Distribution And Amounts Of Nitrous And Nitric Oxide Emissions From British Soils.

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Declaration.

I declare that this thesis has been composed by myself, except where stated otherwise, and has not been submitted in any previous application for a degree.

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ABSTRACT.

This study establishes an empirical predictive model of N_2O and NO emissions for Great Britain based on multivariate regression analysis of field measurement data from several studies in European countries and the USA for which the results have been published in the last 18 years. The significance of studying the emissions of these gases is due to the role of N_2O as a greenhouse effect gas and NO participation in reactions with ozone. Soils are known to be an important source of N_2O and also contribute significant amounts of NO into the atmosphere. Knowledge of N_2O and NO emissions from soils at a national scale is important due to the signed international agreements which oblige Great Britain to produce inventories of greenhouse effect gases and monitor the emissions of NO_x gases. The field studies observed the relationships between the emissions and their controlling factors and on the basis of those relationships, national modelling approaches to predicting the amounts of emissions have been defined. Due to the highly variable nature of emissions, more than one empirical model was developed for each of the gases. The relationships defined in the analysis were later applied to estimate N_2O and NO emissions from British soils with an application of input parameter data of the established controlling factors in the framework of ArcInfo GRID.

Data for N fertiliser input, soil moisture and temperature were not readily available and therefore had to be estimated with existing data. Soil moisture was predicted with the SPACTeach model based on the monthly precipitation sums obtained from the Climate LINK data set. This data source also provided monthly air temperature data used to model soil temperature with the theory of heat flux. N input was estimated as a sum of mineral and organic N fertiliser inputs from agriculture and atmospheric N deposition. The former was estimated from the recommended values according to spatial distribution of land use data provided by the Agricultural Census. The latter was based on the modelled N atmospheric deposition provided by the Review Group on Acid Rain (RGAR). Information on the extent of seminatural land was obtained from the Land Cover Map of Great Britain based on satellite data. The data sets were characterised by varied spatial resolution and were brought to a universal 5 km grid resolution prior to modelling emission as this was the best assumed resolution at the national scale. The predicted total of N_2O emissions from British soils ranged between 128 and 140 kt N y^{-1}, and NO between 7 and 66 kt N y^{-1}, depending on the applied model. The predicted totals of N_2O are higher than the estimates based on the approach of Bouwman (1995) and Skiba *et al.*, (1996) using N emission factors. The higher NO emission rates based explicitly on the N factor suggest that the other approaches underestimate their totals (Simpson *et al.*, 1999).

The lower NO predicted in this study was due to the limiting effect of soil moisture. The different results of the models presented here are the result of the improved modelling approach used in this study, which takes into account the climatic characteristics of soils in addition to N input.

The validation of the established models against field measurements from selected studies in Scotland showed their limited accuracy in predicting N_2O and NO emissions at field scales. This was expected due to great spatial and temporal variability of emissions and the restricted methods of field measurements. While mechanistic models are better designed to reflect the emission processes at small scales, at national scales N_2O and NO emissions are better predicted with simple regression models. This is mainly the result of limited availability of input data for large scale studies.

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CHAPTER ONE

Introduction.

1.1 DEFINITION OF THE PROBLEM.

The aim of this project is to calculate and map regional fluxes of nitrous (N_2O) and nitric oxides (NO) from soils in Britain. Both N_2O and NO contribute to permanent changes in the atmosphere, N_2O as a greenhouse effect gas, NO as an agent responsible for reactions leading to ozone production in the troposphere and for ozone reduction and production of hydroxyl radicals in the stratosphere. Soils contribute large amounts of NO and N_2O emissions into the atmosphere, where the concentrations of these two gases have been increasing since pre-industrial times (IPCC, 1995; Levenberger and Siegentaler, 1992; Machilda *et al.*, 1994). As a result of numerous field studies there are known ranges of N_2O and NO emissions from different environments that have been applied in large-scale models. Despite the developments of methodologies for measuring and predicting these emissions, their distribution at regional and national scales is still uncertain. The main reasons are insufficient data and large spatial and temporal variability, which make modelling the emissions at regional and global scales difficult. This problem has been addressed by Shugart *et al.* (1991) as one of scaling (chapter three). Accurate estimates of N_2O and NO emissions from soils are required as input data to the complex atmospheric models which simulate the changes of the atmosphere and their effects on the climate. Apart from the conceptual reasons behind this research there stands a legislative obligation. The United Nations Framework Convention on Climate Change (1997) recommended that all parties should update and publish national inventories of anthropogenic emissions by sources and removals by sinks of all greenhouse effect gases (Mosier and Kroeze, 1997). New predictive models of N_2O and NO emissions from soils in Great Britain, presented in the current study, aim at increasing the existing knowledge of these phenomena to fulfil the signed agreements.

1.2 ISSUES OUTLINED IN THIS STUDY.

This thesis begins with a discussion of the complex nature of the N_2O and NO emissions and their relationships with factors believed to control their production processes and release from soils, which resulted in several modelling approaches (chapter two). In the context of different models the concept and aims of this study are defined (section 2.4, chapter two). Predicting N_2O and NO emissions at the national scale requires input parameter data, some of which were available for this study, but others had to be derived (chapter three). The spatial resolution of the input data determined the resolution of the model (section 3.5, chapter three). Some of the methods to derive input parameters are validated in a study undertaken in a small region in Northern Britain (chapter four). Regression analysis is used to describe relationships between N_2O and NO emissions and their controlling factors and to define predictive empirical models (chapter five). As this analysis method has well-defined requirements, the measurement data of N_2O and NO emissions are critically assessed in terms of their fulfilment and of the extent to which they represent the environmental conditions of Great Britain (chapters five and seven). Predicted annual and seasonal N_2O emissions from British soils are presented in chapter six, and the results of NO emission models are discussed in chapter seven. The defined models are validated with field measurement data from selected studies in Great Britain (chapters six and seven) and compared with other predictions (chapter eight).

CHAPTER TWO

Relationships between N_2O and NO emissions and their controlling factors; modelling approaches used to define them.

2.1 INTRODUCTION.

Soils are the major source of global N_2O and a small source of global NO emissions (IPCC, 1997; McElroy and Wofsy, 1986 and Yienger and Levy, 1995). Modelling the distribution of N_2O and NO emissions from soils requires a broad knowledge of their production processes and optimal conditions for their release into the atmosphere acquired from field and laboratory experiments. This chapter presents a literature review of N_2O and NO production and consumption processes and the optimal conditions for their emissions. It describes the main approaches of existing models for estimating amounts of N_2O and NO emissions from soils at various scales. The concluding section of this chapter contains a discussion of the methodological approach applied in the ArcInfo Grid Emission Model (AGEM), presented in this study, and outlines the aims of this research.

2.2 LITERATURE REVIEW.

2.2.1 The role of NO and N_2O in the greenhouse effect.

Nitrous oxide absorbs light in the infrared region and reduces atmospheric transparency to thermal radiation from the earth's surface. It is estimated that the present increase in atmospheric N_2O concentration contributes about 5% of the calculated anthropogenic greenhouse effect (IPCC, 1990). The tropospheric lifetime of N_2O is circa 130 years (IPCC, 1990). The stratosphere is the major sink for nitrous oxide, where it reacts with ozone (O_3) and is the main precursor of stratospheric NO_x (Williams *et al.*, 1992), thus contributing to stratospheric O_3 depletion. Recent research on the chemistry of the air captured in ice sheets indicates that the annual input of N_2O to the atmosphere has increased by about

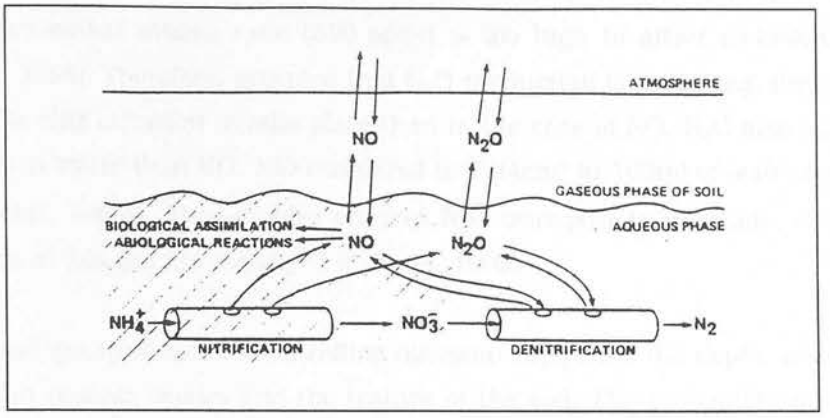
50% since preindustrial times (IPCC, 1990) and is increasing at about 0.2 to 0.3% $year^{-1}$ (IPCC, 1990). Soil microbial processes are generally regarded as the major source of N_2O (Banin, 1986). Globally, soils account for at least 50% of N_2O emission (Bouwman, 1990). The most important anthropogenic sources of N_2O are the use of fertiliser, which contributes up to 1.0 Tg N_2O $year^{-1}$, and animal manure (1.0 Tg N_2O $year^{-1}$) (Bouwman, 1995).

Nitric oxide takes part in the oxidising reactions in the troposphere regulating the concentration of ozone and hydroxyl radicals. Photooxidation of CH_4 and CO in the presence of NO_x gases (NO and NO_2) is the reaction by which ozone is produced (Williams *et al.*, 1992). Through chemical oxidation of NO_x gases to HNO_3, NO_x contributes to acid rain (Williams *et al.*, 1992). The combustion of fossil fuels is the major source of NO_x. The high variability in NO_x tropospheric concentrations and its short lifetime cause problems in establishing a trend for NO_x from atmospheric measurements. Researchers, however, agree that some of its sources in certain regions, predominantly in industrial regions of the Northern Hemisphere, predominantly over Asia, continue to increase. Davidson (1991) estimated soil biogenic emission of NO to be in the range of 4 - 20 Tg N $year^{-1}$ which is a second major source of NO after fossil fuel combustion of over 20 Tg N $year^{-1}$ (Levy, 1989). The emissions from soils contribute to 8-32% of total NO emissions (Bouwman, 1990). The emissions of NO from soils into the atmosphere increases in rural areas (Williams *et al.*, 1992) and therefore in those regions the NO emission from soils is of major importance.

2.2.2 Production processes versus emissions.

Nitrous and nitric oxide emissions from soils occur as a result of the production processes dominating over the consumption of these gases in soils (Conrad, 1995). Firestone and Davidson (1989) suggested that N_2O and NO fluxes are controlled by (1) rates of nitrification and denitrification, (2) amounts of N_2O and NO emitted from soils as a result of those processes and (3) the diffusion of the gases from the site of their production to the atmosphere (figure 2.1).

Figure 2.1 Hole-in-pipe model (Davidson, 1991).



The scope of production processes of N_2O and NO in soils is very wide. Both biotic and abiotic processes are involved and numerous groups of soil microorganisms are responsible for the N gases. The bacterial processes of nitrification and denitrification are accepted as the principal sources of both NO and N_2O in soils and are discussed in detail in sections 2.2.4 and 2.2.3 . Abiotic production of NO is associated with a set of reactions termed chemodenitrification that can occur in anaerobic soils with high concentrations of NO_2^- and NH_3 or NH_4^+ (Bouwman *et al.*, 1990). The examples of these reactions include reduction of nitrous acid (HNO_2) in acid soils, decomposition of hydroxylamine (NH_2OH) and reaction of NO_2^- with the phenolic constituents of soil organic matter (Williams *et al.*, 1992). These reactions are not of great importance in most agricultural soils in temperate climates (Bouwman *et al.*, 1990).

There are two main factors controlling the diffusion of produced gases. The first is a difference between the compensation mixing ratio? (Mc) and the mixing ratio? (Ma). Baumgartner and Conrad (1992) observed that the NO compensation mixing ratio is a changeable variable positively related to the production rate (P) and negatively to the NO uptake (k), which is presented in equation (2.1).

$$Mc = P / k \qquad (2.1)$$

A positive flux of NO from soils into the atmosphere occurs when the compensation point is greater than the mixing ratio (Mc > Ma). Baumgartner and Conrad (1992)

observed that values of Mc for NO ranged between 3 and 1400 ppbv depending on changes of P and k, which define optimum conditions for NO emissions. For N_2O the compensation mixing ratio (310 ppbv) is too high to affect emissions *in situ* (Conrad, 1994). Therefore, provided that N_2O production is occurring, there is more chance for this emission to take place than in the case of NO. N_2O also has higher solubility in water than NO, 130 compared to 7.34cm^3 in 100ml of water for temp = 0 °C (Weast, 1969). This enables efficient N_2O transport in wetlands, where high emissions of this gas are registered (Conrad, 1995).

The second group of factors controlling diffusion comprises the depth at which the production process occurs and the texture of the soil. The probability of emission decreases with the length of the transport through the soil medium. Soil diffusivity that controls the transport of trace gases depends on the texture and water content of the soil and is reduced by a decline in soil aeration. N_2O and NO have different transport ranges for both biotic and abiotic reasons. The biotic reason is because NO is more readily consumed by soil bacteria than N_2O. The abiotic mechanism is linked to the different chemical composition of these two gases, which has significant implications for their behaviour during their transport in soils. N_2O is more chemically stable due to a complete valence shell, hence its pathway through soil is longer than that of NO with incomplete electron bonding.

The role of nitrification and denitrification in the exchange of these researched gases between soils and the atmosphere is of major importance, a description of their mechanisms and optimal conditions follows.

2.2.3 Denitrification.

Denitrification is a process in which organic compounds are oxidised under anaerobic conditions and nitrate (NO_3^-) or nitrite (NO_2^-) are reduced to gaseous products of N (Bouwman *et al.*, 1990). Dinitrogen and N_2O are the main products of denitrification with NO being an intermediate product (equation 2.2).

$$4\,NO_3^- + 5CH_2O + 4H^+ \rightarrow \textit{intermediates} \rightarrow 2N_2 + 5CO_2 + 7H_2O \qquad (2.2)$$

where intermediates are produced in the following sequence:

$$NO_3^- > NO_2^- > NO > N_2O > N_2$$

Many bacteria that under aerobic conditions oxidise organic N using free oxygen, have the capacity to reduce nitrogen oxides when O_2 supply is restricted (Bouwman *et al.*, 1990). The dominant species in this group are *Pseudomonas*, *Bacillus* and *Paracoccus*. Bouwman *et al.* (1990) also stress the importance of *Rhizobia* as denitrifying bacteria, however, their principal role is N fixation in the root zone of leguminous plants. The presence and activity of denitrifying bacteria are controlled by N substrate availability and the characteristics of the soil medium – moisture, temperature, available organic C, redox potential (E_h), pH and texture.

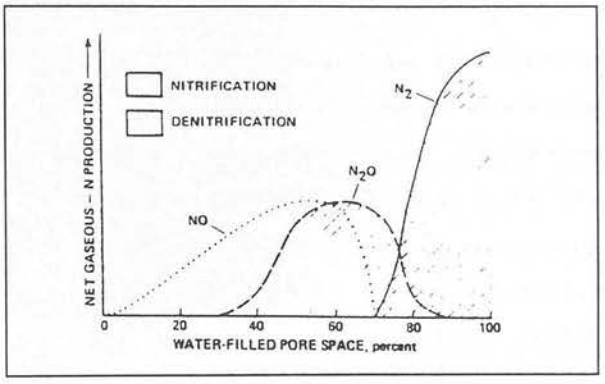
Denitrification requires anaerobic conditions. The location of anaerobic zones in soils depends on the soil type, depth of the water table, root density and extent of the rhizosphere. High denitrification activity was reported at various depths: from 10cm by Henrich and Haselwandter (1997), to 50 cm by Delmas *et al.* (1997) with a mean depth at about 30cm (Klemedtsson *et al.*, 1997).

'Denitrification depends on the micro-scale co-occurrence of nitrate, labile organic matter and anaerobic conditions' (Jordan *et al.*, 1998). Nitrate is the substrate for denitrification, hence its concentration in soils is the main controller of this process (Abbasi *et al.*, 1997; Jordan *et al.*, 1998; Skiba *et al.* 1997 and Skiba *et al.*, 1996). Its concentration depends either on an outside source of N (inputs into the soil through fertilising or atmospheric deposition) or a supply of NO_3^- inside the soil via nitrification (Ashby *et al.*, 1998). C content is regarded as the second most important controlling factor which plays the major role in a considerable number of studies (Ashby *et al.*, 1998; Henrich and Haselwandter, 1991 and Luo *et al.*, 1998). The importance of these two factors is due to their role as substrates in the process of denitrification. When organic C and N concentrations in soils are not limiting, the soil O_2 status plays an important role. Denitrification requires conditions of reduced O_2. These are promoted by soils with high soil moisture (WFPS[1] > 70%, figure 2.2) or in aerobic soils within anaerobic microsites (Smith *et al.*, 1990). The presence of anaerobic microsites in those soils is caused by decomposing organic matter (e.g. a worm or a leaf) as observed by Parkin (1987). The high microbial activity around such a large nutrient source leads to reduced O_2 concentration and promotes conditions favourable for denitrification.

[1] Water filled pore space, defined in section 2.2.5.2, p 31.

Soil acidity and soil temperature also play an important role in regulating denitrification rates. Denitrification is promoted in soils with nearly neutral conditions as the optimal conditions were observed when soil pH was around 7 (Oenema and Velthof, 1993). It diminishes in conditions of soil pH below 4. This relationship is best described by N_2 / N_2O emission ratio which is negatively correlated with soil pH (Granli and Bockman, 1994). Nomnik (1956) observed N_2O as the main denitrification product in the conditions of soil pH between 3.8 and 5.0, but when soil acidity was increased over 6.9 – 8.0, N_2 dominated.

Figure 2.2 Model of the relationship between WFPS of soil and relative fluxes of N gases (Davidson, 1991).

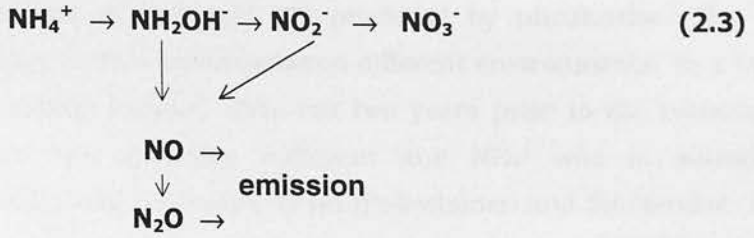


Denitrification is positively related to soil temperature. It can occur at temperatures ranging from -4°C (Mahli *et al.*, 1990) to 75°C, but above 50°C chemodenitrification is a more likely source of N_2O than biological denitrification (Keeney *et al.*, 1979). The optimum range for denitrification is 30 to 67°C (Mahli *et al.*, 1990). Vinther (1990) observed a significant increase in denitrification rates when temperatures rose above 5°C.

Other factors regulating denitrification, and hence N_2O emissions are soil type and plant cover (Beauchamp 1997).

2.2.4 Nitrification.

Nitrification is the biological oxidation of NH_4^+ to NO_2^- and NO_3^- presented by Bouwman *et al.* (1990) as equation (2.3).



(2.3)

The bacteria responsible for this process are both autotrophs and heterotrophs. In the first group the most important species are (1) *Nitrosomonas*, *Nitrosococcus*, *Nitrospira* and *Nitrosolobus* that oxidise NH_4^+ to NO_2^- and (2) *Nitrobacter* that oxidise NO_2^- to NO_3^-. These autotrophic bacteria obtain their energy from the oxidation of NO_2^- or NH_4^+, and depend on the CO_2 as a C source. Keeney *et al.* (1985) observed a positive relationship of nitrification activity with carbon dioxide concentration in the range of 0.3-100%. In conditions of depleted O_2 supply the oxidation of NH_4^+ or NO_2^- may be incomplete and NO and N_2O are produced. Under acid conditions, or at high NO_2^- concentrations, chemodenitrification of NO_2^- in reaction with organic compounds to produce NO_2 may also be an important source of NO (Bremner and Nelson, 1968). Nitrification is believed to be a significant source of NO and N_2O, the latter produced by ammonium oxidisers in anaerobic conditions or in chemodenitrification as an intermediate between NH_4^+ and NO_2^- in acidic conditions (Granli and Bockman, 1994). A number of heterotrophs have been responsible for nitrification in conditions unfavourable to autotrophs e.g. in acidic forest soils as observed by Duggin (1991).

The availability of the substrate (NH_4^+) is the principal controlling factor for nitrification. N input as fertiliser, via precipitation or mineralization of organic N controls the supply of NH_4^+, which has been examined by Delaune *et al.* (1998), Hutchinson and Brahms (1992) and Watson and Mills (1998) among others. Nitrification is an aerobic process that is favoured by WFPS in the range of 20 - 60% with an optimum around 40 % WFPS (figure 2.2). Temperature is another

important environmental factor controlling this process (Williams *et al.*, 1992). The reported optimum temperature for nitrification is 25 - 35°C, but it may vary depending on the climatic region and type of nitrifying bacteria (Bouwman, 1990) due to their climatic adaptation. Soil acidity also plays an important role as a controller of autotrophic nitrifiers that cease their activity in conditions of pH < 5 (Duggin, 1991). It is suggested that in acid soils heterotrophic nitrification is the main source of N_2O and NO produced by nitrification. The importance of the controlling factors varies between different environments. In a forest soil, located in south-eastern Finland, clear-cut two years prior to the measurements, where soil moisture was generally sufficient and NH_4^+ was in abundance, the rate of nitrification was controlled by pH (Paavolainen and Smolander, 1998).

In summary, nitrification occurs in well aerated soils, nitrifier denitrification takes over in conditions of increased water content and denitrification dominates in saturated soils. In practice, however, the distinction among the production processes of nitrous and nitric oxides is not clear, as quite often these processes occur simultaneously (Abbasi *et al.*, 1997). The reasons for this are the complexity of the soil environment and the combined effects of the controlling factors, which are intercorrelated. The optimal conditions for each of the production processes described above are well researched and the principal factors controlling the processes of production of N_2O and NO are also applicable to their emissions.

2.2.5 Factors controlling N_2O and NO emissions.

Emissions are characterised by great spatial and temporal variability, which is related to the complexity of bacterial processes in soils. Field measurements reveal a great variety of responses to changes in controlling factors, which could be graded according to their importance as emission controllers.

The controlling factors are all variables that have an effect on nitrification and denitrification, and the main role is played by N input through fertilising practices, grazing and atmospheric deposition, soil temperature, soil moisture, soil textural class and organic C content. Other significant factors reported in the literature include soil redox potential (E_h) and pH and a number of management practices like

tillage, irrigation, drainage, land use change and biomass burning. The following section presents a discussion of their effects on N_2O and NO emissions.

2.2.5.1 The effect of nitrogen on NO and N_2O emissions.

Soil mineral N is the substrate for nitrification and denitrification and hence its concentration is a major factor controlling the rate of these processes and, consequently, the amounts of N_2O and NO emissions. The concentrations of NH_4^+ and NO_3^- in soils depend on the amounts of nitrogen input as fertiliser, atmospheric deposition and the rate of mineralization of organic N. Fertilising practices, i.e. application rate, fertiliser type and methods of application, control the emissions of N_2O and NO from agricultural land, while atmospheric sources of N dominate on unfertilized land.

Nitrous oxide produced mainly by denitrification and in certain conditions by nitrification, responds to NO_3^- concentration in soils, which Beauchamp (1997) listed as the 'essential' factor of denitrification. Nitrate supply in soil is ensured either directly via the input of NO_3^- fertilisers, or indirectly via nitrification, the latter is limited by the presence of NH_4^+ and the rate of nitrification.

N_2O emissions increase with an application of N fertilisers. On the basis of known fertiliser emission factors, established with field measurement data, global N_2O emissions from agricultural soils are estimated (section 2.3.3). Eichner (1990) presented a summary of existing N_2O emission data based on 16 field studies. On the basis of the compiled data, she estimated median emission factors from five main mineral fertilisers: salts of nitrate excluding ammonium nitrate - 0.03%; urea and salts of ammonium - 0.1%; ammonium nitrate - 0.12% - 0.4% and anhydrous ammonia - 1.63%. Based on these factors Eichner (1990) estimated global fertiliser-derived N_2O at 0.2-2.1 Tg N for 1984. More recent estimates of global agricultural N_2O emissions suggest an increase in the emission ranges due to new established sources (section 2.3.3). The increase observed in the global estimates of agricultural emissions could be partly attributed to recent land use and management changes, especially in the tropics, but the increase in the availability of field data should also have caused the improvement of the estimates.

The N_2O fertiliser-induced emission factors vary considerably depending on fertiliser type, soil and crop type, and management practices. Table 2.1 presents selected

results from a few field studies of those variable conditions. In those cases the mean emission factors ranged from 0.01 to 6.8% of applied N fertiliser. Differences in N_2O emissions rates have been associated with varying fertiliser input. It was observed that anhydrous ammonia produced the highest N_2O emissions due to the method of application by injection to 20cm soil depth that promoted zones of high ammonium concentration (Breitenbeck and Bremner, 1986a). The presence of the previous crop residues can enhance N_2O emissions as noted by Bremner *et al.* (1981), but this varies depending on C/N ratio of the plants (section 2.2.5.2d). High N_2O emissions were also associated with certain land use types like grazed grasslands, potatoes, ungrazed grasslands and arable crops (Skiba *et al.*, 1996).

Table 2.1. N_2O fertiliser-induced emission factors.

Ref	Land use type	Soil characteristics	Fertiliser type	Application rate [kg N ha^{-1}]	N_2O loss (% of N input)
1	bare	silty clay loam	anhydr. amm.	180	0.86
1	bare	silty clay loam	aqueous amm.	180	0.04
1	bare	silty clay loam	urea	180	0.11
1	bare	silty clay loam	calcium nitrate	180	0.06
1	bare	clay loam	anhydr. amm.	180	0.93
1	bare	clay loam	aqueous amm.	180	0.06
1	bare	clay loam	urea	180	0.07
1	bare	loam	anhydr. amm.	180	2.08
1	bare	loam	aqueous amm.	180	0.12
1	bare	loam	urea	180	0.07
2	fallow	clay loam	calcium nitrate	125	0.01*
2	fallow	clay loam	calcium nitrate	250	0.01*
2	fallow	clay loam	urea	125	0.06*
2	fallow	clay loam	urea	250	0.09*
2	fallow	clay loam	amm. sulphate	125	0.09*
2	fallow	clay loam	amm. sulphate	250	0.11*
3	fallow with soya residue	silty clay loam	anhydr. amm.	250	5.3
3	as above	clay loam	anhydr. amm.	250	6.8
3	as above	loam	anhydr. amm.	250	4.0
4	grazed grass	several**	two types**	277-437	3.1**
4	mown grass	several**	two types**	277-437	1.0**
4	spring barley	several**	two types**	ns	0.8***
4	winter wheat	several**	two types**	ns	0.5***
4	potatoes	several**	two types**	ns	1.6***

1/ Breitenbeck and Bremner (1986a); 2/Breitenbeck *et al.* (1980); 3/ (Bremner *et al.*, 1981); 4/ Skiba *et al.* (1996).

*Fertiliser-induced factor calculated from N_2O emission data for the period of 25 days; **data from grasslands presented by Velthof et al. (1994), grazed soil types included sand and clay in the Netherlands and sandy loam in Belgium, mown sites included all the above

soil type and clay loam in Scotland, two types** of fertilisers were used: ammonium nitrate in Belgium and Scotland, and calcium ammonium nitrate in the Netherlands; ***several sites in Scotland, other information not specified (ns).

The observed variability in N_2O emissions from different land use types is associated with nutritional N requirements of crops and grasslands, where the amounts of N fertiliser input depend on the intensity of management practices. Lemke *et al.* (1998) measured increased mean N_2O emissions from wheat fields from 0.9 - 3.4 kg N ha^{-1} yr^{-1} at Ellerslie and Cooking Lake sites in Alberta after an application of 56 and 100 kg N ha^{-1} of urea. An earlier study by Duxbury *et al.* (1982) of N_2O emissions from mineral and organic soils under different crop systems in New York and Florida presented higher N_2O emissions from corn, for which the annual emission ranged from 2.2 to 3.8 kg N ha^{-1} y^{-1} with maximum emissions measured for manure. N_2O emissions from alfalfa were observed to vary from 2.3 to 4.2 kg N ha^{-1} y^{-1} between two years when measurements were taken. Potatoes generated higher N_2O emissions than the arable crops (wheat, barley and corn). Cumulative emissions from those crops grown on fine-silty Dystric Eurochrept soil were observed by Ruser *et al.* (1998), who measured the total emissions of 3.59 kg N ha^{-1} for ridges and 5.07 kg N ha^{-1} for uncompacted interrow soil in the period between May and September.

Managed grasslands are associated with the highest N_2O emissions due to the intensive management practices of high N inputs and grazing. Bouwman (1995) suggested that N_2O emissions from grasslands are at least a factor of two higher than from tilled land as presented in figure 2.3 (Bouwman, 1995). Terry *et al.* (1981) in their study of N_2O emissions from cultivated organic soils of South Florida measured higher annual N_2O emissions from grassland (96.8 kg N ha^{-1} yr^{-1}) than sugarcane plantation (48.4 kg N ha^{-1} yr^{-1}). The intensification of grassland management caused greater emissions in the order: unfertilised < fertilised with mineral N < fertilised and grazed (figure 2.4, Velthof and Oenema, 1995). Different results were obtained by Ellis *et al.* (1998), who observed N_2O emissions in February from Hampshire grass on silty clay loam for three systems of varied intensity: maximised profitability (input= 312 kg N ha^{-1}), maintained production (input=189 kg N ha^{-1}) and reduced stocking rate (input= 139 kg N ha^{-1}). The lowest cumulative emission was observed for the most intensive system with maximum

daily N_2O emission of 2.05 kg N ha^{-1} yr^{-1}, and the highest measured N_2O was recorded for the maintained production system - 5.5 kg N ha^{-1} yr^{-1}.

Figure 2.3 N_2O loss from crops and grasslands measured by long-term studies of mineral soils (Bouwman, 1995).

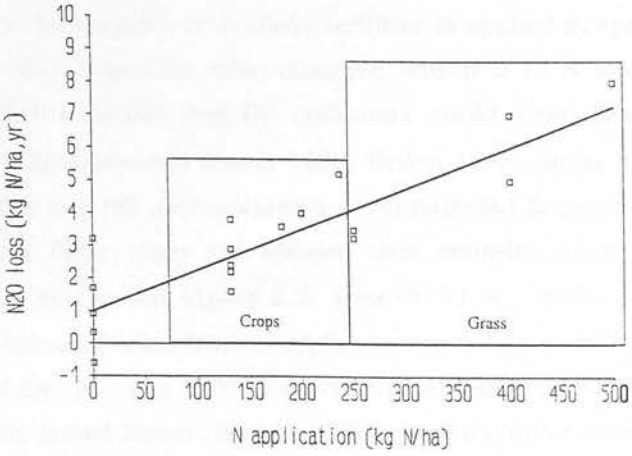
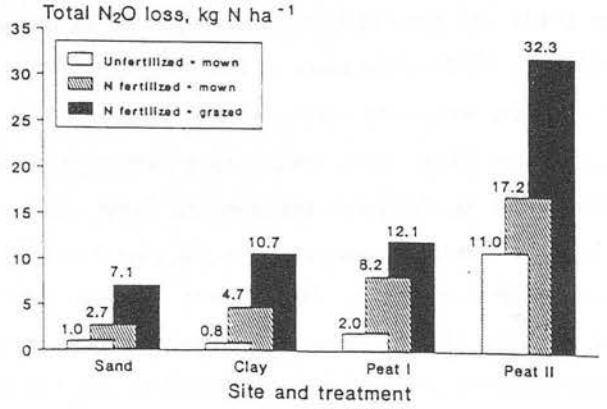


Figure 2.4 Total N_2O losses measured from three grassland soils under different management systems (Velthof and Oenema, 1995).



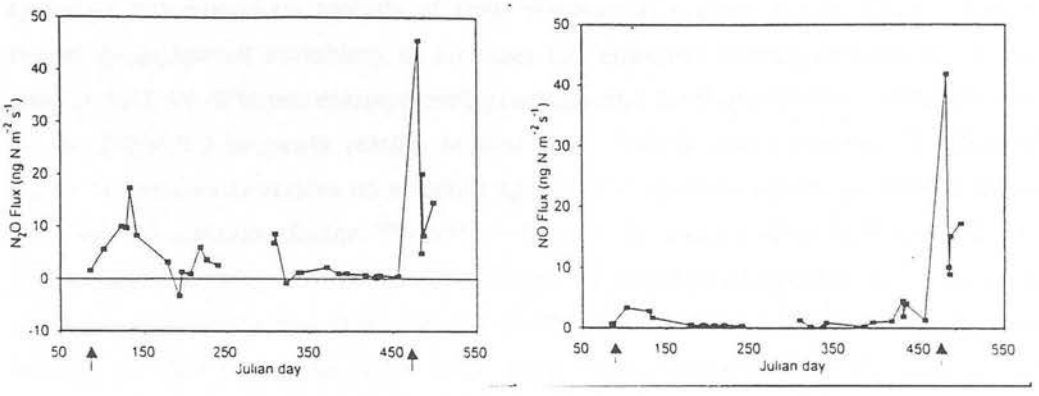
The difference observed in N_2O emissions from crops and grasslands is the combined effect of different fertiliser practises for these two main agricultural systems and contrasting soil characteristics. Grasslands require larger amounts of N input and a high proportion of applied N is in organic form that replenishes the supply of both N and C. On the other hand, they have less demand of well drained soils than crops and often are associated with conditions of restricted aeration.

The temporal distribution of N_2O emissions from agricultural soils during a year is closely related to the timing of the fertiliser application. There are two major peaks in N losses from soils during the year. In spring the increase follows the fertiliser application and in autumn it is an effect of the mineral N release from the mineralisation of organic N from crop residues and the first fertiliser input on winter crops. As the majority of artificial fertiliser is applied in spring and summer, the maximum N_2O emissions were observed within 2 to 3 weeks of a fertiliser application, which indicates that the emissions would reach peaks mainly during these seasons (Eggington and Smith 1986; Ryden 1983; Skiba *et al.* 1993). A two year study of N_2O and NO measurements at Rothamsted Experimental Station on a wheat field with flinty loam soil showed that emission rates followed mineral nitrogen content of the soil (figure 2.5, Yamulki *et al.*, 1995). The increase in N content of soil occurred after Nitram application at a rate of 200 and 150 kg N ha^{-1} on 5 April 1991 and 22 April 1992, respectively. The N_2O emission response in 1991 was delayed and lasted longer, and in 1992 it was instantaneous and pronounced due to different precipitation in those years. In 1992 higher precipitation provided good conditions for denitrification that lead to more dynamic N_2O emissions. Other researchers have observed a similar pattern in which N_2O emissions increase rapidly shortly after N fertiliser input. Ryden (1981) measured high N_2O emissions with a weekly mean of 76 kg N ha^{-1} y^{-1} following the third ammonium nitrate application, when the water content of loam was > 20% and the temperature was above 10 °C. In a drying soil, the response was very weak (< 3.7 kg N ha^{-1} y^{-1}) despite the same N application rate. Smith *et al.* (1998) observed N_2O emissions for a selection of land use types in Scotland. An increase in emissions was observed after approximately 2-3 weeks of the first ammonium nitrate application to potatoes and grassland. The increase from winter wheat was not marked. In practice, however, the temporal variation in emissions due to fertiliser application is very complex as various types of fertilisers can be used simultaneously e.g. synthetic and organic fertilisers that may cause a complex response. Paul and Beauchamp (1993) studied the yield response and analysed the N concentration change in silt loam soil after an application of manure and urea. They found that the inorganic N content in soil decreased on the plots where dairy cattle and solid beef manure was added, other treatments caused the N increase. They also concluded that the manure had the lowest yield response in the year of application, but it increased considerably in the second residual year. This proves that much organic manure is

stored in soil for the next season and therefore less fertiliser might be required in the following year. Studies by Vos *et al.* (1994) and Watson and Mills (1998) also confirm this.

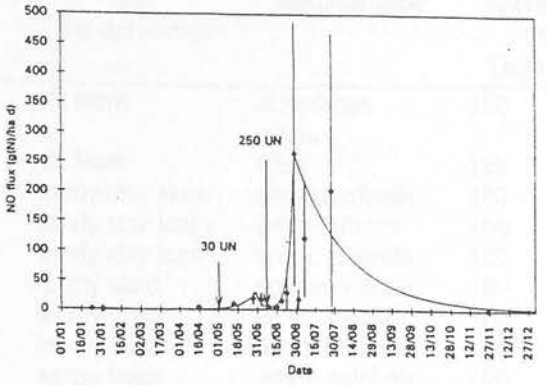
The magnitude of emissions depends on the rate and the type of N fertiliser and on soil conditions. There is considerable variability between the published results, but some management practices are associated with high N_2O emissions. These include incorporation of residues from the remaining crop into fallow soils, supply of N in organic form and the application method of direct injection. Organic N fertilisers produce more N_2O emissions due to the supply of water soluble C that increases the rate of denitrification considerably.

Figure 2.5 Seasonal cycle of N_2O and NO flux measured from a wheat field on a flinty loam soil (Yamulki *et al.*, 1995).



Nitric oxide is a product of nitrification and denitrification, but it also is a substrate for denitrification. Denitrification requires reduced O_2 concentrations. These conditions are frequently associated with wet and heavy soils or the deeper soil horizons. In both cases conditions of low diffusivity are created that obstruct transport of NO produced in denitrification to the soil surface. In effect NO is more likely to be consumed by denitrifying bacteria than emitted into the atmosphere. NO production and emission is N fertiliser dependent and, like N_2O, is characterised by dynamic fluctuations in emissions occurring after fertiliser application (figures 2.5b and 2.6).

Figure 2.6 Temporal distribution of NO emissions from maize field on sandy loam (Delmas *et al.*, 1997).



Veldkamp and Keller (1997) defined NO emissions from agricultural soils with the fertiliser emission factor of 0.5%, and hence indicated N input as the principal factor of NO emissions (details of their method in section 2.3.3). Other studies report great spatial variability in fertiliser NO emission factors caused, as in the case of N_2O, by different management practices and land use types on different soil types. Table 2.2 presents results of four field studies that observed an effect of different fertiliser practices on selected agricultural systems on the estimated mean fertiliser NO emission factor. The value of the factor ranged from 0.04 to 1.52% of the applied N. NH_4^+ is the limiting factor of nitrification processes, hence its abundance in conditions of well aerated soils promoted the highest loss of applied fertiliser as NO emissions (table 2.2). Ammonium chloride led to the largest NO emissions in the field studies included here, while applications of the salts of nitrate were followed by relatively small NO emissions. Soils of coarse texture, i.e. loamy sand and loams, favoured NO soil emissions. Those soils provide the aerobic environment necessary for nitrification and conditions of high diffusivity that enable easy NO transport through the soil profile. The highest NO emission factors were observed for fallow land, where there was no competition from plants for the soil N. Other studies support the observed NO emission variability according to different land use types and soil physical characteristics.

Table 2.2. NO fertiliser-induced emission factors.

Ref	Land use type	Soil characteristics	Fertiliser type	Application rate [kgN ha^{-1}]	N_2O loss [%of N input]
1	corn	silt loam	anhydrous amm.	168	0.11
1	corn	silt loam	urea	168	0.16
2	bare	sandy clay loam	sodium nitrate	100	0.04
2	bare	sandy clay loam	amm. nitrate	100	0.63
2	bare	sandy clay loam	amm. chloride	100	1.52
2	bare	loamy sand	sodium nitrate	100	0.14
2	bare	loamy sand	amm. nitrate	100	0.6-0.7
2	bare	loamy sand	amm. chloride	100	1.23
3	rye grass	sandy loam	amm. sulphate	100	1.1-6.4
3	rye grass	sandy loam	potassium nitrate	100	0.1
4	wheat	flinty loam on clay	nitram	48	0.39
4	wheat	flinty loam on clay	nitram	96	0.36
4	wheat	flinty loam on clay	nitram	192	0.39

1/ Thornton *et al.* (1995); 2/ Slemr and Seiler (1984); 3/ Skiba *et al.* (1993); 4/Harrison *et al.* (1995)

Aneya *et al.* (1998) observed varying NO fluxes from different crop types in North Carolina. They found a strong dependence of NO emissions on location and crop type. The highest mean NO flux of 6.4 kg N ha^{-1} y^{-1} was measured for soyabean, grown on fine sandy loam. NO emissions from corn planted in a similar location was 1.7 kg N ha^{-1} y^{-1}, that contrasted with 2.6 kg N ha^{-1} y^{-1} NO emitted from corn on sandy loam. The lowest mean NO emission was estimated from measurements on a tobacco plantation, where 1.2 kg N ha^{-1} y^{-1} was emitted. Those differences observed in North Carolina are distinct and confirm that although 'NO emissions follow changes in soil temperature, and to some degree follow changes in extractable nitrogen content, the correlation's (sic) are further complicated by the interactions of soil moisture' (Aneya *et al.*, 1998). Similar NO emissions were observed by Guenzi *et al.* (1994) from corn planted on silt loam in eastern Colorado. The NO fluxes varied over the range 0 - 2.1 kg N ha^{-1} y^{-1}. Much higher NO emissions were measured by Jambert *et al.* (1997) from a maize field on podzol (90% sand) in France. The average seasonal NO gaseous loss was estimated at 60.5 ng N m^{-2} s^{-1}, but the peak of 81.4 ng N m^{-2} s^{-1} of NO emissions occurred after the second anhydrous ammonia application of 250 kg N ha^{-1} in June. The highest NO emissions of > 1 mg N m^{-2} h^{-1} were observed from high inputs of cattle and swine

excreta (590 and 1150 kg N ha^{-1}, respectively) by Watanabe *et al.* (1997), who measured NO emissions from grasslands in autumn and winter in the Kanto District, Japan. In autumn, NO emissions were ranging from 0 - 1 mg N m^{-2} h^{-1} and in winter the range of NO emissions was greater - from 0 – 1.7 mg N m^{-2} h^{-1}.

NO emissions induced by fertiliser input also vary temporally. The increase in emissions follows the timing of the fertiliser application and depends on environmental conditions prevailing at the time. Yamulki *et al.* (1995) observed NO fluxes from a wheat field on a flinty loam on clay that was well drained. They reported an increase in NO emissions occurring 2 days after the application of nitram (mixed ammonium nitrate and calcium carbonate), but a large peak of emissions (an increase by a factor of 10) followed a lower application rate (150 kg N ha^{-1} as opposed to 200 kg N ha^{-1}). This was due to lower soil moisture that was negatively correlated with NO emissions. Delmas *et al.* (1997) examined NO emissions from a maize field on sandy soil into which 250 kg N ha^{-1} of anhydrous ammonia was injected. NO emission increased exponentially in three weeks and the enhanced emissions lasted about 25 days, before returning to background levels. The distribution of NO emission during the year can be assumed to be very similar to the N_2O annual cycle. The NO emission peaks occur in spring and summer after the fertiliser application and their number depends on the number of split applications in a year that is modified by climatic conditions prior to and after the N fertiliser input.

Method of estimating emissions due to N input

If the amount of fertiliser input is known, the total loss of nitrogen from the fertiliser can be calculated on the basis of the estimated fraction of N loss. The proportion of emitted fertiliser is estimated as a difference between the total and the background emission measured respectively from a treated and a control plot. Conrad and Seiler (1980) have presented this as an equation (2.4).

$$L = \frac{{}_0\int^t (E_i - E_0)\, dt}{M} \times 100\% \qquad (2.4)$$

Where E_i and E_0 are emission rates of a gas from fertilised and control plots respectively, M is an amount of fertiliser and t describes the period of an experiment. This method has been applied in all studies of fertiliser effects on emissions of nitric and nitrous oxides.

Major types of fertilisers and their N content.

Fertiliser input to soils is either of mineral or organic origin characterised by a different N composition. In the past organic N was the only form of N fertiliser, but the amounts of N returned to soil in animal waste was not sufficient to sustain fertility (Haynes *et al.*, 1986). The development of the production methods of mineral fertilisers during the Industrial Revolution lead to an increase of N input to soils in the developed countries and now it is the most commonly used form of N.

Mineral fertiliser.

The N content of these types of fertiliser is presented in table 2.3. The most common artificial fertilisers used in Britain are NH_4NO_3 (ammonium nitrate), $(NH_4)_2SO_4$ (ammonium sulphate) and $CO(NH_2)_2$ (urea). These are usually applied in combination with phosphates and potassium. Burnhill *et al.* (1995) estimated that straight fertiliser is applied to the majority of spring and winter wheat, winter barley, rye and oil seed rape, while compounds dominate for spring barley, early and maincrop potatoes and turnips. The rate of application varies between crops and is regionally variable (Burnhill *et al.*, 1995). N application rate depends on the crop and soil type and climate. Although the N requirements of crops are well researched, it is difficult to predict the levels of N uptake due to the effect of weather conditions during and soon after the application. To maximise the yield and minimise the fertiliser loss, guidelines of good fertiliser practice are published that specify the levels of application required according to crop type, soil and climate.

Table 2.3. Nitrogen content of most commonly used fertilisers in the UK.

Fertiliser type	Chemical form	Nitrogen content (Approx. %)
anhydrous ammonia	liquid NH_3	82
urea	$CO(NH_2)_2$	45-46
ammonium nitrate	NH_4NO_3	33-34.5
nitrogen solutions	NH_4NO_3 + urea in water	28-32
aqua ammonia	dilute NH_4OH	20-25
calcium cyanamid	$CaCN_2$	22
diammonium phosphate	$(NH_4)_2HPO_4$	21
ammonium sulphate	$(NH_4)_2SO_4$	20-21
cal-nitro and A.N.L.	NH4NO3 and dolomite	20
sodium nitrate	$NaNO_3$	16
calcium nitrate	$Ca(NO_3)_2$	15
ammonium polyphosphates	$(NH_4)HP_2O_7$, $NH_4H_2P_3O_{10}$.	12-15
potassium nitrate	KNO_3	13
monoammonium phosphate	$NH_4H_2PO_4$	11

Source: Brady (1990).

Organic fertiliser.

Organic manure (of animal origin) is commonly applied to agricultural soils in different forms (dry, wet - urine or mixed - slurry) and its N content depends on the animal it originates from, the type of feed used and the storage method of the manure (Bockman *et al.*, 1990). It originates from livestock housed either for the whole year (intensive pig and poultry farming) or during the cold winter period (cattle and dairy farming). This organic manure is applied to soils to increase organic matter and improve the soil structure (Bockman *et al.*, 1990). Fertiliser Manufacturers' Association (FMA) (1998) states that *'farmers do take account of manure nitrogen and adjust fertiliser N accordingly'*. However, current farming practices suggest that even today farmers tend to regard manure as waste rather than fertiliser which is against the recommendations of good fertiliser practice (Dyson, 1990). The fraction of organic N fertiliser uptake by crops varies between 35 and 70% depending on weather conditions during and after the application and its timing (Dyson, pers. comment). The latter is as critical as in the case of synthetic fertiliser and it is suggested that the majority of manure is applied in spring before planting and in summer after silage cut (Dyson, pers. comm).

Nutrient enrichment of soils is also ensured by the increasingly practised application of green manure that comprises the remains of the harvested crop. Plant residues incorporated into soils are believed to increase the rates of both nitrification and denitrification and led to an increase in N_2O (Cochran *et al.*, 1997; Larsson *et al.*, 1998 and Ryden and Lund, 1980) and NO emissions (Vos *et al.*, 1994). The plant residues that provide biologically available N enhance mineralisation and that, in effect, leads to greater decomposition due to increased numbers of heterotrophic bacteria. Anaerobic conditions are created with increased O_2 consumption by heterotrophs that leads to denitrification and N_2O emissions. In any remaining aerobic microsites nitrification may be the source of produced N_2O. Higher N_2O emissions from soils enriched with green manure have been recorded recently by Larsson *et al.* (1998) from heavy clay soil to which grass and alfalfa mulches were added. The increase in emissions depends on the C/N ratio of the plant residues; the lower the ratio, the greater the emissions (section 2.2.5.2d). This pattern was observed by Larsson *et al.* (1998) as alfalfa mulch characterised by the lowest C/N ratio caused the highest increase of N_2O emissions - 347 kg N ha^{-1} y^{-1} compared with a smaller increase of 86 kg N ha^{-1} y^{-1} in treatments with grass mulches. Goodroad *et al.* (1984) observed the effect of residues of alfalfa, rye and straw, the former caused the highest total N_2O release of 3.2 kg N ha^{-1}. The observed total N_2O emissions from rye were 1.6 kg N ha^{-1}, and from straw 2.2 kg N ha^{-1}. The emissions varied between consecutive years, but that could not be explained by climatic variables. Vos *et al.* (1994) measured NO fluxes from a fallow field following oil seed rape harvest on a cambisol fertilised partly with a green manure. The fluxes of the green manure were 2 to 12 times higher than those of the control plot and amounted to 0.62 – 12.7 kg N ha^{-1} y^{-1} compared with 0.46 – 7.76 kg N ha^{-1} y^{-1} for the bare soil. NO emissions were attributed to increased rates of denitrification.

Legumes, members of the *Leguminosae* plant family with the ability to fix atmospheric N_2 through the symbiotic relationship with *Rhizobium*, are often used in green manure. They have an important role in grassland conservation management and form a valuable part of crop rotation systems grown for human and animal consumption. The amount of fixed N is controlled by changing conditions in the atmosphere and soil. Conditions known to reduce the fixing capacity of legumes are extreme temperatures, drought, floods and low pH. High N content in soils is also believed to reduce the benefits of *Leguminosae*, hence good

fertiliser practice guidelines specify the reduced amounts of N input. A reduction of 20 kg N ha^{-1} of annual N input is recommended for grass establishment (Swift, 1988) and for all pulses a reduction of 90 kg N ha^{-1} is proposed when '*Rhizobium* inoculation is used' (MAFF[2] and SOAEFD[3], 1991). Benefits of *Leguminosae* crops like clover in grass management and other legumes used in crop rotation is hindered by the difficulty of controlling the amounts of N incorporated into soils.

Regional and temporal variation of fertiliser application.

In estimating seasonal variability in the amounts of nitrous and nitric oxide emissions from soils, the change in fertilising practices and environmental conditions throughout the year should be considered. Different crop types determine specific fertilising practices with different times of application and amount of fertiliser used as presented in table 2.4.

Table 2.4. Split mineral N fertiliser for different crops and grassland management types.

Crop	application 1	application 2	application 3	application 4	application 5
			(proportion, date)		
Winter cereals	25% - 30/09	38% - 01/03	37% - 21/04		
Spring cereals	50% - 01/04	50% - 21/04			
Oilseed Rape	25% - 21/08	38% - 01/03	37% - 01/04		
Potato	45% - 15/04	55% - 15/06			
Hops	33% - 01/03	33% - 01/04	34% - 01/05		
Vegetables	50 % -01/03	50 % - 01/04			
Grazed grasslands					
South of England	20% - 15/02	20% - 15/04	20% - 31/05	16% - 30/06	24% - 31/07
H.S.D.	23% - 01/03	20% - 15/04	20% - 31/05	20% - 30/06	16% - 31/07
M.S.D.	30% - 01/03	24% - 15/04	24% - 31/05	20% - 30/06	
L.S.D.	77% - 1/03	23% - 15/06			
Mown grasslands					
South of England	36% - 1/03	29% - 15/04	17% - 15/05	18% - 15/06	
H.S.D.	38% - 1/03	31% - 15/04	31% - 15/06		
M.S.D.	58% - 1/03	42% - 1/08			
L.S.D.	57% - 1/03	43% - 1/08			

H.S.D. - high stocking density, M.S.D. - medium stocking density, L.S.D. - low stocking density.
Source: Dyson, 1992; Dyson, 1993; Dyson *et al.*, 1993a; Dyson *et al.*, 1993b; Dyson *et al.*, 1993c; MAFF, 1988; Swift, 1988; Younie *et al.*, 1990 and information from the survey of farmers.

[2] Ministry of Agriculture, Fisheries and Food
[3] Scottish Office of Agriculture, Environment and Fisheries Department

In terms of general fertiliser practices cereals are divided into two major groups: winter and spring crops. Autumn N fertiliser applications are not recommended due to low profits with high losses as a result of high leaching and emissions (Dyson and Sinclair, 1993). It is well known, however, that a small autumn application of N fertiliser is widely practised (Dyson, pers. comm). Dyson and Sinclair (1993) recommend that the main part of annual N requirement is applied to winter cereal varieties in spring as a split of 1 – 2 thirds applied at the start of spring growth, and the remaining part at the growth stage 30-31 (at the start of stem extension). As a small part of the annual application is made in autumn, the current study assumes that the autumn application equals a quarter of annual fertiliser, and the spring application is split evenly (table 2.4). For the spring cereal varieties all recommended N fertiliser is input in spring (table 2.4), a half to seedbed and the other half at 2-3 leaf stage (Dyson and Sinclair, 1993). For oilseed rape that is commonly grown as a winter variety, an autumn application is recommended at sowing, which would provide 50kg N (~ 25% of annual standard application of 175 kg N ha^{-1}). The remainder of recommended N input is normally split in half and applied first at the start of spring growth and second prior to stem elongation (Dyson, 1993). There are two main potato types grown: for seed and main crop ware, the latter requires more N input to prolong the tuber-bulking period (table 2.4, Dyson *et al.*, 1993). According to SAC[4] recommendations ~ 50% of total recommended N should be applied at planting, and the remainder between emergence and tuber incubation (table 2.4, Dyson *et al.*, 1993). Vegetables are not grown in Scotland, hence the recommendations used in the current study were based on those of MAFF and SOAEFD (1991). Vegetables have different requirements in terms of the timing of application that is linked with the planting period. Some crops (e.g. lettuce and radish) prefer split application, others require just a one top-dressing. For a few vegetable crops recommendations were not published (MAFF and SOAF, 1991). It was assumed that two split applications of annual N input to vegetables take place in the beginning of March and April (table 2.4). Grassland management is the most versatile and recommendations vary depending on the purpose of grassland growth, intensity of management (livestock stocking density) and geographical location. The number of split applications varies from 2 - 5 depending on the climatic conditions that control plant growth (table 2.4, Dyson, 1992; MAFF and SOAF, 1991).

[4] Scottish Agricultural College

Grazing practices and their effect on N_2O and NO emissions.

The constant presence of animals on pastures leads on the one hand to continuous N enrichment via direct excreta input, and on the other to N uptake via consumption. There is also an additional effect of animal tramping, which leads to soil compaction and subsequently promotes conditions for denitrification and associated N_2O loss. Field measurements of N_2O emissions by Velthof *et al.* (1996b) confirmed this as the estimated daily means of emissions were greater for the grazed than mown grassland and ranged between 1.6 – 12.7mg N m^{-2} h^{-1} and 0.4 – 6.8 mg N m^{-2} h^{-1}, respectively. The proportion of N enrichment lost due to volatilisation depends on a number of factors among which the composition of excreta and soil moisture are the most important. N_2O emission factors presented in the literature vary, but the characteristic pattern of seasonal variability of emissions is consistently reported. Flessa *et al.* (1996b) observed 3.8% of cattle urine loss due to N_2O emissions and 0.5% of dung loss. Yamulki *et al.* (1997) observed emission factors from dung ranging from 0.03% in July to 0.74% in October and Allen *et al.* (1996) reported no N_2O release from excreta input in summer and 0.8-2.3% in winter. No detailed explanation of this trend was offered, but the higher fluxes in winter could be explained by wetter soil conditions and, in the absence of plants, no competition for the available mineral N in soils. Some researchers noticed a difference in N_2O emissions for different soil types that were subject to grazing. Velthof and Oenema (1995) observed 0.5% loss from sand, 1.4% from clay and 2.3-3.9% from peat. But this was not reported by others (Yamulki *et al.*, 1997). Soil texture has a more important effect when excreta types vary. In Allen *et al.* (1996) total N_2O emissions for autumn and winter from dung and urine were higher from moderately drained loam (207 and 197 mg N kg^{-1} for dung and urine, respectively), but from poorly drained silty clay loam high emissions were reported only for urine (0.2 and 148 mg N kg^{-1}). Generally emission factors from grazed grasslands vary considerably with the mean oscillating around 2% (Fowler *et al.*, 1997; Monaghan and Barraclough, 1993; Vermoesen *et al.*, 1997).

Few studies report NO emissions from excreta input, the emission factors for NO are considerably lower and vary between 0.03% for freely-drained loam covered with ryegrass (Colbourn *et al.*, 1987) and 0.26% for bare agricultural soil in laboratory conditions (Paul *et al.*, 1993). Low emissions from grazed grasslands are associated with the treading effect, which leads to more compacted soils with increased

anaerobic sites and restricted diffusivity that reduces NO production and emissions. Oenema *et al.* (1997) suggested an increase in N_2O emissions by a factor of 2 caused by the treading effect that might suggest its restricting effect on NO.

Livestock excreta production is estimated on the basis of the number of animals and an amount of manure produced per animal head. There are many studies of the manure production rate and the nutritional content for different types of livestock carried out by government organisations, among which ADAS[5], DAIO[6] and SAC are compared and listed in tables 2.5-2.8. There are observed differences in the presented estimates that have a number of causes. Firstly there are variations in the classifications of livestock and the states of organic fertiliser used in the calculations of the production data and nutritional content of manure.

Table 2.5. UK livestock numbers, amount of excreta per animal and N content of livestock manure in 1990.

Livestock	Numbers [millions]	Total excreta [10^6 t]	Excreta per animal [t]	N content [kg N t^{-1}]
Cattle	12	128.6	10.7	2.5
Sheep	43.4	48.9	1.13	N/A
Pigs	7.4	9.4	1.27	8.08
Poultry	161.7	4.6	2.84*	24.35

Source: MAFF, 1990.
*excreta produced by 100 animals

Table 2.6. Manure production and nutrient content in 1989

Livestock	Manure produced per animal annually [t/y]	N content[kg/t]
Dairy cow	23.0^S	4.7^S
10 Pigs	21.0^S	6.3^S
100 Layer hens	10.0^S	5.4^S
100 Layer hens	2.3^M	21.7^M
1000 Chickens	1.1^M	21.5^M

Source: Bockman *et al.* (1990)
^{S} Slurry, ^{M} Manure

[5] Agricultural Development and Advisory Service
[6] Danish Agricultural Information Office

Table 2.7. N content of organic manures and their production rates per animal.

Type of fertiliser	N content
Cattle FYM	6.0 kg N t^{-1}
Pig FYM	7.0 kg N t^{-1}
Poultry manure	29 kg N t^{-1}
Dairy slurries	av. 3.0 kg N m^{-3}
Beef slurries	av. 2.3 kg N m^{-3}
Pig slurries	av. 5.0 kg N m^{-3}

Sources: Chambers and Smith (1993)

Table 2.8. SAC position on N content in manure according to livestock.

Livestock type	Total nutrients [kg N t^{-1}]	Livestock type	Amount of manure [t $week^{-1}$]	Nutrient composition of organic manure [kg N yr^{-1} $animal^{-1}$]
Cattle	6.5	10 dairy cows	2	67.8
		10 young cattle	0.6	20.3
		10 fattening cattle	1.3	44
Pig	7	100 fattening pigs	1.5	11.8
		10 sows + litter	0.5	11.8
Broiler litter	24	1000 broilers + litter	0.2	0.78
Deep litter	17	1000 hens + litter	1.1	0.78
Battery (fresh manure)	17	1000 battery hens (fresh)	0.8	0.78
Battery (air dry)	41	1000 battery hens (air dry)	0.34	0.78

Source: Dyson (1992)

MAFF (1990) does not differentiate between different types of cattle and poultry (table 2.5), while DAIO (Bockman *et al.*, 1990) includes information on dairy cows, layer hens and chickens (table 2.6); Chalmers and Smith (1993) present the N content data for both beef and dairy slurries (table 2.7), and Dyson (1992) distinguishes subgroups within the main animal types (dairy, pigs and poultry) (table 2.8). Secondly, there are inconsistencies with regards to the state of organic fertiliser for which data are presented. MAFF (1990) gives estimates for excreta, which is a general term for animal waste (table 2.5); DAIO, Chalmers and Smith (1993) provide information for both slurry and manure (tables 2.6 and 2.7); Dyson (1992) presents farmyard manure composition (table 2.8). There was no information from the available sources on the proportion of different types of organic waste produced by farmed animals, which resulted in an assumption that all organic waste is applied to fields as manure. This might cause an overestimation due to a higher N content in manures. From the presented information SAC source gives the

most detailed account of animal types and their nutritional content of manures, which decided on its application in the current study.

Atmospheric deposition.

There are few damaging effects of atmospheric N deposition on semi-natural environments. The most commonly recognised are the destruction of plant tissue by high concentrations of NO_3^- and NH_4^+ deposition to forests and acidification of aquatic ecosystems leading to reduction in biota diversity (Geir-Havald Strand, 1995; Henrichsen, 1986). This problem was first recognised at United Nations Conference on the Human Environment in Stockholm when the evidence of large-scale freshwater acidification in southern Scandinavia was presented (Bolin *et al.*, 1972). Contrasting to these reports are the results of studies in Scandinavia and Germany observing temporary accelerated tree growth due to atmospheric N deposition (Gundensen, 1991; Seibt, 1983). Substantial evidence of damaging effects of acid deposition due to transboundary pollution led to the Convention on Long-Range Transboundary Air Pollution (LRTAP) in 1979, which has currently 40 members who agreed to participate in efforts against air pollution. In 1988 LRTAP proposed the Protocol on the Control of Emissions of Nitrogen Oxides or Their Transboundary Fluxes ('Sofia Protocol'), which was the first legislation committing the parties of LRTAP to reduce the NO_x emissions to the 1987 levels by 1994 (DoE, 1997).

There are two main groups of atmospheric N deposition compounds: wet deposition (NH_4^+ and NO_3^-) and dry deposition (NO_2, HNO_3, NH_3, PAN, HONO and particulate material containing N) (DoE, 1994). The distribution of N deposition is variable in different ecosystems. In 1994 total N deposition ranged in Great Britain from < 10 kg N ha^{-1} in the Sutherland and Wester Isles to > 30 kg N ha^{-1} in Lake District, Snowdonia, Exmoor and East Anglia. Atmospheric N deposition is an important source of soil N and plays a major role in enhancing N gaseous losses from soils in semi-natural environments. The highest values of atmospheric N deposition have been observed on high altitude areas where higher concentrations of dissolved ions in rainfall were measured. This has been associated with a seeder-feeder enhancement that is described as scavenging of polluted 'hill cap' clouds by non-polluted raindrops (Dore *et al.*, 1992).

In agricultural systems, on the other hand, N atmospheric deposition is generally only a minor additional source of N that contributes on average <20% of soil N

supply (assuming N deposition rate of 20 kg N ha^{-1} and N fertiliser input rate of > 100 kg N ha^{-1}). There are, however, hot-spots of dry N deposition associated with high livestock intensities; enhanced dry deposition of NH_3 occurs downwind of poultry and pig farms. High NH_3 deposition rates of 80, 50 and 17 kg N $ha^{-1}y^{-1}$ were observed at a distance of 30 and 50m and 250m respectively downwind from a large poultry farm (Pitcairn *et al.*, 1998).

Increased N content in soils due to high atmospheric N deposition leads to higher enzyme activity of nitrifiers and denitrifiers. Many studies (Henrich and Haselwandter, 1997; Papke and Papen, 1998; Skiba *et al.*, 1998b) concerning the influence of N atmospheric deposition on the NO and N_2O emissions indicate that this problem affects mostly semi-natural environments. In Britain most agricultural soils are situated at low altitudes, while semi-natural land dominates at higher altitudes, where seeder-feeder enhancement occurs. High cloud deposition at the summit of Dunslair Heights, in the Scottish Borders, was partly a reason for increased N deposition rates from 6.4 kg N ha^{-1} y^{-1} (below the height of cap cloud formation at 380m) to 24 kg N ha^{-1} y^{-1} at the summit - 615m (MacDonald *et al.*, 1997). Additional enhancement was caused on the summit by the forest canopy, which intercepted acid deposition. Deposition rates can increase by up to 90 % as a result of tree interception and washing off by rainfall (Fowler *et al.*, 1989)

To summarise, N atmospheric deposition is less significant on agricultural land due to intensive fertiliser management practices having a greater effect on the levels of emissions. But on unmanaged land (rough grazing or fallow) the contribution of atmospheric deposition to total N is considerable, especially in areas of enhanced deposition (Tietema and Verstraten, 1991).

Studies of increased atmospheric deposition to forest show that there is a significant increase in N_2O and NO emissions from soils, even in acidic conditions (Henrich and Haselwandter, 1997). In south central Scotland an annual increase in N_2O emissions was estimated at > 3 % of deposited N that amounts to an average of 48 kg N ha^{-1} yr^{-1} (Skiba *et al.*, 1998b). The effect of increased N inputs to forests was observed in a beech woodland in the Solling area in Germany in the period of 1987 - 1988 (Brumme and Beese, 1992). N_2O emissions from sites with higher N content ranged from 0.35 - 1.96 kg N ha^{-1} $month^{-1}$ compared to the control plots, where mean monthly emissions were 0.21 - 1.78 kg N ha^{-1} $month^{-1}$. The effects of

intensive livestock husbandry on the neighbouring forest were studied in southern Scotland by Skiba *et al.* (1998b). The mean emission factor as a proportion of total N deposited was 0.76% for that area and ranged from 0.2 to 15%. Environmental factors have a limiting effect on emissions. High soil moisture provides good conditions for complete denitrification that reduces N_2O to N_2. This was observed by Castro *et al.* (1993) who measured N_2O mean annual fluxes of 0.02 - 0.08 kg N ha^{-1} in the Appalachians that were lower than N_2O emissions measured in similar environments in Wisconsin (Goodroad and Keeney, 1984). Higher temperature has a positive effect on N_2O fluxes from forests enriched with atmospheric N input as observed by Brumme and Beese (1992). They measured peak N_2O emissions in July and August (1.1 - 1.96 kg N ha^{-1} $month^{-1}$) when soil temperatures at 5 cm depth varied between 10 - 15 °C. Emissions of NO were also increased by atmospheric N deposition. The NO emission factor was estimated at 0.35% by Johansson (1984) for pine forest near Stockholm, Sweden. Valente and Thornnton (1993) reported NO emissions > 1kgN ha^{-1} yr^{-1} from a forest in Tennessee which was explained by a possible high N input to soil from a runoff from an upslope agricultural field. Skiba *et al.* (1998b) observed NO losses from mixed woodland in South-central Scotland in the range 1.3 - 20% of atmospheric N input.

Acid deposition effects vegetation directly through the uptake of acid mist by leaves, and indirectly by increasing acidity of soils. Low pH (< 5.5 pH as suggested by Swift, 1988) of soils has fatal effects on agricultural crops and semi-natural vegetation. Neutralising soil pH has been necessary in many affected environments by adding limestone. Liming is a common management practice on agricultural soils and in forested areas of increased atmospheric deposition. It was observed to reduce N_2O emissions from a beech forest in Germany by 8-62% (Brumme and Beese 1992). This, however, varies and some field studies found increased N_2O emissions 1.6 fold (Butterbach-Bahl *et al.*, 1997). Liming was reported to reduce NO emissions, the observed decrease varied from 25-30% in Sweden (Johansson, 1984) to 43-100% in Hoglwald spruce forest in southern Germany (Papke and Papen, 1998).

2.2.5.2 Main management practices that influence N_2O and NO emissions.

Fertiliser N input to agricultural soils in mineral and organic form and grazing are without doubt the most important factors controlling N_2O and NO emissions from agricultural soils. There are, however, other agricultural practices like tillage,

irrigation and drainage, which disturb natural physical, chemical and biological characteristics of soils and disrupt the nature of biological processes. Their effect on N_2O and NO emissions can be substantial. The following section discusses the nature of those changes and their effects on the emissions. Additionally, biomass burning and land use change have been included in this discussion, as they are considered important controlling factors of the emissions and are associated with anthropogenic effects.

Tillage

Mechanical disturbance of soil structure to increase aeration of soils takes place on many arable soils in autumn and spring that results in a fundamental change in the soil physical and biological characteristics and destruction of soil structure. Greater aeration of soils increases microbial activity and mineralisation of organic N. Tillage is also accompanied by incorporation of the previous year's crop residues, which provides a carbon source for the micro-organisms. On several sites for different crops throughout USA, conventional tillage produced 1.6 times more N_2O than no tillage (Mummey *et al.*, 1998). Increased NO emissions following tillage were observed by (Slemr and Seiler, 1991) who reported emission rising from 0 – 0.5 kg N ha^{-1} y^{-1} to 0.9 – 6.4 kg N ha^{-1} y^{-1} from grassland on a sandy loam.

Irrigation

This is an agricultural practice aimed at increasing soil water supply to crops. Increased soil water availability and reduced aeration promote denitrification and an increase in the ratio production of N_2O/NO. Timing and frequency of irrigation were recognised as important factors in the emission response of soil (Mosier, 1994), as large and less frequent water applications resulted in lower N_2O production (Rolston *et al.*, 1984).

Drainage.

Drainage as a management practice is common in Britain on cultivated land, especially on soils characterised by restricted drainage of Land Capability Class - LCC 2, 3 and 4 (Brady, 1990) where drains are used to reduce water logging. Drainage increases aeration and promotes higher rates of nitrification. Colbourn and Harper (1987) observed lower denitrification (reduced from 14 kg N ha^{-1} to 9 kg N ha^{-1}) and a shift in the composition of its products from N_2 to N_2O emissions from drained arable clay soil in Oxfordshire. This was due to restriction of denitrification in more aerated drained soils with increased diffusion of oxygen down to the ground

water level lowered from 20 down to 50 cm by drainage. The highest N_2O emissions from drained clay were observed by Colbourn and Harper (1987) in late autumn, which contrasted with very low N_2O emissions from undrained clay (38 and 1.7 kg N ha^{-1} y^{-1}, respectively).

From all the soil types drained for agriculture, peats are recognised the highest source of N_2O and NO due to their high C content, but they are proportionately a small fraction of all agricultural soils. The HOST[7] classification describes 0.55% of all British soils as drained peats that make up 2.4% of peatlands in Great Britain. Organic soils form the majority of soil cover in North-west Scotland, most upland areas in Britain and in Cambridgeshire, where peatlands are adopted for agriculture through drainage. Undrained raw peats often covered by bog or heathland and moorland vegetation have a very low mean pH of 3 (Avery, 1990). In these conditions rates of decomposition are low which promotes a high organic C content. Drainage practices reduce soil water content and increase aeration that stimulates mineralisation. The high fertility of peats promotes high N_2O and NO emissions, but this increase is not always observed. Freeman *et al.* (1997) reported > 95% decline in N_2O emissions from drained peat in mid-Wales, which was 'balanced' by a 200% increase in N leaching. They suggested that the abundance of organic carbon favoured complete denitrification and led to a decrease in N_2O/N_2 ratio.

Biomass burning.

This source plays a major role as a contributor of N_2O and NO emissions in the tropical and subtropical regions. Burning in those areas can be caused either by natural events, e.g. natural forest fires and savanna burning occurring towards the end of dry season (Yienger and Levy, 1995), or setting fires deliberately for larger scale clearance. In Britain biomass burning occurs on a much smaller scale and is linked to the seasonal burning of heathland to promote regeneration. In the recent past it was also associated with the burning of crop residues, but this has been mostly stopped for environmental reasons. Biomass burning was observed to increase NO emissions as a result of intensified mineralization, lack of competition from N uptake by plants and increased carbon content (Sanhueza, 1997). It also increased N_2O emissions due to reported increased rates of nitrification (Johansson

[7] Hydrology Of Soil Types

and Sanhueza, 1988; Levine *et al.*, 1988; Levine *et al.*, 1990; Levine *et al.*, 1996; Parsons and Scholes, 1996). The reports in the literature are, however, conflicting. Studies by Levine *et al.* (1996) of NO and N_2O emissions from savannas in South Africa suggests no N_2O emissions as a result of fire. This contrasts with an earlier study of N_2O emissions in temperate climate following wetting and burning that showed a considerable enhancement in emissions (Levine *et al.*, 1988).

A global inventory of soil-biogenic NO_x emissions assumes biomass burning to cause a local mean increase of NO emissions by a factor of 3 (Yienger and Levy, 1995). Local studies of the effect of biomass burning on NO emissions report a higher response to burning. Levine *et al.* (1990) observed an increase of emissions from 0.1 to 0.9 and 1.8 after the first and second burning of saturated marshland. Anderson *et al.* (1988) recorded an increase in NO emissions from chaparral forest in California from 0 – 10.8 kg N ha^{-1} y^{-1} to 1.8 – 31.3 kg N ha^{-1} y^{-1}. Those enhanced NO emissions are localised and the measurement periods are short. Yienger and Levy (1995) suggested that the observed emission factors cannot be applied to all ecosystems for longer periods, as the calculated totals would be over-estimated.

Infrequent and highly localised biomass burning in temperate climates might suggest that the range of emissions from wet ecosystems of Britain is much smaller than in the subtropical and tropical regions.

Land use change.

Change of vegetation cover has both natural and anthropogenic origins. Human effects on natural vegetation cover are normally associated with deforestation and reforestation. Bouwman *et al.* (1990) recognised both natural and anthropogenic causes of deforestation. In the first group fires are the main factor. The anthropogenic effects are more complex as there are several different types of human behaviour e.g. traditional, that includes shifting cultivation and fuel wood collection; economic effects that embrace all types of agricultural management and socio-political ones that are associated with population migrations and urbanisation (Bouwman *et al.*, 1990).

Deforestation for economic reasons is widespread in tropical regions, where large-scale permanent clearance of rainforest for plantation crops and timber trade is common. In the past century clear cutting was common in temperate regions, but

presently it occurs on a much smaller scale. Between 1984-1990 deforestation for agriculture in the UK occurred in 3.2% of coniferous forest and 6.2% of deciduous woodland, while urban developments damaged only 0.8% of deciduous forest (DoE, 1993). These changes, however, were rather small and might have been temporary.

Deforestation has serious effects on the water balance in soil by increasing runoff, decreasing soil infiltration and reducing plant water uptake (Bouwman, 1990). Further changes involve a reduction of organic matter input and soil acidity and the deterioration of soil structure. With deforestation there is a clear NO emissions increase as observed by Keller *et al.* (1993) in Costa Rica. They reported NO emissions from young tropical pastures of 8.6 kg N ha^{-1} y^{-1} exceeding those from tropical forest of 1.29 kg N ha^{-1} y^{-1}. These soil transformations create good conditions for nitrification as observed in a Norway spruce forest in Finland by Smolander *et al.* (1998), who noted an increase in nitrification rates from aproximately 5 to maximum of 850 μg N g^{-1} 40 d^{-1} in the first year and the peak rate of ~ 1000 μg N g^{-1} 40 d^{-1} in the second year after clear-cutting on a control plot. The increase is due to a lack of competition for the available N in soils and increased mineralization caused by high organic N content in soils originating from the dead biomass. As a result, young pastures, succeeding forests, emit increased amounts of NO. With time, however, when this N source becomes exhausted, the importance of well established grasslands as NO emitters, decreases (Keller *et al.*, 1993).

2.2.5.3 Soil moisture

The most important effect of water on the production of NO and N_2O in soils is the strong influence on the rate of O_2 supply and soil diffusivity. Denitrification occurs only when the oxygen supply is limited by, for example, high soil water content, while nitrification is dependent on a sufficient supply of O_2 (at low to moderate soil water content) (Davidson, 1991). The relationship between relative N fluxes and soil moisture (WFPS) was derived by Davidson (1991) on the basis of several field measurements, in which a changing pattern for production processes of NO and N_2O became apparent (figure 2.2). NO was produced mainly by nitrification with the peak production rate occurring at ~55% WFPS. With increasing soil moisture, denitrification became a dominant bacterial process, with an increasing role for N_2O as its final product (maximum ~ 60-65 % WFPS). When the WFPS > 80% N_2 was the dominant gas produced.

The soil water content depends on the amount of precipitation, soil and the rate of evaporation. WFPS is the proportion of soil pores filled with water and is described as a function of absolute water content in soil and soil porosity (equation 2.5).

$$WFPS = \frac{VWC}{P} * 100\% \qquad (2.5)$$

Where: WFPS - water filled pore space [%],

VWC - volumetric water content [%],

P - porosity [$cm^3\ cm^{-3}$].

Volumetric water content (VWC) indicates soil moisture status (table 2.9) that controls the aeration of soils, an important factor of N_2O and NO emissions, but it does not account for soil texture. Soil porosity is applied in calculation of WFPS that accounts for different textural characteristics of soils (equation 2.5). WFPS hence varies for different soil textural classes (table 2.9).

Table 2.9. Typical porosity and moisture characteristics for main textural classes estimated from Hall *et al.* (1977).

Texture of A horizon	Pore space [%] of total soil volume	WFPS [%]		
		Field capacity	Wilting point	AWC
C	58.6	81.9	49.5	32.4
zC	62.2	78.3	44.1	34.2
zcL	56.8	79.4	37.1	42.3
cL	54.7	79.2	38.8	40.4
scL	49.7	78.3	38.2	40.1
zL	50.9	78.6	29.1	49.5
szL	50.6	69.2	25.7	43.5
sL	50.6	61.3	24.9	36.4
lS	49.1	40.7	13.4	27.3
S	45.3	30.5	6.0	24.5

C - clay, zC - silty clay, zcL - silty clay loam, cL - clay loam, scL - sandy clay loam, zL - silt loam, szL - sandy silt loam, sL - sandy loam, lS - loamy sand, S - sand, AWC - available water capacity = WFPS at field capacity – WFPS at wilting point, WFPS - water-filled pore space.

Soil moisture in field conditions oscillates between field capacity and wilting point. Typical values of WFPS in those water regimes may indicate bacterial processes expected in different soil types. On the basis of Davidson's (1991) model and WFPS estimates for different water regimes some conclusions can be drawn regarding the dominant bacterial processes in soils. Optimal conditions for nitrification are more likely to be found in coarse and medium textured soils, while fine textures can provide more often good conditions for denitrification. Heavy clay soils at field capacity and all saturated soils (with WFPS > 100%) do not provide good conditions for NO and N_2O emissions. Waterlogging promotes complete denitrification with N_2 as the final product and any intermediate products (N_2O and NO) are not expected to escape the soil surface due to the high activity of denitrifiers like *Pseudomonas*, *Bacillus* and *Paracoccus* (Bouwman, 1990) and minimal diffusivity.

Precipitation events control gas emissions from soils into the atmosphere. For all soil texture classes both nitrous and nitric oxides emissions increase following rainfall events. Wetting a dry soil was observed to enhance NO and N_2O emissions (Parton *et al.*, 1988; Mummey *et al.*, 1994; Scholes *et al.*, 1997). The increased amounts of available water in soils activates bacteria, including groups that metabolise inorganic N (Davidson *et al.*, 1993). Especially large N_2O emissions were observed after watering very dry soils of semi-arid environments (Parton *et al.*, 1988

and Mummey *et al.*, 1994). N_2O evolution rates may be one, two or even three orders of magnitude higher than the prevailing rates preceeding the burst. This large response, often referred to as 'pulsing' of N oxides release, was short and occurred immediately after wetting (Mummey *et al.*, 1994). Scholes *et al.* (1997) observed an increase in N_2O and NO emissions from a savanna in South Africa immediately following wetting dry soil (VWC = 1.2%). Just a few hours after wetting the soil N_2O increased from the background levels of 0.03 - 0.27 kg N ha^{-1} y^{-1} to 1.05 - 3.01 kg N ha^{-1} y^{-1}. At the same time an NO peak of 23.6 kg N ha^{-1} y^{-1} was observed, but after 3 days NO emissions returned to the mean fluxes of 3.1 - 9.3 kg N ha^{-1} y^{-1}. In those dry environments nitrification is believed to be the principal source of N_2O (Parton *et al.*, 1988; Scholes *et al.*, 1997) and NO. The short-lived emissions observed by Scholes *et al.* (1997) could not be entirely explained by mineralization and nitrification processes that continued after the observed decline in NO and N_2O emissions. Pulsing is not as common in Britain due to the even distribution of rain throughout the year. In temperate climates N_2O and NO emissions continue at higher levels in conditions of optimal soil moisture (Davidson, 1991) until the N substrate present in the soil is depleted. A sharp increase in soil moisture to field capacity can produce a 'pulse' effect, but the subsequent wetting may cause waterlogging and restrict soil diffusivity.

Bouwman *et al.* (1990) suggested that the release of N_2O from soil into the atmosphere is enhanced by alternate drying and wetting of soils, but the subsequent peaks show decreasing emission rates. Hutchinson *et al.* (1993) observed ungrazed Bermuda grass pasture on well-drained sandy loam. They noted larger peaks of NO emissions of 1.2, 1.3 and 1.43 μg N kg^{-1} h^{-1} for high, medium and low initial soil moisture. The enhanced emission began to drop after 30 hours and reached the minimum level on the fourth day. The second water addition caused NO emissions to increase only for soil of low and medium soil moisture to 0.9 and 0.6 μg N kg^{-1} h^{-1}, while the soil of high initial moisture did not respond to the second wetting. A similar sequence was observed on an alder plantation, where subsequent NO emission peaks reached 0.7, 0.4 kg N ha^{-1} y^{-1} with water applications of 0.7 and 1.0 mm (Skiba *et al.*, 1997). Two days after the second wetting the emissions declined to an average 0.2 kg N ha^{-1} y^{-1} and did not respond to 6.7mm rain.

With an arithmetic increase of soil water content, N_2O emissions increase exponentially as was observed by Fowler *et al.* (1997) on the basis of several studies on grassland sites in Europe. An increase in soil moisture from 22 to 40% dry weight was followed by increase from 0 to approximately 65 kg N ha^{-1} y^{-1} and the response was not observed when soil moisture was below 26.5% dry weight (Fowler *et al.*, 1997).

The presented studies confirm Davidson's model (1991) and suggest a dynamic nature of soil processes controlled by rapidly changing soil water regime.

2.2.5.4 Soil temperature

Soil temperature as a controlling factor for denitrification and nitrification has been reported to have a considerable effect on seasonal variability of both N_2O and NO emissions (Skiba *et al.*, 1994). It is a positive controlling factor of microbial activity, denitrification and nitrification rates (Granli and Bockman, 1994). There is very little bacteria growth when temperature is in the range of 0-5°C and similarly when it reaches very high values. At 65°C denaturation occurs, therefore the production process of NO and N_2O ceases. The optimal temperature for bacterial growth is 30°C in most cases (Saad and Conrad, 1993). The temperature dependence of nitrification and denitrification is described by Q_{10}, or the activation energy (E_a).

