end of November. Soil temperature increased from approximately 15 °C during May, to between 20-30 °C, from days 50-100 (end of June-August). The temperature then gradually decreased to between 4-8 °C in November.

5.2.4 Determination of Residual Fertiliser Value

On 1 May 2007, NH_4NO_3 was re-applied to the mineral N calibration plots at rates of 0, 30, 60, 90 and 120 kg N ha⁻¹. However, no second year growth was observed on the plots amended with biowastes the previous year, so no further harvests of the experiment were taken.

5.2.5 ICP-AES Analysis

Grass samples selected for full elemental analysis were taken from the top rates of application for each treatment and 4 control samples from each block. Samples from the first harvest only were analysed. Samples were digested using an aqua-regia method (MAFF, 1986) prior to ICP-AES (inductively coupled plasma atomic emission spectroscopy). Dried, ground grass samples, 1 g, were weighed into a 300 ml glass digestion tube, 2 ml of deionised water was pipetted to each tube thoroughly wetting the sample. Then 6 ml of HCl and 2 ml of HNO_3 were carefully added to each tube. The samples were heated on a block digestion unit (Gerhardt, Bonn, Germany); the temperature was gradually increased to 100 °C, and the samples were refluxed at this temperature for 2 h. After cooling the samples were mixed with approximately 40 ml deionised water, left to cool again, filtered to <0.45 µm and then diluted to 100 ml in volumetric flasks. Sub-samples of approximately 10 ml were transferred to plastic sample tubes for ICP-AES analysis (Fisons-ARL 3580 B ICP, Ecublens, Switzerland). They were analysed for a spectrum of 28 elements. The instrument was calibrated with standards for each element prepared in a 1M HCl matrix.

A blank sample, containing 2 ml deionised water, 6 ml of HCl and 2 ml of HNO_3 was included in each batch. In addition, a spiked sample containing known concentrations

of the elements to be analysed was digested to check efficiency of the procedure, and 5 % of the samples were replicated.

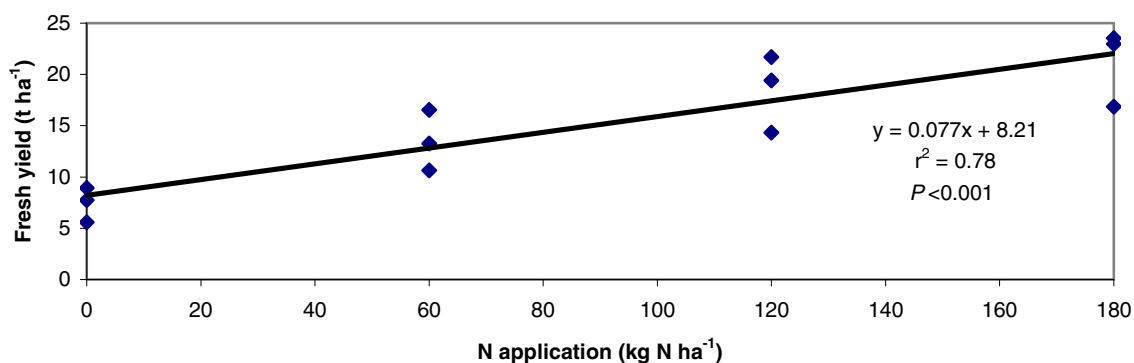
5.3 Results and Discussion

5.3.1 Crop Response to Biowastes Application, and N Equivalencies

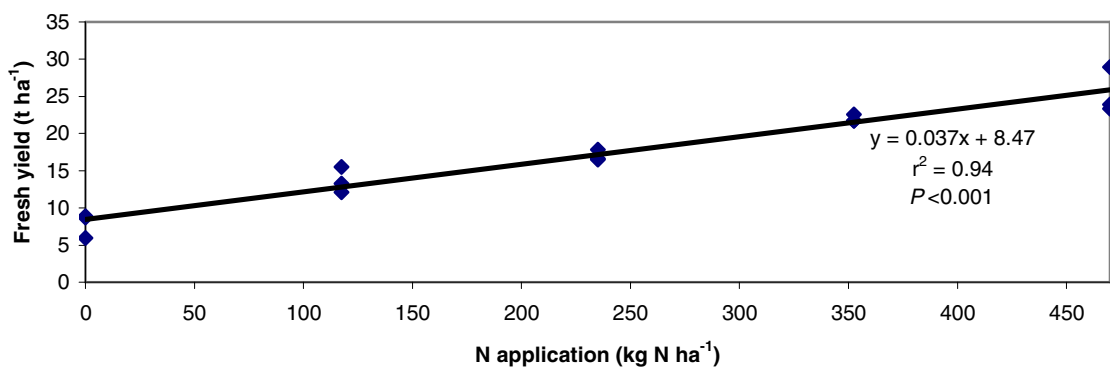
The cumulative response of perennial ryegrass to application of biowastes and mineral N fertiliser application, measured as fresh yield, dry yield and as N offtake is shown in Figures 5.3 - 5.11. The crop response was plotted against rate of total N application in the biowastes and mineral N fertiliser, with the exception of biowastes with a low total N content, where a base or top dressing of N was applied (treatments 3, 4 and 7-11, Figure 5.1), where crop response was plotted against rate of application (DS ha^{-1} ; $\text{m}^3 \text{ha}^{-1}$). Where a significant linear relationship between rate of application of N, or rate of application, and crop response was found, r^2 and P -values from an ANOVA test of significance are given. In the case of a non-significant relationship the mean values are plotted.

Crop response in soil treated with an increasing rate of mineral N reached a maximum before the top rate of application (240 kg N ha^{-1}). Elemental analysis of plant material from the top rates of application from the first harvest, was conducted to investigate the nutrient status of the ryegrass. Tissue content of major nutrient elements are presented in Table 5.1, further tissue element concentrations are given in Appendix A4. Typical nutrient element concentrations in perennial ryegrass, taken from Whitehead (1995), are shown in Table 5.2. This data was examined to determine whether other nutrient elements in the mineral N plots may have been limiting growth at top rates of application when the response became curvilinear. Sulphur may have been limiting in the top rates of application in the mineral N control plots as mean concentrations were $1.34 \text{ mg g}^{-1} \text{ DM}$, which was below the typical S content in perennial ryegrass, of $2\text{-}5 \text{ mg g}^{-1} \text{ DM}$. Plant tissue contents of P and Mg in the mineral N controls were within the normal range. Tissue K content was $33.6 \text{ mg g}^{-1} \text{ DM}$, slightly greater than the typical concentration of $15\text{-}28 \text{ mg g}^{-1} \text{ DM}$, and the Ca content was also slightly greater than the expected range.

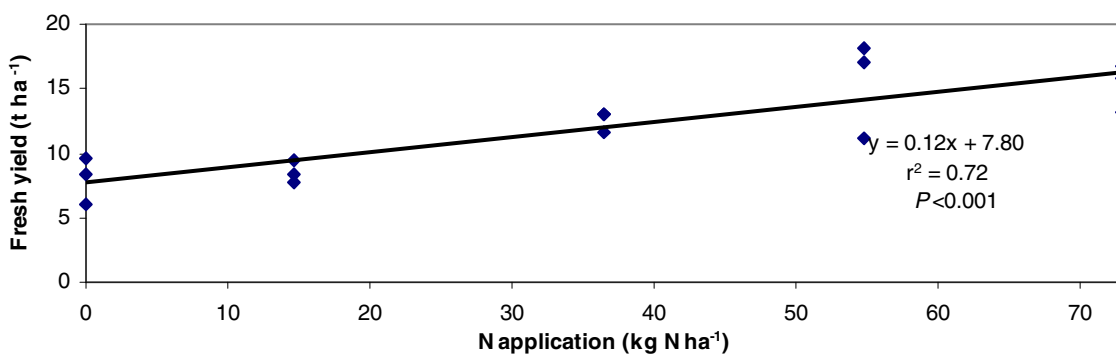
(a) Mineral N control



(b) DMAD



(c) Abattoir



(d) AD fresh & AD stored

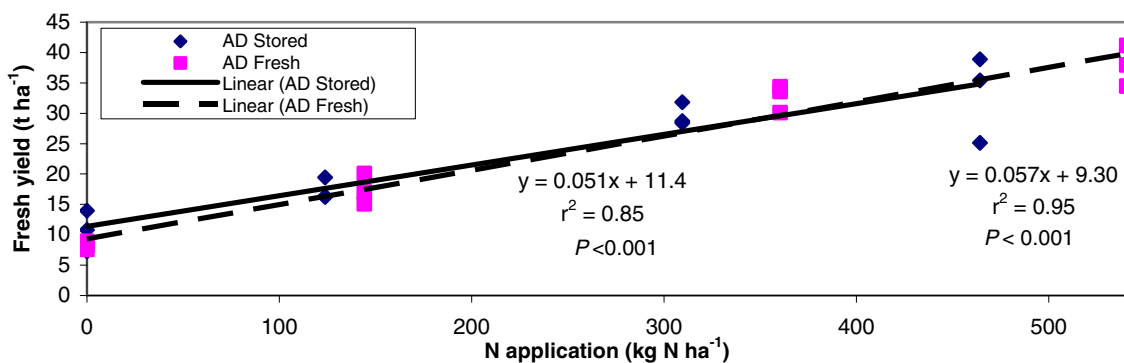
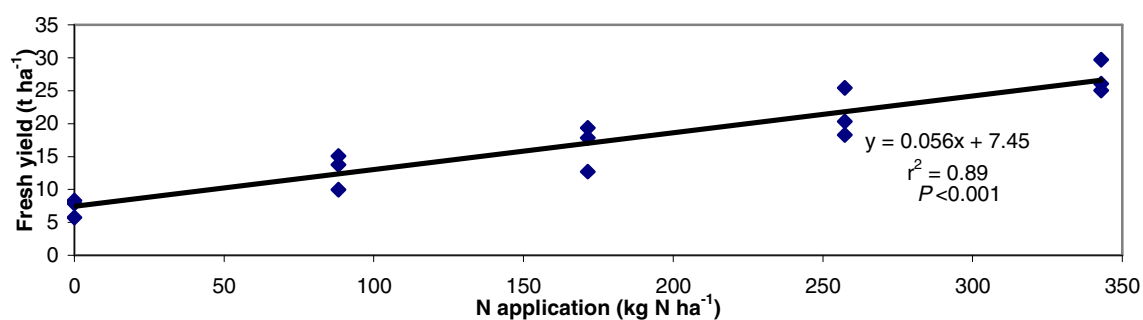


Figure 5.3 Cumulative ryegrass yield (4 harvests, fresh yield) relative to N application from mineral N fertiliser, biosolids and biowastes. Regression equation, r^2 value and P value from an ANOVA test of significance are shown.

(e) TAD



(f) ADMSW

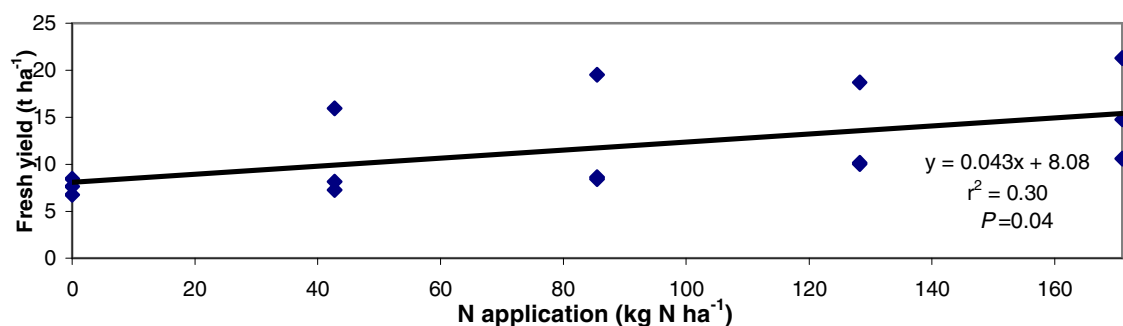
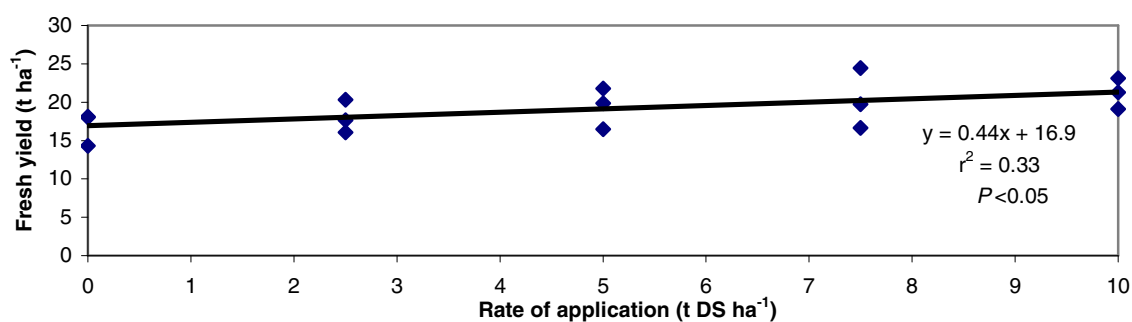


Figure 5.3 cont.

(a) Trout old



(b) KG

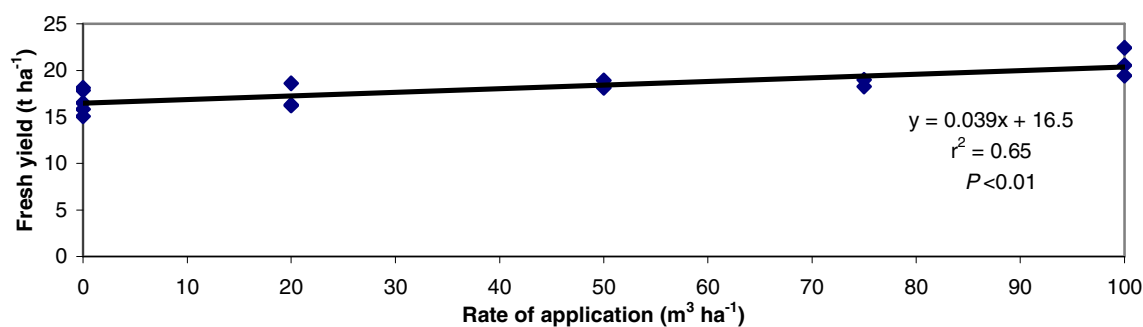
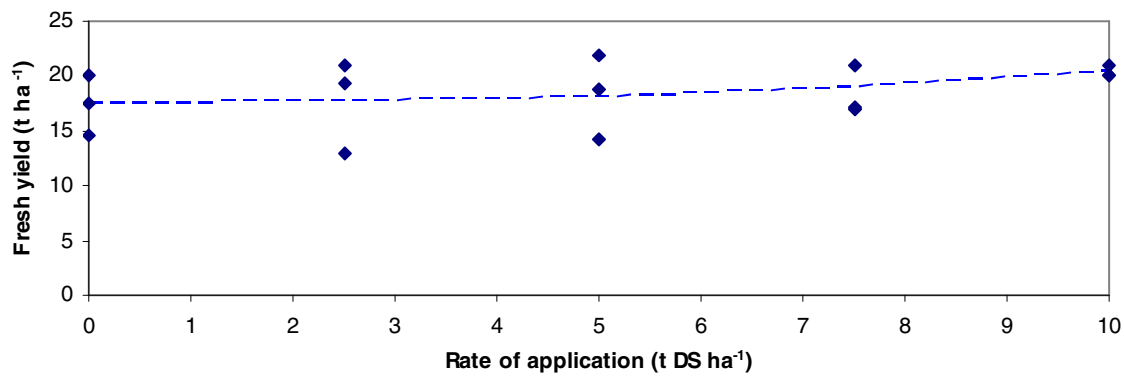
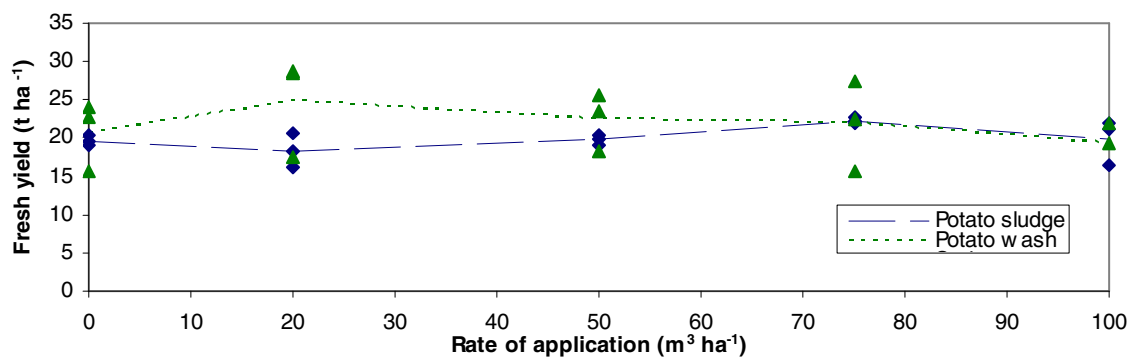


Figure 5.4 Cumulative ryegrass response (4 harvests, fresh yield) relative to rate of application of biowastes (t DS ha⁻¹ or m³ ha⁻¹). Regression equation, r^2 value and P value from an ANOVA test of significance are shown.

(a) Trout Fresh



(b) Potato sludge & Potato wash



(c) Ice-cream & Ice-cream DAF

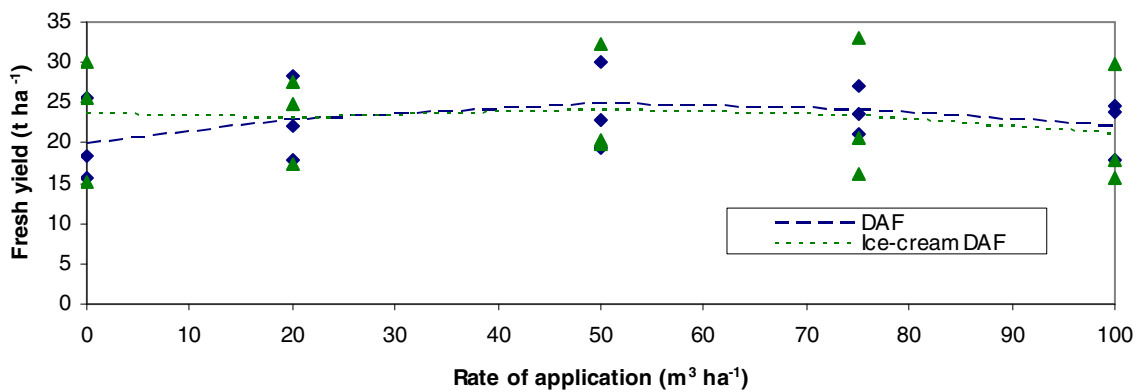
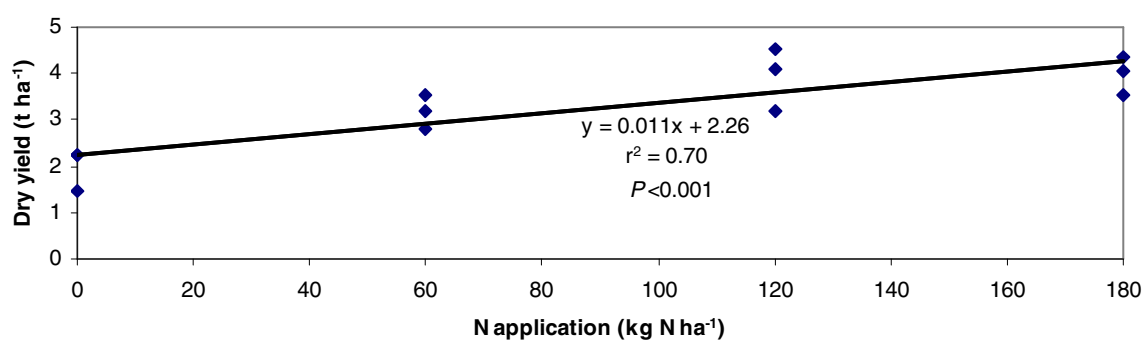
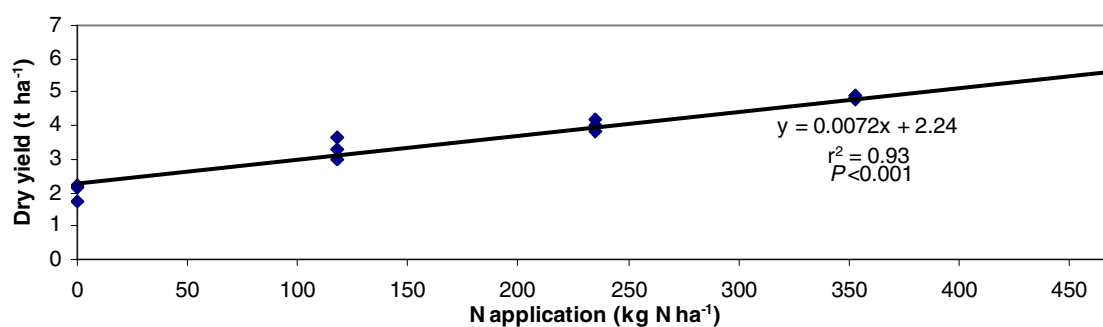


Figure 5.5 Cumulative ryegrass response (4 harvests, fresh yield) relative to rate of application of biowastes (t DS ha⁻¹ or m³ ha⁻¹), --- or --- indicate mean cumulative fresh yield (t ha⁻¹); no significant ($P>0.05$) relationship was detected.

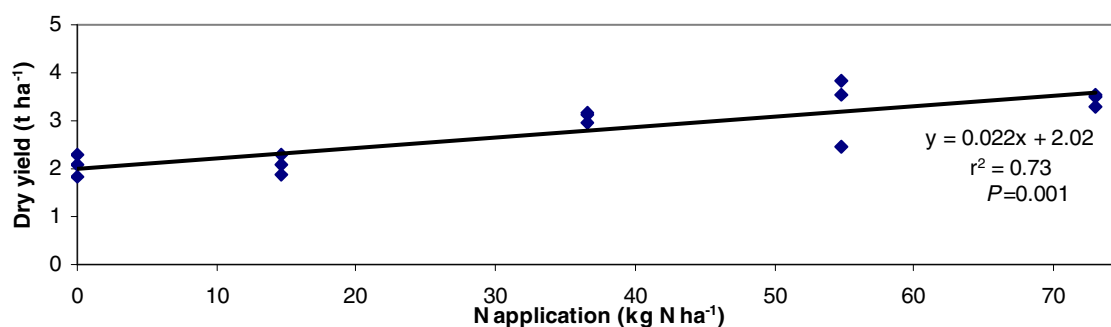
(a) Mineral N control



(b) DMAD



(c) Abattoir



(d) AD fresh & AD stored

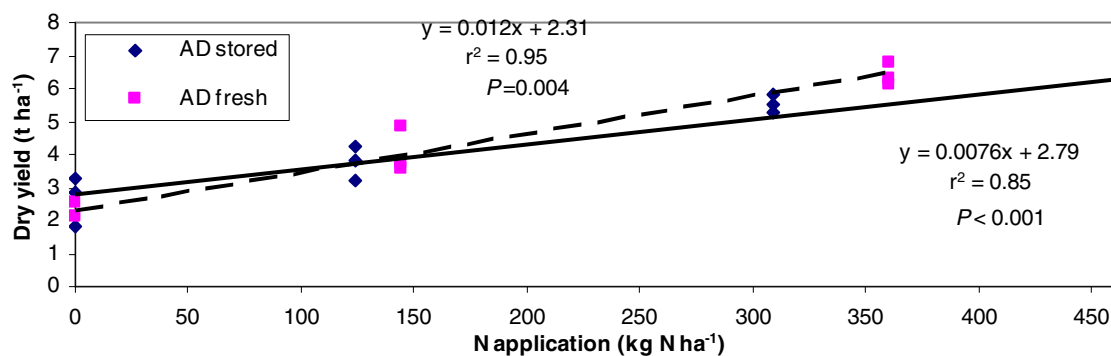
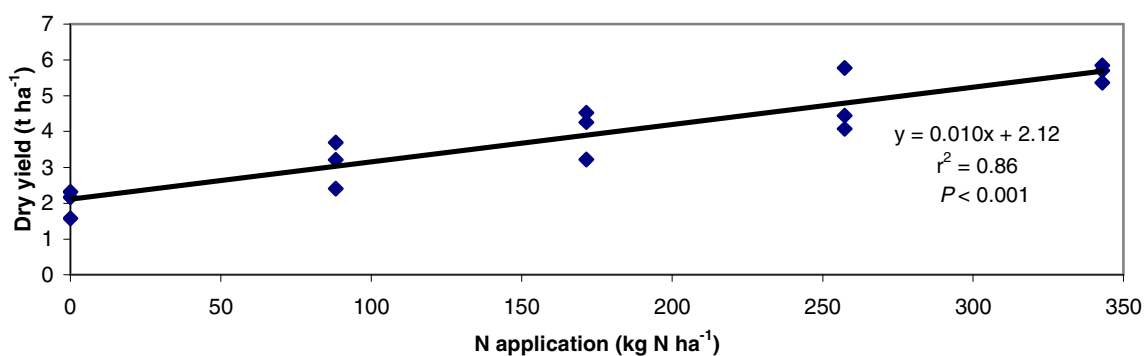


Figure 5.6 Cumulative ryegrass yield (4 harvests, dry yield) relative to N application from mineral N fertiliser and biowastes treatments. Regression equations, r^2 values and P values from ANOVA test of significance are shown on each graph.

(e) TAD



(f) ADMSW

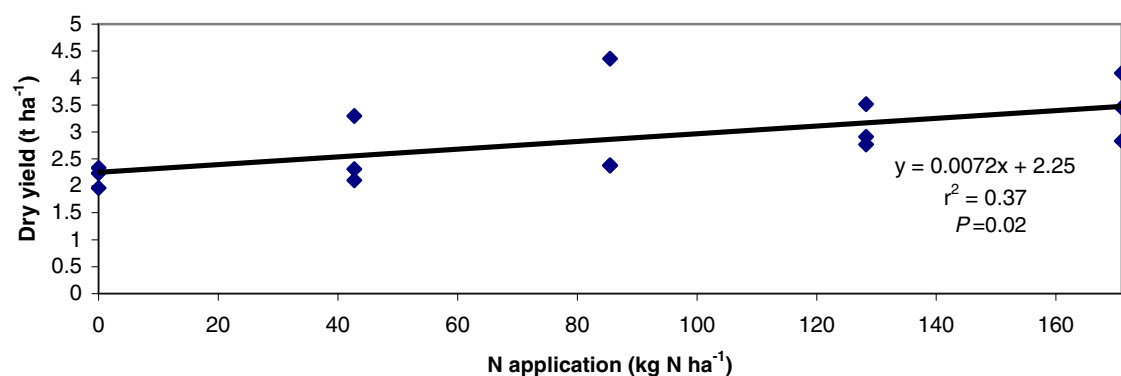


Figure 5.6 cont.

(a) Trout old

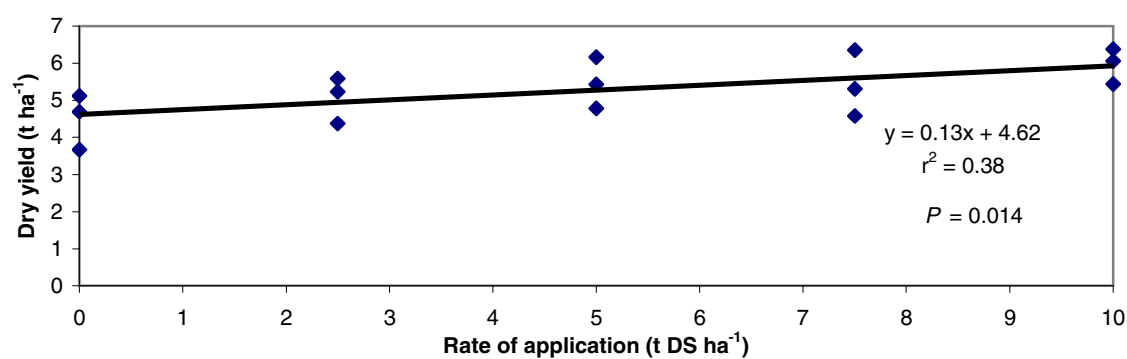
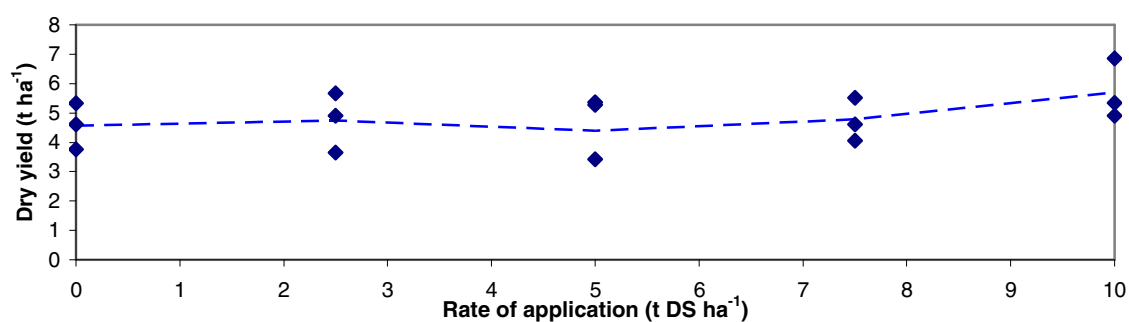
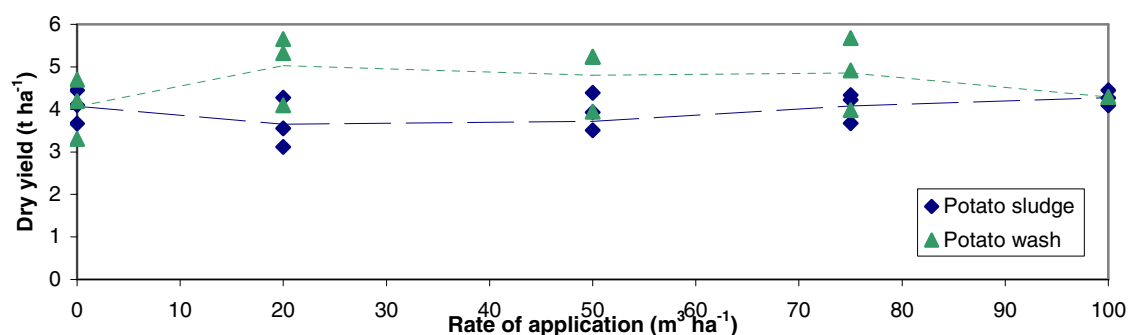


Figure 5.7 Cumulative ryegrass response (4 harvests, dry yield) relative to rate of application of biowastes (t DS ha⁻¹ or m³ ha⁻¹). Regression equation, r^2 value and P value from an ANOVA test of significance are shown.

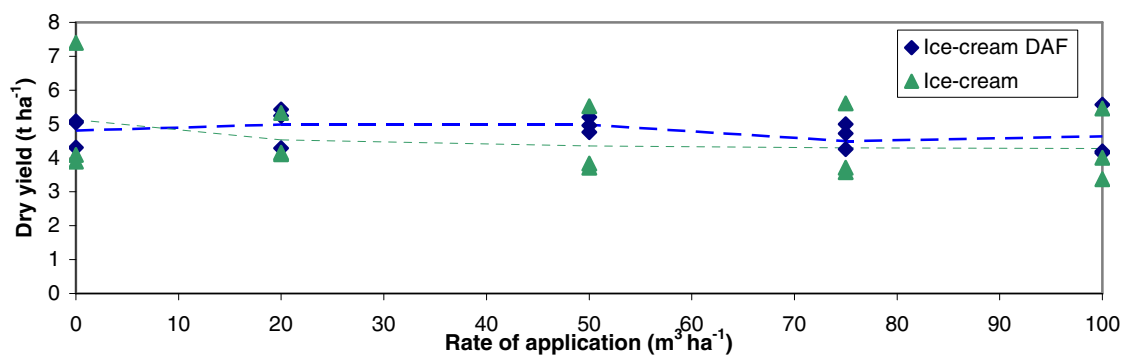
(a) Trout fresh



(b) Potato sludge & Potato wash



(c) Ice-cream & Ice-cream DAF



(d) KG

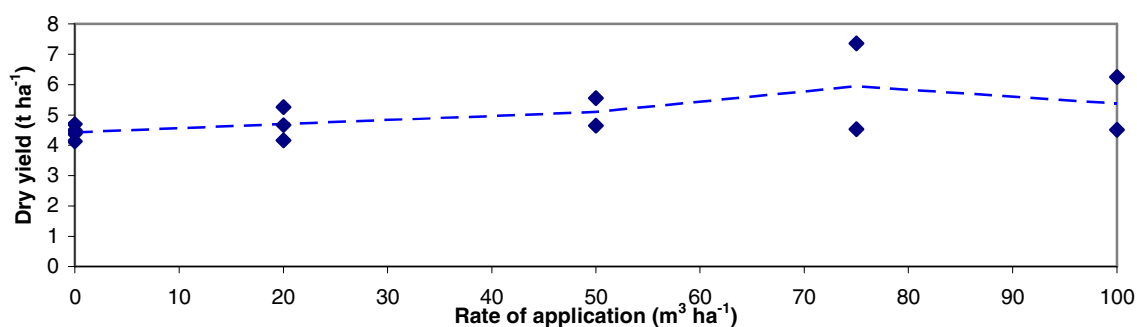
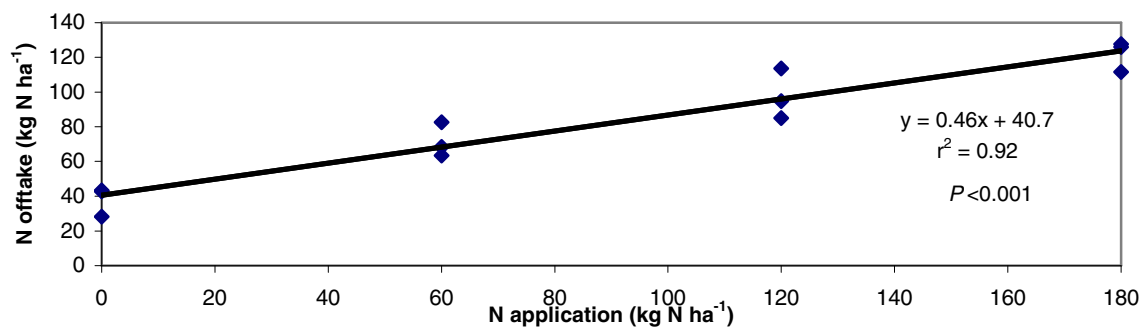
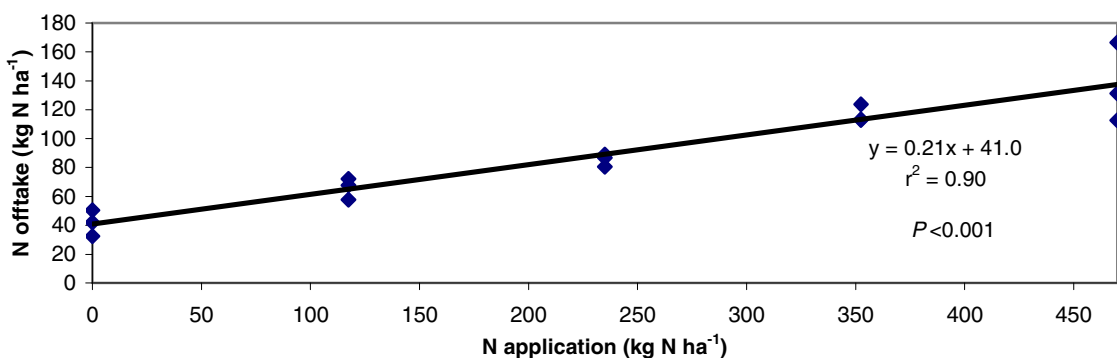


Figure 5.8 Cumulative ryegrass response (4 harvests, dry yield) relative to rate of application of biowastes (t DS ha⁻¹ or m³ ha⁻¹), --- or --- indicate mean cumulative fresh yield (t ha⁻¹); no significant relationship was detected ($P > 0.05$).

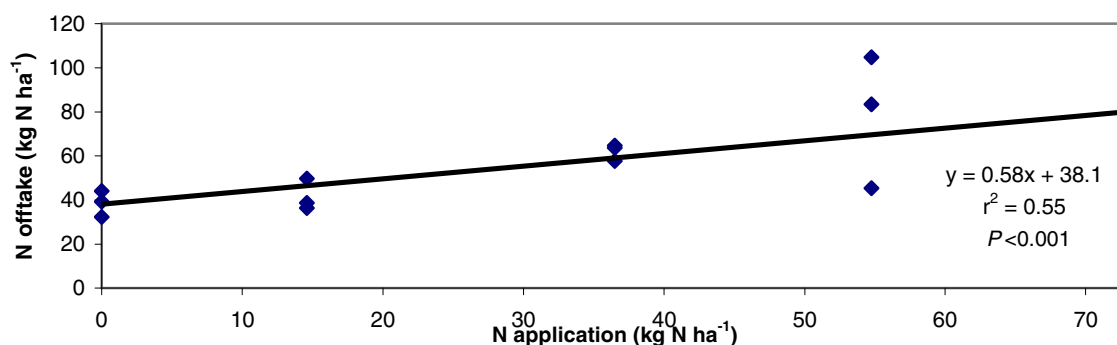
(a) Mineral N control



(b) DMAD



(c) Abattoir



(d) AD fresh & AD stored

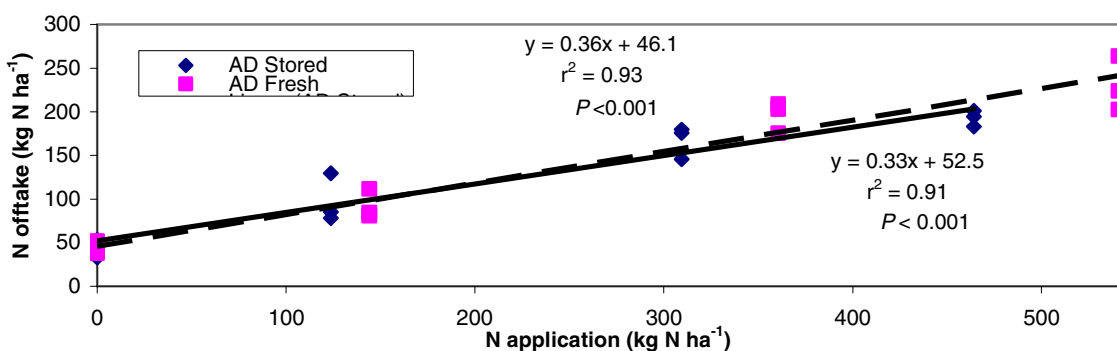
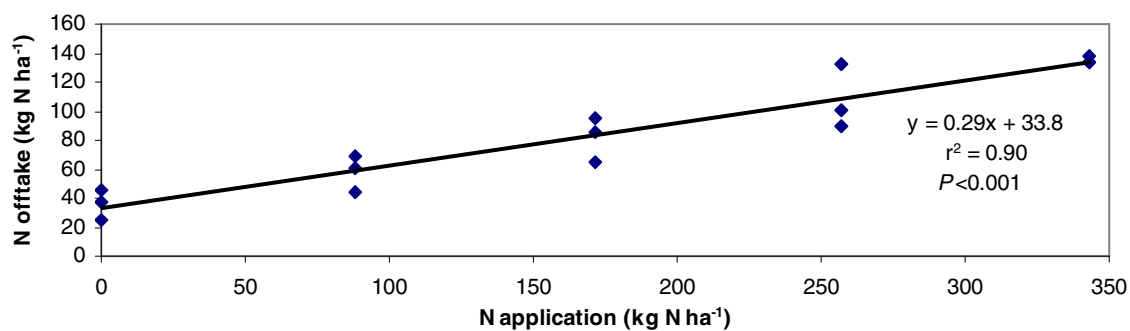


Figure 5.9 Cumulative ryegrass response (4 harvests, N offtake) relative to N application from mineral N fertiliser, biosolids and biowastes. Regression equations, r^2 values and P values from ANOVA test of significance are shown on each graph.

(e) TAD



(f) ADMSW

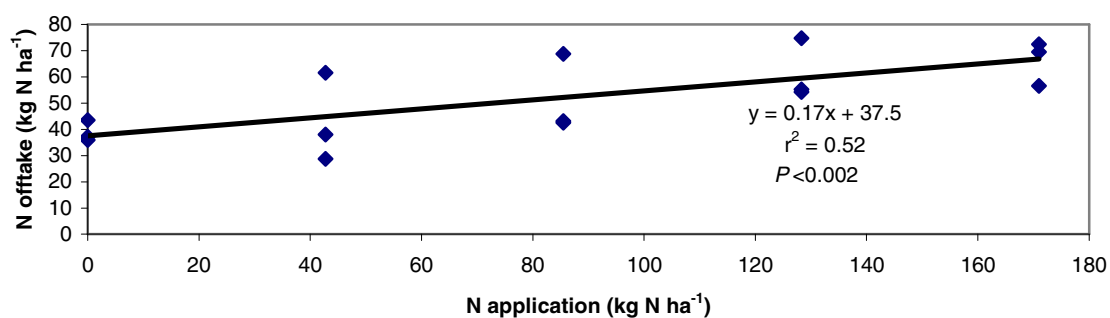
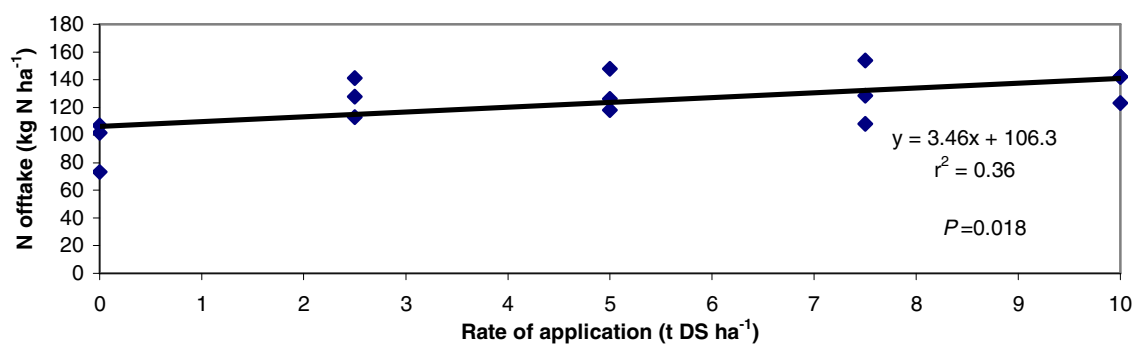


Figure 5.9 cont.

(a) Trout old



(b) Ice-Cream DAF

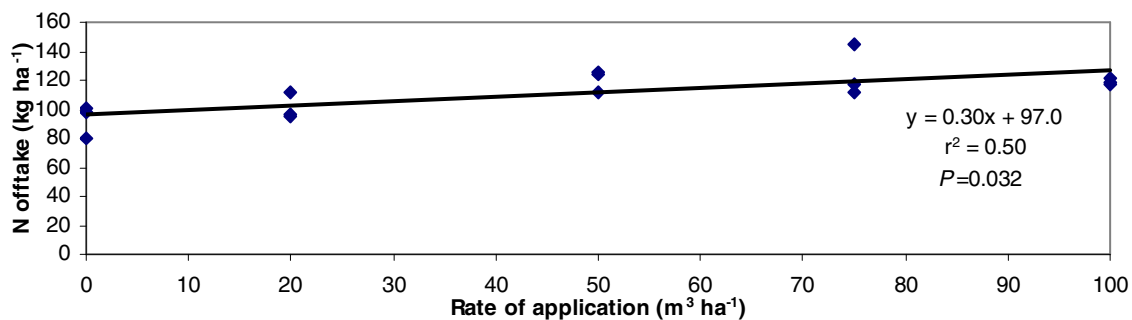
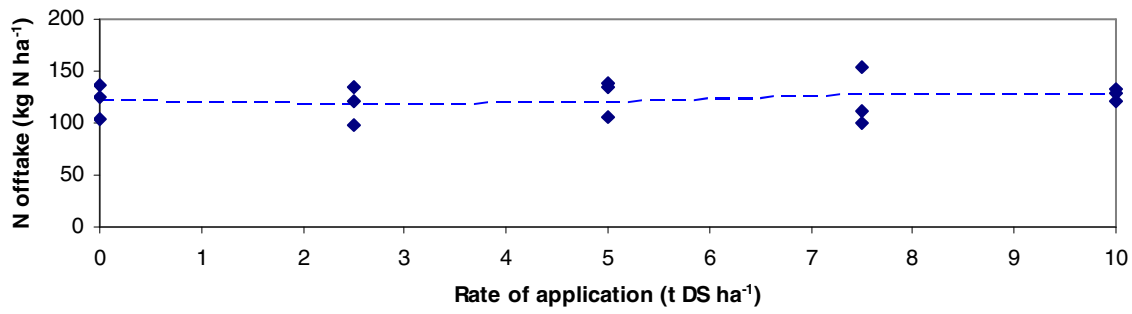
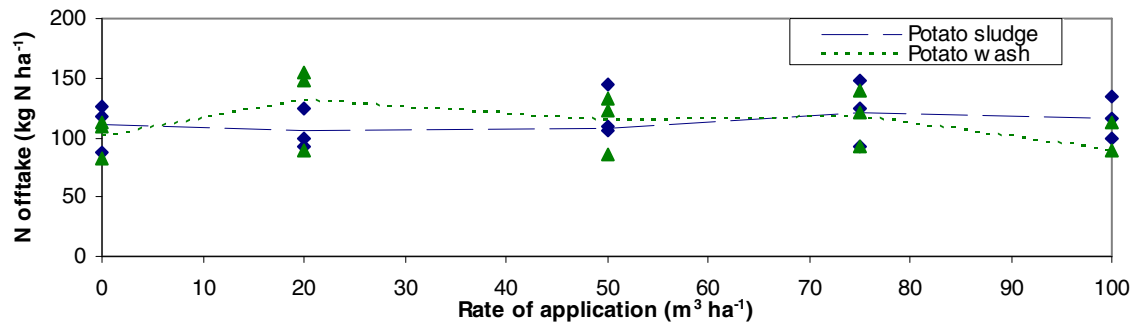


Figure 5.10 Cumulative ryegrass response (4 harvests, N offtake) relative to rate of application of biowastes (t DS ha⁻¹ or m³ ha⁻¹). Regression equation, r^2 value and P value from an ANOVA test of significance are shown.

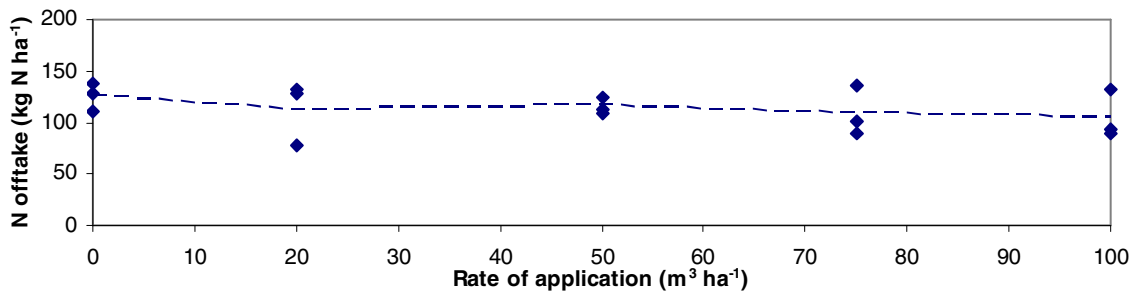
(a) Trout fresh



(b) Potato sludge & Potato wash



(c) Ice-cream



(d) KG

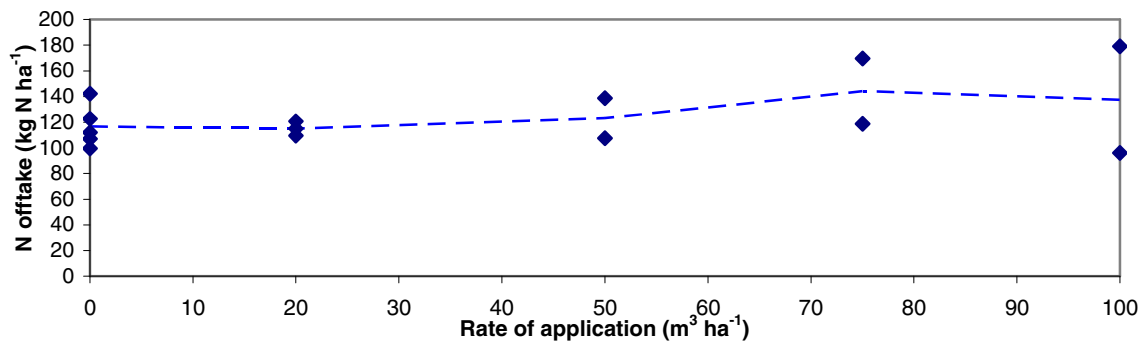


Figure 5.11 Cumulative ryegrass response (4 harvests, N offtake) relative to rate of application of biowastes (t DS ha⁻¹ or m³ ha⁻¹), --- or --- indicate mean cumulative fresh yield (t ha⁻¹); no significant relationship was detected ($P>0.05$).

Table 5.1 Concentrations of plant nutrient elements (P, K, Mg, Ca, S) in ryegrass grown on unamended and mineral N-, biosolids- and biowastes-amended soil.

Treatment	Element concentration (mg g ⁻¹ DM)				
	P	K	Mg	Ca	S
Control A [†]	3.02	30.9	1.88	12.0	1.47
Control B [†]	3.16	28.2	2.25	11.7	1.94
Control C [†]	3.02	32.4	1.67	11.6	2.22
Mean Control	3.06	30.5	1.93	11.8	1.88
Mineral N A	3.58	32.9	2.46	16.2	1.50
Mineral N B	3.62	33.1	1.95	15.8	1.23
Mineral N C	3.14	34.6	1.77	10.9	1.29
Mean Mineral N	3.44	33.6	2.06	14.3	1.34
DMAD A	2.61	36.9	1.91	13.7	4.51
DMAD B	3.46	38.5	1.46	12.4	5.66
DMAD C	2.56	35.2	1.58	10.3	4.96
Mean DMAD	2.88	36.8	1.65	12.1	5.04
Abattoir A	4.18	36.1	2.35	13.7	1.95
Abattoir B	3.99	36.1	1.53	14.1	1.61
Abattoir C	2.64	30.4	1.10	7.9	1.46
Mean Abattoir	3.60	34.2	1.66	11.9	1.68

Table 5.1 cont.

	Element concentration (mg g ⁻¹ DM)				
Treatment	P	K	Mg	Ca	S
Trout old A	1.50	23.2	2.50	9.24	1.82
Trout old B	1.97	20.1	2.09	14.0	2.69
Trout old C	2.07	23.9	1.69	10.6	2.38
Mean Trout old	1.85	22.4	2.09	11.3	2.30
Trout new A	1.92	22.2	1.95	10.9	2.13
Trout new B	2.00	20.2	2.35	11.3	1.55
Trout new C	1.70	19.2	1.64	12.5	2.24
Mean Trout new	1.87	20.6	1.98	11.6	1.98
Potato sludge A	3.65	33.8	2.57	11.9	1.78
Potato sludge B	3.81	44.9	1.92	7.8	1.37
Potato sludge C	3.37	36.1	1.67	11.5	2.92
Mean Potato sludge	3.61	38.3	2.05	10.4	2.02
Potato wash A	2.64	35.0	2.41	14.1	2.96
Potato wash B	3.18	32.3	1.80	8.62	1.01
Potato wash C	3.31	33.8	1.34	12.9	3.47
Mean Potato wash	3.04	33.7	1.85	11.9	2.48

Table 5.1 cont.

	Element concentration (mg g ⁻¹ DM)				
Treatment	P	K	Mg	Ca	S
KG A	2.42	25.0	1.98	9.10	1.52
KG B	2.08	21.6	1.58	8.39	1.50
KG C	1.70	18.3	1.62	14.3	2.74
Mean KG	2.07	21.6	1.73	10.6	1.92
Ice-cream A	2.82	21.9	1.63	10.6	1.77
Ice-cream B	2.07	21.0	1.95	7.10	1.41
Ice-cream C	2.25	24.4	1.26	7.96	2.00
Mean Ice-cream	2.38	22.4	1.61	8.55	1.73
DAF A	1.56	20.2	1.76	10.2	2.19
DAF B	2.08	32.2	2.16	10.2	2.06
Mean DAF	1.82	26.2	1.96	10.2	2.12
AD fresh A	2.71	43.0	2.22	11.1	2.36
AD fresh B	3.63	40.2	2.34	17.7	2.12
AD fresh C	2.94	27.1	1.51	8.88	1.85
Mean AD fresh	3.09	36.8	2.02	12.5	2.11

Table 5.1 cont.

	Element Concentration (mg g ⁻¹ DM)				
Treatment	P	K	Mg	Ca	S
AD stored A	3.67	41.1	1.76	12.8	3.17
AD stored B	2.97	38.7	1.77	7.11	2.11
AD stored C	3.03	46.5	1.19	6.61	2.48
Mean AD Stored	3.22	42.1	1.57	8.83	2.58
TAD A	2.55	39.2	1.12	7.48	2.82
TAD B	3.00	44.3	1.19	5.68	1.69
TAD C	2.60	39.4	0.96	5.62	1.79
Mean TAD	2.72	41.0	1.09	6.26	2.10
ADMSW A	3.58	37.7	1.72	11.8	2.99
ADMSW B	3.37	34.9	1.95	12.4	4.39
ADMSW C	2.92	30.0	1.56	13.7	4.20
Mean ADMSW	3.29	34.2	1.74	12.6	3.86

[†] Mean value (n=4)

Table 5.2 Typical perennial ryegrass tissue nutrient element composition (Whitehead, 1995).

Element concentration (mg g ⁻¹ DM)					
N	P	K	Mg	Ca	S
20-35	3-6	15-28	1-3	4-8	2-5

A summary of the linear regression coefficients and r^2 values is provided in Table 5.3. Nitrogen equivalency values were calculated for biowastes treatments that demonstrated a significant relationship between rate of N application and crop response at $P \geq 0.05$, by comparing linear regression coefficients with mineral fertiliser N as described in Section 3.7.2. Values were determined using the three measures of crop response, dry yield, fresh yield and N offtake, these are shown in Table 5.4. The N equivalency values were summarised by expressing as a mean of the three measures of crop response. N equivalencies calculated from yield data, with the exception of AD stored were greater than for N offtake, so the mean values from the yield data are also shown separately. Mineralisable N contents of each of the wastes were calculated from the mean N equivalency values and the mineral N contents of the biosolids or biowastes are expressed as a percentage of total or organic N, these values are also shown in Table 5.4.

The N equivalency value relative to mineral N obtained for abattoir wash water was 1.6. It was not possible to calculate a mineralisable N value for this waste as the N equivalency value was greater than the total amount of N supplied in the abattoir wash water. Although the available N in abattoir waste was higher than the other biowaste materials at 65 % (Table 3.13), this value was unusual as an N equivalency of 1 or below would be expected if the crop response was dependent on N input alone. Therefore, it was assumed that other factors were contributing to the crop response, for example the input of K, Mg and S or trace elements may have improved the nutritional status of the soil. However, following nutrient analysis of plant material from the top rates of application, no difference was found in the major nutrient element concentrations between the mineral N control and abattoir wash water.

Other researchers have found greater yields from similar types of animal protein wastes in comparison to inorganic N fertiliser. In a three year crop response experiment with ryegrass, Douglas *et al.* (2003) also found that abattoir waste applied at a rate of 250 kg total N ha⁻¹ produced yields that were equal to or significantly greater than mineral N fertiliser applied at the same rate of N, apparent N recovery was also larger in the crop fertilised with abattoir waste.

Table 5.3 Summary table of linear regression coefficients and r^2 values for mineral fertilisers, biosolids and biowastes in 2006 field experiment.

	Fresh yield		Dry yield		N offtake	
	Slope	r^2	Slope	r^2	Slope	r^2
Ammonium nitrate	0.077	0.78	0.011	0.70	0.46	0.92
DMAD	0.037	0.94	0.0072	0.93	0.21	0.90
Abattoir	0.12	0.72	0.022	0.73	0.58	0.55
Trout old [†]	0.44	0.33	0.13	0.38	3.46	0.36
Ice-Cream DAF [†]	NS	NS	NS	NS	0.30	0.50
KG [†]	0.039	0.65	NS	NS	NS	NS
AD fresh	0.057	0.95	0.012	0.95	0.36	0.93
AD stored	0.051	0.85	0.0076	0.85	0.33	0.91
TAD	0.056	0.89	0.01	0.86	0.29	0.90
ADMSW	0.043	0.30	0.0072	0.37	0.17	0.52

NS=not significant at $P \leq 0.05$

[†] Low total N wastes: regression relative to rate of application

Table 5.4 Nitrogen equivalency values of biosolids and biowastes for each measure of crop response (fresh yield; dry yield and N offtake) based on comparison of linear regression coefficients with mineral N control, and mineralisable N contents of each material

Biowaste	Fresh yield	Dry yield	N offtake	Mean yield data	Mean all	Mineralisable N [†]	
						(% total N)	(% organic N)
DMAD	0.48	0.64	0.45	0.56	0.52	42.1	47.0
Abattoir	1.51	1.92	1.24	1.78	1.60	-	-
AD fresh	0.74	1.03	0.78	0.98	0.85	45.5	75.0
AD stored	0.66	0.68	0.70	0.67	0.68	21.4	40.1
ADMSW	0.56	0.64	0.37	0.61	0.52	34.3	41.9
TAD	0.73	0.93	0.63	0.81	0.76	68.0	74.1

[†] Mineralisable N = N equivalency (mean all) (%) – Mineral N content of biosolids/biowastes

The abattoir waste was blood and gut contents, so was less dilute than the wash water used in this experiment, however, the materials are likely to be similar in terms of the N-containing compounds. Smith and Hadley (1988) found that base-applied dried blood, at rates between 125-500 kg N ha⁻¹, produced greater yields than NH₄NO₃. They suggested that the mode of N release from organic N sources may explain the increased response, and that plant roots were not sufficiently developed to absorb the large pool of available N from inorganic fertiliser sources immediately after planting. It may be that the sources of N in abattoir wash water, which were mainly NH₄-N and simple organic molecules were better utilised than NH₄NO₃, which may have been more at risk from leaching from the root zone. The DS content of the abattoir waste was very low, 0.13 %, so the application rate of N was between 15-75 kg N ha⁻¹ compared to 60–240 kg N ha⁻¹ for the mineral N calibration plots. Therefore, the range of crop response to application of this biowaste was not well represented by the mineral N fertiliser gradient. This may partially account for the high apparent N equivalency value as the application rate of N in abattoir waste was at the low end of the mineral N response curve.

A biosolids treatment, DMAD, was included as a reference material as the N fertiliser value and agronomic benefit of this product has been well researched, and has been shown to behave consistently (Terry *et al.*, 1979; Parker and Sommers, 1983; Smith *et al.*, 1998b;c;d; Smith and Bellett-Travers, 2001; Breedon *et al.*, 2003; Smith *et al.*, 2002; Morris *et al.*, 2003; Petersen *et al.*, 2003). There was a significant linear relationship between the rate of application of DMAD and crop response ($r^2 = 0.90-0.94$) and an N equivalency of 0.52 was calculated. This value was greater than values found in previous field trials. In a programme of trials at Silwood Park, a yield of 0.30 relative to mineral N was measured for DMAD treated soil (Smith *et al.*, 2001; Smith and Bellett-Travers, 2002; Morris *et al.*, 2003).

The high N equivalency for DMAD obtained in the 2006 trial may have been a result of other nutrients such as P, K, Mg or S influencing the crop response. Morris *et al.* (2003) applied a base dressing of K₂SO₄ across the field site. Here, however, the aim was to measure the gross agronomic value of the biowastes without correcting the background nutrient status of the soil. Nutrient availability measurements were primarily focussed on the N fertiliser value as this nutrient is usually the most important of agronomic value supplied to soil in biosolids and biowastes and is the most limiting to agricultural yields (Cooke, 1982). It is interesting to note that the N equivalency for N offtake measured here was lower than the equivalencies calculated for yield, 0.45 for

N offtake compared to 0.48 and 0.64 for fresh and dry yields respectively. This indicated that, as suggested by Kiemnec *et al.* (1987), N offtake may have been a more sensitive indicator of N availability than yield. However, if the supply of nutrients other than N were contributing to increased crop growth in DMAD treatments relative to the mineral N control, then N offtake would, of course, increase to some extent as a function of increased yield. The N equivalency of DMAD calculated from dry yield was particularly high, this may be explained by examining the mineral N control response curve for dry yield. It appeared that there was a diminishing increase in response of dry yield to N application of 180 kg N ha⁻¹, however, the linear regression was highly significant ($P < 0.001$).

