NITROUS OXIDE FROM INCORPORATED CROP RESIDUES AND GREEN MANURES

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Thesis submitted for the degree of Doctor of Philosophy in the Faculty of Science and Engineering, Institute of Ecology and Resource Management, University of Edinburgh

1997

DECLARATION

I, Elizabeth Mary Baggs, declare that this thesis was composed by myself, and the work described was carried out by myself, except for the instances detailed in the text and acknowledgements.

Elizabeth Baggs

ACKNOWLEDGEMENTS

The work carried out in this thesis was funded by the Ministry of Agriculture, Fisheries and Food.

I would like to thank everyone who has helped me throughout this work, and particularly my supervisors Bob Rees and Keith Smith for their advice and guidance. I would also like to thank Andy Vinten, Iain McTaggart, Doug Lewis, Lianhai Wu, Becky Hood, and Katrina Castle for their advice and assistance at various stages. I am also grateful to Lesley Swan, Rab Howard, Frances Wright, Ian Crichton, Angelo Fierro and John Parker for their help in the field and lab. A big thanks to Lillias, Julia and Katrina for making the work a lot more bearable at times!

Finally, I would like to thank Billy and both my parents for their continual encouragement and support.

ABSTRACT

A series of field and laboratory experiments were undertaken to examine the effects of incorporation of plant material on emissions of N_2O from agricultural soils. The overall aim was to increase understanding of that part of the agricultural N cycle, associated with the release of N after incorporation of crop residues and green manures into soil, and subsequent N_2O emissions to the atmosphere. N_2O emissions from growing crops and following addition of various residues and green manures to soil were measured and compared. The effects of crop type, fertiliser application, cultivation techniques, soil type, and climatic conditions, and also of the addition of high C substrate in the form of paper waste, on these emissions were investigated.

Emissions of N_2O were increased after cultivation of soil, attributed to increased accessibility of organic matter to soil microbes, and improved gaseous diffusion. Emissions were higher following incorporation of plant material than emissions from bare soil. Generally, fluxes were increased within a few hours or days after cultivation and/or incorporation, but the effect was short-lived. Most of the N_2O was emitted during the first 2 weeks. The magnitude and timing of N_2O released within this period was highly dependent on temperature and rainfall following incorporation, and the cultivation technique employed.

The C:N ratio of the incorporated plant material had a considerable effect on rates of decomposition, and on subsequent N_2O production during nitrification and denitrification. Higher emissions were typically measured after incorporation of material with a low C:N ratio, such as legumes, than when material with higher ratios, such as cereal straw, was involved. When material with a high C:N ratio was added, N was immobilised. Nevertheless, the presence of high C:N paper waste increased N_2O emissions from incorporated vegetable crop residues. This was attributed to the creation of more anaerobic sites in the soil.

Emissions of N_2O increased within a few days of applying mineral N fertiliser to spring-sown cereal crops. Again, these fluxes were short-lived. Use of ^{15}N-labelling in this experiment showed that approximately 50 % of crop N at harvest was derived from applied fertiliser. In other experiments, the presence of a growing crop, particularly a legume, increased emissions, compared with those measured from bare soil.

The measurements of soil mineral N (the substrate for N_2O) were compared with the amounts predicted by various N models. Practical suggestions were made for ways to lower N_2O emissions from agricultural systems, thereby reducing detrimental effects on the ozone layer and global warming.

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CHAPTER 1 INTRODUCTION

During the present century concentrations of nitrous oxide (N_2O) in the atmosphere have dramatically increased. Over approximately the last 20 years they have been rising at a rate of 0.25 % yr^{-1}, i.e. an addition of 3.5 Tg N_2O-N yr^{-1} (Robertson, 1993). This increasing N_2O is of concern due to its roles in the destruction of stratospheric ozone (O_3) (Crutzen, 1981) and as a "greenhouse" gas (Hansson *et al.*, 1990). O_3 screens out ultraviolet radiation, thus the depletion of the O_3 layer is of concern as ultraviolet increases the risk of skin cancer, immune deficiencies, and possible harm to crops and aquatic systems. Robertson (1993) states that N_2O is approximately 250 times more potent than CO_2 as an absorber of infrared radiation, resulting in a rise in temperature at the earth's surface (Wang *et al.*, 1976). N_2O has an atmospheric lifetime of about 150-170 years, so these detrimental effects will be long-lasting, and any corrective response will be slow (Robertson, 1993).

The precise contribution of each of the numerous anthropogenic sources to the global N_2O budget still remains to be quantified (Robertson, 1993). Estimated emission rates from agriculture vary considerably (Granli and Bøckman, 1994), but primarily result from the activity of soil micro-organisms (Haynes, 1986), particularly after application of N fertiliser (Mosier, 1994; Bouwman, 1996). Organic N inputs to soil in the form of plant material, either as whole green manures or as post harvest residues, have been found to increase N_2O emissions compared with emissions measured from bare soil (Denmead *et al.*, 1979; Aulakh *et al.*, 1983, 1984b, 1991a; de Catanzaro and Beauchamp, 1985). This organic material is readily decomposed, and N_2O is released during nitrification and/or denitrification, according to the aeration of the soil (Ryden and Lund, 1980; Aulakh *et al.*, 1984a; Groffman, 1991). Such emissions vary depending on the type of plant material, its composition, and the amount of biomass incorporated (Reinertsen *et al.*, 1984), and are further complicated by soil temperature, moisture content, aeration, soil type and cultivation (Frankenberger and Abdelmagid, 1985). In organic agricultural systems, where incorporated plant material is used as a vital source of N (Millington, 1989), such emissions of N_2O represent an important loss of N from the system, and reductions in this loss would be highly beneficial.

In previous field trials undertaken at Bush Estate, near Edinburgh, large emissions of N_2O were measured following ploughing-in of grass and grass/clover swards, and were higher than emissions from uncultivated swards (Davies, 1996). High fluxes were measured immediately after cultivation, with most of the N_2O emitted during the first 13 days. Over a 48 day period 3.3 kg N ha^{-1} was measured from the ploughed grass/clover swards. This high flux was attributed to the high N content of the clover, and the stimulation of mineralisation of organic matter after ploughing. This work indicated the potential importance of organic residue incorporation as a source of N_2O emissions from agriculture, but to establish a more complete picture further work was required, particularly comparisons of emissions from plant material with different N contents (Aulakh *et al.*, 1984b). To date, little work has been undertaken examining N_2O emissions after incorporation of green manures (Granli and Bøckman, 1994), although there is great potential for N_2O production due to their often high N contents, especially if incorporated at an immature stage, and high biomass input if incorporated as a whole crop.

The overall aim of this work was to increase understanding of the N cycle, with respect to N release from incorporated plant material, and losses of N_2O associated with this practice. This would enable N_2O emissions to be predicted under certain management practices, and, where applicable, suggestions to be made for changes in strategy to reduce such emissions. It was hypothesised that N_2O emissions would be raised after incorporation of plant material into soil, but the magnitude of fluxes would be highly dependent on the composition of the material, and would fluctuate in response to varying environmental conditions in field trials. Therefore, the timing and method of cultivation were likely to be of importance.

The effects of incorporating different crop residues and green manures were investigated in a series of field trials and laboratory experiments involving different C:N ratios, cultivation treatments, soil types and variations in environmental parameters. Emissions were also measured from growing crops prior to their incorporation. Data obtained from field trials were used in the validation of models predicting changes in soil available N and losses of N through denitrification. Suggestions are made for the improvement of these models.

CHAPTER 2 LITERATURE REVIEW

2.1 The soil N cycle

There are 3 main forms of N in mineral soils - organic N associated with soil humus, NH_4^+-N fixed by clay minerals and soluble inorganic NH_4^+ and NO_3^-. Rosswall (1976) calculated that, in the absence of inorganic fertiliser, less than 1 % of terrestrial N was in the form of available soil N, 4 % was stored in plants, 1 % in plant litter, 0.2 % in micro-organisms and 94 % in soil organic matter. Most of the N in surface soils is associated with the organic matter and protected from rapid microbial release. Typically, only 2-3 % of N a year is mineralised from organic matter (Brady, 1990).

The amount of N in soils to ploughing depth often exceeds 4000 kg N ha^{-1} (Stevenson, 1982). Soil organic N is divided into pools, of which the living biomass, fresh debris and old passive material are particularly important.(Bjarnason, 1989). The biomass significantly contributes to the pool of mobile, plant available nutrients in the soil (Paul, 1984). Jenkinson and Ladd (1981) estimated that the quantity of N in the microbial biomass of an unmanured wheat field was 95 kg N ha^{-1} to 230 mm depth. Both NH_4^+ and NO_3^- can be immobilised into microbial tissue, for example during decomposition of residues with a low N content. NH_4^+ ions can also be fixed by clay minerals. Most of the mineral N pool not immobilised is absorbed and assimilated by plants (section 2.2.3). This organic N in plant material is either consumed by animals or returned to soil after plant death.

The main additions of N to the soil are from plant material, inorganic fertiliser, green and farm manures, wet and dry deposition and biological fixation of N_2. Losses of N occur through leaching, erosion and surface runoff, volatilisation of NH_3, gaseous losses of N_2 and N_2O, and removal by plants and animals. Soils have been identified as a major source of N_2O, accounting for 65 % of total global N_2O emissions (Prather *et al.*, 1995). As discussed below in section 2.2.5, this N_2O is produced during microbial nitrification and denitrification in the soil. Thus, N_2O from soils is directly related to the amount of N being cycled within the soil, with increased emissions measured following additions of both organic and inorganic N to the soil (sections 2.2.5.6 and 2.2.5.8).

2.2 Processes of the N cycle

2.2.1 Organic matter decomposition

Decomposition results in organic N and other essential plant nutrients being accessible in available forms. During decomposition some of the C and N is assimilated into microbial tissue and some is converted to humus under the action of micro-organisms. The turnover rate depends on agricultural practices and soil and vegetation type (Paul, 1984). Mineral N is the essential substrate for N_2O in the processes of nitrification and denitrification (section 2.2.5). Thus, decomposition of organic material added to the soil has the potential to increase N_2O production (section 2.2.5.8).

Above-ground crop residues remain in arable fields after harvest. They are either cut and incorporated prior to sowing of the following crop, or they are composted on the farm and incorporated at a later date (Dixon and Holmes, 1987). If taken off early, arable silage crops are sometimes allowed to regrow, and the residue then ploughed in (Dixon and Holmes, 1987). Incorporated crop residues provide an important source of N for the following crop after their decomposition (McKenney *et al.*, 1993), and are fundamental in the replenishment of soil organic matter (Janzen and Kucey, 1988). As discussed below in section 2.2.5.8, decomposition of incorporated crop residues may, under certain conditions, result in production of N_2O during nitrification and denitrification. The potential contribution of N to the soil depends on the crop species incorporated. Until residues are completely mineralised their value as an immediate source of available N is limited (Faris *et al.*, 1986). Ladd *et al.* (1985) found that after 8 years decomposition, 28-35 % of the crop residue N remained as organic residues in the top 0.2 m of the soil, compared with 45-50 % remaining after 4 years (Ladd *et al.*, 1981b).

On occasion the whole crop is used as a source of N for the following arable crop (Parsons, 1984; MacRae and Mehuys, 1985; Millington, 1989). Such crops - "green manures" - are important in rotations, especially within organic farming systems (Millington, 1989; Lampkin, 1990). Green manuring enriches the soil by incorporating fresh plant material other than just residues (Atallah and Lopez-Real, 1991). During their growth green manures take up C, N and other nutrients, thereby reducing leaching losses (Parsons, 1984). They also protect the soil from erosion (Weeraratna, 1979; Lampkin, 1990). On decomposition after incorporation they provide a source of N for the following crop (McKenney *et al.*, 1993), reducing fertiliser requirements (Atallah and Lopez-Real, 1991), particularly if incorporated whilst still green and rich in N. Such addition of N-rich material has been found to increase N_2O emissions from soil (section 2.2.5.8).

Benefits from green manures depend on how effectively they are incorporated into the soil (Davis, 1989; Millington, 1989), with an optimum time interval between incorporation and sowing of the next crop (Rayns and Lennartsson, 1995). This time interval is also important in reducing gaseous N emissions after incorporation. Often different species of green manures are grown together (Millington, 1989), such as slow and fast growing species, to optimise the use of time available.

It has been found that incorporation of a green manure, even a legume, may not necessarily increase soil organic matter levels (Ladd *et al.*, 1983; MacRae and Mehuys, 1985; Frankenberger and Abdelmagid, 1985). Russell (1973) stated that globally green manures are more effective as an immediate N source than as a source of organic matter. This is because of their rapid decomposition due to their often low C:N ratios, with N usually released quickly and in large flushes. In agreement with this, Sarrantonio (1995) reported that 140 kg NO_3^- ha^{-1} was made available within one week of incorporating a green manure.

2.2.1.1 Mineralisation and Immobilisation

Heterotrophic micro-organisms require C for respiration and cell synthesis. To accompany this C they also require N and other nutrients. If insufficient organic N is present micro-organisms use the mineral N in soil, transforming it into organic N constituents of their cells and tissues. This process is immobilisation and results in net incorporation of mineral N, usually NH_4^+, into microbial tissue during decomposition (Jansson and Persson, 1982). The release of N from the soil organic matter into inorganic forms of NH_4^+ or NH_3 is known as mineralisation (Jansson and Persson, 1982; Haynes, 1986). These processes are continually occurring in the soil, defined as the mineralisation-immobilisation turnover (Shields *et al.*, 1973; Jenkinson and Ladd, 1981; Juma and Paul, 1984), and so the availability of NH_4^+ for nitrification or plant uptake may be considered as a net effect. The balance between mineralisation and immobilisation is a function of the C:N ratio of cells synthesised, the energy efficiency of the micro-organisms, and the C:N ratio of the material undergoing decomposition. The latter is the most important (Brady, 1990). Decomposing microbial tissue can significantly contribute to the readily mineralisable soil organic N (Marumoto *et al.*, 1982), thereby acting as both a nutrient source and sink (Jansson *et al.*, 1989). After plant material has undergone substantial decomposition micro-organisms may be the primary source of mineralisable nutrients in soil (Jansson *et al.*, 1989). Mineralisation rates in soil generally decrease with depth due to a decrease in organic matter and micro-organisms. Nevertheless, according to Cassman and Munns (1980) a substantial proportion of N released may be mineralised at up to 1 m depth.

2.2.1.2 Factors affecting decomposition

The effects of crop residue type and quality on residue decomposition have been well documented (for example, Harper and Lynch, 1981; Reinertsen *et al.*, 1984; Christensen, 1986). Large differences in decomposition rates and nutrient release patterns have been observed among various plant materials, particularly in the early stages of decomposition. These differences have been ascribed to differences in crop residue characteristics, including concentrations of N and other nutrients, lignins, carbohydrates and water soluble C (Reinertsen *et al.*, 1984; Janzen and Kucey, 1988). According to Andrén (1987) decomposition rates are controlled by the crop's influence on soil moisture as well as its concentration of water soluble components.

The C:N ratio of the decomposing organic substrate is generally considered to be the major factor determining the balance between mineralisation and immobilisation, and is the best residue characteristic for predicting decomposition rates (Harper and Lynch, 1981; Jenkinson, 1984; Reinertsen *et al.*, 1984; Christensen, 1986; Granstedt, 1995). The C:N ratios of organic substrates vary considerably. Dead plant material may contain between about 5 and 0.1 % N, and so decomposition may potentially range from C:N ratios of 20-500 (Heal *et al.*, 1997). The lowest C:N ratios of about 8:1 are found in microbial tissue. Legume residues are reported as having C:N ratios in the range of 13:1 to 23:1, whilst cereal straws typically have ratios of 60:1 to 80:1 (Haynes, 1986).

A low C:N ratio generally results in net mineralisation, as a result of a high rate of decomposition. Materials with C:N ratios of <20 decompose rapidly, often with a release of NH_3 as N compounds are metabolised as C sources (Heal *et al.*, 1997). Short-lived immobilisation of N may occur immediately after incorporation of plant material with a high C:N ratio, such as cereal straw, and may last for up to several weeks (Aulakh *et al.*, 1991b). The critical value above which there is generally immediate net immobilisation is thought to be with a C:N ratio of greater than approximately 25-30 (Haynes, 1986). However, this value is not precise due to other aspects of substrate quality, such as lignin and polyphenol content. Fungi and bacteria can decompose substrates with higher ratios. This critical value is supported by Jenkinson (1984) who added substrate with a C:N ratio of about 30 to soils which resulted in N immobilisation over a period of several weeks.

The mineralisation-immobilisation turnover continuously repeats itself until the supply of any added material is exhausted (Jenkinson and Ladd, 1981; Juma and Paul, 1984). During decomposition the C:N ratio progressively decreases so that at some point N is no longer limiting to activity. At that point the balance changes from net immobilisation to net mineralisation. In accordance with this, Janzen and Kucey (1988) found that after incorporating wheat, lentil and rape residues the critical N concentration, below which significant immobilisation occurred, decreased in time with progressive decomposition (1.9 % on day 14 to 1.1 % on day 84). Phases of net immobilisation followed by net mineralisation after a period of time have been reported by Black (1968), Carter and Rennie (1984) and Nicolardot (1988). Thus, the long-term effect of continued straw incorporation is increased mineralisation (Powlson *et al.*, 1987), as net immobilisation is followed by a slow release of N by mineralisation.

Residue lignin and polyphenol contents also influence decomposition rates. When plant material contains high concentrations of lignin or polyphenols there may be little mineralisation of plant N, despite high N concentrations (Fox *et al.*, 1990; Palm and Sanchez, 1991). Frankenberger and Abdelmagid (1985) found an inverse relationship between the lignin content of plant materials and the cumulative amount of N mineralised. With a given C:N ratio, N mineralisation decreased slightly as the lignin content of the residues increased. Müller *et al.* (1988) concluded that lignin concentration was better than N concentration, and N concentration was better than C:N ratio in predicting the amount of N mineralised from crop residues. This is in contrast to other workers (for example, Frankenberger and Abdelmagid, 1985) who have found the lignin content to be less important than the N content or C:N ratio. Combining both schools of thought, Fox *et al.* (1990) proposed the (lignin+polyphenol):N ratio to be a good predictor of N mineralisation rates after residue incorporation.

Temperature has a fundamental effect on decomposition as it controls microbial activity (Swift *et al.*, 1979). The optimum temperature for organic matter decomposition is approximately 35 °C (Alexander, 1977). Rates generally rise rapidly with increasing temperature over the range normally found in temperate field soils (Haynes, 1986), with a Q_{10} of between 2 and 3 between 10 to 40 °C (Brady, 1990). Microbial activity is greatly reduced below temperatures of about 2 °C. Fluctuations around freezing point may produce more marked effects, with frequent freeze-thaw cycles increasing mineralisation rates. These factors result in large seasonal differences in mineralisation rates in the UK. In the cooler parts of the UK the release of mineral N from manures and soil organic matter is too slow in the spring to provide a satisfactory supply of N to spring-sown cereals (Stockdale *et al.*, 1995). In contrast, vegetable or potato crops, whose main demands for N occur later in the growing season, are better provided for by such delayed mineralisation. Date of incorporation of residues is an important determinant of their decomposition, as earlier incorporation in the autumn increases the number of days the soil remains above the critical temperature for decomposition (Harper, 1988).

Soil moisture content also affects decomposer activity (Swift *et al.*, 1979). The combined effect of high temperature and moisture on decomposition is more important than that of temperature alone, as these conditions favour microbial activity (Haynes, 1986). Stanford and Epstein (1974) found that optimum mineralisation rates occurred around 0.33 and 0.1 bar, and increased between permanent wilting point and field capacity. Above field capacity mineralisation rates fall because of restricted aeration, as rates of decomposition by aerobic bacteria are greater than by anaerobic bacteria (Patrick, 1982). The distribution of moisture in the soil is important in controlling net mineralisation (Cassman and Munns, 1980). High moisture contents of litter on the soil surface reduce decomposition rates (Haynes, 1986). Drying and rewetting cycles are also important (Haynes, 1986). Microbial activity is stimulated both by the physical disruption of soil aggregates caused by swelling and shrinking, which exposes organic matter not previously accessible, and by the accumulation of microbial cells with a low C:N ratio killed during the dry period.

Aerobic conditions in sandy soils usually result in more rapid decomposition than occurs in fine-textured soils (Allison, 1973). Clay soils hold more moisture than sandy soils and therefore may inhibit decomposition under wet conditions by slowing O_2 diffusion. They may also absorb molecules onto lattices, reducing substrate availability to micro-organisms. Ladd *et al.* (1981b) found slower decomposition in heavy clay soils than in sandier soils during the first 16 weeks after incorporation of residues. Low mineralisation rates in clay soils have also been reported by Cerri and Jenkinson (1981) and Azam *et al.* (1989).

Decomposition proceeds more readily in neutral than in acidic soils, as very low or high pH restricts the activity of soil micro-organisms, particularly bacteria (Alexander, 1977). Rates are also affected by the nature of the inorganic N present and its relationship with soil pH. Soil organisms utilise NH_4^+ preferentially over NO_3^- so the amount of NH_4^+ immobilised increases with increasing pH, since NH_4^+ is physiologically acidic (Power and Broadbent, 1989). Conversely, immobilisation of NO_3^- tends to increase with decreasing pH.

Cultivation increases aeration, evaporation and enhances the accessibility of crop residues to soil micro-organisms, resulting in increased mineralisation of N (Ross, 1990). Physical disruption of soil aggregates exposes organic matter microsites to micro-organisms, thereby increasing mineralisation (Haynes, 1986). Coarse organic material is more resistant to decomposition than organic matter with a greater surface area:volume ratio. According to Groffman *et al.* (1987), tillage practices affect the timing of N availability more than the total amount of N available.

Incorporated crop residues initially decompose faster than residues left on the soil surface (Parker, 1962; Douglas *et al.*, 1980; Wilson and Hargrove, 1986; Smith and Sharpley, 1990; Varco *et al.*, 1989, 1993). For example, Wilson and Hargrove (1986) found that N from clover residues was removed faster when the residues were buried (24 % of residue remaining after 120 days), than when they were placed on the soil surface (32 % of residue remaining after 120 days). Similarly, Varco *et al.* (1989) found that incorporation of vetch residues resulted in greater releases of soil inorganic N throughout the plough layer, and greater recovery by corn in the first year than when the residues were surface placed. In one year 21 % of the residue remained 120 days after conventional tillage, and 43 % where there was no tillage. In another year 13 % of the residue remained 75 days after conventional tillage, and 36 % where there was no tillage. Crop residues incorporated deep into the soil decompose faster than those only shallowly incorporated.

Decomposition of residues is largely dependent on rate of addition (Jenkinson, 1977a; Azam *et al.*, 1993; Rees *et al.*, 1993). Large additions of organic matter usually decompose more slowly than small additions, due to N deficiency in soils (Jenkinson, 1981), or development of anaerobic zones (Rees *et al.*, 1993). The rate of residue incorporation is important because it determines the duration of the early stages of decomposition when residue close to seeds or roots can inhibit crop establishment, primarily through the prevention of moisture uptake (Harper and Lynch, 1981). Toxins produced by decaying residues, especially in anaerobic conditions after sowing into wet soil, may suppress seed germination and seedling emergence (Wallace and Elliott, 1979; Baggs, 1993). Bartholomew (1965) suggested that a concentration of 10-20 g N kg^{-1} of residue after the rapid stage of decomposition was necessary to satisfy the microbial requirements for continued degradation.

Christensen (1985) reported that the presence of growing plants decreased or retarded decomposition by modifying the soil environment. Both roots and soil micro-organisms may compete for nutrients from the decomposing plant material, microbial activity may be inhibited by root exudates, or soil micro-organisms may show a preference for fresh material released from roots (Jenkinson, 1977b; Christensen, 1985 and Nicolardot *et al.*, 1995). However, in contrast to this, other work, for example, that by Clarholm (1985), found that the presence of living roots actually increased the biodegradation of plant residues and the mineralisation of native soil organic matter. There is a continuous supply of readily available C from root cell death and exudation of soluble C compounds.

Plant material may decompose more rapidly in soil after successive seasons of incorporation, implying that the microbial biomass adapts to the input of substrate (Allison and Kilham, 1988). Powlson *et al.* (1987) found that despite a steady increase in soil biomass following regular straw incorporation, there was no long-term change in the biomass C:N ratio. However, Allison and Kilham (1988) reported greater increases in the C:N ratio of the biomass after straw inputs to soil with a history of straw incorporation than soil with no previous incorporation history. This suggests that organic matter turnover in soil can become progressively more rapid. Nevertheless, Sørensen (1979) found that the overall pattern of decomposition was similar whether the soil had been amended with one or with several successive straw applications. He also found that the size of the microbial biomass decreased in response to successive straw applications. Similarly, Williams *et al.* (1995) reported that long-term straw incorporation had little effect on N release from a mustard green manure.

2.2.1.3 Priming effect

As early as 1926 Löhnis found that additions of fresh plant material to soil stimulated mineralisation of indigenous soil organic N. Since then many reports have shown that the addition of N, either organic or inorganic, to soil promotes the mineralisation of soil N (for example, Broadbent and Nakashima, 1971; Jenkinson *et al.*, 1985; Dalenberg and Jager, 1989; Azam, 1990; Fox *et al.*, 1990; Azam *et al.*, 1991). In 1985 Jenkinson *et al.* introduced the term 'added nitrogen interaction' (ANI) to describe any increase (positive ANI) or decrease (negative ANI) in the mineralisation of native soil N following fertiliser application (Jansson, 1971). The reasons for the ANI have been described by Jenkinson *et al.*(1985). An ANI can be either real or apparent (Sørensen, 1982; Haynes, 1986; Azam *et al.*, 1993).

Controversy exists regarding the occurrence and origin of the ANI and may depend on the form of N added (Hart *et al.*, 1986). For example, Azam *et al.* (1993) found that 3 different plant materials had different effects on the mineralisation of soil N, resulting in either a positive or negative ANI. Negative ANIs were found after addition of soybean and corn residues, whilst addition of vetch increased native soil mineralisation. Mineralisation and plant availability of N from plant residues with low C:N ratios, such as leguminous green manures, may be increased by applications of inorganic N, particularly as NH_4^+ (Azam *et al.*, 1995).

The priming effect has been studied using ^{15}N tracers (Broadbent and Nakashima, 1971; Yaacob and Blair, 1980; Azam *et al.*, 1985). Yaacob and Blair (1980) found that addition of ^{15}N-labelled organic residues stimulated the release of native soil organic N, and thus had a positive priming effect, resulting in 13.8 % and 39.2 % of N uptake. Azam *et al.* (1985) reported that losses of N from ^{15}N-labelled legume material were increased in the presence of ^{15}N ammonium sulphate, which they claim is indirect evidence of increased mineralisation of the legume. However, addition of this ^{15}N-labelled ammonium sulphate had no apparent priming action on the soil N.

2.2.2 Leaching

Leaching is the removal of nutrients in solution from soil (Legg and Meisinger, 1982). Losses may range from 2-100 kg N ha^{-1} yr^{-1} (Hauck and Tanji, 1982). N is leached mainly as NO_3^-, although NH_4^+ may also be leached from sandy soils (Haynes, 1986). Thus, leaching represents the movement of the substrates for denitrification and nitrification down the soil profile. This has been shown to result in N_2O production during denitrification in subsoils and groundwater (Dowdell *et al.*, 1979).

The amount of N leached depends on the type of cropping system. Cultivation increases mineralisation and nitrification (section 2.2.1.2), resulting in enhanced leaching losses (Legg and Meisinger, 1982). Additions of fertiliser N can result in large losses, especially when combined with irrigation on light-textured soils (Haynes, 1986; Wild, 1988). Kolenbrander (1972) found that 3-5 % of 60 kg N ha^{-1} fertiliser applied to cultivated land was leached, but only 1 % of 250 kg N ha^{-1} applied to grassland was leached. The NO_3^- was assumed to be assimilated as rapidly as it was formed in the grassland. Leaching losses are strongly influenced by seasonal effects. The NO_3^- susceptible to leaching during temperate winters is mainly derived from organic N mineralised in the late summer and autumn, and any excess fertiliser N remaining in the soil after harvest (Powlson, 1988). Such leaching reduces the substrate for denitrification that might otherwise occur in these soils. In the spring nitrification and application of fertiliser may potentially lead to an accumulation of NO_3^- in the soil. Heavy rains before crop establishment can result in significant leaching of this inorganic N (Allison, 1973).

2.2.3 Plant recovery of N

Nitrogen is essential to plant growth as a component of chlorophyll, amino acids and enzymes. It is essential for carbohydrate utilisation, root development and activity, and is supportive to uptake of other nutrients (Alexander, 1977; Olson and Kurtz, 1982). N is usually taken up by plants as NH_4^+ and/or NO_3^-.Rate of available N uptake is controlled by its concentration in soil solution and by plant metabolism (Rao and Rains, 1976). Olson and Kurtz (1982) state that if any preference exists it is usually for NH_4^+ early, and NO_3^- late in the growing season. Available N is the substrate for nitrification and denitrification (section 2.2.5), and thus these processes are in competition with plants for available N. At times of greater plant requirement for N the potential for nitrification and denitrification is reduced. Recovery of applied N is lowered when there is a long fallow period before sowing of the following crop mainly as a result of losses by leaching, nitrification and denitrification. Therefore, it is important that incorporation of plant material, particularly leguminous, is succeeded by a crop that is efficient in taking up N, especially during the autumn (Ladd *et al.*, 1983; Ladd and Amato, 1986).

The demand for N varies between crop species (Wild and Jones, 1988). Differences in N recoveries between different species have been recorded (Yaacob and Blair, 1980). Studies with ^{15}N-labelled fertilisers and residues have shown that during the first season plants can only use between 30 and 70 % of applied fertiliser or crop residue N. Up to 40 % is retained in the soil as organic N, whilst between 10-40 % of applied N is assumed to be lost from the system (Legg and Meisinger, 1982; Ladd *et al.*, 1981b, 1983; Azam *et al.*, 1985, 1986; Wager *et al.*, 1985; Müller, 1987). Most of the N in incorporated plant material has been found to be retained in the soil after 1 year (Ladd *et al.* 1981b, 1983; Wagger *et al.*, 1985; Ladd and Amato, 1986). N recovery from labelled organic residues has been found to be lower than recovery from labelled fertilisers (Rees *et al.*, 1993). In 1981 and 1983 Ladd *et al.* used ^{15}N-labelled legumes, with C:N ratios of 11.1 and 14.9:1, to show that the proportions of legume derived N taken up by a first subsequent wheat crop ranged from 11-28 %. Total recoveries in crop and soil were more than 90 % of the legume N input. Greenhouse studies have shown recoveries of legume N by non-legumes ranging from 5 % (Azam *et al.*, 1985) to 55.5 % (Yaacob and Blair, 1980).

2.2.4 N fixation

The ability of nodulated legumes to fix atmospheric N_2 through the symbiotic relationship with rhizobium provides an additional source of N to the soil (Faris *et al.*, 1986; Frame and Newbould, 1986; Wagger, 1989; Marschner, 1995). At present the terrestrial input of N from biological N_2 fixation is between 139 to 170 $\times 10^6$ t N yr^{-1}, compared with 65 $\times 10^6$ t N yr^{-1} from inorganic fertiliser (Peoples and Craswell, 1992). Part of the fixed N remains in the soil as root residues and nodules, or returns to the soil in litter. In annual species some of the fixed N after harvest becomes available for the next crop. This fixed N provides a substrate for production of N_2O during nitrification and denitrification (section 2.2.5) after the incorporation of legume residues. Fixation of N is thought to be the main source of tropical forest N_2O.

The rate of fixation and N content vary depending on the species and genotype of the legume (Marschner, 1995). Royal Society (1983) data indicate great variations in amounts of N_2 fixed annually by nodulated temperate legumes. *Vicia faba* may fix 45-600, *Phaseolus* spp. 40-60, and clovers 45-673 kg N ha^{-1} yr^{-1} (Royal Society, 1983). Rhizobial infection, nodulation and N fixation may be inhibited by large amounts of mineral N in the soil, drought, flooding, extremes of temperature and unfavourable soil type or pH. This would explain why some authors have reported no or negative effects of ploughing in legumes on subsequent crops (Faris *et al.*, 1986).

2.2.5 N_2O losses

Nitrous oxide is one of the major greenhouse gases, accounting for 6-8 % of the present greenhouse forcing rate ascribed to anthropogenically derived gases (CO_2, CFC's, CH_4 and N_2O) (Hansson *et al.*, 1990). Because of the strong absorption of these gases in the infrared window (8-12 μm) only about 5 % of long-wave radiation can escape from the earth's surface into space, with more than 90 % of the radiation being radiated back to the earth's surface. Therefore, an increase in the concentration of a greenhouse gas initially reduces the flux of long-wave terrestrial radiation to space, as more becomes trapped in the troposphere. This results in a rise in temperature at the earth's surface, known as the greenhouse effect (Wang *et al.*, 1976). According to Houghton *et al.* (1990), N_2O has a global warming potential (GWP) of 290 per 1 kg of gas, referenced to CO_2 which has a GWP of 1. On a molar basis N_2O is approximately 250 times more potent than CO_2 as an absorber of infrared radiation (Robertson, 1993).

Nitrous oxide is also a major natural regulator of stratospheric O_3, which effectively controls the earth's ultraviolet-B radiation balance. In the stratosphere N_2O is destroyed by the following photochemical reaction with atomic oxygen, forming NO:

$$N_2O + O(^1D) \rightarrow 2NO$$

The NO produced catalyses the reduction in O_3 as follows (Crutzen, 1970; Hahn and Crutzen, 1981):

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO_2 + O \rightarrow NO + O_2$$

This depletion of the ozone layer is of concern because ozone screens out ultra-violet radiation which may cause skin cancer, cataracts and deficiencies in the immune system, and may also harm crops and aquatic systems. Due to the atmospheric lifetime of N_2O of about 150-170 years, these effects will be especially long-lasting (Robertson, 1993). Natural N_2O emissions may come from the soils and oceans, while anthropogenic emissions may come from a large number of weak sources (Khalil and Rasmussen, 1992).

At present the precise global N_2O budget is unknown. Robertson (1993) stated that almost 50 % (6.5 Tg N) of the sources remain to be identified in order to balance the known sinks (14.1 Tg

N). Each source emits small amounts of N_2O, so that precise estimates of annual emission rates may not be known for a long time. Until these anthropogenic sources of N_2O are better determined it will be difficult to devise strategies to reduce N_2O emissions. Its long atmospheric lifetime implies that the response to any corrective measures will be very slow (Robertson, 1993). Knowledge of the extent of contributions from agricultural and other intensively managed landscapes to global N_2O fluxes are particularly poor and estimated emission rates vary greatly (Granli and Bøckman, 1994). N_2O emissions are generally estimated as being higher and more variable from agricultural land than from uncultivated land or natural ecosystems (Bouwman, 1990b). Bouwman (1990a) estimated the contribution of soils to the total global N_2O emission as approximately 90 %. Unknown sources of N_2O account for almost twice the current global atmospheric loading rate of 3.5 Tg N_2O-N yr^{-1} (Robertson, 1993). Until 1989 industrial combustion was considered to be a substantial source of N_2O to the atmosphere (4 Tg N). However, Muzio *et al* (1989) discovered that this was an overestimation, with recent estimates of <0.01 Tg N_2O-N yr^{-1} derived from this source. Biomass burning during land clearing may also be a significant source of N_2O (Robertson, 1993).

In most global assessments the high N_2O fluxes from agriculture are assumed to result from fertiliser use (section 2.2.5.6). Direct fluxes of N_2O from agricultural sources may also result from the hydrologic transport of dissolved N_2O through ground water to surface waters (Granli and Bøckman, 1994). Soil may also act as a sink for atmospheric N_2O, depending on soil conditions and amount of fertiliser N applied (Ryden, 1981). Two microbial processes contribute most to the emission of N_2O from soils: denitrification and nitrification (Sahrawat and Keeney, 1986). Since soil is heterogeneous these two processes can proceed at the same time. Until about 1980 denitrification was considered to be the main source of N_2O production (Delwiche, 1981), but in 1981 Bremner and Blackmer showed that the contribution from nitrification was also significant.

2.2.5.1 Denitrification

Denitrification is the final stage of the N cycle, whereby fixed N is returned to the atmospheric pool of N_2. It is an irreversible process, and therefore represents a loss of N from the biosphere to the atmosphere (Haynes, 1986). Denitrification occurs in anaerobic sites in the soil where NO_3^- is reduced to NO, N_2O and N_2 by soil micro-organisms. These micro-organisms use NO_3^- in place of O_2 as the terminal electron acceptor in respiration (Powlson, 1988).

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

Many micro-organisms are capable of reducing NO_3^- to NO_2^-, but not all are able to completely reduce to N_2. The denitrifying bacteria of most significance in soil are heterotrophic and aerobic (Anderson and Levine, 1986). Denitrifying bacteria have a variety of incomplete reduction pathways, so that some produce only N_2O or N_2, whilst others can produce both (Robertson and Kuenen, 1991). The most prevalent denitrifiers are species of *Pseudomonas*, especially *P. fluorescens*, and *Alcaligenes* (Drury *et al.*, 1991). Some fungi have also been shown to be capable of reducing NO_3^- and NO_2^- anaerobically (Granli and Bøckman, 1994).

Both N_2O and N_2 are released as gaseous products of denitrification; the relative amounts of each gas depends on environmental conditions, especially pH (Focht, 1982). The intermediate products can accumulate and eventually escape from the soil. The rate of denitrification is usually low under environmental conditions reported to favour production of N_2O relative to N_2, such as low pH, low temperature and presence of O_2. Thus the relative production of N_2O is more pronounced under conditions marginal for denitrification, even though the total amount of N_2O may still be small. Under severe anaerobic conditions N_2O may even act as the main electron acceptor for denitrification, representing a sink for atmospheric N_2O (Blackmer and Bremner, 1976). Several reviews of denitrification are available within the literature (Delwiche, 1981; Payne, 1981; Firestone, 1982; Tiedje, 1988).

2.2.5.1.1 Factors affecting denitrification

Presence of NO_3^- or NO_2^- in the soil is necessary for N_2O production by denitrification. Mosier *et al.* (1983) and Blackmer and Bremner (1978) found that N_2O production from denitrification was strongly correlated with the NO_3^- content of the soil. The N_2O:N_2 ratio increases with increased NO_3^- and NO_2^- concentrations (Blackmer and Bremner, 1978). At high NO_3^- concentrations N_2O is the dominant gaseous product of denitrification and the reduction of N_2O to N_2 is inhibited. The environment in which the greatest quantities of NO_3^- are most likely to be found is agricultural land receiving substantial inputs of nitrogen fertilisers or manures (Vinten and Smith, 1993).

Temperature is important in controlling the rate of denitrification in soils (Freney *et al.*, 1979). Denitrification rates increase rapidly between 2 and 37 °C, with an optimum temperature of 25-30 °C (Bremner and Shaw, 1958). With increasing temperature the ratio of N_2O:N_2 evolved is reduced; the N_2O persisting for shorter times (Nômmik, 1956). Melin and Nômmik (1983) found that at 20 °C concentrations of N_2O and N_2 were equal. In the range of 10-35 °C a 10 °C increase doubles the rate of denitrification (Stanford *et al.*, 1975), reflecting the fact that denitrification is a biological process. At temperatures above 50 °C chemodenitrification may be important (Keeney *et al.*, 1979).

Soil moisture content affects denitrification and its gaseous products both directly and indirectly, by affecting the diffusion of O_2 into and through the soil, and by increasing microbial activity (Swift *et al.*, 1979). Denitrification rates are generally considered to be proportional to the moisture content of soils, being greater after rainfall events (Bremner and Blackmer, 1979; Denmead *et al.*, 1979a; Smith and Tiedje, 1979; Aulakh *et al.*, 1983; Vinther, 1984; Sexstone *et al.*, 1985; Mosier *et al.*, 1986; Jarvis *et al.*, 1991). At low soil moisture contents the main gaseous product of denitrification is N_2O (Freney *et al.*, 1979). Conversely, at field capacity N_2O emission rates are lower than N_2 emission rates (Focht *et al.*, 1979). Drying, or air-dry storage, of soil increases the amount of soil organic matter available to denitrifiers (Patten *et al.*, 1980). Alternate anaerobic-aerobic cycles have been shown to increase N_2O emissions, whereas continuous anaerobic conditions only produce relatively small amounts of N_2O (Sahrawat and Keeney, 1986).

The absence of, or restricted availability of, oxygen in soils or microsites is a prerequisite for denitrification (Groffman and Tiedje, 1991). The moisture content also indirectly affects the O_2 content and diffusion rate, and thus affects N_2O production. With reduced aeration the rate of denitrification increases, but the N_2O:N_2 ratio decreases due to the greater rate of reduction of N_2O to N_2 under anaerobic conditions. In accordance with this, Firestone *et al.* (1980) found that increased O_2 content enhanced production of N_2O relative to N_2 during denitrification. Smith *et al.* (1983) found that the critical redox potential for N_2O reduction and production occurred at +250 mV for pH 6.7 and 8.5, and at +300 mV for pH 5.

Organic carbon availability, for example from incorporation of plant material, is one of the most important factors affecting denitrifier activity in soil (Firestone *et al.*, 1980; Beauchamp *et al.*, 1989). Water soluble C and readily decomposable constituents of organic matter are the most effective in promoting denitrification (Lalisse-Grundmann *et al.*, 1988). Denitrifying bacteria use a wide variety of organic acids, carbohydrates and other organic compounds as carbon and energy sources when growing under aerobic conditions. However, under anaerobic conditions, these carbon sources may become limited (Beauchamp *et al.*, 1989; Webster and Goulding, 1989). Denitrification has been found to be proportional to soluble organic C in both unamended and residue amended soils (Paul and Beauchamp, 1989). Increased C supply reduces the ratio of N_2O:N_2 evolved during denitrification.

The optimal pH range for denitrification is between 7 and 8 (Wiljer and Delwiche, 1954). Although denitrification occurs in soils covering a wide range of pH, it is slow below pH 6 (Delwiche, 1981; Firestone, 1982). Below pH 6 the N_2O:N_2 ratio increases, as reduction of N_2O

is inhibited (Koskinen and Keeney, 1982; Firestone and Davidson, 1989). Firestone *et al.* (1980) observed an interaction between pH and NO_3^- substrate levels denitrification, with low pH having a greater effect on the $N_2O{:}N_2$ ratio at high NO_3^- levels.

2.2.5.2 Chemodenitrification

In addition to the above biological process, chemodenitrification may also contribute to production of N_2O (Chalk and Smith, 1983; Anderson and Levine, 1986). However, research has established the importance of biological denitrification and nitrification as the main processes for N_2O production. NO_2^- may react with organic compounds, such as amines, to form N_2, NO and N_2O (Mosier *et al.*, 1983; Sahrawat and Keeney, 1986; Granli and Bøckman, 1994). Accumulation of NO_2^- is reported to occur in both acid and alkaline soils following application of alkaline-producing fertilisers, especially at high pH, or at microsites where the fertiliser band is situated (Chalk and Smith, 1983). The most common product of chemodenitrification is NO, which is found in only trace amounts from biological denitrification. Thus, the presence of large amounts of NO is indicative of chemodenitrification.

2.2.5.3 Nitrification

Nitrification is an aerobic process, performed by both autotrophs and heterotrophs, although autotrophic nitrification is the most studied (Granli and Bøckman, 1994). Nitrification occurs in two stages (Haynes, 1986), mediated by separate groups of micro-organisms: the oxidation of NH_4^+ to NO_2^- by ammonium oxidisers (prefix *Nitroso-*, for example *Nitrosomonas*), and the further oxidation of NO_2^- to NO_3^- by nitrite oxidisers (prefix *Nitro-*, for example *Nitrobacter*):

$$NH_4^+ + 3/2O_2 \rightarrow NO_2^- + 2H^+ + H_2O + E$$

$$NO_2^- + 1/2O_2 \rightarrow NO_3^- + E$$

Nitrification in soil is a significant source of N_2O (Lipschultz *et al.*, 1981; Bremner and Blackmer, 1981; Sahrawat and Keeney, 1986). According to Groffman (1991), N_2O is formed from nitrification as a result of two processes. Ammonium oxidisers can use NO_2^- as an alternative electron acceptor when O_2 is limiting, and produce N_2O (nitrifier denitrification). Also, intermediates between NH_4^+ and NO_2^- can chemically decompose to N_2O, especially under acidic conditions (a kind of chemodenitrification). Nitrite oxidisers do not usually produce N_2O (Goreau *et al.*, 1980). Heterotrophic nitrifiers can also denitrify and produce significant amounts of N_2O.

2.2.5.3.1 Factors affecting nitrification

Nitrifying bacteria have a high optimum temperature for activity reaching a maximum at about 25-30 °C (Haynes, 1986). Under laboratory conditions nitrification rate has been shown to increase with temperature over the range 2.5 °C to 20 °C, but below 4 or 5 °C nitrification is slow (Addiscott, 1983). Bremner and Blackmer (1981) reported that an increase in soil temperature from 5 to 30 °C also increased the rate of emission of N_2O from well aerated soil samples.

Nitrification is an aerobic process. Maximum nitrification rates have been reported at about 50-60 % WFPS (Linn and Doran, 1984). At low moisture contents microbial activity is depressed and mineralisation of organic N will be slow, thereby limiting the amount of NH_4^+ available for nitrification (Goodroad and Keeney, 1984). However, nitrifiers can produce NO_3^- even below the wilting point of plants.

Concentration and availability of NH_4^+ are crucial to nitrification, provided that other environmental factors are not limiting (Yoshida and Alexander, 1970). Oxidation of NH_4^+ is more rapid than formation of NH_4^+ through mineralisation, so that NH_4^+ is often limiting for nitrification (Macdonald, 1986). Blackmer *et al.* (1980) reported that N_2O production increased with increasing NH_4^+ concentration, up to about 1 g NH_4^+-N l water^{-1}. Such high concentrations may occur around fertiliser granules immediately after fertilisation.

Growth and metabolism of autotrophic nitrifying bacteria is optimal between pH 7 and pH 8. As confirmation of this, Yoshida and Alexander (1970) demonstrated that increasing pH from 6 to 8 strongly increased N_2O evolution in cell suspensions of *Nitrosomonas europea*. Bremner and Blackmer (1978, 1981) found that N_2O emission rates increased with increase in pH. Approximately 3-fold higher N_2O emissions were measured from a well aerated and $(NH_4)_2SO_4$ amended soil at pH 7-8 than at pH 6.8 or 5.4.

2.2.5.4 Variability in emissions

Spatial, diurnal, seasonal and annual variabilities in N_2O emissions complicate estimates, and make comparisons of published data very difficult (Goodroad *et al.*, 1984). Several workers have measured marked diurnal variations in the rate of N_2O emission from soils (for example, Denmead *et al.*, 1979b; Ryden *et al.*, 1979; Matthias *et al.*, 1980; Blackmer *et al.*, 1982; Conrad *et al.*, 1983; Christensen, 1983). In general, studies have indicated that the N_2O flux is highest either in the early-mid afternoon (Denmead *et al.*, 1979b; Ryden *et al.*, 1979; Christensen, 1983), or late afternoon/evening (Blackmer *et al.*, 1982). Nevertheless, Blackmer *et al.* (1982) state that there is no short time during a 24 hour period that is always satisfactory for assessing the amount of N_2O evolved during that period. Ryden *et al.* (1979), Conrad *et al.* (1983) and Denmead *et al.* (1979b) attributed the peak emissions in the early afternoon to variations in topsoil temperature, with no time lag between the maximum and minimum N_2O evolution and the maximum and minimum surface soil temperatures. However, in contrast to this, Blackmer *et al.* (1982) observed diurnal changes in N_2O emissions that were 2 - 12 hours behind surface soil temperatures. The important seasonal effect of temperature on N_2O emissions is confirmed by increased emissions reported during the spring, resulting from renewed microbial activity due to increasing temperature (Van Cleemput *et al.*, 1994).

Large spatial variabilities of N_2O fluxes have been measured in the field as a result of changing environmental conditions, especially during warm, wet periods (Goodroad and Keeney, 1985). Spatial variability may be large with N_2O emitted from different positions in the same field often varying by a factor of 10 or more (Granli and Bøckman, 1994). According to Christensen *et al.* (1990), Smith and Arah (1990) and Ryden *et al.* (1979), such spatial variability is mainly caused by hotspots of microbial activity and C in the soil. These may last for periods ranging from days to weeks (Christensen *et al.*, 1990). Any improvement in predicting N_2O losses from soils requires greater understanding of the locations of hotspots, both temporally and spatially (Grundmann *et al.*, 1988).

2.2.5.5 Site of N_2O production in soils

Goodroad and Keeney (1985) found that following heavy rainfall the site of N_2O production moved from the surface deeper down the soil profile. They concluded that nitrification was the predominant source of N_2O production near the soil surface, and N_2O was produced by denitrification at depth after NO_3^- leaching. However, contrary to this, Roiston *et al.* (1976) and Denmead *et al.* (1979b) reported the zone of maximum denitrification to be close to the soil surface.

2.2.5.6 N_2O from fertilised soils

By providing an additional N source, mineral fertilisers increase the short-term emissions of N_2O from soil (Breitenbeck *et al.*, 1980; Ryden and Lund, 1980; Duxbury *et al.*, 1982; McElroy and Wofsy, 1985; Sahrawat and Keeney, 1986; Robertson, 1993; McTaggart *et al.*, 1994; Mosier, 1994; Bouwman, 1996). Bouwman (1996) estimated that 1.25 % of fertiliser N is lost as N_2O-N, representing a global loss of 1 Tg N_2O-N yr^{-1}. According to Ryden and Lund (1980), annual losses of N as N_2O from fertiliser amended soils may be as high as 40 kg ha^{-1}, whereas annual emissions from unfertilised soils are usually <1-2 kg N ha^{-1} (Sahrawat and Keeney, 1986).

Typically, increases in N_2O emissions after fertilisation are either immediate or lag a few days behind the date of application (Conrad *et al.*, 1983; McTaggart *et al.*, 1994). Peak emissions vary considerably in magnitude (Ryden, 1981). This peak may last between several days and a few weeks, often being ended with a sharp decrease (Conrad *et al.*, 1983; Van Cleemput *et al.*, 1994). Secondary peaks may occur following rainfall, until there is a depletion of fertiliser in the upper soil layers (Seiler and Conrad, 1981; Conrad *et al.*, 1983). It should be noted that in most experiments reported in the literature N_2O emissions were only measured over the period immediately after fertilisation, encompassing the large fluxes. Few studies have been undertaken over a long enough time period to measure trends in annual emissions. Therefore, the gradual loss of residual fertiliser N as N_2O remains unquantified. Bouwman (1996) suggested that if N_2O measurements were extended over longer periods, more of the N_2O emissions induced by fertilisation would be captured.

Fertiliser type, the fertiliser's physical state when applied (dry or liquid), the application procedure and timing of application are important in determining N_2O emissions (Mosier and Hutchinson, 1981; Mosier *et al.*, 1982, 1983; Duxbury and McConnaughey, 1986; Bouwman, 1996). Applications of NO_3^- often result in significantly lower N_2O evolution rates than applications of NH_4^+ (Conrad and Seiler, 1980; Breitenbeck *et al.*, 1980; and Bremner and Blackmer, 1981). This is in accordance with nitrification being a process for N_2O production. However, Clayton *et al.* (1997) found that in cool, wet conditions, emissions after NO_3^- application were significantly higher than after NH_4^+ application. Conrad *et al.* (1983) found significantly greater N_2O emissions where the fertiliser had been worked into the upper 0.1 m of soil, compared with where it had been surface distributed and subject to volatilisation following rain. Fertiliser applications in periods when the crop takes up N will potentially reduce losses of N by nitrification, denitrification and leaching. Rainfall following fertilisation often results in subsequent N_2O fluxes (Webster and Dowdell, 1982; Conrad *et al.*, 1983). Powlson *et al.* (1992) estimated that 2.6 % of fertiliser N was denitrified for every 10 mm rain that fell during the critical 3 week period following fertiliser application.

Emissions of N_2O have been reduced through the use of nitrification inhibitors (Magalhães *et al.*, 1984; Willison and Anderson, 1991; Bronson *et al.*, 1992; McTaggart and Smith, 1996). Nitrification inhibitors slow down NH_4^+ oxidation to NO_3^- (Aulakh *et al.*, 1984a; Bronson *et al.*, 1992). For example, nitrapyrin (2-chloro-6-(trichloromethyl)-pyridine) inhibits the NH_4^+ oxidation step for up to 4-8 weeks (Bremner and Blackmer, 1978; Aulakh *et al.*, 1984a; Bronson *et al.*, 1992). When nitrification is inhibited less N is lost by leaching and more is taken up by plants as NH_4^+ or is immobilised. Dicyandiamide (DCD) is another nitrification inhibitor added to some commercial fertilisers that inhibits the first step of nitrification. Skiba *et al.* (1993) found that addition of DCD reduced emissions of N_2O in dry conditions by 40 %. However, in wet conditions, where denitrification was the main source of N_2O, emissions were not reduced by DCD. Similarly, McTaggart and Smith (1996) found that addition of DCD to winter wheat, winter barley and oilseed rape crops reduced emissions by up to 54 %.

2.2.5.7 N_2O from crops and vegetation

Growing plants affect soil microbial processes by stimulation of microbial activity by root material and exudates, root consumption of water and oxygen, depletion of available NO_3^- and NH_4^+, alteration of soil structure and the creation of channels for gas transfer, and a reduction in diurnal variations in soil temperature as a result of plant cover (Stefanson, 1972).

Most studies in the literature have reported higher N_2O losses in the presence of growing plants, particularly legumes, than from bare soil (for example, Duxbury, 1984; Klemedtsson *et al.*, 1987; Kilian and Werner, 1996). Emissions of N_2O from cropped soils have been found to vary depending on species grown, although differences are not consistent. Apart from the difference between legumes and non-legumes the type of crop has been found not to greatly influence N_2O emissions (Mosier *et al.*, 1986; Granli and Bøckman, 1994; Kilian and Werner, 1996). However, variations in timing of emissions may be apparent due to differences in N uptake between crops. Van Cleemput *et al.* (1992) found that N_2O emissions from grassland was 15 % higher than from crops of maize, wheat, sugarbeat and potato. Mosier *et al.* (1986) reported total N_2 and N_2O emissions for the whole growing season of 4.5 kg N ha^{-1} from a maize crop and 1.5 kg N ha^{-1} from a barley crop. Where denitrification is NO_3^- limited the presence of roots can reduce denitrification as both roots and micro-organisms compete for the NO_3^-. Thus in some circumstances bare soil may emit more N_2O than cropped soil. For example, Duxbury *et al.* (1982) found 2-5 times higher annual N_2O emissions from fallow than from soils cropped to sugarcane or St. Augustine grass.

Legume crops can further increase the N_2O emitted from soils. According to Eichner (1990), estimates of N_2O emissions from soils cropped with legumes range from 0.34 to 4.6 kg N_2O-N ha^{-1} yr^{-1}. This includes natural emissions, emissions associated with cultivation, and emissions from N fixed by the legume. Duxbury *et al.* (1982) suggested that the presence of legumes in pastures can increase N_2O emissions by a factor of 2-3. In accordance with this, Galbally (1994) measured an annual average N_2O emission of 0.35 kg N ha^{-1} yr^{-1} from a legume pasture in Australia. Bremner *et al.* (1980) found that emissions from unfertilised soyabean averaged 1.2 kg N_2O-N $ha^{-1}yr^{-1}$. In 1984 Duxbury measured higher annual emissions of 2-4.6 kg N_2O-N $ha^{-1}yr^{-1}$ from unfertilised alfalfa. However, it must be noted that the contribution of residual N fixed by the previous season's legume crop are often not accounted for in these measurements. Rhizobia are thought to contribute to N_2O emissions from growing legumes (Smith and Smith, 1986). Nodule denitrification is continuous, occurring simultaneously with N_2 fixation (Smith and Smith, 1986; Kilian and Werner, 1996).

High N_2O emissions have been found where plants have been cut or damaged and the roots remain in the soil (Conrad *et al.*, 1983; Beck and Christensen, 1987). Beck and Christensen (1987) found that this was noticeable immediately after cutting of grass, when N_2O emissions increased by a factor of 10 or more. This may have been due to organic C released from the roots after cutting, stimulating denitrification. The temperature of the soil may also have been increased due to greater irradiation absorbance.

In general, under a temperate climate, periods of increased N_2O emissions are observed in the spring and early autumn, but this is confounded by the fact that these are times of fertiliser application and irrigation. The main period of cereal crop uptake of NO_3^- is in the early summer. Mosier *et al.* (1986) measured maximum N_2O emissions from a barley crop in May and from a maize crop in July. Fluxes are typically low early in the growing season, increasing after the first irrigation, and then returning to pre-irrigation levels (Eichner, 1990).

2.2.5.8 N_2O emissions after incorporation of plant material

The return of plant material to agricultural soil is considered desirable as it conserves resources (Atallah and Lopez-Real, 1991; McKenney *et al.*, 1993). However, this practice has the potential for increasing N_2O emissions (Aulakh *et al.*, 1983, 1984b). Although there are numerous reports in the literature on the recovery and distribution of N in residue amended soils, data on the effects of addition of plant material on N_2O from nitrification and/or denitrification are comparatively sparse.

Incorporation of plant residues has been reported to stimulate both nitrification and denitrification (Jansson and Clark, 1952; Bremner and Shaw, 1958; Ryden and Lund, 1980; Aulakh *et al.*, 1984b; de Catanzaro and Beauchamp, 1985). The addition of readily biodegradable organic material to well-aerated soil enhances mineralisation (section 2.2.1.1), thereby increasing O_2 consumption by heterotrophs (Drury *et al.*, 1991; McKenney *et al.*, 1995). Anaerobic microsites may be created resulting in denitrification, and gaseous losses of NO, N_2O and N_2 (Dowdell *et al.*, 1979b; Beauchamp *et al.*, 1989; Smith and Arah, 1990; McKenney *et al.*, 1993; Granli and Bøckman, 1994). N_2O is formed unless the decomposition of the organic material creates sufficient anaerobic conditions to cause reduction to N_2 (Firestone *et al.*, 1980), or the temperature is so low that extensive formation of N_2O does not take place before the next crop has taken up the N. Fresh plant material also helps to retain moisture within the soil, often allowing anaerobic conditions to develop (Harper and Lynch, 1981). N_2O may also be released from nitrification under aerobic conditions during decomposition (Haynes, 1986; Groffman, 1991). The losses of N_2O from these two processes after incorporation of plant material have been reported to be higher than losses from bare soil (Jansson and Clark, 1952; Denmead *et al.*, 1979b). For example, Aulakh *et al.* (1984b) found that incorporation of wheat straw residues doubled gaseous N losses over a growing season, compared to those from bare soil, by supplying C to the nitrifying and denitrifying micro-organisms.

Nitrous oxide emissions from plant residue amended soil varies with the type of residue, the residue composition, and biomass incorporated (Reinertsen *et al.*, 1984; Paul and Beauchamp, 1989). Emissions are further complicated by other factors influencing decomposition, such as weather, soil temperature, moisture content, soil type and type of cultivation (Frankenberger and Abdelmagid, 1985). Although the effects of crop type on residue decomposition are well documented (section 2.2.1.2), studies of their influence on N_2O losses are comparatively sparse. In 1991 Aulakh *et al.* emphasised the necessity for further studies comparing different crop residues encompassing a wide range of C:N ratios.

The C:N ratio of the plant material, or that of the soil after addition, is considered important in decomposition (section 2.2.1.2). In accordance with this, greater N_2O emissions have generally been measured after incorporation of material with a low C:N ratio, such as legumes, than cereal straw (Goodroad *et al.*, 1984; de Catanzaro and Beauchamp, 1985; McKenney *et al.*, 1993). For example, Goodroad *et al.* (1984) found that addition of alfalfa residues to soil resulted in greater N_2O emissions than those following addition of rye, which had a higher C:N ratio than the alfalfa. De Catanzaro and Beauchamp (1985) also compared N_2O emissions from alfalfa and cereal straw residue amended soils. They also found that the alfalfa amended soil produced significantly higher amounts of N_2O and CO_2, and lost NO_3^- more rapidly than the same amount of added straw.

McKenney *et al.* (1993) reported that introduction of dried hairy vetch, red clover, annual ryegrass, reed canarygrass and corn residues to soil rapidly promoted denitrification through the supply of available organic C. The increase in net N_2O production was evident almost immediately following establishment of anaerobic conditions. Except for the annual ryegrass, the cumulative losses of N_2O were inversely related to the C:N ratio of the residue.

As discussed above in section 2.2.1, the often rapid decomposition of green manures, releasing N and C to soil micro-organisms, means that there is a great potential for N_2O production after their incorporation. To date, this potential remains almost completely unexamined. Aulakh *et al.*

(1983) found that green manuring of clover resulted in significantly greater gaseous N (N_2O + N_2) losses than when the clover had been removed and the soil fallowed. They emphasised that even though the higher gaseous losses were associated with higher levels of soil NO_3^--N, the addition of such easily decomposable C in the plant material, with a low C:N ratio, greatly enhanced denitrification. These emissions were also dependent on the rainfall, soil moisture and temperature both at and following incorporation. Approximately 40 % of the N added to the soil by green manured clover residues was mineralised by the end of the following fallow period. Similarly, Redman *et al.* (1988) measured rapid initial decomposition of a green manured pea crop, with small fluxes of N_2O measured from denitrification in the autumn.

Different placements of plant material in the soil varies the supply of organic C and N to micro-organisms and changes the soil moisture/aeration status around the incorporated material (Douglas *et al.*, 1980; Aulakh *et al.*, 1991a). Hotspots of microbial activity may occur, resulting in differences in N_2O emissions (Christensen *et al.*, 1990). Placement of plant material at depth may result in N_2O produced at depth being reduced to N_2 before diffusion out of the soil and measurement at the surface (Jury *et al.*, 1982; Arah *et al.*, 1991).

Aulakh *et al.* (1991) found that the inverse relationship between denitrification and C:N ratio of residues was greater when the residues were incorporated into the soil than when they were surface placed. However, this relationship varied with time. Initially, incorporation resulted in higher denitrification rates, but as the experiment proceeded the cumulative denitrification losses between placement methods were not significantly different. Earlier, in 1983, Aulakh *et al.* found that despite gaseous N emissions being greater where clover was green manured compared with where it had been removed, differences between tillage treatments were very small and the contribution of lower soil horizons to losses was low.

2.3 Methods for field measurements of N_2O

Methods for measuring N_2O emissions from agriculture are reviewed by Mosier (1990), but are complicated by large spatial and diurnal variability (section 2.2.5.4).

2.3.1 Chamber method

2.3.1.1 Closed chambers (cover boxes)

This is a simple method by which a sealed enclosure is placed over the soil surface and the change in N_2O concentration in the enclosure is measured over periods of time, normally of 1 hour. Gas samples of a few millilitres are taken, and the N_2O concentration can be directly analysed by gas chromatography, using an electron capture detector. Further details on design are presented in Chapter 3. However, the effects of an increasing N_2O concentration on the rate of diffusion into the chamber are uncertain (Arah, 1988), and the soil under the chamber is isolated from fluctuations in atmospheric pressure which affect mass flow. Nevertheless, the chambers are simple to construct and relatively cheap (Matthias *et al.*, 1980). For examples of use see Ryden *et al.* (1979), Mosier *et al.*, (1982), Goodroad and Keeney (1984), Clayton *et al.* (1994), McTaggart *et al.* (1997).

2.3.1.2 Open chambers

These are chambers through which the atmosphere is continually pumped through a trap which removes the N_2O, preventing a concentration build up. However, uncertainties are introduced relating to the effect of the forced flow of gas over the soil surface. For examples of use see Ryden *et al.* (1979) and Christensen (1983).

2.3.1.3 Large chambers

Fluxes of N_2O can be measured from areas of land 2-3 orders of magnitude greater than those normally studied by the use of small chambers. A series of plastic hoops are covered with either tent fabric or polyethylene sheet to form a hemi-cylindrical chamber. The accumulation of N_2O is measured with a Fourier transform infrared spectrometer (Galle *et al.*, 1994), or with a long-path infrared absorption spectrometer tuned to a N_2O absorption band at 2180-2200 cm^{-1} (Smith *et al.*, 1994).

2.3.2 Measurements in soil

The concentration of N_2O in soil air may be measured at various depths by insertion of probes into the soil (Mosier and Hutchinson, 1981; Arah *et al.*, 1991). This method is cheap and soil is only disturbed initially during probe insertion. However, the usefulness depends on soil conditions. There is minimal spatial and temporal resolution, and there is uncertainty in the value of the soil-gas diffusivity, making the calculation of emission fluxes difficult.

2.3.3 Micrometeorological

Micrometeorological methods integrate large surface areas, reducing problems of spatial variability that are inherent with chambers, and reduce interference of the immediate environment. However, there is a lack of chemical N_2O detectors with a sufficiently rapid response time and sensitivity to permit the eddy correlation method to be used. Most micrometeorological methods are based on the assumption that the flux to or from the surface is identical to the vertical flux measured at the reference level some distance above the surface. They also require extensive uniform surface areas and constant atmospheric conditions during each measurement (Mosier, 1990). The two general techniques used are eddy correlation and flux-gradient methods (Baldocchi *et al.*, 1988; Mosier, 1990). The use of micrometeorological methods are further examined by Smith *et al.* (1994) and Christensen *et al.* (1996).

CHAPTER 3 GENERAL MATERIALS AND METHODS

3.1 Routine storage of soils

Soil samples were stored at 5 ^{o}C overnight, where analysis was to be undertaken the following day. When this was not possible, samples were frozen at -15 ^{o}C, and later thawed for approximately 12 hours prior to analysis.

3.2 Gravimetric soil moisture contents

Unless otherwise stated, soil was sampled in the field to a depth of 0.2 m using an auger. This soil was thoroughly mixed prior to analysis. A known weight of fresh soil (between 10 and 20 g) was oven dried for 48 hours at 100 ^{o}C and then reweighed and the moisture content calculated from the loss of weight.

3.3 Determination of available soil N

A known weight of fresh soil (approximately 20 g) was shaken with 100 ml of 1M KCl extracting solution for one hour, giving a 1:5 ratio of soil to extractant. The extractant was filtered through Whatman No. 42 filter paper, and stored at 5 ^{o}C until analysis, which was always within two weeks of extraction.

The concentration of available N in the filtered extractant was determined by continuous flow analysis on a Chemlab Instruments autoanalyser. Determination of NO_3^--N was by the modified Griess-Ilosvay method (Best, 1976), using copper/hydrazine as a reducing agent in place of cadmium. Determination of NH_4^+-N was by the method of Crooke and Simpson (1971).

3.4 Biomass N and C

Alcohol-free chloroform is required for biomass C fumigation. This was prepared by washing commercial chloroform with 5 % by volume concentrated H_2SO_4, by shaking in a separating funnel. The acid was separated off and the chloroform was then washed with 10 rinses of distilled water (Brookes *et al.*, 1985).

10 g soil was placed in a sealable graduated tube and fumigated in a vacuum oven with 50 ml chloroform. The oven was evacuated with a pump until the chloroform began to evaporate, or

the internal oven pressure was in excess of 800 mbar. The oven was sealed and left for 24 hours. After this time excess chloroform was evaporated by continual re- evacuation. The graduated tube was sealed and incubated in the dark at 20-25 °C for 10 days. The tube headspace was then sampled and analysed for CO_2 using a gas chromatograph (Pye Unicam 104). These fumigated soils were extracted with 1M KCl (1 g:5 ml) and analysed for NH_4^+-N and NO_3^--N (as described above).

The biomass C and N were calculated as follows:

Biomass C ($mg\ kg^{-1}$) = Cf / 0.41

and

Biomass N ($mg\ kg^{-1}$) = Nf / [(-0.014*Cf/Nf) +0.39] (Voroney and Paul, 1984),

where

Cf = CO_2 emitted $mg\ kg^{-1}$;

Nf = final NH_4^+-N ($mg\ kg^{-1}$) - initial NH_4^+-N ($mg\ kg^{-1}$).

3.5 Determination of ^{15}N enrichment of soils

The method of Brookes *et al.* (1989) was followed for determination of the ^{15}N enrichment of the available N pools. Soil samples were analysed for available N (as described above). A volume of 1M KCl extract, sufficient to give a total concentration of between 100-350 μg N, was placed in a kilner jar which had a disc of Whatman GF/D filter paper inserted on a syringe needle attached to the inside of the lid. 10 μl of $KHSO_4$ were pipetted onto this filter paper. Exposure of the filter paper and $KHSO_4$ to the atmosphere was minimised. For ^{15}N-NH_4^+ analysis 0.3 g MgO, or for both ^{15}N-NH_4^+ and ^{15}N-NO_3^- analysis 0.4 g Devarda's alloy followed by 0.3 g MgO, were added to the solution in the kilner jar which was then sealed and left in the dark at room temperature for 6 days. After 6 days the needle and filter paper were dried in a desiccator for at least 24 hours, after which the filter paper was placed in a tin cup, ready for analysis by mass spectrometry. If previous analysis was for ^{15}N-NH_4^+ the procedure was repeated following addition of 0.4 g Devarda's alloy to the solution to reduce the NO_3^- to NH_4^+ for analysis for ^{15}N-NO_3^-.

3.6 Preparation of plant material for analysis

All plant samples were oven dried at 100 °C for 48 hours and dry matter yields were recorded. The dried samples were coarsely milled in a hammer mill, and then subsamples (approximately 5 g) were finely ground in an agate ball mill to produce a fine consistency. This was necessary to achieve adequate homogeneity in the very small samples taken for ^{15}N analysis (Robinson and Smith, 1991). The samples were then ready for analysis of total C and N contents by mass spectrometry.

3.7 Mass spectrometry

Mass spectrometry determines the isotopic composition of a sample by separating charged ions on the basis of their mass to charge ratio, and determining their relative proportions (Robinson and Smith, 1991). In the case of N analysis this involves the conversion of N in the sample to N_2. The N_2 molecules are ionised and then passed through a magnetic field which separates the N into 3 components: $^{14}N_2$, $^{14}N^{15}N$ and $^{15}N_2$, with masses of 28, 29 and 30, respectively. The ^{15}N enrichment of the sample can be determined from the relative amounts of each component, or more commonly from the ratio of the peaks due to $^{14}N_2$ and $^{14}N^{15}N$ (Hauck and Tanji, 1982).

$$\text{atom \% }^{15}\text{N enrichment} = \frac{100}{2\,R+1}$$

Where R = the ratio of the peaks due to $^{14}N_2$ and $^{14}N^{15}N$.

Plant and soil extracts were analysed for ^{15}N content using a single inlet VG Isogas MM622 triple detector mass spectrometer linked to a Carlo Erba 1400 Automatic Nitrogen Analyser, which converts N compounds to N_2 by the Dumas oxidation-reduction procedure. Subsamples of the prepared plant material and the filter papers were accurately weighed out into small tin cups and sealed for analysis. In this system at least 100 µg of N is required to give an accurate reading. For young plant samples with N contents greater than 1.5 %, a sample of 10 mg is sufficient. More mature plant samples, including straw, and the soil extracts may require subsamples of 20-30 mg to ensure that there is sufficient N present for analysis. Reference values are obtained from standards of known N and ^{15}N content in the same batch as the samples. These standards allow the mass spectrometer computer software to calibrate the ion beam currents and current ratios obtained for the samples and calculate values for total percentage N and ^{15}N enrichment.

For analysis of total C in plant samples the C is converted to CO_2. The CO_2 molecules are separated according to their mass/charge ratios by fixed magnetic and electrical fields. Estimation of total C is based on the molecular ion currents detected at masses 44, 45 and 46.

Checks undertaken have shown that the variation between replicate 5 g subsamples of plant material selected for grinding in the agate ball mill, and that between replicate 10 mg portions of the subsequently ground material, is very much less than is commonly observed between replicate field plots (Robinson and Smith, 1991). As a further check, any samples whose replicate ^{15}N enrichment values differed by greater than 0.003 atom % were repeated. Data were corrected for any electronic drift between successive measurements of reference materials.

3.8 Measurement of gas fluxes in the field

Emissions of N_2O were measured in the field using closed flux chambers (cover boxes) installed on each plot. These chambers were 0.2 m lengths of polypropylene piping (0.4 m diameter) fitted with a 45 mm wide outward-facing polyvinylchloride flange at one end (Smith K.A. *et al*, 1995). Squares of 3 mm aluminium sheet, with rubber draught excluder on the underside, were used as removable lids for these chambers (Clayton *et al.*, 1994). Each lid was fitted with a sampling port, closed by a 3-way tap. Chambers were inserted to a depth of approximately 50 mm into the soil, using a metal cutting ring to create a groove first, if necessary. Care was taken to minimise any undue disruption to the soil, particularly to that inside the chamber, during insertion. The chambers remained in place on their respective plots throughout each experiment. Where possible, sampling was undertaken at approximately the same time of day on each sampling date, to minimise any effects of diurnal variation in N_2O emissions. One hour after closing the lid, duplicate gas samples (5 ml) were taken from the chambers using airtight greased glass syringes suitable for sample storage for at least a few hours (Smith K.A. *et al.*, 1995). The samples were brought back to the laboratory for analysis by gas chromatography on the same day.

3.9 Gas analysis by gas chromatography

Gas samples were analysed for N_2O in a Hewlett Packard 5890 gas chromatograph (GC) fitted with an electron capture detector. Detector and oven temperatures were 380 and 50 ^{o}C, respectively. The system was front and back-flushed to prevent any gas with a column retention time less or greater than N_2O from also being analysed.

An autoinjection system for GC analysis of N_2O was used to allow efficient, rapid analysis of multiple gas samples (Arah *et al.*, 1994). The autoinjection system consists of two rotary valves, each with 16 sampling ports, giving a total of 32 ports, to which syringes containing the samples could be attached. The autoinjector is computer controlled and can be programmed to sample over any time interval, from any number of ports, and to allow single or multiple sampling. It has 2 sample loops enabling gas samples to be sent to two different column/detector systems for different gas analyses. The autoinjector control program also controls the front and/or backflushing operation described above.

The N_2O fluxes were calculated as:

$$\text{Nitrous oxide flux (g } N_2O\text{ - N ha}^{-1}\text{ day}^{-1}) = \frac{c \times h \times 168}{t}$$

where c = change in concentration of N_2O (ppm)
h = height of chamber lid above the soil surface (cm)
t = length of time chamber was sealed (minutes)

assuming 1 mole of gas occupies 24 litres at ambient temperature (20 ^{o}C).

A Pye Unicam 104 gas chromatograph fitted with a thermal conductivity detector was used for analysis of CO_2 samples. Detector and oven temperatures were 120 ^{o}C and 70 ^{o}C, respectively.

3.10 Statistical methods

Data were analysed using the MINITAB statistical package. Firstly, treatment means and standard errors were calculated. Error values presented in text and tables, and error bars on graphs represent ± one standard error. Analysis of variance was undertaken on 3 or more replicates. Prior to this analysis, data sets were tested for normality and log-transformed where appropriate (Parkin and Robinson, 1993). In each case the null hypothesis was tested that there was no difference between treatments. Where applicable, t-test, correlation and regression analyses were undertaken to help explain effects of treatments applied.

CHAPTER 4 EMISSIONS OF NITROUS OXIDE FOLLOWING INCORPORATION OF GRASS, CLOVER AND OTHER GREEN MANURES

4.1 Introduction

Previous work has suggested that incorporation of grass swards and crop residues may make a significant contribution to emissions of N_2O from agricultural systems (Jansson and Clark, 1952; Ryden *et al.*, 1979; Aulakh *et al.*, 1983, 1984b; de Catanzaro and Beauchamp, 1985). The N_2O is produced by nitrification and/or denitrification, depending upon the soil environment and nature of the material incorporated (section 2.2.5.8). As discussed above in section 2.2.5.8, the addition of organic material to soil stimulates microbial activity, leading to O_2 consumption, and the development of anaerobic microsites in the soil, creating conditions ideal for denitrification (Drury *et al.*, 1991; Granli and Bøckman, 1994; McKenney *et al.*, 1995). N_2O is lost unless anaerobiosis results in reduction to N_2, or temperature is extremely low. At the same time N_2O may be released during nitrification in the better aerated regions of the soil profile (Haynes, 1986; Groffman, 1991). At present there are no guidelines available for good management practice to limit N_2O emissions after organic amendments to soil.

Microbial activity and production of N_2O varies with the type of residue incorporated, with different species decomposing at varying rates due to their composition, biomass and the amount of plant material incorporated (Reinertsen *et al.*, 1984; Aulakh *et al.*, 1991a,b). Decomposition rates are further determined by soil and air temperatures, soil moisture content, soil type and condition, and type of cultivation (Frankenberger and Abdelmagid, 1985; Stott *et al.*, 1986). The C:N ratio of the plant material, or that of the soil after addition, is generally considered to be an important determinant of rates of decomposition (section 2.2.1.2).

Incorporation of organic material with a low C:N ratio releases mineral N on decomposition, creating conditions suitable for N_2O generation (section 2.2.5.8). Greater N_2O emissions have been observed when the incorporated material had a low C:N ratio, such as legumes (Goodroad *et al.*, 1984; de Catanzaro and Beauchamp, 1985; McKenney *et al.*, 1993). Conversely, incorporation of organic material with a high C:N ratio may stimulate immobilisation of NH_4^+, thereby restricting nitrification and denitrification, and reducing and/or delaying production of N_2O. Aulakh *et al.* (1991a,b) pointed to the need for studies comparing different crop residues having a wide range of C:N ratios. Several studies have been conducted on the influence of one or two crop residues on emissions of N_2O (for example, de Catanzaro and Beauchamp, 1985), but studies comparing different crop residues with a wide range of C:N ratios are scarce (Aulakh *et al.*, 1991a,b).

Ploughing of grassland has been found to result in formation of substantial amounts of NO_3^- (Linden and Wallgren, 1993) with a great potential for increasing N_2O emissions (Ryden, 1981; Addiscott *et al.*, 1991; Davies, 1996). Such emissions are greater if ploughing stimulates mineralisation of any stored N. Increased emissions were emitted after ploughing of grass and grass/clover swards at Bush Estate, near Edinburgh (Davies, 1996). Over 48 days following summer ploughing in 1992, 3.7 and 1.5 kg N_2O-N ha^{-1} were emitted from ploughed grass/clover and grass swards, respectively. Emissions were 0.5 and 0.1 kg N_2O-N ha^{-1} from corresponding unploughed grass/clover and grass swards, respectively.

The practice of green manuring has a great potential for large emissions of N_2O after incorporation due to their often rapid decomposition and release of N and C to soil micro-organisms (section 2.2.1). However, to date only a few studies have examined the effects of green manure incorporation on microbial processes, and particularly immobilisation, nitrification and denitrification (Aulakh *et al.*, 1983; Redman *et al.*, 1988; McKenney *et al.*, 1995).

A laboratory incubation was undertaken to measure N_2O emissions after addition of grass and clover residues to soil. It was hypothesised that amendment of the soil with these residues would increase N_2O emissions, and that these emissions would be greater from clover amended soil. On the basis of the results from this laboratory incubation, field trials were undertaken. N_2O emissions were measured after ploughing-in and rotary tillage of grass and grass/clover swards and after incorporation of various green manures, including both legumes and non-legumes (Appendices I and II). The results were related to environmental parameters in order to ascertain if there are certain conditions where the incorporation of plant material may give rise to undesirably high N_2O emissions.

4.2 Laboratory incubation

4.2.1 Materials and methods

Ten soils of the Biel series were sampled from the Bush Estate, near Edinburgh, were sieved and wetted up to a consistent moisture content of 19 % on a fresh weight basis. Fresh soil (75 g on a dry weight equivalence) was placed in 500 ml conical flasks (3 replicates per soil). Root:shoot ratios of chopped fresh grass of 1.25:1 (0.89:0.71 g) and of a grass/clover mix of

2.26:0.26:1 (1.04 g roots:0.12 g clover shoots:0.46 g grass shoots) were mixed with the soil in the conical flasks. The flasks were then sealed with rubber 'Suba' seals and incubated at a constant temperature of 20 °C.

Emissions of N_2O were measured on days 3, 7 and 13 of the experiment by collection of gas in a 5 ml glass syringe through the Suba seal. Samples were analysed for concentrations of N_2O using gas chromatography (section 3.9). After gas sampling the Suba seals were removed, the flasks were aerated using air from a gas cylinder, and the Suba seals were then replaced. The flasks were aerated to prevent air saturation of N_2O occurring within the flasks. At the end of the experiment the soil pH was measured following the method of McLean (1982). Available NH_4^+ and NO_3^- were determined, as described in section 3.3.

4.2.2 Results

Emissions of N_2O from the residue amended treatments were significantly higher ($p<0.001$) than from the control over the whole experimental period (Fig. 4.1a). These emissions were greatest from the grass/clover mix treatment, and increased over the experimental period, to 0.5 kg N_2O-N g soil^{-1} hour^{-1} on day 13 (Fig. 4.1b). There was no significant difference between the emissions from the grass and grass/clover amended soils on the 3 sampling dates, nor was there any significant difference in pH (Fig. 4.1e).

At the end of the incubation period available NH_4^+ was higher ($p<0.05$) in the residue amended treatments than in the control (Fig. 4.1c). The greatest concentration of 3.2 µg NH_4^+-N g dry soil^{-1} was in the grass treatment. Available NO_3^- in the residue amended treatments was significantly lower ($p<0.001$) than the control (Fig. 4.1d).

4.3 Field trials

4.3.1 Sites, materials and methods

In Spring 1994, 2 experimental sites were established. The first site, on the Bush Estate near Edinburgh, was a sandy loam of the Biel series (Soil Survey of Scotland, 1982a). Two trials were undertaken at this site. The second site, at Aldroughty Estate near Elgin, was a sandy loam of the Boyndie series (Soil Survey of Scotland, 1982b).