Q_{10} is an expression of the increases in a reaction rate for every 10°C rise in temperature. The relationship between the rate of emission and temperature is also described by the activation energy (Ea) that indicates the optimal temperature for bacterial growth. Ea is a measure of the correlation between soil temperature and bacterial activity, as described by the Arrhenius equation (2.6).

$$\text{Flux} = (\text{Ea}/R)(1/T) + \text{constant} \qquad (2.6)$$

Where R - gas constant of 8.31J mol^{-1} K^{-1}
T - absolute temperature in K

The response of bacterial processes to increasing temperature starts with a positive relationship expressed in the bacterial growth curve that rises to an optimum and then decreases. The activation energy and Q_{10} for a particular reaction in soil are variable. Their variability reflects physical and biological factors, e.g. changes in gas solubility in water or changes in microbial populations (Granli and Bockman,

1994). Goodroad and Keeney (1984) observed changes in the production rate of N_2O from Q_{10} = 3.3 for a temperature rise from 10 to 20 °C and Q_{10}=3.1 for a further increase from 20 to 30 °C. Conrad *et al.* (1983) observed daily oscillations in N_2O production processes from a lawn. They measured E_a in the range of 20 to 150 $kJmol^{-1}$ and Q_{10} = 2.8 for the range in temperatures from 13 to 23°C. Changes in the values of the microbial activity parameters were observed for different crops by Johansson and Granat (1984). They estimated E_a and Q_{10} values for NO production of three types of crops: barley and grass lay (E_a=83 KJ mol^{-1} and Q_{10}=3.6), and lucerne (E_a=65 KJ mol^{-1} and Q_{10}=2.7). The temperature dependence of NO and N_2O emissions from aerobic soils can be characterised by the E_a of approximately 80 KJ mol^{-1} (Skiba, 1991).

The seasonal variability in N_2O emissions is well documented in the literature (Bowden *et al.*, 1990b; Conrad and Seiler, 1980; Dunfield *et al.*, 1995; Velthof *et al.*, 1996a and Yamulki *et al.*, 1995). The highest rates of N_2O production and emissions were reported in spring and summer, when an estimated 66 % of annual N_2O were emitted (Yamulki *et al.*, 1995). Velthof *et al.* (1996a) observed a similar trend in N_2O emissions for grassland, where mean emission in June was estimated at 93 kg N ha^{-1} y^{-1} and in September and November about 20.8 kg N ha^{-1} y^{-1}. Diurnal changes in N_2O emissions generally followed temperature, but with a certain delay as observed by Yamulki *et al.* (1995). The time lag between the maxima of emissions and temperature suggested that N_2O was produced by denitrification in deeper soil levels.

NO emissions were also reported to vary annually, with higher fluxes measured in spring and summer (Johansson and Granat, 1984; Anderson and Levine, 1987; Valente and Thornton, 1993; Jambert *et al.*, 1994). On grassland, NO emissions of 1.2 kg N ha^{-1} y^{-1} were reported in summer (June-August) compared to 0.1 kg N ha^{-1} y^{-1} in winter (December - February) by Anderson and Levine (1987). Jambert *et al.* (1994) confirmed a similar trend in NO emissions from a maize field in France, where 0.3 - 0.6 kg N ha^{-1} y^{-1} were reported in January and 11 - 171 kg N ha^{-1} y^{-1} in June. The daily distribution of NO emissions was observed by Yamulki *et al.* (1995) who measured the fluxes to range between 2.17 and 5.27 kg N ha^{-1} y^{-1} and the emissions were observed to follow the temperature curve closely. This suggests that the location of NO sources is closer to the soil surface than in the case of N_2O.

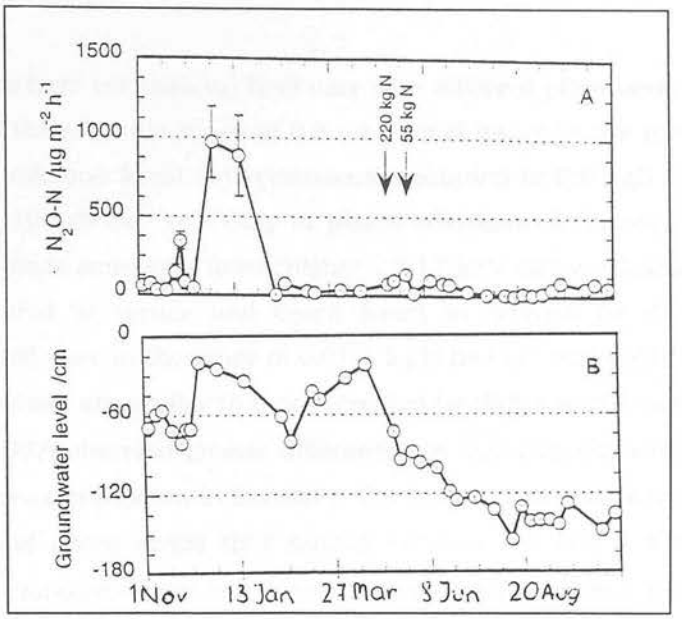
Temperature responses in N_2O emission patterns are not always observed as changes in other important controlling factors like N concentration in soils or soil moisture may override the temperature effect. The N content of soils is a very strong factor for both N_2O and NO emissions that enhances emissions in spring and summer when the N fertiliser is applied. In semi-natural environments the relationship between temperature and N_2O emissions is often more apparent than in agricultural soils (Skiba *et al.*, 1998b).

Freeze-thaw cycle.

In many long-term experiments, measurements throughout the coldest part of the winter period have been ignored due to the limiting effect of low soil temperature on bacterial processes leading to N_2O and NO emissions (Armstrong, 1983). Recently, winter-time N_2O emissions have been shown to significantly contribute to the annual flux, hence the annual N_2O emissions might have been previously underestimated (Brooks *et al.*, 1997; Burton and Beauchamp, 1994; Goodroad and Keeney, 1984 and Van Bochove *et al.*, 1996). The increase in N_2O emissions in winter has been associated with a freeze-thaw cycle, which was observed in many studies. Dorsch *et al.* (1997) observed microbial behaviour patterns during a freeze-thaw experiment on fine-loamy soil with added mustard straw. Freezing caused wide-spread death of soil microorganisms, which in turn provided large amounts of organic matter for the surviving bacteria and caused a 'respiratory burst' during a thaw. Low temperatures in soils caused low N_2O/N_2 ratios and enhanced N_2O production. Mean N_2O emissions of 86.7 and 94.2 kg N ha^{-1} y^{-1} were measured after thawing from plots with an initial temperature of -4 °C and -20 °C. The emission from a control plot that was not frozen was much smaller (0.6 kg N ha^{-1} y^{-1}). Muller *et al.* (1997) observed an increase in N_2O emissions from unfertilised grassland on loamy sand overlying gley that rose within 7 days from 2.1 to 4.3 kg N ha^{-1} y^{-1}. Both studies by Dorsch *et al.* (1997) and Muller *et al.* (1997) are short term (up to 2 weeks) and their findings present limited evidence of higher emissions in the cold period than those during warmer months. A longer study by Rover *et al.* (1998) of N_2O emission rates from arable silty loam soil presents better evidence. Observed fluxes of 5.8 and 9.4 kg N ha^{-1} y^{-1} from unfertilised and fertilised plots during December - February exceeded those from the same plots during March – November that averaged at 0.5 and 1.5 kg N ha^{-1} y^{-1}. Another long-term study of drained peat soil under four management practices was prepared by Flessa *et al.* (1998) who observed the largest N_2O emissions in winter when the groundwater level was high

(figure 2.7). A current PhD study is investigating the effect of the freeze-thaw cycle on NO emissions, which have been observed to increase temporarily (R. Thorman pers. comm).

Figure 2.7 Enhanced winter N_2O emissions measured from peat grassland (Flessa *et al.*, 1998).



The above research suggests that N_2O emissions during the winter period form a substantial proportion of the annual total due to the freeze-thaw cycle.

2.2.5.5 Vegetation cover

Vegetation has an important effect on biological processes in soils due to the production of organic material and removal of available N as NO_3^- and NH_4^+ (Granli and Bockman, 1994). Uptake of N from the soil pool by plants is an important part of the nitrogen cycle and it varies between species, but it also depends on weather conditions. A montane grassland at Llyn Llydaw, Snowdonia, was estimated to take up 162 kg N ha^{-1} (DoE, 1994). Clough *et al.* (1996) reported plant uptake of urine-N applied at a rate of 500 kg N ha^{-1} in managed grassland averaging at 10.9% and 35.4 % for mineral and peat soils, respectively. Much greater uptake was estimated in the hot and humid tropical climate of Costa Rica, where the average uptake of rain forest is about 400 kg N ha^{-1} yr^{-1} and of pasture – 200 kg N ha^{-1} yr^{-1}

(Bouwman, 1995). The effect of vegetation cover on the processes of denitrification and nitrification is variable. Plants can stimulate those processes due to decomposition that is especially active in rhizospheres, and water consumption (Granli and Bockman, 1994) that change the aerobic conditions in microzones. In conditions of restricted amounts of N content in soils, however, plants compete successfully with bacteria for the available NO_3^- and may halt denitrification (Granli and Bockman, 1994).

N_2O emissions from seminatural land vary with different plant cover. In south-east Scotland N_2O fluxes in the range of 0.3 - 1.3 kg N ha^{-1} y^{-1} were reported for grass species. In coniferous forest N_2O emissions amounted to 0.5 kgN ha^{-1} yr^{-1} and on moorland - 1.16 kgN ha^{-1} yr^{-1}. Only in places of enhanced atmospheric deposition were nitrous oxide emissions much higher - 3.17 kgN ha^{-1} yr^{-1} (Skiba *et al.*, 1994). Fluxes registered in spruce and beech forest in Sweden by Klemedtsson and Svensson (1988) were in the range of 0.01-1 kg N ha^{-1} yr^{-1} and 0.01-2 kg N ha^{-1} yr^{-1}, respectively, which are similar to those reported by Skiba *et al.* (1994). Butterbach-Bahl *et al.* (1997) observed greater differences in N_2O emissions from forests with different species composition in Germany. The lowest emissions were observed from a spruce stand (*Picea abies*) that ranged between 0.3 and 1.4 kg N ha^{-1} yr^{-1}. Intermediate emissions were registered from pine forest (*Pinus sylvestris*), where mean N_2O emissions ranged between 0.5 and 4.6 kg N ha^{-1} yr^{-1}. The highest N_2O emissions were observed from a beech plot (*Fagus silvatica*) with the range of 0.7 - 8.9 kg N ha^{-1} yr^{-1}. Much smaller N_2O emissions from moorland at an altitude of 615 m were measured by MacDonald *et al.* (1997) who observed inter-annual variability from 0.6 kg N ha^{-1} yr^{-1} in 1994 to 0.003 kg N ha^{-1} y^{-1} in 1995. Higher N_2O emissions were measured in Germany from minerotrophic fens by Augustin *et al.* (1998) where in 1995 they ranged between 5.3 and 14 kg N ha^{-1} yr^{-1}. These high rates of N_2O emissions in the latter study could be explained by drainage that was reported to enhance emissions (section 2.2.5.1b) and by the high N content of fens that contrast with the low nutrient content normally observed in undisturbed upland peatlands described by MacDonald *et al.* (1997).

NO emissions from seminatural land are much smaller than those registered for N_2O. Studies in south-central Scotland (Skiba *et al.*, 1994) revealed that on different species of grass they vary between a negative flux of -0.1 kg N ha^{-1} yr^{-1} and small emissions of 0.26 kg N ha^{-1} yr^{-1}. On peat covered with coniferous forest and

moorland vegetation uptake of 6.2 * 10^{-3} - 15.5 * 10^{-3} kg N ha^{-1} yr^{-1} was registered. This is due to high soil moisture of peat that restricts NO emissions. Similarly, small values of NO emissions were registered in other areas. Davidson (1991) reported NO emission of 0.18 kg N ha^{-1} yr^{-1} from temperate forests, Johansson (1984) measured similar NO fluxes of 0.029 - 0.25 kg N ha^{-1} yr^{-1} from coniferous forest in Sweden, while Regina *et al.* (1998) observed higher NO emissions from drained forested peatland that ranged between 1.07-2.51 kg N ha^{-1} yr^{-1}. Butterbach-Bahl *et al.* (1997) measured NO emissions from three different tree species at two sites in Germany. The lowest mean NO emissions were observed from pine forest of 0.2 - 2.7 kg N ha^{-1} y^{-1}. Beech tree stands promoted intermediate NO emissions of 0.5 - 4.1 kg N ha^{-1} y^{-1} and the highest and most variable NO fluxes were observed on spruce plots where a range 1.7 - 11.3 kg N ha^{-1} y^{-1} was measured. Spruce woodlands were recognised as a more important source of NO than deciduous woodlands.

2.2.5.6 Soil characteristics important for emissions.

Soils, as a medium in which N_2O and NO are produced, vary in terms of their physical, biological and chemical characteristics, and this generally affects the amounts of these trace gases emitted. Although great variability within the soil environment makes accurate estimates of produced and emitted gases impossible, the general characteristics of soil can give an indication of what types of processes are likely to occur and what effects they lead to. Soil characteristics that control production processes and, subsequently, emissions of N_2O and NO are presented in detail in the following section.

Soil texture, defined by Brady (1990) as a proportionate representation of the various size mineral particles, determines the aeration and drainage of the soil and thereby can be very important in the production processes of NO and N_2O. Soils with large proportions of coarse particles (> 50% of sand with grain size > 0.06 mm as defined by the British Standard Institution, Brady, 1990) characterised by abundant macropores, have low water-holding capacity. In contrast fine-textured soils consisting of > 35% of clay and < 40% of sand are characterised by a high proportion of capillary pores having good water holding capacity. These two types represent two extreme groups of soil textures; the former is good for nitrification

provided the requirements of nitrifiers are fulfilled; the latter creates anaerobic conditions for longer periods that favour denitrification (Bouwman *et al.*, 1990). All the soil of moderately coarse to moderately fine textures, described by Brady (1990) as loamy soils, represent conditions intermediate between the two described types. They are characterised by varying soil moisture with the possibility of local anaerobic microsites existing in the vicinity of aerobic conditions, where both mentioned processes can occur simultaneously.

N_2O emissions vary between soil types in most field studies. Velthof and Oenema (1995) observed a significant effect of soil type on emissions from managed grasslands between sand and clay soils, but for unfertilised soils there was no difference (figure 2.4). Armstrong (1983) noted high peaks of emissions following an application of 200 kg N ha^{-1} from a clay loam site (59 kg N ha^{-1} y^{-1}), with emissions a factor of 8 higher than from sandy loam (maximum 7 kg N ha^{-1} y^{-1}, but the intensive release of N_2O ceased after four days compared with the sandy loam in which consistent emissions were noted throughout the experiment. Arah *et al.* (1991), however, observed higher N_2O emissions from light-textured soils and suggested that in heavier-textured soils its further reduction to N_2 is caused by restricted diffusion.

Organic C either as living plant roots and bacteria or dead remains is important for soils for retaining productivity. Organic C provides reducing agents (electron acceptors) for denitrification, it can also stimulate microbial activity and lead to increases in the number of denitrifiers in soils (Granli and Bockman, 1994). Its main role is, however, considered as a substrate for respiration, which can lead to the development of anaerobic microsites necessary for denitrification (Granli and Bockman, 1994). Some British soils contain very high levels of organic C. Peatlands of North Britain and Cambridgeshire have an average concentration of 172 kt km^{-2}, while mineral soils contain 41 kt C km^{-2} in Scotland and 21 kt C km^{-2} in England and Wales (Milne and Brown, 1997). The value of C concentration varies locally depending on the levels of organic matter in soils, the environmental conditions suitable for decomposition processes and management practices like organic manure inputs and grazing. There are generally more N_2O emissions from drained organic soils (peats) as observed by Velthof and Oenema (1995). Between March and November they measured total N_2O emissions ranging from 2 to 11 kg N ha^{-1} on

two peat sites in the Netherlands. Organic fertilisers generate more N_2O than mineral fertilisers added to mineral soils, where C can be a limiting factor of denitrification (Granli and Bockman, 1994; Slemr *et al.*, 1984; Velthof *et al.*, 1996a).

Soil acidity has a recognised effect on bacterial processes. Optimum pH for both denitrification and nitrification is between 7.0 and 8.0 (Granli and Bockman, 1994) and pH of 4.5 was found to be a lower limit for the latter process according to Duggin (1991), Tietema *et al.* (1992) proposed a limit of 3.5. The pH of most arable soils is maintained at pH 6-7, and grasslands at 5.5 - 6.0 by liming, therefore soil acidity does not represent a major controller on managed land. It affects seminatural soils to a much greater extent, however, especially forest soils. An effect of changing soil acidity on N_2O and NO emissions was observed by Butterbach-Bahl *et al.* (1997) on a forest soil. Limed plots (top soil with pH = 5.7-6.1) had a factor of 2 - 5 greater N_2O emissions than acid plots (top soil with pH = 2.9 - 3.6). The opposite was noted for NO, as higher fluxes were reported from acid plots and emitted NO was a factor of 4 greater than N_2O. According to Granli and Bockman (1994) N_2O emissions increase with increasing pH values when nitrification occurs, this process therefore was responsible for N_2O and NO volatilised. Butterbach-Bahl *et al.* (1997) observed a positive correlation of NO and a negative correlation of N_2O emissions from a spruce forest in Germany with high atmospheric deposition. The observed relationship was complex as it depended on the species composition of the forest (Butterbach-Bahl *et al.*, 1997). Although generally acidification is not the main controller of N_2O and NO emissions as observed for a range of agricultural and seminatural soils in Northern Britain (Skiba *et al.*, 1998), the limiting effect of this factor can become the major controller in some forest environments in highly polluted areas.

Redox potential (E_h) of soils is a parameter describing availability of oxygen in soil, which is a measure of oxidation state of the soil. It is suggested that a negative value indicates optimal conditions for denitrification. Byrnes *et al.* (1993) observed positive values E_h during the fallow dry season when nitrification was the source of small N_2O fluxes, but it fell slightly after water addition with a parallel increase in N_2O emissions. Although E_h could be a good indicator of bacterial production processes of NO and N_2O, it is not determined in the majority of field studies.

2.2.6 Summary.

Both N_2O and NO emissions are spatially and temporally variable. The spatial distribution of emissions is linked to the complexity of bacterial processes in soils and the latter results from heterogeneity of soil characteristics. Field experiments suggest that there are environmental variables, which act as controlling factors of N_2O and NO emissions from soils. Those factors are: N content of soils, organic C content, soil moisture, soil temperature, and other soil characteristics such as soil texture, soil pH and redox potential. Those variables decide on the rates of N_2O and NO production processes and their release from soils. Dynamic emission responses in time can be a result of either a sudden increase in N or C substrates due to management practices on agricultural soils, or changes in weather regimes affecting water characteristics of soils e.g. precipitation after a prolonged dry period and defrosting of topsoil in spring. The controlling factors have a combined effect on the amounts of emissions, which form complex relationships. It is reasonable to assume that the factors controlling N_2O and NO emissions at a field scale are also responsible for variability of these processes at larger scales. The current study addresses this claim by analysing the relationships between the emissions and the above listed variables for temperate climates. Although there might be other existing, presently unknown, factors of N_2O and NO emissions at that scale, their influence is currently difficult to assess in this general approach. They are better definable at the field scales. It is a limitation of this study to restrict the analysis to the variables listed by field studies published in literature. A more detailed account of data used to define models is presented in chapter five. The dynamism of N_2O and NO emissions is difficult to predict and various modelling approaches have been developed. The following paragraph presents the existing models that provide the background for discussion of the simulation approach adopted in this research.

2.3 MODELS ESTIMATING N_2O AND NO EMISSIONS.

Simulation of reality has been practised since the beginning of the computing era when multiple simulations on large data sets were made possible. Models are a simplified imitation of reality that aim at reproducing and describing processes. The complexity of biological, physical and chemical processes in soils is revealed in a great variety of modelling approaches to estimate the amounts, spatial distribution and temporal variability of many parameters including nitric and nitrous oxides

emissions. Models can be characterised by their different objectives, spatial scale of their application and different simulation methods.

The diversity of microbial processes in which N_2O and NO are produced and the great variability of soil characteristics preclude entirely accurate estimation of emissions. Several researchers have observed considerable variability in emissions at a field scale, which amounts to over 200% for N_2O (Fowler *et al.* 1997) and 165% for NO (Davidson and Kingerlee, 1997). Higher spatial variability of N_2O emissions is linked to the heterogenous nature of soils and to the high requirements of anaerobic microsites for the production processes to occur. This is contrasted with the character of NO emissions, which predominantly occur from the surface soil horizons under aerobic conditions. The dynamic nature of soils and the diversity of microbial processes of N_2O and NO production are best described by mechanistic models. This approach estimates the rates of the production processes and defines the conditions of gas emissions (section 2.3.2). This most commonly practised method of mechanistic modelling, however, makes great demands in terms of input data for controlling factors and thus its application is restricted at larger scales for which those parameter data are frequently not available. Another approach to model N_2O and NO emissions is based on mathematical functions describing the relationships between the emissions and their controlling factors. This is an empirical method to establish representative emission values for different environments (background emission) and to observe any pattern of responses to controlling factors. This approach is described in section 2.3.1.

The complexity of soil processes is the greatest problem in scaling up. Kirby *et al.* (1996) in their study of erosion in Canada discussed the necessity of defining different levels of processes when increasing scale from micro-scales via catchments to regions. Inventories at national and global scales aim at establishing the important factors determining the variability of emissions at that resolution level (described in section 2.3.4).

The following discussion examines the models at field and at global and regional scales. The field scale models give an indication of the control variables and the dynamism of processes; the regional and global overviews aim at estimating the nitrous and nitric oxides emissions from known sources. Firstly field empirical models are presented, then the more detailed approach of mechanistic models

follows. Finally those approaches applied to models of global N_2O and NO emissions are discussed.

2.3.1 Empirical models of NO and N_2O emissions at field scale.

Empirical models represent the relationships between emissions and their controlling variables either as linear or non-linear functions. They parameterise the controls on the basis of large data sets, with the use of statistical functions of regression analysis. This approach although restricted by the need for normally distributed data, constant variance and error-free independent variable, provides a simple solution to the complexity of soil processes. Here are a few examples of this approach.

Table 2.10 Selected empirical modelling approaches of N_2O and NO emissions at plot scale.

ref.	Model definition	Area of study	n	R^2	Literature reference
		N_2O			
2.7	log (N_2O) = -6.26 + 1.45 * log (soil NO_3) + 3.61 * log (soil moisture)	South-east Scotland, variety of land use types	22	0.33	Skiba *et al.* (1994)
2.8	Ln (N_2O) = -11.9 + 2.0 ln(NO_3^- + NH_4^+) + 20.7 WFPS - 10.5 WFPS ^{2}	Peat grassland in Zegveld, The Netherlands	25	0.64	Velthof *et al.* (1996a)
		NO			
2.9	log10 (NO) = 0.049 Ta - 0.83	Grassland on sandy loam in Colorado, autumn 1985	15	N/a	Williams *et al.* (1987)
2.10	log10 (NO) = 0.034 Ta - 0.58	Area as above, but data from the entire period of study (July - Nov., 1995)	152	N/a	Williams *et al.* (1987)
2.11	log NO = -3.23 + 1.01* log (soil NO_3) + 0.165 * (Ts)	South-east Scotland, variety of land use types	19	0.61	Skiba *et al.* (1994)

Ts – soil temperature, Ta – air temperature, WFPS – water filled pore space, N/a - not available.

Nitrous oxide.

A study of five sites (3 agricultural and 2 seminatural) in south-east Scotland (Skiba *et al.*, 1994) found a positive correlation between N_2O fluxes and the controlling factors of nitrate content and soil moisture. This relationship was presented in table 2.10 by equation 2.7. The model was based on 22 measurements from a variety of soils and land use types specific for this region, i.e. managed grassland on clay loam, winter wheat on sandy loam, lawn grass on sandy clay loam, coniferous forest on sandy clay loam and moorland on peat. This model

suggests that soil NO_3^- and soil moisture are important controlling factors for estimating N_2O emissions from those environments. Another empirical relationship was defined by Velthof *et al.* (1996a) for peat grasslands in Zegveld, The Netherlands, who observed a stronger quadratic function of the effect of WFPS on emissions and greater correlation function of N content of soils (NO_3^- and NH_4^+). The strength of the relationship between N_2O emissions and the controlling factors described in equation 2.8 was sensitive to seasonal changes (table 2.10). During the entire study soil moisture (WFPS) had a significant effect only in June, while in September and November only N content was important. The strength of the derived function was greater in the latter study (r^2 = 0.64, n=25) than in the former (r^2=0.33, n=22), this, however, does not imply a more suitable function, as the application of the stronger relationship is restricted to a specific soil.

Nitric oxide.

Different controlling variables are proposed for NO. Two studies were chosen for comparison. The first is of a grassland site on sandy loam in Colorado (Williams *et al.*, 1987). Data were collected from six plots and on the basis of those, daily mean NO emissions were estimated. In this study a significant correlation was observed between NO emissions measured between 5 September and 15 November 1985 and air temperature that ranged from -5 to 30 °C. Williams *et al.* (1987) reported a positive relationship defined by equation 2.9 (table 2.10). But that relationship varied and became more uncertain when data from the entire measurement period were included. The observed relationship was then better defined by equation 2.10 (table 2.10). N substrate was not recognised as a significant factor probably due to the fact that fertiliser was not applied to that site and there were no observed changes.

Soil nitrogen content was an important controller proposed by Skiba *et al.* (1994) in their model for the five ecosystems observed in South-central Scotland described above. The model described by Skiba *et al.* (1994) in equation 2.11 was mostly sensitive to changes of NO_3^- concentration in soils and temperature oscillations (60% of NO variability) for 19 measurements (table 2.10).

The empirical modelling approach suggests that relationships between emissions and their controlling factors vary between different locations and environments. This variability provides strong arguments expressed in the literature against an

application of empirical models beyond the boundaries of the environments for which they were defined (Velthof *et al.*, 1996a). The current research applies this modelling approach on a large scale, which is further discussed in section 2.4.2. In the following section a mechanistic approach to the soil processes of N_2O and NO production is presented, which adopts an alternative to empirical models.

2.3.2 Mechanistic approaches to soil dynamics.

There are a number of models that try to describe the processes connected with the N cycle in soils and account for N inputs (fertilising and atmospheric deposition), mineralization/immobilisation, nitrification, denitrification, nitrate leaching and uptake (Wu and McGechan 1998). These models include ANIMO (Berghuijs van Dijk *et al.*, 1985), DAISY (Hansen *et al.*, 1991), SOILN (Johnsson *et al.*, 1987) and SUNDIAL (Bradbury *et al.*, 1993). All the four models describe mechanistic processes in the soil system with pools of different N forms e.g. humus, litter, manure that control the rate of transformations and the outflows from the system, also symbolically represented as pools e.g. uptake, leaching and volatilisation pool of N_2O and N_2. The flow between the pools in all models is represented as a 'first-order rate process' (Wu and McGechan 1998), in which the amount of processed N is proportional to the amount of N in the original pool. Nitrification is an example of such a simple process, and its rate in all the mentioned models depends on the amount of ammonium (NH_4^+) e.g. SOILN measures the rate by excess of ammonium above an assumed equilibrium NH_4^+/NO_3^- (Wu and McGechan 1998). While nitrification is described in a similar way in all four models, there are major differences in defining the controllers of denitrification and estimating its rates. SOILN describes it as a zero-order rate process that is controlled by soil aeration, nitrate concentration (limited by half-saturation constant) and soil temperature. ANIMO highlights the importance of pore size distribution in soil and the amount of decomposable organic matter. DAISY estimates the rate of denitrification on the base of nitrate and anaerobic microsites co-existence. In SUNDIAL the denitrified amount of N is proportional to CO_2 and nitrate.

The main controllers and the algorithms describing the processes vary between the models and hence their coefficients can not be compared directly. The processes are described by physical functions, for which a large variety of parameters are

required. This restricts the application of the models to specific locations of field sites. All four models define total N volatilised in the process of denitrification, but there seems to be no measurement of N_2O and NO emission by nitrification. To apply these models for estimating N_2O and NO emissions would require further investigation in terms of controllers defining the ratios of the different N trace gases.

An application of the mechanistic models describing the N cycle to specific sites and comparison with measured emissions is the best way to evaluate their viability. This has been attempted in a few studies. Baggs (1997) measured N_2O emissions from different crops in south Scotland and compared the results with the predictions of four soil-plant models: NCYCLE, SOILN, N_ABLE and SUNDIAL. The results of SOILN were compared with measurements from spring barley and grassland and revealed that the modelled values were generally underestimated. This was mainly due to the definition of nitrification in the model by a NO_3^-/NH_4^+ ratio observed often in agricultural soils, and not as a microbial process (Baggs, 1997). Dynamic changes of environmental variables like temperature and oscillations in soil moisture were unaccounted for in SOILN (Baggs, 1997). The model does not take into account the available C as a factor controlling denitrification and does not consider the role of soil as an N_2O sink that was frequently observed during measurements. The comparison of N losses estimated by SUNDIAL with field measurements from winter wheat, spring barley and oilseed rape showed a tendency for the model to overestimate gaseous losses of N (Baggs, 1997). This was due to constant scaling factors used to estimate the N losses. These were based on experimental work, but their application is limited and they cause inaccuracies (Baggs, 1997). SUNDIAL also ignores temperature changes in soils.

Another mechanistic approach describing N_2O emissions from soils is the Denitrification-Decomposition (DNDC) model that is rainfall-event driven (Li *et al.*, 1992). There are three components of that model: (1) thermal-hydraulic, which predicts soil temperature and soil moisture, the factors which in turn control the other sub-models of (2) denitrification and (3) decomposition. Modelled amounts of N_2O emitted from soils as results of nitrification are predicted as a function of NH_4^+ concentration in soils that varies with temperature. Denitrification is the other important source of N_2O outlined in the model, and the amounts of N_2O emissions are estimated with an application of adsorption coefficients and air-filled porosity of the soils (Li *et al.*, 1992). This process-simulating model was applied to estimate

N_2O emissions from agricultural sources at the county level in Florida, USA (Li *et al.*, 1994). The input data of variables needed for running the model was obtained from the best available published data for Florida. Most of the variables used were soil parameters generalised according to crop type e.g. NO_3^- and NH_4^+ concentration in soil, or soil textural class e.g. bulk density, pH and organic C content. In reality, these soil characteristics are variable due to heterogeneity of soils. Validation of the model by Li *et al.*, (1996) on three sites: bare soil, sugar cane and grass showed that the DNDC model accurately presented the dynamic changes of N_2O emissions from soils in most cases. In the current study, the DNDC model would have a very restricted application to some field locations for which all input data could be obtained. The required input data sets at the national scale were not available to this study and DNDC model could not be applied to predict N_2O and NO emissions from all British soils. A possible future application of this model could be further investigated at a smaller scale as a results of its successful application in other studies. This, however, goes beyond the scope of this study.

De Willigen (1991) compared several modelling approaches presenting the processes of the N cycle. He found that simpler approaches in functional models, that estimate soil moisture by defining its lower and upper limits, are in general as accurate as more complex mechanistic simulations. The complexity of mechanistic models aims at representing biological processes accurately, but there are restrictions in their applications. The demanding requirements of mechanistic models and the restricted scope for the application of both empirical and mechanistic approaches limit modelling of N_2O and NO emissions. This is especially so when the chosen level of modelling approaches regions and entire world. To propose the best approach for modelling N_2O and NO emissions for Great Britain a discussion of various existing approaches of predicting emissions at global scales is first presented.

2.3.3 Global inventories.

The simplest approach to understand the biogenic sources of these two gases at large spatial scales is to prepare an inventory (or a budget of the scale of all emission sources). This type of modelling involves estimating the magnitude and distribution of known sources and sinks, and establishing the potential for

unknown sources and sinks (Williams *et al.*, 1992). There are a number of such inventories of nitrous and nitric oxide emissions, their description is presented in the following section.

Nitrous oxide.

There are several major sources and sinks of N_2O that have been recognised in global inventories by McElroy and Wofsy (1986) and IPCC (IPCC, 1992; IPCC, 1995; IPCC, 1997) as presented in table 2.11. Natural sources play an important role in the global budget with soils and oceans recognised as the most important. The earlier estimates of global N_2O sources by McElroy and Wofsy (1986) and IPCC (1992) did not recognise livestock as a significant N_2O source. The most recent IPCC inventory estimated that this source contributes an average of 2.1 Tg N yr^{-1}. The contribution of anthropogenic sources has also increased in the most recent inventory (IPCC, 1997) due to the inclusion of mineral and organic fertiliser, crop residue and amount of N biological fixation (table 2.11). The emission estimated from fertiliser input is based on Bouwman's emission factor of 1.25% (Bouwman, 1995) established on 20 measurements that has been uniformly applied to both mineral and organic fertiliser. Estimates of biological fixation and crop residue are very uncertain due to insufficient data world-wide. Among anthropogenic sources biomass burning and conversion of forests to agricultural land are fully recognised and well known through observations (Anderson and Levine, 1988; Crutzen and Andreae, 1990 and Keller *et al.*, 1993).

The stratosphere has been recognised as the main sink for N_2O. The role of soils as an N_2O sink, however, is very uncertain. IPCC has suggested the importance of soils as both source and sink of nitrous oxide (Mosier and Kroeze, 1997). Field measurements provide some evidence of this N_2O sink activity as negative fluxes have been measured by several research groups. Based on the sink strength of a forest and moorland in South Scotland it was estimated that in Great Britain seminatural land provides a sink for 1kt N_2O-N y^{-1} (Skiba *et al.*, in press). While sinks in the atmosphere and the stratosphere are well known, the role of soils as a nitrous oxide sink appears to be insignificant.

IPCC (1997) estimated that all sources contributed 16.2 (6.4-34.4) Tg N yr^{-1} and that is counteracted by total uptake of 16.2 (12.1 - 20.7) Tg N yr^{-1} by both the stratospheric sink and atmospheric increase (Mosier and Kroeze, 1997). This

estimate compares with the earlier inventory by McElroy and Wofsy (1986) who proposed the total production of N_2O at 15.3 (8.6 - 22.0) Tg N yr^{-1} and the total uptake at 14 (10.5-17.5) Tg N yr^{-1} (table 2.11).

Table 2.11. Global N_2O inventories.

	Model 1	Model 2	Model 3	Model 4
		Tg N y^{-1}		
		Sources		
Natural				
Oceans	2 ± 1	1.4-2.6	3 (1-5)	3 (1-5)
Tropical soils				
Wet forest	7.4 ± 4.0	2.2-3.7	3 (2.2-3.7)	3 (2.2-3.7)
Dry savannas		0.5-2.0	1 (0.5-2.0)	1.0 (0.5-2.0)
Temperate soils				
Forests	0.1-0.5	0.5-2.0	1 (0.1-2.0)	1(0.1-2.0)
Grasslands	0.1	?	1(0.5-2.0)	1(0.5-2.0)
Anthropogenic				
Agricultural soils	0.8 ± 0.4	0.03-3.0	3.5 (1.8-5.3)	3.3 (0.6-14.8)
Biomass burning	0.7 ± 0.2	0.2-2.1	0.5 (0.2 –1)	0.5 (0.2 –1)
Industrial sources	4 ± 1	0.8-1.8	1.3 (0.7-1.8)	1.3 (0.7-1.8)
Cattle and feedlots	?	?	0.4 (0.2-0.5)	2.1 (0.6-3.1)
Total sources	**15.3 ± 6.7**	**5.6-15.2**	**14.7 (8-22.4)**	**16.2 (6.4-34.4)**
		Sinks		
Atmospheric increase	3.5 ± 0.5	3-4.5	3.9 (3.1-4.7)	3.9 (3.1-4.7)
Soils	?	?	?	?
Stratospheric sink	10.5 ± 3	7-13	12.3 (9-16)	
Total sources	**14.0 ± 3.5**	**10 – 17.5**	**16.2 (12.1-20.7)**	**3.9 (3.1 – 4.7)**

Model 1 – McElroy and Wofsy (1986); Model 2 – IPCC (1992); Model 3 – IPCC (1995); Model 4 – IPCC (1997).

IPCC estimated total global nitrous oxide emissions from both natural and agricultural soils at 9.3 (3.9 - 24.5) TgN yr^{-1} that can be compared with 8.6 (4 - 13.2) Tg N yr^{-1} proposed by McElroy and Wofsy (1987). Soils are estimated to contribute over 50% of all N_2O emissions world-wide. This estimate is highly uncertain as it is based on fluxes measured on agricultural forest soils in temperate climates and can not be considered to represent all world land use types and soil classes especially those in the tropics.

Nitric Oxide.

There are several recognised sources of NO_x that were presented by Delmas *et al.* (1997), here listed in table 2.12. Fossil fuel combustion is the main source at the earth's surface contributing 22Tg N yr^{-1}, followed by biomass burning, mainly observed in savanna ecosystems of the subtropical region. Yienger and Levy (1995) estimated NO emissions from soils at 5.5 Tg N yr^{-1}. Delmas *et al.* (1997) also distinguished important sources in the troposphere including lightning, ammonia oxidation, aircraft and stratospheric injection. Their estimate of total global nitric oxide emission was 38.2 Tg N yr^{-1}. Davidson and Kingerlee (1997), who used biome stratification to obtain spatial variability proposed another world inventory of nitric oxide. Biome stratification assigns measured emissions to the main vegetation ecosystems in the three climatic zones: boreal, temperate and tropical. It then applies proportionate areas to extrapolate from the established mean emissions for the major biome-climatic ecosystems to global estimates. When the mean emission of 2.7 kg N ha^{-1} yr^{-1} for all reported biomes was applied to all terrestrial ecosystems a total global emission of 35 Tg N yr^{-1} was derived, while stratification reduced that estimate to 21 Tg N yr^{-1}. The latter total is more reliable as it takes into account reduced emissions from wetlands, temperate forests and deserts (Davidson and Kingerlee, 1997). During the process of NO volatilisation from the soil-plant system into the atmosphere, absorption by vegetation occurs that considerably reduces the emitted amount. Yienger and Levy (1995) estimated canopy reduction factors (CRF) that is a measure of the proportion of emitted NO_x deposited almost instantaneously onto the vegetation canopy. They suggested that CRF values in temperate climates vary from 0.39 for conifers to 0.77 for tundra. Davidson and Kingerlee (1997) applied CRF into their inventory and estimated total NO emissions from soils into the atmosphere at 13 Tg N yr^{-1}.

Table 2.12. Global inventory of NO_x sources (Delmas *et al.*, 1997)

NO_x sources	Magnitude [Tg N y^{-1}]
Surface sources	
Fossil fuel combustion	22 (15-29)
Biomass burning	6.7 (3-10.4)
Biogenic soil emission*	5.5 (3.3-7.7)
Tropospheric sources	
Lightning	2 (1-4)
Stratospheric injection	0.5 (0.4-0.6)
Aircrafts	0.55 (0.5-0.6)
Ammonia oxidation	1.0 (0.5 – 1.5)

* Yienger and Levy (1995)

Bouwman's (1995) modelling approach to estimate N_2O emissions on the basis of N fertiliser input was applied by Veldkamp and Keller (1997) to define NO emissions from agricultural soils. Their regression model was based on 12 field sites located in temperate and tropical climatic zones. The results of this analysis suggest that 0.5 % of applied N was emitted as NO and the intercept of the regression line indicates background NO emission of 0.17 kg N ha^{-1} y^{-1}. This model has great uncertainty because it relies on only a small sample of field plots representing temperate and tropical climatic regions (Veldkamp and Keller, 1997).

Global estimates of N_2O and NO emissions are characterised by large uncertainties that are due to the major assumptions and generalisations in the discussed inventories and many areas are still unresearched. Large ranges of error specified in these models can accommodate any variability unaccounted for, but they also imply the urgency of more detailed regional studies that would help in producing more accurate estimates. Global totals can be validated against the regional estimates, but they give no indication of spatial variability in emissions. This aspect is tackled in inventories compiled using empirical and mechanistic models at both global (Bouwman, 1995; Yienger and Levy, 1995) and regional scales (Stohl *et al.*, 1996; Williams *et al.*, 1992).

2.3.4 Coupled inventories with predictive empirical and mechanistic models.

Global potential for N_2O production in natural soils

(Bouwman, 1995).

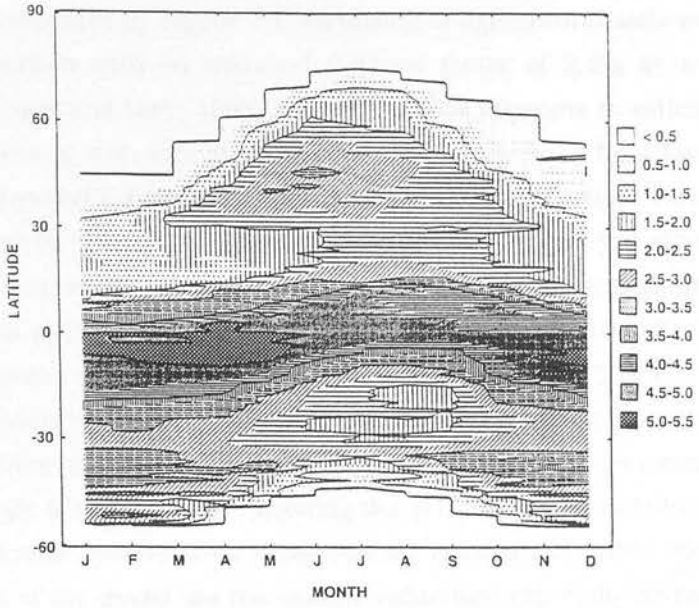
The spatially variable model of N_2O production potential in natural soils is based on the assumption that N_2O emissions are strongly correlated with amounts of N cycled through the 'soil-plant-microbial' biomass (Bouwman, 1995) and soil processes like decomposition and N mineralisation play an important role in the model. Variables that are recognised as controlling nitrous oxide emissions at a global scale include organic matter content, soil fertility, temperature effect on decomposition, soil-water, and soil-oxygen limitation affecting denitrification. The controlling factors were ranked into non-dimensional indices indicative of their relative influence on the rates of soil processes. This approach was necessary due to a lack of quantitative relationships between N_2O emissions and the various controlling factors on a global scale. Model results present monthly nitrous oxide emission potential at 1° x 1° resolution that exhibits a distinct seasonal pattern (figure 2.8). The tropics are recognised as a major source of N_2O emissions from natural soils. Verification of the model's results against field measurements showed a high r^2 of 0.6, but due to a lack of data for some important ecosystems in Asia, Africa and Australia there is great uncertainty in the model in those areas. Regression analysis was applied to estimate real values of nitrous oxide emissions, which for natural soils sum up to 7.0 Tg N y^{-1}, a similar estimate to the IPCC total (table 2.11).

Global N cycle as an effect of anthropogenic changes

(Nevison *et al.*, 1996).

The effects of human disturbance on natural environments have been considered in the Nitrogen Biosphere Model (NBM), a mechanistic simulation of the terrestrial carbon-nitrogen cycle at 0.5° x 0.5° resolution for the period of 1860-1990 (Nevison *et al.*, 1996). Livestock manure and mineral fertiliser and NO_x atmospheric deposition define inputs to existing pools of N, among which fluxes occur controlled by temperature, precipitation, soil type, vegetation cover and land use.

Figure 2.8 Seasonal and latitudinal distribution of the nondimensional N_2O production potential predicted by Bouwman *et al.* (1993).



NBM applies algorithms from the CENTURY model to define external N inputs and assumes a fixed 2% of mineralised N loss to emissions that according to the model are directly related to the former. Based on field observations the NBM model assumes a fixed 2% loss from mineralisation and 5 - 10% as a ratio between N_2O and total N emission. That ratio was obtained from a few existing field studies to which a quadratic fit was applied. In the period of 1860-1990 for which the model was run, nitrous oxide emissions due to mineralisation declined from 5.9 to 5.7 Tg N yr^{-1}. Leaching and volatilisation increased N_2O emissions from 0.3 to 1.2 Tg N yr^{-1} and from 0.15 to 2.1 Tg N yr^{-1}, respectively. The estimated total of global N_2O emissions is 9Tg N yr^{-1} that is comparable with IPCC's estimate (Mosier and Kroeze, 1997). Verification of the model results with 30 field measurements adopted from Bouwman *et al.* (1993) showed a best fit of r^2 = 50%. The advantage of this approach, adopted in the NBM model, is the comprehensive view of mechanisms leading to emissions variable in time and space. On the other hand the model does not account for the effects of soil moisture, oxygen partial pressure and soil fertility that are major limitations of this approach.

Empirical model of NO_x soil-biogenic emissions.

Yienger and Levy (1995) based their model on a combination of effects of changing temperature and precipitation in which emissions are varied according to vegetation

cover. The modification included 'synoptic-scale pulsing', the emission burst that occurs after wetting dry soils, and canopy reduction (CR) due to absorption of emitted nitric oxides by vegetation. Fertilising of agricultural soils was described by a linear function with an assumed fertiliser factor of 2.5% as a mean of eight studies (Yienger and Levy, 1995). This model also attempts to estimate the effect of biomass burning with a crude assumption of an increase by a factor of 3 for the transitional period between dry and wet seasons. Results show that emissions from soils account for 5.5 Tg N yr^{-1} that increased from 3.6 Tg N yr^{-1} since pre-industrial times. The importance of CR is presented by the model scenario in which canopy reduction is excluded and results in total emissions of 10.2 Tg N yr^{-1}, a much higher estimate. The model predicts NO_x emissions in 2025 of 6.9 Tg N yr^{-1}. The spatial distribution presented in this model highlights the importance of tropical regions, where emissions are twice as high as those in temperate regions. The breakthrough of this model is including the 'pulsing' effect contributing 1.3 Tg N yr^{-1} that indicated dynamic NO_x emissions for northern Namibia (figure 2.8). Other advantages of the model are the canopy reduction, especially active in the tropical rain forests and biomass burning represented in a simplified form due to restricted data availability. The model also needs improvement of the agricultural element that does not include any variability in fertilising practices according to crops.

Process modelling of nitrogen trace gases (Potter *et al.*, 1996).

This is another global approach of integrated ecosystem modelling based on satellite data of climatic characteristics, vegetation cover and soil data, in which those characteristics interact as trace gas controllers. In this model Potter *et al.* (1996) used a coupled carbon-nitrogen Carnagie-Ames-Stanford (CASA)[8] model at a 1° x 1° resolution to calculate N mineralisation rates and monthly production of NO, N_2O and N_2 in soils. Nitrogen trace gases are estimated in the model with an assumed 2% of total mineralised N and their proportion (NO: N_2O: N_2) is controlled by water filled pore space (WFPS) described by index (I_w) according to 'hole-in-pipe' theory (figure 2.1). The model predicts total trace gas emission from soils of 6.1 Tg N_2O -N yr^{-1} and 9.7 Tg NO-N yr^{-1}, with the majority of emissions in the tropics (60% of N_2O and 45% of NO). The total estimate of N_2O emissions from soils worldwide compares

[8] The CASA-Biosphere model (Potter *et al.*, 1993) is a simulation of interactive trace-gas model that accounts for 'nutrient substrate availability, soil moisture, temperature, soil texture, and microbial turnover '(Potter *et al.*, 1996).

with Nevison's *et al.* (1996) global N_2O estimate of 6.7 Tg N_2O-N yr^{-1} and 6.6 Tg N yr^{-1} proposed by Bouwman *et al.* (1995). Total NO emission of 5.5 (3.3-7.7) Tg N yr^{-1} estimated by Yienger and Levy (1995) is lower than that suggested by Potter *et al.* (1996), but the former considers canopy uptake that was assumed to reduce the emissions by 50%. This is in line with Bouwman *et al.'s* (1993) observed highest potential for N_2O emissions from natural soils in the tropics. Seasonally the model predicts little variability in N_2O emissions close to equator (up to 15%) and a much greater coefficient of variation (cv) for latitudes of 44 °N of 20-24% (peak in June). For NO, seasonal variability does not change spatially and is estimated at cv 10-15% with highest emissions in August. Uncertainties in the model are associated mainly with the assumed 2% potential production rate of total trace nitrogen gas. Other limitations are linked to the exclusion of N deposition, grazing effects (via soil compaction and animal excreta inputs), fertilising practices and biomass burning from the model. The main advantage of this model is a comprehensive ecosystem view of nitrogen gas emissions world-wide, controlled by soil moisture.

Regional model of N_2O.

Mechanistic model N_2O emissions for New Zealand. GIS application.

This is an example of how a coupled mechanistic model with GIS application predicts the distribution of emissions from soils (Muller *et al.*, 1997). The mechanistic model based on Michaelis-Menten kinetics was developed from a field study of nitrous oxide measurements on grassland treated with urine. Detailed data of measured fluxes, soil temperature, soil N status and water-soluble C content were used to develop relationships applied later to estimate fluxes from nitrification and denitrification from total N_2O. A simple soil moisture model enables soil to be classified into one of three defined water suction groups using precipitation data and unsaturated hydraulic conductivity from a soil inventory data set for New Zealand. This mechanistic model is said to predict overall trends in N_2O emissions rather than exact amounts. GIS application of the mechanistic model for a pilot study of an area of 10 km^2 near Cantenbury proved successful, but implementing this method at a larger scale e.g. whole country requires a revision of the model parameters established on the basis of field measurements on a grassland site.

Regional models of NO.

European inventory.

Stohl *et al.* (1996) observed that national and global emission estimates were based on temporary field measurements extrapolated to annual or seasonal emissions over larger areas. Those estimates (Skiba *et al.*, 1992; Williams *et al.*, 1992 and Yienger and Levy, 1995) were varied spatially depending on temperature, fertiliser input and vegetation cover. The approach used by Stohl *et al.* (1996) was adopted from Williams *et al.'s* (1992) model with minor changes e.g. soil temperature was estimated according to the force-restore method that estimates soil temperature hourly changes in assumed two-layered soil based on a prognostic model (Stull, 1988). The land use emission factor was defined in a similar method to Williams *et al.* (1992) except that the fertiliser induced emission was assumed to amount to 5% of applied N. The estimated annual total of NO emissions for Europe amounted to 535.4 kt N yr^{-1} and for the UK 25.4 kt N yr^{-1}. The model was run for 1994 and according to the results, arable land was the single largest source of NO emissions from soils at the annual scale (72% of all NO emissions) and in summer (81%). Grasslands contributed much more NO emissions (13.8%) than permanent crops (2.6%). NO emissions from soils were compared with pyrogenic NO_x emissions modelled by the EMEP inventory for 1991 (Sandnes, 1993) and they revealed that soils contributed up to 8% of the annual pyrogenic NO_x emissions. But on hot summer days in Albania and Iceland, soils were the major source of atmospheric NO_x (Stohl *et al.*, 1996).

These emissions are well in line with Yienger and Levy's (1995) NO emission total of 740 kt NO_x-N yr^{-1} for Europe and Russia. Uncertainties in the model are high - in the range of factor of 3-4, and primarily due to the application of uniform soil temperature for different land covers and the large variations in fertilising practices across Europe that are unaccounted for.

North American inventory.

Soil NO emission measurements show considerable differences for various biomes and in many areas, where N fertiliser input is high, seasonal high NO emissions are expected. Williams and Fehsenfeld (1991) observed that summer NO emissions from highly fertilised soils approach and even exceed emission levels of urban areas. They estimated a ratio of summer soil NO emissions to industrial NO_x sources at

0.99 in Iowa, 1.34 in Nebraska and 1.92 in South Dakota (Williams and Fehsenfeld, 1991). Temperature is another controller that displays an exponential relationship with emissions. The inventory for the United States was based on an algorithm developed on field measurements from 7 sites, over 350 data points listed by Williams *et al.* (1992). A logarithmic function[9] of NO emissions displayed a weak correlation (0.071) with temperature. The land use factor was varied for agricultural and natural land. The agricultural factor was found from an observed linear relationship between emissions and the amounts of applied fertiliser. For natural land the emission factor was defined on the basis of mean absolute NO emissions observed for those land types. The model predicts 314 Kt N yr^{-1} NO emitted from the USA and the majority of this emission occurs in summer. Agricultural soils are reported to contribute about 66% of total emissions. Williams *et al.'s* (1992) model presents a simple spatial and temporal NO emission distribution for USA. The results of the model have not been evaluated due to a lack of emissions data from soils in the USA, and the authors felt comparing model predictions with the data from other continents would be inappropriate. Moisture was not incorporated into the model, as more data are needed to define the effects on NO emissions. The broad land use classes proposed to estimate the factors of biome emission caused great generalisations in the performance of the model. The method applied to estimate soil temperature via empirical relationships from site observations is also expected to be erroneous. The final results are said to vary from real values by a factor of 3.

2.3.5 Conclusions.

All the models presented here base their estimates of N_2O and NO emissions on field measurements mainly from temperate climate zones with other global climate regions under-represented. The extrapolated emissions are then varied depending on other controlling factors. Although mechanistic approaches describing physical processes and quantifying their products on the basis of controlling parameters are more comprehensive (Nevison *et al.*, 1996; Potter *et al.*, 1996), they have the considerable disadvantage of a great demand for explicit parameters. Data

[9] NO emission = A * exp(0.071±0.07 * T_{soil}); NO emission [ng N m^{-2} s^{-1}], A-land use factor[ng N m^{-2} s^{-1}), Tsoil [°C]

requirements restrict their application. Despite the complexity of the described processes, their performance has been criticised by some researchers (Baggs, 1997; De Willigen, 1991). All the models omit some important controlling factors e.g. Nevison *et al.* (1996) do not consider soil moisture and oxygen partial pressure, while the model presented by Potter *et al.* (1996) does not account for atmospheric nitrogen deposition, grazing practices and fertilising management practices.

The relationships of emissions with the controlling factors are best described in empirical models. Despite the common belief that this modelling method has restricted application, it is employed in the majority of large-scale models at the global (Yienger and Levy, 1995) and regional scales (Stohl *et al.*, 1996; Williams *et al.*, 1992).

2.4 MODELLING APPROACH USED IN THIS PROJECT.

2.4.1 The advantages and limitations of GIS in predicting N_2O and NO emissions.

Geographical Information Systems (GIS) are viewed as *'integrated systems of computer hardware and software for the analysis and display of spatially distributed data'* (Johnston, 1998). This software system is built for data storage and retrieval, performance of spatial analysis, predicting new outputs on the basis of stored data and the production of outputs in digital form (graphical files, tabular displays, ASCII files) or as a hardcopy (maps). GIS as a system, therefore, incorporates characteristics of computer cartography, data base management and computer-aided design.

GIS has incorporated ideas of computer based databases such as statistical software (MINITAB, SPSS) and design methods such as CAD into a spatially referenced system. The geographical reference stored in GIS provides a way of linking data sets together and this principle is the reason for the success of GIS (Maguire *et al.*, 1991). Its capability of producing maps as an output could be substituted by using, for example, high-level languages like FORTRAN, but the functions of spatial analysis are unique for GIS as the other applications do not offer such properties.

The first ideas of applying the GIS method were based on producing map overlays that created the mainstream of GIS applications in 1970s, but since then GIS applications have developed into a variety of modelling strategies such as rule-based, statistical models and coupled mathematical models. GIS became a powerful tool in environmental studies of large scale phenomena involving large data bases and complex relationships. There are many ecological applications of GIS among which studies of the habitat of different faunal species are the most common, such as a study by Johnston *et al.* (1991) of bear habitat, work by Coulson *et al.* (1991) to predict pine beetle outbreaks and multivariate regression model finding the physical controllers effecting the spread of spruce budworm (Johnston *et al.*, 1992) to name a few.

GIS found wide application in the work of environmental agencies that has led to the establishment of global environmental databases at 1° x 1° resolution incorporating information on vegetation, soils, land-use, topography, human population, animal populations etc. as presented by Matthews (1993). GIS databases at national scales are restricted to a few projects, but their establishment is gradually taking place. One of the future issues of GIS application is to incorporate a global data system with national and regional data. This would enable access to accurate data at a variety of scales from the global model down to the local site, but the development of such an integrated system depends on the developments in computer technology.

There are many GIS software applications available for research that have developed recently. In that large group SPANS, ArcView and MapInfo have common application. ArcView has the widest application of all the existing GIS programs for a variety of reasons. It is a Windows based graphical interface written by ESRI[10] that has all the main GIS functions. Its popularity is due to clear and easy-to-learn functions that support the most common needs of the user market e.g. good and easily editable graphical display of results, simple mathematical functions or data manipulation that can be loaded from other data base systems like EXCELL or ORACLE. The additional advantage of ArcView is its price that makes it affordable for individual users. ArcView however has many restrictions in terms of spatial

[10] Environmental Systems Research Institute Inc.

analysis and it often requires links with more complex software e.g. ArcInfo for more sophisticated objectives.

MapInfo Professional build by MapInfo Co. is a comprehensive GIS software combining cartographic functions and spatial analysis. There are direct links with other GIS systems e.g. ArcInfo, ArcView and AutoCAD mapping package. Data can be loaded from several data base packages e.g. EXCELL, DBASE, Access and Lotus that allows for good data management and data analysis can be carried via incorporated SQL commands.

SPANS is a good spatial analysis software created by Intera Tydac plc. that applies in-built modelling language for advanced mathematical functions. Both vector and raster modelling of map overlays can be performed in SPANS that allows additionally for data manipulation. It is a popular educational package that has also found application in research. Compared with ArcView SPANS provides a more sophisticated modelling method that requires, however, certain programming skills.

Among other less common GIS methods there is the Modular GIS Environment (MGE) created by Intergraph. MGE supports the needs of the users that require raster specific modelling tool for more complex models. It provides links with ORACLE and data manipulation can be achieved with SQL language. Although it accommodates for all possible grid functions, it is specific for data in raster format and hence its application is restricted to specific studies.

The GIS software packages described above are representative of the great variety of available programs and their main functionality. This research into N_2O and NO emissions from soils required a system able to accommodate large data sets of several types, offering a good selection of analysis functions and producing good quality outputs. Most of the needs were supported by the above programs, but the size of data sets and required data management functions were provided by another GIS method – ArcInfo.

ArcInfo, ESRI GIS software, is a large module that combines many graphical and modelling functions for both raster and vector data formats. It also offers data management functions through direct coupling with many software systems for easy data input and change of data resolution. Its multiple functions provide a good balance to the high cost and make this GIS method attractive for the higher price

end of the consumer market. A steep learning curve and high cost are the two main reasons why ArcInfo does not appeal to individual users and small companies. ArcInfo is one of the best methods for producing inventories as it allows for the incorporation of different data sets and an empirical model approach established through statistical analysis.

Despite all the advances offered by GIS, which are well known and publicised, it is relatively new in the field of modelling emissions from soils. It is applied for a variety of tasks, among which integrating data of different scales is the most common. But the majority of applications do not involve dynamic modelling. The GIS facility for direct connection with other software systems enabled its application in a pilot study to couple a mechanistic model of N_2O and NO emissions from grasslands in New Zealand by Muller *et al.* (1997). This model proved that the GIS solution to scaling up N_2O and NO emission exercises has many advantages, but also recognised the requirement for detailed data sets that might be one of the factors restricting its modelling applications. Another application of the GIS method for an inventory of ammonia emissions from soils in the UK was recently presented by Dragosits *et al.* (1998). In that work a strategy of mean NH_3 emission factors, established in experimental work, was applied to livestock and fertiliser input data for the UK to estimate ammonia emissions from soils.

Matthews (1993) suggested that GIS provides an *'ideal framework for coherent and systematic estimates of trace gas emissions and for analysing the global distribution of the sources of these gases'*. It is therefore the most convenient method for predicting the distribution of N_2O and NO emissions from soils at national scale.

In view of all the advantages of the GIS method to model gas emissions there remains the question why the application of GIS is so restricted. It is possible that its advantage of large data capacity also brings with it disadvantages, among which the main problem is the substantial processing time at the stage of data preparation prior to modelling. Another important restriction might be linked to the fact that direct coupling with mechanistic models on a grid basis is not an efficient method in terms of processing time. It has, however, no restriction in terms of statistical modelling and coupling with expert systems. GIS is the best system for inventory applications due to the spatial database and overlay functions. More advanced applications such as the previously mentioned knowledge-based models

allow for predicting N_2O and NO emissions on the basis of available data of the controlling factors. In those methods *'relationships developed outside the GIS are applied to data sets in the geographical database'* (Haines-Young *et al.*, 1993). This modelling strategy will be adopted in this work and the method of its application is briefly presented in the following section.

2.4.2 The concept and aims of ArcInfo Grid Emission Model (AGEM).

This study aims at defining a model describing distribution of N_2O and NO emissions from soils on the basis of their controlling factors. The model describing the relationships between the emissions of NO and N_2O and their controlling factors is to be applied to predict the scale of these processes for Great Britain. It concentrates on Britain as a whole for three main reasons. Firstly, Britain has an obligation towards other countries to report on the extent of emissions of greenhouse effect gases including N_2O (IPCC, 1995; Wirth and Lashof, 1990) and as a member of LRTAP[11] is obliged to monitor NO_x emissions (DoE, 1997). Secondly, there are existing data sets of the controlling factors of emissions (e.g. climatic variables, HOST soil classes, land use and land cover data) at the national scale that enable the analysis of the effects that these controlling factors have on the amounts of emissions at that scale. Thirdly, the knowledge of distribution of emissions for the whole country is necessary to define a policy for adopting the best management practices in order to reduce the amounts of emissions. There are already defined guidelines of optimal agricultural management practices for preventing N losses from soils (Cole *et al.*, 1997; Freney, 1997; Jarvis and Pain, 1994; Smith *et al.*, 1997). In order for those guidelines to be implemented it is important to establish a distribution of N_2O and NO emissions and identify areas of the highest emissions, where the problem should be specifically addressed.

Previous sections of this thesis present various methodological solutions that could be applied to predict distribution of N_2O and NO emissions from soils at the national scale. The methods presented have their advantages and limitations which determined the choice of methodology applied to define the models. The following

[11] definition in section 2.2.5.1, p 29.

paragraphs discuss the choice of modelling method best suitable for the subject and aims of this study and attempt at defining a hypothesis.

Mechanistic approaches are preferred modelling methods of dynamic in nature processes such as N_2O and NO emissions. They best describe the temporary changes of the fluxes and take into account complexity of soil physical, chemical and biological processes. Their application is, however, restricted by high requirements of several input variables, availability of which decreases at larger scales. In this study, the presented mechanistic models were assessed, but they could not be applied due to unavailable data (e.g. daily climatic data, concentration of NO_3^- and NH_4^+ in soils, adsorption coefficients) at the national scale. Further collection of data would be required, for which this study had restricted time and financial resources.

An alternative empirical method is characterised by a steady-state approach to the described processes, which is restricted in its application to model dynamic processes, but, on the other hand, has advantage of simplicity and more flexibility in terms of data requirements. This method is also more compatible with GIS ArcInfo, which is applied here to determine spatial distribution of N_2O and NO fluxes in Great Britain.

The model presented by this study, referred to as the ArcInfo Grid Emission Model (AGEM), is a GIS application of ArcInfo software in raster format. The aim of AGEM is to define a range of N_2O and NO emissions spatially dependent on the controlling factors like N soil content due to N input, soil temperature and soil moisture as documented in literature (Bowden *et al.*, 1990a; Conrad and Seiler, 1980; Dunfield *et al.*, 1995; Hutchinson and Brahms, 1992; Skiba *et al.*, 1994; Skiba *et al.*, 1997; Velthof *et al.*, 1996a and Yamulki *et al.*, 1995). Despite the spatial restrictions on the empirical functions outlined in section 2.3.1, establishing a general empirical trend between the dependent (the emissions) and independent variables (the controlling factors) offers a simple method of predicting N_2O and NO emissions for a variety of environments in Great Britain.

As described in this chapter, N_2O and NO emissions are very dynamic and variable processes occurring at microscales in heterogenous soils. Describing their relationships with the controlling factors by means of empirical model presents a

considerable challenge. This concept follows the modelling approach employed before by Eichner *et al.* (1990) and Bouwman (1995) for predicting N_2O emissions from N input. Other environmental factors, however, are expected to limit the effect of N input on the amounts of emissions as suggested earlier in this chapter. This study is trying to define a simple empirical model on the basis of complex relationships between N_2O and NO emissions and all their controlling factors observed in field measurements.

The complex nature of the processes leading to the emissions resulted in a view that modelling their spatial and temporal distribution is restricted by the limits of investigated environments (Jambert *et al.*, 1997b; Velthof *et al.*, 1996a). It is the aim of this study to test and argue that the empirical models can be applied at the national scales to outline factors responsible for the spatial variability of N_2O and NO emissions. Producing an inventory of N_2O and NO emissions for Britain requires some generalisations and assumptions to build a bridge between field studies and global models, but as Bouwman and Asman (1997) said *'scaling can be very useful for testing hypotheses and identifying missing information'.*

Finding the distribution of N_2O and NO fluxes for Britain requires detailed data of the controlling factors and a sound knowledge applied to the strategy of calculating emissions. The data sets used to predict N_2O and NO emissions from British soils with the established models are described in chapter three. Detailed discussion of theoretical background for AGEM is presented in chapter five.

CHAPTER THREE

Data sets used in ArcInfo Grid Emission Model.

3.1 DATA TYPES AND THEIR CHARACTERISTICS.

ArcInfo Grid Emission Model (AGEM) is a predictive statistical model of NO and N_2O emissions estimating the emissions of these gases on the basis of existing data of controlling factors (table 3.1). The empirical model was established using regression analysis of field measurements of N_2O and NO emissions in many parts of the world (chapter five, tables of N_2O and NO data). The model was then applied using existing data of the established controlling factors to estimate N_2O and NO emissions from soils in Great Britain. There were two main modelling issues linked to the data, which affect the outcome of AGEM - data availability and variation in spatial and temporal scale. The first issue is connected with restrictions in the availability of data of factors controlling N_2O and NO emissions for Great Britain versus required information. The second issue of AGEM - spatial and temporal differences among the data of the controlling factors - had an effect on the spatial and temporal resolution of the model. The available data sets are listed in table 3.1 (p 73), which outlines their main characteristics in terms of origin, and spatial and temporal resolution.

Statistical analysis of the field measurement data showed that the main controlling factor of the N_2O and NO emissions is N input from mineral and organic fertiliser application and atmospheric deposition (chapter five). Estimating N_2O and NO emissions requires that a distinction be made between mineral and organic input as different factors were reported for grazed and mown grasslands in several studies (Fowler *et al.*, 1997; Velthof *et al.*, 1994; Velthof and Oenema, 1995). Actual N fertiliser input was not available at a spatial resolution required by this study, hence the use of published recommendations of fertiliser input (section 3.2.5). Recommendations of good fertiliser practice vary according to land use type, which was obtained from the Agricultural Census (AC), the latter also provided information on livestock distribution for deriving organic manure input (section

3.2.2). A discrepancy was expected between the real N inputs and the recommended values especially in the case of organic manure, so the approach of this model was evaluated by a survey of eight selected farms from the East Lothian Region in Scotland (chapter 4). Atmospheric deposition for Great Britain was obtained from modelled results of measurements of wet and dry deposition components (section 3.2.5).

AC data varies between England / Wales and Scotland due to different sources of data (section 3.2.1) especially in the grassland classification (grazed / cut in Scotland and permanent / temporary in England and Wales). The AGEM is based on the Scottish classification of grasslands, and the proportion of grazed grasslands in England and Wales was calculated in the method described in section 3.2.5. The AC does not provide any information about semi-natural land, therefore a separate data source was used, The Institute of Terrestrial Ecology (ITE) Land Cover Map (section 3.2.1). These two data sets were combined to obtain the total land cover of Great Britain.

N_2O was also observed to vary depending on soil moisture, soil temperature and amount of organic C (chapter five). Carbon density was estimated on the basis of soil data provided for England and Wales by SSLRC[1] and for Scotland by MLURI[2] (section 3.2.6). There were no soil moisture and soil temperature data readily available for Great Britain and they had to be estimated using CLIMATE Link data and HOST classes (table 3.1). Other climatic data available from the Meteorological (Met) Office present greater detail, but their high cost meant they were unavailable for this research. Calculating soil moisture was based on the SPACTeach simulation model for which a number of assumptions were made (section 3.3.2), and soil temperature on Fourier's law of heat flux (section 3.3.1).

There are many differences between data sets in terms of their spatial and temporal resolution, which have an effect on their compatibility. The greatest uncertainty is expected of the final map of land cover for Britain due to differences between land use (the AC) and land cover (the LCM) data, which were used to create the complete land cover map of Great Britain. These differences relate to the spatial and temporal resolution of the two data sets and their different classification methods (section 3.2.1). Differences between the data sets in spatial and temporal resolution have an

[1] Soil Survey and Land Research Centre
[2] Macaulay Land Use Research Institute

important effect on the data processing errors. Climatic and N atmospheric deposition data have very coarse resolutions of 10 and 20 km^2, respectively, while land cover, HOST soil classes and carbon densities present details at a resolution of 1km^2, and AC data are intermediate with 5km^2 resolution. Temporal resolution of dynamic data such as climatic characteristics, deposition and fertiliser input also vary considerably. Some data present monthly changes (air temperature and precipitation), others give an indication of seasonal or annual variability (fertiliser recommendations and atmospheric deposition, respectively). The discussion of those differences and their effect on the chosen model resolution is presented in sections 3.4 and 3.5. All these differences among the data are expected to produce uncertainties in the outputs of the model, the definition of which is essential for the validation process. Estimating some types of error is expected to be easier in the cases of the regression model of field measurements (chapters 5 and 7), and land cover for Britain (chapter 4), but more difficult for soil moisture (section 3.3.2), soil temperature (section 3.3.1) and N fertiliser input (chapter 4).

This chapter presents a detailed analysis of all the available data types (table 3.1) and the methodology used to estimate missing data required for AGEM and explores the differences between the various data sets, which might affect uncertainties in the model (sections 3.2.2a, 3.2.4a and 3.4). The aim of this presentation is to define the best spatial and temporal resolution for the model (section 3.5).

Table 3.1 Summary of data used in AGEM model.

Data type	Format and scale of provided data	Sources of data	Time scale
Land cover (seminatural land)	ASCII files, 1km grid resolution	ITE Land Cover Map established on satellite imagery data	1990-1991
Land use (agricultural land)	ASCII files, 5km grid size	Agricultural Census data provided by Data Library	1988
Fertiliser input	Not spatial data published as N input recommendations for England/Wales and Scotland	MAFF for England/Wales; Scottish Agricultural College for Scotland	Recommendations published by MAFF in 1991; and by SAC - 1990 - 1993
N deposition data	ASCII files at a resolution of 20km grid	Acid deposition model	1992-1994
C data	ASCII files, 1km grid resolution	ITE inventory of soil C	Adjusted soil C data from MLURI and SSLRC
Soil temperature estimated from air temperature (heat flow theory)	ASCII files at 10 km resolution	Climate LINK project, University of East Anglia.	Long-term averages from 1961-1990
Soil moisture estimated from precipitation (Climate LINK) and texture-HOST data	Precipitation at resolution of 10km grid; soil wetness classes at 1km grid (both as ASCII files)	Institute of Hydrology provided soil wetness classes, precipitation data - as above	HOST classes from 1995; rainfall fields as above

3.2 EXISTING DATA SETS.

This section describes data sets which were obtained from various sources and input to the AGEM without major processing required apart from adjusting the spatial resolution differences. Each data set is presented in terms of its origin, major characteristics (e.g. resolution and quantity) and uncertainties.

3.2.1 Land cover data set.

The ITE Land Cover Map (LCM) of Great Britain is based on LANDSAT imagery from 1990-1991 which has been interpreted by the ITE Remote Sensing Unit (Fuller *et al.*, 1994). Original satellite data were aggregated into two types: 'the full set of 25 "target" cover-types, or 17 "key" cover-types' (Fuller *et al.*, 1994), which are presented in table 3.2 and described in Appendix 1. The former demonstrate the original data from the interpreted satellite imagery at 25m x 25m resolution, which is claimed to distinguish parcels of land with the minimum area of 5 ha (Fuller *et al.*, 1994). The latter has the resolution of a 1km grid, and was created from the

'full set' via generalisation of the land cover types, which were combined into a proportional representation of all $25m^2$ original cells for every 1km grid cell. Among the land cover types there are classes which represent the original 'target' cover types (class A, B, C, D, J, L, M, N, O, P and Q), but grasslands, heathlands, moorlands and deciduous forests have been distinguished on the basis of a variety of classes (table 3.2). Grasslands represent a complex land cover, which varies in terms of species distribution, altitude, soil characteristics (acidity and wetness) and the type of management. All those factors have a distinctive influence on the reflectance of the vegetation, which in the 'key' classification (table 3.2) was divided between 3-4 types (E-H). This classification, due to restrictions of spectral recognition in the process of separation of discrete classes, makes this data set unique and problematic in combination with other land classifications. In the 25m data set, 2% of land is unclassified (class 0) due to insufficient information either as an effect of cloud cover or unusual reflectance. Unclassified cover is not distinguished as a separate 'key' class in the 1km data set, but it can be estimated from a difference of all the 17 classes from the total land area.

Table 3.2. LCM classification with groupings of land use and cover types used in AGEM Fuller *et al.*, 1994).

'Target' class	**Land cover category**	**Land use/cover in AGEM**
1. Sea/Estuary	A. Sea/Estuary	Excluded
2. Inland Water	B. Inland water	Excluded
3. Beach and Coastal Bare	C. Beach/ Mudflat/ Cliffs	Excluded
4. Saltmarsh	D. Saltmarsh	Excluded
5. Grass Heath	E. Rough Pasture/Dune Grass/ Grass Moor	Heathland
9. Moorland Grass		Heathland
6. Mown/ Grazed Turf	F. Pasture/ Meadow/ Amenity Grass	AC classes
7. Meadow/ Verge/ Seminatural		Meadow
19. Ruderal Weed	G. Marsh/ Rough Grass	AC classes
23. Felled Forest		AC classes
8. Rough/ Marsh grass		AC classes
25. Open Shrub Heath	H. Grass Shrub Heath	AC classes
10. Open Shrub Moor		AC classes
13. Dense Shrub Heath	I. Shrub Heath	AC classes
11. Dense Shrub Moor		AC classes
12. Bracken	J. Bracken	Bracken

14. Scrub/ Orchard	K. Deciduous/ Mixed Wood	Deciduous forest
15. Deciduous Woodland		Deciduous forest
16. Coniferous Woodland	L. Coniferous/ Evergreen Woodland	Coniferous forest
24. Lowland Bog	M. Bog	Bog
17. Upland Bog		
18. Tilled Land	N. Tilled (Arable Crops)	AC classes
20. Suburban/ Rural Development	O. Suburban/ Rural Development	Excluded
21. Continuous Urban	P. Urban Development	Excluded
22. Inland Bare Ground	Q. Inland Bare Ground	Excluded
0. Unclassified		

Description of classes in Appendix 1.

3.2.2 Agricultural data.

The source of the data is an annual survey of 235000 selected 'major' holdings, which are defined differently for England and Wales according to size (>6 ha) and economic activity; and Scotland where economic activity is the explicit qualifier (MAFF and SOAF, 1991). This annual survey is prepared and carried out by MAFF for England and Wales and the Department of Agriculture and Fisheries for Scotland. The results of the survey are combined and presented by the Data Library of Edinburgh University in two formats: vector data with a parish as a reference unit, and grid data at various resolutions (1, 5 and 10km^2).

Data used in this study are the 1988 Agricultural Survey in raster format at 5 km^2 resolution. The older survey was used because the results from the more recent surveys for England and Wales are incomplete, which means that it is impossible to apply fertiliser recommendations.

(1) 1994 Agricultural survey does not give any information about the class of vegetables and fruits, and some sub-groups of sheep types are missing from livestock.

(2) 1993 Agricultural survey - same as for 1994 with more sub-groups missing from the livestock class - calves and cattle and oats, rye, and mixed corn not available.

(3) 1992 Agricultural survey does not include most cereals, grasslands, other crops and vegetables.

(4) 1989 - 1991 Agricultural surveys are not available for England and Wales.

The raster format was selected for two reasons, firstly it was more compatible with other data formats used in this study, and secondly parish boundary data were not available for use with the vector format data due to the 1984 Data Protection Act. Gridded data were created from the parish data set by overlaying them with 1km grid net and assigning each 1km grid cell to either non-agricultural, or agricultural land depending on a proportional contribution of different land categories in that specific grid cell. In some cases woodland and inland water were emphasised in the assignment to *'present a more sensible picture of a larger area'* (MAFF and SOAF, 1991). The 1km data set was then resampled to the lower resolutions of 5 and 10 km and each grid was assigned with the proportional distribution of all land categories estimated for each 5 km grid from the summary of all 1 km grids. The locational errors of this data set are entirely due to the procedure of the assignment; land use classes in each grid cell are not preserved, but their general character is maintained. At the coarser resolution the total area of each land use class is better represented due to the reduction of boundary uncertainties. This fact makes the land use data at 5 and 10km^2 resolution more accurate and hence more attractive for modelling than the 1km data set.

3.2.2a Vegetation classes defined by AC and LCM data sets.

There are a number of conceptual inconsistencies when adopting AC and LCM data sets for the complete land cover map of Great Britain due to the differences between these two sources reported in sections 3.2.2 and 3.2.1. Six main semi-natural vegetation classes of the LCM provided information for non agricultural land (table 3.2) to complete the AC information on the characteristics of agricultural land use. The remaining 'target' classes were expected to be compatible with AC data, i.e. grassland class (AC) was assumed to be an equivalent of 'target' class 6, 19, 23, 8, 25, 10, 11 and 13 and tilled land (AC) with 'target' class 18. Apart from temporal differences, diverse sources of those two classifications are another reason for error. The main uncertainty lies with rough grasslands, which are defined by the Agricultural Census as 'rough grazing on which you have sole grazing rights' (MAFF, 1996). From the definition of LCM 'target' classes corresponding with rough grasslands as defined by AC (table 3.2), it becomes clear that a large proportion of those classes might fall outside the scope of the AC category of rough grazing. LCM defines agricultural grasslands as all variety of grass types from newly sown leys, pastures to unimproved swards, while AC describes this class as productive grasses

e.g. clover, which are subject to agricultural management. Tilled land is defined by the LCM as land under annual tillage for cereals and horticulture including one year old leys (Fuller *et al.*, 1994) while AC excludes horticulture and leys from this type. All these differences indicate a possibility of a larger estimate of tilled land by the LCM than the AC and a lower estimate of grassland by the LCM than the AC. A detailed verification of the LCM and the AC data was carried out for the Tyne-Clyde area (chapter 4) and Great Britain (chapter five) to examine the effect of different classifications on the uncertainty of land cover data.

3.2.3 Climatic characteristics.

Data of mean, minimum and maximum air temperature and rainfall for Britain were obtained from the data sets prepared for the TIGER IV Consortium (Barrow *et al.*, 1993). Those data sets are based on UK Met Office long term averages from 1961-90, which were interpolated and rasterized in order to obtain a 10km grid cover of Britain. Precipitation values were obtained from 7201 sites, from which only 2376 qualified for UNIRAS and 750 for the smoothing spline method. Maximum and minimum temperatures came from 623 Met stations, but the measurements of 356 Met stations were used to produce the Climate LINK data set. The processing was part of the Climate Impacts LINK project and involved a combination of two methods: inverse-distance weighting function (UNIRAS, 1989) and partial plate smoothing spline (Barrow *et al.*, 1993). A detailed description of this methodology and the uncertainty of Climate LINK data set are presented by Barrow *et al.* (1993).

3.2.4 HOST soil classes.

The Hydrology Of Soil Types (HOST) classification has been produced with the co-operation of the Institute of Hydrology (IH), the Soil Survey of Scotland based at the Macaulay Land Use Research Institute (MLURI) and the Soil Survey and Land Research Centre (SSLRC). It was developed in the mid-1980s on the 1970s version of the Winter Rainfall Acceptance Potential (WRAP) map and incorporated the details of the national reconnaissance soil maps at 1:250,000 prepared by the soil survey organisations mentioned above (Boorman *et al.*, 1995). The IH hydrological database was incorporated into the project, which in effect led to defining new soil classes, known presently as HOST classes.

The HOST classification focuses on the types of water movement in soils depending on their structural and textural characteristics, and the depth of the groundwater aquifer or impermeable layer (Boorman *et al.*, 1995). There are eleven response models, A-K, which describe the types of water movement in soil, from the least restricted downward flow to the surface runoff resulting from saturated conditions (table 3.3, Appendix). Within the existing model responses, the HOST classification distinguishes types depending on the rate of flow and the type of water storage. These properties are the result of various soil textural and structural characteristics. In total there are 29 HOST classes (table 3.3, Appendix) covering nearly 94% of the area of England, Wales and Scotland. The remaining 6% are unclassified urban areas and inland waters.

From the HOST classification, one can draw some conclusions about the characteristics of British soils. Over 23% of the area is classified as peats, with just over a third of them available for agriculture (0.55% drained and the remaining 9.93% characterised by groundwater level below 2m depth). The remaining mineral soils exhibit a variety of drainage characteristics: 41.8% are impermeable or slowly permeable with half of them subjected to prolonged waterlogging (gleyed layer within 40cm); 6.65% have good drainage (HOST classes 3 and 5) and 18.74% exhibit moderate drainage characteristics due to the microporous texture of the substrate and varying depths of gleyed and/or impermeable layers (table 3.3, Appendix).

3.2.4a Soil classification differences between HOST and field measurement data sets.