Elemental analysis of plant tissue was conducted here to examine transfer of nutrients from biowastes to crops and to determine whether other elements were contributing to the crop response. Biosolids provided some K, although they were a poor source in relation to TAD for example, which contained approximately 6 times the amount of this element compared to DMAD (Tables 3.6 and 3.8). This is because K is a soluble cation and is largely elutriated from the solids during wastewater treatment and hence DMAD is not considered an agronomically relevant source of K (Hall, 1983a). From the elemental analysis (Table 5.1), it can be seen that plant material fertilised with DMAD had slightly greater concentrations of K, 36.8 mg g⁻¹ DM, compared to 33.6 mg g⁻¹ in the mineral N control. Warman (1986) found that aerobically digested sewage sludge applied to a sandy loam soil at rates of 4.5 and 9 t DS ha⁻¹ produced K concentrations in plant tissue that were as low as an unamended control in some cases and significantly lower than crops fertilised with pig manure and inorganic fertiliser at similar rates of N application. They found that the percentage recovery of K was highest in sewage sludge-amended treatments, but explained this due to the crop drawing on the soil pool. In this experiment, the ryegrass K concentration in DMAD amended treatments was similar to or greater than other treatments, despite its low K content; this may also be a result crop uptake of background soil K.

Plant tissue from the biosolids treatment had much greater S contents, 2.5 times the amount of S, 5.04 mg g⁻¹ DM compared to 1.34 mg g⁻¹ DM in the mineral N control. The typical tissue S content for perennial ryegrass is 2-5 mg g⁻¹ DM. These results indicated that other elements, primarily S, were potentially contributing to the crop response in DMAD-amended soil and explained the higher relative values obtained for DMAD in comparison to the previous programme of experiments at Silwood Park. This might be expected from the nutrient analysis of the materials as DMAD had the

greatest concentration of S, 9.3 g kg^{-1} compared to the amounts of S supplied by the biowastes (Tables 3.6 and 3.8). Biosolids application rates of between $10\text{-}19 \text{ t ha}^{-1}$ DS have previously been found to increase plant available S (Chambers *et al.*, 2003). Previous research has shown that corn and forage grass fertilised with sewage sludge compost and septic sludge have elevated tissue concentrations of S in comparison to mineral fertiliser treatment (Warman and Termeer, 2005). In an experiment to investigate the effectiveness of sewage sludge as a fertiliser for spinach, Türkmen *et al.* (2008) found that applications of sewage sludge at similar rates to the top rate in this investigation (15 t DS ha^{-1}) significantly increased tissue K and S contents in comparison to unamended control soil.

Crop response to the digestates showed a strong linear relationship with increasing rate of application, and N equivalency values similar to, or greater than, DMAD. Nitrogen equivalency for ADMSW was equivalent to DMAD, at 0.52; this is to be expected from the high available N content of ADMSW. Despite its lower total N content, ADMSW had a high available N content of 18.2 % relative to total N, compared to 10.3 % available N in DMAD. This suggested that, as the N equivalency values for each material were the same, of the remaining organic N, DMAD had a larger mineralisable fraction overall, 47 % compared to 42 %. Composted municipal solid waste has previously been found to be a moderate to poor source of N (Wolkowski, 2003) with an N equivalency of 0.17 in the first year. These results suggest that MSW treated by anaerobic digestion may have significantly greater fertiliser N replacement value than composted biowastes, as a high proportion of N may be lost by volatilisation of NH_3 during composting. Elemental analysis also revealed that S may have some contribution to the crop response in ADMSW soils as the concentration in grass was more than double in ADMSW fertilised grass, 3.86 mg g^{-1} compared to 1.34 mg g^{-1} in mineral N treatments (Table 5.1). This is consistent with the relatively high S content demonstrated by initial nutrient analysis of the biowastes (Table 3.8). As found with the response to DMAD application, the N equivalency calculated from N offtake alone was 0.37, much lower than the mean value from yield data of 0.61, supporting the observation that crop response to ADMSW was influenced by other nutrients such as S.

Thermophilic Aerobic Digestate (TAD) had a slightly lower total N and available N (% total N) in comparison to DMAD (Table 3.10 and 3.12), but its N equivalency was 0.76 (Table 5.3), and was comparable to values that might be expected from liquid slurries or biowastes with a high proportion of N in mineral forms. This indicated that, despite

its relatively low mineral N content, TAD had a very high proportion of rapidly mineralisable organic N, 74 % organic N, compared to between 41-47 % organic N in the anaerobically digested wastes, with the exception of AD fresh. There was a greater mineralisable fraction of 75 % organic N in AD fresh. However, this waste had a much greater mineral N content so as a percentage of the total N, the mineralisable organic N in TAD was greater. This is consistent with research that demonstrates that aerobically digested biosolids have a greater pool of mineralisable N than anaerobically digested biosolids (Hall, 1983a; Serna and Pomares, 1991a; Serna and Pomares, 1991b; Hernández *et al.*, 2002). From elemental analysis of plant material, it was determined that TAD was an effective source of available K as the concentration in the plant tissue was 41.0 mg g⁻¹ DM compared to 33.6 mg g⁻¹ DM for the mineral N control.

The AD fresh and AD stored also had greater N equivalencies compared to DMAD of 0.85 and 0.68 respectively. The difference in performance between AD fresh and stored cannot be explained by the nutritional analysis of the biowastes. Although storage of the material resulted in lower total N, both materials had high available N concentrations of approximately 40-45 % of total N content (Table 3.13), compared to 10 % available N in DMAD (Table 3.10). The greater N equivalencies than the mineral N content indicate that a proportion of organic N was mineralised. It is likely that the differences observed between the materials are a result of the organic N fraction of AD fresh being more readily mineralisable than the stored AD, as the more readily degradable organic matter would continue to undergo mineralisation during storage, increasing the stabilisation of the material. The calculated mineralisable N fraction was nearly double for AD fresh, 75 % compared to 40 % organic N in the stored AD. Gilmour *et al.* (2003) also found that biosolids that had undergone extended long-term storage in a lagoon had lower plant available nitrogen (PAN). The material had a similar N equivalency to values determined by Shröder *et al.* (2007) for anaerobically digested cow slurry, which was 63 % in the first year. Elemental analysis of grass fertilised with AD fresh and stored showed that concentrations of K were greater in grass fertilised with the digestates in comparison to grass fertilised with mineral N alone, indicating that these materials may be a good source of available K. This is consistent with the nutritional analysis of the biowastes, which showed that the K contents of AD fresh and stored were 2102 g m⁻³ and 1765 g m⁻³ respectively. This is likely to be a result of the co-digestion of animal slurry. The S content was greater than in the mineral N control, 2.11-2.58 mg g⁻¹ DM in AD fresh/stored, compared to 1.34 mg g⁻¹ DM in the mineral N control. However, this difference in S was not as great as that

observed for ADMSW and DMAD, where the tissue S content was 3-4 times greater in comparison to mineral N fertiliser controls.

A base dressing of 120 kg N ha⁻¹ was applied to plots treated with potato processing waste, as they were expected to have low total N contents. This N fertiliser dressing was applied to ensure that the soil was not N limited and enabled crop response analysis to discern other agronomic benefits conferred by the waste treatment at the rates of application tested in this experiment. Following chemical analysis of the biowastes, KG, the ice-cream wastes and the trout farm wastes were also found to have low total N contents. A top dressing of 120 kg N ha⁻¹ was therefore also applied to these treatments to ensure that the crop was not N limited. Linear regression analysis was performed to determine whether the increase in biowaste application rate resulted in increased crop response, and the r^2 value for significant relationships are shown in Table 5.3. However, N equivalency values were not calculated in the case of a significant relationship when a top/base dressing of mineral N was also applied, as the relative response was not determined by the supply of available N from the biowastes, but some other characteristic that improved soil properties and crop growth.

Chemical analysis of the fresh and mature trout farm waste showed the materials had very similar nutritional characteristics. The trout farm waste was discharged into a settlement lagoon and it would be expected that mineral N would be lost by volatilisation and leaching and the DS content of the waste would increase during this process. The more mature waste had slightly greater DS content (Table 3.8) but the total N content was also slightly greater (Table 3.12). These waste sources may be particularly variable due to seasonal changes in the feeding and stocking regime of the farm and the management and frequency of the discharges to the lagoons. Differences between fresh and old waste collected for this experiment may not necessarily reflect the effects of length of storage, but could also reflect the seasonal variability in waste composition. No linear relationship was found between rate of application and crop response for Trout fresh but there was a linear relationship for Trout old for all measures of crop response (Table 5.3). Trout old had a slightly greater mineral N content (Table 3.12) so this may have influenced the crop response. Alternatively, the addition of Trout old may have resulted in other beneficial improvements to soil structure and WHC. Chambers *et al.* (2003) found improvements in soil physical characteristics with additions of 5-10 t ha⁻¹ OM from biosolids such as water infiltration rate and topsoil available water, and in some cases soil capacity and strength. Application of Trout old added less OM to the soil, 1.6 t ha⁻¹. However, there

may have been temporary improvements to surface soil structure, improving water infiltration rates for example, resulting in increased crop yield.

There was a significant linear relationship between application rate of Ice-cream DAF and N offtake (Figure 5.7). Ice-cream DAF had low total and available N contents (Table 3.13); however, there may have been other benefits such as addition of other nutrients or OM. Similarly, there was a significant linear relationship between fresh yield and application rate for KG, ($r^2=0.65$). In these cases, where significant increases in yield were only detected from one measure of crop response, the result may not be very meaningful; however, it does suggest some agronomic benefit of application of the wastes. There was no significant crop response following application of either of the potato wastes. However, elemental analysis of plant material showed that potato sludge was a good source of K, the concentration in plant tissue was $41.0 \text{ mg g}^{-1} \text{ DM}$ compared to $33.6 \text{ mg g}^{-1} \text{ DM}$ in the mineral N control (Table 5.1). Further investigation may be required for the biowastes that had low total N concentrations, at greater rates of application, in order to detect and isolate the agronomic benefit.

Although the ice-cream waste had a total N content comparable to that of the liquid digestates (5.35 kg N m^{-3} compared to 6.19 kg N m^{-3} in AD stored for example) its available N content was low, only 1.06 % relative to total N, and there was no significant increase in crop yield following Ice-cream application. It may be that some negative effects of waste addition, prevented detection of the benefits; the low pH of the ice-cream waste treatments, 4.4 and 3.5 (Table 3.9), for instance may have increased soil acidity, with detrimental effects on fertility. However, other treatments with high N equivalencies, such as TAD, also had a low pH value, therefore, other characteristics of the ice-cream waste may be responsible for poor crop response such as fat content. Fat or oil contents greater than approximately 4 % have been demonstrated to have detrimental effects on plant growth; the oil coats the soil particles restricting absorption of water by plant roots (Davis and Rudd, 1997). The ice-cream wastes, and DAF in particular, have high fat contents, as Dissolved Air Flotation (DAF) uses air bubbles to remove fats and suspended materials from the ice-cream waste water stream, increasing the fat content in the waste. These initial results suggest that wastes with high fat content may require pre-treatment, such as biological digestion, before landspreading.

5.3.2 Nitrogen Equivalencies Based on Comparison of Individual Yields Relative to Fitted Mineral N Response Curves

In addition to the comparison of linear regression coefficients, N equivalencies were also calculated using an alternative method, as described in Section 3.7.2. This was to calculate N equivalencies of individual yield values of crop response to biosolids and biowastes, which is a standard approach (George, 1994; Jackson *et al.*, 1997; Nicholson *et al.*, 1999; Nicholson *et al.*, 2003; Schröder *et al.*, 2007). The response to mineral N fertiliser application was curvilinear at the top rate of application; nutrient analysis of the plant material (Table 5.1) demonstrated that S may have been limiting as discussed in Section 5.3.1. Previously, the top rate of application was excluded to consider the linear section of the response curve, in this case asymptotic regression equations were fitted to the full set of data for crop response to application of mineral N fertiliser. Individual yield values for each rate of application for the biosolids and biowastes were compared to the regression for mineral N to calculate a relative application of mineral N, this was expressed as a percentage of the total N application in the biosolids or biowastes to give an N equivalency for each rate of application. The parameter estimates and r^2 values for the asymptotic regressions are shown in Table 5.5.

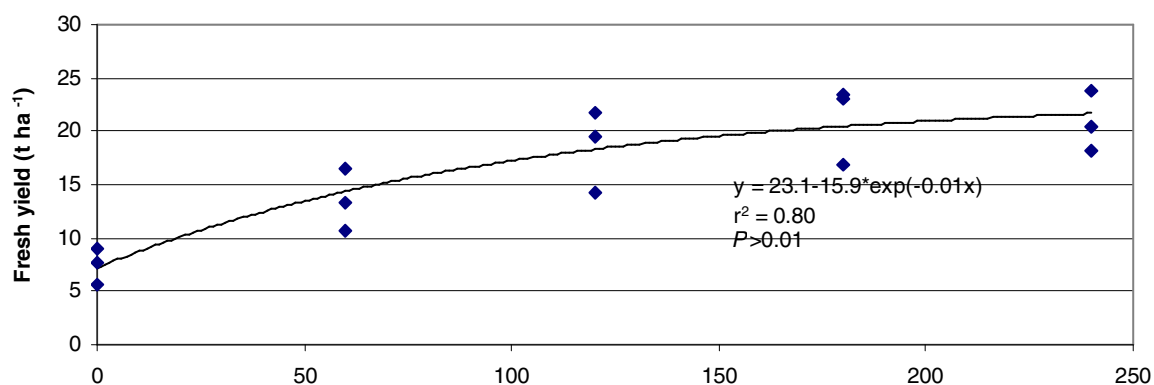
Table 5.5 Summary of parameter estimates and r^2 values for asymptotic regression of each measure of crop response (dry yield, fresh yield and N offtake) to mineral fertiliser N application.

Measure of crop response	Parameter Estimates			r^2
	a	b	c	
Fresh yield	23.1	-15.9	-0.01	0.80
Dry yield	4.02	-2.05	-0.017	0.75
N offtake	131.1	-94.5	-0.009	0.91

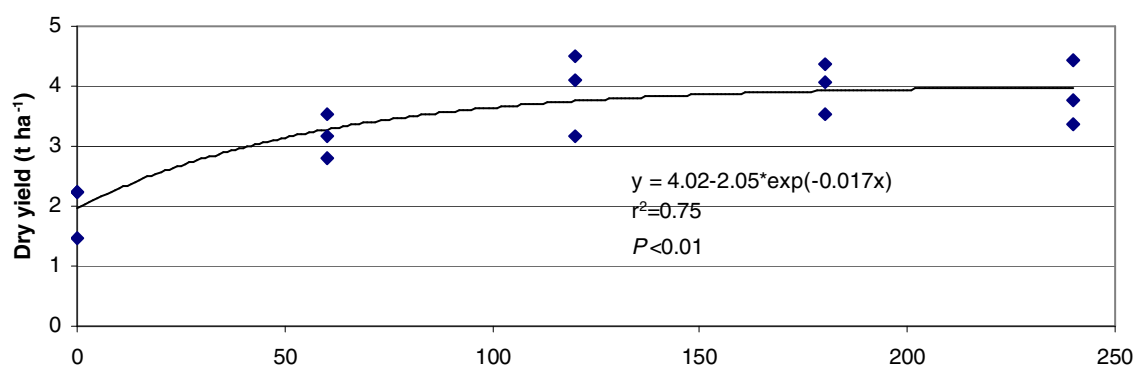
Figure 5.12 shows the fitted curves for each measure of crop response. The asymptotic regression equations, r^2 values and P values from ANOVA tests to demonstrate the significance of the regression are shown on each plot. The r^2 values for fresh yield, dry yield and N offtake showed that the regression curves were a close fit to the data, 0.75, 0.70 and 0.92 respectively, and the relationships were significant at $P < 0.01$.

Table 5.6 shows the N equivalency values calculated using this method. A disadvantage of this method is that it was not possible to calculate N equivalencies when the yield response to biosolids or biowastes was greater than the top response to mineral N fertiliser. It was only possible to calculate N equivalencies for the lowest rate of application for AD fresh and AD stored as the N content of these materials was high, and the yield and N offtake for the greater rates of application was greater than the response to mineral N fertiliser. When the crop response for the biosolids or biowastes was close to the peak value for mineral N fertiliser the N equivalency may be an over-estimate, because in this section of the mineral N fertiliser response curve the response appeared to be limited by the availability of other nutrients. For example, the mean N equivalency value for DMAD at 117.5 kg N ha⁻¹ was 0.44, close to the value of 0.52 calculated by comparison of linear regression coefficients, but at 470 kg N ha⁻¹ the N equivalency was 0.68. As observed previously, N equivalencies calculated from N offtakes were lower than those calculated from yield values; N equivalencies for DMAD, calculated from N offtakes, at application rates of 117.5 and 235 kg N ha⁻¹ were 0.35 and 0.34 respectively. These values are closer to the expected values for DMAD based recent biosolids trials at Silwood Park (Smith *et al.*, 2001; Smith and Bellett-Travers, 2002; Morris *et al.*, 2003). This evidence supported the assumption that crop response in mineral N controls at higher rates of application was limited by other elements, possibly S. The mean N equivalencies calculated for ADMSW ranged from 0.32, at 128.3 kg N ha⁻¹, to 0.40 at the lowest rate of N application, whereas the mean value calculated from the linear regression coefficients was 0.52. The difference in the calculated values may be because for this biowaste there was more variation and the r^2 of linear regressions were lower than the majority of the other biowastes (Table 5.3). The mean N equivalencies calculated for TAD at N application rates of 88.3 kg N ha⁻¹, 171.5 kg ha⁻¹ and 257.3 kg ha⁻¹ were 0.46, 0.89 and 0.73, respectively, compared to a mean of 0.73 from comparison of linear regression coefficients, which was therefore a good approximation of the N equivalency across the range of application rates.

(a) Fresh yield



(b) Dry yield



(c) N offtake

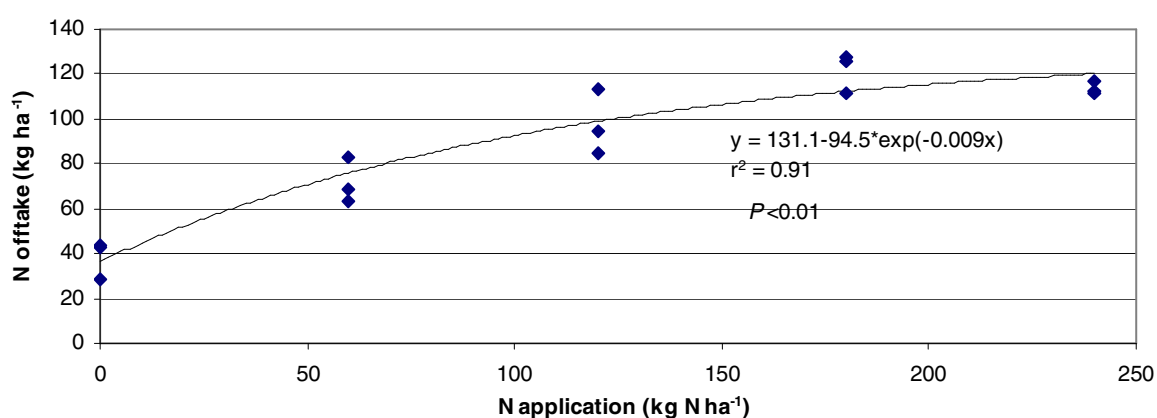


Figure 5.12 Measures of crop response: (a) dry yield; (b) fresh yield and (c) N offtake to N application in mineral N control plots. Asymptotic regression curves were fitted to the data, the equation, r^2 value and P value are shown on each plot. The regression curves were used in the calculation of N equivalency values.

Table 5.6 N equivalency values for biosolids and biowastes where there was a significant response to N application, calculated relative to mineral N fertiliser response asymptotic regression curve.

Biosolids or Biowaste	N application (kg N ha ⁻¹)	Crop response measure (mean)			N equivalency			
		Fresh yield (t ha ⁻¹)	Dry yield (t ha ⁻¹)	N offtake (kg ha ⁻¹)	Fresh yield	Dry yield	N offtake	Mean
DMAD	117.5	13.6	3.30	65.81	0.44	0.53	0.35	0.44
	235	17.0	4.00	85.32	0.40	1.28	0.34	0.67
	352.5	22.0	4.85	116.77	0.76	†	0.59	0.68
	470	25.4	5.47	136.93	†	†	†	†
Abattoir	14.6	8.51	2.08	41.58	0.59	0.23	0.42	0.41
	36.5	12.5	3.07	62.02	1.12	1.24	0.96	1.11
	54.8	15.4	3.27	77.87	1.33	1.09	1.17	1.20
	73.0	15.3	3.45	73.51	0.97	1.03	0.76	0.92
ADMSW	42.8	10.5	2.57	42.81	0.53	0.48	0.18	0.40
	85.5	12.2	3.04	51.49	0.44	0.51	0.22	0.39
	128.3	13.0	3.07	61.44	0.35	0.35	0.27	0.32
	171.0	15.6	3.46	66.19	0.43	0.45	0.24	0.37
TAD	88.3	13.0	3.10	57.78	0.51	0.54	0.32	0.46
	171.5	16.7	4.00	81.66	0.53	1.73	0.42	0.89
	257.3	21.4	4.77	107.69	0.85	†	0.60	0.73
	343.0	27.0	5.64	135.25	†	†	†	†
AD Fresh	144.2	17.4	4.06	92.26	0.71	†	0.69	0.70
	360.5	32.7	6.42	195.73	†	†	†	†
	540.8	37.9	6.78	230.16	†	†	†	†
	721.0	38.3	7.11	238.14	†	†	†	†
AD Stored	123.8	17.3	3.74	97.81	0.82	0.95	0.94	0.90
	309.5	29.6	5.54	166.94	†	†	†	†
	464.3	33.1	6.05	192.85	†	†	†	†
	619.0	34.7	6.26	215.86	†	†	†	†

† Crop response to biosolids or biowastes exceeded maximum response to mineral fertiliser N

The N equivalencies for AD fresh, applied at a rate of 144.2 kg N ha⁻¹, and AD stored, applied at a rate of 123.8 kg N ha⁻¹, were 0.70 and 0.90 respectively, whereas comparison of linear regression coefficients resulted in N equivalencies of 0.84 and 0.67. However, it was only possible to calculate N equivalencies for the lowest rates of application for AD fresh and AD stored, so these values do not represent N availabilities across the full range of application.

Comparing the two methods for calculating N equivalencies demonstrated that they produce similar values at the lower rates of application, but at higher rates of application of biosolids or biowastes, N equivalencies may be over-estimated by the comparison of individual yield values to the asymptotic regression model for mineral N.

This is because the relationship for mineral N became non-linear at the maximum rate of application, 240 kg N ha⁻¹. However, for biosolids and biowastes, crop response did not appear to become non-linear at top rates of application, with the exception of AD fresh and AD stored where the top N application rates were greater than 500 kg N ha⁻¹ as a result of the high total N content. This is likely to be because these materials were sources of other elements such as K and S. Therefore, in this case, it could be argued that, in order to isolate the crop response to N application it is more appropriate to consider the linear section of the response curve. Comparison of linear regression coefficients to response to mineral fertiliser N, rather than individual yield values, provides an approximation of the N equivalency across the whole response curve (Kiemec *et al.*, 1987; Smith *et al.*, 2001; Smith *et al.*, 2002b; Morris *et al.*, 2003). This may be considered inaccurate if there were fewer rates of application, however, the systematic design allowed for five rates of application. Therefore, in this case, it is a more reliable estimate of average N availability over these rates of application. However, in the case of ADMSW, where there was a high level of variability between replicates and the linear regression curve was not a good fit to the data, it may be considered more accurate to use the mean individual yield values.

By using the systematic design, an unamended control subplot can be included in each main plot. A further advantage of using the linear regression model, $y = a + bx$, with a systematically designed experiment, and comparing the regression coefficient, b , is that the mean value for no applied N, which is the intercept, a , is taken into account on an individual treatment basis as it is only the slope of each model that is compared. However, although comparing individual yields from biosolids and biowastes application to the asymptotic regression curve for mineral N response, incorporated the crop response when there is no applied N into the regression model, this data is from the mineral N control plots only. Although this includes an unamended control from each block, it is less precise than on an individual treatment basis.

5.3.3 Residual Value of Biosolids and Biowastes

No second year growth was observed on any of the treatment plots in the second growing season. This indicated that for those treatments that were a significant source of mineral N, the majority of N was mineralised in the first year. This supported the findings of Morris *et al.* (2003) who found that there was little second year response to biosolids applied at normal agronomic rates. In the case of the digested wastes, the findings demonstrated that the organic fraction was stabilised, and the labile organic N

was rapidly mineralised. Shröder *et al.* (2007) found that the residual value of cow slurries was dependent on the degree of stabilisation of the waste. The combined second to fourth year fertiliser replacement value of soil injected anaerobically digested cow slurry was only 8 % compared to 11-20 % for soil injected undigested slurry. The majority of N in the abattoir waste tested here was inorganic so it is unsurprising this was utilised by the crop in the first year. In the case of the other wastes, the ice-cream wastes, KG and the trout wastes, the N applications were not high, so residual value would not be expected.

5.4 Summary

To improve the efficiency of use of nutrients from industrial biowaste and provide guidelines for best practice, a programme of field experiments was established at Silwood Park, the Imperial College campus near Ascot, Berkshire, in spring 2006, on a low nutrient status sandy loam soil. A range of biowastes from industrial and commercial processes were investigated, including examples from the meat, vegetable and dairy processing industries, and from anaerobic and aerobic digestion plants.

The N equivalency for DMAD was 0.52, this was greater than the mean value of 0.30 found in previous trials, which demonstrated that nutrient elements other than N may be affecting the crop response in grass fertilised with this material. Elemental analysis of the plant tissue showed that S concentrations in ryegrass treated with DMAD were nearly 4 times greater than in grass fertilised with mineral N alone, indicating that this element was potentially contributing to the increased crop response to DMAD. Despite the lower total N content, N equivalency for ADMSW was equivalent to DMAD at 0.52, which may reflect its greater mineral N content. There was also a contribution of S to the crop response in this material as tissue content were greater in comparison to the mineral N control. However, differences in S content of grass for the other materials were not great, and were similar to control values; therefore, for these treatments, it was assumed that the crop response was primarily due to N.

Abattoir waste had an N equivalency of 1.6, indicating that factors other than N availability contributed to crop response. Following further elemental analysis, no elements were found to be greater in plant tissue fertilised with Abattoir in comparison to grass fertilised with mineral N fertiliser. The range of yield response to Abattoir did not correspond well with the mineral N calibration plots, due to low total N content of Abattoir; this experimental artefact may explain why the N equivalency was greater

than 1. The fresh and stored co-digestates of food and farm waste (AD fresh and stored) had N equivalencies of 0.85 and 0.68 respectively; these materials are therefore good sources of available N, in the same range as digested animal slurries (Shröder *et al.* 2007). The fresh co-digestate (AD fresh) may contain a pool of readily mineralisable organic N, resulting in a higher N equivalency than AD stored. The N equivalency of TAD was 0.76, similar to the other digested liquids, despite its much lower mineral N content. This indicated that TAD contained a high proportion of rapidly mineralisable N. Application of Trout old and a base dressing of mineral N, resulted in a significant response in fresh and dry yield and N offtake indicating that there were benefits of the addition of organic matter of this waste type to the soil. There was a significant relationship between the rate of application of KG and fresh yield and for Ice-cream there was a significant relationship with N offtake. These treatments received a top dressing of 120 kg N ha⁻¹. This suggested that, under non-limiting N conditions, there were some positive effects of the materials at these rates of application, and increasing application rate may reveal an increased response. There was no significant relationship between fresh and dry yield and rate of application for KG, Trout fresh, potato processing wastes or either ice-cream waste. However, following elemental analysis of the plant material, grass fertilised with Potato sludge and a base dressing of N was found to have greater concentrations of K than grass fertilised with mineral N alone, indicating that Potato sludge conferred agronomic benefit as an effective source of available K. In further experiments the approach taken with wastes with low N content should focus on greater application rates to determine whether the materials confer benefit through improvements to soil structure and organic matter content.

Similar N equivalencies to those obtained by comparison of linear regression coefficients were generally obtained when comparing the individual yield values to biowastes application to the crop response curve for mineral N. However, when the yield exceeded the maximum from the mineral N response curve it was not possible to calculate N equivalencies. When yield responses were close to the maximum for mineral N, equivalency values calculated by the individual yield comparison approach may be an over estimate of availability. Comparison of linear regression coefficients is considered the most suitable method for this experiment (Kiemec *et al.*, 1987; Smith *et al.*, 2001; Smith *et al.*, 2002b; Morris *et al.*, 2003), as the systematic design allows several rates of application. Therefore, a reliable approximation of the N equivalency across different rates of application in the linear section of the crop response curve is obtained.

6 FIELD INVESTIGATION OF THE NITROGEN VALUE AND OTHER AGRONOMIC BENEFITS OF INDUSTRIAL BIOWASTES- 2007

6.1 Introduction

6.1.1 Background

A second field experiment was established at the Imperial College campus at Silwood Park in 2007, where the soil is a low nutrient status sandy loam and is ideally suited to characterise the agronomic potential of industrial biowastes recycled to farmland (Smith and Bellet-Travers, 2001; Smith *et al.*, 2002b; Morris *et al.*, 2003). The experiment followed the same procedures as the 2006 experiment. A systematic design was used to investigate the agronomic benefit of a further range of biowastes. The processed biowastes investigated in the 2006 experiment, from anaerobic and aerobic digestion plants, were included to investigate reproducibility of the results, and to further investigate nutrient transfer from the digestates to crops. As before, mineral N controls and digested biosolids from wastewater treatment were included so that the N release properties of the biowastes relative to these well characterised and understood fertiliser sources could be assessed. In addition, a further selection of mineral fertiliser controls were incorporated into the design, with base dressings of the nutrient elements P and K, and a combination of P and K supplied to the mineral N gradients. The N equivalency values from the 2006 experiment had indicated that in some cases the crop response to biowaste treatments was not due to N alone; N equivalency for Abattoir was greater than 1, and N equivalency for DMAD, the reference material, was greater than values found in previous experiments. These additional controls were included so that the crop response due to N alone from the biowastes could be elucidated, although at this stage the importance of S to the crop response was not fully appreciated as the elemental analyses of the plant tissue was not yet completed. Details of the biowastes, are given in Section 3.4.

6.1.2 Aims

The specific aims of the 2006 experiment were to:

- Characterise the total and mineral nutrient concentrations in a selected range of industrial biowastes;

- Quantify the N release properties of industrial biowastes relative to sewage sludge and mineral fertiliser;
- Examine nutrient transfers, including P, K, Mg and S, from biowastes to crops;
- Develop a strategic approach for investigating agronomic value of biowastes.

In addition, further objectives of the 2007 experiment were to:

- Investigate reproducibility of the crop response to biowastes addition by inclusion of the same processed biowaste materials as were investigated in 2006;
- Investigate the fertiliser equivalency values due to N alone, by inclusion of P and K controls;
- Expand the range of biowastes tested to characterise the agronomic properties of a wider selection of biowaste materials from key industrial sectors and especially the food industry.

6.2 Materials and Methods

6.2.1 Experimental Establishment

The second biowastes trial was established between 25-27 April 2007. General materials and methods are presented in Chapter 3; in addition, details of the field establishment for the 2006 trial at Silwood Park experiments are given in Section 5.2.1. The 2007 experiment followed the same procedure, but differed in the biowastes used; rates of application were adjusted in some cases and additional controls were included. In the 2007 experiment, there were 12 treatments in total including 4 mineral fertiliser controls, a biosolids reference treatment and 7 biowastes treatments. The selection, collection and physical and chemical properties of the biowastes are described in Sections 3.4.1-3.4.3. A list of the biowastes investigated in the experiment and the abbreviations used in this thesis are given in Table 3.5, a diagram of the lay-out of the experiment is given in Figure 6.1

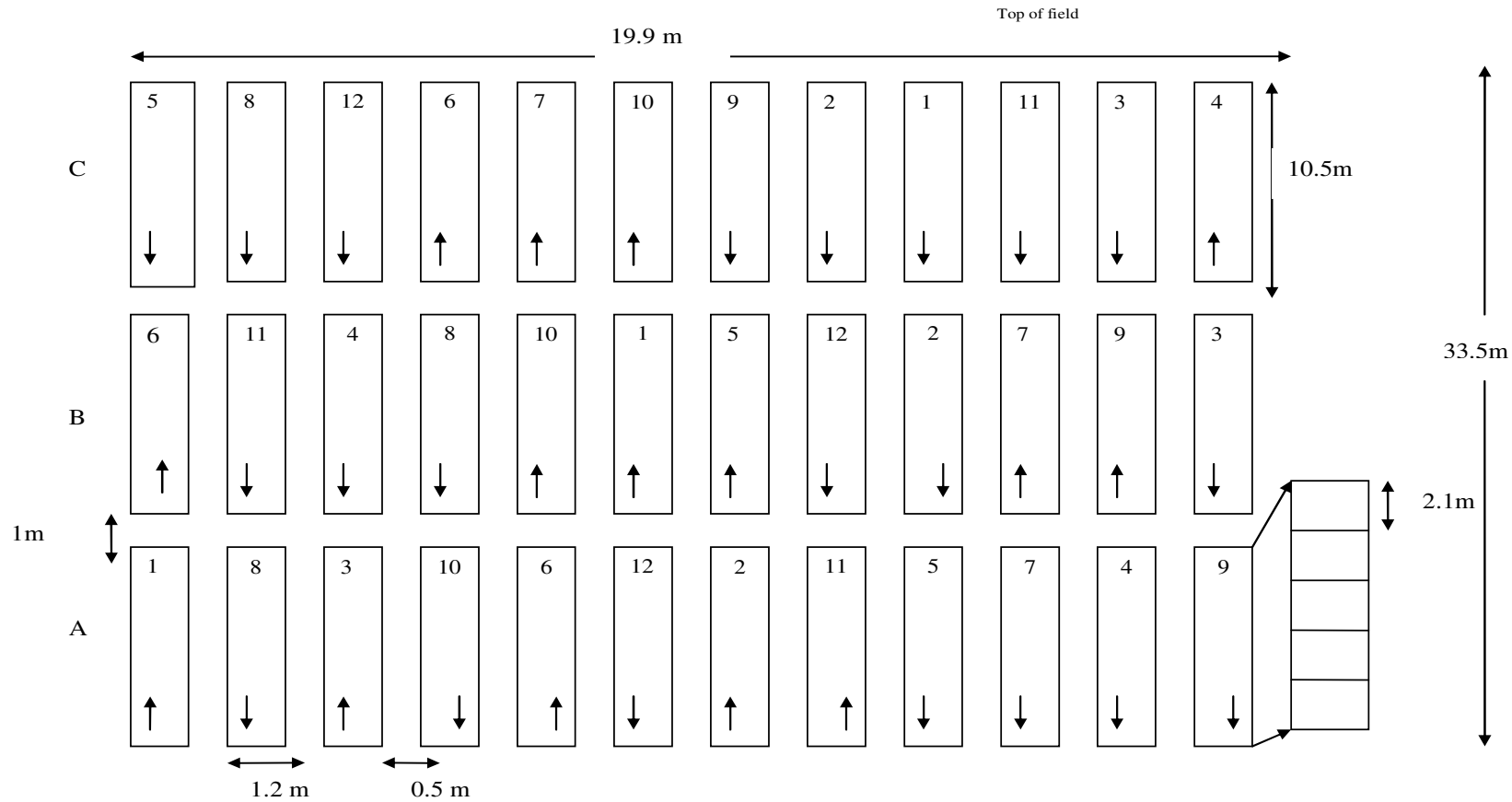


Figure 6.1 Experimental design for 2007 trial, showing arrangement, dimensions and subdivision of plots, direction of arrow indicates direction of gradient of application, low to high. Treatments: 1, mineral N; 2, mineral N + base dressing P; 3, mineral N + base dressing K; 4, mineral N + base dressing P + K; 5, DMAD; 6, ADMSW; 7, TAD; 8, AD Fresh; 9, AD Stored; 10, Vegetable; 11, Yeast; 12, Salt whey (key to abbreviations given in Table 3.5).

In 2007, rates of application for the liquid wastes were reduced to 0, 20, 40, 60 and 80 m³ ha⁻¹ for AD fresh and AD stored and Yeast and the rates of application for Salt whey were 0, 25, 50, 75 and 100 m³ ha⁻¹. This was to supply rates of N for these N rich sources within approximately the linear response range of the crop to N fertiliser application.

The rates of mineral N supplied to the calibration plots were also reduced, based on experience from the 2006 field experiment, to 0, 50, 100, 150 and 200 kg N ha⁻¹, as the top rate applied in 2006, of 240 kg N ha⁻¹ was in excess of the linear section of the crop response curve. Three additional control treatments were included with the same rates of application for mineral N plus a base dressing of P, K or P and K together. Phosphorus was applied as granulated triple-super phosphate at a rate of 22 kg P ha⁻¹ and K was applied as KCl a rate of 50 kg K ha⁻¹. These are the recommended rates given in RB209 for grass establishment (MAFF, 2000). Site management and environmental data collection and are described in Sections 3.6.2 and 3.6.3.

6.2.2 Soil Conditions

Soil temperature and gravimetric content in the 2007 trial are presented in Figure 6.2. Soil moisture was greater during the summer period than in 2006 as a result of exceptional rainfall conditions.

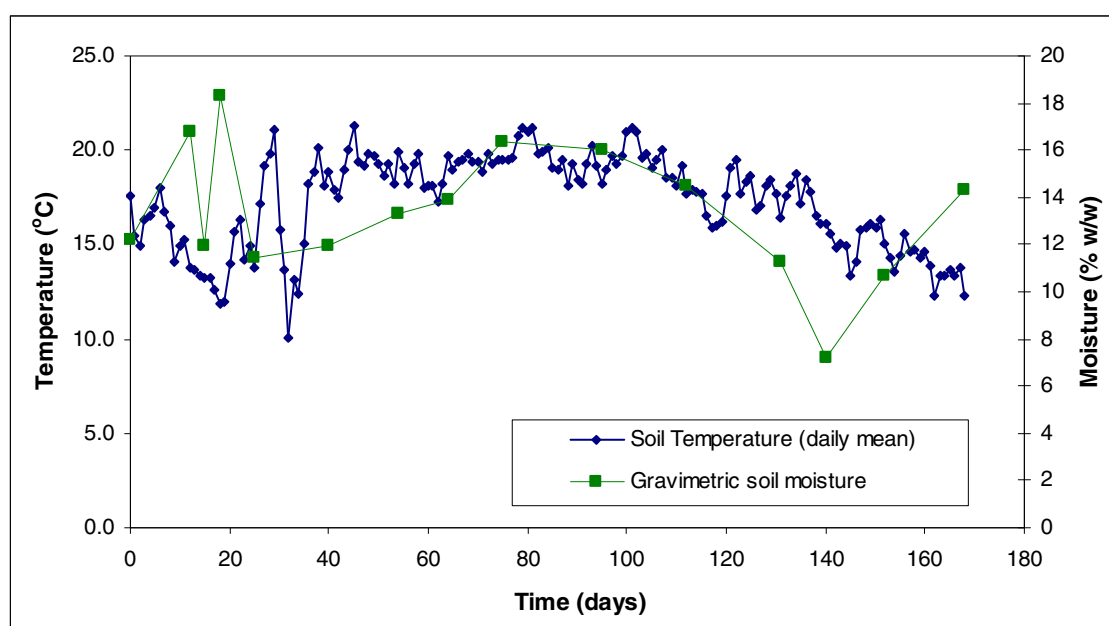


Figure 6.2 Gravimetric soil moisture (% w/w) and temperature (°C), 26 April-11 October 2007 (days 0-168).

Rainfall and air temperature data are available in Appendix A3. In 2007, maximum soil moisture content was approximately 18 % w/w on day 18 in mid-May and generally remained between approximately 12-15 % from June-August; whereas, in 2006 the soil moisture decreased in the summer months to a minimum of 2 %. The lowest moisture content measured during the 2007 trial was in September, at 7.2 %. After this date, moisture content increased again and was above 14 % at the last harvest date on 10 October 2007. Correspondingly, the mean daily soil temperature was lower than recorded in the 2006 experiment. From day 0-45 (June 10) mean daily soil temperature was generally between 10-20 °C, after this mean daily temperature fluctuated between approximately 18-21 °C until day 115 (19 August), and then decreased to approximately 12 °C by the end of the experiment on 10 October 2007. By comparison, in 2006, soil temperatures during July and August were greater, and generally between 20-30°C.

6.2.3 Irrigation

The second trial site was irrigated on 4 May 2007 to aid crop establishment during the early phase of emergence and crop establishment. The irrigation was carefully controlled to ensure an even application and measured with an in-line flow meter, approximately 5.7 l m⁻² was applied across the site. An area the width of two subplots was irrigated at any one time, the angle of spray was adjusted manually. Buckets were set out in pathways and the amount of water collected was measured to monitor the distribution of water.

6.2.4 Harvesting

The same procedure was followed as for the previous experiment. It was only possible to take 2 harvests in 2007, due to poor growing conditions; there was low soil temperature conditions (Figure 6.2) and high rainfall (Appendix A3). The first harvest was taken on 9 June and the second on 10 October.

6.3 Results and Discussion

The cumulative response of perennial ryegrass to applications of biosolids, biowastes and mineral fertiliser controls, measured as fresh yield, dry yield and as N offtake, is shown in Figures 6.3-6.8. In most cases, a significant linear relationship ($P \leq 0.05$) was found between rate of N application in the fertiliser source and the measure of crop

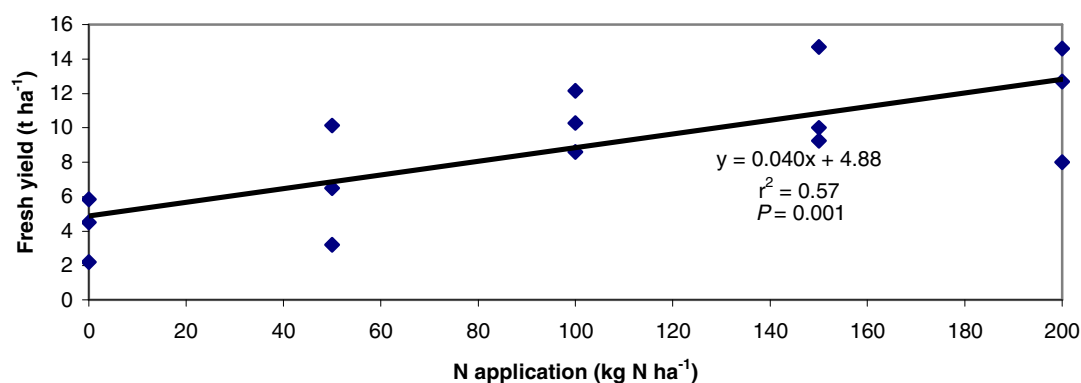
response. The exceptions were ADMSW and Salt whey; for ADMSW there was no significant linear relationship with any of the measures of crop response (Figures 6.4, 6.6 and 6.8), and for Salt whey the only significant linear relationship was with fresh yield. Douglas *et al.* (2003) investigated N availability in salt whey from cheese processing and found it was less than 10 %. The whey had a high salinity of 6430 $\mu\text{S cm}^{-1}$. Therefore, the relatively poor performance of this biowaste may result from the increased soil salinity disrupting osmotic balance and root nutrient uptake (Davis and Rudd, 1997). However, the high rainfall received would mitigate a salinity effect. The low rate of N added in this biowaste, which was only 25-50 % of the amount from most of the other biowastes applied (Figures 6.3, 6.6 and 6.8), may explain the low response.

A significant response to ADMSW was found in the 2006 trial, resulting in an N equivalency value of 0.52. The lack of significant response in 2007, may be explained by the total N content, which was lower than in the previous experiment, and equivalent to 1.5 % DS compared to 1.75 % in the previous year. The low total N content resulted in smaller yield in comparison to the mineral N control in 2007, thereby reducing the ability to detect a statistically significant crop response to application of ADMSW. The biowaste was collected from a stockpile in the open air at the digestion plant. This storage method would have resulted in losses of N by volatilisation and the material may also have begun to compost resulting in further stabilisation of the organic N fraction. Therefore these results may reflect the effects of temporal variations in the stability of the organic N fraction, depending on the length of storage. Consequently, the sample collected in 2007 potentially had a smaller pool of mineralisable N.

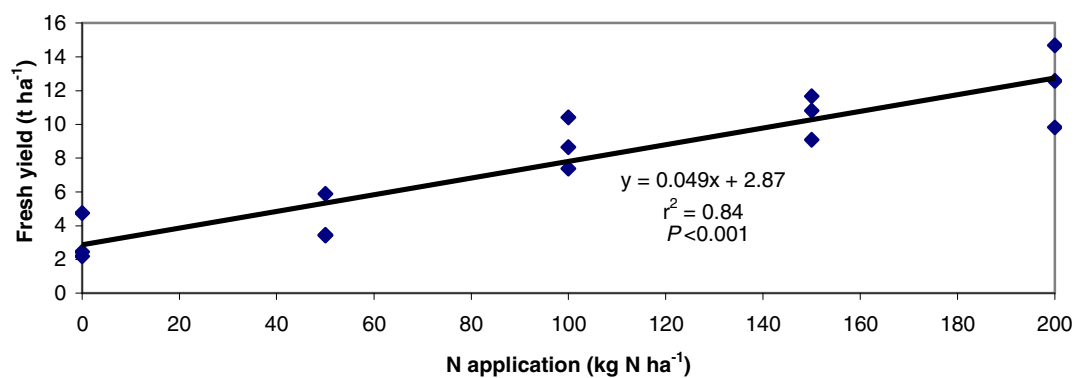
Where there was a significant relationship, the r^2 values for the linear regression and P value from an ANOVA test of significance of the regression are given on the graphs. A summary of r^2 values and regression coefficients for the measures of crop response for each treatment is given in Table 6.1. Nitrogen equivalency values for the biosolids and biowastes relative to each of the mineral fertiliser controls are shown in Tables 6.2-6.5.

The top rate of application for the mineral N controls was reduced from 240 kg N ha⁻¹ in the 2006 trial to 200 kg N ha⁻¹ in the 2007 experiment, which was within the linear section of the response curve. The regression coefficients for the mineral controls demonstrated that the base dressings of K and of K+P contributed to the crop response (Table 6.1).

(a) Mineral N control



(b) Mineral N+K control



(c) Mineral N+P control

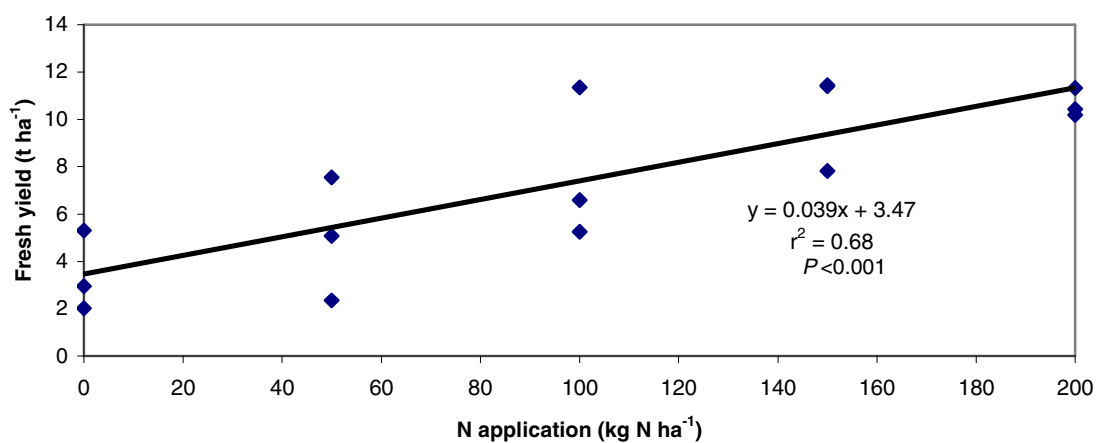
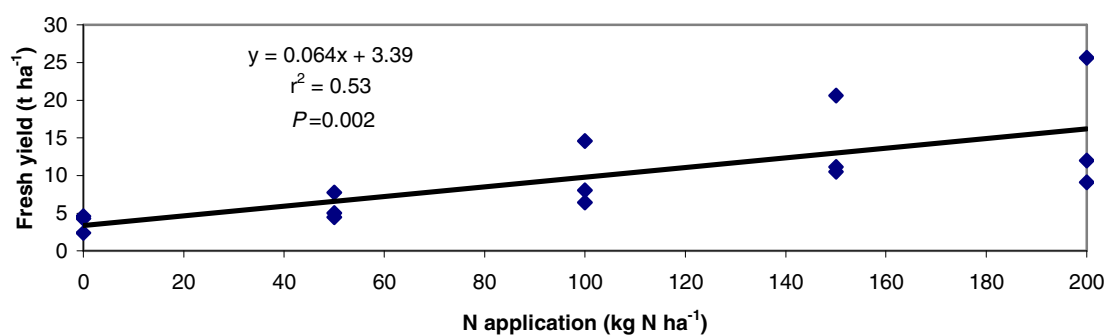
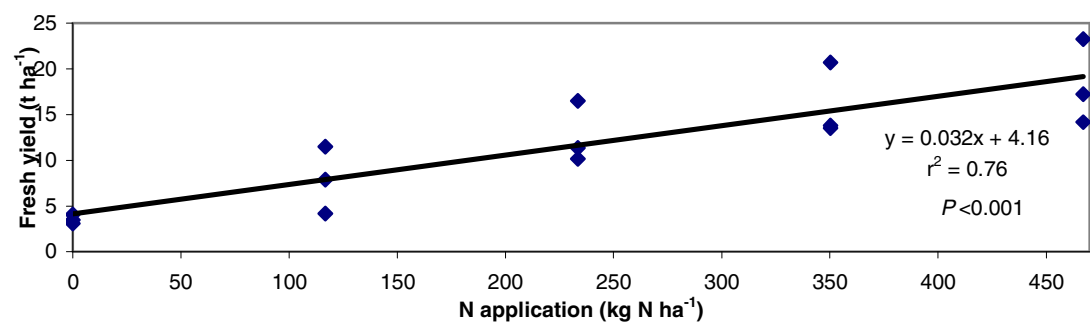


Figure 6.3 Cumulative ryegrass response (2 harvests, fresh yield) relative to N application from mineral N fertiliser, biosolids and biowastes. Regression equation, r^2 value and P value from an ANOVA test of significance are shown.

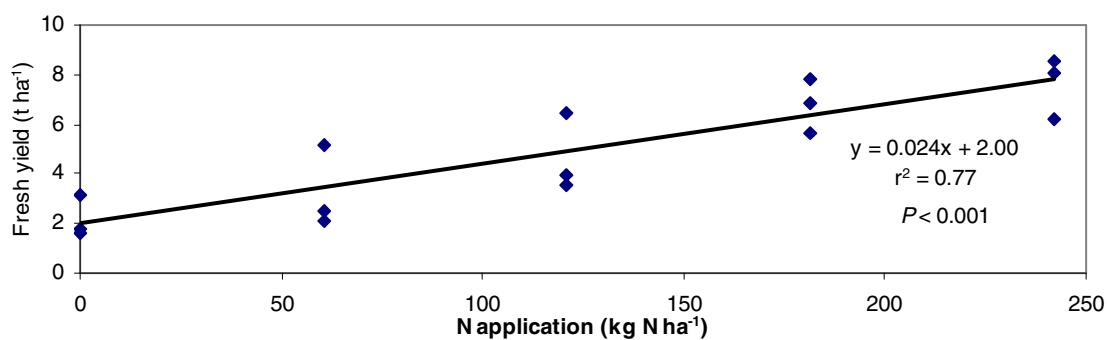
(d) Mineral N+P+K control



(e) DMAD



(f) Vegetable



(g) Salt whey

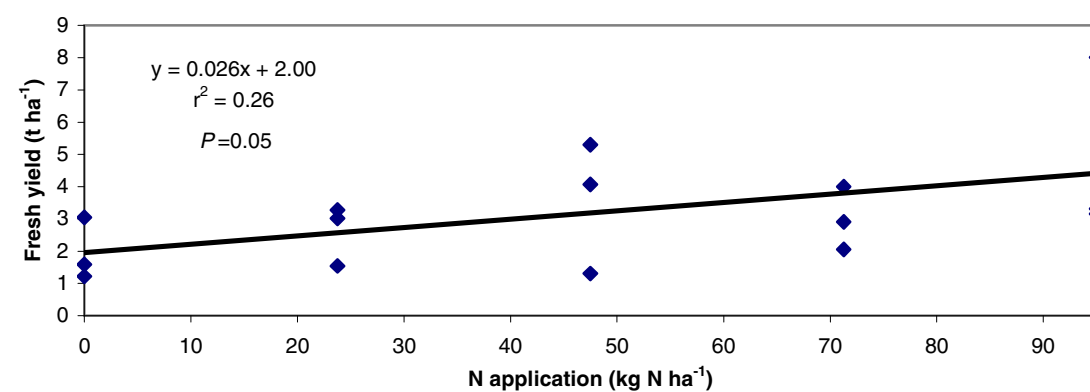
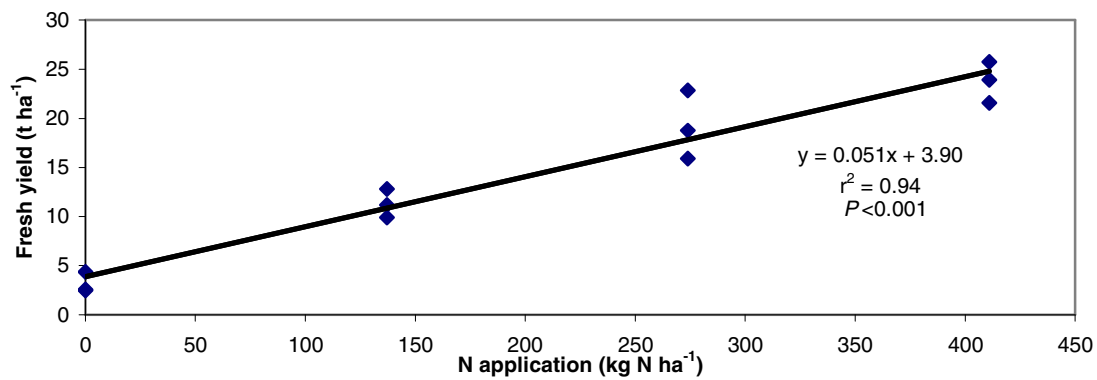
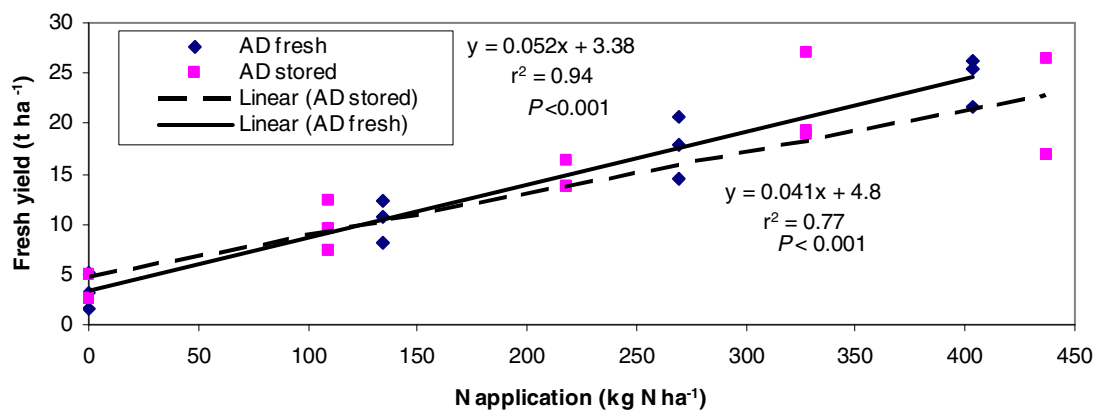


Figure 6.3 cont.

(h) Yeast



(i) AD fresh & AD stored



(j) TAD

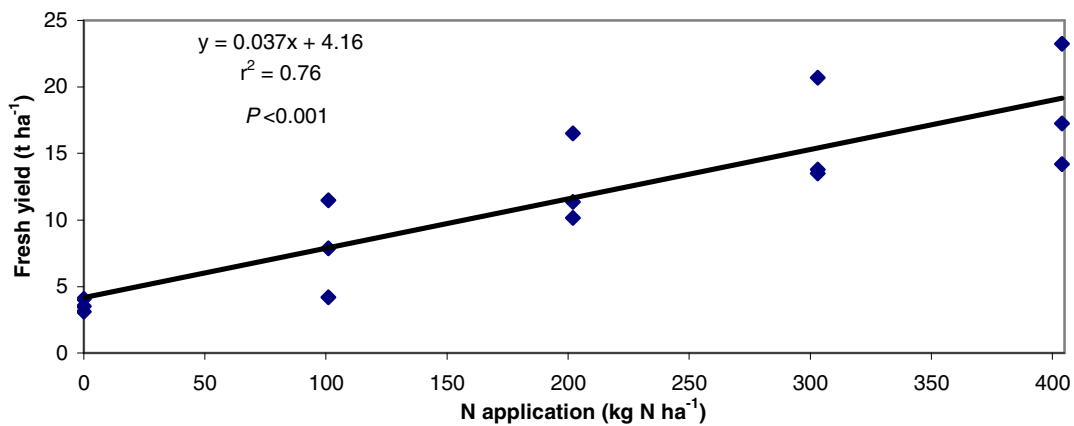


Figure 6.3 cont.

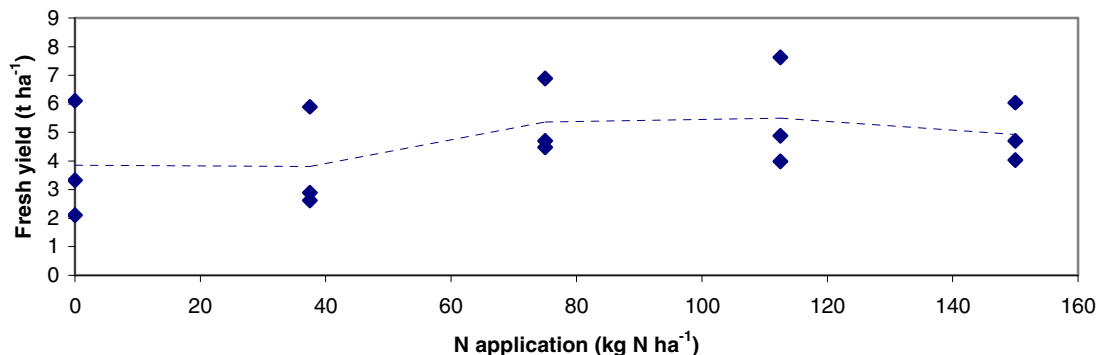
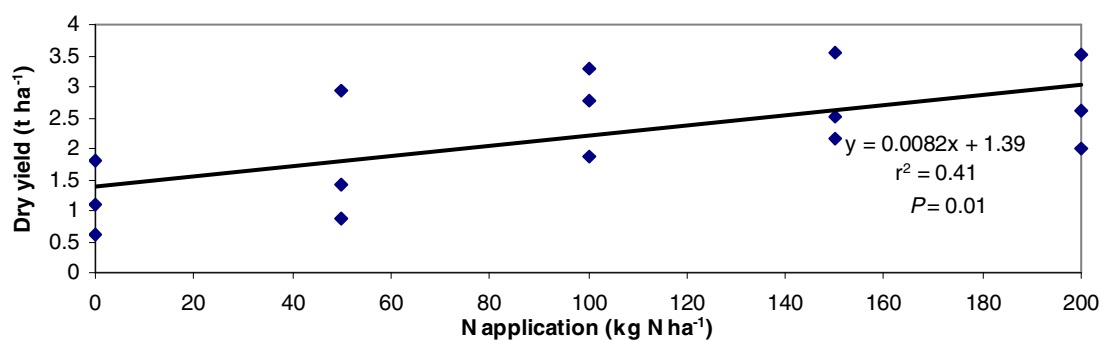


Figure 6.4 Cumulative ryegrass response (2 harvests, fresh yield) relative to N application in ADMSW treated soil, --- represents the mean cumulative fresh weight yield (t ha^{-1}); no significant ($P > 0.05$) relationship was detected.