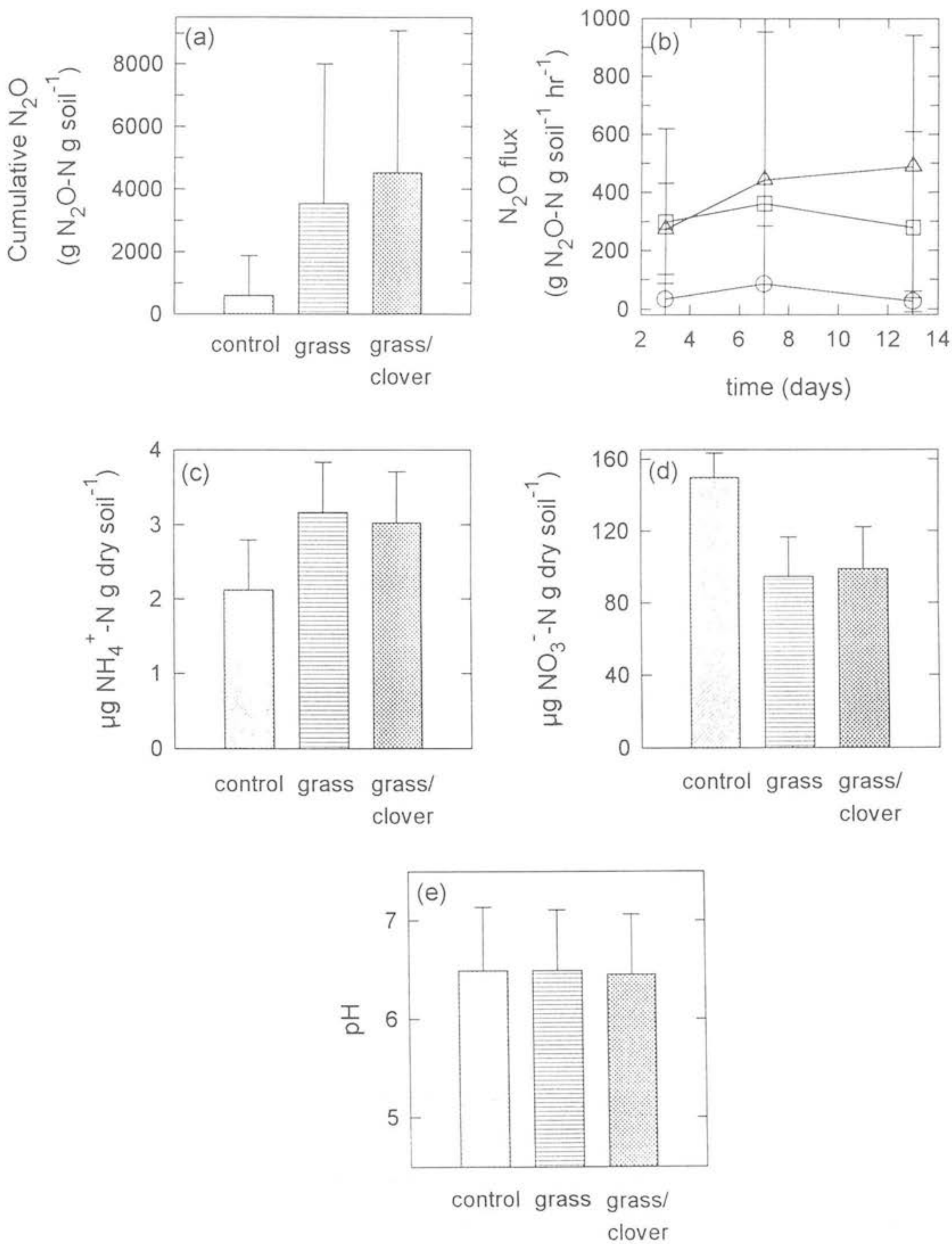

Figure 4.1 (a) Cumulative emissions of N_2O over the whole experimental period, (b) N_2O emissions from control (circles), grass (squares) and grass/clover (triangles) treatments, (c) concentrations of available NH_4^+, (d) concentrations of available NO_3^- and (c) pH values during laboratory incubation.

4.3.1.1 Bush Estate

The first trial at the Bush estate investigated N_2O emissions following incorporation of mixed grass/clover swards (*Menna*, *Kent* and *Huia* varieties of white clover). These swards were subjected to different treatments during the growing season. Half of them had been cut 6 times throughout the growing season (cut treatment). The other half were allowed to grow continuously and were only cut at the end of the growing season (uncut treatment). The second trial at this site investigated N_2O emissions following incorporation of Italian ryegrass (*Augusta*, *85/22* and *Bab 242* varieties). Both of these trials were ploughed on 6 April 1994, rotary tilled, sown to barley and rolled on 28 April 1994.

4.3.1.2 Aldroughty Estate

At Aldroughty Estate N_2O emissions were compared after incorporation of overwintering green manures. The crops used in this trial were white clover (*Trifolium repens* cv. Kent Wild White), white mustard (*Sinapis alba*), oats (*Avena sativa* cv. Dula), birdsfoot trefoil (*Lotus corniculatus*) and forage peas (*Pisum sativum* cv. Magnus). Fallow areas where the natural vegetation had been allowed to regenerate, and bareground where seedlings had been removed by a propane gas burner were also included in this trial. The site was ploughed, rotary tilled, sown to oats and rolled on 14 April 1994. This trial formed part of experimental work established in April 1993 comparing the availability of N from green manures (Appendix II).

At both experimental sites N_2O emissions prior to and following cultivation were measured using cover boxes. Monthly determinations of available soil NH_4^+ and NO_3^- and gravimetric soil moisture contents were made. Details of methods are presented in Chapter 3. Air temperature and rainfall data were obtained for the respective experimental periods from local meteorological stations.

4.3.2 Results

4.3.2.1 Bush Estate

Cumulative emissions of N_2O for the whole 84 day sampling period and over the 25 days after rotary tillage are presented in Fig. 4.2. There was no significant difference in cumulative emissions between treatments and trials. A cumulative emission of 236 g N_2O-N ha^{-1} was measured over 84 days from the uncut grass/clover treatment. Over the whole sampling period the lowest emission of 153 g N_2O-N ha^{-1} was measured from the Italian ryegrass trial. During the first 25 days following rotary tillage 175 g N_2O-N ha^{-1} was emitted from the cut grass/clover treatment, representing 78 % of the 224 g N_2O-N ha^{-1} emitted over the 84 day sampling period.

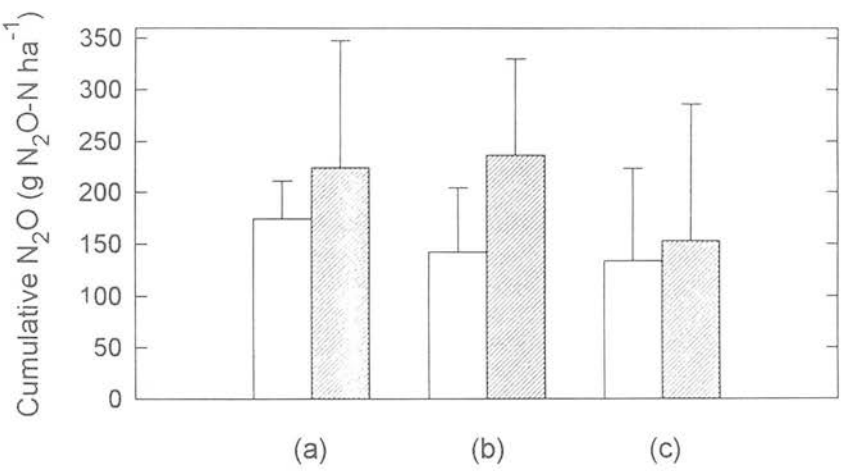

Figure 4.2 Cumulative emissions of N_2O over the whole 84 day sampling period (hatched bars) and between 22 April and 17 May (empty bars) after incorporating (a) cut grass/clover, (b) uncut grass/clover and (c) Italian ryegrass at Bush Estate.

Short-lived fluxes of N_2O were measured immediately after rotary tillage at the Bush Estate, but there was no significant difference between treatments and trials (Fig. 4.3). Ploughing alone had little effect on emissions. Large fluxes of N_2O were measured after rotary tillage of the grass/clover trial, particularly the cut grass/clover swards. Three days after rotary tillage (1 May) fluxes of 23 and 13 g N_2O-N ha^{-1} d^{-1} were measured from the cut and uncut grass/clover swards, respectively. Emissions from this trial fell after this date. However, 6 days after rotary tillage (4 May) 14 g N_2O-N ha^{-1} d^{-1} was measured from the Italian ryegrass trial. Emissions from this trial fell after this date. By 3 June emissions had returned to pre-cultivation levels.

The N_2O fluxes on 1 and 4 May were positively correlated with a rise in air temperature from 4 to 15 °C between 21 and 28 April ($r=0.5$, $p<0.01$ on the grass/clover treatments, and $r=0.3$, $p<0.001$ on the Italian ryegrass trial). The rise in temperature between these dates followed the greatest N_2O emissions. The gravimetric soil moisture contents correlated poorly with N_2O emissions ($r=0.06$, $p<0.01$ on the grass/clover treatments; $r=0.1$, $p<0.01$ on the Italian ryegrass trial).

Ploughing of the grass/clover and Italian ryegrass trials resulted in lowered concentrations of available NH_4^+ (Fig. 4.4a). Concentrations increased again after rotary tillage of the cut grass/clover treatment, with 7.8 μg NH_4^+-N g $soil^{-1}$ measured 3 days after rotary tillage. However, there was no significant difference between treatments on this day. By the end of the sampling period, available NH_4^+ had increased slightly in the uncut grass/clover treatment and Italian ryegrass trial, but had fallen in the cut grass/clover treatment. Available NO_3^- increased after rotary tillage of trials (Fig. 4.4b). On 3 June 18.1, 12.2 and 8.1 μg NO_3^--N g $soil^{-1}$ were measured in the uncut grass/clover, cut grass/clover and Italian ryegrass treatments, respectively.

The soil moisture contents fell after cultivation and particularly after rotary tillage (Fig. 4.3c). Three days after rotary tillage the soil moisture content of the cut grass/clover treatment was significantly higher ($p<0.01$) than that of the Italian ryegrass trial.

4.3.2.2 Aldroughty Estate

Cumulative emissions of N_2O over the 63 day experimental period are presented in Fig. 4.5. There was no significant difference between treatments. A total of 580 g N_2O-N ha^{-1} was measured from the trefoil treatment over the whole experimental period. A comparatively low

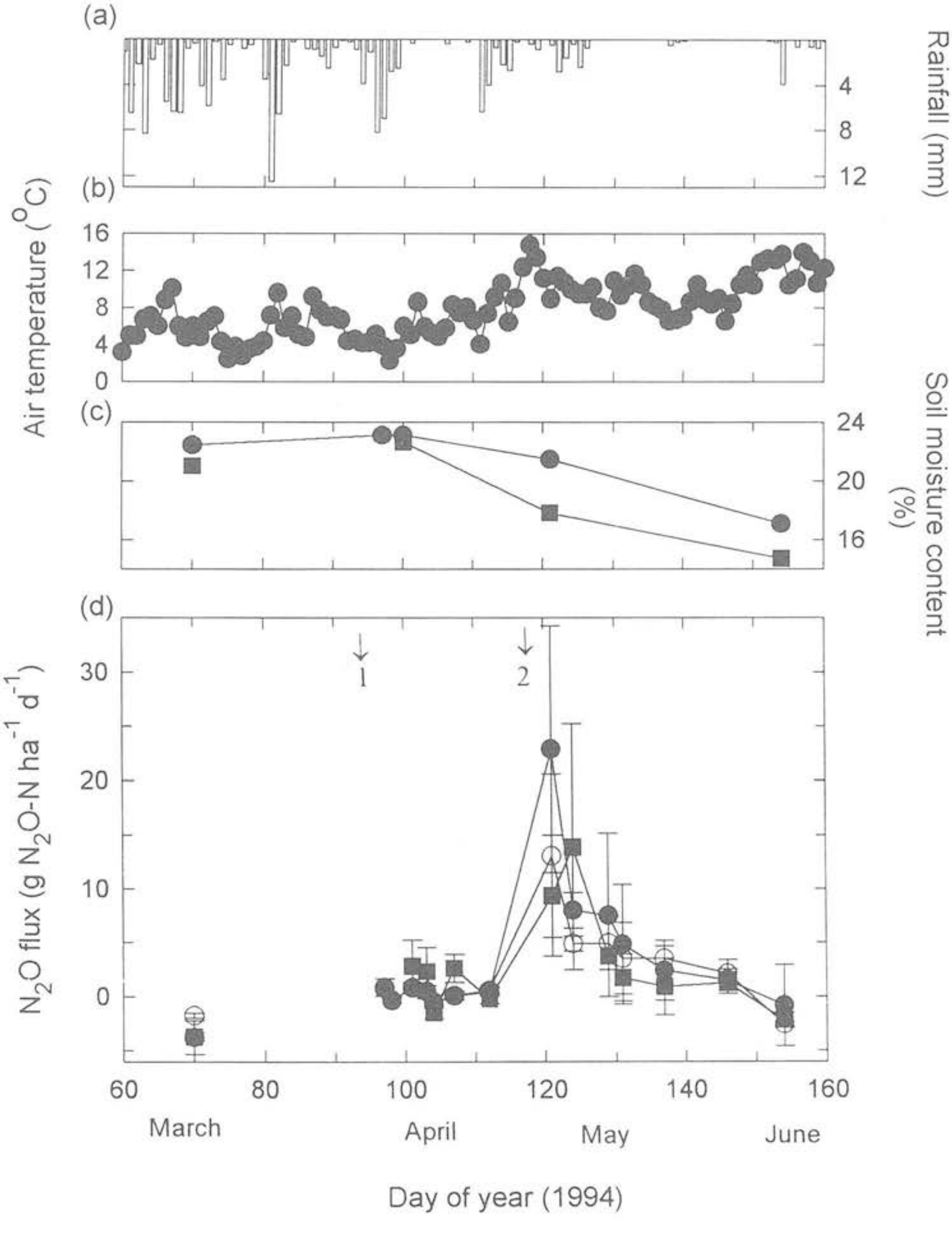

Figure 4.3 (a) Rainfall, (b) air temperature, (c) soil moisture content, (d) average N_2O emissions from cut grass/clover (filled circles), uncut grass/clover (empty circles) and Italian ryegrass (filled squares) at Bush Estate. Arrows indicate times of cultivation: 1. Ploughing, 2. Rotary tillage.

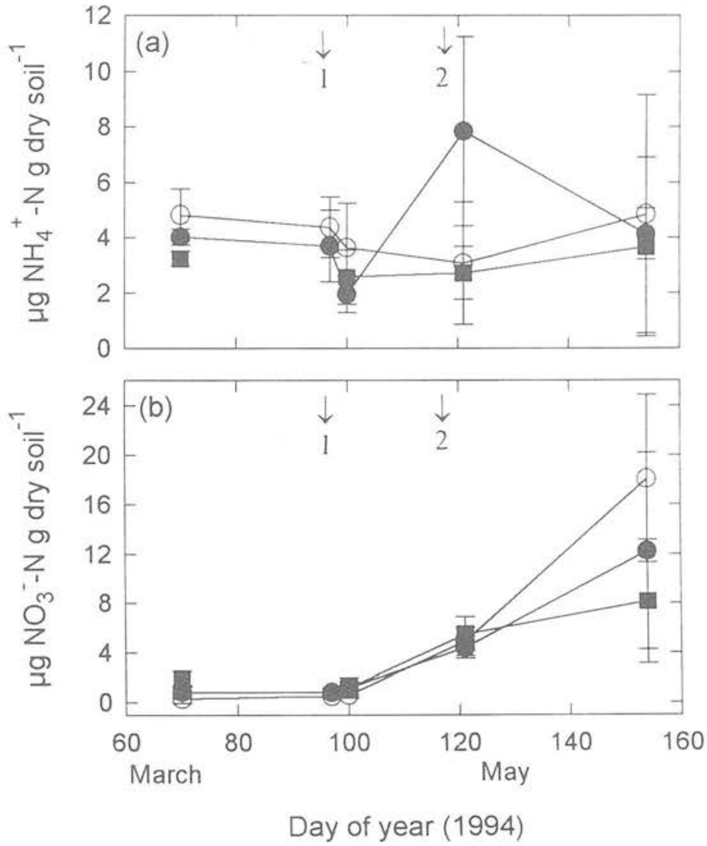

Figure 4.4 Concentrations of (a) available NH_4^+, (b) available NO_3^- on cut grass/clover (filled circles), uncut grass/clover (empty circles) and Italian ryegrass (filled squares) trials at Bush Estate. Arrows indicate times of cultivation: 1. Ploughing, 2. Rotary tillage.

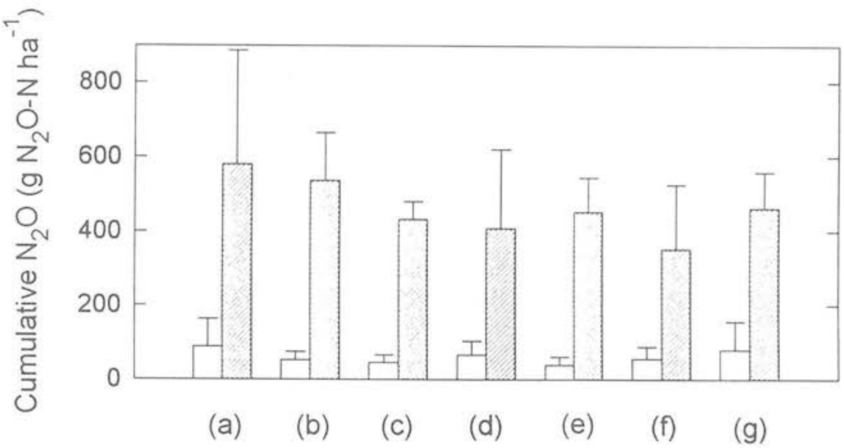

Figure 4.5 Cumulative emissions of N_2O over the whole sampling period (hatched bars) and over the first 3 weeks after cultivation (empty bars) of (a) trefoil, (b) forage pea, (c) mustard, (d) white clover, (e) oats, (f) fallow control and (g) bareground control treatments at Aldroughty Estate.

emission of 353 g N_2O-N ha^{-1} was measured from the fallow treatment. Emissions over the first 3 weeks after cultivation were low, only averaging 13 % of total emissions.

There was no significant difference in daily emissions of N_2O after cultivation at Aldroughty Estate (Fig. 4.6). Increased fluxes of N_2O were measured after cultivation on 14 April. Five days after cultivation a flux of 7.7 g N_2O-N ha^{-1} d^{-1} was measured from the fallow treatment. Further short-lived fluxes were measured from all treatments on 26 April. A flux of 14 g N_2O-N ha^{-1} d^{-1} was measured from the bareground treatment on this day, but was not significantly higher than fluxes from other treatments. On 3 May low emissions were measured from all treatments, but had increased by 18 May, when a flux of 13.7 g N_2O-N ha^{-1} d^{-1} was measured from the trefoil treatment. At the end of the experimental period emissions from all treatments were again low. Throughout the experimental period N_2O emissions from all treatments were strongly correlated with air temperature ($r=0.8$, $p<0.01$).

Available NH_4^+ increased throughout the experimental period (Fig. 4.7a). Concentrations of 5.2 and 15.8 µg NH_4^+-N g $soil^{-1}$ were measured in the trefoil treatment on 19 April and 19 May, respectively. The concentration on 19 April was significantly higher ($p<0.05$) than concentrations in other treatments. 11.7 µg NH_4^+-N g $soil^{-1}$ was measured in the fallow treatment on 19 May. Available NO_3^- increased after cultivation, and throughout the remainder of the experimental period (Fig. 4.7b). On 19 May 21.1 µg NO_3^--N g $soil^{-1}$ was measured in the white clover treatment ($p<0.05$).

Net N mineralisation rates from the decomposing plant residues were calculated by subtracting the accumulated NH_4^+ and NO_3^- of the bareground treatment at each sampling date from concentrations after residues had been incorporated (after Frankenberger and Abdelmagid, 1985). However, this means of calculating net mineralisation assumes that there was no priming effect, no loss of N from the soil or immobilisation. The highest rate of N mineralisation 35 days after cultivation was in the trefoil treatment ($p<0.05$) (Fig. 4.8). Three days after cultivation rates were negative in the oats and fallow treatments. The lowest mineralisation was in the oats treatment ($p<0.05$) 35 days after cultivation.

There was no significant difference in soil moisture contents between the various treatments at any time throughout the experimental period (Fig. 4.6c). Soil moisture contents were increased after cultivation due to rainfall, averaging 21 % on 19 April, but then fell again.

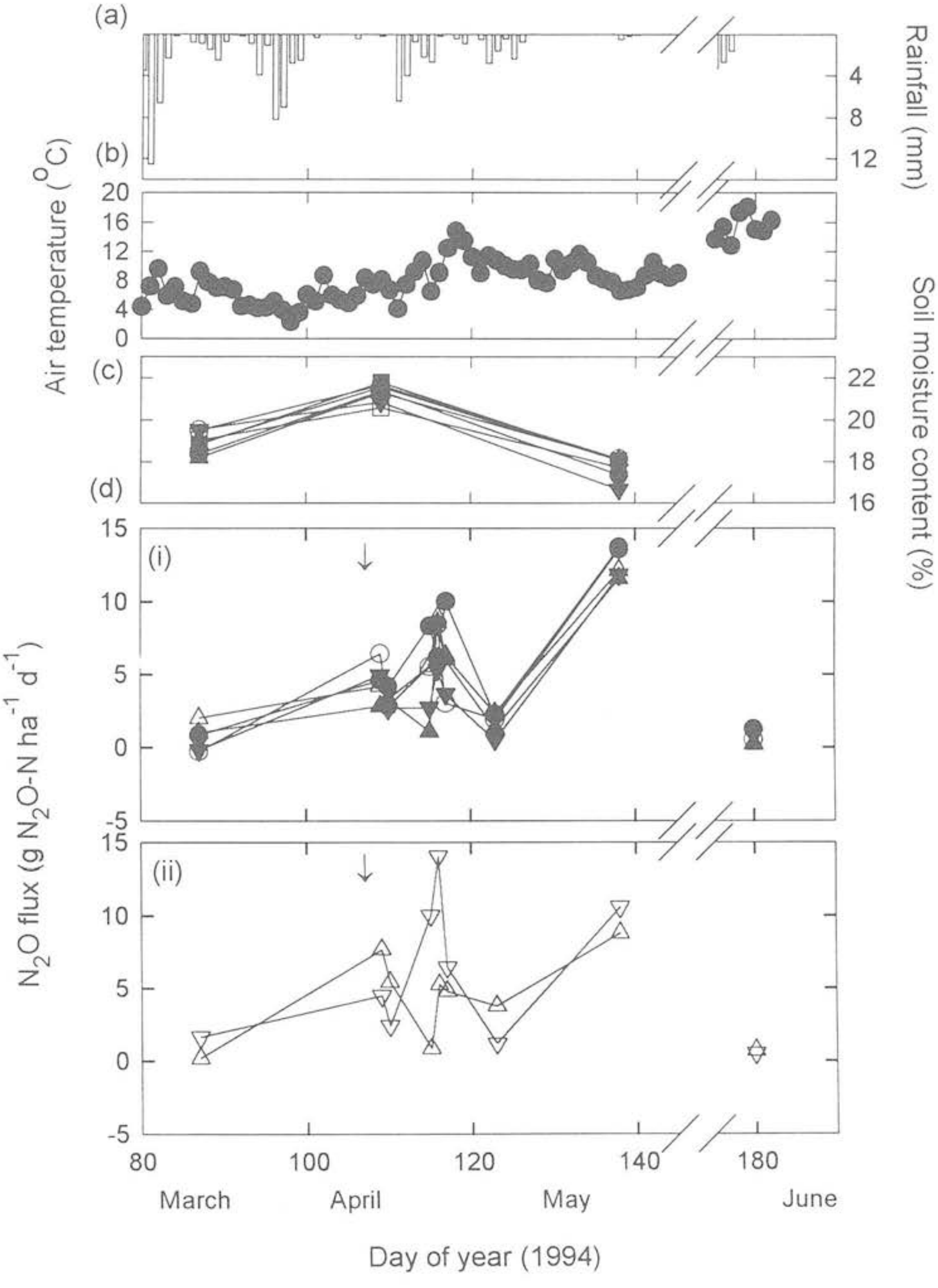

Figure 4.6 (a) Rainfall, (b) air temperature, (c) soil moisture content, (d) (i) N_2O emissions after incorporation of trefoil (filled circles), forage pea (empty circles), mustard (filled upward triangles), white clover (empty upward triangles), oats (filled downward triangles), (d) (ii) emissions from fallow (upward triangles) and bareground (downward triangles) control treatments at Aldroughty Estate. Arrow indicates date of cultivation.

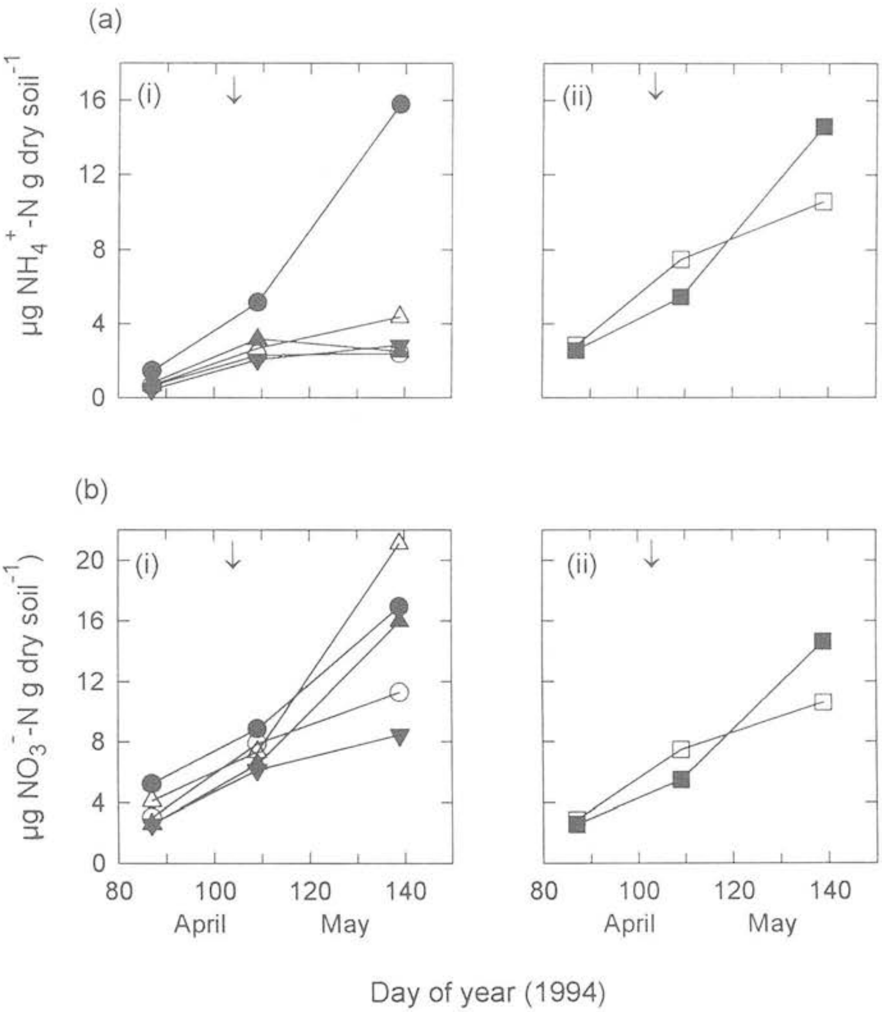

Figure 4.7 Concentrations of (a) available NH_4^+, (b) available NO_3^-, after (i) cultivation of trefoil (filled circles), forage pea (empty circles), mustard (filled upward triangles), white mustard (empty upward triangles), oats (filled downward triangles), (ii) cultivation of fallow (filled squares) and bareground (empty squares) control treatments at Aldroughty Estate. Arrow indicates date of incorporation.

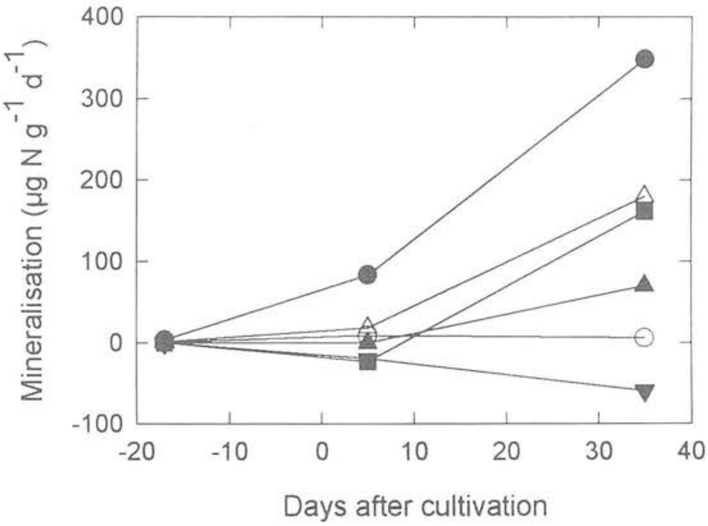

Figure 4.8 Net N mineralisation after cultivation of trefoil (filled circles), forage pea (empty circles), mustard (filled upward triangles), white clover (empty upward triangles), oats (filled downward triangles) and fallow (filled squares) treatments at Aldroughty Estate.

4.4 Discussion

4.4.1 Laboratory incubation

Throughout the incubation N_2O emissions from the plant amended soils were greater than from the control treatment. Soil incorporation of readily degradable plant material stimulates microbial decomposition usually resulting in greater losses of N_2O from nitrification and denitrification than from bare soil (Jansson and Clark, 1952; Denmead *et al.*, 1979b; Ryden *et al.*, 1979). N_2O is also produced from microbial decomposition of organic matter in bare soil (Granli and Bøckman, 1994). Emissions from the grass/clover mix amended soil were 81 and 211 g N_2O-N ha^{-1} hr^{-1} higher than from the grass amended soil on days 7 and 13, respectively. The greatest N_2O flux of 490 g N_2O-N ha^{-1} hr^{-1} was measured from the grass/clover mix treatment on day 13. Such enhanced N_2O emissions after clover incorporation have been reported in the literature (Aulakh *et al.*, 1983; Davies, 1996). Davies (1996) measured emissions from ploughed grass/clover swards twice those from ploughed grass swards over 2 consecutive summers. These emissions, in turn, were higher than those from unploughed grassland. The higher emissions from grass/clover treatments may be attributed to the low C:N ratio of the clover, resulting in rapid decomposition and loss of N_2O from nitrification and denitrification (Goodroad *et al.*, 1984; McKenney *et al.*, 1993).

Soil amendment with plant material resulted in higher ($p<0.05$) concentrations of available NH_4^+ at the end of the incubation period than in the control treatment. The greatest concentration, 3.2 μg NH_4^+-N g dry $soil^{-1}$, was in the grass amended soil. The concentrations of available NO_3^- were significantly lower ($p<0.001$) in the plant amended soils, suggesting that denitrification was the predominant process contributing to N_2O losses during this experiment. This denitrification is likely to have been due to the presence of fresh plant material inducing anaerobic conditions. Addition of plant material to soil increases O_2 consumption during microbial respiration, resulting in the formation of anaerobic microsites (Drury *et al.*, 1991; McKenney *et al.*, 1995). Residues also help to retain moisture within the soil, allowing anaerobic conditions to develop (Harper and Lynch, 1981). Accumulation of high concentrations of N_2O within the flasks between sampling times may have restricted diffusion of N_2O from the soil, resulting in an underestimation of emissions and possible reduction of N_2O to N_2 (Arah *et al.*, 1991). The low concentrations of NO_3^- measured in the plant material amended treatments may also have been due to immobilisation of N. In the absence of NH_4^+ available NO_3^- is immobilised by heterotrophic micro-organisms (Davidson *et al.*, 1990). Immobilisation has been found to occur after addition of plant material to soil (Jenkinson, 1984), and is generally greater where the plant material has a high C:N ratio, such as grass (Haynes, 1986; Aulakh *et al.*, 1991b). However, in this experiment, higher concentrations of available NH_4^+ were measured in the grass treatment than the grass/clover treatment. This may have been due to greater nitrification in the grass/clover treatment. The addition of plant material to the soil had little effect on soil pH, although pH was slightly lowered in the grass/clover mix treatment.

4.4.2 Field trials: Bush Estate

Incorporation of the Italian ryegrass and grass/clover swards by ploughing had an unexpectedly limited effect on gaseous N emissions. Cultivation increases aeration of soil and the accessibility of crop residues to soil micro-organisms (Ross, 1990), thereby making conditions favourable for decomposition (Lynch and Panting, 1980). Generally, ploughing has been found to result in immediate increases in N_2O emissions due to the increased decomposition of organic matter and the release of N_2O enriched soil air after physical disturbance of the soil (Matthias *et al.*, 1980; Bremner and Blackmer, 1981). Tillage operations also increase aeration, but to a shallower depth than conventional ploughing, resulting in a concentration of microbial biomass near the soil surface (Goss *et al.*, 1978). The action of ploughing only resulted in raised N_2O emissions from the Italian ryegrass trial. However, emissions from this trial were also lower than expected. This may have been due to the low temperature at the time of, and following, ploughing-in of the plant material, which would have slowed down microbial activity, thereby reducing rates of mineralisation, nitrification and denitrification (Stott *et al.*, 1986). Davies (1996) also found that rotary tillage rather than ploughing initiated increases in N_2O after incorporation of grass swards.

Large fluxes of N_2O were measured after rotary tillage. However, the relative effects of cultivation and addition of plant material could not be determined as both fields were entirely cropped and a bare ground control was not available. These fluxes may have been stimulated by the physical disturbance of the soil when it was warmer, as well as by the addition of substrate for decomposition in the form of fresh plant material. The highest flux of 23 g N_2O-N ha^{-1} d^{-1} after rotary tillage was measured from the cut grass/clover swards. The lowest emissions were measured from the Italian ryegrass trial.

Comparisons of emissions from different plant varieties, as opposed to species, have not been examined elsewhere in the literature. It was hypothesised that differences between the clover varieties would be minimal, in view of the small differences in N contents. The greatest difference would be expected to be between different crop types (Chapter 6), and particularly between legumes and non-legumes (Chapter 7), with higher emissions expected after incorporation of leguminous material (Goodroad *et al.*, 1984; Eichner, 1990).

There was no significant difference between N_2O emissions from the cut and uncut grass/clover swards. This suggests that, in the absence of livestock, differences in management of grass systems throughout the growing season have little effect on the emissions of N_2O after incorporation. Emissions following such different management practices have not been examined elsewhere in the literature.

Prior to cultivation negative fluxes of N_2O were measured on all treatments of both trials, suggesting that the soil was acting as a sink for N_2O. Ryden (1981) measured N_2O sinks as large as 11.6 ng N m^{-2} s^{-1} when soil moisture was below 20 %, available NO_3^- was below 1 μg N g soil^{-1}, and temperature was above 5-8 ^oC. However, the mechanism responsible for such sinks of N_2O are unknown.

Cumulative emissions of N_2O were higher from the grass/clover swards than from the Italian ryegrass. This is in agreement with the results obtained from the laboratory incubation and from other experimental work reported in the literature. For example, Aulakh *et al.* (1983) found that green manuring with clover resulted in greatly raised gaseous N losses. The C:N ratio of the grass/clover swards was lower than that of the Italian ryegrass. Incorporation of the N-rich clover would have stimulated microbial activity and decomposition. However, the emissions were also dependent on the rainfall, soil moisture and temperature both at and following cultivation. Raised N_2O emissions are generally reported after rainfall as reduced aeration results in greater denitrification (Bremner and Shaw, 1958; Ryden *et al.*, 1979; Rolston *et al.*, 1982; Mosier *et al.*, 1986). The heavy rainfall prior to ploughing of 36.6 mm between 21 March and 4 April had little effect on N_2O emissions. The peak emissions after rotary tillage occurred after further rainfall and coincided with a rise in air temperature from 4 to 15 ^oC between 21 and 28 April. Such a rise in temperature has generally been found to increase N_2O emissions from both nitrification and denitrification (Granli and Bøckman, 1994). Laboratory studies have shown that N_2O production increases strongly with increasing temperature up to 20-40 ^oC (Freney *et al.*, 1979; Keeney *et al.*, 1979; Goodroad and Keeney, 1984). This temperature rise created some difficulty in separating the relative effects of rotary tillage and air temperature on N_2O emissions. After rotary tillage the air temperature was constantly greater than prior to tillage. N_2O emissions from the Italian ryegrass trial showed weaker correlations with air temperature than those from the grass/clover trial.

Soil moisture contents were reduced after both ploughing and rotary tillage and continued to fall throughout the remainder of the experimental period. The action of cultivation is known to dry soil by exposing a greater surface area of soil to the atmosphere, whereas more moisture is retained in soils subject to reduced cultivation (Lynch and Panting, 1980). Both the lower rainfall and increased temperature after ploughing would have contributed to this reduction in soil moisture. The respective effects of cultivation and air temperature on this soil moisture were difficult to ascertain as the air temperature steadily increased throughout the experimental period. On both trials the soil moisture contents correlated poorly with N_2O emissions, suggesting that temperature was the more significant variable influencing gaseous emissions, particularly on the grass/clover trial. Contrary to this, most authors have reported strong positive correlations between N_2O emissions and soil moisture contents both when nitrification (Davidson, 1992) and denitrification (Rolston *et al.*, 1978; Ryden and Lund, 1980) were the main producer of N_2O.

Plant material rich in N generally decays rapidly, with much of the N being mineralised. Decomposition of residues with low N requires additional N that is immobilised from the soil (Schomberg *et al.*, 1994). In the literature greater N_2O emissions have generally been observed when the incorporated material, such as legumes, had a low C:N ratio. For example, de Catanzaro and Beauchamp (1985) compared N_2O emissions from legume (alfalfa) and cereal (straw) amended soils. The alfalfa amended soil produced significantly greater N_2O and CO_2, and lost NO_3^- more rapidly than the same amount of added straw. They concluded that due to the higher lignin and cellulose content of the straw additional C would be decomposed and become available more slowly from this treatment. Similarly, Goodroad *et al.* (1984) found that addition of alfalfa residues increased emissions more than addition of rye, which has a high C:N ratio. Such results are in accordance with those from the Bush Estate and the laboratory incubation, where greater emissions were measured from the grass/clover swards which had a lower C:N ratio than the Italian ryegrass. The importance of C:N ratio was more apparent in the laboratory incubation than the field trials. This is because field trials involve other variables that affect N_2O emissions which cannot be controlled, such as temperature or rainfall (Frankenberger and Abdelmagid, 1985). Additionally, the plant material incorporated during the field trial would have been fresher than that added in the laboratory incubation. Thus, under the same temperature, decomposition would have potentially been more rapid in the field.

Short-lived immobilisation of N may occur immediately after incorporation of plant material with a high C:N ratio and may last for up to several weeks (Aulakh *et al.*, 1991b). Wallgren and Lindén (1991) stated that immobilisation may occur after incorporation of an Italian ryegrass catch crop into soil. In the present work, immediately after rotary tillage concentrations of available NH_4^+ remained low on the uncut grass/clover and Italian ryegrass trials, suggesting that short-lived immobilisation occurred. However, the long-term effect of incorporation of plant material with a high C:N ratio is increased mineralisation, as immobilisation is followed by a slow release of N (Powlson *et al.*, 1987).

Immobilisation may also have occurred immediately after the ploughing of the trials, as concentrations of NH_4^+ in the soil fell. However, this immobilisation was short-lived on the cut grass/clover swards as concentrations of NH_4^+ increased again after rotary tillage, indicating that mineralisation was occurring. The effects of immobilisation on the NH_4^+ concentrations of the uncut grass/clover swards lasted longer. Concentrations of available NO_3^- were also low after ploughing of both cut and uncut swards, but were greatly increased after rotary tillage. Rotary tillage would have increased microbial activity, releasing some of the immobilised N. This would explain why NH_4^+ concentrations were very low immediately after ploughing but greatly increased after rotary tillage of the cut grass/clover swards. The increased concentrations of available NO_3^- after rotary tillage suggest that the high N_2O emissions from both trials resulted from nitrification. The increase in N_2O emissions from the cut grass/clover swards between 22 April and 1 May strongly correlated ($r=0.8$) with concentrations of available NH_4^+.

4.4.3 Field trials: Aldroughty Estate

Emissions of N_2O were raised immediately after incorporation of residues at the Aldroughty Estate. Fluxes measured on 26 and 27 April, the greatest of which was 14 g N_2O-N ha^{-1} d^{-1} from the bareground treatment, may have been stimulated by 16.2 mm rainfall between 21 and 26 April (Conrad *et al.*, 1983). These fluxes also coincided with a rise in temperature from 4 to 11 °C between 21 and 24 April. Throughout the experimental period temperature correlated strongly with N_2O emissions at this site ($r=0.8$, $p<0.01$). The large fluxes measured on 18 May may have been in response to the warmer temperatures from 27 April onwards. However, by the end of the experimental period N_2O emissions were low from all treatments despite a temperature of 18 °C on 26 June. It is probable that the large fluxes measured on 18 May resulted from release of N immobilised immediately after incorporation. In accordance with this, available NH_4^+ in the trefoil and fallow treatments and available NO_3^- in all treatments had increased by 18 May. By 29 June most of the readily degradable plant material would have probably been decomposed.

The flux of 14 g N_2O-N ha^{-1} d^{-1} from the bareground treatment on 26 April confirms reports that emissions from bare cultivated soil may significantly contribute to total emissions from agricultural systems (Bouwman, 1990a). However, it is generally found that incorporation of plant material increases emissions compared to those from bare soil (Ryden *et al.*, 1979; Aulakh *et al.*, 1983; de Catanzaro and Beauchamp, 1985), as was found in the preliminary incubation. Low emissions immediately after incorporation of plant material may have been due to temporary immobilisation of N (Aulakh *et al.*, 1991a,b). Despite the large N_2O flux from the bareground treatment on 26 April the highest cumulative emissions over the experimental period of 359 and 323 g N_2O-N ha^{-1} were measured from the trefoil and forage pea treatments, respectively. This was probably due to their low C:N ratios stimulating mineralisation and nitrification. The lowest cumulative emissions were from the oats treatment - a cereal with a high C:N ratio. As previously stated, higher N_2O emissions are generally measured after incorporation of plant material with a low C:N ratio, than material with a high C:N ratio (Goodroad *et al.*, 1984; McKenney *et al.*, 1993).

The concentrations of available soil N increased throughout the experimental period. The greatest increases of NH_4^+ on the trefoil and bareground treatments corresponded with the high N_2O emissions from these 2 treatments. The increase in NO_3^- concentrations throughout the experimental period suggest that, as at the Bush Estate, nitrification was the main process contributing to gaseous N losses. Nitrification is known to be predominant in such dry soils (Skiba *et al.*, 1993). Low NH_4^+ and NO_3^- concentrations were measured on the oats treatment, suggesting that immobilisation occurred after incorporation due to the high C:N ratio, resulting in the low cumulative emissions from this treatment.

After incorporation all treatments were sown to oats. The growing oat crop may have affected N_2O emissions. Growing plants are known to effect microbial processes by root consumption of N_2O, depletion of soil NH_4^+ and NO_3^-, stimulation of microbial activity by root exudates, alteration of soil structure and creation of channels for gas transfer, and reduction in diurnal temperature variations (Svensson *et al.*, 1991; Kilian and Werner, 1996). Plants have been reported as both increasing and reducing N_2O emissions. In general, higher N_2O emissions have been reported in the presence of growing crops as they increase soil C (Klemedtsson *et al.*, 1987; Kilian and Werner, 1996). However, where available NO_3^- is limiting roots can reduce losses of N_2O from denitrification, as they compete with the soil micro-organisms for NO_3^-. Bakken (1988) found that at low soil moisture contents plants reduced denitrification. It is possible that the low N_2O emissions measured on 29 June may have been due to the presence of the oat crop which would have been almost mature by this day.

Results from this experiment at Aldroughty Estate can be compared with a cover crop trial the previous year at this site (Appendix II). As part of this trial N_2O emissions were measured after spring incorporation of rye, forage rape, winter peas, winter barley, winter wheat and white mustard, as well as after cultivation of fallow and bareground. Low N_2O emissions were measured from this trial. As in this experiment the greatest flux of 3.6 g N_2O-N ha^{-1} d^{-1} was measured from the bareground treatment and was significantly ($p<0.05$) higher than fluxes from the other treatments. Emissions were raised after incorporation of residues, and particularly the forage rape treatment. By the end of the experimental period differences in emissions between treatments were greatly reduced. Significant linear correlations were found between N_2O production and soil NO_3^- content, suggesting that N_2O emissions predominantly resulted from nitrification.

Lower peak emissions were measured at Aldroughty Estate than at Bush Estate, with smaller differences observed between legumes and non-legumes. This may have been due to the drier conditions at Aldroughty where there was less rainfall over the experimental period. Rainfall before incorporation raised soil moisture contents. However, after 24 April soil moisture contents fell until the end of the experimental period due to low rainfall. Temperatures were higher for most of the experimental period at Aldroughty and probably resulted in the greater fluctuations in emissions from this site. Also, soil at this site contained a higher percentage of sand than that of the Bush Estate, which generally is associated with lower emissions (Granli and Bøckman, 1994).

4.5 Summary

Addition of plant material to soil increased N_2O emissions in the laboratory incubation. The greatest emissions were measured from the grass/clover treatment. Field trials at the Bush Estate confirmed these higher emissions after incorporation of grass/clover compared with Italian ryegrass. However, at Aldroughty Estate smaller differences in N_2O emissions were observed after incorporation of legumes and non-legumes. At both field sites temperature was found to be a highly significant variable influencing emissions. Large fluxes of N_2O were expected immediately after ploughing of the soil at the Bush Estate, but did not occur until after rotary tillage. This was attributed to the importance of temperature. It is suggested that in Scotland incorporation of crop residues and overwintering green manures should occur in early spring when temperatures are still low but sufficient for some microbial decomposition. If possible incorporation should take place immediately prior to sowing of the next crop, so that N released during decomposition is available for crop uptake, and losses from the soil are minimised. These experiments have confirmed the importance of C:N ratios on gaseous N emissions from decomposing plant material, with greater emissions generally measured from material with a low C:N ratio. The effect of different cultivation systems on gaseous N emissions need to be examined both in the presence and absence of plant residues, with varying C:N ratios.

CHAPTER 5 NITROUS OXIDE EMISSIONS FOLLOWING INCORPORATION OF VEGETABLE CROP RESIDUES AND PAPER WASTE

5.1 Introduction

The physical action of cultivation increases soil aeration, evaporation and enhances the accessibility of crop residues to soil microbes (section 2.2.1.2). Less soil disturbance in reduced cultivation systems improves soil porosity and increases root growth and microbial biomass near the surface (Goss *et al.*, 1978; Lynch and Panting, 1980). Doran (1980) found a 3-7 times greater population of denitrifiers in the surface of zero-tilled soils compared with the surface of ploughed soils. Cultivation induces conditions favourable for decomposition and so crop residues left on the surface are generally found to decompose more slowly, and at a steadier rate, than incorporated residues (Parker, 1962; Douglas *et al.*, 1980; Wilson and Hargrove, 1986; Smith and Sharpley, 1990; Varco *et al.*, 1993).

Nitrous oxide losses are generally reported to be higher in the presence of crop residues and higher from undisturbed than from cultivated soils despite greater decomposition rates in cultivated soils (Burford *et al.*, 1981; Rice and Smith, 1982; Aulakh *et al.*, 1984c; Staley *et al.*, 1990). In 1984 Aulakh *et al.* measured gaseous N losses from conventional and zero-till cropped fields of 3-7 and 12-16 kg N ha^{-1} yr^{-1} respectively. Both surface mulched and fully incorporated wheat residues doubled the gaseous N losses over a growing season, compared with where there were no residues. The greater emissions following surface mulching were thought to be due to the retention of moisture by the residues.

There are few studies in the literature concerned with N_2O losses from commercial horticulture (for example, Iritani and Arnold, 1960; Ryden and Lund, 1980; Duxbury *et al.*, 1982). The low C:N ratios and high water composition of most vegetable crops would be expected to greatly increase N_2O emissions after their incorporation. Vegetable cropping leaves substantial amounts of mineral N and readily decomposable crop residue N in the soil in the autumn. Rahn *et al.* (1992) found up to 388 kg N ha^{-1} after cauliflower harvest, comprising both residue and soil mineral N. However, on a global scale the N_2O contribution from vegetable crops would probably be small because they only occupy a small total cropped area (Ryden and Lund, 1980; Duxbury *et al.*, 1982). Duxbury *et al.* (1982) measured daily fluxes and annual emissions of N_2O from onions and found considerably greater N_2O production than where alfalfa and field maize were grown. In 1980 Ryden and Lund measured N_2O emissions from irrigated lettuce, celery, broccoli, cauliflower and artichokes. The N_2O fluxes ranged from 70 g N ha^{-1} d^{-1} from the irrigated artichokes to 200 g N ha^{-1} d^{-1} from the lettuce. Unfortunately inadequate measurements of N_2O losses were made after ploughing-in of these crop residues, although they estimated that substantial denitrification occurred after celery incorporation. N_2O emissions are expected to be significantly greater where larger amounts of residues are incorporated.

Immobilisation of soil N has been found to occur after incorporation of organic material with a C:N ratio of more than approximately 20:1 (section 2.2.1.2). However, this value is not precise. Incorporation of a C-rich waste into agricultural soil would therefore be expected to result in initial immobilisation of N (Dolar *et al.*, 1972), potentially reducing NO_3^- leaching and losses of gaseous N. Although immobilisation of fertiliser N in the presence of high C material has been well studied (for example, Rice and Smith, 1984), there is little information available on immobilisation when the N source is organic, or when high-N residues are left on the soil surface (Sarrantonio, 1995). King (1984) reported that applications of paper mill waste with a high C:N ratio resulted in an initial net immobilisation of N. Paper mill waste may be used to conserve soil N and organic matter, as it can contain high concentrations of organic matter (as paper fibres) and calcium carbonate (Zibiliske, 1987; Aitken and Lewis, 1994). Zibilske (1987) applied primary mill sludge to agricultural soil at rates ranging from 0 to 267 g kg soil^{-1}. Initially, N immobilisation was apparent on all treatments. After about 60 days immobilisation had ceased and there was net N mineralisation in the lower sludge application treatments. He concluded that such applications may be useful in reducing winter NO_3^- leaching, and over time may improve soil organic matter. It was hypothesised that application of such paper waste could also reduce losses of N_2O from agricultural soils.

Experimental work was undertaken to investigate the fate of N following different cultivations of vegetable crop residues and paper waste applications. The effects of these different cultivations on N_2O emissions and available soil N were examined both in the presence and absence of crop residues. It was hypothesised that greater N_2O losses would occur where residues were only minimally cultivated despite low autumn temperatures. The presence of paper waste was expected to increase immobilisation of N after residue incorporation, thereby reducing emissions of N_2O.

5.2 Sites, materials and methods

In autumn 1994 two experimental trials were established at Balmalcolm Farm, Cupar, Fife (GR 318084), a commercial vegetable farm. The soils at both trials were freely drained loamy sands, of the Hexpath series. Both sites have a long history of intensive green salad and vegetable cropping. The first of the trial sites, Mackies Field, had previously been double cropped with lettuce (*Lactuca sativa* var. *Saladin*) during summer 1994, and the second trial site, Dipper Field, had been cropped with calabrese (*Brassica oleracea italica* var. *Cymosa*) throughout autumn 1994. A strip-plot experimental design (Little and Hills, 1978) was applied at both of these sites. Further details of experimental design are given in Vinten *et al.* (1996).

5.2.1 Mackies Field

At Mackies Field lettuce residues remaining in the field since harvest (September 1994) were subjected to three different cultivation treatments; deep mouldboard ploughing (350 mm depth), conventional mouldboard ploughing (150 mm depth) and rotary tillage with a power harrow (incorporation to a maximum depth of 50 mm). Areas of 2 m x 1.5 m were cleared of residues prior to cultivation, physical disturbance of the soil being kept to a minimum. Large roots were also removed, but fine roots remained in the soil. All cultivations at this site were undertaken on 13 October 1994. The field was left as winter fallow after cultivation.

Paper mill waste was acquired from GB Papers Ltd, Guardbridge, St. Andrews, Fife. On 10 October 1994, 3 days prior to cultivation, this waste was spread by a rear-delivery manure spreader at rates of 0 and 44.4 ± 7.1 t dry matter ha^{-1}, the traverses of the spreader being at 90^{o} to the direction of cultivation. The nutrient content of this paper mill waste is presented in Table 5.1. The C:N ratio of the paper waste was highly variable, being mainly influenced by the N content of the polyacrylamide flocculants and dyestuffs and surfactants used in the manufacturing process (Vinten *et al.*, 1996).

Table 5.1 Composition of paper waste on a fresh weight basis (Davies, 1995).

Dry matter %	35 ± 7
pH	6.9 ± 0.4
N %	0.48 ± 0.1
C %	11.8 ± 1.4
C:N ratio	25:1

Nitrous oxide was sampled from cover boxes, probes (at 50, 150 and 250 mm depths) and autochambers, both in the absence (-PW) and presence (+PW) of paper waste (Tables 5.2 and 5.3, respectively). Cover boxes were installed on plots of all cultivation treatments, both those

Table 5.2 Nitrous oxide sampling in the absence of paper waste application. Abbreviated nomenclature in parenthesis.

Treatment	Cultivation		
	deep ploughing	conventional ploughing	rotary tillage
lettuce residues (-PW/+R)	cover box x 3 probe 50, 150, 250 mm	cover box x 3 probe 50, 150, 250 mm autochamber	cover box x 3 probe 50, 150, 250 mm
controls (-PW/-R)	cover box x 3 probe 50, 150, 250 mm	cover box x 3 probe 50, 150, 250 mm autochamber	cover box x 3

Table 5.3 Nitrous oxide sampling in the presence of paper waste application (44.4 t dry matter ha^{-1}). Abbreviated nomenclature in parenthesis.

Treatment	Cultivation		
	deep ploughing	conventional ploughing	rotary tillage
lettuce residues (+PW/+R)	cover box x 3 probe 50, 150, 250 mm	cover box x 3 autochamber	cover box x 3
controls (+PW/-R)	cover box x 3 probe 50, 150, 250 mm	cover box x 3	cover box x 3

with crop residues (+R) and bare soil controls (-R), and at 0 (-PW) and 44.4 t dry matter ha^{-1} (+PW) paper mill waste application. These cover boxes were removed during cultivation, and replaced on every plot afterwards. With 3-fold replication a total of 36 cover boxes were used and regularly sampled for N_2O. Probes were inserted in deep ploughing with paper waste both with and without residues (+PW/+R and +PW/-R), deep ploughing without paper waste both with and without residues (-PW/+R and -PW/-R), conventional ploughing without paper waste both with and without residues (-PW/+R and -PW/-R) and rotary tillage without paper waste but with residues (-PW/+R) treatments. Gas samples for N_2O analysis were taken manually from the cover boxes both prior to and following cultivation, following the method described in sections 3.8 and 3.9. Gas samples from the depth probes were taken less frequently using 2 ml glass syringes.

In a parallel study (Scott, 1994, pers. comm.), N_2O was automatically sampled from conventionally ploughed plots using specially designed autochambers (Tables 5.2 and 5.3). Each chamber was made of galvanised steel, 0.2 x 0.2 x 0.7 m height. A cover mounted on pivot arms from the chamber sides was moved by a motor to cover and open the chamber. A timer was set to close the chambers for one hour every 6 hours. Each sampling time, just before reopening the chambers, a pump drew a flow of air from the chamber through a sampling loop of copper tubing. The loop was connected to rotary switching valves for sample storage. Further details of the design are described in Smith K.A. *et al.* (1995).

Air temperature and rainfall data were obtained for the duration of the trial. Weekly determinations of available soil NH_4^+ and NO_3^- and gravimetric soil moisture contents were made as described in sections 3.2 and 3.3. The density of lettuce plants per m^2 remaining after harvest and their percentage ground cover prior to cultivation were visually estimated using a quadrat. Plant samples were analysed for their total C and N contents. On 23 February 1995 soil was sampled at 0-0.2 m and 0.2-0.4 m depths from the conventionally ploughed and rotary tilled residue and control treatments, both in the presence and absence of paper waste. Determinations of biomass N and C were made on this soil (Castle, 1995, pers. comm.). Details of the methods used are presented in section 3.4.

5.2.2 Dipper Field

At the second experimental site, Dipper Field, chopped calabrese residues (following harvest November 1994) were subject to the same cultivation and paper mill waste treatments as at Mackies Field. All cultivations at this site were undertaken on 7 December. As at Mackies

Field, controls consisted of areas of 2 m x 1.5 m cleared of residues. Paper mill waste from GB Papers Ltd was spread at the same rates and in the same manner as at Mackies Field.

Cover boxes were installed on each cultivation treatment, both with residues and controls, and the 0 and 44.4 t dry matter ha^{-1} paper mill waste applications, as at Mackies field. With a 3-fold replication, a total of 36 cover boxes were manually sampled for N_2O. Air temperature and rainfall data were obtained for the duration of this trial. Available soil NH_4^+ and NO_3^- and gravimetric soil moisture contents were also determined and plant samples were analysed for total C and N contents. Determinations of biomass N and C were made on February 23 1995, as at Mackies Field.

5.3 Results

5.3.1 Mackies Field (Lettuce)

5.3.1.1 Cumulative emissions of N_2O

Cumulative N_2O emissions are presented in Fig. 5.1. Over the whole experimental period the greatest emissions ($p<0.05$) from the treatments without paper waste were measured after residue incorporation and particularly the rotary tillage of residues, from which 1640 g N_2O-N ha^{-1} was emitted over the 79 day experimental period. However, cumulative emissions from this treatment were not significantly greater than from the other treatments. Most of this N_2O was emitted during the first 2 weeks after cultivation, particularly after rotary tillage (-PW/+R) where 1080 g N_2O-N ha^{-1} (65 % of the total emission) was emitted over this period. A higher percentage of total emissions were released within these 2 weeks after cultivation of the -PW/+R than the -PW/-R treatments, except after conventional ploughing.

Incorporation of paper waste and residues (+PW/+R) on the deep ploughed and conventional ploughed treatments did not result in significantly higher cumulative losses of N_2O than those from the +PW/-R treatment (Fig. 5.1). Rotary tillage of +PW/+R resulted in significantly lower ($p<0.05$) total losses of N_2O than from the rotary tilled +PW/-R treatment. The highest cumulative emission of 3230 g N_2O-N ha^{-1} over the whole experimental period was measured from the deep ploughed +PW/+R treatment. The presence of paper waste increased the percentage of total N_2O emitted during the first 2 weeks after cultivation. 3040 g N_2O-N ha^{-1} (94 % of the total emission) was emitted during the first 2 weeks after deep ploughing of +PW/+R. The presence of residues increased the percentage released during this period, except after rotary tillage.

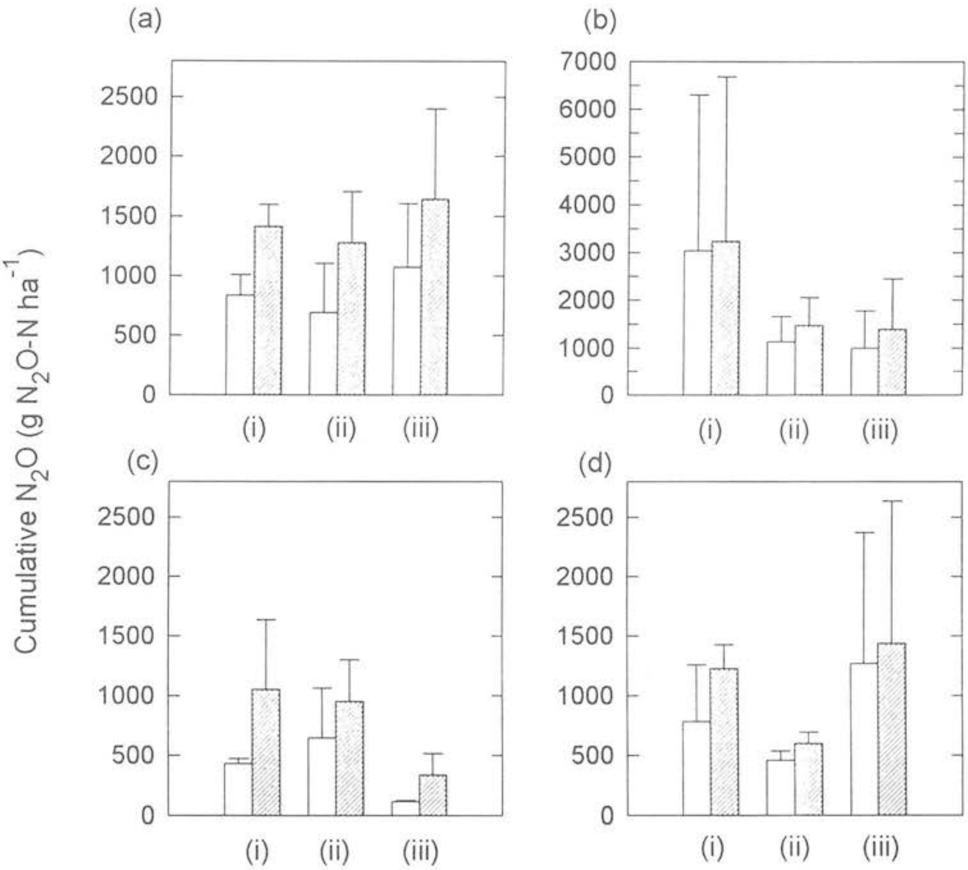

Figure 5.1 Cumulative emissions of N_2O over the whole 79 day sampling period (hatched bars) and over the first 2 weeks after cultivation (empty bars) of (a) lettuce residues (-PW/+R), (b) lettuce residues and paper waste (+PW/+R), (c) controls (-PW/-R), (d) controls with paper waste (+PW/-R) by (i) deep ploughing, (ii) conventional ploughing, (iii) rotary tillage.

5.3.1.2 Daily N_2O fluxes

Nitrous oxide emissions from the treatments without paper waste increased after cultivation (Fig. 5.2). The greatest increase of 36 g N_2O-N ha^{-1} d^{-1} was measured over the 4 days following rotary tillage (-PW/+R). The flux of 45.0 g N_2O-N ha^{-1} d^{-1} measured from this treatment on the first day after cultivation (11 October) was higher ($p<0.05$) than those measured from other treatments. Between 27 September and 11 October emissions from the deep ploughed treatments also increased by 26 g N_2O-N ha^{-1} d^{-1}. However, cultivation immediately resulted in reduced emissions from the conventionally ploughed plots - both -PW/+R and -PW/-R. Similarly, deep ploughing and rotary tillage of -PW/-R resulted in low N_2O emissions, and even uptake, with fluxes of 4.9 and -0.5 g N_2O-N ha^{-1} d^{-1} respectively, on the first day after cultivation. Emissions of N_2O were low after rotary tillage of -PW/-R throughout the experimental period, only increasing on 14 and 21 November, probably in response to rainfall of 27.4 mm and 15.6 mm between 9-14 and 17-20 November, respectively.

On 21 October N_2O fluxes were high from all treatments, except the rotary tilled -PW/-R, probably due to a rise in temperature of 4 °C and 13.2 mm of rainfall between 18 and 21 October. On 21 October 58 g N_2O-N ha^{-1} d^{-1} was emitted from the rotary tilled -PW/+R treatment. Three days later a flux of 67.5 g N_2O-N ha^{-1} d^{-1} was measured from this treatment. The standard deviations of each treatment are shown in Fig. 5.3. These standard deviations tended to be greatest where fluxes were large.

In general, the presence of paper waste increased N_2O emissions (Figs. 5.4 and 5.5), but the effect was short-lived, with very poor responses to any rainfall events after only 3 weeks. Large fluxes of N_2O were measured immediately following cultivation, particularly after rotary tillage of the +PW/-R treatment, with a flux of 99.0 g N_2O-N ha^{-1} d^{-1} measured from this treatment on the first day after cultivation. Emissions increased from all treatments on 21 October, probably in response to the rainfall of 8.6 mm and 2.8 mm on 19 and 20 October, respectively. The large flux of 748 g N_2O-N ha^{-1} d^{-1} from the deep ploughed +PW/+R treatment on 21 October was significantly higher ($p<0.05$) than fluxes from other treatments. However, this was short-lived, and by 24 October there was no significant difference between treatments. A short-lived flux of 169 g N_2O-N ha^{-1} d^{-1} was measured from the conventional ploughed +PW/+R treatment on 21 October. Again, this flux was short-lived. Further rain on 24 October (0.6 mm) may have prolonged emissions, especially from the rotary tilled treatments. The standard deviations from each treatment were greatest where large emissions were measured (Fig. 5.3).

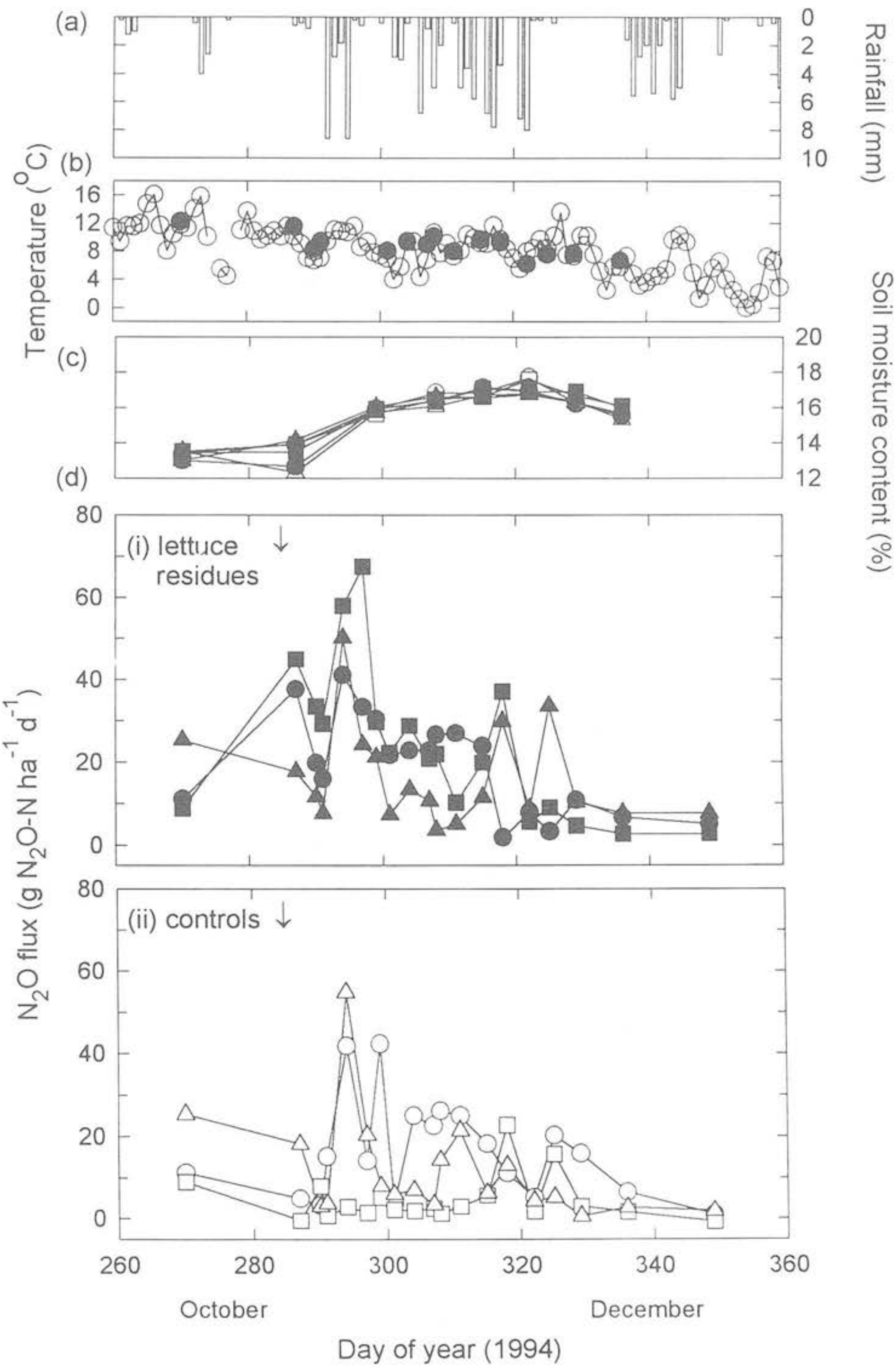

Figure 5.2 (a) Rainfall, (b) air temperature (empty symbols), soil temperature (filled symbols), (c) soil moisture contents, (d) N_2O emissions after deep ploughing (circles), conventional ploughing (triangles) and rotary tillage (squares) of lettuce residues (-PW/+R) and controls (-PW/-R) at Mackies Field. Arrow indicates date of cultivation.

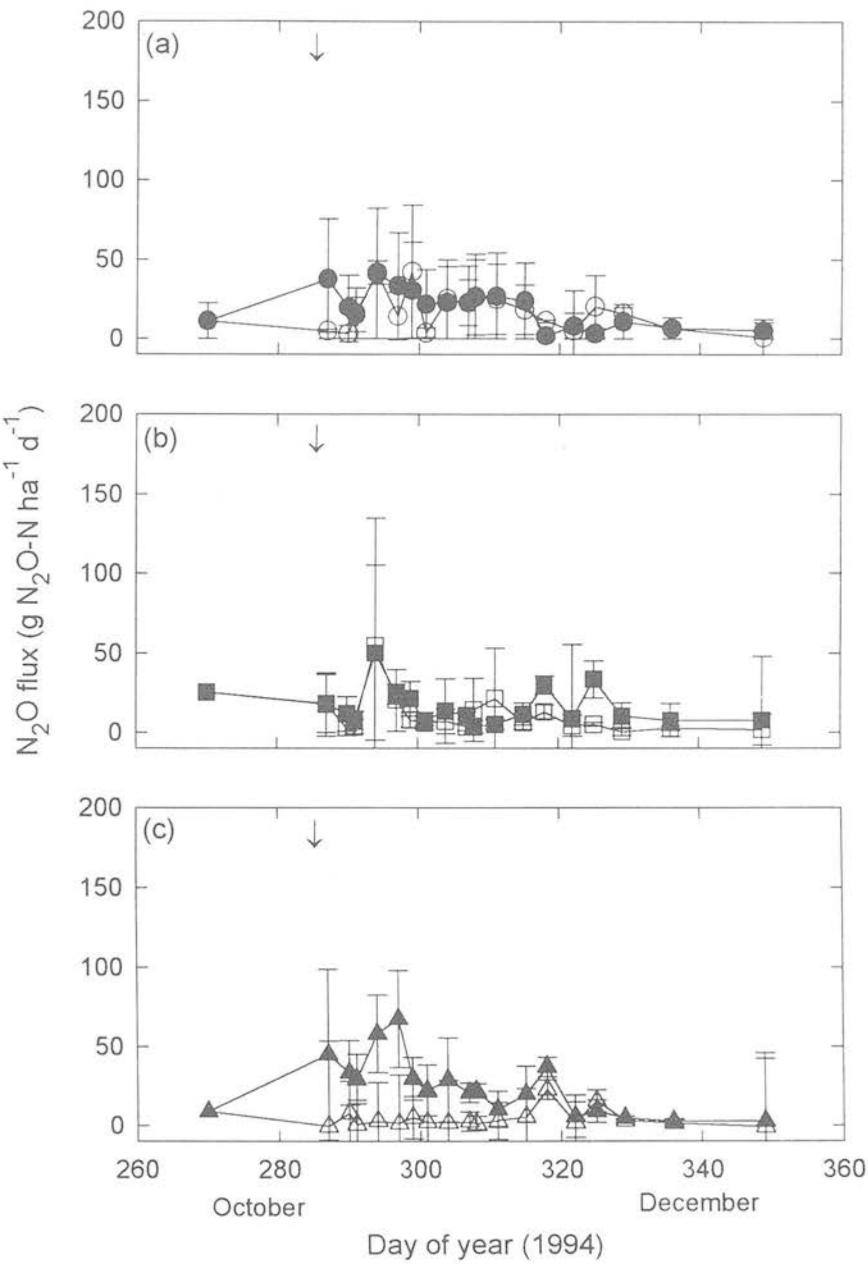

Figure 5.3 Emissions of N_2O after (a) deep ploughing, (b) conventional ploughing, (c) rotary tillage of lettuce residues (-PW/+R) (filled symbols) and controls (-PW/-R) (empty symbols) in the absence of paper waste at Mackies Field. Arrow indicates date of cultivation.

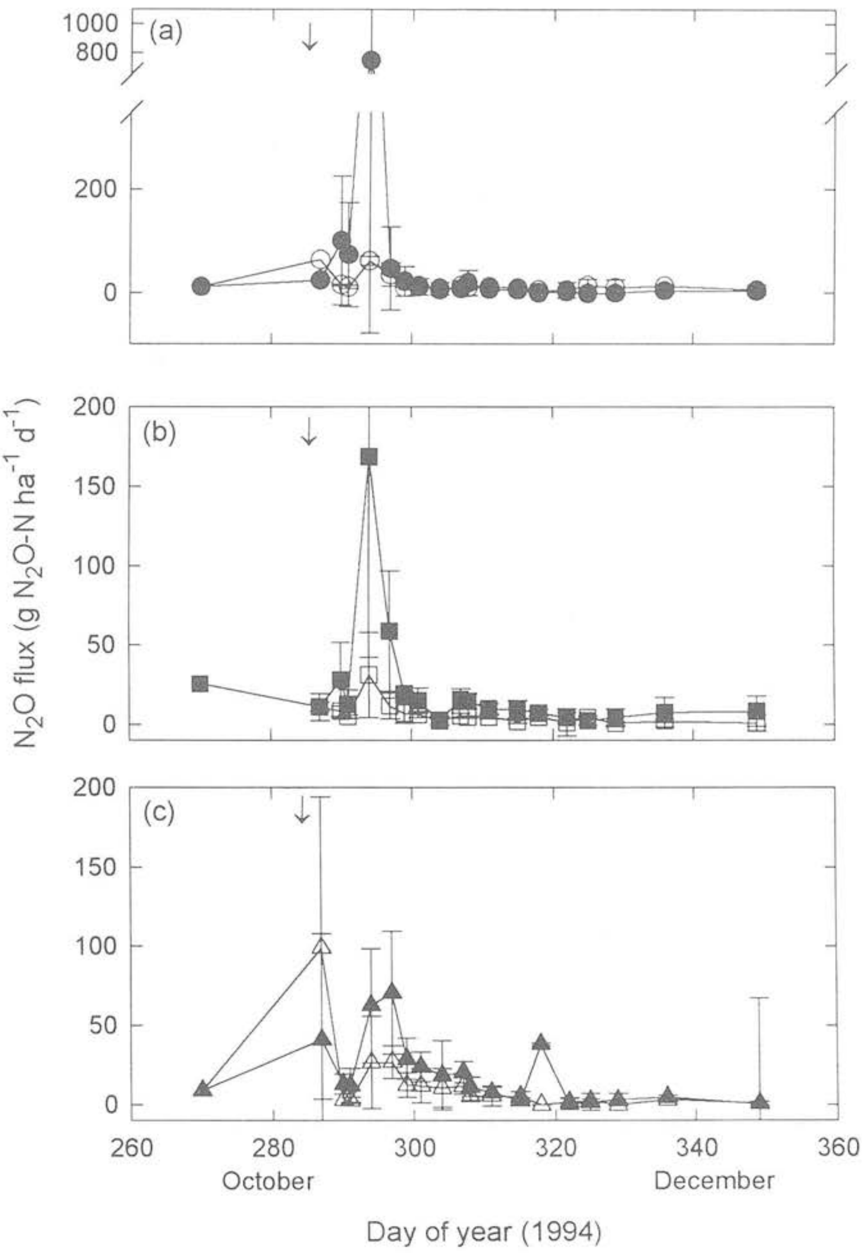

Figure 5.4 Emissions of N_2O after (a) deep ploughing, (b) conventional ploughing, (c) rotary tillage of lettuce residues (+PW/+R) (filled symbols) and controls (+PW/-R) (empty symbols) in the presence of paper waste at Mackies Field. Arrow indicates date of cultivation.

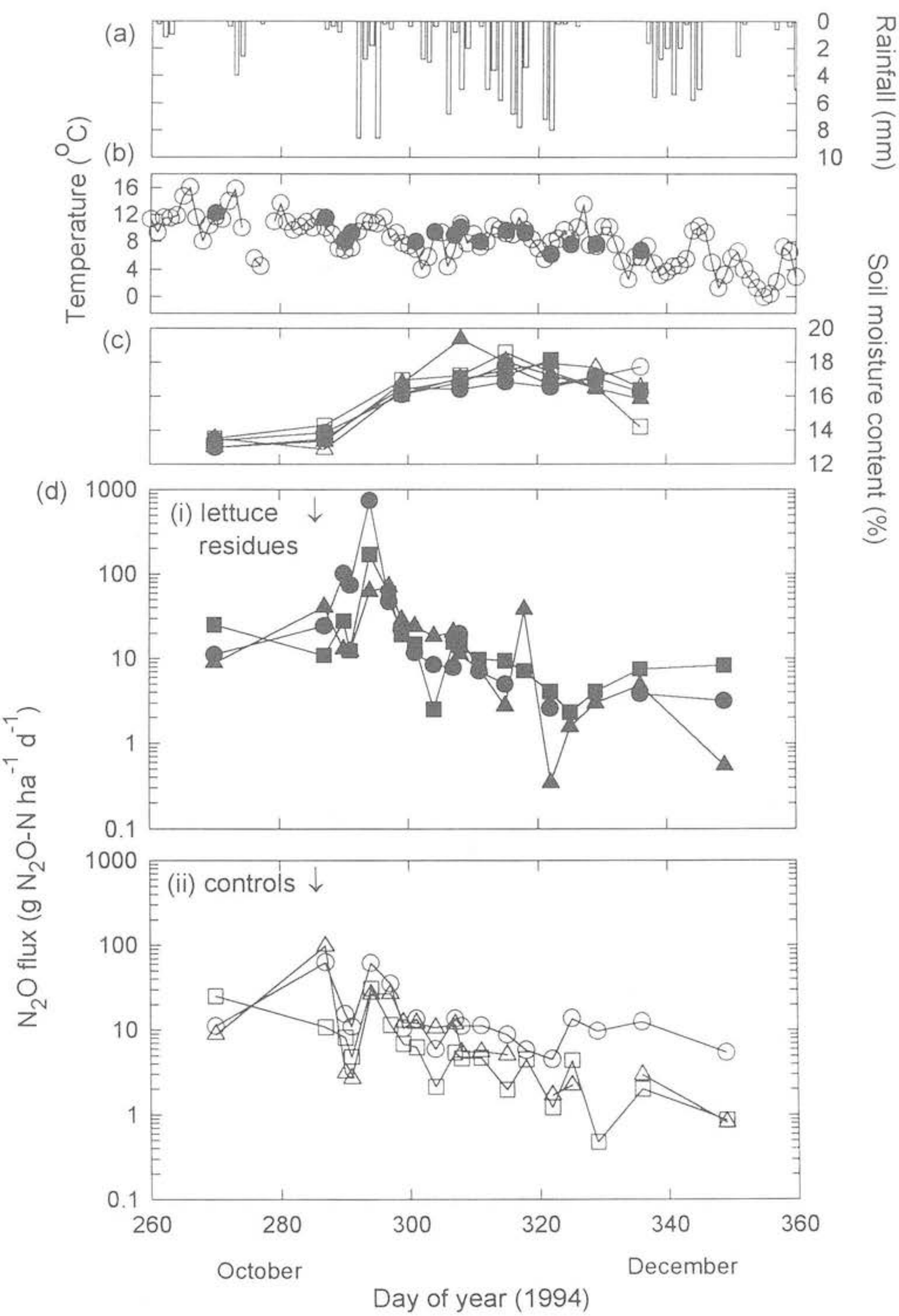

Figure 5.5 (a) Rainfall, (b) air temperature (empty symbols), soil temperature (filled symbols), (c) soil moisture contents, (d) N_2O emissions after deep ploughing (circles), rotary tillage (triangles) and conventional ploughing (squares) of lettuce residues (+PW/+R) and controls (+PW/-R) in the presence of paper waste at Mackies Field. Arrow indicates date of cultivation.

5.3.1.3 N_2O measurements with autochambers

Emissions of N_2O as measured with autochambers are presented in Appendix III. The autochambers sampled every 6 hours, making it possible to investigate diurnal variations in emissions. Emissions increased during the day, peaking at 2 pm and 8 pm, although this was not consistent. In general, greater emissions were measured from the conventionally ploughed +PW/-R treatment, with large fluxes measured on 14, 20-22, 25-28 November and 10-12 December. These were probably in response to rainfall over the few days prior to each of these emissions. The N_2O emissions from cover boxes (generally sampled at 2 pm) and the automatically sampled emissions (for the 2 pm samples only) were compared (Fig. 5.6). Measurements of N_2O from autochambers were high, averaging 0.51 times those from the cover boxes (Rees *et al.*, 1997). The autochamber measurements differed most strongly from the cover box measurements at times when the autochambers recorded large fluxes. A flux of 154 g N_2O-N ha^{-1} d^{-1} was measured from the conventionally ploughed -PW/+R treatment using an autochamber on 14 November. However only 13 g N_2O-N ha^{-1} d^{-1} was measured from cover boxes on this treatment on this day.

5.3.1.4 N_2O in soil profile

In general the greatest differences in N_2O concentrations between treatments were on the first two sampling dates; the N_2O concentrations decreased with time (Fig. 5.7).

Concentrations of N_2O were consistently low at 150 mm depth both on the deep ploughed +PW/+R and +PW/-R treatments, and at 250 and 50 mm depths on the deep ploughed +PW/+R treatment throughout the whole of the sampling period. Comparatively high concentrations of N_2O, 7 and 16.2 ppm were measured at 50 mm on the deep ploughed +PW/-R treatment on 31 October and 3 November, respectively.

Concentrations of N_2O decreased over time in the deep ploughed -PW treatment. At all 3 depths they were higher in the -PW/-R treatment, for example, 7.7 ppm at 250 mm depth on 31 October, compared with 0.4 ppm on the -PW/+R treatment. Concentrations in the deep ploughed -PW/+R treatment remained low throughout the sampling period at this depth.