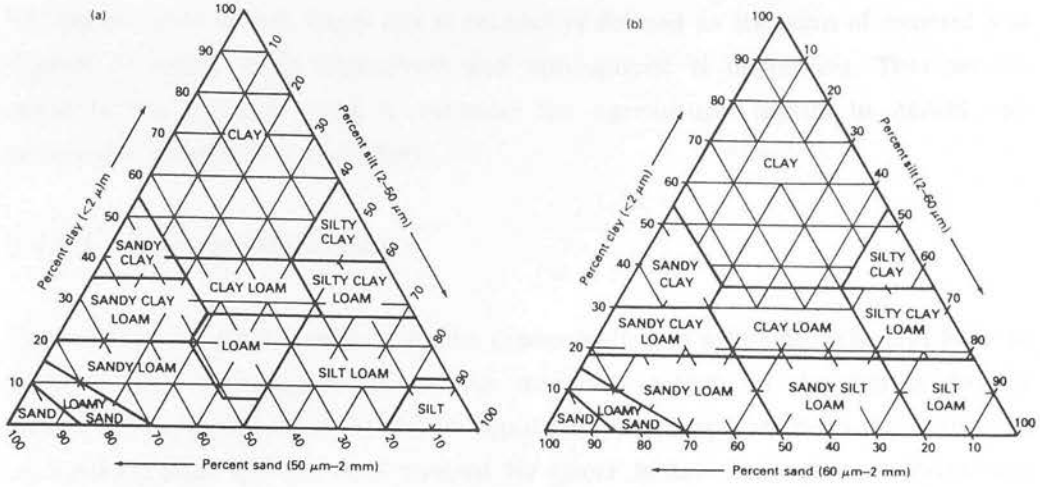
Inconsistencies in soil data sets are linked to the fact that the two systems used in AGEM have different origins. HOST classes are based on the behaviour of water in the soil substrate as described above. The majority of published data sets of NO and N_2O emissions, used in the AGEM to define predictive models, give information on the textural characteristics of the studied soils (85% and 66% for NO and N_2O respectively). The remaining studies do not specify the textural class of the soils, but some of them provide their taxonomic description (e.g. order, suborder and group). There are a number of studies in which no soil details are presented (8.6% and 6.5% for NO and N_2O data, respectively). These differences could increase the uncertainty of established models and therefore the soil data sets had to be made compatible. A simple classification was prepared on the basis of textural characteristics for both HOST and field data, which generates three drainage classes from the HOST classification (table 3.4) and scales field soil classes according to their drainage (table 3.5). The derived coarse classes would decrease the uncertainty caused by the differences presented above.

Table 3.4 Drainage groups of HOST classes

Drainage classes	HOST classes
free drainage	3,5
moderate drainage	1,2,4,6,7,8,10,13,14
poor drainage	9,11,12,15,16,17,18,19,20,21,22,23,24,25,26,27,28,29

In the field data set, soil textural classification was either according to USDA or UK systems as field measurements encompassed both North America and Britain (figure 3.1). These two systems define different limits for soil textural classes and there might be therefore some inconsistencies in the interpretation of the results.

Figure 3.1 Textural (particle-size) classes according to the United States Department of Agriculture (a) and the Soil Survey of England and Wales (b).



There are no major discrepancies observed for sandy loam, but other soil types such as silt loam and clay are defined very differently by the two classification systems, while loam is non existent in the UK textural classification system. In the cases listed below the specified soil types had to be used as described in the UK textural classification: Anderson and Levine (1987); Breitenbeck and Bremner (1986a, b); Burton *et al.* (1997); Cates and Keeney (1987); Cochran *et al.* (1981); Goodroad *et al.* (1984); Matson *et al.* (1992); McKenney *et al.* (1980); Mosier and Hutchinson (1981); Valente and Thornton (1993); Thorton and Valente (1996); Wagner-Riddle *et al.* (1997); Williams *et al.* (1988). Assigning values of drainage characteristics to textural classes partly solves the problem of inter-class differences, but uncertainty due to these differences still accounts for 22% and 17.8% of N_2O and NO emission measurements, respectively.

Table 3.5. Drainage groups assigned to the textural classes of published data sets.

drainage scale	textural classes
1	sand, loamy sand
2	sandy loam
3	loam, silt loam, loam on clay, sandy silt loam
4	loam an clay, clay loam, silty clay loam, loess, fine silty soils, silty soils
5	clay
6	organic soils like peats and humisols

3.2.5 Soil nitrogen content.

For the purpose of this study soil N content is defined as the sum of mineral and organic N inputs from agriculture and atmospheric N deposition. This section presents the methods used to estimate the agricultural inputs in AGEM and acquired atmospheric N deposition.

3.2.5.1 Mineral fertiliser input.

Soil mineral N content, defined by the concentration of available NO_3^- and NH_4^+ in soils, is very changeable because the microbial activity of the soil is directly dependent on the levels of N fertiliser input and N atmospheric deposition. There is no existing data set of soil N content for Great Britain. The present study was based, therefore, on modelled data of N fertiliser input established from existing guidelines, organic N inputs based on animal densities (AC) and modelled atmospheric N input. Good fertiliser practice guidelines were applied in AGEM instead of the British Survey of Fertiliser Practice (BSFP) data (Burnhill *et al.*, 1995), which include the overall fertiliser usage. This choice was due to the fact that the spatial resolution of the latter data was too coarse as it only distinguished six crop types - winter wheat, spring barley, winter barley, maincrop potatoes, oilseed rape and sugar beet (Burnhill *et al.*, 1995). In reality there are many more crops grown in Britain, as indicated in table 3.6, for which different fertiliser guidelines are prescribed. The modelling strategy using the published recommendations of mineral N input would increase the spatial variability of estimated N input to soils. Additionally agricultural advisers claim that farmers do follow the published recommendations (FMA, 1998), which suggests that the loss of detail in BSFP outweighs the uncertainties of the fertiliser recommendations.

Fertiliser recommendations.

These are guidelines published by government advisory bodies on optimal amounts and timing of mineral fertiliser and slurry input to soil according to crop type, soil N status, climatic conditions and soil type, which are primarily aimed at increasing economic use of fertilisers. An important environmental role of the recommendations is to reduce N loss by leaching through reduction of excessive fertiliser input. Fertiliser recommendations are published separately for England and Wales by the Ministry of Agriculture, Fisheries and Food (MAFF, 1988) and for Scotland by the Scottish Agricultural College in Edinburgh (Dyson, 1993; Dyson *et*

al., 1993a; Dyson and Synclair, 1993b; Dyson *et al.*, 1993c; Swift, 1988 and Younie *et al.*, 1990).

Table 3.6. Recommendations of N input to arable land in England/Wales and Scotland (MAFF, 1988; Dyson, 1992; Dyson, 1993; Dyson, 1993a; Dyson 1993b).

crop types	**N input [kg N $ha^{-1}y^{-1}$]**		**Assumed index in AGEM**
land use	England/Wales	Scotland	
	Arable crops		
wheat	200	180	0
winter barley	160	170	0
spring barley	150	130	0
oats	125	100	0
corn / rye	125	ns	0
maize	40	ns	0
	Tillage crops		
potatoes	160	160/130 *	1
sugar beet	75	ns	0
hops	225	ns	1
turnip	100	100	1
kale	125	120	1
other crops	125	100	1
oilseed rape	125	175	1
forage beet/rape	ns	100	0
	Vegetables		
cauliflower/ calabrese	200	200	1
carrots	100	100	0
cabbage	ns	200	1
brussels	ns	250	1
parsnip	100	ns	0
celery	40	ns	0
lettuce	125	200	0/1
sweetcorn	100	ns	0
rhubarb	ns	250	1
beetroot	100	ns	0
beans	150	ns	1
peas	100	100	1

ns - not specified
* amount depends on crop variety;

England and Wales.

The recommended value of N input was estimated on the basis of the crop requirement and the residual N in soil from previous years (MAFF, 1998). The latter was used to define three arbitrary nitrogen Index levels: Index 0 with *'low N reserves and more nitrogen (...) needed compared with'* Index 1; Index 1, the

intermediate class and Index 2 which defines *'highest soil nitrogen reserves'* (MAFF, 1988). The level of nitrogen index is determined by 'the last crop grown' as listed in table 3.7 (MAFF, 1998). Tables of guidelines distinguish between the three index classes, and in many cases (all crops and some vegetables) soil texture is also considered an important factor for crop N requirements that are adjusted accordingly (MAFF, 1998). For grasslands the level of fertiliser input is defined by the management practices and rainfall level (the latter defines N input to hay) (MAFF, 1998).

There were some difficulties in this approach due to limitations of the Agricultural Census data. The raster format of the agricultural data set and its coarse resolution meant that it was not possible to monitor rotational practices at a field level, hence it was decided that the index class would be assigned on the basis of the current year's crop (tables 3.6 and 3.8). Additionally soil type criteria were ignored to simplify the model and it was assumed that all varieties grow on mineral soils which is true for the majority of arable land and grasslands (DoE, 1990).

Table 3.7 Nitrogen Index - based on last crop grown (MAFF, 1998).

Nitrogen Index 0*	**Nitrogen Index 1***	**Nitrogen Index 2***
Cereals	Peas or beans	Any crop receiving large dressings of farmyard manure or slurry
Sugar beet	Potatoes	Lucerne
Maize	Oilseed rape	Long leys, grazed or cut and grazed, high N (b)
Vegetables (<200 kgN ha^{-1})	Vegetables (>200 kgN ha^{-1})	Permanent pasture, cut only, grazed or cut and grazed
Forage crops removed	Forage crops grazed	
Leys grazed or cut and grazed, low N (a)	Leys grazed or cut and grazed, high N (b)	
Leys cut only	Long leys cut only	
Permanent pasture poor quality	Long leys, grazed or cut and grazed, low N (a)	

* Nitrogen Index is established on the basis of the previous year's crop
(a) Low N - less than 250 kgN ha^{-1} per year and/or low clover content
(b) High N - more than 250 kgN ha^{-1} per year and/or high clover content

Another factor defining N input to grasslands in the MAFF system is soil fertility, which is not available from the AC data. The AGEM based N input to grassland on the SAC recommendations according to the N index defined in table 3.8. The SAC system was adopted as it distinguishes between grazed and mown grasslands and

the N_2O and NO emissions from grasslands under these two management systems have been shown to be very different (Galbaly and Roy, 1978; Velthof *et al.*, 1996b). The Agricultural Census for England and Wales provides data only for temporary and permanent grasslands. Information on the proportion of grazed grasslands was obtained from the Countryside Information System (the method is described further in this section). N fertiliser input to mown grasslands was estimated as the mean of equally weighted hay and silage, for which the recommended amount varies according to number of cuts (Swift, 1988).

Table 3.8. Recommendations of N input [kg N ha^{-1} y^{-1}] to grasslands for Britain (MAFF, 1988; Swift, 1988).

stocking density [$SUha^{-1}$]	Mown grassland	Grazed grassland	Index
0 - 2.0	130	110	0
2.1 - 5.0	200	210	1
> 5.0	300	325	1/2

Scotland.

N fertiliser recommendations are estimated in a similar way to the MAFF system for England and Wales, except that SAC defines the 'standard' rates depending on soil N status (low, moderate or high) and other adjustments are made according to the amount of rainfall and soil characteristics.

Technical Notes define soil nitrogen status in a similar way to the MAFF Index system (table 3.9) apart from a few exceptions. Potatoes in the SAC classification are distinguished between the seed and the main crop, vegetables are split by MAFF depending on N input and forage crops are assigned to a higher class by SAC. The AC data does not provide information on the crops grown specifically for forage, this class was therefore not considered in the AGEM. Fertiliser guidelines for grasslands depend on the input of N fertiliser, which in turn is defined by the stocking density (table 3.8) and management system i.e. grazed and cut grass. The former defines soil N status for grazed grasslands, while N status of cut grasslands depends on the level of N input of the previous year (assumed the same as in the current year). The MAFF recommendations were adopted for estimating N input to the majority of crops apart from grasslands, and although some minor inconsistencies in N input are expected, they are not likely to have a noticeable impact compared to other uncertainties linked with this approach (section 3.4).

Table 3.9 Soil nitrogen status - based on previous crop (Dyson, 1990).

Low N status	Moderate N status	High N status
Leys grazed semi-extensively with less that 125 kgN $ha^{-1}y^{-1}$	Leys grazed semi-extensively with 125-150 kgN ha^{-1} y^{-1}	Leys grazed intensively with more than 250kgN ha^{-1} y^{-1} or a strong clover sward
Leys cut	Oilseed rape	Forage crop grazed
Forage crop removed	Potatoes - ware	
Cereals	Peas	
Potatoes-seed	Beans	
	Field vegetables	

Grazed grasslands based on the Countryside Survey 1990 data.

Data for grazed and cut grasslands for England and Wales were estimated from regional proportions of grasslands with grazing animals present, provided by the Countryside Information System (CIS) for Department of the Environment regions, and total grass areas as defined by the AC at the 5km grid scale (section 3.2.2). CIS is a computer-based database system combining remote sensing data from LANDSAT imagery, the results of field survey and ecological sampling as *'an integrated GB picture of land use, land cover, landscape features, habitats, vegetation and plant and freshwater animal species'* (Barr *et al.*, 1993). Information about grazing has been compiled from field surveys carried out in 508 $1km^2$ squares selected in a random stratified sampling method, in which the ITE Land Classification was the sampling framework (Barr *et al.*, 1993). In the field survey, types of animals present in defined areas were observed and recorded (codes 175-184 for the grazed area and 185-192, 195 for animal types as defined in Barr *et al.*, 1993). The proportions of grazed grasslands were then estimated at the regional level (estimates at the county level were also available, but discounted on statistical grounds due to great uncertainty of estimates).

Table 3.10 Proportions of grazed land according to regions in England and Wales (Barr *et al.*, 1993).

region nr	region name	grazed land [%]
1	East Midlands	44.0
2	East Anglia	48.5
3	North	55.4
4	North West	45.7
5	South East	40.3
6	South West	45.1
7	West Midlands	43.9
8	Yorkshire and Humberside	46.9

Computing the total area of grazed and cut grasslands in ArcInfo GRID involved applying CIS grazing proportions at regional level (table 3.10) to AC data of total managed grasslands at 5km resolution. This simple approach ensured spatial variability of grazed grasslands between the regions, but the method assumed that all registered grazing occurred on managed grasslands, the reliability of which is unknown. Additional uncertainty in this method is associated with differences between the sources of data (section 3.4).

3.2.5.2 Organic fertiliser input.

Data used to estimate organic N input to soils were obtained from the Agricultural Census, which provided information on livestock numbers in the same format as the land use data (section 3.2.2). Different livestock types were assigned to major livestock groupings and N input was estimated from the nutrient content of organic manure according to its origin (table 2.8, chapter two). The amounts of organic manure produced by different animals were then compared in order to assign the livestock groupings with stocking units (SU) and to produce a map of stocking density applied in estimation of mineral N input to grasslands (tables 3.8 and 3.11). For simplicity of approach, all cattle and cow types over 2 years old, deer and horses were made equivalent to 1 livestock unit. As information on nutrient content was not available for sheep, the livestock units were assigned for this type according to Chadwick (1995). The method used was based on a commonly applied definition of one livestock unit equivalent to one dairy cow (Chadwick, 1995). Distribution maps of livestock density and organic N inputs to grasslands for Great Britain were produced in ArcInfo GRID at 5 km resolution.

Table 3.11 Stocking unit equivalents of different livestock groupings.

Livestock groupings	Livestock types as defined by the AC	Stocking unit equivalent
Cows and cattle over 2 years old	Cows in milk, cows in calf, heifers in calf, bulls and other cattle	1
Young cattle (not exceeding 2 years of age)	Heifers in calf, bulls for service and other cattle and calves intended for dairy, beef hers, or for slaughter	0.3
Horses and deer	Horses and ponies, farmed deer	1
Pigs	Sows ofr breeding, gilts, boars, barren sows for fattening and other pigs	0.16
Sheep*	Ewes, shearlings and ewe lambs, female sheep not for breeding, rams, ram lambs and other sheep and lambs	0.15
Poultry	Hens, fowls, table chicken, ducks, geese, turkeys and other poultry	0.004

* Stocking units adopted from Chadwick (1995)

3.2.5.3 Atmospheric deposition data

N deposition encompasses dry (e.g. NO_y and NH_3) and wet components (i.e. NO_3^- and NH_4^+) and the data for 1992 – 1994 are used in the AGEM (RGAR, 1997). Rainfall concentrations and NO_2 are measured presently at 32 rural monitoring sites, the number being reduced from 59 in 1988 due to limited resources. The sites comprise a 'Primary Network' where 'wet only' collectors are used, and a 'Secondary Network' with bulk collectors (RGAR, 1997). The site data are interpolated by kriging to obtain 20km^2 cover for UK. The interpolation standard error ranges from 5 to 15μeql^{-1}. The data set is reliable at a national scale, however locally in Cumbria, Pennines and in north west Scotland there are areas with great uncertainty, due to the lack of site monitoring at high altitudes (RGAR, 1997). In upland areas wet deposition is increased as an effect of higher precipitation and the seeder-feeder enhancement. The absence of monitoring stations in upland areas result in modelled atmospheric N deposition being underestimated (RGAR, 1997).

Dry deposition of ammonia, which was not available from measurements for 1992-94, is modelled using the Fine Resolution Ammonia Exchange model (FRAME) which employs land use and surface mean wind speed data (Klimova-Murphy and Fisher, 1996). The outcome of FRAME is considered to be more reliable than the NH_3 concentration map resulting from corrected passive diffusion tube measurements (RGAR, 1997).

3.2.6 Soil organic carbon content.

Soil organic C is one of the main factors controlling the amounts of emitted N_2O and NO by providing substrate for decomposition, which is shown to enhance denitrification (chapter two). The organic C concentration in soils has been estimated and mapped for Great Britain (Milne and Brown, 1997). The method estimating soil C content assumes that concentration of organic carbon in soils is directly related to vegetation cover and therefore soil organic C density can be obtained on the basis of the dominant vegetation type and corresponding carbon density for each land cover type (Milne and Brown, 1997). The highest carbon density is attributed to Scottish peats amounting to 38 - 51 kg m^{-3}. The total amount of carbon in British soils was estimated at 9838 Mt, with over 70% in Scottish soils (Milne and Brown, 1997).

Soil C density data were obtained from the ITE Carbon map as an ASCII file at 1 km grid resolution (Milne and Brown, 1997). This data set was derived from the MLURI and the SSLRC soil data with a revised method of estimating carbon for Scottish peats. From the obtained soil C density data, the proportion of soil carbon was estimated in ArcInfo GRID with the assumed mean bulk densities of 1.1 g cm^{-3} for medium to heavy texture soils, 1.55 g cm^{-3} for light texture soils (Hall *et al.*, 1977) and 0.35 g cm^{-3} for peats (Howard *et al.*, 1994).

There is clearly great spatial variability in organic C content, which is attributed to the heterogeneity of soil characteristics. Estimated % C content in soils ranges from 0 - 72% with the above mean (> 3 %) proportion of soil carbon content in Scotland, Wales and Cornwall. Those areas of high soil C content were related to peat or forest distribution. Milne and Brown (1997) assumed an error of ± 20% for soil C content in non-peat Scottish soils and for all soil types in England and Wales, but for peats a greater uncertainty was expected (about 50%) due to their changeable depth and the uncertainty of bulk density estimates (Milne and Brown, 1997). The proposed error for total C content in British soils is in the region of 25%. An additional uncertainty in % C calculation in this work due to the application of mean bulk densities is expected to increase the error further to 55 % due to the variability of bulk density within the main soil classes (table 3.12).

Table 3.12 Mean and ranges of typical dry bulk densities and porosities of soils (Hall, 1977)

	Dry bulk density [g cm^{-3}]	Porosity [cm^3 cm^{-3}]
Cultivated mineral soils		
Medium-heavy texture	1.1 (0.8-1.4)	0.58 (0.69-0.46)
Light texture	1.55 (1.4-1.7)	0.40 (0.46-0.35)
Subsoils and parent material	1.65 (1.5-1.8)	0.38 (0.43-0.32)
Grasslands and woodland	1.0 (0.8-1.2)	0.58 (0.67-0.50)
Peats	0.2 (0.1-0.35)	0.86 (0.93-0.79)

3.3. DERIVED DATA SETS.

Climatic characteristics are known to control factors of N_2O and NO emissions in many studies (reported in chapter two), and both soil temperature and soil moisture have been used as predictors of the emissions in many models (Bouwman, 1995; Nevison *et al.*, 1996; Skiba *et al.*, 1993; Velthof *et al.*, 1996c; Williams *et al.*, 1987). There were no data sets of soil moisture and temperature readily available for input to AGEM, it was, therefore, necessary to estimate them on the basis of existing climatic data described in section 3.2.3. This section presents the methods in which the required data sets were derived and explores the uncertainties of the applied approach.

3.3.1 Soil temperature.

Soil temperature data were not available for the reasons discussed in section 3.1 and they have therefore been estimated from air temperature and soil moisture data with the empirical SOILTEMP model (Appendix 2).

Model description.

The SOILTEMP model uses inputs of air temperature fields from Climate LINK data set (section 3.2.3) and water filled pore space (WFPS) fields, which were derived in a procedure described in section 3.3.2. It is an ArcInfo Macro Language model, which estimates soil temperature using the theory of heat flow (Appendix 2).

The theory of heat flow in soil was presented by Monteith and Unsworth (1990), who observed that soil thermal properties were defined by the volume fraction of each soil component. These properties determine the amount and the velocity of

heat transferred into the deeper layers of the soil from the surface. If temperature at depth z and time t is T(z.t), the boundary condition which describes a harmonic oscillation of temperature at the depth z describes soil temperature with function presented in equation (3.3).

$$T(z.t) = T_m + A(z)\sin(\omega t - z/D) \qquad \text{(Campbell, 1977)} \qquad (3.3)$$

where $A(z) = A(0)\, e^{-z/D}$ is the amplitude at the level **z**,

$A(0)$ is the amplitude at the soil surface,

$\omega = (2\pi/365)d^{-1}$, T_m is the mean temperature of the air,

z is the soil depth,

$D = (2\kappa'/\omega)^{0.5}$,

κ' - thermal diffusivity, which depends on the soil type and amount of moisture in the soil (table 3.13).

The SOILTEMP varies the diffusivity parameter (table 3.13) depending on a proportional weighting of soil types for each grid cell and can be applied at any user-defined level of soil depth. Soil temperature was estimated at 30cm and 5cm depth (figures A3.1 and A3.2), which were the assumed lower limits for the majority of emitted N_2O and NO, respectively. The depth of emitted N_2O was based on the mean extent of denitrification processes (Delmas *et al.*, 1997; Henrich and Haselwandter, 1997; Klemedtsson *et al.*, 1997) and for NO 5cm level was assumed as it is a short-lived gas in the soil profile (chapter two).

Table 3.13 - Thermal diffusivity (κ') according to the properties of soils (Monteith and Unsworth, 1990).

soils	VWC [%]	Thermal diffusivity κ' [10^{-6} m^2 s^{-1}]
Sandy soil (40% pore space)	0.0	0.24
	0.2	0.85
	0.4	0.74
Clay soil (40% pore space)	0.0	0.18
	0.2	0.53
	0.4	0.51
Peat soil (80% pore space)	0.0	0.10
	0.4	0.13
	0.8	0.12

Model results.

SOILTEMP has been used to determine seasonal changes of soil temperature in Great Britain. Mean seasonal soil temperatures at 30cm depth ranged from -1.1 °C in winter[3] (Glen More, Scotland) to 18.2 °C in summer[4] (Greater London, England) and at 5cm from -3.4 °C in winter (Glen More, Scotland) to 19.3 °C in summer (Greater London, England). There was a distinctive spatial pattern in the seasonal distribution of soil temperature with an observed expansion of warmer air from the Southeast in spring[5] to summer and then the invasion of cold air from the north in autumn[6] and winter (figure A2). Southern coasts of England and Wales, Anglesey and Thames Delta had mean seasonal soil temperatures at the 30cm level above 5°C, and, in few places, even above 6°C throughout the year (figure A2). In those areas temperature was not a limiting factor for N_2O and NO emissions. On the other hand, in the Scottish Highlands, estimated mean soil temperatures at both 5 and 30 cm were below 6°C for a great proportion of a year causing lower activation energies of the bacterial processes of N_2O and NO production (chapter two).

Temporal changes in soil temperature at 5cm depth exhibit a similar pattern to these at 30cm, with an observed relationship between spatial changes of soil temperature and air temperature. A much greater range of soil temperatures at 5cm depth will most probably have an effect on the amount and character of emissions, especially of NO which are likely to follow the pattern of temperature fluctuations (figure A3). Also, much higher soil temperatures closer to the surface in summer might create optimal conditions for the release of NO in the drier areas of south-east England (coinciding with a rainfall deficit of the rain zones 1 and 2 presented on figure A4).

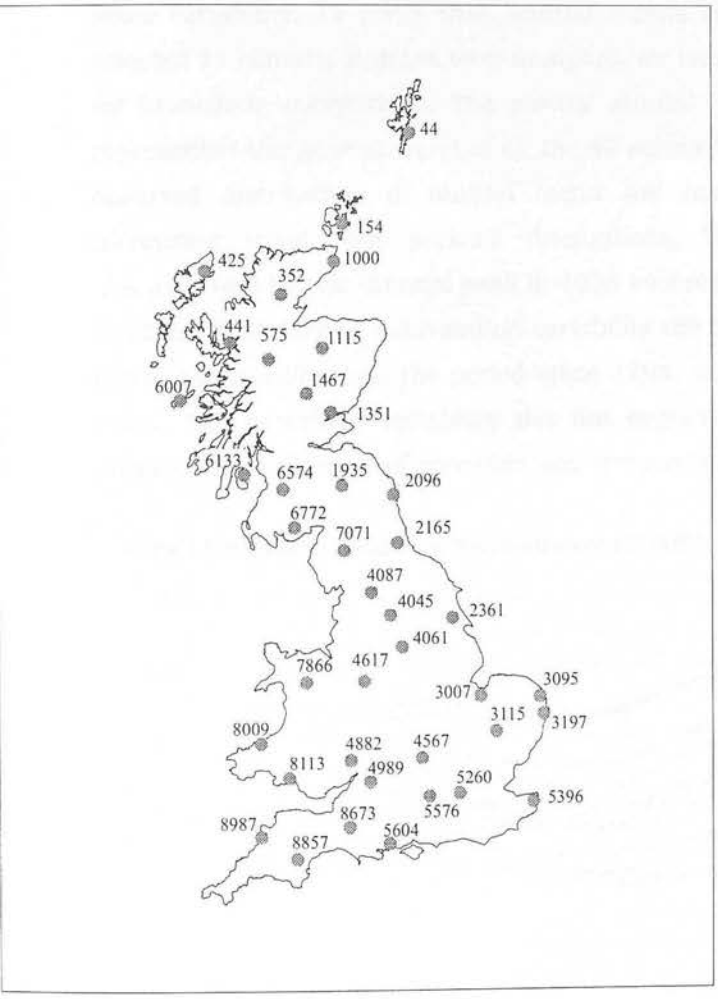
Verification of the estimated soil temperature.

Soil temperature data estimated with the predictive model at 30 cm depth (equation 3.3) were validated with measured soil temperature at 30 cm depth at 41 selected climatic stations (figure 3.2). The modelled data were compared with the data measured in the period 1990-1998 to observe an accuracy of prediction and any deviations due to changes in temperature since the period of 1961-1990, for which the predictions were made. It is important to indicate that more recent climatic data than the Climate LINK were not available for this thesis. The soil temperature data

[3] winter is defined in this thesis as December, January and February
[4] summer represents June, July and August
[5] spring is defined as March, April and May
[6] autumn in this thesis refers to September, October and November

were obtained from the British Atmospheric Data Centre (BADC) supplied as ASCII files of Climate Station Data listing daily soil temperatures measured at 0900 GMT at a depth of 30cm.

Figure 3.2 Location of BADC stations used for validation of the modelled seasonal soil temperature.

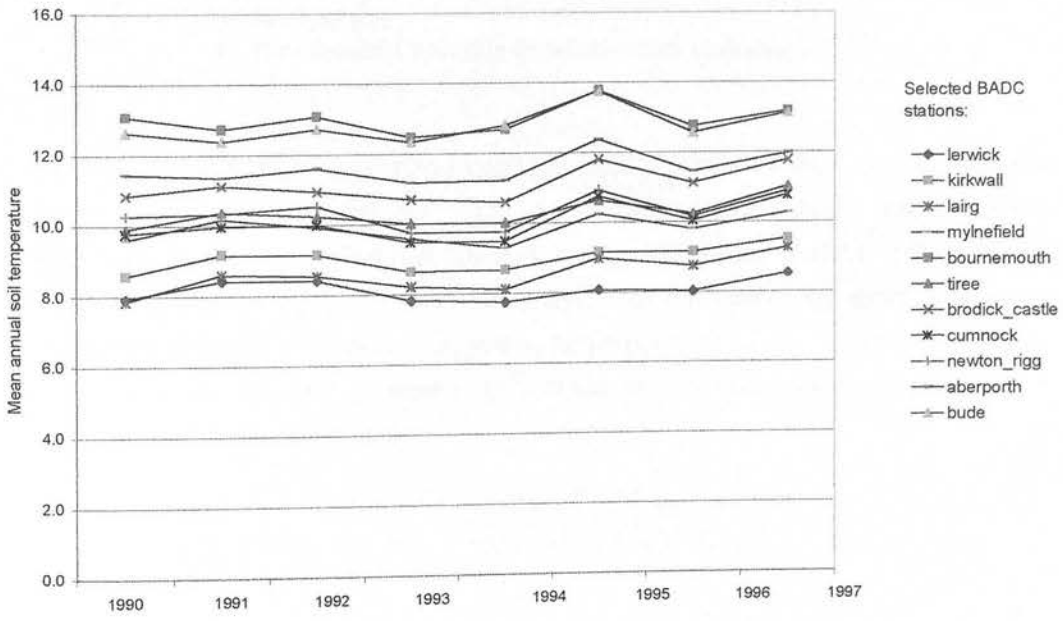


station code	name
44	Lerwick
154	Kirkwall
352	Lairg
425	Stornoway airport
441	Plockton
575	Fort Augustus
1115	Glenlivet
1351	Mylnefield
1467	Faskally
1935	Bowhill
2096	Boulmer
2165	Durham
2361	Hull
3007	Terrington StClement
3095	Hemsby
3115	Brooms Barn
3197	Lowestoft
4017	Malham Tarn
4045	Bradford
4061	Sheffield
4567	Grendon Underwood
4617	Keele
4882	Ross on Wye
4989	Westonbirt
5260	Kew
5396	Manston
5576	Reading
5604	Bournemouth
6007	Tiree
6133	Brodick_castle
6574	Cumnock
6772	Threave
7071	Newton_rigg
7866	Bala
8009	Aberporth
8413	Swansea
8673	Yeovilton
8857	Yarner Wood
8987	Bude
1000	Wick

The selection of BADC meteorological stations providing climate parameters data was reduced to 301 from the total of 1000 due to restricted availability for the period 1990-98. For 1998, only data for winter and spring were available. From the total number of 301 stations a further selection was carried out according to a combination of stratified and random techniques in order to choose one BADC station for each 100 km grid. When soil temperature data were not available for that location the closest station with available data was reselected.

The temporal difference between the Climate LINK data set (old data) and the recent measurement data set, obtained from the BADC stations, was expected to cause some variability. To verify this, annual means of measured soil temperature at selected 11 climatic stations were analysed, air temperature data were not available for immediate comparison. The plotted annual means for the selected stations represented the general trend of all the 40 selected BADC stations (figure 3.3). The observed distribution of annual mean soil temperatures did not reveal any increasing trend, but periodic fluctuations. The period of 1990-1997 was characterised by one thermal peak in 1995 succeeded by a cold year. It also became apparent that despite inter-station variability the beginning of the 1990s was more stable climatically than the period since 1994, when more dynamic changes took place. The described variability did not suggest any trend, which might have affected the validation of modelled soil temperature. The results of this validation

Figure 3.3 Mean soil temperature oscilation in the period 1990-1997.



are presented in the following paragraph.

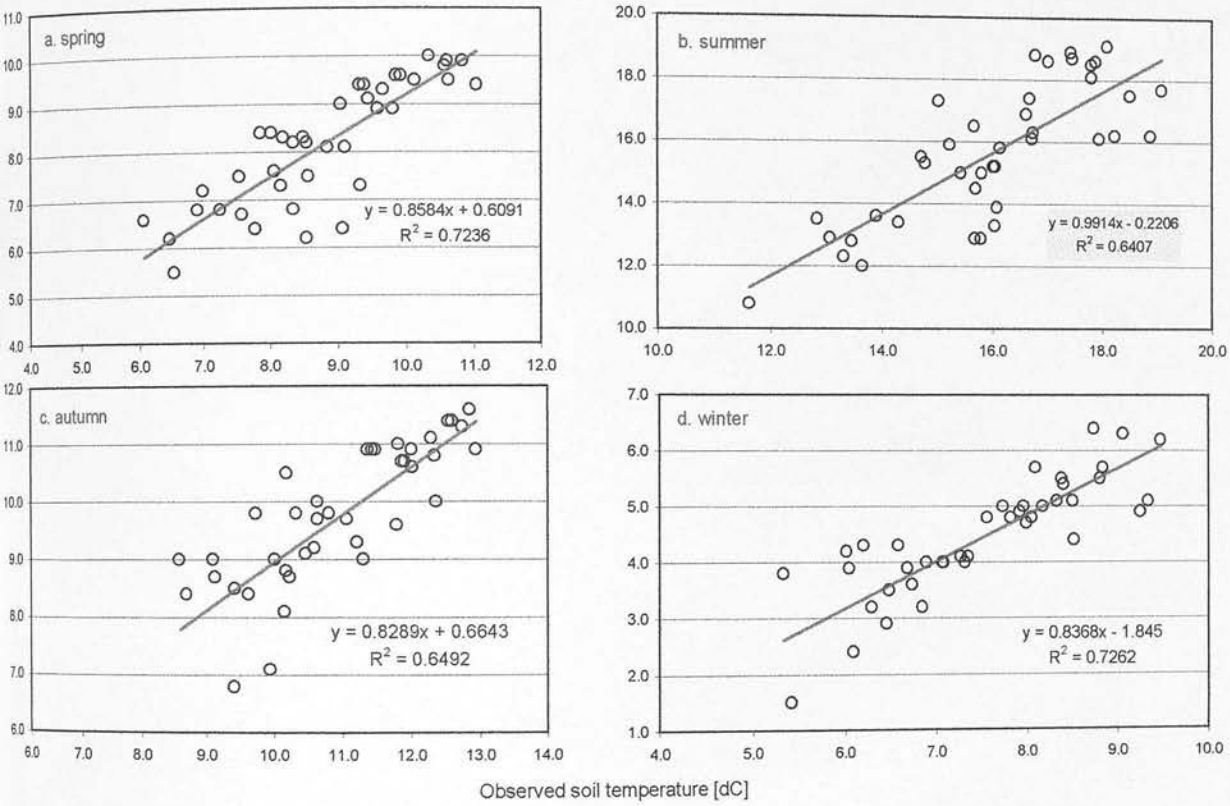
The arithmetic means of soil temperature for each season in the period 1990-1998 were estimated on the basis of measured daily soil temperatures at the selected 40 BADC stations with FORTAN program. The estimated means were then compared with the modelled soil temperature based on the Climate LINK data set. Correlation analysis revealed that the variability of modelled data corresponded with the observed values. The correlation was lower for autumn and summer (0.80) than for winter and spring (0.85). As the data did not fulfil the linear regression requirement of normal distribution, a different approach was undertaken. For each BADC station the residuals were estimated as direct differences between the observed (BADC data) and predicted (soil temperature model) values. On the basis of those residuals, random error (s_y) was estimated with equation (3.4). An analysis of residual error showed a general trend for the empirical model to underestimate soil temperature for all seasons with the highest deviations observed in spring (figure 3.4). The standard error indicated that the modelled mean soil temperature could vary on average in winter by 1.4°C, in spring by 2°C, in summer by 0.4 °C and in autumn by 0.6 °C ($p < 0.05$).

$$s_y = s_{y.x} \sqrt{(1/n) + (x^2/\Sigma x^2)} \qquad (3.4)$$

Where:
s_y - standard error of y (estimated with equation 5.13)
$s_{y.x}$ – standard error of regression equation 5.14
n – sample size
x – independent variable (modelled N_2O emission)

The analysis of temporal changes in soil temperature prior to the validation did not provide any evidence for an increasing trend, which might have caused underestimation of modelled soil temperature for the period of 1961-1990 (Climate LINK data). That analysis, however, was carried out for a relatively short period and the lack of data for the preceeding years, corresponding to the Climate LINK data, did not allow for any positive conclusions linking the observed trend and underestimated soil temperature.

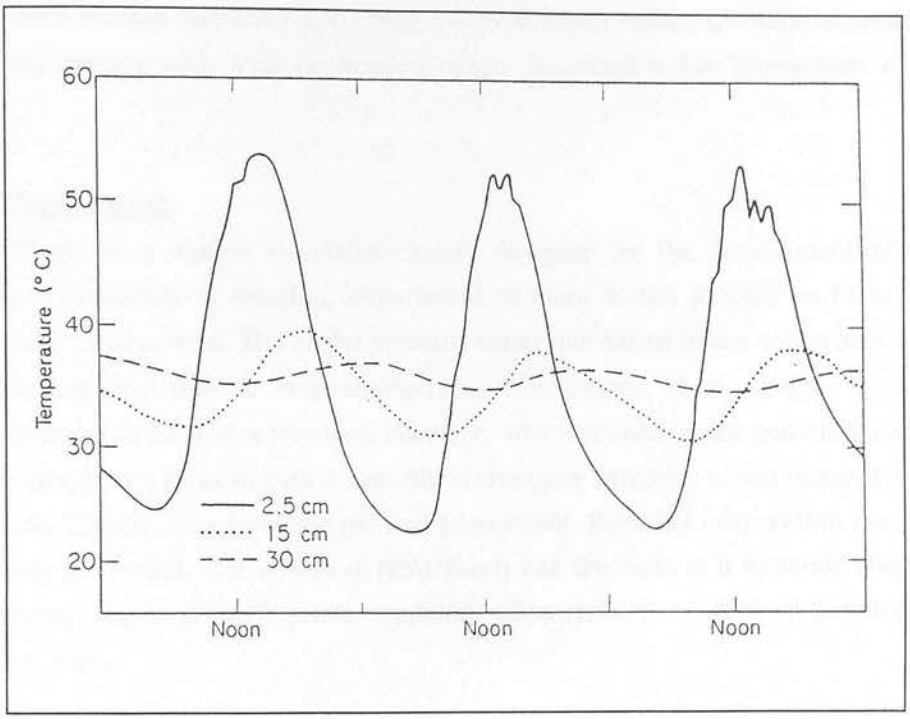
ure 3.4 Validation of soil temperature model with mean seasonal soil temperature measured on selected BADC stations.



As the SE error results of the above validation contrasted with the correlation test it might indicate that the high error in winter and spring was due to large residuals for some stations. In winter the largest residuals (SE > 1 °C) were registered for stations: Fort Augustus; Mylnefield; Faskally and Bowhill. In spring the largest deviations (SE > 3°C) were observed in Malham Tarn, Faskally, Plocton, Fort Augustus and Lerwick. It became clear that certain locations are associated with large residuals of estimates. Those stations have either upland location at high altitudes (Malham Tarn) and low altitudes, in Glens (Faskally, Fort Augustus), or in coastal locations (Lerwick, Plocton). The lower estimated soil temperature, based on air temperature, was affected by the location of the mentioned stations in extreme environments. As the theory of heat flow in soil perceives temperature as a function of position and harmonic changes with time (Monteith and Unsworth, 1990) as presented in figure 3.5, soil temperature depends on the phase angle defined by ($\varpi t - z/D$) (equation 3.3). For seasonal soil temperature oscillation $\varpi = (2\pi/365)d^{-1}$ and t

= $\pi/2$ for maximum temperature (i.e. summer) and t=-$\pi/2$ for minimum indicating winter season (Monteith and Unsworth, 1990).

Figure 3.5 Diurnal course of temperature at three depths in a sandy loam bare soil (Monteith and Unsworth, 1990).



The model of heat flux therefore predicts soil temperature for the day described by t, while the BADC station data represent seasonal means. The large residuals in the stations listed above could be explained by longer winter seasons with low air temperatures that, in turn, affect the model results. The observed uncertainties of the modelled soil temperature are due to the model assumptions. As indicated by the SE mean error, the heat flux model produced better estimates of soil temperature for summer and autumn, and less reliable estimates for winter and spring. The standard error estimated for each individual site indicated that the maximum uncertainty of the model estimates is 3 °C (p=0.05). The estimated uncertainty is further applied in the strategy of sensitivity testing as presented in section 6.5 (chapter six).

3.3.2 Soil moisture.

The effects of soil moisture on N_2O and NO emissions are well documented (section 2.2.5.3, chapter two). As there are no existing readily available data for soil moisture they had to be estimated from CLIMATE Link rainfall fields (section 3.2.3) and HOST classes (section 3.2.4) using the SPACTeach model, a computer-assisted learning module with wide application range, described below (Simmonds *et al.*, 1995).

SPACTeach model.

SPACTeach is a simple simulation model designed by the Department of Soil Science, University of Reading, Department of Plant & Soil Science and CLUES[7], University of Aberdeen. The model presents water movement in the soil profile while considering loss due to evapotranspiration (Simmonds *et al.*, 1995). It is an application in a form of a Windows interface, which enables point-and-click control of the simulation process with a capacity of changing variables of soil textural class, soil bulk density, plant cover (type and proportion), potential evaporation rate and intensity of rainfall. The output of SPACTeach has the form of a dynamic graph of volumetric water content profile updated either hourly or daily depending on requirements.

The reasons for applying this model for estimating soil moisture at the national scale to existing data sets were primarily concerned with its low requirements for input data, wide application range, easily adjustable variables and non-spatial character.

SPACTeach estimates soil moisture for agricultural mineral soils, values for peats had to be estimated with a different method discussed further on in this section.

Assumptions underlying the SPACTeach application.

The assumptions of the SPACTeach model are of two kinds: (1) those linked to the model design and (2) those due to the model application in this work. The first kind of assumption is due to uniformity of the soil profile, unlimited soil layer and simplified soil classification of six textural types: sand, loamy sand, loam, clay loam, silty clay and clay (Simmonds *et al.*, 1995). This had an important effect on

[7] Centre for Computer Based Learning in Land Use and Environmental Science

the drainage character, which had no limitations of gleyed layers and water tables occurring in field conditions. The second type of assumption resulted from the application method of the SPACTeach that is described in the following paragraph.

Method of estimating soil moisture with SPACTeach.

The SPACTeach model was applied to estimate soil moisture by indirect coupling with GIS ArcInfo data sets of HOST wetness soil classes and Climate LINK rainfall data. Prior to running the model, five rainfall zones were defined on the basis of total annual precipitation data for Britain (figure A4).

The first important assumption linked to the method of soil moisture estimation is due to SPACTeach requirements for rainfall intensities. On the basis of the mean precipitation, mean hourly rainfall intensity was estimated for each rainfall zone as a function of time. The rainfall intensities estimated this way were too small to be incorporated into the model, as the model does not accept input of fractional numbers. A strategy of rainfall events and wet and dry days was therefore chosen according to seasonal precipitation in each of the five rainfall zones for Britain (table 3.13). A wet day was assumed as a day, in which rainfall events occurred regularly with duration of two hours, intercepted by dry periods of one hour. On a dry day no precipitation occurred. Three different rainfall intensities were assumed based on the class of moderate intensity defined by the Met Office: 2, 3 and 4 mm hr^{-1}. Those assumed rainfall intensities and the mean rainfall fields from the Climate LINK data set (figure A4) were used to define the proportion of wet days per season and to estimate mean rainfall intensities. Finally the assumed rainfall intensities were assigned to the five rainfall zones for Britain for each season according to the estimated rainfall intensities (table 3.14).

The second assumption originated from the design of the model of simplified soil classification, which recognises only five main textural soil classes listed above. The SPACTeach was used to estimate soil moisture of three contrasting textural classes: sands, loams and clays, which were later associated with the three drainage classes defined on the basis of the HOST classification (table 3.4). The SpacTeach 'sand' class was assigned to freely drained soils, 'loam' to moderately drained soils and 'clay' to poorly drained soils.

Table 3.14. Rainfall intensities applied in SPAC versus real intensities.

Season	Rain zone	Mean rainfall [mm per season]	Range of precipitation [mm per season]	Real range of intensities [mm hr^{-1}]	Real mean intensity [mm hr^{-1}]	Prop. Of wet days [% per season]	Assumed rain intensity [mm hr^{-1}]
spring	1	145.9	95.2 - 168.5	1.29 - 2.28	1.48	50	2
	2	177.5	121.0 - 234.7	1.64 - 3.18	2.41	50	2
	3	230.4	166.6 - 300.0	2.26 - 4.07	3.13	50	3
	4	302.6	243.8 - 396.5	2.09 - 3.39	2.59	80	3
	5	438.4	309.4 - 689.7	2.12 - 4.73	3.01	99	3
summer	1	160.5	110.9 - 187.8	1.51 - 2.55	2.11	50	2
	2	183.3	135.7 - 244.8	1.84 - 3.32	2.41	50	2
	3	235.7	165.8 - 324.7	2.25 - 4.41	3.2	50	3
	4	308	241.0 - 412.6	2.06 - 3.53	2.64	80	3
	5	436.5	302.8 - 750.7	2.59 - 6.42	3.73	80	4
autumn	1	165.5	134.6 - 209.4	1.86 - 2.91	2.29	50	2
	2	235.4	177.8 - 315.4	2.46 - 4.38	3.26	50	3
	3	356.6	274.3 - 443.6	2.34 - 3.79	3.05	80	3
	4	482.9	393.0 - 572.8	2.99 - 4.36	3.68	90	4
	5	731.9	541.2 - 1105.9	3.75 - 7.67	5.08	99	5

Further simplifications of the AGEM method to calculate soil moisture involved soil bulk density and evaporation rate. Soil bulk density was varied according to recommended values by SPACTeach, which are 1.1 (1.0 - 1.2) g cm^{-3} for clays, 1.4 (1.2 - 1.5) g cm^{-3} for loams and 1.7 (1.5-1.9) g cm^{-3} for sandy soils (Simmonds *et al.*, 1995). The three main drainage classes defined on the basis of HOST classes (table 3.4) were used in SPACTeach for the three different scenarios of soil type. Potential evaporation rate was changed according to season as defined in SPACTeach and its value varied from 1.5 – 2.9 mm day^{-1} for spring, 3.0 – 4.9 mm day^{-1} for summer and 0.5 – 1.5 mm day^{-1} for autumn. SPACTeach was run for the extreme values of potential evaporation (table 3.15).

Finally, a very important assumption of SPACTeach application is an effect of its design explicitly for agricultural soils. There are three major crop types recognised by SPACTeach: sorghum, sugar cane and potato. Soil moisture can be also estimated with SPACTeach for bare soils. Due to restricted choice of vegetation types provided by SPACTeach, a strategy of simplified vegetation classes had to be adopted arbitrarily according to season, depending on the assumed stage of crop development (table 3.16). All crops in spring were assigned to the SPACTeach 'sorghum' class with an assumed vegetation cover of 50 % of the soil surface. Their soil cover increased in summer to the maximum of 80 %, and then decreased to 5

% in autumn. Grasslands were assigned to 'sorghum' with a different assumed soil cover, which varied from 91 % in spring to 99 % in summer and autumn.

As the model is not designed for seminatural vegetation, it did not provide information on the effect of forests or heathlands on the water regime, which is expected to have a considerable effect. At this stage seminatural land had to be excluded from the adopted method. Further implications of this limitation are discussed in the following sections.

Table 3.15. SPAC results of seasonal volumetric water content for bare soil and main soil types.

Rain intensity [mm hr^{-1}]	Evaporation defined by SPAC [mm d^{-1}]	Soil type defined by SPAC	VWC on a wet day [%]	VWC on a dry day [%]
	spring			
2mm	1.5	sand	21	14
		loam	46.5	40.5
		clay	61.5	57.5
	2.9	sand	21	11.5
		loam	47	40.5
		clay	61.5	57
3mm	1.5	sand	22	13
		loam	47.5	41
		clay	61.5	57
	2.9	sand	22	13
		loam	48	41
		clay	61	57
	summer			
2mm	3	sand	21	12
		loam	46	40.5
		clay	61.5	57.5
	4.9	sand	21	11
		loam	46	39
		clay	61	57
3mm	3	sand	22	13
		loam	48	41
		clay	61.5	57
	4.9	sand	22	11.5
		loam	47.5	40
		clay	61	56.5

	autumn			
2mm	0.5	sand	21	14.5
		loam	46.5	41.5
		clay	61.5	57.5
3mm	0.5	sand	22	15
		loam	48	41.5
		clay	61.5	57.5
4mm	0.5	sand	22.5	15
		loam	49	42
		clay	61.5	57.5

Table 3.16. Seasonal changes of soil cover for major crops defined by SPAC.

season	SPAC land cover type	Group represented	Proportion of covered soil [%]
spring	bare	Bare soil	0
	sorghum	crops	50
	sorghum	grass	91
	potatoes	Root tilled crops and vegetables	1
summer	bare	Bare soil	0
	sorghum	crops	80
	sorghum	grass	99
	potatoes	Root tilled crops and vegetables	60
autumn	bare	Bare soil	0
	sorghum	crops	5
	sorghum	grass	99
	potatoes	Root tilled crops and vegetables	70

First stage of SPACTeach. Initial modelling strategy.

Initially, the model was run at two extreme values of potential evaporation as defined for the four seasons and the three soil types with different options of vegetation cover, which varied according to season (table 3.16). The default SPACTeach parameters for initial soil moisture at field capacity (FC) and stomatal sensitivity were unchanged. The results of the volumetric water content (VWC) were read for two wet days and two consecutive dry days from the moisture profile at a depth of 30cm and input to EXCELL. Sensitivity analysis showed no significant variability between different vegetation types, various evaporation levels and stomatal sensitivity (tables 3.17 and 3.18, Appendix). On the other hand, bulk density, rainfall intensity and soil type were controlling VWC (figures 3.6, 3.7, 3.8 and 3.9). Therefore a simplified approach was justified and different vegetation covers were excluded from the estimation of soil moisture for Great Britain, which

covers were excluded from the estimation of soil moisture for Great Britain, which was carried out for bare soils. The uncertainty introduced by this simplification can not be verified due to a lack of sufficient field measurements, and is considered one of the important limitations of SPACTeach.

Figure 3.6 Loam moisture profiles predicted by SPACTeach for specified bulk densities [g cm^{-3}].

Figure 3.7 Sand soil moisture profiles predicted by SPACTeach for different rainfall intensities.

Figure 3.8 VWC estimated for different soils for a summer day.

Figure 3.9 VWC estimated by SPACTeach for various soil types on an autumn day.

Figure 3.6

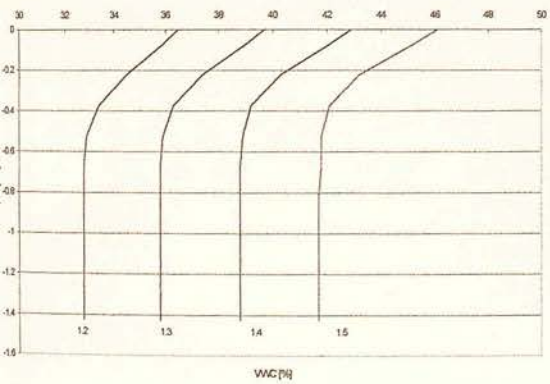


Figure 3.7

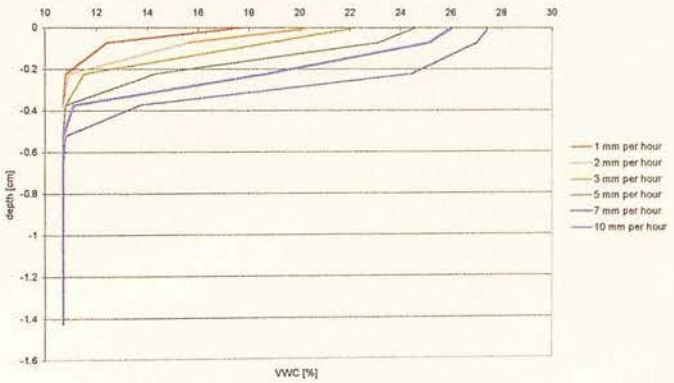


Figure 3.8

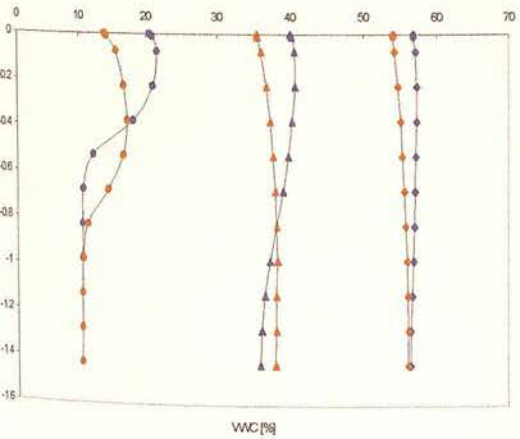
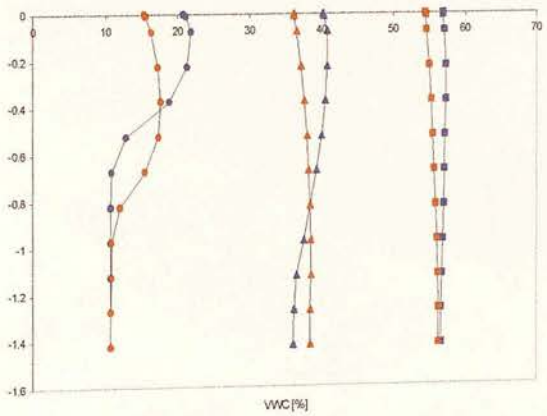


Figure 3.9



Soil moisture for peats.

The SPACTeach model only considered agricultural mineral soils, therefore a different approach was adopted to estimate soil moisture for peats. The latter was estimated from field measurements by MacDonald (1997) at Great Dun Fell (NY710322), NW England. Field experiments took place in March and July, 1995. The vegetation cover was classified as upland moorland. The site was grazed by sheep. On the basis of field measurements of peat water content, mean soil moisture was estimated as % dry weight for winter (March) and summer (July) from 6 and 16 measurements respectively. The results were then converted to water filled pore space (WFPS) and finally assigned to different seasons. Soil moisture from March was assigned to winter and autumn, while the July value was used to obtain moisture for spring and summer. It was decided that due to the fact that peats are predominantly found in upland areas such as the Scottish Highlands, the Lake District and the North York Moors, this strategy would best represent the climatic variations in those areas and solve the problem of data unavailability. However, the results were based on a limited number of samples for two months, which not surprisingly introduced uncertainty in the areas, where peat is the dominant soil (figure A6). Unfortunately, there were no other data that could be used in AGEM. The implications of the limited data availability on the results of soil moisture are discussed further in this section.

Results of the first stage of SPACTeach modelling.

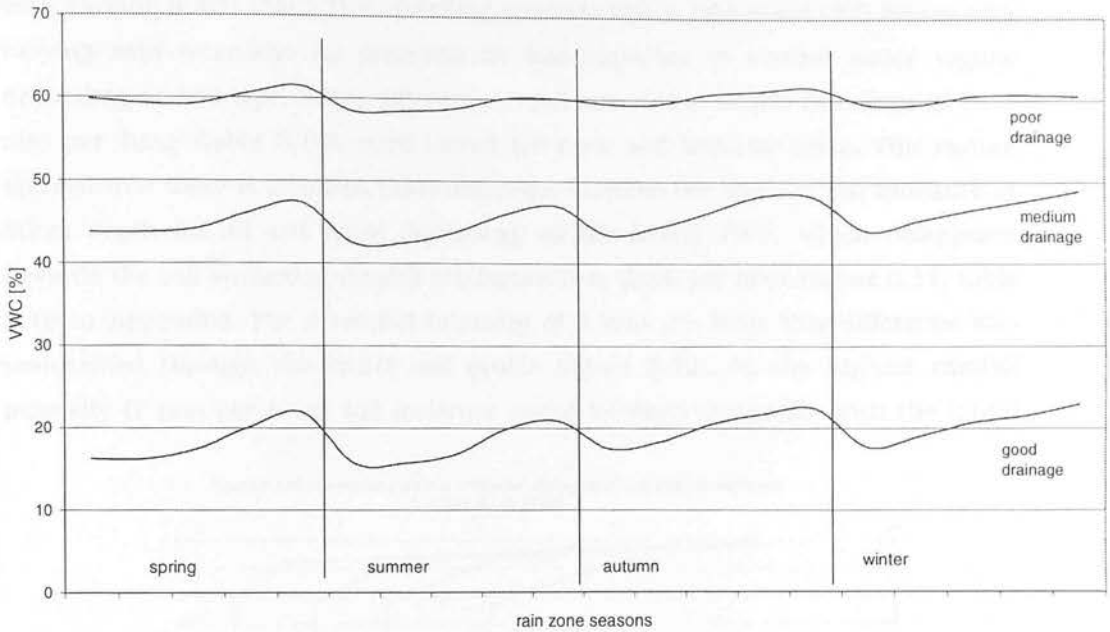
In order to generate grid coverages of seasonal soil moisture, the results of the SPACTeach model were loaded into the INFO database as look-up tables. Tables were created for four seasons with values of VWC for each rainfall zone and each soil type. The values transferred from EXCELL into INFO were estimated as weighted averages on the basis of the proportion of dry and wet periods. The INFO tables were later related to a grid cover of rainfall zones. Estimation of mean soil moisture for each season at 5km grid resolution was carried out in GRID depending on the rainfall zone and the proportion of land under each of three soil types (figure A5). Finally VWC grid coverages for each season were transformed to WFPS with the application of equation 2.3 (chapter two) and the seasonal soil moisture for mineral soils was combined with WFPS estimated for peats.

There was very little seasonal variability of WFPS, which had lower means in winter and autumn (80.9 and 80.7 % respectively) and fractionally higher means in spring

and summer (86.3 and 85.3 % respectively). Spring and summer had very similar spatial distributions of estimated soil moisture, and were different from the distribution of soil moisture in autumn and winter (figure A5). SPACTeach estimated soil moisture at saturation for the Central Scotland and several areas in Wales and England. Those areas were characterised by a large proportion of poorly drained soils (> 90 %). Soil moisture for peats was relatively low to those predicted by SPACTeach, especially in winter and autumn (WFPS = 52.9 %). This resulted in a relatively low mean WFPS in the areas of dominant peat, which was mainly in Scotland where 75 % of British peats are located (Howard *et al.*, 1994). The rather low soil moisture in those areas in autumn and winter was surprising, as they receive high precipitation and raw peats tend to accumulate large volumes of water (figures A3.3 and A3.5). The predicted low peat soil moisture in autumn and winter resulted in a contrast between the British uplands with lower WFPS and lowlands with higher WFPS. This contrast was not recorded for spring and summer, when less spatial variability in soil moisture was observed (figure A5). The character of seasonal distribution of WFPS throughout the country suggested a strong control of soil moisture distribution by a few variables, which were soil drainage class (for all seasons) and the presence of organic soils. Precipitation had a much weaker influence on WFPS.

The presented results were characterised by similar ranges of WFPS for Great Britain for all seasons (aprox. 40 to 106 %) (figure 3.10). Little seasonal variability of soil moisture and large areas of saturated soils confirmed serious limitations of SPACTeach to predict soil moisture. The observed problems with predicted soil moisture were probably caused by the strategy of simplified soil classification and the method estimating mean rainfall intensities according to rain zones. Additionally the limitation of ArcInfo in not directly coupling with dynamic physical models such as SPACTeach restricted the predictions to the mean seasonal moisture (table 3.15). However, other reasons for that uniformity connected to the input parameters used by SPACTeach might have caused the observed uniformity and overestimation of soil moisture. This was tested in the second stage of modelling, the results of which are presented in the following paragraph.

Figure 3.10 Seasonal fluctuations of VWC estimated by SPACTeach for three soil drainage classes.



Second stage of SPACTeach. Sensitivity analysis.

The results produced in the first stage of SPACTeach suggested relatively uniform and very high soil moisture values throughout the year. The estimated soil moisture for loams and sands oscillated around FC and clays were saturated throughout a year (figure 3.10). The initial runs of the model involved single episodes of inter-changeable two wet and dry days with assumed initial soil moisture at FC. In the field, however, soil moisture normally oscillates between wilting point (WP) and FC. The assumed initial soil moisture in SPACTeach was suspected to cause the high predictions of the model.

Sensitivity analysis was applied to observe the importance of the input parameters in the predicting power of the model. SPACTeach was run for the three types of soil with varying initial VWC. The modelling scenario was a rain event of 5 hours with varying rain intensity. As precipitation was expected to control water regime depending on soil type, hence different rainfall intensities, within the range of 1 - 7 mm per hour (table 3.15), were tested for each soil textural class. The results showed that there is a considerable difference between the levels of soil moisture at 30cm depth for all soil types depending on the initial VWC, which disappears towards the soil surface at rainfall intensities over 2mm per hour (figure 3.11, table 3.19 in Appendix). For a rainfall intensity of 1 mm per hour this difference was maintained through the entire soil profile (figure 3.12). At the highest rainfall intensity (7 mm per hour) soil moisture varied between the profile with the initial

Figure 3.11 Sand moisture profile predicted by SPACTeach at different initial moisture levels with assumed rain intensity of 2 mm per hour.

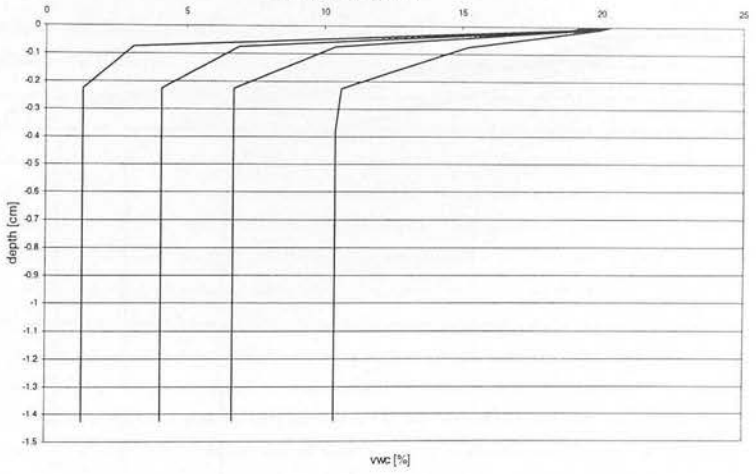
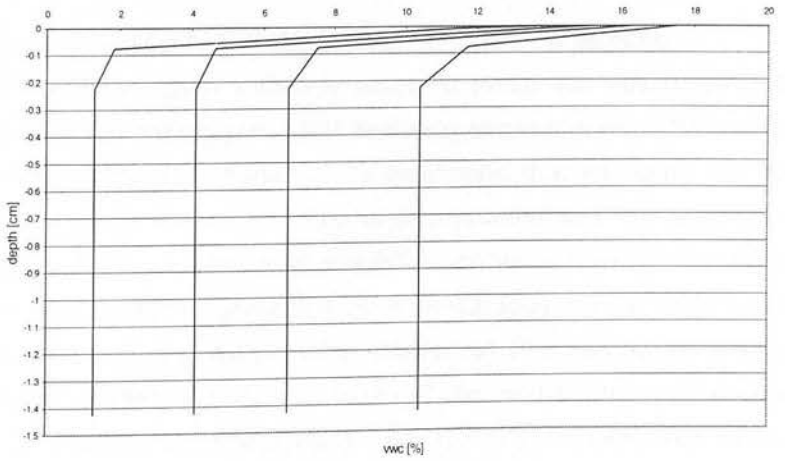


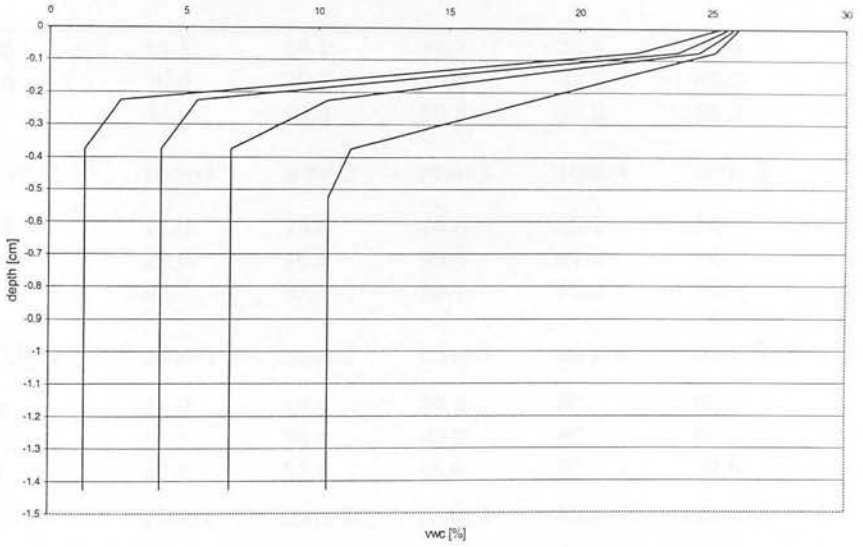
Figure 3.12 Sand moisture profile predicted by SPACTeach at different initial moisture levels with assumed rain intensity of 1 mm per hour.



moisture at FC and the second highest VWC profile by 3 % for clays, 8 % for loams and 4 % for sands (figure 3.13). The difference between the profile with initial moisture at wilting point and the second lowest VWC profile was the highest and oscillated around 10 % for all soil types.

These observations confirm an expected strong dependence of soil moisture on its initial level according to the main soil types. They also provided evidence that SPACTeach overestimated soil moisture in the original approach when the initial water content was assumed at FC. This strategy of modelling was revised and different levels of the initial soil moisture were employed in the next stage of soil moisture modelling with SPACTeach. This method and its results are described in the following paragraph.

Figure 3.13 Sand moisture profile predicted by SPACTeach at different initial soil moisture levels with assumed rain intensity of 7mm per hour.



Third stage of SPACTeach. Results of the final modelling strategy.

SPACTeach was run again with new assumed initial soil moisture (VWC) values, that varied between wilting point (WP) and near saturation level (SAT) depending on soil type (table 3.20). It is important to emphasise that changing soil moisture is caused by the continuous interaction of precipitation with the soil, controlled by soil porosity, bulk density and rainfall variability during the season. This interaction could only be presented by a continuous run of SPACTeach for the whole year with inputs of daily rainfall values, but this was not possible due to (a) insufficient input data and (b) the design of the model. The revised strategy was expected to produce more seasonally and spatially variable soil moisture. The

uncertainty of applying SPACTeach to estimate soil moisture in AGEM, and its effect on the predicted N_2O and NO emissions, will be studied later. In the final modelling approach soil moisture was expected to vary depending on precipitation and soil type and the assumed initial soil moisture was stratified according to rain zones and soil types (table 3.20). According to the stratification, mean soil moisture for soils in zones 4 and 5 in autumn and winter was at FC or near saturation (SAT), and for soils in zone 5 in summer at FC (table 3.20). In other scenarios VWC was estimated with SPACTeach according to the method of the assumed proportions of dry and wet days during the seasons used in the initial stage of modelling (table 3.14).

Table 3.20 Assumed initial soil moisture as volumetric water content [%] input to SPACTeach in the third stage of modelling.

SPRING	zone-1	zone-2	zone-3	zone-4	zone-5
sand	14.1	14.1	16.7	20.0	20.6
loam	30.0	30.0	35.4	42.3	43.0
clay	46.9	46.9	50.8	55.5	56.3
SUMMER	zone-1	zone-2	zone-3	zone-4	zone-5
sand	13.8	13.8	16.8	20.1	FC
loam	29.8	29.8	35.8	41.0	FC
clay	47.1	47.1	50.4	53.8	FC
AUTUMN	zone-1	zone-2	zone-3	zone-4	zone-5
sand	14.9	16.5	20.4	FC	FC
loam	31.2	36.0	43.0	FC	FC
clay	47.6	51.8	55.6	FC	57.6
WINTER	zone-1	zone-2	zone-3	zone-4	zone-5
sand	15.1	17.4	20.5	FC	FC
loam	30.8	30.4	42.1	FC	52.6
clay	47.7	51.8	55.0	FC	57.1

The new estimated WFPS for Great Britain showed improved soil moisture estimates with maximum WFPS < 100 %, and a larger proportion of soils with estimated WFPS < 70 % (figure A7). Although there was an observed similarity in mean soil moisture between all the seasons (aprox. 71 %), there were also noticeable differences in the ranges of soil moisture. This suggests that the strategy of rain zone stratification with adjusted initial soil moisture considerably improved the predictions of SPACTeach. The validation of SPACTeach results is presented in the following section.

Validation of SPACteach results.

Lack of sufficient field measurements considerably restricted validation of the SPACTeach results. The validation was limited to mineral soils in winter. The validation was based on an assumption that in winter 90% of soils in Britain are at field capacity (B. Ball pers. comm). The comparison of mean estimated WFPS for winter with the WFPS at FC confirmed that the SPACTeach model overestimated soil moisture in most areas of Great Britain (figure A8). The difference between the two soil moisture grid coverages estimated as a proportion of FC gave an indication of expected minimum error. This error was higher in England and Wales (mean = 20%) than in Scotland (mean = 10%), which might be caused by a considerable proportion of poorly drained soils that caused the greatest overestimation (> 20 %). The validation results were questioned, however, as the values of field capacity defined for the three soil drainage classes by SPACTeach were higher than those defined by Hall (1977), which were applied for the validation (table 3.21). The difference is largest for clays (9.2 %) and decreases for loams (8.2 %) and sands (0.4 %). This might have caused an uncertainty of the estimated soil moisture and is linked with the issue of SPACTeach limitations, which are presented in the following paragraph.

Table 3.21 A comparison between default SPACTeach soil moisture and observed means used for the validation (Hall, 1977) at saturation (SAT), field capacity (FC) and wilting point (WP) levels.

HOST/ SPACTeach soil drainage class	Hall (1977)			SPACTeach		
	SAT	FC	WP	SAT	FC	WP
Poor drainage/ clay	58	46	25	57.7	55.2	39.3
Moderate drainage/ loam	50	36	15	57.7	44.2	20.6
Free drainage/ sand	47	17	5	57.7	17.4	2.1

Criticism of the model.

In summary, the SPACTeach model has several limitations, which make its application problematic. They are either conceptual or pragmatic in nature.

The SPACTeach model assumes continuous flow and an absence of impermeable layers or ground water levels within a specified 150 cm of soil profile. The HOST classification defines only 20% of British soils with a ground water level at more than 2m below the surface, and there is no certain proportion of soil with an impermeable layer below 150cm. This would suggest that the model underestimates soil moisture for most soil types. The opposite results were caused by the restricted availability of input data and model design and its different interpretation of soil moisture states than that by Hall (1977).

SPACTeach is a simple predictive model, which, despite the main advantage of limited requirements of inputs (the reason for its application in this work), demanded many assumptions. Firstly, only four types of land cover were considered i.e. sorghum, potato, sugar cane and bare soil. The lack of semi-natural land options in the model restricted its application. Sensitivity analysis confirmed, however, that the vegetation types and stomatal sensitivity had no significant effect on VWC. Secondly, there were only six options for soil types and peat soils were not considered in this model, which was a very important restriction of the SPACTeach model in this work. Thirdly, despite the opportunity to adjust the main parameters, such as the physical characteristics of soils and climatic variables, the available ranges were restricted. Some assumptions about the rainfall intensity therefore had to be made, which are described earlier in this paragraph. The main limitation of the model, however, was lack of access to the code of the model, which meant that direct coupling with the GIS for the input and output of large data sets was not possible. It was therefore necessary to run SPACTeach manually as isolated scenarios, which had considerable implications for the results due to the assumed initial soil moisture at FC (the main reason for considerable overestimation of soil moisture in the first stage of modelling), the limited number of scenarios and slow processing time.

3.4 THE INFLUENCE OF DIFFERENT DATA SETS ON THE EMISSION ESTIMATES.

Validation of models is essential to assess their reliability through a comparison of model results with independent data sets. One of the main sources of error is poor quality of input data. There are various sources of this type of error in GIS, among which age of data, map scale, density of observations were the 'most obvious and easy to check' (Burrough, 1996). In this study there are a number of differences among data sets of controlling factors in terms of their spatial and temporal scales, which are caused by their different sources as indicated in section 3.2. These differences create problems with compatibility between the data. In this section an attempt is made to present all the discrepancies and their likely effect on the output of the model.

Differences due to temporal scales of data.

Data for variables controlling NO and N_2O emissions can be classified into three groups in respect of their temporal characteristics.

(1) Data relating to specific short periods lasting a few years, representing phenomena liable to changes - AC, LCM, atmospheric deposition;
(2) Long term data defined as averages from data observed over a long period - Climate LINK data;
(3) Data without temporal scale, for which information is not related to any particular time - HOST classes, fertiliser recommendations.

With these differences there are a number of issues regarding their compatibility and uncertainty of representing reality. As all the data sets are combined in AGEM Data Base System (table 3.1), it is important to consider how all the data relate to each other and what are the implications of the differences between the data on the quality of the output. Another important issue relates to the limited representation of reality by the input data and the consequences of that on the model results.

In terms of relationships among the data types, group (1) causes the greatest uncertainties due to their short duration and/or temporal variability represented by the data sets. Data from groups (2) and (3) define the mean or abiding properties (respectively) and they are less liable to induce errors due to the character of the attributes they represent. In group (1) there are considerable differences between AC (1988) and LCM (1990-91) which can cause great uncertainty in the complete

map of land cover produced for Britain from combined AC and LCM. The regression analysis of the AC and the LCM data for the Tyne-Clyde area describes the differences and explores possible reasons (chapter four). The main issues of their compatibility are the differences between their interpretation of land cover (classification incompatibilities) and variability due to the differences in time scale associated with land use change in the period of 1988 to 1990-91. Important land use changes may occur in such a short period due to the crop rotation, conversion of tilled land into unmanaged grass (in line with the set aside scheme introduced in 1988) and turning agricultural land into urban areas e.g. roads and expanding city boundaries (Barr *et al.*, 1993). There were unfortunately no data available to verify this. Some AC data for Scotland could be used to find changes within agricultural land in the period of 1990-1991, but information on seminatural land for 1988 was not available (LCM) and most information on agricultural land was missing for England and Wales (section 3.2.5). Land use changes have been presented for Great Britain by the Countryside Survey in the period of 1984 – 1990 (Barr *et al.*, 1993). According to this source, tilled land and managed grassland decreased by 4% and 2% respectively, while urban areas and rough grass / marsh increased by 4% and 45% respectively.

Relating individual data to the real world is more complex as it also touches upon the problem of model representation. There is always a discrepancy between the modelled average values and the actual values in the real world, whether we look at the problem of emissions, or the controlling variables of climate characteristics, N input, or soil organic C content. The data types defined in group (2) represent mean values of climatic characteristics (Climate LINK data) and hence they are more convenient to models aiming to reflect general trends. When the predicted phenomena are related to the real world, however, a difference between their results and the processes occurring in the 'real world' determines model uncertainty. This was observed in the validation of soil temperature estimated from long-term monthly averages of air temperature for 1961-1990 with mean measured soil temperature for 1990-97 (section 3.3.1). Group (1) represents data for specific periods, which determine the validity of model predictions. The results can be compared to the real world values by estimating changes within a period of time and relating them to the present values. This touches upon the issue of relativity, which has important implications on the predictive power of models. Combined land use (the AC) and land cover data (the LCM) represent periods of 1988 and 1990 – 1991, respectively. Some changes of land use were expected since 1988,

which affected the estimated N fertiliser input based on the AC data and hence the predictions of N_2O and NO emissions. This problem is addressed in chapter five.

Spatial units represented by data sets and their account of the variable emission processes.

Among the input data sets there are spatial and non-spatial data, e.g. field measurements and climatic data for the former and fertiliser recommendations for the latter.

Climatic variables are characterised by continuity, but Climate LINK data present average values for each 10 km grid (section 3.2.3) hence all the variability of temperature and rainfall is lost for each area defined by the resolution. Similarly HOST classes present soil types at 1 km resolution (section 3.2.4) while in reality they represent continuous type data. The same applies to atmospheric N deposition, land use and land cover, which are defined by the resolution of 20 km, 5 km and 1 km, respectively. It is, therefore, clear that great simplifications are characteristic of input data sets. In line with the general GIS rule, according to which no more details should be expected from outputs of GIS model than given by inputs, the quality of the input data sets has a considerable effect on the output of AGEM (section 5.6, chapter five).

From the spatial data sets the results of actual measurements of NO and N_2O emissions are unique by representing data at a resolution of < 1m. Models predicting the amount and distribution of N_2O and NO emissions at scales larger than that of a plot assume that the obtained results are representative (chapter two). This is linked with a recognised problem of scaling up, which tries to solve the great spatial variability of NO and N_2O emissions. The full discussion of scaling is presented in chapter five. It is important at this point, however, to mention this issue here due to its significance in the modelling process. Scaling up strategy suggests that the AGEM model, representing processes at a national scale, should ignore in-field variability, which could be classified as 'noise', but emphasise inter-field differences, the latter as a measure of differences between the various land use and soil types. This issue affects the important problem of this work - defining the most appropriate scale for the modelling, which is discussed in the conclusions.

3.5 SPATIAL AND TEMPORAL RESOLUTION OF THE MODEL.

The problem of appropriate scale for a model is the primary issue of modelling. It was discussed among others by Johnston (1998) who develops Shugart *et al.'s* (1991) view about the relationship of spatial pattern and resolution which, when too fine, can affect the results by including 'noise' and when too coarse, obscures spatial variability. The definition of the most suitable resolution for the model should then take into account all the input data and the required details of the output so that the spatial and temporal variability of emissions are well presented. In view of the general belief that *'the most suitable resolution is one that conveys meaningful information about a feature of interest'* (Johnston, 1998) based on the available data, a 5km resolution was chosen as the best spatial resolution and seasonal variability as the temporal resolution for representing emissions at a national scale. The variability for the present model is defined by the different land use types, soil classes, environmental characteristics and management practices (N input). Due to the resolution of the AC and the LCM data, which determine the emission variability, the 5km resolution (that of the coarser data set) seemed to be most justified for the model. As some of the remaining input data sets have coarser resolution, the detail of the output in respect of the variability of those data will not be greater than the inputs (e.g. 10 km^2 for climatic variable and 20 km^2 for the impact of atmospheric deposition).

Temporal changes in emissions are primarily an effect of the climatic variables - rainfall and temperature, which are represented by monthly averages, and fertiliser practices for which some dates are defined in published recommendations for different crops. The decision to present seasonal variability of emissions is partly caused by the temporal resolution of the climatic data and partly by the restricted detail on the timing of fertiliser input, which at monthly resolution could cause considerable error.

In summary, this chapter presented the range of data sets used as input variables in AGEM, the variety of their sources, different spatial and temporal scales and variability arising from the character of represented properties. The data sets are discussed in terms of those which already exist, and those, which have had to be derived for the purposes of this study. The problem of the uncertainties in, and variability between, the different data sets are linked to their effect on the likely

error in the AGEM results. Of the presented data, soil moisture bears the greatest uncertainty due to the assumptions underlying SPACTeach application in estimating VWC, which are discussed in detail in section 3.3.2. Soil temperature introduces a smaller error, which is mostly a result of relatively old data of air temperature, their coarse spatial resolution and the uncertainty of the mean values of the parameters used in the equation (3.3). Errors introduced into AGEM by the other types of data are due to the uncertainties of the sources and the incompatibility between the data affected by their varying spatial and temporal scales. The presented uncertainties of input data are bound to have a considerable effect on the quality of the predicted N_2O and NO emissions (chapter five).

APPENDIX 1.

Description of the 'key' cover types (Fuller *et al.*, 1994).

Land cover classes:

A. Sea/Estuary.

This class includes open sea, coastal waters and estuaries except for major estuarine features or sea lochs, which are classified as B.

B. Inland Water.

Inland fresh water and ground covered with water throughout the year excluding temporarily flooded surfaces like winter-flooded meadows.

C. Coastal Bare Ground.

The coastal zones covered by mud, silt, sand, shingle and rocks including features of coastal accretion and erosion.

D. Saltmarsh.

Areas of extensive seaweed development including the green alga or brown wracks and saltmarshes colonised by halophytic grasses up to normal levels of high water spring tides.

E. Rough Pasture/ Dune grass/ Grass Moor.

Lowland grass heaths and upland grass moors are difficult to separate due to similarities in species composition. The former is primarily composed of *Ammophila*, *Festuca* and *Carex* , and herbaceous species, which are occurring at altitudes of 100-200m in north-western Britain and 0 - 200m in north-western Scotland. The latter is represented by *Nardus*, *Festuca*, *Molinia*, *Deschampsia* and *Juncus*, which are quite often lightly grazed by sheep. The fact of similarity between the two 'target' classes encouraged the interpreters to combine those into 'key' cover-type class E.

F. Pasture/Meadow/ Amenity Grass

This class encompasses many types of grasslands from leys of single species to unimproved swards and seminatural grasses. They represent two 'target' cover-types - classes 6 and 7 (table 3.2), the first one consisting of grazed and mown swards, and second one including meadows and verges on which minor

management practices take place. The latter also includes semi-natural grasslands of upland areas and floodplains with restricted access.

G. Marsh/ Rough Grass.

Land cover defined by the three original Landsat classes - 19, 23 and 8 (table 3.2). The first type represents land, which is often bare, covered scarcely by perennial plants, natural colonisers of the derelict arable land or setaside. Class 23 is defined as felled forest covered by brush-wood and ruderal weeds. The last 'target' component of class G encompasses fens, marshes, upper saltmarshes, and all the grass neither mown nor grazed.

H. Grass / Shrub Heath.

It includes the class of open shrub heath in lowland, which mainly is the effect of heath grazing and hence the in-frequent representation of this class; and open shrub moor, which is more common. The latter class dominates northern and western parts of Britain, where *Calluna* is encouraged to provide habitat for grouse and grazing discourages development of dwarf shrub species. Burning of the plant cover ensures vegetation cycle of interchangeable moorland and heather.

I. Shrub Heath.

This land-cover class is created from 'target' class 13 and 11 (table 3.2). Both original types are characterised by the occurrence of heather and ling with the dominance of the species in Dense Shrub Heath and an addition of broom and gorse developed primarily on sands. Dense Shrub Moor represents land cover of more balanced species composition including heather, bilberry and herbaceous species.

J. Bracken.

Vegetation cover is dominated by a single specie of *Pteridium aquilinum*, with very little input of other species. This class is very well defined on winter satellite imagery due to a characteristic reflectance pattern.

K. Deciduous/ Mixed Wood.

This class encompasses all deciduous forests, mixed forests, scrubs and orchards. Scrub species included in this class: sallow, hawthorn, brambles and tree nurseries. Class K is characterised by seasonal changes in reflectance pattern which separates it from the evergreen species.

L. Coniferous/ Evergreen Woodland.

Forest cover consisting of coniferous species, larch, holly, *Rhododendron*, yew and Holm oak. Spectral signature of this class can be easily distinguish from K due to darker leaf colour throughout the year.