(a) Mineral N control



(b) Mineral N+K control

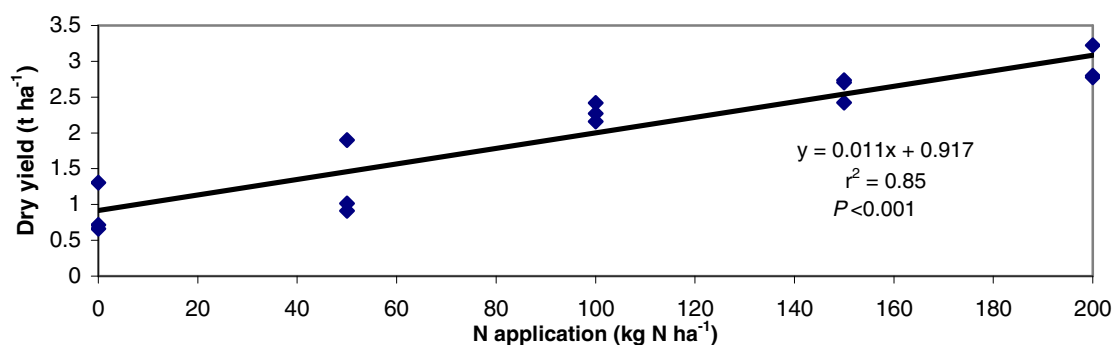
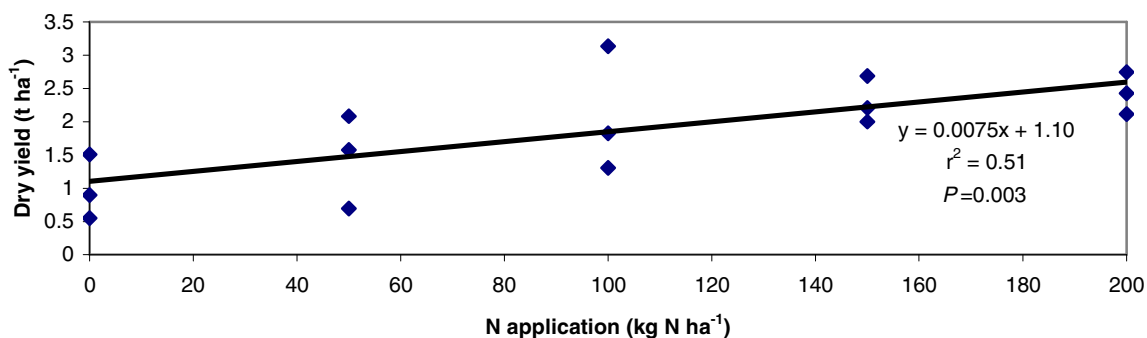
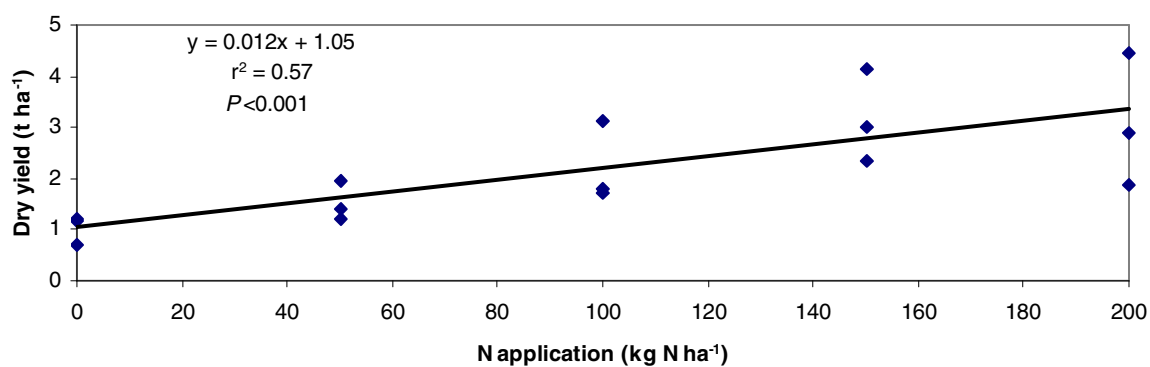


Figure 6.5 Cumulative ryegrass response (2 harvests, dry yield) relative to N application from mineral N fertiliser, biosolids and biowastes treatments. Regression equation, r^2 value and P value from an ANOVA test of significance are shown.

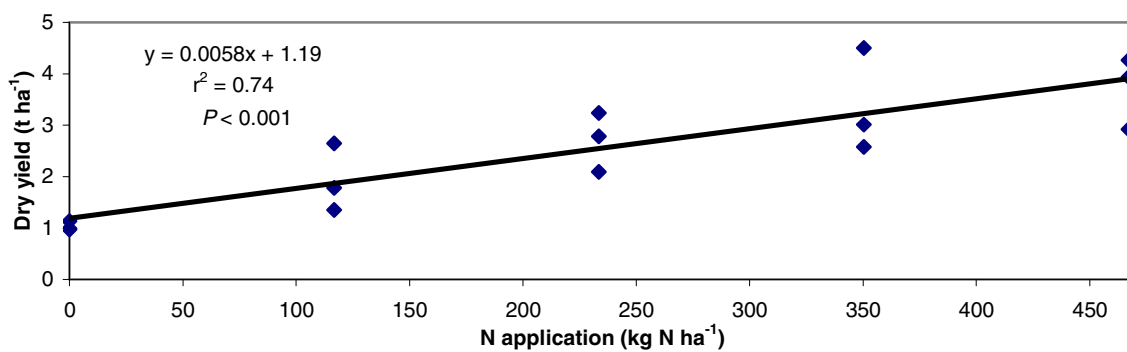
(c) Mineral N+P control



(d) Mineral N+P+K control



(e) DMAD



(f) Vegetable

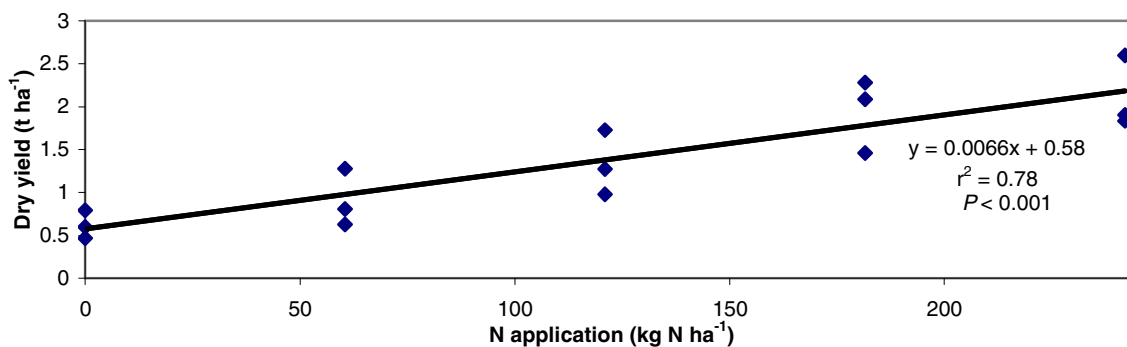
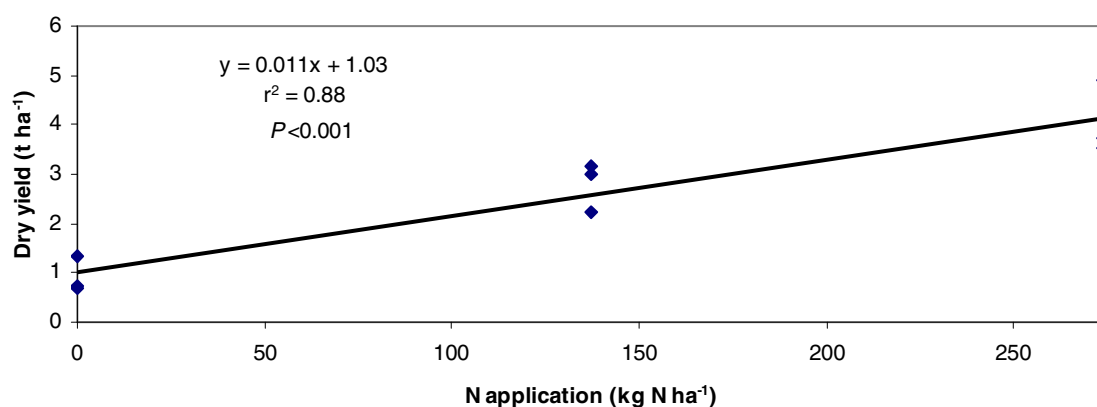
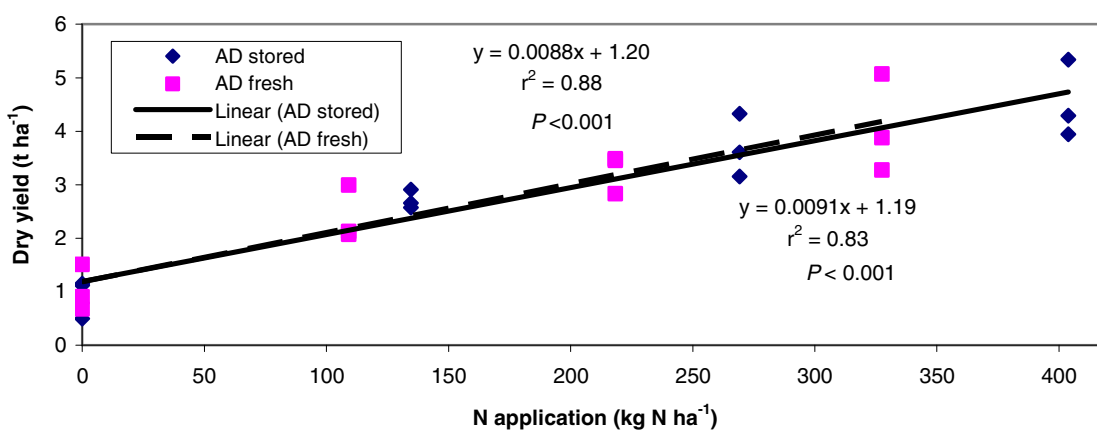


Figure 6.5 cont.

(g) Yeast



(h) AD fresh & AD stored



(i) TAD

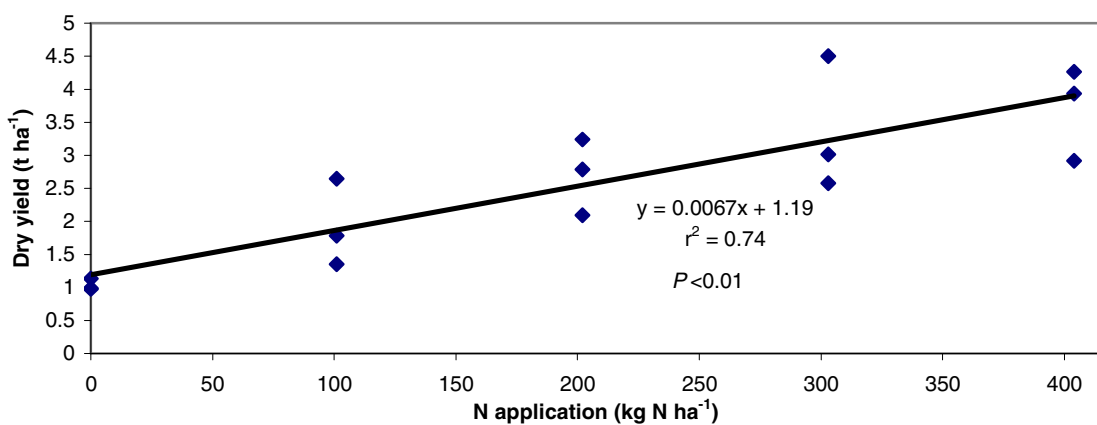
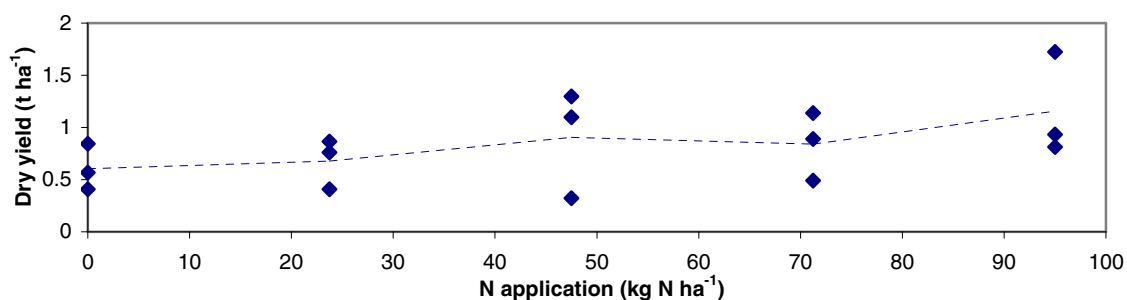


Figure 6.5 cont.

(a) Salt whey



(b) ADMSW

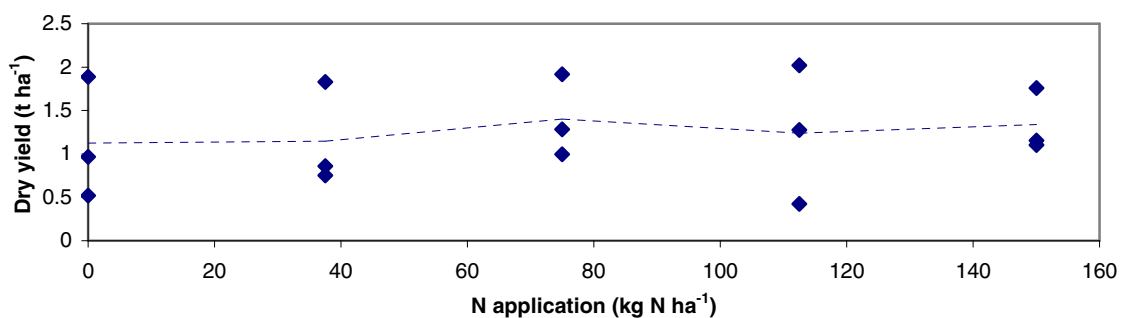
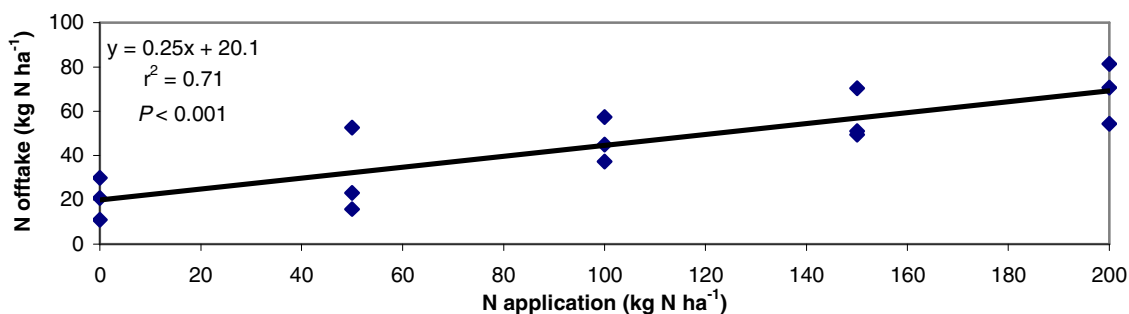


Figure 6.6 Cumulative ryegrass response (2 harvests, dry yield) relative to N application in biowastes treated soil, --- indicates mean cumulative dry yield (t ha^{-1}); no significant ($P > 0.05$) relationship was detected.

(a) Mineral N control



(b) Mineral N+K control

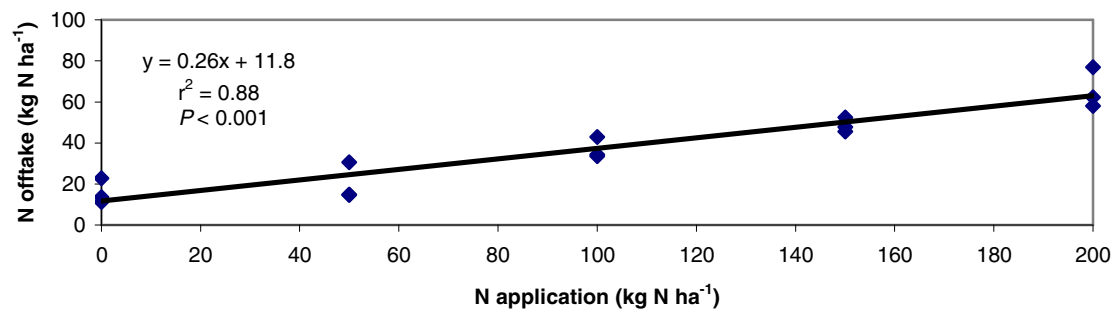
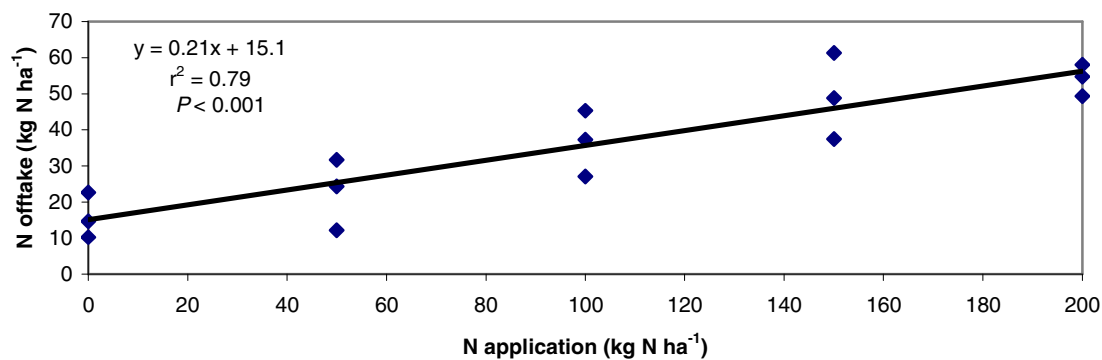
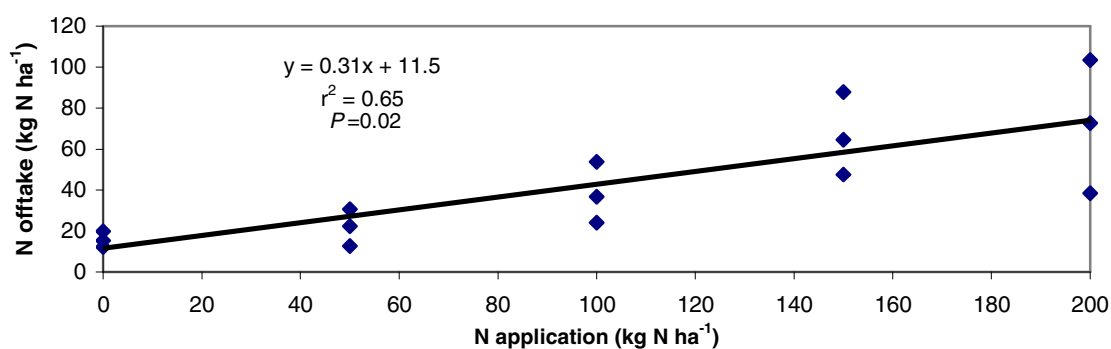


Figure 6.7 Cumulative ryegrass response (2 harvests, N offtake) relative to N application from mineral N fertiliser, biosolids and biowastes. Regression equation, r^2 value and P value from an ANOVA test of significance are shown.

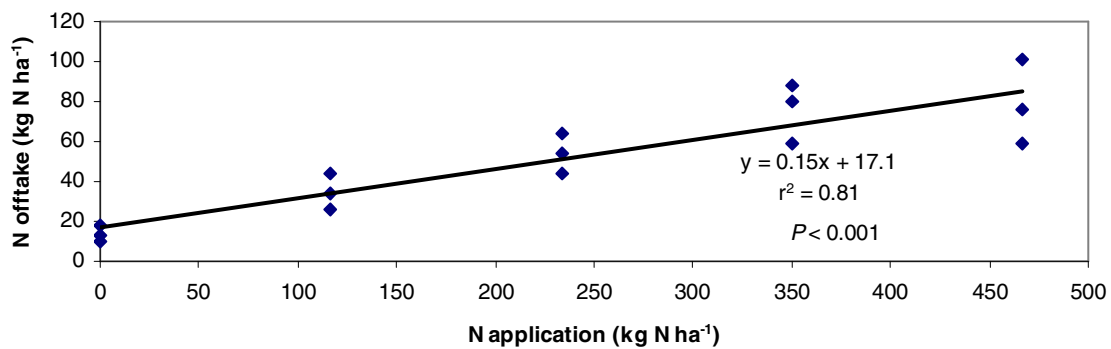
(c) Mineral N control+P



(d) Mineral N control+P+K



(e) DMAD



(f) Vegetable

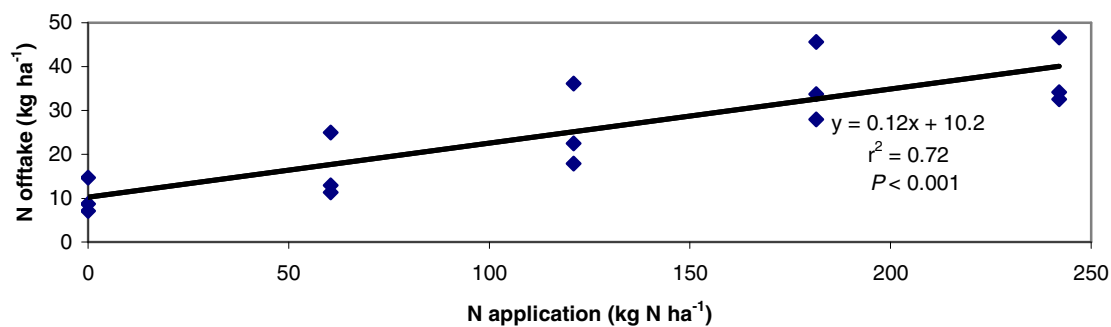
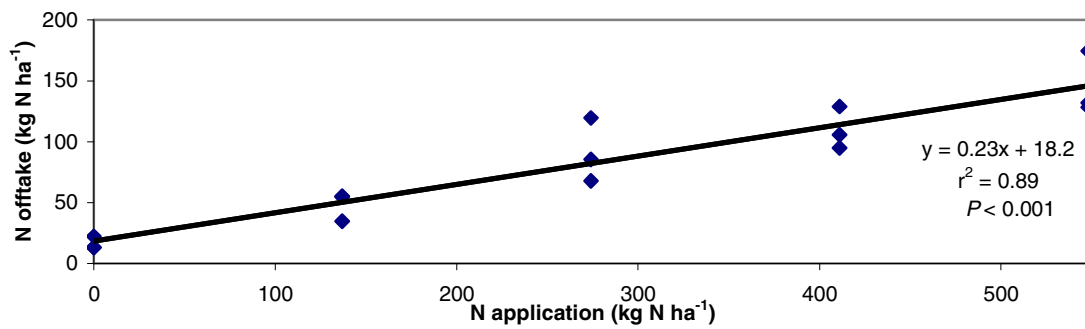
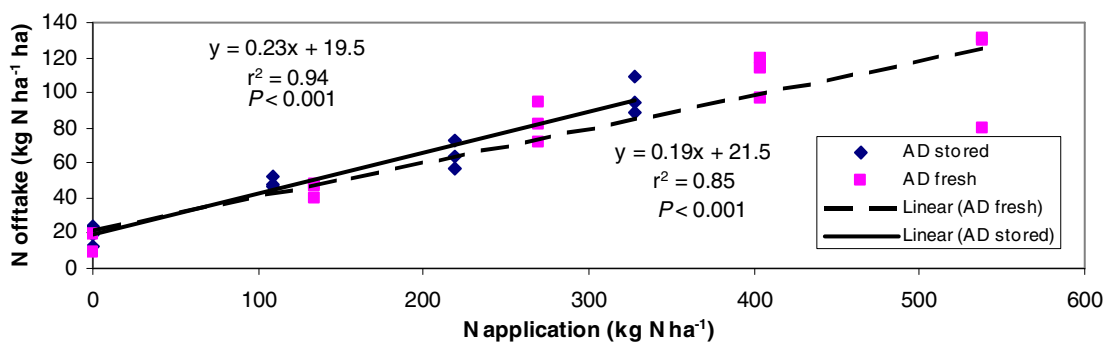


Figure 6.7 cont.

(g) Yeast



(h) AD fresh & stored



(i) TAD

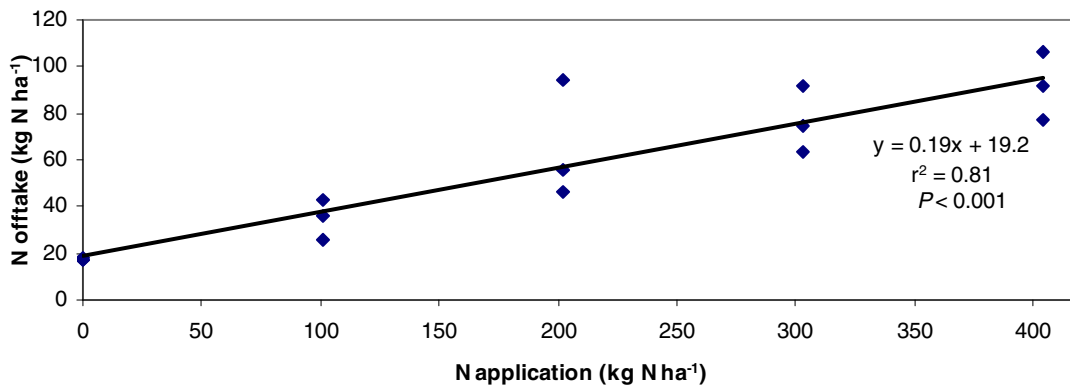
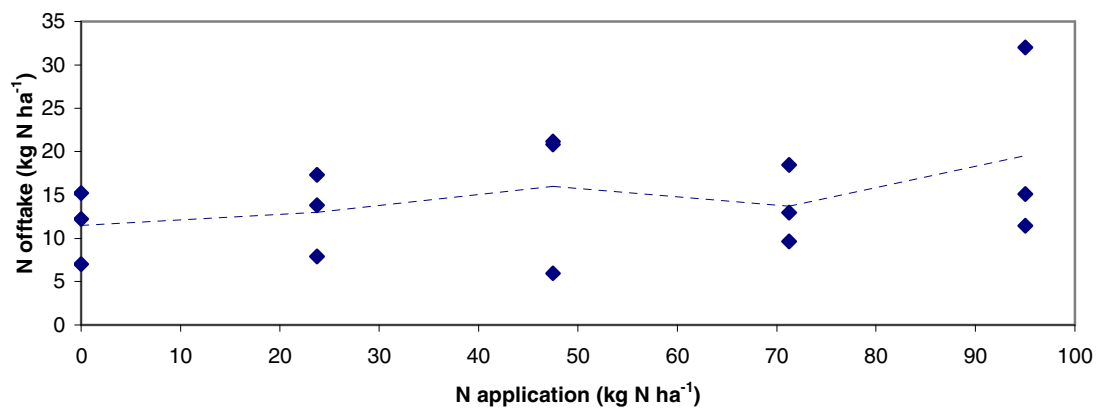


Figure 6.7 cont.

(a) Salt whey



(b) ADMSW

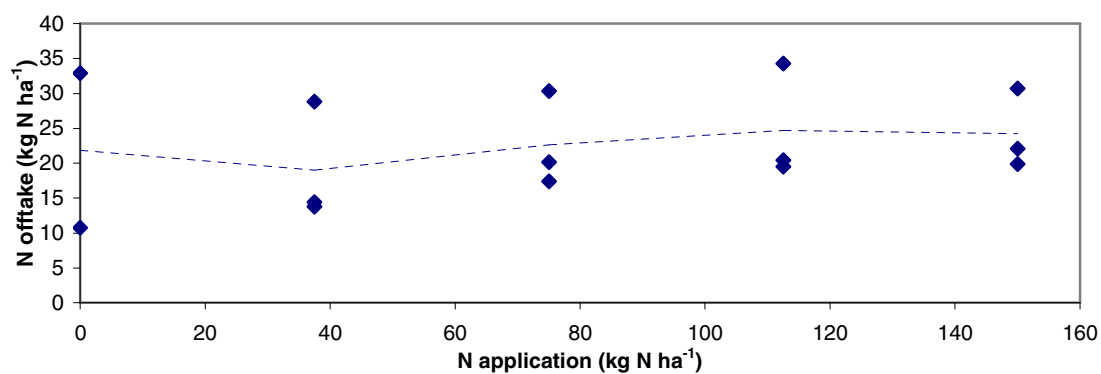


Figure 6.8 Cumulative N offtake (2 harvests) relative to N application in biowastes , ---- indicates mean cumulative dry yield (kg ha⁻¹); no significant ($P>0.05$) relationship was detected.

Table 6.1 Summary table of linear regression coefficients and r^2 values for mineral fertilisers, biosolids and biowastes in 2007 field experiment.

	Fresh yield		Dry yield		N offtake	
	Slope	r^2	Slope	r^2	Slope	r^2
Mineral N	0.04	0.57	0.0082	0.41	0.25	0.71
Mineral N+K	0.049	0.84	0.011	0.85	0.26	0.88
Mineral N+P	0.039	0.68	0.0075	0.51	0.21	0.79
Mineral N+P+K	0.064	0.53	0.012	0.57	0.31	0.65
DMAD	0.032	0.76	0.0058	0.74	0.15	0.81
Vegetable	0.024	0.77	0.0066	0.78	0.12	0.72
Salt whey	0.026	0.26	NS	NS	NS	NS
Yeast	0.051	0.94	0.011	0.88	0.23	0.89
AD fresh	0.052	0.94	0.0092	0.83	0.19	0.85
AD stored	0.041	0.77	0.0088	0.88	0.23	0.94
TAD	0.037	0.76	0.0067	0.74	0.19	0.81
ADMSW	NS	NS	NS	NS	NS	NS

NS= not significant at $P \leq 0.05$

Table 6.2 Nitrogen equivalency values for biosolids and biowastes investigated in 2007 field experiment at Silwood Park, based on comparison of linear regression coefficients in relation to mineral N.

	Fresh yield	Dry yield	Mean (yield)	N offtake	Mean (all)	Mineralisable N	
						(% total N)	(% organic N)
DMAD	0.80	0.71	0.75	0.60	0.70	57.9	66.1
Vegetable	0.60	0.81	0.71	0.48	0.63	54.7	59.7
Salt whey	0.65	NS	0.65	NS	0.65	58.6	62.6
Yeast	1.28	1.39	1.33	0.96	1.21	118.0	119.9
AD fresh	1.30	1.12	1.21	0.76	1.06	52.8	112.6
AD stored	1.03	1.07	1.05	0.92	1.00	28.7	101.7
TAD	0.93	0.82	0.87	0.76	0.83	69.4	80.8

Table 6.3 Nitrogen equivalency values for biosolids and biowastes investigated in 2007 field experiment at Silwood Park, based on comparison with linear regression coefficients in relation to mineral N+K.

	Fresh yield	Dry yield	Mean (yield)	N offtake	Mean (all)	Mineralisable N	
						(% total N)	(% organic N)
DMAD	0.65	0.54	0.60	0.58	0.59	46.5	53.1
AD fresh	1.06	0.85	0.95	0.73	0.88	34.8	74.3
AD stored	1.06	0.81	0.94	1.21	1.03	31.0	109.8
TAD	0.76	0.62	0.69	0.73	0.70	56.1	65.4
Vegetable	0.49	0.61	0.55	0.46	0.52	43.9	47.9
Salt whey	0.53	NS	0.53	NS	0.53	46.6	49.8
Yeast	1.04	1.06	1.05	1.01	1.04	102.1	103.6

Table 6.4 Nitrogen equivalency values for biosolids and biowastes investigated in 2007 field experiment at Silwood Park, based on comparison of linear regression coefficients, in relation to mineral N+P.

	Fresh yield	Dry yield	Mean (yield)	N offtake	Mean (all)	Mineralisable N	
						(% total N)	(% organic N)
DMAD	0.82	0.78	0.80	0.71	0.77	64.7	73.8
Vegetable	0.62	0.89	0.75	0.57	0.69	60.9	66.4
Salt whey	0.67	NS	0.67	NS	0.67	60.6	64.8
Yeast	1.31	1.52	1.42	1.14	1.32	129.4	131.4
AD fresh	1.33	1.22	1.28	0.90	1.15	62.2	132.8
AD stored	1.05	1.17	1.11	1.10	1.11	38.8	137.5
TAD	0.95	0.90	0.92	0.90	0.92	77.6	90.3

Table 6.5 Nitrogen equivalency values for biosolids and biowastes investigated in 2007 field experiment at Silwood Park, based on comparison of linear regression coefficients, in relation to mineral N+P+K.

	Fresh yield	Dry yield	Mean (yield)	N offtake	Mean (all)	Mineralisable N	
						(% total N)	(% organic N)
DMAD	0.50	0.51	0.50	0.48	0.50	37.3	42.5
Vegetable	0.38	0.58	0.48	0.39	0.45	36.4	39.7
Salt whey	0.41	NS	0.41	NS	0.41	40.9	46.3
Yeast	0.80	0.99	0.89	0.89	0.85	82.8	98.5
AD fresh	0.81	0.80	0.80	0.61	0.74	20.9	44.6
AD stored	0.64	0.76	0.70	0.74	0.71	0.00	0.00
TAD	0.58	0.58	0.58	0.61	0.59	45.1	52.5

The regression coefficients for mineral N+K and mineral N+P+K were greater than for Mineral N alone for all three measures of crop response. Phosphorus and K combined had a greater affect on crop response than K alone; however, a base dressing of P did not significantly increase the response to mineral N. Despite reducing the top application rates of AD fresh/stored from 100 m³ ha⁻¹ to 80 m³ ha⁻¹, there was a significant curvilinear relationship between rate of N application from AD fresh and yield response, and for AD stored and N offtake. In these cases, the top rate was removed from the regression so that only the linear section of the response was under consideration. The top rate of application for Yeast was also 80 m³ ha⁻¹, but this waste also had a high N content, and it was also necessary to exclude the top rate of application for the fresh yield response and the top two rates for dry yield, where a significant curvilinear relationship was found.

The reference material, DMAD, in comparison to mineral N fertiliser alone had a N equivalency of 0.70. This is much greater than would be expected; the value obtained in the 2006 trial was 0.52. There was unusually high summer rainfall during the 2007 experiment and it may be that this resulted in loss of N from the mineral N control plots resulting in the greater relative N equivalency of DMAD, a source of organic N. It is rare to have significant NO₃⁻ leaching losses below grassland during the summer period (Whitehead, 1995), but this appeared to be a possibility under the exceptional rainfall conditions experienced at Silwood Park during the field experiment, although leaching losses were not measured directly. However, leaching losses of NO₃⁻ were previously measured during biosolids fertiliser value trials at Silwood Park (Morris, 2006) and were found to be minimal. In the Silwood Park trials to investigate the fertiliser value of biosolids (Smith and Bellett-Travers, 2001; Smith, *et al.*, 2002b; Morris, *et al.*, 2003), the mean N equivalency for DMAD over 3 years of experiments was consistently approximately 0.30. In these experiments a dressing of K₂SO₄ had been applied across the site. The greater value obtained for DMAD in 2006, in addition to an N equivalency greater than 1 obtained for abattoir wash water was assumed to be a result of a contribution of another element to the crop response, therefore, controls for K and P were set up in the 2007 experiment. Nitrogen equivalency values for biosolids and biowastes relative to mineral N were similar to those obtained relative to mineral N with a base dressing of P (Tables 6.2 and 6.4), which demonstrated that there was no crop response to addition of P alone. Nitrogen equivalency values of biosolids and biowastes were smaller relative to mineral N with a base dressing of K (Table 6.3), and smaller still relative to mineral N with P and K combined (Table 6.5). This suggested that there was an interacting effect between P and K on crop response to addition of N,

and demonstrated that, as may be expected, the soil should be maintained at an adequate P and K status to achieve maximum benefit from addition of fertiliser N. These nutrients can be supplied through addition of organic wastes. Thus, biosolids are an important source of P and biowastes may supply P and K, vegetable waste for example is an effective source of K as demonstrated by elemental analysis of grass fertilised with Potato sludge in the 2006 trial. When there was a base dressing of P and K, the N equivalency value obtained for DMAD was 0.50, similar to the value obtained in the 2006 trials. It was therefore considered appropriate to use the N equivalency values obtained relative to the mineral N control plus a base dressing of P and K (Table 6.5) as a comparison between the two years of the investigation. The losses of mineral N from the mineral N control plots due to leaching by heavy rainfall in 2007 may have been reduced indirectly by the dressing of P and K, stimulating root growth and ability of the grass to capture the applied mineral N more effectively.

Full elemental analysis of the plant material from the 2006 experiment was not available when the 2007 trial was established; however, the S content of DMAD fertilised grass in 2006 was found to be over 2.5 times greater than the S content of mineral N fertilised grass (Table 5.1). This suggested that S was limiting at the site and explains the greater N equivalencies found for the reference material, 0.52 (Table 5.3) and 0.50 (Table 6.5). The differences in S concentration in plant tissue fertilised by the biowastes and the grass fertilised by mineral N alone were not so great and so it was assumed that provision of S did not contribute to the N fertiliser equivalencies obtained for these materials to a significant extent.

Mineralisable N values were also calculated and are shown in Tables 6.2-6.5. The mineralisable N content of DMAD was calculated as, 42.5 % organic N (Table 6.5). Again, this may be an over-estimate as the crop response to DMAD may be increased in relation to the mineral N controls, as a result of a response to added S.

The N equivalencies relative to mineral N+P+K for AD fresh/stored were 0.74 and 0.71 respectively (Table 6.5). These were consistent with values found in the 2006 trial of 0.84 for AD fresh and 0.66 for AD stored, and in the same range as would be expected for digested animal slurries (Shröder *et al.*, 2007). It is interesting to note that there was not such a great difference between the fresh and stored material in the 2007 experiment. This may be because AD stored had a higher mineral N content than AD fresh of 72 % total N in comparison to 53 % total N respectively (Table 3.13), which may be due to continued mineralisation during storage, and low rates of volatilisation of

NH₃. The difference in the fresh and stored digestates is reflected in the mineralisable N content, which is 44.6 % organic N for AD fresh; for AD stored, however, the N equivalency was equivalent to its mineral N content, indicating that during the storage period the labile organic N was mineralised and the remaining organic N fraction is resistant to further degradation.

The N equivalency for TAD was 0.59 which was lower than the value of 0.73 obtained in 2006. Elemental analysis of grass fertilised with TAD in 2006 showed enhanced K status compared to mineral N fertilised grass (Table 5.1), so the greater N equivalency in 2006 may be due to a contribution of K to the crop response. Vegetable waste mix was found to be a good source of N with a relative fertiliser N value of 0.45, similar to the N equivalency of DMAD. Yeast had an N equivalency value that was greater than the liquid digestates, of 0.85. It had a high total N content, of 6.85 kg m⁻³, compared to 6.73 kg m⁻³ and 5.46 kg m⁻³ in AD fresh and stored, respectively (Table 3.12), but its mineral N content was very low, 1.5 %. The high N equivalency of Yeast demonstrated that a large proportion of organic N was present in readily degradable forms from the yeast biomass in the waste material; the mineralisable N content was calculated at 98.5 %. Douglas *et al.* (2003) found that pot ale had a high fertiliser replacement value, with herbage yields greater than or equal to yields from mineral N at the same rate of application, due to a high component of amino acids.

In 2006, N equivalencies were also calculated by comparison of individual yield values and N offtakes for biosolids and biowastes, to fitted curves for the mineral fertiliser controls (as described in Section 3.7.2) which is an alternative standard approach to calculating nutrient equivalency (George, 1994; Jackson *et al.*, 1997; Nicholson *et al.*, 1999; Nicholson *et al.*, 2003; Schröder *et al.*, 2007). Asymptotic regression curves were fitted to the 2007 crop response data in relation to application of N for the mineral N, mineral N+K, mineral N+P and mineral N+P+K controls. In some cases the r^2 value for the asymptotic regression of crop response to the mineral fertiliser controls was less than r^2 from the linear regression (Figures 6.3, 6.5 and 6.7); in these cases it was considered more appropriate to use the linear regression for calculating the N equivalencies. This demonstrated that the measures taken to obtain a linear response (supply of P and K, and reduction of rates of application of N) based on experience from the 2006 field trial were effective. In the case of N offtake for all the mineral fertiliser controls and fresh yield for mineral N+K and mineral N+P+K, the linear regression coefficient was a better fit than the asymptotic regression equation. Due to the linear crop response to mineral N+P+K, comparison of regression coefficients was

therefore, in this case, considered the most appropriate method for calculating N equivalencies. A summary of the parameter estimates are summarised in Appendix A5. The fitted asymptotic regression curves for each measure of crop response when the r^2 value was greater than for the linear regression, and N equivalencies calculated by comparison of individual yields to these fitted curves are also given in Appendix A5.

6.4 Summary

A second field experiment was established at the Imperial College campus at Silwood Park in 2007. A further selection of biowaste materials from key industrial sectors and especially the food industry were included. Additional aims were to investigate the reproducibility of the crop response to biowastes addition by inclusion of the same processed biowaste materials as were investigated in 2006. Additional controls were included with base dressings of P and K and combinations of these elements to investigate the fertiliser equivalency values due to N alone. Application of a base dressing of P to mineral N fertiliser controls did not increase the gradient of crop response, however, application of K resulted in an increased response. The greatest increase in response was achieved by a combination of P and K. Nitrogen equivalency for DMAD relative to mineral N control plots plus a base dressing of P and K was 0.50, close to the value of 0.52 relative to mineral N fertiliser obtained in the 2006 trial. Therefore, N equivalencies for the biowastes, relative to the N+P+K control were used as a comparison between years.

Significant linear relationships between the rate of N application in biowastes and crop response were found in most cases, with the exception of Salt whey and ADMSW. Thus, the majority of the materials listed were effective sources of available N. Differences in response to ADMSW between the two years of the experiment demonstrated the potential for variation in the properties of the material probably due to differences in mineral N content and organic matter stability, brought about by variation in length of storage. The salinity of Salt whey may have detrimental effects on soil fertility, outweighing the positive benefits. However, low total N content may explain the non-significant crop response, although a significant response in fresh yield relative to N addition was detected.

Vegetable waste mix had a N equivalency of 0.45, similar to DMAD, indicating that it is an effective source of available N. Despite its low mineral N content Yeast had a high

N equivalency of 0.85, it was therefore a significant source of readily mineralisable organic N compounds which are rapidly degraded in soil to release mineral N.

The N equivalencies for AD fresh/stored were 0.74 and 0.71 respectively, which were relatively consistent with values in 2006 trial of 0.85 and 0.68. The N equivalencies obtained in 2007 were relatively similar between the stored and fresh material, compared to the 2006 values. This may be due to the increased mineral N content in AD stored in 2007, due to continued mineralisation during storage. The thermophilic aerobic digestate (TAD) had a slightly lower N equivalency than the other liquid digestates of 0.59, relative to N+P+K control. It was lower than the value of 0.76 relative to mineral N fertiliser alone achieved in the previous trial indicating influence of K on the crop response or potential variation due to variability of input material and low stability of organic matter content.

7 SHORT-TERM LABORATORY INCUBATION TO INVESTIGATE MICROBIAL BIOMASS N AND MINERAL N DYNAMICS IN BIOWASTES-AMENDED SOIL

7.1 Introduction

7.1.1 Background

Recent research has demonstrated that soil fertility influences N transformation processes in biosolids-amended soil, with more N released in soils of a higher fertility status (Smith *et al.*, 1998b; Breedon *et al.*, 2003). The mechanisms responsible for this observation require further investigation to determine whether they need to be considered in relation to biowastes management practices. Nitrogen mineralised from organic N sources may be immobilised by transfer to microbial biomass where it will not be immediately available to crops. Partitioning of N in microbial biomass may be important in understanding N release kinetics and could be responsible for lower N availability observed in less fertile soils. It is well established that the C:N ratio of organic soil inputs influences the amount of mineralised N (Nicolardot, 2001, Pansu *et al.*, 2003, Vinten, 2002). When soils are amended with organic materials that have a high C:N ratio, N is temporarily immobilised in microbial biomass as available C is assimilated. In general, if the organic fertiliser source has a high C:N ratio, greater than 20:1, organic N tends to be immobilised by the microbial community, whereas when the C:N ratio is less than 20:1 the N content of the substrate is in excess of microbial cellular requirements and organic N tends to be mineralised (Parker and Sommers, 1983). Biowastes represent a diverse range of materials and treatment processes affect their characteristics, relative stability and nutrient availability in different soils.

Microbial biomass N (MBN) may represent an important component of N in biowastes amended soils and is likely to vary with soil type and biowaste. The stability of the added organic matter may be particularly important in modulating microbial and N dynamics in amended soils (Recous and Mary, 1990; Calbrix *et al.*, 2007). Soil incubation studies have been extensively used to determine N availability in organic soil amendments (Terry *et al.*, 1979; Hsieh *et al.*, 1981; Griffin and Laine, 1983; Parker and Sommers, 1983; Wiseman and Zibilske, 1988; Smith *et al.*, 1998b;c; d; Breedon *et al.*, 2003). They enable the kinetics of mineralisation of organic amendments to be

quantified without interferences due to losses of N by crop uptake or leaching through the soil profile.

The objectives of this laboratory incubation study were, therefore, to investigate the effects of biowaste type and soil type on N availability in amended soils under controlled temperature and moisture conditions, and to study immobilisation of N within soil biomass. This was to provide information into its importance in controlling N release to crops from biowastes in contrasting fertility systems. The three processed biowastes investigated the 2006 and 2007 fertiliser response trials (Chapters 5 and 6), in addition to an unamended control, mineral N control and a biosolids reference treatment (DMAD), were selected and mixed with soils with contrasting physical and chemical properties. The two soils from Wye in Kent were collected from the sites of the 2005 field investigation into MBN and mineral N dynamics in biosolids-amended soil (Chapter 4) and the third soil was from Silwood Park, the site of the biowaste crop response trials (Chapters 5 and 6). The selection of soils and materials which have been investigated in the field means that comparisons can be drawn with field data. Two of the biowastes had been treated anaerobically and one had been treated aerobically, therefore differences in relative stability and N mineralisation behaviour in amended soils were expected.

7.1.2 Aims

- To investigate the effects of biowastes type on N mineralisation in amended soil, under controlled moisture and temperature conditions;
- To investigate the interactions between biowaste type, soil type and N dynamics in amended soil under controlled moisture and temperature conditions;
- To study N partitioning within soil microbial biomass for different soil types amended with biowastes, and the subsequent influence on N release;
- To draw comparisons with field data on the fertiliser value of biowaste materials in different soil types.

7.2 Materials and Methods

7.2.1 Introduction

General materials and methods are described in Chapter 3. Site locations and properties of the 3 soils collected for the laboratory incubation experiment are given in Section 3.2. General methods for soil sampling and analysis are given in Section 3.3. Soils were thoroughly mixed and sieved to <5.6 mm in field fresh condition before use, any remaining plant biomass was removed by hand. Selection, collection and physical and chemical characteristics of biosolids and biowastes investigated in the experiment are given in Section 3.4, and a list of the biosolids and biowastes used in this experiment and the field experiments, and abbreviations used in this thesis are given in Table 3.5. Methods specific to this experiment are described here.

7.2.2 Calculating Water Holding Capacity and Adjusting Soil Moisture

The water holding capacity (WHC) was measured using the following procedure, modified from the method described by Harding and Ross (1964). Samples of approximately 100 g of each soil were placed in a small sieve lined with a Whatman 150 mm 1 filter paper, and placed in a dish of water so that the water level was higher than the level of the soil to allow the soil to become saturated. They were left to stand for 12 h to achieve equilibrium. The sieves were then removed from the dish of water, covered with parafilm to avoid evaporation, and left for 3 h to drain.

Three 20 g subsamples of each saturated soil were weighed into aluminium dishes, recording the weight of the dish before adding the soil. The samples were dried overnight at 105 °C for 24 h to achieve constant weight.

The water holding capacity (WHC) was calculated as follows:

$$\text{WHC (\%)} = (\text{mass of drained soil} - \text{mass of oven dried soil}) / (\text{mass of oven dried soil}) \times 100$$

Silwood Park soil had the lowest WHC of 38.4 %, Brices field was 45.4 % and North Sidelands was 65.5 %. The soils were air-dried for 8 hours to reduce their moisture content until they reached approximately 50.0 % WHC which is within the standard

range used for laboratory incubation experiments (Harding and Ross, 1964; Wiseman and Zibilske, 1988; Smith *et al.*, 1998b;c;d).

7.2.3 Incubation Procedure

The experiment was established on 2 February 2007. The solid materials, ADMSW and DMAD, and TAD, which was a liquid with a high dry solids content, were added to the soils at a rate equivalent to 10 t DS ha⁻¹, and the liquid, AD, was applied at a rate of 50 m³ ha⁻¹. An unamended soil and a mineral N control, NH₄Cl, were included for each soil type. The mineral N treatment, NH₄Cl, was applied at a rate equivalent to 200 kg N ha⁻¹. Rates of incorporation were calculated on the assumption that the soils had a bulk density of 1 and the cultivation depth was 10 cm.

The solid materials were weighed out into the required portions for 2.1 kg soil, and thoroughly mixed into a slurry with 50 ml deionised water, a hand blender was used to homogenise ADMSW, which contained fibrous material. Ammonium chloride was dissolved in 75 ml of deionised water, and the unamended control soil also received 75 ml of deionised water to maintain equivalent moisture content. The wastes and mineral N were then carefully mixed into 2.1 kg portions of sieved soil using a hand mixer, and then sieved to pass 5.6 mm, to ensure uniform incorporation.

The amended and control soils were weighed out into triplicate 100 g portions in polythene bags (140 x 140 x 50 cm), for each removal time of the experiment. A gap was left in the seal of each bag to allow gas exchange, and the samples were placed in an incubator and were maintained in the dark at 25 °C. Samples were removed after 0, 3, 6, 13, 20, 34 and 48 days. This time period was chosen as NO₃-N production from the wastes was expected to reach a maximum by approximately 50 days as observed in previous incubation experiments with biosolids at similar temperatures (Smith *et al.*, 1998b; Smith and Durham, 2002; Breedon *et al.*, 2003). The mass of each bag was recorded and moisture was kept constant throughout the incubation experiment by addition of deionised water.

At each removal time soil was weighed out for microbial biomass N and C determination and gravimetric moisture content, and the remaining soil was frozen at -19 °C, and later analysed for mineral N.

Methods for determination of gravimetric moisture content, mineral N and chloroform fumigation-extraction procedure for MBC and MBN analysis are described in Sections 3.3.3, 3.3.4 and 3.3.5 respectively.

7.2.4 Electrical Conductivity

The electrical conductivity of amended and unamended control soils on day 0 was measured, following a standard procedure (MAFF, 1986). Air-dried soil, ground to 2 mm, was shaken for 15 minutes at 20 °C with saturated CaSO_4 solution in a ratio of 1:2.5 soil to CaSO_4 . The samples were then filtered through a Whatman no. 2 filter paper and soil conductivity was measured using a conductivity meter (Hanna Instruments Leighton Buzzard, UK).

7.2.5 Soil pH

The pH of amended and unamended control soils on day 0 was measured following a standard procedure (MAFF, 1986). Air-dried soil, ground to 2 mm, was shaken for 15 minutes with deionised water in a ration of 1:2.5 soil to water. The pH of the resulting suspension was measured.

7.2.6 Statistical Analysis

Analysis of variance was carried out on recovered $\text{TON} + \text{NH}_4\text{-N}$ (% total N) and MBN (% total N). Calculations and statistical analysis of data used are described in Section 3.7.1.

7.3 Results and Discussion

7.3.1 Mineral N Concentrations

Changes in total oxidised nitrogen (TON) and $\text{NH}_4\text{-N}$ from day 0 to day 48 of the incubation experiment are shown in Figures 7.1–7.5. Replicate treatments are shown on the figures and in most cases it can be seen that replicates were in good agreement. In the case of soils amended with NH_4Cl there was little difference in the mineral N concentration between the experimental replicates (Figure 7.1). The organic soil amendments introduced greater variation between replicates (Figures 7.2-7.5); this may reflect the relative difficulty of obtaining complete homogenisation when mixing the

biowastes with the soils. It may also be a consequence of added complexity in soil microbial behaviour when combining organic matter with soil in addition to nutrients. Expected initial mineral N concentrations were calculated from the mineral N content of the biowastes and rate of application and are shown in Table 7.1, actual recoveries of mineral N were close to these values. Initial mineral N recoveries in NH_4Cl amended soil for Silwood, Brices and North Sidelands were approximately 95 %, 84 % and 94 %, respectively. In DMAD-amended soil, initial recoveries of $\text{NH}_4\text{-N}$ were greater than the expected recovery of $42.2 \text{ mg kg}^{-1} \text{ ds}$ (Table 7.1), for Brices and Silwood recoveries were approximately $68 \text{ mg kg}^{-1} \text{ ds}$ and they were greater for North Sidelands, at $72.5 \text{ mg kg}^{-1} \text{ ds}$ (Tables 7.2-7.4). Thus, it appeared that there was some initial rapid mineralisation of DMAD, when this material was added to the soils. There may also have been some mineralisation during the experimental set-up and mineral N determination procedures. The expected initial concentration of mineral N in ADMSW amended soil was $35.5 \text{ mg kg}^{-1} \text{ ds}$, and actual recoveries were close to this value at 44.9, 35.1 and $48.3 \text{ mg kg}^{-1} \text{ ds}$ for soil from Silwood, Brices and North Sidelands, respectively. Actual initial mineral N recoveries for TAD amended soil were very close to calculated initial values, but for AD amended soil concentrations were between 34 and $54 \text{ mg kg}^{-1} \text{ ds}$ greater than the expected concentration of $139 \text{ mg kg}^{-1} \text{ ds}$, with the greatest concentration in North Sidelands soil. Therefore, some mineralisation of AD may have occurred during the experimental set up. This indicated that the mineralisable organic N fraction was rapidly mineralised, especially in the higher fertility soil.

Changes in mineral N concentrations in NH_4Cl -amended soil, in comparison to unamended control soils are shown in Figure 7.1, and N recoveries for each soil are given in Tables 7.2-7.4. During the course of the incubation in all soil types, $\text{NH}_4\text{-N}$ concentrations decreased with a corresponding increase in TON concentrations as nitrification occurred. Nitrification occurred at a faster rate in North Sidelands soil, followed by Silwood soil and Brices soil; Figure 7.1 shows that TON concentrations exceeded $\text{NH}_4\text{-N}$ concentrations on day 3 for North Sidelands soil, day 6 for Silwood and day 13 for Brices. At the end of the incubation period recoveries of TON were approximately 100 % of the mineral N input for all three soils types (Tables 7.2-7.4). The differences in nitrification rates may be explained by the organic matter content (Table 3.1) and microbial biomass concentration, which is discussed in the following Section (Section 7.3.2). The nitrification capacity corresponded with the organic matter and microbial biomass content of each soil. Brices had the lowest organic matter content and MBC contents, of 1.9 % and $60\text{-}120 \text{ mg C kg}^{-1} \text{ ds}$ respectively, compared

to 2.1 % and 150-200 mg C kg⁻¹ ds respectively for Silwood and 4.0 % and 400-500 mg kg⁻¹ ds respectively for North Sidelands. Thus the greater the soil organic matter content, the more fertile and microbiologically active the soil (Zagal, 1993; Silva *et al.*, 2005), which accounts for the higher nitrification rate in North Sidelands. In addition, the lowest fertility soil, Brices, had a lower total N concentration than North Sidelands, 0.12 compared to 0.25 % (Table 3.3) and the lowest available N concentration 6.3 mg kg⁻¹ ds, compared to 11-12 mg kg⁻¹ ds in the other two soils. The higher pore space, resulting from improved soil structure as a consequence of greater soil organic matter content, may also be important in increasing mineralisation and nitrification rates, through increased oxygen availability. For example, Nendel and Reuter (2007) found that N release from grape residues was positively related to the pore volume. However, the greater mineralisation and nitrification rates in North Sidelands are contrary to the findings of Sistani *et al.* (2008), who generally found that mineralisation of broiler litter was negatively correlated to the clay and silt content of the soil, with more broiler litter N being mineralised in lighter, sandy soil types. This was probably because NH₄-N became fixed by clay minerals in the clay soil type. The results presented here suggest that soil fertility and N mineralisation and nitrification rates may be more closely related to organic matter content than texture. Jha *et al.* (1996) also found that a soil with low soil organic matter content and high clay content had fewer free-living nitrifying bacteria than soil containing a larger amount of organic matter, with low clay content.

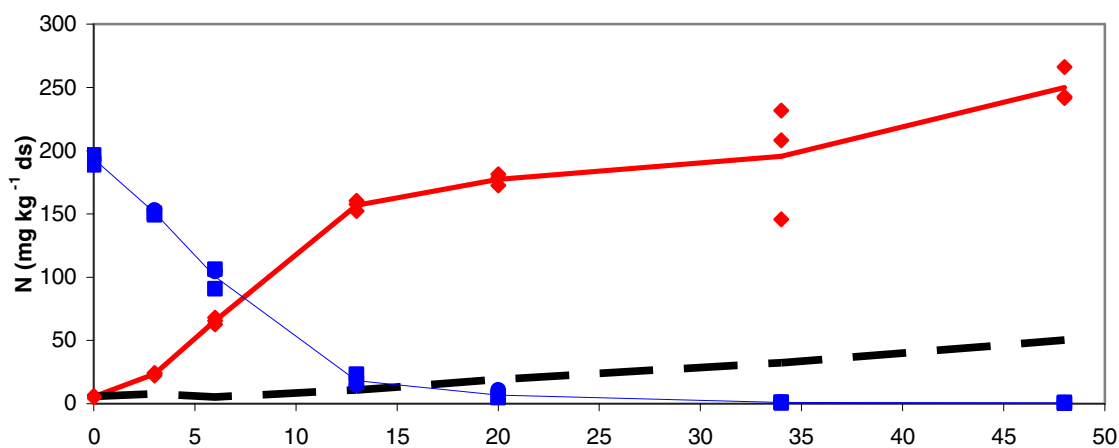
It was in Brices soil that the greatest deficit in expected and actual recovery of mineral N was observed in NH₄Cl treated soil; this may indicate that mineral N was initially immobilised in the microbial biomass. Analysis of the samples for MBN was conducted and the results are discussed in Section 7.4.3. The greater initial mineral N recoveries observed in North Sidelands soil may also be related to its fertility status and a greater capacity for mineralisation. Greater rates of nitrification in the higher fertility soil, North Sidelands, were also observed in the soils with organic amendments (Figures 7.2- 7.5).

Total oxidised-N (TON) and NH₄-N dynamics in soils amended with DMAD, in comparison to unamended control soils, are presented in Figure 7.2. Final mineral N recoveries are given in Tables 7.2-7.4. In each soil, TON concentrations increased above initial values contributed from the mineral N input in DMAD indicating mineralisation of organic N. In Silwood soil, the loamy sand, mineralisation occurred until day 6, at which point NH₄-N concentrations reached a maximum of 105 mg kg⁻¹ ds above control values; TON concentrations continued to increase to 66 mg kg⁻¹ ds

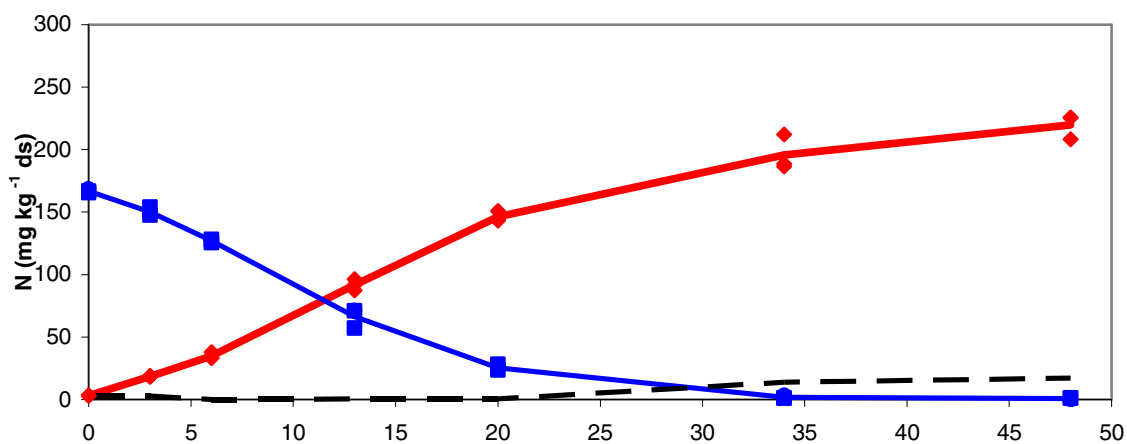
greater than control values, which was equivalent to 14.4 % of total N addition available in the soil, and 5.87 % mineralised organic N (Table 7.2). In Brices soil, the sandy silt loam, TON concentrations had increased to 92 mg kg⁻¹ ds greater than control values by the end of the incubation period, equivalent to approximately 20 % total N additions, this indicated that 12.1 % of the organic N had been mineralised (Table 7.3). In North Sideland soil, the silty clay, TON concentration reached a maximum at day 20 at 72 mg kg⁻¹ ds above unamended soil. At this point N recovery was equivalent to 15.8 % total N additions, and a mineralisable fraction of 7.4 % (Table 7.4). However, after day 20, the TON concentration began to decline. Smith *et al.* (1998b) found that approximately 20–40 % of the total N in lagoon-matured and dewatered digested biosolids was converted to TON, and Breedon *et al.* (2003) recovered between 40–60 % total N in DMAD amended soil, whereas 14–20 % of total N in DMAD was available at day 48 in this experiment. It is possible that not all the mineralisable N had been released from the biowastes after 48 days, however, in previous incubation experiments where the temperature was maintained at 20 °C, maximum TON production from biosolids was observed in a sandy loam between 42 and 56 days and in a clay loam by 42 days (Breedon *et al.*, 2003). In a selection of soil types, incubated at 25 °C, Smith *et al.* (1998b) found that the majority of digested biosolids tested produced a maximum amount of TON within 40 days. The soils for the incubation experiment described here were collected in January 2007. It is possible that the apparently slower rates of N release measured here were explained because the microbial population was not as active due to cold winter temperatures, and required more time to adapt to the input of organic matter and incubation temperature, as mineralisation and nitrification rates increase with temperature (Opperman *et al.*, 1989; Cookson *et al.*, 2003).