The highest concentrations over the first 3 sampling dates in the conventional ploughed -PW were measured from the -PW/+R treatment at 50 mm depth. A concentration of 5.8 ppm was measured in this treatment on 31 October. Over the whole sampling period low concentrations were measured at 250 mm depth on the conventional ploughed -PW/+R treatment.

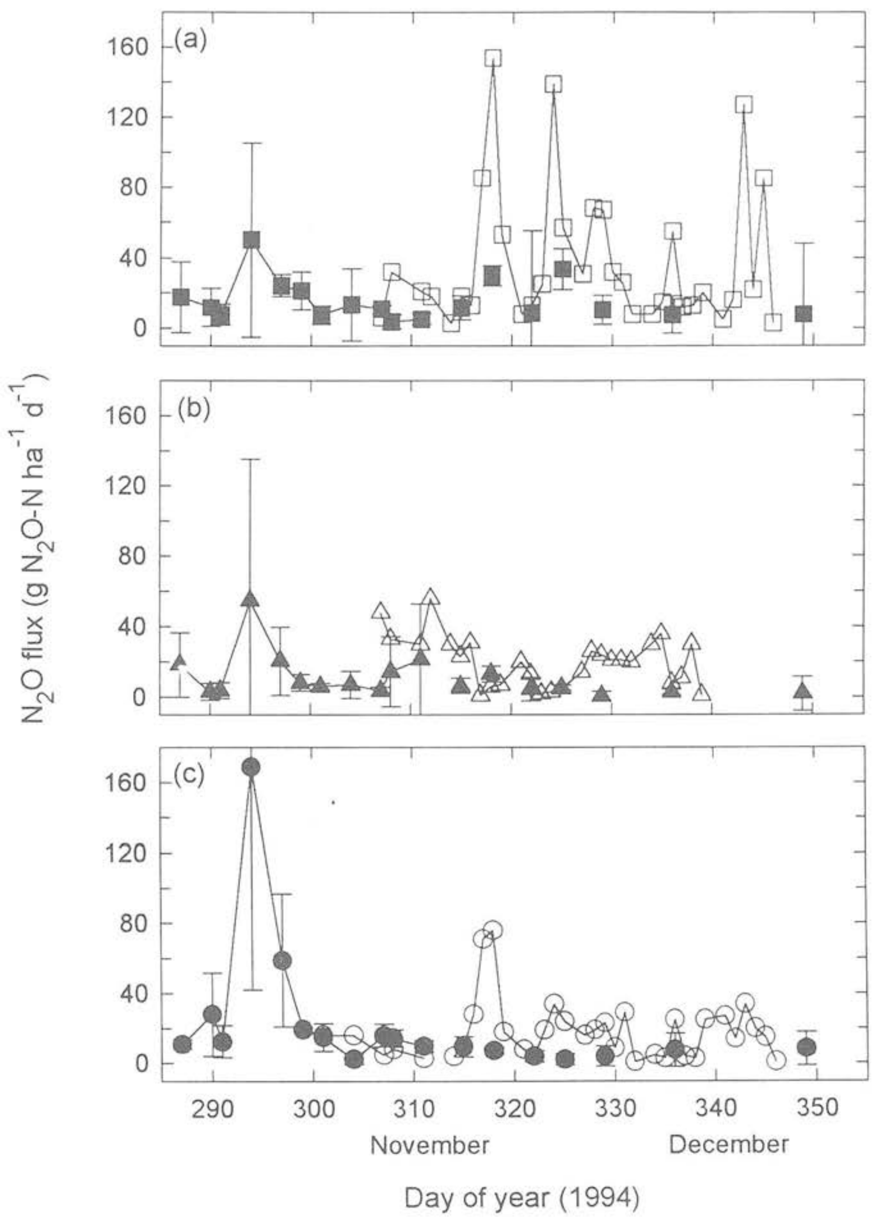

Figure 5.6 Emissions of N_2O from autochambers (empty symbols) and cover boxes (filled symbols) after conventional ploughing of (a) lettuce residues (-PW/+R), (b) control (-PW/-R) and (c) lettuce residues with paper waste (+PW/+R).

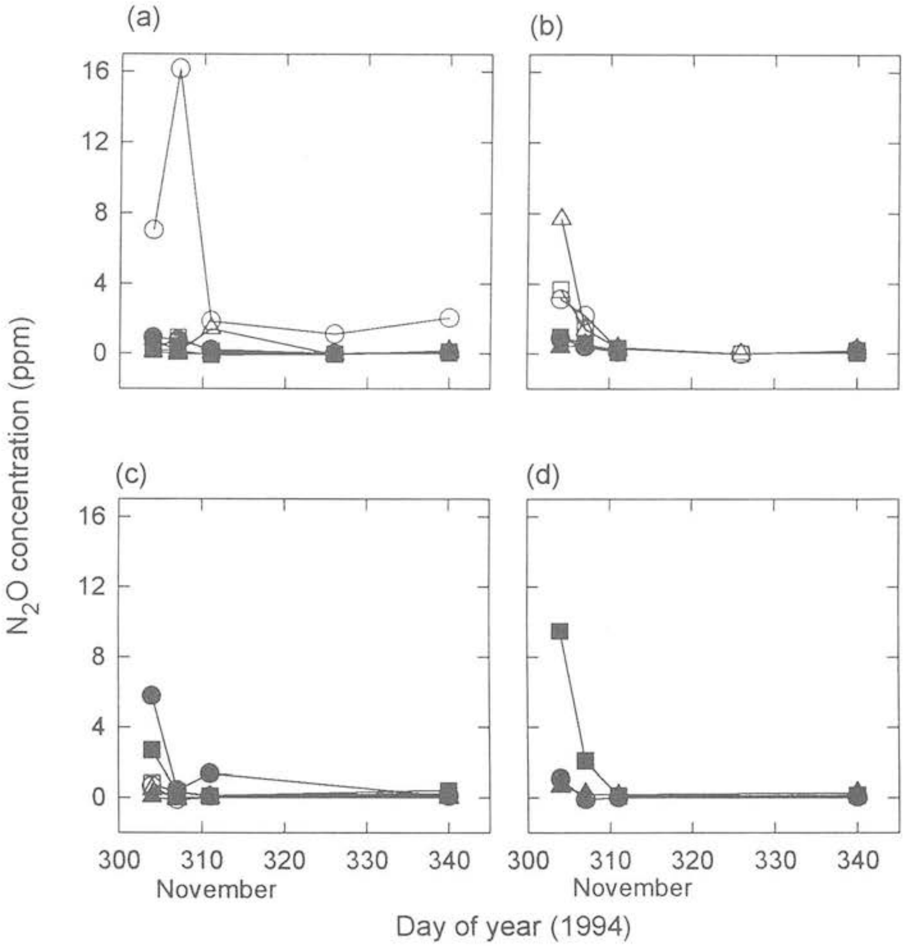

Figure 5.7 Concentrations of N_2O at 50 mm (circles), 150 mm (squares) and 250 mm (triangles) depths on control (empty symbols) and lettuce residue (filled symbols) plots after (a) deep ploughing with paper waste, (b) deep ploughing without paper waste, (c) conventional ploughing without paper waste and (d) rotary tillage without paper waste.

A concentration of 9.5 ppm was measured at 150 mm depth in the rotary tilled -PW/+R treatment on 31 October. This concentration fell over time. From 3 to 6 November the lowest concentrations on this treatment were obtained at 50 mm depth.

5.3.1.5 Available soil N

In general, available soil N increased immediately after cultivation, and then declined throughout the sampling period to concentrations lower than prior to cultivation (Fig. 5.8). Slight increases were measured on most treatments towards the end of the sampling period.

Available NH_4^+ increased in all treatments without paper waste after cultivation, particularly in the -PW/-R treatments, with 5.4 and 6.2 μg NH_4^+-N g dry soil^{-1} measured in the conventionally ploughed -PW/-R treatment on 27 September and 14 October, respectively. Concentrations in the conventionally ploughed -PW/-R were greater ($p<0.05$) than in the -PW/+R treatment. Available NH_4^+ increased towards the end of the sampling period; particularly in the rotary tilled -PW/+R treatment.

Following cultivation the only increase in available NO_3^- was in the rotary tilled treatments, with 4 and 8.2 μg NO_3^--N g dry soil^{-1} measured in the -PW/+R and -PW/-R treatments, respectively on 14 October. These concentrations were not significantly different than those in other treatments. Available NO_3^- then fell until 18 November. A short-lived increase to 1.6 μg NO_3^--N g dry soil^{-1} on 25 November was measured in the rotary tilled -PW/+R treatment. The other treatments exhibited slight increases in available NO_3^- towards the end of the sampling period.

Cultivation of paper waste treatments increased available NH_4^+ in the rotary tilled +PW/+R and conventionally ploughed +PW/-R treatments, but not significantly. By 26 October concentrations in the rotary tilled and deep ploughed +PW/+R treatments had increased to 13.6 and 3.5 μg NH_4^+-N g dry soil^{-1}, respectively. Small increases in available NH_4^+ were measured towards the end of the sampling period in the conventionally and deep ploughed +PW/+R treatments. Cultivation immediately increased available soil NO_3^- in the deep ploughed +PW/-R and conventional ploughed +PW/+R treatments, but not significantly. By 26 October available NO_3^- had fallen in all treatments, and most noticeably in the deep ploughed +PW/-R.

5.3.1.6 Biomass N

There was no significant difference in concentrations of biomass N between residue and control treatments both without and with paper waste, or between the 2 sampling depths (Figs.

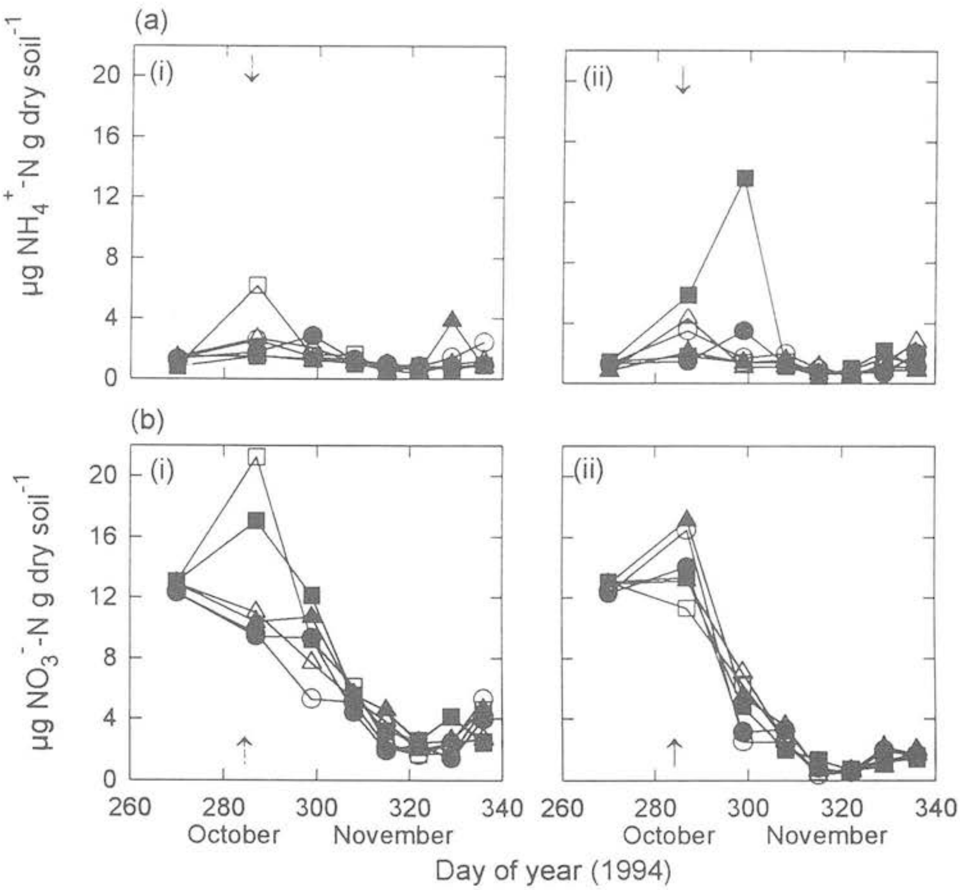

Figure 5.8 Concentrations of (a) available NH_4^+, (b) available NO_3^-, after deep ploughing (circles), conventional ploughing (squares) and rotary tillage (triangles) of lettuce residues (filled symbols) and controls (empty symbols) in the (i) absence and (ii) presence of paper waste at Mackies Field. Arrows indicate date of cultivation.

5.9a and 5.9b). A concentration of 39.1 mg biomass N kg dry soil^{-1} was measured in the rotary tilled -PW/+R treatment at 0-0.2 m depth and 78.6 mg biomass N kg dry soil^{-1} was measured on the conventionally ploughed +PW/+R treatment at 0-0.2 m depth.

5.3.1.7 Biomass C

There was no significant difference in concentrations of biomass C between residue and control treatments both without and with paper waste, or between the 2 sampling depths (Figs. 5.10a and 5.10b). A concentration of 115 mg biomass C kg dry soil^{-1} was measured at 0-0.2 m depth on the rotary tilled -PW/+R treatment and a concentration of 308 mg biomass C kg dry soil^{-1} was measured at 0-0.2 m depth on the conventionally ploughed +PW/+R treatment.

5.3.1.8 Gravimetric soil moisture contents and rainfall

There was no significant difference in soil moisture contents on both -PW and +PW treatments (Figs. 5.2c and 5.4c). Rainfall, especially the 22.6 mm between 19 and 24 October (Figs. 5.2a and 5.4a), increased soil moisture contents.

5.3.1.9 Temperature

The air temperatures at times of gas sampling are shown in Figs 5.2 and 5.4. The average air and soil temperatures taken manually over the sampling period were 10.8 ^{o}C and 8.9 ^{o}C, respectively. The temperatures fluctuated around these averages until towards the end of the sampling period when they fell. The air temperature was consistently higher than the soil temperature except on 14 November when it temporarily fell below that of the soil.

5.3.1.10 Residue density and properties

The density of lettuce plants remaining after harvest and an estimate of their percentage ground cover are presented in Table 5.4. There was no significant difference in plant density or ground cover between different areas of the field prior to cultivation. These lettuce residues had an average dry matter content of 9.6 %, a N content of 5.1 % and a C of 39.9 %, giving a C:N ratio of 7.8:1.

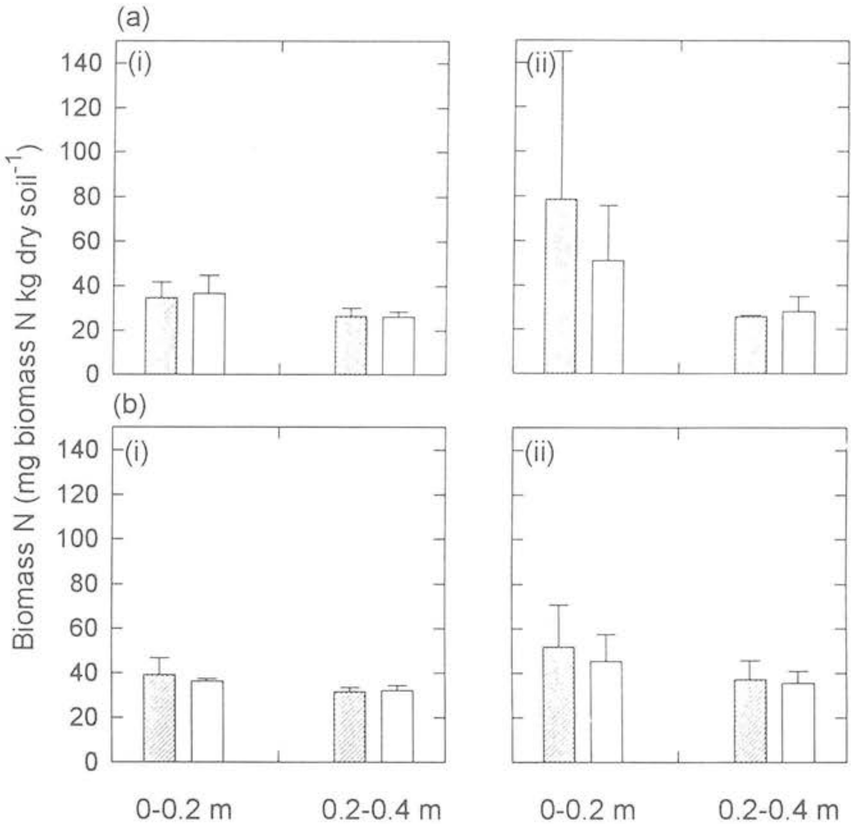

Figure 5.9 Concentrations of biomass N after (a) conventional ploughing, (b) rotary tillage of lettuce residues (hatched bars) and controls (empty bars) in the (i) absence and (ii) presence of paper waste at Mackies Field.

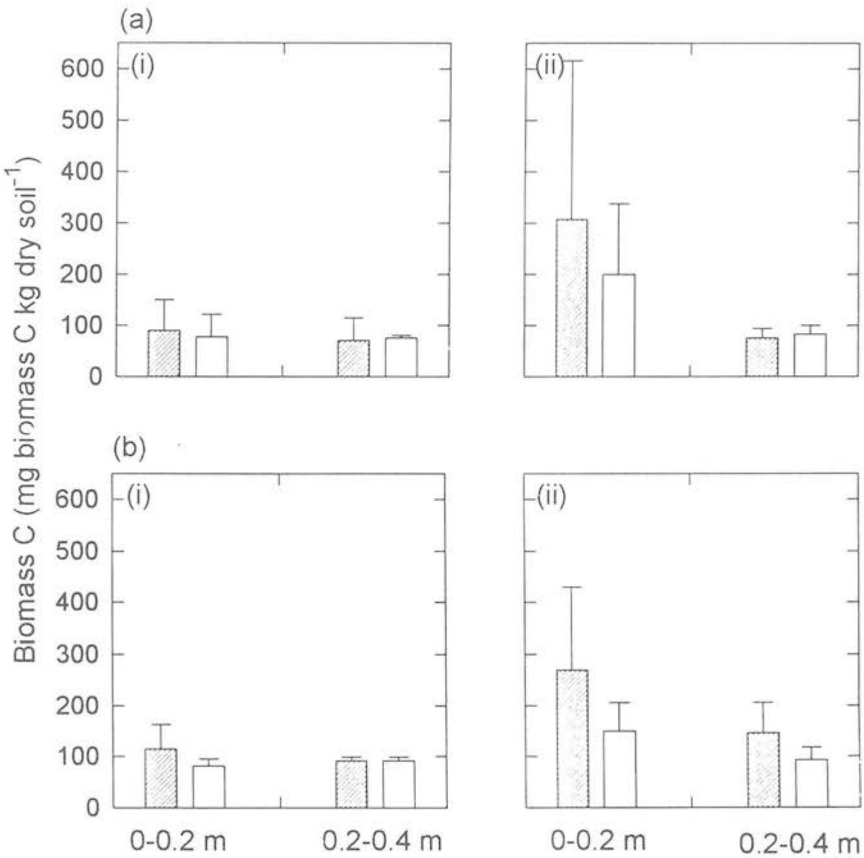

Figure 5.10 Concentrations of biomass C after (a) conventional ploughing, (b) rotary tillage of lettuce residues (hatched bars) and controls (empty bars) in the (i) absence and (ii) presence of paper waste at Mackies Field.

Table 5.4 Post-harvest residue density and ground cover averaged for subsequent cultivation treatment

Cultivation	Density (plants m^{-2})	Ground cover (%)
deep ploughing	5.8 ± 3.4	72.5 ± 18.6
conventional ploughing	5 ± 3.2	67.5 ± 10.8
rotary tillage	6.6 ± 3.4	75.8 ± 13.2

5.3.2 Dipper Field (Calabrese)

5.3.2.1 Cumulative emissions of N_2O

Cumulative N_2O emissions are presented in Fig. 5.11. Emissions from the deep ploughed and rotary tilled -PW/+R treatments were greater than from the -PW/-R treatments ($p<0.05$), but the situation was reversed for the conventional ploughed treatment, where over the whole sampling period the -PW/-R treatment emitted 472 g N_2O-N ha^{-1} compared with 183 g N_2O-N ha^{-1} from the conventional ploughed -PW/+R treatment ($p<0.05$). Over the whole sampling period 353 g N_2O-N ha^{-1} was measured from the deep ploughed -PW/+R treatment. As at Mackies Field, most of the N_2O was released during the first 2 weeks after cultivation. The percentage of total N_2O released over this period was lower after cultivation of calabrese residues, except where they were deep ploughed.

The incorporation of residues in the presence of paper waste resulted in higher (but not statistically significant) cumulative emissions over the whole sampling period from the deep ploughed and conventionally ploughed treatments compared with the +PW/-R treatments (Fig. 5.11). Over the first 2 weeks emissions from the conventionally ploughed +PW/+R were higher ($p<0.01$) than from the conventionally ploughed -PW/+R treatment. The presence of paper waste also increased emissions from the rotary tilled +PW/-R treatment ($p<0.05$), with 194 and 282 g N_2O-N ha^{-1} emitted during the first 2 weeks and the whole sampling period, respectively.

5.3.2.2 Daily N_2O fluxes

Emissions of N_2O from the treatments without paper waste were initially reduced after cultivation, particularly from the deep ploughed -PW/+R treatment (Fig. 5.12). The only increase in N_2O occurred in the conventionally ploughed -PW/+R treatment, of 1 g N_2O-N ha^{-1} d^{-1} between 2 and 9 December. Seven days after cultivation (14 December) there were

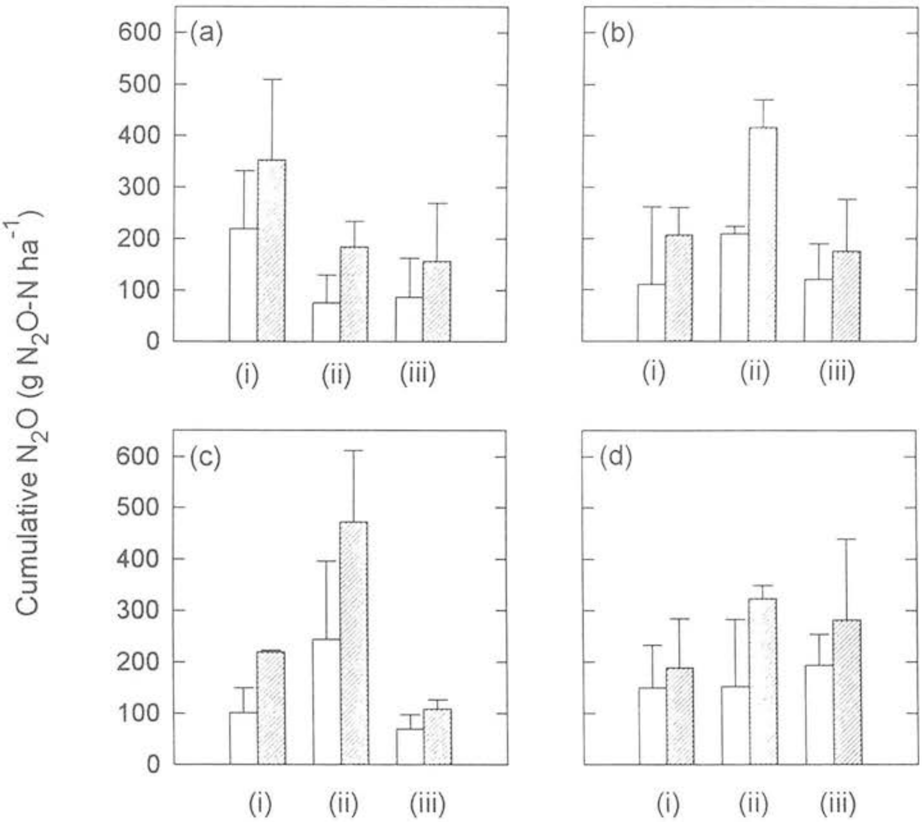

Figure 5.11 Cumulative emissions of N_2O over the whole 33 day sampling period (hatched bars) and over the first 2 weeks after cultivation (empty bars) of (a) calabrese residues (-PW/+R), (b) calabrese residues and paper waste (+PW/+R), (c) controls (-PW/-R), (d) controls with paper waste (+PW/-R) by (i) deep ploughing, (ii) conventional ploughing, (iii) rotary tillage at Dipper Field.

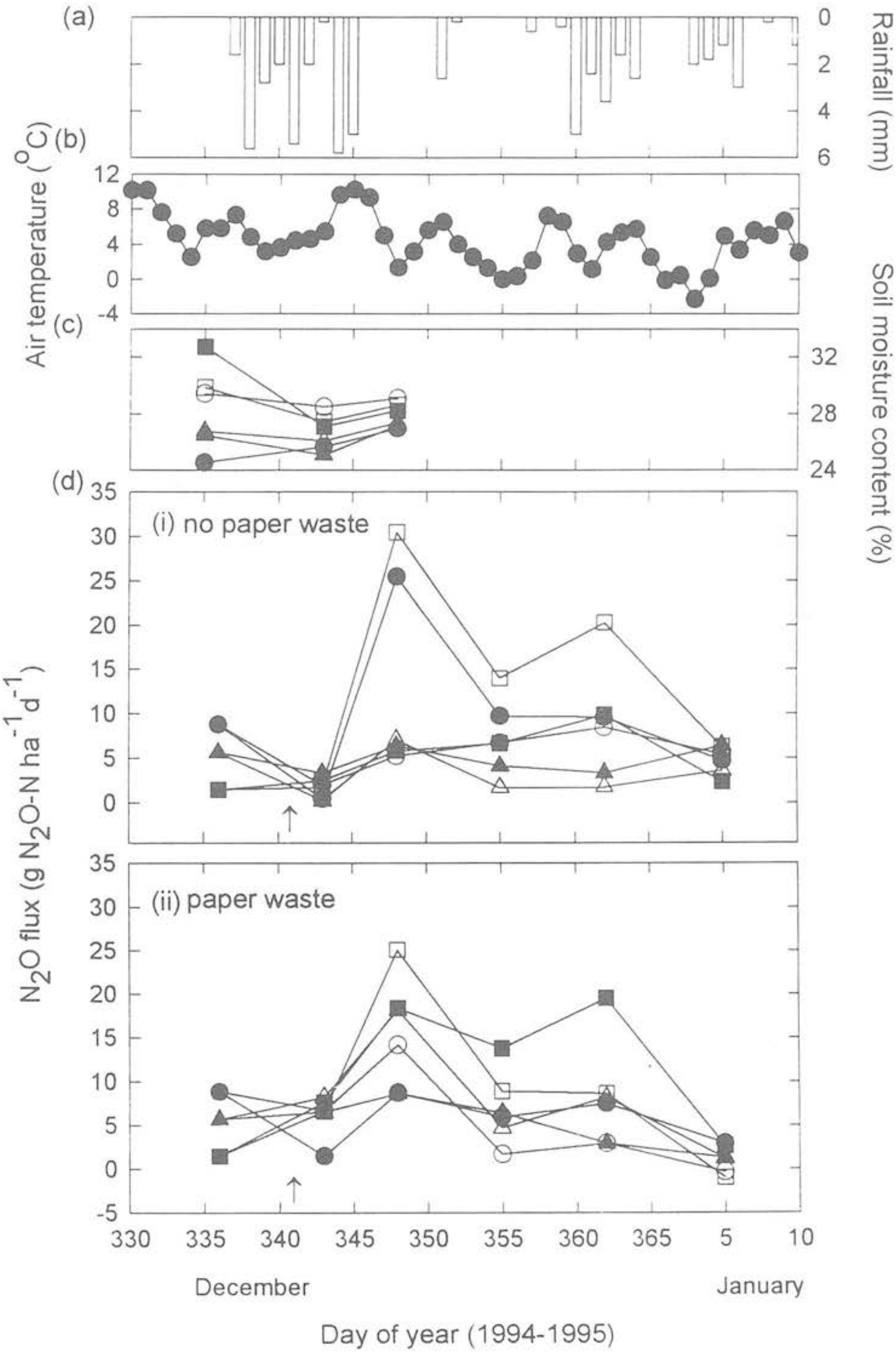

Figure 5.12 (a) Rainfall, (b) air temperature, (c) soil moisture content, (d) N_2O emissions following deep ploughing (circles), rotary tillage (triangles) and conventional ploughing (squares) of calabrese residues (filled symbols) (-PW/+R) and controls (empty symbols) (-PW/-R) in the (i) absence and (ii) presence of paper waste at Dipper Field. Arrows indicate date of cultivation.

large fluxes of N_2O from the conventionally ploughed -PW/-R deep ploughed -PW/+R treatments of 30.5 g N_2O-N ha^{-1} d^{-1} and 25.5 g N_2O-N ha^{-1} d^{-1}, respectively, which were significantly greater ($p<0.01$) than fluxes from other treatments on this day. Between 14 and 28 December high emissions were measured from the conventionally ploughed -PW/-R treatment. The standard deviations of each treatment are shown in Fig. 5.13.

Emissions of N_2O increased immediately after rotary tillage and conventional ploughing in the presence of paper waste, but were reduced after deep ploughing, particularly where residues were incorporated (Figs. 5.12 and 5.13). As in the absence of paper waste, large fluxes of N_2O occurred 7 days after cultivation. The highest observed value was 25.1 g N_2O-N ha^{-1} d^{-1}, from the conventionally ploughed +PW/-R treatment on this day, but this was not significantly higher than fluxes from the other treatments. On 28 December a flux of 19.5 g N_2O-N ha^{-1} d^{-1} was measured from the conventionally ploughed +PW/+R, which was greater ($p<0.05$) than those from other treatments on this day, and was strongly positively correlated ($r=0.6$, $p<0.05$) with a rise in air temperature of 4.3 ^{o}C between 21 and 28 December. By 5 January 1995 emissions from all treatments were low. The standard deviations for each treatment are shown in Fig. 5.13.

5.3.2.3 Available soil N

Throughout the experimental period there was no significant difference between available N in the various treatments (Fig. 5.14). This may have been due to the low temperatures throughout the experimental period (Fig. 5.11b). The presence of paper waste had little effect on either N pool, with the exception of the available NH_4^+ after rotary tillage (+PW/+R). On 14 December 6.5 μg NH_4^+-N g dry $soil^{-1}$ was measured in this treatment. Available NH_4^+ concentrations increased in the conventional ploughed +PW/+R treatment throughout the experimental period, and by 2.7 μg NH_4^+-N g dry $soil^{-1}$ between 28 December 1994 and 15 February 1995. Available soil NO_3^- fell throughout the experimental period. Higher concentrations were measured in the conventionally ploughed +PW/+R than in the corresponding -PW/+R treatment. The greatest decrease in available NO_3^- throughout the sampling period was measured in the deep ploughed +PW/+R treatment.

5.3.2.4 Biomass N

There was no significant difference in concentrations of biomass N between residue and control treatments both without and with paper waste, or between the 2 sampling depths (Figs. 5.15a and 5.15b). In general biomass N was higher (but not significantly) at 0-0.2 m than at 0.2-0.4 m depth and a concentration of 60.1 mg biomass N kg dry $soil^{-1}$ was measured in the

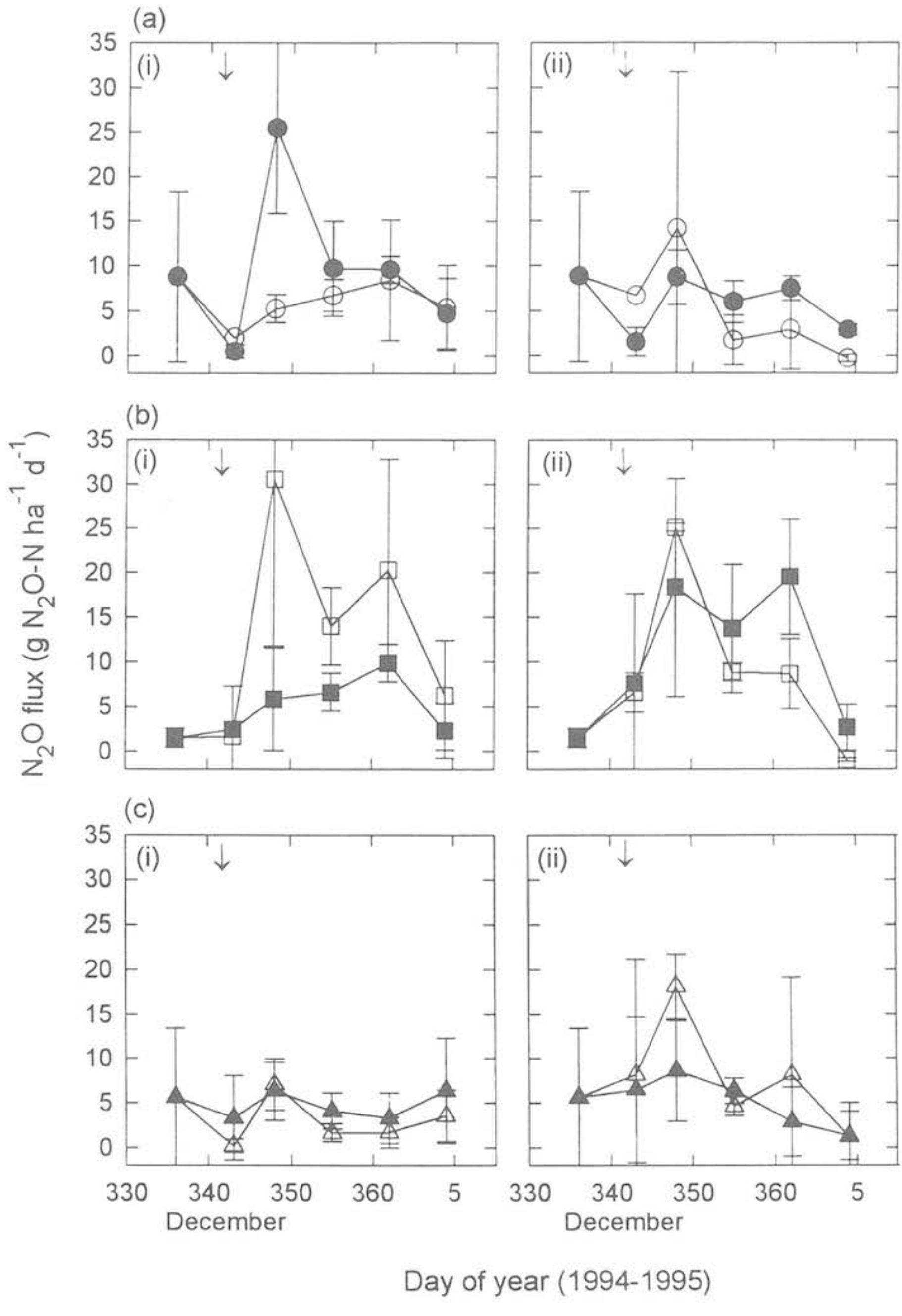

Figure 5.13 Emissions of N_2O after (a) deep ploughing, (b) conventional ploughing, (c) rotary tillage of calabrese residues (filled symbols) and controls (empty symbols) in the (i) absence and (ii) presence of paper waste at Dipper Field. Arrows indicate date of cultivation.

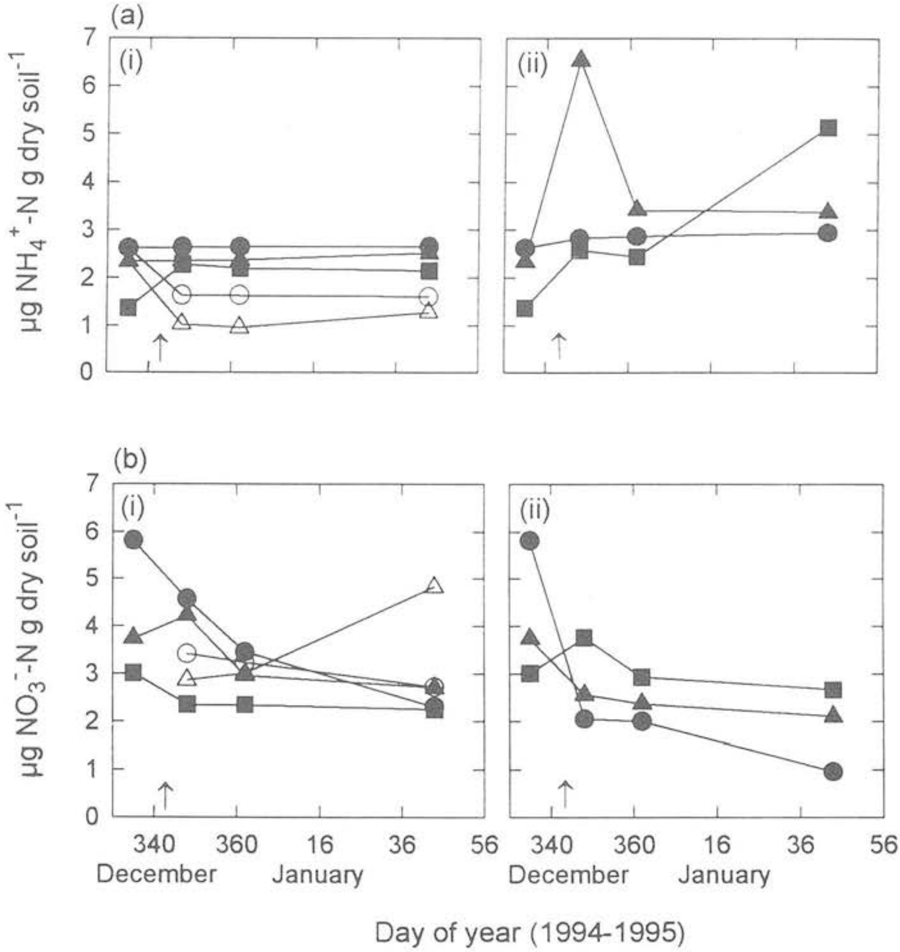

Figure 5.14 Concentrations of (a) available soil NH_4^+, (b) available soil NO_3^-, after deep ploughing (circles), rotary tillage (triangles) and conventional ploughing (squares) of calabrese residues (filled symbols) and controls (empty symbols) at Dipper Field with (i) no paper waste, (ii) paper waste. Arrows indicate date of cultivation.

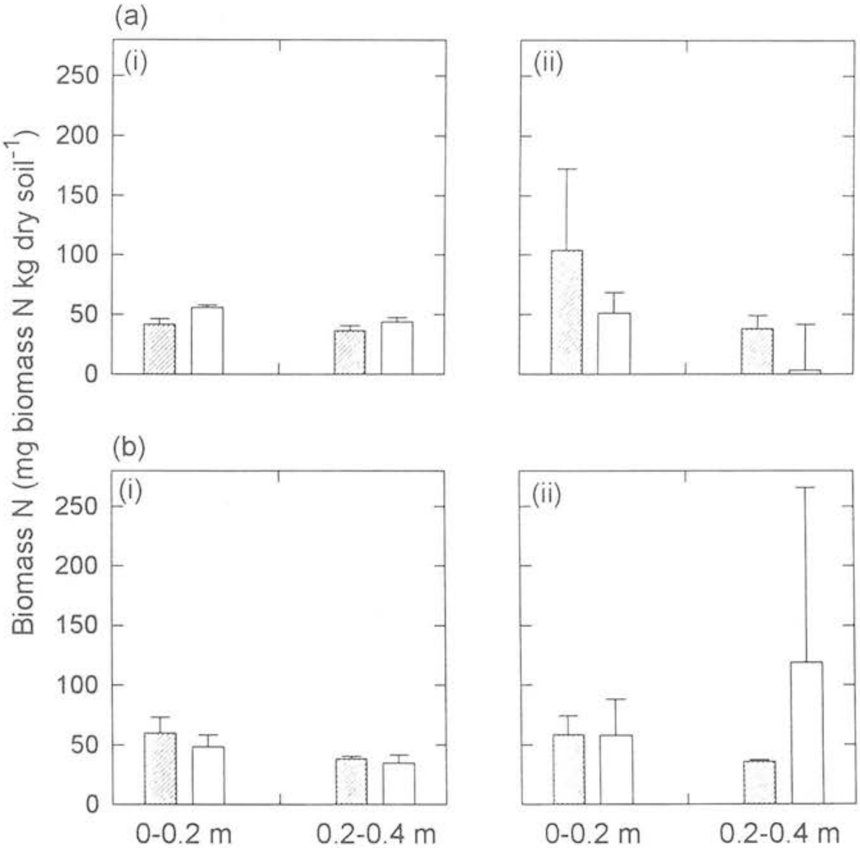

Figure 5.15 Concentrations of biomass N after (a) conventional ploughing, (b) rotary tillage of calabrese residues (hatched bars) and controls (empty bars) in the (i) absence and (ii) presence of paper waste at Dipper Field.

lightly tilled -PW/+R treatment at 0-0.2 m depth. A concentration of 120 mg biomass N kg dry soil^{-1} was measured in the rotary tilled +PW/-R treatment.

5.3.2.5 Biomass C

There was no significant difference in concentrations of biomass C between residue and control treatments both without and with paper waste, or between the 2 sampling depths (Figs. 5.16a and 5.16b). In general biomass C was higher (but not significantly) at 0-0.2 m than at 0.2-0.4 m depth. A concentration of 195 mg biomass C kg dry soil^{-1} was measured in the conventionally ploughed -PW/-R treatment at 0-0.2 m depth, and 478 mg biomass C kg dry soil^{-1} was measured at 0-0.2 m depth in the conventionally ploughed +PW/+R treatment.

5.3.2.6 Gravimetric soil moisture contents

There was no significant difference in soil moisture contents throughout the experimental period, although application of paper waste appeared to raise moisture contents, and reduced differences between treatments towards the end of the experimental period (Fig. 5.12). Average moisture contents were 28 and 27 % in the presence and absence of paper waste, respectively.

5.3.2.7 Residue properties

The calabrese residues had an average dry matter content of 11.9 %. The heads, leaves and stems had respective dry matter contents of 11.9, 13.9 and 9.9 %. These residues had a N content of 2.5 %, a C content of 40.0 % and a C:N ratio of 16:1.

5.3.2.8 Temperature

Both the air and soil temperatures fell between 11 and 21 December, the air temperature falling from 10.3 to -0.1 ^{o}C (Fig. 5.12b). After 21 December the air temperature steadily increased, but the soil temperature remained low.

5.4 Discussion

5.4.1 Effect of cultivation in the absence of paper waste

Nitrous oxide emissions were increased by cultivation. At Mackies Field the greatest increase occurred immediately after cultivation, when 36 g N_2O-N ha^{-1} d^{-1} was emitted after rotary tillage of residues (-PW/+R). However, emissions of N_2O were consistently low throughout the experimental period from the rotary tilled -PW/-R treatment. This suggests that after the initial N_2O fluxes it was the presence of residues that induced emissions and not the action of

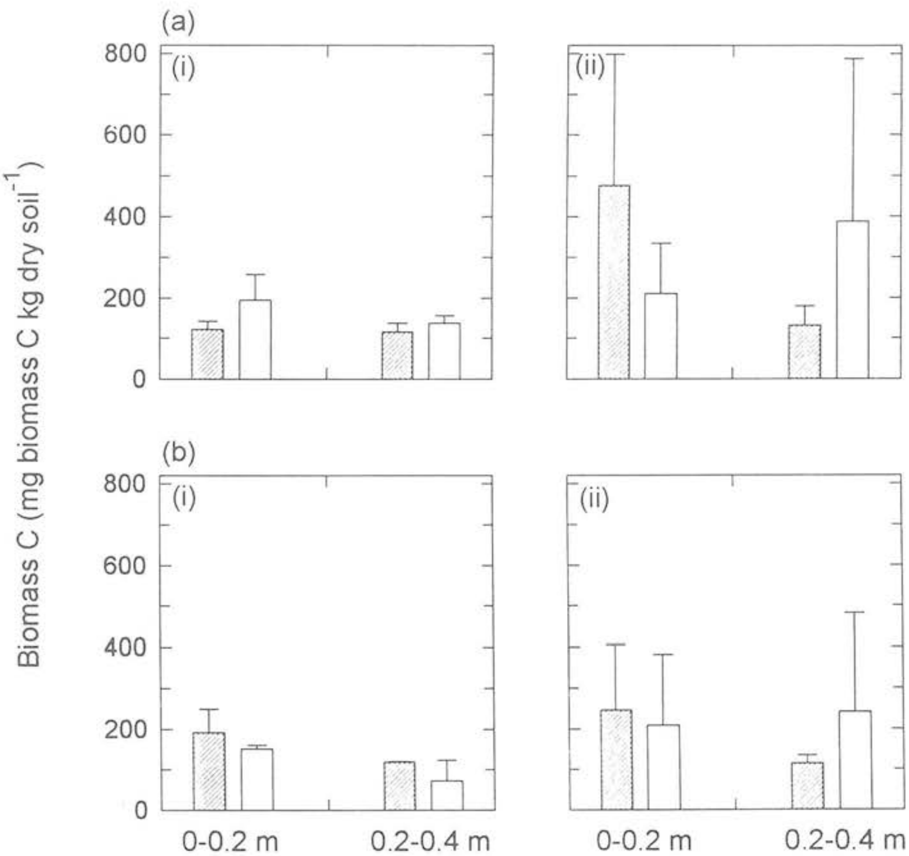

Figure 5.16 Concentrations of biomass C after (a) conventional ploughing, (b) rotary tillage of calabrese residues (hatched bars) and controls (empty bars) in the (i) absence and (ii) presence of paper waste at Dipper Field.

cultivation alone. The presence of fresh crop residues within the soil is known to stimulate microbial activity, resulting in gaseous losses of N_2O via nitrification and denitrification (Goodroad *et al.*, 1984; de Catanzaro and Beauchamp, 1985; Drury *et al.*, 1991; McKenney *et al.*, 1995).

Large N_2O emissions following tillage or minimal cultivation are reported in the literature. N_2O losses have been found to be higher from completely undisturbed or lightly cultivated soils than from ploughed soils, even in the absence of crop residues (for example, Burford *et al.*, 1981; Aulakh *et al.*, 1984b; Linn and Doran, 1984; Aulakh and Rennie, 1986; Staley *et al.*, 1990). Burford *et al.* (1981) estimated annual N_2O emissions of between 5.4 and 8.6 kg N_2O-N ha^{-1} from zero cultivated soils and between 0.9 and 5.6 kg N_2O-N ha^{-1} from ploughed soils. Such a difference between cultivation treatments is often attributed to changes in pore-space distribution, aeration, soil moisture content, growth of roots and micro-organisms with reduced cultivation of soils (Burford *et al.*, 1981). These factors are primary regulators of gaseous N losses (Focht, 1974). The action of ploughing dries the soil by exposing a greater surface area of soil to the atmosphere (Ross, 1990). The presence of fresh crop residues remaining on the surface of a zero tilled soil helps to maintain soil moisture and nutrients in the top layers of the soil (Lynch and Panting, 1980), resulting in a favourable environment for microbial growth, immobilisation of N and denitrification. This is confirmed by the difference in soil moisture contents after light tillage in this experiment. The action of the power harrow was sufficient to dry the soil in the absence of residues, whereas soil moisture contents were raised in the presence of residues.

Aulakh *et al.* (1991b) found higher concentrations of soil NO_3^- where residues were surface-placed or there were no residues, compared with where residues were incorporated into the soil. However, at Mackies Field concentrations of available NO_3^- increased after conventional ploughing but declined after rotary tillage and deep ploughing. Available NH_4^+ increased after cultivation, particularly in the absence of lettuce residues. The lower NH_4^+ in the presence of residues suggests that their incorporation may have resulted in immobilisation of N. Emissions of N_2O may have been from both nitrification and denitrification. The high concentrations of available NH_4^+ and NO_3^- in the conventionally ploughed -PW/-R treatment suggest that cultivation resulted in increased mineralisation and nitrification, which was the probable cause of the large fluxes observed from this treatment on 21 October.

On 21 October large N_2O fluxes followed all cultivations at Mackies Field, except after rotary tillage of the -PW/-R. These fluxes 8 days after cultivation were most likely to be in response to the 13.2 mm rainfall between 18 and 21 October. Denmead *et al.* (1979a) found that increases in N_2O emissions from a grass sward occurred almost immediately after addition of water. The greatest flux of 67.5 g N_2O-N ha^{-1} d^{-1} on 24 October measured after rotary tillage of residues may have partly been due to the residues conserving soil moisture for longer than in the other treatments, resulting in anaerobic conditions and loss of N_2O during denitrification (Focht *et al.*, 1979). Unfortunately, under such field conditions it is not completely possible to determine the respective effects of rainfall and cultivation on the N_2O emissions. However, the N_2O fluxes on 14 October probably resulted from increased microbial activity stimulated by cultivation alone, whereas the emissions measured between 21 and 27 October probably resulted from further activity induced by rainfall over this period.

At Dipper Field the delay of the first large N_2O fluxes until 6 days after cultivation was most probably due to the lower temperatures after cultivation compared with those after cultivation of Mackies Field. Microbial activity is temperature-dependent (Addiscott, 1983; Stott *et al.*, 1986). Low temperatures slow down microbial activity within the soil, thereby reducing the rates of mineralisation, nitrification and denitrification. In contrast to trends observed in Mackies Field, the greatest N_2O fluxes at Dipper Field of 30.5 and 25.5 g N_2O-N ha^{-1} d^{-1} on 14 December were measured from the conventionally ploughed -PW/-R and deep ploughed -PW/+R treatments, respectively. These fluxes were most probably induced by the 30.4 mm rainfall between 3 and 10 December, as well as the action of cultivation (Conrad *et al.*, 1983; Frankenberger and Abdelmagid, 1985). The 5 ^{o}C temperature increase between 9 and 11 December would also have induced a flush of microbial activity resulting in these N_2O fluxes. The occurrence of mineralisation after cultivation is confirmed by the comparatively greater NH_4^+ concentrations after deep ploughing of residues. NO_3^- concentrations in this treatment fell throughout the experimental period due to denitrification and/or leaching losses. Emissions from the conventionally ploughed -PW/-R treatment remained the highest until the end of the experimental period. This may have been due to increased aeration of the soil by ploughing stimulating microbial activity (Ross, 1990). The fluxes measured from this treatment on 28 December probably resulted from increased denitrifier activity after rainfall.

Overall, N_2O emissions were lower after cultivation of Dipper Field than after cultivation of Mackies Field. This may in part be attributed to lower temperatures both prior to and following the later cultivation of Dipper field. Low temperatures reduce N_2O production by lowering rates of microbial activity (Harper, 1988). More than half of the above-ground material of brassica crops remains in the field after harvest (Ryden and Lund, 1980). Thus the presence of brassica residues on the surface and their incorporation have a greater potential for N_2O losses. However, this was not apparent after incorporation of calabrese residues in this experiment.

The composition of the residues must also be taken into account. Higher N_2O emissions have been observed when the incorporated plant material had a low C:N ratio (Goodroad *et al.*, 1984; McKenney *et al.*, 1993), such as the lettuce residues at Mackies Field. Short-lived immobilisation of N usually occurs after incorporation of plant material with a high C:N ratio (Dolar *et al.*, 1972; Jenkinson, 1984). The calabrese residues had a higher C:N ratio (16:1) than the lettuce residues (7.8:1), resulting in lower losses of N_2O from nitrification and denitrification. The greater concentrations of biomass N found after incorporation of calabrese residues also suggests that immobilisation of soil N occurred at this site (Castle, 1995, pers. comm.).

5.4.2 Effect of paper waste application

The application of paper waste resulted in increased N_2O emissions after cultivation at both sites. This was particularly marked 8 days after deep ploughing of residues at Mackies field, where a maximum flux of 748 g N_2O-N ha^{-1} d^{-1} was measured. A large flux of 169 g N_2O-N ha^{-1} d^{-1} was also observed on this day after conventional ploughing of residues. The presence of residues resulted in larger fluxes of greater duration. However, by about 1 November N_2O emissions had fallen to levels found where no paper waste was applied.

Emissions of N_2O were raised 7 days after cultivation of Dipper Field, particularly from the conventionally ploughed +PW/-R and +PW/+R treatments. However, emissions from the conventionally ploughed +PW/-R and deep ploughed +PW/+R treatments were lower than where no paper waste had been applied. This may have reflected the higher C:N ratio of the calabrese residues than the lettuce residues, resulting in greater immobilisation of N in residue amended treatments at Dipper Field, lowering N_2O emissions after deep ploughing of residues.

In the literature, paper waste has been reported as potentially being able to conserve soil N and organic matter (Zibilske, 1987). However, to date, no studies have been made on the effects of paper waste on gaseous N losses from soils. The high C:N ratio of most paper waste usually results in a net immobilisation of N after application to soil (King, 1984; Aitken and Lewis, 1994). Clearly the extent of this depends on the rate of application and the C and N composition of the waste, which is known to be highly variable. The paper waste was found to have a C:N ratio of 25:1, although the N content of the material was highly variable. Values of up to 46:1 were recorded for some samples (Paterson, 1995). Immobilisation may have occurred after incorporation of such high C material. Zibilske (1987) found that where 17-33 g paper waste kg soil^{-1} was applied to soil immobilisation only lasted about 60 days, and approximately 150 days where 67 g kg^{-1} was applied. Such immobilisation has reduced NO_3^- leaching after application of paper mill waste. The occurrence of immobilisation after addition of paper waste is confirmed by increased concentrations of biomass C and N in the rotary tilled and conventionally ploughed +PW/-R and +PW/+R treatments at both 0-0.2 and 0.2-0.4 m depths (Castle, 1995, pers. comm.). Cumulative leaching losses of 94.1 kg NO_3^--N ha^{-1} were measured from the paper waste treatments compared with 177 kg ha^{-1} from treatments with no paper waste at Mackies Field between October 1994 and March 1995 (Davies, 1995). The reduction in NO_3^- leaching may have been attributable to both gaseous N losses and immobilisation.

The application of paper waste may have interacted with the residues resulting in gaseous losses of N_2O via nitrification and denitrification. The extremely large peaks measured may have resulted from release of some of the N immobilised after application of paper waste stimulated by the incorporation of fresh material with a lower C:N ratio. Thus, addition of residues with a high N content decreased the organic C:N ratio so immobilisation was reduced (Haynes, 1986; Janzen and Kucey, 1988). In accordance with this, concentrations of available soil NH_4^+ were slightly greater in +PW than -PW treatments. Dolar *et al.* (1972) found that NPKS fertilisation of paper sludge amended soil resulted in greater uptake of nutrients (particularly N) by a subsequent oat crop, and that the fertiliser N served to reduce the organic C:N ratio so that immobilisation was reduced and NH_4^+ concentrations remained high. They assumed that some characteristic of the sludge inhibited nitrification. At Mackies Field the concentration of NH_4^+ was only significantly raised on 26 October after conventional ploughing of lettuce residues. In all other treatments the NH_4^+ concentration remained low throughout the experimental period indicating the occurrence of immobilisation after application of paper waste. However, concentrations of available NO_3^- generally fell over the experimental period, especially between 14 and 26 October. This period of greatest reduction in NO_3^- coincided with the period of greatest N_2O losses. The lowest NO_3^- concentrations on 26 October were in the deep ploughed treatments. This suggests that denitrification was the main process contributing to N_2O production in the presence of paper waste, although leaching of NO_3^- also occurred during this period (Davies, 1995). It is also possible that the paper waste inhibited nitrification (Dolar *et al.*, 1972).

A laboratory incubation confirmed that application of paper waste may have significant effects on microbial activity (Luo, 1995, pers. comm.). Calabrese residues and paper waste were added to soil at rates of 0.6 g kg dry soil^{-1}, and 11.1 g kg dry soil^{-1}, respectively. The release of CO_2 was monitored over 107 days at 15 °C. The highest soil respiration rates were measured where paper waste was combined with residues. For the first 8 days the presence of calabrese residues resulted in greater CO_2 emissions than those caused by paper waste, but between days 21 and 107 respiration was found to be higher from the paper waste treatment. N_2O losses from denitrification were measured over the first 8 days. The paper waste immediately resulted in a short-lived flux of 153 μg N_2O-N kg dry soil^{-1} d^{-1}. The calabrese residues also increased N_2O emissions over the first 3 days. Their combined additions resulted in lower emissions than their individual additions. Concentrations of soil NH_4^+ were greatly raised, and concentrations of NO_3^- lowered following the combined application. It is uncertain if this reduction in NO_3^- was a result of nitrification inhibition by the paper waste, or due to leaching and denitrification (Vinten *et al.*, 1996). This reduction in concentrations of NO_3^-, whilst concentrations of available NH_4^+ increased may have resulted from dissimilatory reduction of NO_3^- (Stanford *et al.*, 1975; Buresh and Patrick, 1978; de Catanzaro *et al.*, 1987; McKenney *et al.*, 1995). De Catanzaro *et al.* (1987) found that addition of 50 g alfalfa kg soil^{-1} promoted dissimilatory NO_3^- reduction. Such reduction is favoured by strict anaerobic conditions, a high pH and large quantities of readily oxidisable organic matter (Stanford *et al.*, 1975; Buresh and Patrick, 1978). Nitrification may have been inhibited due to partial anoxia, or to the chemical properties of the paper waste (Vinten *et al.*, 1996).

The addition of paper waste to a sandy soil has been reported to increase the soil moisture content (Dolar *et al.*, 1972), thereby increasing the potential for denitrification within the amended soil. This was apparent at Mackies Field where soil moisture contents were significantly raised between 14 and 26 October on all treatments where paper waste had been applied. The moisture content of the deep ploughed +PW/-R treatment also greatly increased between 26 October and 4 November. This increase in moisture content may have been sufficient to raise denitrification through the creation of anaerobic microsites. The waste was heterogeneously distributed within the soil, probably resulting in hotspots of microbial activity within the soil (Vinten *et al.*, 1996). Incorporation of fresh plant material would have locally exacerbated these conditions (Grundmann *et al.*, 1988) resulting in greater fluxes from the ploughed treatments, particularly where residues had been deep ploughed.

5.4.3 N_2O from probes

Measurements of N_2O at depth enable the main site of N_2O production to be determined under the different cultivation and paper waste application treatments. The N_2O concentrations from the probes at the 3 depths corresponded well with the cover box emissions at Mackies Field on 31 October and 3 November. After rotary tillage higher concentrations of N_2O were measured at 150 mm depth than at 50 and 250 mm, on both 31 October and 3 November. The lowest concentrations were measured at 250 mm depth. Tillage would be expected to produce more N_2O near the soil surface than ploughed soils due to a greater organic matter content and greater biological activity near the surface (Lynch and Panting, 1980; Aulakh *et al.*, 1984c). However, on 31 October higher concentrations of N_2O were measured near the surface after conventional ploughing than rotary tillage of residues. In accordance with this, Rolston *et al.* (1976) found the greatest concentrations of both N_2O and N_2 in the field to be at 50 mm depth. The application of paper waste to the deep ploughed -PW/+R treatment increased N_2O concentrations by a factor of 7 at 50 mm depth on 3 November. This indicates that the presence of paper waste in the soil moved the main site of N_2O production nearer to the soil surface. The concentrations at all other depths were lower throughout the whole of the experimental period where paper waste had been applied.

Goodroad and Keeney (1985) found that, following rainfall, the main site of N_2O production moved from the surface deeper into the soil profile. From this they suggested that nitrification was the main source of N_2O near the soil surface, and denitrification the main source at depth, particularly after rainfall had leached NO_3^- into the soil. Similarly, Denmead *et al.* (1979a) stated that the aerobic conditions of surface layer soils are more favourable for nitrification. Groffman (1985) found that potential nitrification activity was greater after zero-tillage than conventional tillage, but at 50-130 mm depth potential denitrification was greater under conventional tillage. N_2O produced deeper in the profile remains in the profile for longer (Jury *et al.*, 1982) and therefore may be reduced before reaching the soil surface (Arah *et al.*, 1991).

5.4.4 N_2O emissions measured by autochambers

In general, higher emissions of N_2O were measured on the conventionally ploughed -PW/+R treatment. This is confirmed by other studies in the literature where incorporation of residues increased emissions of N_2O (for example, Aulakh *et al.*, 1984b; Goodroad *et al.*, 1984; de Catanzaro and Beauchamp, 1985; Drury *et al.*, 1991; McKenney *et al.*, 1995). The presence of paper waste resulted in lower emissions where residues were incorporated. This may have been due to immobilisation of lettuce residue N induced by the presence of paper waste.

Although diurnal variations in N_2O emissions were observed throughout the sampling period, they were less pronounced and less consistent than expected (Appendix III). N_2O emissions are generally found to be greatest in the early evening and at a minimum near sunrise (Denmead *et al.*, 1979a; Blackmer *et al.*, 1982). The greatest fluxes after conventional ploughing of residues in the presence of paper waste on 14, 20-22, 27 November and 12

December were all sampled at 8 pm, whereas the greatest fluxes on 25, 26 November, and 5, 11 December were all sampled at 8 am. Such diurnal variations are normally attributed to variations in topsoil temperature (Denmead *et al.*, 1979a; Ryden *et al.*, 1979; Conrad *et al.*, 1983). Conrad *et al.* (1983) found that N_2O evolution coincided with the diurnal variation in surface temperature, with no time lag between the maximum and minimum evolution and the maximum and minimum soil temperatures.

The N_2O emissions sampled from the autochambers at the same time as manual sampling from cover boxes (2 pm) compared very poorly. On the days when large fluxes were measured from the autochambers comparisons with the cover box measurements were extremely poor - emissions from the autochambers being consistently greater. Only where the emissions from the autochambers were low was there a good comparison with cover box emissions.

With such differences between the two sampling methods the problems of replication and spatial variability must be considered. Three replicate measurements of each treatment were obtained using cover boxes, whereas only one autochamber was placed on each treatment monitored. No more were available because of their high production cost. With no replication and placement on different plots than the cover boxes it is possible that the autochambers were placed over hotspots of microbial activity resulting in greater N_2O emissions. Such hotspots depend on the soil texture and structure, moisture content and distribution of organic matter, and are typically small in size (Folorunso and Rolston, 1985; Parkin, 1987; Grundmann *et al.*, 1988; Christensen *et al.*, 1990). Heterogeneous distribution of residues and/or paper waste within the soil may have resulted in hotspots of denitrification in localised anaerobic zones within the soil (Vinten *et al.*, 1996). Christensen *et al.*(1990) state that at high O_2 availability denitrification will only occur in hotspots where there is a non-limiting supply of organic matter. However, when the O_2 availability is low, such as in the presence of crop residues, denitrification is more likely to occur throughout the entire soil and be less localised.

5.4.5 Influence of soil temperature

The activation energy of the N_2O evolution (Ea) was calculated using the logarithmic form of a modified Arrhenius equation in which the reaction rate *k* is replaced by the N_2O evolution rate *v*, assuming a zero-order process:

$$\ln v = \frac{\mathrm{Ea}}{\mathrm{R}}\frac{1}{\mathrm{T}}$$

Both in the presence and absence of paper waste at Mackies Field the highest activation energies were calculated to be after tillage of residues. The highest activation energy of 126 kJ mol^{-1} (r=-0.74) was calculated for the rotary tilled -PW/+R treatment. This suggests that variations in emissions from this cultivation treatment were mainly due to temperature (Conrad *et al.*, 1983). This is in accordance with the main site of microbial activity being near the soil surface after this cultivation (Goss *et al.*, 1978; Carter and Rennie, 1984) and generally higher N_2O emissions following reduced cultivation (Aulakh *et al.*, 1984c; Staley *et al.*, 1990). Calculated activation energies were higher in the absence, than in the presence of paper waste, except after conventional ploughing of lettuce residues, where low values of 35.8 kJ mol^{-1} (r=-0.2) and 12.1 kJ mol^{-1} (r=-0.1) were calculated for the +PW/+R and -PW/+R treatments, respectively. Cultivation of residues resulted in higher values than cultivation of bare ground, except on the deep ploughed -PW/+R, and conventionally ploughed +PW/+R treatments.

Activation energies were higher at Dipper field, except on the rotary tilled -PW/+R and deep ploughed -PW/-R treatments, confirming the importance of temperature at this site. In the absence of paper waste higher values were calculated after cultivation of the bare ground, except after deep ploughing, for which a value of 168 kJ mol^{-1} (r=-0.58) was calculated. The presence of paper waste at this site raised the activation energies after rotary tillage and conventional ploughing of residues, and deep ploughing of the bare ground.

5.5 Summary

The incorporation of vegetable residues increases emissions of N_2O, even when they are only rotary tilled using a power harrow. Most of the N_2O was emitted within the first 2 weeks after cultivation. Based on other reports in the literature, it was expected that emissions would be greater after tillage. However, this was only apparent at Mackies Field after tillage of residues in the absence of paper waste. The increased emissions after ploughing of lettuce residues in the presence of paper waste indicates that such a practice, although potentially reducing NO_3^- leaching by immobilisation, may increase gaseous N emissions from the soil. The use of ^{15}N labelled residues would have enabled the relative effects of residue and paper waste incorporation on immobilisation, nitrification and denitrification to be determined. It is suggested that paper waste only be applied to systems where the N can be conserved in the soil in a form that is readily available to subsequent crops, not lost through nitrification or denitrification.

CHAPTER 6 THE CONTRIBUTION OF INORGANIC AND ORGANIC NITROGEN SOURCES TO EMISSIONS OF NITROUS OXIDE FROM SOIL

6.1 Introduction

Addition of organic material to soil generally increases emissions of N_2O (for example, Denmead *et al.*, 1979b; Aulakh, *et al.*, 1983; de Catanzaro and Beauchamp, 1985). The magnitude and extent of these emissions depends on several factors, including C:N ratio, quantity and placement of incorporated plant material, type of cultivation, soil type, air and soil temperature, and rainfall at and following the time of addition (Chapters 4 and 5). The contribution of nitrification and/or denitrification to N_2O emissions also depends on these factors (Haynes, 1986; Granli and Bøckman, 1994). The effect of adding plant material with varying C:N ratios to soil has been examined in Chapters 4 and 5. However, the contribution of residue N to the measured N_2O emissions can only be directly determined using isotopically labelled residues.

Addition of N fertiliser to a crop generally increases the short-term emissions of N_2O from the soil (Ryden and Lund, 1980; Duxbury *et al.*, 1982; McElroy and Wofsy, 1985; Sahrawat and Keeney, 1986; Robertson, 1993; McTaggart *et al.*, 1994; Mosier, 1994; Clayton *et al.*, 1997). Bouwman (1996) estimated that an average of 1.25 % of applied fertiliser N is lost as N_2O-N. Increased emissions typically occur either immediately after or within a few days of fertiliser application and normally last for several days, with further fluxes occuring in response to rainfall, until the fertiliser in the upper soil layers is depleted (Conrad *et al.*, 1983). The type and form of fertiliser applied, time of application and weather conditions following application influence the magnitude of these emissions (section 2.2.5.6). Applications of NO_3^- alone have, in some situations, been found to result in significantly lower emissions than applications of NH_4^+, presumably due to the important role of nitrification in N_2O production (Breitenbeck *et al.*, 1980; Conrad and Seiler, 1980; Bremner and Blackmer, 1981; Eichner, 1990).

Use of the stable isotope ^{15}N is now common in N research, particularly in studies of residue decomposition, net transformations of N within the soil, the priming effect of added fresh organic matter or fertiliser N, and plant recovery of applied N (Hauck and Bremner, 1976). Addition of a material with an unusually high or low concentration of ^{15}N to soil will result in an increase or decrease in ^{15}N in all or part of the system, enabling transformations and interactions of the labelled N to be quantified (Hauck and Bremner, 1976). Most experiments reported in the literature have been concerned with the fate of fertiliser N, by adding ^{15}N as $^{15}NO_3^-$ and/or $^{15}NH_4^+$ (for example, Olson *et al.*, 1979; Mulvaney and Vanden Heuvel, 1988; Powlson *et al.*, 1992; Vos *et al.*, 1994). The fate of N from incorporated ^{15}N-labelled crop residues has been followed where crops have been grown using ^{15}N-labelled nutrient solutions or fertilisers (for example, Azam *et al.*, 1985, 1989; Wagger *et al.*, 1985b; Ladd and Amato, 1986).

Contributions of nitrification and/or denitrification to measured N_2O emissions can be determined directly using ^{15}N (Rolston *et al.*, 1982; Mulvaney and Kurtz, 1982; Stevens *et al.*, 1993). Mass spectrometry enables the flux of ^{15}N in N_2O to be quantified. However, because of the high costs, complexity and high concentration of N_2O required for analysis (Arah *et al.*, 1993; Stevens *et al.*, 1993), to date, only a few studies have included direct measurement of the ^{15}N-enriched gases evolved.

Experimental trials were established during 1995 to examine emissions of N_2O throughout the growing season of various crops. Following application of ^{15}N-labelled fertiliser in the spring, and incorporation of ^{15}N-labelled crops in the autumn, the fate of labelled N was monitored. It was hypothesised that the greatest fluxes of N_2O would occur immediately following inorganic fertilisation in the spring and incorporation of residues in the autumn, and after large rainfall events, with most of the N_2O produced during nitrification where NH_4^+ fertilisers or crop residues were applied.

6.2 Sites, materials and methods

Field trials were undertaken throughout spring and autumn 1995 on the Bush Estate, near Edinburgh. These trials were established in the spring on areas within fields of winter wheat (var. *Mercia*), spring barley (var. *Chariot*), oilseed rape (var. *Libravo*) and peas (var. *Magnus*), all sown on sandy loam soils of the Biel series. For all the crops, except the peas, plots were marked out in a randomised block design with 3 replicates per treatment. The treatments were N at standard rates (SAC, 1993), and no applied N. $NH_4^+NO_3^-$ fertiliser was applied to the fertilised plots as a solution, in 2 applications: 60 and 120 kg N to winter wheat on 22 March and 24 April, respectively, and 60 kg N to spring barley on both 13 April and 5 May. 60 and 120 kg N were applied to the oilseed rape on 25 April and 11 May, respectively. The peas were not fertilised, due to their ability to fix N. Controls in the pea trial consisted of areas of bare soil from which emerging seedlings had been removed. Emissions of N_2O were periodically measured using conventional closed cover boxes, as described in sections 3.8 and 3.9. Determinations of available soil N and gravimetric soil moisture contents were also made (sections 3.2 and 3.3).

Microplots of 0.4 x 0.4 m within the main plots were fertilised with $^{15}NH_4{}^{15}NO_3$ at 10 % atom enrichment applied at the same rates and times as the fertiliser on the main plots. Chambers made from lengths of plastic pipe (0.24 m diameter, 0.4 m height) were placed into the soil of the microplots in order to sample N_2O emissions. A 3-way valve was inserted into the side of each chamber, and made gas-tight with silicone sealant. One hour prior to gas sampling, the top of the chamber was securely covered with sheets of plastic tied with string. Gas was sampled using the methodology described for conventional cover boxes (section 3.8). It was hoped that concentrations of N_2O would be high enough to enable the isotopic enrichment of this gas to be determined. Soil was periodically sampled from the microplots, outside the chambers, and determinations were made of soil ^{15}N concentrations as described in section 3.5. Rates of mineralisation were estimated from differences in available N between sampling dates.

Harvesting of the peas, winter wheat, spring barley, and oilseed rape took place on 10, 17, 18 and 25 August, respectively. Plants within 1 m^2 areas within the main plots were cut to 30 mm above the soil surface. Plants were also harvested from within the microplots. Samples were dried and dry matter yields and ^{14}N and ^{15}N contents were determined. The ^{15}N labelled residues that had not been used in analysis were frozen at -15 °C until one day prior to autumn incorporation, when the stubble was coarsely chopped.

The stubbles of the winter wheat and spring barley were ploughed into the soil on 27 October and 1 November, respectively. After these cultivations and sowing to the subsequent winter cereals, areas of 1 m^2 within the plots were cleared of stubble and seedlings. The defrosted and chopped ^{15}N-labelled residues were manually incorporated into the soil of these cleared areas, to a depth of approximately 0.15 m on 31 October in the winter wheat trial and 14 November in the spring barley trial. The oilseed rape was not followed by a winter cereal. Treatments on this trial consisted of bare soil areas cleared of stubble, areas where the stubble was left on the soil surface, and incorporation of ^{15}N-labelled oilseed rape residues to a depth of 0.1 m on areas cleared of stubble. Here the cultivations were carried out manually with a spade. Measurements of N_2O emissions, concentrations and ^{15}N enrichments of soil available N and biomass N, and gravimetric moisture contents were made on each trial throughout the autumn. Mineralisation rates were estimated as in the spring. The percentages of N derived from fertiliser (NDFF) (spring) or residues (NDFR) (autumn) in the available N pools, soil biomass and crops at harvest were calculated using the formula:

$$\text{NDFF or NDFR} = \frac{{}^{15}\text{N (\%) in sample} - {}^{15}\text{N natural background (\%)}}{{}^{15}\text{N (\%) in fertiliser} - {}^{15}\text{N natural background (\%)}}$$
(or residue) applied

6.3 Results

6.3.1 Spring

6.3.1.1 Cumulative emissions of N_2O

Over the whole growing season cumulative emissions of N_2O from the fertilised winter wheat and spring barley were significantly greater ($p<0.05$) than from comparable unfertilised crops (Fig. 6.1). Emissions from the fertilised and unfertilised oilseed rape crop were significantly higher ($p<0.005$) than emissions from the other fertilised and unfertilised crops, respectively. 380 g N_2O-N ha^{-1} was emitted over 54 days from the fertilised oilseed rape.The lowest cumulative emissions from the non-legumes over the sampling period were measured from the spring barley: 47.9 and 13.1 g N_2O-N ha^{-1} over 61 days from the fertilised and unfertilised treatments, respectively. Cumulative emissions over 64 days from the pea crop were not significantly different from those from areas of bare soil.

6.3.1.2 Daily N_2O fluxes

There was no significant difference between N_2O emissions measured from the chambers in the ^{15}N fertilised microplots and N_2O emissions measured with conventional cover boxes in the fertilised main plots (Appendix IV). Unfortunately, concentrations of N_2O from the microplots were not sufficiently high to enable determination of $^{15}N_2O$.

Emissions of N_2O from winter wheat did not significantly increase after both fertiliser applications, and were lower than those measured after fertilisation of the other crops. Fluxes of 3.8 and 3.7 g N_2O-N ha^{-1} d^{-1} were measured from the fertilised winter wheat on 24 March and 4 May, respectively (Fig. 6.2a).

Fertilisation of the spring barley significantly increased ($p<0.01$) N_2O emissions, with fluxes of 11.9 and 13.0 g N_2O-N ha^{-1} d^{-1} measured on 20 April and 5 May respectively (Fig. 6.2b). The response in emissions following the second fertiliser application was more rapid than after the first fertiliser application. Emissions from the unfertilised plots were consistently lower than from the fertilised plots, except on 7 and 14 June prior to harvest where emissions of 5.6 and 2.3 g N_2O-N ha^{-1} d^{-1} were measured from the unfertilised crop, respectively.

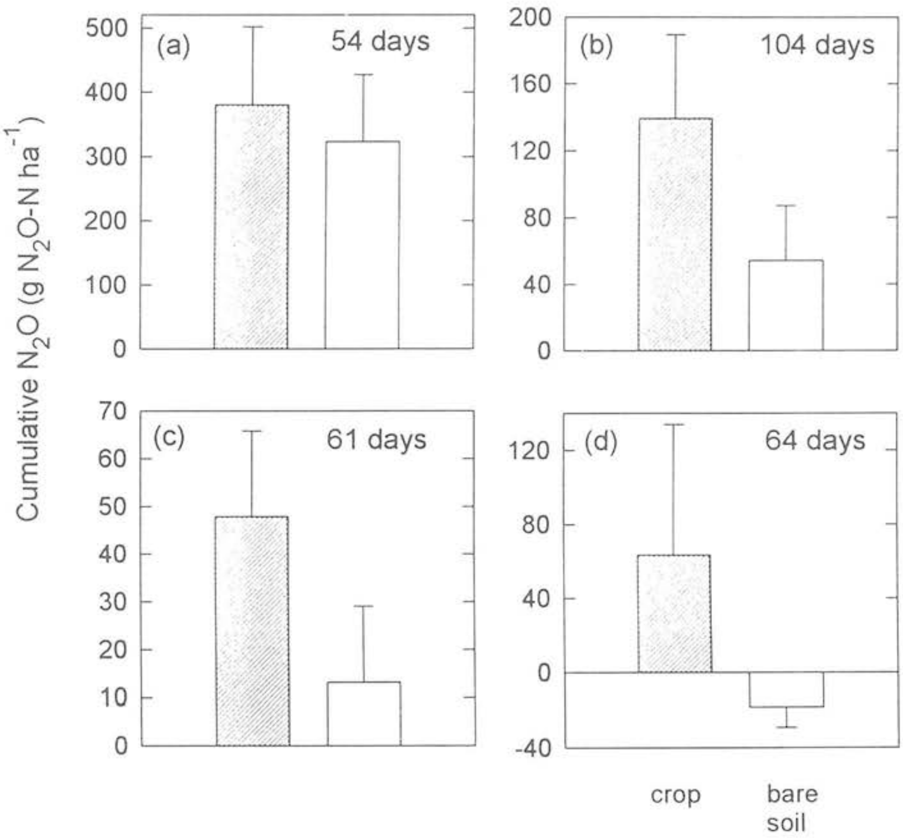

Figure 6.1 Cumulative emissions of N_2O over the spring growing season from fertilised (hatched bars) and unfertilised (empty bars) crops of (a) oilseed rape, (b) winter wheat, (c) spring barley, (d) pea crop (hatched bar), bare soil (empty bar).

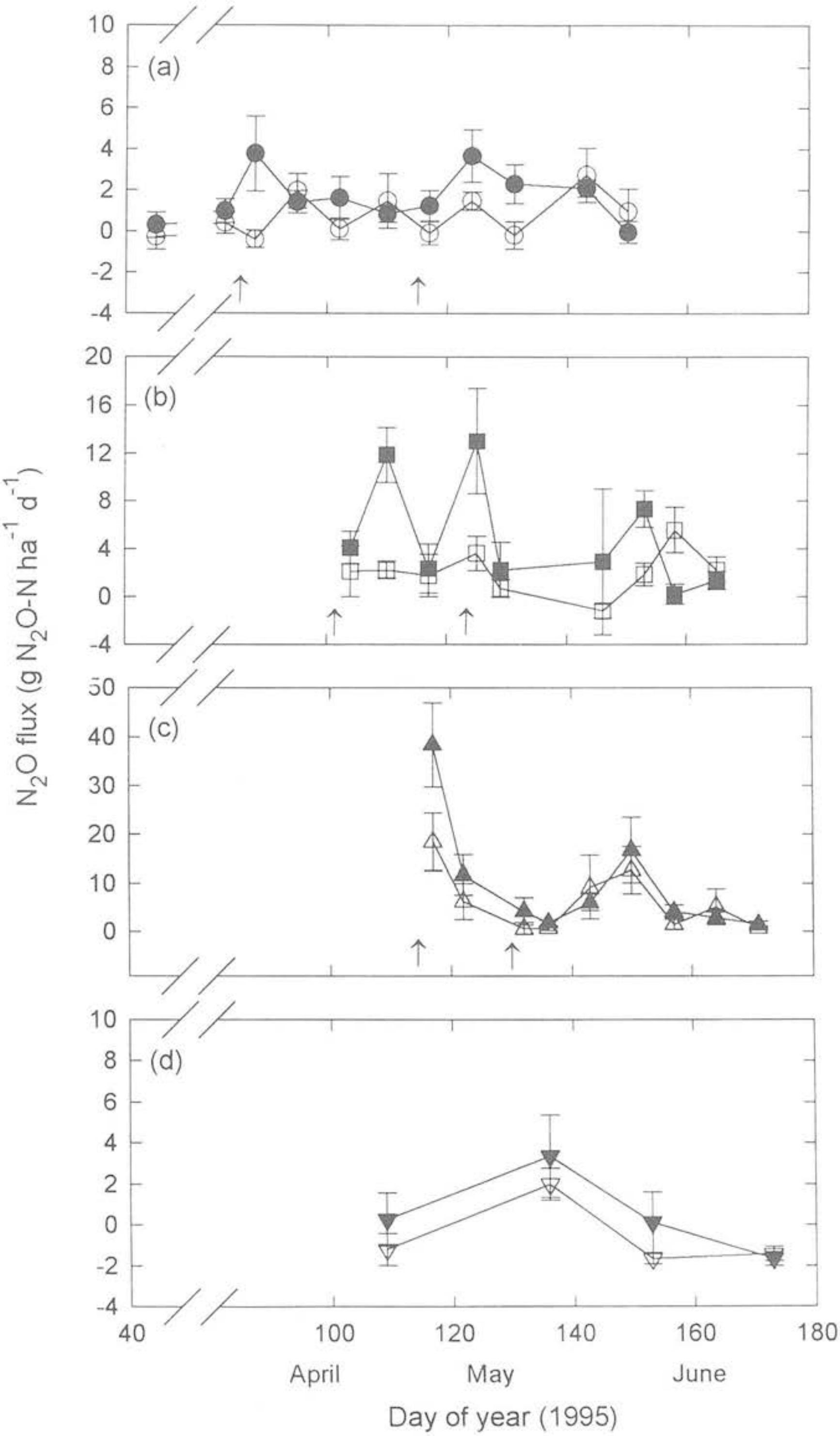

Figure 6.2 Emissions of N_2O during the spring growing season of fertilised (filled symbols) and unfertilised (empty symbols) crops of (a) winter wheat, (b) spring barley, (c) oilseed rape, (d) pea. Arrows indicate times of fertilisation.

The first fertilisation of the oilseed rape on 25 April increased N_2O emissions ($p<0.05$), with a flux of 38.4 g N_2O-N ha^{-1} d^{-1} measured on 27 April (Fig. 6.2c). A flux of 16.7 g N_2O-N ha^{-1} d^{-1} was measured 19 days after the second fertiliser application, but was not significantly different from that measured from unfertilised plots on this day. Emissions from both treatments fell after this date.

Throughout the growing season there was no significant difference between N_2O emissions from the growing pea crop and from the bare soil control (Fig. 6.2d). Emissions increased between 19 April and 16 May, with a flux of 3.4 g N_2O-N ha^{-1} d^{-1} measured from the pea crop on 16 May. After this, emissions fell until the end of the sampling period.