M. Bog.

Land cover representing areas permanently waterlogged or under water for prolonged periods of time (winter) with acid conditions of soils encouraging peat development. Vegetation cover is characterised by grass and dwarf shrub heaths and moors with a generous addition of bog morth and cotton grass. Bog cover mostly occurs in uplands in the north and west Britain, but it is also represented in a few lowland areas on the west coast of Scotland.

N. Tilled.

This category consists of 'all land under annual tillage' (Howard, 1993: 16) e.g. cereals and horticultural crops, one year old leys, and all other vegetated land uncovered in winter e.g. scrub-clearance, development, mining, soil tipping.

O. Suburban/ Rural Development.

All areas on the satellite image with a reflectance pattern characteristic of mixed build-up and vegetated cover. Due to the fact of small urban features this class was distinguished from P.

P. Urban Development.

This cover represents continuous build-up surface cover e.g. cities, large town centres, industrial and commercial complexes and permanent bare ground.

Q. Inland Bare Ground.

As opposed to class P this cover characterises all 'natural surfaces such as rock, sand, gravel or soil' (Howard, 1993: 17) excluding coastal zones of cliffs and beaches, but including 'imported surfaces of sand or gravel' (Howard, 1993: 17) like car parks.

APPENDIX 2.

SOILTEMP model.

AML application estimating soil temperature at a chosen depth with input data of air temperature.
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Dept. of Geography, Edinburgh University.

```
/* this program calculates soil temperature on the basis
/* of known air mean seasonal temperature, soil moisture
/* and other paramenters.

/*SETTING ENVIRONEMENT
grid
setwindow maxof
mapex soil_class
setcell 5
&station 9999
/*checking if old temporary grid was deleted
&if [exists temp_soil -grid] &then
kill temp_soil

/*SETTING PARAMETERS AND GETTING COVERAGES

&sv depth = [response 'type depth in [m] at which you want estimate temp']
&r get_coverages                    /*getting physical data

&r diffusivity %.soil_moisture%          /*setting thermal diffusivity

&r period %.mean_temp%                        /*setting WT parameter
&type 'Period wt ='%.period%
&type 'Input covers are:'%.mean_temp%, %.max_temp%, %.min_temp%,~
%.soil_moisture%

/*ESTIMATING DAMPING DEPTH AND TOTAL DIFFUSIIVITY

/*diffusivity is calculated as a weighted average of parameter
/*for different soil classes - freely, moderately and poorly drained
/* and peats
diff_par = diff_pard * %.weight_good% + diff_parm * %.weight_mod% + ~
diff_parpr * %.weight_poor% + diff_parpt + %.weight_peat%

/*damping depth is the function of diffusivity in aa specified period
damping_depth = POW( 2 * diff_par / %.period%, 0.5)

/*ESTIMATING AMPLITUDE AND SOIL TEMPERATURE
parameter = %depth% / damping_depth

amplit = ( %.max_temp% - %.min_temp% ) * (EXP(- parameter))

temp_soil = %.mean_temp% + amplit * sin ( %.period% - parameter )
&sv season = [before [after %.mean_temp% tmn_] _]

&return
```

APPENDIX.

Table 3.3 The HOST classification (Boorman et al., 1995).

SUBSTRATE HYDROGEOLOGY	MINERAL SOILS				PEAT SOILS	
	Groundwater or aquifer	No impermeable or gleyed layer within 100cm	Impermeable layer within 100cm or gleyed layer at 40-100cm	Gleyed layer within 40cm		
Weakly consolidated, microporous, by pass flow uncommon (Chalk)	Normally present and at > 2m	1 4.31				
Weakly consolidated, microporous, by pass flow uncommon (Limestone)		2 2.12				
Weakly consolidated, macroporous,by pass flow uncommon		3 1.58				
Strongly consolidated, non or slightly porous By-pass flow common		4 3.33	13 0.87	14 0.66	15 9.93	
Unconsolidated, macroporous, by-pass flow very uncommon		5 5.07				
Unconsolidated, microporous, by-pass flow common		6 2.61				
Unconsolidated, macroporous, by-pass flow very uncommon	Normally present and at ≤ 2m	7 1.01		IAC* < 12.5 [< 1m day⁻¹]	IAC* ≥ 12.5 [≥ 1m day⁻¹]	*Drained*	*Undrained*
Unconsolidated, microporous,by pass flow common		8 1.62		9 3.68	10 2.21	11 0.55	12 2.94
			IAC** > 7.5	IAC** ≤ 7.5			
Slowly permeable	No significant groundwater or aquifer	16 0.43	18 5.40	21 4.02	24 13.85	26 2.49	
Impermeable (hard)		17 9.28	19 2.16	22 1.10		27 0.83	
Impermeable (soft)			20 0.69	23 1.31	25 3.64		
Eroded Peat						28 0.58	
Raw Peat						29 5.73	

Small numbers are HOST class numbers. Large numbers are percentage land cover in England, Wales and Scotland. Also unclassified (urban) areas (5.15%) and lakes (0.74%). No extensive UK soil types outside the table or within the shaded portions of the diagram.

*IAC used to index lateral saturated hydraulic conductivity; ** IAC used to index soil water storage capacity

Table 3.17. SPACTeach results for spring.

land cover	Rainfall [mm hr^{-1}]	Evaporation [mm d^{-1}]	VWC after 1wet day [%]	VWC after 1 dry day [%]
bare ground	2	1.5	20	21
	2	1.5	46	47
	2	1.5	61	62
sorghum(50%)	2	1.5	20	21
	2	1.5	46	46
	2	1.5	61	62
sorghum(99%)	2	1.5	20	21
	2	1.5	46	46
	2	1.5	54	55
potatoes (1%)	2	1.5	20	21
	2	1.5	46	47
	2	1.5	61	62
bare ground	2	2.9	21	21
	2	2.9	47	47
	2	2.9	61	62
sorghum(50%)	2	2.9	20	21
	2	2.9	46	47
	2	2.9	61	62
sorghum(99%)	2	2.9	20	21
	2	2.9	46	47
	2	2.9	53	54
potatoes (1%)	2	2.9	20	21
	2	2.9	46	47
	2	2.9	61	62
bare ground	3	1.5	21	22
	3	1.5	47	48
	3	1.5	61	62
sorghum(50%)	3	1.5	20	22
	3	1.5	46	47
	3	1.5	60	61
sorghum(99%)	3	1.5	21	22
	3	1.5	49	49
	3	1.5	62	62
potatoes (1%)	3	1.5	21	22
	3	1.5	47	48
	3	1.5	61	62
bare ground	3	2.9	21	22
	3	2.9	47	48
	3	2.9	60	61
sorghum(50%)	3	2.9	21	22
	3	2.9	47	48
	3	2.9	60	61
sorghum(99%)	3	2.9	21	22
	3	2.9	47	48
	3	2.9	60	61
potatoes (1%)	3	2.9	21	22

	3	2.9	47	48
	3	2.9	60	61

Table 3.18 SPACTeach results for clay at various stomatal sensitivities.

Soil depth [cm]	VWC at stomatal sensitivity of -5000	VWC at stomatal sensitivity of -8000	VWC at stomatal sensitivity of -12000	VWC at stomatal sensitivity of -16000
57.6	57.6	57.6	57.6	57.6
-0.01	57.5	57.6	57.5	57.5
-0.075	57.3	57.4	57.3	57.3
-0.225	56.9	56.9	56.9	56.9
-0.375	56.4	56.4	56.4	56.4
-0.525	56.0	56.0	56.0	56.0
-0.675	55.7	55.7	55.7	55.7
-0.825	55.6	55.6	55.6	55.6
-0.975	55.5	55.5	55.5	55.5
-1.125	55.5	55.5	55.5	55.5
-1.275	55.5	55.5	55.5	55.5
-1.425	55.5	55.5	55.5	55.5

Table 3.19 Results of SPACTeach sensitivity test for sandy soil at various initial moisture levels.

Soil depth [cm]	Rain intensity [mm hr^{-1}]	VWC [%]-	VWC [%]	VWC [%]	VWC [%]
Initial VWC		**0.013 (Wilt.pt.)**	**0.041**	**0.067**	**0.104 (~ FC)**
0	1	13.9	15.2	16.3	17.5
-0.01		11.4	13.9	15.5	17.0
-0.075		1.3	4.4	7.3	11.9
-0.225		1.3	4.1	6.7	10.4
-0.375		1.3	4.1	6.7	10.4
-0.525		1.3	4.1	6.7	10.4
-0.675		1.3	4.1	6.7	10.4
-0.825		1.3	4.1	6.7	10.4
-0.975		1.3	4.1	6.7	10.4
-1.125		1.3	4.1	6.7	10.4
-1.275		1.3	4.1	6.7	10.4
-1.425		1.3	4.1	6.7	10.4
0	2	19.5	19.8	0.2	20.3
-0.01		18.9	19.3	19.5	19.9
-0.075		3.1	6.9	10.4	15.2
-0.225		1.3	4.1	6.7	10.6
-0.375		1.3	4.1	6.7	10.4
-0.525		1.3	4.1	6.7	10.4
-0.675		1.3	4.1	6.7	10.4
-0.825		1.3	4.1	6.7	10.4

-0.975		1.3	4.1	6.7	10.4
-1.125		1.3	4.1	6.7	10.4
-1.275		1.3	4.1	6.7	10.4
-1.425		1.3	4.1	6.7	10.4
-0.975		1.3	4.1	6.7	10.4
0	3	21.4	21.5	21.6	22.0
-0.01		20.9	21.0	21.1	21.7
-0.075		7.0	10.8	14.3	18.5
-0.225		1.3	4.1	6.8	11.0
-0.375		1.3	4.1	6.7	10.4
-0.525		1.3	4.1	6.7	10.4
-0.675		1.3	4.1	6.7	10.4
-0.825		1.3	4.1	6.7	10.4
-0.975		1.3	4.1	6.7	10.4
-1.125		1.3	4.1	6.7	10.4
6.7		1.3	4.1	6.7	10.4
-1.425		1.3	4.1	6.7	10.4
0	7	25.3	25.6	25.8	26.0
-0.01		24.9	25.4	25.7	25.9
-0.075		22.2	23.7	24.5	25.1
-0.225		2.6	6.9	11.5	18.2
-0.375		1.3	4.1	6.7	10.7
-0.525		1.3	4.1	6.7	10.4
-0.675		1.3	4.1	6.7	10.4
-0.825		1.3	4.1	6.7	10.4
-0.975		1.3	4.1	6.7	10.4
-1.125		1.3	4.1	6.7	10.4
-1.275		1.3	4.1	6.7	10.4
-1.425		1.3	4.1	6.7	10.4

CHAPTER FOUR

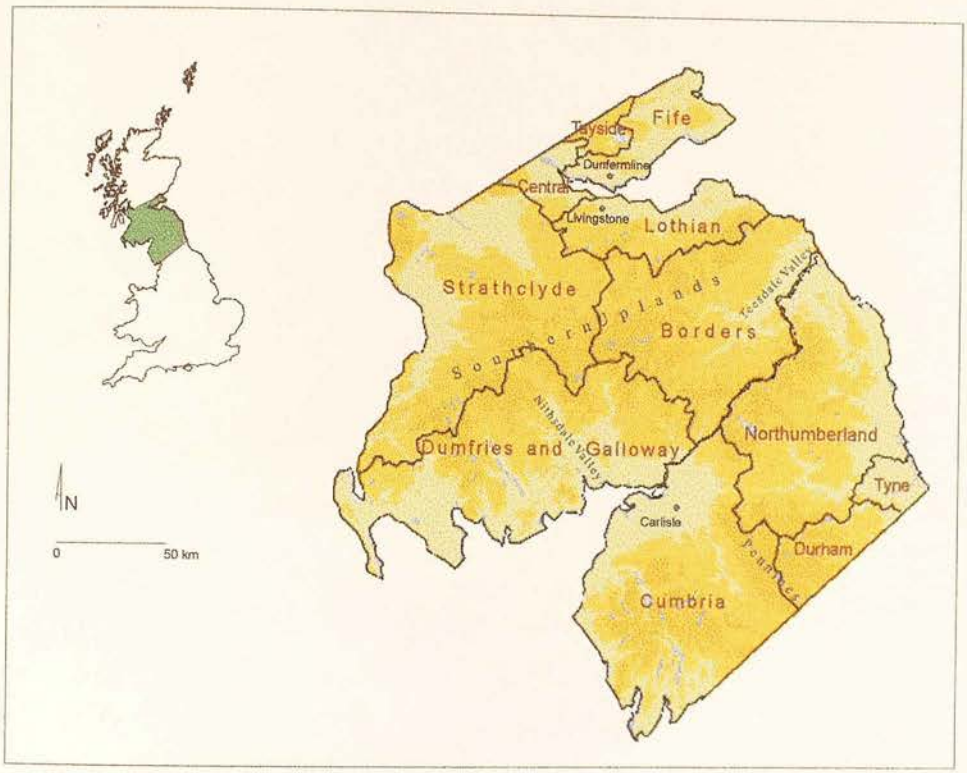
An inventory of soil N_2O emissions in the Tyne-Clyde area.

4.1 INTRODUCTION - AN AREA AND AIMS OF THE STUDY.

Bouwman (1995) based his model of N_2O emissions from agricultural soils on amounts of N fertiliser input. His approach was established on the basis of field observations from a variety of environments, on the basis of which a fertiliser-induced emission factor was derived. This is a commonly applied method used to estimate N_2O emissions at regional and national scales. This simple method was applied to produce an inventory of N_2O emissions from a designated region of Great Britain and is presented in this chapter.

This method estimating N_2O emissions with important controlling factors departs from the empirical approach developed in this thesis. The regional study presented introduces, however, a spatial aspect into predicted N_2O emissions which depend on the distribution of N input to soils. In this context it is a pilot study of the spatial modelling approach presented in this thesis. The outcome of this small study was to (1) establish the reliability of the N fertiliser input approach presented in chapter three for further applications, (2) recognise any problems with modelling N_2O emissions due to the restricted availability of input data and (3) establish the spatial distribution of N_2O emissions at a regional scale.

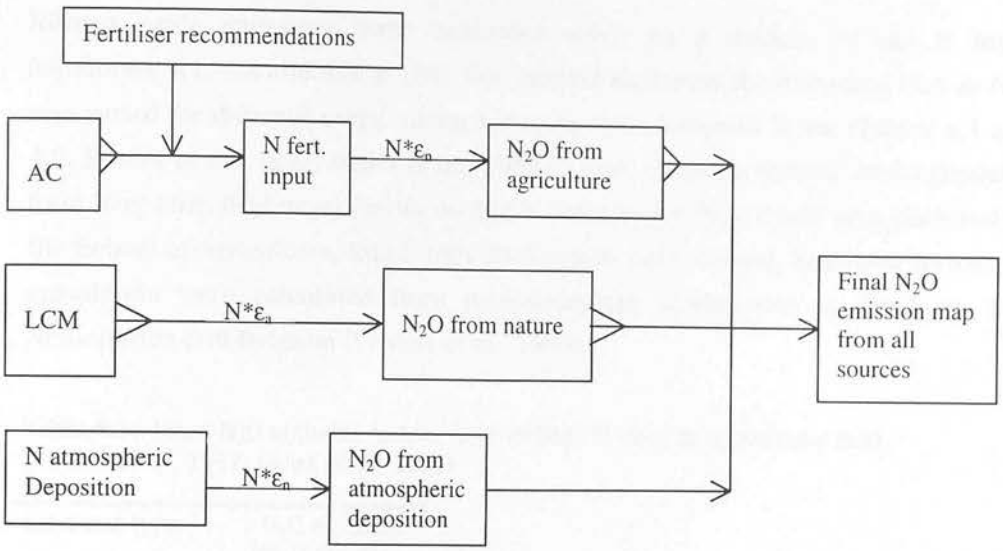
Figure 4.1 Tyne-Clyde area.



The study region was defined by the estuaries of the rivers Tyne and Kent in the south and Tay and Clyde in the north (figure 4.1) straddling the England-Scotland border, and is referred to as the "Tyne-Clyde area". This area was selected for three main reasons. Firstly, the location of most field measurements, applied in the N_2O emission inventory of the Tyne-Clyde area, was in the South of Scotland (section 4.2.1). Secondly, this area has a specifically agricultural character as 75% of the land is used for agriculture. This corresponds with the land use structure in England and Wales, where 84 % of total land is used for agriculture, with 52 % of total area under intensive management (figure 4.2 and 5.2, chapter five). Scotland, however, has a smaller proportion of agricultural land than the Tyne-Clyde area, as only 49 % of the total land is used for agriculture (figure 5.2, chapter five). Finally, the border between Scotland and England lies in the South of the area. This is significant to the study as there are differences between Scotland and England in recommendations of N input to some crops (table 3.6, chapter three) and different

classifications of grasslands, which may have further implications on the method of estimating N fertiliser input to soil in Great Britain.

Figure 4.2 Method of estimating N_2O emissions from the Tyne-Clyde area.



This study estimates N_2O emissions from agricultural and seminatural soils by applying emission factors derived in field studies. The single principal factor controlling emissions applied in this study was N input to soils in the form of agricultural inputs and atmospheric deposition. N inputs as fertiliser were modelled on the basis of published recommendations for Scotland (Dyson, 1992; Dyson, 1993; Dyson *et al.*, 1993a; Dyson *et al.*, 1993b; Dyson *et al.*, 1993c; Swift, 1988 and Younie *et al.*, 1990;) and England and Wales (MAFF, 1988), the approach described in chapter three. Organic inputs to soils were estimated from livestock numbers provided by Agricultural Census data (chapter three). Estimated N fertiliser inputs were verified with actual fertiliser practices obtained from eight farms in a survey of farmers. Finally the N_2O emissions model for the Tyne-Clyde area was validated with a GIS inventory for the Lothian Region (Lilly *et al.*, 1998).

4.2 METHOD OF ESTIMATING N_2O EMISSIONS FROM SOILS WITH EMISSION FACTORS.

4.2.1. Emission factors based on field measurements.

Nitrous oxide emissions were estimated solely as a fraction of the N input (equations 4.1, 4.2 and 4.3, p 132). For mineral fertilisers the fractional loss as N_2O was varied for different crops, using a crop specific emission factor (Tables 4.1 and 4.2, Fowler *et al.*, 1997; Skiba *et al.*, 1996). These emission factors were calculated from long-term field experiments on arable soils in the Tyne Clyde area obtained by the School of Agriculture, Edinburgh (McTaggart, pers. comm). Emission factors for grasslands were calculated from measurements carried out in Scotland, The Netherlands and Belgium (Velthof *et al.*, 1994).

Table 4.1. Mean N_2O emission factors from mineral N input to agricultural land. (Fowler *et al.*, 1997; Skiba *et al.*, 1996)

Land use type	N_2O emission [% N input]
grazed grassland	2.1
mown grassland	1.8
winter wheat	0.5
spring barley	0.8
winter barley	0.5
oats	0.8
oilseed rape	0.5
potatoes	1.6
root tillage crops	1.6

Table 4.2. Mean N_2O emissions from selected seminatural ecosystems (Skiba *et al.*, 1996).

Land cover	N_2O emission [kg N ha^{-1} yr^{-1}]
Deciduous & mixed woodland	0.78
Coniferous woodland	0.28
Unmanaged grassland	0.31
Moorland	0.19

The data used to derive the emission factors were collected in 1992 and 1993 during frequent field measurements with small cylindrical chambers (Skiba *et al.*,

1996). On agricultural soils, measurements were carried out every few days during the growing seasons, and more frequently following fertiliser application. The results of the experimental work lead to the estimate of mean fertiliser emission factors presented in table 4.1. It was observed that grazed grasslands were the largest source of N_2O due to greater proportion of N input in organic form and the side effects of grazing e.g. treading causing soil compaction (Skiba *et al.*, 1996). N_2O emissions from potatoes were higher than from other crops due to the later timing of N fertiliser application and plants' requirement of higher soil moisture (Skiba *et al.*, 1996).

Mean N_2O emissions from seminatural land were measured between 1992 and 1995 at several sites in South-East and Central Scotland, and North England. The N_2O emission measurements were obtained using a similar method to the agricultural experiments with sampling every 2 - 4 weeks (Skiba *et al.*, 1996). Among semi-natural ecosystems, deciduous woodland was the greatest source with a mean emission of 0.78 kg N ha^{-1} y^{-1}. Some deciduous tree species caused very high emissions e.g. alder (*Alnus*) for which the mean measured flux was 1.78 kg N ha^{-1} y^{-1} due to N fixation in their roots (Skiba *et al.*, 1996). High N_2O emissions were also registered for upland moorland due to increased N deposition on higher altitudes as an effect of seeder-feeder enhancement and intercept of acid deposition by forest canopy present on that site (Fowler *et al.*, 1989).

The mean fertiliser factors for agricultural soils and mean emissions for seminatural vegetation were applied in the Tyne-Clyde inventory to land cover data to find the spatial distribution of N_2O emissions.

4.2.2 Description of the inventory.

An N_2O emission inventory was created for the Tyne-Clyde area using ArcInfo GRID through the application of the emission factors taken from the field measurements (tables 4.1 and 4.2). ArcInfo was used to estimate N_2O emissions using simple overlays of different land cover and land use types. This method was applied as the most suitable for obtaining the spatial distribution of annual emission rates controlled by soil N content. As this value was not readily available, however, it was assumed that N content was directly influenced by N input to soils, either via fertilising and grazing, or by atmospheric N deposition.

Initially, agricultural and seminatural land type data at resolutions of 5 and 1km respectively (description of source in chapter three), were converted into ArcInfo input formats with Fortran90 programs. They were then loaded into the Oracle Data Base Management System (DBMS) that had a link with the ArcInfo system, which allowed for the direct input of data into INFO data base tables. Grid coverages for the different crop types, grassland, livestock density and seminatural land cover classes were prepared using AC and LCM data, respectively (figure 4.2). Mineral N input to tilled land and grasslands and organic N input to grasslands were estimated using fertiliser recommendations (tables 3.6 and 3.8, chapter three). Initially, N_2O emissions from seminatural land had a higher resolution of 1 km grid. As processing was to be carried out at 5 km resolution, which was the resolution of the AC data, all grid coverages of input data were brought to that resolution.

For all the agricultural systems, emission factors were applied to N input according to the different crops and grass management (tables 4.1 and 4.2) and N_2O emission grids were produced according to equation (4.1). For the organic N input, a mean N_2O emission factor of 2 % was assumed on the basis of the general variability presented in chapter two. This emission factor is also in-line with the IPCC/OECD suggestions (IPCC, 1997). N_2O emissions from semi-natural land were estimated from mean measured emission factors that were proportionally weighted depending on the dominant land cover type in each grid as presented in equation (4.2). The N_2O emissions for agricultural land and semi-natural ecosystems were combined together with N_2O estimated from total N deposition with an assumed 1% emission factors (IPCC, 1997) that is also close to the mean emission factor of 0.8% estimated by Skiba *et al.* (1998a). The emissions from the different sources were summed to obtain a map of total soil N_2O emissions for the Tyne-Clyde area (equation 4.3).

$$E_{agr} = \Sigma \varepsilon_n * N_r * A \quad (4.1)$$

where : E_{agr} - N_2O emission from agriculture

ε_n - emission factor according to crop type

N_r - amount of N recommended

A - area under agricultural land

$$E_{nat} = \Sigma \varepsilon_a * A \quad (4.2)$$

where : E_{nat} - N_2O emission from seminatural land

ε_a - mean N_2O emission according to vegetation type

A - area under seminatural land

$$E_{N2O} = E_{agr} + E_{nat} + E_{dep} \quad (4.3)$$

where: E_{agr} - N_2O emission from agriculture

E_{nat} - N_2O emission from seminatural land

E_{dep} - N_2O emission caused by atmospheric N deposition (for ε_{dep} = 1% of atmospheric N input).

4.3 RESULTS AND DISCUSSION.

Agricultural activity contributed to the majority of the total annual N_2O in the studied region. N fertiliser input caused N_2O emissions from agricultural soils to range from 0.5 to 20 kg N ha^{-1} y^{-1} with an average flux of 3.2 kg N ha^{-1} y^{-1} (figure 4.3c). N_2O emissions from agricultural land varied depending on the spatial distribution of different crops and grass management. Grasslands were associated with the highest emission values and for the Tyne-Clyde area with mean N_2O emissions of 9.3 ± 12 kg N ha^{-1} y^{-1}. This was due to high inputs of mineral N fertiliser (table 3.8, chapter three) and the additional N input from animal manure. The mean N_2O emissions from grassland soils in the Tyne-Clyde area were higher than average N_2O emissions measured in the growing seasons of 1992 and 1993 by Velthof *et al.* (1994) at 1.6 and 4.1 kg N ha^{-1}. This might be due to the exclusively mineral form of N input examined by Velthof *et al.* (1994). Much higher emission responses were observed from organic forms of N in several studies (Ball *et al.*, 1997; Eggington and Smith, 1986; Killian *et al.*, 1996).

Tilled land was characterised by moderate emissions ranging from 0 - 2.5 kg N ha^{-1} y^{-1} with a mean of 0.4 kg N ha^{-1} y^{-1}. The main source of N input was from mineral fertiliser N applications (table 3.6, chapter three). The range of estimated N_2O emission rates corresponded with mean N_2O emissions measured at 0.5 kg N ha^{-1} y^{-1} from barley, and 1.6 kg N ha^{-1} y^{-1} from oilseed rape in South-central Scotland (Skiba *et al.*, 1998c). The rather low mean of N_2O emissions is due to a small proportion of high-N requiring crops grown in Scotland. The dominant crops that are associated with higher N_2O emissions are oilseed rape, barley and potatoes.

N_2O emissions from semi-natural land ranged from 0 - 0.6 kg N ha^{-1} y^{-1} with the mean value of 0.1 kg N ha^{-1} y^{-1} (figure 4.3a). This source is rather small due to large proportion of moorland in semi-natural ecosystems. As indicated in figure 4.4, 454967 ha of moorland contributed 57 % of seminatural land from which low emissions were observed (Skiba *et al.*, 1996). Mean N_2O emissions from semi-natural land in the Tyne-Clyde area were substantially lower than the IPCC assumed background level of emissions of 1 kg N ha^{-1} y^{-1} (Bouwman, 1995).

Figure 4.3 N_2O emissions in the Tyne-Clyde area from different sources.

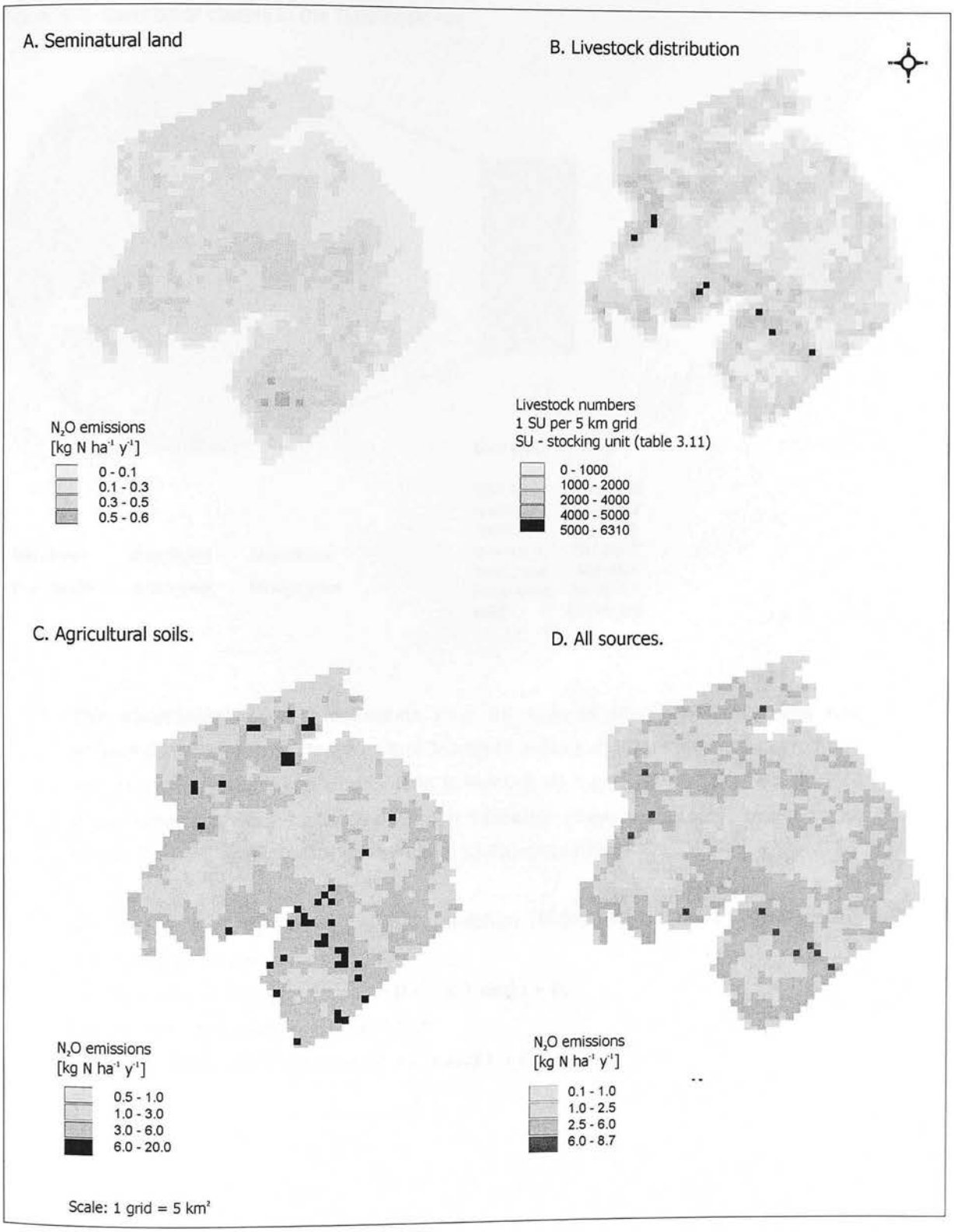
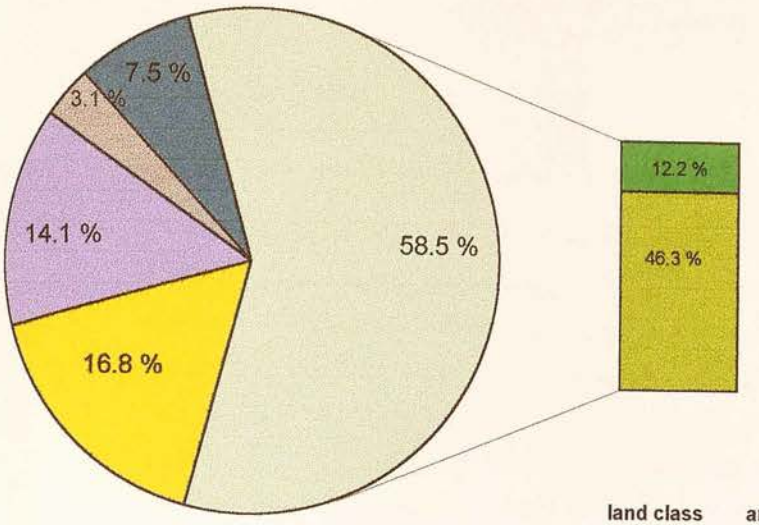


Figure 4.4. Land cover classes in the Tyne-Clyde area.



land class	area [ha]
tilled land	540244.9
heathland	454967.2
deciduous	101297.8
coniferous	241209.6
man grass	391656.8
rough grass	1490039.1
total	3219415.3

The distribution of N_2O emissions from all soils in the Tyne-Clyde area was analysed using ArcInfo Geary (c) and Moran (I) indices that describe autocorrelation between adjacent cells of phenomena presented on a grid basis. They are the two most commonly used statistics giving an indication of spatial autocorrelation for an entire data set within a GIS environment (Johnston, 1998).

On the basis of these two indices, Goodchild (1986) defined three characteristic groups of phenomena:

(1) Clustered and regionalized for $0 < c < 1$ and $I > 0$;

(2) Uncorrelated when $c = 1$ and $I = 0$;

(3) Contrasting, checkerboard for $c > 1$ and $I < 0$.

Table 4.3. Spatial autocorrelation analysis of N_2O emissions for the Tyne-Clyde area according to main land use types.

Land use	Geary index	Moran index
Tilled land	0.24	0.53
Grassland	0.74	0.17
Seminatural ($5km^2$)	0.14	0.78
Seminatural ($1km^2$)	0.24	0.72
All land	0.33	0.62

The statistics estimated for the Tyne-Clyde area indicated that N_2O emissions from both agricultural and semi-natural soils (at 5 km grid resolution) showed a certain degree of clustering as the estimated value for c for those land groups were below 1 (table 4.3). N_2O emissions from semi-natural land at 5km resolution showed a greater clustering than from grasslands as indicated by the Geary statistics of 0.14 and 0.74, respectively. For N_2O emissions from semi-natural soils at its original resolution of 1 km grid the Geary index of 0.24 indicated greater variability of land cover data. This trend of Geary value increase (that coincided with Moran index decrease) might suggest that the clustering of distribution of N_2O emissions disappears at the local level due to the great spatial variability of this phenomenon (chapter two). At 5 km grid resolution, however, more regional characteristics of emissions could be examined. Large areas of the Southern Uplands, Cumbrian Mountains, North Pennines and some parts of Central Scotland had N_2O emissions below 2 kg N ha^{-1} y^{-1}. Lower N_2O emissions (mean ~ 3 kg N ha^{-1} y^{-1}) were registered in East Tyne-Clyde. The West and Southwest had much higher N_2O emissions of ~ 4-5 kg N ha^{-1} y^{-1} with a more clear tendency of grids with higher N_2O emissions to cluster. This was mostly influenced by the location of grasslands, predominantly in the western upland regions of Galloway, Cumbria and Strathclyde (figure 4.1), where managed grasslands contribute to over 80% of total agricultural land (figure 4.5). Tilled land in the Tyne-Clyde area, located predominantly in the East, did not cause as high levels of N_2O emissions (table 4.4).

Table 4.4. N_2O emissions from major land classes according to the Tyne-Clyde inventory.

land cover	Minimum N_2O emissions [kg N $ha^{-1}y^{-1}$]	Maximum N_2O emissions [kg N $ha^{-1}y^{-1}$]	Mean N_2O emissions [kg N $ha^{-1}y^{-1}$]
Coastal areas	0.1	4.4	1.3
Rough grassland	0.2	7.4	2.8
Managed grass	1.9	6.6	4.3
Tilled land	0.2	8.7	2.3
Heathland	0.6	4.1	1.4
Deciduous forest	0.7	0.7	0.7
Coniferous forest	0.4	2.2	0.7

A few local flux hot-spots (> 6 kg N ha^{-1} y^{-1}) were, however, identified near Dunfermline, Livingston, the upper Nithsdale Valley, west and south of Carlisle and around Teesdale Valley (figure 4.3d). These localised areas of high N_2O emission are the result of intensive grassland management. High stocking densities ranging from 3 to 5.6 stocking unit per ha (SU ha^{-1}) were the major reason for those high N_2O emissions of 6 – 38 kg N ha^{-1} y^{-1} from grassland areas (the maximum occurred near Dunfermline). The hot-spots of emissions, as observed on figure 4.3b (over 5000 SU in 5 km^2 areas), were primarily an effect of large numbers of cattle and cows (> 3000), sheep (ranging from 5200 - 18042) and poultry (the maximum livestock density in North Cumbria is associated with a poultry farm with > 20500 birds), which promoted large mineral N inputs to grasslands (table 3.8, chapter three) and produced a surplus of organic N.

N_2O emissions from semi-natural land were the main contributor in the uplands of the Tyne-Clyde area. The dominant natural land cover class was moorland, representing 14.1% of the total area and contributing only 0.12 Kt N y^{-1} that represented 1% of the total N_2O emission (table 4.5). Forests also contributed little (1.6%) to the total N_2O flux, mainly due to their scarcity in this area - 10.6 % (table 4.5), but also as a result of low emission rates of 0.28 kg N ha^{-1} y^{-1} from coniferous forests and 0.78 kg N ha^{-1} y^{-1} from deciduous and mixed forest (Skiba *et al.*, 1996).

Atmospheric deposition had a minor effect on the total amount of emitted N_2O and it contributed just over 5% of the total flux (table 4.5). However, in upland areas, N deposition rates can be the major N input to the soil and therefore significantly influence N_2O emissions. The seeder-feeder effect in upland areas can enhance atmospheric N deposition by 41 - 73 % (Dore *et al.*, 1992). Modelled N deposition rates suggest the largest rates of atmospheric N deposition to occur in central

Cumbria (>30 kg N ha^{-1} y^{-1}). It is expected that the coarse resolution of atmospheric N input data (20km * 20km) and the great uncertainty of modelled ammonia (section 3.2.5, chapter three) underestimated this source. Large amounts of emitted ammonia from intensively grazed grasslands and livestock farms are quickly deposited (Skiba *et al.*, 1998b) and this leads to very high N deposition values. Their importance is lost in the data source applied in this study that represented mean total N input for each 20 km grid. Finer resolution estimates of atmospheric N deposition might further increase the high N_2O emissions from grasslands observed in this study.

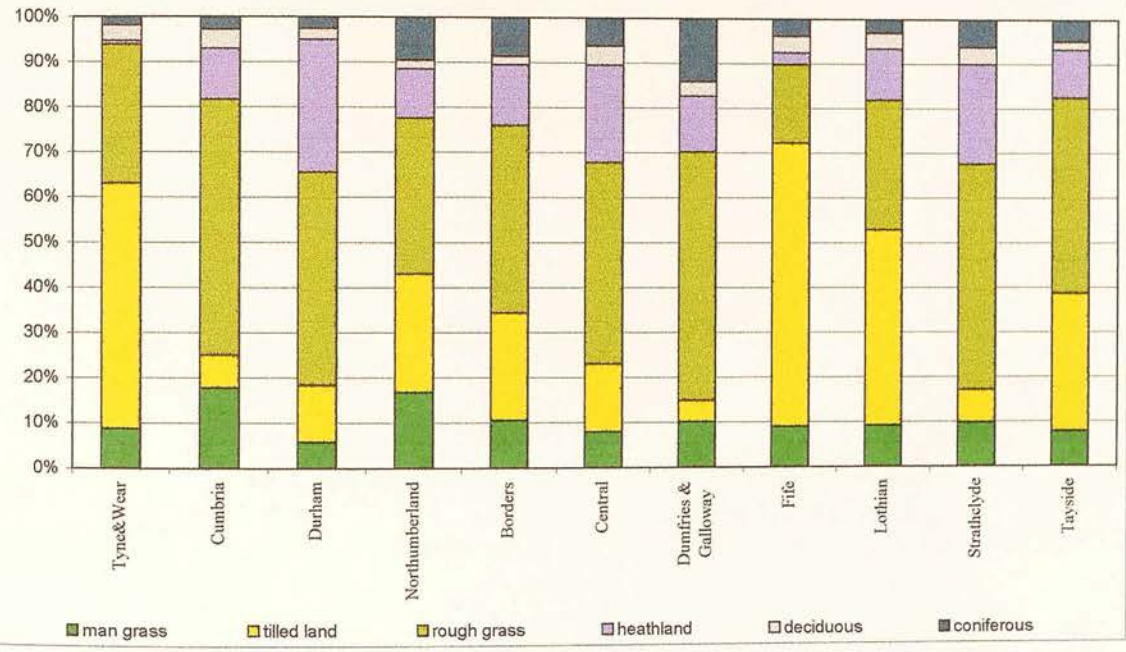
Table 4.5. Estimates of N_2O emissions for the Tyne-Clyde area.

Land use	Area [10^6 ha]	N_2O emission [Kt N y^{-1}]
Tilled land		
Cereals	0.34	0.34
Other crops	0.06	0.11
Managed grasslands		
Grazed grassland	0.64	2.39
Cut grassland	0.40	1.32
Excretal N from grazing animals	171 kt N	3.42
Seminatural land		
Unmanaged grassland	1.02	0.32
Shrub heath and bracken	0.64	0.12
Deciduous & mixed woodland	0.10	0.08
Coniferous woodland	0.24	0.07
Bog	0.04	0.008
N deposition	53.2 kt N	0.53
Total	**3.48**	**9.8**

Distribution of N_2O emission reflects the biological and physical characteristics of seminatural ecosystems and management practices in agricultural systems. Within the Tyne-Clyde area there are 11 administrative units described as regions in Scotland, and counties in England (EDINA, 1991), that outline smaller areas within the area of study and could be individually analysed in terms of N_2O emissions. For the simplicity of this presentation the administrative units are here referred to as regions. The following section observes different environmental characteristics of those regions and corresponding patterns of N_2O emissions. The aim is to establish whether some areas are more similar than others and to associate the similarities of N_2O emissions with anthropogenic and environmental factors. The spatial variability of N_2O emissions from soils was also analysed at the regional level. The highest mean emissions were observed in Cumbria (3.45 kg N ha^{-1} y^{-1}) and

Dumfries and Galloway (2.5 kg N ha^{-1} y^{-1}), the lowest (1.2 kg N ha^{-1} y^{-1}) were noted in Tyne & Wear (figure 4.6). Large spatial variability of N_2O emissions was observed for the regions: Lothian; Cumbria and Fife; whereas Tayside and the Borders had relatively uniform fluxes (figure 4.3d). These differences were related to the distribution of the major land cover classes. According to the proportional distribution of major land classes, four main types of regions could be established on the basis of LCM satellite data: arable, grassland, 'natural' and mixed (figure 4.5).

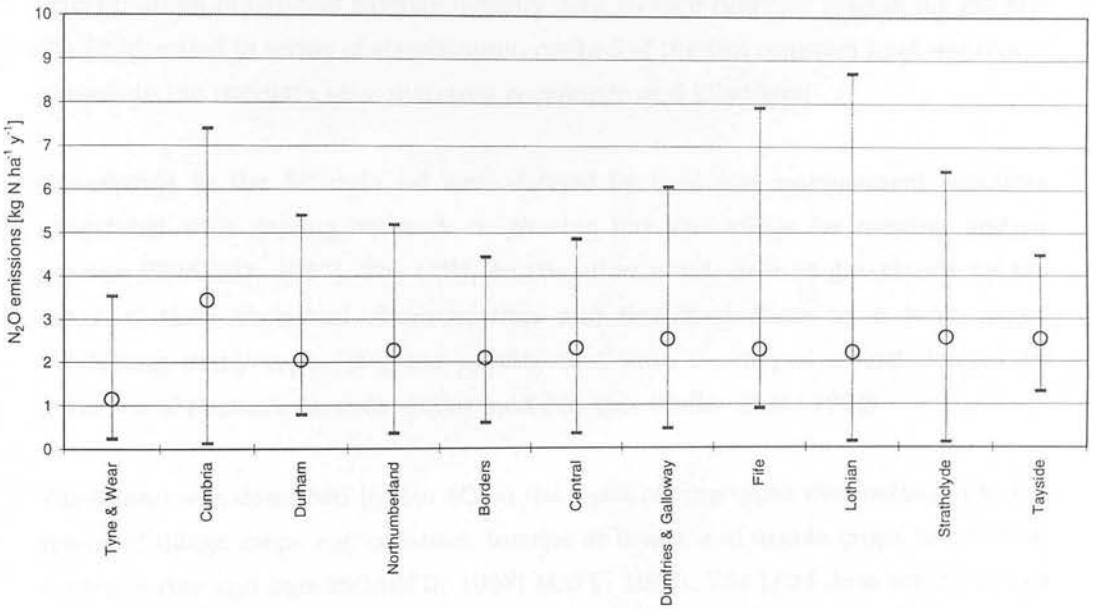
Figure 4.5 Regional distribution of major land cover types.



Three regions i.e. Tyne & Wear, Fife and Lothian were assigned to the arable group as over 40% of their area was classified as tilled land. Cumbria and Dumfries and Galloway had over 65% of grasslands that qualified them into the second main ecosystem group of grassland regions. Four regions: Durham; Central; Dumfries and Galloway and Strathclyde were assigned to the 'natural' group with at least 30% of heathland and woodland and 40 % of rough grasslands. To the group of varied agricultural and semi-natural ecosystems, three regions were assigned: Northumberland; Borders and Tayside. This classification was not explicit as Dumfries and Galloway was described both a 'natural' and grassland region due to the high proportion of woodland (~18%) and 65% of the area as rough and managed

grasslands. There was an observed pattern in N_2O emissions variability among the main region classes. Grassland regions had the highest mean and range of emissions, while 'natural' and mixed regions showed relatively uniform fluxes (figure 4.6). Livestock numbers were recognised as an important factor in N_2O emission variability. Insignificant livestock husbandry led to small variability in mean emissions, e.g. in Tyne & Wear, while in the Fife and Lothian regions, large variability in emissions was caused by having 3% of the total livestock in the study region located in a relatively small area. The Fife and Lothian regions contributed

Figure 4.6 N_2O emissions from soils - regional variability.



only 2.7 and 3.5%, respectively, of all managed grasslands in the Tyne-Clyde area. The high intensity of grazing caused emissions rising up to 38 kg N ha^{-1} y^{-1} in the vicinity of Dumfries. Large livestock numbers, which totalled 504 699 SU in Strathclyde, 507 645 SU in Dumfries and Galloway, and 625 619 SU[1] in Cumbria on the total area of managed grasslands of 243 * 10^3 ha, caused enhanced emissions in the West and the bi-polar West-East character of N_2O variability (figure 4.3c). The observed spatial variability of N_2O emissions was enhanced by other environmental variables such as climatic and soil conditions that promoted different agricultural practices. Precipitation was the most important indirect climatic factor causing greater N_2O emissions in western parts of the Tyne-Clyde area.

[1] Definition in section 3.2.5.2, chapter three

4.4 Uncertainties of this approach due to incompatibility of the land use data sources.

The main limitation of the inventory was associated with the different data sources, principally the Agricultural Census (AC) and the Land Cover Map (LCM), used in this study. The data sets had different dates and varying methods of compilation. The AC, from 1988, was based on a survey of farmers and assigned to old Ordinance Survey maps. The LCM, from 1990-1991, was the result of interpretation of Landsat satellite imagery. Due to their different origins the AC and the LCM varied in terms of classification method of the two common land use/cover classes to the two data sets: managed grasslands and tilled land.

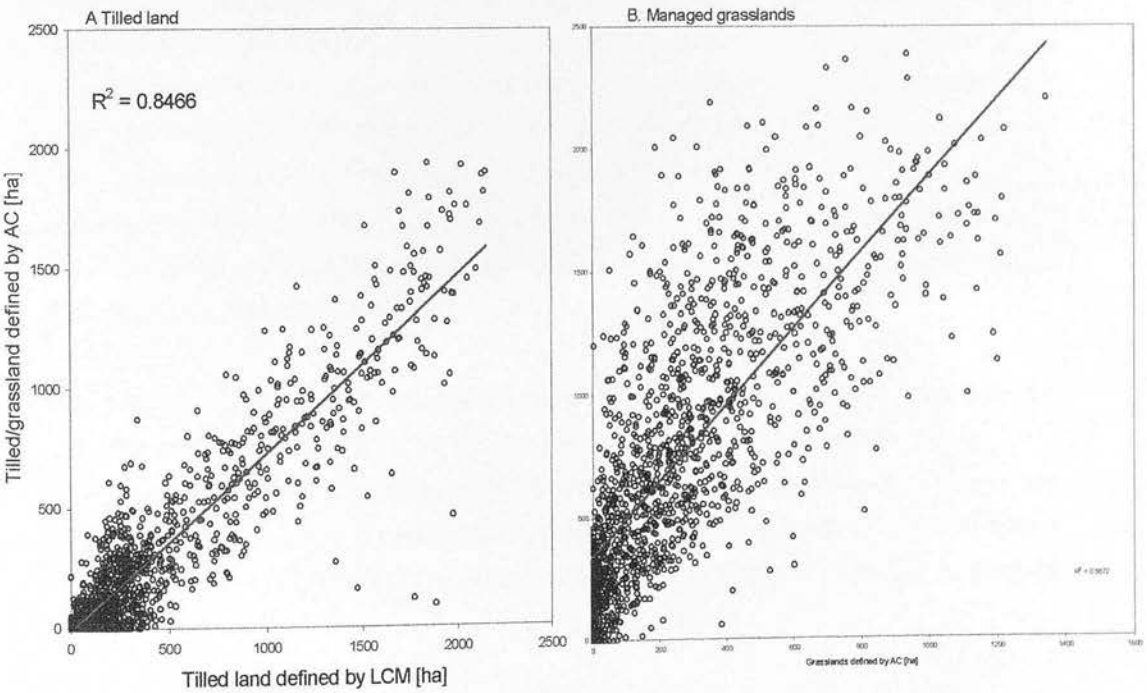
Grasslands in the AC data set were defined by land use management practices associated with grazing livestock or growing hay and silage for mowing and/or grazing (SOAEFD, 1997). The LCM, on the other hand, defined grasslands on the basis of their ecological characteristics and described them as a large group combining many types of grass species that form a cropped sward defined by presence of *Festuca, Agrostis, Lolium* and *Poa* spp. (Fuller *et al.*, 1994).

Tilled land was described by the AC on the basis of crop types that belonged to the group of tillage crops e.g. potatoes, turnips or beans and arable crops like wheat, winter barley and oats (SOAEFD, 1997; MAFF, 1997). The LCM data set described tilled land as *'all land under annual tillage, especially for cereals, horticulture etc.'* The recognition of the tilled land based on a seasonal pattern of bare soil in winter and the presence of vegetation in summer, meant that one year old leys and temporarily bare ground e.g. mining, scrub-clearance (Fuller *et al.*, 1994) were included in this category.

Due to the definitional differences between the AC and the LCM some aerial incompatibilities were expected that could have a significant influence on the results of the emissions inventory, which used the AC as the source of agricultural land use information and the LCM for seminatural land classes. A correspondence between the area of managed grasslands and tilled land, as defined by both the LCM and the AC for each 5 km grid, was observed with linear regression analysis for the Tyne-Clyde area (figure 4.7a and b). As the observed distribution of the data

did not comply with the required conditions of normal distribution of residuals and no spatial autocorrelation (Shaw and Wheeler, 1994), the presented results may show some bias. The requirements of regression analysis were relaxed here as the aim was only to observe general trends in differences between the two data sets. The data sets were linked with an application of COMBINE function of ArcInfo. Linear regression requires error free independent variable (Shaw and Wheeler, 1994). A choice of independent variable for this analysis was difficult as neither of the data sets in question could be considered universal, they were both expected to carry some degree of error. Due to the agricultural character of the analysed land cover classes the AC was chosen as an independent variable in this analysis (figure 4.7a and 4.7b).

Figure 4.7 Correspondence between AC and LCM data sets



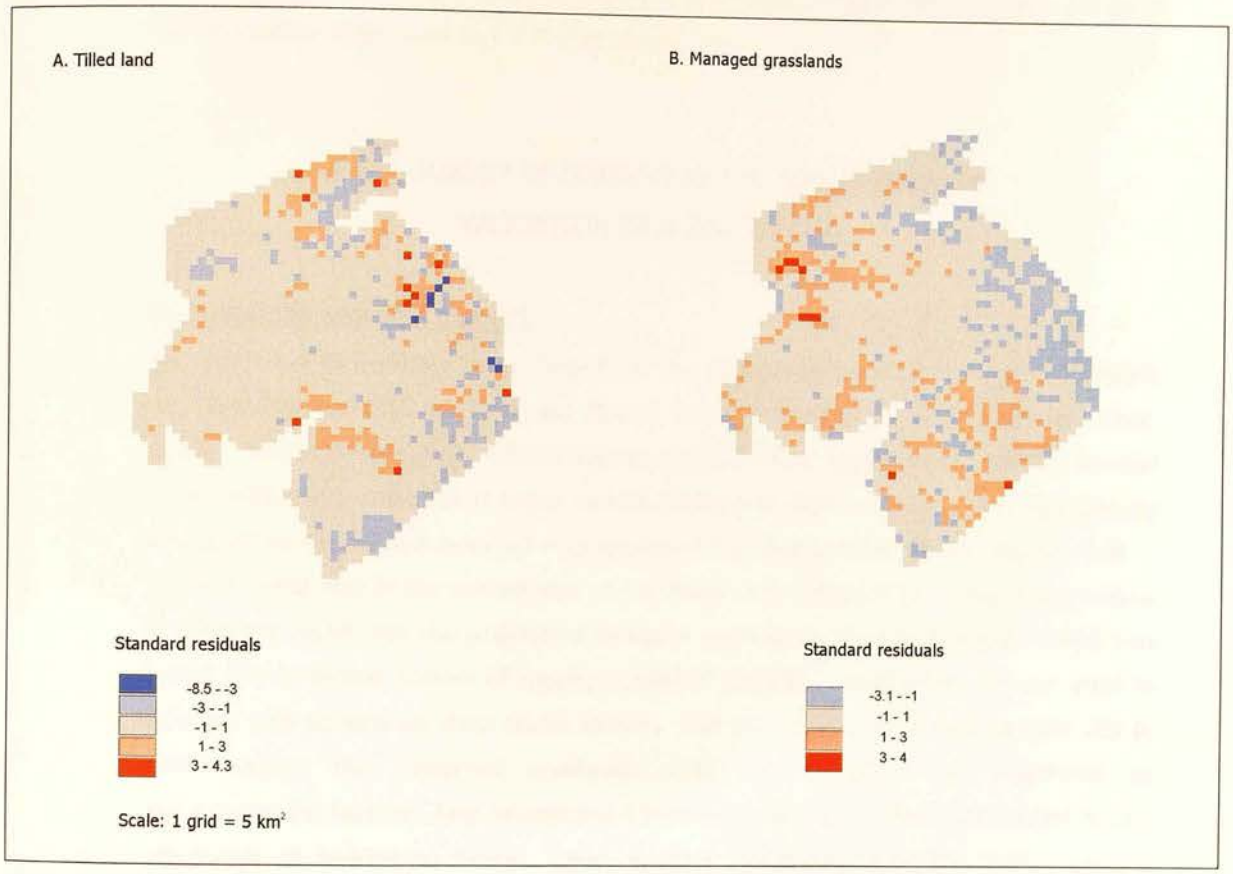
The linear regression analysis showed a general agreement between the two data sets as described by the positive correlation coefficients. On the other hand there were considerable differences between the AC and the LCM in the area of managed grasslands and tilled land showed by the regression coefficients of 0.72 and 1.69. The relationship was also characterised by a great degree of data scatter that was

especially a problem in case of grasslands (figures 4.7a, 4.7b). The linear regression analysis explained 84% of data variability for tilled land (figure 4.7b) and only 59% for grasslands (figure 4.7a). The standard error estimated for grasslands was 346 ha and for tilled land 153 ha. The small coefficient of determination and larger standard error for managed grasslands suggested that simultaneous application of these two data sets could contribute to a larger error of the estimated N_2O emissions for this land class.

The general trends defined by the linear regression results suggested also that there was a tendency by the AC to underestimate tilled land and overestimate grassland areas in comparison with the LCM (figures 4.7a, 4.7b). These differences could be explained by the different methods of data acquisition. The spectral recognition characteristics of crops and grasses, especially at earlier stages of their development, might affect the accuracy of satellite image interpretation as suggested by the definition of tilled land by the LCM. This might explain a tendency of tilled land overestimation by the LCM. But there were also differences due to annual crop rotation and more permanent land use changes that might have occurred between 1988 and 1990-1991. Barr *et al.* (1993) observed small land cover changes between 1984 and 1990 that resulted in a decrease in total managed grassland of 2 % and tilled land of 4% for the whole of Britain over that period. The differences due to crop rotation could not be assessed due to the incomplete AC data sets for 1990 and 1991 (section 3.2.2, chapter three).

The evidence presented above suggested that the main differences between the AC and the LCM were due to the different methods of data acquisition. There were however other factors like differences in their resolution, uncertainties caused by human error during the interpretation of Landsat satellite imagery or generalization methods of the AC, which contributed to the conflicting data (section 3.2.2, chapter three).

Figure 4.8 Distribution of standard residuals from the comparison of the Land Cover Map with the Agricultural Census.



The spatial distribution of standard residuals confirmed a larger incompatibility between these data sets in the areas where tilled land and grasslands predominated (figure 4.8a and 4.8b). Negative values of residuals indicated areas where N_2O emissions would be underestimated due to the smaller agricultural area defined by the Agricultural Census. These errors mainly occurred on the East Coast in the case of N_2O emission from grasslands (figure 4.8b). Positive residuals signified the areas of overestimated emissions and these could be observed generally in the West for grasslands and in the East for tilled land (figure 4.8a). From this analysis, the expected error in N_2O emissions from grasslands and tilled land was calculated. The mean N_2O emissions from grasslands and tilled land in the Tyne-Clyde area were estimated at 4.6 and 1.1 kg N ha^{-1} y^{-1}, respectively. The mean area represented by those land classes for all considered pixels was 1028 ha and 378 ha, respectively. The standard error was estimated as the proportion of mean area at 33.6 % for managed grasslands and at 40.4 % for tilled land. Assuming the proportional relationship between the standard error of N_2O emissions and the standard error of land use/cover due to the described incompatibilities, the

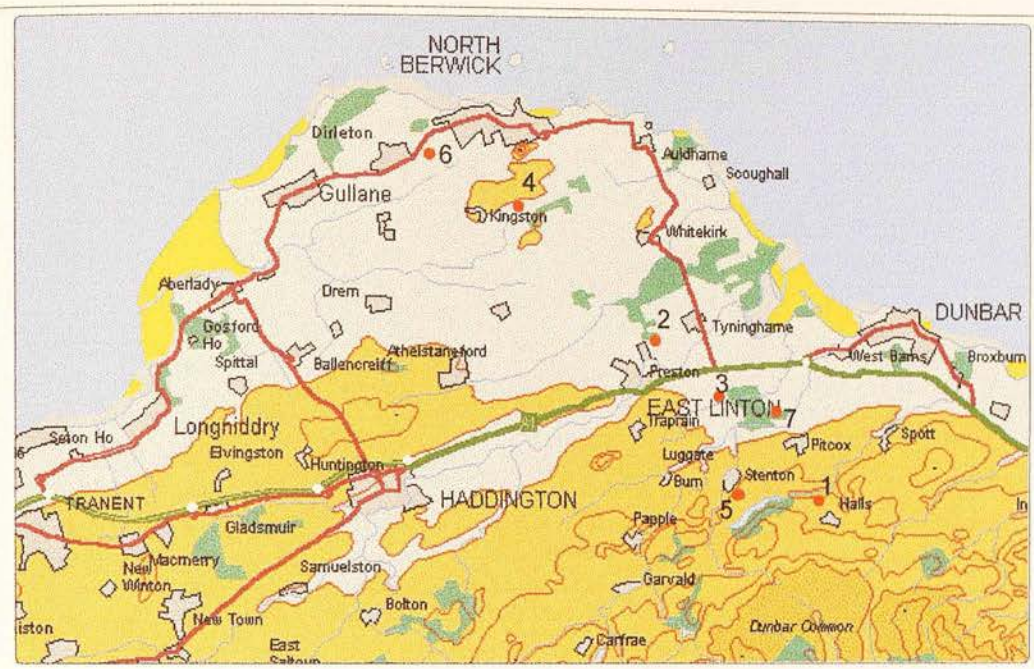
uncertainty of mean N_2O emissions was estimated by multiplying the mean N_2O emissions from the Tyne-Clyde area and the standard errors for tilled land and grasslands, respectively. The uncertainty was greater for grasslands (4.6 ± 1.5 kg N ha^{-1} y^{-1}) than tilled land (1.1 ± 0.4 kg N ha^{-1} y^{-1}).

4.5 SURVEY OF FARMERS IN THE NORTH BERWICK. VALIDATION OF N INPUT MODEL.

Aims and the sampling method.

The model of N fertiliser input based on the guidelines published by MAFF (1988) for England and SAC for Scotland (Swift, 1988; Younie *et al.*, 1990; Dyson, 1992; Dyson, 1993; Dyson *et al.*, 1993a; Dyson *et al.*, 1993b; Dyson *et al.*, 1993c) needed to be evaluated. Data for N input model evaluation were collected in a specifically designed survey of farmers that was carried out in the Lothian Region (figure 4.9).
The principal aim of the survey was to establish the relationship between the actual N fertiliser input and the published fertiliser guidelines. As the N input model was based on standard values of recommended N fertiliser application it was vital to observe any deviations from those values. The survey was intended to find out to what extent the observed residuals could be explained by economic or environmental factors. Any unexplained variability would be then attributed to the character of individual farms. Large positive residuals from the recommended values of N input have negative effects on the environment and might also effect agricultural outputs. The intended outcome of this analysis was to establish whether there are any patterns in the actual N input to different crop types. The survey of farmers had to be also referred to the population of all farmers in Great Britain in order to place its conclusions in a wider context.

Figure 4.9 Location of surveyed farms.



Farm_nr	N input [kg Nha^{-1}y^{-1}]	st_dens [SUha^{-1}]	area [ha]
1	181	0.5	181.0
2	3140	33.6	309.1
3	168	6.6	248.4
4	195	1.6	237.9
5	180	8.2	76.7
6	306	9.9	228.8
7	7062	0.0	184.0

Description of the survey.

Eight farms were chosen using a systematic sampling method in which a transect was drawn between Stenton and North Berwick in East Lothian (figure 4.9). Farms were selected at the interval of 1 - 2km. The main criteria for the location of selected farms were the characteristics of soils described by textural class. This methodology was applied principally for measuring nitrous and nitric oxide emissions in a field campaign carried out by the Institute of Terrestrial Ecology (ITE) and the Scottish Agricultural College (SAC), and of which the farmers' survey was an additional part. For the purpose of the survey a simple questionnaire was prepared which was distributed to the farmers by post prior to the field survey in the first instance (table 4.6, Appendix).

The response rate to this first stage of the survey was poor as only one questionnaire was sent back. The second stage involved visiting farmers to obtain information according to the layout of the designed questionnaire form. At this

stage the response rate improved from one to seven farms. The required data from one farm were not available due to the farmer's absence.

The response of the farmers to the questionnaire varied. Four of the surveyed farmers provided detailed answers on their field names, crops grown and N input often referring to existing documentation that is regularly updated in order to provide information to agricultural surveys. It is therefore safe to assume that the information provided by these four farmers was highly reliable. The remaining three co-operated well, however they did not refer to any documentation at the time of the interview, often giving confusing answers, especially when N input was concerned. The information from those farms, although used in the analysis was therefore less reliable.

Results and discussion.

The information obtained in actual N fertiliser input, both in mineral and organic form, was compared to the recommended values of fertiliser input according to crop type. The guidelines in the analysis were defined according to the Technical Notes published by the SAC (Dyson, 1992; Dyson, 1993; Dyson *et al.*, 1993a; Dyson *et al.*, 1993b; Dyson *et al.*, 1993c; Swift, 1988; Younie *et al.*, 1990). The recommended rates of N fertiliser application are regulated by the available N content in soils and the N status of soil is defined by the crop type of the previous year (table 3.9, chapter three). The AC data set did not provide spatially accurate information on the type of crop grown in the previous year, therefore it was assumed that there was no change in crop type from the previous year. As crop rotation is a common agricultural practice, the assumption is not valid in general terms, but within certain spatial and temporal boundaries it could be applied. These limits were to be established in the survey of the farmers that monitored the crop rotation practice.

Crop rotation was first initiated in the eighteenth century in East Anglia ('Norfolk rotation'), where a four-year cycle comprised wheat, a root crop, barley, and a leguminous crop (Clark, 1993). Another more contemporary crop rotation is a seven year cycle in which 3 years of barley are followed by wheat, potatoes, turnips and fallow (one year each). This rotation is commonly practised in South Scotland (farmer's personal comment). On the basis of results of this short survey for the period of 1996-1997 it was difficult to judge how closely the seven-year rotation was followed, but a trend was observed on six farms where low N status crops were followed by moderate or high N status crops (table 3.9, chapter three). The crop types that created a basis for this analysis were registered for 1996 and 1997. There was an observed change in the crop rotation that was registered for the

majority of farms, with the exception of farm 7 that was a wheat monoculture. On average half of all cereal crops were rotated with potatoes, turnips or oilseed rape. The conclusion from this observation suggests that the main assumption of N input model of no change of crop type in consecutive years and maintained N soil status is true only for the farms that practise monoculture. Other farm units can temporarily maintain the crop type in consecutive years, when the arable crops are grown (mainly barley), but generally soil N status oscillates between low and moderate or high. This might explain certain deviations from the standard N input values assumed in the model.

The advice provided on the amounts of N fertiliser required by crops is complex and varies according to the N status of soil, its type and climate. These factors had to be examined additionally when analysing the variability of N input (table 4.7, Appendix). The relationship between the actual N input and the standard recommended N fertiliser levels was studied. First it was established that the distribution of sampled categories e.g. N input, N recommendations, crop type and stock numbers was not normal (figure 4.10a-e). Due to this fact and the small sample size relative to the total population (table 4.8) Spearman's rank correlation analysis was applied to establish the significance of the correlation between the above categories and N input. Multiple regression analysis was additionally used to examine the amount of variability explained by individual factors (categories).

Table 4.8. Spearman's rank correlation coefficient matrix between N input and other factors accounted in the survey of farmers.

N input	N recommended	crop	Livestock	longitude	latitude	area	Nr of crops	random	soil
N recommended	0.749								
Crop	0.270	0.212							
Livestock	0.415	0.451	0.057						
longitude	-0.028	0.102	0.046	0.045					
latitude	0.103	-0.128	-0.088	-0.033	-0.877				
Area	-0.078	-0.200	-0.390	-0.187	-0.109	0.288			
Nr of crops	-0.062	0.037	0.138	0.109	0.866	-0.844	-0.400		
Random	-0.098	-0.117	-0.016	-0.042	-0.222	0.216	0.235	-0.290	
Soil	-0.277	-0.203	0.032	-0.273	0.107	-0.282	-0.098	0.061	0.101

Figure 4.10. Histograms of data used for the analysis of the farms in North Berwick area.

Figure A - Distribution of observed N input.

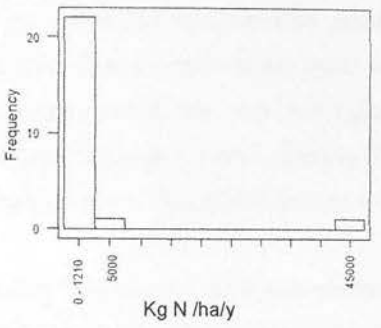


Figure B - Distribution of recommended N input.

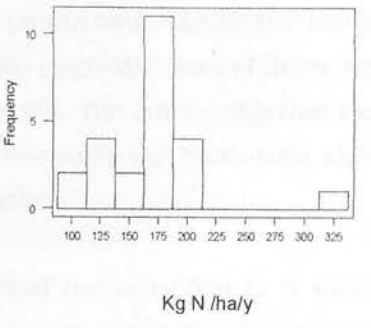
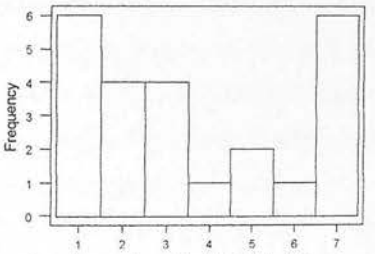


Figure C - Distribution of crop types



Crop types described in table 4.7.

Figure D - Distribution of farms depending on number of crops grown.

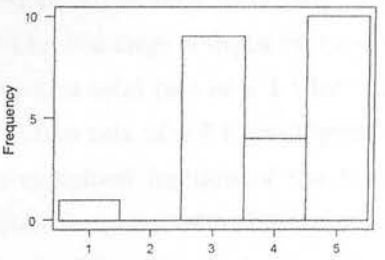
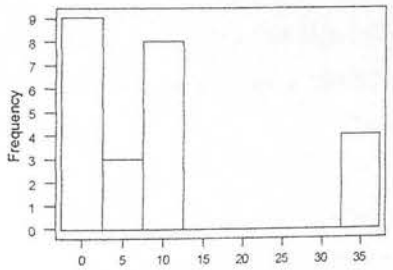


Figure F - Distribution of livestock numbers



Spearman's rank correlation matrix (table 4.8) was analysed for significant correlation between N input and the controlling factors and between the factors themselves. At the chosen significance level of 0.05 the critical values of one- and two-tailed tests were 4.25 and 3.61 respectively. A comparison of the critical values with the correlation coefficients from the survey matrix showed that a very significant correlation existed between N input and N recommendations, and livestock numbers (both relationships have a positive character). Additionally a significant correlation was established between crop type and the area of the field and geographical location and number of crops on the farm. The former correlation indicated that certain crops were associated with particular sizes of fields, but the correlation coefficient was not significant ($p > 0.05$). The latter suggested that the farm type changed when moving from the South-east to the North-west along the transect from a wheat monoculture to crop rotation.

Multiple regression analysis showed that 56 % of the variability in N input was explained by N recommendations. This was not much, especially if one considers a very substantial standard error of residuals of 6520 (factor of 2 - 3 greater than modelled N input). This error could be explained by a few large residuals: a large disposal of pig slurry on farms 2 at a rate of 47 t ha^{-1}; a large N input on farm 6 as a mixture of mineral fertiliser and chicken slurry at a total rate of > 1 t ha^{-1} and a similar practice on farm 7 with a higher N application rate of 6.7 t ha^{-1} (figure 4.9). When soil type was added to the analysis the explained fraction of the N input variability decreased to 53.8%. Taking into account the geographical location of the farm the explained variance decreased further to 52%. The inclusion of stock numbers and of a random factor that represented the individual decision making process of a farmer, caused an even greater reduction of the explained fraction of N input variability to 50%. At the same time the value of the not-adjusted (biased) fraction of explained variance increased to 63.1%. The reason for this discrepancy is unknown.

The statistical analysis did not show an expected influence of environmental factors on the variability of actual N inputs. Spearman's correlation test only established the influence of livestock numbers on the N inputs and recommendations, but this was expected as livestock presence was the main source of organic N. No influence of environmental variables was established in this test either. The shortcomings of the statistical analysis were caused by the very small sample (n=8), which was due to the limited timescale and resources for this survey. It was therefore essential to

analyse the results individually. Different crop groups were looked at to establish N input variability and that was analysed in environmental and economic terms.

There were three arable crops grown on the surveyed farms: winter wheat; winter and spring barley. The standard N fertiliser recommendations for those crops are 180, 170 and 130 kg N ha^{-1} (table 3.6, chapter three). The actual N input for winter wheat relative to the recommended values varied from -66 to up to 10000% (the high input was due to excessive organic fertiliser input on farm 7, figure 4.9). The high N input on farm 7 was explicitly as poultry manure. Even imperfect drainage of the soil (clay loam) did not justify this excessive application that was caused by large organic waste from close-by poultry farms. There is also a considerable error expected due to contradicting farmer's response. When the extreme residual of farm 7 is ignored the upper range of N input is +119%. In the case of barley, actual N input for the winter variety oscillated between 65% and 123% of the standard recommended rate, and for the spring barley the registered N input was between 77% and 116% of the advised N input. The higher inputs of N to wheat might suggest that the crop was used for breadmaking that requires on average 20% more N in order to increase crop output (Dyson and Sinclair, 1993). All the variability could be partly explained by the recommended adjustments for local soil and climatic conditions. Generally higher inputs were required for coarse, sandy textured soils and when average annual rainfall does not exceed 750 mm. From the collected soil samples only farms 2, 5 and 6 (figure 4.9) had sandy loam soil texture that requires additional input of 5 and 8% to winter wheat and spring barley. On those farms higher N input to winter wheat was only registered for farm 6 (figure 4.9). All other higher N inputs to arable crops could be explained by low rainfall in this area *i.e*: not exceeding 400mm per annum (Climate LINK data, section 3.2.3, chapter three) that requires adjustments up to 14, 8 and 20% over standard N input to winter wheat, winter and spring barley, respectively (Dyson and Sinclair, 1993). Generally N input to arable crops was relatively low: that might suggest adjustments due to crop factor *e.g.* lower N content of grain required by malting industry in the case of winter and spring barley. The reduction required by those crops should be in the range 17 and 16%, and in the case when spring barley was used for feed, a further reduction of 4% should be applied. As the purpose of the crops was not known for the farms it was hard to comment on the fertiliser management of the individual farms, but in general terms the N input to arable crops was within the recommended range, except on farm 7 where excessive amounts of organic manure were spread.

Tillage crops, represented on the surveyed farms by potatoes, oilseed rape and calabrese, were grown only on three farms. Actual N input was much higher than required by oilseed rape and potatoes and could not be explained by either climatic conditions or soil texture. The registered N input to oilseed rape was 154% of the recommended amount, and to potatoes 135-143%. Although 10% and 12% of additional N is required in this dry region for those crops and when farmers aim at high yield the extra N input can add up to 20% of N (Dyson *et al.*, 1993), the registered input was well above that recommended value. It was also observed that a considerable proportion of N input to those crops was either in the form of cow manure or slurry. These types of fertiliser can cause larger N_2O emissions, compared to mineral fertilisers, due to increased levels of organic matter and soil moisture that enhance denitrification (Granli and Bockman, 1994).

In almost all cases the grasslands of the surveyed farms received excessive N input that varied from 55% to 266% of the recommended amount, and on farm 2 the amount of N input was a factor of 224 larger than required due to pig slurry disposal. The recommended N fertiliser input was mainly controlled by stocking densities that were considered in the estimation of the standard rate. No further adjustments were envisaged by the Agricultural College (Younie *et al.*, 1990). All N input to grasslands combined mineral and organic fertiliser. Mineral N fertiliser was applied in up to three applications in the spring and summer seasons. Organic manure was either directly deposited by livestock animals during the grazing season, or was applied at the end of summer or/and in autumn. In the case of the high stocking density on farm 2 (34 SU ha^{-1}) it was expected that organic manure was disposed of on grassland throughout the year. Additionally, part of the organic fertiliser was onto potatoes, which received 390 kg N ha^{-1} y^{-1}, 266 % over the recommended 160 kg N ha^{-1} y^{-1}. These very high levels of N input were the effect of not taking organic fertiliser into account as a source of soil N. This is a traditional notion in the farming community where organic manure is regarded as a waste product that needs to be disposed off (Dyson, pers. comm). Levels of soil N are more difficult to predict when N is applied in organic form rather than as mineral fertiliser due to a longer N period before the available N is produced. This pattern is characteristic of intensive livestock farms, where the large amounts of organic waste produced become a burden to farmers and are most commonly disposed of on their fields. This suggestion was supported by two examples: one of the monoculture wheat growing farm, where large amounts of chicken manure were spread; the other of the large pig farm, where pig slurry was applied in large quantities to grasslands belonging to this farmer throughout the year.

In the context of this survey, farmers followed published guidelines of N input on multicrop farms with low and moderate stocking densities, but actual N inputs to grasslands and tilled land were considerably above N recommendations, especially in association with large numbers of livestock (pig and poultry farms).

Conclusions.

The survey of farmers established that the fertiliser practices on the analysed farms very remotely followed the fertiliser practices. The survey was successful in establishing a positive correlation (0.74) between the actual N input and the recommended N. This factor did not prove very strong as it explained only 54% of the N input variability. Other factors expected to improve the correlation through multiple regression analysis failed. The reason for the high unexplained fraction of the variability might lie in the very small sample. It was estimated that up to 266 % more N was applied on the surveyed farms compared with the recommended N input (excluding the very high residuals on farms 2, 6, and 7). There is a high probability that the selected farms might not be representative of the population of all farms in the Lothian Region (table 4.9). It is even more unlikely that they represent the population of all farms in the Tyne-Clyde area, and even less so of Great Britain as a whole.

Table 4.9. Representation of agricultural management in the Lothian regions by the surveyed farms.

	Total area of land classes in Lothian region [10^3ha]	Total area of land classes represented by sampled farms [ha]	Fraction surveyed [%]
number of farms	1163	7	0.6
agricultural land	2134.0	1403.3	0.06
wheat	372.8	589.2	0.16
spring barley	485.1	215.6	0.04
winter barley	165.4	124.4	0.07
potatoes	526.7	58.0	0.001
oilseed rape	707.1	34.4	0.005
grasslands	914.8	240.8	0.03

There were large differences between the farms in terms of preferred management practices even in this small area. It is possible that an increase in the number of surveyed farms might improve the significance of the correlation with other controlling factors like soil type or geographical location. On the other hand enlarging the sampled area might cause greater variability due to environmental

factors. Despite the limits of the results, the selected eight farms are an example of certain management practices that are representative for a large community of farmers. In this respect the presented survey is valid in establishing patterns of N input depending on crop type and livestock husbandry. The sampling methodology that was designed for the field campaign rather than a survey of farmers *per se* was another restriction of this survey. In this type of survey, however, it is very important to use previously established contacts with the farming community and hence gain a high response (7 farms from total of 8) and reliable results. The results of the survey indicated that N input variability was substantial and it might vary from the recommended values by a factor of 3. N input to arable crops established on the basis of recommendations was expected to be most accurate, while inputs to tillage crops and grasslands were unreliable. The established deviations of real N inputs from the recommendations applied in the emission model were used further in the sensitivity analysis (chapter six and seven) to observe the effect of the fertiliser application rates uncertainty on the levels of N_2O and NO emissions.

4.6 VALIDATION OF THE TYNE-CLYDE APPROACH.

Regional inventory of N_2O emissions (Lilly *et al.*, 1998).

The Tyne-Clyde N_2O inventory was compared with a regional inventory of N_2O by Lilly *et al.* (1998) in order to evaluate the approach in this study. The regional inventory of N_2O (Lilly *et al.*, 1998) was prepared for an area located in the East Lothian sub-region, in the vicinity of North Berwick, designated by Eastings 320 and 400, and Northings 650 and 690. Due to its location it is referred to here as the North Berwick inventory. The predictions of N_2O emissions from soils in the North Berwick inventory were based on two controlling factors: soil wetness class and land cover. Soil wetness classes were prepared on the basis of HOST classification and climatic data and they characterised soils in terms of saturation that increases N_2O emissions (Lilly and Mathews, 1994). Land cover data were obtained from the Land Cover of Scotland 1988 (LCS88) map at 1:24000 scale. The modelling of N_2O involved stratification of soils (six wetness classes) and land cover (six categories) in respect of the potential N_2O production that was based on mean emission factors established by Skiba *et al.* (1996). Further analysis of vegetation map led to a sub-division of arable class into three main sub-categories according to altitude (Lilly and Mathews, 1994). In the final stage of modelling, the stratified maps of soil

wetness characteristics and vegetation cover were overlaid to predict N_2O emissions according to established means (Lilly and Mathews, 1994).

Results of the validation.

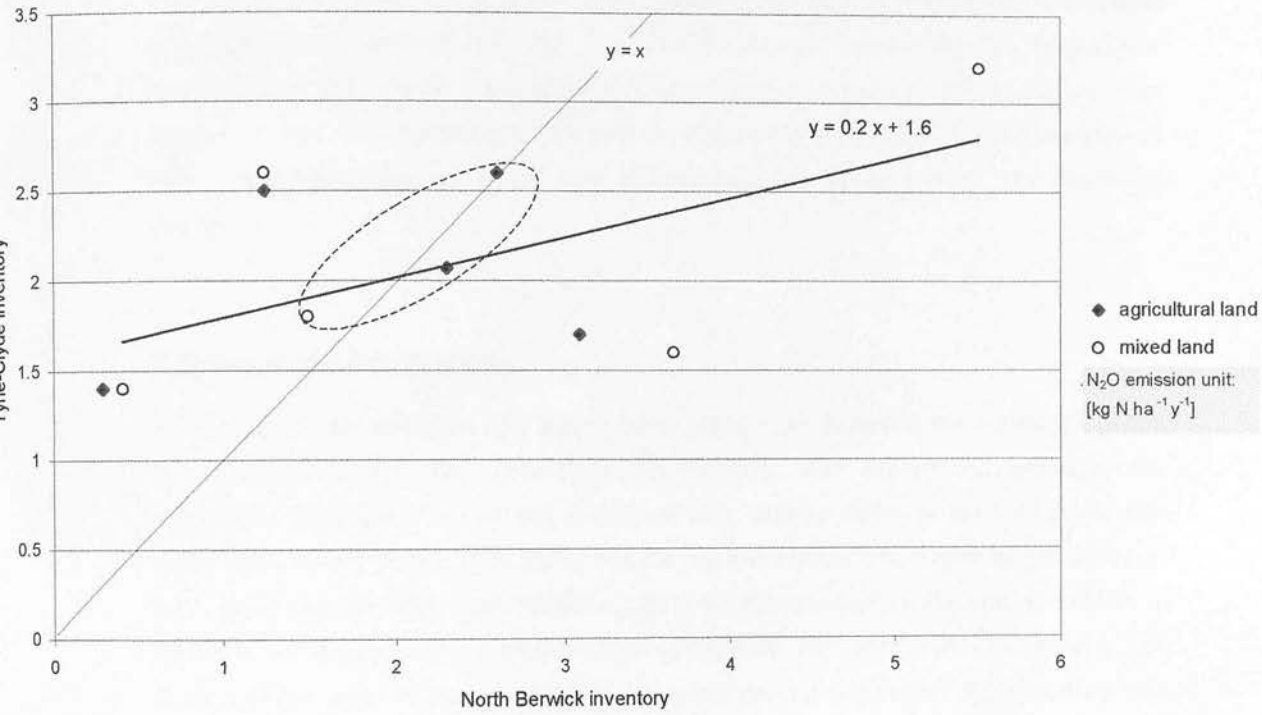
Ten 5 km^2 grids were selected semi-randomly from the area common to both inventories. The selection was based on the land use variability, with five locations of specifically agricultural character and the remainder characterised by mixed agricultural and seminatural land. Land use was the important variable controlling N_2O emissions in both approaches presented here, that applied land-use derived emission factors. The estimates of the two models were compared with an application of linear regression analysis.

Both samples had bi-modal distributions with median N_2O emissions of 2.5 and 1.9 kg N ha^{-1} y^{-1} for the Tyne-Clyde and the North Berwick inventory, respectively. Higher emission variability was suggested for the selected locations in the North Berwick inventory that estimated N_2O emissions in the range of 0.3 – 5.5 (sd=1.6) kg N ha^{-1} y^{-1} compared with the Tyne-Clyde estimates that predicted N_2O emissions range of 1.4 - 3.5 (sd=0.8) kg N ha^{-1} y^{-1}.

The rudimentary requirements of the linear regression method are the normal distribution of input data sets and error-free independent variables (Shaw and Wheeler, 1994). The aim of this analysis to compare the two approaches, justified a relaxation of stringent requirements of the statistical method (chapter five). The estimates for the selected locations did not comply with the normal-distribution requirement, but the data sets were not transformed, as otherwise the interpretation of the results would be impossible.