Mineral N dynamics in ADMSW-amended soil, relative to the unamended control soil, are shown in Figure 7.3. In all Silwood and Brices soil by the final sampling date there was a slight decrease in available N from initial concentrations, and in North Sideland available N fell below control concentrations after day 13. Total oxidised N concentrations remained greater than control concentrations until day 34 in Brices soil but decreased below control concentrations on day 48. Final recoveries and the proportion (%) of mineralised N are presented in Tables 7.2–7.4; the final mineral N concentrations in Brices soil are taken as the day 34 values as concentrations had increased to a maximum on this date.

(a) Silwood (loamy sand)



(b) Brices (sandy silt loam)



(c) North Sidelands (silty clay)

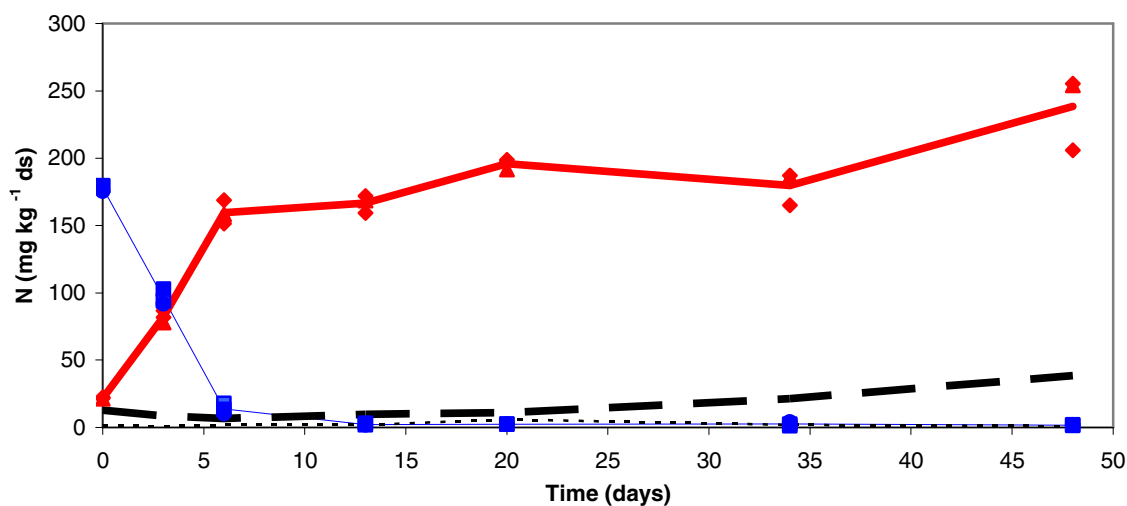
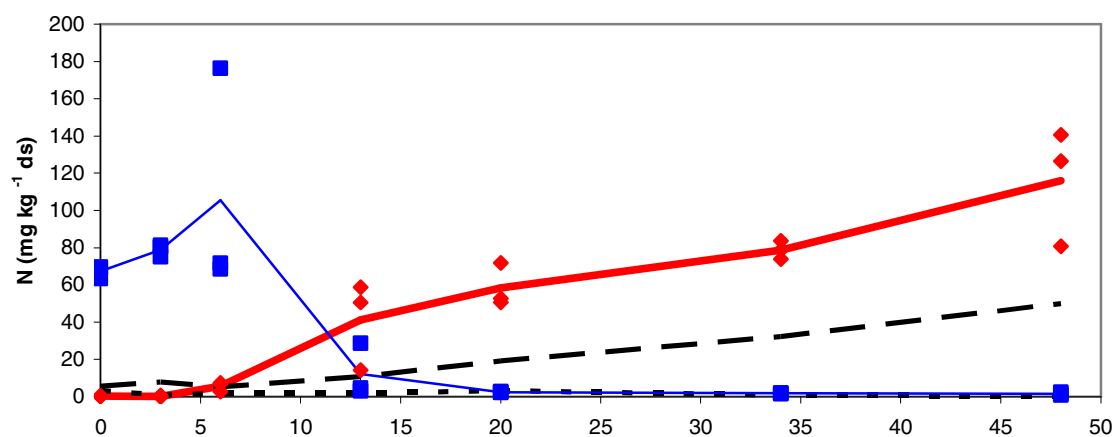
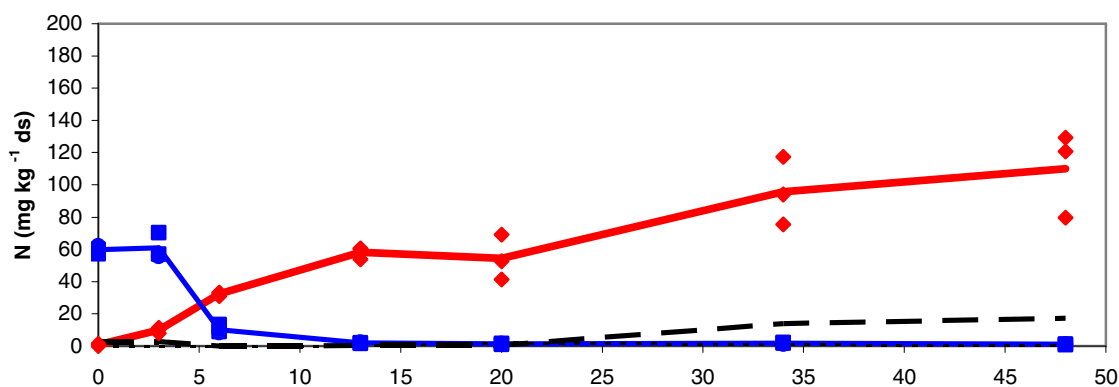


Figure 7.1 Concentration of NH₄-N and TON in relation to time, in three contrasting soils, amended with NH₄Cl (NH₄-N, — ; replicates, ■ ; TON, — ; replicates, ♦) and in unamended control soils (NH₄-N, - - - - ; TON, — — —).

(a) Silwood (loamy sand)



(b) Brices (sandy silt loam)



(c) North Sidlands (silty clay)

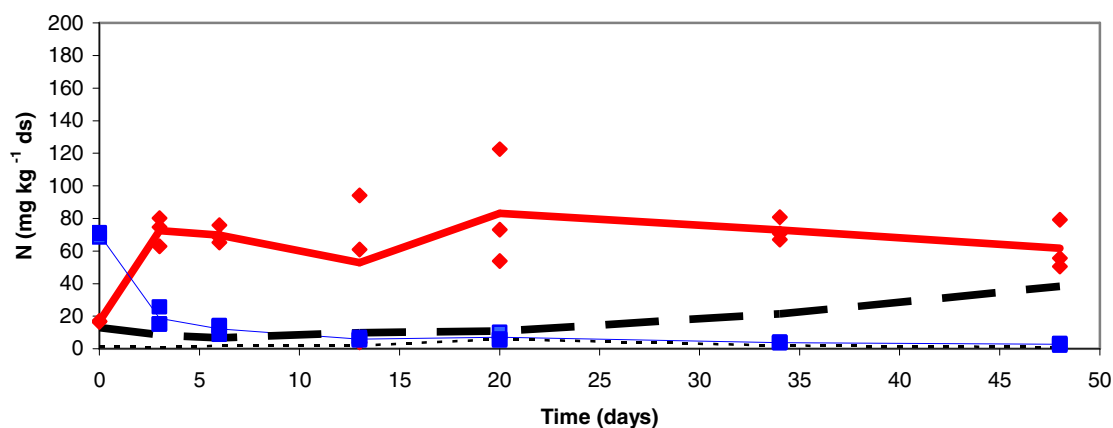
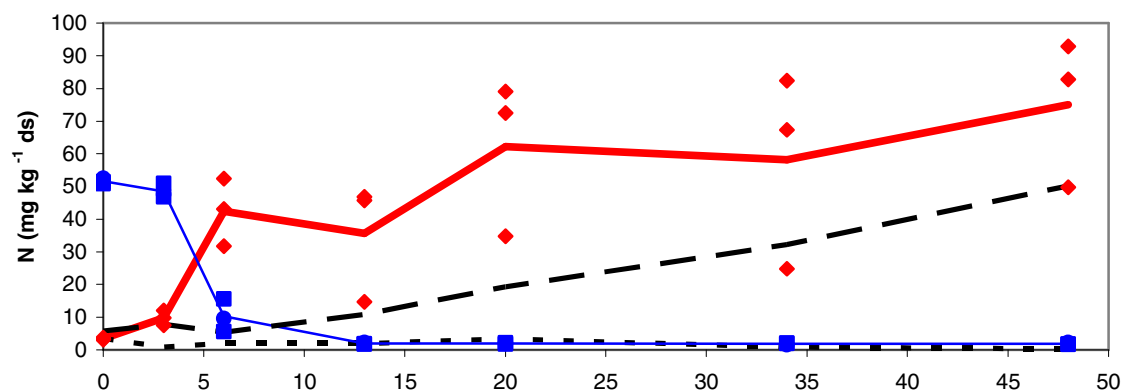
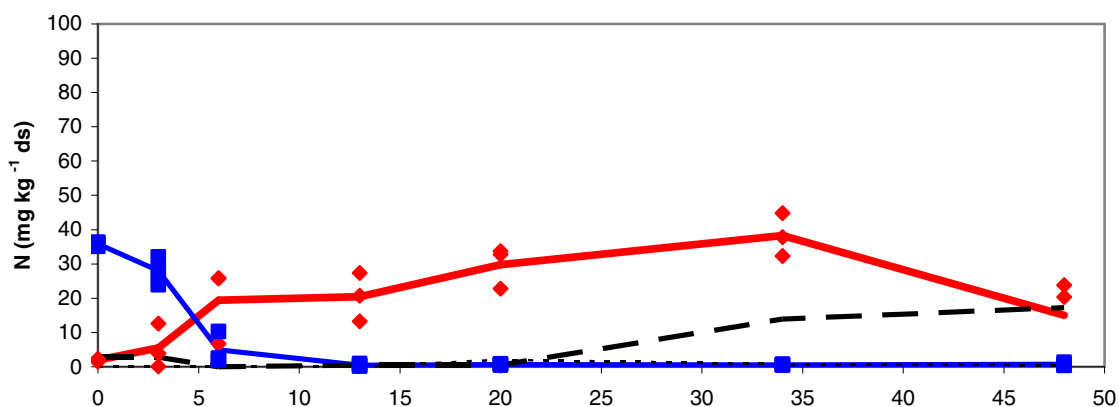


Figure 7.2 Concentration of $\text{NH}_4\text{-N}$ and TON in relation to time, in three contrasting soils, amended with DMAD ($\text{NH}_4\text{-N}$, —■—; replicates, ■; TON, —♦—; replicates, ♦) and in unamended control soils ($\text{NH}_4\text{-N}$, - - - - -; TON, — — —).

(a) Silwood (loamy sand)



(b) Brices (sandy silt loam)



(c) North Sidelands (silty clay)

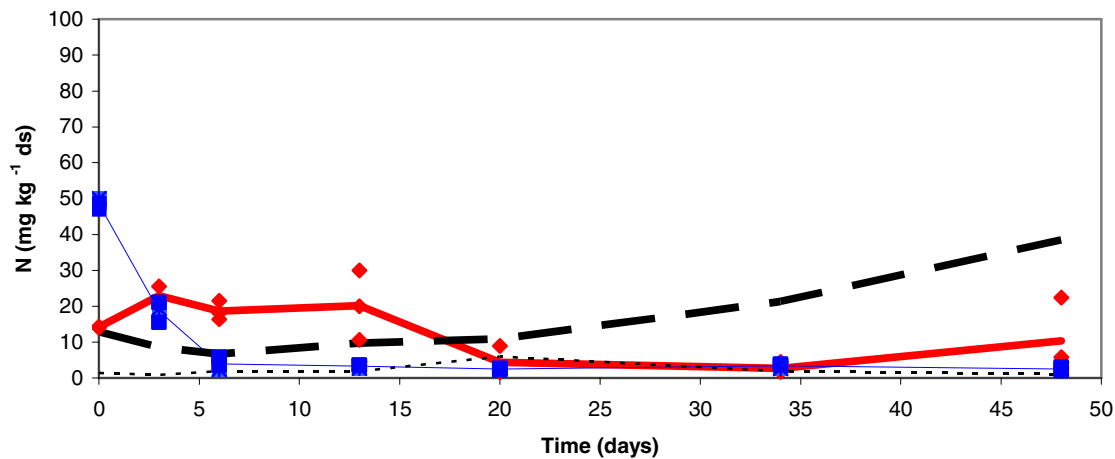
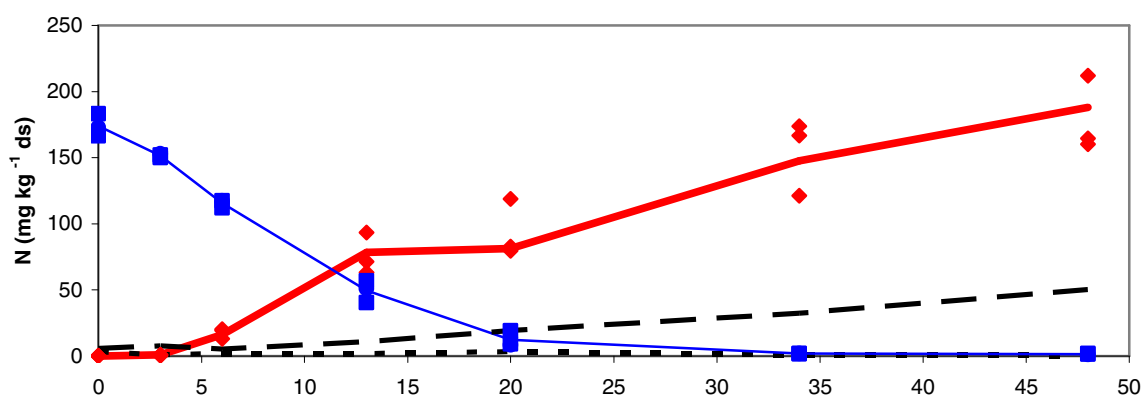
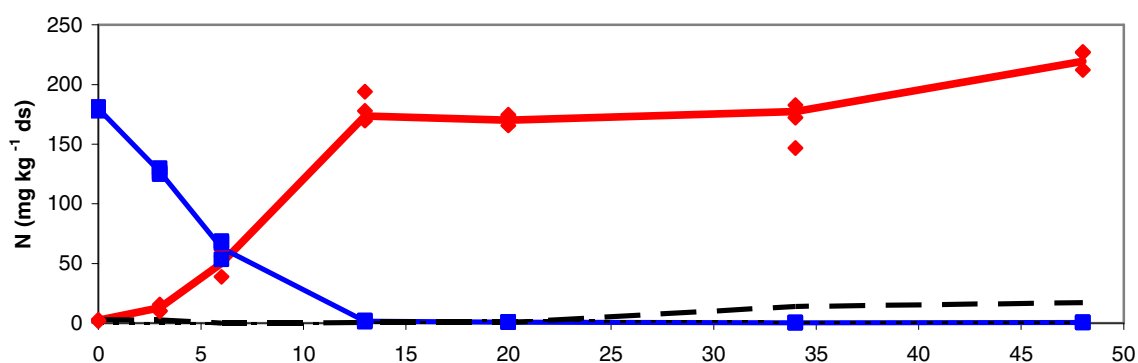


Figure 7.3 Concentration of $\text{NH}_4\text{-N}$ and TON in relation to time, in three contrasting soils, amended with ADMSW ($\text{NH}_4\text{-N}$, —■—; replicates, ■; TON, —◆—; replicates, ◆) and in unamended control soils ($\text{NH}_4\text{-N}$,; TON, — — —).

(a) Silwood (loamy sand)



(b) Brices (sandy silt loam)



(c) AD: North Sidelands (silty clay)

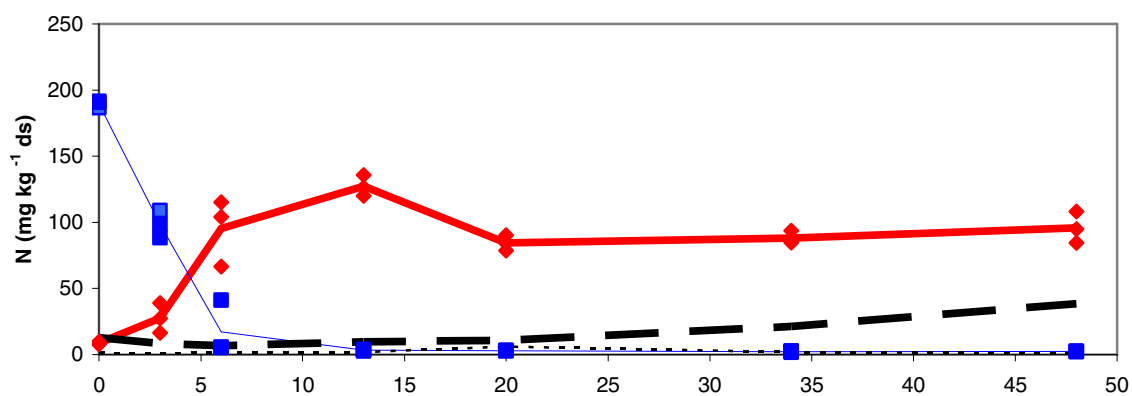
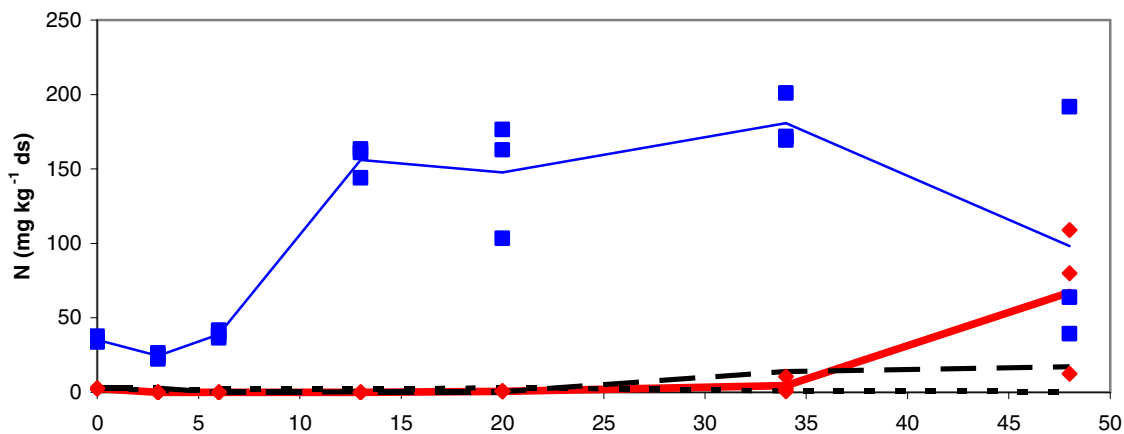
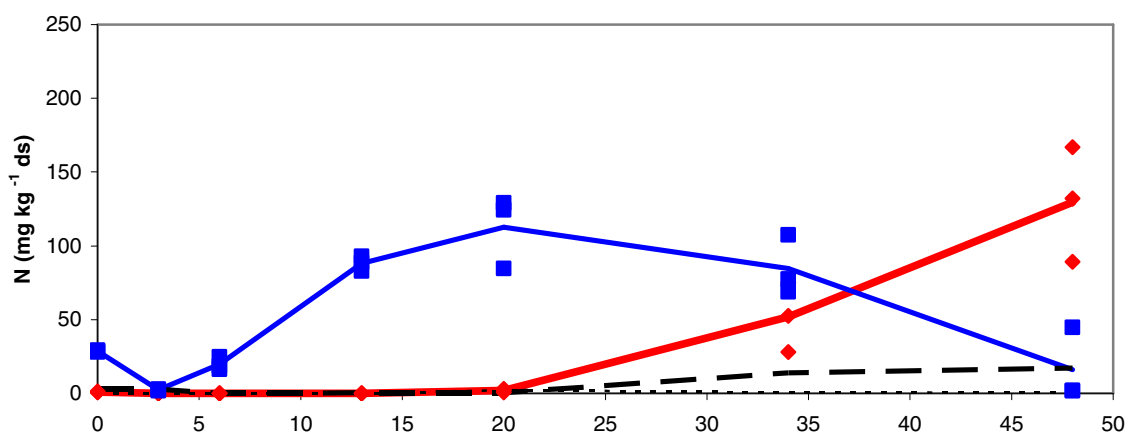


Figure 7.4 Concentration of NH₄-N and TON in relation to time, in three contrasting soils, amended with AD (NH₄-N, — ; replicates, ■; TON, — ; replicates, ♦) and in unamended control soils (NH₄-N, ----- ; TON, — — —).

(a) Silwood (loamy sand)



(b) Brices (sandy silt loam)



(c) North Sidelands (silty clay)

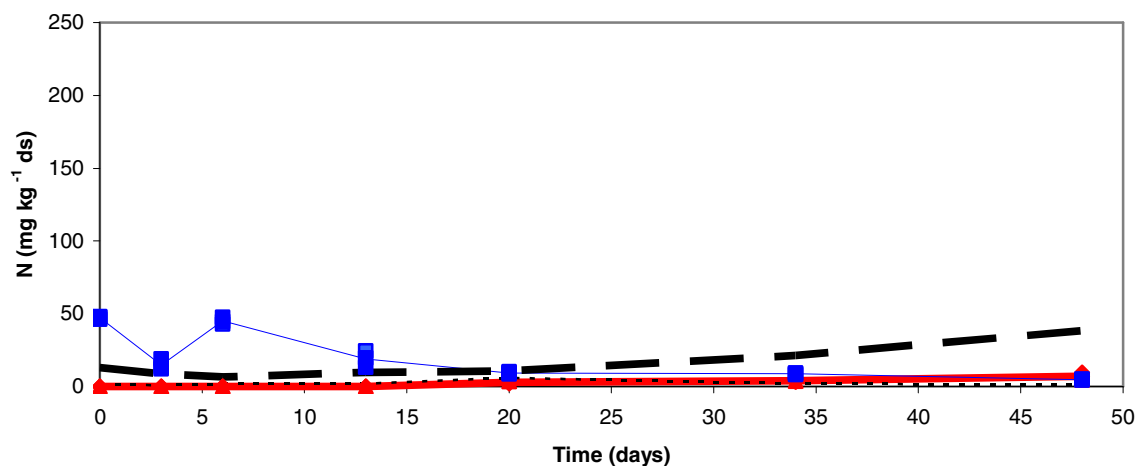


Figure 7.5 Changes in concentration of NH₄-N and TON in relation to time, in three contrasting soils, amended with TAD (NH₄-N, — ; replicates, ■; TON, — ; replicates, ♦) and in unamended control soils (NH₄-N, - - - - ; TON, — — —).

Table 7.1 Nitrogen additions to the soils from biosolids, biowastes and mineral N.

Biowaste or fertiliser	Total N input (mg kg⁻¹ ds)	Organic N input (mg kg⁻¹ ds)	NH₄-N input (mg kg⁻¹ ds)	TON input (mg kg⁻¹ ds)	NO₂-N input (mg kg⁻¹ ds)	Mineral N input (mg kg⁻¹ ds)
NH ₄ Cl	200	0	200	0	0	200
DMAD	464	421.8	34	Trace	8.21	42.2
ADMSW	232	196.5	33.6	Trace	1.91	35.5
AD	296	157	137.8	Trace	1.12	139
TAD	350	322	28.0	Trace	1.87	29.9

Table 7.2 Nitrogen recoveries, incubation study, Silwood Soil.

Soil Treatment	Day 0, NO₃-N (mg kg⁻¹ ds)	Day 0, NH₄-N (mg kg⁻¹ ds)	Day 0, mineral N recoveries (mg kg⁻¹ ds)	Day 0, % total N available	Final NH₄-N (mg kg⁻¹ ds)	Final TON (mg kg⁻¹ ds)	Mineral N recovery (mg kg⁻¹ ds)	Available N (% total N)	Mineralised N (% organic N)
Control	6.61	3.48			0.34	50.2			
NH ₄ Cl	5.50	193.3	188.7	94.4	0.67	250.1	200.3	100.1	
DMAD	0.28	67.4	57.5	12.4	1.55	115.9	67.0	14.4	5.87
ADMSW	3.40	51.6	44.9	19.3	1.87	75.1	26.5	11.4	-4.58
AD	0.083	174.2	164.2	55.5	1.48	188.3	139.3	47.0	0.16
TAD	2.57	35.2	27.6	7.89	98.4	67.2	115.1	32.9	26.6

Table 7.3 Nitrogen Recoveries, Incubation Study, Brices Soil.

Soil Treatment	Day 0, NO ₃ -N (mg kg ⁻¹ ds)	Day 0, NH ₄ -N (mg kg ⁻¹ ds)	Day 0, mineral N recoveries (mg kg ⁻¹ ds)	Day 0, % total N available	Final NH ₄ -N (mg kg ⁻¹ ds)	Final TON (mg kg ⁻¹ ds)	Mineral N recovery (mg kg ⁻¹ ds)	Available N (% total N)	Mineralised N (% organic N)
Control	2.83	0.00			0.49	17.2			
NH ₄ Cl	3.15	166.8	167.1	83.5	0.74	219.7	202.7	101.4	
DMAD	0.72	59.8	57.7	12.4	1.11	109.9	93.3	20.1	12.1
ADMSW	2.00	35.9	35.1	15.1	0.58 [†]	38.3 [†]	24.3	10.5	-5.72
AD	2.30	179.9	179.4	60.6	0.46	219.5	202.3	68.3	40.3
TAD	0.98	28.8	26.9	7.69	16.1	129.4	127.8	36.5	30.6

[†] Final TON and NH₄-N concentrations for ADMSW amended soil taken from day 34, where there was a peak in TON concentration, including adjustment for control values (not shown)

Table 7.4 Nitrogen Recoveries, Incubation Study, North Sidelands

Soil Treatment	Day 0, NO ₃ -N (mg kg ⁻¹ ds)	Day 0, NH ₄ -N (mg kg ⁻¹ ds)	Day 0, mineral N recoveries (mg kg ⁻¹ ds)	Day 0, % total N available	Final NH ₄ -N (mg kg ⁻¹ ds)	Final TON (mg kg ⁻¹ ds)	Mineral N recovery (mg kg ⁻¹ ds)	Available N (% total N)	Mineralised N (% organic N)
Control	12.9	1.45			1.03	38.5			
NH ₄ Cl	21.7	178.0	185.4	92.7	1.70	238.5	200.7	100.4	
DMAD	16.7	70.2	72.5	15.6	7.06 [†]	83.2 [†]	73.4	15.8	7.40
ADMSW	14.1	48.5	48.3	20.8	2.52	10.3	-26.7	-11.5	-31.6
AD	8.76	189.6	184.1	62.2	2.34	96.0	58.8	19.9	-51.1
TAD	0	47.3	33.0	9.44	4.58	6.98	-28.0	-7.99	-18.1

[†] Final TON and NH₄-N concentrations for DMAD amended soil taken from day 20, where there was a peak in TON concentration, including adjustment for control values (not shown)

The amounts of recovered N were greatest in Silwood Park, equivalent to 11.4 %, followed by Brices field, 10.5 %, and in North Sidelands less mineral N was recovered than was added. In all three soils no net mineralisation of organic N was therefore detectable.

In AD-amended soil, the TON concentration increased rapidly in all three soil types, the rates of nitrification followed the same pattern as was observed for the NH_4Cl treatment, with a faster rate of nitrification in the higher fertility soil (Figure 7.4). This is consistent with the rapid nitrification rates observed by Smith *et al.* (1998b) who found that the majority of added $\text{NH}_4\text{-N}$ was transformed to TON within 20 days of incubation at 25 °C. Initial $\text{NH}_4\text{-N}$ concentrations measured in the soil were large as most of the added N was in mineral form, therefore TON concentrations did not increase above initial $\text{NH}_4\text{-N}$ concentrations, although in North Sidelands soil there was a decrease in accumulated TON concentration by the end of the experiment. Final available N concentrations for Silwood and Brices Field were 47.0 and 68.3 %, which were in the range expected for liquid digested biosolids (Coker *et al.*, 1966; Ryan *et al.*, 1973; Hall *et al.*, 1983b.; Kiemnec *et al.*, 1987; Smith *et al.*, 1998b). In North Sidelands, recovered N was lower, at 19.9 % of total added N. The proportion of mineral N in AD was approximately 47 %; therefore, there was full recovery of the mineral N fraction in Silwood and Brices soil, in addition 40 % of the organic N was mineralised in Brices soil.

As was observed in ADMSW-amended soil, there were apparent losses of mineral N in North Sidelands soil following TAD addition (Figure 7.5). In TAD-amended soil there was an increase in $\text{NH}_4\text{-N}$ concentration by approximately 110 mg kg^{-1} ds in Silwood between days 0-34, and approximately 80 mg kg^{-1} ds in Brices between day 0-20, but in North Sidelands the $\text{NH}_4\text{-N}$ concentration decreased below unamended control values on day 20. There was a delay in nitrification in this soil treatment; TON concentrations did not increase until day 34 in Brices soil and day 48 in Silwood soil. There was no increase above unamended control values in North Sidelands soil, although there was an increase of <10 mg kg^{-1} from initial TON concentration. It could be that nitrification was temporarily inhibited in TAD treated soil as a result of high concentrations of $\text{NH}_4\text{-N}$ from the TAD. Nitrification activity in soil has been reported to be inhibited at high concentrations of $\text{NH}_4\text{-N}$ after application of high rates of raw or digested sludge (Epstein *et al.*, 1978). Ryan *et al.* (1973) also found an initial lag in nitrification following high rates of application of digested sludge, when the rates of added $\text{NH}_4\text{-N}$ were 378-756 mg kg^{-1} ds, which may have been a result of inhibitory

effects of high $\text{NH}_4\text{-N}$ concentration; however, they observed an increase in $\text{NO}_3\text{-N}$ by the second week of incubation. Other potential factors that may inhibit nitrifiers were increased salinity or acidity following amendment with TAD, which had a low pH of 4.4 (Table 3.8). The electrical conductivity and pH of the amended soils on day 0 in relation to the unamended controls are shown in Tables 7.5 and 7.6. The electrical conductivity of unamended control soil was between 1.6 and 2.0 mS cm^{-1} , and similar in AD-, DMAD- and ADMSW-amended soils. The electrical conductivity was approximately 0.5 mS cm^{-1} greater than the unamended control soils in TAD and NH_4Cl -amended soil, however, this was still well within a normal soil salinity range (Rowell, 1994). Acidic pH has been reported as a cause of $\text{NH}_4\text{-N}$ accumulation and inhibition of nitrification (Ste-Marie and Paré, 1999; Kemmitt *et al.*, 2006; Pietri and Brookes, 2008). However soil pH in TAD-amended soil was similar to pH in unamended control soil (Table 7.6).

Mean $\text{NO}_2\text{-N}$ concentrations are shown in Figure 7.6. Nitrite-N concentrations were negligible in Brices and Silwood soil and very low in North Sidelands and less than $3 \text{ mg kg}^{-1} \text{ ds}$. Inhibition of nitrification may result in an accumulation of $\text{NO}_2\text{-N}$ (Wiseman and Zibilske, 1988). In TAD treatments in Brices and Silwood soil, small concentrations of $\text{NO}_2\text{-N}$ were observed, whereas in the majority of the other treatments $\text{NO}_2\text{-N}$ concentrations were undetectable. In North Sidelands, however, less $\text{NO}_2\text{-N}$ was measured in TAD treatments in comparison to the other treatments. In this soil type, the concentrations of $\text{NO}_2\text{-N}$ appeared to increase with the amount of $\text{NH}_4\text{-N}$ applied (Figure 7.6). This may be because, whilst nitrification overall is rapid in North Sidelands soil, oxidation of $\text{NH}_4\text{-N}$ to $\text{NO}_2\text{-N}$ was initially more rapid than oxidation of $\text{NO}_2\text{-N}$ to $\text{NO}_3\text{-N}$ leading to a transient increase in the $\text{NO}_2\text{-N}$ pool when $\text{NH}_4\text{-N}$ application was high.

The statistical significance of potential effects of soil, treatment and sampling date effects on the mineral N ($\text{TON} + \text{NH}_4\text{N}$) recovered (% total added N) were examined by ANOVA, which showed that there was a significant effect of soil and treatment and the interaction between soil and treatment was also significant ($P < 0.001$). Mineral N recoveries in each treatment (means of incubation dates) are shown in Figure 7.7a. Tamhane's T2 pairwise comparisons (Tamhane, 1979) showed that, as would be expected, as a proportion of the total N supplied, the recovery of mineral N was significantly greater from NH_4Cl compared to the other treatments ($P < 0.001$). Mineral N recovery in AD was significantly greater than TAD, ADMSW and DMAD ($P < 0.001$); with the smallest amount of mineral N being recovered in North Sidelands soil.

Table 7.5 Soil electrical conductivity (mS cm^{-1}) in Day 0 samples (mean of triplicates).

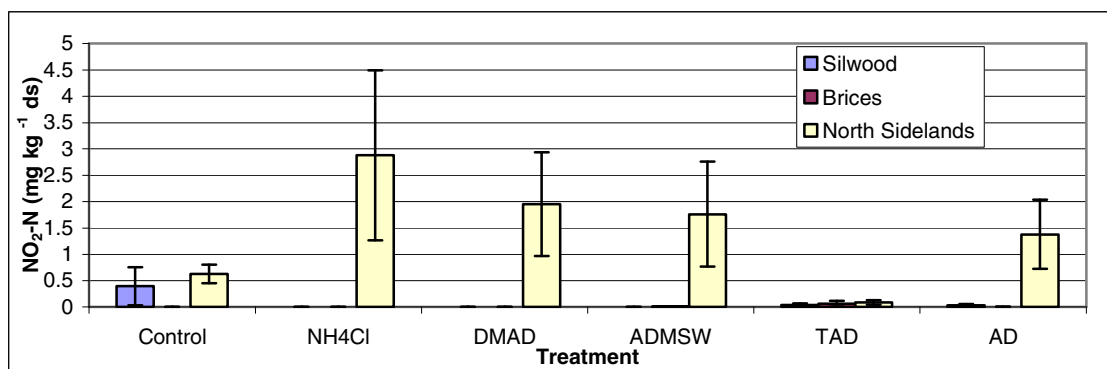
Soil	Silwood		Brices		North Sidelands	
	Mean (mS cm^{-1})	SD	Mean (mS cm^{-1})	SD	Mean (mS cm^{-1})	SD
Control	1.95	0.12	1.69	0.51	1.97	0.08
NH ₄ Cl	2.50	0.13	2.39	0.04	2.41	0.29
DMAD	1.99	0.04	1.98	0.05	2.00	0.07
ADMSW	2.02	0.05	2.00	0.05	2.04	0.08
AD	2.11	0.05	2.11	0.08	2.17	0.04
TAD	2.66	0.52	2.42	0.02	2.45	0.05

Table 7.6 Soil pH in Day 0 samples (mean of triplicates).

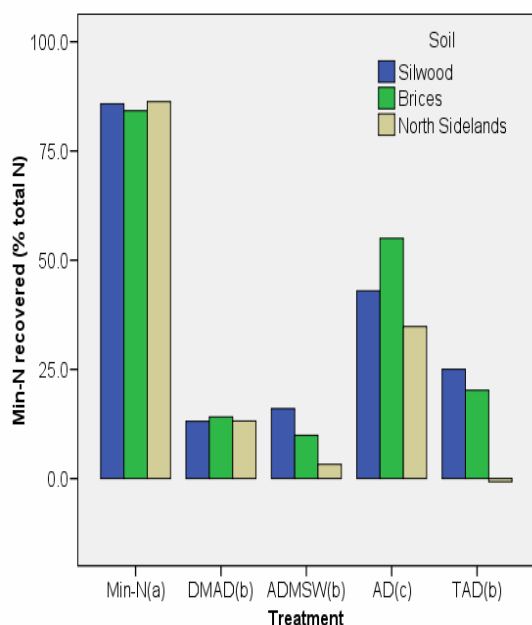
Soil	Silwood		Brices		North Sidelands	
	Mean	SD	Mean	SD	Mean	SD
Control	6.6	0.13	6.8	0.09	8.1	0.02
NH ₄ Cl	7.5	0.01	6.7	0.28	8.4*	
DMAD	7.4	0.07	7.4	0.03	7.9	0.01
ADMSW	7.7	0.03	7.6	0.01	8.1	0.09
AD	7.6	0.01	7.5	0.03	8.0	0.01
TAD	6.4	0.03	6.7	0.27	7.8	0.08

*n=1 (insufficient sample remaining)

Figure 7.6 Mean NO₂-N concentration (days 0-48) in the different treatments for each soil type. Error bars are standard error of the mean.



(a) Effect of soil type and amendment



(b) Effects of amendment and incubation time

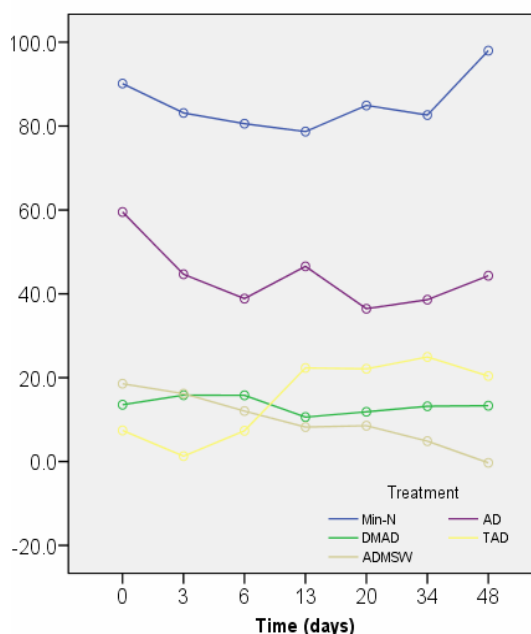


Figure 7.7 The effects of (a) soil type and amendment (mean for all time points) and (b) amendment and time (mean for all soil types) on min-N ($\text{NH}_4\text{-N} + \text{TON}$) recovered (% total added N). Letters in brackets on x axis indicate results of Tamhane's T2 pair-wise comparisons: sampling dates or treatments that do not have the same letter are significantly different at $P < 0.05$.

There was no significant difference in the quantity of mineral N recovered for DMAD, ADMSW and TAD amended soils ($P > 0.05$); however, Figure 7.7a shows that the smallest overall mineral N recoveries occurred in North Sidelands soil for ADMSW and TAD amendments. There was no significant effect of sampling date on mineral N ($\text{NH}_4\text{-N} + \text{TON}$) recovered ($P > 0.05$). This indicated that there was generally no significant net mineralisation in amended soil during the incubation. However, as can be seen from Figure 7.5, net mineralisation did occur in TAD-amended soil during the incubation for Brices and Silwood. The added mineral N was less than $50 \text{ mg kg}^{-1} \text{ ds}$, so the majority of mineral N recovered in these soil types at the end of experiment was mineralised N. The interacting effects of treatment and time on mineral N recovery were examined by ANOVA (Figure 7.7b) and a significant effect was found ($P < 0.001$). This demonstrated that, mineralisation was dependent on treatment type, and the least stabilised waste, TAD, had a pool of readily mineralisable N.

The results indicated that losses of N occurred from the soils in some cases, or that available N had been immobilised. The most significant losses of N in soil from North

Sidelands were from ADMSW and TAD amended soil where mineral N ($\text{NH}_4\text{-N} + \text{TON}$) concentrations decreased below the unamended control concentrations (Figure 7.4). Potential mechanisms for the lower concentrations of N recovered in North Sidelands soil (silty clay) in comparison to the other soil types, in the ADMSW and TAD treatments, are gaseous losses of N by ammonia volatilisation or denitrification, ammonium fixation or microbial immobilisation. Microbial biomass N was measured and is discussed in Section 7.4.2. Ammonium fixation is a possibility and occurs to a greater extent in soils with greater clay content (Tester *et al.*, 1977), so this would be consistent with the reduced recovery of N in North Sidelands, the silty clay, compared to expected recoveries from the behaviour of these biowastes in the other soil types. However, all the mineral N from applied NH_4Cl was recovered in all the soil types, so it is unlikely that $\text{NH}_4\text{-N}$ fixation was a significant factor here. Ammonia volatilisation is reduced by incorporation of organic amendments into the soil (Donovan and Logan, 1973; Robinson and Polgase, 2000), therefore it is also unlikely to account for the observed losses.

Denitrification rates increase under oxygen deficient conditions (Mendoza *et al.*, 2006), and when there is greater water filled pore space (Maag and Vinther, 1996; Webb *et al.*, 2004). In an incubation study with ^{15}N -labelled NO_3 , Epstein *et al.* (1978) reported major losses of N by denitrification from incubated soils rich in available C. The soil-types examined here were air dried to reduce moisture content from the field moisture status to 50-60 % WHC, following addition of biowastes. However, North Sidelands had a higher organic matter content (Table 3.1) and a greater WHC of 65 % compared to 38 - 45 % in the other soils. Therefore, in this soil type, there was more potential for localised anaerobic conditions following addition of organic matter and subsequent losses of N by denitrification (Smith, 1980; Fillery, 1983). Chantigny *et al.* (2002) also reported greater rates of denitrification in a clay soil incubated with organic amendments, in comparison to a sandy loam, and found that N_2O production rates were three times greater in the clay soil. They attributed this to lower oxygen availability in the clay loam soils tested.

Smith *et al.* (1998b) adjusted the moisture content of different soil types used in an incubation experiment with different biosolids products, to a lower moisture content of 40 % WHC. Breedon *et al.* (2003), in an incubation experiment with biosolids-amended soils, used field fresh soils, which were drier than the soils used in this experiment as they were collected from spring-autumn, as opposed to this soil which was collected in January. Thus, drier conditions in the incubation experiments reported

by Smith *et al.* (1998b) and Breedon *et al.* (2003) may have prevented anaerobic conditions developing.

It is interesting to note that there was full recovery of N in mineral N control treatments, even in North Sidelands, which was the most vulnerable soil type to denitrification (Smith, 1980; Fillery, 1983). The moisture status of the control soils was adjusted with deionised water so that it was equivalent to the biosolids and biowastes treatments. Therefore, properties of the organic matter added to the soils in the different biowastes treatments were responsible for the observed reduction in mineral N recovery in North Sidelands soil compared to the other soil types. The results indicated markedly contrasting behaviour of the biowastes in the different soil types, and particularly of TAD and ADMSW in North Sidelands soil compared to the other biowaste and soil types. Indeed, in North Sidelands soil the concentration of mineral N declined below the unamended control for these biowastes treatments. The reduced, or absence of, TON accumulation in the clay loam soil amended with these biowaste materials could be largely related to the stability and mineralisation characteristics of the different waste types and an interaction with soil type. Less stabilised organic wastes usually have greater C:N ratios than more stable products; for example, ADMSW and TAD had C:N ratios of 14:1 and 11:1 respectively, compared to 7.5:1 and 4:1 for DMAD and AD (Tables 3.10 and 3.12). Greater availability of readily mineralisable C, and, therefore, higher BOD of the less stable materials, may lead to localised anaerobic conditions in the soil, increasing rates of denitrification. Ryan *et al.* (1973) observed decreases in N at high rates of application (940-1880 mg kg⁻¹) of digested biosolids, and attributed this to denitrification, as a result of development of anaerobic microsites due to high rates of microbial respiration. They observed a decrease in apparent mineralisable and inorganic fractions, as occurred here with TAD in the silty clay soil (North Sidelands). Since NH₄⁺N released by mineralisation of the organic N fraction was depleted, it would appear that anaerobic and aerobic conditions were occurring simultaneously. Nitrification presumably occurred, but NO₃⁻ was instantaneously removed by denitrification activity in anaerobic microsites within this soil type. Depletion of oxygen by heterotrophs in TAD treated soil may also explain the delay in nitrification observed in this treatment (Figure 7.5), which could not be explained by high salinity or low pH. Nitrate eventually began to accumulate in Silwood and Brices soil, however, in North Sidelands it is likely that nitrate was immediately lost by denitrification. It is generally thought that denitrification may occur in anaerobic microsites within an otherwise aerobic soil, and that this occurs more frequently in clay soils with higher organic matter (Fillery, 1983; Smith, 1980), which is consistent with the results observed here.

Aggregate size may also have an impact on the development of anaerobic microsites; when aggregates are greater than 4 mm diameter oxygen diffusion may be restricted in the centre of the aggregate, however, moisture content may be a more important factor influencing denitrification (Fillery, 1983). In this experiment, the aggregate size was greater than 4 mm, as soil was sieved to 5.6 mm. However, Master *et al.* (2004) found no difference in rates of denitrification between soils sieved to 2 mm and soils sieved to 4.76 mm. Air-drying and re-wetting of soil has been reported as a cause of denitrification in laboratory studies (Fillery, 1983). To reduce the moisture content of the soil for the investigation from field moisture to 50 % WHC it was air-dried for 12 hours, but was not re-wetted. Other researchers have also reported increased N₂O emissions resulting from added organic matter (Clayton *et al.*, 1997; Stevens and Laughlin, 2001; Master *et al.*, 2004). In a laboratory incubation study, Master *et al.* (2004) found that an average of 1.5 % of applied N fertiliser was emitted as N₂O from soils irrigated with reclaimed effluent, in comparison to 0.7 % of applied fertiliser N in fresh water irrigated soil. Maag and Vinther (1996) found that nitrification and denitrification rates were greater in finer textured soils, which is consistent with greater rates of apparent denitrification observed here in the silty clay soil from North Sidelands compared to the other soil types examined. The results presented here indicate that further research is urgently required to quantify the interaction between stability of biowastes, soil moisture conditions and soil type on N transformation processes and potential loss mechanisms in biowaste amended agricultural soil. This is necessary to prevent the agricultural application of biowastes potentially leading to significant emission of greenhouse gases, which it is intended to reduce as a diversion route from biowaste disposal in landfill.

7.3.2 Microbial Biomass C

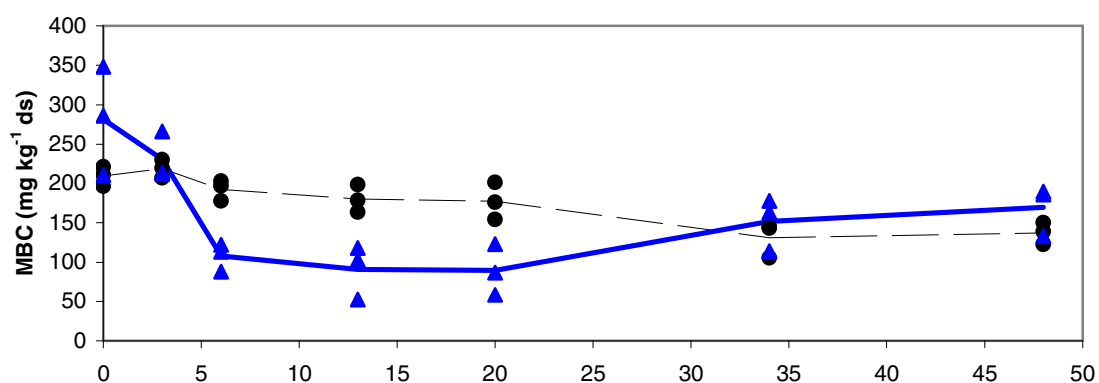
Microbial biomass C (MBC) dynamics in amended and non amended soils are shown in Figures 7.8–7.12. Microbial biomass carbon remained relatively constant in the unamended control soils throughout the incubation period. North Sidelands had the greatest MBC content of between 400-500 mg kg⁻¹ ds, Silwood had a MBC content of between 150-200 mg kg⁻¹ ds and Brices had the smallest MBC concentration between 60-120 mg kg⁻¹ ds. The MBC concentrations in unamended soils were as expected from their organic matter content (Table 3.1) as North Sidelands contained the most organic matter, followed by Silwood soil and soil from Brices had the smallest organic matter content. This demonstrated the higher fertility status of the higher organic

matter soil, and was consistent with Zagal (1993) who also measured greater MBC concentration in finer textured soils due to their ability to preserve organic matter.

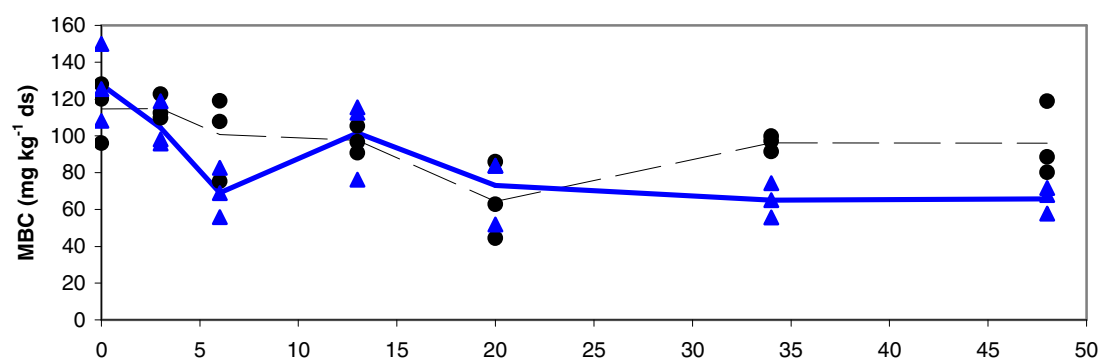
The addition of mineral N to the soil does not supply an organic substrate and may therefore be predicted to have little influence on MBC concentration. In mineral N treated soils (Figure 7.8) there was an approximately equal MBC content to unamended soil in Brices soil, and an apparent negative influence on biomass C content from days 5-20 in soil supplied from Silwood Park. In North Sidelands, MBC concentrations remained below unamended control concentrations from days 0-48. In a field experiment to investigate the effects of surface additions of dairy shed effluent and NH_4Cl on soil MBC, addition of NH_4Cl had no effects on MBC throughout the soil profile, however it increased MBN (Zaman *et al.*, 2002). Only a small increase in soil electrical conductivity was measured in the soil amended with NH_4Cl in the incubation experiment reported here and this was unlikely to have a negative impact on soil MBC (Table 7.5). However, high $\text{NH}_4\text{-N}$ concentration of the soil, following addition of NH_4Cl , may have caused temporary disruption to the microbial community (Ryan *et al.*, 1973; Epstein *et al.*, 1978).

An increase in MBC would be expected in soils amended with biowastes and biosolids as the addition of organic matter provides a substrate for microbial growth (Jedidi *et al.*, 2004; Ayad *et al.*, 2007; Fernandes *et al.*, 2007; Plaza *et al.*, 2007). In all three soil types, following addition of DMAD, there was an increase in MBC concentration above unamended control concentrations on days 0-3, by approximately $100 \text{ mg kg}^{-1} \text{ ds}$ (Figure 7.9). On day 6 in all three soil types MBC concentrations decreased below unamended control values, and then fluctuated at approximately control concentrations in Silwood and North Sidelands. In Brices, concentrations were generally greater than unamended control concentrations until day 48. A similar pattern was observed for ADMSW amended soil in Silwood and Brices soil, however, in North Sidelands, on day 3 concentration decreased below control values and remained less than or equal to control values for the duration of the experiment (Figure 7.10).

(a) Silwood (loamy sand)



(b) Brices (sandy silt loam)



(c) North Sidelands (silty clay)

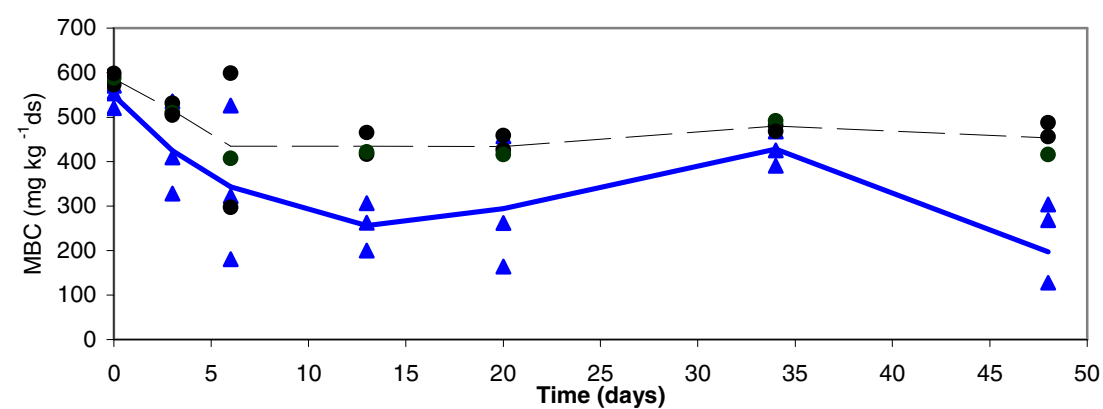
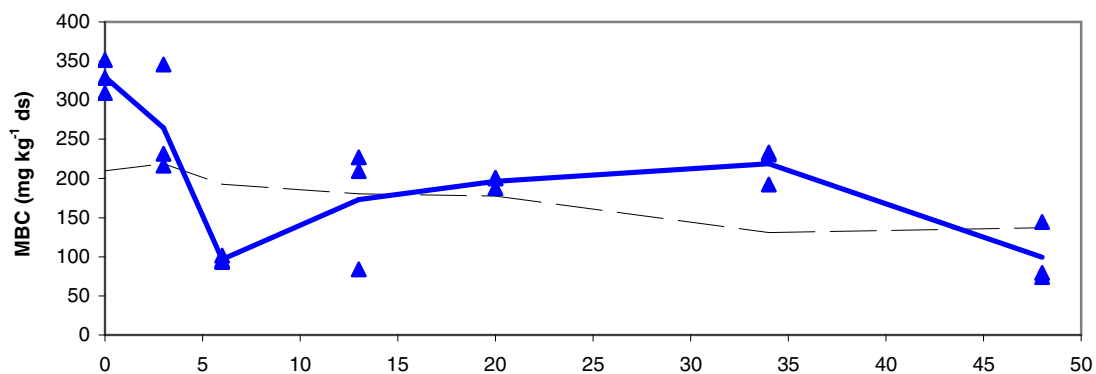
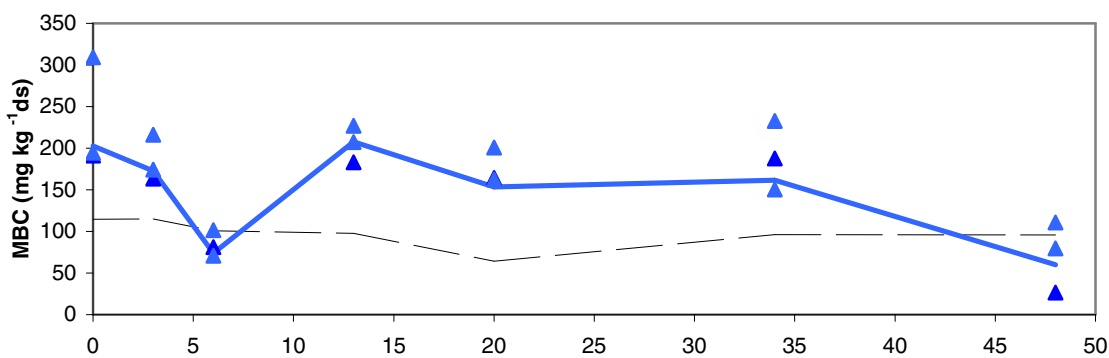


Figure 7.8 Microbial biomass carbon (MBC) concentration ($\text{mg kg}^{-1} \text{ ds}$), in three contrasting soil types, in relation to time in unamended control soil (mean, ---; replicates, •) and mineral N control soil (mean, —; replicates, ▲).

(a) Silwood (loamy sand)



(b) Brices (sandy silt loam)



(c) North Sidelands (silty clay)

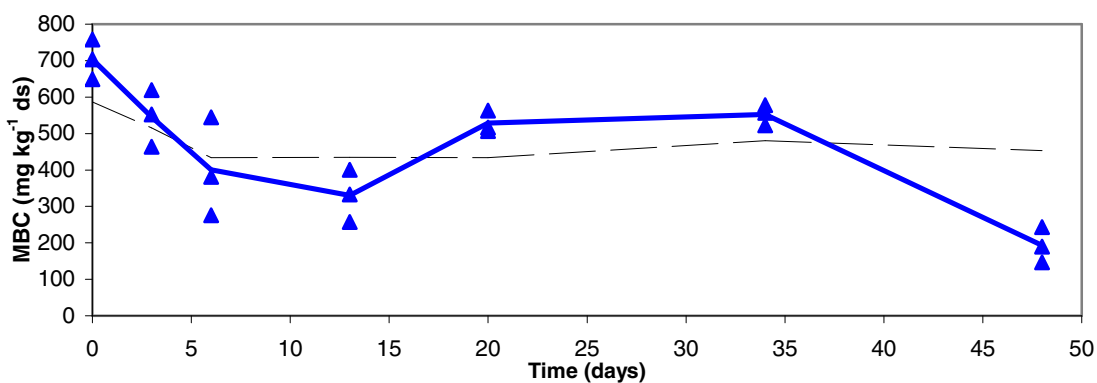
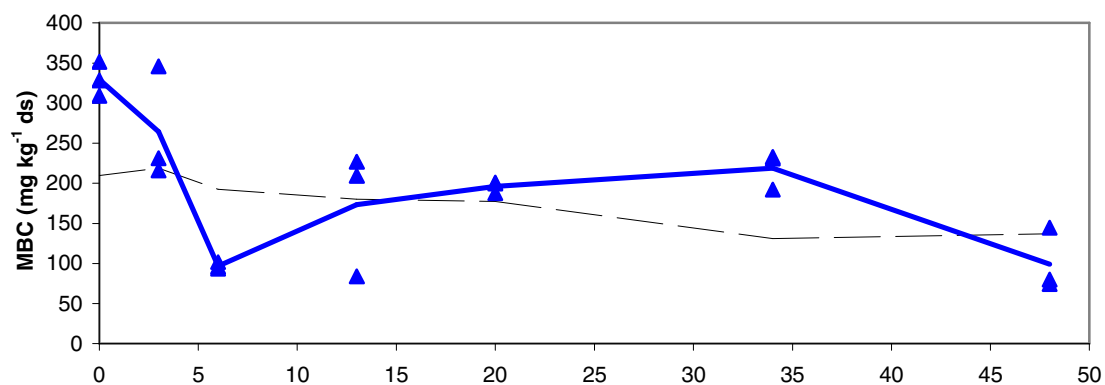
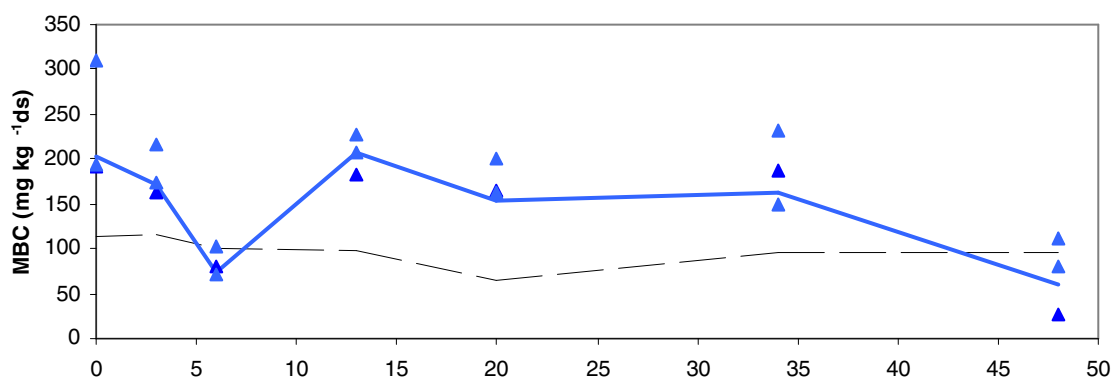


Figure 7.9 Microbial biomass carbon (MBC) concentration ($\text{mg kg}^{-1} \text{ ds}$), in three contrasting soil types, in relation to time in unamended control soil (mean, ---) and DMAD-amended soil (mean, — ; replicates, $\blacktriangle$).