6.3.1.3 Available soil N

Throughout the growing season, there was no significant difference in available soil N in the fertilised and unfertilised winter wheat plots and between soil depths (Fig. 6.3a and 6.4a). Concentrations of 18.8 μg NH_4^+-N g dry $soil^{-1}$ at 0.2-0.4 m and 16.3 μg NH_4^+-N g dry $soil^{-1}$ at 0-0.2 m were measured immediately after fertilisation. A concentration of 21.5 μg NO_3^--N g dry $soil^{-1}$ was measured at 0-0.2 m depth on 12 May.

Variations in contribution of applied fertiliser N to the available soil N pool in the winter wheat plots are shown in Fig. 6.5a. On 4 April, after the first fertiliser application, fertiliser N contributed to 64.7 and 67.2 % of the total available soil N at 0-0.2 and 0.2-0.4 m depths, respectively. On 12 May after the second fertiliser application, 80 % of the available N at 0-0.2 m depth was derived from the fertiliser, and 66 % derived from fertiliser at 0.2-0.4 m depth. However, immediately prior to harvest, the contribution of fertiliser N to the soil available N was lower.

Immediately after fertilisation of spring barley there was no significant difference in available soil N in the fertilised and unfertilised spring barley plots and between soil depths (Fig. 6.3b and 6.4b). On 27 July 8.7 μg NH_4^+-N g dry $soil^{-1}$ was measured at 0.2-0.4 m and 37.9 μg NO_3^--N g dry $soil^{-1}$ ($p<0.05$) was measured at 0-0.2 m in the fertilised plots.

The first addition of fertiliser N to the spring barley contributed 41.6 and 23.1 % of available soil N on 19 April at 0-0.2 and 0.2-0.4 m depths, respectively (Fig. 6.5b). After the second application contributions increased to 58.4 and 43.6 % on 11 May, and 57.1 and 21.2 % on 27 July at 0-0.2 and 0.2-0.4 m depths, respectively. The percentage N derived from fertiliser was lower at 0.2-0.4 m depth.

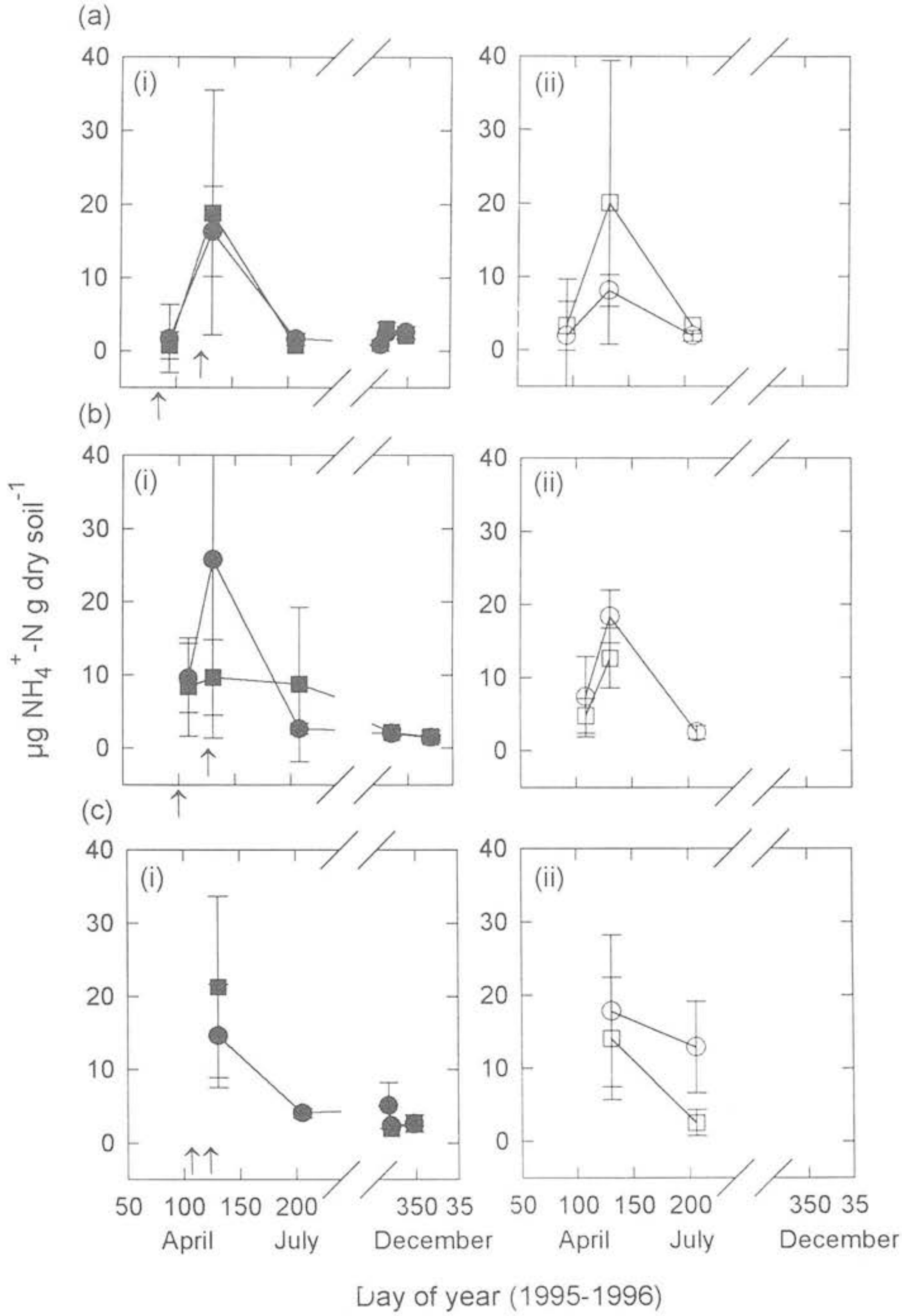

Figure 6.3 Concentrations of soil available NH_4^+ in (i) fertilised, (ii) unfertilised crops of (a) winter wheat, (b) spring barley, (c) oilseed rape at 0-0.2 m (circles) and 0.2-0.4 m (squares) depths. Arrows indicate times of fertilisation.

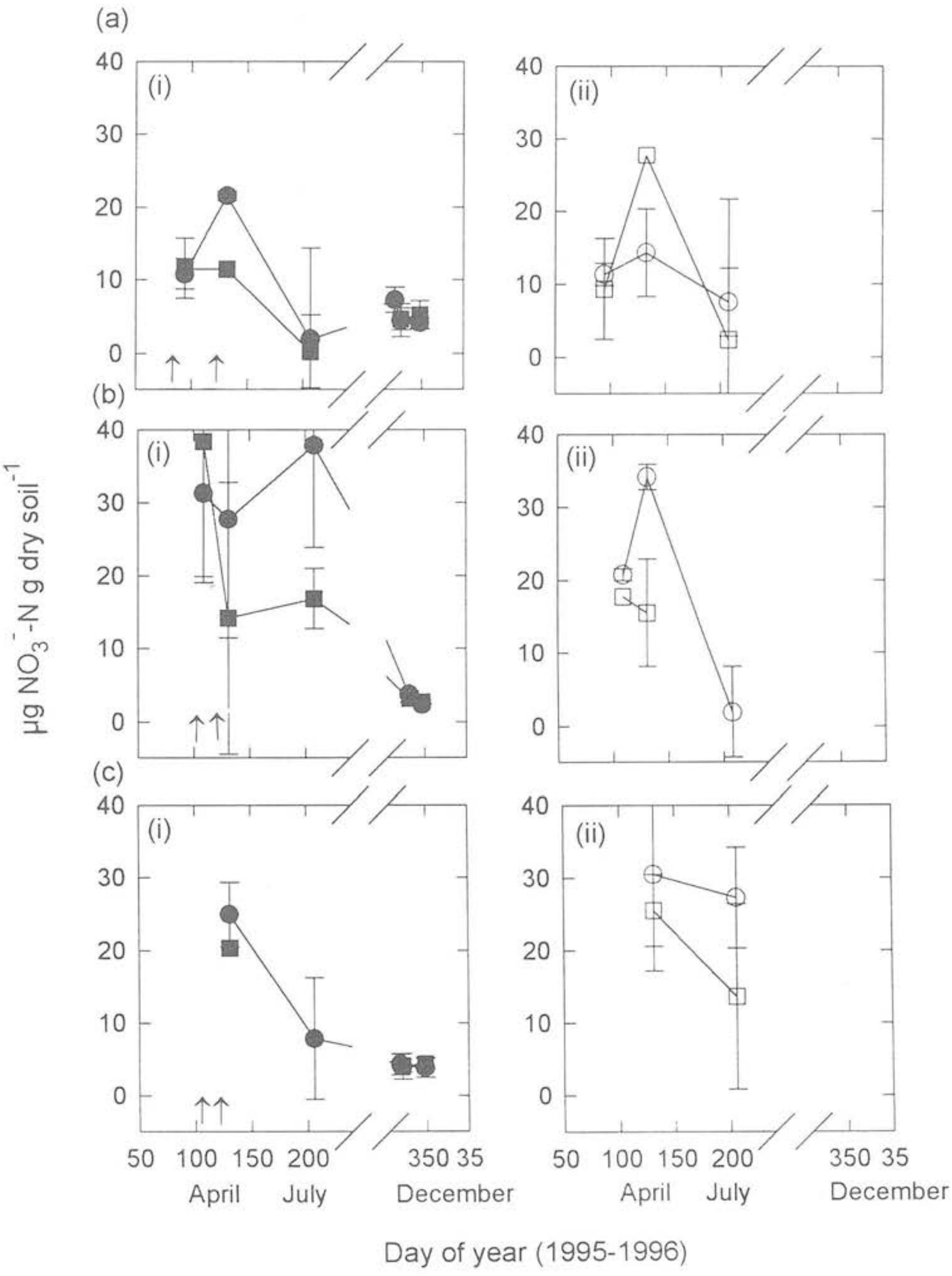

Figure 6.4 Concentrations of soil available NO_3^- in (i) fertilised, (ii) unfertilised crops of (a) winter wheat, (b) spring barley, (c) oilseed rape at 0-0.2 m (circles) and 0.2-0.4 m (squares) depths. Arrows indicate times of fertilisation.

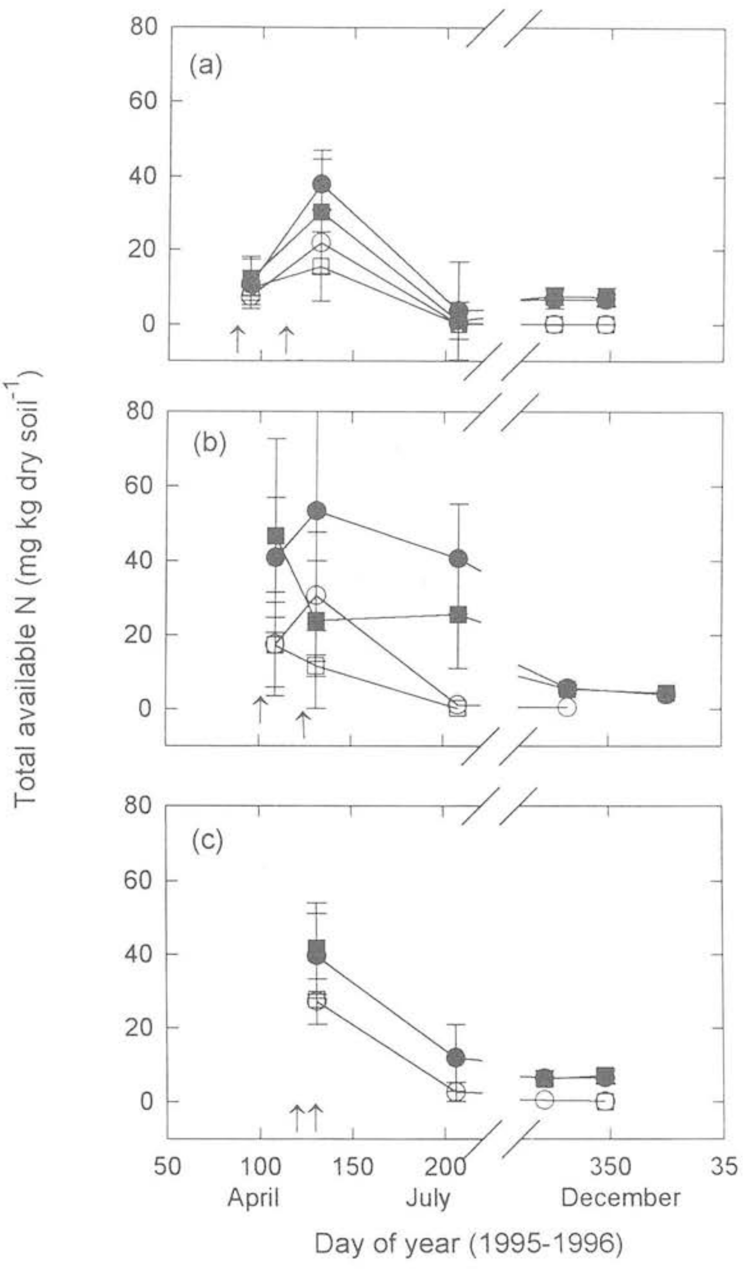

Figure 6.5 Concentrations of total available N (filled symbols) during spring and autumn 1995 on (a) winter wheat, (b) spring barley, (c) oilseed rape trials at 0-0.2 m (circles) and 0.2-0.4 m (squares) depths, and N derived from fertiliser (empty symbols). Arrows indicate times of fertilisation.

Throughout the growing season, there was no significant difference in available soil N in the fertilised and unfertilised oilseed rape plots and between soil depths (Fig. 6.3c and 6.4c). On 11 May 21.3 and 14.7 μg NH_4^+-N g dry soil^{-1} were measured at 0-0.2 and 0.2-0.4 m depths, respectively. Available NO_3^- in the oilseed rape plots fell throughout the growing season (Fig. 6.4c). 30.5 and 25.5 μg NO_3^--N g dry soil^{-1} were measured from the unfertilised plots at 0-0.2 and 0.2-0.4 m on 11 May.

On 11 May 67.4 and 66.4 % of available soil N at 0-0.2 and 0.2-0.4 m depths, respectively, was derived from the first fertiliser application to the oilseed rape (Fig. 6.5c). By 25 July the contribution of fertiliser N to total available soil N was lowered to 26.5 % at 0-20 m, despite the second application on 11 May.

Throughout the growing season available NH_4^+ was lower under the pea crop than the bare ground control, but not significantly so (Fig. 6.6). On 21 April 2.9 and 1.4 μg NH_4^+-N g dry soil^{-1} were measured in the control and cropped areas, respectively. On this day 14.3 μg NO_3^- -N g dry soil^{-1} was measured in the cropped soil, but had fallen by 16 May.

6.3.1.4 Estimated mineralisation rates

Mineralisation rates were estimated to be higher at 0-0.2 m than at 0.2-0.4 m depth under fertilised crops and the unfertilised spring barley and oilseed rape crops (Table 6.1). A rate of 0.92 μg N g^{-1} d^{-1} was estimated at 0.2-0.4 m depth under the unfertilised winter wheat. Lower rates were estimated in the fertilised winter wheat and oilseed rape plots than the unfertilised. Mineralisation was lower under the pea crop than the bare soil.

6.3.1.5 Crop N contents

At harvest the pea crop had a N content of 2.8 %, but this was not significantly higher than the N contents of the winter wheat and spring barley (Table 6.2). The pea crop also had the highest C content of 47.8 %, giving a C:N ratio of 17:1 for this crop. The winter wheat had the highest C:N ratio of 38:1. 59.2 % of the oilseed rape N was derived from the applied fertiliser. Contributions of fertiliser N to the N in the cereals were not significantly different.

6.3.1.6 Dry matter yields

Fertilisation resulted in greater dry matter yields at harvest (Table 6.3). The oilseed rape crop had the highest dry matter yields of 3490 and 2650 kg ha^{-1} on the fertilised and unfertilised areas, respectively. The lowest yields were from the spring barley crop. The dry matter yield of the pea was higher than the unfertilised cereals, or the fertilised spring barley.

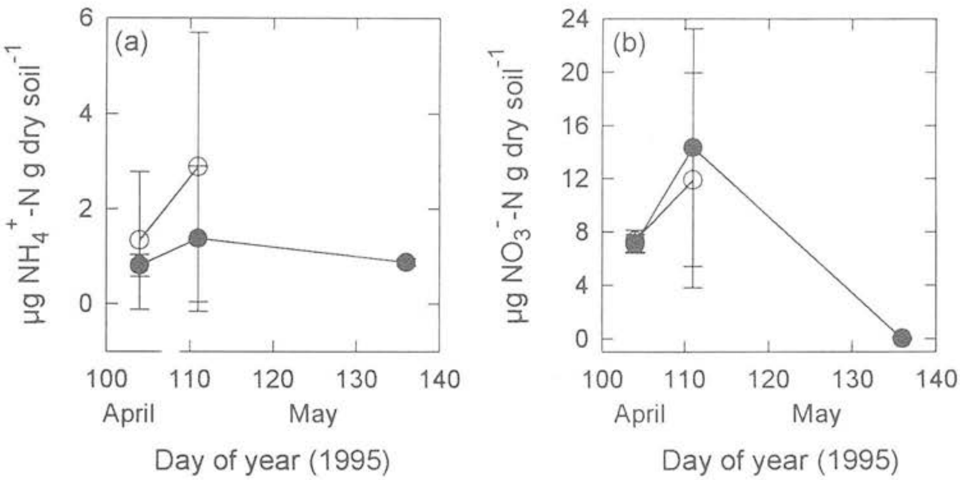

Figure 6.6 Concentrations of (a) available NH_4^+, (b) available NO_3^- on cropped (filled symbols) and bare soil (empty symbols) on the pea trial at Bush Estate.

Table 6.1. Estimated mineralisation rates ($\mu g\ N\ g^{-1}\ d^{-1}$) during spring 1995.

Crop	fertilised		unfertilised	
	0-0.2 m	0.2-0.4 m	0-0.2 m	0.2-0.4 m
winter wheat (38 days)	0.67	0.41	0.24	0.92
spring barley (22 days)	0.57	-1.0	1.11	0.25
oilseed rape (75 days)	-0.36		-0.11	-0.31
	cropped		bare soil	
pea (22 days)	0.08		0.22	

Table 6.2. C:N ratio, recovery of fertiliser N (%), total N uptake (kg ha^{-1}), ^{15}N uptake (kg ha^{-1}) of crops at harvest and. Cereal values are averaged for grain and straw.

Crop	C:N	Recovery of fertiliser N (%)	Total N uptake (kg ha^{-1})	^{15}N uptake (kg ha^{-1})
winter wheat	38:1	54.4 ± 1.9	34	18.5
oilseed rape	30:1	59.2 ± 0.008	51.3	30.4
spring barley	29:1	49.8 ± 0.9	34	17
pea	17:1			

Table 6.3. Dry matter yields at harvest.

Crop	Yield (kg ha^{-1})	
	fertilised	unfertilised
winter wheat	3210 ± 1750	2620 ± 208
spring barley	2540 ± 165	1640 ± 589
oilseed rape	3490 ± 1120	2650 ± 763
pea		2880

6.3.1.7 Rainfall, air temperature and soil moisture contents

Rainfall and air temperature throughout the spring growing season are presented in Fig. 6.7, and the gravimetric soil moisture contents under each crop in Fig. 6.8. Air temperature increased throughout the spring, from an average of 5 ^{o}C in March, to an average of 14 ^{o}C at the end of June. In general, gravimetric moisture contents fell throughout the growing season, except on the spring barley trial, where an increase of 7.1 % was measured between 27 and 29 July (Fig. 6.8b).

6.3.2 Autumn

6.3.2.1 Cumulative emissions of N_2O

Cumulative emissions over the autumn sampling period are presented in Fig. 6.9. Emissions from the incorporated oilseed rape residues (359 g N_2O-N ha^{-1}) were higher ($p<0.05$) than those measured from the incorporated winter wheat (155 g N_2O-N ha^{-1}) and spring barley residues (-26 g N_2O-N ha^{-1}). The lowest total emission of N_2O from the oilseed rape was measured from stubble remaining on the soil surface, and was significantly lower ($p<0.05$) than where residues had been incorporated. On the spring barley trial fluxes were actually negative, indicating uptake by the soil, especially after incorporation of residues. Emissions from the bare ground of the spring barley trial were lower ($p<0.05$) than from the other trials.

6.3.2.2 Daily N_2O fluxes

Emissions of N_2O increased, but not significantly, immediately after incorporation of ^{15}N labelled winter wheat residues, with a flux of 84.5 g N_2O-N ha^{-1} d^{-1} measured on 2 November (Fig. 6.10a). On the same day 68.7 g N_2O-N ha^{-1} d^{-1} was emitted from the bare soil control.

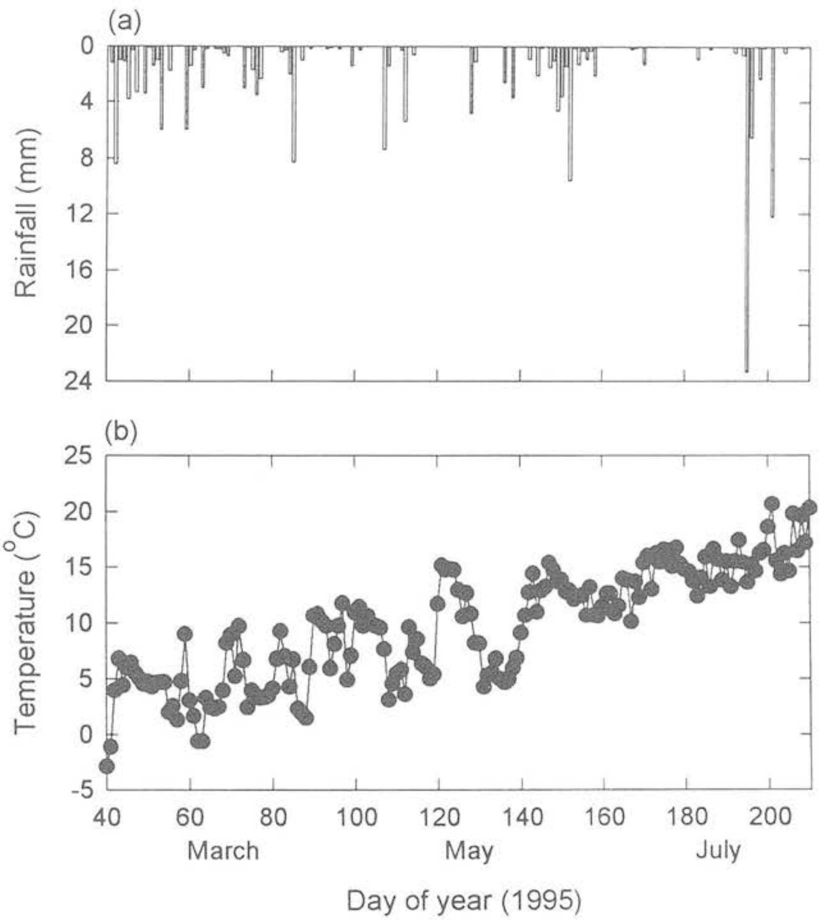

Figure 6.7 (a) Rainfall, (b) air temperature during spring/summer 1995 at Bush Estate.

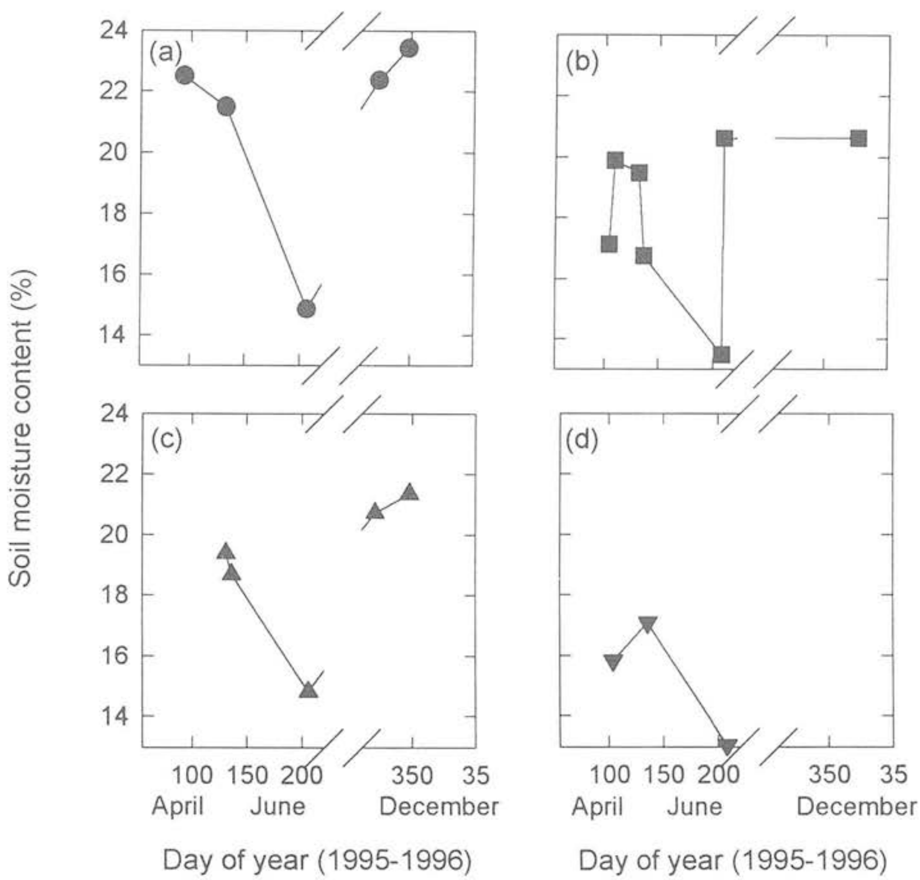

Figure 6.8 Gravimetric soil moisture contents during spring and autumn 1995 in (a) winter wheat, (b) spring barley, (c) oilseed rape, (d) pea trials at Bush Estate.

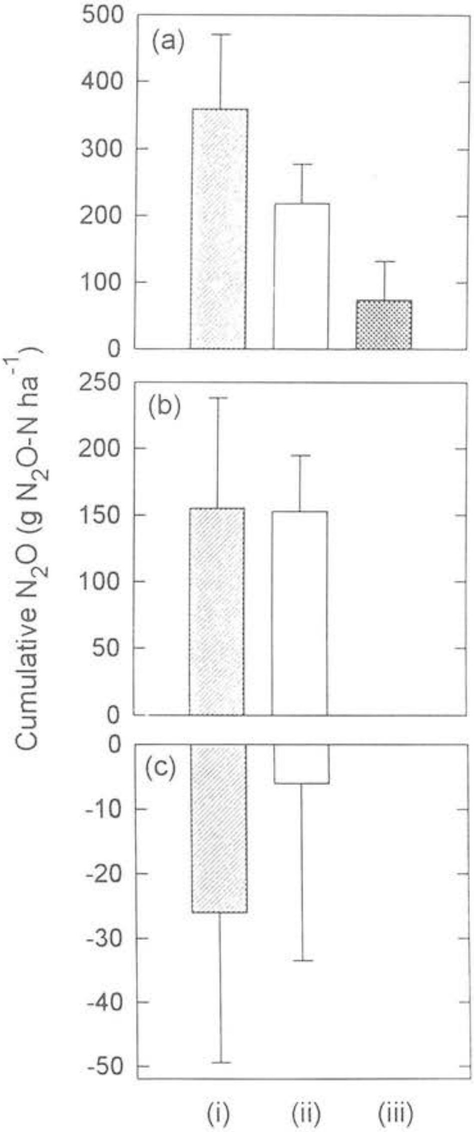

Figure 6.9 Cumulative emissions of N_2O in the autumn from (i) incorporated ^{15}N-labelled residues, (ii) bare soil controls, (iii) stubble of (a) oilseed rape, (b) winter wheat, (c) spring barley crops.

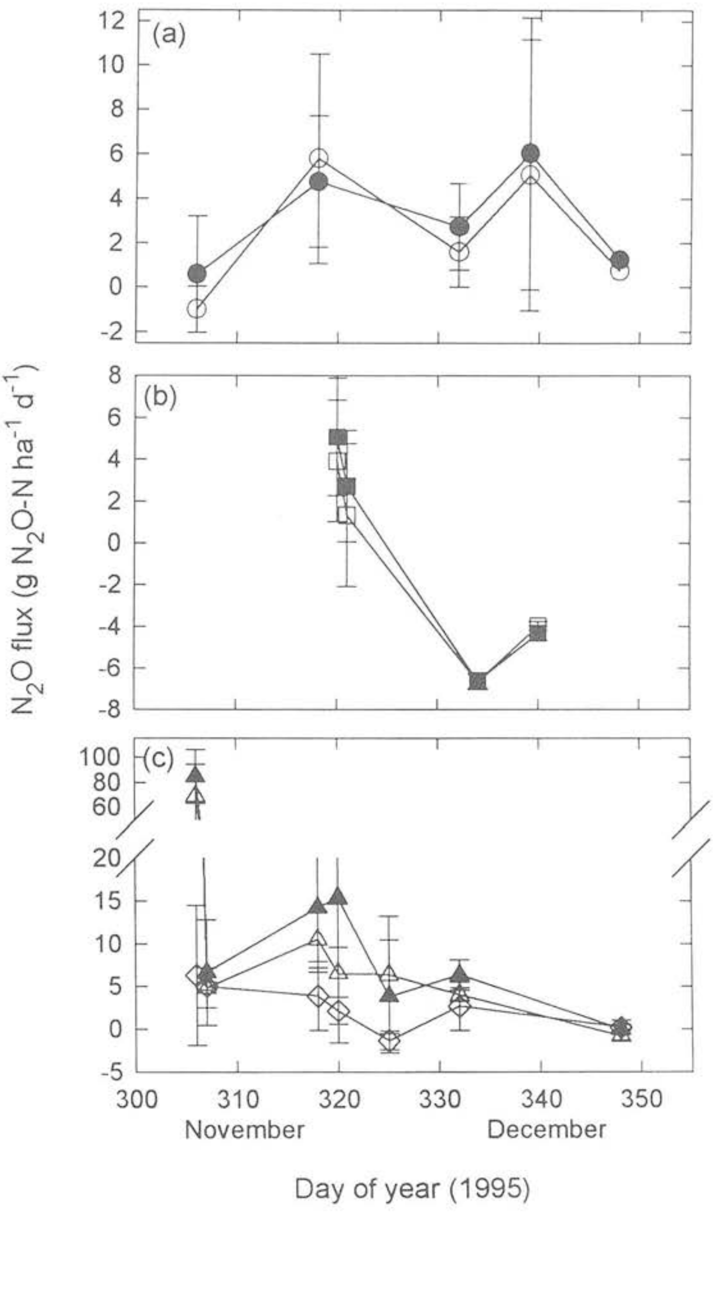

Figure 6.10 Emissions of N_2O following incorporation of labelled residues (filled symbols) and cultivation of bare soil (empty symbols) on (a) winter wheat, (b) spring barley, (c) oilseed rape (stubble = diamond symbols) trials at Bush Estate.

Emissions from areas with stubble remaining on the surface were low throughout the entire sampling period.

After incorporation of labelled spring barley residues N_2O emissions were not significantly raised. A flux of 5.1 g N_2O-N ha^{-1} d^{-1} was measured on 16 November (Fig. 6.10b). Between 16 and 30 November N_2O emissions from the incorporated residue and control treatments fell from 5.1 to 2.7 g N_2O-N ha^{-1} d^{-1} and from 3.9 to 1.3 g N_2O-N ha^{-1} d^{-1}, respectively. Emissions had increased again by 6 December but were still low.

A flux of 84.5 g N_2O-N ha^{-1} d^{-1} was measured on 2 November immediately after incorporation of the ^{15}N labelled oilseed rape residues, and was significantly greater ($p<0.01$) than where stubble was left on the surface, but not greater than the control (Fig. 6.10c). A flux of 68.7 g N_2O-N ha^{-1} d^{-1} was measured from the control on this day. However, these large fluxes were very short-lived. Emissions from stubble left on the soil surface were low throughout the experimental period. Emissions from the incorporated residue treatment increased again until 16 November, when a flux of 15.5 g N_2O-N ha^{-1} d^{-1} was measured, which was higher ($p<0.05$) than those from the other treatments.

6.3.2.3 Available soil N

There was no significant difference between available N at the two sampling depths in any of the trials throughout the autumn (Fig. 6.3). On each trial soil N derived from the autumn incorporated ^{15}N labelled residues was lower than that derived from the fertiliser in the spring (Fig. 6.5). After autumn incorporation of winter wheat available NH_4^+ was slightly higher than at the end of the spring growing season (Fig. 6.3a). On 21 November 2.5 and 3.1 μg NH_4^+-N g dry $soil^{-1}$ were measured at 0-0.2 and 0.2-0.4 m depths, respectively. Concentrations of 7.3 μg NO_3^--N g dry $soil^{-1}$ were measured at 0-0.2 m on 14 November after incorporation of winter wheat (Fig. 6.4a). After incorporation of winter wheat, residue N contributed to 0.97 and 0.33 % of available soil N at 0-0.2 and 0.2-0.4 m depths on 21 November, and 6.3 and 2.2 % on 14 December (Fig. 6.5a).

Available N was low throughout the autumn on the spring barley trial. Concentrations of 2.2 μg NH_4^+-N g dry $soil^{-1}$ (0.2-0.4 m depth) and 3.7 μg NO_3^--N g dry $soil^{-1}$ (0-0.2 m depth) were measured on 28 November (Figs. 6.3b and 6.4b). On 28 November residue N accounted for 9.9 % of the soil available N at 0-0.2 m depth (Fig. 6.5b).

On 14 November 5.1 μg NH_4^+-N g dry $soil^{-1}$ was measured at 0-0.2 m depth after incorporation of oilseed rape (Fig. 6.3c). However, by 17 November the concentration at this depth had fallen to 2.4 μg NH_4^+-N g dry soil^{-1}. Available NO_3^- was also low in the autumn (Fig. 6.4c). Addition of residues in the autumn contributed to only 7.2 % of total available soil N at 0-0.2 m depth on 17 November, and 6.3 and 2.2 % of soil available N at 0-0.2 and 0.2-0.4 m, respectively, on 14 December (Fig. 6.5c).

6.3.2.4 Estimated mineralisation rates

Mineralisation rates in the autumn were estimated to be low (Table 6.4). The highest mineralisation rate of 0.04 μg N g^{-1} d^{-1} was estimated for the incorporated oilseed rape residues at 0.2-0.4 m. Rates were higher at 0.2-0.4 m than at 0-0.2 m depth after incorporation of both the spring barley and oilseed rape residues.

Table 6.4. Estimated mineralisation rates (μg N g^{-1} d^{-1}) in the autumn 1995.

Residues	0-0.2 m	0.2-0.4 m
winter wheat (23 days)	-0.01	-0.02
spring barley (44 days)	-0.08	0.003
oilseed rape (27 days)	0.002	0.04

6.3.2.5 Biomass N

On the winter wheat trial 1.5 and 1.9 % of biomass N was labelled at 0-0.2 and 0.2-0.4 m, respectively, 21 days after incorporation. Between 21 November and 14 December concentrations after incorporation of winter wheat increased at both 0-0.2 and 0.2-0.4 m depths (Fig. 6.11a). On 14 December 40.4 and 38.9 mg biomass N kg dry soil^{-1} were measured at 0-0.2 and 0.2-0.4 m depths, respectively, of which 0.6 mg was labelled. On 21 November 0.7 mg kg^{-1} was labelled. In contrast to this, concentrations of biomass N at 0-0.2 m after oilseed rape incorporation fell slightly between 17 November and 14 December, with 1.8 (4.8 %) and 1.2 (3 %) mg biomass N kg dry soil^{-1} derived from the residues on these days, respectively (Fig. 6.11b), whereas at 0.2-0.4 m depth the value was only 0.4 mg. Of the 32.2 mg kg^{-1} measured 14 days after incorporation of spring barley, 2.0 (6 %) mg was from the residue N (Fig. 6.11c).

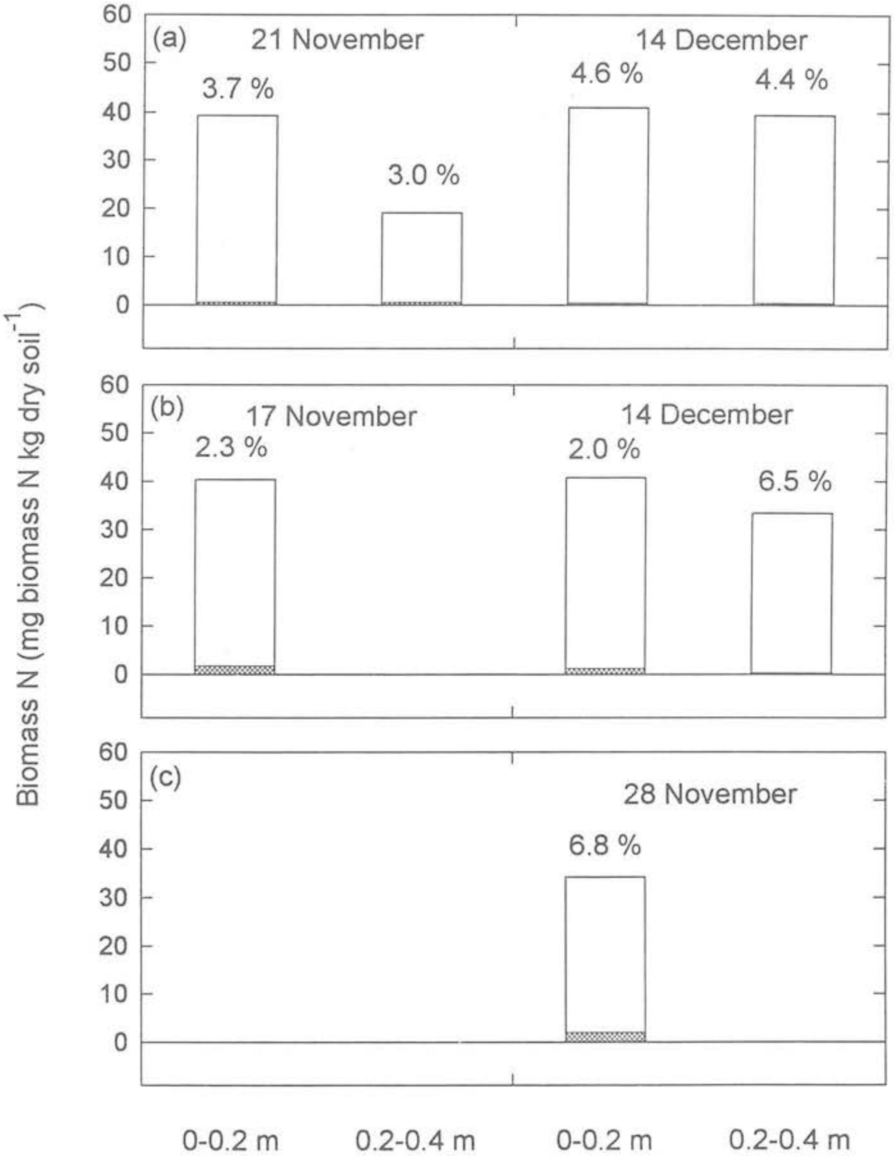

Figure 6.11. Concentrations of biomass N and ^{15}N in the biomass (hatched areas) after incorporation of (a) winter wheat, (b) oilseed rape, (c) spring barley residues. Values are given for % recovery of residue N.

6.3.2.6 Rainfall, air temperature and soil moisture contents

Rainfall and air temperature throughout the autumn are presented in Fig. 6.12. Gravimetric soil moisture contents are presented in Fig. 6.8. Air temperatures fluctuated greatly during the sampling period, but fell from an average of 8 ^{o}C in late October, to an average of 3 ^{o}C in mid December. In general, rainfall was low in the autumn, except for the 35 mm rain on 14 November.

6.4 Discussion

6.4.1 Effect of spring application of fertiliser

Emissions of N_2O increased after application of fertiliser in the spring, particularly on the winter wheat and spring barley trials, from which total emissions of 140 and 47.9 g N_2O-N ha^{-1} were measured, respectively, after fertilisation, compared with 54.2 and 13.1 g N_2O-N ha^{-1} from the unfertilised crops. This is in agreement with other work reported in the literature, where short-term increases in N_2O from soil have been observed after fertiliser application (for example, Ryden and Lund, 1980; Duxbury *et al.*, 1982; McElroy and Wofsy, 1985; Sahrawat and Keeney, 1986; Robertson, 1993; McTaggart *et al.*, 1994).

Although N_2O emissions were raised after fertilisation, the magnitude and timing of emissions varied between trials, confirming findings by Ryden (1981). Any direct comparisons between the 3 fertilised trials are limited because of differences in timing and rate of fertiliser application, site locations, crops, and soil characteristics. Two applications of 60 kg N ha^{-1} were made to the spring barley, but 60 kg N ha^{-1} followed by 120 kg N ha^{-1} was applied to both the winter wheat and oilseed rape crops. The smaller application rate of fertiliser may have been partly responsible for the low total N_2O emissions measured from the barley. N_2O emissions after fertiliser application result from interactions between soil temperature, moisture content, amount and timing of fertiliser applied, and crop uptake of N (Ryden, 1981). Fertiliser applications were made on different days, with different temperature and rainfall at, and immediately following, fertilisation, resulting in a different pattern of N_2O emissions from each trial. It should be noted that the highest emissions were measured from the fertilised oilseed rape, which was sown and fertilised after the two cereal crops. Indeed, the first application to this trial was one day after the second application to the winter wheat trial. Thus, warmer temperatures at time of fertilisation would have increased microbial activity, resulting in greater N_2O production from nitrification and denitrification. This is reflected in the high total emissions from the unfertilised oilseed rape. In confirmation of this, Powlson *et al.* (1992) found that sowing date of winter wheat had a marked effect on loss of spring

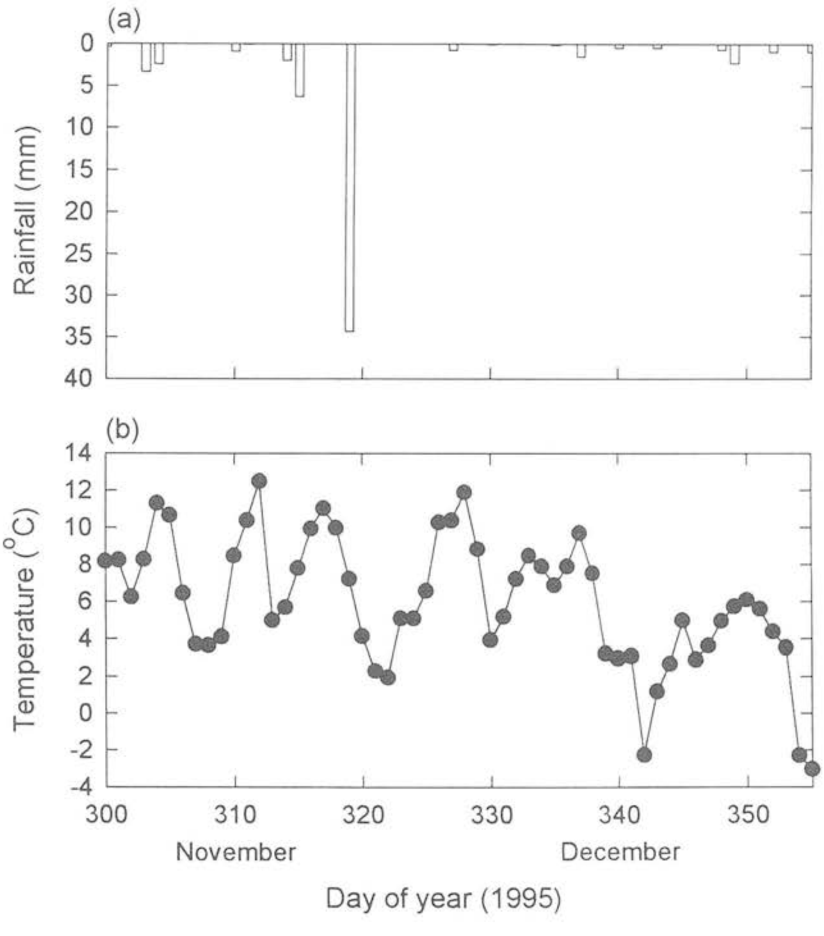

Figure 6.12 (a) Rainfall, (b) air temperature during autumn 1995 at Bush Estate.

applied N fertiliser, with more N lost from a later sown and fertilised crop. Therefore, on no particular day, or period of time after fertilisation, are N_2O emissions from the different trials directly comparable, even over the whole growing season.

N_2O fluxes were low after the first fertiliser application to the winter wheat crop, increasing only by approximately 3.5 g N_2O-N ha^{-1} d^{-1}. A further N_2O flux was measured 10 days after the second fertiliser application. This delay may in part have been an artefact of the sampling regime, with the raised emissions actually occurring sooner, but remaining unquantified. Concentrations of available N at 0-0.2 m depth were raised after this second application. However, concentrations of NH_4^+ at 0-0.2 m were lower than on unfertilised plots. Fertilisation of the winter wheat increased mineralisation of N, within the top 0.2 m of the soil. This was probably due to a higher concentration of fertiliser remaining in this layer, in addition to warmer temperatures near the soil surface, stimulating microbial activity (Olson *et al.*, 1979). However, on unfertilised plots higher concentrations of available NH_4^+ were measured at 0.2-0.4 m depth than at 0-0.2 m depth on 12 May. The increase in concentrations of available N between 4 April and 12 May may reflect increased microbial activity in the spring, due to rising temperatures, although this would be expected to be greater nearer the soil surface than at depth.

Goodroad and Keeney (1985) suggested that nitrification was the main source of N_2O near the soil surface, and denitrification the main source at depth, particularly after rainfall. Webster and Dowdell (1982) found that peaks of N_2O emission from denitrification after summer fertilisation of grass swards resulted from the upper layers of the soil, with little or no increases in N_2O concentrations below 75 mm. However, the contribution at depth may not be apparent, as complete reduction to N_2 may occur before gaseous N reaches the soil surface (Arah *et al.*, 1991). Seiler and Conrad (1981) found high concentrations of N_2O in deeper layers of fertilised soil after the evolution rates at the surface had already returned to background levels.

Both applications of fertiliser to the spring barley increased fluxes of N_2O. After the first fertiliser application low concentrations of available NH_4^+ and high concentrations of available NO_3^- were measured at both 0-0.2 and 0.2-0.4 m depths, prior to the first N_2O peak emissions measured. The low NH_4^+ concentrations indicate immobilisation of N, or nitrification after this application. The second application of fertiliser to the spring barley crop resulted in an immediate increase in N_2O emissions, with a flux of 13.0 g N_2O-N ha^{-1} d^{-1} measured immediately after application. After this second application concentrations of available N were much higher at 0-0.2 m depth, but not at 0.2-0.4 m. Mineralisation was estimated to be greater in the unfertilised spring barley, and greater at 0-0.2 m than 0.2-0.4 m depth. This is in accordance with greater microbial activity in surface layers of soil until washed down by rain. The lower mineralisation in the fertilised crop may have reflected the increased N_2O emissions, losses of NO_3^- via leaching, plant uptake of available N and/or immobilisation. Within the literature addition of N, either organic or inorganic, to soil has typically been reported to increase mineralisation of soil N (for example, Broadbent and Nakashima, 1971; Jenkinson *et al.*, 1985; Azam *et al.*, 1991). However, in some cases addition of fertiliser has resulted in lower mineralisation (Westerman and Tucker, 1974).

Emissions of N_2O increased after the first application of 60 kg N ha^{-1} to the oilseed rape. A flux of 38.4 g N_2O-N ha^{-1} d^{-1} was measured 2 days after this application. High concentrations of available soil N were measured immediately after application, but then declined throughout the growing season. A flux of 16.7 g N_2O-N ha^{-1} d^{-1} was measured 19 days after the second fertiliser application. This was probably stimulated by rainfall at this time, especially as a flux of 12.6 g N_2O-N ha^{-1} d^{-1} was measured from the unfertilised oilseed rape on this day. Such subsequent fluxes of N_2O have often been reported to occur after the immediate fertilisation flux, particularly in response to rainfall (Conrad *et al.*, 1983; Webster and Dowdell, 1982). This occurs until there is a depletion of fertiliser in the upper soil layers. Powlson *et al.* (1992) estimated that 2.6 % of fertiliser N was denitrified for every 10 mm of rain that fell during the critical 3 week period following fertiliser application. Goulding *et al.* (1993) measured denitrification losses of over 1 kg N ha^{-1} d^{-1} from fertilised wheat for short periods following rain. Negative mineralisation rates were estimated throughout the oilseed rape trial, indicating immobilisation and/or loss of N by denitrification or leaching. This mineralisation was greater under unfertilised oilseed rape, and greater at 0-0.2 m than 0.2-0.4 m depth.

According to Conrad *et al.* (1983) such raised emissions after fertilisation are typically measured either immediately after, or within a few days of, application, as was found in these field trials. However, they also stated that such emissions may last for one or a few weeks, often ending with a sharp decrease. Such prolonged raised emissions were not observed in these trials, where emissions quickly fell to pre-fertilisation levels within only a few days. Only the raised emissions after the second application to the winter wheat crop endured over 2 weeks. The responses from the other two trials may have been more short-lived because of the larger and more immediate fluxes of N_2O after fertilisation, suggesting that the applied N source was more rapidly depleted. Similarly, McKenney *et al.* (1980) measured only small losses of fertiliser N as N_2O after fertilisation of maize, and within 80 days emissions of N_2O had returned to "background" rates.

The type of fertiliser applied is known to have an important role in determining emissions of N_2O (Mosier *et al.*, 1982, 1983; Breitenbeck *et al.*, 1980; Eichner, 1990). Solid fertilisers, as applied in these trials, absorb moisture, dissolve, and are distributed throughout the soil by rain. NH_4^+ initially moves more slowly than NO_3^-, but is often nitrified within several days (Granli and Bøckman, 1994). Rapid nitrification near the soil surface would result in the often observed immediate N_2O fluxes after fertiliser application in these trials. The addition of $NH_4^+NO_3^-$ fertiliser to the soil in spring provided the potential substrate for increased production of N_2O from both nitrification and denitrification.

6.4.2 Effect of growing crop

The presence of a growing crop influences emissions of N_2O from soil by altering the soil environment, and taking up available N. Most studies in the literature have reported higher N_2O emissions in the presence of growing plants, despite uptake of N (for example, Stefanson, 1972; Duxbury, 1984; Klemedtsson *et al.*, 1987; Kilian and Werner, 1996). The mechanisms involved and further examples are examined further in Chapter 7, where the differences between legume and non-legume crops are examined.

As a crop grows throughout the season its influence on emissions of N_2O becomes increasingly important. Such effects can be seen on the pea trial, which was unfertilised, and comparisons made between emissions from the growing crop and bare soil. Until harvest emissions were higher from the cropped than the bare soil. This agrees with findings of work reviewed by Eichner (1990). Such enhanced N_2O emissions are thought to be contributed to by legume rhizobia (Daniel *et al.*, 1980; Smith and Smith, 1986). Concentrations of available NH_4^+ were lower on the cropped than uncropped areas, but concentrations of NO_3^- were higher on cropped areas. This suggests that nitrification was the predominant process contributing to the N_2O emissions. The reduction in available NO_3^- after 21 April most likely indicates crop uptake, as opposed to substantial losses of N_2O by denitrification. In the other trials comparisons between cropped and uncropped fertilised soils were not possible as each entire field was sown. However, the effect of the growing crop on the raised N_2O emissions after fertilisation must be considered as contributing to measured fluxes, although the contribution from these crops (non-legumes) would not be expected to be as great as from the pea.

The presence of a growing crop may account for the observed increase in emissions from unfertilised cropped plots towards the end of the spring sampling period, particularly on the spring barley and winter wheat trials. Emissions from these unfertilised crops fell prior to harvest. This may be due to the reduced availability of mineral N, as more N is concentrated above ground. However, mature crops continue to alter the microenvironment of the soil through shading (Mosier *et al.*, 1986). Emissions from the unfertilised oilseed rape also increased between 12 and 30 May, possibly not only in response to rainfall, but also due to the growing crop. The growing crop would be expected to reduce available soil N by plant uptake. Such a reduction was observed on all trials, except for the available NO_3^- of the fertilised spring barley which remained high at 0-0.2 m depth. Reduction in available N was also more gradual on the unfertilised oilseed rape at 0-0.2 m.

6.4.3 Fate of fertiliser N

Bouwman (1996) estimated that 1.25 % of N fertiliser is emitted as N_2O, on the basis of long-term measurements of greater than 1 year. In this study, assuming that the N_2O emissions were completely derived from the fertiliser N input, the percentages were lower than Bouwman's estimate with approximately 0.2 % of fertiliser N lost as N_2O from the oilseed rape crop over the 54 day sampling period, 0.08 % lost as N_2O from the winter wheat over 104 days, and 0.04 % of fertiliser N emitted as N_2O from the spring barley over 61 days. However, the contribution of this labelled fertiliser to these emissions can really only be estimated by comparisons with unfertilised plots, as fluxes were too low as to enable analysis of $^{15}N_2O$. According to Stevens *et al.* (1993) the lowest concentration for detection by mass spectrometry is 2.1 μl N_2O l^{-1}, and determination of isotopic composition at even this concentration would be imprecise.

Total crop recoveries of applied ^{15}N have generally been found to be < 80 % (Ladd and Amato, 1986). In accordance with this, the first fertiliser application to winter wheat contributed 64.7 and 67.2 % of total soil available N at 0-0.2 and 0.2-0.4 m depths, respectively on 4 April. After the second application 80 % of the N at 0-0.2 m was from the fertiliser. Prior to harvest, the concentration of available N had fallen, due to plant uptake, and the proportion of this N coming from the fertiliser had also fallen, suggesting that the N derived from fertiliser was preferentially taken up by the crop, leached or immobilised.

The contribution of applied fertiliser to the available soil N pools was lower in the spring barley and oilseed rape trials. Despite the second application of fertiliser on 11 May to the oilseed rape, only 26.5 % of soil N at 0-0.2 m depth on 25 July was derived from the fertiliser. This may have reflected a greater plant uptake of fertiliser N on the oilseed rape trial, with 59.2 % of crop N derived from the two ^{15}N labelled fertiliser inputs. However, Vos *et al.*

(1994) found relatively low uptake of fertiliser N (40 %) in an oilseed rape crop at harvest. In general, 30-70 % of applied fertiliser N is taken up by plants, 10-40 % is lost and up to 40 % remains in the soil after the first crop (Azam *et al.*, 1986; Powlson *et al.*, 1992). In these field trials approximately 50 % of crop N at harvest was derived from fertiliser. It was assumed that this labelled N was uniformly distributed within the residues, however, this is not necessarily so. Ladd and Amato (1986) found that cereal grain N was of a slightly higher ^{15}N atom % enrichment than straw N. In these trials harvested ^{15}N labelled crops were chopped and only the stubble was incorporated in the autumn, thereby avoiding incorporation of higher enriched grain N.

Generally, higher concentrations of fertiliser N were measured at 0-0.2 m depth than at 0.2-0.4 m depth, except after the first fertilisation of the winter wheat. This is in agreement with the main concentration of fertiliser remaining in the surface layers of the soil, in time being washed to lower layers after rainfall. Olson *et al.* (1979) found that most of the fertiliser N remained in the top 0-0.1 m soil layer. Powlson *et al.* (1992) reported that 84-88 % of labelled N remained within the cultivated layer of the soil (0-0.23 m). This is in agreement with the main site of N_2O production being in the surface layers, and therefore greatly influenced by rainfall events and surface temperatures.

6.4.4 Effect of autumn incorporation of residues

Nitrous oxide emissions did not increase significantly after incorporation of residues. Emissions were lower than expectations based on previous trials (Chapters 4 and 5). Concentrations of both available NH_4^+ and NO_3^- were very low throughout the autumn. This was probably due to the high C:N ratios of the incorporated residues, resulting in immobilisation of soil N. Over the entire autumn sampling period more N_2O was emitted in the presence of residues from the oilseed rape (359 g N_2O-N ha^{-1}) and winter wheat (155 g N_2O-N ha^{-1}), but not from the spring barley, where total emissions were very low. This was probably due to the later cultivation and incorporation of residues in this trial, with low temperatures at the time of, and after, incorporation. Additionally, emissions from this trial were only measured over 20 days. Emissions of N_2O are known to be reduced under low temperatures, as microbial activity, nitrification and denitrification all decrease with falling temperature (Denmead *et al.*, 1979a; Bremner and Blackmer, 1981). This is why emissions of N_2O are higher in the spring than in autumn, and lowest in winter. The soil content of nitrifiable N is also important in these seasonal variations (Goodroad and Keeney, 1984), due to the complex combination of environmental conditions and factors that control mineralisation of N.

In previous trials the incorporation of crop residues has resulted in substantial fluxes of N_2O, typically within the first 2 weeks after incorporation (Chapters 4 and 5). Recently added plant residues are approximately 7 times more mineralisable than native organic matter (Shen *et al.*, 1989), and so N_2O fluxes would be expected after addition. However, in these trials N_2O emissions after incorporation of residues were not significantly greater than emissions from bare soil. Fluxes were measured immediately after cultivation of the oilseed rape and spring barley trials, particularly the former. However, the high flux of 68.7 g N_2O-N ha^{-1} d^{-1} measured from the bare soil of the oilseed rape trial immediately after cultivation indicates that these fluxes were mainly a result of soil disturbance by cultivation, as reported by Matthias *et al.* (1980), rather than due to rapid decomposition of residues. Concentrations of available NH_4^+ were increased immediately after incorporation of oilseed rape residues, indicating increased mineralisation, and that the immediate losses of N_2O were by both nitrification and denitrification. Mineralisation was estimated as being greatest at 0.2-0.4 m depth on this treatment. This mineralisation is reflected in the concentrations of biomass N being slightly lowered between 17 November and 14 December, suggesting that immobilisation was instantaneous, but N was later released from the biomass. Vos *et al.* (1994) also found immediate mineralisation of N from oilseed rape residues after incorporation. Such immobilisation followed by remineralisation later in the season has been reported elsewhere (for example by Wagger *et al.*, 1985b; Powlson *et al.*, 1987).

The lowest emissions from the oilseed rape trial were from areas where stubble remained on the surface. This was probably due to slower decomposition rates compared with circumstances where residues are incorporated (Douglas *et al.*, 1980; Wilson and Hargrove, 1986; Varco *et al.*, 1993). Contrary to this, N_2O emissions are generally reported to be higher from undisturbed than from cultivated soils (Burford *et al.*, 1981; Aulakh *et al.*, 1984c). The presence of stubble helps to maintain moisture in the top few cms of soil, creating a favourable environment for microbial growth, immobilisation of N and denitrification (Chapter 5).

The fluxes of 5.1 and 2.7 g N_2O-N ha^{-1} d^{-1} measured from the incorporated spring barley treatment on 16 and 17 November, respectively, were probably stimulated by heavy rainfall on 14 November. This rainfall probably also increased emissions from the winter wheat and oilseed rape trials on 14 and 16 November. After the initial fluxes following cultivation, emissions from the spring barley trial were very low, with negative fluxes measured on 30 November and 6 December. This was probably a result of the later cultivation of this trial. After incorporation concentrations of available NH_4^+ were very low. This suggests that in addition to low mineralisation as a result of low temperatures incorporation of residues may have resulted in immobilisation of soil N. Biomass N data shows that N was immobilised after incorporation of spring barley residues.

N_2O emissions increased 14 days after incorporation of winter wheat residues, from 0.6 to 4.8 g N_2O-N ha^{-1} d^{-1}. However, on this day higher fluxes were measured from the bare soil control, indicating that these fluxes were in response to heavy rainfall. Concentrations of available NO_3^- went up temporarily after incorporation of winter wheat residues, suggesting that N_2O losses from this trial were predominantly from nitrification, despite high soil moisture contents. Mineralisation was estimated to be higher at 0-0.2 m than 0.2-0.4 m depth. Concentrations of microbial biomass on the winter wheat trial increased over the sampling period.

It must be noted that typically up to 40 % of fertiliser N remains in the soil after harvest (Azam *et al.*, 1986), but this proportion depends on inputs (Ladd and Amato, 1986). This N may contribute to production of N_2O in the following season. However, according to Azam *et al.* (1986) this N is mostly in organic forms, of different availabilities. Indeed, only a small portion of this immobilised N (<15 %) becomes remineralised during the subsequent growing season. Vos *et al.* (1994) measured a flux of NO_3^- after incorporation of oilseed rape residues, and concluded that this NO_3^- was largely derived from soil organic N, not from unused fertiliser applied in spring (Macdonald *et al.*, 1989), or from immobilised fertiliser (Martinez and Guiraud, 1990). Thus, it can be assumed that the N_2O losses mostly resulted from decomposition of incorporated residues, and any contribution from fertiliser derived N was low.

6.4.5 Fate of residue N

Mineralisation was low in the autumn, with very low recoveries of ^{15}N in the available N pools, even assuming that this ^{15}N was primarily derived from the labelled residues. This shows that conditions in a temperate autumn are not always favourable for biological activity (Wagger *et al.*, 1985a). Despite immobilisation being reduced at low temperatures, Olson *et al.* (1979) state that net immobilisation is often greater in the autumn, as more time elapses before the maximum demand for N by a growing crop, than in the spring. Indeed, by the end of the autumn period of sampling, the subsequent crops had only emerged and started to tiller, and so any effects of the growing crop on N_2O emissions, and changes in N pools, were considered to be negligible in the autumn.

Biomass N data show the occurrence of immobilisation of N after incorporation of residues in the autumn. Ladd *et al.* (1981a) found that concentrations of ^{15}N labelled biomass were greater 4-8 weeks after incorporation of medic plant material. After 8 weeks concentrations of biomass ^{15}N fell rapidly at first, then more slowly. Wagger *et al.* (1985a,b) found that only 12-15 % of wheat residue N was mineralised after one cropping season. In accordance with this, Azam *et al.* (1985) found that incorporation of plant material in a pot experiment increased biomass N. After 35 days, up to 10 % of N from the residues was in the microbial biomass, plants had taken up 4.8 % of residue N, and 89 % of residue N remained in the soil, with 6 % unaccounted for. This confirms findings by Ladd *et al.* (1981a). Azam *et al.* (1989) found that the 6-9 % of ^{15}N recovered in microbial biomass after addition of ^{15}N-labelled soyabean changed very little with time.

After incorporation of spring barley residues 6.4 % of the 32.2 mg biomass N kg dry soil^{-1}, measured on 28 November, was labelled. This labelled N may have been derived both from the incorporated labelled residues, and also from ^{15}N immobilised after spring application of ^{15}N fertiliser, that had not yet been remineralised (Wagger *et al.*, 1985b; Martinez and Guiraud, 1990). Due to the low autumn temperatures it cannot be assumed that most of the immobilised N was derived from the residues, since immobilisation is reduced in these conditions (Olson *et al.*, 1979). Concentrations of biomass N fell between 17 and 44 days after incorporation of oilseed rape, with the labelled fraction falling from 4.8 to 3.0 % at 0-0.2 m depth. This indicates that immobilised N was remineralised 17 days after incorporation (Wagger *et al.*, 1985b). The contribution of labelled winter wheat residue N to the microbial biomass was lower, with only 1.5 and 1.9 % of biomass N being labelled at 0-0.2 and 0.2-0.4 m depths, respectively on 21 November.

A longer experimental period would have been desirable to take account of the slow release of N from residues. In 1981 Ladd *et al.* found that 60-65 % of ^{15}N labelled medic remained as organic residues after 32 weeks of decomposition. Organic residue N is generally mineralised over long periods of time (Byrnes, 1990), so N from residues may be only partially available to plants in the first growing season, giving a low contribution of residue ^{15}N to soil mineral N (Ladd *et al.*, 1983; Azam *et al.*, 1989), as was found in these trials. Here, the contribution of residue N to total soil available N was lower than that of the fertiliser in the spring. Despite the long time for total mineralisation from organic residues (Byrnes, 1990), the lower temperatures in the autumn would have reduced microbial activity and slowed the decomposition of residues. After incorporation of winter wheat the contribution of residue N to the total soil N pool increased with time, as a result of progressive decomposition, although by 14 December, residue N still only accounted for 6.3 % of soil N at 0-0.2 m depth. This is in agreement with the comparatively low concentration of biomass ^{15}N, and increased N_2O emissions. The highest contribution of residue N to available N pools of 9.9 % was measured at 0-0.2 m on the spring barley trial on 28 November. Contributions from the oilseed rape residues decreased with time at 0-0.2 m depth, the N probably being washed down the profile with rain.

6.5 Summary

The application of fertiliser to a sown crop increased emissions of N_2O and reduced mineralisation in the top 0-0.2 m of the soil, except in the winter wheat trial. Fluxes after fertilisation were lower than reported by other workers in the literature, and were too low to permit the analysis of $^{15}N_2O$. The application of single labelled fertiliser, such as $^{15}NH_4NO_3$ or $NH_4{}^{15}NO_3$ would have enabled the respective contributions of nitrification and denitrification to N_2O emissions to be evaluated if measurement of $^{15}N_2O$ had been possible. Immobilisation was found to be important, particularly in the autumn, resulting in low N_2O emissions after incorporation of labelled residues. Ideally the autumn trials should have been undertaken over a longer period of time, in order to allow for complete mineralisation of residue N and remineralisation of immobilised N. The spring and autumn trials were on the same field sites, so that residual labelled fertiliser N may have contributed to the autumn labelled biomass, available N pools and N_2O emissions in the autumn after incorporation of labelled residues. It is recommended that future trials to evaluate the contribution of different N sources to emissions of N_2O should be based over a period of several months, during the same season, using higher applications of single labelled fertilisers.

CHAPTER 7 NITROUS OXIDE EMISSIONS FROM GROWING AND INCORPORATED CROPS IN A MEDITERRANEAN CLIMATE

7.1 Introduction

Temperature strongly influences the rate of organic matter decomposition through effects on microbial activity. The optimum temperature for decomposition is approximately 35 °C (Alexander, 1977). Below 2 °C little microbial activity takes place. Between these limits decomposition rates generally rise rapidly as the soil temperature increases (Haynes, 1986). Nitrifying bacteria have an optimum temperature for activity at 25-30 °C, and so temperatures within this range would be expected to result in relatively large emissions of N_2O as a result of nitrification (Granli and Bøckman, 1994). The rate of denitrification increases rapidly between 2 and 37 °C, with an apparent optimum at 25-30 °C (Bremner and Shaw, 1958; Freney *et al.*, 1979). However, with increasing temperature the ratio of $N_2O:N_2$ is reduced, because of the increasing tendency for N_2O reduction to N_2 (Nômmik, 1956).

Provided that available soil N is not limiting, many authors have reported higher N_2O emissions in the presence of growing plants, particularly legumes (Stefanson, 1972; Duxbury, 1984; Klemedtsson *et al.*, 1987; Eichner, 1990; Kilian and Werner, 1996). Plant growth increases the amount of organic substances in soil from root material and exudates, stimulating microbial activity. Differences in emissions of N_2O between crops are most apparent between legumes and non-legumes, otherwise the type of crop has not been found to greatly influence N_2O emissions (Mosier *et al.*, 1986; Kilian and Werner, 1996). However, most of these experiments have compared emissions from fertilised crops. According to Eichner (1990) the level of N_2O emissions from soils cropped with legumes ranges from 0.34 to 4.6 kg N_2O-N ha^{-1} yr^{-1}. Bremner *et al.* (1980) found that emissions from unfertilised soyabean averaged 1.2 kg N_2O-N ha^{-1} yr^{-1}. Rhizobia are thought to contribute to N_2O emissions from growing legumes (Smith and Smith, 1986). Nodule denitrification is continuous, occurring simultaneously with N_2 fixation (Smith and Smith, 1986; Kilian and Werner, 1996).

Experimental work was undertaken on a clay soil in a Mediterranean climate. N_2O emissions were measured from mature growing and incorporated legume and non legume crops. It was hypothesised that the warm temperatures at the time of autumn cultivation would be conducive to microbial activity, resulting in high N_2O emissions, particularly immediately after incorporation of legume crops.

7.2 Sites, materials and methods

In autumn 1995 an experimental site was established at the Centro di Sperimentazione di Castelvolturno (CSCV), in the Low-Volturno basin, an alluvial plain approximately 35 km north of Naples, Italy. The CSCV consists of mainly Entisols and Vertisols; the field used in this experiment was a Vertisol with a silty clay loam texture. The climate can be described as a typical Mediterranean xeric, with a mean annual temperature of 15 °C and annual rainfall of 1100 mm, with approximately 75 rainy days a year.

A strip plot experimental design was established. Crops of maize, soyabean and fababean were grown in strips across the experimental area throughout the summer 1995. Half of these crops were incorporated to a depth of 50 mm in 8 m wide strips, perpendicular to the crop rows, by 2 passes of a rotary tiller on 26 September 1995.

Emissions of N_2O were measured by a chamber method both prior to and following the time of cultivation. Two chambers (0.4 x 0.4 x 0.4 m height) were placed on each plot and also on a control area of bare rotary tilled soil. These chambers differed in design from those described in section 3.8. They were constructed from sheets of PVC joined with a gas-tight sealant. A water-filled channel was constructed around the top of the chamber wall, into which a vertical flange on the PVC lid penetrated as an effective alternative to compression seals. A gas sampling port was inserted through the lid and made gas-tight with sealant. Gas samples were obtained using 5 ml glass syringes, and analysed for concentrations of N_2O as described in section 3.9.

Soil samples were collected at times of gas sampling and analysed for concentrations of available NH_4^+ and NO_3^-, and gravimetric soil moisture content, as described in sections 3.2 and 3.3. This analysis was undertaken in the Dipartimento di Biologia Vegetale, Universita degli Studi di Napoli, "Federico II". Soil temperature (0.1 m depth) was continually monitored in both growing and incorporated maize and soyabean plots using a temperature probe with datalogger. Air and soil (50 mm) temperatures in both growing and incorporated maize plots were manually recorded at the time of gas sampling. Crops were sampled from areas of 1 m^2 and analysed for total C and N contents and above ground biomass and dry matter.

Eight days after rotary tillage areas of 1 m^2 were irrigated with 5 l water m^{-2}, using a watering can. This irrigation encompassed one chamber of each plot, in an attempt to simulate a day's rainfall event, based on meteorological data from that region.

7.3 Results

7.3.1 Cumulative emissions of N_2O

Cumulative N_2O emissions for the whole experimental period after cultivation are presented in Fig. 7.1a. In the absence of irrigation, the greatest cumulative emission over the entire 22 day period after cultivation was 137 g N_2O-N ha^{-1}, measured from the growing soyabean crop, and was significantly higher ($p<0.005$) than emissions from all other treatments. Cumulative emissions after incorporation of fababean and maize were greater than from the growing crops. The cumulative emission of 107 g N_2O-N ha^{-1} from the incorporated maize was significantly greater ($p<0.05$) than the 28.2 g N_2O-N ha^{-1} emitted after 26 September from the growing maize crop. The lowest cumulative emission over this period of 2.7 g N_2O-N ha^{-1} was from the control.

The cumulative emissions before irrigation on 4 October are shown in Fig. 7.1c. 56.3 g N_2O-N ha^{-1} was emitted from the growing fababean plot during this period, and was 94 % of the total emission from this treatment in the absence of irrigation. Incorporation of maize resulted in an emission of 54.5 g N_2O-N ha^{-1}, significantly more than the 23.5 g N_2O-N ha^{-1} from the growing crop ($p<0.05$) over this 14 day period.

7.3.1.1 Irrigation

Irrigation only raised cumulative emissions over the period after cultivation significantly from the incorporated fababean treatment ($p<0.05$), with 98.9 g N_2O-N ha^{-1} and 63.1 g N_2O-N ha^{-1} emitted from irrigated and non-irrigated plots respectively (Fig. 7.1(ii)). Again, the lowest emissions were from the control.

In the absence of irrigation the greatest cumulative emission from 4 October until the end of the experimental period was measured from the growing soyabean crop ($p<0.005$). Irrigation resulted in the greatest cumulative emission of 57.8 g N_2O-N ha^{-1} from the incorporated fababean, which was significantly higher than emissions after irrigation of other incorporated treatments ($p<0.05$), irrigated growing crops ($p<0.05$), and the non-irrigated fababean ($p<0.05$) treatments. Over this period the irrigated control acted as a sink taking up 17.6 g N_2O-N ha^{-1}.

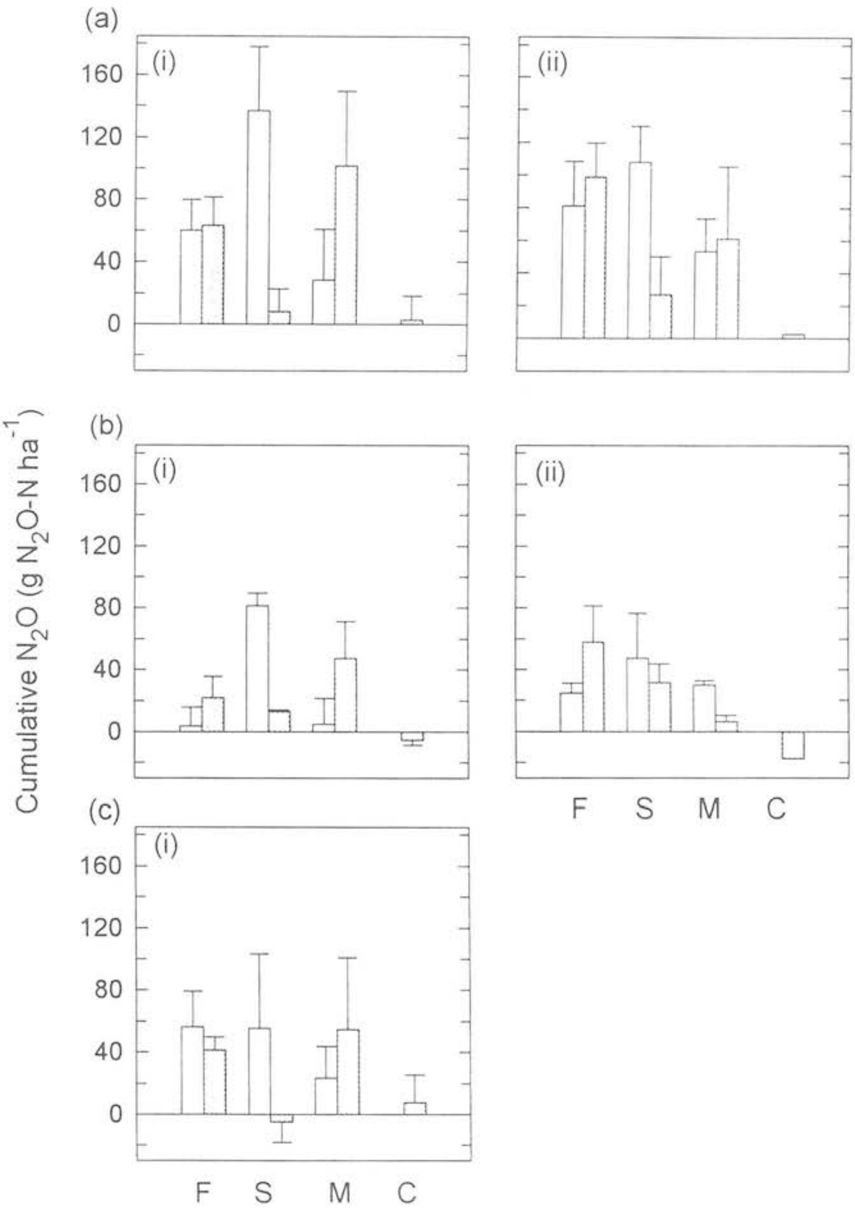

Figure 7.1 Cumulative emissions of N_2O (a) during the whole sampling period (22 days). (b) after irrigation on 4 October (8 days). (c) before irrigation from (i) non irrigated. (ii) irrigated growing (empty bars) and incorporated (hatched bars) fababean (F). soyabean (S). maize (M) and control (C) treatments.

7.3.2 Daily fluxes of N_2O

Fluxes of N_2O fluctuated after cultivation, with negative fluxes measured from both incorporated and growing crop treatments, particularly over the first 3 days (Figs. 7.2 and 7.3). Negative fluxes were measured from the growing soyabean and maize crops prior to cultivation. Negative fluxes were measured on the first day after cultivation (27 September) from all treatments except the incorporated maize, and on 28 September from all treatments except the incorporated maize and growing soyabean and fababean crops. The incorporated soyabean took up 18 g N_2O-N ha^{-1} d^{-1} on 28 September. The magnitude of these negative fluxes were reduced on 29 September. Emissions from the soyabean crop on 20 September were significantly lower ($p<0.05$) than emissions from the maize and fababean crops on this day.

Positive fluxes of N_2O were measured immediately following incorporation of crops on 26 September, but were not significantly different on this day. A flux of 23 g N_2O-N ha^{-1} d^{-1} was measured from the soyabean crop on this day. Emissions from the soyabean crop increased from -2 to 13 g N_2O-N ha^{-1} d^{-1} between 29 September and 6 October, and during this time were significantly greater ($p<0.05$) than emissions from the other growing crops. On 6 October the flux of 12.7 g N_2O-N ha^{-1} d^{-1} measured from the growing soyabean crop was greater ($p<0.005$) than from the incorporated soyabean. By the end of the experimental period all emissions were low.

7.3.2.1 Irrigation

One day after irrigation (5 October) a flux of 30 g N_2O-N ha^{-1} d^{-1} was measured from the incorporated fababean treatment, which was significantly higher ($p<0.005$) than the other treatments on this day (Figs. 7.4 and 7.5). Emissions from the maize crop, incorporated soyabean and control treatment were also raised after irrigation ($p<0.05$).

7.3.3 Available soil N

Available NH_4^+ was raised in all treatments immediately after cultivation on 26 September (Fig. 7.6a). Concentrations on this day were higher ($p<0.05$) where the crops had been incorporated. The greatest increases between 22 and 26 September of 38 and 26 µg NH_4^+-N g dry $soil^{-1}$ were measured in the incorporated maize and incorporated fababean treatments, respectively. Available NH_4^+ was also raised in the control. However, after 26 September available NH_4^+ in all treatments remained low until 12 October, when available NH_4^+ was

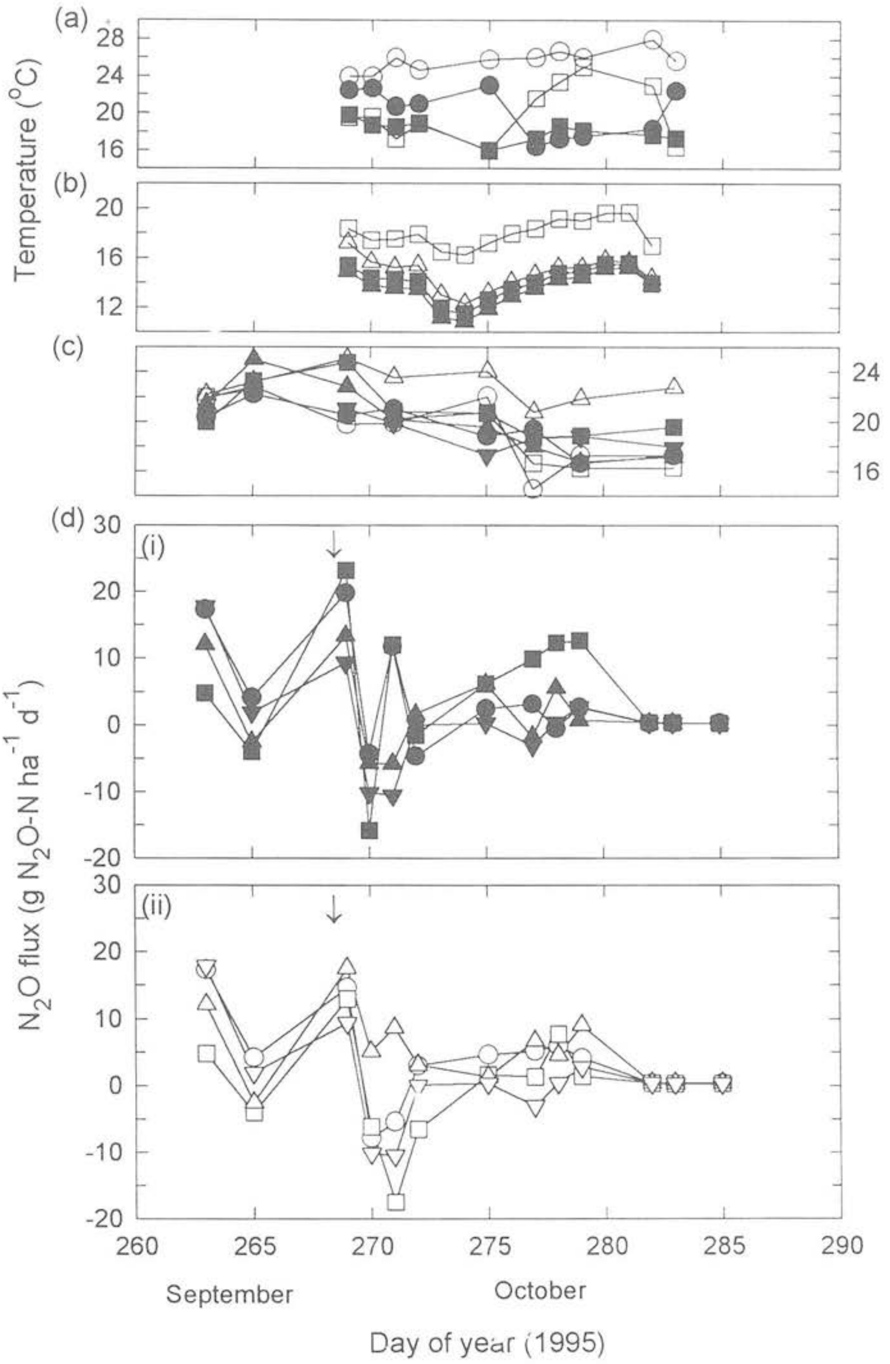

Figure 7.2 (a) Manually obtained air temperatures, (b) data logger soil temperatures at 0.1 m depth, (c) soil moisture contents, (d) N_2O emissions from (i) growing crops (filled symbols), (ii) incorporated crops (empty symbols), of fababean (circles), soyabean (squares), maize (upward triangles), bare soil control (downward triangles). Arrows indicate time of cultivation.