The results of both inventories were also expected to depart from the actual N_2O emissions, the choice of independent variable was therefore related to the resolution of the models. The results of the North Berwick inventory were chosen as the independent variable in the regression analysis due to the data format (vector) and an inclusion of soil wetness and altitude together with N input as important controlling variables. The results of the Tyne-Clyde study were chosen for the dependent variable in the linear regression analysis due to lost details in devising the raster data format and the single variable of N input to soils used to estimate N_2O emissions.

Figure 4.11 Validation of the Tyne-Clyde inventory against the North Berwick model.



The established linear trend was not significant (F=3.13, p=0.11) that might indicate that the presented relationship (figure 4.11), which explains only 28% of the variability between the two approaches, might be biased. The two sets of results were relatively weakly correlated (cv = 0.53). There was no clear trend in the distribution of the residuals that might indicate types of land classes for which the two approaches produced different estimates. The North-Berwick inventory produced higher estimates of emissions in the areas where N_2O calculated by the Tyne-Clyde inventory exceeded 1.9 kg N ha^{-1} y^{-1} (figure 4.11). On the other hand the Tyne-Clyde inventory estimated higher emissions for two locations of agricultural character and two of seminatural for which the North-Berwick inventory estimated emissions below 1.49 kg N ha^{-1} y^{-1} (figure 4.11).

Only on three occasions were similar emissions predicted (difference < 0.4 kg N ha^{-1} y^{-1}). These locations were on agricultural soils: (1) (Easting=353, Northing=683) dominant arable land and intensive poultry and pig farms; (2) (Easting=335, Northing=664) area of dominant grassland (56% of total grid area) with large number of cattle, sheep and pigs; (3) (Easting = 358, Northing = 677) mainly agricultural land with a variety of tillage and arable crops and 3% of deciduous

forest. Other points presented very contrasting estimates with the difference in the range 0 – 2.31 kg N ha^{-1} y^{-1}.

The regression analysis and the direct comparison of the predictions confirmed little agreement between the two models. The overestimation by the Tyne-Clyde study of the areas with expected lower emissions was due to differences in data formats of the two approaches that had an effect on the results. The implications of the differences between these two approaches are presented in the following section.

A review of the two methods.

Linear regression analysis has shown large differences between the estimates of the North Berwick and the Tyne-Clyde inventories. The differences between the estimated emissions in selected locations were due to different data formats and some differences in the strategy of estimating emissions. The regional inventory of N_2O emissions by Lilly *et al.* (1998) applied stratification of landscape according to altitude, soil types and soil wetness characteristics. This increased the detail of the final N_2O emission estimates. With the detailed spatial resolution of input data sets (1:25000) it produced a highly variable N_2O emission model for the area of study.

The Tyne-Clyde inventory used data in raster format and produced final results at a coarser resolution of 5km grid. This inventory was prepared for a larger area and due to restricted data availability it produced less detailed results that represented means of N_2O emissions for each 5 km^2. This is considered the main reason for such different outcomes between the presented models that both used the same approach of land use-variable emission factors. In one selected location (Easting=367, Northing=667) the comparison presented supportive evidence for that. N_2O emission predicted by the Tyne-Clyde inventory was 1.4 kg N $ha^{-1}y^{-1}$, while the North Berwick inventory estimated 0.42 kg N ha^{-1} y^{-1}. The observed difference was the effect of spatial variability of N_2O emissions presented by the North Berwick inventory in vector format. The predicted N_2O emissions suggested that the selected location was forested (table 4.10). As a contrast, The Tyne-Clyde inventory represented mean N_2O emission for all land cover in the 5km grid that contained the selected point. In that area, a small proportion was represented by forest (> 230 ha predominantly coniferous forest), with the remainder dominated by moorland used for hill grazing (> 2000 ha). The presence of sheep (> 7400) led to

some N enrichment of soils that added to atmospheric N deposition (11.4 kg N ha^{-1} y^{-1}). The character of the selected grid dictated the higher N_2O emission estimated by the Tyne-Clyde approach. The differences between the two approaches were therefore the combined effect of data format and differences in methods of estimating N_2O emissions. The following section presents detailed comparison of the methods used by the two inventories for major land categories.

Table 4.10. Mean N_2O emissions for different land classes applied by Lilly *et al.* (1998)

Emission class		Soil wetness					
		I	II	III	IV	V	VI
Rough grass/ moorland	2	0.3	0.3	0.3	0.3	0.3	0.3
Woodland	3	0.42	0.42	0.42	0.42	0.42	0.42
Golf course	4	0.67	0.67	1.21	1.23	1.76	1.76
Improved pasture	5	1.24	1.24	3.04	3.09	4.88	4.88
Ley/arable< 75m	6a	1.49	1.49	2.6	2.76	4.0	4.19
Ley/arable 75m-150m	6b	1.77	1.77	3.52	3.66	5.51	5.65
Ley/arable >150m	6c	2.3	2.3	5.15	5.28	8.18	8.26

N_2O emissions from seminatural land.

In the regional inventory Lilly *et al.* (1998) based their approach on mean absolute values of N_2O emissions obtained in two field campaigns (Skiba *et al.*, 1996; Velthof et al., 1994). In the Tyne-Clyde inventory the emissions from seminatural land were based on a similar approach, although the estimates for forests distinguished between major tree species. For deciduous and mixed forests a higher emission factor of 0.78 kg N ha^{-1} y^{-1} was used in the Tyne-Clyde inventory than the estimate of 0.42 kg N ha^{-1} y^{-1} applied by Lilly *et al.* (1998). On the other hand, the emissions from coniferous woodlands were lower in the Tyne-Clyde approach, as they closely followed the field emission data (Skiba *et al.*, 1996). In areas of greater proportion of coniferous forests N_2O emissions proposed by Lilly *et al.* (1998) were more likely to be overestimated, but for deciduous and mixed woodlands the North Berwick inventory produced too low values.

N_2O emissions from agricultural areas.

For agricultural land a different approach was undertaken in the Tyne-Clyde inventory that estimated N_2O emissions from both mineral and organic N input (figure 4.3). The mean N_2O emission values applied in the North Berwick inventory by Lilly *et al.* (1998) were compared with the calculated N_2O emissions based on the recommended N input as in the Tyne-Clyde inventory. From this comparison it

became apparent that for tilled land higher estimates were used in the former model. Arable crops occurring in the sampled points were represented by two varieties – wheat and spring barley for which comparison was made. Wheat had the recommended N input of 180 kg N ha^{-1}. This produced emissions of approximately 0.9 kg N ha^{-1} y^{-1} when applying the corresponding emission factor of 0.5% (table 4.1). In a similar way N_2O emission from spring barley was estimated at 1.0 kg N ha^{-1} y^{-1}. These two estimates were well below even the lowest mean absolute emissions used by Lilly *et al.* (1998) and presented in table 4.9. An increase in N_2O emissions with the altitude and higher soil wetness class (table 4.9) led to an even larger gap between the models. Those differences were observed for two selected locations (Easting=378, Northing=657 and Easting=335, Northing=668), where the Tyne-Clyde inventory estimated N_2O emissions of 3.2 and 1.6 kg N ha^{-1} y^{-1} and the North-Berwick inventory predicted 5.51 and 3.66 kg N ha^{-1} y^{-1}, respectively.

The Tyne-Clyde inventory assumed that grasslands with medium stocking densities (2-5 SU ha^{-1}) received 200 and 210 kg N ha^{-1} depending on mown or grazed management. In those areas mean N_2O emissions were expected to sum up to 3.6 and 4.2 kg N ha^{-1} y^{-1} according to applied emission factors of 2 and 1.8% (table 4.1). In areas where stocking densities were over 5 SU ha^{-1}, the mean emissions of 5.4 and 6.5 kg N ha^{-1} y^{-1} were expected from mown and grazed grasslands. In areas of intensive livestock husbandry the Tyne-Clyde estimates were higher than those proposed by Lilly *et al.* (1998) even on very wet soils (table 4.10). Three selected locations: (1) Easting=373, Northing=672; (2) Easting=333, Northing=656; (3) Easting=333, Northing=665 were classified by Lilly *et al.* (1998) as managed grassland with estimated N_2O emissions in the range from 1.24 to 3.09 kg N ha^{-1} y^{-1} depending on soil wetness class (table 4.10). N_2O emissions estimated by the Tyne-Clyde inventory for those locations ranged between 1.7 to 2.6 kg N ha^{-1} y^{-1}. The lower estimate by the Tyne-Clyde inventory for location (3) could be explained by a higher proportion of tilled land (51% of total area) and some contribution of forest (8%) that lead to moderate total N input in that 5km grid (276 kg N ha^{-1} y^{-1}).

N input proved to be the main controlling factor of N_2O emissions in several studies (Beauchamp, 1997; Bouwman, 1994; Granli and Bockman, 1994; Skiba *et al.*, 1996; Vos *et al.*, 1994; Yamulki *et al.*, 1995). This factor, varied according to crop types and management practices associated with livestock husbandry with additional consideration of atmospheric N inputs, determined the emissions from soils in the Tyne-Clyde inventory. The North Berwick inventory also applied land use-dependent emission factors and introduced the stratification of arable crops

and grasslands according to soil wetness class and altitude. As the Tyne-Clyde study considered livestock numbers and atmospheric deposition in addition to standard application of mineral N fertiliser, the estimates produced by this inventory should be higher in agricultural areas of intensive livestock husbandry and on semi-natural land with enhanced atmospheric N inputs. On the other hand the absence of soil moisture from the prediction method of N_2O emission in the Tyne-Clyde inventory was a major restriction of this approach.

Uncertainty of the Tyne-Clyde estimates due to spatial variability.

The two models vary considerably for two major reasons. Firstly, the details of the produced output maps were greater for the North Berwick inventory, that explained large variability of the predictions. The design of this inventory accounted for land use types like forests, representing small proportions of the area. Secondly, there were some differences in the methods of estimating N_2O emissions in the presented models that caused higher estimates from arable land by Lilly *et al.* (1998). As the Tyne-Clyde inventory estimated mean N_2O emissions for each 5km grid, the residual differences between the two approaches indicated the loss in spatial variability of N_2O emissions due to generalisation of the input data.

To observe departures of N_2O emissions estimated by the Tyne-Clyde study due to land class variation within the ten selected 5km grids (described above) residuals were derived as differences between the estimates of the two inventories. For each individual location a random error was estimated with equation (3.4) (chapter three). Mean N_2O emission estimated by the Tyne-Clyde inventory for the selected ten locations was in the range of 1.9 ± 1.0 kg N ha^{-1} y^{-1} (p=0.05). The location, for which the estimated N_2O emission range was the largest (1 – 5.4 kg N ha^{-1} y^{-1}), was characterised by mixed land use with grassland and tilled land agricultural practices contrasting with deciduous and coniferous forest (8% of total grid area). The smallest range of uncertainty from 1.3 to 1.9 kg N ha^{-1} y^{-1} was observed on uniformly agricultural land with mixed tilled land and grassland (Easting=335, Northing=668). This analysis showed that N_2O emissions could vary from the estimated mean by 16 – 68%. As some of the differences are caused by the effect of additional variables used in the North Berwick inventory, the locations on which the soil wetness class affected estimated emission (grasslands and tilled land) were excluded. Only two locations (Easting=367, Northing=667; Easting=352, Northing=662) were classified by the North Berwick area as semi-natural land

where soils wetness class did not effect the estimated N_2O emissions. On those locations the mean N_2O emissions estimated by the Tyne-Clyde study for both grids were 1.4 kg N ha^{-1} y^{-1}. After excluding the effect of soil wetness class the residual error indicated that N_2O emission could vary by 0.7 kg N ha^{-1} y^{-1} (50%) due to land use variability in each grid.

Conclusions.

The comparison of the N_2O emissions estimated by the North Berwick and the Tyne-Clyde study showed some major differences between the two studies. The detailed analysis of the two approaches suggested that the different results are due to the additional consideration of soil wetness class and altitude as controlling factors in the North Berwick inventory and consideration of livestock density and atmospheric N inputs by the Tyne-Clyde study. The main difference, however, is caused by data formats (raster and vector) that determined spatial variability of N_2O emissions estimated by each inventory. The North Berwick study used an emission model with preserved spatial detail. The Tyne-Clyde study, on the other hand, has an advantage of a generalised approach more suitable for a larger scale study. An estimated 'error' due to all mentioned differences ranged between 16- 68%, while the loss of spatial detail in the Tyne-Clyde study on the basis of two selected locations was observed to vary N_2O emissions by 50%.

4.7 CONCLUSIONS FROM THE TYNE-CLYDE STUDY.

N_2O emission inventory for the Tyne-Clyde area recognised agriculture as the main source of N_2O due to high N fertiliser input and intensive livestock husbandry. Distribution of N_2O emissions in the studied region showed a certain degree of clustering in areas of intensive grassland management and high stocking densities. The spatial variability of agriculture in the Tyne-Clyde area with a larger proportion of grasslands in the West and of tilled land in the East, caused much higher N_2O emissions in the West.

The single controller of N_2O emissions in the Tyne-Clyde study was N input to soils that was estimated with an application of the recommendations of good fertiliser practice. Reliability of the published recommendations in estimating real fertiliser application rates was tested with a small survey of farmers in the vicinity of North

Berwick. The conclusion from the small survey showed that fertiliser recommendations offered a good basis for estimating general trends in fertiliser management practised on farms, especially on arable land. In areas of high stocking densities and on some tillage crops, however, they proved to be inaccurate as real N inputs were observed on average to exceed the recommendations by a factor of 3. As the inventory was based on the published guidelines of good fertiliser practise, the results of those emissions might have been affected by individual management practices on farms in this area.

The applied emission factors in the inventory of N_2O emissions in the Tyne-Clyde helped to estimate relatively accurate levels of emissions. The comparison of the results with the North-Berwick N_2O emission inventory revealed, however, considerable differences between the two approaches. As the same emission factors were applied in both models this indicated that some other reasons caused the discrepancies. Lilly *et al.* (1998) applied soil moisture as an important environmental factor in estimating N_2O emissions that was not considered by the Tyne-Clyde inventory. The limitation of Lilly *et al.* (1998) approach was not to consider high organic N inputs due to large stocking densities provided for the Tyne-Clyde inventory by the AC. The high organic N inputs associated with intensive livestock farming proved very significant for N_2O emissions in the Tyne-Clyde inventory. Despite large uncertainties in estimating real N application rates established by the survey of farmers (section 4.5), the location and numbers of livestock improve predictions of N_2O emissions.

The reliability of N_2O emission estimates was also influenced by the accuracy of the input data. The two data sources of land use applied in this inventory - the Agricultural Census and the Land Cover Map showed differences in their definition of grasslands and tilled land. The disagreement between the two data sources was expected to vary the estimated N_2O emissions by approximately 30% (section 4.4). The areas of highest error were related to the spatial distribution of tilled land and grassland. The characteristics of the input data and their limited spatial resolution determined the details of the results. The results of the N_2O emissions inventory of the Tyne-Clyde area represent mean N_2O emissions for each studied 5km grid within this region. This inventory was designed to present general regional variability. The comparison with the N_2O emission model by Lilly *et al.* (1998) showed that the latter approach is more accurate at the local scale. The main advantage of the North-Berwick study is the availability of the detailed input land cover and soil data. The spatially detailed N_2O model of Lilly *et al.* (1998) who based

estimates on land cover classes, altitude and soil moisture, presented a good solution for the local scale due to the vector format of the input data that maintains spatial reference. The raster format of the data used in the Tyne-Clyde study has unquestionable disadvantages at the local scale of the N_2O emission study presented here. At a larger scale, however, the coarser resolution of the model offers an advantage of a simplified view that presents general trends more effectively.

Implications for the N_2O emission study for Great Britain.

This regional study outlined a number of problems that need to be considered in the further work. The main issues examined by the pilot study were the sources of N input data and the correspondence of the agricultural and seminatural land data sets. The fertiliser recommendations showed a considerable departure from the fertiliser application rates on some surveyed farms. The observed variability of actual N application from the recommendations will be applied in the sensitivity analysis to establish uncertainty of N_2O emissions due to N input variability. As land use was observed to be an important factor in the N input variability, uncertainties of N_2O emissions should be greater in the West where a higher proportion of grasslands is observed. The largest residuals in actual N inputs were associated by the survey of farmers with very high livestock densities. These sources should be accounted for at the national scale with the AC data of livestock numbers. Some consideration should also be given to the problem of incompatibility of the LCM and the AC in providing information on the vegetation cover. The established incompatibility between these two data sources should be also studied at a national scale in order to observe the areas where this error has an effect on the estimated N_2O emissions. Further modelling of N_2O emissions at the national scale should also include soil moisture and temperature as they were observed to control the N input effect on N_2O emissions (sections 2.2.5.3 and 2.2.5.4, chapter two). The relationship between the controlling factors of N input, soil moisture and temperature with the levels of N_2O emissions is examined in the following chapter.

APPENDIX.

TABLE 4.6 Questionnaire form used in the survey of farmers.

AREA OF CROPS, GRASS AND OTHER LAND AND N INPUT

*Please, state what **fields** you manage, their **area** in **ha** and what **type of crops** (including grasslands, fallow and set aside) were grown on these fields in **1996**. Please, show also the **amount** (in **kg/ha**) and **type** of **mineral N fertiliser** which is applied to those fields and the **month** of the application.Please, specify what type of crops will be grown on these fields this year (**1997**).*

field name	*area [ha]*	*crop type in 1996*	*N FERTILISER IN 1996*			*crop type in 1997*
			amount [kg ha]	*type*	*month*	

MANURE / SLURRY INPUT

Please, sho how much manure/slurry is put onto your fields, what type it is (like cows manure or sheep manure etc.) and when it is applied by specifying the month.

PLEASE, SPECIFY INPUT OF MANURE IN **units**.

field name	**MANURE / SLURRY**			application method
	amount [units]	type	month	

TYPES AND AMOUNT OF LIVESTOCK

Please, show how many animals you keep,the proportion of the year they are kept indoors, grazed outside and in the case of outside grazing - what area of grassland they are grazed on.

	NUMBER	*PERIOD- IN*	*PERIOD- OUT*	*AREA [ha]*
Dairy Cows				
Cattle ***(male and female)***				
2 yr. and over				
under 2 yr.				
Calves				
Sheep ***(male and female)***				
2 yr. and over				
under 2 yr.				
Pigs				
Goats				
Total Poultry				
Other Livestock				

Table 4.7. Data used in the statistical analysis.

Farm Nr	Crop type	Crop type symbol	Number of crops on the farm	Field area [ha]	Stocking density [SUha^{-1}]	N input [kgNha^{-1} y^{-1}]	N recommended [kgNha^{-1} y^{-1}]
4	W/barley	2	5	22.7	1.6	210.0	170
	Wheat	1	5	122.8	1.6	215.0	180
	O/rape	4	5	34.4	1.6	303.3	175
	S/barley	3	5	34.0	1.6	100.0	130
	Grass	7	5	24.0	1.6	60.0	110
1	W/barley	2	3	28.0	0.5	205.0	170
	S/barley	3	3	18.0	0.5	120.0	130
	Grass	7	3	135.0	0.5	243.1	110
2	W/barley	2	4	51.7	33.6	110.0	170
	Wheat	1	4	77.2	33.6	140.0	180
	Potatoes	5	4	25.2	33.6	390.0	160
	Grass	7	4	20.0	33.6	47200.	325
3	S/barley	3	3	120.6	6.6	155.8	130
	Wheat	1	3	103.8	6.6	207.0	180
	Grass	7	3	24.0	6.6	64.0	210
6	W/barley	2	5	22.0	9.9	140.0	170
	Wheat	1	5	110.4	9.9	200.0	180
	Potatoes	5	5	33.2	9.9	216.0	160
	Calabrese	6	5	38.8	9.9	210.0	200
	Grass	7	5	24.4	9.9	1210.0	210
7*	Wheat	1	1	184.0	0.0	7062.0	180
5	Wheat	1	3	20.3	8.2	118.0	180
	S/barley	3	3	43.0	8.2	126.0	130
	Grass	7	3	13.4	8.2	450.0	210

* the high N input might be due to the uncertainty of the data source

CHAPTER FIVE

Empirical model of N_2O emissions.

5.1 INTRODUCTION.

Field measurements have revealed that N_2O emissions are controlled by a variety of physical and biological factors with soil N content, soil temperature and moisture, soil C content and land use being significant. Agricultural N fertilised soils are the main contributor to N_2O emissions in the UK, responsible for 86% of total N_2O emissions from soils (Skiba *et al.*, 1996). The contribution of agriculture to the UK total of N_2O emissions is well above the global mean estimate of 50% from this source (Bouwman, 1990).

This chapter attempts to define a predictive model of N_2O emissions on the basis of observed relationships between the responses in N_2O flux and the controlling factors of N input, soil temperature and moisture, soil C content and land use type. The established model will be applied to determine the distribution and amounts of N_2O emissions from British soils.

Several models predicting amounts of N_2O emissions apply correlation coefficients found for the main controlling factors through regression analysis (Bouwman 1995; Skiba *et al.*, 1997; Velthof *et al.*, 1996a). Multivariate regression analysis was chosen in the current study to establish the controlling factors of N_2O emissions and empirical relationships between those factors and the emissions observed. There are two main issues in the method presented in this study. The first relates to the rules of the statistical analysis method applied to the compiled field measurements to define the empirical relationship. Linear regression analysis has well defined requirements of input data that restrict its application (Ebdon, 1977; Snedecor and Cochran, 1978 and Webster, 1997). Once the regression model describes a valid relationship between the N_2O emissions and the controlling factors, the limits of its application need to be established. This is the second issue in this approach. The models employed in many soil studies at the field level to

describe patterns of N_2O emissions, predict their values and compare the outcomes with the measurements (Skiba *et al.*, 1997; Velthof *et al.*, 1996a). The problem of valid applications of defined models is one of the most important issues of those studies. Bouwman (1995) warned about the restrictions of his model which were mainly due to the limited data that were applied to define that model. Velthof *et al.* (1996a) restricted the application of their model to managed grasslands on peat.

This chapter presents the method in which the empirical regression model of N_2O emissions from soils was defined. The multivariate regression analysis was based on the N_2O experimental data set that was obtained from literature. The N_2O emissions were measured in several locations. The measurement methods and description of the compiled data set are presented in the section below. The following section 5.3 attempts to establish the advantages and limitations of this modelling approach in the view of the presented data set. This discussion is followed by the results of the statistical analysis and the description of the empirical model of N_2O emissions (section 5.4). Finally the certainty limits of the defined model are assessed in terms of the predictions made for the field studies collected from the literature (section 5.5) and the input data parameters (section 5.6).

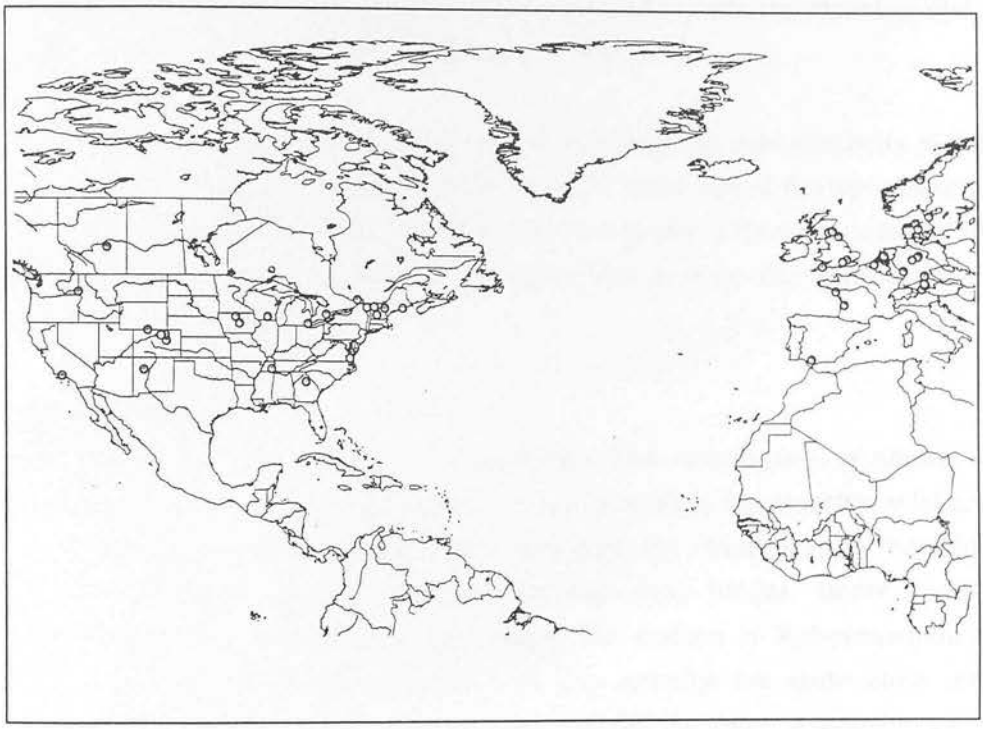
5.2 N_2O EXPERIMENTAL DATA SET.

5.2.1 The origins of the data.

Data of N_2O measurements were compiled from the literature published in the last 18 years that represent a variety of land use and soil types. As insufficient data were available from Britain, the spatial boundaries of the emissions data were extended to the world's temperate climate regions and data were obtained from north-west Europe and North America (figure 5.1). Published field emission results also provided information on the factors controlling the emissions: N inputs, temperature (soil or air), soil moisture, organic C content, soil textural class, land use and other information like the frequency and time scale of measurements, and the site location. The compiled data varied in the extent of information provided for these controlling variables (discussed in detail later in this section). Therefore the complete data set for the multivariate regression analysis was only represented by 107 out of 306 sites. Furthermore, 18 data points had to be discarded from the original data set due to high residual values of either N_2O emissions or the

controlling factors. 29 data points were excluded due to their laboratory origins according to a generally accepted rule they should not be associated with the field measurements, which is discussed further in this section.

Figure 5.1 Spatial distribution of N_2O emission measurements.



5.2.2 Measurement methods.

There are a number of approaches in measuring N_2O fluxes from the soil-atmosphere interface applied in experimental work. The main methods used in the field studies of the compiled N_2O data set are presented in the following section.

Closed box method.

This is most commonly applied field measurement method of N_2O emissions. There are various designs of the equipment used in closed chamber N_2O flux measurements, but the same principle is common to all. This is based on an enclosure, usually a frame with an attachable sealed cover, that is placed on a chosen soil plot for a period of time (frequently lasting 30 minutes) to capture the gases emitted from the soil. Nitrous oxide is estimated as a function of its concentration difference between the ambient gas and the sample drawn from the box as presented by equation (5.1).

$$F = (\rho\ V\ A)\ dc/dt, \qquad \textbf{(5.1)}$$

where F is the emitted nitrous oxide; ρ - density of this gas (2kg m^{-3}); V - volume of the chamber above the ground; A - surface of the soil enclosed by the box; dc - change of volumetric concentration of nitrous oxide inside the chamber and dt - time period of the measurement (Denmead, 1979).

This method is commonly used because of its robustness and simplicity of design. Low cost of maintenance and operation, and the small size of the equipment make it flexible in transport and installation. The drawbacks of its size are linked to the spatial and temporal variability of emissions that increase the uncertainty of the estimated mean values.

Soil incubation.

The complexity of the processes of production and consumption of nitrous oxide and the numerous controlling factors of those processes, result in many laboratory based studies applying soil incubation. Soil cores are obtained from the field and placed in sealed containers, often screw-tap glass bottles, under conditions simulating the environment of their origin. The method of N_2O measurement is based on the closed box principle, and gas samples are quite often directly transported to a gas chromatograph that reduces the error of possible gas leak during transport between the field and the laboratory. The fact of controllable environmental factors e.g. soil temperature and soil moisture makes this technique attractive especially in research establishing relationships between emissions and their controlling factors. There are two problems with measurements of N_2O emissions obtained by incubation. Firstly, the controlled conditions in a laboratory depart considerably from the dynamic and unpredictable *in-situ* environment hence the relationships derived in a laboratory are not transferable to the field situation (Hutchinson *et al.*, 1993; Williams *et al.*, 1998). Secondly, the removal of soil cores from their original location disturbs soil air channels (Jarvis *et al.*, 1994) that may have a big effect on N_2O emissions. Due to the many reservations outlined in literature, the experimental data established in the laboratory environment were excluded from the analysis presented in this chapter.

Micrometeorological method.

The micrometeorological method that estimates mean fluxes from large areas has been introduced in recent years to accommodate the spatial and temporal variability of fluxes (Arah *et al.*, 1994; Mosier and Hutchinson, 1981; Sharpe and Harper, 1997; Smith *et al.*, 1994; Wagner-Riddle *et al.*, 1997). This method is based on a concept of identical fluxes at the soil - air interface and at the reference level of measurement and assumes turbulent transport of gas parcels dictated by the physical conditions of the atmosphere (Bouwman, 1990). The measurement should be obtained over a large, relatively flat and uniform surface on the upwind fetch. The micrometeorological technique estimates vertical fluxes with various methods e.g. flux gradient, aerodynamic method, Bowden ratio or eddy correlation. All of them require elaborate measurements of atmospheric physical properties e.g. wind velocity, temperature gradient and concentration of trace gases within the constant flux layer (Bouwman, 1990). All the mentioned methods have their limitations due to complexity of the processes occurring in the atmosphere and the elaborate measurements. This in turn requires very sensitive equipment that considerably increases costs of maintenance and installation. High costs of equipment, the need for a large uniform parcel of land cover and specific conditions of the atmosphere (e.g. considerable net radiation for the Bowden ratio method, or stable conditions of air turbulence for aerodynamic method) make this methodology difficult to apply in most studies.

Advantages and limitations of the closed box and micrometeorological methods.

The measurement methods of N_2O emissions have different characteristics that cause limitations when trying to account for the great complexity of soil bacterial processes responsible for the production of this gas. Heterogeneous soils present a dynamic environment for the bacterial processes that are responsible for the large spatial and temporal variability of N_2O emissions. A few field campaigns have investigated this problem. Velthof *et al.* (1996b) in a field study of nitrous oxide emissions from clay under grazed and mown grasslands, concluded that the maximum distance between small chambers of 20 cm internal diameter would have to be 6 m to obtain a representative mean flux measurement. Others reported coefficients of variations (cv) for emissions ranging from 42-97% for N_2O (Clayton *et al.*, 1994) to 161-508% for $N_2O + N_2$ (Folorunso and Rolston, 1984). An increased release of N_2O emissions from soils follows immediately after the coincidence of optimal condition of their production processes (principally denitrification and

nitrification) and diffusion through the soil profile that vary temporary. Their variability in time has been researched in a few field studies with the design of automated chambers that enable continuous or very frequent sampling (Mummey *et al.*, 1997; Velthof *et al.*, 1996a; Velthof *et al.*, 1996b). Velthof *et al.* (1996b) found small diurnal flux variations except immediately after fertilisation, while Mummey *et al.* (1997) estimated a range of change at 23-130% and reported variation of 171% during an annual study, with cv of 71% in August.

Micrometeorological methods account for great spatial variability by interpolating the flux over large areas (> 1 ha). Closed chamber methods try to establish the spatial variability by replicate measurement plots. When means from two sample points collected from a maize field in Colorado using the chamber method were compared to the aerodynamic micrometeorological method, the results were corresponding (258 ± 163 ng N m^{-2} s^{-1} from chamber with 350 ng N m^{-2} s^{-1} from aerodynamic method) (Mosier, 1990).

Changes in time are equally difficult to account for, as the continuous measurements are only possible with the use of specially designed automatic chambers. Their application is still very limited due to complexity of the equipment and the restricted length of the measuring period. Long term studies (with the total measuring period over one year) were observed to produce more accurate results. The most common strategy is to use a small chamber method and repeat measurements at similar times on a daily or weekly basis (depending on the length of the field campaign, the prevailing climatic conditions and any N additions to soils). This strategy was based on observations of the diurnal distribution of N_2O emissions that established a certain regularity in the flux oscillations (Aneya *et al.*, 1997; Christensen, 1983).

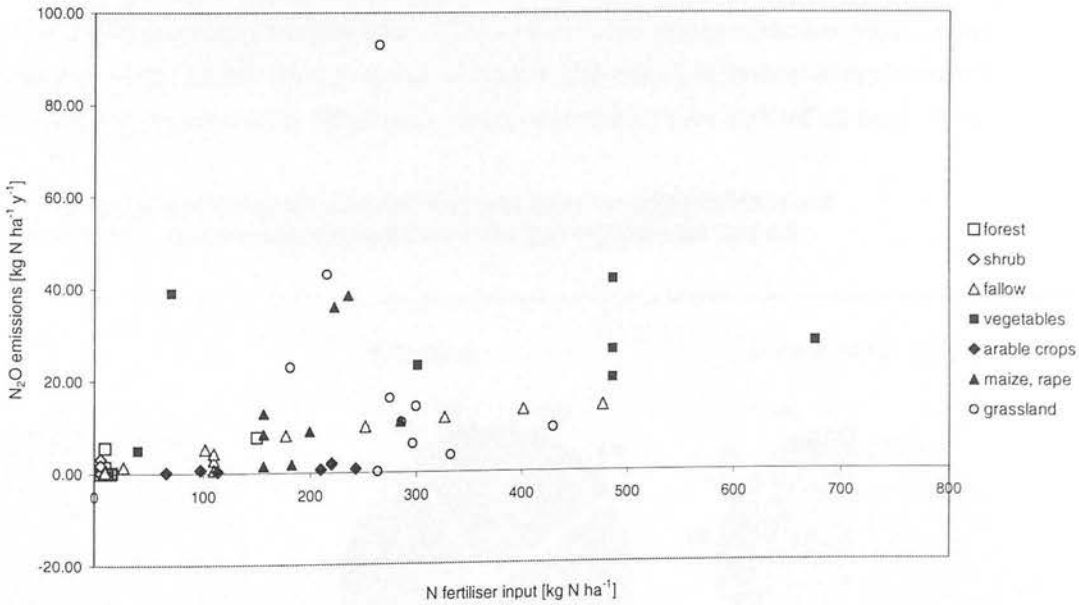
In the field studies used for preparing the experimental data set of N_2O field measurements, the static chamber technique was applied most often (77% of all data were measured using the closed box method). Large temporal variability requires frequent measurements over prolonged periods of time, but only 23% of 78 compiled studies lasted more than one growing season and 23% were short-term experiments, not longer than one month. 14% of field studies carried out only a few measurements through the entire period of study. Spatial and temporal variability lead to uncertainty of the estimated mean emissions at the field level. The unknown spatial variability is reduced with an application of micrometeorological methods. This method is applied, however, only in three of the selected studies (Mosier and

Hutchinson, 1981; Sharpe and Harper, 1997; Wagner-Riddle *et al.* 1997). The implications of the widely applied close chamber method for the model results are that a great data scatter of N_2O emissions is expected and some difficulty in model definition might occur. The variable time-scale of the experiments might result in some incompatibility of the data.

5.2.3 General characteristics of the experimental N_2O data set.

The collected studies showed great variability in N_2O emissions with some differences observed for different land classes (figure 5.2). While N_2O emissions were relatively low from semi-natural land, great variability was observed among the agricultural soils. For grasslands this variability was the most evident, while maize, oilseed rape, fallow land and vegetables were associated with generally high emissions. Cereal crops were at the bottom range of N_2O emissions from agricultural land. As N_2O emissions were observed to vary for different ecosystems, the experimental data set had to be evaluated in terms of the representation of the main land use and soil types.

Figure 5.2 N_2O emissions from different land cover types as a function of N input

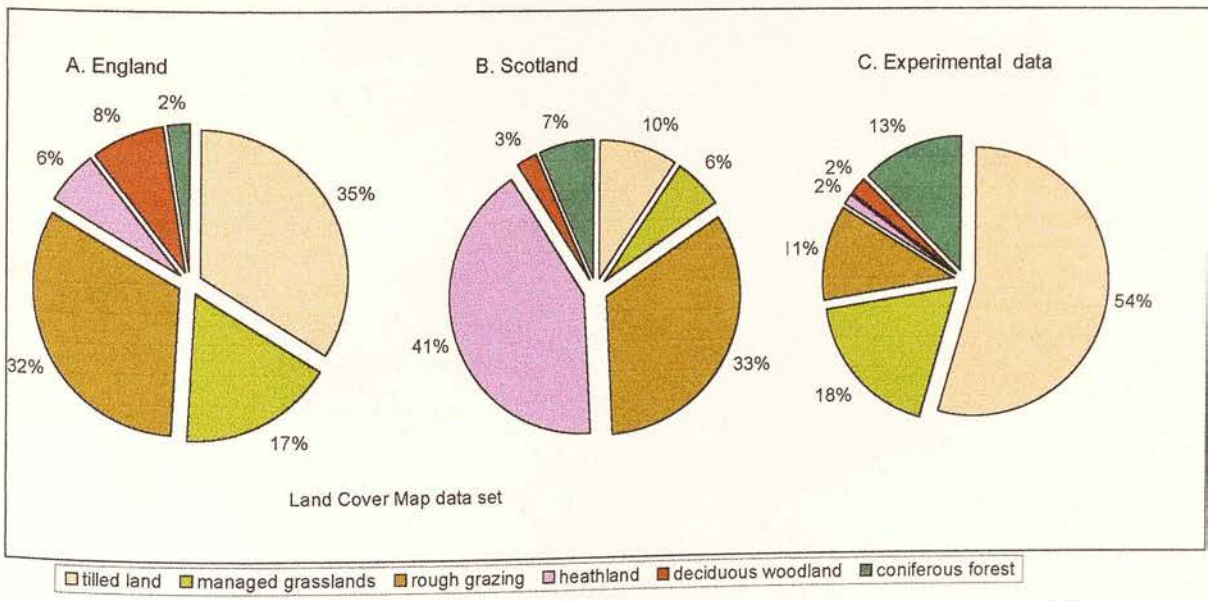


Land use. There were 23 different classes recorded, among which grassland was the largest (21% of managed and unmanaged grasslands). Agricultural land was very well documented (82%) with grasslands, fallow land and cereal crops the largest classes. Semi-natural land contributed to a small part of the data set (18%) and was represented primarily by coniferous forest (13% of all data points). Deciduous and mixed forest were the second largest semi-natural land class (2.5%), and the rest was represented by shrub, meadow and bog, which together only accounted for 2.5% of all data.

Soil type. From 22 soil types recorded, 12 could not be assigned to textural classes due to missing information on soil texture. Among 12 mineral soil texture classes sandy clay and silty clay were not represented. The most widely represented soil texture classes were: sandy loam (17%), silt loam (13.7%), clay (9.4%), sand (10%) and loam (8.7%). Less common were clay loam, silt clay loam, sandy silt loam and loamy silt and they contributed not more than 10% of all observed soils. Soil texture class was not specified in 28% of the studies that gave only the details of the soil taxonomic classification. In three studies, soil type was not specified.

There was a relatively poor coverage for semi-natural land in comparison with agricultural land use. The reason for the under-representation of seminatural environments may be the greater recognised importance of agricultural soils in the nitrous oxide emission budget (over 20% in N_2O total global emission reported in Bouwman *et al.*, 1995). This may cause bias in the model in favour of agricultural land (figure 5.3), especially tilled land which contributed over 50% of all data plots.

Figure 5.3 Comparison of the areal extend of main land classes in England/Wales and Scotland with their proportional representation in the N_2O experimental data set.



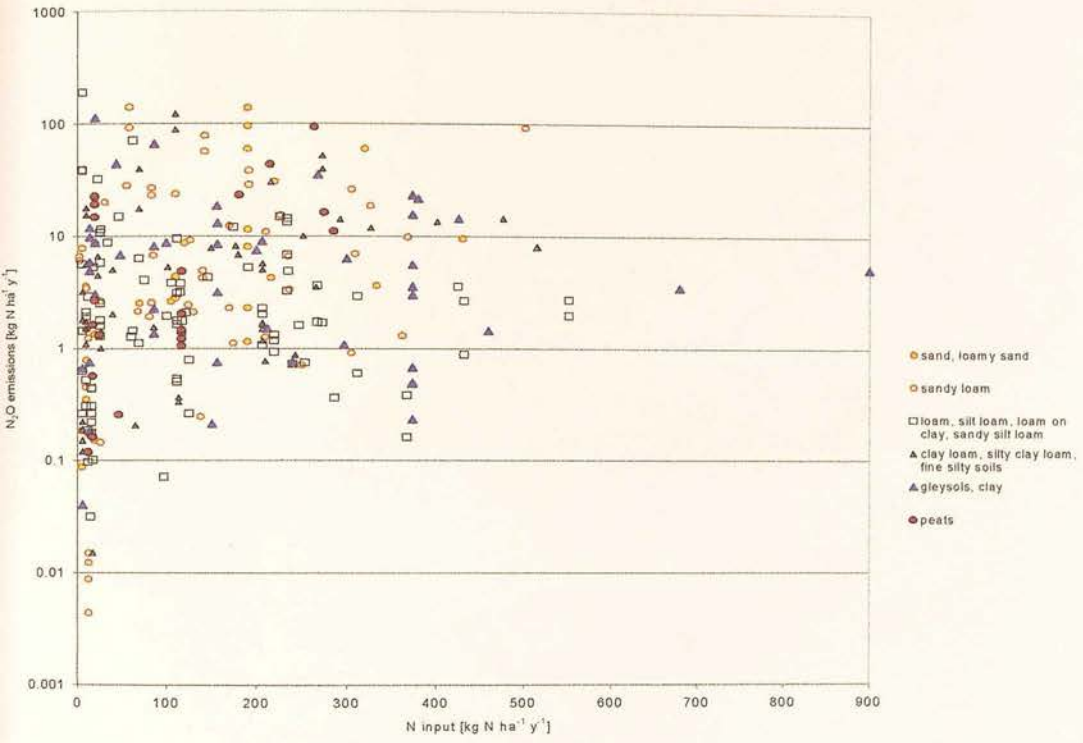
The background emissions described in this model are represented by two land classes: unmanaged grasslands (represented by control plots) and coniferous forest environments contributing to 11% and 13% of all experimental data. Heathlands and moorlands that play an important part in the British landscape, making up 6% and 41% of land cover in England and Scotland, were represented only by a study of a fen environment (Martikainen *et al.*, 1993).

Several studies reported that soil texture was an important variable controlling N_2O emissions (Anderson and Levine, 1987; McKenney *et al.*,1980 and Velthof and Oenema, 1995). As a general rule in similar environmental conditions, fine textured soils have higher denitrification rates than coarse textured soils (Skiba *et al.*, 1993). However, this was not reflected by the data set due to different land use, N input and environmental conditions of studied soils. The presented experimental N_2O data set is characterised by a large variability of N_2O emissions within the major soil groups and fuzzy boundaries between them (figure 5.4). Additionally there is an observed misrepresentation of some soil types in the selection of the compiled studies (e.g. peats).

Table 5.3 Mean N_2O emissions for different land use types represented in the experimental data set.

Land use type	N_2O emissions [kg N ha^{-1} y^{-1}]
Cereals	2.1
Other tillage crops and bare soils	5.8
Horticultural crops	2.6
Grasslands	3.6

Figure 5.4 N_2O emissions for different soil types represented in the experimental data set as a function of N input.



For the experimental data set used in the current study, mean N_2O emission from bare soil and tillage crops was higher than the mean emissions from grasslands, and much lower mean emissions were observed for vegetables and cereals (table 5.3). Relatively high emissions from bare soils might be caused by the remainder of the crop legumes that enhance denitrification in conditions of high organic soil content. Additionally the absence of plant uptake increases the available N in soils for bacterial processes leading to emissions. The great variability of observed emissions from grasslands and cereal crops is due to differences in soil types and management practices. Anderson and Levine (1987) observed N_2O emissions from crops grown on sandy loam in Virginia and clay loam in Colorado and their means were considerably different between the two sites (in Virginia mean N_2O emissions were 27.6 and 19.7 kg N ha^{-1} y^{-1} for corn and barley and in Colorado their values were 2.9 and 17.7 kg N ha^{-1} y^{-1} for winter wheat and fallow). Different mean N_2O fluxes were also measured by McKenney (1980) in Ontario from corn on sandy loam in Harrow where emissions varied depending on N input in the range 0.08 - 0.8 kg N ha^{-1} y^{-1} and on clay from 11.7 - 41.6 kg N ha^{-1} y^{-1}. Velthof and Oenema (1995) observed substantial differences in N_2O emissions from grassland sites on four

soils: sand, clay and two peat soils. They noted an exponential increase in N_2O emissions related to soil type and N soil content, from 1 kg N_2O-N ha^{-1} y^{-1} for untreated sand grassland to 12.1 and 32.3 kg N_2O-N ha^{-1} y^{-1} from two peat soils under intensively managed grasslands (figure 2.4, chapter 2).

In the data set (table 5.1), the differences between the main soil types were not easily distinguishable. The highest median N_2O emissions were observed for well drained soils and poorly drained soils (> 4 kg N ha^{-1} yr^{-1}), but the range was the largest in the case of moderately drained soils (- 0.8 - 188 kg N ha^{-1} yr^{-1}) with the lowest median of 1.57 kg N ha^{-1} yr^{-1}. Peats in the compiled data set recorded relatively low N_2O emissions of 1.8 (-0.5 - 93) kg N ha^{-1} yr^{-1}, despite the highest C content values (38 - 50.6%). This is the result of a few large N_2O emission measurements from mineral soils. Velthof *et al.*, (1997) measured high total emissions of 12% of applied calcium nitrate (189 kg N ha^{-1}). Sharpe and Harper (1997) observed emissions from an oat field on sandy loam where 0.25 – 0.38 kg N_2O-N ha^{-1} d^{-1} flux was measured following an application of ammonium of 58 kg N ha^{-1} in optimal environmental conditions. Nyborg *et al.* (1997) observed a peak flux of N_2O emissions in spring on a fallow field, following an input of 105 kg N ha^{-1} of KNO_3. This enhancement could also be attributed to the presence in soil of the previous crop legumes. The unclear boundaries between soils in terms of N_2O emissions are linked with differences in land use type and reflect complexity of environmental conditions of each site. It was expected that the complex characteristics of the listed sites in the data set, together with differences in data availability would make the definition of the model more difficult.

The observed variability of N_2O emissions from different soil groups is less conspicuous than the variability implied by different vegetation cover. This might effect the outcome of the analysis of the data set. In addition the limited availability of the soil data in the compiled N_2O data set might increase the uncertainty of this variable in the multivariate regression analysis. The discussion of the applied statistical analysis method and its results are presented in the following section.

5.3 REGRESSION ANALYSIS AS A MODELLING METHOD FOR N_2O EMISSIONS.

5.3.1 A case for regression analysis.

The previous section showed that N_2O emissions were observed to respond to the changing biological and physical characteristics of soils that are defined by the controlling factors of N input, soil temperature and moisture, soil C content and land use. These observed controlling factors were expected to be good predictors of N_2O emissions. The regression method was chosen to describe relationships between the emissions and their controlling factors. This section presents arguments for and against its application in the current study.

The regression model offers a simple description of complex relationships between N_2O emissions and the controlling factors. Its principal applications was described by Snedecor and Cochran (1978), who defined it as a method used to establish relationship of Y with X; predict Y from X; find an error when Y is predicted with this method; or to test a theory about a cause and an effect. In this study the regression model was in the first instance applied to describe the complex relationships between N_2O emissions and the controlling variables. In the second stage, the defined model was used to predict the spatial distribution of emissions from the known values of the controllers. Prior to the analysis, the relationships between the dependent and independent variables were observed on the basis of the compiled N_2O data set from field measurements (table 5.1, figure 5.1).

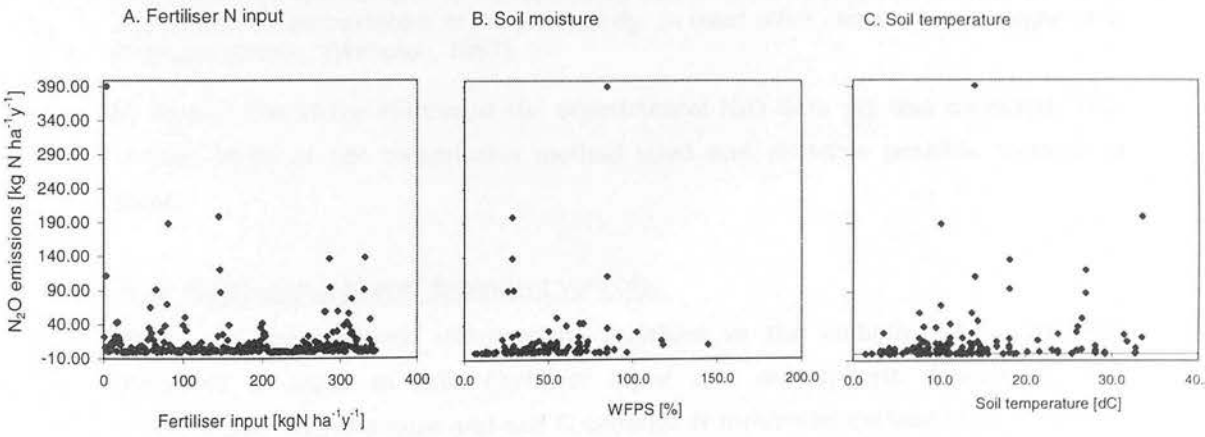
According to Clark and Hosking (1986), a linear model '*is concerned with situations where we are examining how a single variable is functionally dependent on one or more independent variables and when the form of the functional relationship is linear*'. There is some evidence of a trend in the relationship between the N_2O emissions and the group of controlling factors as the emissions, that could be identified as the dependent variable, increase in optimal conditions for their production and diffusion, and decrease in restricting conditions. Plotted values of N_2O fluxes against N input, soil temperature and moisture and C content from the collected data did not however present any recognised trend (figure 5.5 a, b, c). The complex response of emissions to the changing characteristics of soils was interpreted by Davidson (1991) in the 'hole-in-the-pipe' theory. Davidson's model proposed not a single variable, but a group of soil characteristics that cause

different compositions of gases released from soils. Those factors were observed to act together and each displayed a threshold value that limited emissions. The complex relationships between N_2O emissions and their controllers could be best described by multivariate regression analysis that has a general form presented by the equation (5.2)

$$\hat{Y} = \alpha + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \ldots + \beta_n X_n + \varepsilon \qquad (5.2)$$

$\hat{Y}$ - estimated value of dependent variable
$X_1, X_2, X_3, \ldots, X_n$ – independent variables
$\beta_1, \beta_2, \beta_3, \ldots, \beta_n$ – measure of expected change in Y when $X_1, X_2, X_3, \ldots, X_n$ increases by a unit
ε - a measure of error ($= \sqrt{\sigma^2}$).

Figure 5.5 N_2O emissions as a function of the main controlling factors.



That analysis method *'attempts to predict and to explain the variation of a single dependent variable (Y) from a number of predictor terms'* (Shaw and Wheeler, 1994) and aims at defining the function of that relationship. There is a continuing discussion in the literature of the appropriate application of linear regression analysis. Purists like Webster (1997), Snedecor and Cochran (1978) and Ebdon (1977) present well defined requirements for the analysed data and dispute the validity of regression when those requirements are not met. There are many soil scientists that apply regression analysis to describe natural phenomena like N_2O

emissions. They represent a more pragmatic approach that envisages a 'relaxed' application of regression and are represented by Cooper and Weekes (1983). They recognise the application of this method to define *'a notion that two variables may have an association which can be defended by some theory of causation'* (Cooper and Weekes, 1983). These two opposing views, one presented by Webster (1997) who argues that this method is quite often *'misused'* due to violation of the proposed requirements; and the other by scientific pragmatists that employ it to observe relationships, are important in the discussion of its application in this study. The following section looks at the conditions for the valid application of linear regression analysis in the context of this study.

5.3.2 Criteria of regression analysis.

'A regression equation may be used to express a functional relation between two variables that are thought to be related by some simple mathematical law but only where one of the variables is known exactly. In most other circumstances regression is inappropriate.' (Webster, 1997).

In view of the above statement the experimental N_2O data set was assessed. This section looks at the compilation method used and presents possible sources of error.

Error of independent and dependent variables.

There are four interval independent variables in the compiled data set that represent N input to soils (fertiliser input and atmospheric deposition), soil temperature, soil moisture and soil C content. N input was estimated as a sum of regional mean atmospheric N deposition and fertiliser input specified in field studies. When no N deposition values were presented in the published work, long-term averages were obtained from NADP (1997) and Summers (1997). The majority of the experimental studies listed soil temperature data, but it had to be transformed to a uniform level of 30cm depth. The equation of heat flow in soils (equation 3.3, chapter 3) was applied to estimated soil temperature at the comparable level. When no temperature was measured in the experiments, the data were obtained from the nearest weather station (Pearce and Smith, 1990). Soil moisture and soil C content were measured in the field; the former was converted to water-filled-pore-space (WFPS) and the latter to organic C content of soils (%C). There is some uncertainty expected in a case of atmospheric N deposition and soil temperature due to their residual variability from the long-term mean values used

in this data set for some data points. Due to restricted data availability this difference cannot be assessed, but the error is not expected to be significant.

Clark and Hosking (1986) point out that Y has to be free from error. It is probable that this assumption is often not fulfilled. The uncertainties of measurements are mainly due to the dynamic nature of bacterial processes resulting in large spatial and temporal variability of N_2O emissions, which are difficult to account for. This leads to some assumptions of representative mean values of N_2O emissions on the basis of all measured fluxes, which are impossible to verify. Clark and Hosking (1986) suggest that when there are errors in X, the slope of the linear regression is underestimated. When there are errors in the measurement of Y, the error term might be overestimated. But in case of both variables being subject to error '*consequences are not easily determined*'. There are two reasons for data error that might affect the validity of the model. Firstly, there is a possibility of measurement error, that according to Hutchinson and Livingston (1993) is an effect of physical and biological disturbances of the measured soil or sample errors (handling, analysis and flux estimation). It is assumed in this study that the error of N_2O emission measurements is minimal and insignificant. Secondly, the analysed data of N_2O emissions and their controlling factors are expected to represent means of distributions for the listed sites. This has important implications for the established relationships that represent only average responses of N_2O emissions to the controlling factors and do not account for their highly changeable nature. This simplification of analysis was essential to the clear outcome of the model. The variability for each measurement plot could be easily established via the referencing system of site numbers included in tables 5.1 and 5.2 and an application of published standard deviations of N_2O emissions.

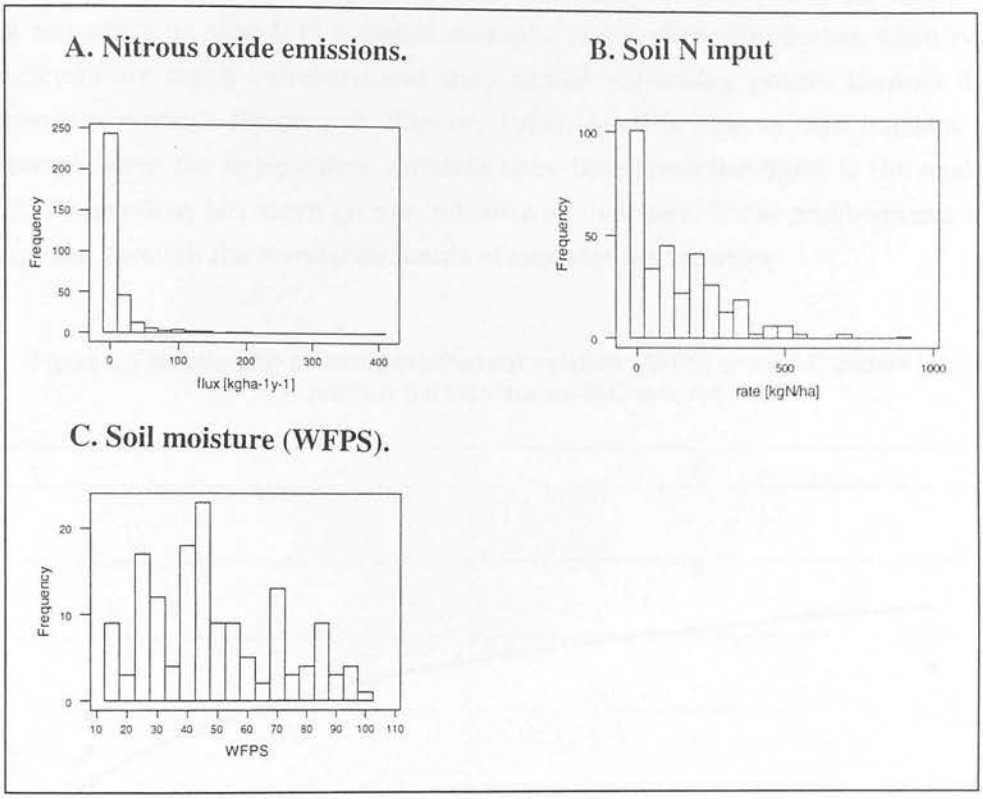
Distribution of the variables.

Different requirements for a valid regression model are presented in literature, but the most common is the normal distribution of independent and dependent variables. This is highlighted in many studies (Ebdon, 1977; Snedecor and Cochran, 1978; Clark and Hosking, 1986; Webster, 1997). Some researchers point out the importance of a normal distribution being required only from the independent variables (Ebdon, 1977; Snedecor and Cochran, 1978), others expand this requirement onto dependent variables (Webster, 1997).

The independent variables in this study were the controlling factors of N input, soil moisture, soil temperature, C content and land classes. The distributions of those

data were observed prior to an application of regression analysis. The distributions of N_2O emissions, N input to soils and soil moisture proved to be not normal (figures 5.6a-c) and for the purpose of regression analysis they were transformed with a natural logarithmic function.

Figure 5.6 Distribution of N_2O emission, soil N and soil moisture from field measurements.



The transformations of variables have consequences for the established relationships in the regression analysis that relate to the transformed factors as presented in the equation (5.3) as observed by Shaw and Wheeler (1994).

$$U = \alpha + \beta_1 V_1 + \beta_2 V_2 + \beta_3 V_3 + \ldots + \beta_n V_n + \varepsilon \qquad (5.3)$$

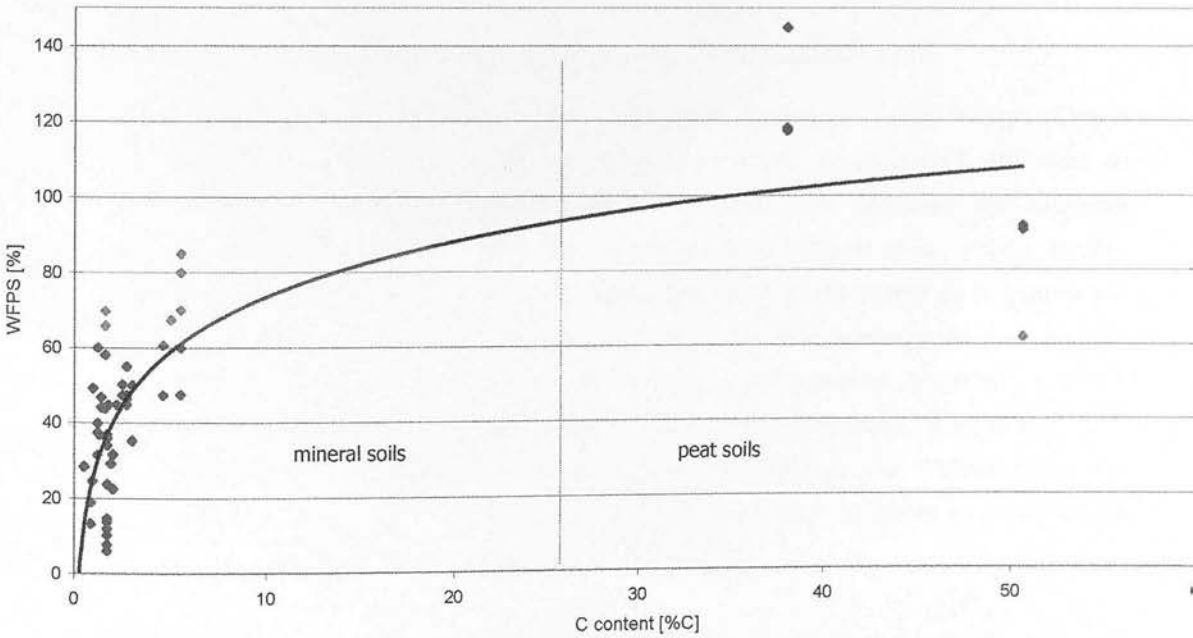
Where U represents a transformed dependent variable, $V_1,\ldots V_n$ - transformed independent variables, $\beta_1, \ldots \beta_n$ - coefficients of correlation, α and ε - intercept and residual error of the linear model defined for the transformed variables. Transformations make an interpretation of the established relationships more difficult and require additional calculations to find the dependent variable from the

known independent factors and to estimate an error ε. This is looked at in detail in chapter six.

Correlation between independent variables.

While a non-normal distribution can be addressed by transformation of the variables, the problem of multi-collinearity and high correlation between variables can not easily be solved. In a classic example, multi-collinearity occurs when two predictors are highly correlated and show similar 'explaining' powers towards the dependent variable (Shaw and Wheeler, 1994). Another case of this problem is observed when the independent variables show little predictive input to the model with one another, but much greater influence on their own. Those problems can be examined through the correlation matrix of independent variables.

Figure 5.7 Relationship observed between soil moisture (WFPS) and soil C content for data points of the experimental N_2O data set.



Pearson's correlation matrix for variables in the experimental N_2O data set (table 5.4) showed high correlation between WFPS and soil C content (0.52 for the original data and 0.714 after logarithmic transformation). The reason for such a close relationship between those variables was caused by the peat characteristics of high

organic C content (>38% C) and soil moisture (from 62 - 144%) as presented on figure 5.7. The proportion of peats in the N_2O data set was rather small (five studies), but they represented sites with the highest WFPS values. Among the plots on mineral soils that contributed to the majority of the compiled data, relatively low soil C content (< 5.5%) corresponded in a majority of cases with WFPS values below 60% (figure 5.7). Only soils of restricted drainage were an exception to this pattern (e.g. imperfectly draining gleysol in the study by Clayton *et. al.*, 1997 or alluvial silt loam studied by Qian *et. al.*, 1997). Some correlation was also observed for land use and N input (>0.3). The three main land use classes: grasslands, tilled land and seminatural had different levels of N input in the experimental data with respective medians of 172, 126 and 12.4 kg N ha^{-1} yr^{-1}.

Table 5.4 Correlations' matrix.

	ln(N)	soil temperature	ln WFPS	ln C
soil temperature	0.124			
ln WFPS	-0.018	-0.200		
ln C	-0.073	-0.107	0.714	
land use	-0.385	-0.032	-0.164	-0.338

Although the N input for different land use types depended on the design of each experiment, they reflected a general trend of fertiliser management practices in their respective countries. Published recommendations for Scotland and England (Dyson, 1993; Dyson *et al.*, 1993a; Dyson *et al.*, 1993b; Dyson *et al.*, 1993c; MAFF, 1988; Swift, 1988 and Younie *et al.*, 1990) list the highest range of N inputs for grasslands that vary from 110 kg N ha^{-1} yr^{-1} for extensive mown grasslands to 325 kg N ha^{-1} y^{-1} for grazed grasslands with high stocking densities (table 3.8, chapter 3). The recommendations for tilled land are lower and vary from 75 kg N ha^{-1} yr^{-1} for sugar beet to 200 kg N ha^{-1} yr^{-1} for wheat (in England and Wales) and some vegetables varieties. Only hops (in England), rhubarb and brussels sprouts (whole country) receive more N input (>200 kg N ha^{-1} y^{-1}).

Some correlations were expected between the variables describing physical soil characteristics - soil moisture and temperature. As indicated by the theory of heat flow in soils, temperature is influenced by changes in soil moisture level. Equation (3.3) (chapter 3) applied to estimate soil temperature shows its dependence on thermal diffusivity of soils (κ) that is a function of thermal conductivity and volumetric specific heat that, in turn, change with soil water content (Campbell, 1977). On the other hand, soil moisture is sensitive to changes of temperature that control saturation vapour pressure of water (Monteith and Unsworth, 1990).

Atmospheric N input, that contributes the majority of total N in seminatural environments, is also correlated with the physical variables. The wet component of atmospheric deposition was observed to vary depending on the meteorological conditions, i.e. precipitation and wind, and the location of industrial sources (Dore *et al.*, 1992). Dry N atmospheric deposition depends on the vertical flux of gases that is controlled by stomatal uptake and a variety of atmospheric parameters (Horvath *et al.*, 1998).

The suggested relationships between the environmental variables were not very important as their correlation coefficients did not exceed 0.20 (table 5.4).

Independence of data points.

The collected N_2O data measurements and their variables came from 60 studies (table 5.2, Appendix). Some studies selected plots in different geographical locations (Anderson and Levine, 1987; Kaiser *et al.*, 1996), but there were few studies carried out in the same location in consecutive years that were treated separately in the N_2O experimental data set (Velthof *et. al.*, 1995; Velthof *et. al.*, 1996a). According to a suggested similarity of adjacent points by Shaw and Wheeler (1994), some relationship was expected between environmental variables of plots within the same site. In view of that observation, the presented variables in the N_2O data set were analysed in the context of possible links between the data points from similar locations. The possibility of autocorrelation was implied by the independent variables. This was caused by the presented data in most studies that included different measurements of N_2O emissions corresponding to different treatments of N input, but only one measurement of the controlling factors characteristic to the studied soil e.g. soil temperature and soil C content. This was expected to produce a considerable autocorrelation between the data points.

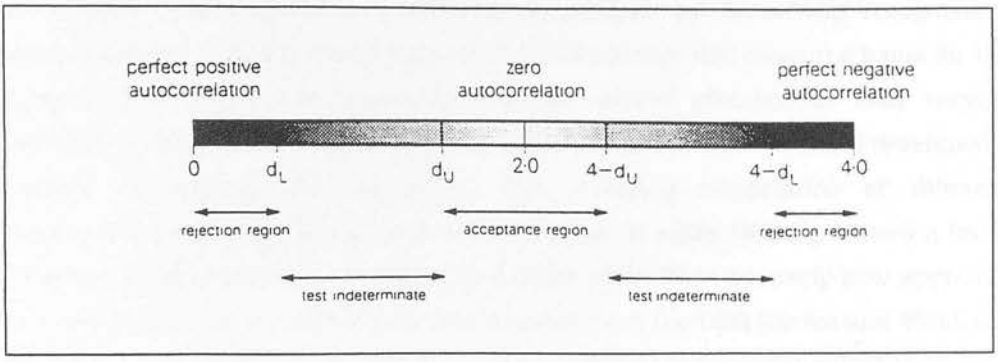
The Durbin-Watson (d) statistic was applied to establish autocorrelation. The d statistic offers a numerical test of independence of data points and is a function of squared successive residual differences to squared sum of residuals (equation 5.4).

$$d = \frac{\Sigma (e_i - e_{i-1})^2}{\Sigma e_i^2} \qquad (5.4)$$

d - Durbin-Watson statistic
e_i , e_{i-1} - consequtive residuals

d statistics indicate whether any autocorrelation occurs between the data points within a chosen significance level and determine the sign of autocorrelation (figure 5.8). The results of this test are included with the multivariate regression analysis (section 5.4).

Figure 5.8 Rejection and acceptance regions for the Durbin-Watson statistic (Shaw and Wheeler, 1994).



The characteristics of the measurement data presented above, used to define the relationship between N_2O emissions and the controlling factors, do not fully comply with the prescribed requirements of the applied analysis method. Observed correlation between some variables of the model, the possibility of autocorrelation between individual data points and great variability of N_2O emissions suggest limitations of the regression model referred to in the introduction (section 5.1) as the first issue of the modelling approach. Another problem of this thesis is to apply the model defined on the basis of the experimental data set at the national scale. This issue is discussed in the following section.

5.3.3 Spatial application of the regression model

The presented regression model of N_2O emissions from soils has two main functions. The first is to describe the variability of N_2O emissions and their dependence on the environmental factors in soils presented in the experimental N_2O data set. The second is to predict levels of N_2O emissions from defined independent variables of N input, soil moisture and temperature, C content and land use data. The accuracy of the predictions would be affected by any problems related to the data set on which the model is based and to the method that was used to derive it. The relationships established from the measurement data are applied in the predictive model based on the concept of scaling that defines

defines important factors of N_2O emissions measured at different scales, from a field to region and the whole country. This section looks at scaling issues, relates them to the field of N_2O emissions and presents implications of these for estimating N_2O emissions from British soils with AGEM (Arc Info Grid Emission Model).

The concept of scaling came from developments in modelling methods that enabled changing scales of models. It originated from an old idea of generalisation in cartographic classification of presented phenomena, by describing recognisable general pattern in highly variable elements. This concept laid down the basis for the generation of maps that presented spatially defined phenomena with varying amounts of detail depending on the map scale. From this old idea there developed a concept of scaling that recognises the changing importance of different characteristics of one phenomenon with a change in scale. Scaling formed a basis on which local research was referred to a wider scale. This relatively new approach was developed in the biogenic emission inventories of the USA (Pierce and Waldruff, 1991) and Castelporziano in Italy (Lenz *et al.*, 1997) or soil erosion model of an area in south-east Spain (Kirby *et al.*, 1996). N_2O emissions measured at field level show great spatial and temporal variability that is related to the complex environmental characteristics of soils. Field studies listed in the experimental N_2O data set attempted to establish relationships between the emissions and the controlling factors. In a few studies, those responses were described empirically but it was argued that the application of those models was restricted to the specific location under defined environmental conditions (Velthof *et al.*, 1996a). On the other hand, the established relationships between N_2O emissions and the controlling factors, described by the means of N_2O emission factors, were extrapolated to a larger scale in the global and national inventories as presented in chapter two. Bouwman (1995) and Veldkamp and Keller (1997) developed this approach even further and predicted N_2O and NO emissions with fertiliser emission factors established from combined studies undertaken in temperate and subtropical climatic zones (presented in chapter two). Since those models were published, more experimental studies have been completed. AGEM continues this idea and tries to recognise a whole range of important controlling factors on the basis of the compiled studies from temperate climatic regions published between 1980 – 1997. Apart from N input that was recognised by Bouwman (1995) as the main controlling factor, this approach tries to establish the important environmental variables with an application of multivariate regression. This study presents an analysis of the experimental measurements of mean N_2O emissions and their controllers and aims at recognising some general emission patterns existing in the temperate climatic

zone. This analysis leads to definition of the empirical predictive model of N_2O emissions that describes their general trends in the temperate climate region. The approach of this study follows the suggestions of the field-scale N_2O emissions models that their valid predictions are strictly limited by the environmental character of the ecosystem for which the model was defined. The application of the empirical model of N_2O emissions, established on the basis of combined European and North American studies, would be defined by the environmental characteristics of the ecosystems represented by the experimental studies and the fertiliser management practices as described in detail in section 5.2.3.

The 60 compiled studies were located in the temperate climatic region of western and northern Europe and North America (figure 5.1). All the countries, from which the studies originate, are generally recognised as countries of the North with intensive agricultural systems. No significant differences were expected between the individual countries in terms of their agricultural practices. The conventional agriculture in those countries could be described by economically defined fertiliser inputs and highly intensive animal husbandry that influence the amounts of N_2O emissions. These similarities are the effects of the Common Agricultural Policy (CAP) in the countries of the European Economic Community (EEC) and technological improvements of post-industrial revolution period. The agricultural management practices of the countries in question that are important for N_2O emissions primarily relate to the intensive management of grasslands and tilled land rotation with specific amounts of N fertiliser input defined for each crop type. Median N input observed in the compiled studies was 111 (2-899) kg N ha^{-1} yr^{-1} that is slightly lower than mean N fertiliser input in Britain of 133 kg N ha^{-1} yr^{-1} to all crops and grass (Owen, 1997). The top N fertiliser inputs were measured in the Netherlands (Velthof *et al.*, 1997) where higher intensity grassland management is observed compared with Great Britain. The experimental data set lists only three countries: England (Velthof *et al.*, 1996b), the Netherlands (Velthof *et al.*, 1995) and Germany (Flessa *et al.*, 1996b) where the effects of grazing on N_2O emissions were studied. Animal density on grassland in southern Germany was noted by Flessa *et al.* (1996b) as 48 cattle ha^{-1} that considerably exceeds the mean stocking density observed in Great Britain (4 cattle ha^{-1}), but is within the range of stocking densities estimated for Great Britain on the basis of AC data (0 – 140 cattle ha^{-1}). Vethof *et al.* (1997) observed soil type to be an important factor for N_2O emissions from grasslands with varying management intensity. Grasslands in the experimental data set were mostly grown on moderate to heavy textured soils e.g. silty loam, clay and organic soils. Similarly in Great Britain permanent grasslands

are associated with heavy textured soils that are not suitable for cereal crops. Fertiliser management of tilled land in the studied agricultural systems provides good representation of the N fertiliser inputs to crops in Great Britain. The great variety of grassland management practices presented in the experimental studies also reflects the variety of grassland management in Great Britain. Some caution should be exercised regarding the N_2O emission studies with exceptionally high N inputs that might influence the relationship represented in the established model.

The environmental characteristics that may influence the validity of the predictions made by the model are described by the physical characteristics of soils in the compiled studies. Among the observed soil characteristics the most important recognised factors were soil temperature, soil moisture and C content. Their measured ranges should be compared with the conditions characteristic of British soils as they have important implications for the predictions of the empirical model. Mean soil temperature of 13.2 °C corresponded well with the mean annual soil temperature estimated for Great Britain (9.4 °C). High soil temperature (>30 °C) was observed by Anderson and Levine (1987) during summer in their study of N_2O emissions from corn and fallow fields in Virginia and Colorado due to the continental climate. The minimum soil temperature in the N_2O data set of –2.9 °C was measured by Bowden *et al.* (1990a) in Harvard forest in January when the soil was frozen. The annual range of soil temperatures estimated for British soils is -0.4 - 19.6 °C. The evidence presented in chapter two clearly suggests that the optimum soil temperature for bacterial growth is at 30 °C and a three-fold increase in bacterial activity was observed with an increase of soil temperature from 20 to 30 °C. Higher soil temperatures characteristic to some field studies might cause bias in the application of the predictive model for Great Britain.

Soil C content represented in the data set was 2.7% on average (median) and corresponded with the mean soil C content of British soils (2.8%). The scope of %C variability in the soils studied by the regression, estimated at 0.1 – 50.6%C, is within the range of organic C content represented by British soils (0 - 72%) as estimated by Milne and Brown (1997). Soils in the British highlands are dominated by peats with C content exceeding 10%. In a few locations in the Pennines, on Iona and The Orkneys, soils contain over 55% organic C. Organic C soil content of 50.6% was measured only in Zegfeld, The Netherlands by Velthof *et al.* (1996a) that represented the highest reported value in the experimental data set. Although there is a correspondence in the presented values of C soil content for Great Britain with the environments of the N_2O data set, a small number of studies of peats might

result in a more accurate definition of the relationship in the model between N_2O emissions and C soil content for mineral than organic soils.

WFPS for the UK is relatively high due to abundance of precipitation and the relatively large proportion of soils with moderate to heavy textures. The range of soil moisture presented by the experimental data is from 12 - 102 % WFPS and the estimated soil moistures with an application of SPACTeach model range between 34 and 99 %. The mean soil moisture from field measurements of 47.4 % WFPS was lower than the estimated mean annual moisture for British soils at 76% WFPS (figure A8). Soil moisture was also estimated to vary between the field plots by 22 % on average, as indicated by the standard deviation (sd). This suggests that the environmental conditions of the experimental data set favour both nitrification and denitrification (Davidson, 1991) (figure 2.3, chapter 2). Soil moisture values estimated for Great Britain, on the other hand, suggest greater importance of denitrification as the main process of N_2O production. There are significant differences observed between soils in the North-west and South-east that are described by water regimes of the soil HOST classes (table 3.3, chapter 3). In northern Britain soil moisture is characteristic of undrained and raw or eroded peats (HOST classes 15, 28, 29, 12) and hard impermeable mineral soils (HOST classes 17, 19, 22). In South-east Britain different water retention is attributed to the dominant mineral soils with good and moderate drainage (HOST 5, 1, 6, 9), slowly permeable mineral soils (HOST 18, 21), localised impermeable soils (HOST 20, 25) and drained peats (HOST 11) (figure A7). These contrary soil drainage characteristics cause regional differences in soil moisture with mean WFPS > 80 % in Scotland and WFPS below 70 % in the South-east (figure A13). The described differences might result in variable accuracy of the predictions throughout Great Britain. The predictions of N_2O emissions from wet environments of heathlands and moorlands are expected to bear larger uncertainty than those for mineral soils.

The above comparison of the independent model variables from the experimental data set with their ranges for Great Britain, reveals their general agreement. Some differences exist, however, and they might have important implications for the application of the model to predict N_2O emissions in Britain. Sites with very high N inputs and high soil moisture might effect the model bias when applied to predict N_2O emissions from soil in Great Britain. The limited representation of peat sites in the experimental data set further increases model uncertainty for predicting N_2O emissions from this soil type which forms > 20 % of British soils.

5.4 RESULTS OF MULTIVARIATE REGRESSION.

Relationships between the independent variables of N input to soils and the environmental characteristics of soils and N_2O emissions were observed using multivariate regression analysis performed by MINITAB. Prior to the analysis N_2O emissions, N input, soil moisture and organic C content were transformed with natural logarithms to make them comply with the normal distribution requirement of the regression method. There were three phases of the analysis: factor analysis that was applied to define the significant factors or group of factors on the basis of all variables; regression tests that aimed at defining the model and model validation via a simple regression test. The multivariate regression analysis was repeated until the best description was found. The following section presents the results of the multivariate regression analysis and their interpretation.

Table 5.5 Factor loadings.

Variable	Factor1	Factor2	Factor3	Factor4
Ln N_2O	0.096	0.611	0.471	0.629
ln N	-0.286	0.351	0.709	-0.532
ln WFPS	0.863	0.297	-0.130	-0.167
soil temperature	-0.042	0.793	-0.542	-0.113
ln C	0.872	0.198	0.105	-0.144
Land use	-0.787	0.449	-0.198	-0.066
Eigenvalue	2.218	1.454	1.084	0.744
% Variance	0.370	0.242	0.181	0.124

Factor analysis was applied to the N_2O experimental data set to identify groups of inter-related factors from the the dependent variable ($\ln(N_2O)$) and the five independent variables of the regression model: ln(N), ln(WFPS), soil temperature, ln(C) and land use. From the six factors listed three had eigenvalues > 1.0 (table 5.5), which are a measure of variance of all data accounted for by each factor (Shaw and Wheeler, 1996). The loadings of variables on those factors defined the character of each established factor (table 5.5). Transformed WFPS and organic C with land use had high loadings on factor 1 that could be described as a 'biological' factor. Factor 2 was highly influenced by soil temperature that defined its character as a 'climatic' factor. The third factor could be described as a 'substrate' factor due to a high loading of logarithm of N input (table 5.5). The loadings of the logarithmically transformed dependent variable suggested important relationships of $\ln(N_2O)$ with factor 2 and factor 4 indicated by factor score coefficients of 0.42

and 0.84, respectively (table 5.6). It is interesting to observe that factor 4, as in the case of factor 3, is highly loaded by transformed N input, but the loading in the former is negative. That might indicate that factor 4 counteracts, due to its high coefficient score with ln(N_2O), the effects of the 'substrate' factor (factor 3). This confirms complex relationships between the dependent variable and its expected best predictor - ln(N). The 'biological' factor that is responsible for 37% of all data variance (table 5.5) is concurrently weakly loaded by the dependent variable. The variables that determine the 'biological' character of the relationship were observed to be highly correlated (table 5.4) and this might suggest weakness of the following regression analysis. Soil temperature is observed to be relatively strong in factor 2 that proved important to the dependent variable, as indicated by a factor score coefficient of 0.43 (table 5.6).

Table 5.6 Factor Score Coefficients

Variable	Factor1	Factor2	Factor3	Factor4
Ln N_2O	0.043	0.420	0.434	0.845
Ln N	-0.129	0.241	0.654	-0.715
Ln WFPS	0.389	0.204	-0.120	-0.225
soil temperature	-0.019	0.546	-0.499	-0.152
ln C	0.393	0.136	0.097	-0.193
land use	-0.355	0.309	-0.182	-0.089

Factor analysis confirmed the complexity of relationships between the dependent variable and all independent variables considered in the following regression analysis. The variables defining factor 1 should be particularly considered in the following analysis in respect to their implications for the empirical relationship between ln(N_2O) and the independent variables.

In the regression analysis phase a relationship between the dependent variable and each independent variable was studied first. The results showed that the natural logarithm of N input was the most significant single predictor of logarithmically transformed N_2O emissions accounting for 21% of their data variability, the defined relationship was presented by equation (5.5). Land use was the second most important single 'predictor' of transformed N_2O emissions that accounted for 10.7% of ln(N_2O) variability (equation 5.6). Caution is advised towards using land use as a single predictor of N_2O emissions, as the values represented by that data set were assigned to distinguish main land class groups and to explore their effect in connection with the other controlling factors on the studied relationship. Relationships of the dependent variable with transformed soil moisture (WFPS) and soil temperature presented by the equations (5.7) and (5.8)

were rather weak as indicated by a standard error of 1.9 in both cases. Ln(WFPS) explained significantly only 4% (F=5.25, p = 0.024) and soil temperature explained 1.7 % (F= 3.13, p = 0.078) of ln(N_2O) data variability. The results of the multivariate regression analysis, which suggested soil temperature was a weak single predictor of ln(N_2O), contrasted with the results of the factor analysis, which described it as an important variable. The relationship between ln(N_2O) and ln(C) was not significant (r^2=0.2%, F=0.37, p= 0.543), C content was therefore excluded from the multivariate regression analysis. The contrasting results of simple regression and factor analysis suggest complex interactions in the group of variables.

Table 5.7 Results of multivariate regression analysis of the N_2O experimental data.