(a) Silwood (loamy sand)



(b) Brices (sandy silt loam)



(c) North Sidelands (silty clay)

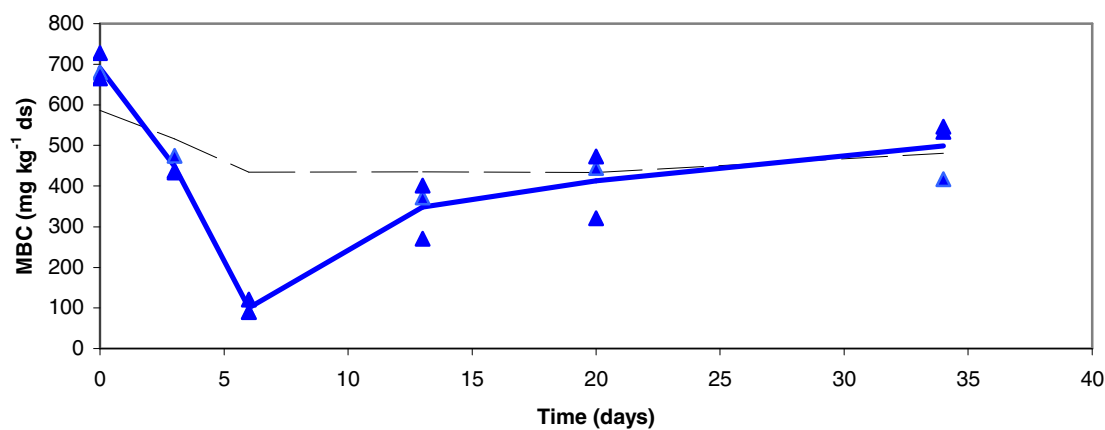
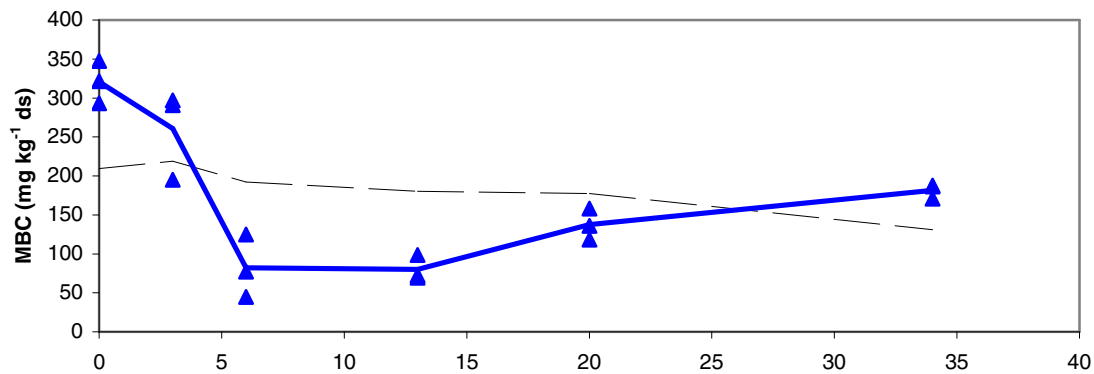
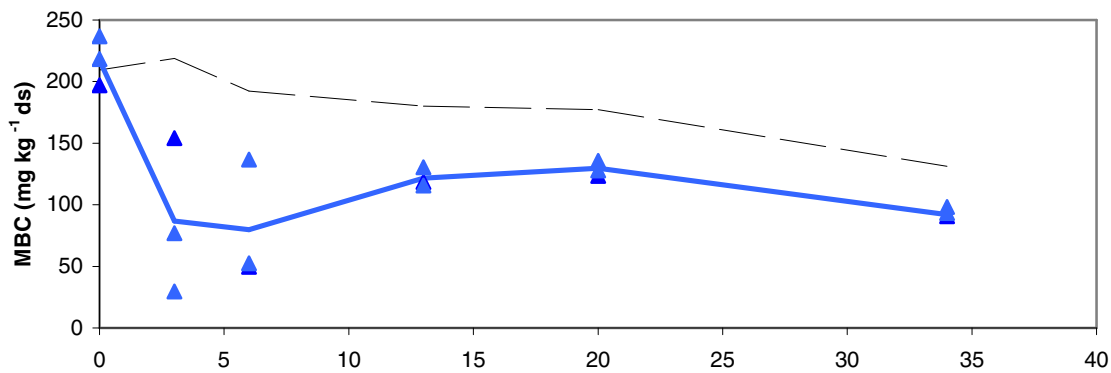


Figure 7.10 Microbial biomass carbon (MBC) concentration ($\text{mg kg}^{-1} \text{ ds}$), in three contrasting soils, in relation to time in unamended control soil (mean, ---) and ADMSW-amended soil (mean, — ; replicates, $\blacktriangle$).

(a) Silwood (loamy sand)



(b) Brices (sandy silt loam)



(c) North Sidelands (silty clay)

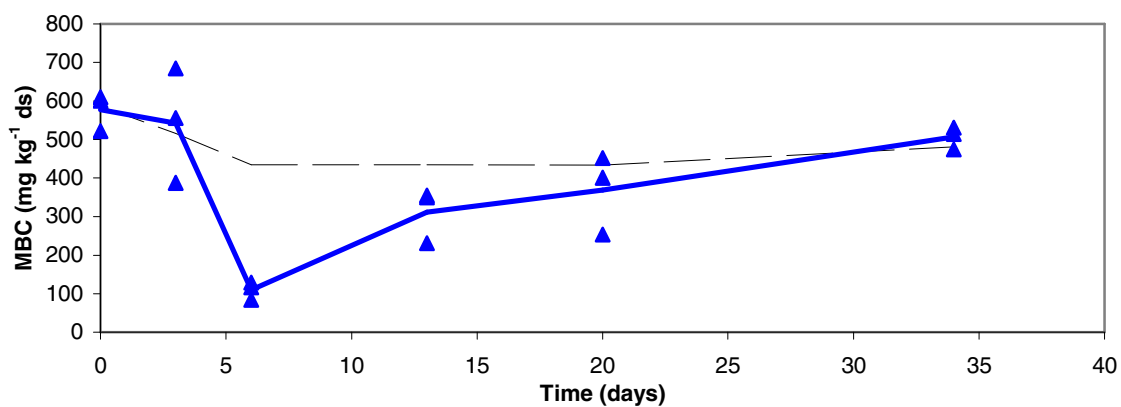
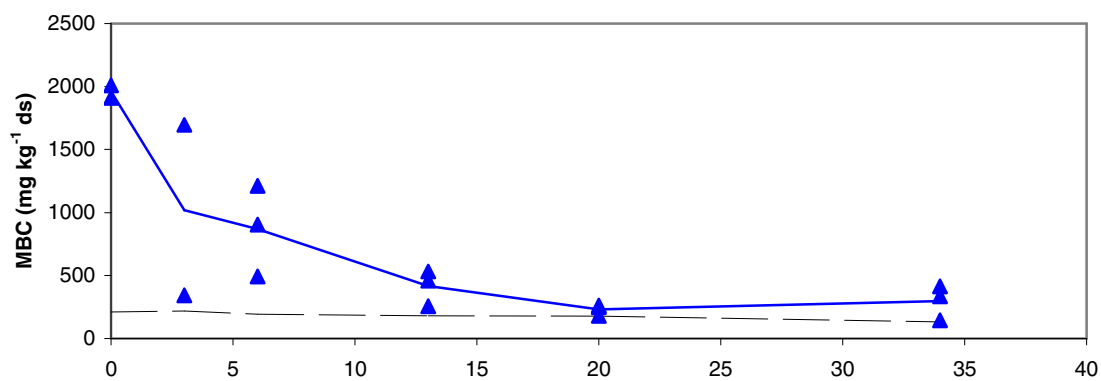
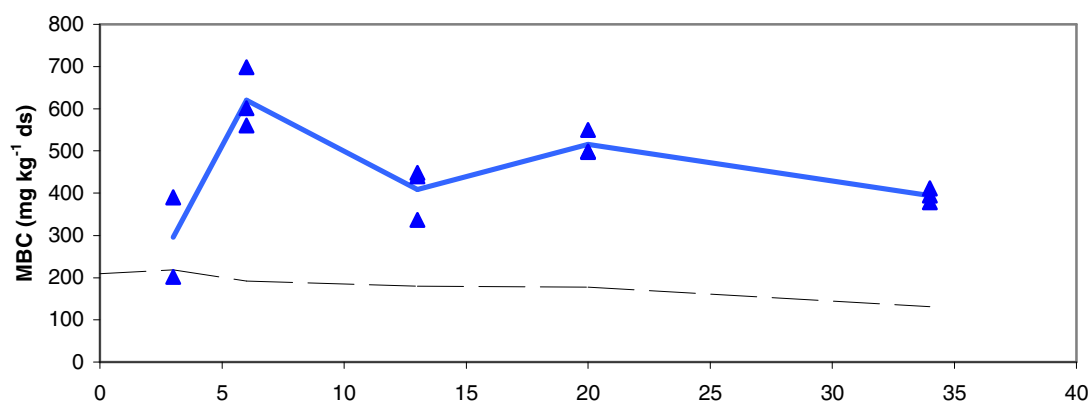


Figure 7.11 Microbial biomass carbon (MBC) concentration (mg kg⁻¹ ds), in three contrasting soils, in relation to time in unamended control soil (mean, --) and AD-amended soil (mean, — ; replicates, ▲).

a) Silwood (loamy sand)



(b) Brices (sandy silt loam)



(c) North Sidelands (silty clay)

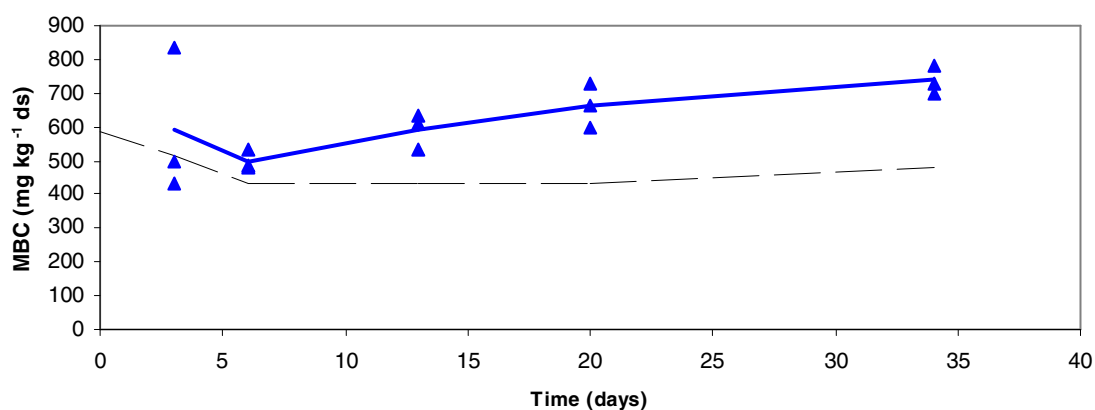


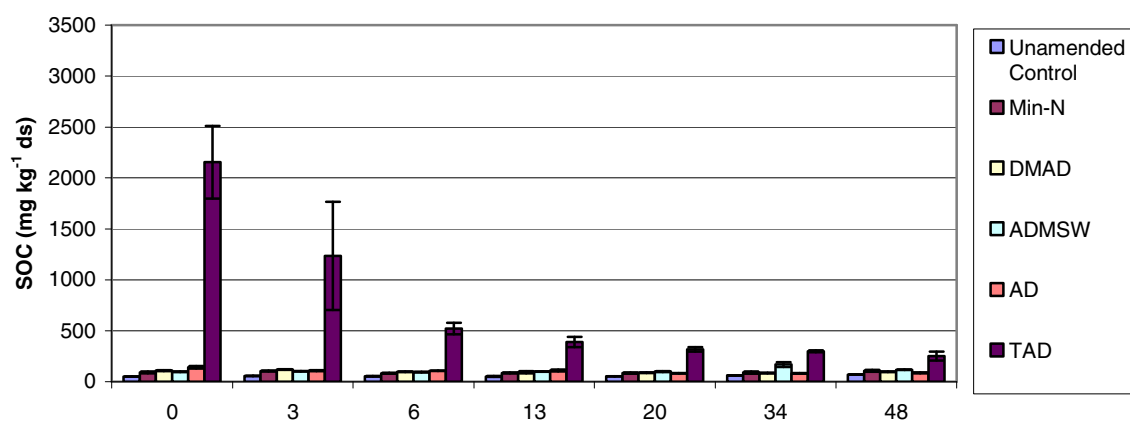
Figure 7.12 Microbial biomass carbon (MBC) concentration ($\text{mg kg}^{-1} \text{ ds}$), in three contrasting soils, in relation to time in unamended control soil (mean, --) and TAD-amended soil (mean, — ; replicates, $\blacktriangle$).

Results for the AD treated soils did not follow the pattern expected based on the response observed for the other anaerobically digested products (Figure 7.11). Microbial biomass carbon (MBC) concentrations were initially greater than unamended control values in Silwood soil, and were equivalent to control values in Brices and North Sidelands, but decreased to approximately 100 mg kg^{-1} below unamended control values in soil from Silwood and Brices, and 400 mg kg^{-1} below unamended control in North Sidelands soil. Following that, concentrations gradually increased to similar values as in the unamended control. A similar decrease was observed in NH_4Cl amended soil and may be due temporary disruption of the microbial community by the high $\text{NH}_4\text{-N}$ concentration (Ryan *et al.*, 1973; Epstein *et al.*, 1978). Salinity was unlikely to be a significant factors as the electrical conductivity of amended soils were close to unamended control values (Table 7.6).

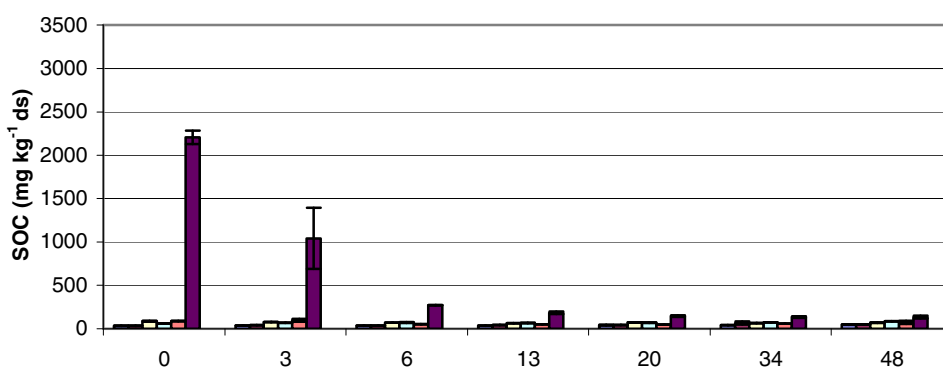
Erroneous values were observed in TAD-amended soil on day 0 and day 3 of the experiment, and negative values obtained for MBC, in some cases. In these cases, extractable soluble organic C (SOC) was less in fumigated TAD-amended soil than in unfumigated soil. The chloroform fumigation-extraction method generally has advantages over the fumigation-incubation method, as it is suitable for determination of MBC in soils with a low pH and added degradable organic matter (Martens, 1993). However, due to the high concentrations of labile organic matter introduced in the TAD, it is likely that the negative values were a result of high concentrations of K_2SO_4 extractable soluble organic C in non-fumigated soils. These values have been excluded from Figure 7.12; this reduces the reliability of the initial data for this biowaste, however, in the majority of cases MBC concentrations measured in all three experimental replicates were greater than the unamended control.

The soluble organic carbon (SOC) concentrations in the different treatments are shown in Figure 7.13. Soluble organic carbon concentrations in TAD amended soil were approximately 60 times greater than in unamended control Silwood soil, 40 times greater in Brices and 30 times greater in North Sidelands, compared to their respective unamended control soils. Concentrations in the other treatments were similar to control values. In the second week, SOC remained above control values for Silwood and Brices soil by 20-30 times, but was only 3 times greater in North Sidelands soil. This demonstrated the higher fertility of North Sidelands; the microbial biomass was able to process the labile organic matter at a faster rate than the other two soils, reducing the concentration of SOC measured in this soil type.

(a) Silwood (loamy sand)



(b) Brices (sandy silt loam)



(c) North Sideland (silty clay)

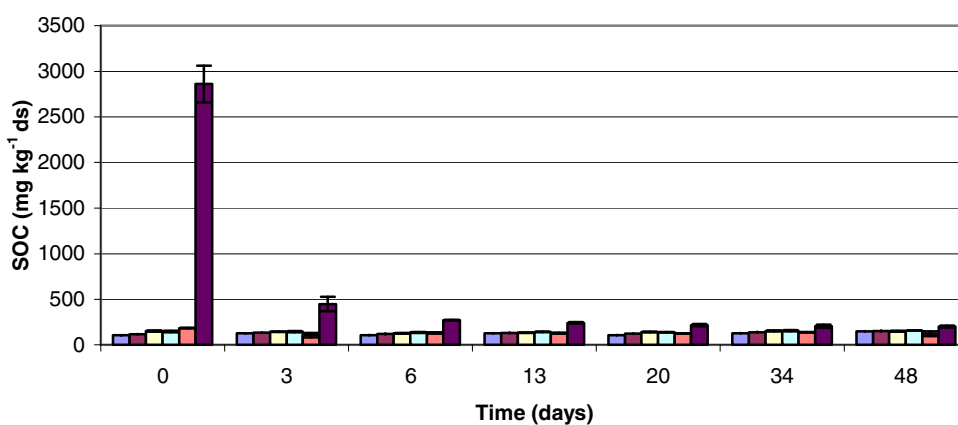


Figure 7.13 Soluble organic carbon (SOC) concentration ($\text{mg kg}^{-1} \text{ ds}$), in three contrasting soil types, in relation to time. Error bars are standard error of the mean.

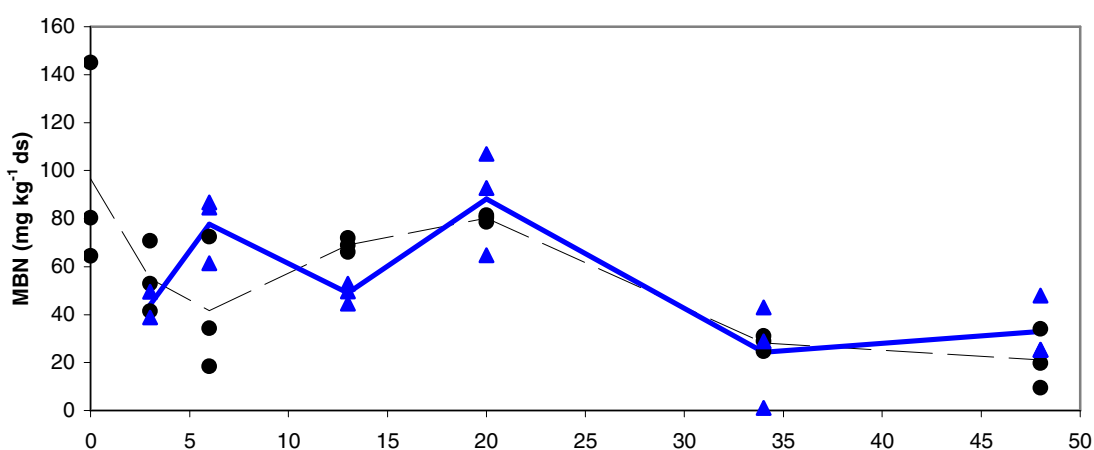
From days 13-48, the SOC concentration in TAD amended soil was much closer to the unamended control values; whereas in all TAD treated soils MBC concentrations remained above the unamended control for the duration of the experiment. This can be explained by the high concentration of readily mineralisable organic matter that might be expected from the aerobically digested waste, stimulating microbial biomass growth. The TAD was only aerobically digested for a limited period of time to comply with the ABPR (SI, 2005b), and was not digested to achieve stability of the organic matter as is the objective of AD treatment. Other researchers have also found that MBC is related to the availability of readily degradable organic matter. For example, MBC has been measured during composting of biodegradable municipal solid waste (MSW) (Jedidi *et al.*, 2004; Ayad *et al.*, 2007) and was found to decrease as the compost matured and the stability of the organic matter increased.

7.3.3 Microbial Biomass N

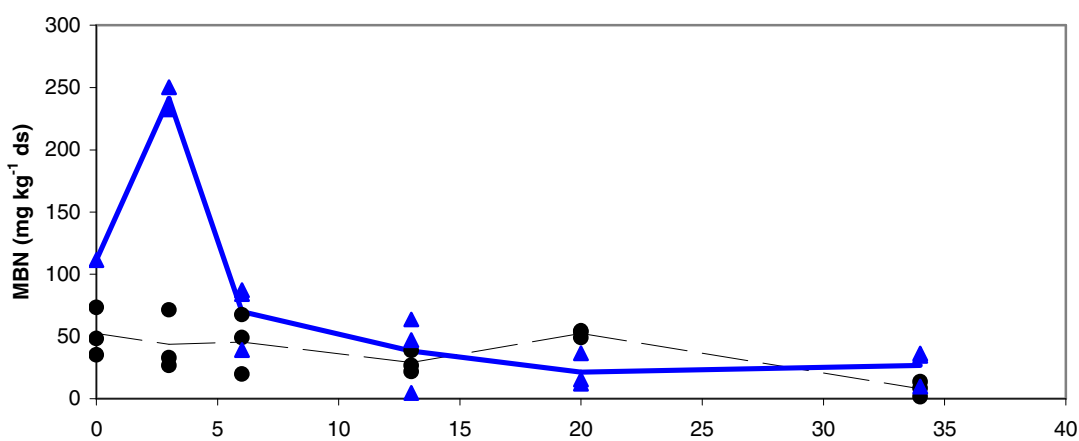
Microbial biomass N (MBN) dynamics in biosolids, biowastes and NH_4Cl amended soil relative to unamended control soil are presented in Figures 7.14-7.18. As observed with for MBC, in a few cases on day 0, there were some erroneous values resulting in negative measurements of MBN. This was observed for some replicates in NH_4Cl , TAD and DMAD amended soil and is likely to be due to high background concentrations of $\text{NH}_4\text{-N}$ or soluble organic nitrogen (SON) in the non-fumigated soil (Figures 7.1-7.5), resulting in difficulties in detecting differences in MBN concentration in fumigated soil. It was observed mainly in Brices Field, which may be explained by the lower nitrification rate observed in this soil type resulting in greater accumulation of $\text{NH}_4\text{-N}$.

The MBN concentration in unamended control soils was between 20-100 $\text{mg N kg}^{-1} \text{ ds}$ for Silwood Park and Brices soil and was approximately twice this value in North Sidelands, which contained between 100-180 $\text{mg N kg}^{-1} \text{ ds}$, consistent with the MBC concentrations. Thomsen *et al.* (2003) also found MBN concentration was related to the organic C content of the soil. The soil with the highest sand content (41 %) and the lowest organic C content of 1.37 % had a MBN content of 20-40 $\text{mg N kg}^{-1} \text{ ds}$, compared to 30-70 $\text{mg N kg}^{-1} \text{ ds}$ in a soil with a lower sand content (of 28 %) and an organic C content of 1.54 %. In the NH_4Cl treatments there was an initial rise in MBN for all three soil types in comparison to unamended control soil on day 3 (Figure 7.14).

(a) Silwood (loamy sand)



(b) Brices (sandy silt loam)



(c) North Sidelands (silty clay)

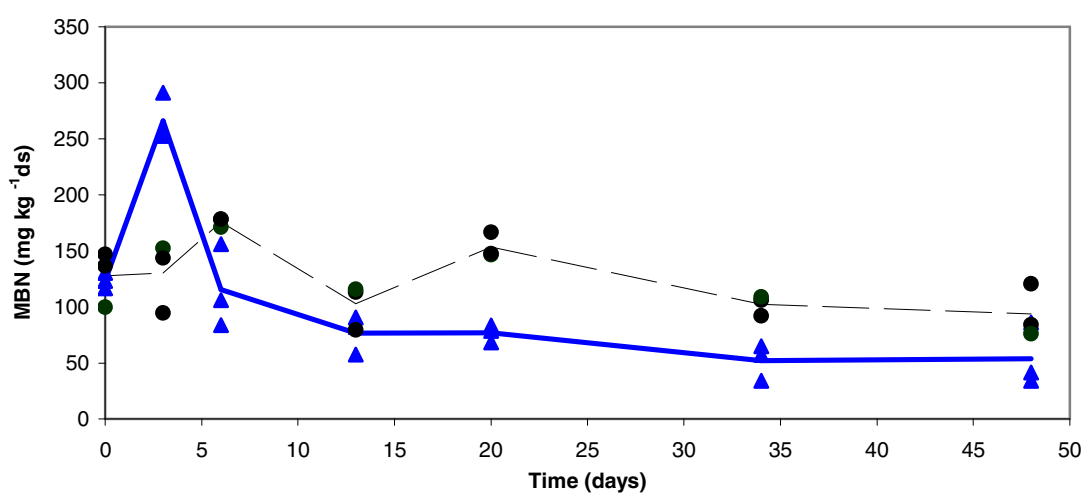
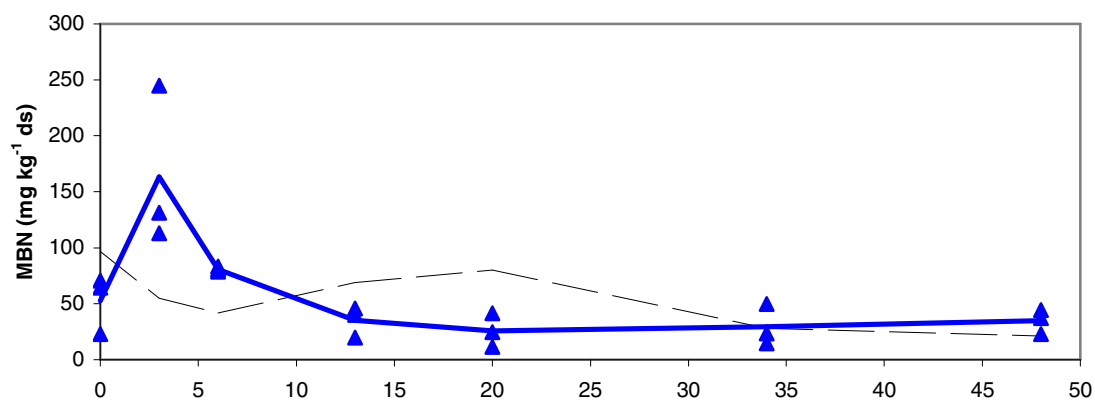
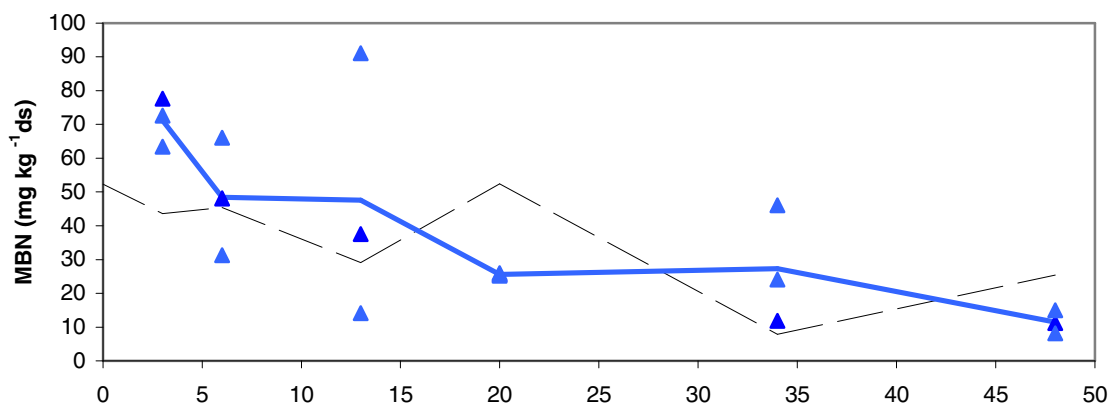


Figure 7.14 Microbial biomass nitrogen (MBN) concentration ($\text{mg kg}^{-1} \text{ds}$), in three contrasting soil types, in relation to time in unamended control soil (mean, ---; $\bullet$, replicates) and mineral N control soil (mean, —; replicates, $\blacktriangle$).

(a) Silwood (loamy sand)



(b) Brices (sandy silt loam)



(c) North Sidelands (silty clay)

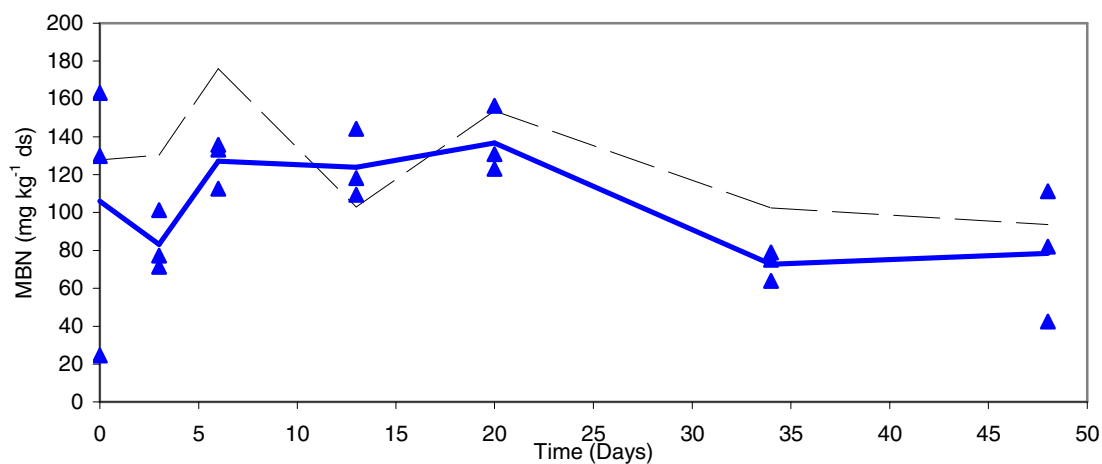
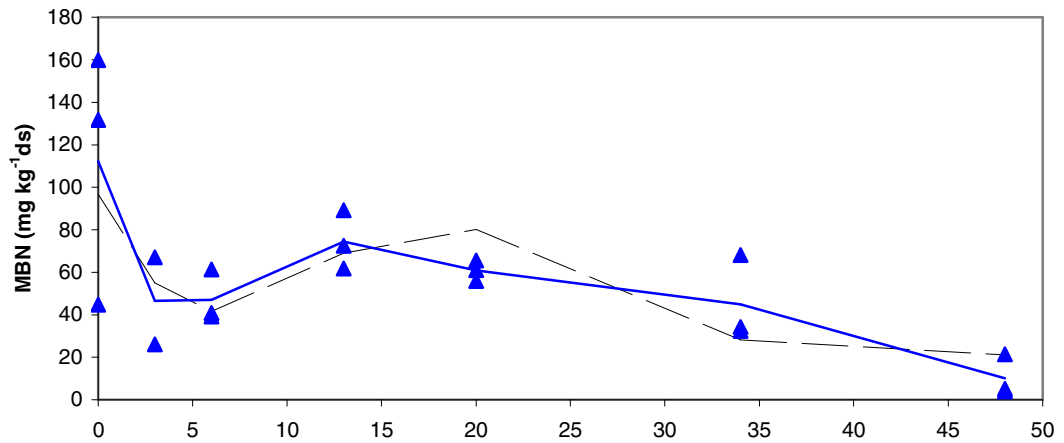
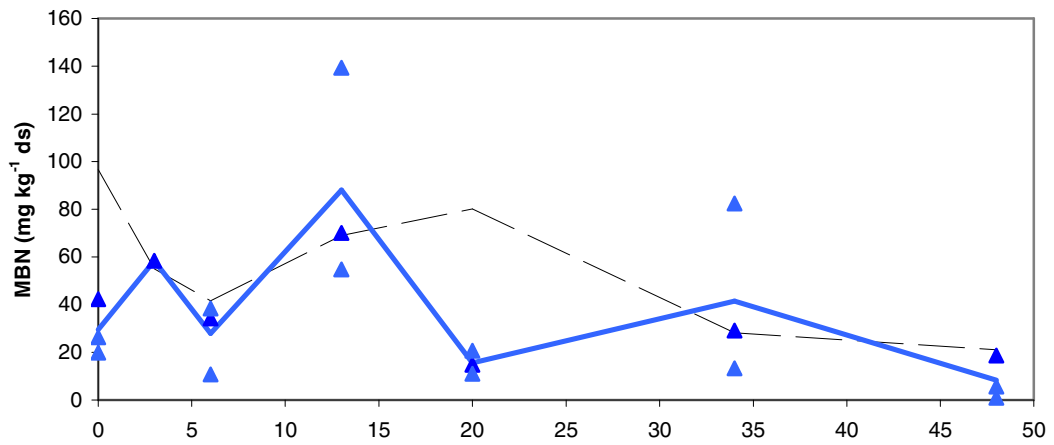


Figure 7.15 Microbial biomass nitrogen (MBN) concentration ($\text{mg kg}^{-1} \text{ ds}$), in three contrasting soils, in relation to time in unamended control soil (mean, --) and DMAD-amended soil (mean, — ; replicates, ▲).

(a) Silwood (loamy sand)



(b) Brices (sandy silt loam)



(c) North Sidelands (silty clay)

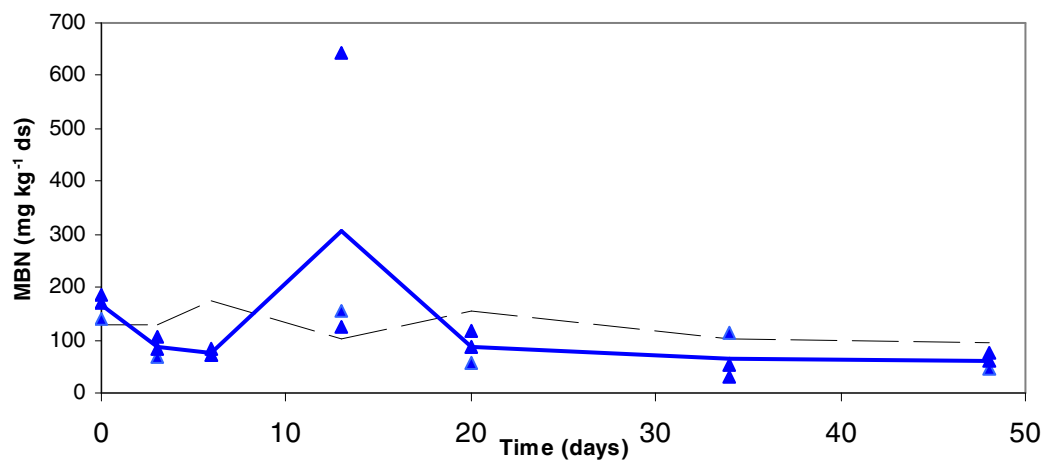
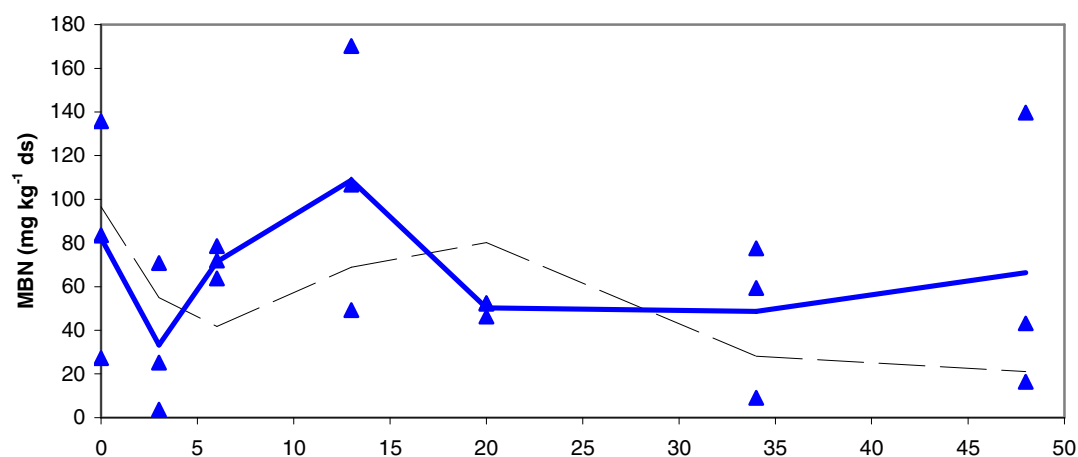
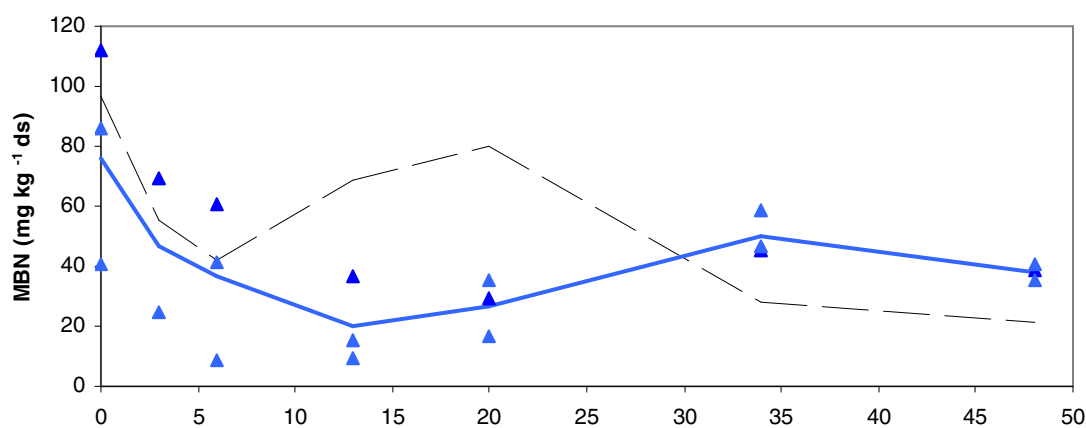


Figure 7.16 Microbial biomass nitrogen (MBN) concentration ($\text{mg kg}^{-1} \text{ ds}$), in three contrasting soil types, in relation to time in unamended control soil (mean, $---$) and ADMSW-amended soil (mean, $---$; replicates, $\blacktriangle$).

(a) Silwood (loamy sand)



(b) Brices (sandy silt loam)



(c) North Sidelands (silty clay)

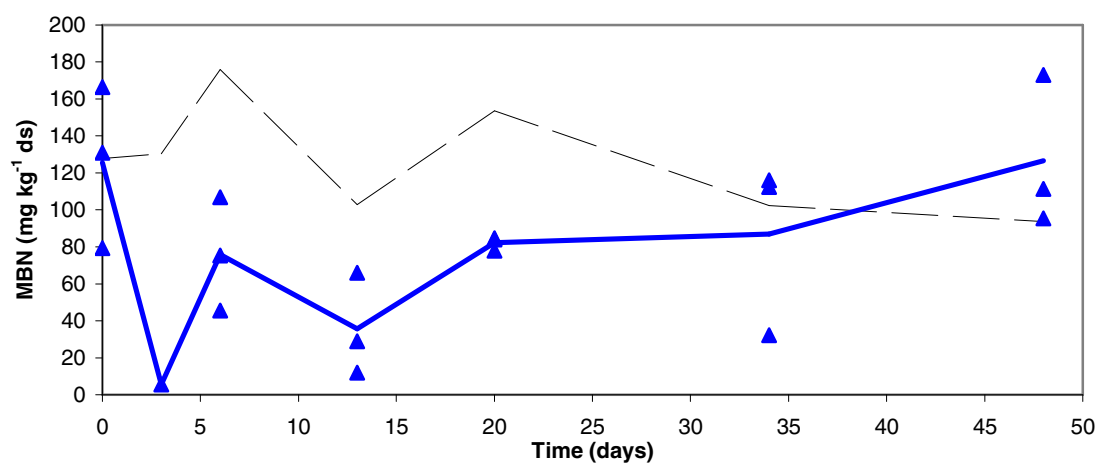
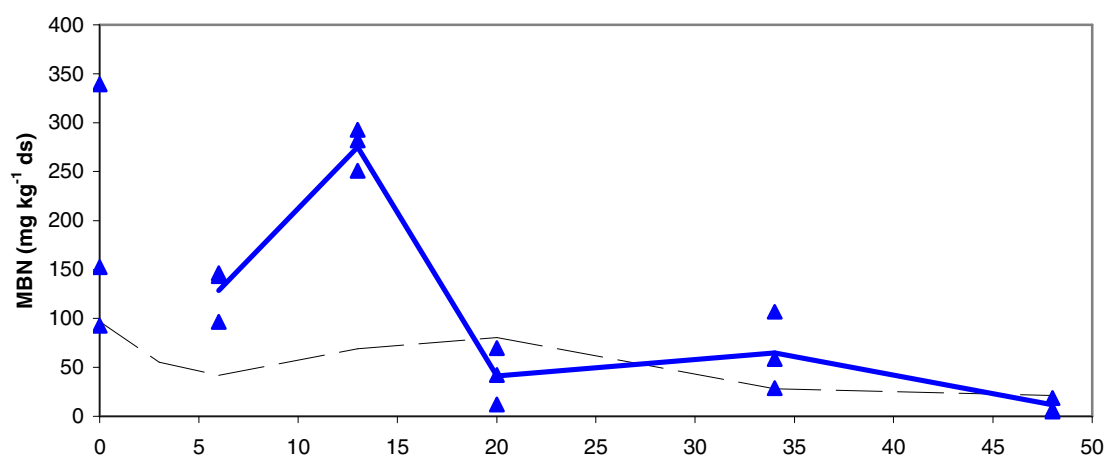
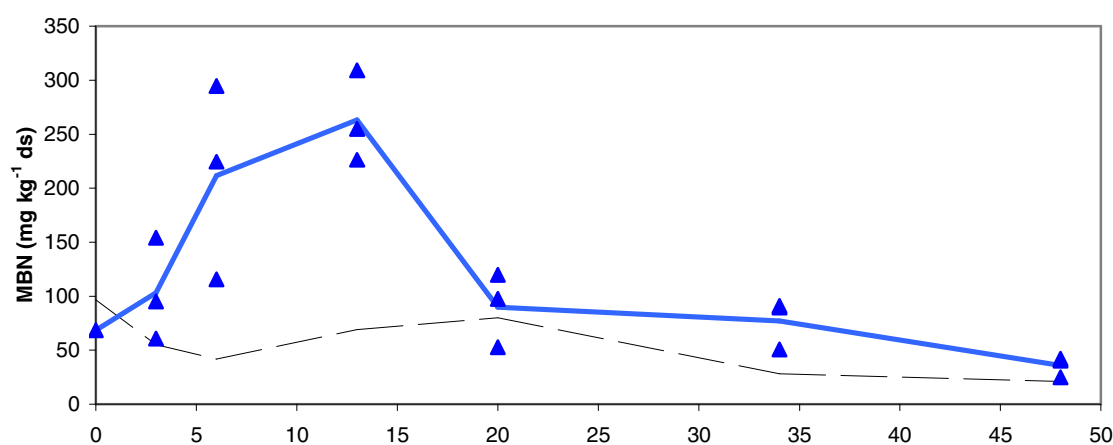


Figure 7.17 Microbial biomass nitrogen (MBN) concentration (mg kg⁻¹ ds), in three contrasting soils, in relation to time in unamended control soil (mean, --) and AD-amended soil (mean, — ; replicates, ▲).

(a) Silwood (loamy sand)



(b) Brices (sandy silt loam)



(c) North Sidelands (silty clay)

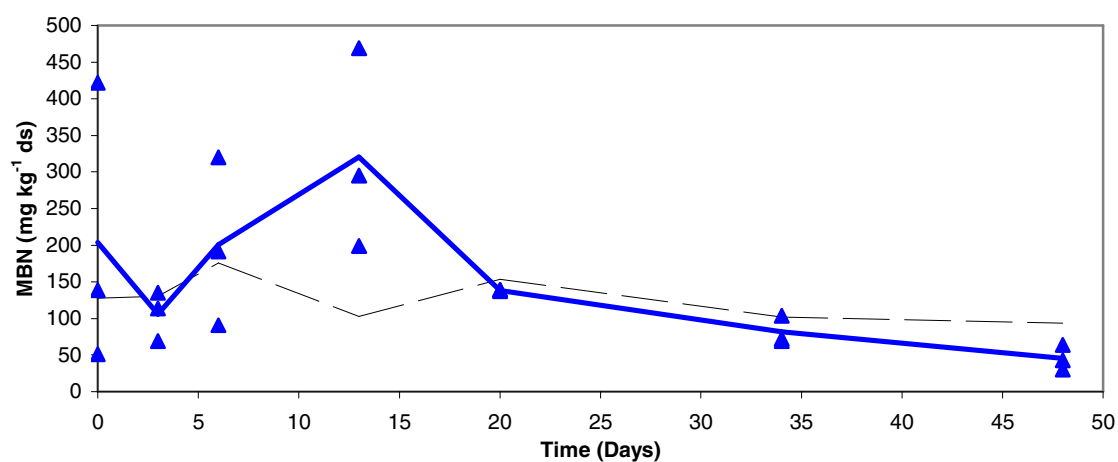


Figure 7.18 Microbial biomass nitrogen (MBN) concentration ($\text{mg kg}^{-1} \text{ ds}$), in three contrasting soils, in relation to time in unamended control soil (mean, $--$) and TAD-amended soil (mean, $---$; replicates, $\blacktriangle$).

This initial increase may be due to initial utilisation of the added N by the nitrifying bacterial community. For example, Zaman *et al.* (2002), also observed an increase in MBN following soil amendment with NH_4Cl . This initial rise in MBN was greatest in soil from Brices Field, where MBN concentrations increased by approximately 4 times compared to the control values on day 3. However, for this sample there were only 2 replicates so this observation may not be significant. After this time point, MBN concentrations remained approximately equivalent in the mineral N and unamended controls in all 3 soils for the duration of the experiment. This behaviour was expected as there was no addition of organic matter in these soils, so no additional substrate was available to support growth of the microbial biomass.

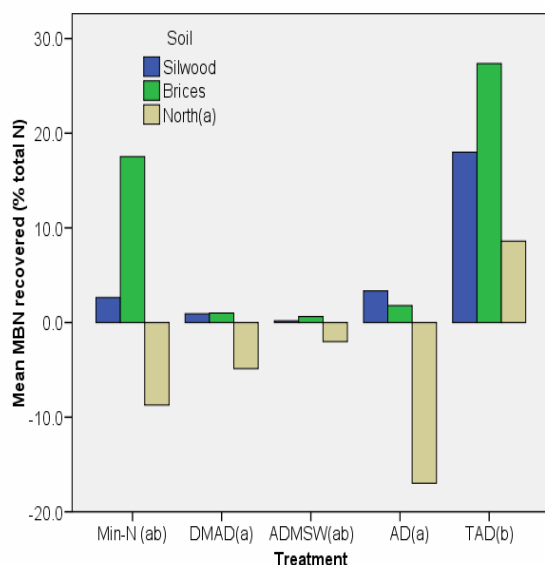
Franco-Hernández *et al.* (2003) reported that a significant portion of $\text{NH}_4\text{-N}$ added to a sandy clay loam in aerobically digested biosolids, in a laboratory incubation experiment, was not recovered. This was due to N immobilisation since the pH was too low for significant NH_3 volatilisation. However, in this experiment, microbial immobilisation is not a significant factor in DMAD-amended soil. Figures 7.15 and 7.16 show changes in MBN following soil amendment with DMAD and ADMSW, and MBN concentrations were approximately equal to unamended control values in all three soils for these treatments. Therefore the decrease in mineral N that was observed in ADMSW amended soil cannot be accounted for in the microbial biomass, indicating that denitrification is the most likely mechanism as discussed in Section 7.2.1. Microbial biomass N concentrations in TAD amended soil corresponded with the observations for MBC. Microbial biomass N (MBN) concentrations in all three soil types amended with TAD were generally greater than the unamended controls until day 20 when concentrations returned to approximately control values. In Silwood and Brices soil, maximum concentrations of MBN were approximately $200 \text{ mg kg}^{-1} \text{ ds}$ greater than unamended control values, and they were $150 \text{ mg kg}^{-1} \text{ ds}$ greater than the unamended control for North Sidelands. This represents an increase of nearly 4 times the background concentration in Silwood and Brices and 3 times the control values in North Sidelands. This may be related to the stability of the aerobically digested food waste, which contains a high proportion of readily degradable organic matter. Therefore, in contrast to the more stabilised anaerobically digested residues addition of this labile organic matter source to the soils stimulated the microbial community resulting in initial immobilisation of N. This appeared to occur to a lesser extent in North Sidelands, which may support the view that there is reduced potential immobilisation of organic N in soils with a higher fertility status. However, there were also other interacting factors; smaller concentrations of N were recovered in North

Sidelands soil treated with TAD compared to the other treatments examined, so this observation may be a reflection of lower N availability due to losses from this silty clay soil type. However, Thomsen *et al.* (2003) also measured increased concentrations of ^{15}N derived from sheep faeces in the microbial biomass in a sandy soil with a low organic matter content, equivalent to a recovery of 13 % ^{15}N , in comparison to a finer-textured soil with a greater organic matter content, where a maximum of 9 % of ^{15}N was recovered in the microbial biomass in this soil type.

Microbial Biomass N (MBN) dynamics in AD amended soil followed a similar pattern to that observed with MBC, with an apparent reduction in MBN with AD addition in comparison to the unamended control soils. This effect may be due to a temporary inhibition of microbial activity as a result of high $\text{NH}_4\text{-N}$ concentrations in the incubated soil (Ryan *et al.*, 1973; Epstein *et al.*, 1978).

Analysis of variance (ANOVA) demonstrated that there were significant soil ($P=0.001$), time ($P<0.001$) and amendment ($P<0.001$) effects on the quantity of N recovered as MBN. There were no overall significant interacting effects of soil type and incubation time or soil type and amendment type ($P>0.05$). The effects of soil type and amendment on MBN (% total N) are shown in Figure 7.19a; the greatest MBN recoveries were in Brices soil, followed by Silwood and then North Sidelands. Tamhane's pairwise comparisons showed that significantly less N was recovered as MBN in North Sidelands soil ($P<0.001$). Microbial biomass N was significantly greater in NH_4Cl ($P<0.001$) and TAD ($P<0.001$) amended soils in comparison to the other treatments. The effects of soil and incubation time on MBN (% total N) are shown in Figure 7.19b; Tamhane's pair-wise comparisons showed that there was significantly less N immobilised in soil after 20 days, in comparison to 0, 13, 34 and 48 days. This may reflect temporary inhibition of microbial biomass caused by AD and NH_4Cl amendments, however, concentrations of recovered N recovered in the MBN increased significantly by the end of the incubation period. The findings from MBN and MBC analysis of the samples demonstrated greater microbial activity in soils amended with TAD, which contained unstabilised organic matter compared to the anaerobically digested products, which are treated to stabilise the organic fraction. There was significantly less recovered MBN in North Sidelands than the other soils, but this may be related to the lower availability of mineral N in this soil type, due to losses associated with potential denitrification activity

(a) Effect of amendment and soil type



(b) Effect of soil type and sampling date

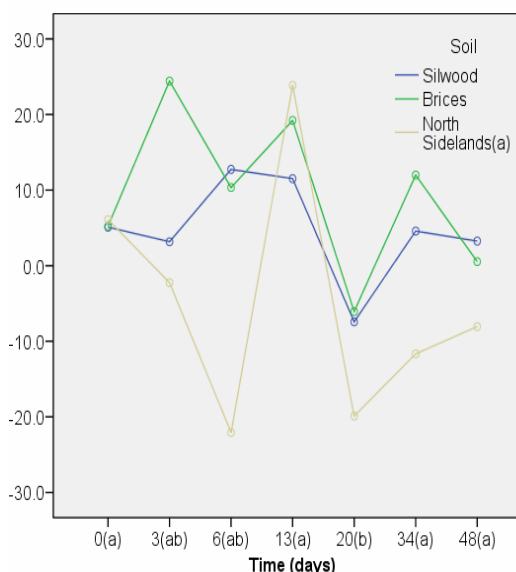


Figure 7.19 Effects of (a) soil type and amendment (mean for all time points) and (b) soil type and incubation time (means for all treatments) on MBN recovered (% total N added). Letters in brackets, next to treatment, incubation date or soil type, indicate results of Tamhane's pair-wise comparisons: soils or treatments that do not have the same letter are significantly different at $P<0.05$.

7.4 Summary

A laboratory incubation study was established with a silty clay, loamy sand and a sandy silt loam amended with anaerobically (AD and ADMSW) and aerobically (TAD) digested biowastes; anaerobically digested biosolids (DMAD) and mineral N were included as reference comparison. The aim was to investigate the effects of biowaste type and soil type on N availability in amended soils under controlled temperature and moisture conditions, and to study immobilisation of N within soil biomass, to provide information into its importance in controlling N release to crops from biowastes in contrasting fertility systems.

Final N recoveries in mineral N controls were approximately 100 % total N additions in all three soil types. This indicated that, at the end of the experiment, in soils treated with mineral N and no organic matter additions, there was no immobilisation or loss of added N. Differences in nitrification rates were observed between soil types, with

greater nitrification rates in the higher fertility soil (North Sidelands: silty clay) following addition of mineral N or organic N sources. Of the organic soil amendments, final recoveries of N were greatest in soil amended with liquid anaerobic co-digestate of food waste and animal slurry (AD), between 20–68 % total N. This was to be expected from the high proportion of mineral N in this biowaste type of 47 %. The order of greatest recovery was: sandy silt loam > loamy sand > silty clay. Final recoveries of N in DMAD amended soil ranged between 14.5-20 % of the total N addition, with order of greatest recovery: sandy silt loam > silty clay > loamy sand. Final recoveries of N in ADMSW amended soil were between -11.5-11.5 % of the total added N, with order of greatest recovery: loamy sand > sandy silt loam > silty clay. Final recoveries of N in TAD amended soil ranged between -8-33.0 % of the total added N, with order of greatest recovery: sandy silt loam > loamy sand > silty clay.

In soil amended with DMAD for all 3 soil types, and TAD and AD for the sandy silt loam and loamy sand, final available N was greater than the initial input of mineral N to the soil in the products indicating net mineralisation of the organic N fraction. Net mineralisation was greatest in the sandy silt loam. However, in all 3 soils amended with ADMSW there was no net mineralisation of organic N in any of the soil types. In addition, in the silty clay no net mineralisation was detected for AD or TAD.

The findings of the laboratory incubation study indicate that losses of N occurred from biowastes amended soil. The losses of N were most significant in North Sidelands soil, which had greater clay and organic matter contents compared to the other soil types examined. The results suggested that the most likely mechanism of N loss was by denitrification as a result of localised anaerobic conditions in the soil. The greatest amounts of unrecovered N occurred in ADMSW and TAD amended soil, which suggested that these materials were less stabilised than AD and DMAD, and their degradation in soil potentially led to greater O₂ depletion compared to the other waste types.

Microbial biomass C concentrations were greater in soil from North Sidelands, the silty clay with high organic matter content followed by Brices soil, the sandy silt loam, and then Silwood, the loamy sand. Microbial biomass C concentrations and MBN concentrations were greater in TAD amended soil than unamended soil in all three soil types, indicating greater microbial activity and reflecting the lower stability of this organic matter source compared to the other biowastes tested. This supported the hypothesis that increased microbial activity stimulated by addition of unstabilised, or

partially stabilised, biowastes materials to soil may lead to O₂ deficits and denitrification losses in vulnerable soil types. Microbial biomass C in DMAD and ADMSW amended soil were generally equivalent to unamended soil in all three soil types. Microbial biomass C and MBN concentrations decreased below control values in AD amended soil, possibly in response to an inhibitory effect of the high NH₄-N concentrations in incubated soils amended with this type of digestate.

8 GENERAL DISCUSSION

8.1 Industrial Biowastes

8.1.1 Background

The term 'biowastes', in this thesis, is used to refer to organic residuals from industrial and commercial processes, excluding agriculturally-derived wastes and wastewater treatment sludges. An estimated 7 million tonnes of these materials are spread on agricultural land annually in the UK (Gendebien *et al.*, 2001), and this is regarded as the main potential alternative management route to landfill disposal (Gendebien *et al.*, 2001; Defra, 2007). Under the waste management licensing regulations (WMLR) (SI, 2005a), certain industrial biowastes are exempt from waste management licensing, but necessary to register the exemption prior to landspreading. Those wishing to spread industrial biowastes to agricultural land must demonstrate that they are of agricultural benefit (Section 2.2.2.4). Biowastes represent a diverse range of materials from the food and drinks industry, pharmaceutical, leather and tanneries and textile industries. Hence, they are highly variable in terms of physical and chemical properties, such as organic matter and nutrient element content.

Total nutrient concentrations in organic fertiliser sources do not reflect availability. In addition to mineral forms, nutrients will be in organic forms not all of which will be available for crop uptake. To gain maximum economic benefit and prevent environmental damage by losses of nutrients to the environment, it is important to accurately quantify nutrient availability in organic residuals. In addition, under the Nitrates Directive (CEC, 1991), the supply of N to crops from fertilisers and organic sources must not exceed crop requirements. There has been much research into the use of livestock manures and slurries in agriculture (Smith *et al.*, 1984; Nicholson *et al.*, 1996; Jackson and Smith, 1997; Nicholson *et al.*, 1999), and biosolids from wastewater treatment (Hall, 1983a;b; Serna and Pomares, 1991a; Serna and Pomares, 1991b; Hernández *et al.*, 2002; Cogger *et al.*, 1999; Smith and Bellett-Travers, 2001; Smith *et al.*, 2002b; Smith *et al.*, 2003; Breedon *et al.*, 2003; Morris *et al.*, 2003.; Corrêa *et al.*, 2004; Cogger *et al.*, 2004; Tarrasón *et al.*, 2007), and fertiliser guidelines exist for these materials (MAFF, 2000). However, with the exception of paper wastes (King, 1984; Aitken *et al.*, 1998; Douglas *et al.*, 2003; Levy and Taylor., 2003; Gibbs *et al.*, 2005; Burgos *et al.*, 2006), there has been little quantitative research on the properties

or agronomic characteristics of industrial biowastes, and the availability of N from these organic residuals. The complexity and variability of the materials require the development of fertiliser guidelines, to improve confidence in their agronomic value, gain maximum economic benefit from their use in agriculture and to prevent release of excess nutrients to the environment.

8.1.2 Characterisation of Physical and Chemical Properties of a Selected Range of Biowastes

A range of biowastes from industrial processes were selected for field and laboratory investigation (Chapters 5, 6 and 7), these included examples from meat and fish production industries, vegetable processing, dairy processing, the brewing industry and examples of anaerobic and aerobically digested biowastes. An initial aim was to characterise the physical and chemical characteristics of the selected range of biowastes. There were a range of solid and liquid biowastes, some of the liquids were very dilute with DS contents of less than 2.5 %; these were kieselguhr (KG) and potato sludge and wash water (Potato sludge/wash). There was a wide range of pH values from 3.6 for TAD to 8.8 for ADMSW (Tables 3.8 and 3.9). Many of the biowastes were a significant source of total N (Tables 3.12 and 3.13) including; mixed vegetable waste, yeast from brewing (Yeast), ice-cream waste (Ice-cream), anaerobically digested municipal solid waste (ADMSW), thermophilic aerobic digestate of food waste (TAD) and anaerobic co-digestate food waste and animal slurry (AD stored/fresh). The greatest total N contents in liquid biowastes were in AD stored/fresh, between 5.5-7.2 kg N m⁻³, as expected due to the animal slurry component in the input material (Gendebien *et al.*, 2001; Payne, 2006), and Yeast, 6.9 kg N m⁻³. Ice-cream also had a high total N content of 5.4 kg N m⁻³, but a low mineral N content of 1.0 % total N. The TAD had a slightly lower total N content than DMAD, equivalent to 3.5-4.0 % compared to 4.6-6.0 % on a DS basis, and they had a similar available N content of approximately 10 %. Anaerobically digested municipal solid waste (ADMSW) had a lower total N content between 1.5-2.3 % on a dry solids basis. Some of the biowastes types were not a significant source of total N including the trout farm wastes (Trout old/fresh), Potato sludge and Potato wash, Salt whey, keiselguhr (KG), Ice-cream DAF and abattoir wash water (Abattoir). This was due to admixture with sediment and loss of N by volatilisation in the case of the trout wastes, and due to the low solids contents in the liquid wastes. However, Abattoir had a high mineral N content of 65 %.

The majority of the biowastes were a source of P (Tables 3.8 and 3.9), with the exception of KG, Potato sludge/wash and Abattoir. Many of the biowastes were a better source of K than DMAD, which has a low K content as it is elutriated during the wastewater treatment process (Hall, 1983b). In particular, AD fresh/stored contained high concentrations of K, due to animal slurries in the input material (Gendebien, 2001; Payne, 2006) and the vegetable wastes also had a high K content. Dewatered digested biosolids (DMAD) and ADMSW were a significant source of S, 9-11 mg kg⁻¹ DS and 5.8 mg kg⁻¹ DS respectively.

8.2 The Effects of Biosolids Type and Livestock Wastes Type on N Availability in Amended Soil under Field Conditions

The fertiliser value of raw sewage sludge and conventionally treated biosolids has been extensively researched (Coker, 1966; Tester *et al.*, 1977; Hall, 1983a;b; Parker and Sommers, 1983; Coker and Carlton-Smith, 1986; Coker *et al.*, 1987; Smith *et al.*, 1998b;c;d; Cogger *et al.*, 1999) (Section 2.8.3). Recent investigations have demonstrated that biosolids treated to 'enhanced' status to eliminate pathogens to meet the standards set by the Safe Sludge Matrix (ADAS, 2001) may have different nutrient release characteristics to conventionally treated products (Cogger *et al.*, 1999; Smith and Bellett-Travers, 2001; Smith *et al.*, 2002b; Morris *et al.*, 2003; O'Connor *et al.*, 2004).

A field investigation was conducted at the Imperial College farm in Wye, Kent, in 2005 (Chapter 4), to investigate N availability in two contrasting agricultural soils amended with conventional and enhanced treated biosolids to further investigate N transformation dynamics of new biosolids products under field conditions. Livestock wastes were included as reference materials as their fertiliser value has been well established (Smith *et al.*, 1984; Nicholson *et al.*, 1996; Jackson and Smith, 1997; Nicholson *et al.*, 1999) (Section 2.8.2) and detailed fertiliser guidelines exist for these organic residuals (MAFF, 2000; Defra, 2001a;b) (Section 2.8.1).