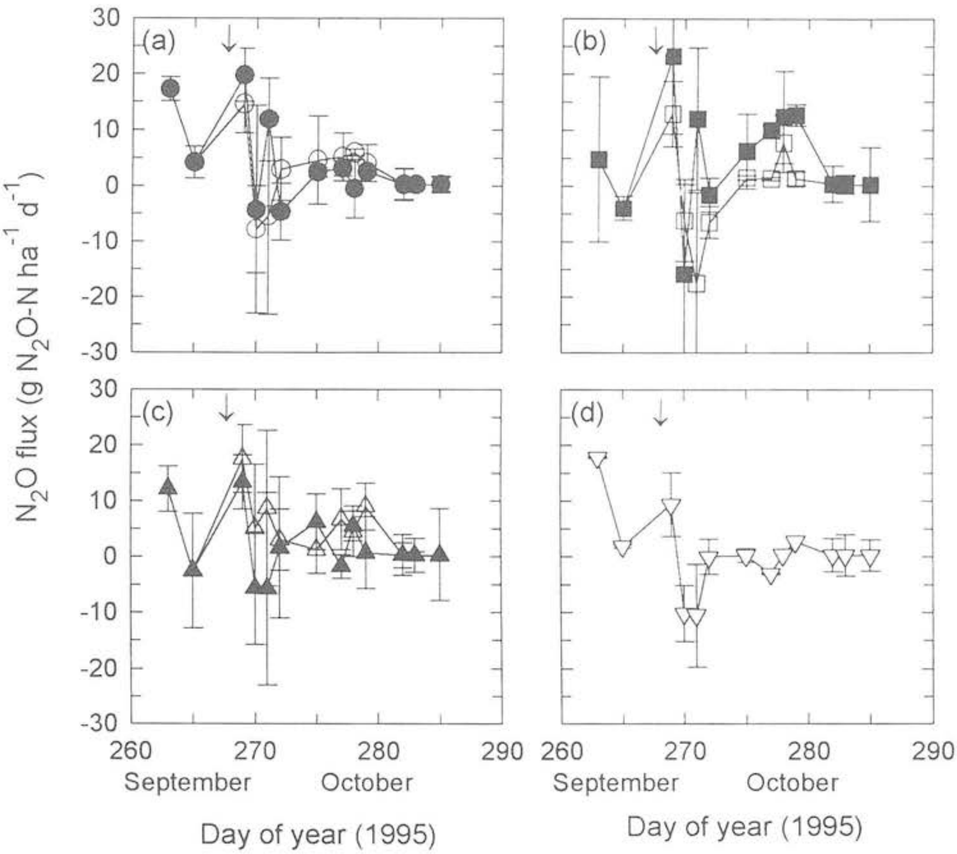

Figure 7.3 Emissions of N_2O from growing (filled symbols) and incorporated crops (empty symbols) of (a) fababean, (b) soyabean, (c) maize, (d) bare soil control. Arrows indicate time of cultivation.

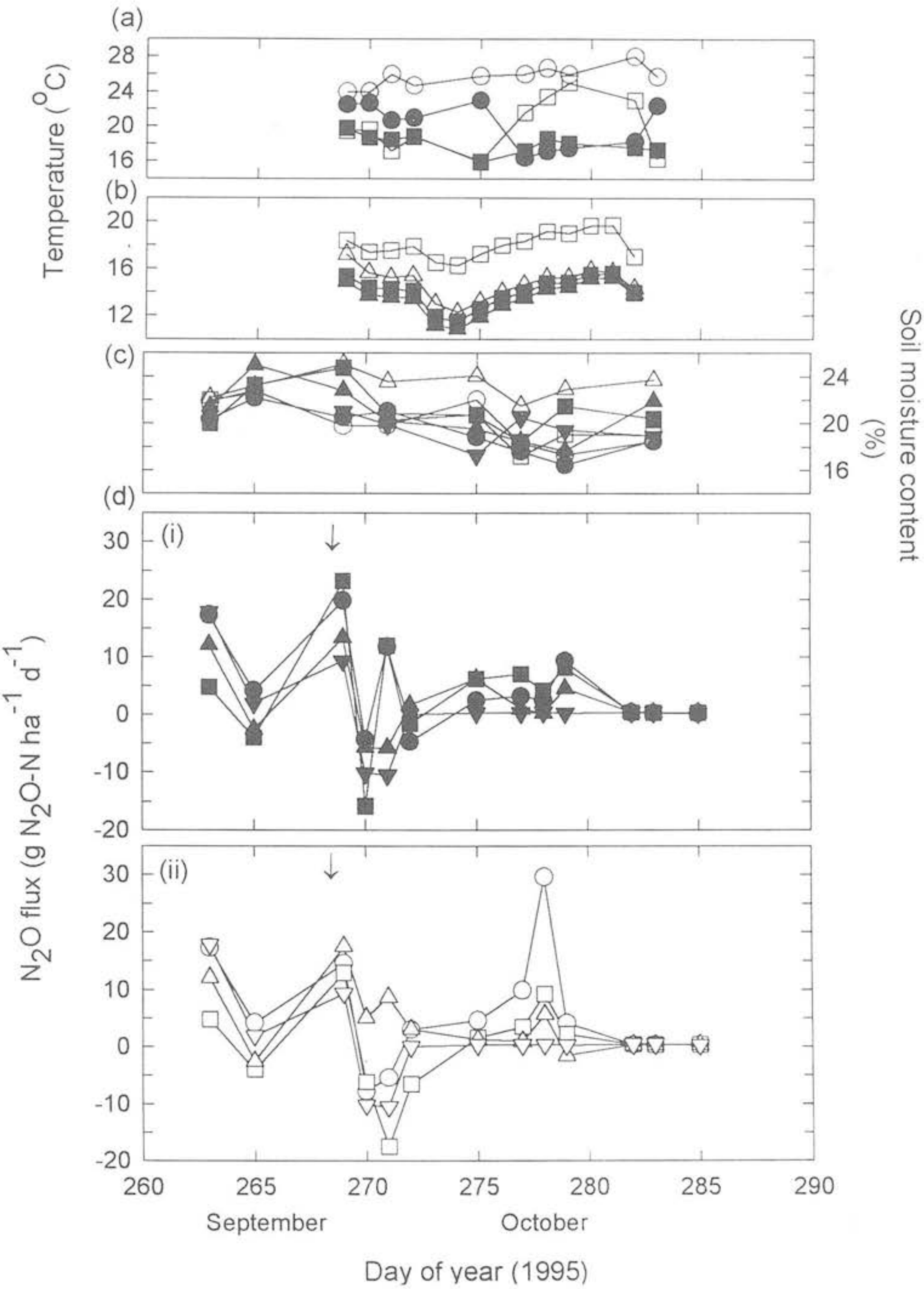

Figure 7.4 (a) Manually obtained air temperatures, (b) data logger soil temperatures at 0.1 m depth, (c) soil moisture contents, (d) N_2O emissions from (i) growing crops (filled symbols), (ii) incorporated crops (empty symbols), after irrigation on 4 October, of fababean (circles), soyabean (squares), maize (upward triangles), bare soil control (downward triangles). Arrows indicate time of cultivation.

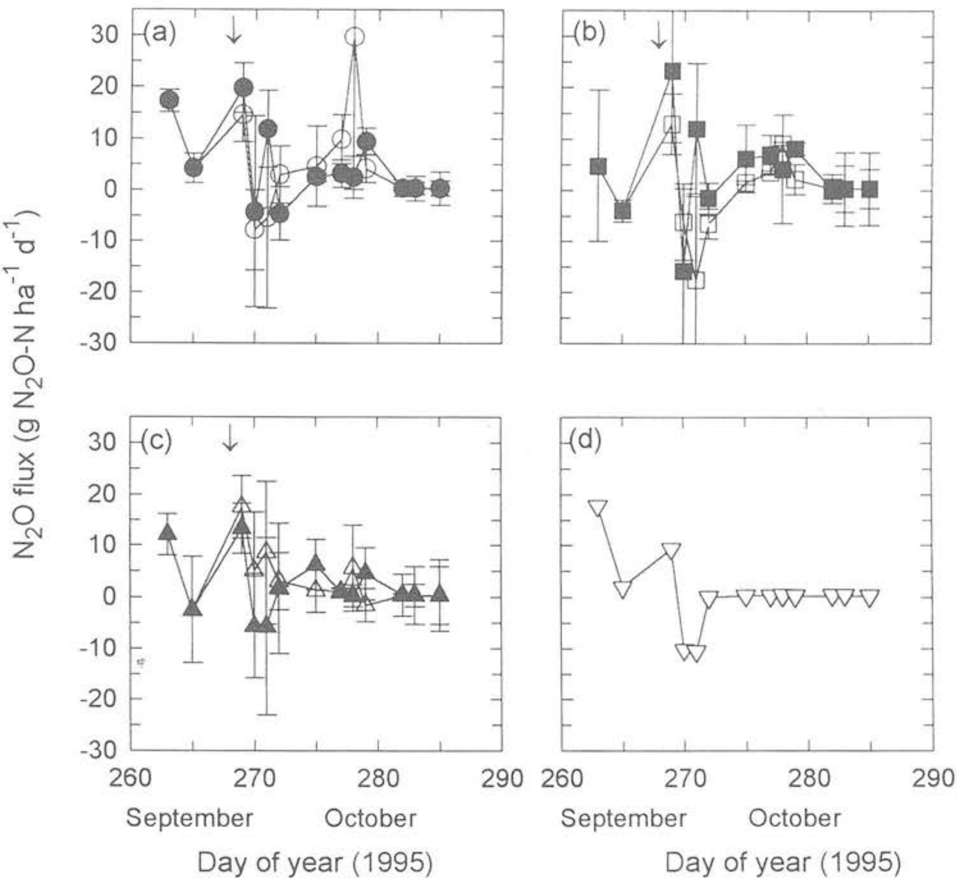

Figure 7.5 Emissions of N_2O from growing (filled symbols) and incorporated crops (empty symbols) with irrigation on 4 October of (a) fababean, (b) soyabean, (c) maize, (d) bare soil control. Arrows indicate time of cultivation.

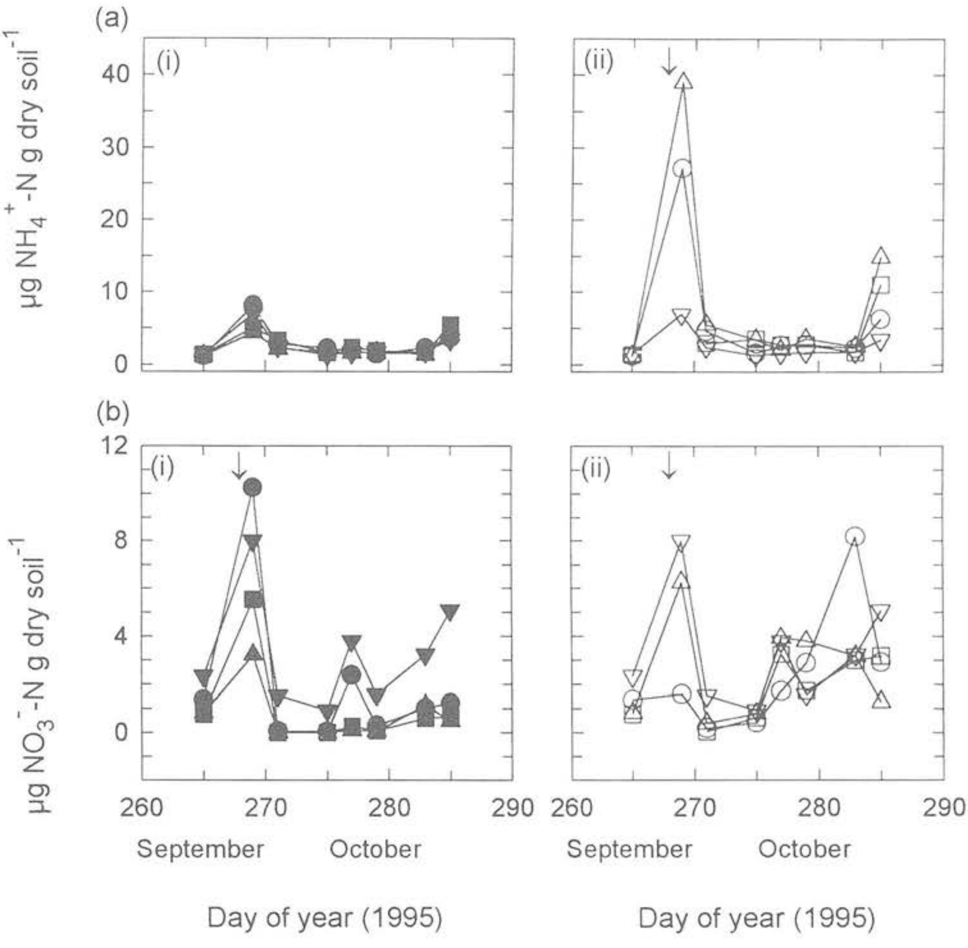

Figure 7.6 Concentrations of (a) available NH_4^+, (b) available NO_3^- in (i) cropped (filled symbols) and (ii) incorporated crop (empty symbols) treatments of fababean (circles), soyabean (squares), maize (upward triangles), control (downward triangles). Arrows indicate time of cultivation.

raised again, particularly in the maize and soyabean treatments; both incorporated and growing crops.

Available NO_3^- was also raised in all treatments immediately after cultivation on 26 September (Fig. 7.6b). On this day 10 µg NO_3^--N g dry soil^{-1} was measured under the fababean crop, and 1.6 µg NO_3^--N g dry soil^{-1} was measured in the incorporated fababean treatment. Concentrations in the control were also raised on this day. By 28 September available NO_3^- had fallen. Further increases between 2 and 4 October occurred in all treatments, except maize and soyabean crops. By 10 October available NO_3^- under the growing crops was significantly lower ($p<0.05$) than where they had been incorporated. 8 µg NO_3^--N g dry soil^{-1} was measured in the incorporated fababean treatment on 10 October.

7.3.3.1 Irrigation

Irrigation increased the differences in available NH_4^+ between treatments, particularly in the growing crop treatments (Fig. 7.7a). On 4 October irrigation temporarily increased the available NH_4^+ in the control. Concentrations were also raised in the incorporated maize treatment. On 12 October available NH_4^+ was still significantly greater ($p<0.05$) after incorporation despite irrigation.

Irrigation initially reduced available NO_3^- under the fababean crop, and in the incorporated soyabean treatment ($p<0.05$) (Fig. 7.7b). On 4 and 10 October the concentrations were greater in the incorporated treatments than under the growing crops ($p<0.05$), despite the reduction in concentrations in the incorporated fababean treatment after irrigation.

7.3.4 Gravimetric moisture contents

There was no rainfall either during the sampling period or for the 2 weeks prior to cultivation. However rainfall had been high in late August. Gravimetric soil moisture contents decreased throughout the sampling period on most treatments (Fig. 7.2c). Incorporation of maize immediately increased the soil moisture content by 2 %. Soil moisture contents on this treatment remained high for the rest of the experimental period, but were only significantly greater on 2 October ($p<0.05$). The moisture content of the soil under the soyabean crop also increased between 22 and 26 September. Irrigation raised soil moisture contents by an average of 1.5 %, with no significant difference between treatments.

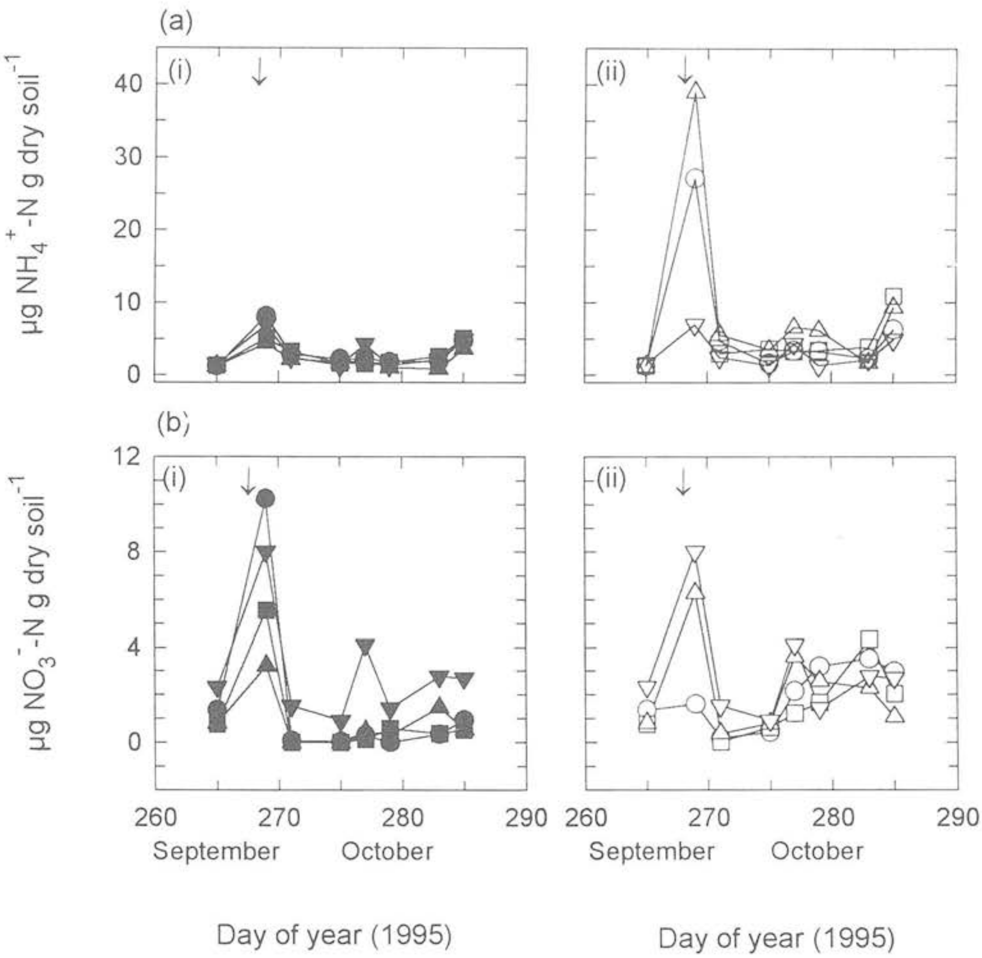

Figure 7.7 Concentrations of (a) available NH_4^+, (b) available NO_3^- in (i) cropped (filled symbols) and (ii) incorporated crop (empty symbols) treatments of fababean (circles), soyabean (squares), maize (upward triangles), control (downward triangles), with irrigation on 4 October. Arrows indicate time of cultivation.

7.3.5 Temperature

Records of air and soil (50 mm) temperatures from the ploughed maize areas taken manually, were consistently higher than within the growing maize crop (Fig. 7.2a). The soil temperature under the maize crop varied less throughout the sampling period than the soil temperature of the incorporated maize treatment. The datalogger highlighted great diurnal variations in soil temperature at 0.1 m depth (Figs. 7.2b and 7.8). These temperatures were lower than the air or at 50 mm depth. Daily averages showed consistently higher soil temperatures where the crops had been incorporated, particularly soyabean which had an average temperature of 18 ^{o}C at 0.1 m depth.

7.3.6 Properties of crops

The fababean crop had the highest N content and lowest C:N ratio and dry matter yield of the three crops (Table 7.1). Maize had the lowest N content of 1.33 % and a comparatively high C:N ratio of 28.6:1. Soyabean had the highest dry matter yield of 5210 kg ha^{-1}.

Table 7.1. Crop composition.

Crop	Crop C (%)	Crop N (%)	C:N ratio	Dry matter yield ($kg\ ha^{-1}$)	Fresh crop weight ($kg\ ha^{-1}$)
fababean	37.6	2.58	14.6:1	2180	27400
soyabean	37.2	2.38	15.6:1	5210	32200
maize	38.0	1.33	28.6:1	4480	35000

7.4 Discussion

7.4.1 Growing crops

Over the whole experimental period higher N_2O emissions were measured in the presence of growing crops than from the bare soil control. Many authors have reported such higher N_2O losses in the presence, than in the absence, of growing plants (for example, Stefanson, 1972; Duxbury, 1984; Klemedtsson *et al.*, 1987; Eichner, 1990; Kilian and Werner, 1996). Plants alter the soil environment in various ways. Plant growth increases the quantity of organic

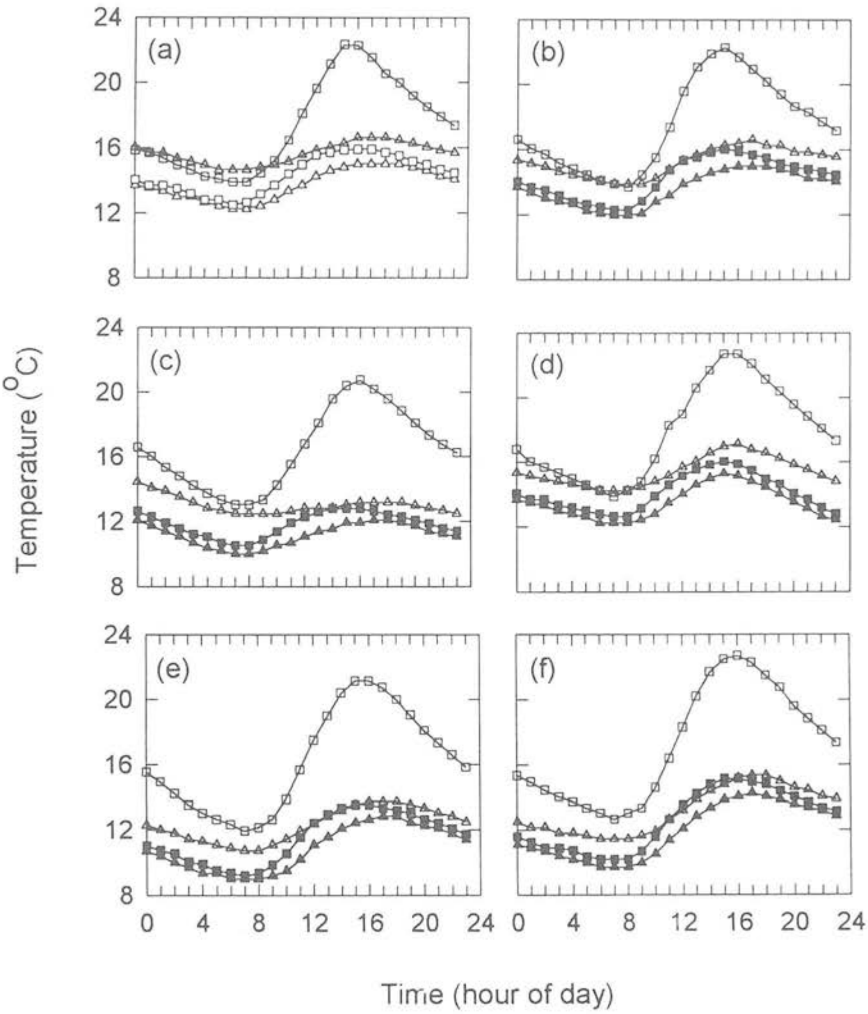

Figure 7.8 Data logged soil temperatures at 0.1 m depth on (a) 27 September, (b) 28 September, (c) 29 September, (d) 30 September, (e) 1 October, (f) 2 October on growing (filled symbols) and incorporated (empty symbols) crops of maize (triangles) and soyabean (squares).

substances in the soil from root material and exudates, stimulating microbial activity and increasing N_2O emissions (Svensson *et al.*, 1991; Kilian and Werner, 1996). Plant roots take up water, soil NO_3^- and NH_4^+ from the soil, and also alter soil structure, creating channels for gas transfer. Plants also provide cover for the soil, reducing diurnal soil temperature fluctuations. However, plants have also been found to suppress denitrification by depletion of soil NO_3^- and reduction of soil moisture (Duxbury *et al.*, 1982; Bakken, 1988).

The total emissions from the 2 legume crops were higher ($p<0.05$) than from the maize crop. The emission of 136.7 g N_2O-N ha^{-1} emitted from the soyabean was greater than that from the fababean ($p<0.05$) or maize ($p<0.01$). Such enhanced emissions from growing legumes have been reported in the literature, and summarised by Eichner (1990). According to Eichner (1990) emissions from agricultural soils cropped with legumes range from 0.34 to 4.6 kg N_2O-N ha^{-1} yr^{-1}, including background emissions, those after cultivation, and emissions from fixed N. In 1984 Duxbury compared N_2O emissions from cropped alfalfa and a weedy pasture of timothy grass. Emissions from the alfalfa ranged from 2-4.6 kg N_2O-N ha^{-1} yr^{-1}, whereas emissions from the pasture were lower, ranging from 0.7-1.9 kg N_2O-N ha^{-1} yr^{-1}, despite probably containing a few legumes. Bremner *et al.* (1980) measured N_2O emissions averaging 1.2 kg N_2O-N ha^{-1} yr^{-1} from cropped soyabean. Using the same method of extrapolation as Bremner *et al.* (1980) to a longer time period, annual emissions from the cropped soyabean, fababean and maize in this trial were calculated to be approximately 1.07, 0.47 and 0.24 kg N_2O-N ha^{-1} yr^{-1}, respectively, assuming a vegetative growth period of 4 months, followed by bare soil. Thus, emissions from this trial were at the lower end of the range reported by Eichner (1990). Annual emissions from the control were calculated to be 0.06 kg N_2O-N ha^{-1} yr^{-1}.

Continual slow degradation of N-rich nodulated legume roots would increase the stimulation of micro-organisms more than would occur with non-legumes (Kilian and Werner, 1996). Thus there is a greater potential for losses of N_2O from both nitrification and denitrification from soil cultivated with legumes (Svensson *et al.*, 1991). Kilian and Werner (1996) found higher denitrification rates from soils cultivated with N_2 fixing *V. faba* plants than soils cultivated with non-fixing plants. Svensson *et al.*, (1991) also reported higher denitrification rates from growing lucerne than fescue grass or barley.

Such enhanced N_2O emissions from soil cropped with legumes may also partly result from rhizobial denitrification (Smith and Smith, 1986). Many strains of rhizobia can denitrify as either nodule bacteroids or free-living bacteria (Kilian and Werner, 1996). Bhandari and Nicholas (1984) measured $^{15}N_2O$ from soyabean bacteria after applying $^{15}NO_3^-$ to the soil.

When measuring N_2O from cropped soyabeans Smith and Smith (1986) concluded that continuous nodule denitrification was occurring simultaneously with N_2 fixation. Daniel *et al.*, (1980) suggested that denitrification by rhizobia may result in significant loss of soil NO_3^-. In this trial emissions measured from the cropped soyabean and fababean treatments may have been contributed to by bacteroids and/or enhanced microbial activity around the nodulated roots.

Concentrations of available soil N were low under the growing crops, and were less than the bare soil control, except on 26 September, indicating crop uptake of NH_4^+ and NO_3^-. The lower emissions measured from the cropped maize compared with the cropped legumes and incorporated maize may have partly been due to lower soil and air temperatures within this crop resulting from shading. The 2 m height of the maize crop resulted in interrow shading, except when the sun was directly overhead. Less shading of the soil would have occurred under the shorter legume crops. Mosier *et al.* (1986) have suggested that the differences in N_2O evolved between various crops may simply reflect their different growth and developmental patterns.

7.4.2 Incorporated crops

Cultivation promotes good aeration and enhances the accessibility of crop residues to soil microbes (Ross, 1990), resulting in increased mineralisation and N_2O production (Chapter 4). In this trial, emissions of N_2O increased after crop incorporation, compared with the bare soil control. The highest total emission of 102 g N_2O-N ha^{-1} ($p<0.005$) over the 22 day trial period was measured after incorporation of maize. This may have been due to its greater aboveground biomass compared to that of the legumes. The large amount of fresh organic C in the maize residues would have stimulated microbial activity, and may have created anaerobic conditions in the top 50 mm of the soil, conducive to losses of N_2O from denitrification. The soil moisture content was increased by 2 % after incorporation of maize, which would have promoted such a development. N_2O emissions after incorporation of legumes have been found to be greater than after incorporation of non-legumes (Chapter 4). This is usually attributed to the low C:N ratio of legumes and their associated more rapid decomposition (Aulakh *et al.*, 1991b), with consequent production of NO_3^-. This is discussed in more detail in Chapter 4. Maize had a higher C:N ratio (28.6:1) than the two legumes, and so greater immobilisation of N would have been expected after its incorporation (Aulakh *et al.*, 1991a,b). According to Haynes (1986) the critical value for which there is generally net immobilisation is with a C:N ratio of greater than 25-30:1, encompassing that of the maize crop. The flush of available NH_4^+ immediately after incorporation of maize on 26 September may have resulted from decomposition of the large amount of biomass incorporated (Lampkin, 1990), with subsequent immobilisation resulting in low concentrations after this date.

Total N_2O emissions were unexpectedly low after incorporation of the soyabean crop. This process would have been expected to result in emissions of similar magnitude to those from the other legume, fababean, due to their similarly low C:N ratios of 15.6:1 and 14.6:1, respectively (McKenney *et al.*, 1993; Goodroad *et al.*, 1994). Unfortunately, soil sampled from the incorporated soyabean treatment on 26 September was lost and so the immediate effect of the crop's incorporation on concentrations of available N was not known for this treatment. However, it is unlikely that the low N_2O emissions were associated with immediate immobilisation of N on this treatment, due to the low C:N ratio of the soyabean material.

The changes in concentration of available NH_4^+ indicate that mineralisation was very rapid during the first few days of the trial, particularly after crop incorporation. This was probably due to the warm temperature being favourable for microbial activity (Haynes, 1986). However, after 28 September concentrations of available NH_4^+ remained low until 12 October. Emissions of N_2O during this period were low suggesting that immobilisation occurred after the initial flush of mineralisation. The immobilised N appears to have been remineralised by 12 October. Concentrations of available NH_4^+ were also immediately raised after rotary tillage of the control. This indicates the effect of cultivation alone in the absence of plant material, in stimulating mineralisation of native soil organic matter, through exposure of organic matter microsites to micro-organisms (Ross, 1990).

7.4.3 Irrigation

Under a Mediterranean climate irrigation is important. In agricultural regions with low summer rainfall and no irrigation, emissions of N_2O have been found to be low (Ryden *et al.*, 1979). In Western Oregon (Mediterranean climate) Myrold (1988) measured gaseous losses of only 1.7 and 0.7 kg N ha^{-1} yr^{-1} from cropped ryegrass and winter wheat respectively, despite additions of N fertiliser and high temperatures. Thus, they reported a strong negative correlation between denitrification and temperature. However, with frequent wetting in the summer under a Mediterranean climate there is the potential for gaseous N emissions to be much greater than from temperate regions (Ryden *et al.*, 1979).

Wetting of soil can lead to rapid activation of soil micro-organisms, particularly after a dry period, resulting in increased production of N_2O (Ryden and Lund, 1980; Sexstone *et al.*, 1985; Vinther, 1992), and redistribution of C and NO_3^- in the soil (Haynes, 1986). Thus, large N_2O fluxes are usually measured after rainfall or irrigation events (Webster and Dowdell, 1982). Despite there being no rainfall over the experimental period soil moisture contents remained high below 50 mm depth and sufficiently moist for microbial decomposition to occur. This was a result of heavy rain in late August. The addition of 5 l water m^{-2}, simulating a day's rainfall raised soil moisture contents but only significantly ($p<0.05$) raised N_2O emissions in the incorporated fababean treatment, suggesting that soil moisture had previously been limiting on this treatment, whilst substrate for nitrification was present in the soil. Increased concentrations of available NO_3^- after irrigation of this treatment, confirm that nitrification contributed to N_2O losses after irrigation.

7.4.4 Possible reasons for low emissions of N_2O

In trials reported in previous chapters, temperature was found to be an important parameter affecting N_2O losses after incorporation of plant material in a Scottish climate, primarily due to the sensitivity of soil micro-organisms to temperature. An increase in temperature is known to raise microbial activity within the soil (Haynes, 1986), thereby increasing rates of decomposition, nitrification and denitrification (Stanford *et al.*, 1975). Nitrifiers have an optimum temperature for activity at about 25-30 °C (Bremner and Blackmer, 1981; Haynes, 1986). Within the range of 10-35 °C a 10 °C increase doubles the rate of denitrification (Stanford *et al.*, 1975). During this field trial air temperatures averaged 25.7 °C and soil temperatures (0.1 m depth) averaged 16 °C. These comparatively high temperatures, favourable for microbial activity, would have been expected to result in large emissions of N_2O, especially after incorporation of fresh plant material rich in N. However, microbial activity may have been so high that mineralised N, even from legumes, was rapidly immobilised into the soil biomass.

According to Sexstone *et al.*, (1985), a clay soil may act as both a source and a sink for N_2O depending on the soil conditions and the amount of N, such as in the form of crop residues. In this trial negative fluxes, or sinks, of N_2O were measured from all treatments, particularly between 27 and 29 September. These may have been a result of the clay mineralogy. In general, higher N_2O emissions have been measured from clay soils than from sandier soils (McKenney *et al.*, 1980; Webster and Dowdell, 1982; Skiba *et al.*, 1992 and Vinther, 1992), but reports differ. Although clay soils have a high potential for sustained N_2O formation from denitrification, in such soils there is a tendency for N_2O produced at depth to be reduced to N_2 as it moves up the profile, as diffusion in a clay soil is slow (Arah *et al.*, 1991). This is exacerbated by moist soil conditions within the profile. Therefore, emissions measured at the soil surface may be misleadingly low indicators of denitrification. Parkin *et al.* (1985) and

Sexstone *et al.* (1985) reported evolution of N from clay soils and those with coarser substrates to be of about the same order of magnitude.

In 1981 Ryden. measured N_2O sinks as large as 11.6 ng N m^{-2} s^{-1}, the mechanism for which remains unknown. Such sinks of N_2O have been observed even 2 weeks following fertilisation when raised N_2O emissions would have been expected (Conrad *et al.*, 1983). In this trial the negative fluxes measured on 27 and 28 September suggest that on these dates the soil was acting as a sink for N_2O. Ryden (1981) partly attributed such sinks to low concentrations of available NO_3^-. The low concentrations of NO_3^- measured on 2 October were not concurrent with negative fluxes on this day. Clearly, low concentrations of available NO_3^- would only limit N_2O from denitrification and not nitrification. It is possible that anaerobic conditions developed after the addition of fresh plant material into the soil (Beauchamp *et al.*, 1989). However, this does not explain the negative fluxes measured from the growing crop treatments.

Many studies have shown that clays with a 2:1 mineralogy may temporarily fix NH_4^+ in their interlayers (McBeth, 1917; Kowalenko and Cameron, 1978; Scherer, 1993; Smith S.J. *et al.*, 1995). After penetration into the interlayers of clay minerals these NH_4^+ ions are protected from nitrification until later released, but may be available to plants (Scherer, 1993). Such NH_4^+ fixation is known to be most rapid during the first few minutes after addition of plant material, but this process usually continues for several weeks (McBeth, 1917), with fixed NH_4^+ only released when the concentration of available soil NH_4^+ becomes very low, such as due to nitrifier activity or plant uptake (Norman and Gilmour, 1987). Cropping may lower the content of non-exchangeable NH_4^+-N in surface soils (Praag *et al.*, 1980). Vermiculites have the greatest capacity for NH_4^+ fixation, whilst montmorillonites are thought only to fix negligible amounts of NH_4^+ ions (Scherer, 1993; Allison *et al.*, 1953). However, montmorillonites may contain zones of vermiculite or illite structures which are capable of fixation. In this field trial at CSCV montmorillonite was the dominant clay mineral. It is possible that the low and negative fluxes of N_2O measured during this trial partly resulted from NH_4^+ fixation, as well as from immobilisation of soil N into the microbial biomass.

7.5 Summary

Despite the warm temperature throughout the experimental period, and soil moisture contents averaging 20 %, emissions of N_2O were low. Negative fluxes were measured from all treatments over the first 3 days of the trial, even from uncultivated cropped treatments, indicating that the soil was acting as a sink for N_2O. This may have been due to a variety of factors, or a combination of these. It was suggested that immobilisation of N, reduction of N_2O to N_2 before reaching the soil surface, or NH_4^+ fixation in clay interlayers may have been contributory factors. A laboratory experiment comparing N_2O emissions from clay and sandy soils is described in section 8.3, with the aim of elucidating reasons for the low emissions measured during this trial.

CHAPTER 8 NITROUS OXIDE EMISSIONS UNDER CONTROLLED ENVIRONMENTAL CONDITIONS

8.1 Nitrous oxide emissions after incorporation of crop residues with varying C:N ratios

8.1.1 Introduction

In field trials (Chapters 4, 5, 6) N_2O emissions were increased after incorporation of plant material into soil. These results confirm those of other authors (for example, Denmead *et al.*, 1979a; Aulakh *et al.*, 1983, 1984b, 1991a,b; de Catanzaro and Beauchamp, 1985). The magnitude of these emissions depends on the nature of the incorporated material, particularly the C:N ratio (Aulakh *et al.*, 1991b; McKenney *et al.*, 1993; Goodroad *et al.*, 1994). The field trials emphasised the importance of environmental parameters on decomposition and N_2O emissions, particularly air and soil temperature, rainfall and resulting soil moisture contents. Denitrification is generally considered to be dependent on the moisture content of soils, being greater after rainfall events (Bremner and Blackmer, 1979; Mosier *et al.*, 1986), whereas under drier conditions nitrification tends to predominant (Skiba *et al.*, 1993). Temperature has an important effect on soil micro-organisms. Microbial activity increases with temperature up to 25-30 °C (Haynes, 1986), thereby increasing the potential for losses of N_2O from nitrification and/or denitrification (Freney *et al.*, 1979; Bremner and Blackmer, 1981).

In order to study the effect of incorporation of plant material on production and losses of N_2O from soil, it is desirable to keep temperature and soil moisture constant, to eliminate the fluxes caused by rainfall or fluctuating temperatures experienced under field conditions. A laboratory experiment was undertaken to determine the effects of incorporation of different crop residues with varying C:N ratios on N_2O emissions, in which temperature and soil moisture contents were kept constant throughout. It was hypothesised that comparatively higher emissions of N_2O would be measured after addition of residues with a low C:N ratio to soil, than after addition of residues with a high C:N ratio. Addition of high C:N residues would probably result in immobilisation of N.

8.1.2 Materials and methods

Emissions of N_2O and concentrations of soil available N were measured after addition of various fresh crop residues to a sandy loam soil. This soil, of the Biel series, was obtained from the Bush Estate. It was fresh sieved to <10 mm, and 2.3 kg was placed in each of 25 buckets (240 mm diameter). Crop residues were coarsely chopped and added to the soil surface and then covered with 50 mm soil. Treatments consisted of soil to which various residues (vegetative tissues only) had been added (Table 8.1). The cereal and pea residues applied consisted of straw only. A control consisted of soil to which no residues had been added. Each treatment was replicated 5 times. The quantity of residues applied to each treatment was calculated on a fresh weight basis from the harvest at the Bush Estate in 1995 (Chapter 6) and the density of lettuce residues at Balmalcolm Farm, in 1994 (Chapter 5). The C:N ratios of the crop residues are presented in Table 8.1.

Table 8.1. Weight and C:N ratios of added residues.

Residue	Weight added (g)	C:N ratio
spring barley	4.6	29.3:1
oilseed rape	13.8	29.8:1
lettuce	10.1	7.8:1
pea	8.0	16.8:1

N_2O emissions were periodically measured from 3 of the replicates using 5 ml glass syringes for sampling (section 3.8), and analysis by gas chromatography (section 3.9). 1 hour prior to gas sampling, sealable gas-tight lids were placed on the buckets. Gas sampling ports had previously been inserted into these lids and made gas-tight with rubber sealant. The temperature was kept at a constant 22 °C, and soil moisture contents were maintained at 19 % on a weight basis - the soil moisture content of the fresh soil at the start of the experiment. Water was added to the soils by spraying evenly over the soil surface. This was done after gas sampling. Concentrations of soil available N were also determined throughout the experimental period (section 3.3). Soil for this analysis was sampled from replicates that were not used for analysis of N_2O.

8.1.3 Results

Over the whole 21 day experimental period the greatest cumulative N_2O emissions, 116 and 98.7 g N_2O-N ha^{-1}, were measured from the pea and oilseed rape treatments, respectively (Fig. 8.1). These were not significantly different from each other, but were significantly greater ($p<0.05$) than the emissions from the lettuce, spring barley and control treatments. Most of the emissions from the oilseed rape (79 %) and pea (76 %) treatments were measured between days 9 and 21 (Fig. 8.1c). 4.4 g N_2O-N ha^{-1} was emitted from the control over the

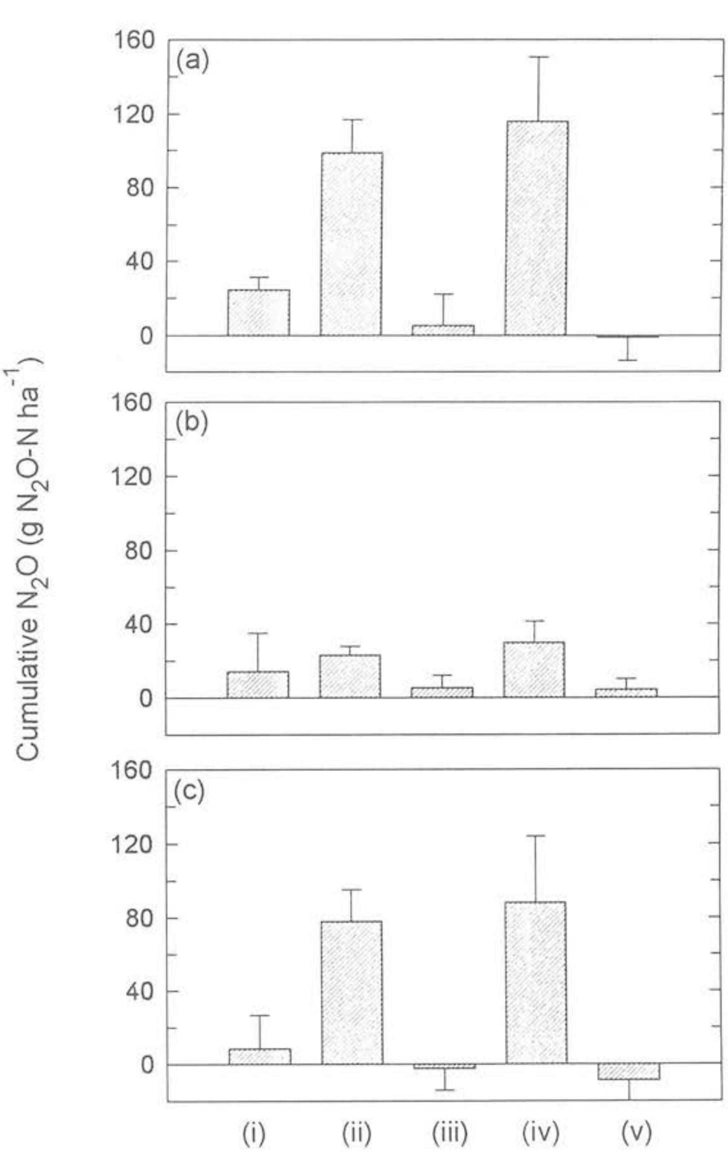

Figure 8.1 Cumulative emissions of N_2O (a) during the whole experimental period (21 days), (b) over the first 9 days, (c) between days 9-21, from (i) spring barley, (ii) oilseed rape, (iii) lettuce, (iv) pea, (v) control treatments.

first 9 days, despite a net uptake of -1.3 g N_2O-N ha^{-1} ($p<0.05$) over the whole experimental period.

Daily fluxes of N_2O over the experimental period are presented in Figs. 8.2 and 8.3(a). Emissions increased one day after the amendments were introduced, with a flux of 5.6 g N_2O-N ha^{-1} d^{-1} measured from the pea treatment on this day (Fig. 8.2(d)). However, by day 9 emissions from all treatments had fallen. Emissions from the spring barley, oilseed rape and pea treatments increased between days 9 and 15 (Fig. 8.2(a,b,d)). This increase was delayed in the lettuce and control treatments (Fig. 8.2(c,e)). On day 15, fluxes of 14.0 and 11.9 g N_2O-N ha^{-1} d^{-1} were measured from the pea and oilseed rape treatments, respectively, and were significantly greater ($p<0.01$ and $p<0.05$, respectively) than the control. After this date emissions then fell in all treatments except the control until the end of the experimental period. A flux of 8.5 g N_2O-N ha^{-1} d^{-1} from the control was measured on day 20.

Available NH_4^+ was low throughout the experiment (Fig. 8.3b). The only significant difference between treatments was on day 15, when 2.1 and 0.5 μg NH_4^+-N g dry $soil^{-1}$ ($p<0.05$) was measured in the lettuce and control treatments, respectively. After day 14 concentrations fell in all treatments except spring barley until the end of the experimental period. 0.9 μg NH_4^+-N g dry $soil^{-1}$ was measured in the spring barley treatment on day 17. At the beginning of the experiment the presence of all residues except oilseed rape resulted in lower available NO_3^- than that in the control treatment (Fig. 8.3c). Throughout the first 15 days of the experiment the highest available NO_3^- was measured in the oilseed rape treatment. For the remainder of the experimental period concentrations were highest in the pea treatment. 17.0 μg NO_3^--N g dry $soil^{-1}$ was measured in this treatment on day 17 ($p<0.05$).

8.1.4 Discussion

Higher cumulative emissions of N_2O were measured after amendment of soil with residues than those from the control. This confirms results from field trials presented in previous chapters, and results reported in the literature, of increased N_2O emissions after residue incorporation (for example, Jansson and Clark, 1952; Denmead *et al.*, 1979a; Aulakh *et al.*, 1984b). The addition of organic material to soil stimulates microbial activity (Haynes, 1986), and N_2O release from both nitrification and denitrification (de Catanzaro and Beauchamp, 1985; Groffman, 1991). Denmead *et al.* (1979a) found that losses of N_2O from both nitrification and denitrification were higher after incorporation of plant material than losses from bare soil, due to the supply of C and N to soil micro-organisms during decomposition.

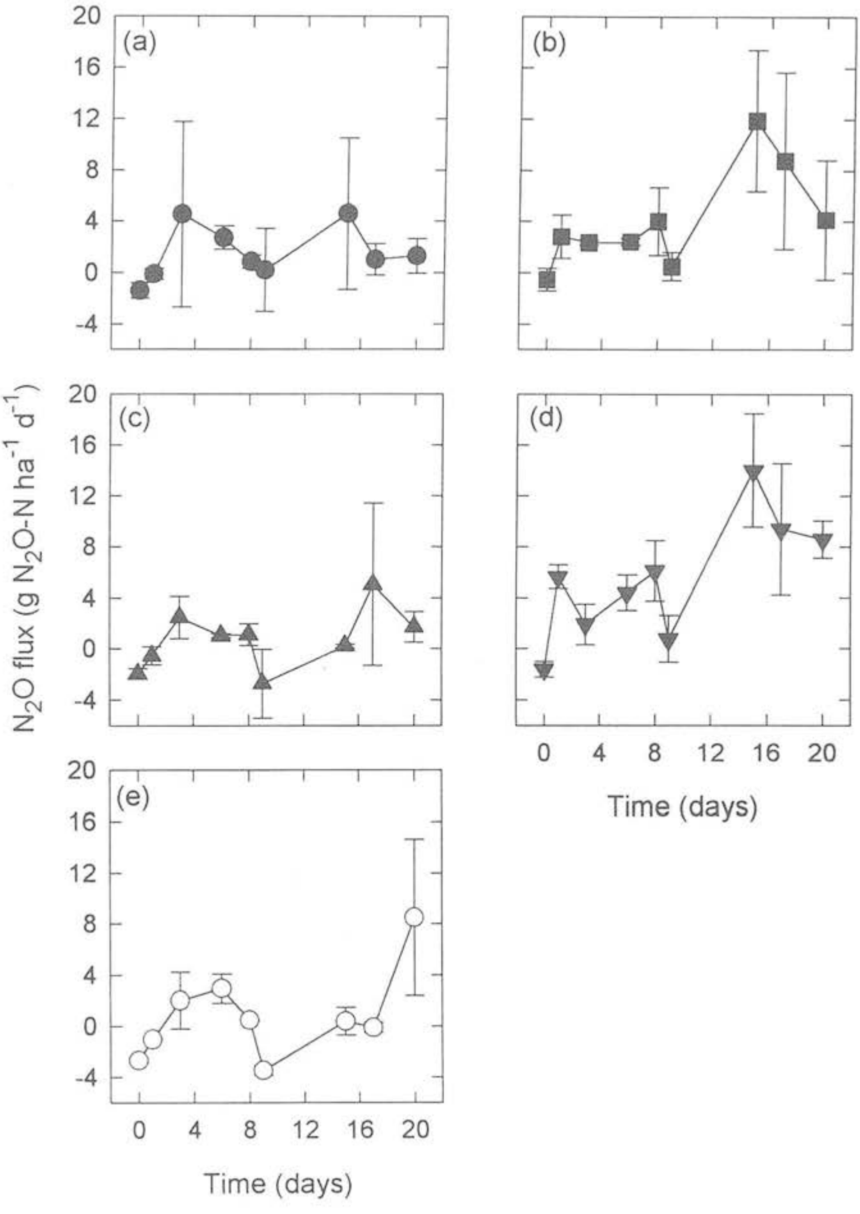

Figure 8.2 Emissions of N_2O from (a) spring barley, (b) oilseed rape, (c) lettuce, (d) pea, (e) control treatments.

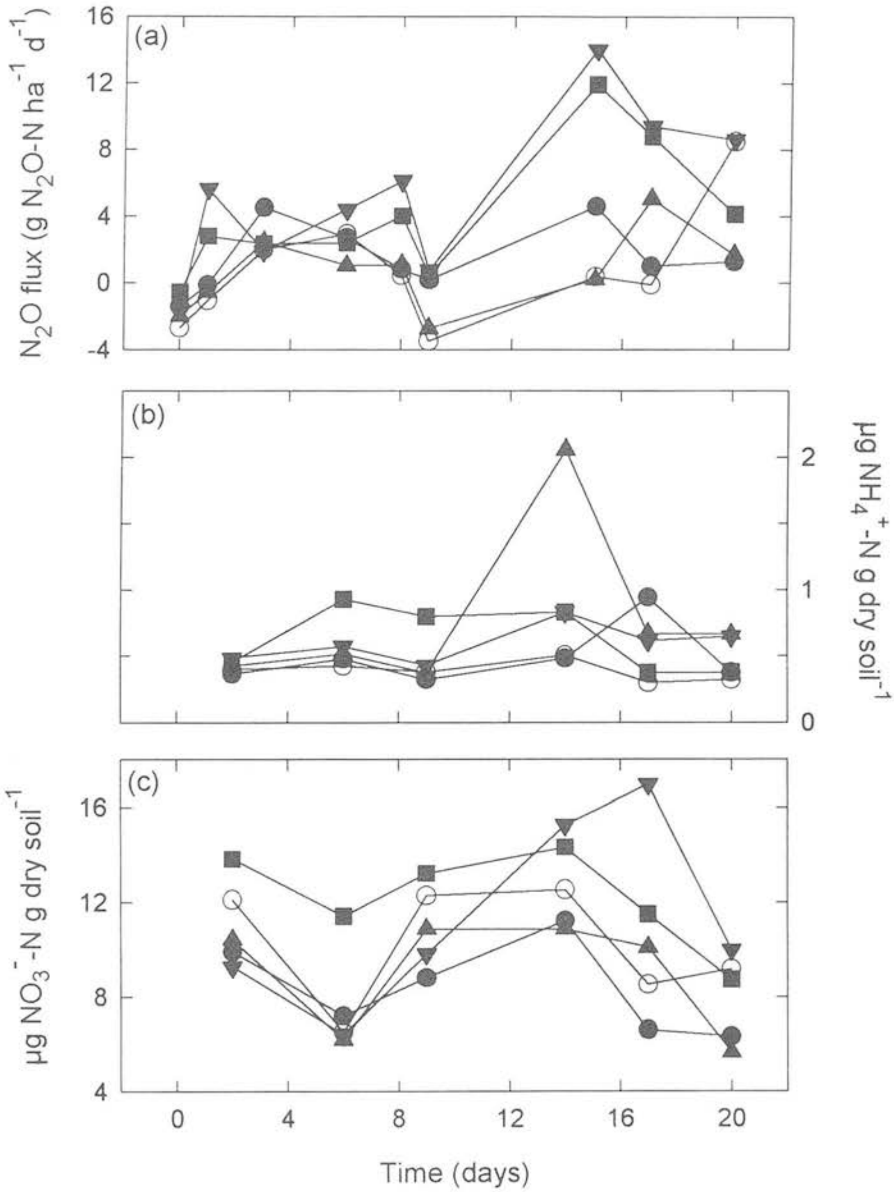

Figure 8.3 (a) Emissions of N_2O, (b) concentrations of available NH_4^+, (c) concentrations of available NO_3^- in spring barley (filled circles), oilseed rape (filled squares), lettuce (filled upward triangles), pea (filled downward triangles), control (empty circles) treatments.

The occurrence of high N_2O emissions after incorporation of leguminous material is also well documented (Chapter 4). This is usually attributed to the low C:N ratio of leguminous material, resulting in rapid decomposition on incorporation (Goodroad *et al.*, 1984; Reinertsen *et al.*, 1984; de Catanzaro and Beauchamp, 1985; Redman *et al.*, 1988; McKenney *et al.*, 1993). For example, McKenney *et al.* (1993) found that cumulative losses of N_2O were inversely related to the C:N ratio of incorporated vetch, red clover, reed canarygrass and corn residues. In this experiment the highest emission of 116 g N_2O-N ha^{-1} was measured from the pea treatment, in which pea residues had a C:N ratio of 16.8:1. However, of the residues applied in this experiment, the lettuce residues had the lowest C:N ratio, but their incorporation resulted in the lowest cumulative emission (5.2 g N_2O-N ha^{-1}) of all the residue amended treatments. On the basis of the large fluxes measured at Mackies Field, Balmalcolm (Chapter 5) following incorporation of lettuce residues, a higher cumulative emission from this treatment was expected. It is possible that large fluxes from the lettuce treatment in this experiment may have been missed as an artefact of the times of gas sampling. The high moisture content of the lettuce residues may have resulted in the development of anaerobic conditions within the soil, particularly at the 50 mm depth of residue placement (Harper and Lynch, 1981). Thus any losses of N_2O from this treatment would probably have been from denitrification. This is confirmed by low concentrations of available NO_3^- on this treatment, resulting from low nitrification and the potential for rapid denitrification. Denitrification may have resulted in reduction of N_2O to N_2 in soil, thereby resulting in low N_2O fluxes measured from the surface (Jury *et al.*, 1982; Arah *et al.*, 1991).

Emissions of N_2O increased on all treatments on the first day of the experiment. As emissions were also increased on the control, these increases may in part have been due to disturbance of the soil in sampling, sieving and establishment of the experiment, releasing air enriched in N_2O (Matthias *et al.*, 1980), and exposing organic matter microsites to micro-organisms (Ross, 1990). The greatest immediate increase was measured from the pea treatment, from which a flux of 5.6 g N_2O-N ha^{-1} d^{-1} was measured on day 1. This confirms the generally observed rapid decomposition of plant material with a low C:N ratio (Jenkinson, 1984; Reinertsen *et al.*, 1984).

The increase in N_2O emissions between days 9 and 15 from the pea treatment coincided with an increase in available NO_3^- between these days, suggesting that the flux of 14.0 g N_2O-N ha^{-1} d^{-1} measured on day 15 resulted from nitrification after decomposition of pea residues. A high concentration of available NH_4^+ was measured in the lettuce treatment on day 15, indicating the occurrence of mineralisation of residue N on this treatment, but possible inhibition of nitrification. This is reflected in the low emissions measured from this treatment.

Incorporation of material with a high C:N ratio, such as cereal straw, has often been found to result in immobilisation of soil N (Jenkinson, 1984; Aulakh *et al.*, 1991a,b). Low concentrations of available NH_4^+ after amendment of soil with spring barley residues suggest that immobilisation occurred in this treatment. Remineralisation may have occurred between days 15 and 18, when available NH_4^+ rose slightly in this treatment. Such remineralisation has been shown to occur once the N resource is exhausted, and N is released from dead microbial cells (Black, 1968; Nicolardot, 1988). Powlson *et al.* (1987) also measured periods of net immobilisation followed by net mineralisation after straw incorporation. However, amendment with oilseed rape residues, which had a slightly higher C:N ratio than the spring barley, resulted in higher available NH_4^+ and NO_3^- than the other treatments during the first 10 days of the experiment.

8.1.5 Summary

Addition of residues to soil increased emissions of N_2O, compared with the bare soil control, especially after addition of the legume. However, low emissions were measured from the treatment to which the residue with the lowest C:N ratio had been added, despite the occurrence of mineralisation of N. The low fluxes measured throughout this experiment indicate the importance of variations in soil temperature on microbial activity, and the effect of irrigation and rainfall events on N_2O losses, particularly from denitrification, under field conditions. In future work the use of ^{15}N labelled residues and determinations of biomass N would be desirable to examine the fate of residue N within the soil.

8.2 An experiment to examine the effects of crop residue type and placement on emissions of N_2O from soil

8.2.1 Introduction

In the two field trials described in Chapter 5 different cultivation treatments resulted in different amounts and patterns of N_2O losses from soil. In addition to release of N_2O after physical disturbance of soil (Matthias *et al.*, 1980), these differences in emissions may have resulted from the different placement of residues within the soil (Douglas *et al.*, 1980; Smith and Sharpley, 1990; Varco *et al.*, 1993). Generally, residues remaining on the soil surface have been found to have a much slower rate of decomposition, which is more linear with time, than incorporated residues (Harper and Lynch, 1981; Christensen, 1986; Douglas and Rickman, 1992). However, to date, studies examining the effects of residue placement in soil on decomposition rates and gaseous losses of N have only investigated differences between surface placed and incorporated residues, and not differences between depths and densities of residue placement in the profile, such as result from mixing or placement in a single dense layer.

Cultivation may result in uneven distribution of residues within the soil, and areas of high and low residue densities (Douglas and Rickman, 1992). Such differences in placement of residues varies the supply of organic C and N to soil micro-organisms, and changes the soil moisture/aeration status around these residues (Douglas *et al.*, 1980; Aulakh *et al.*, 1991a). Thus, differences in N_2O emissions may result. Concentration of residues in a single layer at depth within the soil would be expected to induce localised anaerobic conditions resulting in a hotspot of denitrifier activity and production of N_2O during denitrification (Christensen *et al.*, 1990). However, N_2O produced at depth in the soil may be largely reduced to N_2 before diffusion out of the soil and subsequent measurement (Jury *et al.*, 1982; Arah *et al.*, 1991).

Conversely, with a greater mixing of residues with soil, decomposition would be expected to be more rapid (Parker, 1962), with increased surface area contact between residues and soil micro-organisms (Sain and Broadbent, 1977). In accordance with this, Brown and Dickey (1970) observed that the percentage decomposition of wheat straw was inversely related to the rate of application. However, Wagger *et al.* (1985b) stated that rate of residue application is unlikely to have a significant effect on the total amount of N mineralised.

Nitrification inhibitors have been applied to agricultural systems in an attempt to reduce emissions of N_2O (section 2.2.5.6). However, at present, their use is still limited (Granli and Bøckman, 1994). Nitrification inhibitors work by slowing NH_4^+ oxidation to NO_3^-, thereby reducing losses of N_2O produced during nitrification and denitrification (Aulakh *et al.*, 1984a; Magalhães *et al.*, 1984; Bronson *et al.*, 1992). Dicyandiamide (DCD) is a commercially available inhibitor added to some fertilisers, which can achieve this effect in the field (Skiba *et al.*, 1993).

A laboratory experiment was established to investigate the fate of N from different placements of straw and pea residues in soil, both in the presence and absence of a nitrification inhibitor. The effects of residue placement and nitrification inhibitor on N_2O emissions were examined. It was hypothesised that measurements of N_2O would be higher where residues were thoroughly mixed with the soil as a result of more rapid decomposition and gaseous diffusion from soil, but that they would be reduced after application of nitrification inhibitor.

8.2.2 Materials and methods

The soil used in this experiment was the same sandy loam of the Biel series used in the previous experiment (section 8.1), fresh sieved to <4 mm. Replicate treatments were established in 250 mm lengths of PVC piping, 28 mm in diameter, with a plastic bag secured over one end to hold the soil. 75 g of sieved soil was placed in each tube. Finely chopped pea and straw residues were either completely mixed with this soil, or placed in a layer within the soil at approximately 70 mm depth. Where the latter treatment was applied the residues were placed on top of 38 g of soil, with 37 g of soil then placed on top of the residues. Residues were added at the equivalent N content of approximately 120 kg N ha^{-1}; this required 0.09 and 0.46 g of pea and straw residues, respectively. All treatments were fertilised with the equivalent of 60 kg N ha^{-1} of NH_4NO_3, in solution. A control treatment consisted of 75 g soil to which 60 kg N ha^{-1} as NH_4NO_3 had been added. Each treatment was replicated 3 times.

Replicates were incubated in the dark at a constant temperature of 12 °C for the whole of the 21 day experimental period. Measurements of N_2O emissions, soil moisture contents (section 3.2), available soil N (section 3.3) and biomass N (section 3.4) were made initially, and periodically throughout the experimental period. One hour prior to gas sampling a suba seal was fitted into the open end of each piece of PVC piping, and gas samples taken through these seals using 5 ml glass hypodermic syringes. These gas samples were analysed by gas chromatography as described in (section 3.9). The gravimetric moisture contents of the soils were measured initially, and maintained constant throughout the experiment on a weight basis. The experiment was repeated and run for 21 days with 60 kg N ha^{-1} of the nitrification inhibitor DCD added to each replicate.

8.2.3 Results

8.2.3.1 No nitrification inhibitor

The addition of residues significantly ($p<0.05$) raised emissions of N_2O in the absence of nitrification inhibitor (Fig. 8.4a). Cumulative emissions of 104 and 103 μg N_2O-N kg $soil^{-1}$ were measured from the layered and mixed pea treatments, respectively. These emissions were not significantly different from those from the straw. Emissions from the fully mixed straw were higher ($p<0.05$) than from the layered straw, with cumulative values of 82.0 and 26.6 μg N_2O-N kg $soil^{-1}$ measured respectively.

Throughout the experimental period there was no significant difference between emissions of N_2O from fully mixed and layered pea and straw residues (Fig. 8.5(i)). Fluxes of 60.5 and

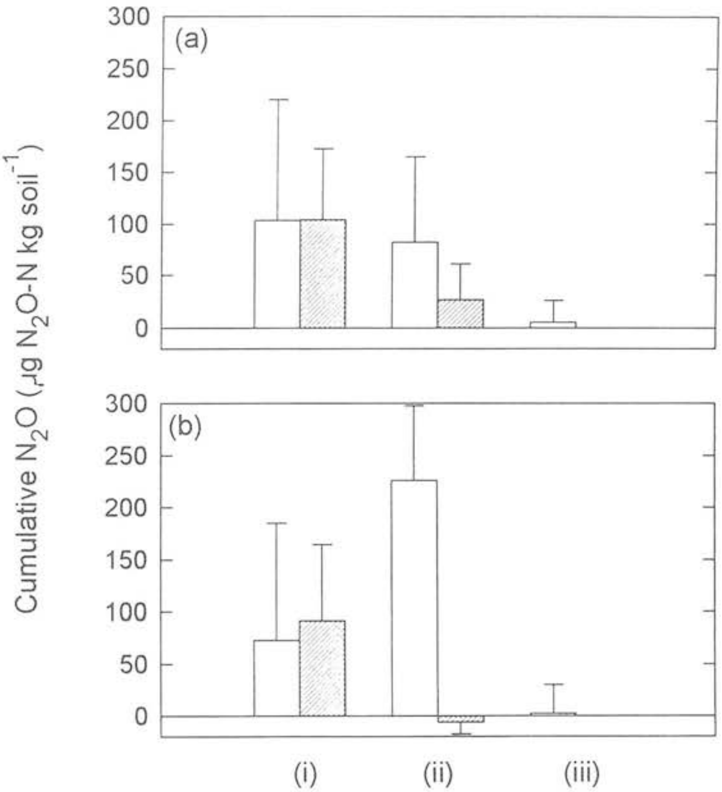

Figure 8.4 Cumulative emissions of N_2O in the (a) absence, (b) presence of nitrification inhibitor from fully mixed (empty bars) and layered (hatched bars) (i) pea, (ii) straw, (iii) control treatments.

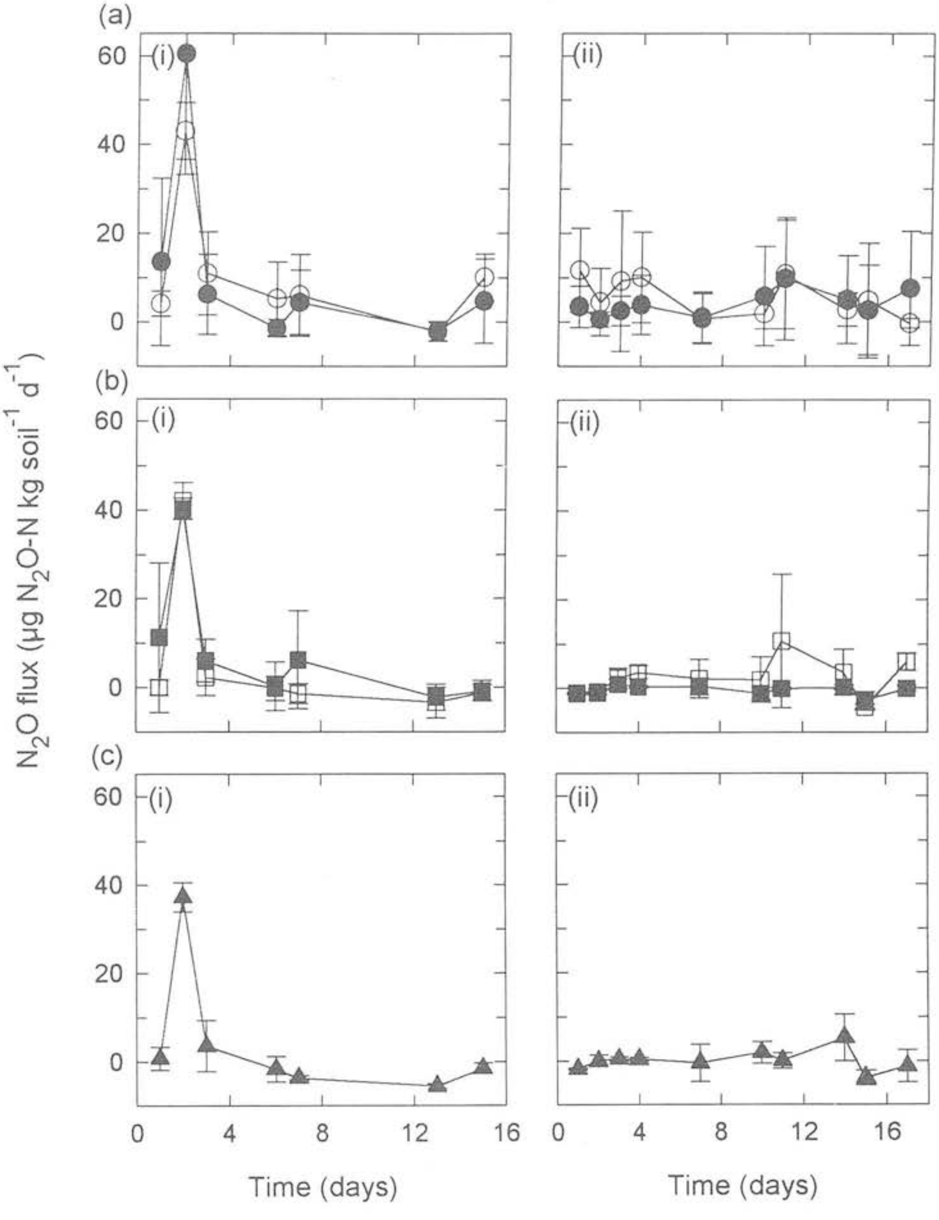

Figure 8.5 Emissions of N_2O in the (i) absence, (ii) presence of nitrification inhibitor from fully mixed (filled symbols) and layered (empty symbols) (a) pea, (b) straw, (c) control treatments.

43.1 μg N_2O-N kg soil^{-1} d^{-1} were measured on day 2 from the mixed and layered pea residues, respectively, but these were short-lived. By day 3 N_2O emissions from all treatments had fallen and remained low for the remainder of the experimental period. Emissions from the fully incorporated pea and straw residues slightly increased between days 6 and 7, but by day 13 fluxes were again low. Emissions from all treatments were raised on day 15 at the end of the experimental period, particularly from both pea treatments.

There was no significant difference in concentrations of available NH_4^+ between the two different placements of residues (Fig. 8.6(i)). On day 2 available NH_4^+ in the layered pea treatments was significantly higher ($p<0.005$) than in the control. The available NH_4^+ in the fully mixed straw treatment on this day was significantly higher ($p<0.001$) than in the fully mixed pea treatment, but not greater than the control. By day 4 concentrations had fallen.

On day 2 available NO_3^- in the straw treatment was significantly lower than in both the pea treatments ($p<0.001$) and the control ($p<0.01$) (Fig. 8.7). By day 4 available NO_3^- in the straw treatments had increased to 30.7 and 31.4 mg NO_3^--N kg dry soil^{-1} in the fully mixed and layered treatments, respectively, but were not significantly different from the control on this day. Concentrations remained high on all treatments for the remainder of the experiment. On day 21 available NO_3^- in the layered straw was significantly higher ($p<0.05$) than in the mixed straw treatment.

From the start of the experiment biomass N increased in the straw and control treatments (Fig. 8.8(i)). Concentrations fell in the pea treatments, but on day 2 were not significantly different from the control. This was because of the higher ($p<0.05$) initial biomass measured in the pea treatments on day 0. On day 4 the 142 mg biomass N kg dry soil^{-1} measured in the mixed straw was significantly ($p<0.05$) higher than the 128 mg biomass N kg dry soil^{-1} measured in the layered straw treatment, and both values were significantly higher ($p<0.05$) than the control (Fig. 8.6). After day 4 concentrations fell. On day 21 the 100 mg biomass N kg dry soil^{-1} measured in the fully mixed straw was significantly higher ($p<0.005$) than the concentration in the layered straw and the control.

8.2.3.2 Nitrification inhibitor

In the presence of a nitrification inhibitor total N_2O emissions from the fully mixed pea and straw layered pea treatments were not significantly greater than the control (Fig. 8.4b). The highest total emission of 226 μg N_2O-N kg soil^{-1} was measured from the fully mixed straw treatment, but was not significantly greater than the other treatments. Despite lower total emissions in the presence of inhibitor, these differences were not statistically significant.

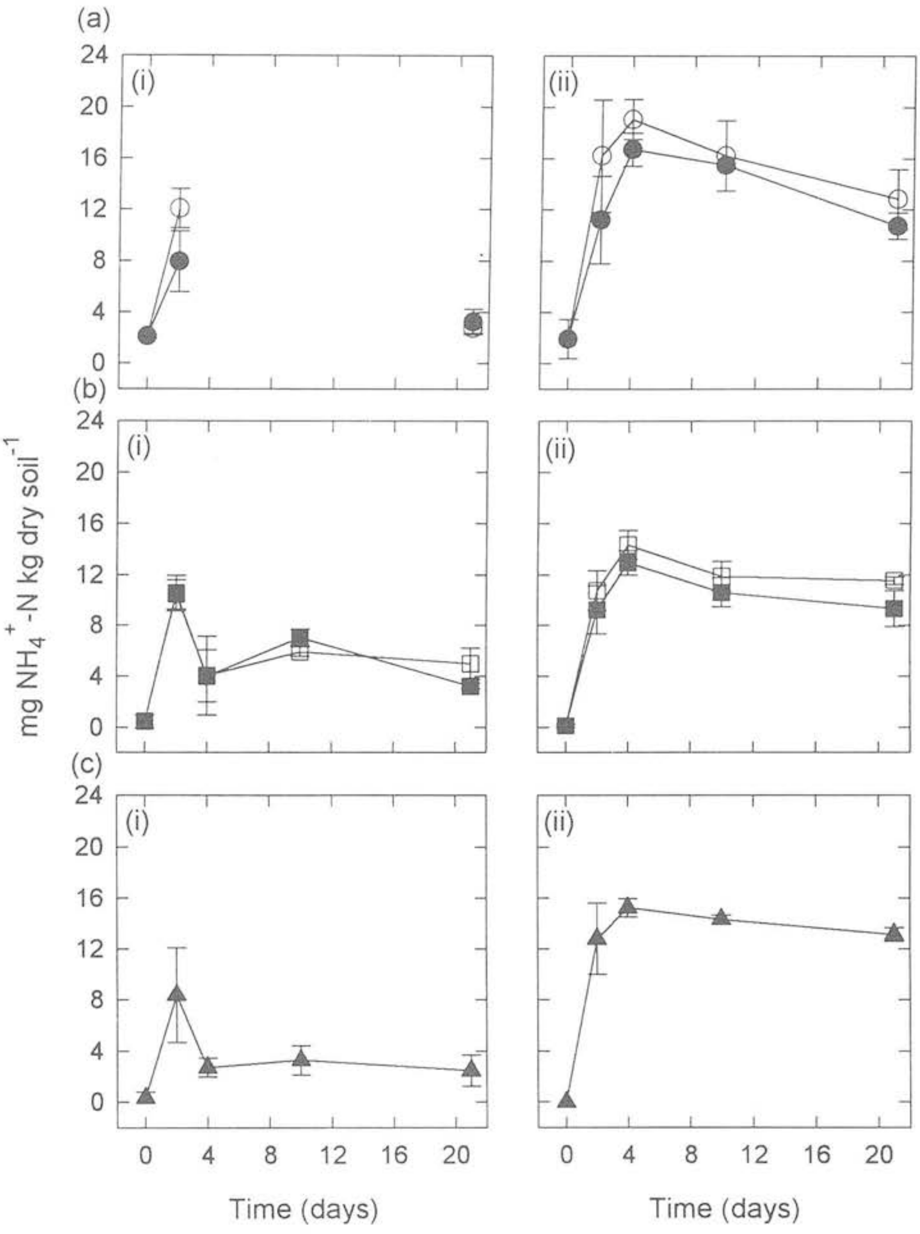

Figure 8.6 Concentrations of available NH_4^+ in the (i) absence, (ii) presence of nitrification inhibitor in fully mixed (filled symbols) and layered (empty symbols) (a) pea, (b) straw, (c) control treatments.

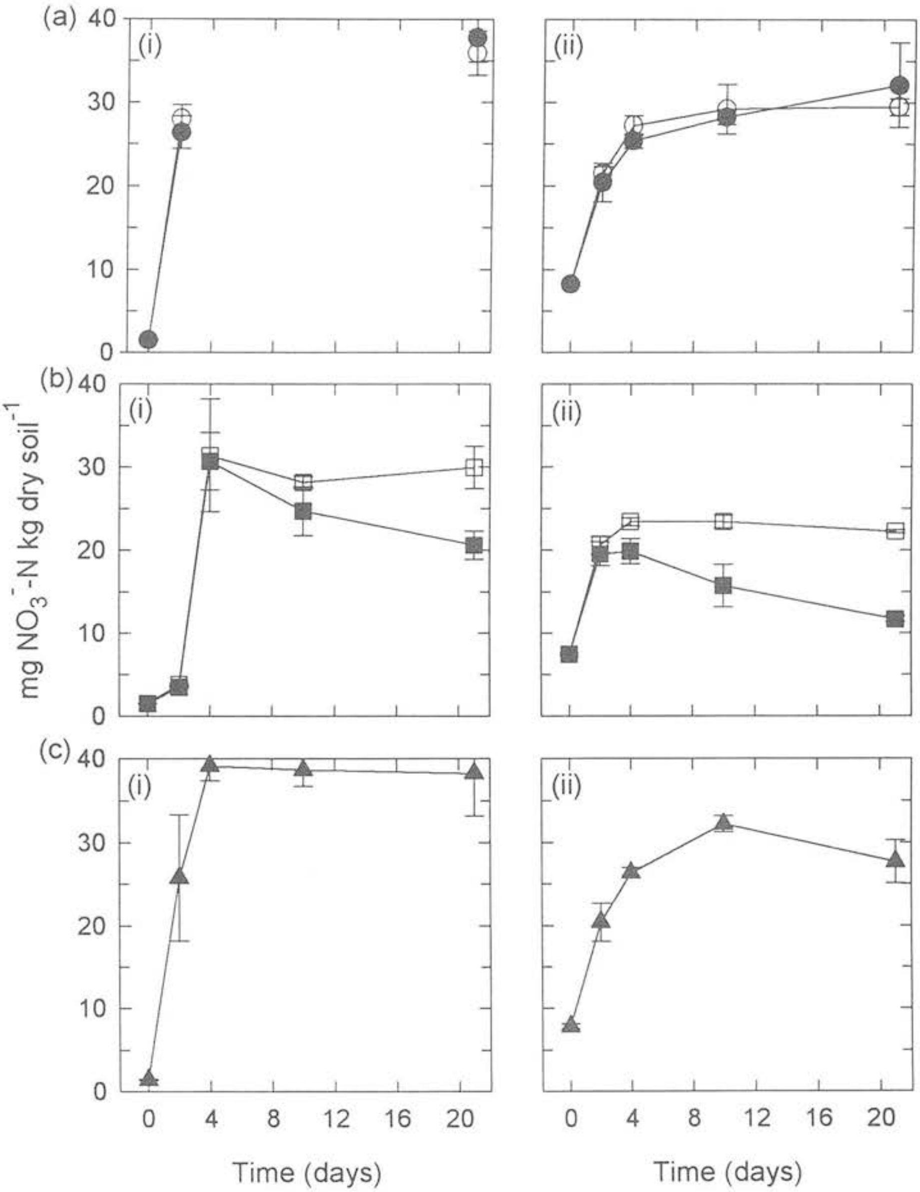

Figure 8.7 Concentrations of available NO_3^- in the (i) absence, (ii) presence of nitrification inhibitor in fully mixed (filled symbols) and layered (empty symbols) (a) pea, (b) straw, (c) control treatments.

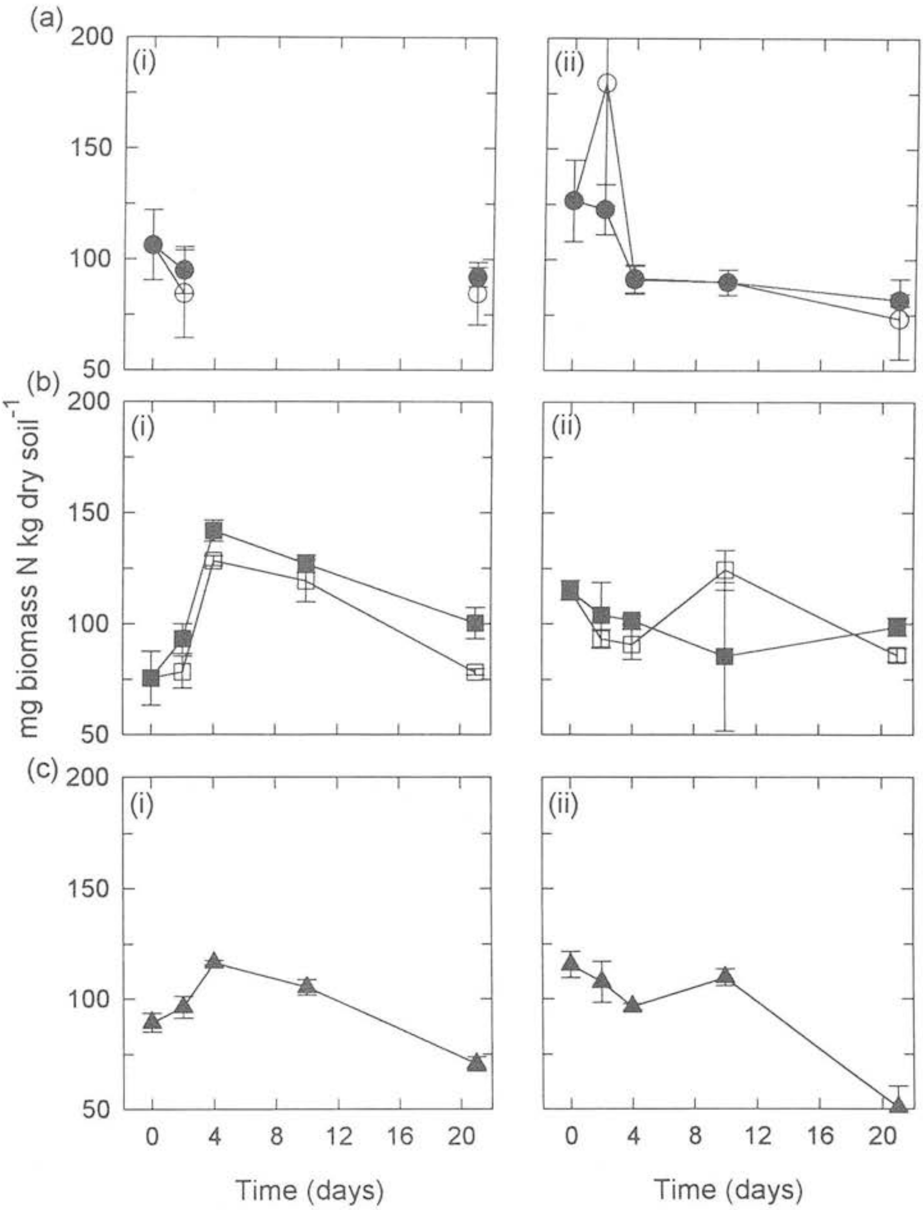

Figure 8.8 Concentrations of biomass N in the (i) absence, (ii) presence of nitrification inhibitor in fully mixed (filled symbols) and layered (empty symbols) (a) pea, (b) straw, (c) control treatments.