Model definition	n	r^2	p	eq
$Ln(N_2O)$= - 1.7 + 0.64 * ln N	296	21.9	0.0	(5
$Ln(N_2O)$= 2.9 - 0.99 * A	299	10.7	0.0	(5
$Ln(N_2O)$= - 1.8 + 0.75 * ln WFPS	133	3.9	0.024	(5
$Ln(N_2O)$= 0.6 + 0.04 * Ts	185	1.7	0.078	(5
$Ln(N_2O)$= 1.6 + 0.09 * ln C	159	0.2	0.543	(5
$LnN_2O)$= - 4.9 + 0.71 * ln N + 0.75 * ln WFPS	130	28.3	0.0	(5
$Ln(N_2O)$= - 6.0 + 0.75 * ln N + 0.83 * ln WFPS + 0.035 * Ts	107	31.1	0.0	(5
$Ln(N_2O)$= - 2.7 + 0.60 * ln N + 0.61 * ln WFPS + 0.035 * Ts - 0.99 * A	107	39.8	0.0	(5

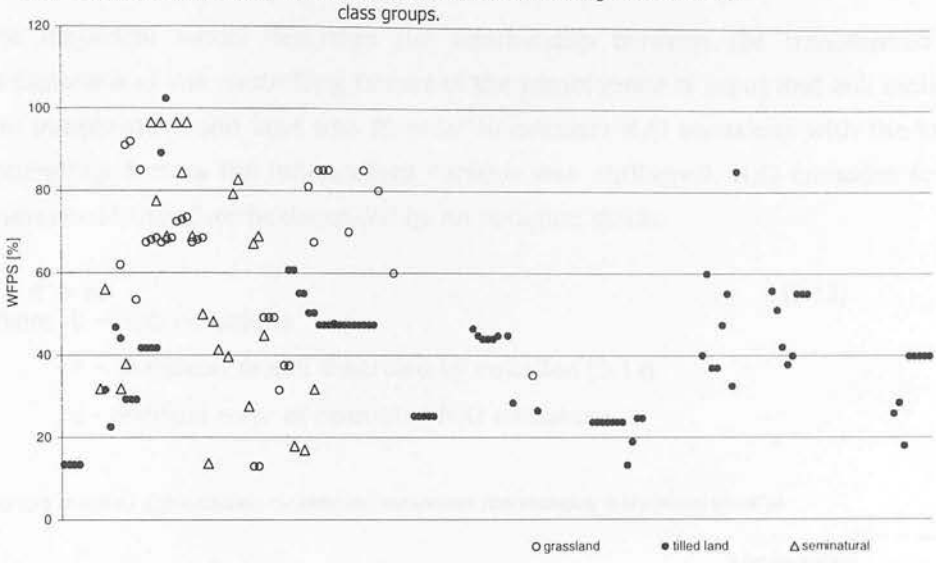
Where N_2O emissions are expressed in [kg N ha^{-1} y^{-1}],
N – nitrogen input [kg N ha^{-1} y^{-1}],
WFPS – water-filled-pore-space [%],
Ts – soil temperature [°C],
A – land use type

The multivariate regression, that followed the preliminary simple regression, looked at groups of variables and explored their combined relationships with ln(N_2O). A first regression was applied to independent variables of ln(N) and ln(WFPS). The described equation (5.10) explained 28.3% of variability of the dependent variable (F=25.05, p=0.0). The introduction of soil temperature to the predictive power of the above variables moderately improved the model presented by the equation (5.11) (r^2=33.6%, s=1.636, F=15.5, p=0.0). As land use was a strong single factor of transformed N_2O emissions it was added to the group of independent variables in the final stage of the multivariate regression analysis. The regression model defined by those four significant controlling factors is presented in equation (5.12)

The presented regression model defines almost 40% of the variability of N_2O with the four significant independent variables. The importance of the controlling factors indicated by the correlation coefficients were in order: land use; log-transformed

soil moisture; log-transformed N input and soil temperature. A comparison of the correlation coefficients of individual factors, when acting as single predictors and in a group, revealed no significant differences that indicates that the presented variables did not cause multicollinearity and the model is relatively stable. It was observed, however, that ln (N), soil temperature and ln(WFPS) had slightly higher coefficients in equation (5.11) than in the group with land use (equation 5.12) (table 5.7). This might suggest that the relationship between the dependent variable and the three land classes i.e. grasslands, tilled land and seminatural land was offsetting the strength of the transformed WFPS and N input. The offset of ln(WFPS) corresponds with the observations made by the factor analysis that recognised a relationship between land use class and ln(WFPS) in factor 1. The influence of land use on the strength of ln(N) is confirmed by the Pearson's correlation of -0.385 that indicates a negative relationship between these two variables (table 5.4). These results confirmed a general relationship existing between soil N input, soil moisture and land use type. It is not surprising to observe a high correlation between ln(N) and land use as N input depends on different crop type and management practice. There is also an observed great variability of soil moisture within each defined land class with similar ranges of their distribution for the three classes (figure 5.9). The median soil moisture values for the three main classes of land use are significantly different. Median WFPS for grasslands has the highest value - 68%, for seminatural land median WFPS was estimated at 53%, and tilled land has on average the lowest WFPS of 41%. This reflects a tendency for different land use types to favour distinct drainage properties of soils. Light textured soils are more suitable for cereals and other tillage crops and they generally are characterised by better drainage. Soils with poor drainage that are not suitable for economical management practices are abandoned as seminatural land or sparingly utilised for hill grazing. Despite a huge simplification implied in this statement, the presented pattern is reflected in the land-use capability classification defined by Klingebiel and Montogomerry (1961) for the USA and adopted by Bibby and Mackney (1969) in Great Britain.

Figure 5.9 Soil moisture variability for the field measurements according to the three land class groups.



In the final regression analysis of the relationship between ln(N_2O) and the independent variables of ln(N), ln(WFPS), soil temperature and land use group (equation 5.12, table 5.7), the Durbin-Watson test was applied to observe a degree of independence between individual data points. The Durbin-Watson statistic estimated by MINITAB (d) was compared with a critical lower (d_l) and upper (d_u) levels. The estimated d of 1.15 was well within the rejection region designated by the d_l of 1.59 ($p = 0.05$) and 1.46 ($p = 0.1$) (figure 5.8). The N_2O data were considerably autocorrelated. The value of d implies that there is a positive autocorrelation between the data points and the adjacent residuals are similar (Shaw and Wheeler, 1994). The similarity of the residuals is likely to be the result of common environmental characteristics between the plots within the same experimental site (section 5.3.2).

The presented relationships between the independent variables contribute to the uncertainty of the established empirical model and a large proportion of unexplained variability of the dependent variable (>60%).

5.5 PREDICTING N_2O EMISSIONS WITH THE EMPIRICAL MODEL.

The empirical model describes the relationship between the transformed N_2O emissions and the controlling factors of the transformed N input and soil moisture, soil temperature and land use. In order to estimate N_2O emissions with the known controlling factors the independent variable was antilogged. N_2O emission for any point could therefore be described by an equation (5.13).

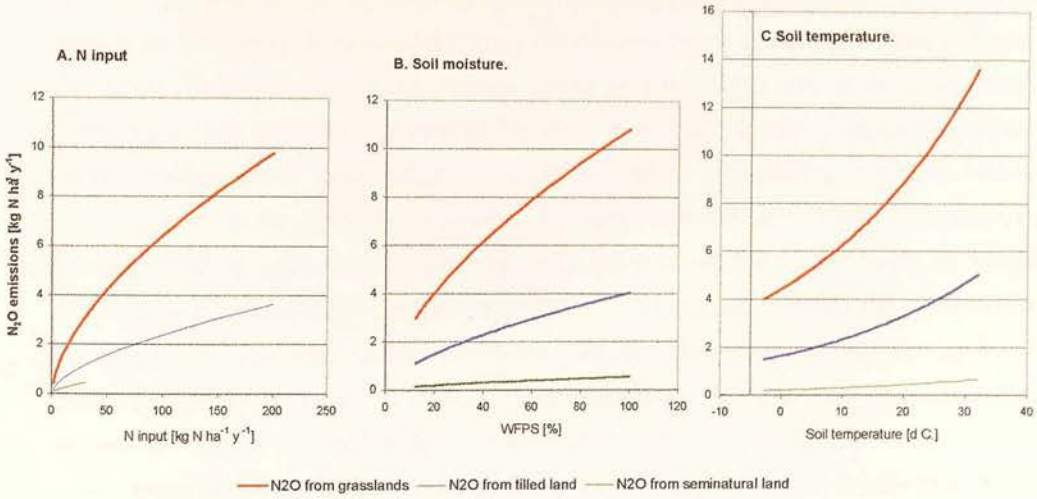
$$E = e^F + \varepsilon \qquad (5.13)$$

Where E – N_2O emissions

F – empirical model described by equation (5.12)

ε - residual error of estimated N_2O emissions

Figure 5.10 Modelled N_2O emissions for different land classes with changing independent variables.



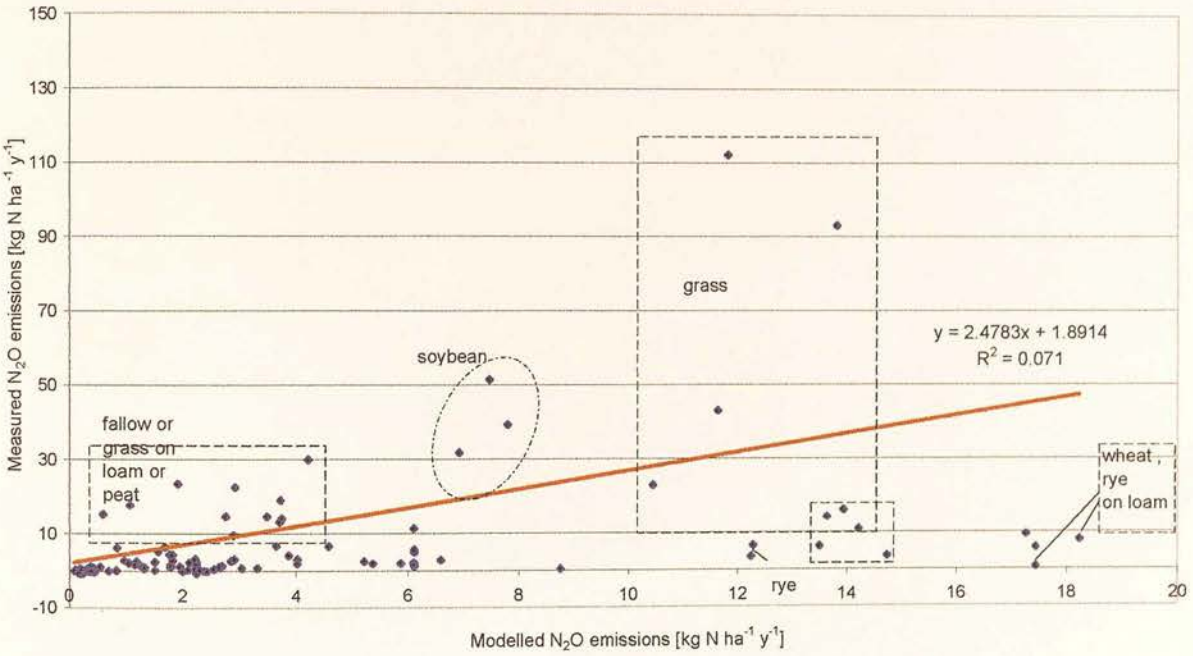
In order to observe the characteristic trends of the empirical model, N_2O emissions were estimated for different land classes (grasslands, tilled land and seminatural land) for three different scenarios that varied each of the independent variables while the values of others were fixed. The model (equation 5.12) predicted the highest N_2O emissions for grasslands that were on average a factor of 2.5 higher than the emissions from tilled land for the same environmental conditions of soil moisture, soil temperature and N input (figure 5.10 a-c). The definition of the model had implications for the predicted values of N_2O emissions that showed a slight asymptotic trend with an increase in both soil moisture (WFPS) and N input. This trend might suggest that there is a limit to growth for N_2O emissions but within the presented ranges of WFPS and N input the model could not indicate the value of

the asymptote. An increase in soil temperature caused an exponential growth in N_2O emissions for grasslands and tilled land, and consistently with the other variables the observed increase was more pronounced for grasslands (figure 5.10 c). This trend could be explained by observations of bacterial activity that increases exponentially with an arithmetic increase in temperature (chapter two).

The differences between the three defined land classes (figure 5.10a, b, c) reflected observed differences in field measurements (section 5.2). Very low N_2O emissions were observed from seminatural land. The difference between agricultural and seminatural land in terms of N_2O emissions was not that surprising due to considerably lower N input in semi-pristine environments where atmospheric N deposition was the single source of soil N content. This was reflected by figures 5.10b and 5.10c where assumed N input for the seminatural land was 20 kg N ha^{-1} yr^{-1} as opposed to 111 kg N ha^{-1} yr^{-1} for tilled land and grasslands (the values were based on the mean N input data from the experimental data set). As the differences between the three main land classes could be considered an effect of agricultural practices, they are also controlled by environmental variables of air temperature and precipitation that have a variable effect depending on soil textural characteristics. Grasslands represent the most variable environment in which the presence of N substrate is hardly ever limited due to very high N fertiliser applications, while the principal controllers of N_2O emissions are soil moisture and temperature. The soils under grasslands, represented in the experimental data set with moderate to heavy textures, cause dynamic changes between aerobic and anaerobic states controlled by soil moisture. The grassland environment is more favourable for denitrification that is the principal source of N_2O production and the high moisture levels in those soils enhance the production of N_2O as a result of NO reduction by bacteria. Tilled land in the data sets was mostly characterised by soils with good drainage that caused lower soil moisture and created an optimal environment for nitrification and a higher ratio of NO/N_2O due to increased soil diffusivity. This was reflected by the trends presented by the model (figures 5.10 b,c) that established grasslands as the highest source of N_2O emissions.

The predicted N_2O emissions and the measured N_2O emission were plotted to assess uncertainty in the model. The observed distribution presented in figure 5.11 suggested considerable variability. The distribution of plotted points was best defined by a linear trend. A simple linear regression was applied to describe this distribution and to validate the estimated N_2O emissions.

Figure 5.11 Existing trends in the empirical model of N_2O emissions.



The data analysed in the linear regression did not fulfil the requirements of the normal distribution of variables and residuals. This analysis, however, was carried out specifically to compare the predicted N_2O emissions with the measured mean N_2O emissions. The requirements of valid regression analysis were therefore relaxed here, as the presented equation (5.14) is listed explicitly to describe a trend of the relationship and to observe departures of the predicted values from the observed N_2O emissions.

$$E = 1.9 + 2.5 * e^{F} + \varepsilon \qquad (5.14)$$

The relationship was very weak as indicated by a small coefficient of determination (r^2), which suggested that the model accounted only for 7% of observed variability in N_2O emissions. The large uncertainty of the empirical model was also indicated by a large standard error (s=40.36). The trend presented in figure 5.11 suggested

that the defined empirical model has a tendency to underestimate N_2O emissions by a factor of 2.5.

The observed linear trend, however, represents the underestimating pattern of the predictions. In order to evaluate the true predictive power of the defined model, the modelled N_2O emissions for all data plots were compared directly with the measured emission values from the experimental data set. This comparison aimed at outlining the ecosystems with the best and the worst predictions made by the defined model. The results of this comparison indicated that the model underestimated N_2O emissions in 26% of the analysed plots and overestimated in 30.5% of studies. The predictions for the remaining part of the data plots were within 1kg N ha^{-1} yr^{-1} range from the measured emissions and were considered close. The studies best described by the model were located in The Netherlands (grasslands on clay and peat, the latter was unmanaged), Denmark (rye), Germany (uncultivated and wheat sites, both with moderate N inputs) and in the USA (studies of N_2O emissions from tobacco, fallow fields in Iowa and Washington and several forest sites). The prediction of the defined model was good for only one data plot in Great Britain. Its significance, however, is low as it represents a control plot on a wheat field in Rothamsted (Harrison *et al.*, 1995). This suggests that the trend of N_2O emission responses to the controlling factors presented by the predictive model inclined towards the North American and some European studies from other countries. The studies from Great Britain listed in the experimental data set were not well represented.

The uncertainty of the model was partly due to a general trend to underestimate presented by the simple regression analysis (equation 5.14). This uncertainty could be described by a standard error of the observed trend, multiplied by the Student's t statistic, that describes departures of real values from the observed means (Snedecor and Cochran, 1978). For some data plots the error was expected to exceed the standard error limits defined by t with 95 and 97.5 % probability. The error for each data plot was calculated with an equation (3.4) (chapter three). The sites that had large residual error were all defined as agricultural land. The sites with a large positive residual unaccounted for by the standard error variation were: a peat site in the Netherlands (Velthof *et al.*, 1996a); mown and grazed grass (Velthof *et al.*, 1996b) in North Wyke (UK); fallow fields in Colorado (Anderson and Levine, 1987) and in southern England (Armstrong, 1983); a soybean field in Iowa (Bremner *et al.*, 1981); a beet field cleared in Germany (Conrad *et al.*, 1983) and a fallow field in Germany (Kamp *et al.*, 1996). Among the agricultural systems for

which the predictions of the model were too high were the following: a grass in Belgium (Kaiser *et al*, 1996); grass in Spain (Slemr *et al*, 1984); ryegrass in Berkshire, UK (Ryden 1983) and in Denmark (Jorgenssen *et al*, 1997); unplanted soils in Iowa (Breitenbeck and Bremner, 1986); a tobacco plantation in Wisconsin (Goodroad *et al.*, 1984); grassland in Rothamstead (Yamulki *et al.*, 1997) and grassland in Glencourse Main, UK (Clayton *et al.*, 1997). It was very difficult to observe any patterns that might suggest specific weaknesses of the empirical model. Both land use and the location of the sites confirmed the difficulty of predicting the variability of N_2O emissions. The characteristics of the largest residuals suggested that very high N input, the presence of plant residues in soils or drainage of peats might promote exceptionally high N_2O emissions that are not accounted for by the empirical model. Exceptionally low N_2O emissions were observed from soils of poor drainage like gleysols and silt clay loam in saturated conditions. Soil moisture and temperature were observed to act as limiting factors on unplanted loam, clay loam and silt clay loam soils that received high N input in Iowa where Breitenbeck and Bremner (1986) measured WFPS of 47.4% and soil temperature of 28 °C.

5.6 VALIDATION OF INPUT DATA PARAMETERS.

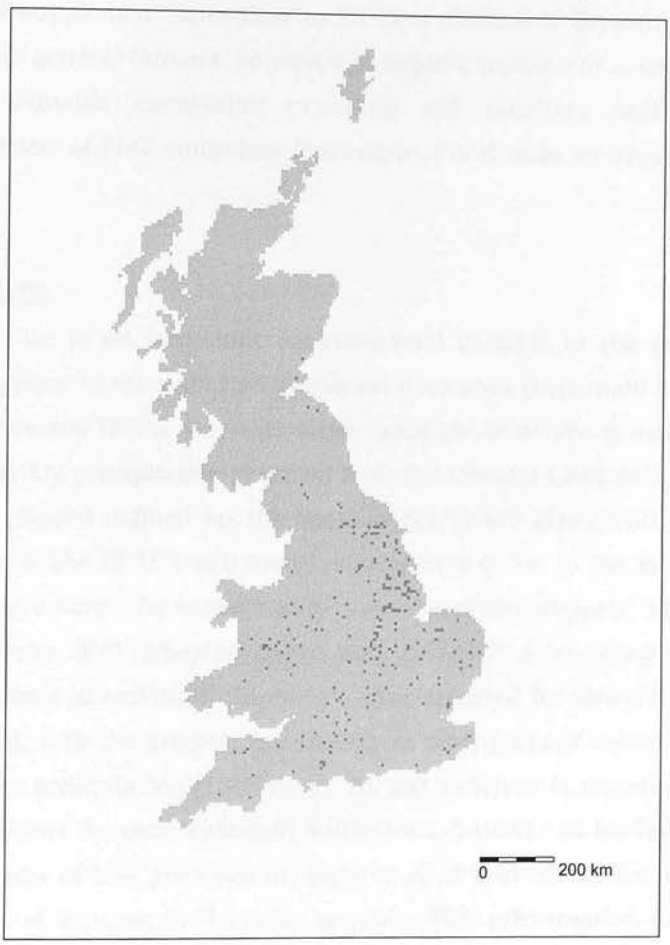
The performance of the AGEM model to estimate N_2O emissions from British soils is affected by the reliability of the empirical equation in estimating N_2O emissions and by the reliability of the input data used as predicting parameters. There are four main controlling factors that decide on the predicted levels of N_2O emissions: N input to soils; soil moisture; soil temperature and the dominant land class. In the previous chapters some validation of the input data sets was carried out. The following section presents the reliability of input data sets in the context of Great Britain, and discusses their likely effect on the uncertainty of predictions.

N input.

N input to agricultural soils is the sum of mineral and organic N fertiliser application and atmospheric N deposition, while on seminatural land soil N is assumed to be provided exclusively from the atmosphere. Atmospheric N is the sum of interpolated site measurements of the wet components of atmospheric deposition and dry deposited oxidised N (RGAR, 1997), and modelled ammonia deposition

(Singles *et al.*, 1998). The interpolation error of wet deposition was estimated in the range from 5 to 15 μeql^{-1} with uplands identified as the areas of greatest uncertainty (section 3.2.5, chapter three). N fertiliser input estimated for different crops according to guidelines of good fertiliser practice (chapter three) reveals some uncertainty due to the differences between the recommended amounts and the actual N input, and as a result of the Agricultural Census (AC) data errors. The guidelines of good fertiliser practice were chosen for estimating N fertiliser inputs to soils due to the greater spatial detail of this approach than the published overall rates of mineral N input to grasslands and cereals for major areas in Great Britain. N application rates exceeding the national average of 130 kg N ha^{-1} (Owen, 1997) were observed in most parts of England, in Wales in Pembrokeshire and The Vale of Glamorgan, and in Scotland in East and West Lothian, Fife, East Renfriewshire, North Lanarkshire and Aberdeenshire (figure A9). If the national mean application rate was assumed as the N input rate in those areas, N_2O emissions would be underestimated. Contrasting to those areas, in large parts of Scotland, North Wales and in England: Richmondshire; Teesdale; Wear Valley and Tynedale (figure A9) the assumed overall N rate of 130 kg N ha^{-1} would cause some overestimation in predicted N_2O emissions due to dominance of non-intensive management practices. The issue of reliability of the fertiliser recommendations as an indicator of N fertiliser input was addressed by the Survey of Farmers in the Lothian region (chapter four). The survey estimated that N input might vary from the estimated value on average by a factor of 3, with decreasing reliability of recommendations as indicators of actual N inputs in the order cereal crops > other tillage crops > grasslands. The results of the survey are applied in the sensitivity analysis as guidelines of varying N input variable (chapter six). The total of mineral N inputs to British agricultural soils, based on the AC data from 1988, was estimated at 1860 kt N y^{-1}. This corresponded well with the published data of UK consumption of mineral N fertiliser, that amounted to 1525 and 1514 kt y^{-1} for 1987/88 and 1988/89, respectively (FMA, 1998). The mineral fertiliser levels were therefore overestimated in this approach by 21.9 % or 22.8 % depending on the period to which the estimated N fertiliser input is referred to. The higher estimate of mineral N input is caused by a combination of the land use data errors and the recommendation approach.

Figure 5.12 Location of pixels with overestimated agricultural land.



There were 213 5 km grid squares in Great Britain where total agricultural area presented by the AC exceeded the maximum possible land area (2500 ha). Most of the erroneous grids were located in England and Wales, but no noticeable spatial pattern was recognised (figure 5.12). The reason for their spatial occurrence in England is likely to be due to a higher proportion of agricultural land. The check-board distribution of the grids with overestimated agricultural land might be caused by the method of allocating the parish information from the Agricultural Census to 1 km grids (method described in chapter three). The total surplus of mineral N fertiliser input estimated on the basis of the 1988 mean N application rate of 130 kg ha^{-1} (Owen, 1997) and the surplus agricultural area only explained a difference of 7 kt N y^{-1}. The remainder of 328 kt N y-1 or 339 kt N y^{-1} (for 1987/88 or 1988/89) is the result of the mineral N input departures from the recommended values, which contributes to the proportionate difference of 21-22 %. This error was partly due to some N inputs to grasslands and tilled land in organic form, the amounts of which are not registered. All of the produced organic fertiliser, based on

the livestock total, would easily supplement most of the N input to those agricultural crops (approx. 1568 kt y^{-1}) even with an assumed standard efficiency of organic N supplement equivalent to 70 % of mineral N (Dyson, pers. comm). This reflects the general farmers' approach to organic manure as a waste product rather than a valuable commodity providing soil nutrition and results in high concentration of N_2O emissions from agricultural soils in areas of high livestock densities.

Soil moisture.

Soil moisture is an important environmental variable in the predictive empirical models applied to estimate N_2O emissions from soils (equations 5.11 and 5.12). The data of seasonal WFPS were estimated using the SPACTeach model on the basis of mean monthly precipitation obtained from the Climate LINK data set and major soil drainage classes defined on the basis of the HOST classification (chapter three). Validation of the SPACTeach model was restricted due to the limited availability of soil moisture data. The model results were therefore compared with soil moisture at field capacity (FC) (chapter three) and revealed a tendency of SPACTeach to overestimate soil moisture. The mean error reported for Great Britain was 22.4 % (4.2 - 26.4), with the greatest uncertainty in most parts of western Britain receiving the highest precipitation (1800 mm). As soil moisture is expected to remain below FC throughout the year, especially within well drained and moderately drained soils and in areas of low precipitation (figures A3.3 and A3.6), the observed error for winter would increase in the other seasons. This presumption can not be verified, however, due to lack of data. Further analysis of the effects of soil moisture variability on the predicted N_2O emissions is explored by sensitivity analysis (chapter six).

Soil temperature

Soil temperature is the least important factor controlling N_2O emissions in models (5.11) and (5.12). It is therefore justified to assume that the uncertainty introduced by this variable will not be important at large scales, however, locally it might reduce accuracy of predicted N_2O emissions on seminatural land in relatively dry areas. Seasonal soil temperature at 30 cm depth was estimated using SOILTEMP model, which applied theory of heat flux (section 3.3.1, chapter three). Predicted soil temperature was validated with mean seasonal soil temperature measured at 41 selected BADC stations at 30 cm depth (section 3.3.1, chapter three). High correlation coefficients (0.80 for summer and autumn and 0.85 for winter and

spring) confirmed relatively good fitness of the model. Residual errors indicated, however, a general underestimating trend of SOILTEMP, and the standard errors for different seasons suggested that predicted soil temperature in winter could vary from the measured values by 1.4 °C, in spring by 2 °C, in summer by 0.4 °C and in autumn by 0.6 °C ($p < 0.5$). The climatic stations with the largest residual error in winter and spring were located in extreme environments, where soil temperature is not expected to have important effect on N_2O emissions (section 3.3.1, chapter three). Any uncertainty introduced by the estimated soil temperature is investigated further by sensitivity analysis in chapter six.

Land use data.

The AC and the LCM are applied in the AGEM (table 3.1, chapter three) to define the dominant land class within each 5 km grid for which mean N_2O emissions are predicted with model (5.12). Considerable uncertainties are expected in the defined land use caused by differences between the two data sets. Compatibility of the AC and the LCM data was analysed for the pilot study of the Tyne-Clyde area in chapter four. The regression analysis for all the grids within the study area revealed that large differences exist within the two land classes common to both data sets: managed grasslands and tilled land. The analysis indicated that due to the differences identified, N_2O emissions were likely to be overestimated in the West as an effect of greater spatial extent of grasslands presented by the AC compared to the LCM, and in the East caused by similar differences in tilled land.

In this section the land use data set for Great Britain, which was derived from the combined AC with the LCM, is validated against the total grid area. That area was defined as the total LCM area brought to the resolution of a 5km grid. Due to great uncertainties in coastal grids presented by the LCM (with an accuracy to 1 km grid) only the inland area was validated. A comparison of the maximum possible grid area (2500 ha) with the total land use data suggested considerable departures of the estimated total land from the combined AC with the LCM, and in some areas the overestimation exceeded a factor of 2 (figure A10). The highest error was recorded near Stafford (Easting=377, Northing=337), where the large agricultural area of > 4800 ha was classified by the AC as mixed grassland and cereals.

In order to analyse the effect of those discrepancies on the predicted N_2O emissions, the grids with overestimated total area (> 2500 ha) were grouped according to the dominant land class, as defined by the variable of model 2 (equation 5.12). Managed grasslands were estimated to be the largest contributor to

the overestimated grids (11.9 %), with a similar input from seminatural land (10.8 %) and a smaller proportion represented by the dominant tilled land (6.4 %). Assuming the dominant class indicates the land use type responsible for introduced uncertainty into the model, grasslands are the reason for overestimation of N_2O emissions in the West, while tilled land causes prediction errors in the East. The uncertainty was difficult to assess, but it was expected to be proportional to the estimated N inputs and the area of overestimation. The larger proportion of grassland areas in the West are associated with high N inputs (max. 780 kg N ha^{-1} y^{-1}), while the greater proportion of tilled land in the East resulted in lower N inputs (200 - 500 kg N ha^{-1} y^{-1}). On the basis of the N_2O emission rates predicted with model (5.11) and model (5.12), the uncertainty associated with land use area was assessed according to the equation (5.15).

$$e_{LU} = E_{N2O} * e_A \qquad (5.15)$$

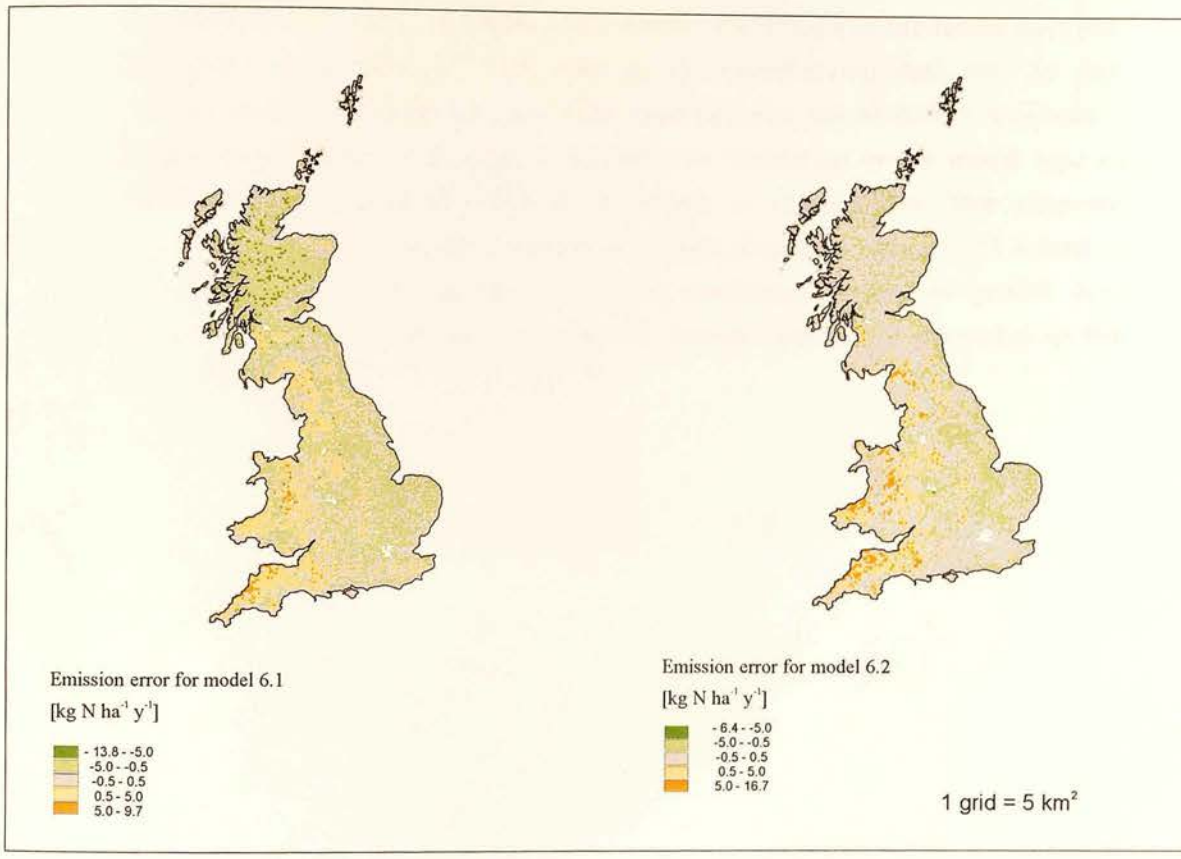
Where e_{LU} - emission error caused by land use inaccuracies

E_{N2O} - predicted mean N_2O emissions from soils

e_A - fraction error estimated as a difference between the total land use and the grid area of 2500 ha.

The emission error was estimated for annual N_2O emissions as predicted by model (5.11) and model (5.12). Mean error due to land use inaccuracies was low as the uncertainty of mean N_2O emissions was defined by model (5.11) as 5.3 ± 0.18 kg N ha^{-1} y^{-1} and by model (5.12) as 3.9 ± 0.2 kg N ha^{-1} y^{-1}. On the other hand, the range of error observed for the two models was very large, and varied from underestimation with model (5.11) by > 5 kg N ha^{-1} y^{-1} in North Scotland (figure 5.13 a) to overestimation with model (5.12) by > 7 kg N ha^{-1} y^{-1} in the areas where grasslands were the dominant land class (figure 5.13 b).

Figure 5.13 Uncertainty of predicted N_2O emissions due to land use inconsistencies.



In summary the described limitations of input data are expected to influence the accuracy of predictions made by the AGEMs. Soil moisture and land use are expected to contribute the largest uncertainty, followed by N input and soil temperature.

5.7 CONCLUSIONS.

The empirical model of N_2O emissions established on the basis of field measurements from a variety of environments in temperate climates, showed a tendency to underestimate N_2O emissions from agricultural systems by a factor of 2.5. Seminatural environments, mostly represented in the experimental data set by coniferous forests, were well described by the empirical relationship. A large proportion of the analysed sites showed high residual error unaccounted for by the presented trend of the model. The sites with high residual error were different in terms of land use, soil characteristics, N input and geographical location. Some common general characteristics of those sites, however, suggested ecosystems for which an application of the model is limited. The general overestimating trend for

intensive agricultural systems suggests a high sensitivity of the model to N input. The limiting environmental factors that were expected to restrict the release of N_2O emissions are not strong variables in the model. Predictions of the model were not particularly good for the British sites in the experimental data set. As this comparison was based on the same data used to derive the models, it was only a preliminary indicator of the AGEM performance. Validation of the model against further field measurement data is presented in chapter six. The observed limitations due to the model definition and input parameters data need a further sensitivity analysis. An application of the established model to predict N_2O emissions and the model sensitivity in the British context are presented in the following chapter.

APPENDIX.

Table 5.1 N_2O experimental data set.

Ref*	land use	soil type	N_2O emission flux [kg N ha^{-1} y^{-1}]	Fertiliser application rate [kg N ha^{-1}]	WFPS [%]	soil temperature [°C]	fertiliser type	soil C content [%]
3	grassland	Argic Cryobolt	0.2	7.6				
8	grassland	humisol	-0.5	17.2		21.2		
9	grassland	humisol	1.2	117.2		21.2	$CO(NH_2)_2$	
10	grassland	humisol	1.4	117.2		21.2	$NaNO_3$	
11	grassland	humisol	1.6	17.2		21.5		
12	grassland	humisol	2.0	117.2		21.5	$CO(NH_2)_2$	
13	grassland	humisol	4.8	117.2		21.5	$NaNO_3$	
14	grassland	humisol	0.6	17.2		16.9		
15	grassland	humisol	1.0	117.2		16.9	$CO(NH_2)_2$	
16	grassland	humisol	1.5	117.2		16.9	$NaNO_3$	
17	grassland	humisol	0.2	17.2		4.2		
19	grassland	peat (Terric Histosol)	93.0	263.7	62.0	14.4	mix	50.6
20	grassland	peat (Terric Histosol)	19.1	19.7	91.0	14.8		50.6
22	grassland	peat (Terric Histosol)	22.6	19.7	92.0	7.7		50.6
23	grassland	sandy loam	6.6	234.7	53.4	15.6	u/sified	
24	mown	poorly drained clay	112.2	150.3	85.0	14.2	NH_4NO_3	
26	grassland	sand	1.3	19.7	67.5	10.7		
27	mown	sand	3.6	332.7	68.0	10.7	$Ca(NO_3)_2$	
28	grazed	sand	9.5	430.0	68.5	10.7	cow excreta	
29	grassland	clay	1.1	19.7	67.5	10.1		
30	mown	clay	6.3	296.7	68.0	10.1	$Ca(NO_3)_2$	
31	grazed	clay	14.3	299.7	68.5	10.1	excreta	

32	grassland	peat 1 (16.3gN/kg)	2.7	19.7	72.5	11.0		
33	mown	peat 1 (16.3gN/kg)	10.9	285.7	73.0	11.0	$Ca(NO_3)_2$	
34	grazed	peat 1 (16.3gN/kg)	16.1	274.7	73.5	11.0	excreta	
35	grassland	peat 2 (18.6gN/k)	14.7	19.7	67.5	11.3		
36	mown	peat 2 (18.6gN/k)	22.9	180.7	68.0	11.3	$Ca(NO_3)_2$	
37	grazed	peat 2 (18.6gN/k)	43.1	214.7	68.5	11.3	$Ca(NO_3)_2$	
38	mown	clay, silt loam	1.3	25.3				
39	mown	clay	43.9	425.3			$CO(NH_2)_2$	4.0
40	mown	silt loam	22.2	425.3			$Ca(NO_3)_2$	2.3
54	grassland	sandy loam	3.6	9.2		4.9		
56	grassland	sandy loam	6.9	309.2		4.9	$Ca(NO_3)_2$	
57	grassland	sandy loam	0.5	9.2		4.9		
58	grassland	sandy loam	1.1	174.2		4.9	slurry	
59	grassland	sandy loam	1.3	209.2		4.9	$Ca(NO_3)_2$	
60	pasture	sandy silt loam	3.5	9.8				
62	grass lawn	loamy sand	0.1	4.9	12.9	29.2		
63	grass lawn	loamy sand	2.6	104.9	12.9	29.2	NH_4NO_3	
65	ryegrass	loam overlying clay	-0.6	15.7	49.1	14.8		
66	ryegrass	loam overlying clay	3.5	265.7	49.1	14.8	NH_4NO_3	
67	ryegrass	loam overlying clay	8.0	515.7	49.1	14.8	NH_4NO_3	
72	rye	sandy loam	2.1	129.8	31.5	13.7	NH_4NO_3	1.2
73	rye	sandy loam	1.5	9.8	37.5	10.9		1.2
74	rye	sandy loam	6.7	84.8	37.5	10.9	NH_4NO_3	1.2
75	corn	sandy loam	0.1	25.9	13.4			
76	corn	sandy loam	0.2	137.9	13.4		NH_4NO_3	
77	corn	sandy loam	0.7	249.9	13.4		NH_4NO_3	
78	corn	sandy loam	1.3	361.9	13.4		NH_4NO_3	
79	corn	clay	18.4	43.6				
80	corn	clay	35.2	155.6			NH_4NO_3	
81	corn	clay	21.5	267.6			NH_4NO_3	
82	corn	clay	65.6	379.6			NH_4NO_3	
83	corn	sandy loam	27.8	55.3	31.7	31.4	u/sified	2.0

84	barley	sandy loam	19.8	30.7	22.6	21.4	u/sified	2.0
85	winter wheat	clay loam	3.0	19.9	46.8	21.6	u/sified	1.4
86	fallow	clay loam	17.8	9.9	44.2	31.8		1.4
87	fallow	sandy loam	3.4	9.8	29.3			1.9
88	fallow	sandy loam	10.8	209.8	29.3		NH4NO3	1.9
89	fallow	sandy loam	91.7	501.8	29.3		cow slurry	1.9
90	fallow	silt loam	0.0	5.8	41.7	7.6		
91	fallow	silt loam	0.6	60.8	41.7	7.6	liquid NH_3	
92	fallow	silt loam	1.3	115.8	41.7	7.6	liquid NH_3	
93	fallow	silt loam	3.1	225.8	41.7	7.6	liquid NH_3	
94	fallow	loamy sand	4.2	215.7	89.1	3.5	$Ca(NO_3)_2$	
95	fallow	clay loam	30.0	215.7	102.4	3.6	$Ca(NO_3)_2$	
96	fallow	loamy sand, clay loam	0.2	215.7		11.2	$Ca(NO_3)_2$	
97	fallow	sandy loam	4.9	139.8			cattle slurry	
98	fallow	sandy loam	4.2	139.8			UAN	
99	fallow following barley	Chernozem, loam	14.7	5.7		9.6		5.7
100	fallow following barley	Chernozem, loam	38.1	62.7		9.6	KNO_3 (N^{15})	5.7
101	fallow following barley	Chernozem, loam	1.4	5.7				5.7
102	fallow following barley	Chernozem, loam	1.4	62.7			KNO_3 (N^{15})	5.7
103	fallow following barley	Chernozem, loam	70.1	5.7		10.2		5.7
104	fallow following barley	Chernozem, loam	188.8	105.7		10.2	KNO_3 (N^{15})	5.7
109	fallow	silt loam	3.8	25.9		10.7		3.7
110	fallow	silt loam	10.7	145.9		10.7	dairy manure	3.7
111	alfalfa	silt loam	4.3	25.9		10.7		3.7
112	grass	silt loam	1.8	75.9		10.7	NH_4NO_3	3.7
113	fallow	silt loam	4.0	25.9		6.3		3.7
114	fallow	silt loam	5.8	115.9		6.3	manure	3.7
115	alfalfa	silt loam	3.8	25.9		6.3		3.7
116	grass	silt loam	-0.1	25.9		6.3		3.7
117	barley	silt loam	1.3	100.9		4.4	NH_4NO_3	3.7
118	soybeans	silt loam	1.9	25.9		4.4		3.7
119	canola	silt loam	1.6	125.9		4.4	NH_4NO_3	3.7

120	grass	silt loam	0.3	25.9		4.4		3.7
121	corn	silt loam	2.5	125.9		4.4	NH_4NO_3	3.7
122	wheat field	flinty loam	0.8	367.8		8.0	Nitram	
123	wheat field	flinty loam	0.2	367.8		15.7	Nitram	
124a	wheat field	flinty loam	0.4	17.8				
124b	wheat field	flinty loam	0.1	17.8		4.2		
125	soybean cleared	Harps, silty clay loam	4.5	23.0	60.7	26.1		4.6
126	soybean cleared	Harps, silty clay loam	39.4	273.0	60.7	26.1	liquid NH_3	4.6
127	soybean cleared	Webster, clay loam	6.6	23.0	55.0	26.5		2.7
128	soybean cleared	Webster, clay loam	51.5	273.0	55.0	26.5	liquid NH_3	2.7
129	soybean cleared	Canisteo, loam	5.3	23.0	50.3	25.9		2.5
130	soybean cleared	Canisteo, loam	31.8	273.0	50.3	25.9	liquid NH_3	2.5
131	unplanted	Canisteo, loam	1.7	26.7	47.4	28.1		2.5
132	unplanted	Canisteo, loam	11.5	206.7	47.4	28.1	liquid NH_3	2.5
133	unplanted	Canisteo, loam	2.2	206.7	47.4	28.1	NH_4OH	2.5
134	unplanted	Canisteo, loam	2.0	206.7	47.4	28.1	$CO(NH_2)_2$	2.5
135	unplanted	Harps, silty clay loam	1.0	26.7	47.4	28.1		4.6
136	unplanted	Harps, silty clay loam	5.0	206.7	47.4	28.1	liquid NH_3	4.6
137	unplanted	Harps, silty clay loam	1.2	206.7	47.4	28.1	NH_4OH	4.6
138	unplanted	Harps, silty clay loam	1.5	206.7	47.4	28.1	$CO(NH_2)_2$	4.6
139	unplanted	Webster, clay loam	1.3	26.7	47.4	28.1		2.7
140	unplanted	Webster, clay loam	5.7	206.7	47.4	28.1	liquid NH_3	2.7
141	unplanted	Webster, clay loam	1.6	206.7	47.4	28.1	NH_4OH	2.7
142	unplanted	Webster, clay loam	1.7	206.7	47.4	28.1	$CO(NH_2)_2$	2.7
143	unplanted with corn resid.	Canisteo, clay loam	1.4	26.7				3.8
144	unplanted with corn resid.	Canisteo, clay loam	5.3	101.7			liquid NH_3	3.8
145	unplanted with corn resid.	Canisteo, clay loam	8.1	176.7			liquid NH_3	3.8
146	unplanted with corn resid.	Canisteo, clay loam	10.0	251.7			liquid NH_3	3.8
147	unplanted with corn resid.	Canisteo, clay loam	11.8	326.7			liquid NH_3	3.8
148	unplanted with corn resid.	Canisteo, clay loam	13.4	401.7			liquid NH_3	3.8
149	unplanted with corn resid.	Canisteo, clay loam	14.3	476.7			liquid NH_3	3.8
150	uncultivated	Eolian sand	0.8	9.8	25.2	15.3		

151	uncultivated	Eolian sand	0.3	9.8	25.2	15.3		
152	uncultivated	Eolian sand	2.8	109.8	25.2	15.3	NH_4NO_3	
153	uncultivated	Eolian sand	4.3	109.8	25.2	15.3	NH_4CL	
154	uncultivated	Eolian sand	4.3	109.8	25.2	15.3	NaNO3	
155	broccoli and cauliflower	Plano silt loam	1.1	312.2			NH_4NO_3	1.8
156	broccoli and cauliflower	Plano silt loam	0.6	552.2			mix	2.7
157	broccoli and cauliflower	Plano silt loam	2.7	432.2			mix	2.7
158	broccoli and cauliflower	Plano silt loam	0.9	112.2			NH_4NO_3	1.6
159	broccoli and cauliflower	Plano silt loam	0.5	112.2			NH_4NO_3	1.6
160	broccoli and cauliflower	Plano silt loam	0.5	112.2			NH_4NO_3	1.6
161	tobacco	Plano silt loam	9.4	312.2			NH_4NO_3	1.8
162	tobacco	Plano silt loam	2.9	552.2	46.6	13.8	mix	2.7
163	tobacco	Plano silt loam	2.0	432.2	44.8	12.8	mix	2.7
164	tobacco	Plano silt loam	2.6	112.2	44.0	11.3	NH_4NO_3	1.6
165	tobacco	Plano silt loam	1.6	112.2	44.0	11.3	NH_4NO_3	1.6
166	tobacco	Plano silt loam	1.8	112.2	44.0	11.3	NH_4NO_3	1.6
167	tobacco	Plano silt loam	3.1	267.2	44.8	12.8	NH_4NO_3	1.8
168	tobacco	Plano silt loam	1.7	122.2			NH_4NO_3	2.3
169	tobacco	Plano silt loam	2.1	267.2	44.8	12.8	NH_4NO_3	2.2
170	beet field, cleared	loess, brown soil	23.5	109.8	28.4	14.6	$NaNO_3$	0.5
172	meadow, unman	loess pararendzina	121.1	109.8		13.7	$NaNO_3$	0.8
173	meadow, unman	loess pararendzina	87.9	109.8		13.7	NH_4Cl	0.8
174	maize	acidic sandy podzol	0.2	4.9				
175	maize	acidic sandy podzol	0.9	304.9			mix	
176	maize	acidic sandy podzol	25.8	304.9			mix	
177	maize	acidic sandy podzol	7.7	4.9				
178	maize	sandy loam	2.3	169.7	26.6	11.3	u/sified	
179	maize	fine loam (Kidder)	3.6	191.0		12.6	mix	0.1
180	maize	fine loam (Kidder)	5.2	247.0		12.6	mix	0.1
181	wheat	silty distric Eutrochrept	2.0	39.8		8.2	u/sified	1.5
182	wheat	silty distric Eutrochrept	17.4	69.8		8.2	u/sified	1.5
183	potatoes	silty distric Eutrochrept	5.0	39.8		8.2	u/sified	1.5

184	potatoes	silty distric Eutrochrept	39.1	69.8		8.2	u/sified	1.5
185	winter wheat	loamy silt	1.6	9.8				
186	winter wheat	loamy silt	1.9	219.8			u/sified	
187	winter barley	loamy silt	1.3	9.8				
188	winter barley	loamy silt	2.1	219.8			u/sified	
191	barley	sandy loam (Otero)	1.2	12.0	23.7	8.8		1.7
192	barley	sandy loam (Otero)	2.1	68.0	23.7	8.8	NH_4NO_3	1.7
193	barley	sandy loam (Otero)	2.4	124.0	23.7	8.8	NH_4NO_3	1.7
194	barley	sandy loam (Otero)	3.3	236.0	23.7	8.8	NH_4NO_3	1.7
195	barley	sandy loam (Otero)	1.9	81.0	23.7	8.8	sewage sludge	1.7
196	barley	sandy loam (Otero)	2.5	83.0	23.7	8.8	sewage sludge	1.7
197	barley	sandy loam (Otero)	9.7	368.0	23.7	8.8	sewage sludge	1.7
201	winter wheat	sandy silt loam	1.2	117.8	13.3	15.1	NH_4NO_3	0.9
202	winter barley	sandy silt loam	1.7	69.8	19.0	15.1	NH_4NO_3	0.9
203	winter wheat	silt loam	1.1	219.8	24.7	14.5	NH_4NO_3	0.9
204	winter wheat	silt loam	0.9	69.8	24.7	14.5	NH_4NO_3	0.9
205	winter wheat	Denchworth clay	8.1	86.1			NH_4NO_3	
206	winter wheat	Denchworth clay	1.4	86.1			NH_4NO_3	
207	winter wheat	Lawford clay	2.3	86.1			NH_4NO_3	
208	winter wheat	Lawford clay	0.8	86.1			NH_4NO_3	
209	winter oilseed rape	Denchworth clay	12.9	156.1			NH_4NO_3	
210	winter oilseed rape	Denchworth clay	8.4	156.1			NH_4NO_3	
211	winter oilseed rape	Lawford clay	3.2	156.1			NH_4NO_3	
212	winter oilseed rape	Lawford clay	1.5	156.1			NH_4NO_3	
218	corn - w.wheat - w.barley	brown earth from loess	1.7	9.8				1.1
219	corn - w.wheat - w.barley	brown earth from loess	6.8	179.8			u/sified	1.1
220	corn - w.wheat - w.barley	brown earth from loess	14.0	292.8			mix	1.3
221	corn	alluvial silt loam	6.3	12.1	40.0	23.1		1.2
222	corn	alluvial silt loam	2.9	12.1	60.0	20.3		1.2
223	corn	fine clay	7.4	211.0	37.0		NH_4-N	1.3
224	sugar beet	silty clay loam (calcerous)	1.5	86.0	37.0		NO_3-N	1.7
225	winter wheat	fine-loamy dystric Eutrochrept	1.1	9.8	47.4	11.1		

226	fallow	fine-loamy dystric Eutrochrept	15.3	9.8	55.0	11.4		
230	rape seed	leached brown soil	1.8	182.3	32.5		u/sified	
231	rape seed	organic rendzina	36.0	221.8	85.0		u/sified	
232	rape seed	clay	9.0	199.3			u/sified	
233	lettuce		41.8	485.8			mix	
234	cellery		20.2	485.8			mix	
235	broccoli		26.4	485.8			mix	
236	cauliflower		28.0	675.8			mix	
237	artichokes		23.3	300.8			manure	
238	decidous	acidic cambisol	5.6	9.8				5.7
239	decidous	acidic cambisol	7.8	149.8			$(NH_4)_2SO_4$	4.1
240	decidous	acidic cambisol	1.5	9.8				5.5
241	decidous	sandy loam	0.0	12.4		-1.5		
242	decidous	sandy loam	0.0	12.4		3.2		
243	decidous	sandy loam	0.0	12.4	31.9	20.9		
244	decidous	sandy loam	0.0	12.4	56.0	8.7		
246	coniferous	sandy loam	0.0	12.4		-2.9		
247	coniferous	sandy loam	0.0	12.4		0.6		
248	coniferous	sandy loam	0.0	12.4	31.9	20.9		
249	coniferous	sandy loam	0.0	12.4	37.9	9.3		
250	coniferous	clayey skeletal soil	0.7	205.4			NH_4NO_3	
251	coniferous	clayey skeletal soil	0.0	5.4				
252	coniferous	clayey skeletal soil	0.2	5.4				
253	coniferous	spodosol	0.2	16.0				
254	coniferous	spodosol	0.4	16.0	96.6	1.7		
255	coniferous	spodosol	0.2	16.0	77.6	10.9		
256	coniferous	spodosol	0.0	16.0	96.6	8.0		
257	coniferous	spodosol	0.3	16.0	69.0	9.0		
258	coniferous	spodosol	0.2	16.0				
259	coniferous	spodosol	0.4	16.0	96.6	5.7		
260	coniferous	spodosol	0.3	16.0	84.5	12.9		
261	coniferous	spodosol	-0.3	16.0	96.6	13.0		

262	coniferous	spodosol	0.2	16.0	69.0	12.0		
263	coniferous	spodosol	0.0	10.0				
264	coniferous	spodosol	0.5	10.0	50.0	7.4		
265	coniferous	spodosol	0.3	10.0	13.8	12.9		
266	coniferous	spodosol	-0.8	10.0	48.3	15.0		
267	coniferous	spodosol	-0.7	10.0	41.4	12.0		
268	coniferous	spodosol	0.0	15.0				
269	coniferous	spodosol	-0.3	15.0	39.7	5.0		
270	coniferous	spodosol	-0.1	15.0	79.3	11.6		
271	coniferous	spodosol	-0.1	15.0	82.8	13.0		
272	coniferous	spodosol	0.0	5.5				
273	coniferous	spodosol	0.0	5.5	27.6	6.4		
274	coniferous	spodosol	0.3	5.5	67.2	13.3		
275	coniferous	spodosol	0.3	5.5	69.0	15.0		
276	coniferous	spodosol	-0.5	5.5	44.8	14.0		
277	cut grass	silty clay loam	0.3	113.8	81.0	11.2	$(NH_4)_2SO_4$	
278	grassland	loam	5.6	253.5	67.4		mix	5.0
279	winter wheat	loam	0.7	97.5	55.8		NH_4NO_3	
280	grassland	gleysol	-0.1	13.5	85.0	9.7		5.5
281	grassland	gleysol	0.7	373.5	85.0	9.7	$CO(NH_2)_2$	5.5
282	grassland	gleysol	5.9	373.5	85.0	9.7	NH_4NO_3	5.5
283	grassland	gleysol	-0.1	13.5	47.5	14.7		5.5
284	grassland	gleysol	3.0	373.5		14.7	$CO(NH_2)_2$	5.5
285	grassland	gleysol	0.7	373.5		14.7	NH_4NO_3	5.5
286	grassland	gleysol	-0.1	13.5	70.0	13.6		5.5
287	grassland	gleysol	15.4	373.5		13.6	$CO(NH_2)_2$	5.5
288	grassland	gleysol	4.9	373.5		13.6	NH_4NO_3	5.5
289	grassland	gleysol	0.5	13.5	85.0	7.7		5.5
290	grassland	gleysol	5.5	373.5		7.7	$CO(NH_2)_2$	5.5
291	grassland	gleysol	11.8	373.5		7.7	NH_4NO_3	5.5
292	grassland	gleysol	0.5	13.5	80.0	12.8		5.5
293	grassland	gleysol	23.1	373.5		12.8	$CO(NH_2)_2$	5.5

294	grassland	gleysol	9.7	373.5		12.8	NH_4NO_3	5.5
295	grassland	gleysol	0.2	13.5	60.0	14.7		5.5
296	grassland	gleysol	3.5	373.5		14.7	$CO(NH_2)_2$	5.5
297	grassland	gleysol	3.0	373.5		14.7	NH_4NO_3	5.5
298	coniferous forest	orthic podzol	0.1	12.0				
299	coniferous forest	orthic podzol	0.1	47.0			NH_4NO_3	
300	coniferous forest	peat	0.1	12.0				
301	coniferous forest	peat	0.3	47.0			NH_4NO_3	
302	winter wheat	silty loam	14.7	233.8	51.1	8.7	slurry	
303	winter wheat	silty loam	14.2	233.8	42.1	14.0	slurry	
304	winter wheat	silty loam	6.7	233.8	37.8	15.2	slurry	
305	winter wheat	silty loam	13.3	233.8	39.9	14.7	slurry	
306	corn	silt loam	3.2	34.4	55.0			
307	corn	silt loam	8.7	174.4	55.0		NH_4NO_3	
308	corn	silt loam	11.9	286.4	55.0		NH_4NO_3	
309a	grassland	clay	8.7	19.7		4.3		4.7
309b	grassland	clay	8.7	99.7		4.3	mix	4.7
309c	grassland	poorly drained sand	8.7	19.7		7.7		2.7
309d	grassland	poorly drained sand	2.3	189.7		7.7	$(NH_4)_2SO_4$	2.7
309e	grassland	poorly drained sand	1.1	189.7		7.7	$(NH_4)_2SO_4$	2.7
309f	grassland	poorly drained sand	59.2	189.7		7.7	$Ca(NO_3)_2$	2.7
309g	grassland	poorly drained sand	59.2	189.7		7.7	$Ca(NO_3)_2$	
309h	grassland	poorly drained sand	1.1	189.7		7.7	$CO(NH_2)_2$	
309l	grassland	poorly drained sand	21.7	19.7		18.1		2.7
309j	grassland	poorly drained sand	11.4	189.7		18.1	$(NH_4)_2SO_4$	2.7
309k	grassland	poorly drained sand	1.1	189.7		18.1	$(NH_4)_2SO_4$	2.7
309l	grassland	poorly drained sand	136.6	189.7		18.1	$Ca(NO_3)_2$	2.7
309m	grassland	poorly drained sand	94.5	189.7		18.1	$Ca(NO_3)_2$	2.7
309n	grassland	poorly drained sand	8.0	189.7		18.1	$CO(NH_2)_2$	2.7
309s	grassland	poorly drained sand	0.2	19.7		13.8		2.7
309t	grassland	poorly drained sand	2.5	69.7		13.8	$Ca(NO_3)_2$	2.7
309u	grassland	poorly drained sand	8.6	119.7		13.8	$Ca(NO_3)_2$	2.7

309v	grassland	poorly drained sand	12.2	169.7		13.8	$Ca(NO_3)_2$	2.7
309w	grassland	poorly drained sand	30.3	219.7		13.8	$Ca(NO_3)_2$	2.7
309z	grassland	poorly drained sand	59.5	319.7		13.8	$Ca(NO_3)_2$	2.7
309y	grassland	calcerous clay	0.8	19.7				2.7
309x	grassland	calcerous clay	1.4	239.7			$Ca(NO_3)_2$	2.7
309aa	grassland	calcerous clay	3.4	459.7			$Ca(NO_3)_2$	2.7
309ab	grassland	calcerous clay	5.1	679.7			$Ca(NO_3)_2$	2.7
309ac	grassland	calcerous clay	6.7	899.7			$Ca(NO_3)_2$	2.7
310	maize	podzol (90% sand)	11.0	284.9			liquid NH_3	19.0
311	maize	podzol on sand	0.4	4.9				3.0
312	maize	podzol on sand	38.5	234.9			mix	3.0
313	maize	podzol on sand	4.9	4.9				3.0
314	forest	podzol on sand	0.0	4.9				3.0
318	bare soil	sandy loam	56.3	142.0			uncomp.NPK	2.2
319	bare soil	sandy loam	37.9	191.0			uncomp.CS	2.2
320	bare soil	sandy loam	26.7	83.0			uncomp.CS	2.2
321	bare soil	sandy loam	6.6	2.0				2.2
322	bare soil	sandy loam	77.9	142.0			comp.NPK	2.2
323	bare soil	sandy loam	28.4	191.0			comp.CS	2.2
324	bare soil	sandy loam	23.0	83.0			comp.CS	2.2
325	bare soil	sandy loam	6.0	2.0				2.2
326	bare soil	sandy loam	2.6	25.9				1.8
327	bare soil	sandy loam	9.1	125.9			NH_4NO_3	1.8
328	bare soil	sandy loam	15.2	225.9			NH_4NO_3	1.8
329	bare soil	sandy loam	18.5	325.9			NH_4NO_3	1.8
330	shrub	coarse-silty XerollicCamborthid	0.2	5.8	18.0			
331	shrub	coarse-silty XerollicCamborthid	0.2	5.8				
332	shrub	coarse-silty XerollicCamborthid	0.2	5.8	17.0			
333	shrub	coarse-silty XerollicCamborthid	0.1	5.8				
334	shrub	coarse-silty XerollicCamborthid	3.2	5.8	31.8			
335	shrub	coarse-silty XerollicCamborthid	1.8	5.8				
338	oat	loamy sand and sandy loam	91.3	58.2	25.9		NH_4	

339	oat	loamy sand and sandy loam	138.7	58.2	28.4		NH_4
340	grassland	imperfectly drained loam	5.6	240.0	35.2		mix
341	wheat	imperfectly drained loam	0.7	86.0	18.0		NH_4NO_3
342	spruce forest	acid hapludalf	0.4	35.0		13.3	
343	spruce forest	acid hapludalf	0.7	35.0		13.3	
349	wheat	flinty loam on clay	0.0	17.8	39.8	10.9	
350	wheat	flinty loam on clay	0.2	65.8	39.8	10.9	Nitram
351	wheat	flinty loam on clay	0.4	113.8	39.8	10.9	Nitram
352	wheat	flinty loam on clay	0.8	209.8	39.8	10.9	Nitram
353	wheat	flinty loam on clay	0.9	242.8	39.8	10.9	FYM

Ref* - reference to literature in table 5.2
u/sified – unspecified fertiliser type
mix – mixed fertilisers
UAN – urea ammonium nitrate
FYM – farmyard manure

Table 5.2 Literature referencing of the experimental data.

Ref*	source
3	Matson *et al.* (1991)
8 - 17	Dunfield *et al.* (1995)
19, 20, 22	Velthof *et al.* (1996a)
23	Kaiser *et al.* (1996)
24	Velthof *et al.* (1996b)
26 - 37	Velthof *et al.* (1995)
38, 39, 40	Webster *et al.* (1982)
54 - 59	Egginton and Smith (1986)
60	Flessa *et al.* (1996b)
62, 63	Slemr *et al.* (1984)
65, 66, 67	Ryden (1983)
72, 73, 74	Jorgenseen *et al.* (1997)
75 - 82	McKenney *et al.* (1980)
83 - 86	Anderson and Levine (1987)
87, 88, 89	Christensen (1983)
90 - 93	Cochran *et al.* (1981)
94, 95, 96	Armstrong (1983)
97, 98	Kaiser *et al.* (1996)
99 - 104	Nyborg *et al.* (1997)
109 - 121	Wagner-Riddle *et al.* (1997)
122, 123, 124a,b	Yamulki *et al.* (1995)
125 - 130	Bremner *et al.* (1981)
131 - 142	Breitenbeck and Bremner (1986a)
143 - 149	Breitenbeck and Bremner (1986b)
150 - 154	Conrad and Seiler (1980)
155 - 169	Goodroad *et al.* (1984)
170 - 173	Conrad *et al.* (1983)
174 - 177	Jambert *et al.* (1994)
178	Kaiser *et al.* (1996)
179, 180	Cates and Keeney (1987)
181 - 184	Ruser *et al.* (1996)
185 - 188	Kohrs *et al.* (1996)
191 - 197	Mosier *et al.* (1982)
201 - 204	Kaiser *et al.* (1996)
205 - 212	Burford *et al.* (1981)
218, 219, 220	Killian *et al.* (1996)
221, 222	Qian *et al.* (1997)
223, 224	Mosier and Hutchinson (1981)
225, 226	Kamp *et al.* (1996)
230, 231, 232	Henault *et al.* (1996)
233 - 237	Ryden and Lund (1980)
238, 239, 240	Brumme and Beese (1992)
241 - 249	Bowden *et al.* (1990)
250, 251, 252	Matson *et al.* (1992)
253 - 276	Castro *et al.* (1993)
277	Yamulki *et al.* (1997)
278, 279	Ball *et al.* (1997)
280 - 297	Clayton *et al.* (1997)

298 - 301	Klemedtsson *et al.* (1997)
302 - 305	Clemens *et al.* (1997)
306, 307, 308	Thornton and Valente (1996)
309a – 309ac	Velthof *et al.* (1997)
310 - 314	Jambert *et al.* (1997)
318 - 325	Hansen *et al.* (1993)
326 - 329	Shepherd *et al.* (1991)
330 - 335	Mummey *et al.* (1997)
338, 339	Sharpe and Harper (1997)
342, 343	Butterbach-Bahl *et al.* (1997)
349 - 353	Harrison *et al.* (1995)

CHAPTER SIX

N_2O emissions from British soils.

General trends of distribution.

6.1. INTRODUCTION.

The control of N_2O emissions from soils by the four factors: N input to soils; soil temperature; soil moisture and land cover class has been described by two empirical models (equation 5.11 and 5.12, chapter five). These models are presented in this chapter by equations (6.1) and (6.2). They were applied to estimate distribution of N_2O emissions from soils in Great Britain, using N input to soils, soil temperature, soil moisture and the dominant land cover described in chapter three (figure 6.1) as input variables. While N input to soils, soil temperature and soil moisture could explain 31 % of N_2O emission variability (equation 6.1), the addition of land class as a predictor of emissions (equation 6.2) explained 40% of measured N_2O variability. The presented models offer two different approaches as suggested from different characteristics of the models in terms of the strength of the independent variables, described by coefficients of determination, and different values of intercept. This chapter presents the results of the two models, assesses their performance in predicting N_2O emissions in four field locations and outlines major differences between their approaches.

$$E_{N2O} = e^{(-6.0 + 0.75 * \ln N + 0.83 * \ln WFPS + 0.035 * Ts)} \quad (6.1)$$

$$E_{N2O} = e^{(-2.7 + 0.60 * \ln N + 0.61 * \ln WFPS + 0.035 * Ts - 0.99 * A)} \quad (6.2)$$

Where: E_{N2O} – N_2O emissions

N – total N input to soils defined as the sum of all agricultural inputs and atmospheric deposition [kg N ha^{-1} y^{-1}];

WFPS – soil moisture [%];

Ts – soil temperature at 30 cm depth [°C];

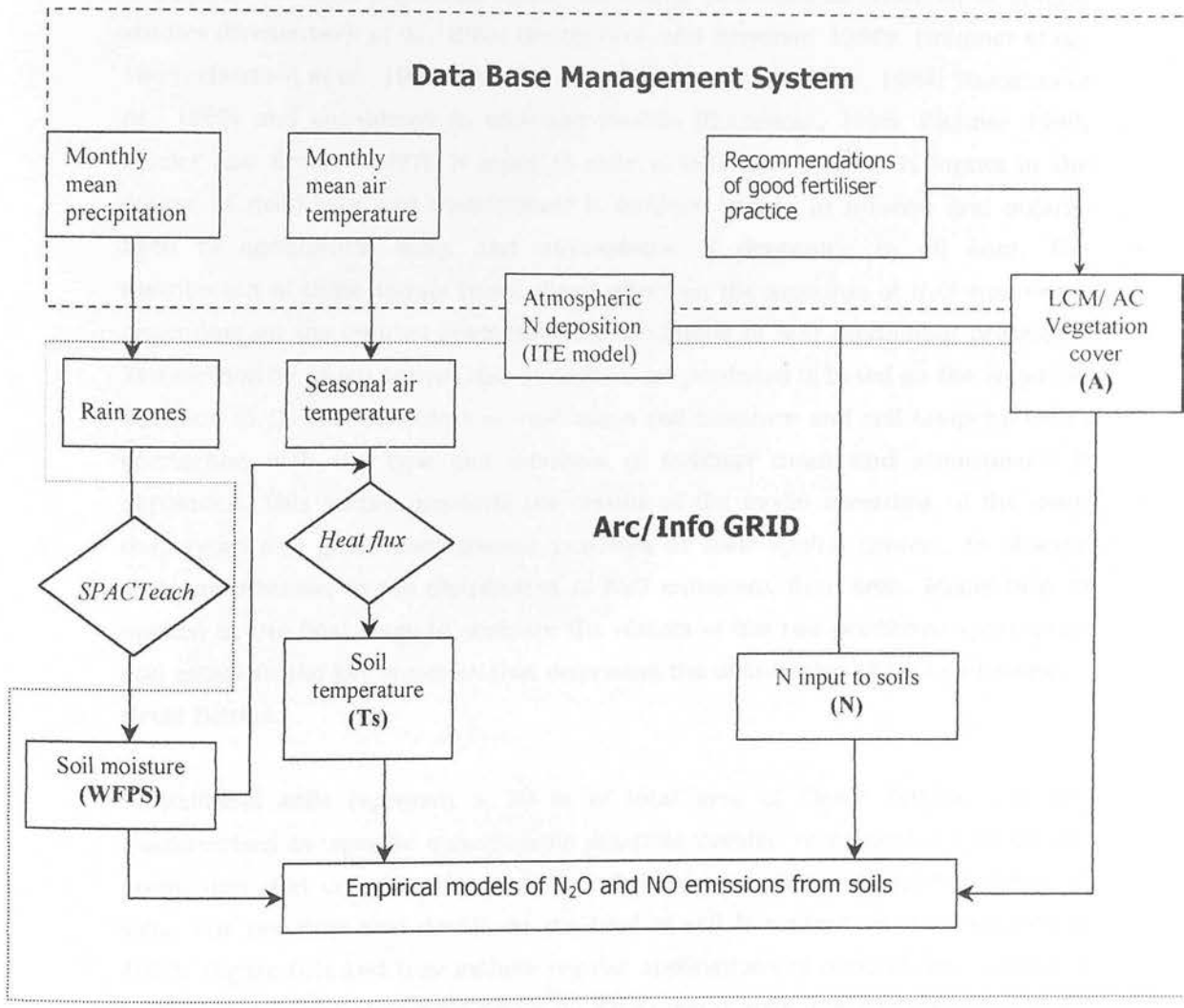
A – the dominant land class described as 1 for managed grasslands, 2 – tilled land and 3 – all semi-natural land.

The field measurements showed large spatial and temporal variability of N_2O emissions that caused considerable uncertainty of the model with 60 % of data variability not accounted for by the regression equation (6.2) and even greater uncertainty, of 70 %, with equation (6.1). The large variability of N_2O emissions not accounted for by the empirical models was expected to affect the estimated N_2O emissions. The assessment of the model (equation 6.2) performance for the 60 field sites (chapter five) showed greater uncertainty of the model for agricultural soils compared with semi-natural environments, especially under grasslands and fallow land where a great variability of soil characteristics like soil drainage and C content was observed. The model did not predict N_2O emissions well for the British sites listed in the N_2O data base e.g. a grassland site in North Wyke (site reference 24 and 25, table 5.1, chapter five), a fallow site in southern England (94-96), ryegrass in Berkshire (65-67), cut grass in Rothamstead (277) and grassland in Glencourse Mains (280-297). The issue of the suitability of the models for the British environment, addressed preliminarily in chapter five, is further investigated by their validation against field measurements and sensitivity testing of the models' performance for Great Britain.

This chapter presents the application of the predictive models (6.1 and 6.2) in the framework described as ArcInfo Grid Emission Model (AGEM) to estimate N_2O emissions from British soils (figure 6.1). In the first section the spatial distribution of N input to British soils is analysed in connection with the effect of that variable on the spatial variability of annual N_2O emissions. Dynamic changes in soil temperature and soil moisture result in seasonal changes of the emissions and emphasise the effect of seasonal N input variability. This is discussed in section

6.3. The uncertainty in the derived results due to the models formulation is examined in section 6.4. The chapter ends with a presentation of the sensitivity testing of the models' performance for Great Britain.

Figure 6.1. Arcin/Info Grid Emission Model (AGEM) structure.



6.2. ANNUAL N_2O EMISSIONS FROM SOILS AS AN EFFECT OF N INPUT TO SOILS.

N input is the most important factor controlling emissions as observed in several studies (Breitenbeck *et al.*, 1980; Breitenbeck and Bremner, 1986a; Bremner *et al.*, 1981; Harrison *et al.*, 1995; Skiba *et al.*, 1996; Slemr and Seiler, 1984; Thornton *et al.*, 1995) and considered in emission models (Bouwman, 1995; Eichner 1990; Mosier and Kroeze, 1997). N input to soils is both the effect of N inputs in the course of deliberate and undeliberate N fertiliser inputs in mineral and organic form to agricultural soils, and atmospheric N deposition to all land. The distribution of those inputs has a direct effect on the amounts of N_2O emissions, depending on the optimal environmental conditions of N_2O production processes. The method by which annual N_2O emissions are predicted is based on the empirical equation (6.1). This considers annual mean soil moisture and soil temperature in connection with the type and amounts of fertiliser input and atmospheric N deposition. This section presents the results of the model according to the main crop types and grass management practices in their spatial context, to observe their contribution to the distribution of N_2O emissions from soils. Model (6.2) is applied at the final stage to compare the results of the two predictive approaches and establish the key variables that determine the distribution of N_2O emissions in Great Britain.

Agricultural soils represent > 70 % of total area of Great Britain, and are characterised by specific management practices created to maximise agricultural production that considerably alter the physical and chemical characteristics of soils. The practices that decide on the level of soil N content were considered in AGEM (figure 6.1) and they include regular applications of mineral and organic N fertilisers, disposal of organic waste on agricultural soils and grazing animals on managed grasslands and rough grazing dominating upland areas. The management practices vary according to crop type on tilled land and intensity of livestock on managed grasslands. The distribution of mineral N fertiliser input to soils planted with cereals reflects the contribution of their area to the total agricultural land, and the structure of crop types that directly affect the application rate according to fertiliser recommendations (table 3.6, chapter three).

Cereals are grown mainly in England, while they are absent from upland areas of Great Britain. The highest mineral N inputs were registered in English 'triangle' of Central and Southeast England where the application rate exceeded 175 kg N ha^{-1} y^{-1}, and in some areas 190 kg N ha^{-1} y^{-1} (figure A11). The mineral N input represents the mean application rate to all cereal crops. The observed difference between Scotland, Wales and England is the effect of both the dominant crop types with a much higher proportion of wheat in England, and barley in Scotland, and the levels of fertiliser inputs to crops that vary for Scotland and England (table 3.6, chapter three), with generally lower N recommendations for Scottish soils. Estimated N_2O emissions from soils planted with cereals show a different spatial distribution (figure A12). High emissions (> 6 kg N ha^{-1} y^{-1}) are still observed in the English 'arable' triangle, but equally high N_2O emissions are estimated for Cornwall, South Wales, western Midlands, the Tweed Valley and coastal areas of Northumberland. The change in the spatial distribution of N_2O emissions is emphasised by an increase in the Geary[1] indices from 0.05 to 0.15 (definition in section 4.3, chapter four), which suggests some loss of the clustered character in the spatial distribution of the emissions relative to N input. This observed change is due to the strong influence of soil moisture, the second strongest factor in N_2O emissions in the AGEM model, indicated by a high coefficient of determination (equation 6.1). The areas where the enhancement of N_2O emission from arable land with cereals is observed receive precipitation exceeding 1000 mm (figure A4) and /or are dominated by soils with poor drainage (figure A6). These conditions result in the prediction of high mean annual soil moisture (WFPS > 75 %) and indicate optimal conditions for denitrification (figure A13). Soil moisture has more effect on the spatial distribution of N_2O emissions from soils planted with cereals than N input, as observed within the English 'arable' triangle (figure A12). This is entirely due to a greater spatial variability of soil moisture in the range of 35 and 90 % WFPS (figure A7) in comparison with uniform mineral N fertiliser inputs (figure A11).

Recommended mineral N inputs to ***other tillage crops*** are generally lower than to cereal crops with the exception of hops and some vegetable varieties in England/Wales, and oilseed rape and potatoes in Scotland (table 3.6, chapter three). The spatial distribution of mean mineral N application rate to tillage crops is more variable than on land planted with cereals with higher contributions of tillage crops to fertiliser N input in Scotland (figure A14). This is confirmed by the much

[1] Definition and description of the application in section 4.2.3 (chapter four)

higher value of the Geary index (0.17 compared to 0.04 for cereals). In England and Wales, agricultural soils receiving >150 kg N ha^{-1} y^{-1}, are localised in the South-east of England, Hereford and Worcester, South-west Wales, Cheshire Plain and the foot slopes of The Pennines and The Lake District. Estimated mean N_2O emissions from tillage crops are higher in Scotland than England and Wales relative to the emissions from cereals. The higher recommendations of N fertiliser for oilseed rape in Scotland result in an increase of 1 kg N ha^{-1} y^{-1} in the rate of N_2O emissions in large areas of Lothian, Fife and The Borders regions, where that crop is dominant. In England the very localised areas of the highest N_2O emissions from tillage crops are characterised by similar rates of N_2O emissions to cereals (figures A6.5 and A6.2). The spatial distribution of N_2O emissions from tillage crops is influenced by the effect of soil moisture, to a lesser extent, however, than from cereals, as the Geary statistic increases by barely 0.02. However, the soil moisture still enhances the N_2O emissions in some areas and limits the effect of N application in others, and the effect is most evident in the English 'arable' South-central triangle.

Different fertiliser practices are recommended for ***grasslands*** compared to tilled land, as they depend on livestock density (table 3.8, chapter three), which not only decides on the mineral N input, but also introduces an additional organic N input through grazing and production of organic waste on farms. The highest stocking density (> 5 SU ha^{-1}) is observed on grasslands associated with lower altitudes of the Scottish Highlands and Islands, the Southern Uplands, The Cheviot Hills, The Pennines, The Lake District, Welsh mountains, Exmoor and a few locations of East Anglia (figure A16). Those intensively managed grasslands receive the mineral N inputs of > 300 kg N ha^{-1} according to the recommendations of good fertiliser practice based on the livestock distribution (table 3.8, chapter three, figure A6.7). In those areas the organic fertilisers contribute surplus N inputs to soils equal to the amounts of mineral N fertiliser, and in some areas of western British uplands managed grasslands receive >50 % of their total N inputs in organic form. N_2O emissions from grasslands follow the spatial distribution of N fertiliser inputs more than soil moisture in contrast to tilled land (figures A6.8, A6.9). This might be caused by: (1) relatively higher N inputs to grasslands, with maximum of > 750 kg N ha^{-1} y^{-1} in comparison with 200 kg N ha^{-1} y^{-1} N input to tilled land; and (2) their spatial coincidence with high soil moisture (figure A13).

The distribution of mineral and organic N inputs to agricultural soils (figure A20) defines five major agricultural management types: (1) fringes of agricultural land with dominant hill grazing where N inputs of < 80 kg N ha^{-1} y^{-1} occur on steeper

slopes and at high altitudes of upland areas and wetlands of the North; (2) mixed tilled land with extensively managed grasslands, where N inputs range from 80 to 200 kg N ha^{-1} y^{-1} on lower altitudes than type (1); (3) intensive, mixed tilled land and grassland management with N inputs 200-300 kg N ha^{-1} y^{-1} that form the core of the British lowlands; (4) dominant intensive grassland management with some tilled land where N inputs range from 300 to 400 kg N ha^{-1} y^{-1} that occur in localised areas of lowlands with optimal agricultural conditions; (5) intensive grassland management with N inputs > 400 kg N ha^{-1} y^{-1} mostly in organic form, in localised areas of uplands and a few lowland locations e.g. on intensive dairy farms in East Anglia and the Midlands (England), The Tweed Valley, Fife and Aberdeenshire (Scotland). The highest N inputs of > 1 tN ha^{-1} y^{-1} are observed in three locations in Fife, West Lothian and Teesdale due to very intensive poultry farming ($280*10^3$ – over $1000*10^3$ birds).

N_2O emissions from agricultural soils range from < 1 kg N ha^{-1} y^{-1} in agricultural areas (1) to > 12 kg N ha^{-1} y^{-1} in localised areas described as type (5) (figure A19). It is observed that the spatial distribution of N_2O emissions < 8 kg N ha^{-1} y^{-1} is more strongly influenced by soil moisture than N input opposed to the areas of the highest emissions assigned to the agricultural areas of types (4) and (5). This might be explained by the fact of the location of intensively managed grasslands on soils characterised by poor drainage with high soil moisture that does not limit N_2O emissions enhanced by high N inputs. In agricultural soils within area type (3), where amounts of N substrate in soil are sufficient, soil moisture is observed to enhance N_2O emissions. In those areas N_2O emissions from soils with restricted drainage exceed 8 kg N ha^{-1} y^{-1} as opposed to drier areas where emissions are reduced to the range 4 – 8 kg N ha^{-1} y^{-1}. Soil moisture is an important limiting factor of N_2O emissions caused by N fertiliser inputs to tilled land (figure A13).

Semi-natural soils receive N inputs from atmospheric N deposition, with higher levels of N inputs in the upland areas that exceed the lowland atmospheric N deposition by a factor of 3-5 (according to total atmospheric N deposition data for 1992-94 used in AGEM, section 3.2.5, chapter three). N_2O emissions from semi-natural soils are the combined effect of N inputs from the atmosphere, soil moisture and temperature. Soil temperature has a diminished effect on the distribution of N_2O emissions due to its weak relationship with the emissions reflected in the model by the coefficient < 0.04 (equation 6.1). In contrast, soil moisture is a very strong environmental variable controlling N_2O emissions, enhancing their rate in lowlands by an average factor of 2. In upland areas the seeder-feeder enhancement

effect of atmospheric N input is the main cause of higher N_2O emissions from semi-natural soils, with their spatial distribution showing characteristic coarse block shapes corresponding to N inputs (figures A6.11 and A6.12). This is confirmed by the Geary statistic of 0.07 and Moran index of 0.878 that indicate regional distribution of N_2O emissions (description of the statistics in section 4.3, chapter four). The observed differences between the lowlands and uplands in terms of atmospheric N input have only a small effect on total annual N_2O emissions limited to upland areas with no agricultural land or within the agricultural management type (1). In those areas the increase in N_2O emissions of > 1 kg N ha^{-1} y^{-1} due to atmospheric N input is observed. The mean annual N_2O emission rate is the result of the intensity of agricultural management and its contribution to the total area (figure 5.14, chapter five). As agricultural land is dominant in England, the contribution of agricultural management practices to the total N_2O emissions result in higher emission rates of > 6 kg N ha^{-1} y^{-1}. In Scotland, a greater proportion of semi-natural land with extensive areas of non-intensive management practices results in mean N_2O emission rates of 4-5 kg N ha^{-1} y^{-1}, and extensive areas where emission rates do not exceed 1 kg N ha^{-1} y^{-1}.