The biosolids and livestock wastes investigated included: farmyard manure (FYM); two liquid livestock slurries, pig slurry (PIG) and cow slurry (COW); dewatered untreated sewage sludge (DRAW); liquid anaerobically digested biosolids (LMAD); dewatered anaerobically digested biosolids (DMAD); thermally dried anaerobically digested biosolids (TDMAD) and lime treated raw cake (LC). Lime cake and TDMAD were examples of biosolids treated to enhanced standards.

Mean TON recoveries for both soil types showed that quantities of recovered N as TON at 0-20 cm for NH_4Cl , pig slurry (PIG) and LMAD were significantly greater ($P < 0.05$) than the recoveries from the other amendments (Figure 4.24). This confirms that liquid livestock manures and liquid digested biosolids can act as rapidly available N sources, and comparable fertiliser sources to mineral N fertiliser, due to their high mineral N content (Table 3.11). The recovery of N after 76 days for NH_4Cl at 0-20 cm was 70-85 % (Tables 4.4 and 4.5), this indicated that there was some movement of N below the top 20 cm. For pig slurry-amended soil the final recovery was equivalent to NH_4Cl in one soil type, at 72 % of the total N applied, but recoveries were variable, as, in the other soil type, 28 % of total N applied was recovered as mineral N. Of the total N applied in LMAD, 47-63 % was recovered as mineral N, which indicated that up to 11 % of the organic N was mineralised in addition to readily available $\text{NH}_4\text{-N}$. This is consistent with recent findings (Smith *et al.*, 2002) that 50-60 % of total N in LMAD is available, and with current fertiliser recommendations (MAFF, 2000), which suggest 55 % of N in spring-applied, incorporated LMAD is available for crop uptake.

Despite a high mineral N content of 50 % total N (Table 3.11) there were lower recoveries in cow slurry-amended soil, equivalent to 28-36 % of applied total N (Table 4.4 and 4.5). There was no statistically significant difference between overall TON recoveries in cow slurry-amended soil and TDMAD- and DMAD-amended soil.

Recoveries of TON from TDMAD and DMAD were less than the liquid digested biosolids and pig slurry, as expected from their lower mineral N content, but N recoveries were greater than from DRAW, LC and FYM. Despite the low mineral N content of TDMAD, there was a rapid increase in $\text{NH}_4\text{-N}$ concentration in both soil types following initial application (Table 4.1), and overall, more TON was available in TDMAD-amended soil in comparison to DMAD amended soil at the mid-point of the trial (Tables 4.2 and 4.3). The lack of statistically significant difference (Figure 4.24) in the overall amounts of total N recovered as TON from the enhanced-treated, TDMAD and conventionally-treated, DMAD, were consistent with previous findings (Gilmour *et al.*, 2003; Morris, 2006). In TDMAD-amended soil, 32-41 % of applied total N was recovered at 0-20 cm after 76 days and 26-33 % total N was recovered in DMAD-amended soil (Tables 4.4 and 4.5). This is consistent with recent findings for TDMAD of between 30-60 % of total N available (Cogger *et al.*, 1999; Smith and Durham, 2002; Morris *et al.*, 2003), and of approximately 30 % total N availability for DMAD (Smith and Bellett-Travers, 2001; Smith *et al.*, 2002b; Breedon *et al.*, 2003; Morris *et al.*, 2003; Patersen *et al.* 2003). Therefore, although TDMAD had less total and mineral N than

DMAD, it had a larger mineralisable pool of N and was an effective rapid release N source for crop production.

Dewatered raw sewage sludge (DRAW), FYM and LC were in a group with the lowest mean recoveries overall, compared to other materials examined (Figure 4.24). However, DRAW and LC were still adequate sources of mineral N; in LC-amended soil 18–31 % of total N was recovered as TON after 76 days, and in DRAW-amended soil 21–23 % total N was available (Tables 4.4 and 4.5) under field conditions. In FYM-amended soil, between 8–13 % of applied total N in this material was released as TON after 76 days. The low mean mineral N recoveries are partially because the release of N from FYM, DRAW and LC was less rapid than for the digested and liquid slurries (Figures 4.7, 4.8 and 4.13). This group of livestock wastes and sludges is characterised by an unstabilised or partially stabilised OM component, and the less rapid release of N may be due to immobilisation of N in the microbial biomass. This has previously been suggested as a mechanism to explain unrecovered N in soils amended with untreated livestock wastes and slurries (Chae and Tabatai, 1986; Sims, 1986; Plaza *et al.* 2007). The MBN component was not measured for livestock wastes in this experiment, but was measured in biosolids amended soil and is discussed in Section 8.6.

8.3 Quantification of the N Release Properties of Industrial Biowastes Relative to Anaerobically Digested Biosolids Cake and Mineral N Fertiliser

There has been little quantitative investigation into N availability from industrial biowastes, although approximately 7 million tonnes are spread to land annually in the UK (Gendebien *et al.*, 2001). Nitrogen in organic residuals is present in mineral and organic forms; the mineral N component is readily available, however only a fraction of the organic N will be released on addition to agricultural soil. It is necessary to be able to accurately predict N availability from organic residuals to gain maximum economic benefit and prevent environmental damage through leaching and runoff of mineral N (Hansen *et al.*, 2007; Surampalli *et al.*, 2008) and gaseous emissions of N (Day *et al.*, 1978; Galbally and Roy, 1983). The Nitrates Directive (CEC, 1991) restricts the amount of total N that can be applied in organic residuals and an annual field-based limit of 170 kg N ha⁻¹ applies within NVZs to areas not in grass; in addition total application of N must not exceed crop requirements (Section 2.3.1). There are detailed fertiliser guidelines for livestock wastes and animal slurries (MAFF, 2000; Defra, 2001a;b) and guidelines are also available for biosolids from wastewater treatment

(MAFF, 2000). However, there are no guidelines available for industrial biowastes. Landspreading of biowastes for agricultural benefit is an important management route and a means of diverting biodegradable waste from landfill in accordance with the Landfill Directive (CEC, 1999). It is important to develop guidelines by providing precise information on the N availability in these materials; this will facilitate further use in agriculture by improving confidence in their N fertiliser value. In addition this will prevent oversupply of inorganic fertiliser N, reducing negative environmental effects and reducing fertiliser inputs and costs.

A programme of field experiments into the agronomic benefits of industrial biowastes was conducted at Silwood Park, the Imperial College campus near Ascot, Berkshire, from 2006-2007 (Chapters 5 and 6). Nutrient availability measurements were primarily focussed on N as this is the most important nutrient of agronomic benefit in organic residuals and is the most limiting to agricultural yields (Cooke, 1982). A range of biowastes from industrial processes were selected. These included examples of biowastes from meat and fish production industries, vegetable processing, dairy processing biowastes, the brewing industry and examples of anaerobic and aerobically digested biowastes. Their physical and chemical characteristics were summarised in Section 8.1. A systematic design was adopted for the field experimentation (Cleaver *et al.*, 1970; Greenwood *et al.*, 1980a;b; Smith and Hadley, 1988). Biowastes were incorporated immediately into the soil to minimise NH_3 volatilisation losses and maximise N recovery. Perennial ryegrass was used as an indicator crop as it is effective at capturing available soil N (Addiscott *et al.*, 1991; Christian and Richie, 1998). The N availability in the biowastes was compared to the availability in biosolids and mineral N fertiliser as these fertiliser sources are well characterised.

The majority of the materials were a significant source of N, and an increase in crop yield and N offtake was observed with increasing rates of application of N. Linear regression coefficients of crop response to biosolids and biowastes application were compared to linear regression coefficients for mineral fertiliser N to obtain N equivalency values for the biowastes. In 2006, the N equivalency value for DMAD was 0.52 (Table 5.3), which was greater than the value of approximately 0.30 previously obtained in a programme of experiments at Silwood Park into the N fertiliser value of biosolids (Smith and Bellett-Travers, 2001; Smith, *et al.*, 2002; Morris *et al.*, 2003). Full elemental analysis of plant tissue demonstrated that DMAD was a significant source of S (Table 5.1), and this probably contributed to the crop response increasing its relative response in comparison to mineral N fertiliser. Anaerobically digested municipal solid

waste (ADMSW) was also a significant source of S, but the plant tissue S contents from the other biowastes treatments were comparable to the mineral N fertiliser control; therefore S was not assumed to be contributing to crop response in these treatments. Previously a base dressing of K_2SO_4 had been applied across the site at Silwood Park (Smith and Bellett-Travers, 2001; Smith, *et al.*, 2002b; Morris, *et al.*, 2003), but this was not done for the biowastes experiments as an additional aim was to assess transfer of other plant nutrient elements to the crop, in addition to quantification of N availability.

In 2007, a further selection of mineral N controls was established, which included a mineral N gradient, plus base dressings of P and K, and a combination of P and K. At this stage, the importance of S was not fully appreciated, and S controls were not established. In 2007, the N equivalency value of DMAD relative to mineral N fertiliser was extremely high, at 0.70 (Table 6.2). The N equivalency values relative to mineral N fertiliser, with a base dressing of P and K was 0.50 (Table 6.5), similar to the value of 0.52 obtained in 2006. Leaching losses at Silwood Park have previously been measured following biosolids-amendment, and were found to be minimal under the ryegrass crop amended with biosolids (Morris, 2006). However, there was exceptionally high rainfall in 2007, and it is highly probable that leaching of fertiliser mineral N took place, which would explain the high N equivalencies relative to mineral N fertiliser. The losses of mineral N from the control plots may have been reduced indirectly by the base dressing of P and K in 2007, due to stimulated root growth and improved efficiency of capture of applied mineral N. The N equivalencies relative to the mineral N gradient with applied P+K were considered to be an appropriate comparison of N availabilities in the biowastes between years, on the basis that N equivalency for the reference material, DMAD, was consistent with the value obtained in 2006.

Despite the lower total N content, the N equivalency obtained for ADMSW in 2006 was equivalent to DMAD at 0.52 (Table 5.3), which may reflect its greater mineral N content of 18 % compared to 10 % total N in DMAD (Tables 3.10 and 3.12). As was observed for DMAD, the S content of plant tissue from ADMSW-amended soil was greater than the mineral N fertiliser controls (Table 5.1), therefore the N equivalency may have been overestimated to a degree. Nevertheless, the findings demonstrated similarities between biosolids from wastewater treatment and mechanically separated municipal solid waste that has undergone a similar biological stabilisation process. By contrast, in 2007, there was no significant crop response to N addition from ADMSW. This may have been due to variation in length of storage of the material in 2007 and difference in stability of the applied product in the two years. The ADMSW had a lower total N

content in 2007, which may have been a result of loss of NH_3 by volatilisation as a result of an extended storage period. In addition extended storage of ADMSW may have resulted in composting and increased stability of the organic matter, reducing the component of mineralisable N.

The N equivalencies for AD fresh and stored were 0.85 and 0.68 respectively, in 2006 (Table 5.3); similar values of 0.74 and 0.71 were also obtained in 2007 (Table 6.5). These values are in the same range as would be expected for digested animal slurries (Shröder *et al.*, 2007). The fresh and stored AD had relatively similar N equivalencies in 2007, whereas there was a difference of 0.17 obtained in 2006. The mineral N content of AD stored in 2007 was greater than AD fresh, 71.8 % total N in comparison to 53.1 %, whereas in 2006 mineral N contents were similar, 39.3 % total N for AD fresh and 46.6 % for AD stored (Table 3.13). This suggested that, in 2007, there had been continued mineralisation of N in AD during storage. Storage also increased stabilisation of the organic matter; the N equivalency for AD stored in 2007 was equal to its mineral N content, which indicated that there was little further mineralisation of organic N. However, the mineralisable N fraction in AD fresh was calculated as 44.6 organic N (Table 6.4). In 2006, mineralisable N was also greater in AD fresh, equivalent to 75 % organic N, compared to 40 % organic N in AD stored (Table 5.3).

Despite a low mineral N content in comparison to the liquid anaerobic digestates, N equivalencies for TAD were similar to the other digested liquids, and were 0.76 in 2006 (Table 5.3) and 0.59 in 2007 (Table 6.5). This indicated that TAD contained a larger pool of rapidly mineralisable N than anaerobically digested biosolids as has previously been reported for aerobically digested sludge (Hall, 1983a; Serna and Pomares, 1991a; Serna and Pomares, 1991b; Hernández *et al.*, 2002). The greater N equivalency obtained in 2006, may be a result of a contribution of K to the crop response, as the mineral fertiliser gradient received no base dressing of K in 2006. Alternatively, it may simply be due to variation in the composition and availability of the N in the input material.

Abattoir wash water, investigated in the 2006 crop response trial had an N equivalency of 1.6 (Table 5.3). This indicated that the abattoir wash water was a significant source of available N, as expected from its high mineral N content. The N equivalency was greater than 1, which suggested that factors other than available N were contributing to the crop response. However, the concentrations of nutrient elements in the plant tissue were similar to those for the mineral N fertiliser control (Table 5.1). The high N

equivalency may be explained as an artefact, as the total N application from this source was low and the yield response was at the lower end of the range of response for the mineral fertiliser control.

Vegetable waste mix investigated in 2007 had an N equivalency of 0.45 (Table 6.5), similar to DMAD, indicating that it was an effective source of available N. Despite its low mineral N content of 1.5 %, yeast waste from brewing was also a significant source of readily mineralisable N, with an N equivalency of 0.85 (Table 6.5). This is consistent with the findings of Douglas *et al.* (2003), who found that brewing wastes applied at equivalent rates of total N to mineral N fertiliser produced equivalent or greater yields.

A significant response in fresh yield relative to N addition was found for Salt whey, but there was no significant relationship for dry yield or N offtake (Table 6.1). This may have been due to its low total N content of 0.95 kg m⁻³, compared to 6.85 kg m⁻³ in Yeast, for example (Table 3.13) .

In addition, N availability in biowastes-amended soil was investigated in a laboratory incubation experiment under controlled temperature and moisture conditions (Chapter 7), in three different soil types. The experiment included an unamended control and mineral N (NH₄Cl) and dewatered digested biosolids (DMAD) were included as reference treatments. This experiment was established primarily to investigate MBN dynamics, which are discussed in Section 8.6. Final N recoveries in mineral N controls were approximately 100 % total N additions in all three soil types, and so there were no N loss mechanisms operating in soil in the absence of organic matter addition. The recoveries of N from the biosolids and biowastes amendments were smaller overall than were measured in the field investigation. Final recoveries of N in DMAD-amended soil ranged between 14-20 % total N, this is at the lower end of previously reported N availabilities for this biosolids type (Smith *et al.* 1998b; Breeden *et al.*, 2003). The incubation period was chosen based on findings from previous incubation experiments at 25 °C (Smith *et al.*, 1998b). However, the lower recoveries may be due to incomplete mineralisation of DMAD, potentially due to a less active microbial population, as the soils were collected during the winter period. Final recoveries of N were greatest in soil amended with liquid anaerobic co-digestates of food waste and animal slurry, between 20–68 % total N. In two of the soil types investigated, N availabilities for AD were within the range that would be expected for liquid digested biosolids (Coker *et al.*, 1966; Ryan *et al.*, 1973; Hall, 1983a.; Kiemnec *et al.*, 1987; Smith *et al.*, 1998b). This supported the findings of the biowastes field investigation

and indicated that anaerobic co-digestates of animal slurries and food wastes have similar N release characteristics to anaerobically digested biosolids. The mineral N recovered in AD-amended soil was significantly greater than in the other biowastes and biosolids treatment ($P<0.05$). This is to be expected from the high proportion of mineral N in this biowaste type of 47 %. Final recoveries of N in TAD-amended soil ranged between -8-33.0 % total added N, These values were lower than expected from the field investigation, in which N was 59-76 % as available as mineral N fertiliser in TAD-amended soil (Tables 5.3 and 6.5), and in one of the soil types, less mineral N was recovered than the amount of total N added initially. In ADMSW-amended soil, final N availability was -11.5-11.5 % of the total added N. Again, this is much lower than expected, as in ADMSW-amended soil, added N was found to be 52 % as available as mineral N fertiliser in the 2006 field experiment (Table 5.3). The recoveries of mineral N were lower than expected, especially in TAD and ADMSW amended soil in one of the soil types. There were suspected losses of N in these treatments, the interactions between soil type and biowastes type are discussed further in Section 8.5.

8.4 Agronomic Benefits of Industrial Biowastes

8.4.1 Findings of Crop Response Trials

In addition to assessing the N availability in the range of industrial biowastes investigated in the 2006/7 biowastes crop response trials; a further aim was to quantify other agronomic benefits and to examine nutrient transfers from biowastes to crops.

In the 2006 experiment, the soils treated with materials which were considered to be a poor source of N received a dressing of 120 kg N ha⁻¹ so that other beneficial aspects could be assessed. These were the potato processing wastes (Potato wash/sludge), trout farm wastes (Trout old/fresh), the ice-cream wastes (Ice-cream DAF and Ice-cream) and keiselguhr from brewing (KG).

It is likely that higher nutrient concentrations in the biowastes will lead to greater concentrations and accumulation in the ryegrass. Hu and Barker (2004) found greater concentrations of N, P, K, Ca and Mg in leaves of tomato plants fertilised with a nutrient rich agricultural waste compared to those fertilised with less nutrient-rich sewage sludge and a yard waste. Full elemental analysis of the plant material from the top rates of application, for the first harvest in 2006, was conducted to provide evidence of

elements other than N in the biowastes improving the nutritional status of the crop (Table 5.1). A significant crop response to rate of application (Table 5.2), for the combination of trout farm waste and mineral N fertiliser demonstrated that benefit arose through the addition of organic matter to the soil. This may be a result of beneficial improvements to the soil structure and water holding capacity through the addition of organic matter (Chambers *et al.*, 2003). There was no significant crop response following soil amendment with Trout fresh; this may reflect temporal variation in the composition of the material as fish feed and faeces composition may vary with the stage of fish maturity and stocking of the fish farm.

Under non-limiting N conditions there was also a significant response between rate of application of Ice-cream DAF and N offtake and KG and fresh yield, this indicated that there were additional benefits of application of these wastes, such as addition of organic matter or trace elements, although elemental analysis of plant tissue did not detect any element effects in these treatments. However, it is possible that the supply of trace elements in these biowastes was important in stimulating root growth, but root development was not measured in this investigation.

There was no significant crop response following application of either of the potato processing wastes, however plant tissue analysis demonstrated that potato sludge were an effective source of N. Tissue K content was 41.0 mg g⁻¹ DM compared to 33.6 mg g⁻¹ in the mineral N control (Table 5.1). Full elemental analysis of plant tissue was not conducted in 2007, however, the vegetable waste mix was also a significant source of K; it contained 38.3 g kg⁻¹ compared to less than 10 g kg⁻¹ in the other solid biowastes, and therefore may supply K for crop growth.

8.4.2 Developing a Strategic Approach for Investigating the Agronomic Value of Biowastes

The principal aim of the programme of industrial biowastes field experiments (Chapters 5 and 6) was to address the deficit of information on the nutritional value of these materials. However, technical difficulties arise due to the variable nature of these wastes, so an additional aim was to develop an appropriate strategy for accurately assessing the agronomic benefit which can be applied, and easily adapted for a wide range of materials. It is necessary to obtain representative samples for experimentation, in the case of some liquid biowastes such as the liquid digestates the material is well homogenised; in other cases, for instance with KG and Potato sludge,

the solid material was found to settle quickly and it was necessary to re-mix the materials to obtain a representative sample prior to application.

A dressing of N was applied to wastes with a low total N content in order to ensure the crop was not N limited so that other benefits could be detected. This approach was successful to some extent, as a significant crop response to Trout old was detected; for KG and Ice-cream DAF, for some measures of crop response, there was a significant positive relationship with rate of application. However, in a further field experiments it may be necessary to apply wastes with very low N content at a much greater rate to assess benefits to the soil and crop response. At higher rates the input of organic matter and trace elements may have a significant impact on structure, fertility and nutritional value.

Biowaste materials have been found to act as slow release sources of nutrients (Wolkowski, 2003; Zheljazkov, 2005), and the input of organic matter to the soil may result in initial immobilisation of nutrients by the microbial community, especially when the ratio of C to nutritional elements is high (Vinten, 2002; Ghani, *et al* 2005). Eriksen *et al* (1999) found soil NO₃-N decreased in the year of application of MSW compost with a C to N ratio of 40. Therefore, although beneficial nutrients may not be immediately available to the crop the waste application may have residual benefits. In previous experiments (Morris *et al.*, 2003), the residual value of sewage sludge was determined by taking further cuts of the grass grown on sewage sludge amended soil the year following application of the waste. Controls were set up in the second year of the biowastes experiment (Chapter 5) to provide complete fertiliser guidelines for the second year fertiliser N value of the biowastes, but no second year growth was observed, suggesting the majority of organic N was mineralised in the first year. Residual value of industrial biowastes has been detected previously (Douglas *et al.*, 2003); the yield of Italian ryegrass fertilised with 250 kg total N ha⁻¹ from distillery waste was significantly greater than mineral N fertiliser applied at the same rate, and the unamended control in the year following application. Therefore it may be of benefit to assess second year growth with a different selection of biowastes.

Additional controls were set up in the 2007 experiment to provide mineral N calibration plots that were also supplied with P and K and a combination of P and K, to determine the crop response from the biowastes that was due to N alone. Following full elemental analysis, high concentrations of S relative to the mineral N control, were found in grass fertilised with DMAD, and to a lesser extent in the ADMSW treatments.

This probably accounted for the high N equivalency for DMAD obtained in these experiments relative to a previous programme of experiments at Silwood Park, in which a base dressing of K_2SO_4 was applied so the soil was adequately supplied with S in addition to K. This demonstrates the need for S to be included in controls in further experiments.

Two different statistical approaches were used to assess the N equivalency of biowastes relative to mineral N controls, these are described in Section 3.7.2. Firstly, regression coefficients from linear regression analysis for the measures of crop response relative to N application in the biowastes were compared to regression coefficients (Kiemec *et al.*, 1987; Smith *et al.*, 2001; Smith *et al.*, 2002b; Morris *et al.*, 2003). An alternative method is to compare individual yields produced by known concentrations of total N to a yield response curve for a mineral N control to obtain a fertiliser N equivalency value (George, 1994; Jackson *et al.*, 1997; Nicholson *et al.*, 1999; Nicholson *et al.*, 2003; Schröder *et al.*, 2007). Nitrogen equivalencies were also calculated by this method as a comparison; asymptotic regression curves were fitted to the mineral N response data, and yields and N offtakes from biowastes amended soil were compared to the fitted curves to obtain N equivalencies. Similar N equivalencies were generally obtained by both methods. However, when the yield exceeded the maximum from the mineral N response curve it was not possible to calculate N equivalencies (Table 5.5). In addition, when yields were close to the maximum for mineral N the N equivalencies may have been an overestimate. This is because, in the 2006 field experiment the response to mineral N was non-linear at top rates of application (Figure 5.9), whereas in the biosolids and biowastes amendments the response was generally linear. The linear response due to biowastes application may have been due to supply of other nutrients such as P, K and S, which may have limited crop response in the top rate of application for the mineral N controls.

In 2007, measures were taken to ensure that there was a linear response in the mineral N controls. The top rate of application in the mineral N control plots was reduced and additional controls were included with base dressings of P and K, and a combination of P and K in addition to a gradient of mineral N. Sulphur was not included in the control treatments, as at this point the tissue nutrient content data was not available and the importance of S to the crop response at the Silwood Park site was not fully appreciated. The rates of application were also reduced for the biowastes which were expected to have a high total and available N content, so that the yield response would be within the same range as the mineral N fertiliser control. In the

mineral N fertiliser gradient with a base dressing of K and P+K, the linear regression was a better fit than asymptotic regression, therefore in this case comparison of linear regression coefficients were considered the most appropriate method for calculating N equivalencies.

Overall, comparison of linear regression coefficients is considered the most suitable method for the design of experiment. The systematic design incorporated an unamended control into each main plot, therefore the mean unamended control value is taken into account on an individual treatment basis, improving the precision of the calculation. The systematic design also allows for several rates of application, and is therefore a reliable approximation of N equivalencies across different rates of application in the linear section of the response curve is obtained.

8.5 The Interactions between Organic Residual Type and Soil Type on N Dynamics under Field and Laboratory Conditions

The availability of N in organic residuals-amended soil may be dependent on soil type (Tester *et al.*, 1977; Terry *et al.*, 1979; Hall, 1983b; Hernández *et al.*, 2002) (Section 2.9.4). Higher rates of mineralisation have been reported in more sandy soils due to better aeration. However, sandy soils may also be more prone to movement of NO_3^- below the surface layer due to leaching (Koo and O'Connell, 2006). There may be lower N availability in clay soils due to $\text{NH}_4\text{-N}$ fixation (Tester *et al.*, 1977; Shen *et al.* 1997; Steffens and Sparks, 1997). Conversely, soils with a high clay content have a greater capacity to protect soil organic matter (Zagal, 1993), and organic matter content may be positively correlated with rates of mineralisation and nitrification, due to a larger and more active microbial population (Zagal, 1993; Jha *et al.*, 1996; Silva *et al.*, 2005). Soils with a higher organic matter content may also have greater pore space, therefore improved aeration, and greater water holding capacity due to improved structure, therefore greater retention of NO_3^- , and less leaching below the surface layer (Addiscott *et al.*, 1991).

The 2005 biosolids and livestock wastes trial in Wye, Kent (Chapter 4), was established on two contrasting soil types, a fine textured silty clay (North Sidelands) and a coarser-textured sandy silt loam (Brices Field) (Table 3.1). The laboratory incubation experiment (Chapter 7) was established with 3 soil types under controlled temperature and moisture conditions. The soils used for the incubation were North Sidelands, Brices Soil and the loamy sand from Silwood Park, Berkshire, the site of the

biowastes crop response trials (Chapters 5 and 6). North Sidelands had a higher organic matter content (4.1-4.6 % ds) compared to Silwood Park (2.1-3.2 % ds) and Brices Field (1.9-2.2 % ds). Microbial biomass C (MBC) concentration in the different soil types was consistent with the organic matter content (Zagal, 1993; Jha, 1996; Silva *et al.*, 2005). In the field experiment, the MBC content of the higher fertility silty clay (North Sidelands) was between 300-1200 kg C ha⁻¹ and the lower fertility sandy silt loam (Brices Field) had a MBC concentration between 80-150 kg C ha⁻¹ (Figure 4.16). The findings of the laboratory experiment were slightly lower but consistent with differences in MBC observed between soil types in the field; North Sidelands had the greatest MBC content of between 400-500 mg kg⁻¹ ds in unamended soil, followed by Silwood, which had a concentration of between 150-200 mg kg⁻¹ ds and Brices had a concentration of between 60-120 mg kg⁻¹ ds (Figures 7.8-7.12).

In the field experiment at Wye, mineral fertiliser nitrification controls (NH₄Cl) were established and demonstrated a faster rate of nitrification in the higher fertility soil type (Figure 4.4). The same pattern was observed in organic residual soil amendments; after 6 days in the sandy silt loam there was an accumulation of NH₄-N in the majority of the amendments, whereas, in the silty clay, there was a decrease in NH₄-N with a corresponding increase in TON concentration in the majority of amendments (Figures 4.5-4.13). Soil mineral N recoveries at the mid-point of the trial showed greater recoveries in the higher fertility soil type, consistent with higher rates of mineralisation and nitrification. The majority of the added N in the mineral N controls was recovered at 0-20 cm in the silty clay by 34-41 days, whereas in the sandy silt loam recoveries were approximately 70 % total N added in the mineral N controls (Tables 4.2 and 4.3). The soil with the higher clay content was not significantly affected by NH₄-N fixation, which is a possibility in clay soils (Tester *et al.*, 1977; Shen *et al.* 1997; Steffens and Sparks, 1997). This was demonstrated by the full recovery of mineral N observed in the silty clay at the mid-point of the field trial, and the greater initial recoveries of NH₄-N in organic residual-amendments in this soil type, in comparison to the sandy silt loam (Table 4.1). Despite the initial differences in mineralisation and nitrification rates, the TON production after 76 days was similar for both soil types for the majority of treatments, demonstrating an initial lag in microbial activity in the lower fertility soil type (Tables 4.4 and 4.5).

A mineral N control (NH₄Cl) was also included in the laboratory incubation, and, as was observed in the field, there were also greater rates of nitrification in the higher fertility silty clay (North Sidelands) followed by the lower fertility sandy loam (Silwood) and then

the sandy silt loam (Brices) (Figure 7.1). This is consistent with their MBC concentrations (Figures 7.8-7.12), and therefore related to the size of the microbial population in each soil type. Silwood and Brices soils had a similar organic matter content (Table 3.1), therefore the differences in fertility between these two soil types may be related to the sand contents of the soils. Silwood soil contained 75-80 % sand compared to 35-41 % sand in Brices soil. Hence, it was a lighter, coarser-textured soil and therefore better aerated; Hernandez *et al.* (2002) reported increased microbial activity in a sandy soil due to improved aeration properties.

Soil type and organic residual type may influence N availability in organic residuals-amended soil. In the 2005 biosolids and livestock wastes field investigation, measurements of TON were made at two depths, 0-10 cm and 10-20 cm to investigate NO_3^- mobility. As would be expected, the liquid organic residual amendments and mineral N fertilisers were more prone to NO_3^- -N movement below the incorporation depth of 0-10 cm as greater concentrations of TON were measured at 10-20 cm in these treatments in comparison to the others (Figures 4.14 and 4.15). There was greater movement of NO_3^- -N below the 0-10 cm in sandy silt loam, as initial concentrations of TON at 10-20 cm in mineral N fertiliser treated soil were up to 20 kg N ha⁻¹ greater than in the silty clay. This is as might be expected in sandy soil types (Addiscott *et al.*, 1991); however, the end recoveries of between 70-85 % added N at 0-20 cm in the mineral fertiliser controls in both soil types (Tables 4.4 and 4.5), indicated that further movement below 20 cm was not significantly greater in the sandy soil. In DMAD-amended plots sown with ryegrass, concentrations of TON at 10-20 cm did not increase above the unamended control, which indicated that, as expected, the grass crop was effective at capturing available N released from the biosolids (Addiscott *et al.*, 1991; Christian and Richie, 1998).

The DMAD plots treated with a protozoa inhibitor in the field investigation showed delayed nitrification rates in Brices Field (sandy silt loam) (Figure 4.11). This may have demonstrated the importance of protozoa grazing on stimulating microbial activity. Alternatively, delayed nitrification rates may have been due to more general non-selective inhibition to microbial biomass activity, including the nitrifying population, and showed that the higher fertility soil was generally resilient to disruption to soil ecology.

The laboratory incubation experiment (Chapter 7) was established primarily to investigate MBN dynamics in biowastes amended soil in comparison to DMAD- and

mineral N-amended soil. Microbial biomass N dynamics are discussed further in Section 8.6.

Mineral N recoveries in the incubation experiment indicated that there were losses of N from the soils, in particular from the silty clay soil amended with TAD and ADMSW. Furthermore, recoveries of mineral N in the silty clay amended with TAD and ADMSW were lower than the unamended control (Table 7.4). The unrecovered N was not immobilised in the microbial biomass (Figure 7.14 and 7.18), despite an increase in MBN concentration in TAD-amended soil between days 0-20 in the silty clay (Figure 7.18). Ammonium fixation is also a potential mechanism, and it occurs to a greater extent in soils with a high clay content (Tester *et al.*, 1977). However, this was not thought to be a significant factor here as the majority of the added N was recovered in the mineral N controls. In addition, greater recoveries of $\text{NH}_4\text{-N}$ were observed in the silty clay (North Sidelands) in comparison to the sandy silt loam (Brices Field) in the 2005 field investigation (Chapter 4). Loss of ammonia by volatilisation is also a possibility. Here the amendments were thoroughly mixed with the soils, this would act to reduce NH_3 volatilisation, which is reduced by incorporation of organic amendments into the soil (Donovan and Logan, 1983). In addition, reduction of TON which had already accumulated in ADMSW, AD and DMAD amended soil in the silty clay (North Sidelands), led to the assumption that N was lost by denitrification.

It is generally thought that denitrification may occur in anaerobic microsites within an otherwise aerobic soil, which occur more frequently in clay soils with higher organic matter (Fillery 1983; Smith 1980). This is consistent with the greater losses of N observed in the silty clay soil in comparison to the coarser textured soils. Denitrification occurs under anaerobic conditions, which may arise due to the high biological oxygen demand associated with the microbial delay of organic amendments, or high moisture conditions. The losses of N observed in the silty clay were a function of the added organic matter, as there was full recovery of N in the NH_4Cl control (Figure 7.1). The greater apparent losses observed in TAD and ADMSW suggested that these biowastes were less stabilised than AD and DMAD, and supported greater microbial growth and activity and consequently oxygen depletion. Findings of the programme of field experiments support these observations, as TAD was demonstrated to have a large pool of mineralisable N (Tables 5.3 and 6.5). Previous research has also shown that aerobically digested organic wastes contain a higher proportion of mineralisable C than anaerobically digested wastes (Hall, 1983b; Serna and Pomares, 1991a; Serna and Pomares, 1991b; Hernández *et al.*, 2002). Soluble organic carbon (SOC) data in the

laboratory incubation experiment (Figure 7.13) also demonstrated the high proportion of labile organic matter in comparison to the other biowastes. In addition, MBC and MBN analysis of TAD-amended soil, indicated that there was greater microbial activity following soil-amendment with this waste type (Figures 7.11 and 7.16) in comparison to the other amendments, which would have led to depletion of oxygen and resulted in the development of anaerobic microsites, leaving the silty clay soil more prone to denitrification losses. Anaerobically digested municipal solid waste may contain less stable organic C than DMAD due to greater variation in the input material, for example there may be a high proportion of green waste containing complex organic matter with varying degrees of resistance to microbial degradation under anaerobic digestion conditions, which may be degraded under aerobic soil environments.

8.6 Partitioning of N within Soil Microbial Biomass in Different Soil Types Amended with Biosolids and Biowastes and the Subsequent Influence on N Release

Microbial biomass N (MBN) is an important fraction of total soil N and may account for approximately 2-6 % of total soil N (Brookes *et al.*, 1985b). When organic matter or nutrients are added to the soil, nutrients may become immobilised in the soil biomass, therefore becoming temporarily unavailable for crop uptake, but represent a labile source of nutrients for crops. The net amount of N mineralised from organic matter may be a balance between total mineralisation and immobilisation. Greater immobilisation of N has been observed when organic soil amendments have a high C:N ratio, greater than 20:1 (Parker and Sommers, 1983). Thus, the addition of high concentrations of available C in unstabilised organic matter sources may result in immobilisation of N (Recous and Mary, 1990; Jedidi *et al.*, 2004; Calbrix *et al.*, 2007). Soil type may also influence the amount of N immobilisation as slower rates of mineralisation of biosolids N has been observed in lower fertility soils (Smith *et al.*, 1998b; Breedon *et al.*, 2003). There has been some investigation into microbial biomass N (MBN) in biosolids-amended soil in laboratory investigations (Jedidi *et al.*, 2004). In addition, MBN has been measured in field investigations with a single soil and sludge type (Banerjee *et al.*, 1997; Fernandes *et al.*, 2005), but there is a lack of information on the effects of soil type on microbial immobilisation of N. However, generally, research in this area is limited.

Microbial biomass N (MBN) was measured in biosolids- and DRAW-amended soil in the 2005 field investigation at Wye, Kent (Chapter 4) in two soils, North Sidelands (a

silty clay) and Brices Field (a sandy silt loam). In addition, a laboratory incubation experiment was set up to measure MBN in biosolids (DMAD)- and biowastes-amended soil under controlled temperature and moisture conditions (Chapter 7). The biowastes were the 3 digested materials that were investigated in the programme of field experiments, the liquid anaerobic co-digestate of food waste (AD), the liquid aerobic digestate of food wastes (TAD) and the anaerobic digestate of municipal solid waste (ADMSW). The soil types selected were the silty clay and the sandy silt loam from the 2005 biosolids and livestock wastes field investigation and the loamy sand from the 2005/2006 industrial biowastes field trials. These soils were selected in order to investigate MBN dynamics following biowastes amendment in contrasting soil types and to allow comparisons with field data.

Findings from the field investigation demonstrated that the MBN content in DRAW- and LC-amended soil was significantly greater than for DMAD- and TDMAD- amended soil for both soil types (Figure 4.17). In the laboratory incubation experiment, added N recovered in the microbial biomass was significantly greater in TAD amended soil than in the anaerobically digested biosolids (DMAD) and anaerobically digested biowastes (ADMSW and AD). Microbial biomass C in DMAD and ADMSW amended soil were generally equivalent to unamended soil in all three soil types. This indicated that there was greater microbial activity resulting from addition of a low stability organic matter source. This was consistent with previous findings that greater microbial immobilisation of N occurs with less stable sources of organic matter (Recous and Mary, 1990; Jedidi *et al.*, 2004; Calbrix *et al.*, 2007).

As observed for MBC concentrations, MBN concentrations were greater in the silty clay in comparison to the sandy silt loam, equivalent to 100-140 kg N ha⁻¹ and 15-40 kg N ha⁻¹ respectively. However, there was some evidence for differences between soil types in the amount of added N recovered in the microbial biomass. There was an initial increase in N recovered in the microbial biomass in LC and DRAW amended soil in the sandy silt loam (Brices Field), whereas there was no increase in the silty clay (North Sidelands). There was also a significant difference overall in the amount of MBN recovered, with greater concentrations ($P=0.03$) of added N recovered in the microbial biomass in the sandy silt loam (Brices Field) (Figure 4.23). In addition, MBN concentrations in DMAD-amended soil were generally greater than the unamended control, whereas in the silty clay they fluctuated at approximately the same concentration as the unamended control.

Despite subtle differences in MBN recovered in the different soil types, the N recovered in the microbial biomass in the lower fertility soil did not account for the initial differences in mineral N production observed between the soil types. There were lower recoveries of mineral N observed in the sandy silt loam than initially expected in DMAD amended soil, 5 % total N compared to an expected 15 % (Table 4.1), but this was not recovered as microbial biomass N. In addition the mineral N recoveries in DRAW and LC in the sandy silt loam (Brices Field) at the mid-point of the trial were approximately 50 % of the mineral N recoveries in the higher fertility silty clay soil (North Sidelands) (Tables 5.2 and 5.3). There were also lower recoveries of mineral N in TDMAD- and DMAD- amended soil at this stage. However, the added N recovered in the microbial biomass, from days 34-41, was similar in both soil types (Figures 4.18-4.21). Therefore the initial differences in net production of TON between soil types are primarily due to a larger and more active bacterial population in the high fertility soil type, and lower capacity of the less fertile soil to turnover the added organic matter and N.

Microbial biomass N was not measured in livestock waste amended soils, but low recoveries of N were observed in FYM-amended soil, 8-13 % total N was recovered, in comparison to 27-33 % total N recovered in digested biosolids cake (DMAD) (Tables 4.4 and 4.5). This may reflect the lower stability of this organic matter source. It is likely that, as observed for LC and DRAW, there was microbial immobilisation of N in FYM-amended soil. Alternatively the FYM may have been stabilised by incidental composting during storage. There were also low initial recoveries of $\text{NH}_4\text{-N}$ for both soil types for pig slurry and cow slurry amended soil than LMAD (Table 4.1). There was full recovery of the added mineral N in the silty clay for LMAD and less than 50 % recovery for PIG and COW. In the sandy silt loam there was just over 50 % recovery of the added mineral N for LMAD and 16-30 % recovery of added mineral N for PIG and COW. These differences may also be explained by differences in microbial immobilisation of N in the lower stability untreated animal slurries, and the digested liquid biosolids as was observed between lower stability biosolids cakes compared to anaerobically digested biosolids cakes. The lower recoveries of mineral N in livestock wastes- amended the lower fertility soil type may be due to greater immobilisation of N in comparison to the higher fertility soil. However, as observed in biosolids-amended soil, where there was greater immobilisation of N observed in the lower fertility soil, this may not fully account for the lower recoveries of N.

9 CONCLUSIONS

9.1 Nitrogen Transformation Processes and Microbial N Dynamics in Biosolids- and Livestock Wastes-Amended Agricultural Soils with Contrasting Properties

- Despite the low mineral N content of DRAW and TDMAD there was an increase in $\text{NH}_4\text{-N}$ concentration in both soil types following initial application, indicating that these materials were a source of rapidly mineralisable organic N.
- Initial recoveries of mineral N were smaller than expected for biosolids-amended soil at one of the field sites. This may have been due to a combination of immediate differences in mineralisation and nitrification at the two sites, low levels of NH_3 volatilisation or ammonium fixation, or movement of small amounts of TON below the surface layer. There was no strong evidence to suggest that initial differences were a result of microbial immobilisation.
- Higher rates of mineralisation and nitrification were measured in the more fertile soil at North Sidelands (silty clay) than in Brices Field (sandy silt loam), as demonstrated by the NH_4Cl control, which is consistent with previous research. From day 0-34 in North Sidelands, the nitrification rate was 4.4 kg N ha^{-1} compared to 2.0 kg N ha^{-1} at Brices. Nitrate concentrations in biosolids- and livestock wastes-amended soil also increased more rapidly in the high fertility soil.
- Soil mineral N recoveries at the mid-point of the trial were greater in the higher fertility soil type, consistent with higher rates of mineralisation and nitrification.
- Recoveries of TON at 10-20 cm suggested that there had not been significant movement below the surface 10 cm on day 6 from biosolids and livestock wastes in either soil type. Subsequently, higher concentrations of TON were measured in Brices, the sandy silt loam, at 10-20 cm indicating that this soil may have been more prone to NO_3^- mobility and to leaching. Higher concentrations of TON in 10-20 cm samples were observed primarily with liquid biosolids and biowastes types. However, final recoveries at 0-20 cm demonstrated movement of between 15-30 % mineral N from control plots independent of soil type.
- Lower concentrations of mineral N in DMAD+grass plots at 0-20 cm in both soil types in comparison to unamended controls indicated that the ryegrass crop was effective at capturing the available N mineralised in amended soil.

- Microbial biomass C and N concentrations were greatest in the soil with the higher organic matter content, North Sidelands, demonstrating its higher fertility status.
- Microbial biomass N contents of soil receiving different biosolids amendments indicated that there were subtle differences in N immobilisation processes in soils of differing fertility status, with greater retention of N in the microbial biomass amended with DMAD in the lower fertility soil with the smaller initial MBN (Brices Field, sandy silt loam).
- The greatest increases in MBN in both soil types occurred with addition of unstabilised or less stabilised biosolids, DRAW and LC, consistent with previous findings.
- The greatest final recovery of inorganic N from the biosolids and livestock wastes in North Sidelands was from pig slurry, which was expected from its high mineral N content. However, recoveries were lower in Brices Field, which were assumed be a result of immobilisation through addition of an unstabilised C source or increased NO_3^- mobility in the sandy loam soil. Microbial biomass C and MBN were not measured in livestock wastes amended soil, however findings for unstabilised biosolids types supported the assumption that the greatest increases in MBN occurred with the least stable organic residual types.
- Whereas net mineralisation was measured in liquid digested biosolids amended soil at North Sidelands, no net mineralisation was measured from liquid livestock wastes. This indicated that a proportion of released N was not accounted for or had been lost from the system, and may be due to biological immobilisation by addition of less stable organic matter.
- With the exception of DMAD+grass treatments, the lowest recovery of N in both soil types was from FYM. This is probably due to increased stability of FYM during storage and minimal release of N.
- The greatest recovery of N from biosolids was in liquid digested biosolids in both soil types, equivalent to 47-63 % of the applied total N, this can be explained by its high stability and mineral N content.
- In both soil types, for the biosolids cakes, the order of recovery of N was TDMAD>DMAD>LC. In TDMAD-amended soil, 32-41 % total N was recovered at 0-20 cm, 26-33 % total N was recovered in DMAD-amended soil and 18–31 % in LC-amended soil. Although TDMAD had less total and mineral N than DMAD, it had a larger mineralisable pool of N and is an effective as a rapid release N source for crop production.

- The patterns and rates of N recovery dynamics were dependent on biosolids or livestock waste type, and initially on soil type. However, overall release of N was similar in both soil types. The results indicated that, despite subtle differences in N immobilisation in biosolids-amended soil between soil types, differences in net production of TON are primarily due to a more active bacterial population in the high fertility soil type.
- The results indicated that it is unnecessary to consider fundamental aspects of the biological and mineralisation properties of different soil types when developing fertiliser recommendations for different biosolids and livestock waste types.

9.2 Field Investigation of the Nitrogen Value and Other Agronomic Benefits of Industrial Biowastes-2006

- N equivalency for DMAD was 0.52, greater than the mean value of 0.30 found in previous trials. Elemental analysis of the plant tissue showed that S concentrations in ryegrass treated with DMAD were nearly 4 times greater than in grass fertilised with mineral N alone, indicating that this element was potentially contributing to the increased crop response to DMAD.
- Despite the lower total N content, N equivalency for ADMSW was equivalent to DMAD at 0.52. This may reflect its greater mineral N content. There was also indication of a contribution of S to the crop response in this material as concentrations were also greater in comparison to the mineral N control.
- Differences in S content of grass for the other materials were not great, and were similar to control values; therefore, it was assumed that the crop response was primarily due to N for these treatment types
- Nitrogen equivalencies of AD fresh and AD stored were 0.85 and 0.68 respectively; these materials were therefore effective sources of available N, and AD fresh may contain a larger pool of readily mineralisable organic N, resulting in a higher N equivalency than stored AD.
- The N equivalency of TAD was 0.76, similar to the other digested liquids, despite its much lower mineral N content. This indicated that TAD was a less stabilised biowaste, and contained a high proportion of rapidly mineralisable N.
- Abattoir waste had an N equivalency of 1.6, which indicated that factors other than N availability contributed to the crop response. Following further elemental analysis of the grass crop, no elements were found to be greater in Abattoir

fertilised grass in comparison to grass fertilised with mineral N alone. However, the range of N application rates to soil supplied in Abattoir did not correspond well with the mineral N calibration plots, due to its low total N content, and this experimental artefact may explain why the N equivalency was greater than 1.

- Crop response for mineral N calibration plots reached a maximum value before the top rate of application. Following elemental analysis of plant material it was determined that DMAD was an effective source of S and TAD and AD fresh/stored were also effective sources of K. Therefore these elements may have been limiting in top rates of application for the mineral N plots, and contributed to the improved yields observed at the higher rates of application of these materials.
- Application of Trout old and a base dressing of mineral N, resulted in a significant response in fresh and dry yield and N offtake indicating that there were detectable agronomic benefits from the addition of organic matter in this waste type to the soil.
- There was a significant relationship between the rate of application of KG and fresh yield and for Ice-cream there was a significant relationship with N offtake. These treatments received a top dressing of 120 kg N ha⁻¹. This suggested that, under non-limiting N conditions, there were positive agronomic effects of the materials at these rates of application, and increasing application rate may have revealed further increased responses.
- There was no significant relationship between fresh and dry yield and rate of application for KG, Trout fresh, potato processing wastes or either ice-cream waste. However, following elemental analysis of the plant material, grass fertilised with Potato sludge and a base dressing of N had greater concentrations of K than grass fertilised with mineral N alone. This demonstrated that that Potato sludge is an effective source of available K, and therefore contributes agronomic benefit.
- Similar N equivalencies to those obtained by comparison of linear regression coefficients were generally obtained when comparing the individual yield values to biowastes application to the crop response curve for mineral N. However, when the yield exceeded the maximum from the mineral N response curve it was not possible to calculate N equivalencies; when yields were close to the maximum for mineral N, equivalency values calculated by the individual yield comparison approach may over estimate the apparent N availability value.

- Comparison of linear regression coefficients was considered the most suitable method for this experiment (Kiemec *et al.*, 1987; Smith *et al.*, 2001; Smith *et al.*, 2002; Morris *et al.*, 2003), as the systematic design allows several rates of application. Therefore, a reliable approximation of the N equivalency across different rates of application in the linear section of the crop response curve was obtained.

9.3 Field Investigation of the Nitrogen Value and Other Agronomic Benefits of Industrial Biowastes-2007

- Significant linear relationships between the rates of N application in biowastes and crop response were found in most cases, with the exception of Salt whey and ADMSW. Thus, the majority of the materials listed were effective sources of available N.
- Application of a base dressing of P to mineral N fertiliser controls did not increase the gradient of crop response, however, application of K resulted in an increased response. The greatest increase in response was achieved by a combination of P and K in the basal fertiliser applied to the mineral N gradient.
- N equivalency for DMAD relative to mineral N control, plus a base dressing of P and K, was 0.50, close to the value of 0.52 relative to mineral N fertiliser obtained in the 2006 trial. Therefore, N equivalencies for the biowastes, relative to the N+P+K control were used as a comparison between years.
- Differences in response to ADMSW between the two years of the experiment demonstrated the potential for variation in the properties of the material probably due to differences in mineral N content and organic matter stability, brought about by variation in length of storage.
- The salinity of Salt whey could potentially impact soil fertility. However, there was no direct evidence of a negative effect of salt whey application to crop yield. Indeed, a significant response in fresh yield relative to N addition was detected, although no statistically significant relationship with N offtake or dry weight yield was measured. This could be explained by the low total N content of this waste type.
- The N equivalencies for AD fresh/stored were 0.74 and 0.71 respectively, and were relatively consistent with values of 0.85 and 0.68 respectively, obtained in the previous year. The N equivalencies obtained in 2007 were relatively similar between the stored and fresh material, compared to the 2006 values. This may

be have been due to the increased mineral N content in AD stored in 2007, due to continued mineralisation during storage.

- Thermophilic anaerobic digestate (TAD) had a slightly lower N equivalency than the other liquid digestates of 0.59, relative to N+P+K control. It was lower than the value of 0.76 relative to mineral N fertiliser alone achieved in the previous trial, potentially demonstrating variation in input materials in this less stabilised biowaste.
- Vegetable waste mix had a N equivalency of 0.45, similar to DMAD, indicating that it was an effective source of available N.
- Despite its low mineral N content, Yeast had a high N equivalency of 0.85, it was therefore a significant source of readily mineralisable organic N compounds that are rapidly degraded in soil to release mineral N.

9.4 Short-Term Laboratory Incubation to Investigate Microbial Biomass N and Mineral N Dynamics in Biowastes-Amended Soil.

- Final N recoveries in incubated soils for the mineral N controls were approximately 100 % total N additions in three contrasting soil types. This indicated that, at the end of the incubation experiment, in soils treated with mineral N and no organic matter additions, there was no biological or chemical immobilisation or loss of added N.
- Differences in nitrification rates were observed between soil types, with greater nitrification rates in the higher fertility soil following addition of mineral N or organic N sources.
- Final recoveries of N were greatest in soil amended with liquid anaerobic co-digestates of food waste and animal slurry, between 20–68 % total N. This was to be expected from the high proportion of mineral N in this biowaste type of 47 %. The order of greatest recovery was: sandy silt loam > loamy sand > silty clay.
- Final recoveries of N in DMAD-amended soil ranged between 14.5-20 % total N, with order of greatest recovery: sandy silt loam > silty clay > loamy sand.
- Final recoveries of N in TAD-amended soil ranged between -8-33.0 % total added N, with order of greatest recovery: sandy silt loam > loamy sand > silty clay.

- Final recoveries of N in ADMSW-amended soil were between -11.5-11.5 % total added N, with order of greatest recovery: loamy sand > sandy silt loam > silty clay.
- In soil amended with DMAD for all 3 soil types, and TAD and AD for the sandy silt loam and loamy sand, final available N was greater than initial available N. This indicated that there was net mineralisation from the organic waste sources, which was greatest in the sandy silt loam.
- In all 3 soil types amended with ADMSW there was no net mineralisation of organic N. In addition, in the silty clay there was no net mineralisation for AD or TAD.
- Findings from the laboratory incubation study indicated that losses of N occurred from biowastes amended soil. The losses of N were most significant in North Sidelands soil, which had greater clay and organic matter contents compared to the other soil types examined, suggesting that the most likely mechanism was by denitrification resulting from localised anaerobic conditions in the soil.
- The greatest losses of N occurred in ADMSW and TAD amended soil, which suggested that these materials were less stable than AD and DMAD. Their microbial degradation in soil potentially led to greater localised O₂ depletion compared to the other waste types.
- Microbial biomass C concentrations were greater in soil from North Sidelands, the silty clay with high organic matter content followed by Brices soil, the sandy silt loam, and then Silwood, the loamy sand.
- Microbial biomass C and N concentrations were greater in TAD amended soil than unamended soil in all three soil types. This demonstrated greater microbial activity resulting from addition of a low stability organic matter source. This supported the hypothesis that increased microbial activity stimulated by addition of unstabilised, or partially stabilised, biowastes materials to soil may lead to O₂ deficits and denitrification losses in vulnerable soil types.
- Microbial biomass C in DMAD and ADMSW amended soil were generally equivalent to unamended soil in all three soil types.
- Microbial biomass C and MBN concentrations decreased below control values in AD amended soil, possibly in response to an inhibitory effect of the high NH₄-N concentrations in incubated soils amended with this type of digestate.

9.5 Overall Conclusions

- The greatest recoveries of mineral N in the 2005 field investigation at Wye, Kent in one soil type were from pig slurry, as predicted from its high mineral N content. Liquid digested biosolids had high available N contents of 47-63 %, consistent with previous findings due to high available N and stability of organic matter content. Available N content of DMAD was 26-33 % total N. Despite a lower total and mineral N content, TDMAD had a larger mineralisable N content, consistent with previous findings, resulting in an available N content of 32-41 % total N. Slow rates of TON production were observed for LC, but it was an adequate source of mineral N, equivalent to 18-31 % total N.
- N equivalency values for DMAD determined by the biowastes crop response trials (2006/2007) at Silwood Park were 0.50-0.52. This was greater than previous values probably as a result of a contribution of S to the crop response.
- Anaerobic digestate of MSW (ADMSW) had a N equivalency equivalent to DMAD of 0.52 in 2006. This may also be an over-estimate as S contributed to the crop response. In 2007 there was no significant crop response to ADMSW. This may be due to increased stability and NH_3 volatilisation during stockpiling.
- Thermophilic aerobic digestate (TAD) of food waste had a N equivalency of 0.59-0.76, it was therefore an effective source of available N. The variation in N value may be due to differences in input feedstock materials to the batches of waste tested.
- Anaerobic co-digestates of livestock slurries and food waste (AD fresh/stored) had N equivalencies between 0.68-0.85, in the same range as liquid digested biosolids. Lower N equivalencies were observed in 2006 for AD fresh (0.68), due to NH_3 volatilisation during storage.
- Abattoir wash water was an effective source of available N and had an N equivalency of 1.6. The value was greater than 1, possibly due to an experimental artefact as a result of the low total N content.
- Fish farm wastes were not a significant source of available N, but the addition of organic matter may be of agronomic benefit.
- Ice-cream production wastes did not have a significant impact on crop response and may require pre-treatment to reduce the fat content. There was also no significant response to Salt whey, this may be due to the low total N content. These waste types require further investigation to establish more quantitatively their agronomic benefit.

- Vegetable waste was an effective source of available N, with an N equivalency value of 0.45.
- Yeast was an effective source of available N with an N equivalency of 0.85.
- Vegetable wastes may be significant sources of K; DMAD and ADMSW are an effective source of S.
- Salt whey, KG and potato processing wastes require further investigation at greater rates of application to determine their agronomic benefit.
- The rates of mineralisation and nitrification in the field investigation were greater in silty clay (North Sidelands) compared to the sandy silt loam (Brices Field). The findings of the laboratory investigation were consistent with greater rates of mineralisation and nitrification in the silty clay (North Sidelands)>sandy loam (Silwood Park)>sandy silt loam (Brices Field). Greater rates of mineralisation and nitrification corresponded with higher organic matter and microbial biomass content.
- There were subtle differences in immobilisation of added N in biosolids-amended soil between soil types. In the 2005 field investigation, there was greater immobilisation in the lower fertility soil (Brices Field) in comparison to the higher fertility soil (North Sidelands). However, differences in rates of TON production were mainly due to a more active bacterial population in the higher fertility soil, and a greater amount of time required to turnover the added organic matter in the lower fertility soil.
- Greater immobilisation of N was observed in soils amended with unstabilised or lower stability organic residuals, regardless of soil type. Soils amended with DRAW and LC in the field investigation and TAD in the laboratory investigation showed greater increases in MBN. This was due to increased microbial activity resulting from high concentrations of labile C. Microbial biomass N was not measured in livestock wastes amended soil, but slower rates of TON production in soil amended pig and cow slurry indicated that there may also have been initial immobilisation in these soil types.
- Findings from the laboratory incubation study indicated that losses of N may occur from biowastes-amended soil under certain conditions. The greatest quantities of unrecovered N were in the silty clay soil with higher organic matter content, and with lower stability waste types. The most likely mechanism to account for the N losses under these conditions was denitrification, resulting from the development of localised anaerobic conditions in the soil in response to high rates of microbial degradation of the applied labile C.

10 FURTHER RESEARCH

10.1 Nitrogen Value and Other Agronomic Benefits of Industrial Biowastes

Biowastes from industrial processes represent a wide range of materials and research is required with a further selection of biowastes to determine their N value and other agronomic benefits. For example, wastes that require investigation include: biological sludges from pharmaceutical processes, of which 8000 t are spread to agricultural land annually (Gendebien, 2001); leather and tannery wastes, of which 9000 t are spread to land annually (Gendebien, 2001) and textile wastes of which 3500 t are spread to land annually (Gendebien, 2001). In addition to those investigated in this thesis, there are a wide variety of other food wastes which require investigation. For example, food wastes spread on land in the Thames region include: fruit skins and pips from jam production, baking wastes and wastes from coffee processing (Payne, 2006).

The approach taken in the biowastes crop response trials at Silwood Park (Chapters 5 and 6) is suitable for future investigation, although some modifications may be required. Comparison of linear regression coefficients (Kiemec *et al.*, 1987; Smith *et al.*, 2001; Smith *et al.*, 2002b; Morris *et al.*, 2003) was considered a suitable method for determination of N equivalency in the linear section of the crop response curve, and is appropriate for use in further investigation. The N equivalency values for DMAD were 0.50-0.52, which were greater than previously measured N equivalencies for this biosolids type at Silwood Park, which were consistently approximately 0.30, over 3 years of investigation (Smith and Bellett-Travers, 2001; Smith *et al.*, 2002b; Morris *et al.*, 2003). Elemental analysis of plant tissue revealed that this was probably due to a contribution of S to the crop response; ADMSW was also a source of S. In the 2007 field investigation additional controls were included with base dressings of P and K and a combination of P and K in addition to mineral N fertiliser gradients. In future experimentation mineral fertiliser controls with a base dressing of P, K and S and combinations of these elements should be included with a gradient of mineral fertiliser N. This will enable the response due to the supply of N alone from the biowastes to be isolated. It is emphasised that the purpose of the research programme described in this thesis was to examine the overall agronomic responses to biowaste additions to soil, so no additional nutrients were supplied with the biowastes.

Elemental analysis of plant tissue is necessary to examine transfer of major nutrient elements and trace elements from biowastes to crops. For example, plant tissue analysis in the 2006 biowastes crop response trial showed that potato sludges were a source of K. Liquid wastes with a low DS content, such as potato processing wastes, salty whey from cheese production and kieselguhr had a low total N content. These biowastes, and similar materials, should be investigated at greater rates of application to determine whether there are benefits other than N fertiliser value, such as addition of organic matter or trace elements. Aitken *et al.* (1998) applied a paper mill sludge with a total N content of 1.17 % DS at a rates between 30-100 t DS ha⁻¹. This does not exceed the limit in of 250 kg N ha⁻¹, from organic sources, for grassland in NVZs (CEC, 1991) and may mean other agronomic benefits can be detected. Benefits to soil structure may be conferred by addition of organic matter; for example; Chambers *et al.* (2003) found improvements in soil physical characteristics with additions of 5-10 t ha⁻¹ organic matter from biosolids such as improved water infiltration rate and topsoil available water, and in some cases soil capacity and strength. It may also be necessary with low total N wastes to apply a base dressing of N, as was done in the biowastes crop response trials at Silwood Park (Chapters 5 and 6), to ensure that the soil is not N limited, which may also result in bacterial immobilisation of N (Sabey *et al.*, 1975; Nicolardot *et al.*, 2001; Vinten, 2002; Pansu *et al.*, 2003).

Findings from the biowastes crop response trials (Chapters 5 and 6) indicated that length and method of storage may influence the amount of available N. For example there was a significant response to application of ADMSW in 2006, but not in 2007. This was possibly due to loss of NH₃ during stockpiling of this biowaste, prior to collection. In addition, in 2006 AD stored had a lower N equivalency than AD fresh and a lower mineralisable N content, due to continued mineralisation during storage and loss of N by volatilisation. Future investigations should include controlled experiments with different storage periods to determine and quantify the significance of this for N release and availability. Storage conditions and the influence of covering on NH₃ volatilisation losses also require investigation. The method of application may influence the N fertiliser value of biowastes; for example surface broadcasting may result in losses of N due to NH₃ volatilisation (Beauchamp *et al.*, 1978; Sutton *et al.*, 1982; Robinson and Polglase, 2000). Timing of application is also important: autumn applications of biowastes may result in lower N equivalencies, as the mineralised N may be leached from soils over winter, and not available for uptake during the growth period of the crop. Therefore it is necessary to investigate the effects of different methods and timing of application to optimise the fertiliser value of the biowastes. This

could be investigated by using field-scale equipment, as has been done for animal manures and slurries (Nicholson *et al.*, 1999). The field trials should include different methods of application, such as sub-soil injection in comparison to surface broadcasting, replicated areas of field and guard areas. Mineral fertiliser and unamended control areas should be included. It is important that the treatments are appropriately replicated to allow for any unevenness of spread that may arise through use of field-scale equipment on a smaller scale. Nicholson *et al.* (1999) used 3 rates of application, with four replicates and sub-plot sizes of 3.75 x 36 m.