In the presence of a nitrification inhibitor daily emissions of N_2O were lower and less variable over time (Fig. 8.5 (ii)). On day 4 fluxes of 10.1 and 3.9 μg N_2O-N kg soil^{-1} d^{-1} were measured from the layered and fully mixed pea residues, respectively. Emissions increased between day 2 and day 4 from both layered and mixed treatments, but then fell again by day 7. A further increase was measured between days 7 and 11. A flux of 10.7 μg N_2O-N kg soil^{-1} d^{-1} was measured on day 11 from the layered straw treatment, and was significantly greater than the control ($p<0.05$), and the mixed straw treatment ($p<0.01$), but was short-lived. Emissions from this treatment also increased at the end of the experimental period. In the presence of inhibitor N_2O emissions from the control were generally lower than where no inhibitor had been applied, particularly in the first half of the experimental period.

On day 4 16.7 and 19.1 mg NH_4^+-N kg dry soil^{-1} were measured in the mixed and layered pea treatments, respectively (Fig. 8.6 (ii)). After day 4 concentrations fell in all treatments. Available NH_4^+ in the two straw treatments was significantly lower ($p<0.05$) than in the control on day 10. On day 2 the available NH_4^+ in the layered pea treatment was higher ($p<0.01$) in the presence of inhibitor than in its absence. On day 21 concentrations in all treatments were higher ($p<0.005$) with inhibitor than without.

During the first 4 days of the experiment available soil NO_3^- increased in all treatments (Fig. 8.7 (ii)). Concentrations continued to increase until day 10 in all treatments except the fully mixed straw residues. On this day the 15.7 mg NO_3^--N kg dry soil^{-1} in the fully mixed straw treatment was lower ($p<0.01$) than that in the layered straw residue treatment. Available NO_3^- in both of these straw treatments was lower ($p<0.001$) than in the control, and lower ($p<0.05$) than in the pea treatments on day 10. On day 21 available NO_3^- in the layered straw was higher ($p<0.005$) than in the mixed straw treatment. Available NO_3^- in the incorporated and layered pea treatments on day 2 were significantly lower ($p<0.001$; $p<0.01$) with, than without, nitrification inhibitor. However, on the same day, concentrations in the straw treatments were significantly higher ($p<0.001$) with, than without, inhibitor. At the end of the experiment available NO_3^- was higher ($p<0.05$) without, than with, inhibitor, except in the mixed pea treatment.

On day 2 180 mg biomass N kg dry soil^{-1} was measured in the layered pea treatment, and was significantly higher ($p<0.05$) than in the layered straw treatment (Fig. 8.8 (ii)). On day 10 124 mg biomass N kg dry soil^{-1} was measured in the layered straw treatment. At the end of the experiment concentrations were low in all treatments. Biomass N was higher ($p<0.05$)

with, than without, inhibitor in both pea treatments and the layered straw treatment on the second day of the experiment.

8.2.4 Discussion

8.2.4.1 Effect of residue addition and placement

Complete mixing of residues with soil increases the amount of residues directly accessible to soil micro-organisms, with better contact between residues and soil (Sain and Broadbent, 1977). Thus, the residues would be rapidly decomposed (Parker, 1962). This probably explains the high fluxes measured immediately after complete mixing of pea residues with soil in the absence of inhibitor. Conversely, concentration of residues in a single layer at depth within the soil would have minimised soil contact, and could have resulted in development of anaerobic conditions within and below the layer. Denitrification would therefore have been likely to be more important in the layered treatment.

The site of N_2O production is important in determining the concentrations of N_2O emitted and measured from the soil surface (Rolston *et al.*, 1976; Jury *et al.*, 1982; Goodroad and Keeney, 1985). In the fully mixed residue treatments N_2O would have been produced more uniformly throughout the soil than in the other treatments. N_2O produced during denitrification from the layer of residues would have taken time to reach the surface resulting in a lag in time before the first N_2O flux was measured at the surface. Initial fluxes from the layered treatments most likely resulted from N_2O released from the soil overlying the residue layer. These immediate fluxes were probably predominantly from nitrification, even on the layered treatment. They may also have been due to release of soil air enriched in N_2O after physical disturbance of soil in the establishment of the experiment (Matthias *et al.*, 1980). N_2O produced during denitrification at depth in soil may be totally reduced to N_2 before diffusion out of the soil and measurement (Jury *et al.*, 1982; Arah *et al.*, 1991), reducing measurements at the surface.

Under field conditions the concentration of micro-organisms is lower at depth (Lynch and Panting, 1980), with increased biological activity near the soil surface (Davis, 1989). However, in the establishment of this experiment, the soil had been sieved and thoroughly mixed, so that the distribution of micro-organisms in the soil could be assumed to be uniform. Aulakh *et al.* (1984c) found that the contribution of lower soil horizons to gaseous N losses was low, regardless of placement of residues. Compaction of residues and soil is capable of increasing anaerobic conditions and denitrification (Bakken *et al.*, 1987; Hansen *et al.*, 1993). However, in this experiment the layered residues were loosely placed in the soil, the only compaction being induced by the weight of the overlying 37 g soil.

Large fluxes of N_2O were measured from all treatments on day 2 of the experiment, even the control. It should be noted that these fluxes would have resulted from both addition of residues and application of inorganic N. Raised emissions from the control reflect the increased nitrification and denitrification due to addition of NH_4NO_3 to all treatments. As discussed in Chapter 6, such increases in N_2O emissions from soil have been found following application of fertiliser to agricultural soil (Duxbury *et al.*, 1982; Conrad *et al.*, 1983; McElroy and Wofsy, 1985; McTaggart *et al.*, 1994). The addition of residues, particularly pea residues, raised emissions of N_2O compared with the control. This is in agreement with Aulakh *et al.* (1983; 1991b) who found that the presence of plant material increased microbial activity and production of N_2O from nitrification and denitrification (Chapter 4). The C:N ratio of the plant material is an important determinant of decomposition, with high emissions frequently measured after incorporation of material with a low C:N ratio, such as legumes (Goodroad *et al.*, 1984; de Catanzaro and Beauchamp, 1985; McKenney *et al.*, 1993). This is discussed in more detail in Chapter 4. However, combined additions of both organic and inorganic N, such as in this experiment, may result in greater emissions than after individual treatments. For example, Azam *et al.* (1985) found that losses of N from incorporated plant material were greater in the presence of ammonium sulphate fertiliser. The presence of residues raised the concentration of fertiliser derived N in the biomass. Wojcik-Wojtkowiak (1978) also reported enhanced mineralisation of organic N in the presence of inorganic N.

The increase in biomass N by day 4 on the control and straw treatments in the absence of inhibitor is reflected in lower available NH_4^+ on this day, indicating that immobilisation of N had occurred on these treatments. Greater immobilisation of N would have been expected after addition of straw than pea residues, due to the higher C:N ratio of the straw (Aulakh *et al.*, 1991b). In this experiment the quantity of straw and pea residues applied to each treatment were calculated on the basis of an equivalent N content, so that greater quantities of straw than pea residues were added to treatments.

8.2.4.2 Effect of nitrification inhibitor

The addition of nitrification inhibitor to soil had an important effect on N_2O emissions. In the presence of inhibitor total cumulative emissions of N_2O were reduced from all treatments, except the fully mixed straw residues. The lower N_2O emissions and raised concentrations of available NH_4^+ after addition of inhibitor reflect the important contribution of nitrification to N_2O emissions from soil, even where the residues had been placed in a layer at depth. The fluxes measured on day 2 were much larger in the absence of inhibitor. This confirms that the immediate N_2O fluxes resulted from nitrification, probably from soil near the soil surface

(Goodroad and Keeney, 1985). In the presence of inhibitor the fluxes of N_2O measured would have been from denitrification of both native soil NO_3^- and fertiliser applied NO_3^-.

Such reduction in N_2O emissions after application of nitrification inhibitor have been reported in the literature (for example, Aulakh *et al.*, 1984a; Magalhães *et al.*, 1984; Willison and Anderson, 1991; Bronson *et al.*, 1992; McTaggart and Smith, 1996). McTaggart and Smith (1996) found that addition of the nitrification inhibitor DCD to winter wheat, winter barley and spring oilseed rape reduced N_2O emissions by 54, 43 and 33 %, respectively. Bronson *et al.* (1992) measured lower N_2O fluxes and lower concentrations of available NO_3^- after addition of nitrapyrin to maize. N_2O losses were reduced from 3.2 to 1.1 kg N_2O-N ha^{-1} over a 14 week period after addition. Concentrations of available NO_3^- were raised over the first 10 days of the experiment in the presence of inhibitor in all treatments, except the fully mixed straw. This suggests that inhibition of denitrification may have occurred, despite the lower concentrations, compared with where inhibitor was absent.

Concentrations of biomass N in the residue treatments were increased in the presence of inhibitor on day 2. This is in accordance with other work reviewed by Granli and Bøckman (1994). The greatest increases were in the pea treatments, particularly the layered pea treatment. This suggests that the inhibition of nitrification increased immobilisation, particularly after addition of the pea residues with a low C:N ratio. Inhibitor raised concentrations of available NH_4^+ on day 2 in the pea and control treatments, but only significantly in the layered pea treatment. Such raised NH_4^+ concentrations indicate continual decomposition of residues, with removal of NH_4^+ only to the biomass in the presence of inhibitor.

8.2.5 Summary

Addition of plant residues to soil raised N_2O emissions, with high emissions measured following addition of pea residues. This was attributed to the low C:N ratio of this material. There was no significant difference in total emissions from the fully mixed and layered residue treatments. Thus, placement of residues had little effect on N_2O production. However, the 2 placements resulted in different patterns of N_2O emissions over the experimental periods. As hypothesised, N_2O emissions were reduced in the presence of nitrification inhibitor, except from the incorporated straw treatment. This suggests that emissions from this treatment were mainly produced during denitrification. Inhibitor also increased the immobilisation of N, particularly in the layered pea treatment.

8.3 Nitrous oxide emissions after addition of residues to sandy loam and clay loam soils

8.3.1 Introduction

Different soil types result in different rates of decomposition of organic material (section 2.2.1.2). Generally, slower rates of mineralisation have been found in soils with a high clay content (Allison, 1973; Cerri and Jenkinson, 1981b; Ladd *et al.*, 1981). Clay soils retain more moisture and may inhibit organic matter decomposition under wet conditions by slowing O_2 diffusion, and by providing physical protection. Thus, incorporation of plant material into a clay soil would be expected to result in lower N_2O emissions from nitrification, due to a limited amount of NH_4^+ available as substrate (Goodroad and Keeney, 1984).

Generally, higher N_2O emissions are found from fine textured clay soils than from coarse sands, but results differ considerably (Granli and Bøckman, 1994). Greater N_2O losses from fine textured soils are most likely to be due to differences in supply of NO_3^- and C, physical variations in soil structure, pore size, aggregation and water infiltration rates affecting aeration and the microenvironment (Aulakh *et al.*, 1991a). More anaerobic sites occur in a clay soil, resulting in greater N_2O losses from denitrification than in sandy soils (Groffman and Tiedje, 1991). Arah *et al.* (1991) emphasised that denitrification is favoured over nitrification in heavy soils. However, as previously discussed, diffusion of N_2O up the profile is slow, and so N_2O produced at depth may be reduced to N_2 as it moves up the profile (Arah *et al.*, 1991).

The type of clay mineral present, and particularly its ability to fix NH_4^+ within its interlayers may also be an important determinant of N_2O emissions from clay soils. Such fixation lowers the availability of NH_4^+ (Scherer, 1993; Smith S.J. *et al.*, 1995), thereby restricting the processes of nitrification and subsequent denitrification. The occurrence and implications of NH_4^+ fixation is further discussed in section 7.4.4.

A laboratory experiment was undertaken to compare N_2O emissions after addition of residues to clay loam and sandy loam soils. Temperature and soil moisture content were kept constant. This would allow the occurrence of low and negative N_2O fluxes measured at CSCV (Chapter 7) to be verified as attributable to intrinsic soil characteristics. It was hypothesised that available NH_4^+ would be low in the clay soil after addition of residues, indicating NH_4^+ fixation.

8.3.2 Materials and methods

The soil used in this experiment was the same sandy loam of the Biel series used in the previous two experiments (sections 8.1 and 8.2), and a 2:1 clay soil of the Stirling series, from Kincardine. Both soils were fresh sieved to <2 mm. 200 g of fresh sieved soil was placed in each of 30 1 litre glass kilner jars. These jars had airtight sealable lids. A hole had been drilled into the top of each lid through which a gas sampling port was inserted and permanently sealed with gas-tight sealant.

The treatments applied to both sandy loam and clay soils were chopped fresh pea and winter wheat straw residues. 0.4 g and 0.8 g of these, respectively, were placed in a layer in the soil, with 100 g soil beneath and 100 g above the residues. A control treatment consisted of jars containing 200 g soil. All treatments were replicated 5 times. Two of these replicates were used for periodic sampling of soil for analysis.

Emissions of N_2O were measured from the jars. The lids were closed for 1 hour prior to gas sampling. Gas was sampled using 5 ml glass syringes and analysed using gas chromatography (section 3.9). Between gas samplings the lids were left partly open to allow aeration of the jars, but to try and minimise drying of the soil. The soil moisture contents were maintained at 19 % on a weight basis. Soils were weighed, dried and rewetted with the required volume of water after gas sampling so as to avoid immediately enhanced emissions in response to this wetting. Determinations of concentrations of available soil N were made as described in section 3.3.

8.3.3 Results

Cumulative emissions of N_2O from the sandy loam and clay loam treatments were not statistically different (Fig. 8.9). Cumulative emissions of N_2O throughout the experimental period of 16.5 and 16.3 g N_2O-N kg soil^{-1} were measured from the sandy loam straw and pea treatments, respectively. A low total emission of 11.2 g N_2O-N kg soil^{-1} was measured from the control of the clay loam. The presence of plant material raised emissions of N_2O from both soil types ($p<0.05$).

On day 2 of the experiment a flux of 4.2 g N_2O-N kg soil^{-1} d^{-1} was measured from the sandy loam pea treatment (Fig. 8.10). This flux was significantly higher ($p<0.05$) than from the clay loam pea and control ($p<0.05$) treatments on this day. Emissions from all treatments were

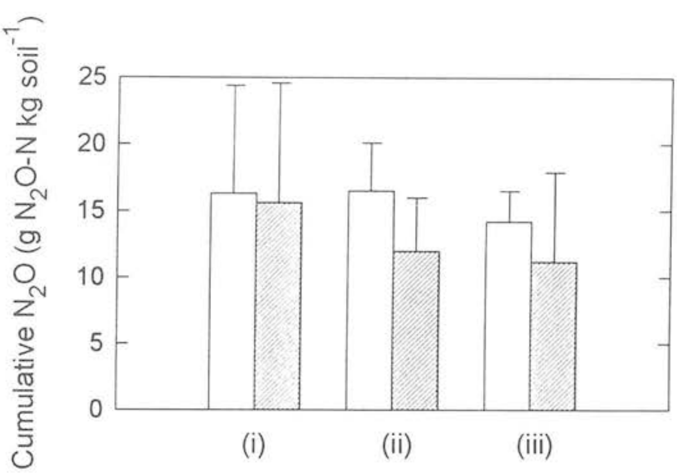

Figure 8.9 Cumulative emissions of N_2O from (i) pea, (ii) straw and (iii) control treatments in sandy loam (empty bars) and clay loam (hatched bars) soils.

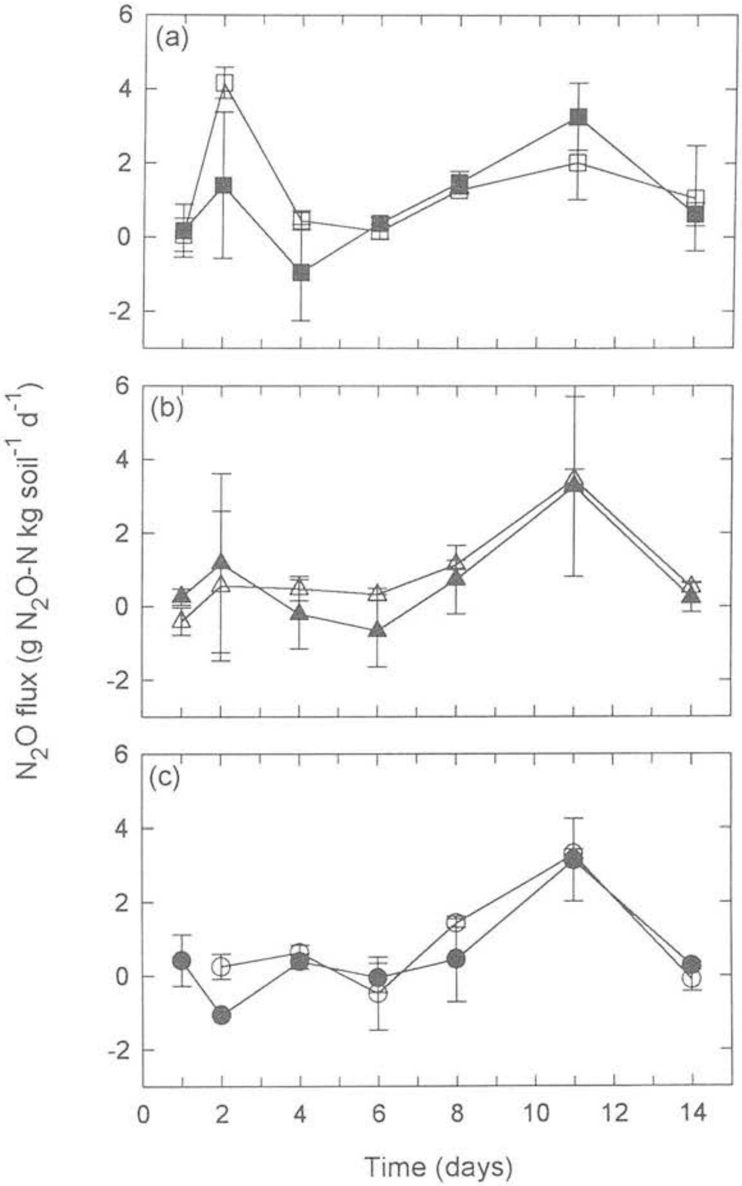

Figure 8.10 Emissions of N_2O from (a) pea, (b) straw, (c) control treatments in sandy loam (empty symbols) and clay loam (filled symbols) soils.

raised between days 6 and 11, with fluxes of 3.1, 3.3 and 3.3 g N_2O-N kg soil^{-1} d^{-1}, measured from the control, pea and straw clay loam treatments, respectively, on day 11.

Available NH_4^+ was low throughout the experimental period, except in the clay pea treatment, with 18.1 μg NH_4^+-N g dry soil^{-1} ($p<0.05$) measured on day 5 (Fig. 8.11(i)). However, this was short-lived. On day 9 available NH_4^+ was higher ($p<0.005$) in the sandy loam than the clay loam pea treatment. Available NO_3^- generally increased throughout the experimental period, and was higher in the sandy loam soil ($p<0.05$, in control, pea and straw treatments between days 1 and 9, and in control and pea treatments on day 15) (Fig. 8.11(ii)). Between days 9 and 15 available NO_3^- in the sandy loam straw treatment fell to 7.1 μg NO_3^--N g dry soil^{-1} on day 15. A concentration of 17.6 μg NO_3^--N g dry soil^{-1} was measured in the sandy loam pea treatment on day 9.

8.3.4 Discussion

Emissions of N_2O were low throughout the experimental period. There was no significant difference in total emissions between the two soil types. The only significant difference between treatments was found on day 2, where fluxes measured from the pea and control sandy loam treatments were higher than fluxes measured from the corresponding clay loam treatments. Generally, higher losses of N_2O have been found from clay soils than sandier soils (McKenney *et al.*, 1980; Webster and Dowdell, 1982; Vinther, 1992). Such differences are most likely caused by the effects of soil texture on O_2 availability. Fine-textured soils have smaller pores that become anaerobic more easily then the larger pores of sandy soils (Groffman and Tiedje, 1991). Even in well-aerated clay loam soils anaerobic microsites are likely to be present. These anaerobic conditions result in N_2O losses from denitrification. However, under the controlled conditions of this experiment, the soil moisture was maintained at a constant 19 %, and may explain the similarity in emissions from both soil types. Under continuous anaerobic conditions relatively small amounts of N_2O may be produced (Sahrawat and Keeney, 1986).

Maintaining soil moisture contents at 19 % would have resulted in different water potentials as clay soils hold more moisture than sandy soils. The moisture content may have actually been too low for denitrification to occur in the clay soil. Under wet conditions the decomposition of organic matter may be inhibited in clay soils (Allison, 1973; Cerri and Jenkinson; 1981; Ladd *et al.*, 1981b), resulting in a limited amount of NH_4^+ available as substrate for nitrification (Goodroad and Keeney, 1984). Ladd *et al.* (1981b) found that variations in clay contents between two soils resulted in significantly different decomposition

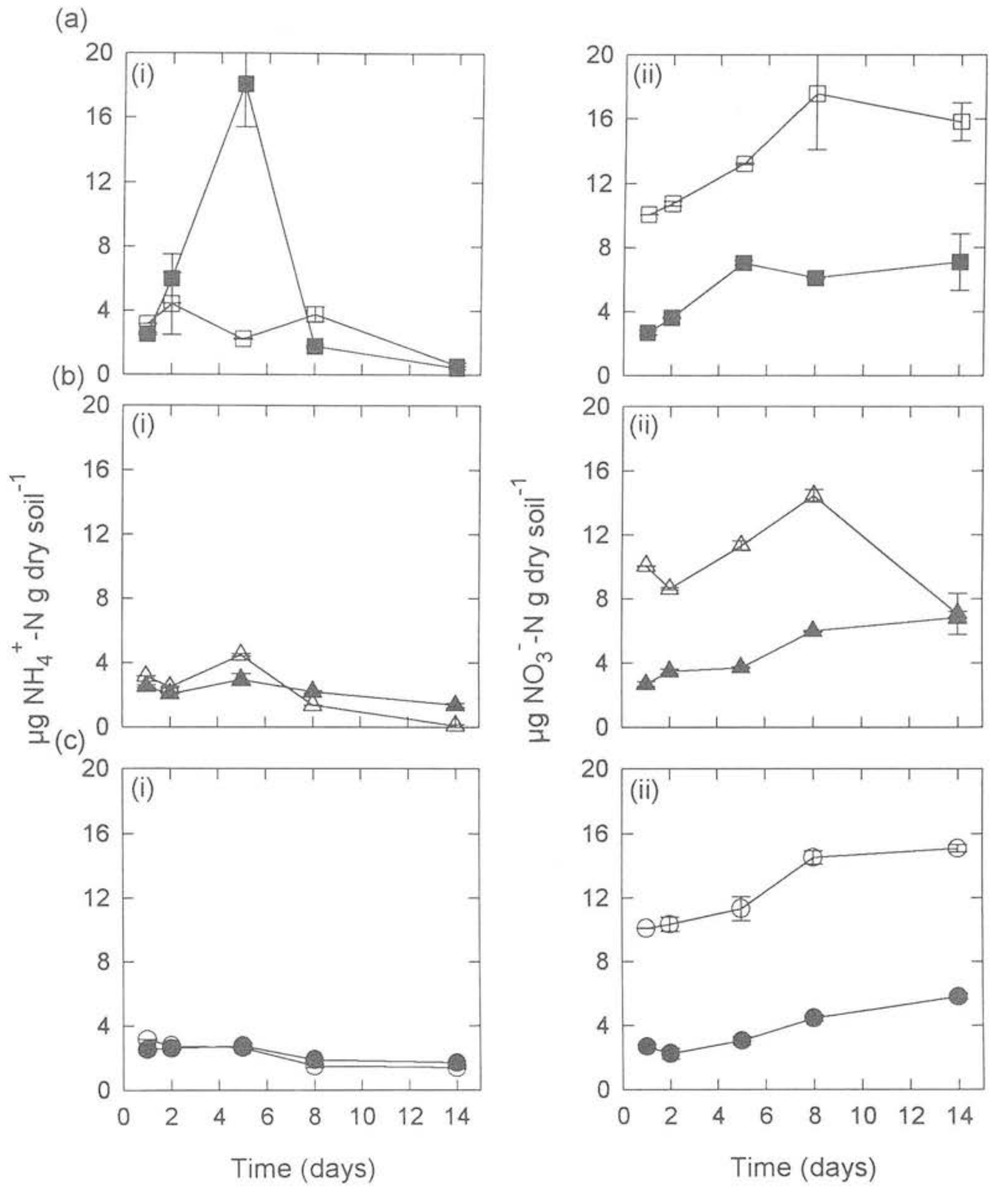

Figure 8.11 Concentrations of (i) available NH_4^+, (ii) available NO_3^- in (a) pea, (b) straw, (c) control treatments in sandy loam (empty symbols) and clay loam (filled symbols) soils.

rates of ^{14}C and ^{15}N labelled medic material. Increased C supply, such as residue addition, has been found to reduce the ratio of N_2O:N_2 evolved during denitrification (Paul and Beauchamp, 1989). Therefore measurements of N_2O from the soil surface may underestimate denitrification.

Negative fluxes were measured from the clay loam soil treatments on days 2, 4 and 6, and confirm the tendency of soils to act as sinks for N_2O when concentrations of NO_3^- are low (Ryden, 1981). As previously discussed, such low fluxes of N_2O during denitrification may reflect the reduction of N_2O to N_2 as it moves up the profile of a clay soil (Arah *et al.*, 1991). In agreement with this, Armstrong (1983) compared N_2O losses from denitrification after autumn fertilisation of clay and sandy loam soils. A rapid reduction in N_2O flux was measured after fertilisation of the clay loam. This was attributed to an increase in the N_2:N_2O ratio in the clay loam due to the greater reducing environment with restricted diffusion.

The concentrations of available NH_4^+ were low throughout the experiment, except the concentration of 18.1 μg NH_4^+-N g dry soil^{-1} measured on the pea amended clay soil on day 5. This was significantly greater than the concentration on the corresponding sandy loam soil treatment on this day. Both this high concentration, and the lack of any significant difference in total N_2O emissions between soil types, implies that the NH_4^+ was not fixed within the interlayers of the clay soil, as clearly, this process does not occur in a sandy loam soil. It is assumed that the low available NH_4^+ in both soils throughout the experiment were a result of immobilisation and/or nitrification. Thus it is suggested that the low emissions of N_2O, and negative fluxes, measured during the field trial at CSCV, near Naples (Chapter 7), were not a result of NH_4^+ fixation, but were due to immobilisation and/or reduction of N_2O to N_2 within the soil.

Available NO_3^- was significantly higher ($p<0.05$) in the sandy loam than in the clay soil, even in the control treatment. This suggests that the N_2O losses from the sandy loam soil were predominantly from nitrification. The lower available NO_3^- in the clay soil indicates that denitrification was predominant. This is in accordance with high losses of N_2O from denitrification being measured from clay soils (Arah *et al.*, 1991; Groffman and Tiedje, 1991). Conversely, nitrification is usually prevalent in sandy soils, with denitrification activity generally low (Vinther, 1992).

8.3.5 Summary

There was no significant difference in total emissions between the two soil types. This meant that low emissions and negative fluxes measured at CSCV (Chapter 7) were probably not a result of NH_4^+ fixation. They may have resulted from immobilisation of N after incorporation of plant material, substantial plant uptake of available N on cropped treatments, and/or reduction of N_2O to N_2 within the clay soil. The use of ^{15}N labelled plant material and acetylene blockage would help clarify the relative contributions of immobilisation and N_2O reduction to N_2, respectively. N_2O was thought to be mainly produced during denitrification in the clay loam and during nitrification in the sandy loam soil. The highest flux was measured from the soil to which leguminous material had been added. The lower C:N ratio of the lettuce residues resulted in low N_2O emissions, probably due to reduction of N_2O to N_2 during denitrification.

CHAPTER 9 COMPARISONS BETWEEN FIELD MEASUREMENTS AND MODEL PREDICTIONS

9.1 Introduction

Several different approaches have been adopted in modelling the N cycle in soil/plant systems (Tanji, 1982). The extent to which the basic concepts are mechanistic and the degree of sophistication of the mathematical relationships varies between models. This chapter describes comparisons made between field measured N_2O emissions and soil available N (described in Chapters 4, 5 and 6) and values for denitrification and available N predicted by four soil/plant models: NCYCLE, SOILN, N_ABLE and SUNDIAL. This project has shown that denitrification significantly contributes to N_2O emissions measured from soils, particularly after incorporation of plant material. None of these four models predicts emissions of N_2O, but the significant contribution of denitrification to such emissions makes comparisons between measured N_2O fluxes and predicted denitrified N valuable.

9.2 NCYCLE

NCYCLE is a simulation model developed at the Institute of Grassland and Environmental Research, North Wyke. The model simulates the cycling of N in grassland systems, and predicts the annual amount of N in liveweight gain, and amounts lost through ammonia volatilisation, leaching and denitrification on the basis of fertiliser application and soil and site characteristics. The main purpose of the model is to increase understanding of interactions of soil, climate and management factors using a mass balance approach (Scholefield *et al.*, 1991). Comparisons between arable field and model predicted values were made, even though some of the animal-related pathways were irrelevant.

The model program initially requires a simple site description, from which it estimates the amount of nitrogen that is added to various pools of the N cycle following mineralisation of soil organic matter. Some of the factors controlling the transfer of N from one pool to another can be changed, as can the application of fertiliser N. The N (kg ha^{-1}) in each pool is expressed on an annual basis.

The inorganic pool is central to the calculations of the model. N enters this pool via the mineralisation of organic nitrogen, additions of urine from livestock, deposition of atmospheric N, and the addition of N fertiliser. N is removed from this pool by plant uptake, or as a result of denitrification, leaching and volatilisation. All of the N not transferred from the plant component to animals is returned to the soil organic pool as plant litter.

The annual amount of N added to the system through the mineralisation of organic matter in the soil is calculated in a sub-model based on the initially chosen parameters, with 220 kg ha^{-1} yr^{-1} for long-term grassland, 30 kg ha^{-1} yr^{-1} for long-term arable and 75 kg ha^{-1} yr^{-1} for a ley-arable rotation. These values are adjusted for climate, age of sward, soil type and drainage status. In addition to the nitrogen mineralised from soil organic matter, a proportion of dung N and litter N is mineralised. The proportion of plant N mineralised is related to its N content (Whitehead *et al.*, 1990), assuming that half of the N in legumes of 2 % N concentration, would be mineralised in 1 year (Bartholomew, 1965).

Total losses of N from the system via denitrification, leaching and volatilisation are calculated as the fraction of soil inorganic N not taken up by plants. Losses from leaching and denitrification are estimated according to soil type and drainage status. Volatilisation is dependent upon the amounts of urine and dung N, and on the proportion of urine N volatilised as ammonia.

9.2.1 Comparisons between model predicted and field measured data

The climatic zone, sandy loam soil type with moderate drainage, and the long-term arable cropping history were initially entered into the model. The model was then run with fertiliser applications of 0, 120 and 180 kg N ha^{-1} yr^{-1}. Comparisons between measurements made during the spring arable field trials at Bush Estate, 1995 (Chapter 6) and the model predictions are shown in Fig. 9.1. The Italian ryegrass trial at Bush Estate, 1994 (Chapter 4), was not included in this comparison as this trial was unfertilised.

The model predicted an exponential increase in N lost from denitrification with increased fertiliser application (Fig. 9.1a). With no fertiliser input 0.46 kg N ha^{-1} yr^{-1} was predicted to be lost from denitrification. This compared well with losses from the unfertilised winter wheat and spring barley trials at Bush Estate, from which 0.19 and 0.08 kg N_2O-N ha^{-1} yr^{-1} were estimated to be lost, respectively. However, 2.19 kg N_2O-N ha^{-1} yr^{-1} was estimated to be lost from the unfertilised oilseed rape trial. Comparisons between model predicted losses from fertilised grassland and measured N_2O emissions from fertilised arable crops were poor. Fertilisation of crops at Bush Estate in 1995 did not significantly increase annual N_2O emissions, whereas the model predicted an exponential increase in N losses with increased

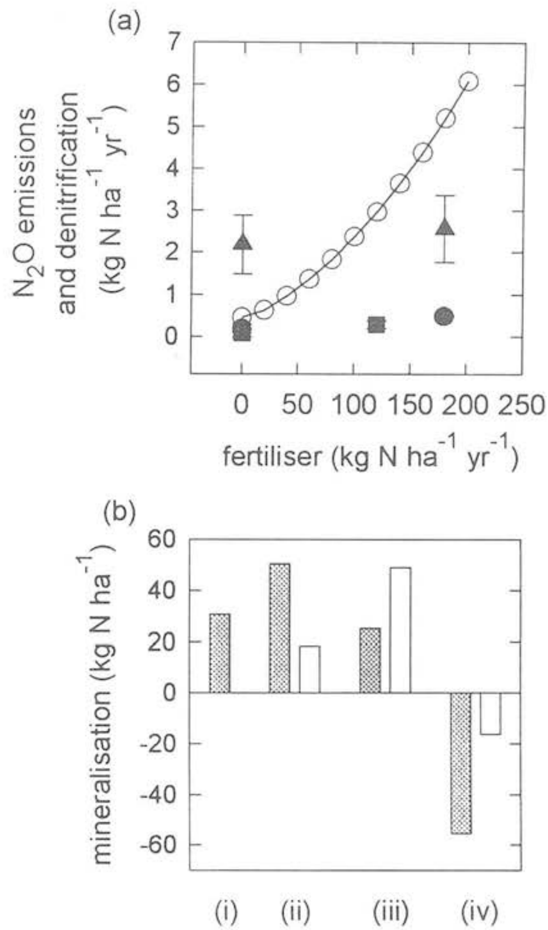

Figure 9.1 (a) Emissions of N_2O from crops of winter wheat (filled circles), spring barley (filled squares), oilseed rape (filled triangles) and denitrification predicted by NCYCLE (empty circles), (b) mineralisation of fertilised (180 kg N ha^{-1}) (hatched bars) and unfertilised (empty bars) crops; (i) model prediction, (ii) winter wheat, (iii) spring barley, (iv) oilseed rape.

rates of fertiliser application. This poor comparison may in part be due to a reduction in the N_2O:N_2 ratio with increased substrate for denitrification after fertilisation.

Emissions of N_2O from denitrification vary between crop types (Chapters 6 and 7). Here, comparisons were made between cereal and grass systems, as the grassland used in this project (Chapter 4) was unfertilised. Van Cleemput *et al.* (1992) measured 15 % higher N_2O emissions from grassland than from maize, wheat, sugarbeet and potato crops. This was attributed to mixed grass/clover swards in grassland systems which would be expected to increase N_2O emissions (Chapter 7). In addition to this, periodic cutting of grassland may increase N_2O emissions ten-fold (Beck and Christensen, 1987).

In a long-term arable system the model uses a constant mineralisation rate of 30.7 kg N ha^{-1} yr^{-1}, even with increased fertiliser applications (Fig. 9.1b). This was higher than estimated rates in the oilseed rape, unfertilised winter wheat and fertilised spring barley trials at Bush Estate (Chapter 6). After application of 180 kg N ha^{-1} to the winter wheat crop at Bush Estate, mineralisation rates of 25.3 kg N ha^{-1} over 38 days, and 50.6 kg N ha^{-1} yr^{-1} were calculated.

9.2.2 Weaknesses of model

The poor comparisons between predicted and measured values were primarily due to the simplicity of NCYCLE and its orientation towards grassland systems. The model was devised in south-west England, and it is suggested that although it may be fairly accurate in predicting transformations and losses of N in grassland in this area (Scholefield, *et al.*, 1991), the potential for extrapolation to other regions is limited, even for grassland systems. This is confounded by restrictions in permitted inputs of soil and site characteristics.

The simplicity of the model results in inaccurate calculations of the N contents of the various pools. For example, denitrified N is expressed as being highly dependent on leaching losses. The proportion of N lost during denitrification is calculated as a proportion of loss due to denitrification + leaching, based on soil texture and drainage. These proportions are based on assessments from 10 systems (Scholefield *et al.*, 1988). Denitrification losses are calculated as being highest for clay soils with poor drainage. The model does not allow the division of this pool into N_2O and N_2 components, and therefore direct comparisons with field measurements of N_2O are limited. Additionally, the important contribution of nitrification to gaseous losses of N from agricultural systems (Lipschultz *et al.*, 1981; Sahrawat and Keeney, 1986) is not accounted for in NCYCLE. The use of the inorganic N pool in calculating losses of N is restricted by this pool not being sub-divided into components. Losses from denitrification and leaching could be calculated using the concentration of available NO_3^- in this pool, and not as the difference between inputs to this pool and uptake by plants.

The mineralisation sub-model is also extremely simplified, with constant mineralisation rates under different fertiliser applications. Using a constant rate for both fertilised and unfertilised grass ignores any priming effect of fertiliser on mineralisation of soil N (Jenkinson *et al.*, 1985; Dalenberg and Jager, 1989). NCYCLE does not have a separate biomass pool, presumably it is included within the organic N pool. This organic N pool is presented as the difference between dung and litter N and mineralisation, representing a balance of flows.

NCYCLE is based on a continuous grassland system, with N pools calculated on an annual basis. This means that seasonal patterns in the soil N cycle are not apparent in the model. For example, effects of increased spring temperatures on microbial activity are not simulated. There is no allowance within the model for differences in times of sowing and application of fertiliser, which have been shown to be important in determining the extent of gaseous N losses from arable systems (Chapter 6). Similarly, there is no allowance for split applications of fertiliser, which with careful application have the potential to lower losses of N (Powlson *et al.*, 1992). There is no facility for changing the N content of the crop, despite this being shown to be fundamental to decomposition and losses of N throughout this project. No account is taken of inputs during N fixation by clover. It is suggested that the model could be extended to include an option for ploughing-out of the grassland system.

It should be noted that the main aim of NCYCLE is to increase understanding of the way the various components of the N cycle interact, with changes in soil, climate and management factors. Although predictive use and extrapolation have been shown to be limited, due to its inherent simplicity, it provides a useful teaching aid and introduction to the various components of the N cycle.

9.3 SOILN

SOILN is a physically based model developed by the Swedish University of Agricultural Sciences. The model simulates C and N flows in soils and plants, in an attempt to quantify and increase understanding of N processes, and with emphasis on leaching, in agricultural and forest systems.

A water and heat model, SOIL (Jansson and Halldin, 1979), surface runoff, infiltration, water flow between soil layers, soil water content and soil temperature parameters. It requires daily meteorological data of air temperature, humidity, rainfall, radiation and windspeed.

In SOILN the soil profile is divided into layers, each of which includes replicated pools of organic and inorganic N. The organic N is divided into litter (crop residues, dead roots and microbial biomass), faeces and humus. The plant component includes N in above and below ground biomass and root distributions within the soil profile. Most of the N transformations are determined by temperature and soil moisture. Nitrification is also determined by pH. Denitrification is represented as a function of soil moisture content, providing a measure of anaerobiosis.

Inputs of manure, inorganic fertiliser and atmospheric deposition can be made to the top soil layer, and losses from denitrification and leaching can occur from each layer. The model contains a submodel of plant growth and development. Plant uptake of N is controlled by root distribution in the profile and a total potential demand. Incorporation of plant material into the litter component is simulated after harvest and after ploughing. At harvest the below ground residues are incorporated into the litter pools in respective layers. At ploughing above ground residues are incorporated into the plough layer, assuming a specific residue C:N ratio. The amount of N incorporated into the plough layer is determined by:

$$N_{p \rightarrow l}(z) = (f_{ar} + f_{lr})N_p$$

where N_p is the plant N prior to harvest, z represents the soil layer, f_{ar} is the fraction of plant N remaining above ground after harvest, and f_{lr} is the live root fraction of plant N after harvest. The C incorporated is proportional to this equation, assuming a constant C:N ratio for above ground residues.

Mineralisation/immobilisation of N is determined by:

$$N_{l \leftrightarrow NH4}(z) = \left[\frac{N_l(z)}{C_l(z)} - \frac{f_e}{r_o}\right] C_{l(d)}(z)$$

where N_l and C_l are the N and C contents of the litter, respectively, f_e is a synthesis efficiency constant, r_o is a constant C:N ratio of biomass and humification products and $C_{l(d)}$ is the amount of litter C decomposed. The change from net immobilisation to mineralisation of N occurs at a C:N ratio equal to r_o/f_e. Net immobilisation occurs when $N_{l \leftrightarrow NH4}(z) < 0$.

Nitrification is not modelled as a microbial process. A NH_4^+:NO_3^- ratio characteristic is assumed for a particular soil type. Nitrification is calculated from the excess of NO_3^- when the NH_4^+:NO_3^- ratio becomes greater than an assumed equilibrium, affected by pH, soil temperature and soil water content. Decomposition, mineralisation and nitrification are regulated by a Q_{10} relationship.

The denitrification rate for each soil layer is expressed as:

$$N_{NO3\rightarrow}(z) = k_d(z)\, e_{md}(z)\, e_t(z)\left[\frac{[N_{NO3}(z)]}{[N_{NO3}(z)] + c_s}\right]$$

where $k_d(z)$ is a potential denitrification rate (g N m^{-2} d^{-1}), $e_{md}(z)$ is the soil water/aeration status, $e_t(z)$ is a temperature factor and c_s is a constant controlling the NO_3^- concentration.

Further details of the model structure, and applications are examined in Johnsson *et al.* (1987).

9.3.1 Comparisons between model predicted and field measured data

Comparisons were made between measurements made during the Italian ryegrass trial (Chapter 4), the spring barley trial (Chapter 6) and model predictions.

9.3.1.1 Italian ryegrass

Measured N_2O emissions and predicted denitrified N are shown in Fig. 9.2. Over the whole modelled period SOILN predicted zero denitrification below 0.4 m depth. Predicted denitrified N increased throughout the spring. This increase was steadier at 0.2-0.4 m than nearer the surface, reflecting the effect of changing air temperature on gaseous emissions from surface soils (Conrad *et al.*, 1983). After ploughing, the simulated denitrified N increased, particularly at 0.2-0.4 m depth. One week after ploughing, the model predicted zero denitrification at 0-0.2 m depth. There was no significant difference between measured N_2O and simulated denitrified N at 0-0.2 m depth. N_2O emissions measured after incorporation of the Augusta variety were significantly lower ($p<0.01$) than simulated denitrified N at 0.2-0.4 m depth. This may have been a result of temperature and/or immobilisation of soil N following the incorporation of the C rich ryegrass (Aulakh *et al.*, 1991b). The flux of 13.9 g N_2O-N ha^{-1} d^{-1} measured on 4 May was probably produced during nitrification..

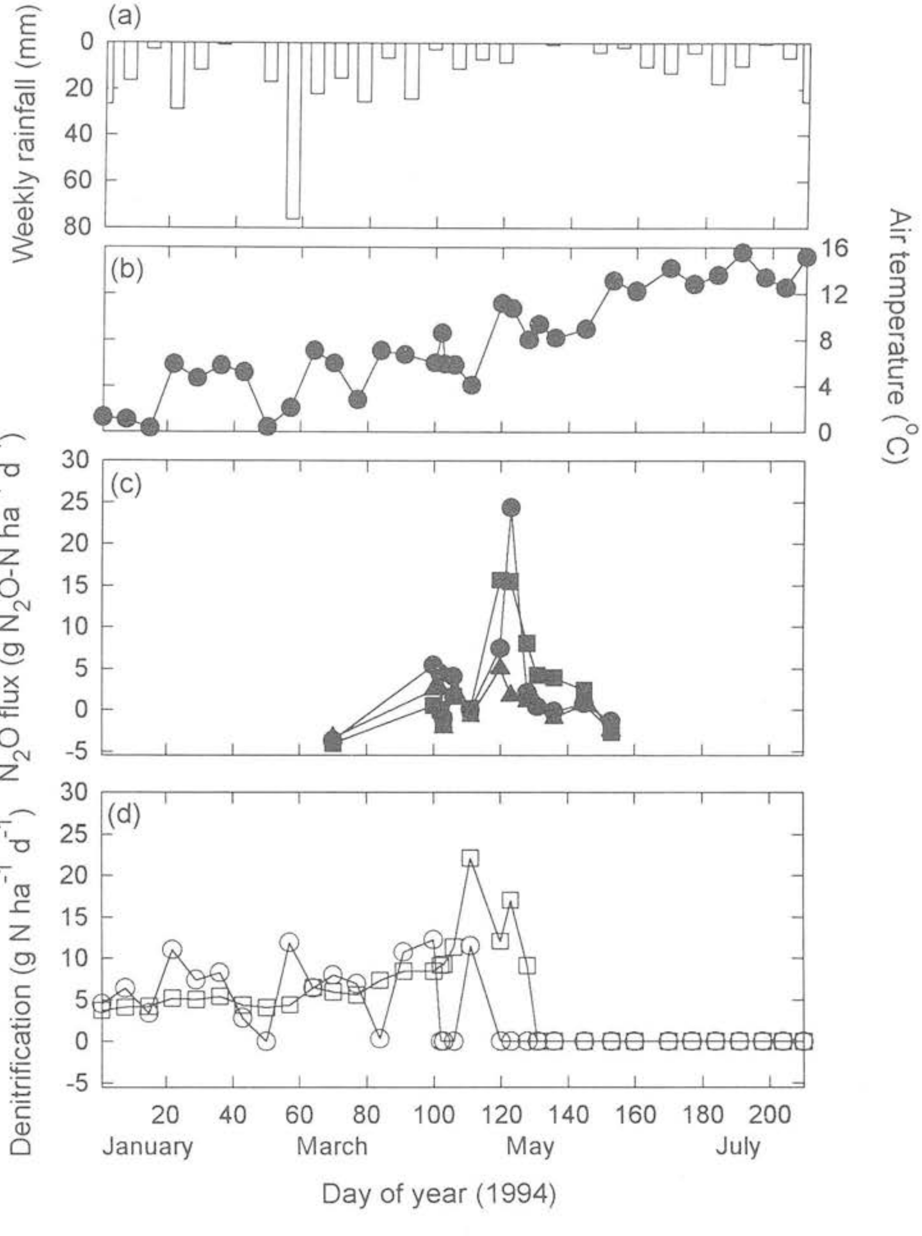

Figure 9.2 (a) Weekly rainfall, (b) air temperature, (c) N_2O emissions measured after incorporation of *Bab 424* (circles), *85/22* (squares), *Augusta* (triangles) Italian ryegrass varieties, (d) model predicted denitrification at 0-0.2 m (circles) and 0.2-0.4 m (squares) depths.

The model predicted that 35 days after incorporation of Italian ryegrass there was no further denitrification, presumably due to an exhaustion of substrate, or higher temperatures drying the soil, resulting in aerobic conditions. However, the rainfall over the summer would have been expected to have stimulated N_2O production (Webster and Dowdell, 1982). Additionally, the trial field was sown to spring barley after ploughing-in of the Italian ryegrass, with the potential for raised N_2O emissions under the growing crop (Chapters 6 and 7).

Predicted available NH_4^+ and NO_3^- were low throughout the modelled period (Fig. 9.3). Available NH_4^+ was predicted to be higher at 0-0.2 m than at 0.2-0.4 m depth, particularly before rotary tillage. After rotary tillage measured available NH_4^+ was higher ($p<0.05$) than that predicted at 0.2-0.4 m depth. Available NO_3^- increased after rotary tillage and was significantly higher ($p<0.05$) than predicted concentrations at this time. After tillage available NO_3^- was predicted to be higher at 0-0.2 than at 0.2-0.4 m depth.

In accordance with the low available N predicted by SOILN, mineralisation changed little over the modelled period, even after incorporation. However, mineralisation rates increase in the spring due to the onset of warmer temperatures stimulating microbial activity (Haynes, 1986) and also increase following addition of organic N to the soil, such as plant material (Aulakh *et al.*, 1983).

9.3.1.2 Unfertilised spring barley

SOILN predicted high fluxes of denitrified N prior to sowing of the spring barley (Fig. 9.4), which were probably in response to rainfall prior to cultivation (Fig. 9.5). A flux of 15.7 g N ha^{-1} d^{-1} was predicted at 0-0.2 m depth on 4 April. Fluxes were predicted at all depths on 26 May, the highest of which was at 0.2-0.4 m. Between 14 April and 14 June measured N_2O was significantly different ($p<0.01$) from predicted denitrified N at each depth. As in the Italian ryegrass simulation, there was no denitrification predicted during the summer months.

Predicted available N was very low throughout the modelled period, with no significant difference between depths, and with no apparent response to increased temperatures in the spring, or after autumn incorporation (Fig. 9.6). After cultivation and sowing of the spring barley measured available N was not significantly higher than that predicted by SOILN. Only the available NO_3^- measured at 0.2-0.4 m was significantly greater ($p<0.01$) than predicted concentrations. Predicted available NO_3^- was raised after harvest and incorporation of the barley crop. As in the Italian ryegrass simulation, mineralisation rates did not change throughout the year.

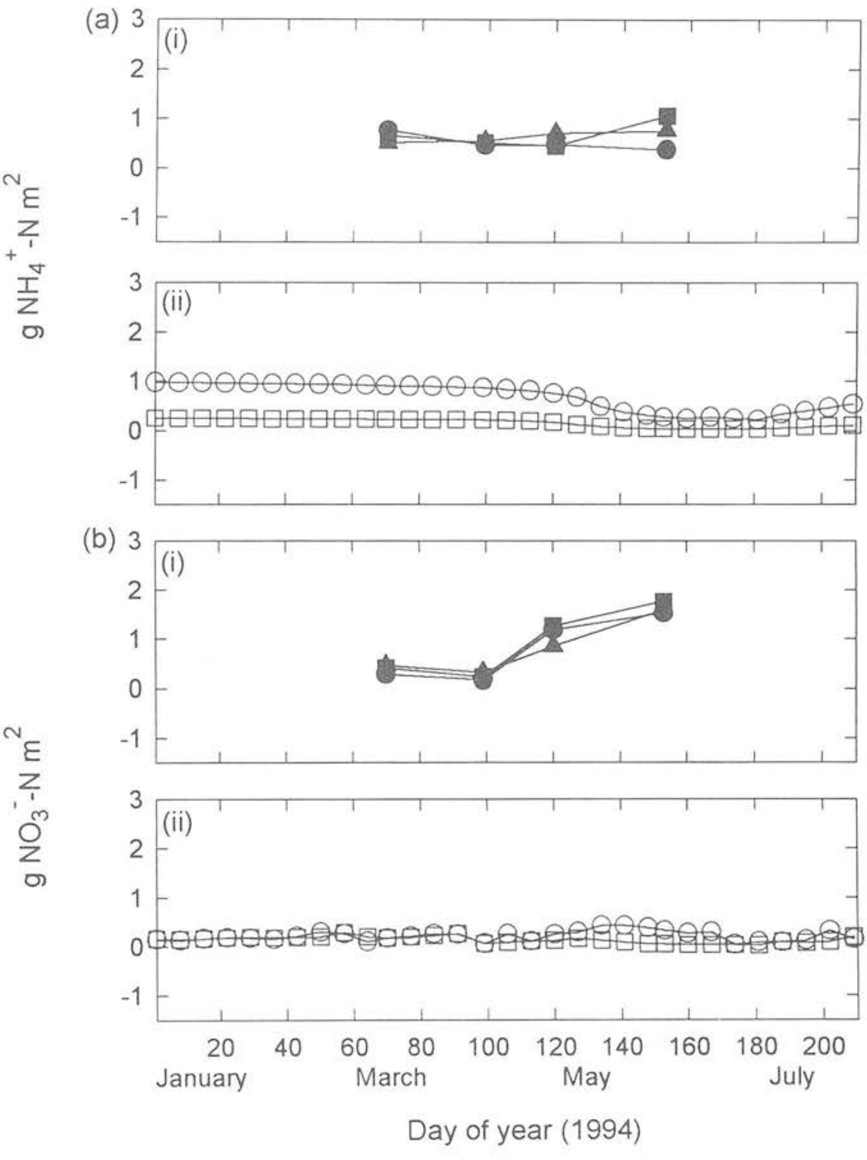

Figure 9.3 (a) Available NH_4^+, (b) available NO_3^- (i) measured after incorporation of *Bab 424* (circles), *85 22* (squares), *Augusta* (triangles) Italian ryegrass varieties, (ii) predicted by SOILN at 0-0.2 m (circles) and 0.2-0.4 m (squares) depths.

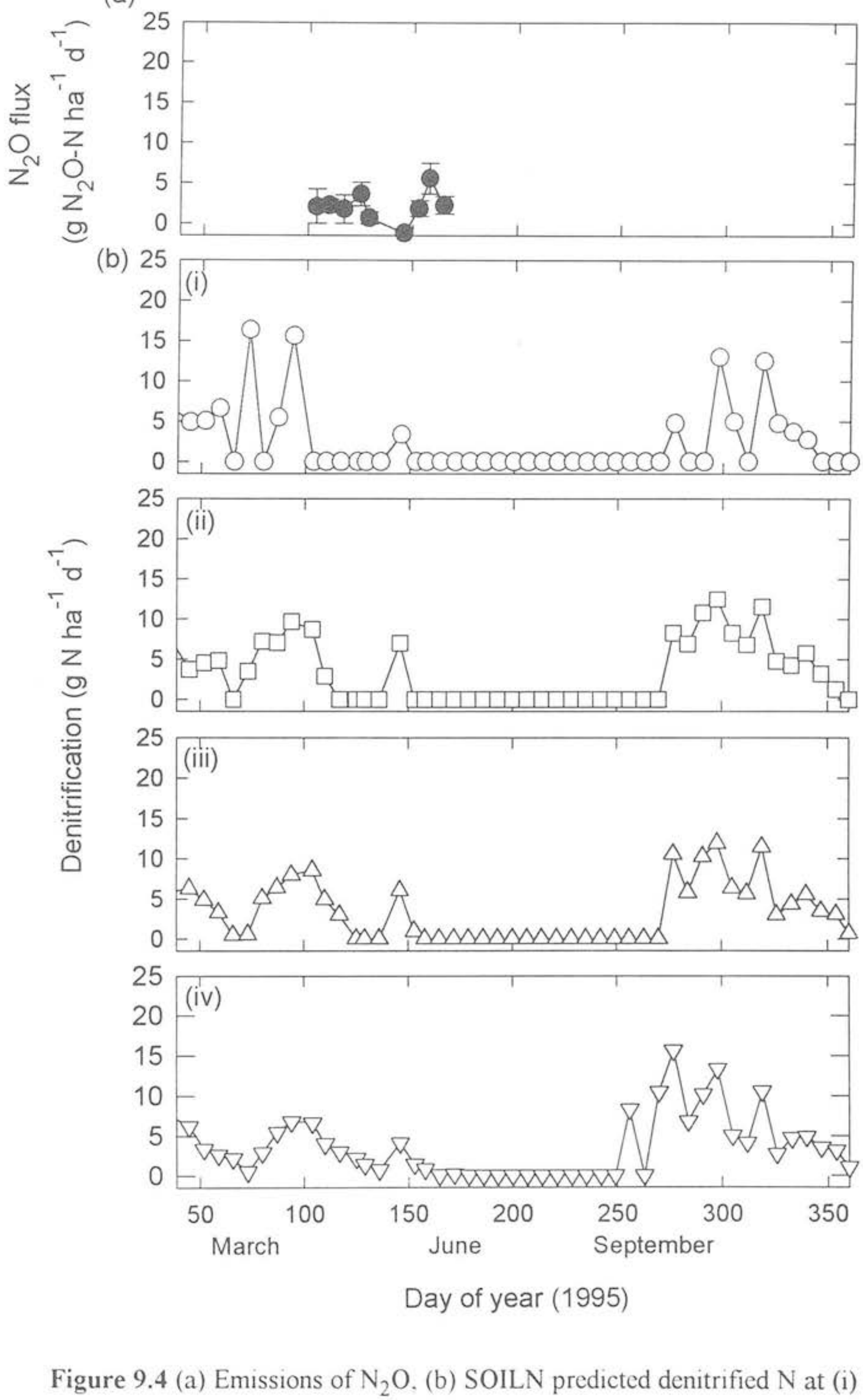

Figure 9.4 (a) Emissions of N_2O. (b) SOILN predicted denitrified N at (i) 0-0.2 m, (ii) 0.2-0.4 m, (iii) 0.4-0.6 m and (iv) 0.6-0.8 m depths from unfertilised spring barley.

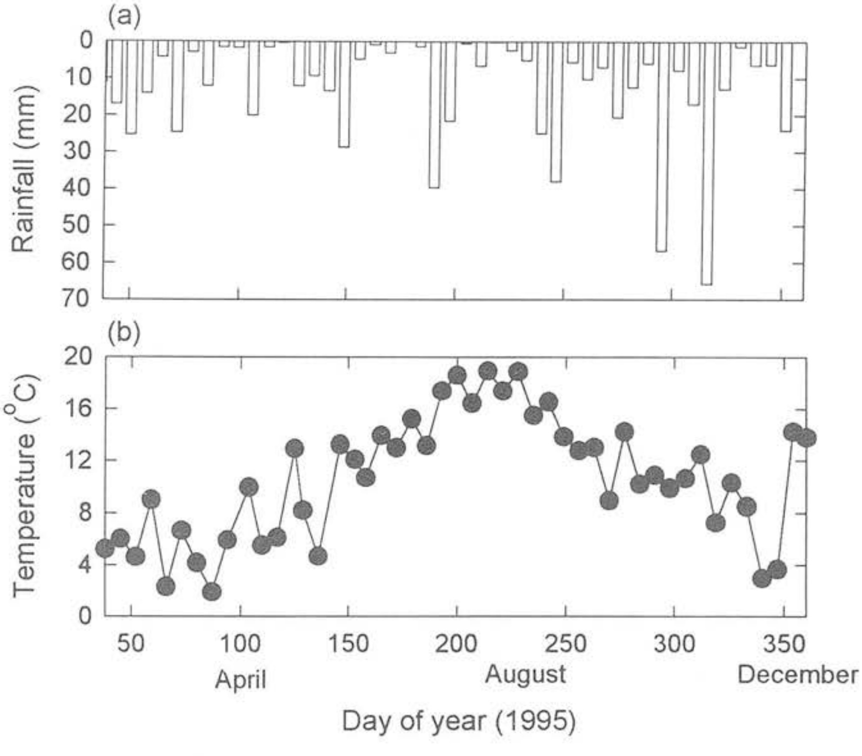

Figure 9.5 (a) Weekly rainfall, (b) air temperature used in SOILN simulation of spring barley trials.

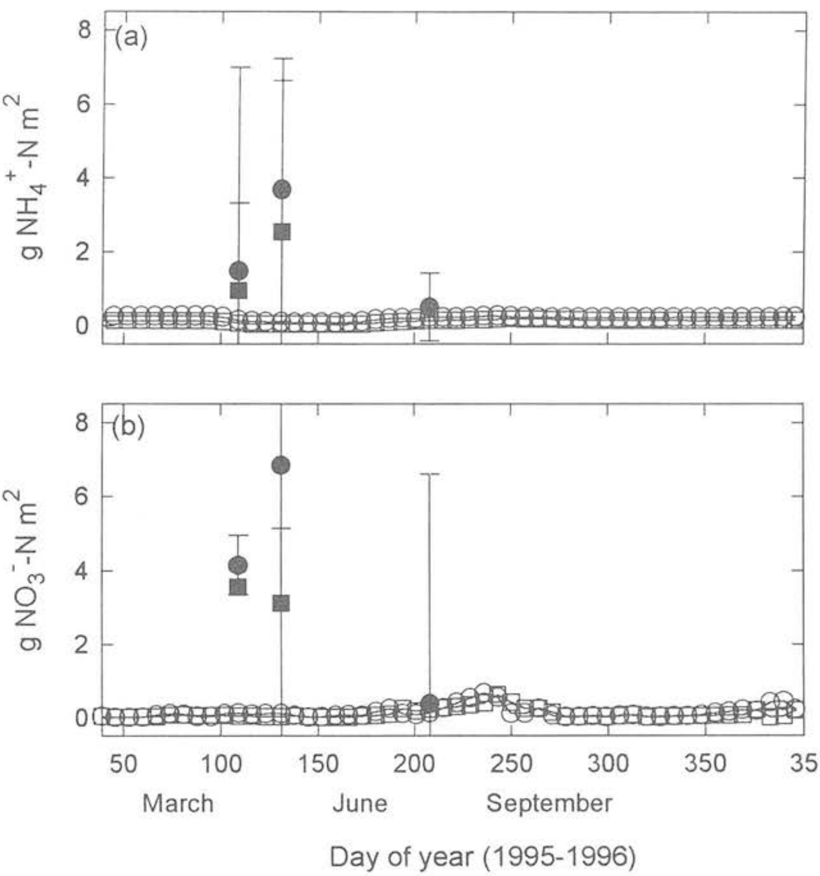

Figure 9.6 (a) Available NH_4^+, (b) available NO_3^- measured (filled symbols) and predicted by SOILN (empty symbols) at 0-0.2 m (circles) and 0.2-0.4 m (squares) depths in the unfertilised spring barley trial.

9.3.1.3 Fertilised spring barley

As for the unfertilised spring barley, high fluxes of denitrified N were predicted prior to cultivation and sowing of the crop (Fig. 9.7). There was no significant difference between predicted denitrified N and measured N_2O after both fertiliser applications. On 20 April 5.9, 8.7 and 10.8 g N ha^{-1} d^{-1} were predicted at 0.2-0.4, 0.4-0.6 and 0.6-0.8 m depths, respectively, and 11.9 g N_2O-N ha^{-1} d^{-1} measured. High losses of N were predicted on 26 May with 22.2 g N ha^{-1} d^{-1} at 0.2-0.4 m depth. This corresponded with an increase in measured N_2O in the following week. As in the other simulations, there was no N denitrified over the summer. There was no difference in predicted denitrified N in the autumn between fertilised and unfertilised spring barley crops. During the autumn there was no significant difference between predicted denitrified N and measured fluxes of N_2O.

Prior to cultivation predicted available NH_4^+ at 0-0.2 m depth steadily decreased (Fig. 9.8a). During the spring there was no significant difference between measured and predicted available NH_4^+ at 0-0.2 m depth. However, measured concentrations were significantly higher ($p<0.001$) than those predicted by SOILN at 0.2-0.4m. After the second fertiliser application 5.2 and 2.8 g NH_4^+-N m^2 were measured and predicted at 0-0.2 m depth, respectively. There was no significant difference between measured and predicted available NH_4^+ in the autumn.

After fertilisation measured available NO_3^- was significantly higher ($p<0.05$) than that predicted by SOILN (Fig. 9.8b). During the autumn there was no significant difference between measured and predicted available NO_3^- at both depths. Predicted negative mineralisation inferred the occurrence of immobilisation in the spring, followed by remineralisation after incorporation in the autumn.

9.3.2 Weaknesses of model

SOILN does not model nitrification as a microbial process, but assumes a $NO_3^-:NH_4^+$ ratio characteristic for a particular soil. Johnsson *et al.* (1987) stated that this simplification was appropriate for rapid nitrification, and low concentrations of NH_4^+ often observed in agricultural soils. However, the poor comparisons between measured and predicted concentrations of available NO_3^- suggest that such a representation of nitrification is inadequate. As a microbial process nitrification is dependent on temperature, moisture content, and substrate availability (Goodroad and Keeney, 1984), and should be modelled allowing for variations in these parameters throughout the growing season, resulting in greater variations in available N throughout the growing season, particularly within the 0-0.2 m layer. In previous chapters nitrification has been shown to be a significant source of N_2O, especially from near

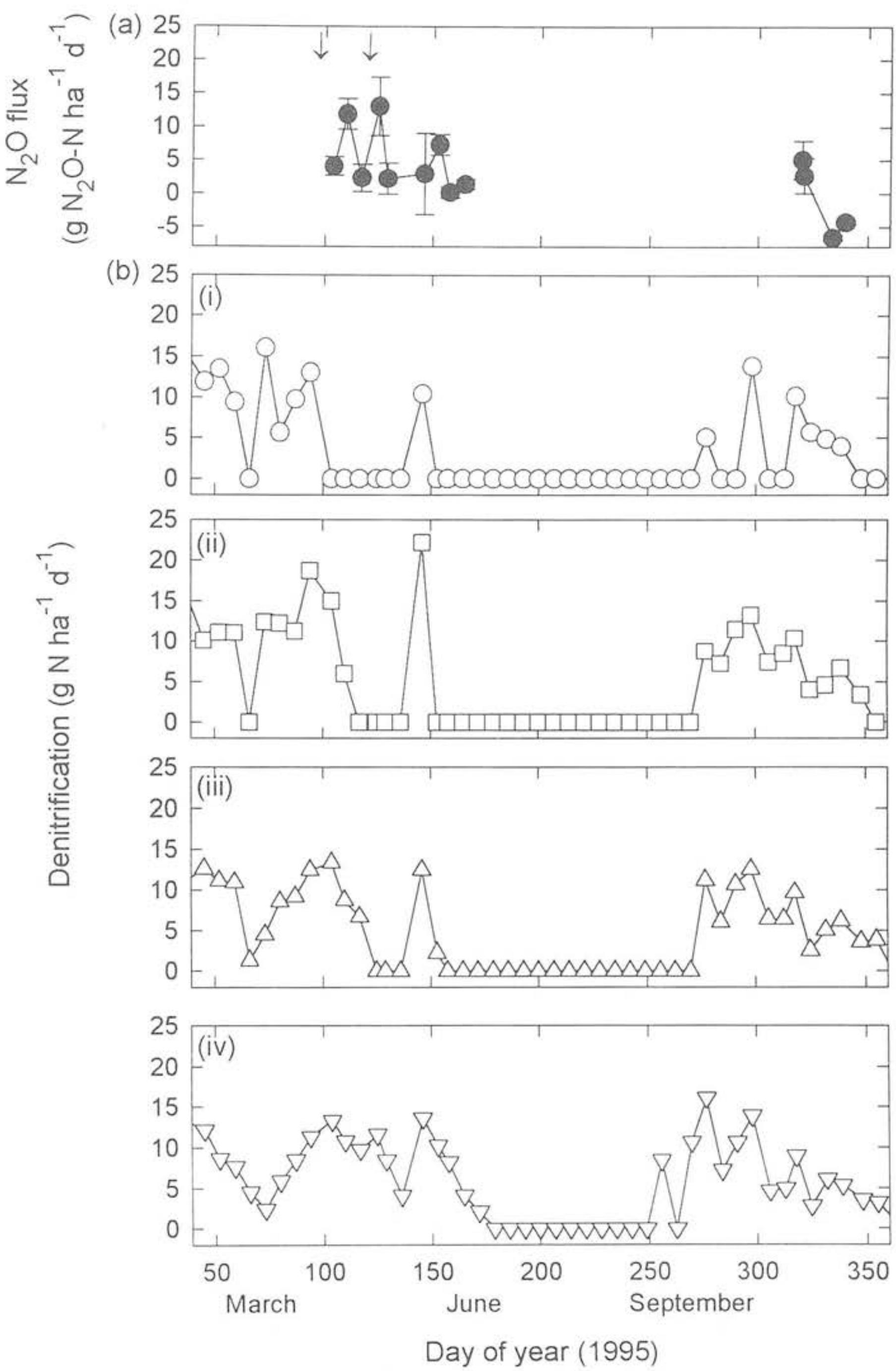

Figure 9.7 (a) Emissions of N_2O, (b) SOILN predicted denitrified N at (i) 0-0.2 m, (ii) 0.2-0.4 m, (iii) 0.4-0.6 m and (iv) 0.6-0.8 m depths from fertilised spring barley. Arrows indicate times of fertilisation.

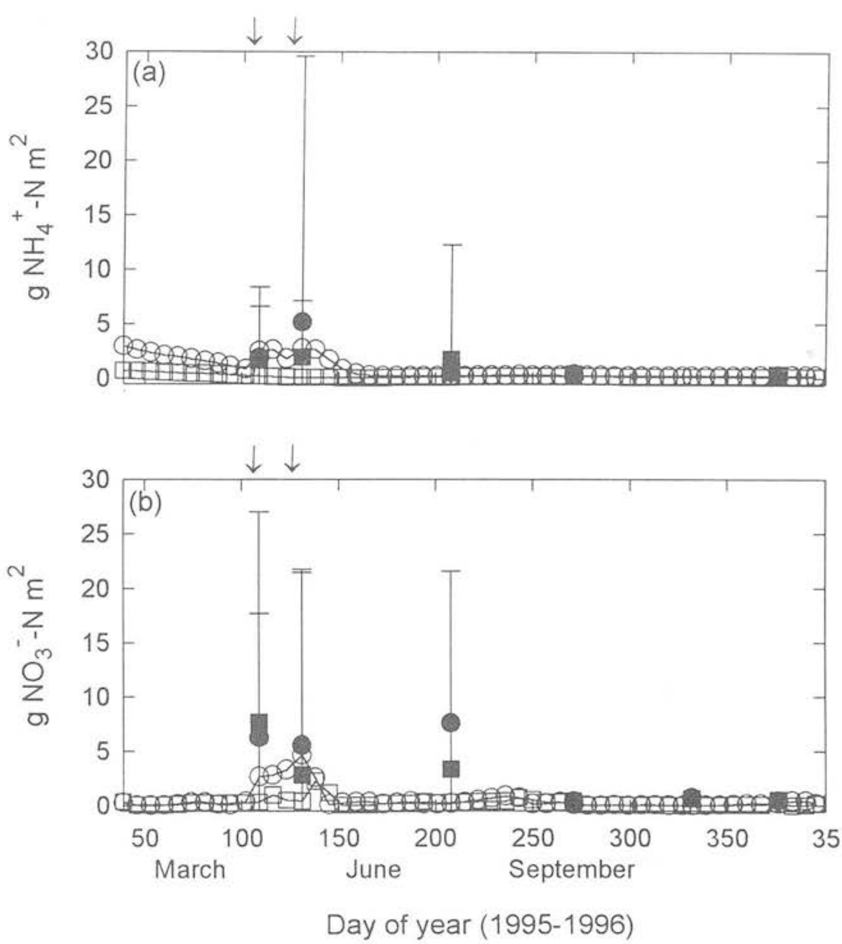

Figure 9.8 (a) Available NH_4^+, (b) available NO_3^- measured (filled symbols) and predicted by SOILN (empty symbols) at 0-0.2 m (circles) and 0.2-0.4 m (squares) depths in the fertilised spring barley trial. Arrows indicate times of fertilisation.

the soil surface. SOILN does not account for losses of gaseous N from nitrification, and therefore is underestimating losses from arable soils. Nitrification may have accounted for the high flux of 13.9 g N_2O-N ha^{-1} d^{-1} measured from the Italian ryegrass trial on 4 May, that was not predicted by SOILN.

As with NCYCLE, the potential applicability of SOILN in predicting losses of N from denitrification would be increased if the model allowed for division of the denitrification product into N_2O and N_2 components. With increasing depth in the soil the N_2O:N_2 ratio would be expected to decrease, with more complete reduction and higher anaerobiosis expected at depth (Jury *et al.*, 1982). No account is taken of the role of available C in determining denitrification, despite affecting denitrifier activity in soil (Beauchamp *et al.*, 1989). Negative measurements of N_2O have been made from soils in this project, and by other authors (for example, Freney *et al.*, 1978; Ryden, 1981), indicating that the soil was temporarily acting as a sink for N_2O. However, the SOILN does not allow for the soil to act as a sink, apart from initial inputs of N during atmospheric deposition.

SOILN includes the microbial biomass N in the litter pool. A separate biomass pool would provide a direct estimate of immobilised N. Simulation of immobilisation needs to take account of the N status of the soil, the C:N ratio of the plant material, and the size of the biomass pool.

Throughout the periods modelled the predicted denitrification and available N showed less temporal variability than expected, or those measured throughout this project. Predicted available N did not increase during the spring despite increasing temperatures which would have stimulated microbial activity after the winter (Haynes, 1986), thereby increasing decomposition, nitrification and denitrification (Stanford *et al.*, 1975). Despite rainfall events during the summers of 1994 and 1995, which would have been expected to increase microbial activity and denitrification within 1-3 days (Schnürer *et al.*, 1986), there was no denitrification predicted at any depth over these periods. Similarly, Johnsson *et al.* (1991) found that denitrification events measured from grass and barley, associated with rain in July 1983, did not occur in the model simulation. They stated that despite rainfall resulting in anaerobic zones in the surface soil, more rainfall was required to raise the simulated water content to the level allowed for denitrification in the model. Thus, the model's sensitivity to soil drying and wetting needs to be increased.

The very small increase in mineralisation predicted after ploughing-in and rotary tillage of the Italian ryegrass indicates that sensitivity to cultivation events need to be increased.. Predicted available N was not raised after this cultivation. However, the action of cultivation and incorporation of fresh plant material stimulates decomposition (section 2.2.1.2), although incorporation of material with a high C:N ratio may result in short-lived immobilisation of N (Aulakh *et al.*, 1991b).

9.4 N_ABLE

N_ABLE was developed at Horticulture Research International, Wellesbourne. The main purpose of the model is to calculate the N dynamics in cropping systems where residues are incorporated, with the aim of improving fertiliser practice.

In N_ABLE the soil is divided into 50 mm thick layers. For each day during the simulation the following calculations are made for each layer: mineralisation of soil organic matter, mineralisation and immobilisation of N as a result of microbial activity on freshly incorporated crop debris, upward and downward movement of water and NO_3^-, and concentrations of NO_3^- in each layer. The model calculates the potential maximum crop demand for N for each day from plant weight and N concentration, the maximum plant weight that could be attained by the end of the day and the critical % N of a plant of that size. The N uptake is calculated from the potential maximum crop demand and the amount of available N within the rooting zone after adjusting for immobilisation, denitrification, etc. A new calculated plant dry matter percentage is used with the plant weight and temperature to calculate each increment in plant weight.

In calculating decomposition of crop residues it is assumed that the organic products of decomposition have a C:N ratio of 10, and do not decompose further. Crop dry matter is assumed to be 40 % C (Vigil and Kissel, 1991). If incorporated plant material is rich in N, mineral N is released, and the decomposition rate is calculated by:

$$-DC / Dt = K_{c,\,rate}\,g(S_{temp})C$$

where t is time, S_{temp} is soil temperature (°C), C is the amount of C in crop residues (t ha^{-1}), $K_{c,rate}$ is the rate constant (0.035 d^{-1}) and $g(S_{temp})$ is defined as:

$$g(S_{temp}) = (4^{0.1S_{temp}}) / 16$$

where $S_{temp} \leq 20$ °C

$$g(S_{temp}) = (S_{temp} - 10) / 10$$
where $S_{temp} > 20$ °C

If the plant material contains little N and there is a low soil N content, then decomposition is at a slower rate than defined by these equations, as there is insufficient N for formation of material with a C:N ratio of 10. Irrespective of the N concentration of the incorporated plant material, the balance of mineralisation and immobilisation is always determined by 75 % of the C being converted to CO_2, while 25 % is converted into resistant soil organic matter.

Further details of the model are examined by Greenwood *et al.* (1996).

9.4.1 Comparisons between model predicted and field measured data

Comparisons were made between measurements of available N from pea and spring barley trials, 1995 (Chapter 6), a lettuce trial, 1994 (Chapter 5) and predicted model outputs.

9.4.1.1 Pea

Immediately after sowing measured available N was significantly higher ($p<0.05$) than that predicted by SOILN (Fig. 9.9). On 20 May the measured available N was lower than that predicted by N_ABLE. Predicted available N in the 0-0.1 m layer increased throughout the spring, and was higher than concentrations at lower depths. Predicted concentrations were raised after harvest, particularly at 0-0.1 and 0.1-0.2 m depths. However, they were only slightly raised immediately after incorporation of residues on 1 November, presumably due to the low temperature at this time.

9.4.1.2 Fertilised spring barley

After fertilisation of the spring barley measured available N at 0-0.2 m was significantly higher ($p<0.05$) than predicted concentrations at 0.1-0.2 and 0.2-0.3 m, but not at 0-0.1 m depth (Fig. 9.10a). 81.7 and 78.0 kg N ha^{-1} were measured (0-0.2 m) and predicted (0-0.1 m), respectively, on 20 April. After the second application of fertiliser predicted available N was raised at 0-0.1 m depth, but not at the lower soil depths. Prior to harvest measured available N at 0.1-0.2 m was higher ($p<0.05$) than predicted concentrations. However, 51.0 kg N ha^{-1} was both measured and predicted at 0.2-0.4 and 0.1-0.2 m depths, respectively on 29 July. There was no significant difference between measured and predicted available N after autumn incorporation.

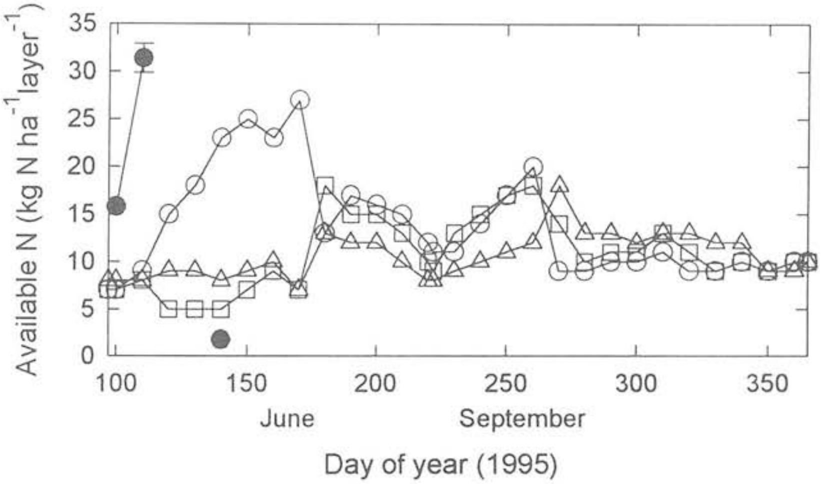

Figure 9.9 Concentrations of available N measured at 0-0.25 m (filled symbols) and predicted by N_ABLE (empty symbols) at 0-0.1 m (circles), 0.1-0.2 m (squares), 0.2-0.3 m (triangles) depths in the pea trial.

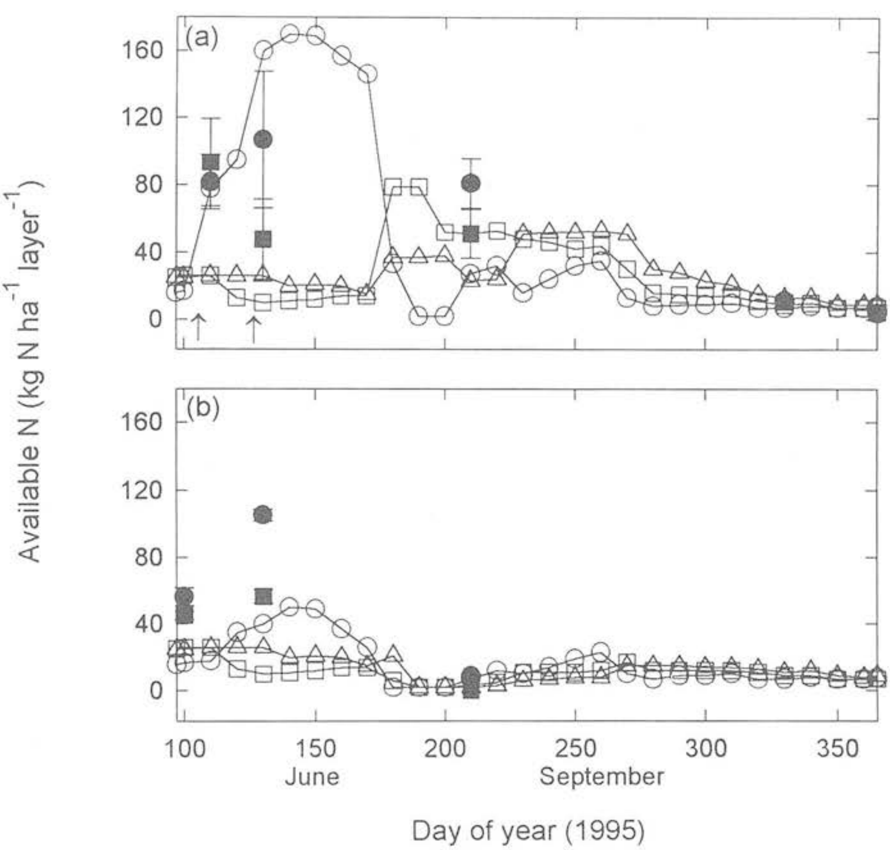

Figure 9.10 Concentrations of available N measured (filled symbols) at 0-0.2 m (circles), 0.2-0.4 m (squares) depths, and predicted by N_ABLE (empty symbols) at 0-0.1 m (circles), 0.1-0.2 m (squares), 0.2-0.3 m (triangles) depths in (a) fertilised, (b) unfertilised spring barley trials. Arrows indicate times of fertilisation.

9.4.1.3 Unfertilised spring barley

After sowing of the spring barley and prior to harvest there was no significant difference between measured and predicted available N (Fig. 9.10b). On 10 May measured available N was higher ($p<0.05$) than that predicted by N_ABLE. Predicted concentrations at 0-0.1 m increased over the spring up to 19 June, whilst those between 0.1-0.3 m depths were the same as where the crop had been fertilised. However, after 19 June concentrations remained low.

9.4.1.4 Lettuce

Application of 150 kg N ha^{-1} to the lettuce on 30 March immediately raised model predicted available N at 0-0.1 m depth (Fig. 9.11a). After harvest predicted available N increased, particularly at 0.1 m depth. Prior to, and following incorporation of lettuce residues there was no significant difference between predicted available N and those measured after rotary tillage, deep and conventional ploughing. On 27 September 27.7 and 27.5 kg N ha^{-1} were measured after deep and conventional ploughing, respectively, whilst 14, 24 and 24 kg N ha^{-1} were predicted for the 3 soil depths, respectively.

9.4.2 Weaknesses of model

N_ABLE requires many inputs that are not typically measured or considered in field trials, such as the "weight (t ha^{-1}) when the roots take up N from the mid-point between the rows", and the "weight of soil mineral N (kg ha^{-1}) at which uptake is half maximum". If these inputs are not known then the model uses default values. This lowers the accuracy and applicability of the model, and potentially reduces differences between crops. The applicability of the model would be increased if simulations could be run over a few years allowing for a number of growing crops to be simulated. This would allow for the soil N status of previous cropping to be accounted for.