The application of model (6.2) to estimate annual mean N_2O emissions resulted in a different distribution of emission rates from soils than that predicted by model (6.1) (figures A6.13 and A6.14). Although the mean N_2O emission predicted for Great Britain decreased to 3.9 kg N ha^{-1} y^{-1}, there was a considerable increase in the predicted variability of N_2O emissions, ranging between 0.1 and 20.4 kg N ha^{-1} y^{-1} (sd=4.5). The spatial distribution was more uniform and it closely followed the dominant land class, the strongest predicting factor of the model (6.2). In areas where semi-natural land was the dominant class, the predicted emissions ranged from 0.1 - 3 kg N ha^{-1} y^{-1} depending on the total N input. Tilled land was the dominant land use type in the East (figure A10), where N_2O emissions predicted by model (6.2) ranged from 3 - 6 kg N ha^{-1} y^{-1}. The highest predicted N_2O emissions corresponded to the extent of managed grasslands, and they varied between 6 and 21 kg N ha^{-1} y^{-1}. Those high rates of emissions were observed in the areas of intensive livestock farming, where high mineral N inputs were intensified with organic manure. The values of N_2O emissions from the intensively managed grasslands predicted by model (6.2) exceeded the predictions made by equation (6.1) by 5 -6 kg N ha^{-1} y^{-1}. The differences are caused by the introduction of the dominant land class. In some locations small areas of managed grasslands with intensive livestock farming adjoin extensive areas of semi-natural land cover. The effect of high N inputs localised on those managed grasslands is considerably

reduced by model (6.2), which predicts N_2O emissions 10 - 11 kg N ha^{-1} y^{-1} lower than model (6.1) when taking into account the dominant land class. These large differences are the result of land use type variability lost with the assignment of the dominant land class to each 5 km grid.

In model (6.1) the distribution of annual N_2O emissions is controlled by the amounts of N input. Areas with the highest N_2O emissions are predicted to be on intensively managed grasslands and on tilled land receiving large mineral N inputs. This contrasts with model (6.2), where the strongest predictor is the dominant land class. The main differences in the predicted distributions of N_2O emissions by the two models are within upland areas. The greatest contrast in N_2O emissions predicted by equation (6.1) is observed in The Scottish Highlands, where intensive farming on the lower slopes and in the valleys develops in the vicinity of extensive hill grazing on the upper slopes. Welsh and English Uplands are characterised by a more gradual increase in the rate of N_2O emissions that is the effect of both high N inputs and soil moisture. In those areas, model (6.2) predicts considerably lower N_2O emissions. In the lowlands, intensive agricultural practices determine the distribution of the areas with high N_2O emissions that are generally associated with intensive livestock farming. N_2O emissions in those areas as predicted by model (6.2) are 3 - 4 kg N ha^{-1} y^{-1} lower than the results of model (6.1). The rate of N_2O emissions is altered by a limiting factor of soil moisture, which is responsible for an increase of 1.5 - 3 kg N ha^{-1} y^{-1} proportionate to N fertiliser input (as observed in some areas of the 'arable' triangle of Southeast-Central England). The observed variation in the N_2O emission response to different environmental conditions is better represented by seasonal N_2O emissions, that are presented in the following section of this chapter.

N_2O emissions from agricultural soils in 1997.

The mineral N input to agricultural soils was estimated in AGEM on the basis of the AC data for 1988 (table 3.1, chapter three) as the most recent data sets were incomplete (chapter three). N input levels vary in time as a result of the land use changes and the variable mineral N input application. There are consistent annual changes as a result of crop rotation practiced in most areas, but those changes are temporary in character. They are submerged by more permanent changes related to some economic and political factors (e.g. response to market prices and current agricultural policy). Those changes are likely to have an effect on annually fluctuating amounts of N inputs to soils. This paragraph presents a review of N

fertiliser inputs and estimated N_2O emissions due to changes in land use between 1988 and 1997.

The comparison of N input levels to agricultural soils between 1988 and 1997 was complex, as the AC data set for 1997 did not provide information on rough grasslands. The missing data resulted in a higher overall mean mineral and organic N input rate that increased from 257 kg N ha^{-1} in 1988 to 338 kg N ha^{-1} y^{-1} in 1997. This increase contrasted with a change observed in mean application rates of mineral fertiliser between the two years. For cereals the mean mineral N application decreased from 156 kg N ha^{-1} to 122 kg N ha^{-1}, for other tillage crops it fell from 122 kg N ha^{-1} to 91 kg N ha^{-1} and for grasslands from 172 kg N ha^{-1} to 138 kg N ha^{-1}. The decrease in the mean N fertiliser input indicates a shift in the crop structure towards a greater proportion of less N demanding crops. The change in fertiliser N application rate would result in lower predicted N_2O emissions from agricultural soils. Another factor that would effect the emissions was the change in the extent of all agricultural soils that received the fertiliser. Although no significant change in total managed agricultural land was observed, there was a change of some cereal crops and grasslands to other tillage crops that affected 4.7 % of total agricultural land (table 6.1).

Table 6.1 Land use change between 1988 and 1997 as indicated by the AC data set.

Land use	1988 [10^6 ha]	1997 [10^6 ha]	1988 [%]	1997 [%]	% change
Cereals	3.8	3.5	36.4	33.5	-8.0
Other tillage crops	0.8	1.3	7.7	12.5	61.5
Managed grasslands	5.9	5.7	55.8	54.0	-3.2
Stocking units* [10^6]	12.4	11.1			-10.8
Total agricultural land	**10.6**	**10.6**			**-0.01**

1 stocking unit [SU] = 1 dairy cow equivalent (table 3.12, chapter three).

The changes in the application rates of mineral N input and in the crop structure of agricultural land between 1988 and 1997 caused a decrease of modelled mean rates of N_2O emissions from 5.2 to 4.7 kg N ha^{-1} y^{-1}. A change in the spatial distribution of N_2O emissions (figure A25) resulted from the exclusion of rough grasslands. This was suggested by lower N_2O emissions for 1997 estimated for upland areas, while in the lowlands great variability of responses was observed, with some increase in N_2O emissions due to higher N inputs in organic form. The

observed spatial shift in N_2O emissions (figure A26) and the change in the structure of main agricultural classes (table 6.1) suggest a greater contribution of tillage crops to the predicted rates of N_2O emissions at the expense of grasslands. This might explain an overall decrease in N_2O emission rates from all agricultural soils, as grasslands and cereals were more important sources of N_2O in 1988. Smaller N_2O emissions from grasslands were due to a decrease in their proportion of the total agricultural land and a decrease of 11 % in the total number of stocking units in comparison with 1988 (table 6.1). The observed changes were partly a result of temporary crop rotation, but a specific decrease in the grassland area and livestock reduction might be related to a crisis in livestock farming caused by the EU-implemented beef ban (Commission of the European Communities, 1996; Council of the European Union, 1996). The observed trend had some positive effect in a reduction of N_2O emissions in some upland areas, but in the lowlands, the response varied. The current depression of livestock farming, however, is probably short-lived and with the lifting of the ban a revival of livestock farming and an increase in N_2O emissions caused by organic N inputs to grasslands is expected.

6.3. SEASONAL VARIATION IN N_2O EMISSIONS AS AN EFFECT OF CLIMATIC VARIABLES.

Annual predictions of N_2O emissions with the two empirical models (6.1 and 6.2) revealed considerable differences. There was an observed strong influence of land cover type, the most important predicting factor in model (6.2), that caused a decrease in the results by a factor of 3 (section 6.2). The distribution of N_2O emissions in Great Britain in that model was more uniform than in model (6.1), due to considerable differences in N_2O emissions from the main land classes. N input had some reduced effect on the ranges of N_2O emissions within the recognised major classes (figure A10). The distribution of N_2O emissions predicted by model (6.1) was more variable and N input was the strongest controlling factor, with some considerable effect of soil moisture. The effect of soil moisture was more pronounced in this model than in model (6.2), which could be explained by a stronger correlation coefficient of this variable. The environmental variables cause seasonal variability of N_2O emissions as they emphasise the effect of N input in the optimal conditions of high soil moisture and soil temperature. N inputs to

agricultural soils vary throughout the year as described by the recommendations of good fertiliser practice (table 2.4, chapter two). The recommendations were applied to estimate seasonal fertiliser input variability with an AML program that used funtion described in equation (6.3).

$$N_S = \sum_{i=1}^{n} \sum_{j=1}^{m} p * N_A \qquad (6.3)$$

where N_S – seasonal N input
N_A – annual N input
S=<winter, spring, summer, autumn>
p – proportion of annual N input applied on date I (table 2.4, chapter two)
i – all application dates (table 2.4, chapter two)
j – all crop types (tables 3.6 and 3.8, chapter three)
In spring i= <01.03 – 31.05>; in summer i = <01.06-31.08>;
in autumn i = <01.09-30.11>; in winter i= <01.12 – 28.02>

As little information is available on the variability of atmospheric N deposition during a year, an equal split was assumed (program in Appendix 6.1). Data of seasonal total N inputs to soils (figure A27), and seasonal variability of soil moisture (figure A7) and soil temperature (figure A2) were applied to estimate N_2O emissions with model (6.1) and (6.2). The seasonal results of the two models are presented in the following section.

Results of model (6.1).

The predictive model (equation 6.1) estimating N_2O emissions with the data of N input to soils, soil moisture[2] and soil temperature[3] was applied to estimate seasonal[4] oscillations in N_2O emission rates. The highest predicted N_2O emissions were observed for spring, when mean emission rates amounted to 2.5 (0.09 - 6.4) kg N ha^{-1} 3 $month^{-1}$ (figure A28a). This was expected as most of the annual N fertiliser is applied in spring (mean=65, range=1 - 175 kg N ha^{-1} 3 $month^{-1}$), which also coincided with soil moisture conditions optimal for denitrification (mean WFPS = 73 %). In summer, mean N_2O emission rates were estimated at 1.6 kg N ha^{-1}. Spring and summer N_2O emissions were a factor of 3 higher than emission rates estimated for autumn and winter (0.7 and 0.5 kg N ha^{-1} 3 $month^{-1}$, respectively)

[2] Modelled with the method presented in section 3.3.2, chapter three
[3] Method used to derive seasonal soil temperature is presented in section 3.3.1, chapter three
[4] seasons are defined in section 3.3.1, chapter three

(figures A6.18 b-d). The spatial distribution of N_2O emissions in Great Britain also varied seasonally. In winter and summer there was an observed difference between the East and the West, while more evenly distributed N_2O emissions were predicted for spring and autumn (figure A28). The highest N_2O emissions in spring (> 5 kg N ha^{-1} 3 $month^{-1}$) were estimated for north Wales, and for Scotland in Renfriewshire and Ayrshire (figure A28a). The characteristic two-phase distribution of N_2O emissions in Great Britain was observed to correspond closely with the seasonal distribution of mean N inputs to soils (figures A6.17 and A6.18). The distribution of N input levels to soils in winter and summer was linked to the distribution of managed grasslands that receive organic manure in winter from grazing, and mixed N in organic and mineral form throughout the summer in split applications (table 2.4, chapter two). Not surprisingly, N_2O emissions were spatially related with N enrichments of soils that were further emphasised by high soil moisture in those areas (figure A13). The limiting soil moisture effect in summer could be observed in South East and Central England where estimated WFPS < 50 % caused a reduction of N_2O emissions to < 1 kg N ha^{-1} 3 $month^{-1}$. In areas where soil moisture was not limiting (> 60 %), N_2O emissions were estimated in the range 1 - 2 kg N ha^{-1} 3$month^{-1}$ for similar levels of N input (figures A6.3 and A6.18b). The more even distribution of N inputs in spring, when all crops receive annual inputs of N in the beginning of the growing season, is associated with high N_2O emissions from agricultural land. Localised areas in the western uplands with soil moisture exceeding 80 % of WFPS, produce accelerated emission rates of 1-1.5 kg N ha^{-1} 3$month^{-1}$. In winter, mean rates of emissions > 1 kg N ha^{-1} 3$month^{-1}$ were predicted only for Wales and the South West of Great Britain (figure A28d). In autumn, similar rates of N_2O emissions were predicted for larger areas randomly distributed in most parts of Wales and England, and small areas in Scotland. This spatial distribution of N_2O emissions was caused by N inputs to grasslands in the West and winter crops in the East (table 2.4, chapter two). The limiting effect of soil moisture was again observed in the East.

The Geary autocorrelation indices estimated for the seasonal distribution of N_2O emissions varied between 0.06 - 0.1, while Moran[5] indices ranged between 0.8 - 0.9, that suggested the regional character of the spatial distribution of predicted N_2O emissions in Great Britain. Although considerable differences in N_2O emissions, especially in spring, were observed between the Northwest and the West, there was not much variability observed between the neighbouring grids. This suggests that the differences between the semi-natural land and agricultural soils

observed in the annual variability of N_2O emissions (section 6.2) were lost at smaller scales in the seasonal distribution.

Results of model (6.2).

The empirical model describing the relationship between N_2O emissions and N input, soil moisture, soil temperature and land class (equation 6.2) was applied to estimate the seasonal variability of N_2O emission rates from soils to compare its performance with model (6.1).

Predicted N_2O emissions for spring and summer were a factor of 2 higher than for winter and autumn, but the spatial pattern was uniform for all the seasons (figure A29). The effect of environmental variables was hence restricted by a non-dynamic parameter, land cover. The highest N_2O emissions were observed in south-west Wales, the Midlands (characteristic crescent-shape), an extensive area from Salisbury to Exmoor and Dartmoor, northern Cumbria and some minor hot-spots in the South and the North of Great Britain (figure A29). In these areas the dominant land class was managed grassland (map 6.13). Compared with the West, where great spatial differences were observed and N_2O emissions in spring ranged from below 1 kg N ha^{-1} 3 $month^{-1}$ to over 7 kg N ha^{-1} 3$month^{-1}$, estimated emissions were more uniform in the East (especially in the Midlands and East Anglia) (2 - 4 kg N ha^{-1} 3$month^{-1}$). The uniform N_2O emissions in the East were predicted for tilled land, while in the West the lowest N_2O emissions were associated with semi-natural land, contrasting with managed grasslands with the highest emission rates (figure A29a-b). Apart from a few emission hot-spots (> 7 kg N ha^{-1} 3$month^{-1}$) in Inverclyde, Aberdeenshire, Fife and Dumfries and Galloway, Scotland produced considerably lower N_2O emissions in spring compared with England and Wales. This was due to a large proportion of heathlands and boglands with small areas utilised by hill grazing and the small proportion of tilled land in south Scotland. In areas of dominant semi-natural land cover N_2O emissions did not exceed 1 kg N ha^{-1} 3$month^{-1}$, even in spring and summer, and from September until April they were below 0.2 kg N ha^{-1} 3$month^{-1}$ (figure A29c-d). The differences in N_2O emissions between managed grasslands, tilled land and semi-natural land were the combined effect of land cover (the strongest variable), N input to soils and soil moisture. The differences in N_2O emissions estimated for winter (< 0.5 kg N ha^{-1} 3$month^{-1}$) and autumn (0.5 - 1 kg N ha^{-1} 3$month^{-1}$) in the East, especially in East Anglia, were

[5] Definition of this index is presented in section 4.2.3 (chapter four).

caused by higher N inputs to winter crops in autumn estimated at 5 - 20 kg N ha^{-1} $3month^{-1}$ and soil moisture in some areas exceeding 70 % WFPS. The effect of soil temperature on N_2O emissions was insignificant as was observed for model (6.1).

In contrast to the results of model (6.1), N_2O emission rates predicted with equation (6.2) had much greater spatial variability at a smaller scale. This was statistically supported by a higher Geary indices (0.31 - 0.35) and lower values of Moran autocorrelation statistics (0.62 - 0.67) than those estimated for model (6.1). The spatial differences between the two models were large despite similar mean N_2O emissions. N_2O emissions estimated for spring with model (6.2) were 2.1 (0.05 - 10.9) kg N ha^{-1} $3month^{-1}$ and with model (6.1) were 2.5 (0.09 - 6.4) kg N ha^{-1} $3month^{-1}$. The differences in spatial variability predicted by the two models could be explained by the strong effect of land cover in model (6.2) that reduced the influence of N input and soil moisture. Model (6.1) followed N inputs to soils more closely, which combined with the effect of soil moisture resulted in seasonal changes of N_2O spatial distribution. The emissions were considerably higher from managed grasslands, when land cover was applied as a predictor (model 6.2), but semi-natural land was regarded as a minor source of N_2O.

6.4. VALIDATION OF THE N_2O EMISSION MODEL WITH FIELD MEASUREMENTS.

The N_2O emission empirical models defined for AGEM were validated against the measured N_2O emissions from four additional field sites: Dunslair Height and Earlston in The Borders, Devilla in Central Scotland and North Berwick in East Lothian region. These field data sets were applied for the validation because they were not employed in the original field data set used to define the models and their location within Great Britain. This validation was to evaluate the AGEM models' suitability to predict N_2O emissions from British soils.

The field sites typified a variety of environments. Agricultural land was represented by an oilseed rape field (North Berwick) and a grazed grassland (Doo Brae), while the remaining data represented a number of semi-natural sites including moorland (in Dunslair Height), mixed forest (Earlston), coniferous forest (Devilla and Dunslair Height) and shrubland with sparse deciduous trees (North Berwick). The soil type at the majority of sites was classified as brown earth with the exception of Dunslair

Height where soil had a peaty surface horizon. The N_2O emissions were measured on those sites during the period of 1994-1995 with a static chamber method described in detail by Skiba *et al.* (1998). The data are presented in table 6.2.

The empirical models described by equation (6.1) and (6.2) were applied to estimate N_2O emissions with the variables of N input, soil temperature and soil moisture measured at each site. A comparison of the measured and the modelled N_2O emission values showed lack of agreement and no consistent trend for all field data (figures 6.2 and 6.3). There were observed differences between the sites in the performance of the models that was expected due to variable soil characteristics and different vegetation cover. Predicted N_2O emissions from the oilseed rape field were considerably over-estimated, while the semi-natural land showed great variability in the performance of the empirical model with some field measurements considerably exceeding the predictions of the model. The performance of the two models was therefore observed for each individual field, and residual error (s_y) was estimated for each measurement according to equation 3.4 (chapter three).

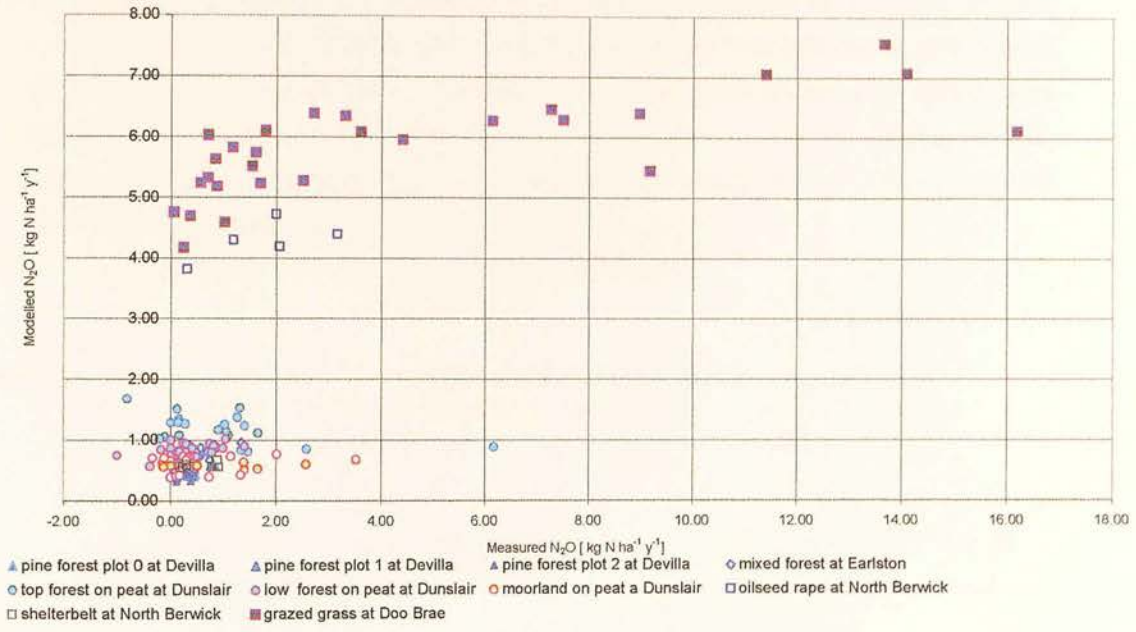
Table 6.2 Field measurements data of N_2O emissions used for model validation.

Site location	Site characteristics of soil type and land use class	Time of study	Measured means and ranges of N_2O emissions [kg N ha^{-1} y^{-1}]	Predicted means and ranges N_2O emissions (model 6.1) [kg N ha^{-1} y^{-1}]	Predicted means and ranges N_2O emissions (model 6.2) [kg N ha^{-1} y^{-1}]	n
Dunslair	Moorland and forest on peat	Apr,1994 – Oct,1995	0.61 (-1.01 - 6.16)	0.84 (0.38-1.68)	0.3 (0.16-0.54)	26
Devilla	Pine forest on brown forest soil	June - Sept,1994	0.29 (0 - 0.85)	0.44 (0.32-0.57)	0.18 (0.15-0.24)	10
Earlston	Mixed forest on brown forest soil	Sept-Nov, 1995	0.48 (0.06-1.33)	0.74 (0.50-0.96)	0.26 (0.19-0.32)	12
North Berwick agricultural	Oilseed rape	June-July,1995	0.74 (0.41-1.19)	4.26 (3.8-4.7)	3.0 (2.8-3.3)	5
North Berwick semi-natural	Shelterbelt of mixed woodland	As above	0.17 (0.12-0.30)	0.55 (0.55-0.67)	0.21 (0.21-0.25)	5
Doo Brae	Sheep-grazed grass on sandy loam	Sept, 1995-March,1996	4.4 (0.05-16.18)	5.8 (4.1-7.6)	19.4 (14.5-24.9)	13

Dunslair Height. This site represented semi-natural land with a mixture of moorland and woodland on peaty soils. The measurements were collected from April 1994 to October 1995 (Skiba *et al.*, 1998a). N_2O emissions measured on that site were low with mean emission of 0.6 (sd=1.0) kg N ha^{-1} y^{-1}, and deposition of small rates of N_2O recorded on eleven occasions. The modelled N_2O emissions for that environment had a higher mean value of 0.8 (sd=0.28) kg N ha^{-1} y^{-1}, with minimum estimated emission of 0.38 kg N ha^{-1} y^{-1}. There was no agreement between the modelled and measured N_2O emission values (figures 6.2 and 6.3). The lowest N_2O emissions were predicted for moorland, and the highest for the top forest site, while no such clear contrast was observed in measured N_2O emissions for the different plots. The mean predicted N_2O emissions were 0.82 ± 0.41 kg N ha^{-1} y^{-1} from the low forest plot, 1.11 ± 0.84 kg N ha^{-1} y^{-1} for top forest and 0.6 ± 0.58 kg N ha^{-1} y^{-1} for moorland. The measured values for these sites were 0.22, 0.37 and 0.31 kg N ha^{-1} y^{-1}, respectively. Model uncertainty for this site, estimated as a proportional difference of the 95% confidence limits from the estimate, ranged for the mentioned plots between 46-60 % for the low forest, 70-97% for the top forest and from 96-112% for moorland. The large uncertainty of the model for the environments represented in this site, especially for moorland, might be due to peaty soils being under-represented in the N_2O field data set that was the basis for deriving that equation (moorland was not represented in that data set, chapter five). In order to observe whether the inclusion of the land class in the model improves the accuracy of the made predictions, equation (6.2) was applied to predict N_2O emissions for the above site. The mean N_2O emission predicted for the three plots was 0.3 kg N ha^{-1} y^{-1} and no significant trend was observed between the predicted and measured N_2O emissions ($F < 0.77$, df=22). This indicated that despite the limitations discussed above the model described by equation (6.1) was performing better than the one described by equation (6.2).

Figure 6.2 Validation of N_2O emission model 6.1 with field measurements

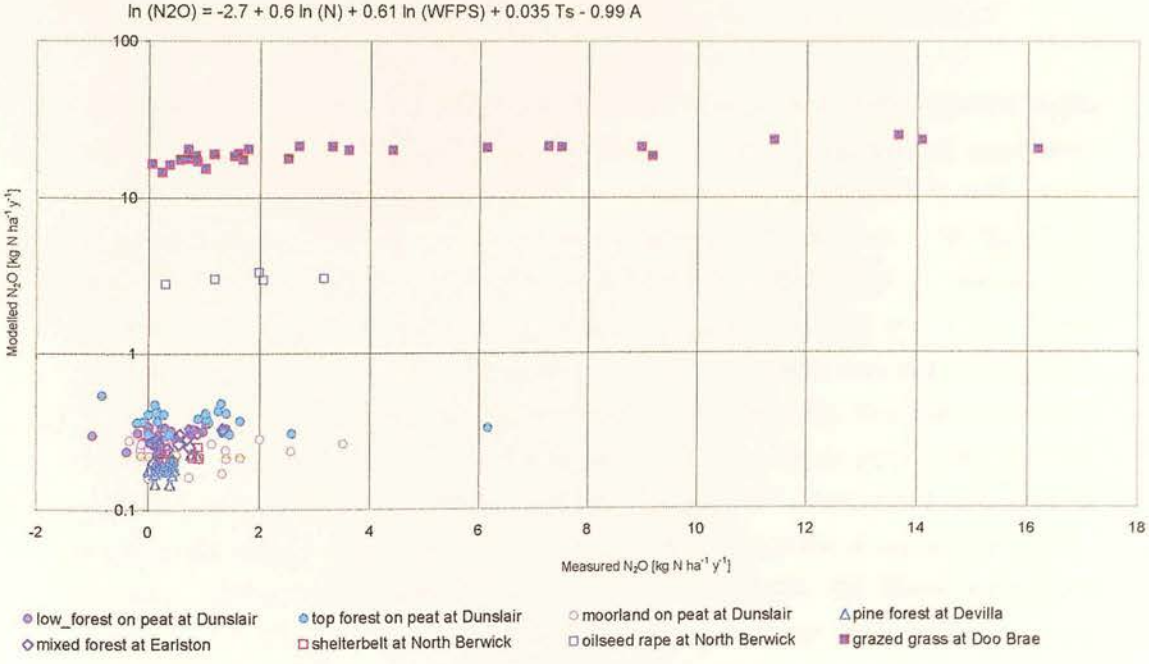
ln (N2O) = -6.0 + 0.75 ln(N) + 0.83 ln (WFPS) + 0.035 Ts



Devilla This site is a pine forest on brown forest soil, where N_2O emissions were measured from June-Sept 1994 on three replicate plots (Skiba *et al.*, 1998a). The trend between the predicted and measured N_2O emissions suggested a tendency for model (equation 6.1) to overestimate the emissions for the sites, where measured N_2O did not exceed 0.48 kg N ha^{-1} y^{-1} (figure 6.2). The two measurements that were under-estimated by the model were obtained in optimal environmental conditions

for N_2O emissions of the highest observed moisture (WFPS > 50%) and high soil temperature (t > 10°C). In those environmental conditions the empirical model did not predict accurate N_2O emissions, which might be caused by a poor relationship established for soil temperature. Mean N_2O emission measured for all the plots was 0.29 (sd=0.22) kg N ha^{-1} y^{-1}, while the estimated values were higher (mean=0.44 ± 0.13 kg N ha^{-1} y^{-1}, p=0.05, n=27). The uncertainty of estimation varied for different measurements between 29 and 31%. The model described by equation (6.2) was also applied to observe the difference in the performance of the two models (similarly to Dunslair Height). The mean N_2O emission was estimated with model (6.2) at 0.18 ± 0.02 kg N ha^{-1} y^{-1} (p=0.05, n=27), but model uncertainty varied from 88 to 175 %. Model (6.1) was more accurate as indicated by a lower mean s_y of 0.06 (compared with 0.1 of model 6.2) and narrower uncertainty limits of 31% (compared with 175% for model 6.2).

Figure 6.3 Validation of N_2O emission model 6.2 with field measurements data.



Earlston. This site was a mixed woodland on brown forest soil. The measurements of N_2O emissions were carried out between Sept-Oct 1995 on three replicate plots (Skiba *et al.*, 1998a). The comparison of N_2O measurements with the predicted values showed that the model over-estimated emissions when measured N_2O was below 0.85 kg N ha^{-1} y^{-1}, which included most of the collected data (figures 6.2 and

6.3). Model (6.1) failed to predict the highest observed N_2O emissions (1.3 kg N ha^{-1} y^{-1}) on the occasion of near saturation of soil when soil temperature was 11.7 °C. The predicted N_2O emission for that date was also the highest noted and the difference between the measured and modelled values did not exceed 0.4 kg N ha^{-1} y^{-1}. The observed difference between the estimated and measured N_2O emission on that date might be caused by a weak soil temperature influence as a predictor in the model that was also observed on a few points in Devilla site. Mean measured N_2O emission at Earlston forest was 0.48 (sd=0.38) kg N ha^{-1} y^{-1}, while mean predicted N_2O emission was 0.74 (sd=0.13) kg N ha^{-1} y^{-1}. The 95% confidence limits for the mean predicted N_2O emission were estimated as 0.75 ± 0.38 kg N ha^{-1} y^{-1} (p=0.05, n=12) with the uncertainty of prediction ranging between 51 and 57%. When land class was included as a predictor with an application of equation (6.2) the predicted mean N_2O emissions were below the measured mean as they were estimated at 0.26 (sd=0.03) kg N ha^{-1} y^{-1}. The observed trend between the new modelled and measured N_2O emissions, however, was not significant (F=1.74, df=10). This corresponded with the performance of model (6.2) on the other semi-natural sites at Dunslair Height and Devilla.

North Berwick. Two plots were selected within this site. One, oilseed rape, representing agricultural land and the other a mixed semi-natural ecosystem described as 'shelterbelt' that could be classified as a shrubland with some deciduous trees. The measurements were carried out in the period of May-June 1995 (Skiba *et al.*, 1998a). There was a considerable difference in the relationship between the measured and estimated N_2O emissions for the two plots. Mean measured N_2O emissions for oilseed rape and the shelterbelt were 0.74 (sd = 0.33) kg N ha^{-1} y^{-1} and 0.17 (sd = 0.07) kg N ha^{-1} y^{-1}, respectively. The performance of model (6.1) varied for the two measurement plots, as there was a considerable overestimation of N_2O emissions from agricultural land and varied accuracy of predictions for the semi-natural land (figure 6.2). The uncertainty of predictions was very large for the shelterbelt plot (230-285%), while for the oilseed rape it did not exceed 64%. The predicted confidence limits of mean N_2O emissions were estimated at 4.26 ± 2.67 kg N ha^{-1} y^{-1} and 0.55 ± 1.57 kg N ha^{-1} y^{-1} (p=0.05, n=10) for oilseed rape and shelterbelt, respectively. When model (6.2) was applied, the predictions were improved for agricultural land by 1 kg N ha^{-1} y^{-1} (figure 6.3), as observed uncertainty decreased to 52 % (mean predicted emissions declined to 3.0 ± 1.58 kg N ha^{-1} y^{-1}) and s_y decreased from 1.16 (model 6.1) to 0.68 (model 6.2). Despite a similar decrease observed in s_y for the shelterbelt (from 0.67 to 0.44) with the application of model (6.2), the uncertainty of the predictions increased

considerably to a maximum of 480% and, the mean predicted N_2O emission decreased with confidence limits remaining high (0.21 ± 1.04 kg N ha^{-1} y^{-1}). This comparison shows the greater reliability of equation (6.2) to predict N_2O emissions from agricultural land, but its predictions for semi-natural ecosystems are very uncertain.

Doo Brae. N_2O emissions were measured from a sheep grazed grassland on sandy loam soil in the period September, 1995 - July, 1996 (Fowler *et al.*, 1997). The field received 93 kg N ha^{-1} of mineral fertiliser and 68.8 kg N ha^{-1} of excreta (total N=162 kg N ha^{-1}). Mean measured N_2O emissions were 4.4 (sd = 4.8) kg N ha^{-1} y^{-1}. Model (6.1) estimated slightly higher mean N_2O emission at 5.8 ± 1.25 kg N ha^{-1} y^{-1}, while model (6.2) considerably over-estimated N_2O emissions with the mean predicted value at 19.4 ± 8.78 kg N ha^{-1} y^{-1}. The predictions made by the two models departed considerably from the trend presented for the oilseed rape site in North Berwick, where model (6.2) was more accurate in estimating N_2O emissions (figure 6.3). N_2O emissions predicted by model (6.2) had a mean s_y a factor of 3.5 higher than those estimated for model (6.1) (figure 6.2). Although both approaches had similar uncertainty limits (42.4% for model 6.1 and 44% for model 6.2), the considerable difference in standard error suggests a better approach for grasslands offered by model (6.1).

Discussion.

The variability of the models' performance described above showed differences between agricultural and semi-natural land (table 6.2). The validation of the models against field measurements suggested that the inclusion of land class as a predictor in equation (6.2) considerably changed the range of predicted emissions. For agricultural land, represented here by oilseed rape and grazed grassland, those estimates varied. On oilseed rape, model (6.1) over-estimated N_2O emissions by 1 – 3.5 kg N ha^{-1} y^{-1} and the application of model (6.2) reduced the difference to 0 – 2 kg N ha^{-1} y^{-1}. For grazed grassland, however, the residual difference increased from the average of 3.8 kg N ha^{-1} y^{-1} for model (6.1) to 17.5 kg N ha^{-1} y^{-1} for model (6.2). On the other hand, for semi-natural land there was a tendency for model (6.2) to underestimate mean N_2O emission compared with the measured values, while model (6.1) over-estimated the emissions. The inclusion of land class types in the prediction (model 6.2) increased the maximum uncertainty of prediction from 285% (model 6.1) to 480% (model 6.2) for the shelterbelt plot at North Berwick and from 31% (model 6.1) to 175 % (model 6.2) for pine forest at Devilla. At the other sites,

the predictions of model (6.2) did not significantly represent the measured variability of N_2O emissions. Lack of significance for the predictions of model (6.2) suggests that predictions made without consideration of land class are more reliable in estimating N_2O emissions from semi-natural land. The uncertainty of the model (6.1) decreased for the represented ecosystems in the order: grazed grassland on sandy loam > pine forest on brown soil > mixed forest on brown soil > oilseed rape on brown soil > pine forest on peat > moorland on peat soil > shrubland with some deciduous trees. The observed high variability of measured N_2O emissions was not represented well by the two models, especially by the reduced range of N_2O emissions predicted by equation (6.2) as observed on figures 6.2 and 6.3 and table 6.2. This was expected due to the aim of the predictive model to indicate mean N_2O emissions for various ecosystems, defined by the levels of soil N and the environmental conditions described by soil moisture and soil temperature, and its limited ability to represent great spatial and temporal variability of N_2O emissions. Other field research established, however, large spatial and temporal variability of N_2O emissions (Clayton *et al.*, 1994; Folorunso and Rolston, 1984; Mummey *et al.*, 1997 and Velthof *et al.*, 1996b). Great uncertainty should be therefore expected from field measurements in representing mean N_2O emissions from different environments, which questions the validation results presented above.

The observed differences in the performance of the two models for the selected sites suggest a different characterisation of the predictions of N_2O emissions from soils in Great Britain depending on land use type. Model (6.1) has a tendency to produce higher estimates of mean N_2O emissions, especially for agricultural soils. Model (6.2) suggested considerable differences between the three major land use types in terms of produced emissions, which might have been slightly exaggerated. Its predictions for semi-natural land were rather conservative as it showed a trend to under-estimate N_2O emissions on those sites. On the other hand, it considerably over-estimated N_2O emissions from grasslands, but yielded a more accurate representation of emissions from tilled land (as represented by the field measurements in North Berwick) compared with model (6.1). This reflected a general trend observed in the field measurements of very low N_2O emissions from semi-natural environments and considerably higher emissions from agricultural soils receiving N fertiliser input. The highest N_2O emissions were measured from grasslands as a result of additional organic inputs.

6.5 SENSITIVITY TESTING OF THE PREDICTIVE MODEL.

The predictive models of N_2O emissions are affected by their limited capacity to represent the great spatial variability of N_2O emissions (section 6.4) and by uncertainties in the input parameters (section 5.6, chapter five). These limitations of the AGEM models were tested with sensitivity analysis. The aim was to establish the key variables for N_2O emissions in the two predictive models and to observe the change in their predictions with change in values of the model parameters. Sensitivity of the two models (6.1 and 6.2) was tested in two experiments. In experiment 1 each parameter was excluded successively from the prediction as presented in table 6.3.

Table 6.3 Predictive models applied in experiment 1.

Factor excluded	Definition of model 1*	Definition of model 2*
N input	$E_{N2O} = e^{(-6.0 + 0.83 * \ln WFPS + 0.035 * Ts)}$	$E_{N2O} = e^{(-2.7 + 0.61 * \ln WFPS + 0.035 * Ts - 0.99 * A}$
Soil moisture	$E_{N2O} = e^{(-6.0 + 0.75 * \ln N + 0.035 * Ts)}$	$E_{N2O} = e^{(-2.7 + 0.6 * \ln N + 0.035 * Ts - 0.99 * A)}$
Soil temperature	$E_{N2O} = e^{(-6.0 + 0.75 * \ln N + 0.83 * \ln WFPS)}$	$E_{N2O} = e^{(-2.7 + 0.6 * \ln N + 0.61 * \ln WFPS - 0.99 * A)}$
Land class		$E_{N2O} = e^{(-2.7 + 0.6 * \ln N + 0.61 * \ln WFPS + 0.035 * Ts)}$

* For explanation of symbols used here refer to table 5.7

The results of experiment 1 confirmed the suspected sensitivity of both models (6.1 and 6.2) to N input and soil moisture. The mean annual N_2O emissions predicted with model (6.1) decreased exponentially from 5.3 kg N ha^{-1} y^{-1} to 0.11 and 0.15 kg N ha^{-1} y^{-1} with an exclusion of N input and WFPS, respectively. Similarly for model (6.2) a considerable decrease of mean N_2O emissions was observed from 3.9 to 0.16 and 0.28 kg N ha^{-1} y^{-1} with the successive removal of N input and soil moisture. The observed response was expected due to the high correlation coefficients for those parameters in both models, especially in model (6.1). This was confirmed by the observed greater response of that model to the changes in input parameters. N_2O emissions estimated by model (6.2) depended also on the dominant land class that was observed to have the strongest relationship with the emission rates as indicated by the negative coefficient of correlation. When this variable was tested (table 6.3) there was a considerable increment in mean annual N_2O emissions from

3.9 to 25.3 kg N ha^{-1} y^{-1}. Soil temperature was the weakest variable in the presented models. The exclusion of that variable caused only an arithmetic decrease in mean N_2O emission rates from 5.3 to 3.9 kg N ha^{-1} y^{-1} (model 6.1) and from 3.9 to 2.9 kg N ha^{-1} y^{-1} (model 6.2).

Table 6.4 Different scenarios for model parameters applied in experiment 2.

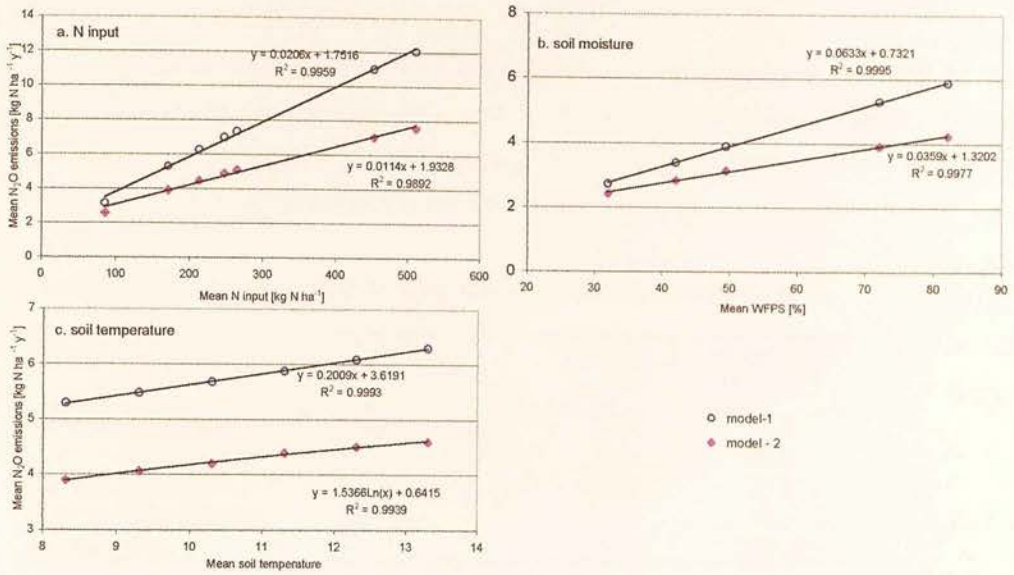
N input scenarios	Soil moisture scenarios	Soil temperature scenarios
50 % of N (lower confidence limit of N to arable crops)	WFPS - 22.4 % (mean soil moisture error from comparison with the field capacity)	Ts + 1 (within the error limits of soil temp)
125 % of N (upper confidence limit of N to arable crops)	WFPS - 30 % (the above plus loss of moisture due to climate change)	Ts + 2 (as above)
145 % of N (variability of N input to potatoes)	WFPS - 40 % (as above)	Ts + 3 (error limits of predicted soil temperature)
155 % of N (variability of N input to oilseed rape)	WFPS + 10 % (soil moisture error plus increase in precipitation due to climate change)	Ts + 4 (the above plus climate warming)
266 % of N (lower confidence limit of N to grasslands)		Ts + 5 (as above)
300 % of N (upper limit of the above)		

In the second stage of the sensitivity testing experiment, the change in mean annual N_2O emission rates was observed with adjusted values of the predictive parameters. This experiment was to indicate the extent to which N_2O emissions may vary depending on the confidence limits of the model variables established in the validation of input data sets (table 6.4), and due to any possible future trends. The values of N input were varied according to the results of the North Berwick survey of farmers (chapter four). Soil moisture was adjusted by the value of mean error established in the comparison with the field capacity (chapter three) and an assumed oscillation as an effect of climate change (table 6.4). Soil temperature was varied by up to 5 °C as an expected effect of the estimated confidence limits of input data (section 5.6, chapter five) and possible effects of widely defined climate warming (table 6.4).

There was a linear increase in mean N_2O emission rates observed for all the parameters that were varied (figure 6.4). Change in N input from 50% of fertiliser input (as observed on some cereal crops in the survey of farmers) to 300%, indicating the average upper limit of N inputs to grasslands (chapter four), corresponded to an increase in N_2O emissions from 3.1 to 12 kg N ha^{-1} y^{-1} as predicted by equation (6.1) (figure 6.7a). For model (6.2), the same variance of N input resulted in N_2O emission rates ranging between 2.5 and 7.5 kg N ha^{-1} y^{-1} (figure 6.7a). This suggests that a reduction in N fertiliser input by 50% would cause a decrease in N_2O emission rates by 2.1 and 1.4 kg N ha^{-1} y^{-1} for model (6.1) and (6.2), respectively. On the other hand, the great uncertainty of N inputs to grasslands, that on average exceeded standard recommended rates by a factor of 3, would result in a possible variation of N_2O emissions by 6.8 and 3.7 kg N ha^{-1} y^{-1}, depending on the model applied.

Soil moisture modelled with the application of SPACTeach model (chapter three) was over-estimated by approximately 22.4%, as indicated by a comparison with the field capacity (chapter three). When WFPS was adjusted by the value of the mean error, N_2O emissions were observed to decrease from 5.3 to 3.9 kg N ha^{-1} y^{-1} and from 3.9 to 3.14 kg N ha^{-1} y^{-1} when estimated by model (6.1) and model (6.2), respectively (figure 6.7 b). Further oscillations in soil moisture (between - 40% and + 10%) resulted in the N_2O emissions ranging between 2.7 and 5.9 kg N ha^{-1} y^{-1} for model (6.1) and between 2.4 and 4.2 kg N ha^{-1} y^{-1} (figure 6.7 b) for model (6.2). A gradual increase in soil temperature variable between 1 - 5 °C caused only slight changes in N_2O emission rates (figure 6.7 c). The observed maximum difference for model (6.1) did not exceed 1kg N ha^{-1} y^{-1} and 0.7 kg N ha^{-1} y^{-1} for model (6.2).

Figure 6.4 Sensitivity of N_2O emission models (6.1 and 6.2) to model variables.



Adjustments in the values of N input in both predictive models, as described by the scenarios in table 6.4, resulted in the greatest increase of N_2O emissions as indicated by the sharp linear trend (figure 6.7) compared to the other controlling factors. Soil temperature was suggested to be the weakest controlling factor by the slope of the linear relationship presented in figure 6.7 c. Model (6.1) was also observed to have a greater response than model (6.2) to changes in the controlling variables. The results of this experiment, related to the strength of the controlling variables and greater sensitivity of model (6.1), supported the observations made in experiment 1.

The two models discussed (6.1 and 6.2) estimate N_2O emissions on the basis of similar controlling factors of N input, soil moisture and soil temperature. There are major differences between the two approaches that were outlined by the sensitivity experiments. Model (6.2) is strongly affected by the land class that coincides with a weaker relationship of the other controlling factors as indicated by the different responses of both models in the sensitivity analysis. The strength of the parameters in the predictive models is in the order land class (model 2 only) > N input > soil moisture > soil temperature.

6.6 PREDICTED TOTALS OF N_2O EMISSIONS.

Total N_2O emissions from soils in Great Britain were estimated at 140.2 kt N y^{-1} with model (6.1) and 127.5 kt N y^{-1} with model (6.2). The results of models (6.1) and (6.2) were surprisingly close considering the differences between their predictions from different ecosystems at the field level (section 6.4).

Table 6.5 N_2O emission totals for Great Britain according to main sources.

Emission source	Model (6.1) [kt N y^{-1}]	Model (6.2) [kt N y^{-1}]
Cereals, other tillage and horticultural crops	26.2	20.6
Grazed and mown grasslands	36.0	35.1
Organic fertiliser	56.8	50.1
Atmospheric deposition	21.2	20.7
All sources:	**140.2**	**127.5**

The main differences between the predictions of those models for Great Britain were in upland areas, where model (6.2) estimated much smaller emissions than model (6.1) in areas of high organic N inputs. The observed higher rates of N_2O emissions estimated by model (6.2) for managed grasslands (figure A24) did not affect the totals due to the smoothing of 'hot-spots' in uplands (table 6.5). Fertiliser emission factors in models (6.1) and (6.2) were estimated at 2% and 1%, respectively, on the basis of the linear trend of N_2O emission sensitivity to variable N input (figure 6.7). Both models (6.1 and 6.2) suggested livestock as the most important source of N_2O emissions, which was followed by managed grasslands.

6.7 CONCLUSIONS.

The two empirical models presented in this chapter estimate N_2O emissions on the basis of the controlling factors defined by the regression analysis presented in chapter five. Model (6.1) estimates emission rates on the basis of N input, soil moisture and soil temperature. The predictions of annual and seasonal distribution of N_2O emissions were strongly influenced by the amounts of N input. Soil moisture was the limiting factor in areas of lower N inputs. Model (6.2) uses land class in addition to the above controlling factors. Land use was the strongest factor that determined the distribution of annual N_2O emissions, with considerable differences

between mean estimates for managed grasslands, tilled land and semi-natural land. The predicted spatial distribution of N_2O emissions did not change during a year as the land class considerably reduced the limiting effects of soil moisture and N inputs. Those variables had restricted influence on N_2O emissions, causing variability within the observed ranges for the main land classes and between the mean seasonal emissions. Soil temperature did not have any significant effect on the distribution of N_2O emissions in either model. Surprisingly, the predictions of model (6.1) were characterised by greater spatial variability with simultaneous smaller prediction ranges than the estimates of model (6.2). N_2O emissions from semi-natural land predicted by model (6.1) were considerably higher than from model (6.2), contrasting to managed grasslands where the highest emission rates from model (6.2) exceeded those predicted by model (6.1) by 10 kg N ha^{-1} y^{-1}.

Validation of the two models against field measurements suggested that while means calculated by model (6.1) for the observed field studies over-estimated N_2O emissions, model (6.2) under-estimated emissions for semi-natural land. Its approach was more accurate for the agricultural soil in North Berwick. The question of accuracy of the model predictions is related to the problem of great spatial and temporal variability of N_2O emissions measured in the field. While that variability is impossible to replicate, the predictions of mean emission rates from different ecosystems seem more feasible to achieve. Following the results of the validation the optimal approach (with minimised error) would combine the two models by applying equation (6.1) to predict emissions from semi-natural land, and equation (6.2) to agricultural soils.

An additional concern regarding the performance of the model was related to the validity of the input data of the controlling factors as observed in section 5.6 (chapter five). The limitations of model accuracy by the uncertain input data were tested in sensitivity analysis. As land use class was observed to be the strongest factor in model (6.2), the AC and the LCM incompatibility were the greatest contributors to the model error. The uncertainties of land use data indirectly effected N input levels, estimated according to crop types, which emphasises their effect on the accuracy of predictions. Although both models were sensitive to changing values of N input and soil moisture, model (6.1) was more affected by the values of those variables. In all the tests, N_2O emissions showed linear response to changing variables determined by the definition of AGEM models. Total N_2O emissions from soils in Great Britain were estimated with the AGEMs at 127.5 - 140.2 kt N y^{-1}.

CHAPTER SEVEN

NO emissions from soils in Great Britain as predicted by empirical models.

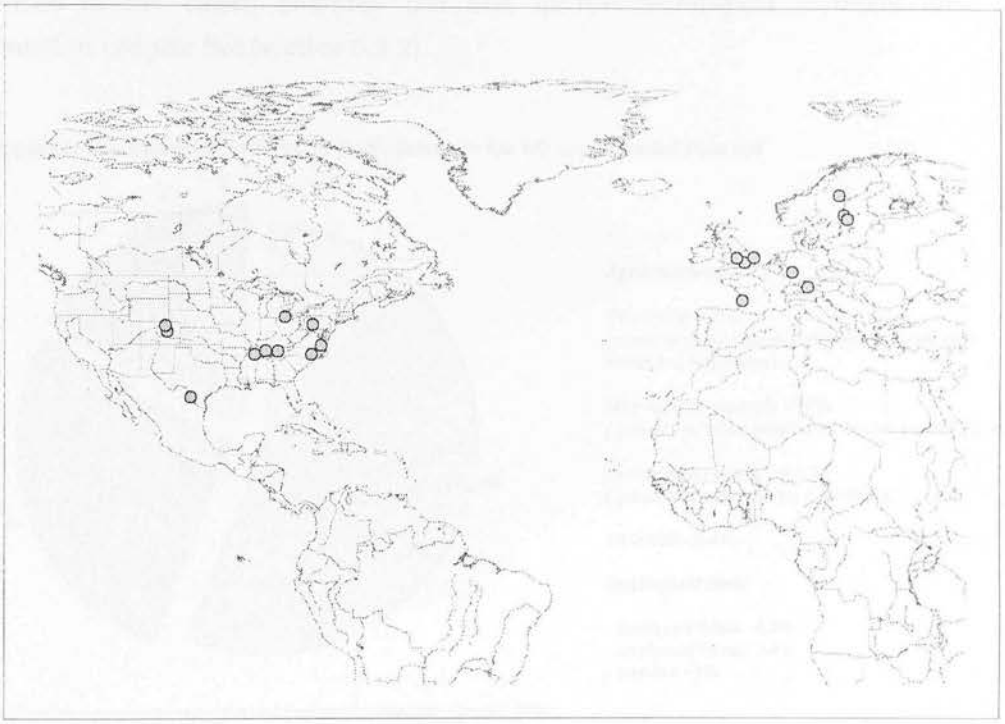
7.1 INTRODUCTION.

NO is produced and emitted in specific conditions that have been researched by field studies in different ecosystems. Field research established that the important controlling factors for NO emissions are N input, soil temperature, soil moisture and vegetation type (Anderson and Levine, 1987; Aneya *et al.*, 1988; Harrison *et al.*, 1995; Jambert *et al.*, 1994; Johansson and Granat, 1984; Skiba *et al.*, 1993; Slemr and Seiler 1984 and Thornton *et al.*, 1995 and Valente and Thornton, 1993). A detailed account of the bacterial processes of NO production and the conditions favourable for NO emissions from soils is presented in chapter two. This chapter aims to recognise general relationships between NO emissions and their controlling factors on the basis of the compiled data of NO field measurements in temperate climates in the last fifteen years. Those relationships established through multivariate regression analysis were used to define an empirical model of NO emissions from soils. This approach is similar to the method by which the empirical model of N_2O emissions was defined (described in chapter five). The predictive model of NO emissions is applied to establish their spatial distribution in Great Britain.

This chapter begins with a presentation of the NO experimental data used to define the relationships existing between NO emissions and the controlling factors, and a discussion of the extent to which the studied environments affect the outlined relationships (section 7.2). Section 7.3 presents the NO emission models defined in the regression analysis and their performance in predicting emissions for the field sites from the NO experimental data set. In the same section, the defined equations are applied to predict NO emissions from soils in Great Britain with the known controlling factors. The results of the models are also compared with field

measurements of NO emissions in South-east Scotland (section 7.5). Finally the results of sensitivity analysis are presented for the model of NO emissions (section 7.6).

Figure 7.1 Location of field measurements used to define predictive model of NO emissions.



7.2. DESCRIPTION OF NO DATA SET.

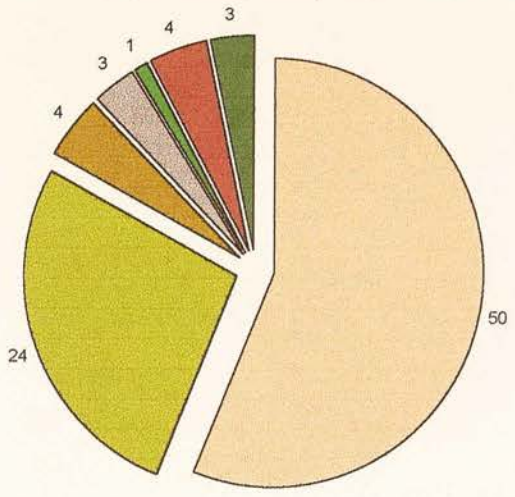
The NO experimental data set consists of 84 point measurements from 25 studies (tables 7.1 and 7.2, Appendix). The location of study sites is illustrated in figure 7.1. The principal methods of measuring emissions of N gases from soils employed by these studies were open chamber, closed chamber and the micrometeorological technique.

The open chamber design allows a steady flow of air through the interior of the box and the flux is estimated from the concentration difference between the air at the inlet and outlet of the chamber (equation 7.1).

$$F = \rho \delta \upsilon / A ; \qquad \textbf{(7.1)}$$

where F is NO flux, ρ - density of nitric oxide, δ - concentration difference between the inlet and outlet of the chamber, υ - volume flow rate of the air through the chamber and **A** - the area of soil enclosed by the chamber (Denmead, 1979). The principles of the closed chamber box and micrometeorological methods are presented in chapter five (section 5.2.2).

Figure 7.2 Proportional representation of major land classes in the NO experimental data set



Agricultural land

Tilled land - 56%
(arable crops like wheat and barley, lucerne, soya beans and vegetables)

Managed grasslands - 27%
(grazed and mown grasslands that receive N fertilisers)

Unmanaged grass - 4.5%
(grasslands not receiving N fertilisers)

Bare soil - 3.4%

Seminatural land:

- deciduous forest - 4.5%
- coniferous forest - 3.4%
- meadow - 1%

89 field measurements were obtained from seven main land classes. This graph presents number of measurements for each land class in the NO data set.

tilled land | managed grassland | unmanaged grass | bare soil | meadow | deciduous forest | coniferous forest

The open chamber technique is the most common method of measurement, used in 16 of the studies in the NO experimental data set. Its popularity is due to requirements of high air flow rates by conventional chemiluminescent analysers used to measure NO concentration. The closed chamber is also applied frequently (Anderson and Levine, 1987; Johansson and Granat, 1984; Thornton *et al.* 1995; Valente and Thornton, 1993 and Watanabe *et al.* 1997) with the micrometeorological method used in only three studies (Hargreaves *et al.* 1992; Jambert *et al.* 1997 and Valente and Thornton,1993).

The factors controlling NO emissions are observed to vary for different land use types and soil classes. Ecosystems represented by the NO experimental data set thus have influence on the defined model. The following section outlines the main characteristics of the NO experimental data set by describing the representation of different vegetation types and soil classes and the corresponding emission variability.

Seven main land use/ land cover types were represented by the NO experimental data set (figure 7.2). The NO data were mostly obtained from agricultural soils (> 90 % of all field measurements) with only a small coverage of seminatural land by four studies of deciduous forest, three of coniferous forest and one of a meadow site in Germany. The agricultural soils studied by the field NO measurements covered a number of different arable and tillage crops, and mown and grazed grasslands from several locations in the USA and Europe (figure 7.1). The land class distribution according to the LCM data set for England/Wales and Scotland (figure 5.3, chapter five) suggested that this distribution might better reflect the English/Welsh environment than that of Scotland. The reason is the more agricultural character of English landscape, where 52 % of land cover is classified as tilled land and grasslands, while in Scotland those land classes represent only 16 % of the total area. Managed grasslands were investigated in 27% of all field studies, which contrasted with only four field measurements on unmanaged grasslands. Areas not receiving N inputs are not well represented by the NO field measurements. The specific character of seminatural land in Scotland, in which heathlands are the major ecosystem contributing to 41 % of the total area, is represented by only one site in Jadras, Sweden (ref. 77A, table 7.1). Woodlands were only studied in seven locations, and although this reflects the small proportion of forest cover in Great Britain (figure 5.3, chapter five), it indicates a limited representation of their contribution to NO emissions in the defined model.

Table 7.3a. Range of NO emissions for different land use types as represented by the NO experimental data set.

Land use	grasslands	arable crops	vegetables	Fallow land	Deciduous forest	Coniferous forest
			NO emission [kg N ha^{-1} y^{-1}]			
minimum	0.1	0.1	-0.4	1.5	0.1	0.1
maximum*	73.9	2.9	2.9	38.4	2.0	7.4
median	1.2	1.1	0.4	1.8	0.6	3.5

* the above measurements seem rather high due to scaling short term fluxes to annual emissions

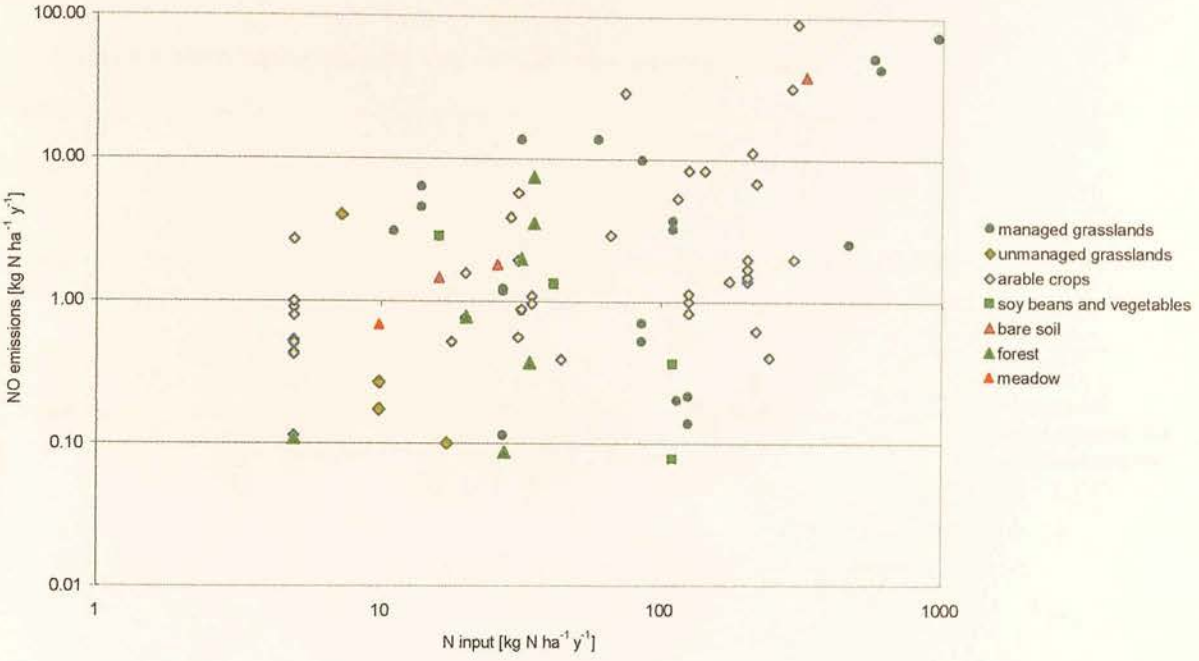
Table 7.3b. Range of NO emissions for major soil types represented by the NO experimental data set.

Soil textural class	median	minimum	maximum*	mean	n
	NO emissions [kg N ha^{-1} y^{-1}]				
sand	1.00	0.11	91.35	24.99	5
sandy loam	0.90	-0.43	38.40	2.78	41
loam, silty loam, loam on clay	1.49	0.10	13.70	3.14	21
clay loam, silty clay loam	1.33	0.20	29.35	4.32	10

* the above measurements seem rather high due to scaling short term fluxes to annual emissions

The different soil conditions in the NO experimental data set determine the character of the established relationships. Among nine soil types specified in the data set, seven were mineral soils and the remaining two could be classified as organic. In the group of mineral soils, sandy loam (48 %), silt loam (14 %) and clay loam (11 %) were the most frequently described classes. Two studies did not specify soil type (ref 17 and 77, table 7.1).

Figure 7.3 NO emissions from different land classes as a function of N input

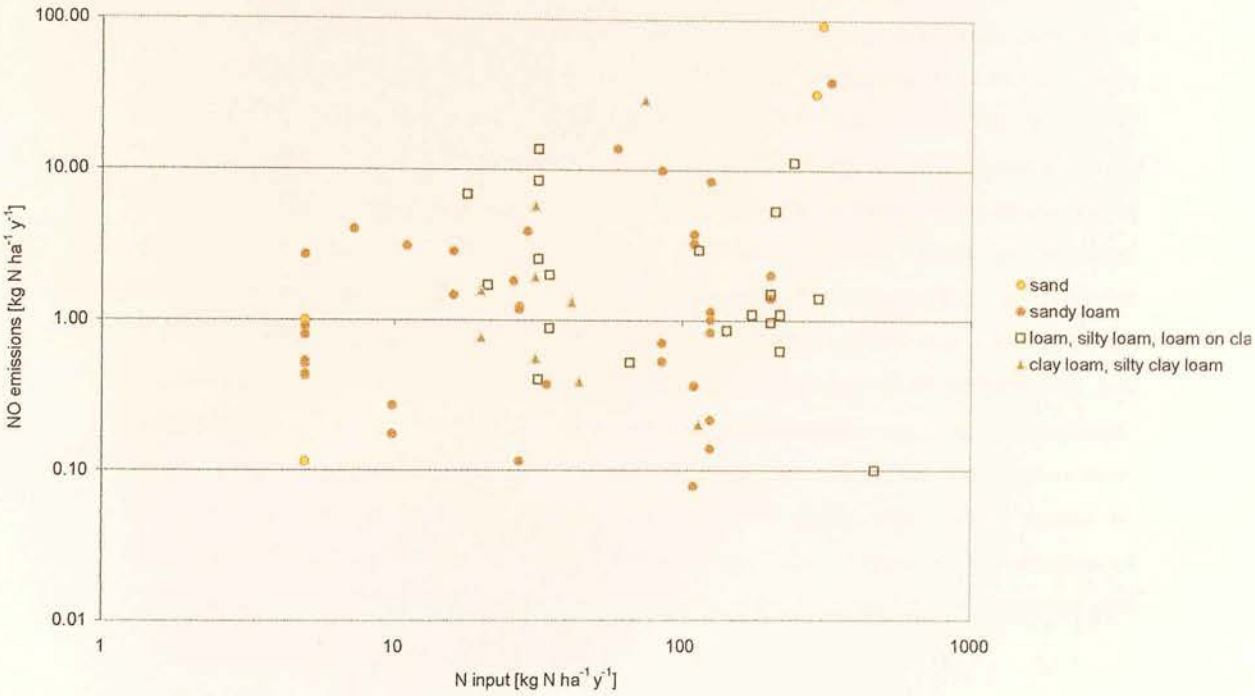


The data of NO field measurements showed an emphasis towards agricultural soils with tilled land forming the largest proportion. High NO emissions are associated with agricultural land due to the surplus of soil N applied through fertiliser application. The disproportionately small number of field sites on semi-natural land might result in a bias of the defined model towards the environments with N input as the strongest controlling factor. The enhancing effect of N fertiliser on NO emission response was observed in a majority of studies in the NO experimental data set.

The highest NO emissions were observed from managed grasslands and bare soils, followed by those from arable land (table 7.3a). Managed grasslands and arable land were also characterised by large variability of NO emissions that showed a weak relationship with N inputs, as observed on figure 7.3. Vegetables had a low median NO emission of 0.4 kg N ha^{-1} y^{-1}. The lowest median NO emission was observed on unmanaged grassland (0.2 kg N ha^{-1} y^{-1}). Surprisingly, high median NO emission of 3.5 kg N ha^{-1} y^{-1} was observed on the forest field plots (table 7.3a), but this was caused by high residual values recorded by Butterbach-Bahl *et al.* (1997)

in an upland forest in Bavaria, where atmospheric deposition contributed 35 kg N ha^{-1} y^{-1} of N input.

Figure 7.4 NO emission from different soil types as a function of N input



There was also some difference observed between different soil drainage classes in the median NO emissions and their variability (figure 7.4). The soil types with the highest median emissions of 1.49 kg N ha^{-1} y^{-1} had characteristics of moderate drainage e.g. loams, silt loams and loams on clay. Soils with poor drainage e.g. clay loams and silty clay loams also had relatively high median NO emissions, higher than those observed for sandy loams and sands (table 7.3b). In contrast, the greatest variability of NO emissions was observed on sands and sandy loams. This could be explained by the dynamically changing moisture conditions in well aerated soils, which lead to some of the highest NO emission measurements. The maximum NO emissions of 91.3 kg N ha^{-1} y^{-1} were measured in June from a sandy soil cropped to maize in south-western France, while only 0.1 kg N ha^{-1} y^{-1} of NO emissions were measured from the same field in November (Jambert *et al.*, 1994). This difference could be explained by seasonal variability; unfortunately, lack of information on the environmental conditions in the soil does not allow for further assessment of the reasons for such great variability. NO emissions from organic

soils were considerably higher than those from mineral soils (median NO emissions for forest soils and marshland were estimated at 2.3 and 6.37 kg N ha^{-1} y^{-1}, respectively). This is consistent with research on NO emissions from acid forest soils by Butterbach-Bahl *et al.* (1997), who measured higher NO than N_2O emissions from those soils (chapter two). Drained peats are also considered a large source of both NO and N_2O due to increased mineralization and high fertility of those soils. In contrast, raw peats do not promote NO emissions, due to very high soil moisture that causes prolonged anaerobic conditions. Relatively high NO emissions from marshland soil of 6.37 kg N ha^{-1} y^{-1}, measured by Hargreaves *et al.* (1992) from Halvergate Marshes on 15.09.1989, are not representative of the great variety of organic soils in semi-natural ecosystems. This study of drained marshland represented only a small proportion of peats converted to pastures located in Cambridgeshire. An additional limitation of this study was its very short duration due to the measurement method (micrometeorological techniques are reliable over short periods of time caused by high requirements of atmospheric conditions - chapter five, section 5.2.2). Those high NO emissions contrasted with very low measurements in September and October from oak-hickory forest in Tennessee by Williams and Fehsenfeld (1991), who observed mean NO emissions of 0.09 kg N ha^{-1} y^{-1}. Large variability in NO emissions from all soil types suggests soil N content was more important controlling factor.

The compiled data set of NO emission measurements from published results presents different land use types and soil classes. Agricultural soils with the dominant class of arable land are the largest group among all studied ecosystems. This unfortunately is not balanced by semi-natural land. Among the best represented soil types are sandy loams and loams mainly used for agriculture. Soils of relatively good or moderate drainage with high N inputs are likely to have an impact on the definition of the model.

7.3 EMPIRICAL MODELS OF NO EMISSIONS ESTABLISHED IN REGRESSION ANALYSIS.

Relationships existing between NO emissions and the factors controlling their amounts were studied with multivariate regression analysis according to the method with which N_2O emission model was defined (chapter five presents a detailed discussion of the method). From the original number of 25 studies (n=89 plots) two studies were excluded (Australia and Japan), as there was high probability they were not representative of the studied regions.

Prior to the application of regression analysis the requirements of this method were considered for the NO experimental data set. The combined data from 23 studies were analysed regarding their distribution, correlation between the independent variables and a possibility of error in the cases of independent and dependent variables (chapter five). N input to soils and NO emissions data showed a skewed distribution, therefore they required a logarithmic transformation. The distribution of the other variables (soil moisture and soil temperature) did not improve with transformation (figure 7.5). A high correlation of 0.65 was observed only between the logarithmically transformed N input and untransformed soil moisture (WFPS - water filled pore space) as presented in table 7.4. There was no clear pattern, which would indicate that this relationship was dependent on land use type or geographical location. It was, however, observed that relatively low soil moisture was characteristic of the majority of American studies measuring NO emissions from grasslands, and many European studies did not record soil moisture. The correlation might therefore be an effect of limited knowledge of soil moisture conditions in a large proportion of studies (WFPS n = 32), and high residuals in a few studies (Thornton *et al.*, 1995; Thornton and Valente, 1996; Yamulki *et al.*, 1995). These studies of the controlling factors of NO emissions from wheat in Rothamsted, the UK (ref 41, table 7.1) and corn in Tennessee (ref 36, 37, 84, 85, table 7.1) reported high N inputs (>170 kg N ha^{-1} y^{-1}) with simultaneous optimal soil moisture for the NO emissions (> 50 % WFPS) as suggested by Davidson (1991).

Figure 7.5 Data distribution of the variables used to define the NO emission model.

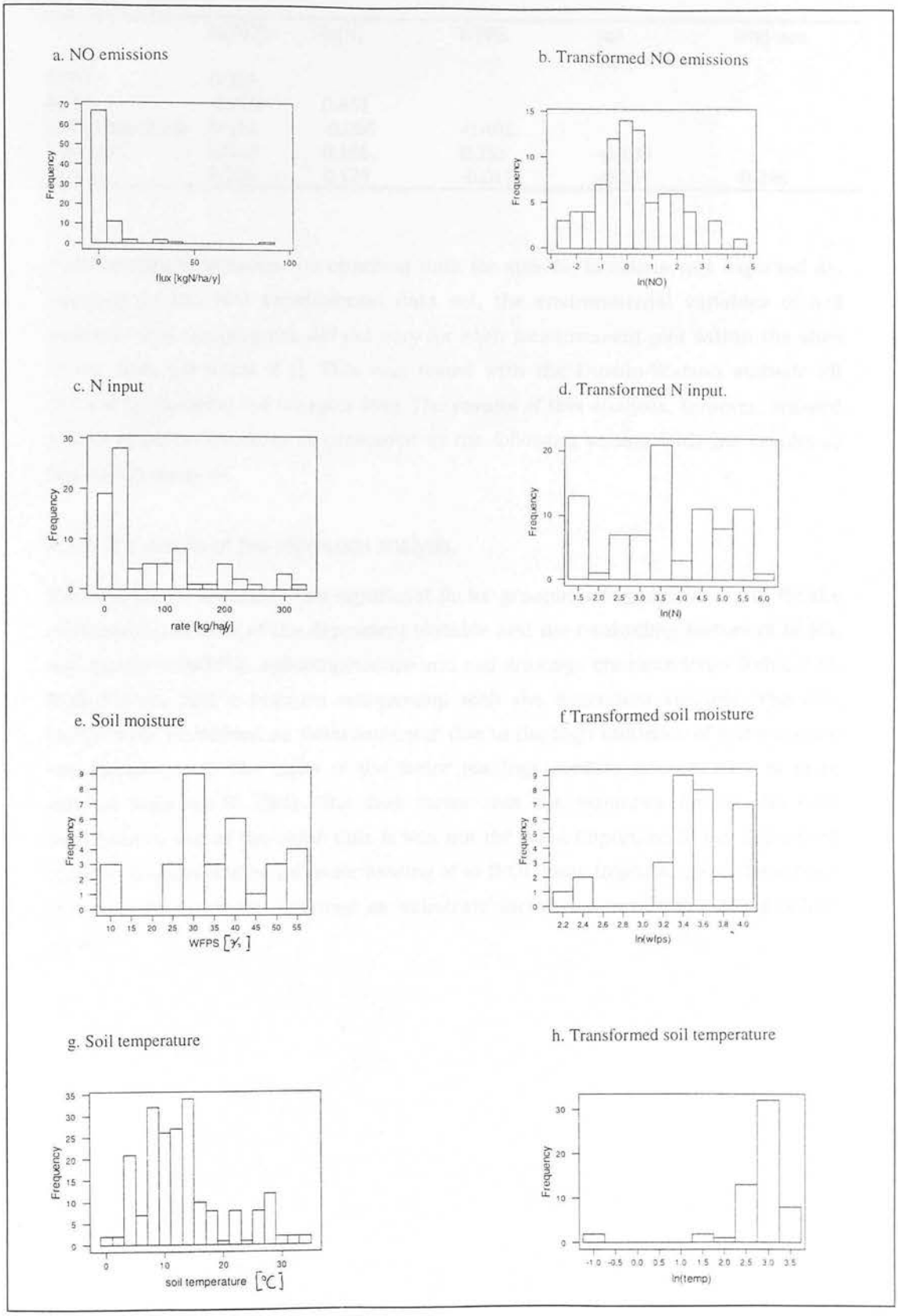


Table 7.4. Pearsons correlation matrix.

	ln(NO)	ln(N)	WFPS	soil temperature	land use
ln(N)	0.361				
WFPS	-0.078	0.651			
soil temperature	0.184	-0.096	-0.401		
land use	0.028	0.156	0.355	-0.136	
$WFPS_2$	0.286	0.124	-0.017	-0.164	-0.246

Autocorrelation between the observed data for specific locations was expected as, similarly to the N_2O experimental data set, the environmental variables of soil moisture and temperature did not vary for each measurement plot within the sites of the data set (table 7.1). This was tested with the Durbin-Watson statistic (d) defined by equation 5.4 (chapter five). The results of this analysis, however, showed a lack of autocorrelation as presented in the following section with the results of regression analysis.

7.3.1 The results of the regression analysis.

Factor analysis indicated two significant factor groupings (eigenvalue > 1.0) for the combination of data of the dependent variable and the controlling factors of ln (N), soil moisture (WFPS), soil temperature and soil drainage characteristics (table 7.5). Both factors had a negative relationship with the dependent variable. The first factor could be defined as 'environmental' due to the high influence of soil moisture and temperature. The signs of the factor loadings confirm an influence of more aerated soils on ln (NO). The first factor was the strongest for all the data distribution, but at the same time it was not the most important to the dependent variable as indicated by its factor loading of ln (NO). More important was the second factor, which could be described as 'substrate' factor due to a high loading of ln(N input).

Table 7.5. Factors described in the analysis of the NO experimental data set.

Variable	Factor1	Factor2	Factor3
Ln (NO)	-0.561	0.031	0.776
Ln (N)	-0.765	-0.184	0.022
WFPS	-0.813	-0.109	-0.255
Soil temperature	0.273	0.819	0.197
Land use	-0.521	0.597	-0.346
$WFPS_2$	-0.774	0.160	-0.015
Eigenvalue	2.505	1.099	0.827
% Variance	0.418	0.183	0.138

The regression analysis indicated that logarithmically transformed N input was the only significant predictor of the dependent variable of ln (NO emissions), as the other tests showed too large uncertainty ($p>0.15$) and no improvement in the value of coefficient of determination (r^2) as presented below in table 7.6. The Durbin-Watson statistic (d) was estimated for the data, on the basis of which the equation (7.2) was defined, to observe the compliance of the data with autocorrelation requirements as discussed in detail in chapter five. Estimated d at 1.97 was compared with the upper (d_U) and lower limit (d_L) of the rejection region at two significance levels: (1) for $p = 0.05$ $d_U = 1.66$ and $d_L = 1.61$; (2) for $p = 0.01$ $d_U = 1.51$ and $d_L = 1.51$ ($n = 81$, $k=1$). As the estimated value of d exceeded d_U at significance of 0.05, the test confirmed that there was no autocorrelation between data of the independent variable (figure 5.8, chapter five).

Table 7.6 The results of the first stage of regression analysis of the NO data set.

Ref	equation	r^2	p	n
(7.2)	ln (NO) = -1.21 + 0.411 ln (N)	13.0	0.001	81
(7.3)	ln (NO) = -0.367 + 0.523 ln (N) - 0.0363 WFPS	12.4	0.155	31
(7.4)	ln (NO) = -0.49 + 0.615 ln (N) - 0.0469 WFPS + 0.005 Ts	13.8	0.362	25

The application of the predictive model of NO emissions (equation 7.5) resulted in the distribution of NO emissions in Great Britain as presented on figure A30.

$$E_{NO} = e^{F1} + \varepsilon \qquad (7.5)$$

Where E_{NO} - NO emissions from soils

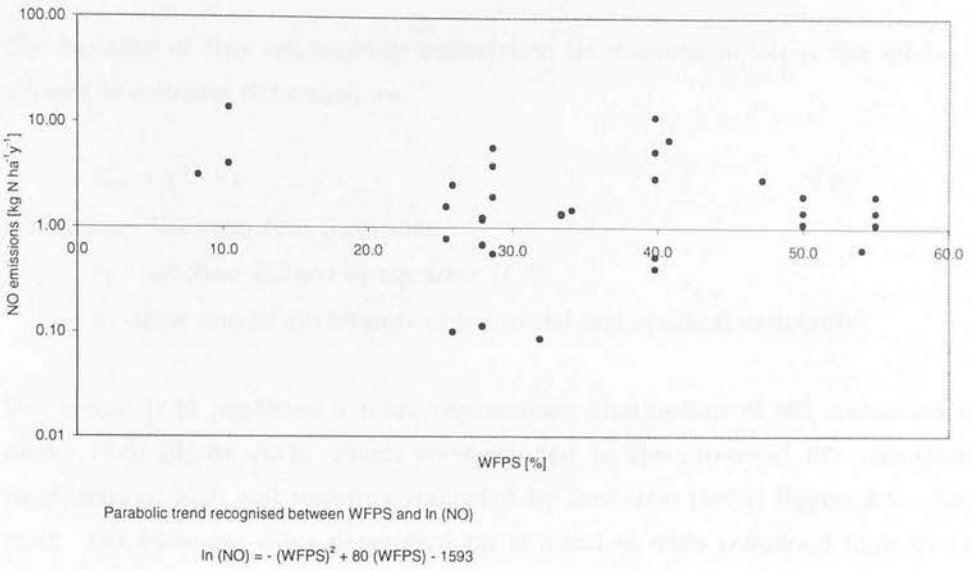
F_1 - function defined by equation (7.2)

ε - error due to uncertainty of the model and residual variability

The pattern in the spatial distribution of predicted NO emissions followed the pattern of N input to soils (figure A30). The predicted mean NO emission for Great Britain was 2.3 (0.5 - 4.6) kg N ha^{-1} y^{-1}, a very similar estimate compared to the predicted mean N_2O emissions of 3.9 kg N ha^{-1} y^{-1} by equation (6.2, chapter six). NO emissions below 1 kg N ha^{-1} y^{-1} were only predicted for The Scottish Highlands and Islands, and in most parts of the country the predicted NO emissions ranged between 2 and 3 kg N ha^{-1} y^{-1}. The highest predicted rates of NO emissions occurred in randomly distributed localised spots, where high N inputs due to large livestock numbers and production of excessive amounts of organic manure occurred. This distribution was the opposite of expected NO emissions, according to field research. Soil moisture was observed to be an important controller of NO emissions from soils in dry environments with distinct wet seasons (Mummey *et al.*, 1994; Parton *et al.*, 1988 and Scholes *et al.*, 1997). NO emissions predicted by model (7.5) at > 2 kg N ha^{-1} y^{-1} for large areas of the North-west Scotland, where mean annual soil moisture was modelled above 60 % WFPS, were too high. A limiting effect of soil moisture was expected to reduce NO emissions in those areas according to Davidson (1991) (figure 2.2, chapter two).

The relationship between soil moisture and NO emissions was re-analysed on the basis of the NO experimental data set. It was observed that within the range of WFPS values presented by the data (8 - 55 %), there was a clear parabolic relationship between the dependent variable of the logarithmically transformed measured NO emissions and the independent variable of soil moisture (figure 7.6). On the basis of the observed distribution a relationship was defined, in which an intermediate variable '$WFPS_2$' was established as a quadratic function of soil moisture (equation 7.6). This relationship was estimated on the basis of figure 7.5 with an assumed maximum WFPS at point A (40.0, 7.0).

Figure 7.6 Soil moisture controlling NO emissions



$$WFPS_2 = - WFPS^2 + 80\ WFPS - 1593 \qquad (7.6)$$

The regression analysis was performed again with soil moisture defined with the above function. The new variable had a reduced correlation coefficient with ln (N) compared with the original WFPS (table 7.4). This was expected to improve the reliability of the model due to reduced multicolinearity caused by correlated independent variables of ln (N) and the original WFPS (table 7.4). Factor analysis with the new introduced variable suggested two significant factor groupings with an eigenvalue > 1.0, but only the first factor was significant to ln (NO) as indicated by factor loading of -0.56. This factor was influenced by soil moisture and ln (N). Multivariate regression analysis revealed that the introduction of the newly defined $WFPS_2$ slightly improved the model (7.7) as indicated by the coefficient of determination (r^2 = 16.8%).

$$Ln\ (NO) = -0.82 + 0.354\ ln\ (N) + 0.0036\ WFPS_2 \qquad (7.7)$$

The new deterministic model has a limited significance as indicated by p = 0.101 and n=28. The Durbin-Watson statistic (d) was estimated for the input data used to define this relationship in a similar method applied to test model (7.5) for autocorrelation. The estimated d of 1.92 was found to exceed d_U=1.56 (p=0.05,

n=28, k=2) and therefore the regression analysis complied with the requirement of no-autocorrelation of the independent variables (figure 5.7, chapter five).