10.2 The Influence of Soil Type and Biowaste Stability on Rate of Denitrification in Biowastes-Amended Soil

Findings from the laboratory incubation study (Chapter 7) indicated that losses of N occurred from biowastes amended soil. The greatest quantities of unrecovered N were in the silty clay soil with higher organic matter content, and with lower stability waste types, suggesting that the most likely mechanism is by denitrification as a result of localised anaerobic microsites in the soil (Smith, 1980; Fillery, 1983). Therefore, further research is required to measure denitrification in biowastes-amended soil. A laboratory investigation could be established in soil types with differing organic matter contents, and biowastes with differing degrees of stability, such as the anaerobic and aerobic digestates investigated in this thesis. Higher moisture content will reduce O₂ availability in the soil and increase the likelihood of development of anaerobic conditions (Webb *et al.*, 2004). Therefore, the temperature should be kept constant and moisture content of the incubated soils varied at rates between 30-100% WHC, for example. Soils should be incubated in closed containers with sufficient headspace to prevent anaerobic conditions; Maag and Vinther (1996) incubated 50 g of soil in a sealed 250 ml bottle. Gas samples can then be taken with a syringe at intervals to analyse for N₂O and NO_x content. Unamended soils and soils treated with mineral N fertiliser should be included to determine the denitrification rate due to addition of the organic N source.

Denitrification in biowastes-amended soil also requires investigation under field conditions, because denitrification observed in laboratory experiments may be an experimental artefact (Fillery, 1983). Field experiments can be established with closed chambers over amended soil so that gas samples can be collected and analysed for N₂O (Clayton *et al.*, 1997). It is important to determine the influence of soil type, biowaste stability and moisture status on N₂O emissions from amended soil. It is

important to precisely predict N availability from biowastes to crops to ensure that they are used efficiently to gain maximum benefit. This information is necessary to ensure potential emissions of important greenhouse gases, N₂O and NO_x, from biowastes-amended soil, are managed and minimised (Day *et al.*, 1978; Galbally and Roy, 1983). This information would assist in the development of fertiliser recommendations for biowastes, which may need to also consider the implications of waste type and soil type and the timing of application, to minimise risks of denitrification losses. This will improve confidence in their fertiliser value and increase the use of organic residuals in agricultural, diverting them from landfill and contributing to nutrient recycling (Green Alliance, 2007).

GLOSSARY OF ABBREVIATIONS

APHA	American Public Health Association
ANOVA	analysis of variance
ATP	adenosine triphosphate
BOD	biological oxygen demand
BRC	British Retail Consortium
BREFS	best available technique reference documents
°C	degrees centigrade
CEC	Council of the European Communities
CEC	cation exchange capacity
COM	Commission of the European Communities
cm	centimetres
Defra	Department of Environment, Food and Rural Affairs
DMAD	dewatered mesophilic anaerobically digested biosolids
DRAW	dewatered raw sewage sludge
DM	dry matter
DNA	deoxyribonucleic acid
DoE	Department of Environment
ds	dry soil
DS	dry solids
e⁻	electron
EC	European Communities
EU	European Union
FW	fresh weight
FYM	farmyard manure
g	gram
h	hours
ha	hectare
H₂O	water
l	litre
kg	kilograms
MAD	Mesophilic anaerobic digestion
MAFF	Ministry of Agriculture, Food and Fisheries
MBC	microbial biomass carbon
MBN	microbial biomass nitrogen

m	metres
Mg	magnesium
mg	milligrams
Mn	manganese
mm	millimetres
MSW	municipal solid waste
Na	sodium
NAMAS	National Accreditation of Measurement and Sampling
N	nitrogen
N₂	nitrogen gas
NH₃	ammonia
NH₃-N	ammonia nitrogen
NH₄⁺	ammonium
NO	nitrogen oxide
N₂O	nitrous oxide
NO₂⁻	nitrite
NO₂-N	nitrite nitrogen
NO₃⁻	nitrate
NO₃-N	nitrate nitrogen
NO_x	nitrous oxides
NPOC	Non-purgeable organic carbon
NVZs	Nitrate Vulnerable Zones
NRA	National Rivers Authority
NRM	Natural Resource Management Ltd.
O₂	oxygen
OM	organic matter
P	Phosphorus
<i>P</i>	Probability
PAHs	polycyclic aromatic hydrocarbons
PCBs	polychlorinated biphenyls
PTEs	Potentially toxic elements
RNA	ribonucleic acid
S	sulphur
s	seconds
SI	Statutory Instrument
SOC	soluble organic carbon
t	tonnes

TOC	total organic carbon
TON	total oxidised nitrogen
µg	microgram
US	United States
USEPA	United States Environmental Protection Agency
UK	United Kingdom
VS	volatile solids
WFPS	water filled pore space
WHC	water holding capacity
WMLR	Waste Management Licensing Regulations
WRAP	Waste and Resources Action Programme
WRc	Water Research Centre
%	per cent

REFERENCES

ADAS (2001) The Safe Sludge Matrix: Guidelines for the application of sewage sludge to arable and horticultural crops 3rd Ed. (<http://www.assuredproduce.co.uk/code/common/item.asp?id=4033093>)

Addiscott, T.M.; Whitmore, A.P. and Powlson, D.S. (1991) *Farming, Fertilizers and the Nitrates Problem*. CAB International, Oxon, UK.

Aitken, M.N.; Evans, B. and Lewis, J.G. (1998) Effect of applying paper mill sludge to arable land on soil fertility and crop yields. *Soil Use and Management* 14 (4), 215-222.

Allison, M.F.; Fowler, J.H. and Allen, E.J. (2001) Factors affecting the magnesium nutrition of potatoes (*Solanum tuberosum*). *Journal of Agricultural Science, Cambridge* 137 (4), 397–409.

Alvarez-Bernal, S.M.; Contreras-Ramos, S.M.; Trujillo-Tapia, N.; Olalde-Portugal, V.; Frías-Hernández, J.T.; Dendooven, L. (2006) Effects of tanneries wastewater on chemical and biological soil characteristics. *Applied Soil Ecology* 22 (3), 269-277.

Al-Widyan, M.I.; Al-Abed, N. and Al-Jalil, H. (2005) Effect of composted olive cake on soil physical properties. *Communications in Soil Science and Plant Analysis* 36 (9-10), 1199-1212.

Antolín, M.C.; Pascual, I.; García, C.; Polo, A.; Sánchez-Díaz, M. (2005) Growth, yield and solute content of barley in soils treated with sewage sludge under semiarid Mediterranean conditions. *Field Crops Research* 94 (2-3), 224-237.

APHA: American Public Health Association (1985) *Standard Methods for Examination of Water and Waste Water* 16th Ed. (eds) Greenberg, A.E.; Trussel, R.R. and Clesceri, L.S, United Book Press, Maryland, USA.

Arias-Estévez, M.; López-Periago, E.; Nóvoa-Muñoz, J.C.; Torrado-Agrasar, A. and Simal-Gándara, J.S. (2007) Treatment of an acid soil with bentonite used for wine fining: effects on soil properties and the growth of *Lolium multiflorum*. *Journal of Agriculture and Food Chemistry* 55 (18), 7541-7546.

Arnaez, J.; Lasanta, T.; Ruiz-Flaño, P. and Ortigosa, L. (2007) Factors affecting runoff and erosion under simulated rainfall in Mediterranean vineyards. *Soil and Tillage Research* 93 (2), 324-334.

Arvanitoyannis, I.S.; Ladas, D. and Mavromatis, A. (2006) Potential uses and applications of treated wine waste: a review. *International Journal of Food Science and Technology*, 41 (5), 475-487.

Ayad, L.B.; Hassan, A.; Jedidi, N.; Saidi, N.; Bouzaine, O. and Murano, F. (2007) Microbial C and N dynamics during composting process of urban solid waste. *Waste Management Research*, 25 (1), 24-29.

Banerjee, M.R.; Burton, D.L. and Depoe, S. (1997) Impact of sewage sludge application on soil biological characteristics. *Agriculture, Ecosystems and Environment*, 66 (3), 241-249.

Batey, T. (1988) *Soil Husbandry: A Practical Guide to the Use and Management of Soils*. Soil and Land Use Consultants, Aberdeen, UK.

Beauchamp, E.G.; Kidd, G.E. and Thurtell, G. (1978) Ammonia volatilization from sewage sludge applied in the field. *Journal of Environmental Quality* 7 (1), 141-146.

Beckwith, C.P.; Cooper, J.; Smith K.A. and Shepherd, M.A. (1998) Nitrate leaching loss following application of organic manures to sandy soils in arable cropping. I. Effects of application time, manure type, overwinter crop cover and nitrification inhibition. *Soil Use and Management* 14 (3), 123-130.

Bellett-Travers, M.D.; Rowlands, C.; Smith, S.R. (2002) A model to predict the release of mineral nitrogen following the mineralisation and nitrification of organic matter in MAD cake. Proceedings of the Joint CIWEM and Aqua Enviro Technology Transfer 7th European Biosolids and Organic Residuals Conference, 8-20 November, Wakefield, UK.

Bellett-Travers, M.D; Breedon, T.D; Morris, R.; Topp, K.F.; Butler, A.P.; Jackson, B. and Smith, S.R. (2003) Predicting the availability of mineral nitrogen following the mineralisation and nitrification of organic nitrogen in conventional and enhanced treated biosolids. Proceedings of the Joint CIWEM and Aqua Enviro Technology Transfer 8th European Biosolids and Organic Residuals Conference, 24-26 November, Wakefield, UK.

Bengtson, P. and Bengtsson, G. (2005) Bacterial immobilization and remineralization of N at different growth rates and N concentrations. *FEMS Microbial Ecology* 54 (1), 13-19.

Bengtson, P., Falkengren-Grerup, U. and Bengtsson, G. (2005) Relieving substrate limitation-soil moisture and temperature determine gross N transformation rates. *Oikos* 111 (1), 81-90

Beyer, L., Frund, R. and Mueller, K. (1997) Short-term effects of a secondary paper mill sludge application on soil properties in a Psammentic Haplumbrept under cultivation. *Science of the Total Environment* 197 (1-3), 127-137.

Bitzer, C.C. and Sims, J.T. (1988) Estimating the availability of nitrogen in poultry manure through laboratory and field studies. *Journal of Environmental Quality* 17 (1), 47-54.

Bonkowski, M. (2004) Protozoa and plant growth: the microbial loop in soil revisited. *New Phytologist* 162 (3), 617-631.

Bowden, W. and Hann, M.J. (1997) The availability of nitrogen following topsoil application of liquid digested sludge. *Nutrient Cycling in Agroecosystems* 47 (2), 167-172.

Boyle, M. and Paul, E.A. (1989) Nitrogen transformations in soil previously amended with sewage-sludge. *Soil Science of America Journal* 53 (3), 740-744.

Breedon, T. J., Bellett-Travers, D. M., and Smith, S. R. (2003) A laboratory incubation study of nitrogen transformations in biosolids-amended agricultural soil as influenced by soil type and temperature. Proceedings of the Joint CIWEM and Aqua Enviro Technology Transfer 8th European Biosolids and Organic Residuals Conference, 24-26 November, Wakefield, UK.

Bremner, J.M. and Shaw, K. (1957) The mineralization of some nitrogenous materials in soil. *Journal of the Science of Food and Agriculture* 8, 341-347.

Brookes, P.C., Powlson, D.S., Jenkinson, D.S. (1982) Measurement of microbial biomass phosphorus in soil. *Soil Biology and Biochemistry* 14 (4), 319-329.

Brookes, P.C.; Kragt, J.F.; Powlson, D.S. and Jenkinson, D.S. (1985a) Chloroform fumigation and the release of soil nitrogen: the effects of time and temperature. *Soil Biology and Biochemistry* 17 (6), 831-835.

Brookes, P.C.; Landman, A.; Pruden, G. and Jenkinson, D.S. (1985b) Chloroform fumigation and the release of soil nitrogen: a rapid direct extraction method to measure microbial biomass nitrogen in soil. *Soil Biology and Biochemistry* 17 (6), 837-842.

Bruce, A.M. and Evans, T.D. (2002) *Sewage Sludge Disposal: Operational and Environmental Issues. A Review of Current Knowledge*. Foundation for Water Research, Marlow, Bucks, UK.

Burford, J.R. and Bremner, J.M. (1975) Relationships between the denitrification capacities of soils and total, water-soluble and readily decomposable soil organic matter. *Soil Biology and Biochemistry* 7 (6), 389-394.

Calbrix, R.; Barrey, S.; Chabrierie, O.; Furrie, L. and Laval, K. (2007) Impact of organic amendments on the dynamics of soil microbial biomass and bacterial communities in cultivated land. *Applied Soil Ecology* 35 (3), 511-522.

Cass, J.; Rogers, M. and Smith S.R. (2005) Enteric pathogen decay kinetics in biosolids amended agricultural soils. Proceedings of the CIWEM/Aqua Enviro Consultancy Services 10th European Biosolids and Biowastes Conference. Aqua Enviro, 13-16 November, Wakefield, UK.

Cassman, K.G. and Munns, D.N. (1980) Nitrogen mineralization as affected by soil moisture, temperature and depth. *Soil Science Society of America Journal* 44 (6), 1233-1237.

CEC: Council of the European Communities (1975) Waste Framework Directive (75/442/EEC). *Official Journal of the European Communities*, No. L194/39-50.

CEC: Council of the European Communities (1986) Council Directive on the protection of the environment and particular of the soil, when sewage sludge is used in agriculture (86/278/EEC). *Official Journal of the European Communities*, No. L181/6-12.

CEC: Council of the European Communities (1991a) Council Directive amending Directive 75/442/EEC on waste (91/156/EEC). *Official Journal of the European Communities*, No. L78/32-37.

CEC: Council of the European Communities (1991b) Council Directive concerning the protection of waters against pollution caused by nitrates from agricultural sources (91/676/EEC). *Official Journal of the European Communities*, No. L375/1-8.

CEC: Commission of the European Communities (1992) *Treatment and Use of Sewage Sludge and Liquid Agricultural Wastes. Review of COST 68/681 Programme, 1972-90* (eds) Hall, J.E.; L'Hermite, P. and Newman, P.J. Commission of the European Communities, Luxembourg.

CEC: Council of the European Communities (1996) Council Directive concerning integrated pollution prevention and control (96/61/EC). *Official Journal of the European Communities*, No. L257/26-40.

CEC: Council of the European Communities (1998) Council Directive concerning urban waste-water treatment (98/15/EC). *Official Journal of the European Communities*, No. L135/40–52.

CEC: Council of the European Communities (1999) Council Directive on the landfill of waste (99/31/EC). *Official Journal of the European Communities*, No. L182/1–19.

CEC: Council of the European Communities (2001) Disposal and recycling routes for sewage sludge. Part 3 – Scientific and technical report. Council of the European Communities, Luxembourg.

CEC: Council of the European Communities (2002) Community Regulation laying down health rules concerning animal by-products not intended for human consumption (1774/2002). *Official Journal of the European Communities*, No. L273/1-95.

CEC: Council of the European Communities (2003) Council Directive providing for public participation in respect of the drawing up of certain plans and programmes relating to the environment and amending with regard to public participation and access to justice Council Directives 85/337/EEC and 96/61/EC (2003/35/EC). *Official Journal of the European Communities*, L156/17-24.

CEC: Council of the European Communities (2006) Council Directive on Waste (2006/12/EC). *Official Journal of the European Communities*, No. L114/9-21.

Chadwick, D.R.; John, F.; Pain, B.F.; Chambers, B.J. and Williams, J. (2000) Plant uptake of nitrogen from the organic nitrogen fraction of animal manures: a laboratory experiment. *Journal of Agricultural Science, Cambridge* 134 (2), 159-168.

Chae, Y.M and Tabatai, M.A. (1986) Mineralization of nitrogen in soils amended with organic wastes. *Journal of Environmental Quality* 15 (2), 193-198.

Chambers, B.J.; Lord, E.I.; Nicholson, F.A. and Smith, K.A. (1999) Predicting organic nitrogen availability and losses following application of organic manures to arable land: MANNER. *Soil Use and Management* 15, 137-143.

Chambers, B.J.; Nicholson, N. and Smith, K. (2001a) Managing livestock manures-making better use of livestock manures on arable land. Booklet 1. ADAS, Notts, UK.

Chambers, B.J.; Nicholson, N. and Smith, K. (2001b) Managing livestock manures. Making better use of livestock manures on arable land. Booklet 2. ADAS, Notts, UK.

Chambers, B.J.; Nicholson, F.A.; Aitken, M. and Cartmell, E. (2003) Benefits of biosolids to treat soil quality and fertility. *Journal of the Chartered Institution of Water and Environmental Management* 17 (3), 162-167.

Chambers, P.A.; Meissner, R.; Wrona, F.J.; Rupp, H.; Guhr, H.; Seeger, J.; Culp, J.M. and Brua, R.B. (2006) Changes in nutrient loading in an agricultural watershed and its effects on water quality and stream biota. *Hydrobiologia* 556 (1) 399–415.

Chantigny, M.H.; Angers, D.A. and Rochette, P. (2002) Fate of carbon and nitrogen from animal manure and crop residues in wet and cold soils. *Soil Biology and Biochemistry*, 34 (4) 509-517.

Chaussod, R.; Gupta, S.K.; Hall, J.E.; Pommel, B. and Williams, J.H. (1985) Nitrogen and phosphorus value of sewage sludges. Revision of document Nr. SL/82/82-XII/ENV/35/82 (eds) Hall, J.E. and Williams J.H. Commission of the European Communities, Luxembourg.

Chiou, I.J.; Wang, K.S., Chen, C.H. and Lin, Y.T. (2006) Lightweight aggregate made from sewage sludge and incinerated ash. *Waste Management* 26 (12), 1453-1461.

Christian, D.G. and Riche, A.B. (1998) Nitrate leaching losses under *Miscanthus* grass planted on a silty clay loam soil. *Soil Use and Management* 14 (3), 131-135.

Clayton, H.; McTaggart, I.P; Parker, J. and Swan, L. (1997) Nitrous oxide emissions from fertilized grassland: A 2-year study of the effects of N fertilizer form and environmental conditions. *Biology and Fertility of Soils* 25 (3), 252-260.

Cleaver, T.J.; Greenwood, D.J. and Wood, J.T. (1970) Systematically arranged fertilizer experiments. *Journal of Horticultural Science and Biotechnology* 45 (4), 457.

Cogger, C.G.; Sullivan, D.M.; Bary, A.I. and Fransen, S.C (1999) Nitrogen recovery from heat-dried and dewatered biosolids applied to forage grasses. *Journal of Environmental Quality* 28 (3), 754-759.

Cogger, C.G.; Bary A.I.; Fransen, S.C. and Sullivan, D.M. (2001) Seven years of biosolids versus inorganic nitrogen applications to tall fescue. *Journal of Environmental Quality* 30 (6), 2188-2194.

Cogger, C.G.; Bary, A.I.; Sullivan, D.M. and Myhre, E.A. (2004) Biosolids processing effects on first- and second-year available nitrogen. *Soil Science Society of America Journal* 68 (1), 162-167.

Coker, E.G. (1966) The effects of liquid digested sewage sludge. I. The effects of liquid digested sludge on the growth and composition of grass-clover swards in south-east England. *Journal of Agricultural Science, Cambridge* 67 (1), 91-97.

Coker, E.G.; Davis, R.D.; Hall, J.E. and Carlton-Smith, C.H. (1982) Field experiments on the use of consolidated sewage sludge for land reclamation. Water Research Centre Report 257-M. Water Research Centre, Stevenage, Herts, UK.

Coker, E.G. and Carlton-Smith, C.H. (1986) Phosphorus in sewage sludges as a fertiliser. *Water Management and Research* 4 (3), 303-319.

Coker, E.G.; Hall, J.E.; Carlton-Smith, C.H. and Davis, R.D. (1987a) Field investigations into the manurial value of lagoon-matured digested sewage sludge. *Journal of Agricultural Science* 109 (3), 467-478.

Coker, E.G.; Hall, J.E.; Carlton-Smith, C.H. and Davis, R.D. (1987b) Field investigations into the manurial value of liquid undigested sewage sludge when applied to grassland. *Journal of Agricultural Science* 109 (3), 479-494.

Cooke, G.W. (1982) *Fertilizing for Maximum Yield* 3rd Ed. Granada, London, UK.

COM: Commission of the European Communities (2003) Communication from the Commission. Towards a Thematic Strategy on the prevention and recycling of waste (301 final). Commission of the European Communities, Brussels.

COM: Commission of the European Communities (2005) Communication from the Commission. Taking sustainable use of resources forward: A Thematic Strategy on the prevention and recycling of waste (666 final). Commission of the European Communities, Brussels.

COM: Commission of the European Communities (2006) Report from the Commission to the Council and the European Parliament on implementation of the Community waste legislation for the period 2001-2003 (406 final). Commission of the European Communities, Brussels.

Conry, M.J. (1997) Effect of fertiliser on the grain yield and quality of spring malting barley grown in five contrasting soils in Ireland. *Biology and Environment* 97 (3), 185-196.

Cordovil, C.M.D.S.; Cabral, F. and Coutinho, J. (2007) Potential mineralization of nitrogen from organic wastes to ryegrass and wheat crops. *Bioresource Technology* 98 (17), 3265–3268.

Corrêa, R.S. (2004) Efficiency of five biosolids to supply nitrogen and phosphorus to ryegrass. *Balanço social, pesquisa agropecuária brasileira* 39 (11), 1133-1139.

Corrêa, R.S.; White, R.E. and Weatherley, A.J. (2005) Biosolids effectiveness to yield ryegrass based on their nitrogen content. *Scientia Agricola* 62 (3) 274-280.

Dahlén, J.; Karlsson, S.; Bäckström, M.; Hagberg, J. and Pettersson, H. (2000) Determination of nitrate and other water quality parameters in groundwater from UV/Vis spectra employing partial least squares regression. *Chemosphere* 40 (1), 71-77.

Davis, R.D.; Sweet, N.; Woods, V. and Yang, G (1996) Advantages of thermally dried sludge for various end uses. Proceedings of the Aqua-Enviro Conference on Sludge Derived Products, 1-2 October, Wakefield, UK.

Davis, R.D. (1983) Operation aspects. In Sludge utilisation to farmland, Water Research Centre regional seminar report (eds) Hall, J.E. and Davis, R.D. Water Research Centre, Marlow, Bucks, UK.

Davis, R.D. and Rudd, C. (1997) Investigation of the criteria for, and guidance on, the landspreading of industrial wastes. Final report to the Environment Agency and the Ministry of Agriculture, Fisheries and Food. Report No. 4088/5. Water Research Centre, Marlow, Bucks, UK.

Day, P.R.; Doner, H.E; McLaren, A.D. (1978) Relationships among microbial populations and rates of nitrification and denitrification in a Hanford soil. In *Nitrogen in the Environment, Volume 2. Soil-Plant-Nitrogen Relationships* (eds) Nelson, D.R. and MacDonald, J.G. Academic Press, London.

Defra: Department of Environment, Food and Rural Affairs (1998) Code of Good Agricultural Practice for the Protection of Water. Defra, London, UK.

Defra: Department of Environment, Food and Rural Affairs (2002) Sewage treatment in the UK: UK implementation of the EC Urban Waste Water Directive. Defra, London, UK (<http://www.defra.gov.uk/environment/water/quality/uwwtd/report02/default.htm>)

Defra: Department of Environment, Food and Rural Affairs (2005) Draft statutory guidance to Environment Agency in England and Wales regarding Waste Management Licensing Regulations (Amendment and Related Provisions). Defra, London, UK (<http://www.defra.gov.uk/ENVIRONMENT/WASTE/management/pdf/ea-draftguidance.pdf>).

Defra: Department of Environment, Food and Rural Affairs (2006a) Sewage sludge arisings and management 1996/7-2005. E-digest of environmental statistics. Defra, London, UK (<http://www.defra.gov.uk/environment/statistics/waste/index.htm>).

Defra: Department of Environment, Food and Rural Affairs (2006b) Industrial and commercial waste arisings by material. Environment Agency waste survey 2002/3. E-digest of environmental statistics. Defra, London, UK (<http://www.defra.gov.uk/environment/statistics/waste/index.htm>).

Defra: Department for Food Environment and Rural Affairs (2007) Waste Strategy for England. Defra, London, UK (<http://www.defra.gov.uk/environment/waste/strategy/index.htm>).

Defra: Department of Environment, Food and Rural Affairs (2008) Nitrates-reducing water pollution from agriculture. Defra, London, UK (<http://www.defra.gov.uk/environment/water/quality/nitrate/default.htm>).

De Haan, S. (1980) Sewage sludge as a phosphorus fertilizer. *Phosphorus in Agriculture* 78 (1), 33-41.

De Resende, A.S.; Xavier, R.P.; de Oliveira, O.C.; Urquiaga, S., Alves, B.J.R. and Boddey, R.M. (2006) Long-term effects of pre-harvest burning and nitrogen and vinasse applications on yield of sugar cane and soil carbon and nitrogen stocks on a plantation in Pernambuco, N.E. Brazil. *Plant and Soil* 281 (1-2), 339-351.

Dewes, T.; Schmitt, L.; Valentin, U. and Ahren, E. (1990) Nitrogen losses during the storage of livestock manures. *Biological Wastes* 31 (3), 214-250.

DoE: Department of the Environment (1996) Code of practice for agricultural use of sewage sludge 2nd Ed. HMSO, London, UK.

Donovan, W.C. and Logan, T.J. (1983) Factors affecting ammonia volatilization from sewage sludge applied to soil in a laboratory study. *Journal of Environmental Quality* 12 (4) 584-590.

Douglas, J.T.; Aitken, M.N. and Smith, C.A. (2003) Effects of five non-agricultural organic wastes on soil composition, and on the yield and nitrogen recovery of Italian ryegrass. *Soil Use and Management* 19 (2) 135-138.

Douglas, B., F. and Magdoff, F.R. (1981) An evaluation of nitrogen mineralization indexes for organic residues. *Journal of Environmental Quality* 20 (2), 368-371.

Driver, J.; Lijmbach, D. and Steen, I. (1999) Why recover phosphorus for recycling and how? *Environmental Technology* 20 (7) 651-662.

Ekelund, F. and Rønn, R. (1994) Notes on protozoa in agricultural soil with emphasis on heterotrophic flagellates and naked amoeba and their ecology. *FEMS Microbiology Reviews* 15 (4), 321-353.

Environmental Protection Act (1990) Section 34, HMSO, London.

Epstein, E.; Keane, D.B.; Meisinger, J.J. and Legg, J.O. (1978) Mineralization of nitrogen from sewage sludge and sludge compost. *Journal of Environmental Quality* 7 (2), 217-221.

Erdem, N. and Ok, S.S. (2002) Effect of brewery sludge amendments on some chemical properties of acid soil in pot experiments. *Bioresource Technology* 84 (3), 271-273.

Eriksen, G. N.; Coale, F. J. and Bollero, G. A. (1999) Soil nitrogen dynamics and maize production in municipal solid waste amended soil. *Agronomy Journal* 91 (6), 1009-1016.

Evans, T. (2001) The journey to sustainable use or disposal of wastewater biosolids. In *Recycling and Reuse of Sewage Sludge: Proceedings of the International Symposium organised by the Concrete Technology Unit and held at the University of Dundee, Scotland, UK, 19-20 March* (eds) Dhir, R.K.; Limbachiya, M.C. and McCarthy, M.J. Thomas Telford, London, UK.

Evanylo, G.K. (2003) Effects of biosolids application timing and soil texture on nitrogen availability for corn. *Communications in Soil Science and Plant Analysis* 34 (1-2), 125-143.

Fernandes, S.A.P.; Bettiol, W. and Cerri, C.C. (2005) Effect of sewage sludge on microbial biomass, basal respiration, metabolic quotient and soil enzymic activity. *Applied Soil Ecology* 30 (1), 65-77.

Fillery, I.R.P. (1983) Biological denitrification. In *Gaseous Loss of Nitrogen From Plant-Soil Systems. Developments in Plant and Soil Sciences Volume 9* (eds) Freney, J.R. and Simpson, J.R. Martinus Nijhoff/Dr W. Junk Publishers, The Hague.

Foley, B. J. and Cooperband, L. R. (2002) Paper mill residuals and compost effects on soil carbon and physical properties. *Journal of Environmental Quality* 31 (6), 2086-2095.

Franco-Hernández, O.; Mckelligan-Gonzalez, A.N.; Lopez-Olguin, A.M.; Espinosa-Ceron, F.; Escamilla-Silva, E. and Dendooven, L. (2003) Dynamics of carbon, nitrogen and phosphorus in soil amended with irradiated, pasteurized and limed biosolids. *Bioresource Technology* 87 (1), 93-102.

Freney, J.R.; Simpson, J.R. and Denmead, O.T. (1983) Volatilisation of ammonia. In *Gaseous Loss of Nitrogen From Plant-Soil Systems. Developments in Plant and Soil Sciences Volume 9* (eds) Freney, J.R. and Simpson, J.R. Martinus Nijhoff/Dr W. Junk Publishers, The Hague.

Frey, S.D.; Norr, M.; Parrent, J.L. and Simpson, R.T. (2004) Chronic nitrogen enrichment affects the structure and function of the soil microbial community in temperate hardwood and pine forests. *Forest Ecology and Management* 196 (1), 159-171.

Galbally, I.E. and Roy, C.R. (1983) The fate of nitrogen compounds in the atmosphere. In *Developments in Plant and Soil Sciences Volume 9: Gaseous Loss of Nitrogen from Plant-Soil Systems Volume 9.* (eds) Freney, J.R. and Simpson, J.R. Martinus Nijhoff/Dr W. Junk Publisers, The Hague.

Garcia-Gomez, A.; Bernal, M.P. and Roig, A. (2002) Growth of ornamental plants in two composts prepared from agroindustrial wastes. *Bioresource Technology* 83 (2), 81-87.

Gendebien, A.; Ferguson, R.; Brink, J.; Horth, H.; Sullivan, M.; Davis, R.; Brunet, H.; Dalmier, F.; Landrea, B.; Krack, D.; Perot, J.; Orsi, C. (2001) European Commission-Directorate-General for Environment. Survey of wastes spread on land - final report. Study contract B4-3040/99/110194/MAR/E3. Report No.:CO 4953-2. Water Research Centre, Marlow, Bucks, UK.

George, B.J. (1994) Design and interpretation of nitrogen response experiments. In *Nitrogen Requirements of Cereals, MAFF reference book 385.* HMSO, London, UK.

Ghani, A., Dexter, M., Sarathchandra, U., and Waller, J. (2005) Effects of dairy factory effluent application of nutrient transformation in soil. *New Zealand Journal of Agricultural Research* 42 (2), 241-253.

Gibbs, P.A.; Chambers, B.J.; Muir, I.; Richardson, S.; Hickman, G.; Hawkis; Barraclough, D.; Marsden; Creed and Davis, R.D. (2005) Paper Waste Production and Type of Materials. Proceedings of the CIWEM/Aqua Enviro Consultancy Services 10th European Biosolids and Biowastes Conference. Aqua Enviro, 13-16 November, Wakefield, UK.

Gilmour, J.T.; Cogger, C.G.; Jacobs, L.W.; Evanylo, G.K. and Sullivan, D.M. (2003) Decomposition and plant-available nitrogen in biosolids: laboratory studies, field studies and computer simulation. *Journal of Environmental Quality* 32 (4), 1498-1507.

Green Alliance (2007) The nutrient cycle: closing the loop (ed) Hislop, H. Green Alliance, London, UK.

Greenwood, D.J.; Cleaver, T.J.; Turner, M.K.; Hunt, J.; Niendorf, K.B. and Loquens, S.M.H. (1980a) Comparison of the effects of potassium fertilizer on the yield, potassium content and quality of 22 different vegetable and agricultural crops. *Journal of Agricultural Science, Cambridge* 95, 441-456.

Greenwood, D.J.; Cleaver, T.J.; Turner, M.K.; Hunt, J.; Niendorf, K.B. and Loquens, S.M.H. (1980b) Comparison of the effects of nitrogen fertilizer on the yield, content and quality of 21 different vegetable and agricultural crops. *Journal of Agricultural Science, Cambridge* 95, 441-456.

Griffin, G.F. and Laine, A.F. (1983) Nitrogen mineralization in soils previously amended with organic wastes. *Agronomy Journal* 75 (1), 124-129.

Griffiths, B.S. (1989) Enhanced nitrification in the presence of bacteriophagous protozoa. *Soil Biology and Biochemistry* 21 (8), 1045-1051.

Gunn, A.P. (2004) *Use of sewage sludge in construction*. CIRIA, London, UK.

Hall, J.E. and Coker, E.G. (1981) Some effects of sewage sludge on soil physical conditions and plant growth. The Influence of Sewage Sludge Application on Physical and Biological Properties of Soils. Proceedings of a seminar organized jointly by the Commission of the European Communities, Directorate-General for Science, Research and Development and the Bayerische Landesanstalt für Bodenkultur und Pflanzenbau, June 23-24, Munich, Germany.

Hall, J.E. (1983a) Predicting the Nitrogen Value of Sewage Sludges. Processing and Use of Sewage Sludge. Commission of the European Communities. Proceedings of the Third International Symposium, September 27-30, Brighton, UK.

Hall, J.E. (1983b) Manurial value of different sewage sludge types. In Sludge utilisation to farmland, Water Research Centre regional seminar report (eds) Hall, J.E. and Davis, R.D. Water Research Centre, Marlow, Bucks, UK.

Hall, J.E. (1983c) Field investigations into the manurial value of lagoon-matured digested sewage sludge, Water Research Centre report 510-M. Water Research Centre, Marlow, Bucks, UK.

Hall, J.E. (1984) The cumulative and residual effects of sewage sludge nitrogen on crop growth. Long Term Effects of Sewage Sludge and Farm Slurries Applications. Proceedings of a round-table seminar organized by the Commission of the European Communities, Directorate-General Science, Research and Development, Environmental Research Programme, 25-27 September, Pisa, Italy.

Hall, J.E. and Franklin, B. (1984) Serburn-in-Elmt field trial: a comparison of effects of grass of four Yorkshire Water sewage sludges. Water Research Centre report 786-M. Water Research Centre, Marlow, Bucks, UK.

Hansen, E. M.; Eriksen, J. and Vinther, F. P. (2007) Catch crop strategy and nitrate leaching following grazed grass-clover. *Soil Use and Management* 23 (4), 348–358.

Harden, T., Joergensen, R.G., Meyer, B., Wolters, V. (1993) Soil microbial biomass estimated by fumigation-extraction and substrate-induced respiration in two pesticide-treated soils. *Soil Biology and Biochemistry* 25 (6), 679-683.

Harding, D.E. and Ross, D.J. (1964) Some factors in low-temperature storage influencing the mineralisable-nitrogen of soils. *Journal of the Science of Food and Agriculture* 15, 829-834.

Harding, S.A.; Capp, C.E. and Larson, W.E. (1985) Nitrogen availability and uptake from field soils five years after addition of sewage sludge. *Journal of Environmental Quality* 14 (1), 95-100.

Hayman, D.S. (1975) Phosphorus cycling by soil micro-organisms and plant roots. In *Soil Microbiology* (ed) Walker, N. Butterworth and Co. Ltd., London, UK.

Hermans, C.; Johnson, G.N.; Strasser, R.J. and Verbruggen, N. (2004) Physiological characterisation of magnesium deficiency in sugar beet: acclimation to low magnesium differentially affects photosystems I and II. *Planta* 220 (2), 344-355.

Hérmendez, T.; Moral, R.; Perez-Espinosa, J.; Moreno-Caselles, M.D.; Perez-Murcia, M.D. and García, C. (2002) Nitrogen mineralisation potential in calcareous soils amended with sewage sludge. *Bioresource Technology* 83 (3), 213-219.

Hewitt, E.J. (1975) *Plant Mineral Nutrition* (eds) Hewitt, E.J. and Smith, T.A. English University Press, London, UK.

Honeycutt, C.W.; Potaro, L.J. and Halteman, W.A. (1991) Predicting nitrate formation from soil, fertilizer, crop residue, and sludge with thermal units. *Journal of Environmental Quality* 20 (4), 850-856.

Horwath, W.R. and Paul, E.A. (1994) Microbial biomass. In: *Methods of Soil Analysis, Part 2. Microbiological and Biochemical Properties* (eds) Weaver, R.W., Angle, S., Bottomley, P., Bezdicek, D., Smith, S., Tabatabai, A. and Wollum, A. Soil Science Society of America, Segoe, WI, USA.

Hseih, Y.P.; Douglas, L.A.; Motto, H.L. (1981) Modelling sewage sludge decomposition in soil: II Nitrogen transformations. *Journal of Environmental Quality* 10 (1), 59-64.

Hu, Y.F.; Barker, A.V. (2004) Effect of composts and their combinations with other materials on nutrient accumulation in tomato leaves. *Communications in Soil Science and Plant Analysis* 35 (19-20), 2809-2823.

Huang, S.C.; Chang, F.C.; Lo, S.L.; Lee, M.Y.; Wang, C.F. and Lin, J.D. (2007) Production of lightweight aggregates from mining residues, heavy metal sludge, and incinerator fly ash. *Journal of Hazardous Materials* 144 (1-2), 52-58.

IPPC: Intergovernmental Panel on Climate Change (2001) Climate change 2001: synthesis report (eds) Watson, R.T. and the Core Writing Team. Cambridge University Press, Cambridge.

Jackson, D.R. and Smith, K.A. (1997) Animal manure slurries as a source of nitrogen for cereals; effect of application time on efficiency. *Soil Use and Management* 13 (2), 75-81.

Jardin, N. and Pöpel, H.J. (1994) Phosphate release of sludges from enhanced biological P-removal during digestion. *Water Science Technology* 30 (6), 281-292.

Jeanmaire, N. and Evans, T. (2001) Technico-economic feasibility of P-recovery from municipal wastewaters. *Environmental Technology* 22 (11), 1355-1361.

Jedidi, N.; Hassen, A.; van Cleemput, O.; M'Hiri, A. (2004) Microbial biomass in a soil amended with different types of organic wastes. *Waste Management Research* 22 (2), 93-99.

Jenkinson, D.S. and Powlson, D.S. (1976) The effects of biocidal treatments on metabolism in soil V. - A method for measuring soil biomass. *Soil Biology and Biochemistry* 8 (3), 167-177.

Jha, P.B.; Singh, J.S. and Kashyap, A.K. (1996) Dynamics of viable nitrifier community and nutrient availability in dry tropical forest habitat as affected by cultivation and soil texture. *Plant and Soil* 180 (2), 277-285.

Joergensen, R.G. (1995) The fumigation extraction method to estimate soil microbial biomass: extraction with 0.01 M CaCl₂. *Agribiology Research* 48 (3-4), 319-324.

Joergensen, R.G. and Mueller, T. (1996) The fumigation-extraction method to estimate soil microbial biomass: calibration of the k_{EN} value. *Soil Biology and Biochemistry* 28 (1), 33-37.

Joshua, W.D; Michalk, D.L.; Curtis, I.H.; Salt, M. and Osborne, G.L. (1997) The potential for contamination of soil and surface waters from sewage sludge (biosolids) in a sheep grazing study, Australia. *Geoderma* 84 (1-3), 135-156.

Kaushik, A.; Nisha, R.; Jagjeeta, K. and Kaushik, C.P. (2005) Impact of long and short term irrigation of a sodic soil with distillery effluent in combination with bioamendments. *Bioresource Technology* 96 (17), 1860-1866.

Kemmitt, S.J.; Wright, D.; Goulding, K.W.T. and Jones, D.L. (2006) pH regulation of carbon and nitrogen dynamics in two agricultural soils. *Soil Biology and Biochemistry* 38 (5), 898-911.

Kiemnec, G.L.; Jackson, T.L.; Hemphill, Jr. D.D. and Volk, V.V. (1987) Relative effectiveness of sewage sludge as a nitrogen fertilizer for tall fescue. *Journal of Environmental Quality* 16 (4), 354-356.

Killham, K. (1994) *Soil Ecology*. Cambridge University Press, Cambridge, UK.

King, L.D. (1984) Availability of nitrogen in municipal, industrial and animal wastes. *Journal of Environmental Quality* 13 (4), 609-612.

King, K.W. and Torbert, H.A. (2007) Nitrate and ammonium losses from surface-applied organic and inorganic fertilizers. *Journal of Agricultural Science* 145 (4), 385–393.

Koo, B.K. and O'Connell, P.E. (2006) An integrated modeling and multicriteria analysis approach to managing nitrate diffuse pollution: 2. A case study for a chalk catchment in England. *Science of the Total Environment* 358 (1-3), 1-20.

Kowalenko, C.U. and Yu, S. (1996) Solution, exchangeable and clay-fixed ammonium in south coast British Columbia soils. *Canadian Journal of Soil Science* 76 (4), 473-483.

Krogstad, T.; Son, T.A.; Asdal, A. and Sæbø A (2005) Influence of chemically and biologically stabilized sewage sludge on plant-available phosphorus in soil. *Ecological Engineering* 25 (1), 51-61.

Krom, M. (1980) Spectrophotometric determination of ammonia: a study of modified Berthlot reaction using salicylate and dichloroisocyanurate. *The Analyst* 105 (1249) 305-316.

Kuile, M.; White, R.E. and Beckett, P.H.T. (1983) The availability to plants of phosphate in sludges precipitated from the effluent from sewage treatment. *Water Pollution Control* 82 (4), 582-589.

Kütük, C.; Cayci, G.; Baran, A.; Baskan, O. and Hartmann, R. (2003) Effects of beer factory sludge on soil properties and growth of sugar beet (*Beta vulgaris saccharifera* L.). *Bioresource Technology* 90 (1), 75-80.

Kyle, M.A. and McClintock, S.A. (1995) The availability of phosphorus in municipal wastewater sludge as a function of the phosphorus removal process and sludge treatment method. *Water Environment Research* 67 (3), 282-289.

Lampe, C.; Dittert, K; Sattelmacher, B.; Wachendorf, M.; Loges, R. and Taube, F. (2006) Sources and rates of nitrous oxide application of N-15-labelled emissions from grazed grassland after mineral fertilizer and slurry. *Soil Biology and Biochemistry* 38 (9), 2602-2613.

Levy, J.S. and Taylor, B.R. (2003) Effects of pulp mill solids and three composts on early growth of tomatoes. *Bioresource Technology* 89 (3), 297-305.

Li, X.G.; Li, F.M.; Zed, R. and Zhan, Z.Y. (2007) Soil physical properties and their relations to organic carbon pools as affected by land use in an alpine pastureland. *Geoderma* 139 (1-2), 98–105.

Lowe, P.; Brown, M. and Hudson, K. (1996) The influence of fibres on the structure of thermally dried sludge product. *Water Science Technology* 34 (3-4), 469-473.

Luxhøi, J.; Bruun, S.; Jensen, L.S and Magid, J. (2007) Modelling C and N mineralization during decomposition of anaerobically digested and composted municipal solid waste. *Waste Management Research* 25 (2), 170-176.

Maag, M. and Vinther, F.P. (1996) Nitrous oxide emission by nitrification and denitrification in different soil types and at different soil moisture contents and temperatures. *Applied Soil Ecology* 4 (1), 5-14.

Macdonald, A.J.; Poulton, P.R.; Stockdale, E.A.; Powlson, D.S. and Jenkinson, D.S. (2002) The fate of residual ¹⁵N-labelled fertilizer in arable soils: its availability to subsequent crops and retention in soil. *Plant and Soil* 246 (1), 123-137.

Madejón, E.; Burgos, P.; López, R. and Cabrera, F. (2003) Agricultural use of three organic residues: effect on orange production and on properties of a soil of the Comarca Costa de Huelva (SW Spain). *Nutrient Cycling in Agroecosystems* 65 (3), 281-288.

MAFF: Ministry of Agriculture Fisheries and Food (1986) *The Analysis of Agricultural Materials. Reference Book 427* 3rd Ed. HMSO, London, UK.

MAFF: Ministry of Agriculture Fisheries and Food (1992) *Code of Good Agricultural Practice for the Protection of Air*. HMSO, London, UK.

MAFF: Ministry of Agriculture Fisheries and Food (1993) *Code of Good Agricultural Practice for the Protection of Soil*. HMSO, London, UK.

MAFF/DoE: Ministry of Agriculture Fisheries and Food/Department of the Environment (1993) Review of the rules for application of sewage sludge to land-soil fertility aspects of potentially toxic elements. Report of the Independent Scientific Committee, PB 1561. MAFF Publications, London, UK.

MAFF: Ministry of Agriculture Fisheries and Food (1998) *Code of Good Agricultural Practice for the Protection of Water*. HMSO, London, UK.

MAFF: Ministry of Agriculture Fisheries and Food (2000) *Fertiliser Recommendations for Agricultural and Horticultural Crops. Reference Book 209* 7th Ed. HMSO, London.

Magdoff, F.R. and Amadon, J.F. (1980) Nitrogen availability from sewage sludge. *Journal of Environmental Quality* 9 (3), 451-455.

Mantovi, P.; Baldoni, G. and Toderi, G. (2005) Reuse of liquid, dewatered, and composted sewage sludge on agricultural land: effects of long-term application on soil and crop. *Water Research* 39 (2-3), 289-296.

Markus, D.K., McKinnon, J.P. and Buccafuri, A.F. (1985) Automated analysis of nitrite, nitrate, and ammonium nitrogen in soils. *Soil Science of America Journal* 49 (5), 1208-1215.

Martens. R. (1995) Current methods for measuring microbial biomass C in soil: potentials and limitations, *Biology and Fertility of Soils* 19 (2-3), 87-99.

Mbagwu, J.S.C. and Ekwealor, G.C. (1990) Agronomic potential of brewers spent grain. *Biological Wastes* 34 (4), 335-347.

Mendoza, C.; Assadin, N.W. and Lindemann, W. (2006) The fate of nitrogen in a moderately alkaline and calcareous soil amended with biosolids and urea. *Chemosphere* 63 (11), 1933-1941.

Mohr, R.M.; Grant, C.A.; May, W.E. and Stevenson, F.C. (2007) The influence of nitrogen, phosphorus and potash fertilizer application on oat yield and quality. *Canadian Journal of Soil Science* 87 (4), 459-468 [Abstract].

Morris, R., Smith, S.R., Bellett-Travers, D.M., and Bell, J.N.B. (2003) Reproducibility of the nitrogen response and residual fertiliser value of conventional and enhanced-treated biosolids. Proceedings of the Joint CIWEM and Aqua Enviro Technology Transfer 8th European Biosolids and Organic Residuals Conference, 24-26 November, Wakefield, UK.

Morris, R.K. (2006) A quantitative investigation of the crop yield response and nutrient value of treated biosolid materials used in agricultural production, PhD thesis. University of London, UK.

Nendel, C. and Reuter, S. (2007) Kinetics of net nitrogen mineralisation from soil-applied grape residues. *Nutrient Cycling in Agroecosystems* 79 (3), 223-241.

Nicholson, F.A.; Chambers, B.J. and Smith, K.A. (1996) Nutrient composition of poultry manure in England and Wales. *Bioresource Technology* 58 (3), 279-284.

Nicholson, F.A.; Chambers, B.J.; Smith, K.A. and Harrison, R. (1999) Spring applied organic manures as a source of nitrogen for cereal crops; experiments using field-scale equipment. *Journal of Agricultural Science, Cambridge* 133 (4), 353-363.

Nicholson, F.A.; Chambers, B.J. and Dampney, P.M.R. (2003) Nitrogen value of poultry litter applications to root crops and following cereal crops. *Journal of Agricultural Science, Cambridge* 140 (1), 53-64.

Nicolardot, B. (2001) Simulation of C and N mineralisation during crop residue decomposition: A simple dynamic model based on the C:N ratio of the residues, *Plant and Soil* 228 (1), 83-103.

Nikitas, C.; Pocock, R.; Toleman, I. and Gilbert, E.J. (2008) The state of composting and biological waste treatment in the UK 2005/06. The Composting Association, Northamptonshire, UK.

NRA: National Rivers Authority (1992) The influence of agriculture on the quality of natural waters in England and Wales. The report of the National Rivers Authority. Water Quality Series, No. 6. NRA, Bristol, UK.

O'Connor, G.A.; Sarkar, D.; Brinton, S.R.; Elliot, H.A. and Martin F.G. (2004) Phytoavailability of biosolids P. *Journal of Environmental Quality* 33 (2), 703-712.

O'Keefe, B.E.; Axley, J. and Meisinger, J.J. (1986) Evaluation of nitrogen availability indexes for a sludge compost amended soil. *Journal of Environmental Quality* 15 (2), 121-128.

Ojeda, G.; Alcañiz, J.M and Ortiz, O. (2003) Runoff and losses by erosion in soils amended with sewage sludge. *Land Degradation and Development* 14 (6), 563-573.

Ojeda, G.; Tarrasón, D.; Ortiz, O.; Alcaniz, J.M. (2006) Nitrogen losses in runoff waters from a loamy soil treated with sewage sludge. *Agricultural Ecosystems and Environment* 117 (1), 49-56.

Opperman, M.H.; Wood, M. and Harris, P.J. (1989) Changes in inorganic N following the application of cattle slurry to soil at two temperatures. *Soil Biology and Biochemistry* 21 (2), 319-321.

Oropeza, M.R.; Cabirol, N.; Ortega, S.; Castro Ortiz, S. and Noyola, A. (2001) Removal of fecal indicator organisms and parasites (fecal coliforms and helminth eggs) from municipal biologic sludge by anaerobic mesophilic and thermophilic digestion. *Water Science and Technology* 44 (4), 97-101.

Otabbong, E.; Arkhipchenko, B.; Orlova, O.; Barbolina, I. and Shubaeva, M. (2007) Impact of piggery slurry lagoon on the environment: A study of groundwater and river Igolinka at the Vostochnii Pig Farm, St. Petersburg, Russia. *Acta Agriculturae Scandinavica, Section B - Plant Soil Science* 57 (1), 74 – 81.

Pansu, M.; Thuries, L.; Larre-Larrouy, M.C. and Bottner, P. (2003) Predicting N transformations from organic inputs in soil in relation to incubation time and biochemical composition. *Soil Biology and Biochemistry* 35 (3), 353-363.

- Parker, C.F. and Sommers, L.E. (1983) Mineralization of nitrogen in sewage sludges. *Journal of Environmental Quality* 12 (1), 150-156.
- Parks, J. (2006) Biosolids in the pharmaceutical industry. Proceedings of the Joint CIWEM and Aqua Enviro Technology Transfer 11th European Biosolids and Organic Residuals Conference, 13-15 November, Wakefield, UK.
- Pathak, H.; Joshi, H. C.; Chaudhary, A.; Chaudhary, R.; Kalra, N. and Dwiwedi, M. K. (1999) Soil amendment with distillery effluent for wheat and rice cultivation. *Water, Air and Soil Pollution* 113 (1-4), 133-140.
- Paul, E.A. and Clark, F.E. (1996) *Soil Microbiology and Biochemistry*. Academic Press, California, USA.
- Payne, G. (2006) Analysis of Industrial Biowaste for Landspreading, MSc thesis. University of London, UK.
- Pedreño, J. N.; Gómez, L.; Moral, R. and Mataix, J. (1995) Improving the agricultural value of a semi-arid soil by addition of sewage sludge and almond residue. *Agriculture, Ecosystems and Environment* 58 (2-3), 115-119.
- Perez-Viana, F.; Rogers, M. and Smith, S.R. (2005) Microbial biomass dynamics in biosolids amended agricultural soils. Proceedings of the CIWEM/Aqua Enviro Consultancy Services 10th European Biosolids and Biowastes Conference. Aqua Enviro, 13-16 November, Wakefield, UK.
- Petersen, S.O.; Petersen, J. and Rubæk, G.H. (2003) Dynamics and plant uptake of nitrogen and phosphorus in soil amended with sewage sludge. *Applied Soil Ecology* 24 (2), 187-195.
- Petts, K.W. and Belcher, M.B. (1980) An automated method for simultaneous determination of nitrogen and phosphorus in plant material, sludge and soil. *Water Pollution Control* 79 (3), 399-404.
- Pietri, J.C.A. and Brookes, P.C. (2008) Nitrogen mineralisation along a pH gradient of a silty loam UK soil. *Soil Biology and Biochemistry* 40 (3), 797-802.

- Plaza, C.; García-Gil, J.C. and Polo, A. (2007) Microbial activity in pig slurry-amended soils under aerobic incubation. *Biodegradation* 18 (2), 159–165.
- Rashid, M. T. and Voroney, R. P. (2005) Nitrogen fertiliser recommendations for corn grown on soils amended with oily food waste. *Journal of Environmental Quality* 34 (6), 2045-2051.
- Recous, S. and Mary, B. (1990) Microbial immobilization of ammonium and nitrate in cultivated soils. *Soil Biology Biochemistry* 22 (7) 913-922.
- Recous, S.; Robin, D.; Darwis, D. and Mary, B. (1995) Soil inorganic N availability: effect on maize residue decomposition. *Soil Biology and Biochemistry* 27 (2), 1529-1538.
- Reed, S.C.; Crites, R.W. and Middlebrooks, E.J. (1995) *Natural Systems for Waste Management and Treatment* 2nd Ed. McGraw-Hill, Inc., U.S.A.
- Rezende, L. A.; Assis, L. C., and Nahas, E. (2004) Carbon, nitrogen and phosphorus mineralization in two soils amended with distillery yeast. *Bioresource Technology* 94 (2), 159-167.
- Rigby, H.R. and Smith, S.R. (2005) Nitrogen transformations in contrasting agricultural soils amended with conventional and enhanced treated biosolids. Proceedings of the CIWEM/Aqua Enviro Consultancy Services 10th European Biosolids and Biowastes Conference. Aqua Enviro, 13-16 November, Wakefield, UK.
- Robinson, M.B. and Polgase, P.J. (2000) Volatilization of nitrogen from dewatered biosolids. *Journal of Environmental Quality* 29 (4), 1351-1355.
- Roem, W.J.; Klees, H. and Berendse, F. (2002) Effects of nutrient addition and acidification on plant species diversity and seed germination in heathland. *The Journal of Applied Ecology* 39 (6), 937-948.
- Rowell, D.L. (1994) *Soil Science: Methods and Applications*. Longman Group UK Ltd., Harlow.

Rowell, D.M.; Prescott, C.E. and Preston, C.M. (2001) Decomposition and nitrogen mineralisation from biosolids and other organic materials: relationship with initial chemistry. *Journal of Environmental Quality* 30 (4), 1401-1410.

Ryan, J.A.; Keeney, D.R. and Walsh, L.M. (1973) Nitrogen transformations and availability of an anaerobically digested sewage sludge in soil. *Journal of Environmental Quality* 2 (4), 489-492.

Sabey, B.R.; Agbim, N.N. and Markstrom, D.C. (1975) Land application of sewage sludge: III. Nitrate accumulation and wheat growth resulting from addition of sewage sludge and wood wastes to soils. *Journal of Environmental Quality* 4 (3), 388-393.

Saggar, S.; Bettany, J.R. and Steward, J.W.B. (1981) Measurement of microbial sulphur in soil. *Soil Biology and Biochemistry* 13 (6), 493-498.

Sameni, M. and Pour, A.T. (2001) Effect of root refuse of liquorice on different characteristics of soil from southern regions of Iran. I. microbial characteristics. *Communications in Soil Science and Plant Analysis* 32 (19-20), 3259-3275.

Sánchez-Monedero, M.A.; Mondini, C.; de Nobili, M.; Leita, L. and Roig, A. (2004) Land application of biosolids. Soil response to different stabilization degree of the treated organic matter. *Waste Management* 24 (4), 325-332.

Sanders, J.R., McGrath, S.P. and Adams, T. McM. (1986) Zinc, copper and nickel concentrations in ryegrass grown on sewage-sludge contaminated soils of different pH. *Journal of the Science of Food and Agriculture* 37 (10), 961-968.

SCA: Standing Committee of Analysts (1986) *Total Nitrogen and Total Phosphorus in Sewage Sludge*. HMSO, London, UK.

Scherer, H.W. (2001) Sulphur in crop production—invited paper. *European Journal of Agronomy* 14 (2), 81–111.

Schulte auf'm Erley, G.; Kaul, H.P.; Kruse, M.; Aufhammerb, W. (2005) Yield and nitrogen utilization efficiency of the pseudocereals amaranth, quinoa, and buckwheat under differing nitrogen fertilization. *European Journal of Agronomy* 22 (1), 95-100.

Schulz, S.; Tian, G.; Oyewole, B. and Bako, S. (2003) Rice mill waste as organic manure on a degraded Alfisol. *Agriculture, Ecosystems and Environment* 100 (2-3), 221-230.

Schröder, J.J.; Uenk, D. and Hilhorst, G.J. (2007) Long-term nitrogen fertilizer replacement value of cattle manures applied to cut grassland. *Plant and Soil* 299 (1-2), 83-99.

Schwedt, G. (1996) *The Essential Guide to Environmental Chemistry*. Translated by Haderlie, B. John Wiley & Sons Ltd., Chichester, UK.

Serna, M.D. and Pomares, F. (1992a) Indexes of assessing N availability in sewage sludges. *Plant and Soil* 139 (1), 15-21.

Serna, M.D. and Pomares, F. (1992b) Nitrogen mineralisation of sludge-amended soil. *Bioresource Technology* 39 (3), 285-290.

Shankar, B.S. and Usha, H.S. (2007) Environmental degradation due to industrialization - A case study of Whitefield industrial area, Bangalore, India. *Environmental Engineering Science* 24 (9), 1338-1342.

Sharpley, A.N.; Smith, S.J.; Jones, O.R.; Berg, W.A. and Coleman, G.A. (1992) The transport of bioavailable phosphorus in agricultural runoff. *Journal of Environmental Quality* 21 (1), 30-35.

Sharpley, A.N.; Chapra, S.C.; Wedepohl, R.; Sims, J.T.; Daniel, T.C. and Reddy, K.R. (1994) Managing agricultural phosphorus for protection of surface waters: issues and options. *Journal of Environmental Quality* 23 (3), 437-451.

Shen, S.Y.; Tu S.I. and Kemper W.D. (1997) Equilibrium and kinetic study of ammonium adsorption and fixation in sodium-treated vermiculite. *Soil Science Society of America Journal* 61 (6), 1611-1618.

Shimadzu (2003) Shimadzu TOC-5000 analyzer user manual 638-94247A. Shimadzu corporation, Kyoto, Japan.

SI: Statutory Instrument (1989) No. 1263 The Sludge (Use in Agriculture) Regulations 1989. HMSO, London, UK.

SI: Statutory Instrument (1990) No. 880 The Sludge (Use in Agriculture) (Amendment) Regulations 1990. HMSO, London, UK.

SI: Statutory Instrument (1994) No. 1056 The Waste Management Licensing Regulations 1994. HMSO, London, UK.

SI: Statutory Instrument (1999) No. 880 The Sludge (Use in Agriculture) (Amendment) Regulations 1999. HMSO, London, UK.

SI: Statutory Instrument (2005a) No. 1728 The Waste Management Licensing (England and Wales)(Amendment and Related Provisions) (No. 3) Regulations 2005. HMSO, London, UK.

SI: Statutory Instrument (2005b) No. 2346 The Animal By-Products Regulations 2005. HMSO, London, UK.

Silva, R.G.I.; Jorgensen, E.E.; Holub, S.M. and Gonsoulin, M.E. (2005) Relationships between culturable soil microbial populations and gross nitrogen transformation processes in a clay loam soil across ecosystems. *Nutrient Cycling in Agroecosystems* 71 (3), 259-270.

Simpson, J.R. and Steele, K.W. (1983) Gaseous nitrogen exchanges in grazed pastures. In *Gaseous Loss of Nitrogen From Plant-Soil Systems. Developments in Plant and Soil Sciences Volume 9* (eds) Freney, J.R. and Simpson, J.R. Martinus Nijhoff/Dr W. Junk Publishers, The Hague.

Sims, J.T. (1986) Nitrogen transformations in a poultry manure amended soil: temperature and moisture effects. *Journal of Environmental Quality* 15 (1), 59-63.

Sims, J.T. (1990) Nitrogen mineralization and elemental availability in soils amended with cocomposted sewage sludge. *Journal of Environmental Quality* 19 (4), 669-675.

Sistani, K.R.; Adeli, A.; McGowen, S.L.; Tewolde, H. and Brink, G.E. (2008) Laboratory and field evaluation of broiler litter nitrogen mineralization. *Bioresource Technology* 99 (7), 2603-2611.

Smarta, S.M.; Bunceb, R.G.H.; Marrsc, R.; LeDucc, M.; Firbanka, L.G.; Maskella, L.C. ; Scotta, W.A. ; Thompsond, K. and Walkere, K.J. (2005) Large-scale changes in the abundance of common higher plant species across Britain between 1978, 1990 and 1998 as a consequence of human activity: Tests of hypothesised changes in trait representation. *Biological Conservation* 124 (3), 355-371.

Smith, S.J. and Stanford, G. (1971) Evaluation of a chemical index of soil nitrogen availability. *Soil Science* 111 (4), 228-232.