N_ABLE also includes various approximations and assumptions further reducing its accuracy and applicability. For example, the organic products of decomposition are assumed to have a C:N ratio of 10, which is taken to be approximately the ratio for organic matter in a well-drained near-neutral arable soil (Greenwood, *et al.*, 1996). Crop dry matter is assumed to be 40 % C, based on work by Vigil and Kissel (1991).

Mineralisation is assumed to convert NH_4^+ immediately to NO_3^-, without any accumulation of NH_4^+ in the soil. This underestimates the available N in the soil, as NO_3^- is subject to leaching and denitrification. The model would benefit from the available N pool being divided into NH_4^+ and NO_3^- components. Losses of N are not calculated individually, but bulked

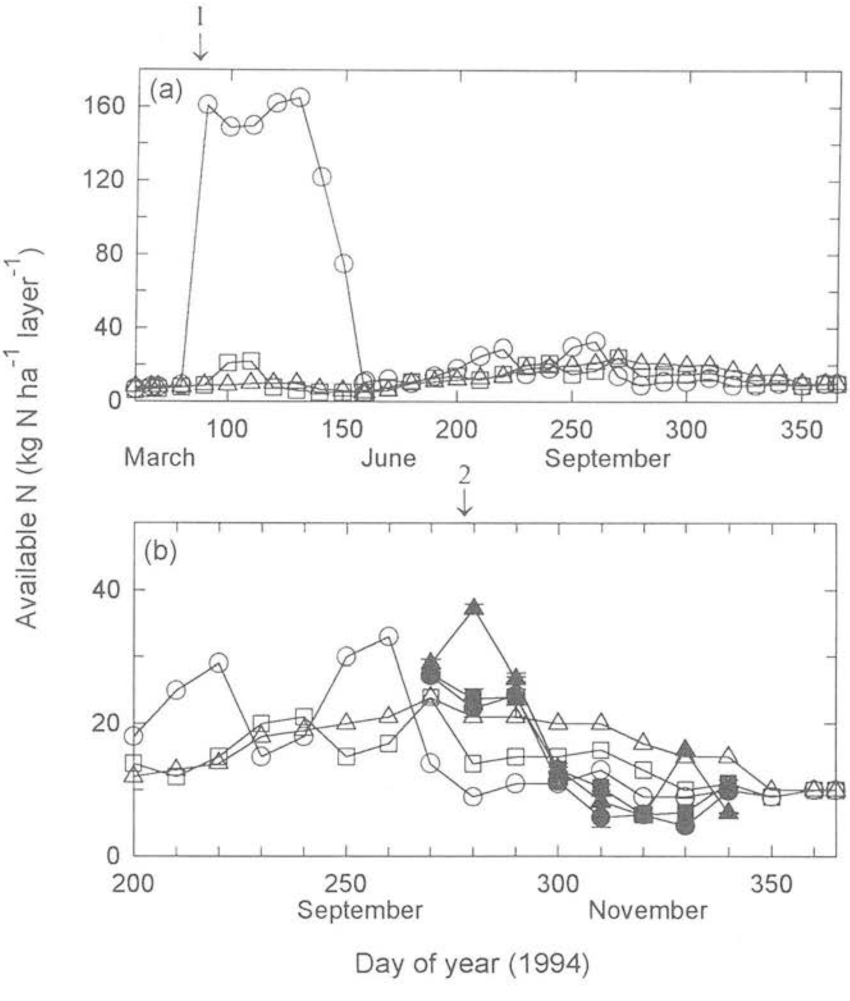

Figure 9.11 Concentrations of available N predicted by N_ABLE (empty symbols) at 0-0.1 m (circles), 0.1-0.2 m (squares), 0.2-0.3 m (triangles) depths, and measured (filled symbols) after deep ploughing (circles), conventional ploughing (squares) and rotary tillage (triangles) of lettuce (a) from planting until the end of the year, (b) after harvest. Arrows indicate times of: 1. Fertilisation, 2. Incorporation.

together to include immobilisation, leaching and denitrification. These pools need to be considered separately to improve the accuracy and applicability of the model. N_ABLE assumes that during growth of the crop a fixed proportion of N is immobilised. This proportion is the same irrespective of crop type, soil and climatic conditions, which is unrealistic (Greenwood, 1986). Gaseous losses during nitrification are not considered, particularly as NH_4^+ is immediately converted to NO_3^-. Greenwood *et al.* (1996) consider other weaknesses of the model to be the exclusion of ammonia volatilisation from crop debris, not accounting for the dependence of crop N uptake and residue breakdown on soil moisture, and not modelling the fixation and release of NH_4^+ from clay lattices.

9.5 SUNDIAL

SUNDIAL (simulation of nitrogen dynamics in arable land) is a user-friendly, PC-based version of the Rothamsted Nitrogen Turnover Model. The N processes involved are described by a set of parameterised zero and first-order equations. The aim of the model is to deal with all of the major processes affecting the behaviour of N in a cereal/soil system, even though each individual process is expressed in a simplified form. The model determines how much N a soil could supply to a crop over the growing season, from a knowledge of soil, its cropping history and weather. The amount of fertiliser required can be calculated. This model has much in common with SOILN.

SUNDIAL is run on a weekly time basis. N is entered by atmospheric deposition, application of fertiliser or organic manures, and is lost through denitrification, leaching, volatilisation, and removal in harvested crops. Organic N is contained in crop residues, soil microbial biomass and humus. Inorganic N is contained in separate NH_4^+ and NO_3^- pools. N is transferred between these pools during mineralisation, immobilisation, nitrification, leaching, denitrification and plant uptake.

The model requires inputs of soil type, mean weekly air temperature, rainfall and evapotranspiration, which are used to drive soil water and temperature sub-models. SUNDIAL also allows for the addition of ^{15}N labelled fertiliser and follows its progress through the crop/soil system.

The soil is divided into layers, and the top 2 layers are each subdivided into 50 mm depths. The amount of N input from seed, rain, dry deposition, symbiotic and non-symbiotic fixation is set at 0.8 kg N ha^{-1} $week^{-1}$ (Powlson *et al.*, 1986). Fertiliser can be applied as either NH_4^+, NO_3^- or any combination of both.

Nitrification is expressed as:

$$P = N_A(1 - e^{-smq})$$

where P is the amount of NO_3^- (kg ha^{-1}) formed in 1 week, N_A is the quantity of NH_4^+ present in the soil layer, s is the soil moisture rate modifier, m is the temperature rate modifier and q is a rate constant (0.6 $week^{-1}$).

SUNDIAL simulates decomposition of organic C as it moves through the various compartments of the model, and calculates the N content of these compartments from assumed C:N ratios. The calculations take account of temperature, soil water content and soil texture.

The return of C in plant material to soil is calculated as:

$$CAO = 1.25\left[1 + 1.12(1 - e^{-0.22G})\right]$$

where C_{AO} is the annual return of C to the soil (t ha^{-1}), and G is the grain yield (t ha^{-1}) at 85 % dry matter. The scaling factor 1.25 allows for C returned to the 0.25-0.5 m layer. This is based on estimates by Jenkinson (1988).

The return of N is calculated as:

$$NAO = 60(1 - e^{-0.5G}) + 0.12(U_G + U_S)$$

where N_{AO} is the annual return of N to soil (kg ha^{-1}), U_G is the N in the grain at harvest and U_S is the N in the returned plant material. The term $60(1\text{-}e^{-0.5G})$ is based on estimates by Powlson *et al.* (1986).

During each week the release of N from plant material returned to soil is calculated as:

$$zC_O(1 - e^{-smr})$$

part of this release is built into the biomass:

$$(= xaC_O(1 - e^{-smr}))$$

and part into the humus:

$$(= xbCo(1-e^{-smr}))$$

where x is the reciprocal of the C:N ratio of biomass and humus components, and z is the reciprocal of the C:N ratio of plant material returned to soil. If z>x(a+b) then there is net release of N, if z<x(a+b) N is immobilised.

The amount of N denitrified in a layer is assumed to be proportional to the quantity of CO_2 produced by the layer, and its NO_3^--N concentration. Loss in a layer is given by:

$$D = q(W / 5)NN\left[(\psi f - \psi c) / \psi f\right]$$

where D is the denitrification loss (kg N ha^{-1}), θ is a denitrification factor, N_N is the amount of NO_3^--N in a layer, ψ_f is the available water holding capacity of the layer, and ψ_c is the calculated moisture deficit in the layer. The model assumes that denitrification only occurs in the 0-0.25 m layer.

Further details of the model structure, particularly calculations for plant uptake of N, leaching, volatilisation of NH_3 and behaviour of ^{15}N fertiliser are examined by Bradbury *et al.* (1993).

9.5.1 Comparisons between model predicted and field measured data

9.5.1.1 Winter wheat

At harvest of the unfertilised winter wheat crop SUNDIAL predicted that 23 kg N ha^{-1} had been denitrified, 60 kg N ha^{-1} leached and only 2 kg N ha^{-1} taken up by the crop. 73 kg N ha^{-1} remained in the soil in available forms (Fig. 9.12a)

At harvest of the fertilised winter wheat crop SUNDIAL predicted that 21 kg N ha^{-1} (18 %) of the 120 kg N ha^{-1} applied was denitrified (Fig. 9.12a). This percentage was higher than the 0.05 % of fertiliser N emitted as N_2O during 104 days of sampling from the winter wheat crop at Bush Estate. The predicted denitrified fertiliser N represented 47 % of total denitrification at harvest. 16 kg N ha^{-1} of applied fertiliser became available NH_4^+ and NO_3^-, representing 22 % of the available soil N at harvest. 109 kg N ha^{-1} of fertiliser had been taken

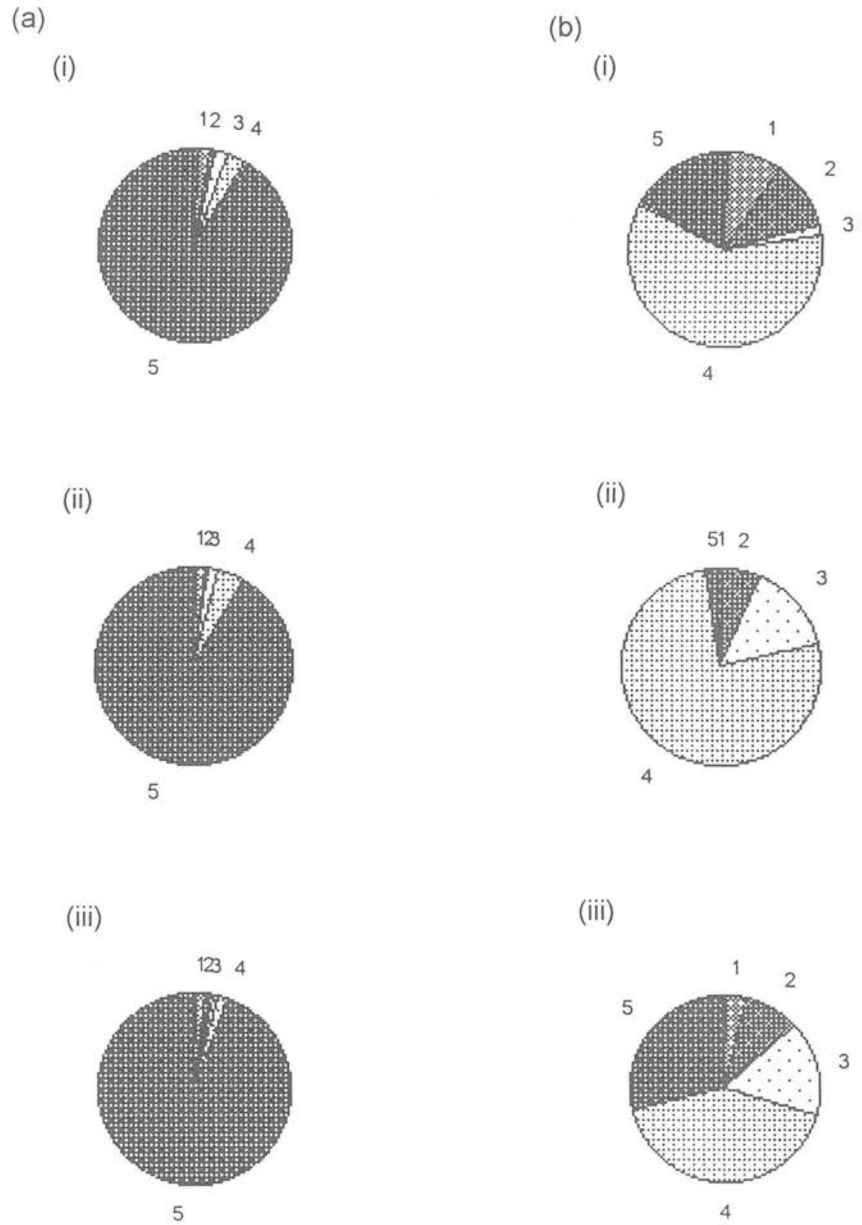

Figure 9.12 (a) Nitrogen balance at harvest (kg N ha^{-1}), (b) fate of labelled fertiliser N (kg N ha^{-1}) predicted by SUNDIAL for (i) winter wheat, (ii) oilseed rape and (iii) spring barley; 1. mineral N, 2. denitrified N, 3. leached N, 4. crop uptake of N, 5. organic N.

up by the winter wheat crop, representing 77 % of total crop uptake. However, crop N derived from fertiliser was measured to be 54.4 % at harvest of winter wheat at Bush Estate.

By the third week after harvest the predicted available N pool had increased, particularly the available NO_3^- (Fig. 9.13a). Throughout the period modelled, the available NO_3^- pool showed greater changes than the available NH_4^+ pool. Concentrations of humus and biomass N decreased immediately after harvest, and then fluctuated until 12 weeks after harvest (4-11 November), when concentrations of 0.8 and 0.9 kg N ha^{-1} were predicted for the humus and biomass, respectively (Fig. 9.13b). Changes in denitrified, nitrified and leached N were comparatively small for the whole period modelled following harvest (Fig. 9.13c). Nitrified N increased on the third week after harvest.

9.5.1.2 Oilseed rape

At harvest of the unfertilised oilseed rape crop SUNDIAL predicted that 17 kg N ha^{-1} had been denitrified, 27 kg N ha^{-1} leached and 29 kg N ha^{-1} taken up by the crop. 61 kg N ha^{-1} remained in the soil in available forms (Fig. 9.12b).

SUNDIAL predicted that 11 kg N ha^{-1} (6 %) of the 180 kg N ha^{-1} fertiliser applied to the oilseed rape crop was denitrified by harvest, representing 38 % of total denitrification. At Bush Estate (Chapter 6) it was calculated that only 0.03 % of fertiliser N was lost as N_2O over 54 days. The model predicted that 27 kg N ha^{-1} (50 %) of this fertiliser was leached, and 137 kg N ha^{-1} (81 %) was taken up by the crop. Only 5 kg N ha^{-1} (0.1 %) became organic N. 59.2 % of labelled fertiliser applied at Bush Estate was taken up by the oilseed rape crop. Although this percentage is lower than that predicted by SUNDIAL, the oilseed rape was both measured and predicted to have the greatest percentage uptake of the 3 crops examined.

Predicted changes in available N were lower over the first 5 weeks after harvest of oilseed rape than winter wheat (Fig. 9.14a). Concentrations of available NO_3^- increased between the sixth and eighth weeks, temporarily fell and then fluctuated between weeks 12 and 16. Changes were less marked in the available NH_4^+ pool. Humus and biomass N fluctuated between approximately 7 and 0 kg N ha^{-1} 7 to 16 weeks after harvest (Fig. 9.14b). As with the winter wheat, changes in denitrified, nitrified and leached N were lower over most of the simulated period (Fig. 9.14c).

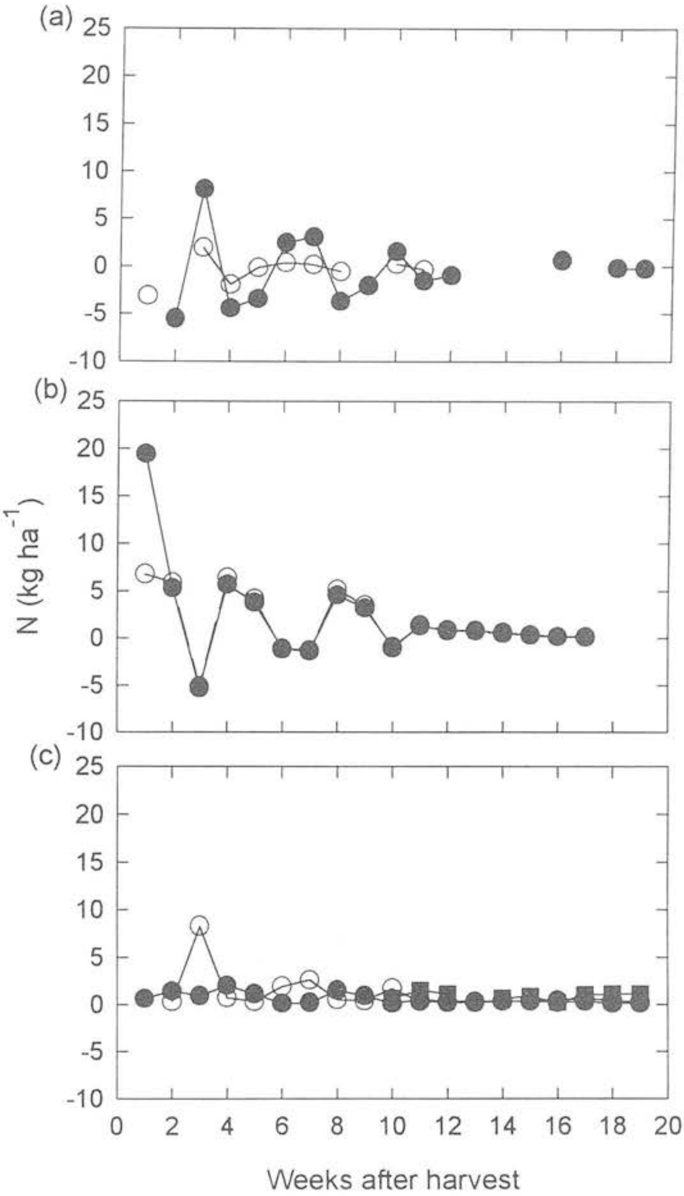

Figure 9.13 (a) Changes in NO_3^- (filled circles) and NH_4^+ (empty circles) pools, (b) changes in humus (filled circles) and biomass (empty circles) and (c) denitrified N (filled circles) nitrified N (empty circles) and leached N (filled squares) predicted by SUNDIAL in the weeks following harvest of winter wheat.

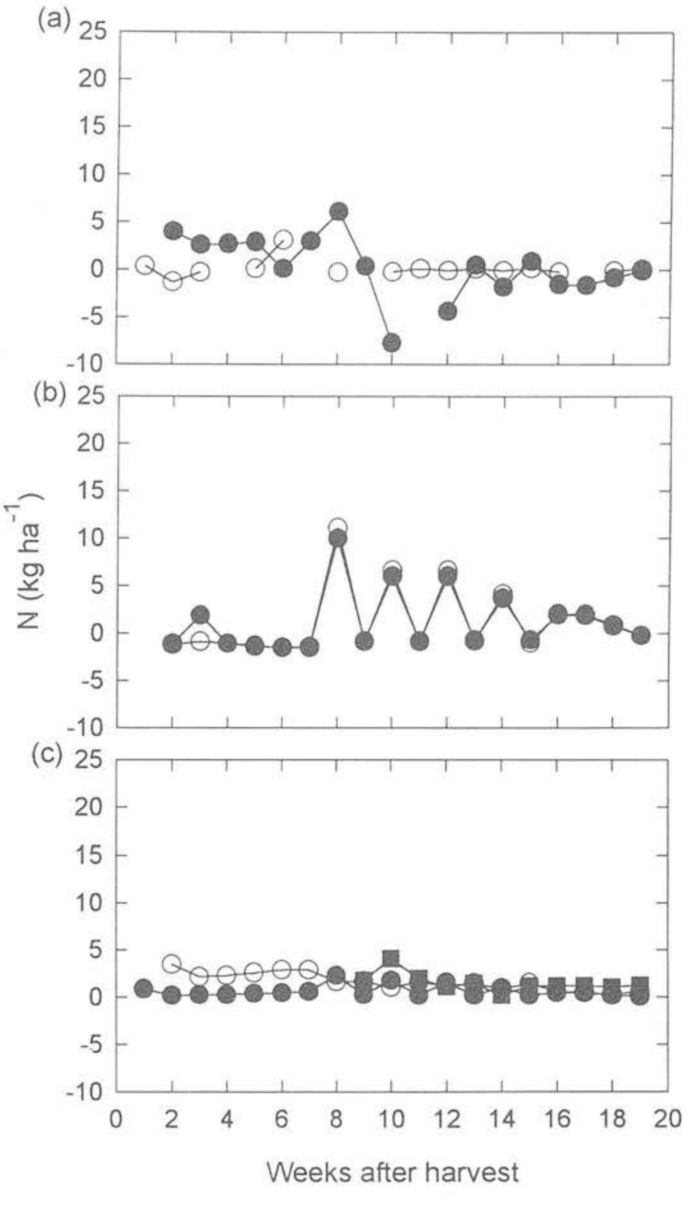

Figure 9.14 (a) Changes in NO_3^- (filled circles) and NH_4^+ (empty circles) pools, (b) changes in humus (filled circles) and biomass (empty circles) and (c) denitrified N (filled circles), nitrified N (empty circles) and leached N (filled squares) predicted by SUNDIAL in the weeks following harvest of oilseed rape.

9.5.1.3 Spring barley

At harvest of the unfertilised spring barley crop SUNDIAL predicted that 17 kg N ha^{-1} had been denitrified, 27 kg N ha^{-1} leached and only 4 kg N ha^{-1} taken up by the crop. 61 kg N ha^{-1} remained in the soil in available forms (Fig. 9.12c).

At harvest of the fertilised spring barley 11 kg N ha^{-1} (9 %) of the 120 kg N ha^{-1} fertiliser applied was denitrified, representing 37 % of total denitrification. Fertiliser applied to spring barley at Bush Estate only contributed to 0.03 % of measured N_2O over a 61 day period. SUNDIAL simulated that 50 kg N ha^{-1} (68 %) had been taken up by the crop, and 34 kg N ha^{-1} (1 %) remained as available soil N. Measurements of the fate of labelled fertiliser at Bush Estate established that 49.8 % was taken up by the spring barley crop, and was lower than that predicted by SUNDIAL.

Predicted changes in available N pools after harvest of spring barley were lower, and less marked, than for winter wheat and spring barley (Fig. 9.15a). Concentrations of humus and biomass N fell between the second and third week after harvest, and then were stable for the remainder of the modelled period (Fig. 9.15b). Changes in denitrified, nitrified and leached N were low over most of the simulated period (Fig. 9.15c). Denitrified N temporarily increased in the second week after harvest, and leached N was raised after week 10.

9.5.2 Weaknesses of model

SUNDIAL includes many simplifications of processes, particularly for plant uptake. Denitrification is calculated from the quantity of CO_2 produced in a layer. This assumes that the respiratory quotient of the soil is approximately 1, so that evolution will give a good measure of O_2 consumption, which is the driving force for denitrification. The model does not allow for denitrification below 0.25 m, whereas denitrification has been found to occur at depth in soil (Granli and Bøckman, 1994). It is also assumed that denitrification does not reduce the concentration of available NO_3^- in any layer below a set residual concentration. The calculation of nitrification assumes that the soil always contains sufficient nitrifiers for nitrification. However, this may not always be the case, particularly after addition of large quantities of fertiliser N, when nitrification may be zero (Bradbury *et al.*, 1993). As with the other models examined (sections 9.2, 9.3 and 9.4), no account is made for gaseous losses of N during nitrification.

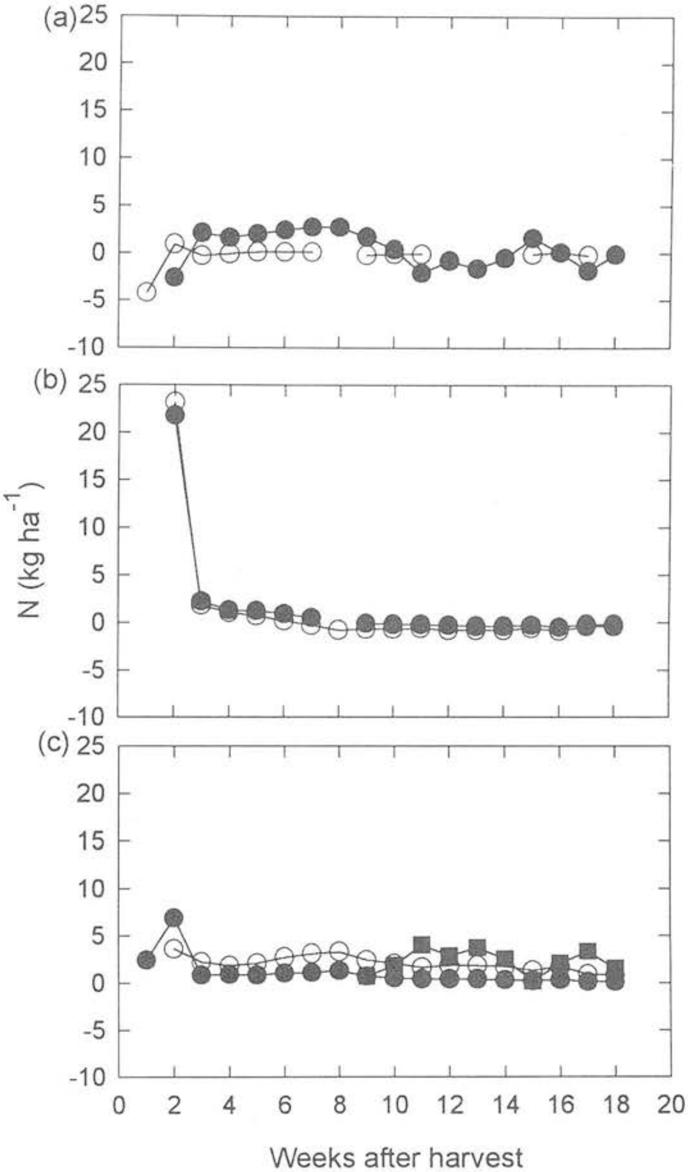

Figure 9.15 (a) Changes in NO_3^- (filled circles) and NH_4^+ (empty circles) pools, (b) changes in humus (filled circles) and biomass (empty circles) and (c) denitrified N (filled circles), nitrified N (empty circles) and leached N (filled squares) predicted by SUNDIAL in the weeks following harvest of spring barley.

SUNDIAL uses constants and scaling factors based on previous estimates and experimental work. This lowers the accuracy of predictions. The model also mainly ignores the temperature dependence of most of the soil processes.

This model is still being developed, limiting its applicability at present. For example, it is not possible to produce weekly N balance sheets throughout the growing season, only balance sheets between consecutive harvests. However, the model has great potential due to its simplicity to run and due to the N budget being calculated for several years, allowing for the growth of many crops, and greater accuracy in prediction of fertiliser requirements.

9.6 Summary

The degree of complexity and applicability for the different processes of the N cycle varied considerably between the four models examined. The models examined have several areas for improvement in common. Their sensitivity needs to be improved, particularly with respect to mineralisation and responses to changes in temperature. This was particularly apparent in the use of SOILN where changes in simulated rates of mineralisation were minimal, even after fertilisation, or autumn incorporation of crop residues. Improvements are required in modelling of the processes of immobilisation and mineralisation/immobilisation turnover with a separate pool for microbial biomass being a necessity. When calculating denitrification the degree of anaerobiosis of the soil needs to be modelled, and subdivision into N_2O and N_2 components would be beneficial. Gaseous losses of N during nitrification are not accounted for, even though these have been shown to be significant, particularly after fertilisation and residue incorporation. Nevertheless, the desired application and simplicity both in structure and in use should be considered when comparing the validity of models.

CHAPTER 10 GENERAL CONCLUSIONS

10.1 N_2O emissions

The original hypothesis of this work was that N_2O emissions would be increased after incorporation of crop residues and green manures. The field trials that were carried out did in fact confirm that such incorporation increased N_2O emissions; thus the results were in keeping with previous work (for example, Denmead *et al.*, 1979a; Ryden and Lund; 1980; Aulakh *et al.*, 1983, 1984b, 1991a,b). Where comparisons were made with emissions from bare soil incorporation of plant material resulted in greater emissions. However, the determination of background emissions from bare, uncultivated soil was not always possible to compare with emissions from incorporated plant material. This was usually due to the use of commercial agricultural fields where the entire field was cultivated, sown and/or fertilised, or there were problems with spatial variability.

Cultivation of bare soil increased N_2O emissions, probably by exposing organic matter to soil micro-organisms, and releasing N_2O from soil air (Matthias *et al.*, 1980). Most of the N_2O measured throughout this project was emitted during the first two weeks after addition of plant material, reflecting the stimulation of microbial decomposition immediately after incorporation (Haynes, 1986), and increased substrate for nitrification and denitrification (Aulakh *et al.*, 1984b; Frankenberger and Abdelmagid, 1985; de Catanzaro and Beauchamp, 1985). These studies provided comparisons of emissions between a wide range of incorporated and growing (fertilised and unfertilised) crops. Such a comparison has long been needed in this area of research (Aulakh *et al.*, 1991a,b).

Generally, higher N_2O emissions were measured after incorporation of material with a low C:N ratio than material with a high C:N ratio, in agreement with other authors (for example, Aulakh *et al.*, 1983; Goodroad *et al.*, 1984; McKenney *et al.*, 1993). N_2O emissions were higher after incorporation of grass/clover swards than after incorporation of Italian ryegrass (Chapter 4). This was attributed to the low C:N ratio of the clover, confirming findings by Davies (1996). Large emissions were measured after autumn incorporation of high N lettuce residues (Chapter 5), with a flux of 67.5 g N_2O-N ha^{-1} d^{-1} measured 8 days after tillage. Reports of emissions from vegetable crops are scarce, particularly after their incorporation. However, this trial emphasised the potential enormity of emissions from incorporated vegetable crops, and the necessity for further quantification.

Immobilisation of N after incorporation reduced the substrate available for nitrification and denitrification. Incorporation of green manures at Aldroughty Estate (Chapter 4) resulted in short-lived immobilisation of N, with the highest flux 12 days after cultivation measured from cultivated bare ground. Autumn incorporation of ^{15}N labelled cereal and oilseed rape straw with a high C content (Chapter 6) resulted in significant immobilisation of N into the microbial biomass, and subsequently low N_2O emissions (Chapter 6). Although the C:N ratio of the organic substrate has been shown to significantly effect N_2O emissions, analysis for other characteristics, such as lignin, water soluble C and cellulose contents would have increased understanding of the decomposition of the various residues.

The method of residue incorporation was shown to affect the magnitude and pattern of N_2O emissions. Cultivation increases soil aeration and mineralisation of N by stimulating microbial activity (Haynes, 1986; Drury *et al.*, 1991). Residues incorporated into the soil initially decompose faster than those left on the soil surface, or only shallowly incorporated (Douglas *et al.*, 1980; Aulakh *et al.*, 1984b; Varco *et al.*, 1993). Despite this, higher N_2O emissions were measured after rotary tillage than after ploughing of lettuce residues (Chapter 5). This was attributed to greater microbial activity near the soil surface and the development of anaerobic conditions near the surface due to the concentration of fresh residues there. Such higher N_2O losses from undisturbed or shallowly cultivated soils than from deeply cultivated soils have been reported elsewhere in the literature (for example, Burford *et al.*, 1981; Staley *et al.*, 1990). Lower emissions from deeper cultivations may be due to reduction of N_2O to N_2 during denitrification at depth before diffusion from the soil (Jury *et al.*, 1982; Arah *et al.*, 1991).

Spring application of NH_4NO_3 fertiliser to arable crops increased N_2O emissions (Chapter 6) by providing an additional substrate for nitrification and/or denitrification. These increases confirm work by other authors (for example, Duxbury *et al.*, 1982; McElroy and Wofsy, 1985; McTaggart *et al.*, 1994; Mosier, 1994). Determinations of available soil N suggested that nitrification significantly contributed to the emissions after fertilisation. This was confirmed by use of a nitrification inhibitor in a laboratory experiment (Chapter 8). Increased emissions are generally short-lived, and their magnitude varies considerably depending on the timing, quantity and type of fertiliser applied (Ryden, 1981; Eichner, 1990; Van Cleemput *et al.*, 1994). Emissions over the whole growing season from fertilised oilseed rape (Chapter 6) were significantly higher than from fertilised winter wheat and spring barley crops. Such large differences between fertilised crops have not previously been found. Indeed, in 1994, Granli and Bøckman stated that there were no major differences in N_2O emissions between various types of fertilised crops.

Addition of N has been found to increase mineralisation of soil N (Jenkinson *et al.*, 1985; Azam *et al.*, 1991), thereby increasing the substrate for nitrification and potential losses of N_2O. However, in these trials mineralisation was estimated to have increased after fertilisation of winter wheat, and decreased on the spring barley and oilseed rape trials.

Unfertilised growing crops significantly contributed to measured N_2O emissions, with higher emissions measured from cropped soil than from bare soil (Chapters 6 and 7), despite crop uptake of available N. Crops stimulate microbial activity by root material and exudates, create channels for gas transfer, and reduce diurnal variations in soil temperature (Granli and Bøckman, 1994). Emissions varied, depending on the species grown, with the highest emissions being detected from a spring oilseed rape crop (Chapter 6). These differences in emissions may have been due to differences in N uptake and growth forms of crops (Mosier *et al.*, 1986; Van Cleemput *et al.*, 1992). However, in other studies, such large differences between unfertilised crops have only been found between legumes and non legumes. At CSCV (Chapter 7) emissions from soil cropped with legumes were higher than from soil cropped with non-legumes. This was attributed to the additional N resulting from the ability of legumes to fix N (Duxbury, 1984; Kilian and Werner, 1996), and denitrification by rhizobia (Smith and Smith, 1986).

Field trials highlighted the importance of rainfall and temperature on the magnitude and timing of N_2O emissions from agricultural soils. Rainfall increased soil moisture contents and fluxes of N_2O from denitrification, usually within three days. This confirms findings by other workers (for example, Conrad *et al.*, 1983; Webster and Dowdell, 1982; Schnürer *et al.*, 1986). The presence of fresh residues in soil may exacerbate the effects of rainfall on moisture contents and aeration of microsites (Harper and Lynch, 1981), increasing the potential for denitrification. The influence of temperature on N_2O emissions was particularly apparent when comparing emissions measured at different times of the year. Lower emissions were measured after winter incorporation of calabrese residues than after autumn incorporation of lettuce residues (Chapter 5). This was attributed to the reduction in microbial activity due to lower temperatures at the time of winter incorporation (Bremner and Blackmer, 1981). N_2O fluxes measured after spring incorporation of grass/clover swards and Italian ryegrass (Chapter 4) coincided with an increase in air temperature. The occurrence of these fluxes was delayed until the temperature increased. Higher emissions than those measured were expected after incorporation of residues under a Mediterranean climate (Chapter 7).

Use of autochambers (Chapter 5) showed that N_2O emissions during field trials were subject to diurnal, as well as seasonal, variations in response to temperature. This confirms findings of other authors, that N_2O emissions coincide with diurnal variations in surface soil temperature (Denmead *et al.*, 1979a; Ryden *et al.*, 1979; Conrad *et al.*, 1983). Sampling at 6 hour intervals gives a truer representation of daily emissions, accounting for diurnal variations (Appendix III). However, discrepancies were found between emissions measured from autochambers and those from manually sampled cover boxes (Chapter 5). The time of gas sampling is of paramount importance when taking daily samples from cover boxes, due to the effect of temperature on microbial activity and N_2O production (Bremner and Blackmer, 1981). Accordingly, in this project, whenever possible sampling was undertaken at the same time of day. However, even when such a sampling regime is employed, there is still the possibility of fluctuations in N_2O emissions between sampling times. Thus, lines on graphs joining N_2O fluxes measured at daily intervals should be regarded with caution.

Higher N_2O emissions were measured from sandy loam than from clay loam soils in a laboratory experiment to which pea and straw residues had been added (Chapter 8). This supports the contention that decomposition in aerobic sandy soils is more rapid than in fine-textured clay soils (Allison, 1973; Cerri and Jenkinson, 1981; Ladd *et al.*, 1981; Azam *et al.*, 1989), resulting in higher losses of N_2O from nitrification (Skiba *et al.*, 1993). Nitrification was considered to be predominant in dry sandy soils (Chapter 4), and in the spring and summer (Chapter 6). Low emissions of N_2O at CSCV (Chapter 7) were initially thought to have been due to the clay properties of the soil lowering the NH_4^+ available for nitrification, but the laboratory experiment (Chapter 8) did not support this hypothesis.

A selection of N_2O emissions from different cropping treatments are presented in Table 10.1, enabling the magnitude of emissions measured in this work to be placed in context with those of comparable studies. In accordance with measurements made within this work, other authors show the low background emissions from bare soil, and higher emissions from cropped legumes, fertilised crops and after incorporation of residues and grassland. Measurements made within this work fall within the range reported within the literature.

Comparisons between studies are difficult because of different sampling periods and different environmental conditions. Eichner (1990) stated that emissions from cropped legumes range from 0.34-4.6 kg N_2O-N ha^{-1} yr^{-1}. In agreement with this, annual emissions from the cropped soyabean and fababean at CSCV, near Naples, were estimated to be 0.47 and 1.07 kg N_2O-N ha^{-1} yr^{-1}, respectively. The estimated annual emission from fertilised oilseed rape crop of

Table 10.1. Emissions of N_2O (kg N_2O-N ha^{-1}) from various cropping treatments.

Crop/treatment	kg N_2O-N ha^{-1}	Time period (days)	Source
bare soil	-0.6-3.2	365	Bouwman (1996)
cultivated bare soil	0.2	365	Denmead *et al.* (1979a)
	-0.02-0.46	64	this work (Chapter 6)
soyabean	0.34-1.97	365	Bremner *et al.* (1980)
	0.14	22	this work (Chapter 7)
alfalfa	2-4.6	365	Duxbury (1984)
barley:			
fertilised with 112 kg ha^{-1} NH_4NO_3	1.04	153	Mosier *et al.* (1982)
unfertilised	0.82	153	
fertilised with 120 kg ha^{-1} NH_4NO_3	0.05	61	this work (Chapter 6)
unfertilised	0.01	61	
grass:			
fertilised with 100 kg ha^{-1} NH_4NO_3	2.38	100	Christensen (1983)
unfertilised	0.67	100	
oilseed rape:			
fertilised with 180 kg ha^{-1} NH_4NO_3	0.38	54	this work (Chapter 6)
incorporated wheat residues	9.0	365	Aulakh *et al.* (1984b)
	0.16	42	this work (Chapter 6)
incorporated straw	0.7-2.2	250	Goodroad *et al.* (1984)
incorporated alfalfa	0.3-3.2	190-200	
incorporated oilseed rape	0.36	42	this work (Chapter 6)
incorporated maize	0.62	355	Bremner *et al.* (1981)
	0.11	22	this work (Chapter 7)
incorporated grass/clover swards	3.7	48	Davies (1996)
	0.8	81	
	0.24	84	this work (Chapter 4)
incorporated Italian ryegrass	0.15	84	
incorporated trefoil	0.58	63	
incorporated lettuce (rotary tilled)	1.6	79	this work (Chapter 5)

1.1 kg N_2O-N ha^{-1} yr^{-1} was in the range of emissions detected after fertilisation. The 0.2 kg N_2O-N ha^{-1} yr^{-1} from the winter wheat was at the lower end of this range. Emissions measured after incorporation of residues and green manures also fall within the range reported.

10.2 Strategies for reducing N_2O emissions

Although the magnitude of N_2O emissions after incorporation of plant material and fertilisation of crops have been shown to vary, they may potentially be reduced by changes in farming strategies. Proposed strategies should be integrated with those to reduce production of other greenhouse gases such as CO_2 and CH_4. Required strategies will vary regionally, depending on soil type, climate, farming system and current agricultural practices. Those suggested here would be applicable to UK arable cropping systems under a temperate climate.

Where possible, incorporation of green manures and crop residues should be delayed until just before the following crop is sown. N uptake by the following crop would lower the substrate available for nitrification and denitrification thereby reducing N_2O production in the soil and retaining N within the plant-soil system. Thus, timing of incorporation in relation to establishment of the following crop is important in the spring, when soil temperatures are increasing, stimulating microbial activity and increased mineralisation (Haynes, 1986). Timing of incorporation in the autumn is also important due to increased denitrification after rainfall (Bremner and Blackmer, 1979; Sexstone *et al.*, 1985) and the potential for NO_3^- leaching (Vinten *et al.*, 1996). Extensive fallow periods between crops should be avoided, particularly in the autumn. Catch crops or green manures may be grown as an alternative to fallow land, or the following cash crop grown almost immediately.

The method of incorporation affects the magnitude of N_2O emissions (Chapter 5). A concentration of crop residues near the soil surface may result in N_2O production during denitrification and/or nitrification (Aulakh *et al.*, 1991b). This N_2O has little distance to diffuse out of the soil and into the atmosphere, and losses may be high after reduced , or shallow, cultivations. Emissions following ploughing were found to be lower. It is recommended that in order to reduce gaseous emissions all cultivations of the same field should be undertaken on the same day, and not, for example, ploughed on one day, and rotary tilled and rolled a few days later. N_2O is released from soil air after disturbance of the soil during cultivation (Matthias *et al.*, 1979), and disturbances of the soil over several days may increase immediate losses of N_2O.

Decomposition of incorporated plant material, particularly immature green manures, may contribute substantial quantities of N to the soil (McKenney *et al.*, 1993). Sarrantonio (1995) reported that 140 kg NO_3^- ha^{-1} was made available within 1 week of incorporating a green manure. However, organic N from incorporated plant material and soil reserves of N are rarely considered when fertiliser N is applied to the following crop. If incorporation of residues occurs immediately, or within a few days, prior to sowing, as recommended, then the contribution of these residues to soil N needs to be considered. This would prevent excess application of fertiliser to requirements, and reduce losses of N. Increased emissions of N_2O were measured immediately after application of N fertiliser (Chapter 6). Lower fertiliser applications would potentially reduce emissions.

Rainfall increases soil moisture contents and denitrification (Bremner and Blackmer, 1979; Sexstone *et al.*, 1985). Large emissions have been found when rainfall occurs after fertiliser application (Conrad *et al.*, 1983). To prevent such large losses fertiliser should not be applied to wet soils, particularly clays, and irrigation should not be scheduled within a few weeks following application. Split applications would appear to be a desirable option, but are not always practical. Powlson *et al.* (1992) suggested split fertiliser applications, basing the second application on the amount lost in the first 3 weeks after the first application. However, such predictions are complicated by changing weather.

Application of high C paper waste to agricultural soils has been found to reduce NO_3^- leaching as a result of increased immobilisation of soil N (Vinten *et al.*, 1996). However, it should be applied with caution as extremely large N_2O emissions were measured after ploughing of residues where paper waste had been applied to the field. Such paper waste should only be applied in systems where N can be conserved in the soil in a form available to the subsequent crop, as occurs when it is immobilised in microbial tissue.

10.3 Further work

Negative fluxes, or sinks, of N_2O were measured during field trials. These were particularly apparent from growing and incorporated crops under a Mediterranean climate (Chapter 7). Despite measurement of N_2O sinks by other authors (Ryden, 1981), the mechanisms involved, and the soil conditions associated with their occurrence, have not been identified and invite further investigation. Studies are required to measure N_2O emissions over a greater range of environmental conditions and agricultural systems than experienced in a temperate climate. Lower emissions than expected were measured at CSCV (Chapter 7), and this emphasises the importance of such studies. Losses of N_2O would be expected to be substantial under a tropical climate (Granli and Bøckman, 1994) due to the warm, wet conditions conducive to rapid mineralisation and denitrification.

The effects of simultaneous applications of both organic and inorganic N on N_2O emissions requires further investigation. Azam *et al.* (1995) found that N_2O emissions were raised after such a joint application, compared to soil where just organic or inorganic N had been applied. Availability of N from green manures with low C:N ratios was increased by applications of inorganic N, particularly as NH_4^+. This has implications for fields where incorporation of crop residues is soon followed by fertilisation of the subsequent sown crop. Any interactions between these 2 forms of N need to be examined. It is known that N applied in residues behaves differently from fertiliser derived N, as residue N is more rapidly immobilised due to the addition of C (Van Veen *et al.*, 1984). Clearly, immobilisation rates of fertiliser N may be increased in the presence of plant material (Recous *et al.*, 1990), thereby reducing immediate N_2O production.

Measurements of annual N_2O emissions from agricultural systems that include times of residue incorporation are required. To date, most annual N_2O emissions have been estimated over part of a growing season, usually after fertilisation. More long-term field trials are required that encompass seasonal variations in climate and N_2O emissions. Emissions also need to be monitored over a period of years after residue incorporation, as substantial percentages of incorporated residue N may remain in the topsoil for several years (Ladd *et al.*, 1981b, 1985). More studies are also required on diurnal variations of N_2O emissions, providing more precise estimates of daily emissions. Autochambers are suited to such studies, although reasons for discrepancies between N_2O sampled using autochambers and manual closed chambers require prior investigation. The problems of spatial variability in emissions and the interacting influence of multiple variables remain in field trials. The relative contributions of these variables may be identified in further laboratory experiments.

In future field trials, application of $^{15}NH_4NO_3$ and $NH_4{}^{15}NO_3$ as separate treatments to crops, and measurement of available ^{15}N and $^{15}N_2O$ would enable the contribution of N_2O from nitrification and denitrification to be determined, respectively. To date, their relative contributions have only been assumed, but not quantified. Emissions from trials after application of double labelled $^{15}NH_4{}^{15}NO_3$ were too low to enable analysis of $^{15}N_2O$. Applications of more highly labelled fertiliser to soil under controlled laboratory conditions would enable such analysis of $^{15}N_2O$ to be made.

Comparisons between field measurements of available N and N_2O and simulations of available N and denitrified N by various models emphasise the need for greater sensitivity when modelling soil processes, particularly mineralisation and immobilisation. Inadequate representation of the processes involved result in poor predictions. Losses of N_2O from nitrification need to be included in these models, as does representation of the microbial biomass. Calculation of denitrification requires an estimation of the degree of anaerobiosis and the effect of C supply.

REFERENCES

Addiscott, T.M. 1983. Kinetics and temperature relationships of mineralisation and nitrification in Rothamstead soils with differing histories. *Journal of Soil Science*, **34**, 343-353.

Addiscott, T.M., Bailey, N.J., Bland, G.J. and Whitmore, A.P. 1991. Simulation of nitrogen in soil and winter wheat crops: A management model that makes best use of limited information. *Fertiliser Research*, **27**, 305-312.

Aitken, M.N. and Lewis, J.G. 1994. The agronomic and environmental effects of applying paper mill sludge to agricultural land. Paper presented at European Waste and Sludge conference.

Alexander, M. 1977. *Introduction to Soil Microbiology*. Second Edition. Wiley and Sons. New York.

Allison, F.E. 1973. *Soil Organic Matter and its Role in Crop Production.* Elsevier Scientific Publishing Co., New York.

Allison, F.E., Doetsch, J.H. and Roller, E.M. 1953. Availability of fixed ammonium in soils containing different clay minerals. *Soil Science*, **75**, 373-381.

Allison, M.F. and Killham, K. 1988. Response of soil microbial biomass to straw incorporation. *Journal of Soil Science*, **39**, 237-242.

Anderson, I.C. and Levine, J.S. 1986. Relative rates of nitric oxide and nitrous oxide production by nitrifiers, denitrifiers and nitrate respirers. *Applied and Environmental Microbiology*, **51**, 938-945.

Andrén, O. 1987. Decomposition of shoot and root litter of barley, lucerne and meadow fescue under field conditions. *Swedish Journal of Agricultural Research*, **17**, 113-122.

Arah, J.R.M. 1988. Measurement and modelling of denitrification in soil. *Ph.D. Thesis, University of Edinburgh.*

Arah, J.R.M., Smith, K.A., Crichton, I.J. and Li, H.S. 1991. Nitrous oxide production and denitrification in Scottish arable soils. *Journal of Soil Science*, **42**, 351-367.

Arah, J.R.M., Crichton, I.J. and Smith, K.A. 1993. Denitrification measured directly using a single-inlet mass spectrometer and by acetylene inhibition. *Soil Biology and Biochemistry*, **25**, 233-238.

Arah, J.R.M., Crichton, I.J., Smith, K.A., Clayton, H. and Skiba, U. 1994. Automated gas chromatographic analysis system for micrometeorological measurements of trace gas fluxes. *Journal of Geophysical Research*, **99**, 16593-16598.

Armstrong, A.S.B. 1983. Nitrous oxide emissions from two sites in Southern England during winter 1981/1982. *Journal of Science, Food and Agriculture*, **34**, 803-807.

Atallah, T. and Lopez-Real, J.M. 1991. Potential of green manure species in recycling nitrogen, phosphorus and potassium. *Biological Agriculture and Horticulture*, **8**, 53-65.

Aulakh, M.S., Rennie, D.A. and Paul, E.A. 1983. The effect of various clover management practices on gaseous N losses and mineral N accumulation. *Canadian Journal of Soil Science*, **63**, 593-605.

Aulakh, M.S., Rennie, D.A. and Paul, E.A. 1984a. Acetylene and N-serve effects upon N_2O emissions from NH_4^+ and NO_3^- treated soils under aerobic and anaerobic conditions. *Soil Biology and Biochemistry*, **16**, 351-356.

Aulakh, M.S., Rennie, D.A. and Paul, E.A. 1984b. The influence of plant residues on denitrification rates in conventional and zero-tilled soils. *Soil Science Society of America Journal*, **48**, 790-794.

Aulakh, M.S., Rennie, D.A. and Paul, E.A. 1984c. Gaseous nitrogen losses from soils under zero-till as compared with conventional-till management systems. *Journal of Environmental Quality*, **13**, 130-136.

Aulakh, M.S. and Rennie, D.A. 1986. Nitrogen transformations with special reference to gaseous nitrogen losses from zero-tilled soils of Saskatchewan, Canada. *Soil and Tillage Research*, **7**, 157-171.

Aulakh, M.S., Doran, J.W., Walters, D.T. and Power, J.F. 1991a. Legume residue and soil water effects on denitrification in soils of different textures. *Soil Biology and Biochemistry*, **23**, 1161-1167.

Aulakh, M.S., Doran, J.W., Walters, D.T., Mosier, A.R. and Francis, D.D. 1991b. Crop residue type and placement effects on denitrification and mineralization. *Soil Science Society of America Journal*, **55**, 1020-1025.

Azam, F. 1990. Comparative effects of organic and inorganic nitrogen sources applied to a flooded soil on rice yield and availability of nitrogen. *Plant and Soil*, **125**, 255-262.

Azam, F., Malik, K.A. and Sajjad, M.I. 1985. Transformations in soil and availability to plants of ^{15}N applied as inorganic fertilizer and legume residues. *Plant and Soil*, **86**, 3-13.

Azam, F., Malik, K.A. and Sajjad, M.I. 1986. Uptake by wheat plants and turnover within soil fractions of residual nitrogen from leguminous plant material and inorganic fertilizer. *Plant and Soil*, **95**, 97-108.

Azam, F., Mulvaney, R.L. and Stevenson, F.J. 1989. Transformation of ^{15}N-labelled leguminous plant material in three contrasting soils. *Biology and Fertility of Soils*, **8**, 54-60.

Azam, F., Lodhi, A., Ashraf, M. 1991. Interaction of ^{15}N-labelled ammonium nitrogen with native soil nitrogen during incubation and growth of maize (*Zea mays* L.). *Soil Biology and Biochemistry*, **23**, 473-477.

Azam, F., Simmons, F.W. and Mulvaney, R.L. 1993. Mineralization of N from plant residues and its interaction with native soil N. *Soil Biology and Biochemistry*, **25**, 1787-1792.

Azam, F., Mulvaney, R.L. and Simmons, F.W. 1995. Effects of ammonium and nitrate on mineralization of nitrogen from leguminous residues. *Biology and Fertility of Soils*, **20**, 49-52.

Baggs, E.M. 1993. Effect of different cultivation systems on the physical characteristics of the seedbed. *M.Sc. Thesis, University of Nottingham.*

Bakken, L.R. 1988. Denitrification under different cultivated plants; effects of soil moisture tension, nitrate concentration and photosynthetic activity. *Biology and Fertility of Soils*, **6**, 271-278.

Bakken, L.R., Børresen, T. and Njøs, A. 1987. Effect of soil compaction by tractor traffic on soil structure, denitrification and yield of wheat. *Journal of Soil Science*, **38**, 541-552.

Baldocchi, E.D., Hicks, B.B. and Meyers, T.P. 1988. Measuring biosphere-atmosphere exchanges of biologically related gases with micrometerological methods. *Ecology*, **69**, 1331-1340.

Bartholomew, W.V. 1965. Mineralisation and immobilisation of nitrogen in the decomposition of plant and animal residues. In; W.V. Bartholomew and F.E. Clark (eds.) *Soil Nitrogen*. ASA, Madison. pp. 285-306.

Beauchamp, E.G., Trevors, J.T. and Paul, J.W. 1989. Carbon sources for bacterial denitrification. *Advances in Soil Science*, **10**, 113-142.

Beck, H. and Christensen, S. 1987. The effect of grass maturing and root decay on nitrous oxide production in soil. *Plant and Soil*, **103**, 269-273.

Best, E.K. 1976. An automated method for determining nitrate-N in soil extracts. *Queensland Agricultural Journal*, **33**, 161-165.

Bhandari, B. and Nicholas, D.J.D. 1984. Denitrification of nitrate to nitrogen gas by washed cells of *Rhizobium japonicum* and by bacteroids from *Glycine max*. *Planta*, **161**, 81-85.

Bjarnason, S., 1989. The long-term fertility experiments in southern Sweden. III. Soil carbon and nitrogen dynamics. *Acta Agriculture Scandinavia*, **39**, 361-371.

Black, C.A. 1968. *Soil-Plant Relationships*. Second edition, Wiley, New York. pp. 792.

Blackmer, A.M. and Bremner, J.M. 1976. Potential of soil as a sink for atmospheric nitrous oxide. *Geophysical Research Letters*, **3**, 739-742.

Blackmer, A.M. and Bremner, J.M. 1978. Inhibitory effect of nitrate on reduction of N_2O to N_2 by soil microorganisms. *Soil Biology and Biochemistry*, **10**, 187-191.

Blackmer, A.M., Bremner, J.M. and Schmidt, E.L. 1980. Production of nitrous oxide by ammonia-oxidizing chemoautotrophic microorganisms in soil. *Applied and Environmental Microbiology*, **40**, 1060-1066.

Blackmer, A.M., Robbins, S.G. and Bremner, J.M. 1982. Diurnal variability in rate of emission of nitrous oxide from soils. *Soil Science Society of America Journal*, **46**, 937-942.

Bouwman, A.F. 1990a. Exchange of greenhouse gases between terrestrial ecosystems and the atmosphere. In A.F. Bouwman (ed.) *Soils and the Greenhouse Effect*. Proceedings of the International Conference Soils and the Greenhouse Effect. Wiley and Sons. pp. 61-126.

Bouwman, A.F. 1990b. Soil processes involved in the production of greenhouse gases, with special relevance to soil taxonomic systems. In; A.F. Bouwman (ed.) *Soils and the Greenhouse Effect*. Proceedings of the International Conference Soils and the Greenhouse Effect. Wiley and Sons.

Bouwman, A.F. 1996. Direct emission of nitrous oxide from agricultural soils. *Nutrient Cycling in Agroecosystems*, **46**, 53-70.

Bradbury, N.J., Whitmore, A.P., Hart, P.B.S. and Jenkinson, D.S. 1993. Modelling the fate of nitrogen in crop and soil in the years following application of ^{15}N-labelled fertiliser to winter wheat. *Journal of Agricultural Science*, **121**, 363-379.

Brady, N.C. 1990. *The Nature and Properties of Soils*. Tenth Edition. Maxwell Macmillan.

Breitenbeck, G.A., Blackmer, A.M. and Bremner, J.M. 1980. Effects of different nitrogen fertilisers on emission of nitrous oxide from soil. *Geophysical Research Letters*, **7**, 85-88.

Bremner, J.M. and Shaw, K. 1958. Denitrification in soil. II. Factors affecting denitrification. *Journal of Agricultural Science*, **51**, 40-52.

Bremner, J.M. and Blackmer, A.M. 1978. Nitrous oxide: Emission from soils during nitrification of fertiliser nitrogen. *Science*, **199**, 295-296.

Bremner, J.M. and Blackmer, A.M. 1979. Effects of acetylene and soil water content on emission of nitrous oxide from soils. *Nature*, **280**, 380-381.

Bremner, J.M. and Blackmer, A.M. 1981. Terrestrial nitrification as a source of atmospheric nitrous oxide. In; C.C. Delwiche (ed.) *Denitrification, Nitrification and Atmospheric Nitrous Oxide*. John Wiley and Sons, Chichester. pp. 151-170.

Bremner, J.M., Breitenbeck, G.A. and Blackmer, A.M. 1981. Effect of nitrapyrin on emission of nitrous oxide from soil fertilised with anhydrous ammonia. *Geophysics Research Letters*, **8**, 353-356.

Bremner, J.M., Robbins, S.G. and Blackmer, A.M. 1980. Seasonal variability in emission of nitrous oxide from soil. *Geophysical Research Letters*, **7**, 641-644.

Bremner, E. and van Kessel, C. 1992. Plant available nitrogen from lentil and wheat residues during a subsequent growing season. *Soil Science Society of America Journal*, **56**, 1155-1160.

Broadbent, F.E. and Nakashima, T. 1971. Effect of added salts on nitrogen mineralisation in three California soils. *Soil Science Society of America Journal*, **35**, 457-460.

Bronson, K.F., Mosier, A.R. and Bishnoi, S.R. 1992. Nitrous oxide emissions in irrigated corn as affected by nitrification inhibitors. *Soil Science Society of America Journal*, **56**, 161-165.

Brookes, P.C., Landman, A., Pruden, G. and Jenkinson, D.S. 1985. 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**, 837-842.

Brookes, P.D., Stark, J.M. and McInteer, B.B. 1989. Diffusion method to prepare soil extracts for automated nitrogen-15 analysis. *Soil Science Society of America Journal*, **53**, 1707-1711.

Brown, P.L. and Dickey, D.D. 1970. Losses of wheat straw residue under simulated field conditions. *Soil Science Society of America Proceedings*, **34**, 118-121.

Buresh, R.J. and Patrick Jr., W.H. 1978. Nitrate reduction to ammonium in anaerobic soil. *Soil Science Society of America Journal*, **42**, 913-918.

Burford, J.R., Dowdell, R.J. and Crees, R. 1981. Emission of nitrous oxide to the atmosphere from direct-drilled and ploughed clay soils. *Journal of the Science of Food and Agriculture*, **32**, 219-223.

Byrnes, B.H. 1990. Environmental effects of N fertilizer use - an overview. *Fertiliser Research*, **26**, 209-215.

Carter, M.R. and Rennie, D.A. 1984. Dynamics of soil microbial biomass nitrogen under zero and shallow tillage for spring wheat, using ^{15}N wheat. *Plant and Soil*, **76**, 157-164.

Cassman, K.G. and Munns, D.N. 1980. Nitrogen mineralisation as affected by soil moisture, temperature and depth. *Soil Science Society of America Journal*, **44**, 1233-1237.

Cerri, C.C. and Jenkinson, D.S. 1981. Formation of microbial biomass during the decomposition of ^{14}C labelled ryegrass in soil. *Journal of Soil science*, **32**, 619-626.

Chalk, P.M. and Smith, C.J. 1983. Chemodenitrification. In; J.R. Freney and J.R. Simpson (eds.) *Gaseous Loss of Nitrogen from Plant-Soil Systems*. Dordrecht, The Netherlands. pp. 65-90.

Christensen, S. 1983. Nitrous oxide emission from a soil under permanent grass: Seasonal and diurnal fluctuations as influenced by manuring and fertilisation. *Soil Biology and Biochemistry*, **15**, 531-536.

Christensen, B.T. 1985. Wheat and barley straw decomposition under field conditions: Effect of soil type and plant cover on weight loss, nitrogen and potassium content. *Soil Biology and Biochemistry*, **17**, 691-697.

Christensen, B.T. 1986. Barley straw decomposition under field conditions: Effect of placement and initial nitrogen content on weight loss and nitrogen dynamics. *Soil Biology and Biochemistry*, **18**, 523-529.

Christensen, S, Ambus, P., Arah, J.R.M., Clayton, H., Galle, B., Griffith, D.W.T., Hargreaves, K.J., Klemedtsson, L., Lind, A.M., Maag, M., Scott, A., Skiba, U., Smith, K.A., Welling, M. And Wienhold, F.G. 1996. Nitrous oxide emission from an agricultural field: Comparisonbetween measurements by flux chamber and micrometerological techniques. *Atmospheric Environment*, **30**, 4183-4190.

Christensen, S., Simkins, S. and Tiedje, J.M. 1990. Spatial variation in denitrification: Dependency of activity centers on the soil environment. *Soil Science Society of America Journal*, **54**, 1608-1613.

Clarholm, M. 1985. Interactions of bacteria, protozoa and plants leading to mineralisation of soil nitrogen. *Soil Biology and Biochemistry*, **17**, 181-187.

Clayton, H., Arah, J.R.M. and Smith, K.A. 1994. Measurement of nitrous oxide emissions from fertilized grassland using closed chambers. *Journal of Geophysical Research*, **99**, 16599-16607.

Clayton, H., McTaggart, I.P., Parker, J., Swan, L. And Smith, K.A. 1997. Nitrous oxide emissions from fertilised grassland: A 2-year study of the effects of N fertiliser form and environmental conditions. *Biology and Fertility of Soils*, in press.

Conrad, R. and Seiler, W. 1980. Field measurements of the loss of fertiliser nitrogen into the atmosphere as nitrous oxide. *Atmospheric Environment*, **14**, 555-558.

Conrad, R., Seiler, W. and Bunse, G. 1983. Factors influencing the loss of fertiliser nitrogen into the atmosphere as nitrous oxide. *Journal of Geophysical Research*, **88**, 6709-6718.

Crooke, W.M. and Simpson, W.E. 1971. Determination of NH_4 in Kjedahl digests of crops by an automated procedure. *Journal of the Science of Food and Agriculture*, **22**, 9-10.

Crutzen, P.J. 1970. The influence of nitrogen oxides on the atmospheric ozone content. *Quaterly Journal of the Royal Meteorological Society*, **96**, 320-325.

Crutzen, P.J. 1981. Atmospheric chemical processes of the oxides of nitrogen, including nitrous oxide. In; C.C. Delwiche (ed.) *Denitrification, Nitrification and Atmospheric Nitrous Oxide*. pp. 17-44. John Wiley, New York.

Dalenberg, J.W. and Jager, G. 1989. Priming effect of some organic additions to ^{14}C-labelled soil. *Soil Biology and Biochemistry*, **21**, 443-448.

Daniel, R.M., Steele, K.W. and Limmer, A.W. 1980. Denitrification by Rhizobia. A possible factor contributing to nitrogen losses from soils. *New Zealand Journal of Agricultural Science*, **14**, 109-112.

Davidson, E.A. 1992. Sources of nitric oxide and nitrous oxide following wetting of dry soil. *Soil Science Society of America Journal*, **56**, 95-102.

Davidson, E.A., Stark, J.M. and Firestone, M.K. 1990. Microbial production and consumption of nitrate in an annual grassland. *Ecology*, **71**, 1968-1975.

Davies, M.G. 1996. The mineralisation and fate of nitrogen following the incorporation of grass and grass-clover swards. *Ph.D. Thesis, University of Edinburgh.*

Davies, R. 1995. The use of paper mill waste to reduce nitrate leaching in a nitrate sensitive area. *Undergraduate dissertation, University of Edinburgh.*

Davis, L. 1989. Green manures for growers. *The case for organic agriculture*. Proceedings of the 1989 National Conference on Organic Food Production. pp. 50-52.

de Catanzaro, J.B. and Beauchamp, E.G. 1985. The effect of some carbon substrates on denitrification rates and carbon utilization in soil. *Biology and Fertility of Soils*, **1**, 183-187.

de Catanzaro, J.B., Beauchamp, E.G. and Drury, C.F. 1987. Denitrification vs dissimilatory nitrate reduction in soil with alfalfa, straw, glucose and sulfide treatments. *Soil Biology and Biochemistry*, **19**, 583-587.

Delwiche, C.C. 1970. The nitrogen cycle. *Scientific America*, **223**, 136-146.

Delwiche, C.C. (ed.) 1981. *Denitrification, nitrification and atmospheric nitrous oxide*. Wiley and sons Ltd. Chichester.

Denmead, O.T., Freney, J.R. and Simpson, J.R. 1979a. Studies of nitrous oxide emission from a grass sward. *Soil Science Society of America Journal*, **43**, 726-728.

Denmead, O.T., Freney, J.R. and Simpson, J.R. 1979b. Nitrous oxide emission during denitrification in a flooded field. *Soil Science Society of America Journal*, **43**, 716-718.

Dixon, P.L. and Holmes, J.C. 1987. *Organic Farming in Scotland*. Edinburgh School of Agriculture in association with the Scottish International Education Trust.

Dolar, S.G., Boyle, J.R. and Keeney, D.R. 1972. Paper mill sludge disposal on soils: Effects on the yield and mineral nutrition of oats (*Avena sativa L.*). *Journal of Environmental Quality*, **1**, 405-409.

Doran, J.W. 1980. Soil microbial and biochemical changes associated with reduced tillage. *Soil Science Society of America Journal*, **44**, 765-771.

Douglas, C.L.Jr, Allmaras, R.R., Rasmussen, P.E., Ramig, R.E. and Roager, N.C.Jr. 1980. Wheat straw composition and placement effects on decomposition in dryland agriculture of the Pacific northwest. *Soil Science Society of America Journal*, **44**, 833-837.

Douglas, C.L.Jr and Rickman, R.W. 1992. Estimating crop residue decomposition from air temperature, initial nitrogen content, and residue placement. *Soil Science Society of America Journal*, **56**, 272-278.

Dowdell, R.J., Burford, J.R. and Crees, R. 1979. Losses of nitrous oxide dissolved in drainage water from agricultural land. *Nature*, **278**, 342-343.

Drury, C.F., McKenney, D.J. and Findlay, W.I. 1991. Relationships between denitrification, microbial biomass and indigenous soil properties. *Soil Biology and Biochemistry*, **23**, 751-755.

Duxbury, J.M. 1984. Factors affecting nitrous oxide production by denitrification in soils. In; V.P.Aneja (ed.) *Environmental Impact of Natural Emissions*. Air Pollution Control Association. Pittsburgh.

Duxbury, J.M., Bouldin, D.R., Terry, R.E. and Tate, R.L. 1982. Emissions of nitrous oxide from soils. *Nature*, **298**, 462-464.

Duxbury, J.M. and McConnaughey, P.K. 1986. Effect of fertiliser source on denitrification and nitrous oxide emisssions in a maize-field. *Soil Science Society of America Journal*, **50**, 644-648.

Eichner, M.J. 1990. Nitrous oxide emission from fertilised soils: Summary of available data. *Journal of Environmental Quality*, **19**, 272-280.

Faris, M.A., Smith, D.C. and Coulman, B.E. 1986. Plow down effects of different forage legume species, cultivars, cutting strategies and seeding rates on the yields of subsequent crops. *Plant and Soil*, **95**, 419-430.

Firestone, M.K. 1982. Biological denitrification. In; F.J. Stevenson (ed.) *Nitrogen in Agricultural Soils*. ASA, CSSA, SSSA, Madison, Wisconsin. pp. 289-326.

Firestone M.K. and Davidson, E.A. 1989. Microbial basis of NO and N_2O production and consumption in soil. In; M.O. Andreae and D.S. Schimel (eds.) *Exchange of Trace Gases between Terrestrial Ecosystems and the Atmosphere*. Wiley and Sons Ltd. pp 7-21.

Firestone, M.K., Firestone, R.B. and Tiedje, J.M. 1980. Nitrous oxide from soil denitrification: Factors controlling its biological production. *Science*, **208**, 749-751.

Focht, D.D. 1974. The effect of temperature, pH and aeration on the production of nitrous oxide and gaseous nitrogen - a zero kinetic model. *Soil Science*, **118**, 173-179.

Focht, D.D. 1982. Denitrification. In; R.G. Burns and J.H. Slater (eds.) *Experimental Microbial Ecology*. Blackwell Scientific, Oxford. pp. 194-211.

Focht, D.D., Stolzy, L.H. and Meek, B.D. 1979. Sequential reduction of nitrate and nitrous oxide under field conditions as brought about by organic amendments and irrigation management. *Soil Biology and Biochemistry*, **11**, 37-46.

Folorunso, O.A. and Rolston, D.E. 1985. Spatial and spectral relationships between field-measured denitrification gas fluxes and soil properties. *Soil Science Society of America Journal*, **49**, 1087-1093.

Fox, R.H., Myers, R.J.K. and Vallis, I. 1990. The nitrogen mineralization rate of legume residues in soil as influenced by their polyphenol, lignin and nitrogen contents. *Plant and Soil*, **129**, 251-259.

Frame, J. and Newbould, P. 1986. Agronomy of white clover. *Advances in Agronomy*, **40**, 1-88.

Frankenberger, W.T. Jr. and Abdelmagid, H.M. 1985. Kinetic parameters of nitrogen mineralization rates of leguminous crops incorporated into soil. *Plant and Soil*, **87**, 257-271.

Fredrickson, J.K., Koehler, F.E. and Cheng, H.H. 1982. Availability of ^{15}N-labeled nitrogen in fertilizer and in wheat straw to wheat in tilled and no-till soil. *Soil Science Society of America Journal*, **46**, 1218-1222.

Freney, J.R., Denmead, O.T. and Simpson, J.R. 1978. Soil as a source or sink for atmospheric nitrous oxide. *Nature*, **273**, 530-532.

Freney, J.R., Denmead, O.T. and Simpson, J.R. 1979. Nitrous oxide emission from soils at low moisture contents. *Soil Biology and Biochemistry*, **11**, 167-173.

Galbally, I.E. 1994. The role of legume pasture in greenhouse gas emissions from Australia. *Final Report of RIRDC Project CSD-47A*.

Galle, B., Klemedtsson, L. and Griffith, D.W.T. 1994. Application of a Fourier transform IR system for measurements of N_2O fluxes using micrometerological methods, an ultralarge chamber system and conventional field chambers. *Journal of Geophysical Research*, **99**, 16575-16583.

Goodroad, L.L. and Keeney, D.R. 1984. Nitrous oxide production in aerobic soils under varying pH, temperature and water content. *Soil Biology and Biochemistry*, **16**, 39-43.

Goodroad, L.L. and Keeney, D.R. 1985. Site of nitrous oxide production in field soils. *Biology and Fertility of Soils*, **1**, 3-7.

Goodroad, L.L., Keeney, D.R. and Peterson, L.A. 1984. Nitrous oxide emissions from agricultural soils in Wisconsin. *Journal of Environmental Quality*, **13**, 557-561.

Goreau, T.J., Kaplan, W.A., Wofsy, S.C., McElroy, M.B., Valois, F.W. and Watson, S.W. 1980. Production of nitrite and nitrous oxide by nitrifying bacteria at reduced concentrations of oxygen. *Applied Environmental Microbiology*, **40**, 526-532.

Goss, M.J., Howse, K.R. and Harris, W. 1978. Effects of cultivation on soil water retention and water use by cereals in clay soils. *Journal of Soil Science*, **29**, 475-488.

Goulding, K.W.T., Webster, P., Powlson, D.S. and Poulton, P.R. 1993. Denitrification losses of nitrogen fertilizer applied to winter wheat following ley and arable rotations as estimated by acetylene inhibition and ^{15}N balance. *Journal of Soil Science*, **44**, 63-72.

Granli, T. and Bøckman, O.C. 1994. Nitrous oxide from agriculture. *Norwegian Journal of Agricultural Sciences*, supplement **12**.

Granstedt, A. 1995. The mobilization and immobilization of soil nitrogen after green-manure crops at three locations in Sweden. In; H.F. Cook and H.C. Lee. *Soil Management in Sustainable Agriculture*. Wye College Press. pp. 265-275.

Greenwood, D.J. 1986. Prediction of nitrogen fertiliser needs of arable crops. *Advances in Plant Nutrition*, **2**, 1-61.

Greenwood, D.J., Rahn, C., Draycott, A., Vaidyanathan, L.V. and Paterson, C. 1996. Modelling and measurement of the effects of fertiliser-N and crop residue incorporation on N-dynamics in vegetable cropping. *Soil Use and Management*, **12**, 13-24.

Groffman, P.M. 1985. Nitrification and denitrification in conventional and nc tillage soils. *Soil Science Society of America Journal*, **49**, 329-334.

Groffman, P.M. 1991. Ecology of nitrification and denitrification in soil evaluated at scales relevant to atmospheric chemistry. In; J.E.Rogers and W.B.Whitman (eds.) *Microbial Production and Consumption of Greenhouse Gases: Methane, Nitrogen Oxides and Halomethanes*. American Society for Microbiology, Washington, D.C. pp. 201-217.

Groffman, P.M., Hendrix, P.F. and Crossley, D.A. Jr. 1987. Nitrogen dynamics in conventional and no-tillage agroecosystems with inorganic fertilizer or legume nitrogen inputs. *Plant and Soil*, **97**, 315-332.

Groffman, P.M. and Tiedje, J.M. 1991. Relationships between denitrification, CO_2 production and air-filled porosity in soils of different texture and drainage. *Soil Biology and Biochemistry*, **23**, 299-302.

Grundmann, G.L., Rolston, D.E., Kachanoski, R.G. 1988. Field soil properties influencing the variability of denitrification gas fluxes. *Soil Science Society of America Journal*, **52**, 1351-1355.

Hahn, J. and Crutzen, P.J. 1981. The role of fluxed nitrogen in atmospheric photochemistry. *Proceedings of the Royal Society of London, B*, **196**, 219-240.

Hansen, S., Maeklum, J.E. and Bakken, L.R. 1993. N_2O and CH_4 fluxes in soil influenced by fertilisation and tractor traffic. *Soil Biology and Biochemistry*, **25**, 621-630.

Hansson, A.C., Andrèn, O., Boström, S., Boström, U., Clarholm, M., Lagerlöf, J., Lindberg, T., Paustian, K., Pettersson, R. and Sohlenius, B. 1990. Structure of the agroecosystem. *Ecological Bulletins*, **40**, 41-83.

Harper, S.H.T. 1988. Straw decomposition. In; Drew, R.D. and Smith, B.D. (eds.) *Changing Straw Disposal Practices*. HGCA research review, **11**, pp. 12-14.

Harper, S.H.T. and Lynch, J.M. 1981. The chemical components and decomposition of wheat straw leaves, internodes and nodes. *Journal of the Science of Food and Agriculture*, **32**, 1057-1062.

Hart, P.B.S., Rayner, J.H. and Jenkinson, D.S. 1986. Influence of pool substitution on the interpretation of fertilizer experiments with ^{15}N. *Journal of Soil Science*, **37**, 389-403.

Hauck, R.D. and Bremner, J.M. 1976. Use of tracers for soil and fertiliser nitrogen research. *Advances in Agronomy*, **28**, 219-266.

Hauck, R.D. and Tanji, K.K. 1982. Nitrogen transfers and mass balances. In; F.J. Stevenson (ed.) *Nitrogen in Agricultural Soils*. American Society of Agronomy. pp. 891-925.

Haynes, R.J. 1986. Nitrification. In; R.J. Haynes, and F.L. Orlando (eds.) *Mineral Nitrogen in the Plant-Soil System*. Academic Press, New York. pp. 127-165.

Heal, O.W., Anderson, J.M., Swift, M.J. 1997. Plant litter quality and decomposition: An historical overview. In; G. Cadisch and K.E. Giller (eds.) *Driven By Nature. Plant Litter Quality and Decomposition*. pp. 3-30.

Houghton, J.T., Jenkins, G.J., and Ephraums, J.J. 1990. *Climate Change: The IPCC Scientific Assessment*. Cambridge University Press.

Iritani, W.M. and Arnold, C.Y. 1960. Nitrogen release of vegetable crop residues during incubation as related to their chemical composition. *Soil Science*, **89**, 74-82.

Jansson, M.D., Elliott, L.F., Papendick, R.I. and Campbell, G.S. 1989. The decomposition of ^{14}C-labeled wheat straw and ^{15}N-labeled microbial material. *Soil Biology and Biochemistry*, **21**, 417-422.

Jansson, P.E. and Halldin, S. 1979. As quoted by; Johnsson, H., Bergström, L., Jansson, P.E. and Paustian, K. 1987. Simulated nitrogen dynamics and losses in a layered agricultural soil. *Agriculture, Ecosystems and Environment*, **18**, 333-356.

Jansson, S.L. 1971. Use of ^{15}N in studies of soil nitrogen. In; A.D. McLaren and T. Skujins (eds.) *Soil Biochemistry*, **2**, 129-166.

Jansson, S.L. and Clark, F.E. 1952. Losses of nitrogen during decomposition of plant material in the presence of inorganic nitrogen. *Soil Science Society of America Proceedings*, **16**, 330-334.

Jansson, S.L. and Persson, J. 1982. Mineralisation and immobilisation of soil nitrogen. In; F.J. Stevenson (ed.) *Nitrogen in Agricultural Soils*. American society of Agronomy. pp. 229-252.

Janzen, H.H. and Kucey, R.M.N. 1988. C, N and S mineralization of crop residues as influenced by crop species and nutrient regime. *Plant and Soil*, **106**, 35-41.

Jarvis, S.C., Barraclough, D., Williams, J. and Rook, A.J. 1991. Patterns of denitrification loss from grazed grassland: Effects of N fertiliser inputs at different sites. *Plant and Soil*, **131**, 77-88.

Jenkinson, D.S. 1977a. Studies on the decomposition of plant material in soils. IV. The effect of rate of addition. *Journal of Soil Science*, **28**, 417-423.

Jenkinson, D.S. 1977b. Studies on the decomposition of plant material in soil. V. The effects of plant cover and soil type on the loss of carbon from ^{14}C labelled ryegrass decomposing under field conditions. *Journal of Soil Science*, **28**, 424-434.

Jenkinson, D.S. 1981. The fate of plant and animal residues in soils. In; D.J. Greenland and M.H.B. Hayes (eds.) *The Chemistry of Soil Processes*. Wiley and Sons, Chichester. pp. 505-562.

Jenkinson, D.S. 1984. The supply of nitrogen from the soil. In; *The Nitrogen Requirement of Cereals*. MAFF reference book 385. HMSO, London. pp. 79-92.

Jenkinson, D.S. 1988. Determination of microbial biomass carbon and nitrogen in soil. In; J.R. Wilson (ed.) *Advances in Nitrogen Cycling in Agricultural Ecosystems*. Wallingford: CAB International. pp. 368-386.

Jenkinson, D.S., Fox, R.H. and Rayner, J.H. 1985. Interactions between fertilizer nitrogen and soil nitrogen - the so-called 'priming' effect. *Journal of Soil Science*, **36**, 425-444.

Jenkinson, D.S. and Ladd, J.N. 1981. Microbial biomass in soil: Measurement and turnover. In; Paul, E.A. and Ladd, J.N. (eds.) *Soil Biochemistry*. Marcel Dekker, New York. pp. 415-471.

Johnsson, H., Bergström, L., Jansson, P.E. and Paustian, K. 1987. Simulated nitrogen dynamics and losses in a layered agricultural soil. *Agriculture, Ecosystems and Environment*, **18**, 333-356.

Johnsson, H., Klemedtsson, L., Nilsson, Å. and Svensson, B.H. 1991. Simulation of field scale denitrification losses from soils under grass ley and barley. *Plant and Soil*, **138**, 287-302.

Juma, M.G. and Paul, E.A. 1984. Mineralisable soil nitrogen: Amounts and extractability ratios. *Soil Science Society of America Journal*, **48**, 76-80.

Jury, W.A., Letey, J. and Collins, T. 1982. Analysis of chamber methods used for measuring nitrous oxide production in the field. *Soil Science Society of America Journal*, **46**, 250-256.

Keeney, D.R., Fillery, I.R. and Marx, G.P. 1979. Effect of temperature on the gaseous nitrogen products of denitrification in a silt loam soil. *Soil Science Society of America Journal*, **43**, 1124-1128.

Khalil, M.A.K. and Rasmussen, R.A. 1992. The global sources of nitrous oxide. *Journal of Geophysical Research*, **97**, 14651-14660.

Kilian, S. and Werner, D. 1996. Enhanced denitrification in plots of N_2-fixing faba beans compared to plots of a non-fixing legume and non-legumes. *Biology and Fertility of Soils*, **21**, 77-83.

King, L.D. 1984. Availability of nitrogen in municipal, industrial and animal wastes. *Journal of Environmental Quality*, **13**, 609-612.

Klemedtsson, L., Svensson, B.H. and Rosswall, T. 1987. Dinitrogen and nitrous oxide produced by denitrification and nitrification in soil with and without barley plants. *Plant and Soil*, **99**, 303-319.

Knapp, E.B., Elliott, L.F. and Campbell, G.S. 1983. Carbon, nitrogen and microbial biomass interrelationships during the decomposition of wheat straw: A mechanistic simulation model. *Soil Biology and Biochemistry*, **15**, 455-461.

Kolenbrander C.J. (1972). Eutrophication from agriculture with special reference to fertilisers and animal waste. In; *Effects of Intensive Fertiliser Use on the Human Environment*. FAO Soils Bulletin no. 16, Rome. pp. 305-327. As quoted by Legg and Meisinger, 1982.

Koskinen, W.C. and Keeney, D.R. 1982. Effects of pH on the rate of gaseous production of denitrification in a silt loam soil. *Soil Science Society of America Journal*, **46**, 1165-1167.

Kowalenko, C,G, and Cameron, D.R. 1978. Nitrogen transformations in soil-plant systems on three years of field experiments using tracer and non-tracer methods on an ammonium fixing soil. *Canadian Journal of Soil Science*, **58**, 195-208.

Ladd, J.N. and Amato, M. 1986. The fate of nitrogen from legume and fertilizer sources in soils successively cropped with wheat under field conditions. *Soil Biology and Biochemistry*, **18**, 417-425.

Ladd, J.N., Amato, M. and Oades, J.M. 1985. Decomposition of plant material in Australian soils. III. Residual organic and microbial biomass C and N from isotope-labelled legume material and soil organic matter decomposing under field conditions. *Australian Journal of Soil Research*, **23**, 603-611.

Ladd, J.N., Amato, M., Jackson, R.B. and Butler, J.H.A. 1983. Utilization by wheat crops of nitrogen from legume residues decomposing in soils in the field. *Soil Biology and Biochemistry*, **15**, 231-238.

Ladd, J.N., Oades, J.M. and Amato, M. 1981a. Microbial biomass formed from ^{14}C, ^{15}N-labelled plant material decomposing in soils in the field. *Soil Biology and Biochemistry*, **13**, 119-126.

Ladd, J.N., Oades, J.M. and Amato, M. 1981b. Distribution and recovery of nitrogen from legume residues decomposing in soils sown to wheat in the field. *Soil Biology and Biochemistry*, **13**, 251-256.

Lalisse-Grundmann, G., Brunel, B. and Chalamet, A. 1988. Denitrification in a cultivated soil: Optimal glucose and nitrate concentrations. *Soil Biology and Biochemistry*, **20**, 839-844.

Lampkin, N. 1990. *Organic Farming*. Farming Press.

Legg, J.O. and Meisinger, J.J.1982. Soil nitrogen budgets. In; F.J. Stevenson (ed.) *Nitrogen in Agricultural Soils*. pp. 503-566. American Society of Agronomy.

Linden, B. and Wallgren, B. 1993. Nitrogen mineralization after leys ploughed in early or late autumn. *Swedish Journal of Agricultural Research*, **23**, 77-89.

Linn, D.M. and Doran, J.W. 1984. Effect of water-filled pore space on carbon dioxide and nitrous oxide production in tilled and nontilled soils. *Soil Science Society of America Journal*, **48**, 1267-1272.

Lipschultz, F., Zafiriou, O.C., Wofsy, S.C., McElroy, M.B., Valois, F.W. and Watson, S.W. 1981. Production of NO and N_2O by soil nitrifying bacteria. *Nature*, **294**, 641-643.

Little, T.M. and Hills, F.J. 1978. Agricultural experimentation. *Design and Analysis*. Wiley, New York.

Löhnis, F. 1926. Nitrogen availability of green manure. *Soil Science*, **22**, 253-290.

Lynch, J.M. and Panting, L.M. 1980. Cultivation and the soil biomass. *Soil Biology and Biochemistry*, **12**, 29-33.

Macdonald, A.J., Powlson, D.S., Poulton, P.R. and Jenkinson, D.S. 1989. Unused fertilizer nitrogen in arable soils - its contribution to nitrate leaching. *Journal of the Science of Food and Agriculture*, **46**, 407-419.

Macdonald, R.McL. 1986. Nitrification in soil: An introductory history. In; J.I. Prosser (ed.) *Nitrification*. IRL Press, Oxford. pp. 1-16.

MacRae, R.J. and Mehuys, G.R. 1985. The effect of green manuring on the physical properties of temperate-area soils. *Advances in Soil Science*, **3**, 71-94.

Magalhães, A.M.T., Chalk, P.M. and Strong, W.M. 1984. Effect of nitrapyrin on nitrous oxide emission from fallow soils fertilized with anhydrous ammonia. *Fertiliser Research*, **5**, 411-421.

Marschner, H. 1995. *Mineral Nutrition of Higher Plants*. Second Edition. Academic Press.

Martinez, J. and Guiraud, G. 1990. A lysimeter study of the effects of a ryegrass catch crop during a winter wheat/maize rotation, on nitrate leaching and on the following crop. *Journal of Soil Science*, **41**, 5-16.

Marumoto, T., Anderson, J.P.E. and Domsch, K.H. 1982. Mineralization of nutrients from soil microbial biomass. *Soil Biology and Biochemistry*, **14**, 469-475.

Matthias, A.D., Blackmer, A.M. and Bremner, J.M. 1979. Diurnal variability in the concentration of nitrous oxide in surface air. *Geophysical Research Letters*, **6**, 441-443.

Matthias, A.D., Blackmer, A.M. and Bremner, J.M. 1980. A simple chamber technique for field measurement of emissions of nitrous oxide from soils. *Journal of Environmental Quality*, **9**, 251-256.

McBeth, I.G. 1917. Fixation of ammonium by soils. *Journal of Agricultural Research*, **9**, 141-155.

McElroy, M.B. and Wofsy, S.C. 1985. Nitrous oxide sources and sinks. In; *World Meteorological Organization, Atmospheric Ozone*, **1**. NASA, Washington D.C. pp. 81.

McKenney, D.J., Shuttleworth, K.F. and Findlay, W.I. 1980. Nitrous oxide evolution rates from fertilized soil: Effects of applied nitrogen. *Canadian Journal of Soil Science*, **60**, 429-438.

McKenney, D.J., Wang, S.W., Drury, C.F. and Findlay, W.I. 1993. Denitrification and mineralization in soil amended with legume, grass and corn residues. *Soil Science Society of America Journal*, **57**, 1013-1020.

McKenney, D.J., Wang, S.W., Drury, C.F. and Findlay, W.I. 1995. Denitrification, immobilisation and mineralisation in nitrate limited and nonlimited residue-amended soil. *Soil Science Society of America Journal*, **59**, 118-124.

McLean, E.O. 1982. Soil pH and lime requirement. In; A.L.Page (ed.) *Methods of Soil Analysis. Part 2*. American Society of Agronomy, Madison. pp. 199-224.

McTaggart, I.P., Clayton, H., Parker, J., Swan, L. And Smith K.A. 1997. Nitrous oxide emissions from grassland and spring barley following N fertiliser application with and without nitrification inhibitors. *Biology and Fertility of Soils*. In Publication.

McTaggart, I., Clayton, H. and Smith, K. 1994. Nitrous oxide flux from fertilised grassland: Strategies for reducing emissions. In; Van Ham, J. *et al.* (eds.) *Non CO_2 Greenhouse Gases*. Kluwer Academic Publishers. pp. 421-426.

McTaggart, I.P. and Smith, K.A. 1996. Nitrous oxide emissions from arable and grassland soils: Effects of crop type and nitrification inhibitors. In; *Transactions of the 9th Nitrogen Workshop*. pp. 523-526.

Melin, J. and Nômmik, H. 1983. Denitrification measurements in intact soil cores. *Acta Agricultura Scandinavica*, **33**, 145-151.

Meyers, R.J.K. and Paul, E.A. 1971. Plant uptake and immobilisation of ^{15}N-labeled ammonium nitrate in a field experiment with wheat. In; *Nitrogen-15 in Soil-Plant Studies*. International Atomic Energy Agency, Vienna. pp. 55-64.

Millington, S. 1989. Green manures for growers. *The Case for Organic Agriculture*. Proceedings of the 1989 National Conference on Organic Food. pp. 48-50.

Mosier, A.R. 1990. Gas flux measurement techniques with special reference to techniques suitable for measurements over large ecological uniform areas. In; A.F. Bouwman (ed.) *Soils and the Greenhouse Effect*. John Wiley and sons, Chichester. pp. 289-301.

Mosier, A.R. 1994. Nitrous oxide emissions from agricultural soils. *Fertiliser Research*, **37**, 191-200.

Mosier, A.R., Guenzi, W.D. and Schweizer, E.E. 1986. Soil losses of dinitrogen and nitrous oxide from irrigated crops in North Eastern Colorado. *Soil Science Society of America Journal*, **50**, 344-348.

Mosier, A.R. and Hutchinson, G.L. 1981. Nitrous oxide emissions from cropped fields. *Journal of Environmental Quality*, **10**, 169-173.

Mosier, A.R., Hutchinson, G.L., Sabey, B.R. and Baxter, J. 1982. Nitrous oxide emissions from barley plots treated with ammonium nitrate or sewage sludge. *Journal of Environmental Quality*, **11**, 78-81.

Mosier, A.R., Parton, W.J. and Hutchinson, G.L. 1983. Modelling nitrous oxide evolution from cropped and native soils. *Environmental Biogeochemistry Ecological Bulletin*, **35**, 229-241.

Müller, M.M., Sundman, V., Soininvaara, O. and Merilainen, A. 1988. Effect of chemical composition on the release of nitrogen from agricultural plant materials decomposing in soil under field conditions. *Biology and Fertility of Soils*, **6**, 78-83.

Mulvaney, R.L. and Kurtz, L.T. 1982. A new method for determination of ^{15}N-labelled nitrous oxide. *Soil Science Society of America Journal*, **46**, 1178-1184.

Mulvaney, R.L. and Vanden Heuvel, R.M. 1988. Evaluation of nitrogen-15 tracer techniques for direct measurement of denitrification in soil: IV. Field studies. *Soil Science Society of America Journal*, **52**, 1332-1337.

Muzio, L.J., Teague, M.E., Kramlich, J.C., Cole, J.A., McCarthy, J.M. and Lyon, R.K. 1989. Errors in grab sample measurements of N_2O from combustion sources. *Journal of Air Pollution Control Association*, **39**, 287-293.

Myrold, D.D. 1988. Denitrification in ryegrass and winter wheat cropping systems of Western Oregon. *Soil Science Society of America Journal*, **52**, 412-416.

Nicolardot, B. 1988. Behaviour of newly immobilised nitrogen in three agricultural soils after addition of organic carbon substrates. In; Jenkinson, D.S. and Smith, K.A. (eds.) *Nitrogen Efficiency in Agricultural Soils*. Elsevier Applied Science, London. pp. 340-354.

Nicolardot, B., Denys, D., Lagacherie, B., Cheneby, D. and Mariotti, M. 1995. Decomposition of ^{15}N-labelled catch-crop residues in soil: Evaluation of N mineralisation and plant N uptake potentials under controlled conditions. *European Journal of Soil Science*, **46**, 115-123.

Nômmik, H. 1956. Investigations on denitrification in soil. *Acta Agricultura Scandinavica*, **6**, 195-228.

Norman, R.J. and Gilmour, J.T. 1987. Utilization of anhydrous ammonia fixed by clay minerals and soil organic matter. *Soil Science Society of America Journal*, **51**, 959-962.

Olson, R.A. and Kurtz, L.T. 1982. Crop nitrogen requirements, utilisation and fertilisation. In; F.J. Steveson (ed.) *Nitrogen in Agricultural Soils*. American Society of Agronomy. pp. 503-566.

Olson, R.V., Murphy, L.S., Moser, H.C. and Swallow, C.W. 1979. Fate of tagged fertilizer nitrogen applied to winter wheat. *Soil Science Society of America Journal*, **43**, 973-975.

Palm, C.A. and Sanchez, P.A. 1991. Nitrogen release from some tropical legumes as affected by lignin and polyphenol contents. *Soil Biology and Biochemistry*, **23**, 83-88.

Parker, D.T. 1962. Decomposition in the field of buried and surface applied cornstalk residue. *Soil Science Society of America Proceedings*, **26**, 559-562.

Parkin, T.B. 1987. Soil microsites as a source of denitrification variability. *Soil Science Society of America Journal*, **51**, 1194-1199.

Parkin, T.B. and Robinson, J.A. 1993. Statistical evaluation of median estimators for lognormally distributed variables. *Soil Science Society of America Journal*, **57**, 317-323.

Parkin, T.B., Sexstone, A.J. and Tiedje, J.M. 1985. Comparison of field denitrification rates determined by acetylene-based soil core and nitrogen-15 methods. *Soil Science Society of America Journal*, **49**, 94-99.

Parsons, J.W. 1984. Green manuring. *Outlook on Agriculture*, **13**, 20-23.

Paterson, J. 1995. Report on the analysis of papermill sludge for GB Papers Ltd, Guardbridge, Fife. Central Analytical Laboratory, SAC, Edinburgh.

Patrick, W.H. 1982. Nitrogen transformations in submerged soils. In; F.J. Stevenson (ed.) *Nitrogen in Agricultural Soils*. American Society of Agronomy. pp. 449-466.

Patten, D.K., Bremner, J.M. and Blackmer, A.M. 1980. Effects of drying and air-dry storage of soils on their capacity for denitrification of nitrate. *Soil Science Society of America Journal*, **44**, 67-70.

Paul, E.A. 1984. Dynamics of organic matter in soils. *Plant and Soil*, **76**, 275-284.

Paul, J.W. and Beauchamp, E.G. 1989. Denitrification and fermentation in plant-residue-amended soil. *Biology and Fertility of Soils*, **7**, 303-309.

Payne. W.J. 1981. The status of nitric oxide and nitrous oxide as intermediates in denitrification. In; C.C. Delwiche (ed.) *Denitrification, Nitrification and atmospheric Nitrous Oxide. John Wiley and sons*. New York. pp. 85-103.

Peoples, M.B. and Craswell, E.T. 1992. Biological nitrogen fixation: investments, expectations and actual contributions to agriculture. *Plant and Soil*, **141**, 13-39.

Power, J.F. and Broadbent, F.E. 1989. Proper accounting for N in cropping systems. In; *Developments in Agricultural and Managed-Forest Ecology*, **21**, Managing nitrogen for ground water protection. pp. 160-182.

Powlson, D.S. 1988. Measuring and minimising losses of fertilizer nitrogen in arable agriculture. In; D.S. Jenkinson and K.A. Smith (eds.) *Nitrogen Efficiency in Agricultural Soils*. Elsevier, London. pp. 231-245.

Powlson, D.S., Brookes, P.C. and Christensen, B.T. 1987. Measurement of soil microbial biomass provides an early indication of changes in total soil organic matter due to straw incorporation. *Soil Biology and Biochemistry*, **19**, 159-164.

Powlson, D.S., Hart, P.B.S., Poulton, P.R., Johnston, A.E. and Jenkinson, D.S. 1992. Influence of soil type, crop management and weather on the recovery of ^{15}N-labelled fertilizer applied to winter wheat in spring. *Journal of Agricultural Science*, **118**, 83-100.

Powlson, D.S., Pruden, G., Johnston, A.E. and Jenkinson, D.S. 1986. The nitrogen cycle in the Broadbalk wheat experiment: Recovery and losses of ^{15}N-labelled fertiliser applied in spring and inputs of nitrogen from the atmosphere. *Journal of Agricultural Science*, **107**, 591-609.

Praag, van H.J., Fischer, V. and Riga, A. 1980. Fate of fertiliser nitrogen applied to winter wheat as $Na^{15}NO_3$ and $(^{15}NH4)_2SO_4$ studied in micrplots through a four-course rotation. 2. Field ammonium turnover and nitrogen reversion. *Soil Science*, **130**, 100-105.

Prather, M., Derwent, R., Ehhault, D., Fraser, P., Sanhueza, E. and Zhou, X. 1995. Other trace gases and atmospheric chemistry. In; J.T. Houghton *et al.* (eds.) *Climate Change 1994; radiative forcing of climate change and an evaluation of the IPCC IS92 Emission Scenarios*. Cambridge University Press. pp. 77-126.

Pruden, G., Powlson, D.S. and Jenkinson, D.S. 1985. The measurement of ^{15}N in soil and plant material. *Fertiliser Research*, **6**, 205-218.

Rahn, C., Vaidyanathan, L.V. and Paterson, C.D. 1992. Nitrogen residues from brassica crops. *Aspects of Applied Biology*, **30**, 263-270.

Rao, K.P. and Rains, D.W. 1976. Nitrate absorption by barley. 1. Kinetics and energetics. *Plant Physiology*, **57**, 55-58.

Rayns, F.W. and Lennartsson, E.K.M. 1995. The nitrogen dynamics of winter green manures. In; H.F. Cook and H.C. Lee (eds.) *Soil Management in Sustainable Agriculture*. Wye College Press. pp. 308-311.

Recous, S., Mary, B. and Faurie, G. 1990. Microbial immobilisation of ammonium and nitrate in cultivated soils. *Soil Biology and Biochemistry*, **22**, 913-922.

Redman, M.H., Wigglesworth, S.A. and Vinten, A.J.A. 1988. Nitrogen dynamics of a leguminous green manure. Proceedings of ISWA/DAKOFA/AVC Seminar on *Nitrogen in Organic Wastes Aplied to Soils*, Aalborg, Denmark.

Rees, R.M., Baggs, E.M., Castle, K., Scott, A., Smith, K.A. and Vinten, A.J.A. 1997. Nitrous oxide emissions and changes in microbial biomass after cultivation of vegetable crop residues. In composition.

Rees, R.M., Yan, L. and Ferguson, M. 1993. The release and plant uptake of nitrogen from some plant and animal manures. *Biology and Fertility of Soils*, **15**, 285-293.

Reinertsen, S.A., Elliott, L.F., Cochran, V.L. and Campbell, G.S. 1984. Role of available carbon and nitrogen in determining the rate of wheat straw decomposition. *Soil Biology and Biochemistry*, **16**, 459-464.

Rice, C.W. and Smith, M.S. 1982. Denitrification in no-till and plowed soils. *Soil Science Society of America Journal*, **46**, 1168-1173.

Rice, C.W. and Smith, M.S. 1984. Short-term immobilisation of fertiliser nitrogen at the surface of no-till and plowed soils. *Soil Science Society of America Journal*, **48**, 295-297.

Robertson, G.P. 1993. Fluxes of nitrous oxide and other nitrogen trace gases from intensively managed landscapes: A global perspective. In; *Agricultural Ecosystem Effects on Trace Gases and Global Climate Change*. ASA Special Publication 55. pp. 95-108.

Robertson, L.A. and Kuenen, J.G. 1991. Physiology of nitrifying and denitrifying bacteria. In; J.E. Rogers and W.B. Whitman (eds.) *Microbial Production and Consumption of Greenhouse Gases: Methane, Nitrogen Oxides and Halomethanes. American Society for Microbiology*. Washington, D.C. pp. 189-199.

Robinson, D., Griffiths, B., Ritz, K. and Wheatley, R. 1989. Root-induced nitrogen mineralisation: A theoretical analysis. *Plant and Soil*, **117**, 185-193.

Robinson, D. and Smith, K.A. 1991. Analysis of nitrogen isotope ratios by mass spectroscopy. In; Smith, K.A. (ed.) *Soil Analysis*. Marcel Dekker, New York. pp. 465-503.

Rolston, D.E., Fried, M. and Goldhamer, D.A. 1976. Denitrification measured directly from nitrogen and nitrous oxide gas fluxes. *Soil Science Society of America Journal*, **40**, 259-266.

Rolston, D.E., Hoffman, D.L. and Toy, D.W. 1978. Field measurement of denitrification. 1. Flux of nitrogen and nitrous oxide. *Soil Science Society of America Journal*, **42**, 863-869.

Rolston, D.E., Sharpley, A.N., Toy, D.W. and Broadbent, F.E. 1982. Field measurement of denitrification. 3. Rates during irrigation cycles. *Soil Science Society of America Journal*, **46**, 289-296.

Ross, S.M. 1990. Soil processes altered by ploughing and drainage. In, *Soil Processes: A Systemstic Approach*. pp. 232-265. Longmans, London.

Rosswall, T. 1976. The internal nitrogen cycle between micro-organisms, vegetation and soil. In; B.H. Svensson and R. Söderlund (eds.) *Nitrogen, Phosphorus and Sulfur-Global Cycles*. pp. 157-167.

Royal Society 1983. *The Nitrogen Cycle of the United Kingdom: A Study Group Report*. The Royal Society, London.

Russell, E.W. 1973. *Soil Conditions and Plant Growth*. Tenth Edition. Longmans, London.

Ryden, J.C. 1981. N_2O exchange between a grassland soil and the atmosphere. *Nature*, **292**, 235-236.

Ryden, J.C. and Lund, L.J. 1980. Nature and extent of directly measured denitrification losses from some irrigated vegetable crop production units. *Soil Science Society of America Journal*, **44**, 505-511.

Ryden, J.., Lund, L.J., Letey, J. and Focht, D.D. 1979. Direct measurement of denitrification loss from soils. 2. Development and application of field methods. *Soil Science Society of America Journal*, **43**, 110-118.

SAC. 1993. *Fertiliser Series No. 5 Recommendations for Cereals: Nitrogen*. Technical Note.

Sahrawat, K.L. and Keeney, D.R. 1986. Nitrous oxide emission from soils. *Advances in Soil Science*, **4**, 103-148.

Sain, P. and Broadbent, F.E. 1977. Decomposition of rice straw in soils as affected by some management factors. *Journal of Environmental Quality*, **6**, 96-100.

Sarrantonio, M. 1995. Microbial activity and nitrogen dynamics following a winter annual green manure. In; H.F. Cook and H.C. Lee (eds.) *Soil Management in Sustainable Agriculture*. Wye College Press. pp. 300-307.

Scherer, H.W. 1993. Dynamics and availability of the non-exchangeable NH_4-N - a review. *European Journal of Agronomy*, **2**, 149-160.

Schmidt, E.L. 1982. Nitrification in soil. In; F.J. Stevenson (ed.) *Nitrogen in Agricultural Soils*. ASA, CSSA,SSSA. Madison, Wisconsin. pp. 253-288.

Schnürer, J., Clarholm, M., Boström, S. and Rosswall, T. 1986. Effects of moisture on soil microorganisms and nematodes: A field experiment. *Microbial Ecology*, **12**, 217-230.

Scholefield, D., Garwood, E.A. and Titchen, N.M. 1988. The potential of management practices for reducing losses of nitrogen from grazed pastures. In; D.S. Jenkinson and K.A. Smith (eds.) *Nitrogen Efficiency in Agricultural Soils*. Elsevier, London. pp. 220-231.

Scholefield, D., Lockyer, D.R., Whitehead, D.C. and Tyson, K.C. 1991. A model to predict transformations and losses of nitrogen in UK pastures. *Plant and Soil*, **132**, 165-177.

Schomberg, H.H., Steiner, J.L. and Unger, P.W. 1994. Decomposition and nitrogen dynamics of crop residues: Residue quality and water effects. *Soil Science Society of America Journal*, **58**, 372-381.

Seiler, W. and Conrad, R. 1981. Field measurements of natural and fertiliser induced N_2O release rates from soils. *Journal of Air Pollution Control Association*, **31**, 767-772.

Sexstone, A.J., Parkin, T.B., Tiedje, J.M. 1985. Temporal response of soil denitrification rates to rainfall and irrigation. *Soil Science Society of America Journal*, **49**, 99-103.

Shen, S.M., Hart, P.B.S., Powlson, D.S. and Jenkinson, D.S. 1989. The nitrogen cycle in the broadbalk wheat experiment: ^{15}N-labelled fertilizer residues in the soil and in the soil microbial biomass. *Soil Biology and Biochemistry*, **21**, 529-533.

Shields, J.A., Paul, E.A., Lowe, W.E. and Parkinson, D. 1973. Turnover of microbial tissue in soil under field conditions. *Soil Biology and Biochemistry*, **5**, 753-764.

Skiba, U., Hargreaves, K.J., Fowler, D. and Smith, K.A. 1992. Fluxes of nitric and nitrous oxides from agricultural soils in a cool temperate climate. *Atmospheric Environment*, **26A**, 2477-2488.

Skiba, U., Smith, K.A. and Fowler, D. 1993. Nitrification and denitrification as sources of nitric oxide and nitrous oxide in a sandy loam soil. *Soil Biology and Biochemistry*, **25**, 1527-1536.

Smith, C.J., Wright, M.F. and Patrick, W.H. Jr. 1983. The effect of soil redox potential and pH on the reduction and production of nitrous oxide. *Journal of Environmental Quality*, **12**, 186-188.

Smith, G.B. and Smith, M.S. 1986. Symbiotic and free-living denitrification by Bradyrhizobium japonicum. *Soil Science Society of America Journal*, **50**, 349-354.

Smith, K.A. and Arah, J.R.M. 1990. Losses of nitrogen by denitrification and emissions of nitrogen oxides from soils. *The Fertiliser Society Proceedings*, **299**, London.

Smith, K.A., Clayton, H., Arah, J.R.M., Christensen, S., Ambus, P., Fowler, D., Hargreaves, K.J., Skiba, U., Harris, G.W., Wienhold, P.G., Klemedtsson, L. And Galle, B. 1994. Micrometeorological and chamber methods for measurement of nitrous oxide fluxes between soils and the atmosphere: Overview and emissions. *Journal of Geophysical Research*, **99**, 16541-16548.

Smith, K.A., Clayton, H., McTaggart, I.P., Thomson, P.E., Arah, J.R.M. and Scott, A. 1995. The measurement of nitrous oxide emissions from soil by using chambers. *Philosophical Transactions of the Royal Society, London, A*, **351**, 327-338.

Smith, K.A., Scott, A., Galle, B. and Klemedtsson, L. 1994. Use of a long-path infrared gas monitor for measurement of nitrous oxide from soil. *Journal of Geophysical Research*, **99**, 16585-16592.

Smith, M.S., Frye, W.W. and Varco, J.J. 1987. Legume winter cover crops. *Advances in Soil Science*, **7**, 95-139.

Smith, M.S. and Tiedje, J.M. 1979. The effects of roots on soil denitrification. *Soil Science Society of America Journal*, **43**, 951-955.

Smith, S.J., Power, J.F., Kemper, W.D. and Sharpley, A.N. 1995. The exchangeability of fixed ammonium in soils. In; H.F. Cook and H.C. Lee (eds.) *Soil Management in Sustainable Agriculture*. Wye College Press. pp. 290-292.

Smith, S.J. and Sharpley, A.N. 1990. Soil nitrogen mineralization in the presence of surface and incorporated crop residues. *Agronomy Journal*, **82**, 112-116.

Soil Survey of Scotland. 1982a. 7 South-East Scotland. Macaulay Institute for Soil Reserach, Aberdeen.

Soil Survey of Scotland. 1982b. 5 Eastern Scotland. Macaulay Institute for Soil Reserach, Aberdeen.

Sørensen, L.H. 1979. Decomposition of straw in soil after stepwise repeated additions. *Soil Biology and Biochemistry*, **11**, 23-29.

Sørenson, L.H. 1982. Mineralisation of organically bound nitrogen in soil as influenced by plant growth and fertilisation. *Plant and Soil*, **65**, 51-61.

Staley, T.E., Caskey, W.H. and Boyer, D.G. 1990. Soil denitrification and nitrification potentials during the growing season relative to tillage. *Soil Science Society of America Journal*, **54**, 1602-1608.

Stanford, G. and Epstein, E. 1974. Nitrogen mineralization - water relations in soils. *Soil Science Society of America Proceedings*, **38**, 103-107.

Stanford, G., Legg, J.O., Dzienia, S, and Simpson Jr., E.C. 1975. Denitrification and associated nitrogen transformations in soils. *Soil Science*, **120**, 147-152.

Stefanson, R.C. 1972. Soil denitrification in sealed soil-plant systems. I. Effect of plants, soil water content and soil organic matter content. *Plant and Soil*, **37**, 113-127.

Stevens, R.J., Laughlin, R.J., Atkins, G.J. and Prosser, S.J. 1993. Automated determination of nitrogen-15-labelled dinitrogen and nitrous oxide by mass spectrometry. *Soil Science Society of America Journal*, **57**, 981-988.

Stevenson, F.J. 1982. Organic forms of nitrogen. In; F.J. Stevenson (ed.) *Nitrogen in Agricultural Soils*. ASA, CSSA, SSSA. Madison, Wisconsin. pp. 67-122.

Stockdale, E.A., Rees, R.M. and Davies, M.G. 1995. Nitrogen supply for organic cereal production in Scotland. In; H.F. Cook and H.C. Lee (eds.) *Soil Management in Sustainable Agriculture*. Proceedings of the Third international Conference on Sustainable Agriculture. Wye College, 1993. pp. 254-264.

Stott, D.E., Elliott, L.F., Papendick, R.I. and Campbell, G.S. 1986. Low temperature or low water effects on microbial decomposition of wheat residue. *Soil Biology and Biochemistry*, **18**, 577-582.

Stott, D.E., Stroo, H.F., Elliott, L.F., Papendick, R.I. and Unger, P.W. 1990. Wheat straw loss from fields under no-till management. *Soil Science Society of America Journal*, **54**, 92-98.

Svensson, B.H., Klemedtsson, L., Simpkins, S., Paustian, K. and Rosswall, T. 1991. Soil denitrification in three cropping systems characterised by differences in nitrogen and carbon supply. I. Rate-distribution frequencies, comparison between systems and seasonal nitrogen losses. *Plant and Soil*, **138**, 257-271.

Swift, M.J., Heal, O.W. and Anderson, J.M. 1979. *Decomposition in Terrestrial Ecosystems*. Studies in Ecology 5, Blackwell, Oxford.

Tanji, K.K. 1982. Modelling of the soil nitrogen cycle. In; F.J. Stevenson (ed.) *Nitrogen in Agricultural Soils*. ASA, CSSA,SSSA. Madison, Wisconsin. pp. 721-772.

Tiedje, J.M. (1988). Ecology of denitrification and dissimilatory nitrate reduction to ammonium. In; A.J.B. Zehnder (ed.) *Biology of Anaerobic Microorganisms*. Wiley, New York. pp. 179-244.

Van Cleemput, O., Van Hoorde, J. and Vermoesen, A. 1992. As quoted by Granli, T. and Bøckman, O.C. 1994. Nitrous oxide from agriculture. *Norwegian Journal of Agricultural Sciences*, supplement **12**.

Van Cleemput, O., Vermoesen, A., De Groot, C.J. and Van Ryckeghem, K. 1994. Nitrous oxide emission out of grassland. *Environmental Monitoring and Assessment*, **31**, 145-152.

Van Veen, J.A., Ladd, J.N. and Frissel, M.J. 1984. Modelling C and N turnover through the microbial biomass in soil. *Plant and Soil*, **76**, 257-274.

Varco, J.J., Frye, W.W., Smith, M.S. and Mackown, C.T. 1989. Tillage effects on nitrogen recovery by corn from a nitrogen-15 labeled legume cover crop. *Soil Science Society of America Journal*, **53**, 822-827.

Varco, J.J., Frye, W.W., Smith, M.S. and Mackown, C.T. 1993. Tillage effects on legume decomposition and transformation of legume and fertilizer nitrogen-15. *Soil Science Society of America Journal*, **57**, 750-756.

Vigil, M.F., and Kissel, D.E. 1991. Equations for estimating the amount of nitrogen mineralised from crop residues. *Soil Science Society of America Journal*, **55**, 757-761.

Vinten, A.J.A., Davies, R., Castle, K. and Baggs, E.M. 1996. Control of nitrate leaching from a nitrate vulnerable zone. *Transactions of the 9th Nitrogen Workshop*. pp 365-368.

Vinten, A.J.A. and Smith, K.A. 1993. Nitrogen cycling in agricultural soils. In; Burt, T.P., Heathwaite, A.L. and Trudgill, S.T. (eds.) *Nitrate: Processes, Patterns and Management*. John Wiley and Sons Ltd. pp. 39-73.

Vinther, F.P. 1984. Total denitrification and the ratio between N_2O and N_2 during the growth of spring barley. *Plant and Soil*, **76**, 227-232.

Vinther, F.P. 1992. Measurements and simulated denitrification activity in a cropped sandy and loamy soil. *Biology and Fertility of Soils*, **14**, 43-48.

Voroney, R.P. and Paul, E.A. 1984. Determination of Kc and Kn in situ for calibration of the chloroform fumigation-incubation method. *Soil Biology and Biochemistry*, **16**, 9-14.

Vos, G.J.M., Bergevoet, I.M.J., Védy, J.C. and Neyroud, J.A. 1994. The fate of spring applied fertilizer N during the autumn-winter period: Comparison between winter fallow and green manure cropped soil. *Plant and Soil*, **160**, 201-213.

Wade, M.K. and Sanchez, P.A. 1983. Mulching and green manure applications for continuous crop production in the Amazon basin. *Agronomy Journal*, **75**, 39-45.

Wagger, M.G. 1989. Time of dessication effects on plant composition and subsequent nitrogen release from several winter annual cover crops. *Agronomy Journal*, **81**, 236-241.

Wagger, M.G., Kissel, D.E. and Smith, S.J. 1985a. Uniformity of nitrogen-15 enrichment in different plant parts and subsequent decomposition monitoring of labeled crop residues. *Soil Science Society of America Journal*, **49**, 1205-1208.

Wagger, M.G., Kissel, D.E. and Smith, S.J. 1985b. Mineralization of nitrogen from nitrogen-15 labeled crop residues under field conditions. *Soil Science Society of America Journal*, **49**, 1220-1226.

Wallace, J.M. and Elliott, L.F. 1979. Phytotoxins from anaerobically decomposed wheat straw. *Soil Biology and Biochemistry*, **11**, 325-330.

Wallgren, B. and Lindén, B. 1991. Residual nitrogen effects of green manure crops and fallow. *Swedish Journal of Agricultural Research*, **21**, 67-77.

Wang, W.C., Yung, Y.L., Lacis, A.A., Mo, T. and Hansen, J.E. 1976. Greenhouse effects due to man-made perturbations of trace gases. *Science*, **194**, 685-690.

Webster, C.P. and Dowdell, R.J. 1982. Nitrous oxide emission from permanent grass swards. *Journal of the Science of Food and Agriculture*, **33**, 227-230.

Webster, C.P. and Goulding, K.W.T. 1989. Influence of soil carbon content on denitrification from fallow land during autumn. *Journal of the Science of Food and Agriculture*, **49**, 131-142.

Weeraratna, C.S. 1979. Pattern of nitrogen release during decomposition of some green manures in a tropical alluvial soil. *Plant and Soil*, **53**, 287-294.

Westerman, R.L. and Tucker, T.C. 1974. Effect of salts plus nitrogen-15-labelled ammonium chloride in mineralisation of soil nitrogen, nitrification and immobilisation. *Soil Science Society of America Proceedings*, **38**, 602-605.

Whitehead, D.C., Bristow, A.W. and Lockyer, D.R. 1990. Organic matter and nitrogen in the unharvested fractions of grass swards in relation to the potential for nitrate leaching after ploughing. *Plant and Soil*, **123**, 39-49.

Wijler, J. and Delwiche, C.C. 1954. Investigations on the denitrifying process in soil. *Plant and Soil*, **5**, 155-169.

Wild, A. 1988. Plant nutrients in soil:Nitrogen. In; A. Wild (ed.) *Russell's Soil Conditions and Plant Growth*. 11th edition. Longman, Harlow. pp. 652-694.

Wild, A. and Jones, L.H.P. 1988. Mineral nutrition of crop plants. In; A. Wild (ed.) *Russell's Soil Conditions and Plant Growth*. 11th edition. Longman, Harlow. pp. 69-112.

Williams, S., Atkinson, D. and Sinclair, A. 1995. The effect of past soil management on the release of nitrogen from a green manure. In; H.F. Cook and C.L. Howard (eds.) *Soil Management in Sustainable Agriculture*. Wye College Press. pp. 597-502.

Willison, T.W. and Anderson, J.M. 1991. Dicyandiamide as an inhibitor of denitrification in coniferous forest soils. *Soil Biology and Biogeochemistry*, **23**, 605-607.

Wilson, D.O. and Hargrove, W.L. 1986. Release of nitrogen from crimson clover residue under two tillage systems. *Soil Science Society of America Journal*, **50**, 1251-1254.

Wojcik-Wojtkowiak, D. 1978. Nitrogen transformations in soil during humification of straw labelled with ^{15}N. *Plant and Soil*, **49**, 49-55.

Yaacob, O. and Blair, G. 1980. Mineralization of ^{15}N-labelled legume residues in soils with different nitrogen contents and its uptake by rhodes grass. *Plant and Soil*, **57**, 237-248.

Yoshida, T. and Alexander, M. 1970. Nitrous oxide formation by *Nitrosomonas europaea* and heterotrophic microorganisms. *Soil Science Society of America Proceedings*, **34**, 880-882.

Zibilske, L.M. 1987. Dynamics of nitrogen and carbon in soil during papermill sludge decomposition. *Soil Science*, **143**, 26-33.

APPENDIX I

Nitrous Oxide Emissions from Soil Incorporation of Crop Residues

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Abstract

The practice of incorporating plant residues may significantly contribute to emissions of nitrous oxide (N_2O) from agricultural systems. Field trials were undertaken on two experimental sites in Scotland; a sandy loam and a loamy sand. At the first site, N_2O emissions were compared after incorporation of different varieties of Italian ryegrass, and different mixes of grass/clover varieties. At the second site comparisons of N_2O emissions were made between five different crop residues - white clover, mustard, oats, trefoil and forage peas. These emissions were related to measurements of soil available N, temperature and gravimetric soil moisture content. Short-lived fluxes of N_2O occurred immediately after incorporation of residues at both sites. The greatest emissions of 23 g N_2O-N ha^{-1} d^{-1} occurred after incorporation of the grass/clover trial, and were positively correlated with a rise in air temperature ($r=0.5$, $p<0.01$). Soil available N increased throughout the experiments; the greatest increases being at the second experimental site.

Introduction

Previous work has shown that emissions of N_2O after incorporation of plant residues may make a significant contribution to emissions from agricultural systems (Aulakh *et al.* 1983 and Ryden *et al.* 1979). Such addition of degradable organic material enhances microbial activity, leading to oxygen consumption, and the development of anaerobic microsites in the soil. The decomposition of plant residues can also lead to N_2O production as a result of nitrification. Such N_2O emissions are of concern since it has been estimated to contribute to 5 % of greenhouse warming (Van Breemen and Feitjel, 1990). Nitrous oxide also destroys stratospheric ozone through the formation of NO (Sahrawat and Keeney, 1986). Granli and

Bøckman (1994) state that it is not at present possible to make a precise estimate of the global N_2O production from agricultural land given that there are too few field measurements, with widely variable results, and an incomplete coverage of potentially important areas and sources. This work compares emissions after incorporation of different types of crop residues, including both legumes and non legumes, and considers the importance of various controlling soil environmental variables.

Sites, materials and methods

Sites and treatments

Two experimental sites were used. The first site, was a sandy loam at the Edinburgh School of Agriculture's experimental farm on the Bush estate, where two trials were established. The second was a loamy sand at Aldroughty estate, near Elgin, north-east Scotland. At Bush comparisons were made following the incorporation of different varieties of Italian ryegrass and grass/clover swards in a blocked experimental design. *Augusta*, *85/22*, *Bab 424* varieties of Italian ryegrass, and *Menna*, *Kent*, and *Huia* varieties of clover were included in the trials on plots of 5 m by 1.2 m. The grass/clover swards had been cut 6 times throughout the growing season in an attempt to simulate grazing.

At Aldroughty Estate an overwintering trial of various green manures had been set up which included white clover, mustard, oats, trefoil and forage peas. The residues of these crops were incorporated in the spring on replicated plots (12 x 3.65 m). Bare fallow soil, both with and without weeds, was also included in this comparison.

At both sites crop residues were ploughed into the soil, and followed by rotary tillage. The plots were sown to barley at Bush and oats at Aldroughty, and rolled. Ploughing took place on 6 April (Julian day 96) and rotary tillage, sowing and rolling on 28 April (Julian day 118) at Bush. At Aldroughty all cultivation was undertaken on 14 April (Julian day 104).

Nitrous oxide measurements

Circular chambers of 40 cm diameter by 20 cm height were inserted 5 cm into the soil on each plot. Gas samples were taken from these chambers both prior to and periodically following cultivation. The chambers were closed with an airtight lid for a known period of time (1 hour), after which samples were taken. These samples were analysed for their N_2O content by gas chromatography using an electron capture detector in the laboratory. Measurements of air temperature were made at the time of gas sampling.

Mineral N

Monthly determinations of available NH_4^+ and NO_3^- were made by soil extraction using 1 M KCl in a 1:5 soil:solution ratio. Extracts were filtered and NO_3^- and NH_4^+ determined by continuous flow analysis. Gravimetric soil moisture contents were also determined at monthly intervals.

Results and discussion

Nitrous oxide

Short-lived fluxes of N_2O occurred immediately after rotary tillage in both trials at the Bush estate (Fig.1). Ploughing alone appeared to have little or no effect on emissions. Maximum N_2O emissions at Julian days 121 and 124 were greater on the grass/clover trial than the Italian ryegrass trial, obtaining values of 23 and 14 g N_2O-N ha^{-1} d^{-1} respectively. This may have been due to a lower C:N ratio of the clover residues, stimulating microbial activity.

These N_2O fluxes were positively correlated with a rise in air temperature ($r=0.5$, $p<0.01$ on the grass/clover plots, and $r=0.3$, $p<0.001$ on the ryegrass plots), but not with soil moisture content. All varieties of Italian ryegrass showed weaker correlations with air temperature than varieties of grass/clover mix. The sudden rise in temperature from 4 to 15 °C on Julian day 120 coincided with the greatest N_2O emissions. This created some difficulty in separating the effects of rotary tillage and temperature. The gravimetric soil moisture contents correlated poorly with N_2O emissions ($r=0.06$, $p<0.01$ for grass/clover; $r=0.1$, $p<0.01$ for ryegrass), suggesting that temperature is a more significant variable for gaseous emissions.

Nitrous oxide emissions were less pronounced following residue incorporation at Aldroughty Estate (Fig.2), with no significant difference between treatments. A minor flux of N_2O occurred on all treatments immediately after incorporation. The greatest emissions of 14 g N_2O-N ha^{-1} d^{-1} were from the fallow - weeds plots on Julian day 116, but this was very short-lived. Cultivation did not appear to have a large effect on emissions, confirming the importance of temperature. The peak N_2O emission of 14 g N_2O-N ha^{-1} d^{-1} on day 140 corresponded with a rise in temperature from 11 to 12 °C at this site. The temperature correlated strongly with N_2O emissions throughout the sampling period ($r=0.8$, $p<0.01$).

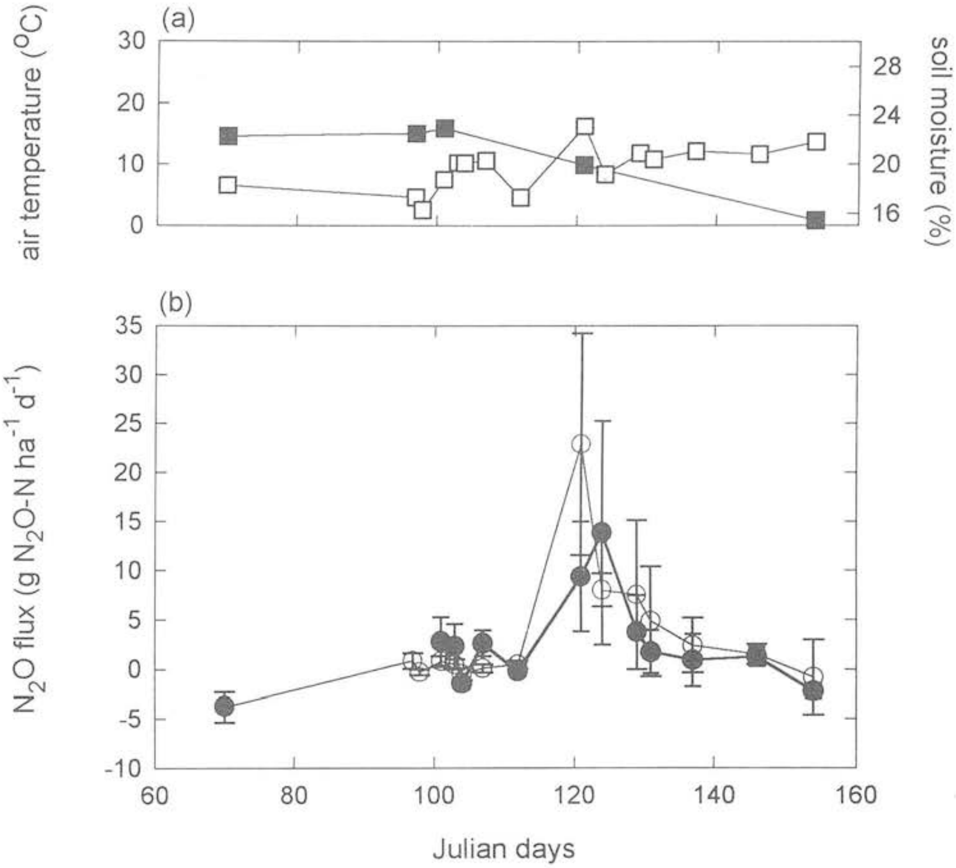

Figure 1. (a) Air temperature (empty squares), soil moisture content (filled squares) (b) N_2O emissions after incorporation of grass/clover swards (empty circles) and Italian ryegrass (filled circles) at Bush Estate.

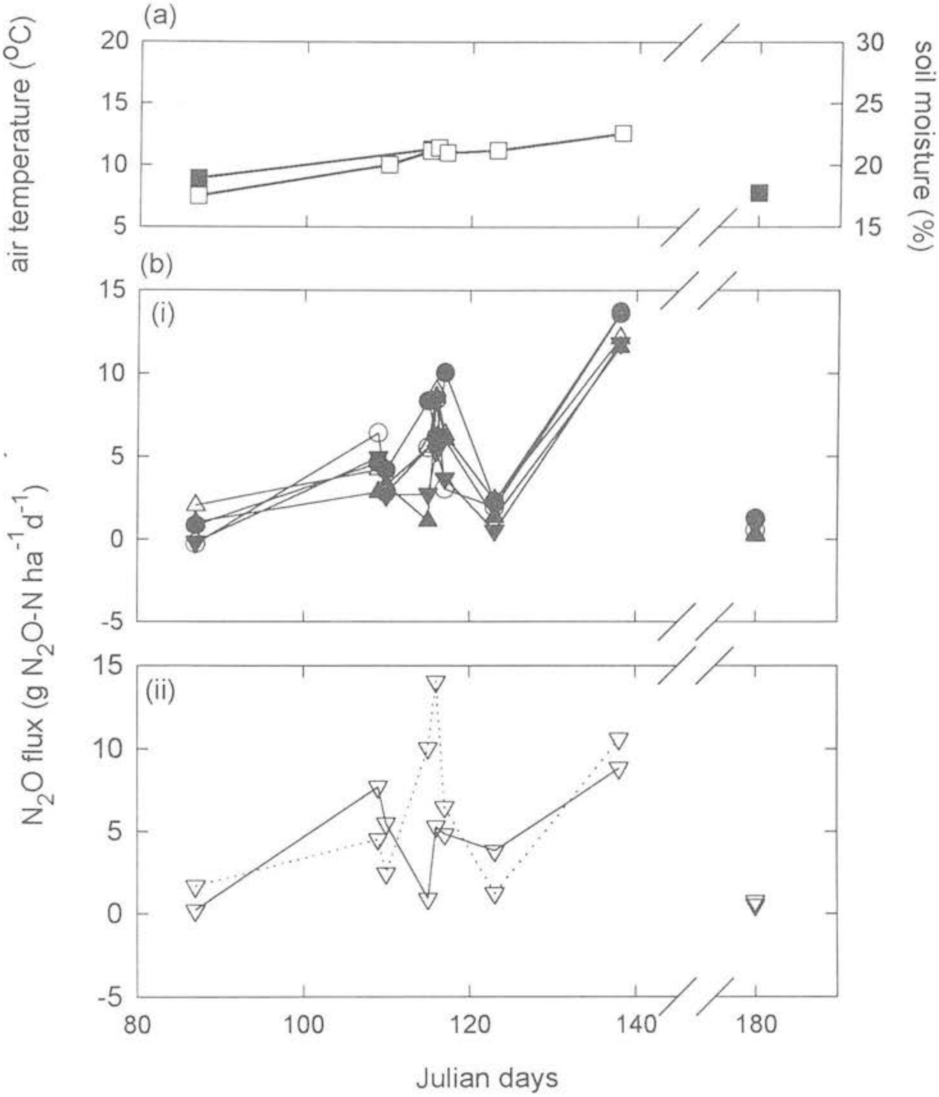

Figure 2. (a) Air temperature (empty squares), soil moisture content (filled squares) (b) N_2O emissions following (i) incorporation of trefoil (filled circles), forage pea (empty circles), mustard (upward filled triangles), white clover (upward empty triangle), oats (downward filled triangles (ii) cultivation of fallow + weeds (solid line) and fallow - weeds (dotted line) treatments at Aldroughty Estate.

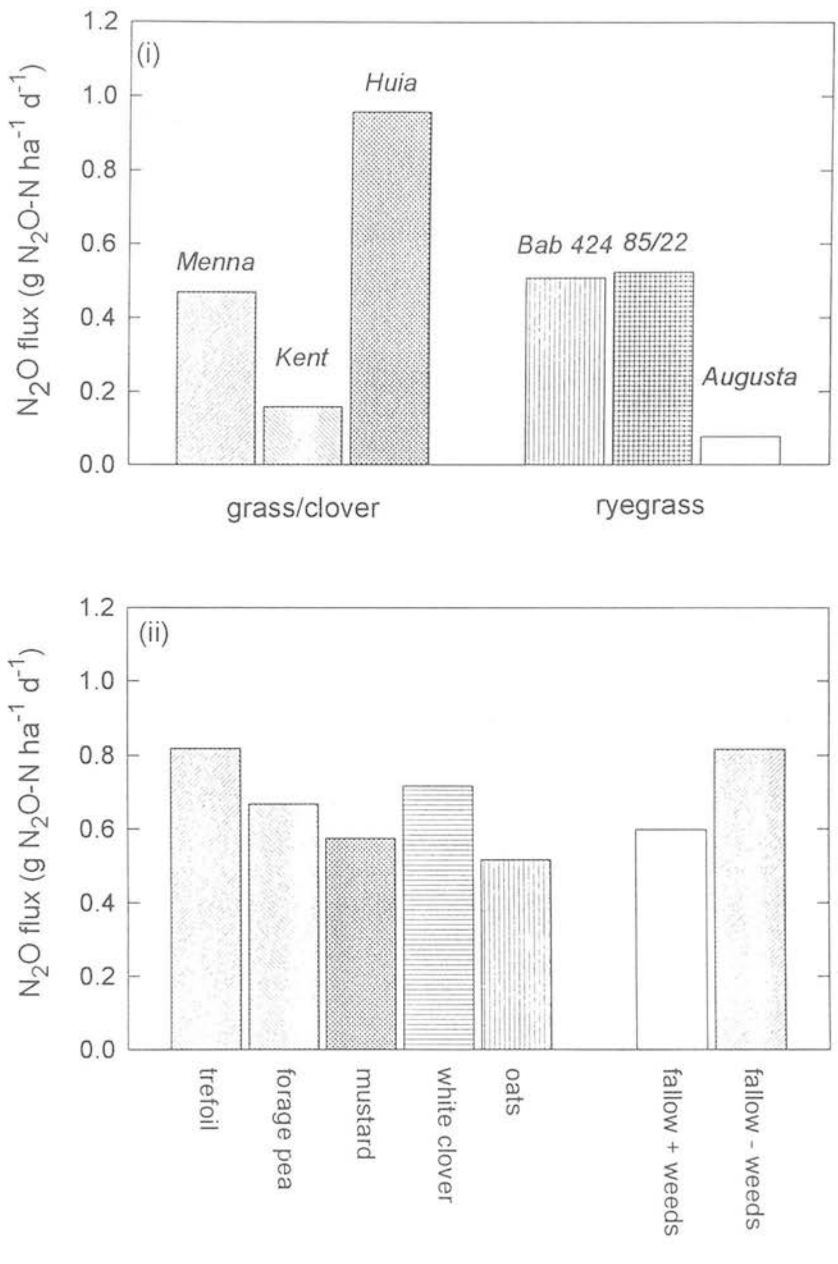

Figure 3. Mean daily N_2O over sampling period at (i) Bush Estate, (ii) Aldroughty Estate.

The mean daily N_2O emissions from both sites (Fig.3.) show that the greatest total emissions over the sampling period resulted from the incorporation of the *Huia* variety of clover. Incorporation of *Augusta* resulted in the lowest emissions from the two trials at the Bush Estate. Nitrous oxide emissions from the various crop residues at Aldroughty Estate were relatively similar (Fig. 3).

Mineral N

The available N concentrations of the soils increased in all plots during the sampling period from April until June, with largest increases following the incorporation of crop residues at Aldroughty Estate. The greatest increase in available NO_3^--N from 3 to 15 μg N g soil^{-1} occurred on the fallow + weeds treatment, with available NH_4^+-N increasing from 0.5 to 12 μ g N g soil^{-1}. Available NH_4^+-N on the trefoil plots increased from 1 to 16 μg N g soil^{-1} over this period.
At the Bush estate the largest increases in available N were found on the grass/clover trial, with increases of available NO_3^--N from 1 μg g soil^{-1} to 11 μg N g soil^{-1}, and available NH_4^+-N from 2 μg N g soil^{-1} to 4 μg N g soil^{-1}.

Nitrous oxide may be released from soils as a product of either nitrification or denitrification (Bremner and Blackmer, 1981). The relative contributions of these two processes to the N_2O fluxes in these trials are unquantifiable without the use of selective nitrification inhibitors, or ^{15}N methodology. However, the work presented here suggests the importance of nitrification as a source of N_2O emission, and further process based studies will be undertaken to verify this.

Acknowledgements

Funding for this work was provided by the Ministry of Agriculture, Fisheries and Food, Scottish Natural Heritage, and the Scottish Office Agriculture and Fisheries Department.

References

Aulakh, M. S., Rennie, D. A. and Paul, E. A. 1983. The effect of various clover management practices on gaseous N losses and mineral N accumulation. *Canadian Journal of Soil Science*, **63**, 593-605.

Bremner, J. M. and Blackmer, A. M. 1981. Terrestrial nitrification as a source of atmospheric nitrous oxide. In; *Denitrification, Nitrification and Atmospheric Nitrous Oxide*. C. C. Delwiche (ed.). pp 151-170. Wiley and Sons.

Granli, T. and Bøckman, O. C. 1994. Nitrous oxide in agriculture. *Norwegian Journal of Agricultural Sciences*, supplement 12.

Ryden, J. C., Lund, L. J., Letey, J. and Focht, D. D. 1979. Direct measurement of denitrification loss from soils II Development and application of field methods. *Soil Science. Society of America Journal*, **43**, 110-118.

Sahrawat, K. L. and Keeney, D. R. 1986. Nitrous oxide emissions from soils. *Advances in Soil Science*, **4**, 103-148.

Van Breemen, N. and Feijtel, T. C. J. 1990. Soil processes involved in the production of greenhouse gases, with special relevance to soil taxonomic systems. In; A. F. Bouwman (ed.). *Soils and the Greenhouse Effect. Proceedings of the International Conference Soils and the Greenhouse Effect*. pp 195-223. Wiley and Sons.

APPENDIX II

The Fate of Nitrogen from Incorporated Crop Residues

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In; D. Younie (ed.). 1996. *Legumes in Sustainable Farming Systems, BGS Occasional Symposium no. 30*. pp. 113-118.

Introduction

Nitrogen is the most important plant nutrient in cropping systems, but is subject to leaching and gaseous losses. The return of N to a following crop is important in any agricultural system, but particularly in organic systems where mineralisation of incorporated crop residues makes N available for crop uptake. However, substantial losses of N may occur after residue incorporation particularly where the soil remains fallow between crops. The growth of cover crops over winter between arable crops reduces such losses and supplies N from mineralisation of their incorporated residues (Jackson *et al.*, 1993). Annual green manure crops, particularly legumes, are grown specifically for the purpose of enriching the soil by their incorporation and retain N within the system (Parsons, 1984). They are grown for a complete summer growing season and ploughed down prior to sowing the subsequent arable crop.

This study was designed to assess the fate of N from incorporated crop residues, including cover crops and green manures, and availability of this N for crop uptake. The effect of crop growth on soil mineral nitrogen was investigated, as was mineralisation potential, nitrous oxide production and subsequent crop yield after residue incorporation.

Sites, materials and methods

Two field trials were undertaken at Woodside Organic Unit, Aldroughty Estate, near Elgin in Morayshire. The first trial comparing winter cover crops was established in August 1992, and the second trial comparing green manures was established in April 1993.

Winter cover crops

This experiment was of a replicated four block design. Treatments of grazing rye (*Secale cereale* cv. Humbolt at 250 kg ha^{-1}), forage rape (*Brassica napus* var. *oleifera* cv. Emerald at 8 kg ha^{-1}), winter peas (*Pisum sativum* cv. Froidure at 250 kg ha^{-1}), Italian ryegrass (*Lolium multiflorum* cv. Atalja at 35 kg ha^{-1}), winter barley (*Hordeum sativum* cv. Manitou at 250 kg ha^{-1}), winter wheat (*Triticum aestivum* cv. Mercia at 250 kg ha^{-1}), white mustard (*Sinapis alba* cv. Albatross at 15 kg ha^{-1}), fodder radish (*Raphanus sativus* var. *campestris* cv. Siletta Nova at 13 kg ha^{-1}), fallow and bare fallow (kept plant free using a propane gas burner) were established in autumn 1992, ploughed down and sown to spring oat (*Avena sativa* cv. Dula) on 8 April 1993 and harvested on 30 September 1993.

Determinations of available NH_4^+ and NO_3^- were made by soil extraction using 1M KCl in a 1:5 soil:solution ratio. Extracts were filtered and NH_4^+ and NO_3^- determined by continuous flow analysis. Potential mineralisation of soil sampled in April 1993 was determined by measuring mineral N after incubating the soils for 13 days at 17 °C. The amount of N accumulated was used as a measure of mineralisation.

Measurements of nitrous oxide (N_2O) fluxes were obtained by a chamber method on the bare fallow, grazing rye, forage rape, winter peas, winter barley, winter wheat and mustard treatments following sowing of the oat crop. Gas samples were analysed for their N_2O content by gas chromatography using an electron capture detector in the laboratory.

The cover crops were sampled on 9 December 1992 and 1 April 1993 from random quadrats (0.25 m^2) cut to ground level. Samples were dried, milled and analysed for total N using a Europa Scientific Roboprep CN. Between May and harvest the oat crop was sampled and analysed monthly.

Green manure crops

The following treatments were established on 20 April 1993 in a randomised block design; red clover (*Trifolium pratense* cv. Essex Broad Red at 15 kg ha^{-1}); white clover (*Trifolium repens* cv. Kent Wild White at 5 kg ha^{-1}); birdsfoot trefoil (*Lotus corniculatus* at 75 kg ha^{-1}); black medick (*Medicago lupulina* at 75 kg ha^{-1}); forage peas (*Pisum sativum* cv. Magnus at 250 kg ha^{-1}); oats (*Avena sativa*, cv. Dula at 250 kg ha^{-1}); white clover at 2 kg ha^{-1} with wild flower mix at 30 kg ha^{-1}; white mustard (*Sinapis alba* cv. at 15 kg ha^{-1}); fallow (natural vegetation allowed to regenerate); bare ground (seedlings removed by propane gas burner). The oat treatment was harvested for grain on 23 September 1993 and straw was left on the surface. All treatments were ploughed down on 14 April 1994 and sown on 15 April 1994 with oats (cv. Dula) at 300 kg ha^{-1}. Plots were harvested on 5 September 1994.

The green manure crops were sampled and analysed at monthly intervals between July and October 1993, and further samples were taken in November 1993, February and April 1994. Determinations of available soil NH_4^+ and NO_3^- and emissions of N_2O were made both prior to and periodically following cultivation of the white clover, birdsfoot trefoil, forage peas, oats, mustard, fallow and bare ground treatments.

Results and discussion

Winter cover crops

Both the available NH_4^+ and NO_3^- increased between December 1992 and April 1993 under all crops except winter wheat as a result of N release by mineralisation and nitrification. The greatest increase of inorganic N of 3.3 kg ha^{-1} was under bare ground. Over the same period the aboveground N content of all cover crops increased except in white mustard. As soil inorganic N was greatest when cover crop N was greatest the crop N can not alone be used as an indicator of reduction of NO_3^- leaching. Following cover crop incorporation greater concentrations of available NH_4^+ and NO_3^- occurred in plots that had previously been bare fallow suggesting that incorporation of crop residues enhanced immobilisation. Immobilisation may have been responsible for the relatively low rates of mineralisation observed following incorporation, although no significant ($p>0.05$) crop effect was found. By July 1993 the N content of oats following bare ground was significantly ($p<0.05$) greater than those following cover crops confirming the occurrence of immobilisation immediately after incorporation. Highest grain yields at harvest were from oats following bare ground, mustard and forage rape.

In general N_2O emissions were low. The greatest peak emission of N_2O of 3.6 g N_2O-N ha^{-1} d^{-1} was from the bare fallow treatment on 28 April, and was significantly ($p<0.05$) higher than from the cropped treatments. Emissions from this treatment remained the greatest throughout April. Between 21 and 28 April emissions increased from all treatments except Italian ryegrass. Rape showed the greatest increase of 1.6 g N_2O-N ha^{-1} d^{-1}. By May differences between treatments were greatly reduced. Significant linear correlations were found between N_2O production and soil NO_3^- content and between N_2O production and

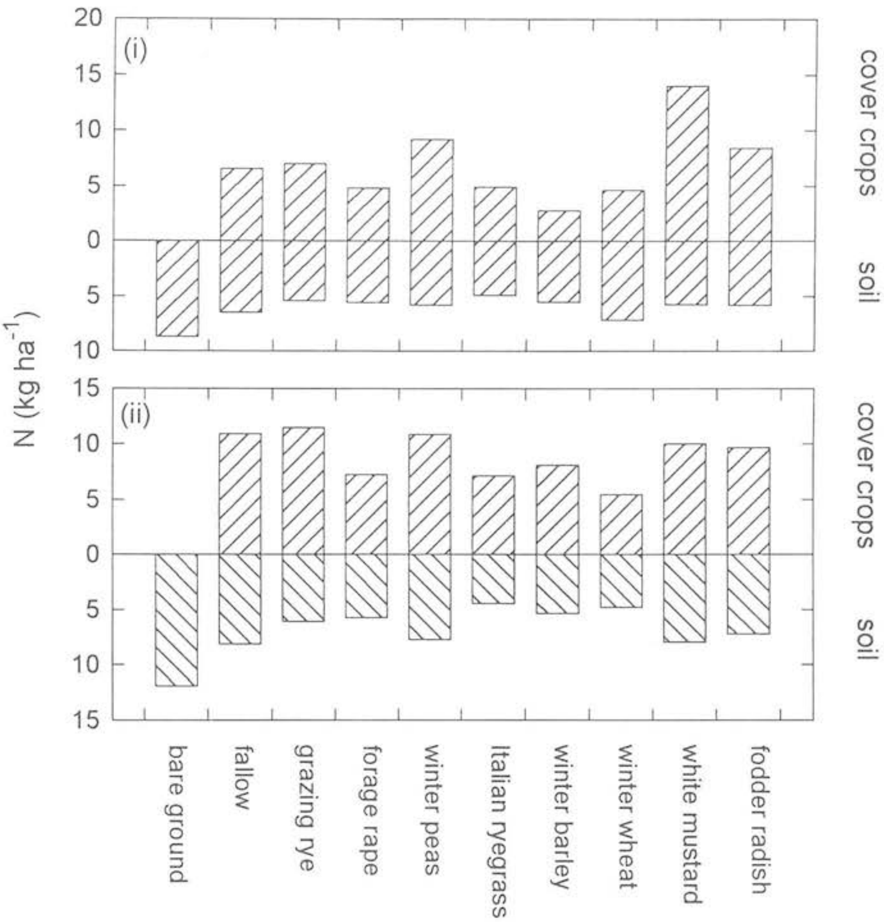

Figure 1. Partitioning of N between cover crops and inorganic N in (i) December 1992 (ii) April 1993.

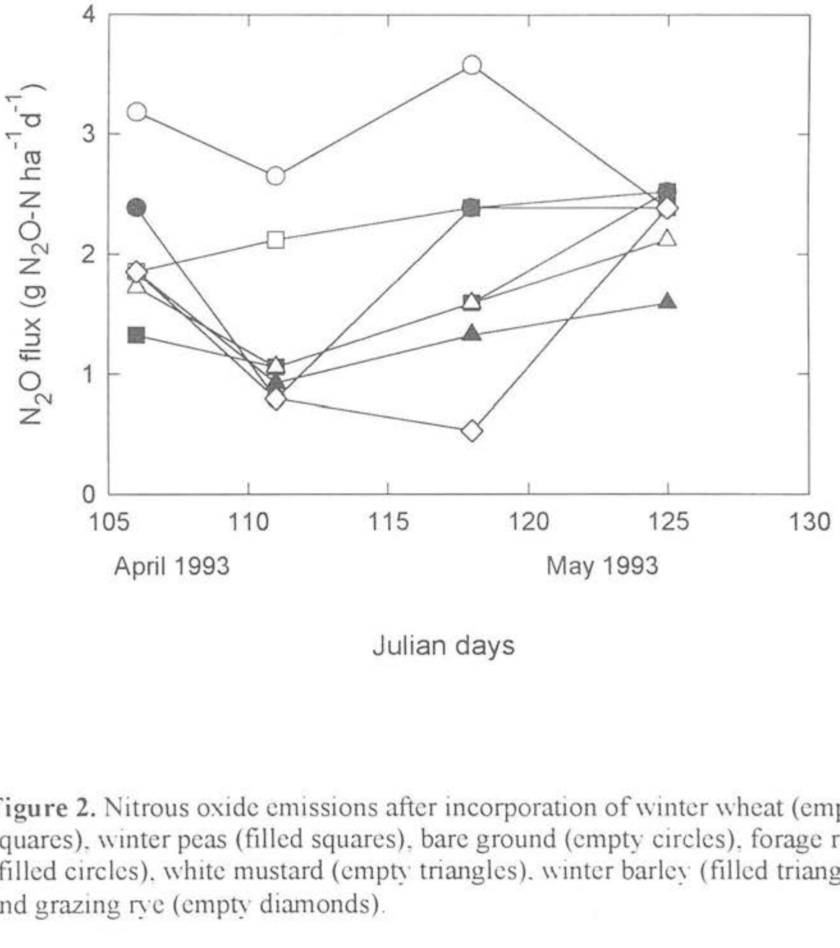

Figure 2. Nitrous oxide emissions after incorporation of winter wheat (empty squares), winter peas (filled squares), bare ground (empty circles), forage rape (filled circles), white mustard (empty triangles), winter barley (filled triangles) and grazing rye (empty diamonds).

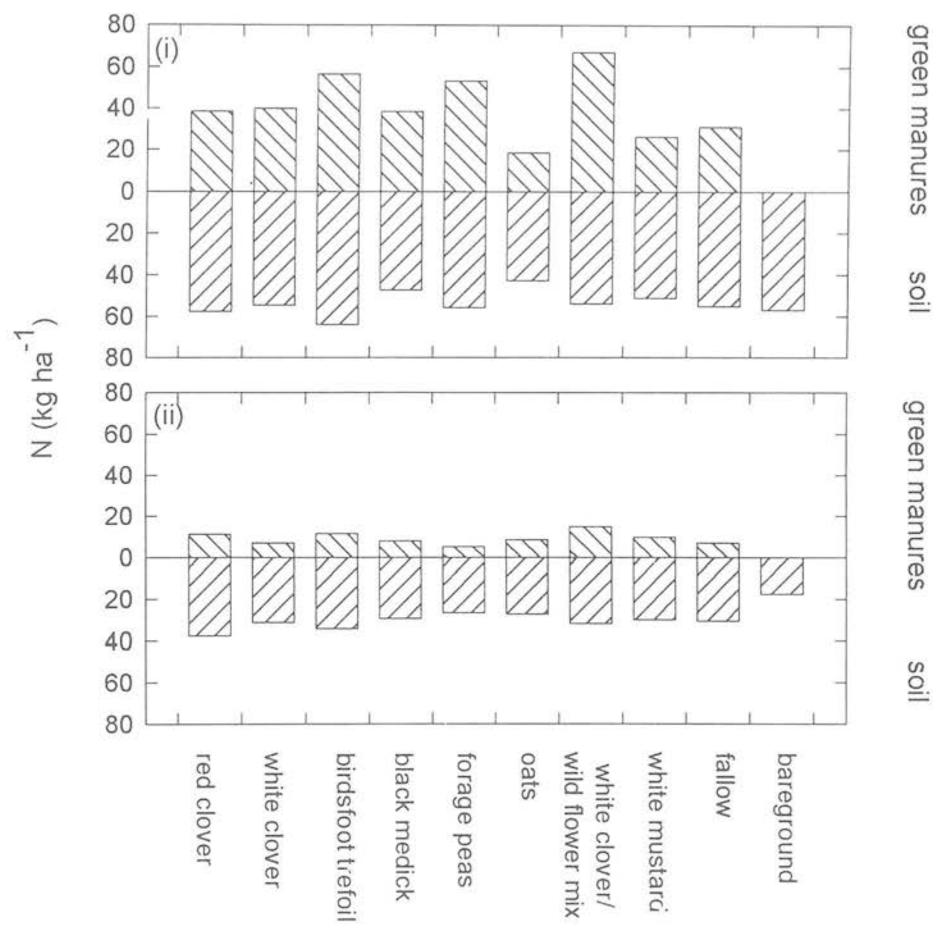

Figure 3. Partitioning of N between green manures and inorganic N in (i) November 1993 (ii) March 1994.

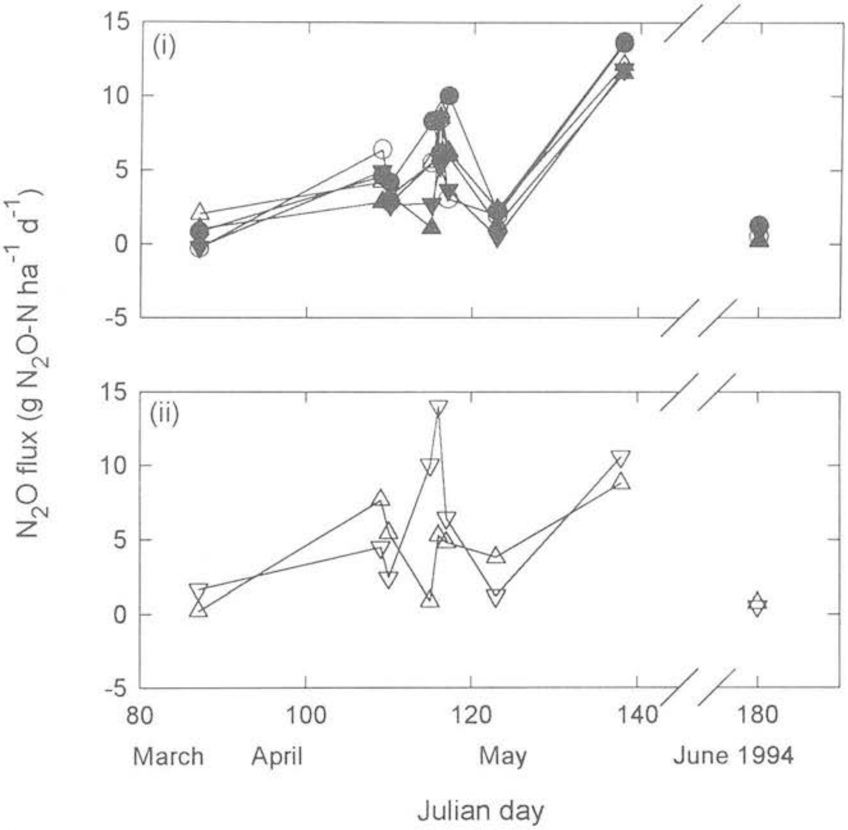

Figure 4. Nitrous oxide emissions after incorporation of (i) trefoil (filled circles), forage pea (empty circles), mustard (filled upward triangles), white clover (empty upward triangles), oats (filled downwrd triangle) (ii) fallow + weeds (upward triangle), fallow - weeds (downward triangle).

potential N mineralisation. High rates of N_2O production in the presence of NO_3^- may be ascribed to denitrification, as may the strong correlation with potential N mineralisation. The latter relationship may also result from nitrification which is known to be important in relatively dry soils such as these (Skiba *et al.*, 1993).

Green manure crops

Soil available NO_3^- fell over winter possibly as a result of leaching. During this period there were differences in N crop uptake, the highest percentage N in the dry matter being in the legumes (for example 138 kg N ha^{-1} in mustard). These values decreased over winter due to crop senescence. Prior to incorporation all crops contained less than 12 kg N ha^{-1}. This biomass N may have been lost in gaseous form or leached from the soil. Following incorporation soil available N increased under all treatments, particularly the fallow treatment where available NO_3^--N increased from 3 to 15 μg N g soil^{-1} between April and June suggesting that residue incorporation induced immobilisation. At harvest no significant difference in oat yields was found. This is not uncommon (Jackson *et al.*, 1993), as mineralisation is dependent on several factors including timing and method of incorporation.

A minor flux of N_2O occurred on all treatments immediately after incorporation with no significant difference between treatments. The greatest emissions of 14 g N_2O-N ha^{-1} d^{-1} were from the fallow treatment 11 days after incorporation, but this was very short-lived. A further increase in emissions was observed between days 120 and 140 with the birdsfoot trefoil attaining a peak of 14 g N_2O-N ha^{-1} d^{-1} on day 140.

The results demonstrate that cover crops and green manures can reduce soil NO_3^- over the winter. Higher rates of N_2O production from previously bare fallow soil suggest that the use of overwintering cover crops and green manures may have the potential to reduce both NO_3^- leaching and N_2O emissions before and following spring incorporation thereby conserving N within the system.

Acknowledgements

Funding for this work was provided by the Ministry of Agriculture, Fisheries and Food, the European Commission, Horticultural Development Council, Scottish Natural Heritage, Scottish Office Agriculture and Fisheries Department and the Scottish Development Agency.

References

Jackson, L.E., Wyland L.J. and Stivers L.J. 1993. Winter cover crops to minimise nitrate losses in intensive lettuce production. *Journal of Agricultural Science*, **121**, 55-62.

Parsons, J.W. 1984. Green manuring. *Outlook on Agriculture*, **13**, 20-23.

Skiba, U., Smith, K.A. and Fowler, D. 1993. Nitrification and denitrification as sources of nitric oxides and nitrous oxide in a sandy loam soil. *Soil Biology and Biochemistry*, **25**, 1527-1536.

APPENDIX III

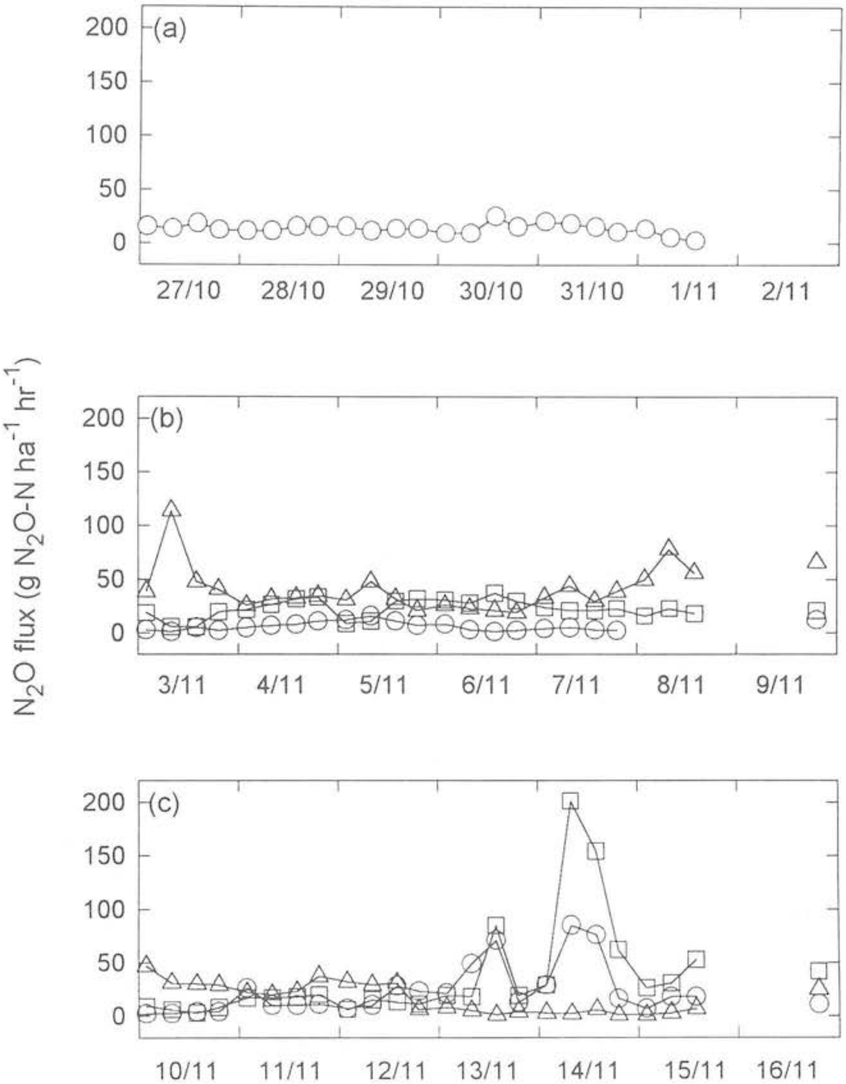

Figure 1. Nitrous oxide measured by autochambers between (a) 27 October-2 November (b) 3-9 November (c) 10-16 December after conventional ploughing of lettuce residues (-PW/+R) (squares), control (-PW/-R) (triangles) lettuce residues with paper waste (+PW/+R) (circles) at Mackies Field.

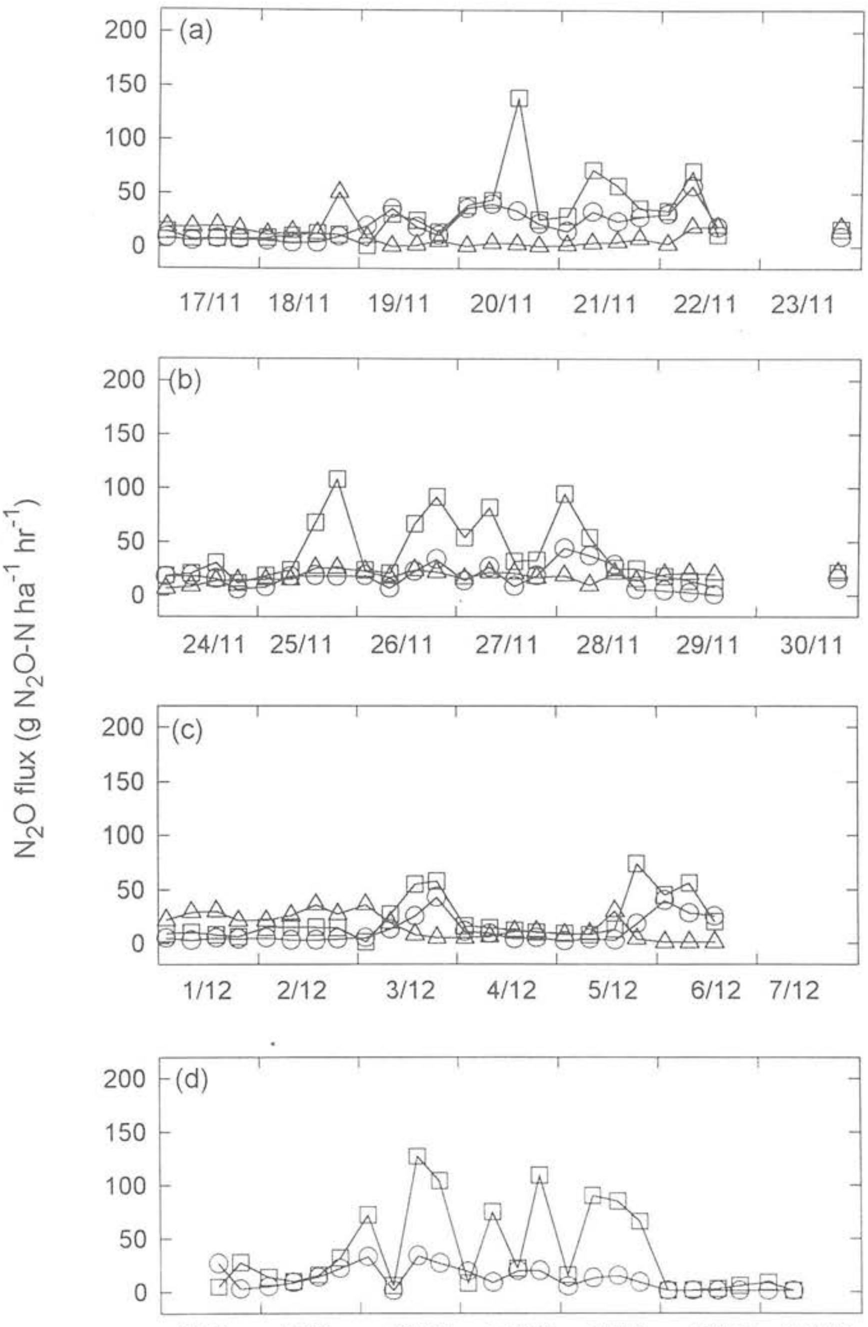

Figure 2. Nitrous oxide measured by autochambers between (a) 17-23 November (b) 24-30 November (c) 1-7 December (d) 8-14 December after conventional ploughing of lettuce residues (-PW/+R) (squares), control (-PW/-R) (triangles) lettuce residues with paper waste (+PW/+R) (circles) at Mackies Field.

APPENDIX IV

Table 1. N_2O emissions from main plots and microplots of fertilised oilseed rape on 3 sampling dates.

Date	N_2O flux (g N_2O-N ha^{-1} d^{-1})	
	main plots	microplots
12 May	4.25 ± 2.81	6.74 ± 4.01
13 June	2.9 ± 1.5	3.0 ± 3.30
20 June	1.5 ± 0.64	4.43 ± 6.10

Table 2. N_2O emissions from main plots and microplots of fertilised spring barley on 3 sampling dates.

Date	N_2O flux (g N_2O-N ha^{-1} d^{-1})	
	main plots	microplots
5 May	13.0 ± 4.39	16.72 ± 8.31
9 May	2.25 ± 2.33	1.89 ± 3.32
2 June	7.40 ± 1.50	4.30 ± 2.0

Table 3. N_2O emissions from main plots and microplots of fertilised winter wheat on 3 sampling dates.

Date	N_2O flux (g N_2O-N ha^{-1} d^{-1})	
	main plots	microplots
5 April	1.42 ± 0.55	-1.32 ± 2.02
4 May	3.66 ± 1.28	1.34 ± 1.20
11 May	2.29 ± 0.95	1.16 ± 0.73