Smith, K.A.; Unwin, R.J. and Williams, J.H. (1984) Experiments on the fertiliser value of animal waste slurries. Long Term Effects of Sewage Sludge and Farm Slurries Applications. Proceedings of a round-table seminar organized by the Commission of the European Communities., Directorate-General Science, Research and Development, Environmental Research Programme, 25-27 September, Pisa, Italy.

Smith, S.R. and Hadley, P. (1988) A comparison of the effects of organic and inorganic nitrogen fertilizers on the growth response of summer cabbage (*Brassica oleracea* var. *capitata* cv. Hispi F₁). *Journal of Horticultural Science* 63 (4), 615-620.

Smith, S.R. and Hadley, P. (1992) Nitrogen fertilizer value of activated sewage derived protein: effect of environment and nitrification inhibitor on NO₃⁻ release, soil microbial activity and yield of summer cabbage. *Fertilizer Research* 33 (1), 47-57.

Smith, K.A.; Chalmers, A.G.; Chambers, B.J. and Christie, P. (1998a) Organic manure phosphorus accumulation, mobility and management. *Soil Use and Management* 14,156-159.

Smith, S.R.; Woods, V. and Evans, T.D. (1998b) Nitrate dynamics in biosolids-treated soils.I. Influence of biosolids type and soil type. *Bioresource Technology* 66 (2), 139-149.

Smith, S.R.; Woods, V and Evans T.D. (1998c) Nitrate dynamics in biosolids-treated soils, II. Thermal-time models of the different nitrogen pools. *Bioresource Technology* 66 (2), 151-160.

Smith, S.R.; Woods, V. and Evans T.D. (1998d) Nitrate dynamics in biosolids-treated soils, III. Significance of the organic nitrogen, a twin-pool exponential model for nitrogen management and comparison with the nitrate production from animal wastes. *Bioresource Technology* 66 (2), 161-174.

Smith, K. A.; Jackson, D. R.; Misselbrook; T. H.; Pain, B. F.; Johnson, R. A. (2000) Reduction of Ammonia Emission by Slurry Application Techniques. *Journal of Agricultural Engineering Research* 77 (3), 277-287.

Smith, S.R. and Bellett-Travers, D.M. (2001) Field trials to develop fertiliser advice for enhanced treated and conventional biosolids. Proceedings of the CIWEM/Aqua Enviro Consultancy Services 6th European Biosolids and Organic Residuals Conference., 12-14 November, Wakefield, UK.

Smith, K.A.; Jackson, D.R. and Pepper, T.J. (2001a) Nutrient losses by surface run-off following the application of organic manures to arable land. 1. Nitrogen. *Environmental Pollution* 112 (1), 41-51.

Smith, K.A.; Jackson, D.R. and Pepper, T.J. (2001b) Nutrient losses by surface run-off following the application of organic manures to arable land. 2. Phosphorus. *Environmental Pollution* 112 (1), 53-60.

Smith, S.R. and Durham, E. (2002) Nitrogen release and fertiliser value of thermally-dried biosolids. *Water and Environmental Management* 16 (2), 121-126.

Smith, S.R.; Bellett-Travers, M.D.; Morris, R. and Bell, J.N.B. (2002a) Fertiliser value of enhanced-treated and conventional biosolids products. Proceedings of CIWEM Conference- Biosolids: The Risks and Benefit, an Update on the Latest Research, 9 January, Chartered Institute of Water and Environment Management, London, UK.

Smith, S. R.; Morris, R.; Bellett-Travers, D. M.; Ferrie, M.; Rowlands, C. L. and Bell, N. (2002b) Implications of the Nitrates Directive and the provision of fertiliser advice for the efficient agricultural use of conventional and enhanced-treated biosolids products. Proceedings of the Joint CIWEM and Aqua Enviro Technology Transfer 7th European Biosolids and Organic Residuals Conference, 8-20 November, Wakefield, UK.

Smith, S.R.; Morris, R., Bellett-Travers, D.M. and Bell, J.N.B. (2003) Managing the phosphate supply from sewage sludge amended agricultural soil. Proceedings of the Joint CIWEM and Aqua Enviro Technology Transfer 8th European Biosolids and Organic Residuals Conference, 24-26 November, Wakefield, UK.

Smith, M.T.E. and Tibbett, M. (2004) Nitrogen dynamics under *Lolium perenne* after a single application of three different sewage sludge types from the same treatment stream. *Bioresource Technology* 91 (3), 233-241.

Soon, Y.K.; Bates, T.E. and Moyer, J.R. (1978) Land application of chemically treated sewage sludge: II effects on plant and soil phosphorus, potassium, calcium, and magnesium and soil pH. *Journal of Environmental Quality* 7 (2), 269-268.

Sørensen, P. (2001) Short-term nitrogen transformations in soil amended with animal manure. *Soil Biology and Biochemistry* 33 (9), 1211-1216.

Spatharis, S.; Tsirtsis, G.; Danielidis, D.B.; Chi, T.D. and Mouillot, D. (2007) Effects of pulsed nutrient inputs on phytoplankton assemblage structure and blooms in an enclosed coastal area. *Estuarine, Coastal and Shelf Science* 73 (3-4), 807-815.

Sprent, J. (1987) *The Ecology of the Nitrogen Cycle* (eds) Barnes, R.S.K.; Birks, H.J.B.; Conner, E.F.; Harper, J.L. and Paine, R.T. Cambridge University Press, Cambridge, UK.

Sripanomtanakorn, S. and Polpresert, C. (2002) Plant available nitrogen from anaerobically digested sludge and septic tank sludge applied to crops grown in the tropics. *Waste Management Research* 20 (2), 143-149.

Stanford, G. and Epstein, E. (1974) Nitrogen mineralization-water relations in soil. *Soil Science of America Proceedings* 38 (1), 103-107.

- Stanford, G. and Smith, S.J. (1972) Nitrogen mineralisation potential of soils. *Soil Science of America Proceedings* 36 (3), 465-472.
- Stanford, G. and Smith, S.J. (1978) Oxidative release of potentially mineralizable soil nitrogen by acid permanganate extraction *Soil Science* 126 (4), 210-218.
- Stark, S.A. and Clapp, C.E. (1980) Residual nitrogen availability from soils treated with sewage sludge in a field experiment. *Journal of Environmental Quality* 9 (3), 505-512.
- Steffens, D. and Sparks, D.L. (1997) Kinetics of non-exchangeable ammonium release from soils. *Soil Science Society of America Journal* 61 (2), 455-462.
- Ste-Marie, C. and Paré, D. (1999) Soil, pH and N availability effects on net nitrification in the forest floors of a range of boreal forest stands. *Soil Biology and Biochemistry* 31 (11), 1579-1589.
- Stephenson, A.H.; McCaskey, T.A. and Ruffin, B.G. (1990) A survey of broiler litter composition and potential value as a nutrient resource. *Biological Wastes* 34 (1), 1-9.
- Stevens, R.J. and Laughlin, R.J. (2001) Cattle slurry affects nitrous oxide and dinitrogen emissions from fertilizer nitrate. *Soil Science Society of America Journal* 65 (4), 1307-1314.
- Stockdale, E.A. and Rees, R.M. (1995) Release of nitrogen from plant and animal residues and consequent plant uptake efficiency. *Biological Agriculture and Horticulture* 11 (1-4), 229-245.
- Sullivan, D.M.; Bary, A.I.; Thomas, D.R.; Fransen, S.C. and Cogger, C.G. (2002) Food waste compost effects on fertiliser nitrogen efficiency, available nitrogen and tall fescue yield. *Soil Science Society of America Journal* 66 (1), 154-161.
- Surampalli, R.Y; Lai, K.C.K; Banerji, S. K.; Smith, J. and Tyagi R. D. (2008) Long-term land application of biosolids - a case study. *Water Science and Technology* 57 (3), 345-352.

Sutton, A.L.; Nelson, D.W.; Hoff, J.D. and Mayrose, V.B. (1982) Effects of injection and surface applications of liquid manure on corn yield and soil composition. *Journal of Environmental Quality* 11 (3), 468-472.

Tamhane, A.C. (1979) A comparison of procedures for multiple comparisons of means with unequal variances. *Journal of the American Statistical Association*, 74, 47–480.

Tarrasón, D.; Ojeda, G.; Ortiz, O.; Alcañiz, J.M. (2008) Differences on nitrogen availability in a soil amended with fresh, composted and thermally-dried sewage sludge. *Bioresource Technology* 99 (2), 252-259.

Templer, P., Findlay, S. and Lovett, G. (2003) Soil microbial biomass and nitrogen transformations among five tree species of the Catskill Mountains, New York, USA. *Soil Biology and Biochemistry* 35 (4), 697-613.

Terry, R.E.; Nelson, D.W. and Sommers, L.E. (1979) Decomposition of Anaerobically Digested Sewage Sludge as Affected by Soil Environmental Conditions. *Journal of Environmental Quality* 8 (3), 342-347.

Tester, C.F.; Sikora, L.J.; Taylor, J.M. and Parr, J.F. (1977) Decomposition of sewage sludge compost in soil: I. Carbon and nitrogen transformations. *Journal of Environmental Quality* 6 (4), 459-462.

Tester, C.F.; Sikora, L.J.; Taylor, J.M. and Parr, J.F. (1982) Nitrogen utilization by tall fescue from sewage sludge compost amended soils. *Agronomy Journal* 74 (6), 1013-1018.

Thomsen, I.K.; Schjønning, P.; Olesen, J.E. and Christensen, B.T. (2003) C and N turnover in structurally intact soils of different texture. *Soil Biology and Biochemistry* 35 (6), 765-774.

Torrey, S. (1979) Sludge characteristics and pre-treatment. In *Sludge Disposal by Landspreading Techniques* (ed) Torrey, S. Noyes Data Corporation, New Jersey, U.S.A.

Trehan, S.P. (1996) Immobilisation of 15NH_4^+ in three soils by chemical and biological processes. *Soil Biology and Biochemistry* 28 (8), 1021-1027.

Türkmen, Ö.; Sensoy, S.; Dursum, A. and Turan, M. (2008) Sewage sludge as a substitute for mineral fertilization of spinach (*Spinacia oleraceae* L.) at two growing periods. *Acta Agriculturae Scandinavica, Section B – Plant Soil Science* 54 (2), 102-107.

USEPA (US Environmental Protection Agency) (1993) Part 503 standards for the use and disposal of sewage sludge. *Federal Register* 58, 9248-9415.

USEPA (2007) Guide for industrial waste management (<http://www.epa.gov/epaoswer/non-hw/industd/guide/chap7cs.htm>).

Vance, E.D.; Brookes, P.C. and Jenkinson, D.S. (1987a) An extraction method for measuring soil microbial biomass-C. *Soil Biology and Biochemistry* 19 (6), 703-707.

Vance, E.D.; Brookes, P.C. and Jenkinson, D.S. (1987b) Microbial biomass measurements in forest soils-the use of the chloroform fumigation incubation method in strongly acid soils. *Soil Biology and Biochemistry* 19 (6), 697-702.

Vesilind, P.A. (1974) *Treatment and Disposal of Wastewater Sludges*. Abb Arbor Science publishers inc., Michigan, USA.

Vinten, A.J.A. (2002) Factors affecting N immobilisation/mineralisation kinetics for cellulose-, glucose- and straw-amended sandy soils. *Biology and Fertility of Soils* 36 (3), 190-199.

Walter, I.; Martinez, F. and Cuevas, G. (2006) Biosolid amendment of a calcareous, degraded soil in a semi-arid environment. *Spanish Journal of Agricultural Research* 4 (1), 47-54.

Watanabe, H.; Kitamura, T.; Ochi, S. and Ozaki, M (1997) Inactivation of pathogenic bacteria under mesophilic and thermophilic conditions. *Water Science and Technology* 36 (6-7), 25-32.

Warman, P.R. (1986) Effects of fertilizer, pig manure, and sewage sludge on timothy and soils. *Journal of Environmental Quality* 15 (2), 95-100.

Warman, P.R. and Termeer, W.C. (2005) Evaluation of sewage sludge, septic waste, and sludge compost applications to corn and forage: Ca, Mg, S, Fe, Mn, Cu, Zn and B content of crops and soils. *Bioresource Technology* 96 (9), 1029-1038.

Webb, J.; Sylvester Bradley, R. and Seeney, F.M. (1997) Responses of cereals to residual fertiliser nitrogen applied to the preceding potato crop. *Journal of the Science of Food and Agriculture* 73 (1), 63-80.

Webb, J.; Harrison, R. and Ellis, S. (2000) Nitrogen fluxes in three arable soils in the UK. *European Journal of Agronomy* 13 (2-3), 207-223.

Webb, J.; Ellis, S.; Harrison, R. and Thorman, R. (2004) Measurement of N fluxes and soil N in two arable soils in the UK. *Plant and Soil* 260 (1-2), 253-270.

Whitehead, D.C. (1995) *Grassland Nitrogen*, CAB International, Oxon, UK.

Wickliff, C.; Volk, V.V.; Tingey, D.L.; Griffis, W.L.; Trunk, M.Y. and Witherow, J.L. (1982) Reactions of chrome tannery sludge with organic and mineral soils. *Water Air Soil Pollution* 17 (1), 61-74.

Widmer, P.; Brookes, P.C. and Parry, L.C. (1989) Microbial biomass nitrogen measurements in soils containing large amounts of inorganic nitrogen. *Soil Biology and Biochemistry* 21 (6), 865-867.

Wilhelm, W.W; Liebig M.A.; Varvel, G.E. and Blackmer T.M. (1999) Midseason stalk breakage in corn as affected by crop rotation, hybrid, and nitrogen fertilizer rate. *Agronomy Journal* 91 (1), 160-165.

Wiseman, J.T. and Zibilske, L.M. (1988) Effects of sludge application sequence on carbon and nitrogen mineralization in soil. *Journal of Environmental Quality* 17 (2), 334-339.

Withers, P.J. and Sharpley, A.N. (1995) Phosphorus Fertilisers. In *Soil Amendments and Environmental Quality* (ed) Rehcigl, J.E. CRC Press, Boca Raton.

Wolkowski, R.P. (2003) Nitrogen management considerations for landspreading municipal solid waste compost. *Journal of Environmental Quality* 32 (5), 1844-1850.

WRAP: Waste and Resources Action Programme (2007) Waste resources in the UK: applying life-cycle thinking in the framework of cost-benefit analysis. A final report for WRAP. Eunomia Research and Consulting Ltd., Bristol, UK.

Zagal, E. (1993) Measurement of microbial biomass in rewetted air-dried soil by fumigation-incubation and fumigation extraction techniques. *Soil Biology and Biochemistry* 25 (5), 553-559.

Zak, D.R.; Grigal, D.F.; Gleeson, S.; Tilman, D. (1990) Carbon and nitrogen cycling during old-field succession-constraints on plant and microbial biomass. *Biogeochemistry* 11 (2), 111-129.

Zaman, M.; Cameron, K.C.; Di, H.J. and Inubushi, K. (2002) Changes in mineral N, microbial biomass and enzyme activities indifferent soil depths after surface applications of dairy shed effluent and chemical fertilizer. *Nutrient Cycling in Agroecosystems* 63 (2-3), 275–290.

Zeng, S.; Chen, B.; Jiang, C. and Wu, Q. (2007) Impact of fertilization on chestnut growth, N and P concentrations in runoff water on degraded slope land in South China. *Journal of Environmental Sciences* 19 (7), 827-833.

Zhang, F. S.; Yamasaki, S.; and Nanzyo, M. (2002) Waste ashes for use in agricultural production: I. Liming effect, contents of plant nutrients and chemical characteristics of some metals. *The Science of The Total Environment* 284 (1-3), 215-225.

Zheljazkov, V.D. (2005) Assessment of wool waste and hair waste as soil amendment and nutrient source. *Journal of Environmental Quality* 34, 2310-2317.

APPENDIX A1 TOTAL HEAVY METAL CONCENTRATION IN SOILS

Table A1.1 Total heavy metal concentration in soil (dry soil basis) at Brices Field, North Sidelands and Silwood Park.

		Total Heavy Metal Concentration (mg kg ⁻¹ ds)							
Soil	Experiment	Depth (cm)	Cu	Pb	Cd	Hg	Ni	Cr	Zn
Brices Field	2005 Biosolids Trial	0-10	45.4	42.4	0.19	-	16.9	23.8	56.5
	2005 Biosolids Trial	10-20	40.6	42.6	0.20	-	16.2	21.1	59.1
	2007 Lab Incubation	0-15	26.8	49.1	0.17	0.28	15.7	17.9	62.9
North Sidelands	2005 Biosolids Trial	0-10	31.5	17.1	0.49	-	6.9	10.6	77.9
	2005 Biosolids Trial	10-20	24.0	16.9	0.50	-	6.7	10.2	75.7
	2007 Lab Incubation	0-15	9.8	10.2	0.34	0.07	8.9	7.0	63.9
Silwood Park	2006 Biowastes Trial	0-15	6.4	27.3	0.17	0.05	3.1	10.6	25.3
	2007 Biowastes Trial	0-15	8.1	42.5	0.16	0.07	<10	10.9	35.2
	2007 Lab Incubation	0-15	6.0	31.2	<0.1	0.07	6.2	10.5	30.4

APPENDIX A2 HEAVY METAL CONCENTRATION IN BIOSOLIDS, LIVESTOCK WASTES AND BIOWASTES

Table A2.1 Heavy metal concentrations in biosolids cakes and solid livestock wastes (dry solids basis), investigated in the 2005 field trial at Wye; the industrial biowastes crop response trials at Silwood Park (2006/7) and the laboratory incubation study.

	Experiment	Total Concentration (mg kg ⁻¹ DS)						
Type		Cu	Zn	Pb	Cd	Hg	Ni	Cr
DRAW	2005 Field Trial	389	342	30.9	0.75	0.8	13.5	20.1
DMAD	2005 Field Trial	407	581	105	2.57	2.0	25.0	35.2
	2006 Field Trial	476	1111	122	0.932	0.979	28.9	34.3
	2007 Field Trial	491	1854	161	1.52	1.16	32.0	55.6
	Laboratory Incubation	509	1150	113	1.11	1.34	33.5	53.5
TDMAD	2005 Field Trial	317	971	277	7.9	2.9	36.6	89.9
LC	2005 Field Trial	161	250	33.8	0.66	2.7	8.5	23.1
FYM	2005 Field Trial	48.7	239	4.9	0.34	<0.05	7.00	8.8

Table A2.2 Heavy metal concentrations in liquid biosolids and livestock wastes (fresh weight basis), investigated in the 2005 field trial at Wye.

	Total Concentration (g m ⁻³)						
Type	Cu	Zn	Pb	Cd	Hg	Ni	Cr
COW	1.51	2.91	0.11	0.01	<0.05	0.14	0.36
PIG	0.79	3.99	0.01	<0.001	<0.05	<0.01	0.160
LMAD	6.38	5.88	2.97	0.08	<0.05	0.70	1.55

Table A2.3 Heavy metal concentrations in solid biowastes (dry solids basis), investigated in the crop response trials at Silwood Park (2006/2007), and the laboratory incubation study.

		Total Concentration (mg kg ⁻¹)						
Biowaste	Experiment	Cu	Zn	Pb	Cd	Hg	Ni	Cr
Trout old	2006 Field Trial	16.4	193	28.3	0.356	0.058	9.60	20.6
Trout fresh	2006 Field Trial	18.6	195	40.1	0.384	0.072	10.2	16.8
Vegetable	2007 Field Trial	7.84	33.7	2.04	0.225	<0.05	7.25	14.6
TAD	2006 Field Trial	2.27	10.1	0.58	0.044	0.25	0.46	0.78
	2007 Field Trial	14.5	49.4	0.75	0.045	<0.20	1.28	1.32
	Laboratory Incubation	10.4	99.3	8.55	0.197	<0.30	4.86	16.1
ADMSW	2006 Field Trial	159	399	470	0.722	0.274	20.5	25.9
	2007 Field Trial	222	481	531	1.23	0.570	25.4	41.4
	Laboratory Incubation	189	786	513	1.21	0.610	31.8	42.8

Table A2.4 Heavy metal concentrations in liquid biowastes (fresh weight basis), investigated in the crop response trials at Silwood Park (2006/2007), and the laboratory incubation study.

		Total Concentration (g m ⁻³)						
Biowaste	Experiment	Cu	Zn	Pb	Cd	Hg	Ni	Cr
Abattoir	2006 Field Trial	<0.01	<0.01	<0.01	<0.001	<0.05	0.014	0.062
Potato sludge	2006 Field Trial	0.074	<0.01	0.010	0.001	<0.05	<0.01	0.026
Potato wash	2006 Field Trial	<0.01	<0.01	0.067	0.001	<0.05	0.039	0.098
Ice-cream	2006 Field Trial	<0.01	<0.01	0.011	0.001	<0.05	0.041	0.082
Ice-cream DAF	2006 Field Trial	0.943	<0.01	0.034	0.004	<0.05	0.041	0.096
Salt whey	2007 Field Trial	0.515	2.70	0.058	<0.01	<0.05	0.155	0.093
KG	2006 Field Trial	<0.01	<0.01	0.020	<0.001	<0.05	<0.01	0.034
Yeast	2007 Field Trial	7.04	10.1	0.204	0.066	<0.05	0.803	0.621
AD fresh	2006 Field Trial	5.80	12.0	0.096	0.035	<0.05	0.348	0.272
	2007 Field Trial	0.240	0.218	0.035	<0.01	<0.05	0.039	0.017
AD stored	2006 Field Trial	4.71	9.29	0.137	0.035	<0.05	0.288	0.334
	2007 Field Trial	6.88	8.95	0.257	0.089	<0.05	0.605	0.666
	Laboratory Incubation	5.85	9.28	0.393	0.042	<0.05	0.568	0.735

APPENDIX A3 RAINFALL AND AIR TEMPERATURE

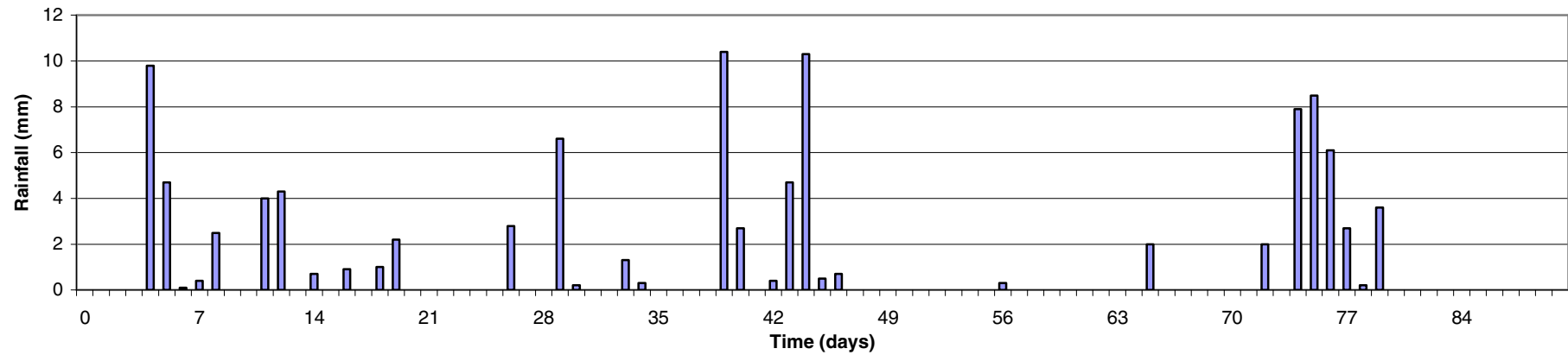


Figure A3.1 Daily rainfall (mm) at the Imperial College Farm in Wye Kent, 20 April-19 July 2005 (days 0-90)

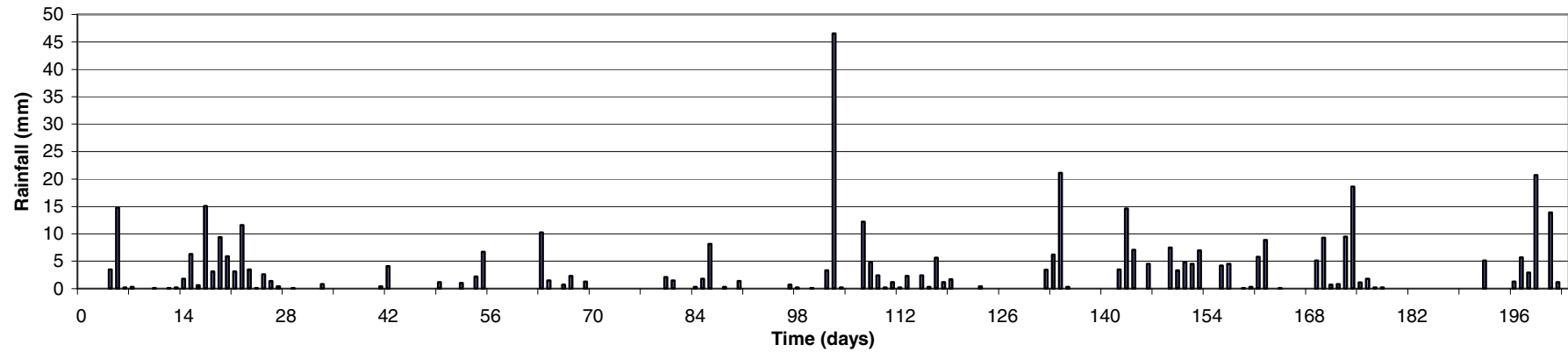


Figure A3.2 Daily rainfall (mm) at Silwood Park, 3 May-11 November 2006 (days 0-203)

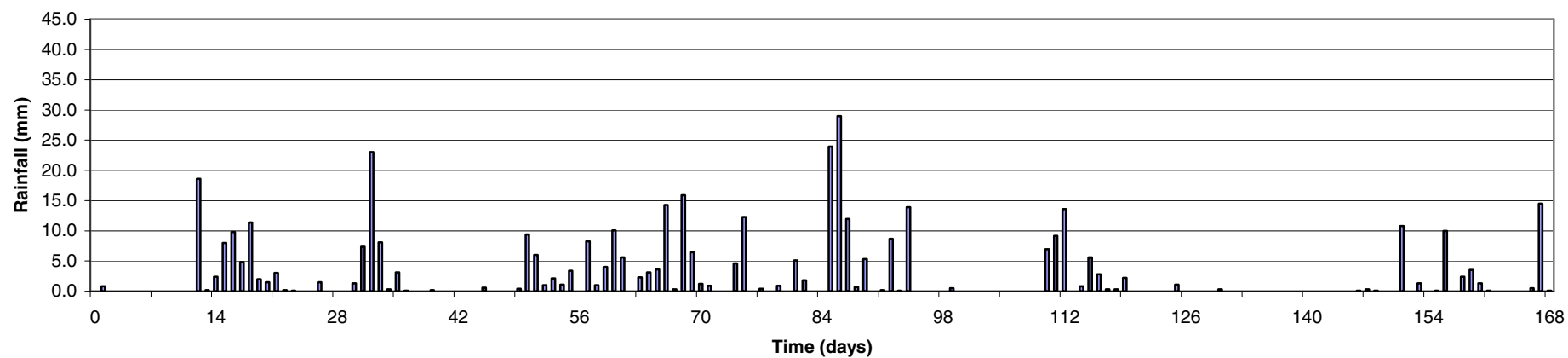


Figure A3.3 Daily rainfall (mm) at Silwood Park, 26 April-11 October 2007 (days 0-168)

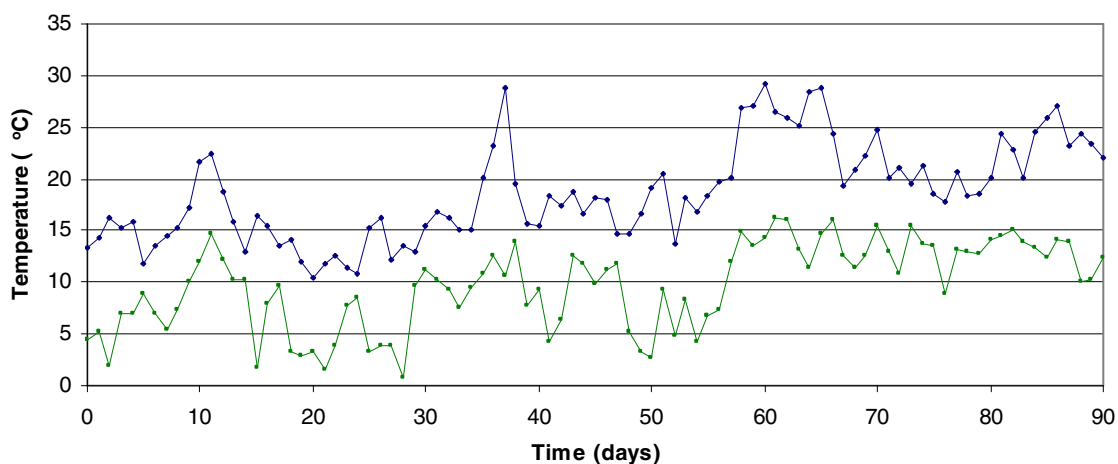


Figure A3.4 Air temperature (°C) at Imperial College Farm, Wye, Kent, 20 April-19 July 2005 (days 0-90); — indicates daily maximum, — indicates daily minimum.

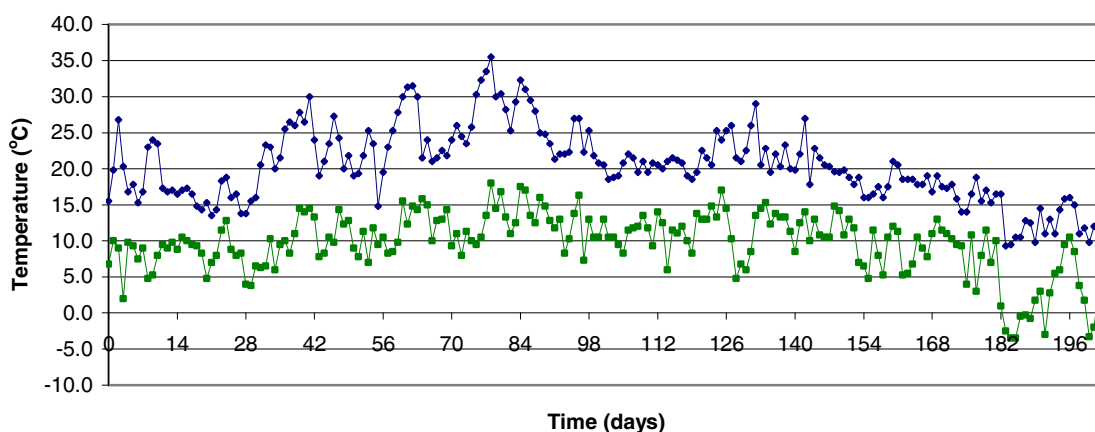


Figure A3.5 Air temperature (°C) at Silwood Park, 3 May-11 November 2006 (days 0-203); — indicates daily maximum, — indicates daily minimum.

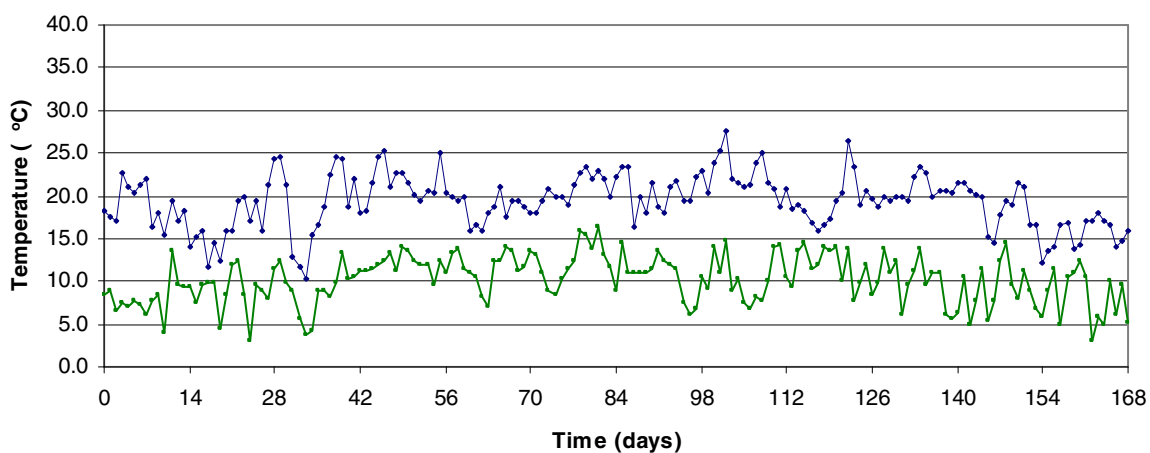


Figure A3.6 Air temperature (°C) at Silwood Park, 26 April-11 October 2007 (days 0-168); — indicates daily maximum, — indicates daily minimum.

APPENDIX A4 GRASS TISSUE ELEMENT CONCENTRATIONS- BIOWASTES CROP RESPONSE TRIAL-2006

Table A4.1 Concentrations of elements in plant tissue grown on biowastes-amended soil.

	Element Concentration ($\mu\text{g g}^{-1}$ DM)													
Treatment	Na	Fe	Mn	Zn	Cu	Pb	Cd	Ni	Cr	Co	Ag	Al	As	Ba
Control A [†]	60.8	526.4	77.9	52.1	3.03	1.67	0.41	1.67	<0.001	4.17	0.88	353.5	3.24	34.1
Control B [†]	<0.001	1035.7	115.4	35.6	1.76	0.88	1.05	2.87	<0.001	1.89	1.10	330.1	4.05	11.3
Control C [†]	170.4	488.5	141.3	38.7	0.54	0.00	0.67	2.66	<0.001	1.34	0.57	252.2	3.39	12.7
Mean Control	77.1	683.5	111.5	42.1	1.78	0.85	0.71	2.40	<0.001	2.47	0.85	311.9	3.56	19.4
Min-N A	<0.001	200.7	117.0	36.5	0.00	0.00	0.59	3.17	<0.001	1.76	0.88	163.4	3.32	10.5
Min-N B	<0.001	182.0	128.2	37.0	0.00	0.00	0.30	2.10	<0.001	0.00	0.00	127.5	2.20	10.1
Min-N C	<0.001	70.0	174.7	66.5	0.00	0.00	0.32	2.67	<0.001	0.86	0.21	93.1	2.67	11.9
Mean Min-N	<0.001	150.9	140.0	46.7	0.00	0.00	0.40	2.65	<0.001	0.87	0.36	128.0	2.73	10.8
DMAD A	<0.001	162.0	91.5	59.6	0.00	0.00	0.09	1.09	<0.001	0.38	0.00	108.3	2.27	21.2
DMAD B	<0.001	109.0	94.4	19.5	0.00	0.00	0.42	2.32	<0.001	0.00	0.00	87.6	2.63	1.37
DMAD C	<0.001	189.3	124.8	44.4	0.00	0.00	0.99	5.29	<0.001	0.77	0.33	95.0	2.76	6.28
Mean DMAD	<0.001	153.4	103.6	41.2	0.00	0.00	0.50	2.90	<0.001	0.38	0.11	97.0	2.55	9.62
Abattoir A	<0.001	61.2	54.3	22.8	0.00	0.00	0.00	0.00	<0.001	0.00	0.00	87.8	2.28	5.43
Abattoir B	<0.001	465.0	91.8	19.2	0.00	0.00	0.60	0.60	<0.001	0.10	0.00	267.6	2.31	4.72
Abattoir C	<0.001	237.8	123.3	17.8	0.00	0.00	0.30	1.20	<0.001	0.70	0.00	156.9	2.11	10.6
Mean Abattoir	<0.001	254.6	89.8	19.9	0.00	0.00	0.30	0.60	<0.001	0.27	0.00	170.8	2.23	6.93

Table A4.1 cont.

	Element Concentration ($\mu\text{g g}^{-1}$ DM)													
Treatment	Na	Fe	Mn	Zn	Cu	Pb	Cd	Ni	Cr	Co	Ag	Al	As	Ba
Trout old A	<0.001	<0.001	89.1	39.3	0.00	0.00	0.43	2.24	<0.001	0.75	0.43	41.4	3.19	10.0
Trout old B	<0.001	<0.001	70.1	26.8	0.00	0.00	1.26	3.79	<0.001	1.68	2.00	42.7	5.05	3.05
Trout old C	<0.001	<0.001	108.5	51.8	0.00	0.00	0.10	3.49	<0.001	1.33	1.64	0.00	4.21	12.5
Mean Trout old	<0.001	<0.001	89.3	39.3	0.00	0.00	0.60	3.17	<0.001	1.25	1.36	28.1	4.15	8.53
Trout new A	<0.001	<0.001	77.5	29.9	0.00	0.00	0.61	2.28	<0.001	0.18	0.26	36.5	2.89	8.86
Trout new B	<0.001	<0.001	68.4	22.3	1.53	0.00	0.69	1.96	<0.001	0.98	0.78	0.00	2.64	1.47
Trout new C	<0.001	<0.001	96.8	31.4	0.00	0.00	0.00	2.88	<0.001	1.73	1.44	34.5	3.84	8.84
Mean Trout new	<0.001	<0.001	80.9	27.9	0.51	0.00	0.43	2.37	<0.001	0.96	0.83	23.7	3.13	6.39
Potato sludge A	<0.001	1133.1	79.2	27.4	0.00	0.00	0.63	0.00	<0.001	1.46	0.10	543.6	3.13	8.46
Potato sludge B	<0.001	259.1	76.4	20.8	0.00	0.00	0.83	2.49	<0.001	0.93	0.93	165.7	3.95	10.6
Potato sludge C	<0.001	261.9	0.00	62.0	0.00	0.00	0.54	0.00	<0.001	1.27	0.15	158.0	2.38	26.9
Mean Potato sludge	<0.001	551.4	51.9	36.7	0.00	0.00	0.66	0.83	<0.001	1.22	0.40	289.1	3.15	15.3
Potato wash A	<0.001	628.3	74.9	26.4	82.0	0.19	0.86	3.94	<0.001	2.38	1.90	184.4	4.37	9.60
Potato wash B	<0.001	181.9	51.4	28.9	0.00	0.00	0.18	0.00	<0.001	0.45	0.00	338.3	2.69	9.68
Potato wash C	<0.001	243.0	81.4	27.0	0.65	0.00	0.39	2.16	<0.001	0.92	0.15	279.0	2.70	6.24
Mean Potato wash	<0.001	351.1	69.3	27.4	27.5	0.06	0.47	2.03	<0.001	1.25	0.69	267.2	3.25	8.51

Table A4.1 cont.

	Element Concentration ($\mu\text{g g}^{-1}$ DM)													
Treatment	Na	Fe	Mn	Zn	Cu	Pb	Cd	Ni	Cr	Co	Ag	Al	As	Ba
KG A	<0.001	<0.001	114.2	32.9	0.00	0.00	0.66	1.60	<0.001	0.56	0.56	56.1	3.29	8.08
KG B	<0.001	<0.001	123.6	33.9	0.00	0.00	1.24	3.90	<0.001	1.62	1.71	48.9	4.09	5.04
KG C	<0.001	<0.001	105.9	38.6	0.00	1.48	0.09	6.56	<0.001	2.03	2.31	52.6	4.44	11.7
Mean KG	<0.001	<0.001	114.6	35.1	0.00	0.49	0.66	4.02	<0.001	1.40	1.53	52.5	3.94	8.29
Ice-cream A	<0.001	<0.001	84.3	31.9	0.00	0.00	0.68	1.86	<0.001	0.88	0.68	27.3	2.54	9.10
Ice-cream B	<0.001	<0.001	122.1	26.3	0.00	0.00	1.12	3.71	<0.001	1.38	1.73	37.7	3.89	7.34
Ice-cream C	<0.001	<0.001	242.6	53.9	0.00	0.00	0.19	3.95	<0.001	2.63	2.26	38.2	4.42	19.8
Mean Ice-cream	<0.001	<0.001	149.7	37.4	0.00	0.00	0.67	3.17	<0.001	1.63	1.56	34.4	3.62	12.1
DAF A	<0.001	307.7	117.4	43.0	0.00	0.00	0.66	2.28	<0.001	0.57	0.19	244.1	2.28	15.2
DAF B	1212.2	0.00	223.3	34.7	0.00	0.00	1.05	3.58	<0.001	1.79	2.00	40.4	5.05	12.2
Mean DAF	606.1	153.9	170.3	38.9	0.00	0.00	0.86	2.93	<0.001	1.18	1.09	142.2	3.67	13.7
AD fresh A	941.5	41.5	122.8	48.3	0.00	0.00	0.89	4.43	<0.001	2.41	2.71	113.9	4.64	15.7
AD fresh B	<0.001	376.2	81.2	17.5	0.00	0.00	0.52	1.89	<0.001	0.52	0.00	201.2	2.62	7.65
AD fresh C	<0.001	774.7	91.1	14.7	0.00	0.00	0.77	2.22	<0.001	1.35	0.58	338.4	2.80	17.31
Mean AD fresh	313.8	397.5	98.4	26.8	0.00	0.00	0.73	2.85	<0.001	1.43	1.10	217.8	3.36	13.6

Table A4.1 cont.

	Element Concentration ($\mu\text{g g}^{-1}$ DM)													
Treatment	Na	Fe	Mn	Zn	Cu	Pb	Cd	Ni	Cr	Co	Ag	Al	As	Ba
AD stored A	<0.001	116.0	65.5	26.3	<0.001	<0.001	0.00	0.00	<0.001	0.00	0.00	125.5	2.00	3.80
AD stored B	<0.001	1858.1	110.4	27.2	<0.001	<0.001	0.65	3.34	<0.001	1.61	0.00	668.0	3.23	8.72
AD stored C	<0.001	0.00	239.7	12.8	<0.001	<0.001	1.07	4.80	<0.001	1.07	0.53	105.6	6.13	0.80
Mean AD Stored	<0.001	658.0	138.6	22.1	<0.001	<0.001	0.57	2.71	<0.001	0.89	0.18	299.7	3.79	4.44
TAD A	307.8	513.9	0.00	48.5	<0.001	<0.001	0.50	0.00	<0.001	0.70	0.50	224.1	2.79	26.3
TAD B	106.1	44.4	72.1	16.1	<0.001	<0.001	0.00	0.72	<0.001	0.10	0.00	74.1	1.28	3.05
TAD C	875.0	218.5	101.3	31.4	<0.001	<0.001	0.47	2.08	<0.001	0.85	0.47	139.1	2.64	9.92
Mean TAD	429.6	259.0	57.8	32.0	<0.001	<0.001	0.32	0.93	<0.001	0.55	0.32	145.8	2.24	13.1
ADMSW A	<0.001	350.1	0.00	51.9	<0.001	<0.001	0.34	0.00	<0.001	0.74	0.10	186.9	2.61	26.4
ADMSW B	446.0	143.6	57.3	22.1	<0.001	<0.001	0.32	1.74	<0.001	0.17	0.09	97.6	2.16	4.40
ADMSW C	<0.001	873.2	71.8	23.0	<0.001	<0.001	0.64	1.64	<0.001	1.55	0.00	375.9	3.92	8.38
Mean ADMSW	148.7	455.7	43.0	32.3	<0.001	<0.001	0.43	1.13	<0.001	0.82	0.06	220.1	2.90	13.1

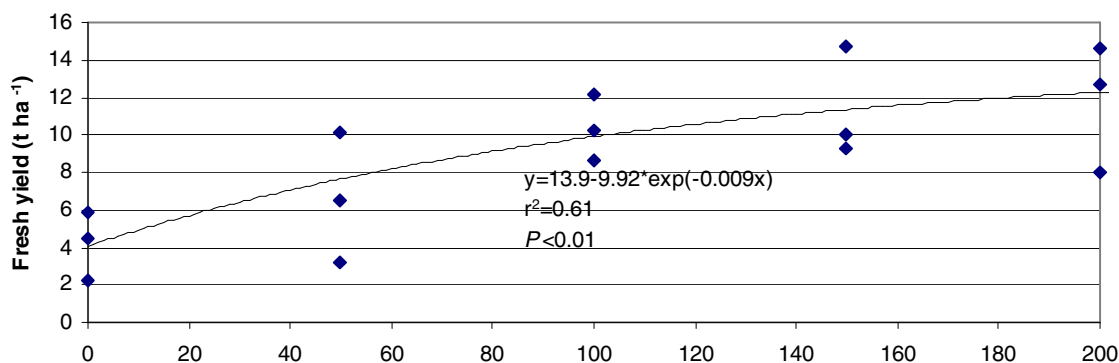
APPENDIX A5 NITROGEN EQUIVALENCIES BASED ON COMPARISON OF INDIVIDUAL YIELDS RELATIVE TO FITTED MINERAL N RESPONSE CURVES-BIOWASTES CROP RESPONSE TRIAL-2007.

Table A5.1 Summary of parameter estimates and r^2 values for asymptotic regression of each measure of crop response (dry yield, fresh yield and N offtake) to mineral fertiliser N application

Fertiliser treatment	Measure of crop response	Parameter Estimates			r^2	<i>P</i> value
		a	b	c		
N	Dry yield	3.02	-1.90	-0.012	0.47	<0.01
	Fresh yield	13.9	-9.92	-0.009	0.61	<0.01
	N offtake	287.1	-267.6	-0.001	0.71†	<0.01
N+P	Dry yield	2.89	-1.94	-0.008	0.54	<0.01
	Fresh yield	20.3	-17.2	-0.003	0.69	<0.01
	N offtake	40.7	-24.8	-1.2	0.37†	<0.01
N+K	Dry yield	4.95	-4.14	-0.004	0.87	<0.01
	Fresh yield	42.5	-39.8	-0.001	0.84†	<0.01
	N offtake	611.2	-599.8	0.000	0.88†	<0.01
N+P+K	Dry yield	5.56	-4.61	-0.003	0.58	<0.01
	Fresh yield	91.1	-87.8	-0.001	0.53†	<0.01
	N offtake	816.2	-804.8	0.000	0.65†	<0.01

† r^2 value was $\leq r^2$ for linear regression; linear regression model was used in these cases

(a) Fresh yield



(b) Dry yield

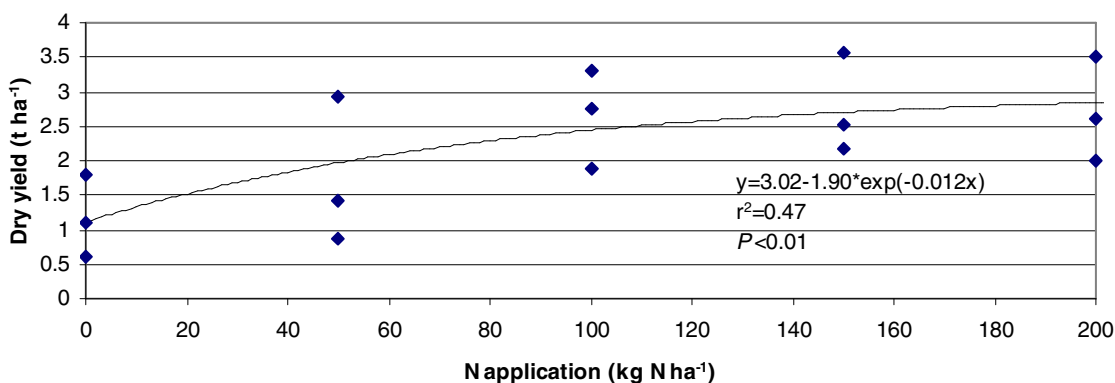


Figure A5.1 Measures of crop response: (a) fresh yield and (b) dry yield in relation to N application in mineral N control. Asymptotic regression curves were fitted to the data; the equation, r^2 value and P value are shown on each plot. The regression curves were used in the calculation of N equivalency values.

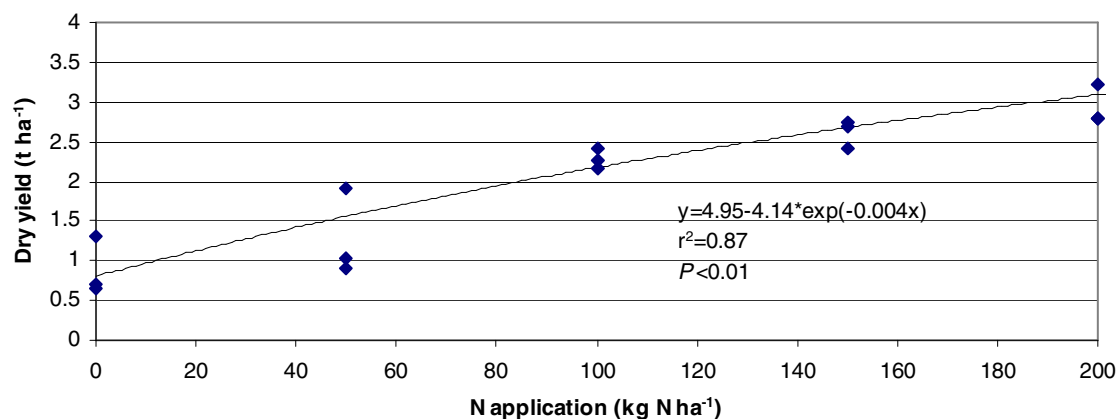
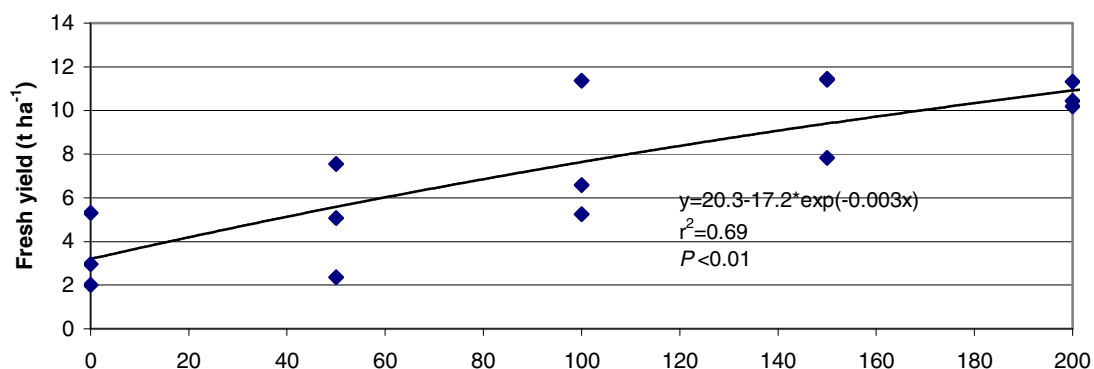


Figure A5.2 Dry yield in relation to N application in mineral N+K control. Asymptotic regression curves were fitted to the data; the equation, r^2 value and P value are shown on each plot. The regression curves were used in the calculation of N equivalency values.

(a) Fresh yield



(b) Dry yield

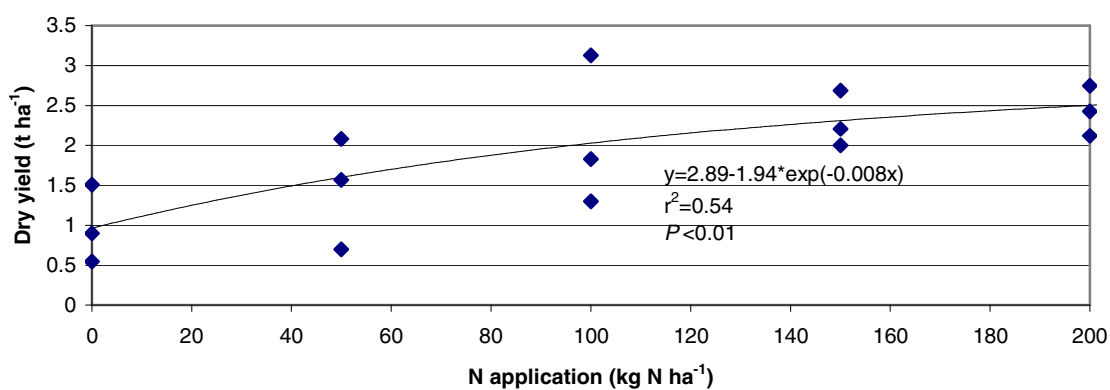


Figure A5.3 Measures of crop response: (a) fresh yield and (b) dry yield in relation to N application in mineral N+P control. Asymptotic regression curves were fitted to the data; the equation, r^2 value and P value are shown on each plot. The regression curves were used in the calculation of N equivalency values.

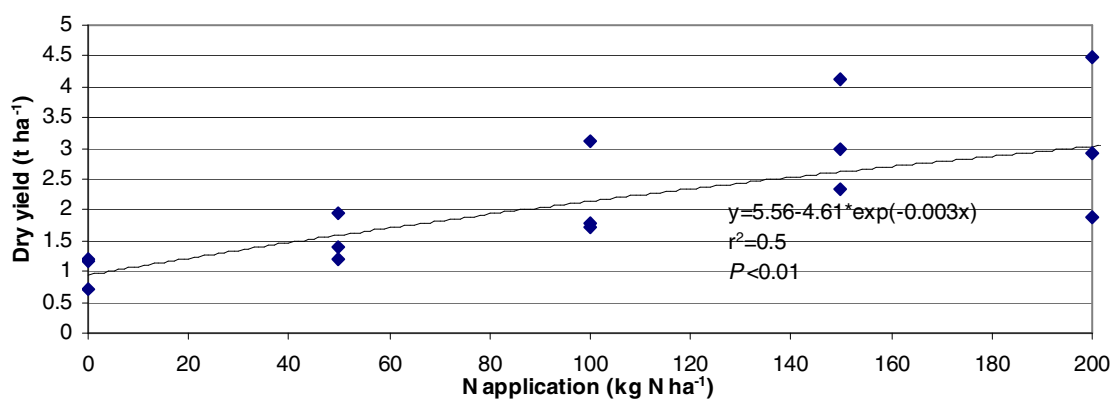


Figure A5.4 Dry yield in relation to N application in mineral N+P+K control. Asymptotic regression curves were fitted to the data; the equation, r^2 value and P value are shown on each plot. The regression curves were used in the calculation of N equivalency values.

Table A5.5 N equivalency values for biosolids and biowastes where there was a significant response to N application, calculated relative to mineral fertiliser response curves fitted by asymptotic or linear regression when appropriate.

Biosolids or Biowaste	Crop response measure				N equivalency relative to mineral N				N equivalency relative to mineral N + P			
	N rate (kg N ha ⁻¹)	Fresh yield (t ha ⁻¹)	Dry yield (t ha ⁻¹)	N offtake (kg ha ⁻¹)	Fresh yield ⁽¹⁾	Dry yield ⁽¹⁾	N offtake ⁽²⁾	Mean	Fresh yield ⁽¹⁾	Dry yield ⁽¹⁾	N offtake ⁽²⁾	Mean
DMAD	116.7	7.85	1.93	34.5	0.65	0.40	0.50	0.52	0.75	0.91	0.79	0.82
	233.5	12.7	2.71	54.1	1.85	0.65	0.59	1.03	1.09	1.16	0.80	1.01
	350.3	16.0	3.37	75.7	†	†	0.65	0.65	†	1.31	0.82	1.07
	467.0	18.2	3.71	78.4	†	†	0.51	0.51	†	1.51	0.65	1.08
Vegetable	60.5	3.26	0.90	16.43	†	†	†	†	†	†	0.10	0.10
	121.0	4.65	1.33	25.50	0.07	†	0.18	0.12	0.22	†	0.41	0.32
	181.5	6.78	1.94	35.80	0.20	†	0.35	0.28	0.49	†	0.54	0.52
	242.0	7.62	2.11	37.82	†	†	0.30	0.30	0.47	†	0.45	0.46
Yeast	137.0	11.3	2.80	48.3	1.09	1.32	0.84	0.96	2.76	†	1.16	1.96
	274.0	19.2	4.05	91.0	†	†	1.05	1.05	†	†	1.32	1.32
	411.0	23.8	4.49	109.8	†	†	0.89	0.89	†	†	1.10	1.10
	548.0	27.0	4.87	145.0	†	†	0.80	0.80	†	†	1.13	1.13
TAD	101.0	7.85	1.93	35.0	0.55	0.46	0.60	0.54	0.87	†	0.94	0.90
	202.0	12.7	2.71	65.4	1.16	0.75	0.91	0.94	1.45	†	1.19	1.32
	303.0	16.0	3.37	76.5	†	†	0.76	0.76	†	†	0.96	0.96
	404.0	18.2	3.71	91.8	†	†	0.72	0.72	†	†	0.90	0.90
AD Fresh	134.6	10.4	2.71	44.8	0.87	1.14	0.75	0.92	2.20	1.37	1.05	1.54
	269.2	17.7	3.69	82.6	†	†	0.94	0.94	†	2.34	1.19	1.77
	403.8	24.4	4.53	110.1	†	†	0.91	0.91	†	†	1.12	1.12
	538.4	24.8	4.61	113.4	†	†	0.70	0.70	†	†	0.87	0.87
AD Stored	109.2	9.77	2.40	48.7	0.90	0.86	1.09	0.95	1.56	1.49	1.49	1.51
	218.4	14.6	3.26	64.7	†	†	0.83	0.83	†	1.67	1.08	1.37
	327.6	21.7	4.07	97.4	†	†	0.96	0.96	†	†	1.20	1.20
	436.8	20.0	4.00	95.0	†	†	0.70	0.70	†	†	0.87	0.87

† Crop response to biosolids or biowastes exceeded maximum response to mineral fertiliser N or did not meet minimum response

⁽¹⁾ Asymptotic regression curve fitted to mineral N response data ⁽²⁾ Linear regression fitted to mineral N response data

Table A5.6 Cont. N equivalency values for biosolids and biowastes where there was a significant response to N application, calculated relative to mineral fertiliser response curves fitted by asymptotic or linear regression when appropriate.

Biosolids or Biowaste	Crop response measure				N equivalency relative to mineral N + K				N equivalency relative to mineral N + P + K			
	N rate (kg N ha ⁻¹)	Fresh yield (t ha ⁻¹)	Dry yield (t ha ⁻¹)	N offtake (kg ha ⁻¹)	Fresh yield ⁽²⁾	Dry yield ⁽¹⁾	N offtake ⁽²⁾	Mean	Fresh yield ⁽²⁾	Dry yield ⁽¹⁾	N offtake ⁽¹⁾	Mean
DMAD	116.7	7.85	1.93	34.5	0.86	0.67	0.76	0.77	0.68	0.60	0.63	0.64
	233.5	12.7	2.71	54.1	0.85	0.66	0.71	0.74	0.69	0.62	0.58	0.63
	350.3	16.0	3.37	75.7	0.76	0.69	0.71	0.72	0.71	0.56	0.59	0.62
	467.0	18.2	3.71	78.4	0.67	0.64	0.56	0.62	0.65	0.50	0.46	0.54
Vegetable	60.5	3.26	0.90	16.43	0.13	0.09	0.30	0.17	†	†	0.26	0.26
	121.0	4.65	1.33	25.50	0.30	0.27	0.44	0.34	0.24	0.16	0.37	0.26
	181.5	6.78	1.94	35.80	0.44	0.44	0.52	0.46	0.45	0.29	0.43	0.39
	242.0	7.62	2.11	37.82	0.40	0.39	0.42	0.40	0.40	0.27	0.35	0.34
Yeast	137.0	11.3	2.80	48.3	1.25	1.19	1.04	1.16	1.25	0.90	0.86	1.00
	274.0	19.2	4.05	91.0	1.20	1.39	1.12	1.24	1.36	0.90	0.93	1.06
	411.0	23.8	4.49	109.8	1.03	1.34	0.93	1.10	1.19	0.78	0.76	0.91
	548.0	27.0	4.87	145.0	0.89	1.79	0.95	1.21	1.15	0.68	0.78	0.87
TAD	101.0	7.85	1.93	35.0	1.00	0.78	0.90	0.89	0.79	0.69	0.74	0.74
	202.0	12.7	2.71	65.4	0.98	0.76	1.03	0.93	0.79	0.72	0.85	0.79
	303.0	16.0	3.37	76.5	0.88	0.79	0.83	0.83	0.79	0.65	0.69	0.71
	404.0	18.2	3.71	91.8	0.77	0.74	0.77	0.76	0.74	0.57	0.64	0.65
AD Fresh	134.6	10.4	2.71	44.8	1.14	1.14	0.96	1.08	1.19	0.82	0.79	0.93
	269.2	17.7	3.69	82.6	1.12	1.11	1.02	1.08	1.12	0.83	0.84	0.93
	403.8	24.4	4.53	110.1	1.08	1.41	0.95	1.15	1.23	0.81	0.78	0.94
	538.4	24.8	4.61	113.4	0.83	1.16	0.73	0.91	0.98	0.62	0.61	0.73
AD Stored	109.2	9.77	2.40	48.7	1.28	1.11	1.32	1.23	1.15	0.91	1.57	1.21
	218.4	14.6	3.26	64.7	1.08	1.02	0.94	1.02	1.06	0.80	0.95	0.94
	327.6	21.7	4.07	97.4	1.16	1.19	1.02	1.12	1.15	0.87	0.72	0.92
	436.8	20.0	4.00	95.0	0.80	0.84	0.74	0.79	0.83	0.60	0.49	0.64

†Crop response to biosolids or biowastes did not meet minimum response to mineral fertiliser N control

⁽¹⁾Asymptotic regression curve fitted to mineral N response data ⁽²⁾Linear regression fitted to mineral N response data