The benefits of this relationship outweighed its limitations when the model was applied to estimate NO emissions.

$$E_{NO} = e^{F2} + \varepsilon \qquad (7.8)$$

Where E_{NO} - NO emissions from soils

F_2 - function defined by equation (7.7)

ε - error due to uncertainty of the model and residual variability

The model (7.8) predicted a more regionalised distribution of NO emissions than model (7.5) (figure A31), which corresponded to the observed NO reduction in conditions of high soil moisture indicated by Davidson (1991) (figure 2.2, chapter two). NO emission rates dependent on N input to soils remained high in areas where mineral soils of good and moderate drainage were dominant (> 70 %), as presented by figure A4. In those areas, estimated mean soil moisture ranged between 25 - 50 % WFPS. The quadratic function (7.6) assumes optimal conditions of NO emissions at WFPS = 40 %. In a few parts of Great Britain, where those conditions prevail, mean annual NO emissions predicted with the new model were fractionally higher than NO emissions predicted with only N input as the controlling factor (model 7.5). Such an increase was observed at a few locations in the north-east East Anglia: Easting=612, Northing=337; Easting=607, Northing = 342, where model (7.8) estimated higher NO emissions than model (7.5) by 0.3 and 0.2 kg N ha^{-1} y^{-1} respectively. In large areas of Great Britain, where modelled WFPS exceeds 50 %, the predicted NO emissions showed a considerable reduction from 2-3 kg N ha^{-1} y^{-1} predicted by model (7.5), to below 0.5 kg N ha^{-1} y^{-1} according to model (7.8).

The mean annual NO emission rate for Great Britain was an order of magnitude lower than the original values predicted by model (7.5). Model (7.5) estimated 2.2 (0.0 – 4.6) kg N ha^{-1} y^{-1} compared with model (7.8) estimate of 0.2 (0.0 - 3.5) kg N ha^{-1} y^{-1}. The observed changes in the spatial distribution of NO emissions predicted by the model (7.8) were supported by a fractional increase in the values of Moran autocorrelation index from 0.52 (for model 7.5) to 0.62 (model 7.8). This suggests a slightly more regional character of NO emissions predicted with N input and soil moisture as illustrated by figure A31.

7.3.2 Model performance studied for changing variables.

Models (7.5) and (7.8) have been applied to estimate NO emissions for varied amounts of N input and WFPS to observe the importance of the predictive variables and their effect on the changing NO emissions. When N input was varied, both models showed a non-linear increase of NO emissions (figure 7.7a). Model (7.5) predicts NO emissions explicitly on the basis of N input. The increase of NO emissions varied with changing N input. Greater changes were estimated in the range of N input from 0 - 100 kg N ha^{-1}, and thereafter the rate of change decreased constantly as suggested by the parabolic shape of their distribution (figure 7.7a). The smaller increase in the upper range of N input suggests reduced bacterial activity for large amounts of available N substrate. A similar parabolic distribution was presented by model (7.8), but an introduction of soil moisture of 33.4 % WFPS (mean soil moisture from all experimental measurements, table 7.1) caused smoothing of the NO emission curve (figure 7.7a). In the range of N input from 0 - 90 kg N ha^{-1}, model (7.8) predicted higher NO emissions in conditions of moderately dry soil (WFPS = 33.4 %). For N input over 90 kg N ha^{-1}, predicted NO emissions were lower than those estimated with the single variable of N input (equation 7.5). This suggests that in moderately dry soil conditions there is a greater effectiveness of bacterial processes in environments with low and moderate N inputs.

Figure 7.7 NO emissions predicted by two empirical models

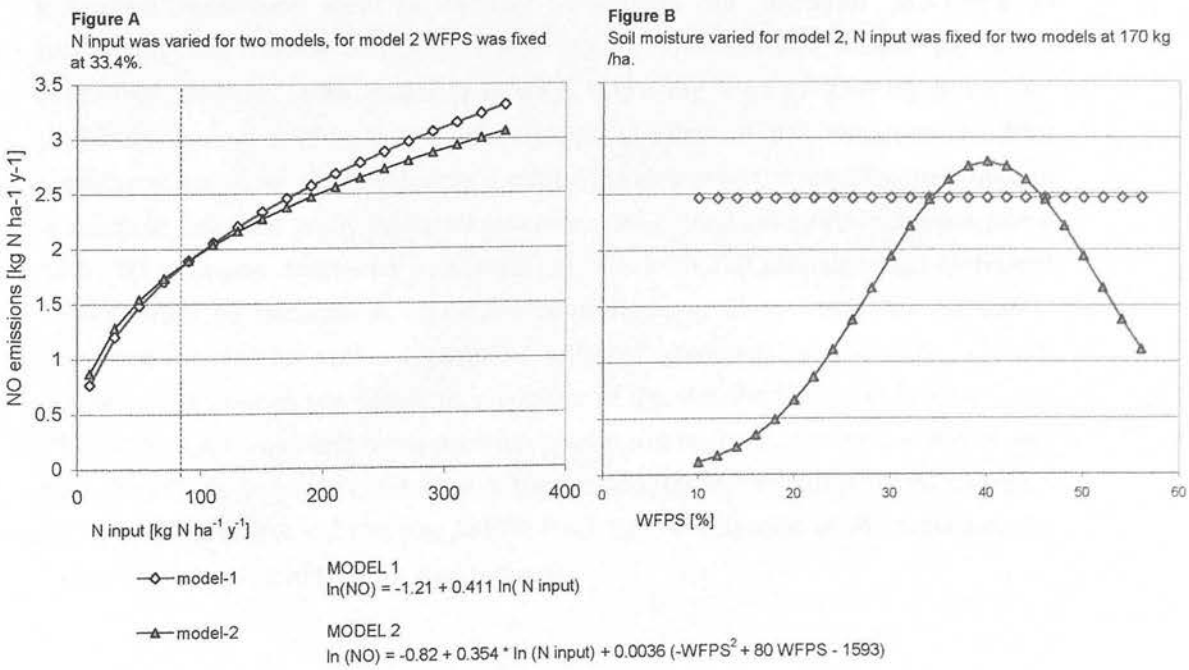
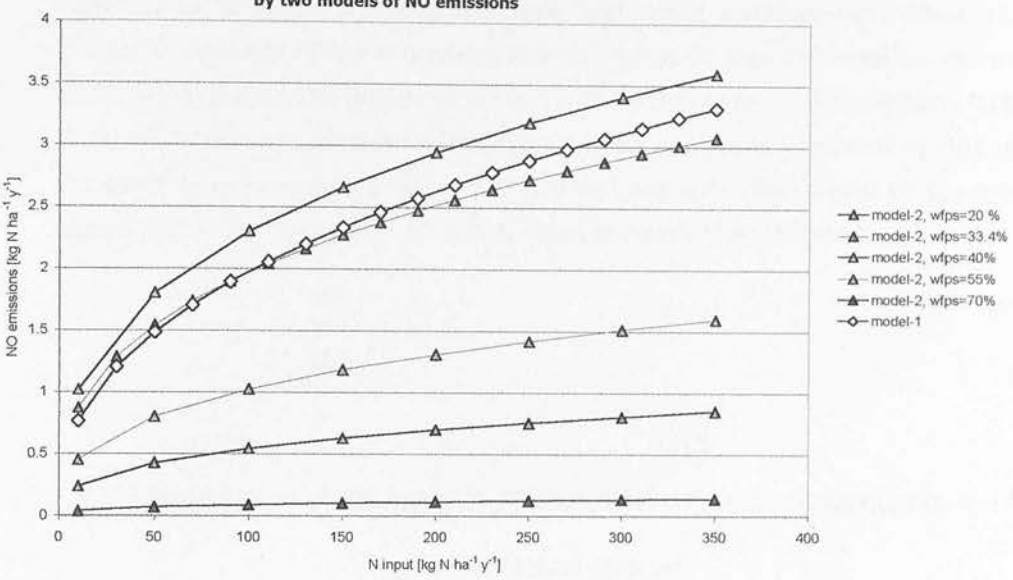


Figure 7.8 The effect of changes in N input and WFPS on predictions made by two models of NO emissions



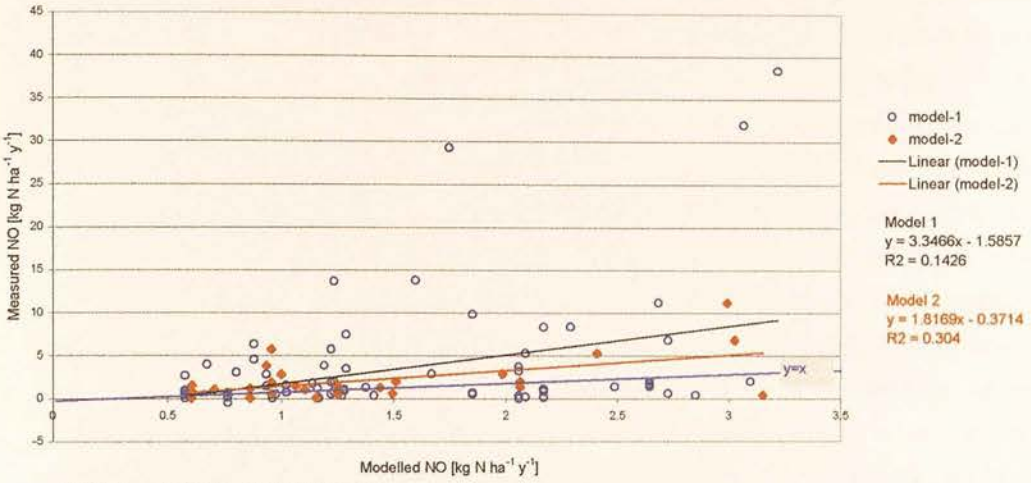
Varying the soil moisture factor had a considerable impact on the amounts of NO emissions predicted by model (7.8). For an assumed N input at 170 kg N ha^{-1}, NO emissions followed the distribution of an inverse quadratic function of soil moisture with the maximum flux at WFPS of 40 % (figure 7.7b). A comparison of the results of this model (7.8) with the predicted NO emissions of 2.46 kg N ha^{-1} y^{-1} using the N input variable with equation (7.5) revealed a considerable controlling effect of soil moisture. In conditions of soil moisture in the range of 34 - 46 % WFPS, this factor enhanced emissions due to optimal conditions for bacterial processes of nitrification and release of NO from soils (figure 7.7b). Outside those regions, NO emissions predicted with model (7.8) were below the level of 2.46 kg N ha^{-1} y^{-1} predicted by model (7.5) due to the restricting effect of soil moisture. In drier conditions, bacterial processes were diminishing as a result of insufficient amounts of water in soil vital to the bacterial processes. When soil moisture increased above 46%, NO emission decreased as a result of restricted soil diffusion and increased consumption by bacteria in anaerobic environments. Changes in NO emissions were also studied for varied N input at different assumed levels of soil moisture (figure 7.8). Although the parabolic character of the distribution was preserved, the effect of N input was most recognised at optimal soil moisture (in the regions of 34 - 46 % WFPS). In moisture conditions not favourable for the production and emission of NO (i.e. for WFPS < 20 % and WFPS > 60 %) the response of NO emissions to increasing amounts of N input was reduced.

The responses of the two empirical models, as presented above, suggest that the variables of N input and soil moisture both have an important effect on the predicted amounts of NO emissions, but soil moisture was observed to restrict the effect of N input on the results of model (7.8). As this important controlling factor of NO emissions is absent from model (7.5) the NO emissions predicted by this model are likely to be over-estimated in very dry and wet soils. This might be particularly significant in localised areas of high N input in North-west Britain (figure A20).

7.3.3 Performance of the model in different environments represented by the NO experimental data set.

Both NO emissions models (7.5) and (7.8) were validated against measured NO emissions with the known experimental data from the field sites in the NO experimental data set (table 7.2, Appendix). The results showed considerable departures from the measured values for the two modelling approaches; this was due to a great proportion of unexplained variability (small r^2) and considerable residual error. The following section looks in detail at the two predictive models in terms of their performance for different soil environments represented by the NO experimental data set (table 7.7 a-b, Appendix).

Figure 7.9 Differences in predictions made by two regression models of NO emissions



Model 1: ln (NO) = -1.21 + 0.411 ln (N)

Model 2 : ln (NO) = -0.82 + 0.35 ln (N) + 0.0035 (- $wfps^2$ + 80 wfps - 1593)

Model (7.5) predicted median NO emissions at 1.3 ± 2.6 kg N ha^{-1} y^{-1}. This model explained only 14% of data variability as indicated by figure 7.9, with mean deviations of the predicted values from the measured NO emissions of a factor of 2. The results of validation suggested insignificant predictions ($F = 0.44$, $p>>0.1$). The field plots for which the model (7.5) was the most uncertain, were either semi-natural or agricultural soils with no added N fertiliser and very low NO emissions from soils due to restricted substrate availability for the bacterial processes (Hutchinson and Brahms, 1992; Jambert *et al.*, 1994 and Johansson and Granat, 1994). The difference between the predicted NO emissions and the confidence limits approached a factor of 4. Estimates of NO emissions were more accurate on sites with added N fertiliser on a pasture (Hutchinson and Brahms, 1992), a grassland (Slemr and Seiler, 1991), a corn field (Williams *et al.*, 1988), a vegetable plantation (Slemr and Seiler, 1991), a wheat field (Harrison *et al.*, 1995) and grass ley (Johansson and Granat, 1984), as indicated by relatively small uncertainty limits (proportional error < 190 %) in table 7.7a (Appendix). Soil N availability increased with fertiliser applications and was the key factor improving the accuracy of the predictions. This confirmed that N treatment as the single predictive variable was the most significant factor in the performance of the model.

The predictive model applying N input and soil moisture as the controlling variables (equation 7.8) showed much improved performance in estimating NO emissions, as suggested by an increase in the coefficient of determination from 14.3 to 30.4% (figure 7.9). Mean NO emissions were estimated at 1.1 ± 1.0 kg N ha^{-1} y^{-1}. As in model (7.5) the NO emissions predicted by model (7.8) were most uncertain for the control plots on agricultural soils receiving low N inputs from atmospheric deposition as reported by Colbourn *et al.* (1987) and Anderson and Levine (1987) for grassland, Anderson and Levine (1987) for wheat and Thornton and Valente (1996) for corn (table 7.7 b, Appendix). The model under-predicted NO emissions for all of the reported plots, with the exception of grassland studied by Colbourn *et al.* (1987), as the observed emissions were exceptionally high, considering low N input and dry soil conditions in the majority of cases (table 7.1). As all of the mentioned sites were on agricultural land, some N substrate could be available to bacteria from the previous years. The relatively low measured soil moisture does not exclude the possibility of anaerobic aggregates with enhanced soil moisture due to soil heterogeneity. Those areas can provide conditions for bacterial processes forming NO that readily escapes the soil through the well aerated soil environment. The environments for which the model predictions are the most certain are, not surprisingly, the agricultural soils with high N inputs and optimal soil moisture conditions. The best predictions were made for corn sites studied by Thornton *et al.* (1995) and Thornton and Valente (1996), wheat fields by Harrison *et al.* (1995) and Yamulki *et al.* (1995) and soybeans, from which the emissions were measured by Anderson and Levine (1987). Those sites were characterised by optimal soil moisture conditions for NO emissions (40 – 55 % WFPS), which was well represented by the model. Still in some plots large differences between the predicted and estimated NO emissions were observed and uncertainty was approaching 100%. In those cases other variables e.g. microsites with enhanced C content or soil pH, that are unaccounted for by the model, may play an important part as controllers of high residual NO emissions.

7.4 SEASONAL DISTRIBUTION OF NO EMISSIONS AS PREDICTED BY EQUATION (7.8).

Model (7.8) was applied in order to estimate the seasonal distribution of NO emissions from soils in Great Britain (figure A32). Seasonal N input was estimated with the method presented in section 6.3 (chapter six). Seasonal changes in soil moisture were modelled in an approach discussed in section 3.3.2 (chapter three). As expected, the highest NO emissions were estimated for spring with a mean of 0.2 and a range of 0.0 - 2.6 kg N ha^{-1} 3 $month^{-1}$, and fluxes of over 2 kg N ha^{-1} 3 $month^{-1}$ were observed in some areas of East Anglia, Nottinghamshire, Lincolnshire and Shropshire (figure A31). Those areas were also observed to contribute to the highest NO emissions in other seasons. However, emission rates did not exceed 1 kg N ha^{-1} 3 $month^{-1}$ in most areas (figure A31). Mean NO emissions did not vary much between the other seasons, but the greatest variability was observed in summer due to N inputs to grasslands (table 7.8).

Table 7.8. NO emissions estimated for four seasons with equation (7.7).

Season*	Mean NO emission [kg N ha^{-1} 3 $month^{-1}$]	Minimum NO emission [kg N ha^{-1} 3 $month^{-1}$]	Maximum NO emission [kg N ha^{-1} 3 $month^{-1}$]	Standard deviation
Spring	0.2	0.0	2.6	0.42
Summer	0.13	0.0	1.96	0.27
Autumn	0.11	0.0	1.26	0.17
Winter	0.12	0.0	1.04	0.17

* seasons as described in section 3.3.1, chapter three.

Seasonal variability of NO emissions was mainly the result of soil moisture changes between the seasons. The rates of NO emissions of over 1 kg N ha^{-1} 3 $month^{-1}$ in spring and summer, and of 0.5 kg N ha^{-1} 3 $month^{-1}$ in autumn and winter were the result of optimal soil moisture in the range of 30 - 50 % WFPS. Those soil moisture conditions are characteristic of the areas with the highest proportions of freely drained and moderately drained soils (figure A6). The greatest NO emissions in spring are partly due to the application of most annual fertiliser in that season, especially on the majority of arable and tillage crops (table 2.4, chapter two), and optimal soil moisture conditions in spring in areas listed earlier (map 3.6, chapter three).

A seasonal variability in NO emissions from semi-natural land was also observed. While in spring and summer on large areas of Sutherland, the Western Isles and The Highlands in Scotland and in English and Welsh Uplands NO emission did not exceed 0.1 kg N ha^{-1} 3 $month^{-1}$, in autumn and winter they increased by 0.2 - 0.3 kg N ha^{-1} 3 $month^{-1}$ (figure A32). This higher background emission was spatially linked with the distribution of peats (figure A6). Peats in semi-natural environments are associated with very moist conditions, particularly in autumn and winter. A large proportion of peats also occur in the areas of highest precipitation, exceeding 1800 mm per annum (indicated by rain zone 5, figure A4). The soil moisture estimated for peats in AGEM is based on limited measurement data from drained peatlands (section 3.3.2, chapter three). A WFPS of 52 %, measured for drained peats in the cold season and adopted for this model, was considerably lower than WFPS for spring and summer (76 %), and does not represent the soil moisture characteristics of raw peats, which dominate areas of North Scotland and the British Uplands. The increase in estimated NO emissions from those areas in autumn and winter is therefore exaggerated.

The seasonal distribution of predicted NO emissions is the result of changing soil moisture. N input has a restricted effect, mainly associated with the high NO emissions in spring.

7.5 MODEL VALIDATION AGAINST FIELD MEASUREMENTS.

The two empirical models (7.5 and 7.8) of NO emissions from soils were validated using additional field measurements of NO emissions from two data sets from several sites in South-east Scotland. This validation was carried out to observe the performance of the defined models in different field conditions to those represented by the data sets used to define the models and to evaluate their suitability for predicting NO emissions from soils in Great Britain.

The first data set was compiled from eight sites: winter wheat and rye grass (1990); mown grass (1991), measurements of NO emissions from alder, *Nothofagus obliqua*, birch and Sitka plantation with acid mist treatment (1991); coniferous forest and moorland study at Dunslair Heights (1992). A summary of these studies was presented by Skiba *et al.* (1994). The second data set was a result of a one-year

field study in the North Berwick area in which NO emissions were measured from cereals in the summer and autumn of 1997 (unpublished data, U. Skiba).

7.5.1 Measurement sites during the campaign in 1990 - 92.

The predicted values of NO emissions with the application of the two models (7.5 and 7.8) were validated against median NO emissions measured on several sites in South-east Scotland in the period of 1990-1992 (table 7.9, Appendix). The data for NO emissions were obtained from agricultural and semi-natural environments. The observed NO emissions were low, as indicated by the median of 0.02 kg N ha^{-1} y^{-1} for all of the sites. Only on two sites were NO emissions of over 1 kg N ha^{-1} y^{-1} measured (Sitka spruce with acid mist treatment and winter wheat, table 7.9, Appendix). A preliminary comparison suggested that the predictions made by the two models (7.5 and 7.8) were over-estimates, especially in the case of model (7.5) (figure 7.10 a- b). The soil moisture factor introduced a greater variability into the NO emission predictions of model (7.8), as observed by the distribution of measured versus modelled values (figure 7.10 a-b). The measurement results were compared with the NO emissions predicted by the two models (7.5 and 7.8) with the method used to validate N_2O predictions described in detail in chapter six.

Figure 7.10 Validation of empirical models of NO emissions with field measurements from 1990 - 1992.

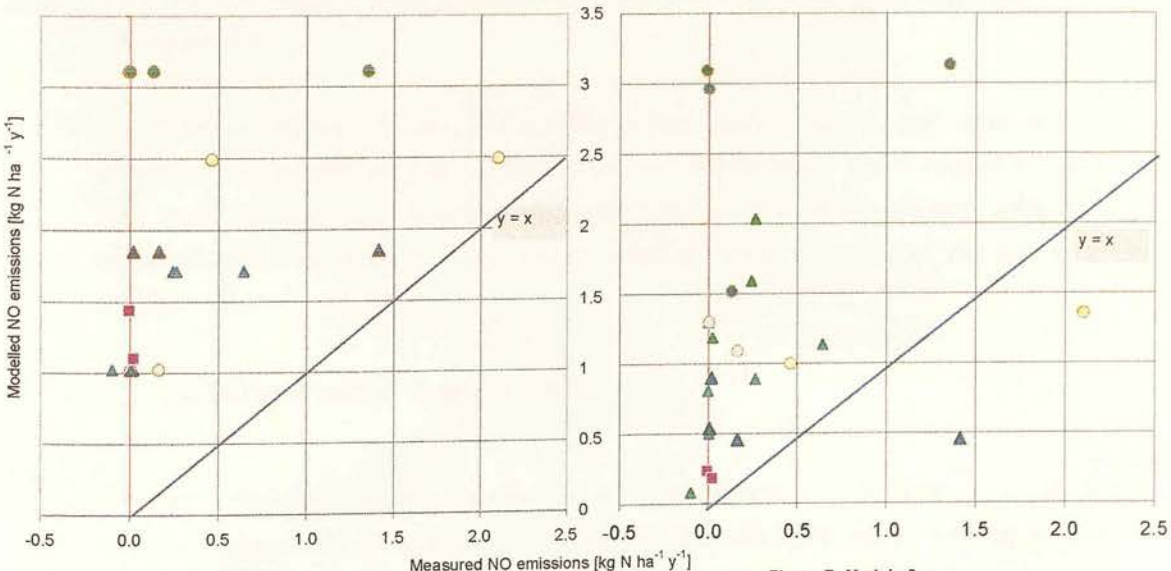


Figure A. Model - 1

E_{NO} = EXP (-1.21 + 0.411 ln (N))

Figure B. Model - 2

E_{NO} = EXP (-0.82 + 0.36 ln (N) + 0.0036 $WFPS_2$)

model 1, wheat
model 1, alder, birch
model 1, Sitka site
model 1, rye grass
model 1, cut grass
model 1, peat

Model (7.5) predicted a median NO emission for all the sites at 1.7 ± 0.98 kg N ha^{-1} y^{-1} and the median residual error of all the estimates (s_y) estimated with equation (3.4) (chapter three) was 0.47. The average uncertainty due to the 95 % probability limits was estimated at 57 (44 - 81) %. Model (7.5) was the least uncertain on the semi-natural plots with very low N input from atmospheric deposition (N = 20 kg N ha-1) and on the peat plots (table 7.9, Appendix). The uncertainty of NO predictions for those ecosystems was above the average of 57 %. Surprisingly, the SE recorded for those sites was at the lower range of estimated error (< 0.45). The results of this validation are compared with model (7.8) in the following section.

Model (7.8) predicted a lower median NO emission at 1.04 ± 0.70 kg N ha^{-1} y^{-1} for all the experimental sites, with a higher accuracy than model (7.5) as indicated by a lower median s_y of 0.34. This model showed, however, a greater uncertainty of 67 (43 - 708) %. This was a similar pattern to that observed in the case of model (7.5) as the sites, for which the predictions were least accurate, were linked with the highest N input i.e. winter wheat and rye grass, and the alder site where optimum soil moisture (WFPS ~ 40 %) was measured. The greatest uncertainty, corresponding to model (7.5), was observed on the semi-natural plots (birch, two Sitka spruce sites, one cut grass site and peat sites), where the uncertainty described by 95 % probability limits exceeded 100 %. Both N input and soil moisture affected the uncertainty of the predictions. On the Sitka spruce site where N input was increased due to the acid treatment, the predictions were more uncertain for higher values of soil moisture (WFPS > 60.8 %) as presented in table 7.9 (Appendix).

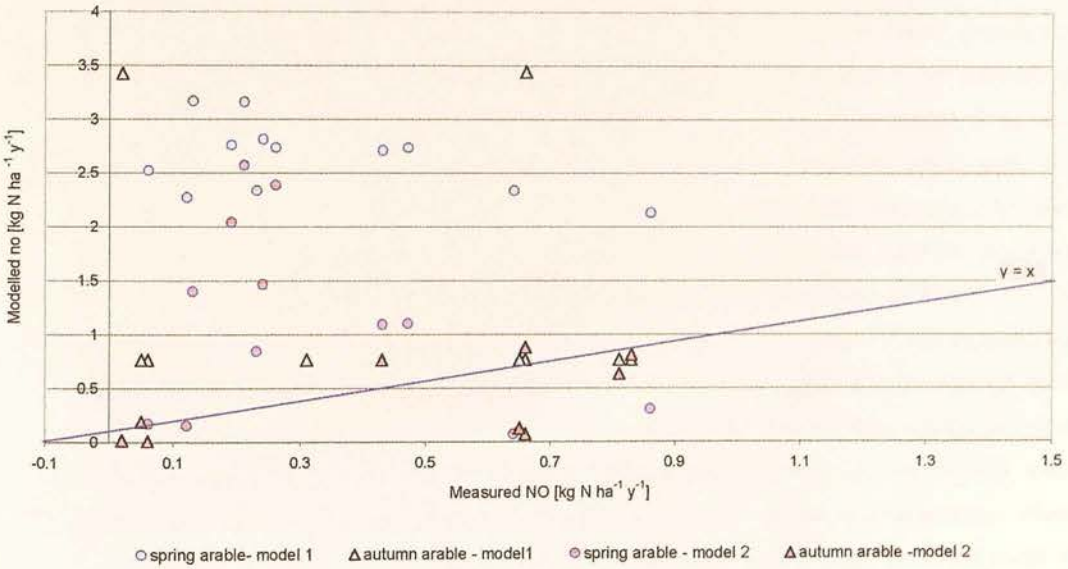
The observed pattern for the two models of the more accurate, but considerably uncertain predictions for semi-natural land, caused by low N input (model 7.5 and 7.8) and limiting soil moisture (model 7.8), is further examined with the measurement data from a more recent study in North Berwick in the following section.

7.5.2 North Berwick sites studied in 1997.

The North Berwick data set consisted of 13 plots of cereal crops grown on soils of different texture. NO emissions were measured from all sites within a 3-day period in May and October 1997 (unpublished data, U. Skiba) (table 7.10, Appendix). N input values were obtained directly from the farmers. Mean NO emission was

measured at 0.37 kg N ha^{-1} y^{-1}, but great variability was observed between the fields (sd = 3.82, n= 13). This variability was an effect of one site on which a very high residual value of NO emissions was measured (6.83 kg N ha^{-1} y^{-1} in May and 18.7 kg N ha^{-1} y^{-1} in October). It was expected that this measurement plot will have an effect on the results of the validation, which is discussed further in this section. The distribution of predicted versus measured values showed a tendency for the two models to over-estimate NO emissions (figure 7.11). The observations made by

Figure 7.11 Validation of NO emissions predicted with two regression models with field measurements from North Berwick.



a detailed analysis for the two models are presented in the following section.

Model (7.5) predicted median NO emission for all the study area at 2.3 ± 2.4 kg N ha^{-1} y^{-1}. The uncertainty of the predictions described by the 95 % probability limits was on average 105% ($F=5.6$, $p<<0.01$). When considered individually, many plots showed a greater uncertainty described by the range of error for all data plots of 93 - 230%. The highest uncertainty (> 200 %) was incidentally linked with the very low NO emission measurements (< 0.8 kg N ha^{-1} y^{-1}). This coincided with the observation made during the validation of the model with the original NO experimental data set, which also showed the greatest uncertainty for the plots with low N input. The median s_y estimated for the North Berwick field data set was 1.17. There was considerably better correspondence between the predicted and measured NO emissions in autumn, when less N input was registered (figure 7.11). The

highest error (s_y > 1.4) was observed for the plots with the largest N input (> 300 kg N ha^{-1}) as presented in table 7.10 (Appendix). The extremely large NO emission measurement on site 2 (table 7.10) had a high s_y (1.47), but relatively low uncertainty (94 %) in spring. Predicted NO emission for that site in spring was under-estimated, but was surprisingly close to the measured value, as indicated by the residual of -3.2. For other sites model (7.5) was observed to overestimate NO emissions due to the large influence of the N input variable, but the greatest uncertainty was registered on the plots with low N input (table 7.10, Appendix).

Model (7.8) estimated median NO emissions for the North Berwick sites at 0.76 ± 2.0 kg N ha^{-1} y^{-1}. The accuracy of the estimates improved compared with model (7.5), as the median s_y decreased from 1.17 to 0.96. On the other hand the uncertainty of predictions of the model (7.8) increased considerably to an average of 261 %. A similar pattern of the predictions to those described for model (7.5) was observed in model (7.8), which showed the largest s_y (> 1.9) for the plots with the highest N input (> 220 kg N ha^{-1} y^{-1}), but the greatest uncertainty was characteristic of the plots with low N input. The limiting factor of soil moisture caused great uncertainty for the few sites where high soil moisture of WFPS > 61 % was observed. In autumn this effect was observed on site 13 (table 7.10, Appendix), where high N did not improve the certainty limits of the estimate compared with model (7.5). A similar limiting effect of soil moisture was observed in spring on sites 2, 8, 12 and 13 (table 7.10). For site 2, where the highest NO emissions were measured, the predicted NO emissions for spring were considerably more underestimated than the result of model (7.5) as observed by high residual error of -6.2. The uncertainty limits estimated for that site were also large (680 %). When that measurement was excluded from the validation of model (7.8) no improvement in model confidence was observed, as sites characterised by low N input had considerably larger uncertainty of predictions than site 2 (table 7.10, Appendix).

7.5.3 Performance of the two models in view of the validation results.

Both models are characterised by large uncertainty of their predictions. The greater uncertainty of model (7.8) was due to a relatively high residual error compared with the error described by the regression model and a small sample size (n = 24), which led to a small F ratio of 0.97 and low significance of the analysis (p > 0.1). Model (7.5) showed much greater residual variability for individual plots in comparison

with the error due to the regression model and a much greater F ratio of 5.6 ($p << 0.01$). These observations indicate that both approaches (model 7.5 and 7.8) have advantages and limitations. Model (7.5) offers a significant method by which the predictions are considerably over-estimated ($p < 0.05$), but the uncertainty of the predictions is lower. Model (7.8) makes more accurate predictions with a considerable uncertainty due to higher residual variability compared with variability of the general trend offered by the model, hence its low significance. The validation indicated that models (7.5) and (7.8) did not predict accurate mean NO emissions for the environments represented by the selected sites in Scotland. The validation results against the field measurements should, however, be treated with caution due to very short term studies, that might have not accounted for the variability of NO emissions. Model predictions reflect general trends in emission processes. Very low NO emissions measured on few occasions, with small deposition fluxes on the sites of semi-natural land and rye grass in the period 1990-92 (table 7.9, Appendix), were not reflected by the models (7.5) and (7.8). This indicates a weakness of the presented empirical approaches, which did not account for the processes leading to deposition that appear to be very important in those environments. The validation nevertheless suggests that general trends of NO emissions are better predicted by model (7.8) than model (7.5).

7.6 MODEL SENSITIVITY.

The two models (7.5 and 7.8) represented two distinct approaches of estimating NO emissions from soils with different characteristic results. There are two important issues of their application for estimating NO emissions. The first one is linked to the very limited accuracy that is affected by the model definition as emphasised by section (7.5). This uncertainty is caused by the high variability of the individual measurements of NO emissions. Description of the two models (section 7.3.2) demonstrated their varied response to changing predictive variables of N input (model 7.5 and 7.8) and soil moisture (7.8). This is related to the second modelling issue of limited accuracy of the input parameters data. Detailed account of that problem was presented in section 5.6 (chapter five). In order to observe how the predictions of the NO emission models change with varying the model parameters for Great Britain, a sensitivity analysis was applied.

Sensitivity analysis was carried out according to the method employed for the N_2O emission models presented in chapter six (section 6.5). In the first stage of this analysis only model (7.8) was tested by excluding each parameter as presented below in table 7.11.

Table 7.11 Definition of NO model (7.8) as tested in experiment 1.

Factor excluded	Definition of the model (7.8)
N input	$E_{NO} = e^{-0.82 + 0.0036\ WFPS-2}$
WFPS	$E_{NO} = e^{-0.82 + 0.354\ ln\ (N)}$

Model (7.8) was shown to be particularly sensitive to soil moisture due to its strong negative influence on NO emissions as described by equation (7.6). This strong effect manifested itself in both phases of experiment 1. When N input was excluded from the model, NO emissions were estimated at 'null' (ArcInfo symbol -9999). Removal of the soil moisture parameter from model (7.8) resulted in a considerable increase in mean NO emissions from 0.2 (0 - 3.5) kg N ha^{-1} y^{-1} (without changes to the model definition) to 2.6 (0.7 - 4.6) kg N ha^{-1} y^{-1} (after the change). The increase, observed especially in the lower range of NO emissions, suggested the strong effect of soil moisture on the predicted background emissions.

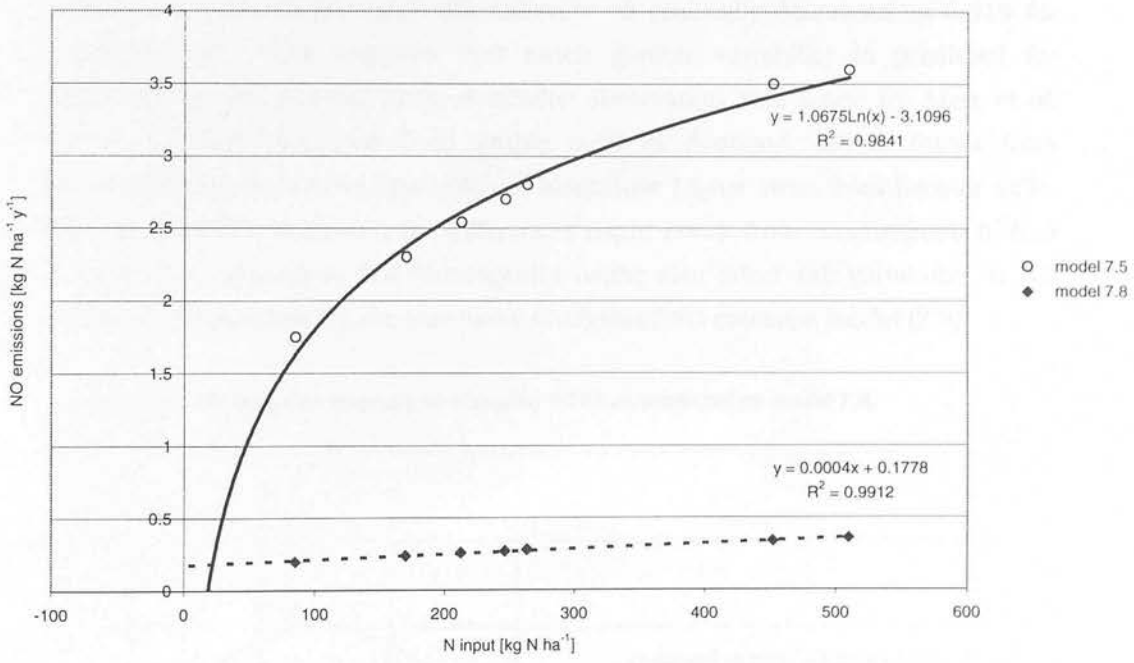
Experiment 2 of the sensitivity analysis varied model parameters as presented in table 7.12, for models (7.5) and (7.8). The multiplication factors for N input were based on the results of the survey of farmers in the North Berwick area as described in chapter six (section 6.5). Adjustments made to soil moisture were based on a strategy to observe the possible variations caused by uncertainty of estimated WFPS and responses to the future trends in climate (section 6.5). Additionally, options five and six were added to observe model (7.8) response to extreme soil moisture conditions (a decrease of 40 % and an increase of 50 %).

Table 7.12 Different scenarios of parameter change in experiment 2.

N input multiplication factors [%]	Soil moisture adjustments [%]
50	- 22.4
125	- 30
145	- 40
155	10
266	30
300	50

The responses of model (7.5 and 7.8) to the adjustments in N input parameter as presented in table 7.12 were observed as changes of mean NO emissions for Great Britain (figure 7.12). The two models responded with different trends. Model (7.5) showed a slightly curved trend with an increase in NO emissions positively related with the N parameter. The distribution had an asymptotic character, which suggested an existing limit to growth in NO emissions.

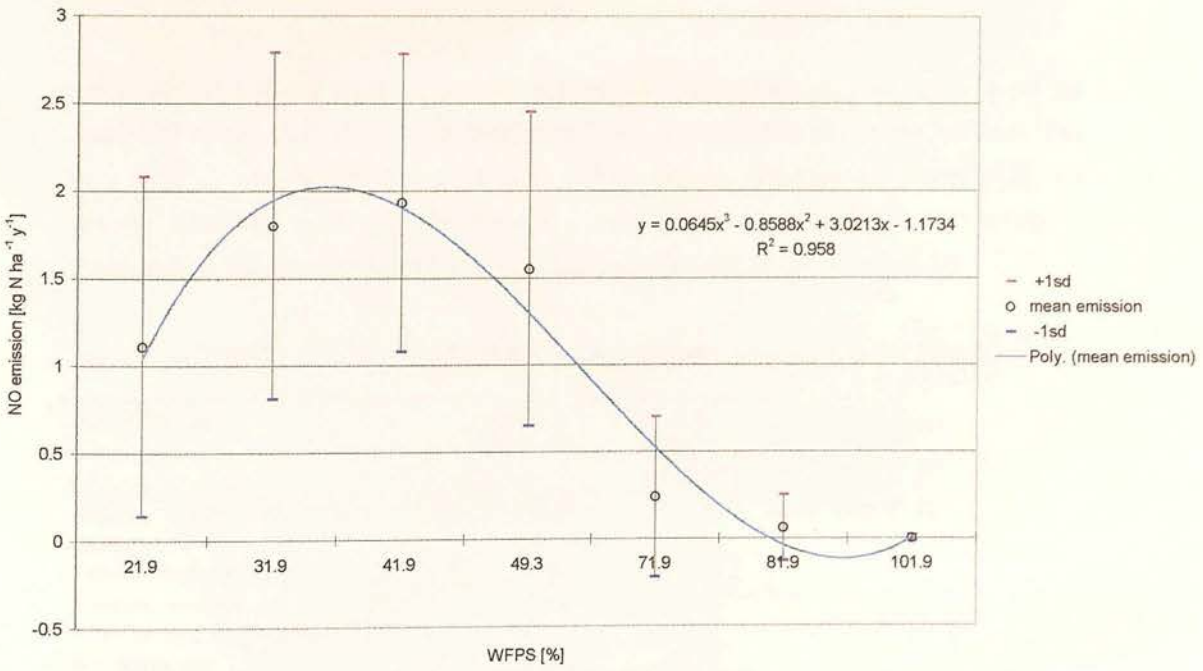
Figure 7.12 Mean NO emissions for different scenarios of N treatment.



Model (7.8) presented a linear trend with a small response to the changes in N input. This was primarily associated with a smaller correlation coefficient of N input factor in model (7.8) than model (7.5). The response of model (7.8) to the varied N input for fixed soil moisture at 33.4 % WFPS as described in section 7.3.2 (figure 7.6) was, however, considerably different and it corresponded with model (7.5). This different model (7.8) behaviour was based on the NO experimental data set (section 7.2) which reflected soil moisture conditions different from those in Great Britain. Mean WFPS for all the sites in the NO experimental data set (33.4 %) was more favourable for NO emissions than the soil moisture conditions of British soils (mean = 71.9 %). In optimal conditions of soil moisture this parameter does not restrict the responses due to changes in N input (figure 7.6). The sensitivity of model (7.8)

was controlled by soil moisture. Responses of model (7.8) to changes in soil moisture, as presented in table 7.12, were studied through the observation of the mean NO emission responses and their standard deviations (figure 7.13). The distribution of mean NO emissions showed, not surprisingly, a parabolic trend described by the third degree equation (figure 7.13) explaining 95 % of data variability. The maximum NO emission was estimated for WFPS of 41.9 %, with the emissions decreasing for higher and lower soil moisture. This corresponded with the observations made for the model performance in section 7.3.2 (figure 7.6). Standard deviation (sd) was variable and large for soil moisture values below 50 % WFPS. In conditions of higher soil moisture sd gradually decreased to 0.019 for saturated soils. This suggests that much greater variability is predicted for conditions of well aerated soils. A similar observation was made by Arah *et al.* (1991) for N_2O measured from arable soils in Scotland, where fluxes from lighter-textured soils were one order of magniture higher than from heavier soils. Arah *et al.* (1991) suggested the differences might result from consumption of N_2O in anaerobic microsites. Soil heterogenity might also affect the variability in NO emissions as observed by the sensitivity analysis of NO emission model (7.8).

Figure 7.13 NO emission response to changing WFPS as predicted by model 7.8.



The sensitivity analysis emphasised differences between models (7.5) and (7.8). The importance of soil moisture as the strongest parameter in model (7.8) was shown by the two experiments discussed above. Soil moisture conditions in Great Britain are considerably different from the NO experimental data that were the basis of the definition of the model. The limiting effect of soil moisture in Great Britain considerably reduces the response of the model to increased N input. This might suggest that in areas of intensive agriculture, NO emissions would be more affected by the textural properties of soils than the amounts of fertiliser input. Changes in soil moisture might therefore result in a considerable variability of NO emissions. If a decrease in soil moisture occurs in South-east England, NO emissions in that area (that are currently the highest in Great Britain) would probably decrease. The effect of climatic changes in other areas would depend on the textural properties of soils and the level of N input. The predictions reflected by model (7.8) are more complex than those offered by model (7.5) due to the higher sensitivity of the former. Model (7.5) strongly supports efforts of better fertiliser management irrespective of climate and soil textural class.

7.7 PREDICTED TOTALS OF NO EMISSIONS.

Total NO emissions from soils in Great Britain were estimated at 65.8 kt y^{-1} by model (7.5) and 7.4 kt y^{-1} by model (7.8). The considerable difference between the two models was caused by the limiting effect of soil moisture in model (7.8), as mean annual estimate in most parts of Great Britain exceeded 55 % WFPS (figure A13) and in those conditions NO emissions were restricted (section 7.3.1).

Table 7.13 Total NO emissions from soils according to major sources in Great Britain.

Emission source	Model (7.5) [kt N y^{-1}]	Model (7.8) [kt N y^{-1}]
Arable, tillage and horticultural crops	11.9	1.94
Grazed and mown grasslands	15	1.0
Organic N input	17.8	2.0
Atmospheric Deposition	21.1	2.5
All sources	**65.8**	**7.4**

Model (7.5) estimated a mean emission factor from all N inputs at 2%, and the background emissions at 0.3 kg N ha^{-1} y^{-1}. For model (7.8) the established

background emission was 0.17 kg N ha^{-1} y^{-1}, and the fertiliser emission factor was 0.04 % (figure 7.12). The very small effect of N fertiliser input was caused by limited production and release of NO from soils in dominant wet conditions (Davidson, 1991). NO emissions from soils in Great Britain predicted by model (7.8) did not exceed 0.1 kg N ha^{-1} y^{-1} in most areas, with the exception of North-east East Anglia, where a fractional increase in NO emissions of 0.2 - 0.3 kg N ha^{-1} y^{-1} was observed. Only in optimal conditions of soil moisture (35 - 45 % WFPS) an increase in NO emissions was indicated by model (7.8). Those areas were very restricted in Great Britain (figure A31), and the fractional increase did not affect the total NO emissions from tilled land, which was dominant in that area. In most parts of Great Britain there was a considerable decrease in NO emission rates from 2 -3 kg N ha^{-1} y^{-1}, predicted by model (7.5), to 0.5 kg N ha^{-1} y^{-1} (figures A7.1, A7.3). The limiting effect of soil moisture reduced the predictions of total NO emissions from all major sources by an average factor of 10 (table 7.13).

7.8 CONCLUSIONS.

This chapter presented two models to estimate NO emissions from soils in Great Britain. These models were defined on the basis of published experimental data and they describe relationships observed between the NO emissions and their controlling factors established in multivariate regression analysis. Model (7.5) estimates NO emissions as a function of N input and the relationship showed a parabolic trend with smaller increases observed for higher values of N input. The spatial distribution of NO emissions predicted in model (7.5) not surprisingly corresponds with great spatial variability of N input to soils. This model considerably overestimates NO emissions, but on the other hand it presents a more statistically significant approach than model (7.8). The predictions of model (7.5) for Great Britain are strongly affected by the validity of predicted N input as the single controlling parameter. N input applied in AGEM was affected by the uncertainties due to land use data and departures of actual application rates from the assumed recommendations (figure 6.1, chapter six). The errors due to the method of estimating N input were not very large (section 5.6, chapter five), which suggests that the accuracy of predicted NO emissions with model (7.5) would be mainly the result of the model definition.

Model (7.8) estimates NO emissions with variables of N input and soil moisture. The inclusion of the environmental variable, controlling the production processes of NO and its release from soils, considerably improved the accuracy of the model as reflected by an increase in a coefficient of determination (r^2) from 14.3 % (model 7.5) to 30.4 % (model 7.8). This model is very sensitive to the changes in soil moisture, which dominate the effects of N input. Only in optimal soil moisture conditions did model (7.8) show a similar response to changing N input to model (7.5). Those conditions, however, are restricted to very small areas in Great Britain, primarily in East Anglia. The trend predicted for Great Britain is characterised by reduced NO emissions in most parts of the country. The sensitive nature of model (7.8) makes its predictions dependent on the accuracy of soil moisture. This variable, modelled with SPACTeach for mineral soils and based on limited measurements, is very uncertain. Simple validation of predicted soil moisture indicated a possibility of over-estimation by an average of 22.4 % (section 3.3.2, chapter three). The sensitivity analysis predicted a considerable increase in NO emissions from 0.24 (0.0 - 3.49) to 1.55 (0.0 - 4.42) kg N ha^{-1} y^{-1} when soil moisture was adjusted by the difference indicated by the mean error. This suggests that due to the uncertainty of the soil moisture parameter, NO emissions could be considerably underestimated by model (7.8) in many parts of Great Britain. The validation of the two presented approaches with field data, however, confirmed greater accuracy of model (7.8) in reflecting general trends of NO emissions. Total NO emissions from soils in Great Britain were estimated with the AGEMs at 7.4 - 65.8 kt N y^{-1}.

APPENDIX.

Table A7.1 NO experimental data set.

site	land use	soil texture or other soil classification characteristics	NO flux [kg N ha^{-1} y^{-1}]	N input [kg N ha^{-1} y^{-1}]	WFPS [%]	soil temperature [°C]	fertilizer type
1	pasture	freely-drained loam	0.10	17.1	25.9	23.0	
2	pasture	freely-drained loam	2.54	464.1	25.9	23.0	$CO(NH_2)_2$
3	pasture	silt loam	13.70	31.5		25.8	
4	pasture	silt loam	0.85	31.5		11.5	
5	pasture	sandy loam	3.11	11.0	8.3	26.0	
6	grassland	sandy loam	1.23	27.1	27.9	20.9	
7	grassland	sandy loam	1.18	27.1	27.9	5.3	
8	grassland	sandy loam	0.11	27.1	27.9	12.6	
9	grassland	sandy loam	0.68		27.9	34.1	
10	grazed	marsh soil, gleysoil	4.58	13.8		17.6	
11	pasture	sandy loam	4.01	7.2	10.3	26.2	
12	pasture	sandy loam	13.78	59.2	10.3	26.2	$(NH_4)_2SO_4$
13	pasture	drained marshland,	6.37	13.8			
17	meadow		0.68	9.8			
21	grass, clover dandelions	sandy loam	0.27	9.8		21.4	
22	grass, clover dandelions	sandy loam	0.17	9.8		20.7	
23	grass, clover dandelions	sandy loam	3.71	109.8		21.4	NH_4Cl
24	grass, clover dandelions	sandy loam	3.23	109.8		20.7	NH_4Cl
25	vegetables	sandy loam	-0.43	9.8		n/a	
26	vegetables	sandy loam	0.00	109.8			$NaNO_3$
27	vegetables	sandy loam	0.37	109.8			NH_4Cl
28	vegetables	sandy loam	0.08	109.8			$CO(NH_2)_2$
32	cornfield	clay loam	29.35	73.8		23.0	$CO(NH_2)_2$,NH_4NO_3
33	corn	silt loam	8.39	142.5		24.7	compound
34	corn	silt loam	0.89	31.5		16.8	compound
35	corn	silt loam	1.09	34.4	50.0		
36	corn	sandy loam	1.40	202.4	50.0		Liquid NH_3
37	corn	sandy loam	1.99	202.4	50.0		$CO(NH_2)_2$
38	corn	sandy loam	3.88	28.9	28.6	33.6	
39	fallow following corn	sandy loam	1.46	16.0	34.1	20.5	
40	wheat field	clay loam	0.39	43.8		16.2	
41	wheat field	flinty loam on clay	0.62	217.8	54.1	10.8	NH_4NO_3
42	wheat field	flinty loam on clay	6.83	217.8	40.8	16.2	NH_4NO_3
43	wheat field	clay loam	0.77	19.9	25.4	28.2	
44	wheat field	clay loam	1.57	19.9	25.4	19.4	
45	soy beans	clay loam	1.34	41.1	33.4	31.8	
46	soy beans	clay loam	1.32	41.1	33.4	0.4	
47	winter wheat	clay loam	5.76	30.7	28.6	0.4	
48	winter wheat	clay loam	0.56	30.7	28.6	20.0	

49 winter wheat	clay loam	1.93	30.7	28.6	18.0	
50 soy beans	sandy loam	2.86	16.0	47.2	14.8	
51 wheat	flinty loam on clay	0.52	17.8	39.8	16.1	
52 wheat	flinty loam on clay	2.92	65.8	39.8	16.1	Nitram
53 wheat	flinty loam on clay	5.30	113.8	39.8	16.1	Nitram
54 wheat	flinty loam on clay	11.20	209.8	39.8	16.1	Nitram
55 wheat	flinty loam on clay	0.40	242.8	39.8	16.1	FYM
56 barley	sandy loam	0.51	4.9		6.6	
57 barley	sandy loam	0.53	4.9		11.3	
58 barley	sandy loam	2.71	4.9		22.6	
59 barley	sandy loam	0.43	4.9		16.9	
60 barley	sandy loam	0.43	4.9		18.0	
61 barley	sandy loam	0.90	4.9	17.5		
62 barley	sandy loam	0.83	124.9	11.5		$Ca(NO_3)_2$
63 barley	sandy loam	8.35	124.9	22.6		$Ca(NO_3)_2$
64 barley	sandy loam	1.01	124.9	13.9		$Ca(NO_3)_2$
65 barley	sandy loam	1.13	124.9	11.8		$Ca(NO_3)_2$
66 grass ley	sandy loam	0.22	124.9	11.4		$Ca(NO_3)_2$
67 grass ley	sandy loam	0.14	124.9	10.0		$Ca(NO_3)_2$
68 grass ley	sandy loam	9.85	84.9	22.2		$Ca(NO_3)_2$
69 grass ley	sandy loam	0.71	84.9	12.6		$Ca(NO_3)_2$
70 grass ley	sandy loam	0.53	84.9	21.0		$Ca(NO_3)_2$
71 lucerne	sandy loam	0.90	4.9		15.0	
72 lucerne	sandy loam	0.43	4.9			
73 lucerne	sandy loam	0.80	4.9		19.7	
74 mixed wood	sandy loam	0.37	33.8		26.0	
75 oak-hickory	forest soil	0.09	27.5	31.9	17.2	
76 oak-hickory	silt loam	1.99	31.5		21.0	
77 coniferous		0.11	4.9			
79 maize	sand	0.51	4.9			
80 maize	sand	1.00	4.9			
81 maize	sand	91.35	304.9			Liquid NH_3, $CO(NH_2)_2$
82 maize	sand	0.11	4.9			
83 corn	silt loam	1.09	34.4	55.0		
84 corn	silt loam	1.40	174.4	55.0		NH_4NO_3
85 corn	silt loam	1.99	296.4	55.0		NH_4NO_3
86 maize	podzol (90% sand)	32.00	289.8			Liquid NH_3
87 bare soil	sandy loam	1.80	25.9			
90 bare soil	sandy loam	38.40	325.9			
91 corn	silt loam	0.96	34.4			
92 corn	silt loam	1.49	202.4			Liquid NH_3
93 corn	silt loam	1.71	202.4			$CO(NH_2)_2$
94 grassland	no details	43.48	600.0		14.5	cattle excreta
95 grassland	no details	26.09	1160.0		14.5	poultry excreta
96 grassland	no details	52.17	570.0		7.0	cattle excreta
97 grassland	no details	73.91	960.0		7.0	poultry excreta
98 spruce forest	acid hapludalf	7.44	35.0	4.7		
99 spruce forest	acid hapludalf	3.53	35.0			(lime)
100 beech forest	acid hapludalf	0.77	20.0			(lime)
101 cut grass	silty clay loam	0.20	113.8	15.1		$(NH_4)_2SO_4$

Compound = NPK; FMY = farmyard manure; empty spaces indicate no fertiliser added and/or not available data of soil moisture and soil temperature

Table 7.2. Literature references of the experimental data.

site number	source
1,2	Colbourn *et al.* (1987)
3,4,33,34,76	Valente and Thornton (1993)
5, 75	Williams and Fehsenfeld (1991)
6-9,38,43-49	Anderson and Levine (1987)
10	Remde *et al.* (1993)
11,12	Hutchinson and Brahms (1992)
13	Hargreaves *et al.* (1992)
14-16	Galbaly and Roy (1978)
17	Slemr and Seiler (1984)
21-28	Slemr and Seiler (1991)
32, 74	Williams *et al.* (1988)
35-37	Thornton *et al.* (1995)
39, 50	Aneya *et al.* (1997)
40, 74	Williams *et al.* (1988)
41,42	Yamulki *et al.* (1995)
51-55	Harrison *et al.* (1995)
56-73	Johansson and Granat (1984)
77,77A	Johansson (1984)
79-82	Jambert *et al.* (1994)
83-85	Thornton and Valente (1996)
86	Jambert *et al.* (1997)
87,90	Shepherd *et al.* (1991)
91-93	Thornton *et al.* (1995)
94-97	Watanabe *et al.* (1997)
98-100	Butterbach-Bahl *et al.* (1997)
101	Yamulki *et al.* (1997)

Table 7.7. Model performance for the sites represented in the NO experimental data set.

A. Model 1: $E_{NO} = e^{(-1.21 + 0.411\ln(N))}$

site	N input [kg N ha^{-1}]	Measured NO flux [kg N ha^{-1} y^{-1}]	Modelled NO flux [kg N ha^{-1} y^{-1}]	Residual	Standard error (SE)	Proportional uncertainty [%]
1	17.1	0.10	0.96	0.86	1.3	274.6
3	31.5	13.70	1.23	-12.46	1.3	214.0
4	31.5	0.85	1.23	0.38	1.3	214.0
5	11	3.11	0.80	-2.31	1.4	343.4
6	27.1	1.23	1.16	-0.07	1.3	225.4
7	27.1	1.18	1.16	-0.02	1.3	225.4
8	27.1	0.11	1.16	1.04	1.3	225.4
10		4.58	0.88	-3.70	1.3	305.4
11	13.8	4.01	0.67	-3.34	1.4	430.5
12	7.2	13.78	1.60	-12.18	1.5	188.8
13	59.2	6.37	0.88	-5.49	1.3	305.4
17	13.8	0.68	0.76	0.08	1.4	365.0
21	9.8	0.27	0.76	0.49	1.4	365.0
22	9.8	0.17	0.76	0.59	1.4	365.0
23	9.8	3.71	2.06	-1.66	2.0	189.7
24	109.8	3.23	2.06	-1.17	2.0	189.7
25	109.8	-0.43	0.76	1.19	1.4	365.0
26	9.8	0.00	2.06	2.06	2.0	189.7
27	109.8	0.37	2.06	1.69	2.0	189.7
28	109.8	0.08	2.06	1.98	2.0	189.7
32	109.8	29.35	1.75	-27.60	1.6	187.0
33	73.8	8.39	2.29	-6.10	2.2	194.3
34	142.5	0.89	1.23	0.35	1.3	214.0
35	31.5	1.09	1.28	0.19	1.3	208.4
36	34.4	1.40	2.64	1.25	2.7	202.3
37	202.4	1.99	2.64	0.66	2.7	202.3
38	202.4	3.88	1.19	-2.69	1.3	220.2
39	28.9	1.46	0.93	-0.53	1.3	283.6
40	16	0.39	1.41	1.02	1.4	196.7
41	43.8	0.62	2.73	2.10	2.8	204.2
42	217.8	6.83	2.73	-4.11	2.8	204.2
43	217.8	0.77	1.02	0.25	1.3	255.9
44	19.9	1.57	1.02	-0.55	1.3	255.9
45	19.9	1.34	1.37	0.03	1.4	199.2
46	41.14	1.32	1.37	0.05	1.4	199.2
47	41.14	5.76	1.22	-4.55	1.3	215.7
48	30.74	0.56	1.22	0.66	1.3	215.7
49	30.74	1.93	1.22	-0.72	1.3	215.7
50	30.74	2.86	0.93	-1.93	1.3	283.6
51	16	0.52	0.97	0.45	1.3	269.5
52	17.8	2.92	1.67	-1.25	1.6	187.5
53	65.8	5.30	2.09	-3.21	2.0	190.2
54	113.8	11.20	2.68	-8.51	2.7	203.2
55	209.8	0.40	2.85	2.45	2.9	207.0
56	242.8	0.51	0.57	0.06	1.5	528.7

57	4.9	0.53	0.57	0.04	1.5	528.7
58	4.9	2.71	0.57	-2.14	1.5	528.7
59	4.9	0.43	0.57	0.15	1.5	528.7
60	4.9	0.43	0.57	0.14	1.5	528.7
61	4.9	0.90	0.57	-0.33	1.5	528.7
62	4.9	0.83	2.17	1.34	2.1	191.7
63	124.9	8.35	2.17	-6.18	2.1	191.7
64	124.9	1.01	2.17	1.16	2.1	191.7
65	124.9	1.13	2.17	1.04	2.1	191.7
66	124.9	0.22	2.17	1.95	2.1	191.7
67	124.9	0.14	2.17	2.03	2.1	191.7
68	124.9	9.85	1.85	-8.00	1.7	187.2
69	84.9	0.71	1.85	1.14	1.7	187.2
70	84.9	0.53	1.85	1.32	1.7	187.2
71	84.9	0.90	0.57	-0.33	1.5	528.7
72	4.9	0.43	0.57	0.14	1.5	528.7
73	4.9	0.80	0.57	-0.22	1.5	528.7
74	4.9	0.37	1.27	0.89	1.3	209.5
75	33.8	0.09	1.16	1.08	1.3	224.2
76	27.5	1.99	1.23	-0.76	1.3	214.0
77	31.5	0.11	0.57	0.46	1.5	528.7
79	4.9	0.51	0.57	0.06	1.5	528.7
80	4.9	1.00	0.57	-0.42	1.5	528.7
81	4.9	91.35	3.13	-88.22	3.3	212.9
82	304.9	0.11	0.57	0.46	1.5	528.7
83	4.9	1.09	1.28	0.19	1.3	208.4
84	34.4	1.40	2.49	1.09	2.5	198.7
85	174.4	1.99	3.09	1.11	3.3	212.2
86	296.4	32.00	3.06	-28.94	3.2	211.6
87	289.8	1.80	1.14	-0.67	1.3	229.2
90	25.9	38.40	3.22	-35.18	3.5	214.7
91	325.9	0.96	1.28	0.31	1.3	208.4
92	34.4	1.49	2.64	1.15	2.7	202.3
93	202.4	1.71	2.64	0.94	2.7	202.3
98	202.4	7.44	1.29	-6.16	1.3	207.4
99	35	3.53	1.29	-2.24	1.3	207.4
100	35	0.77	1.02	0.25	1.3	255.4
101	20	0.20	2.09	1.89	2.0	190.2

B. Model - 2: $E_{NO} = e^{(-0.82 + 0.354 \ln(N) + 0.0036 WFPS-2)}$

site	N input [kg N ha^{-1}]	WFPS [%]	Measured NO flux [kg N ha^{-1} y^{-1}]	Modelled NO flux [kg N ha^{-1} y^{-1}]	Residual	Standard error (SE)	Proportional uncertainty [%]
1	17.1	25.9	0.10	0.60	0.50	0.64	218.1
6	27.1	27.9	1.23	0.86	-0.37	0.54	128.3
7	27.1	27.9	1.18	0.86	-0.32	0.54	128.3
8	27.1	27.9	0.11	0.86	0.74	0.54	128.3
35	34.4	50.0	1.09	1.10	0.01	0.47	87.5
36	202.4	50.0	1.40	2.06	0.67	0.60	60.3

37	202.4	50.0	1.99	2.06	0.08	0.60	60.3
38	28.9	28.6	3.88	0.93	-2.95	0.51	112.9
39	16	34.1	1.46	1.06	-0.40	0.48	92.5
41	217.8	54.1	0.62	1.49	0.87	0.45	61.5
42	217.8	40.8	6.83	3.02	-3.81	1.08	73.8
43	19.9	25.4	0.77	0.61	-0.16	0.63	215.9
44	19.9	25.4	1.57	0.61	-0.97	0.63	215.9
45	41.14	33.4	1.34	1.44	0.09	0.44	63.3
46	41.14	33.4	1.32	1.44	0.12	0.44	63.3
47	30.74	28.6	5.76	0.95	-4.81	0.51	109.1
48	30.74	28.6	0.56	0.95	0.39	0.51	109.1
49	30.74	28.6	1.93	0.95	-0.98	0.51	109.1
50	16	47.2	2.86	1.00	-1.86	0.49	101.6
51	17.8	39.8	0.52	1.25	0.73	0.45	73.4
52	65.8	39.8	2.92	1.98	-0.94	0.57	59.5
53	113.8	39.8	5.30	2.41	-2.89	0.76	65.1
54	209.8	39.8	11.20	2.99	-8.21	1.07	73.4
55	242.8	39.8	0.40	3.15	2.75	1.15	75.4
75	27.5	31.9	0.09	1.15	1.06	0.46	82.0
83	34.4	55.0	1.09	0.70	-0.38	0.59	173.9
84	174.4	55.0	1.40	1.25	-0.15	0.45	73.4
85	296.4	55.0	1.99	1.51	-0.48	0.45	61.1

Table 7.9. Validation with measurements from 1990-92.

Land use	Soil type	N input	wfps	NO flux [kg N ha^{-1} y^{-1}]			Res*-1	SE-1	E-1** [%]	Res*-2	SE-2	E-2** [%]
				Measured	Model-1	Model-2						
wheat	sandy loam	175	54.25	2.100	2.49	1.35	0.39	0.58	48.0	-0.75	0.37	57.4
wheat	sandy loam	175	56.96	0.460	2.49	1.00	2.03	0.58	48.0	0.54	0.33	69.2
rye grass	clay loam	300	55.00	0.130	3.11	1.51	2.98	0.67	44.6	1.38	0.40	54.1
rye grass	clay loam	300	45.17	-0.010	3.11	3.09	3.12	0.67	44.6	3.10	0.64	43.0
rye grass	clay loam	300	44.83	1.350	3.11	3.13	1.76	0.67	44.6	1.78	0.65	42.9
rye grass	clay loam	300	46.21	0.001	3.11	2.96	3.11	0.67	44.6	2.96	0.62	43.4
alder		70	31.72	0.240	1.71	1.59	1.47	0.47	57.2	1.35	0.41	52.9
alder		70	55.17	0.260	1.71	0.89	1.45	0.47	57.2	0.63	0.32	75.3
alder		70	27.24	0.640	1.71	1.13	1.07	0.47	57.2	0.49	0.35	63.7
alder		70	39.66	0.260	1.71	2.03	1.45	0.47	57.2	1.77	0.47	47.9
Nothofagus 1991	sandy clay loam	20	45.17	0.020	1.02	1.18	1.00	0.40	81.3	1.16	0.35	61.9
Nothofagus 1992	sandy clay loam	20	51.55	-0.003	1.02	0.81	1.02	0.40	81.3	0.81	0.32	80.9
Nothofagus 1993	sandy clay loam	20	38.62	0.001	1.02	1.30	1.02	0.40	81.3	1.29	0.37	58.8
birch	sandy clay loam	20	67.76	-0.102	1.02	0.08	1.12	0.40	81.3	0.18	0.28	708.0
birch	sandy clay loam	20	56.38	0.002	1.02	0.50	1.02	0.40	81.3	0.49	0.29	121.9
cut grass		20	41.03	0.002	1.02	1.30	1.02	0.40	81.3	1.30	0.37	58.7
cut grass		20	47.07	0.160	1.02	1.09	0.86	0.40	81.3	0.93	0.34	65.3

sitka	sandy clay loam	85	60.86	1.410	1.85	0.45	0.44	0.49	54.8	-0.96	0.29	132.1
sitka	sandy clay loam	85	60.86	0.160	1.85	0.45	1.69	0.49	54.8	0.29	0.29	132.1
sitka +acid mist	sandy clay loam	85	55.69	0.017	1.85	0.90	1.83	0.49	54.8	0.88	0.32	74.7
sitka +acid mist	sandy clay loam	85	55.69	0.017	1.85	0.90	1.83	0.49	54.8	0.88	0.32	74.7
sitka	sandy clay loam	20	55.69	0.004	1.02	0.54	1.02	0.40	81.3	0.53	0.29	113.5
conifer	peat	46	16.42	-0.005	1.44	0.24	1.44	0.44	63.5	0.24	0.28	246.0
moorland	peat	24	16.21	0.020	1.10	0.18	1.08	0.41	76.7	0.16	0.28	319.4

* Res – Standard residual; E – Proportional uncertainty.

Table 7.10. Validation results with North Berwick measurements.

site	soil texture	N input	WFPS	NO emissions			resid-1	SE - 1	error-1	resid - 2	SE-2	error- 2
		[kg N ha^{-1}]	[%]	[kg N ha^{-1} y^{-1}]					[%]			[%]
				measured	Model-1	Model-2						
4	loam	220	48.2	0.26	2.74	2.39	2.48	1.31	98.7	2.13	2.23	194.0
6	Silt loam	225	50.6	0.19	2.76	2.04	2.57	1.31	98.4	1.85	1.91	194.5
5	loam	220	56.8	0.47	2.74	1.10	2.27	1.31	98.7	0.63	1.15	216.7
3	Loam clay loam	314	55.8	0.13	3.17	1.40	3.04	1.45	94.7	1.27	1.37	202.4
2	Sandy loam	334	66.8	6.43	3.25	0.27	-3.18	1.48	94.1	-6.16	0.88	680.9
8	sandy loam	150	72.0	0.64	2.34	0.07	1.70	1.18	104.6	-0.57	0.93	2872.5
9	Sandy loam	120	64.1	0.86	2.13	0.30	1.27	1.12	108.9	-0.56	0.88	599.9
7	Silty clay	150	57.9	0.23	2.34	0.84	2.11	1.18	104.6	0.61	1.00	246.2
11	Clay loam	235	54.5	0.24	2.81	1.47	2.57	1.33	97.9	1.23	1.42	200.7
10	Sandy clay loam	312	49.0	0.21	3.16	2.57	2.95	1.45	94.8	2.36	2.40	194.1
12	Sandy loam	140	68.1	0.12	2.27	0.15	2.15	1.16	105.8	0.03	0.90	1226.2
13	Sandy loam	180	67.9	0.06	2.52	0.17	2.46	1.24	101.6	0.11	0.90	1082.9
14	Loam free	215	56.8	0.43	2.71	1.09	2.28	1.30	99.0	0.66	1.14	217.4
4	loam	10	47.9	0.83	0.77	0.81	-0.06	0.86	230.5	-0.02	0.98	251.4
6	Silt loam	26			1.14							
5	loam	10		0.31	0.77		0.46	0.86	230.5			
3	Loam /clay loam	10	51.6	0.81	0.77	0.63	-0.04	0.86	230.5	-0.18	0.91	301.0
2	Sandy loam	124	55.5	18.7	2.16	1.05	-16.54	1.13	108.2	-17.65	1.11	220.8
8	sandy loam	10	67.5	0.66	0.77	0.07	0.11	0.86	230.5	-0.59	0.93	2874.0
9	Sandy loam	10	76.5	0.06	0.77	0.01	0.71	0.86	230.5	-0.05	0.95	23386.8
7	Silty clay	10	64.1	0.65	0.77	0.13	0.12	0.86	230.5	-0.52	0.91	1508.6
11	Clay loam	385	60.0	0.66	3.44	0.88	2.78	1.55	92.9	0.22	1.02	240.1
10	Sandy clay loam	10	49.0	0.43	0.77	0.76	0.34	0.86	230.5	0.33	0.96	261.7
12	Sandy loam	10			0.77							
13	Sandy loam	380	78.5	0.02	3.43	0.02	3.41	1.54	93.0	0.00	0.94	11029.9
14	Loam free	10	61.6	0.05	0.77	0.19	0.72	0.86	230.5	0.14	0.89	968.4

CHAPTER EIGHT

Conclusions.

8.1 INTRODUCTION.

The aim of this study was to estimate N_2O and NO emissions from British soils with parameters considered to be their controlling factors. Relationships were established on the basis of field measurements which provided information on the amounts of emissions and their controlling factors.

Soils are the largest source of N_2O emissions in the UK (Skiba *et al.*, 1996), which also contribute a large proportion of NO emissions. N_2O contributes to 5 % of greenhouse effect and it has a very long atmospheric lifetime of 130 years (IPCC, 1990). NO participates in oxidation reactions leading to ozone and acid rain production. The concentration of these two gases in the atmosphere has increased since pre-industrial times as documented by Antarctic ice cores. This study contributes to the current research of estimating the emission range of these gases at the national scale, to which Great Britain is committed as a signatory of LRTAP[1] (DoE, 1997) and participant of multilateral agreements on reduction of greenhouse effect gases (Wirth and Lashof, 1990). The current field measurement data of N_2O and NO emissions from British soils, especially in the case of NO, is limited. Therefore to obtain sufficient input data for this analysis, the studies used to define models were extended to other regions of temperate climate in North-west Europe and the North America. The relationships were established with experimental data from studies in the period 1979-1997.

8.2 SUMMARY OF THE APPLIED MODELLING METHOD.

The method used here to establish the trends in N_2O and NO emissions followed the approach of modelling methods applied at field (Skiba *et al.*, 1994; Velthof *et al.*, 1996 and Williams *et al.*, 1987) and global scales (Bouwman, 1995 and Veldkamp and Keller, 1997), which were described in chapter two. Those models use

[1] the Convention on Long-Range Transboundary Air Pollution

regression analysis, which describes existing relationships between the amounts of emissions and their controlling factors. Regression analysis is commonly applied because of its simplicity in describing complex relationships. The approach in the current study assumed that there are controllers common to all field measurements in temperate climates that could be applied to predict general patterns of N_2O and NO emissions from Great Britain, which is based on the scaling concept (Kirkby *et al.*, 1996; Lenz *et al.*, 1997; Pierce and Waldruff, 1991). Multivariate regression analysis revealed the important controlling factors regulating the general trends of N_2O and NO emissions in all the compiled experimental results. The key controlling factors used in this study are:

- N input, as a substrate for bacterial processes;
- Soil moisture, which determines the rate of nitrification and denitrification, according to the theory by Davidson (1991), and the gas diffusion in soils;
- Soil temperature, which was established to be a weak controller of N_2O emissions and was a non-significant factor for NO emissions in the experimental data set;
- Land use is an important factor for N_2O emissions.

Other variables such as drainage class, fertiliser type, C content were not important predictors in the established models as their inclusion did not improve the regression results. The results presented indicate that with an increasing scale of modelling, the number of key variables decrease.

8.3 DATA AVAILABILITY ISSUES LIMITING THE PREDICTIONS.

The complexity of environmental conditions presented by the field studies, and the N_2O and NO emission responses lead to the definition of more than one empirical model describing the behaviour of each of the gases. These models were applied to estimate N_2O and NO emissions from soils in Great Britain in the framework of ArcInfo Grid Emission Model (AGEM) (figure 6.1, chapter six). Data of input variables for Great Britain had to be acquired and formatted prior to the modelling stage. There were several problems connected with input parameters for AGEM, which could be summarised in three phases of data acquisition:

- Obtaining necessary data for modelling;
- Incorporating all the data sets into the AGEM, which involves the transformation of data to obtain a uniform resolution. This problem relates closely with the choice of scale for modelling;
- Assessing compatibility of different data sources, which provide complementary information.

Most parameters for the AGEMs were not readily available, as soil moisture, soil temperature and N input had to be estimated on the basis of existing data (chapter three). Sometimes the problems with data availability are the result of a very restricted access to the existing data sources due to the high cost (Meteorological Office soil temperature data), legal prohibition (protected parish boundaries limited the choice of the AC data to the raster format) or simply denial of access (detailed results of the British Survey of Fertiliser Practice). As academic research normally has restricted resources, the expectation of a similar payment for data from academic and commercial users denies the former access to good quality data.

All input data sets were in raster format and varied in resolution. The most detailed data of HOST classes and the LCM were at 1 km grid resolution, while climatic and atmospheric deposition data had the resolution of 10 and 20 km grid, respectively. The resolution of the model was defined by taking into account the spatial details of the input data according to their importance for the emissions and the required detail of the model results for Great Britain. The best resolution for the AGEM model was 5 km^2 due to the spatial variability of the AC data. All the data parameters were brought to the required resolution by ArcInfo GRID prior to modelling soil temperature, soil moisture and N_2O and NO emissions in the AGEM framework.

The issue of data compatibility emerged throughout this research on several occasions. Most published studies of N_2O and NO emission measurements used soil textural classifications relevant to this study. There were a few studies, which described soils according to taxonomic classification without specification of their physical characteristics. This resulted in incompatibility of 28 % of N_2O studies and 1 % of NO studies. Discrepancy between the definition of soil moisture at field capacity by SPACTeach and by Hall *et al.*, (1977) led to the uncertain validation results of the predicted soil moisture. But the incompatibility between the AC and LCM data sets had the greatest impact on the outcome of this study. The differences between these two data sources in their definition of the land classes lead to considerable uncertainties in predicted N_2O and NO emissions. The strong effect of land use type on the outcome of the AGEM model is due to its direct effect on the estimated total agricultural N inputs to soils, which is also emphasised in model (6.2) by its role as a separate controlling factor.

8.4 N_2O EMISSIONS.

Both models (6.1) and (6.2) associated the highest N_2O emissions with intensively managed grasslands, where the organic N inputs exceeded 750 kg N ha y^{-1} and added to the high mineral N inputs of 300 – 325 kg N ha^{-1} y^{-1}. Those 'hot spots' where predicted N_2O emissions were in the range 12 –17 kg N ha^{-1} y^{-1} (model 6.1) are: in Wales - North-west Gwynedd and East of Aberystwyth; in England - Devon, localised areas in Midlands, Lancashire and Tynedale and in Scotland - West Lothian, the Valley of Tweed, and several locations in Southern Uplands and the Highlands, where stocking densities exceed 10 SU ha^{-1}. Total N_2O emissions from soils in Great Britain were estimated at 140.2 kt N y^{-1} with model (6.1) and 127.5 kt N y^{-1} with model (6.2). According to other models total N_2O emissions from soils in Great Britain were 56.4 kt N y^{-1} (Skiba *et al.*, 1996 based on emission factors presented in chapter four) and 53 kt N y^{-1} (Bouwman, 1995; details presented in chapter two). The estimates by Skiba *et al.* (1996) and Bouwman (1995) do not consider soil moisture and soil temperature, which might be the main reason for their under-estimation. This was confirmed by the fact that mean fertiliser induced emission factors in models (6.1) and (6.2) of 2 % and 1 %, respectively, were comparable with Bouwman (1995) and in the range suggested by Skiba *et al.* (1996). Total N_2O emissions predicted by models (6.1) and (6.2) corresponded with the recent aircraft N_2O flux measurements (Fowler *et al.*, 1999), which estimated total N_2O emission from the UK from all sources at 305 kt N_2O y^{-1} (146 kt N y^{-1} assuming 75 % of total N_2O originates from soils in line with IPCC, 1997 and Skiba *et al.*, 1996).

Table 8.1 Total N_2O emissions from soils in Great Britain.

Model reference	Mean fertiliser-induced emission factor [%]	Total N_2O emissions [kt N y^{-1}]
Model (6.1)	2.0	140.2
Model (6.2)	1.0	127.5
Bouwman (1995)	1.25	53
Skiba *et al.* (1996)	0.5-2.1	56.4

8.5 NO EMISSIONS.

Model (7.8) highlighted areas with the highest emission rates (2.0 – 3.5 kg N ha^{-1} y^{-1}) as the coastal area of East Anglia, on Cheshire Plain, in the vicinity of Birmingham, in Nottinghamshire, in the Valley of Eden (Cumbria), the Valley of Tweed and coastal regions of the Moray Firth. In those areas intensive agriculture coincides with optimal soil drainage conditions (sands and loamy sands contribute to 70 % of all soils). Total NO emissions from soils in Great Britain were estimated at 65.8 kt N y^{-1} by model (7.5) and 7.4 kt N y^{-1} by model (7.8). The considerable difference between the two models was caused by the limiting effect of soil moisture in model (7.8), as mean annual estimates in most parts of Great Britain exceeded 55 % WFPS, for which NO emissions decreased (figure 7.5, chapter seven). In comparison with other existing models total NO emissions estimated by model (7.5) considerably exceeded other predicted totals, which varied for Great Britain from 6 kt N y^{-1} (Simpson *et al.*, 1999 using methodology of Skiba *et al.*, 1997) and 23 kt N y^{-1} (Simpson *et al.*, 1999 using the model developed by Williams *et al.*, 1992) to 37-44 kt N y^{-1} (Davidson and Kingerlee, 1997). This could be partly explained by differences in modelling approaches e.g. the mean fertiliser emission factor of 2 % in model (7.5) considerably exceeds 0.3 % applied by Skiba *et al.* (1997). Contrasting to model (7.5) total NO emissions estimated by model (7.8) correspond with the lowest predictions by Skiba *et al.* (1997). Also the fertiliser-induced emission factor estimated by this model for soil moisture of 60 – 70 % WFPS varies between 0.09 and 0.47%, which corresponds with mean emission factor estimated by Skiba *et al.* (1997) on the basis of field measurements in Scotland. This suggests a better performance of model (7.8) in predicting NO emissions from British soils. The variety of predictions confirms still great uncertainty of NO emissions mainly associated with limited data of field measurements.

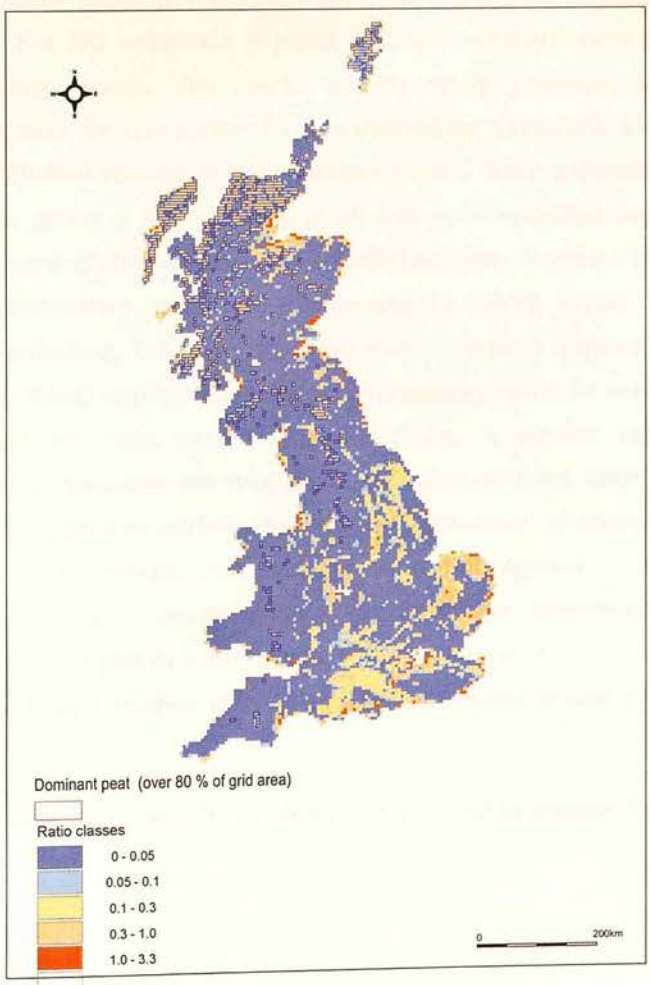
Table 8.2 Total NO emissions from soils in Great Britain.

Model reference	Model (7.5)	Model (7.8)	Skiba *et al.* (1996)	Williams *et al.* (1992)	Davidson and Kingerlie (1997)
Total NO emissions [kt N y^{-1}]	65.8	7.4	6	23	37-44

8.6 DOMINANT SOIL BACTERIAL PROCESSES IN GREAT BRITAIN INDICATED BY NO/N_2O RATIO.

This ratio is examined in many studies in order to relate the amounts of measured emissions with their production processes (Skiba *et al.*, 1993; Watanabe *et al.*, 1997). N_2O and NO emissions predicted with the empirical models presented in this work (model 6.1 and model 7.8 respectively) were applied to estimate NO/ N_2O ratio for British soils (figure 8.1). In most areas, where soil moisture exceeded 75 % of WFPS, the ratio stayed below 0.1, with the exception of southern and South-east England, some parts of Midlands, southern coast of Moray Firth and parts of Caithness and Western Isles (figure 8.1). The highest ratio values (1 - 3.3) were observed at coastal regions, where dominant freely drained soils ensured optimal moisture conditions for NO production and undisturbed emissions from soils. The ratio predicted for peats is liable to overestimation due to the suspected underestimation of soil moisture, which can not be quantified (figure 8.1) The results of NO/ N_2O ratios and estimated mean annual soil moisture (figure A13) suggest that the majority of British soils provide optimal conditions for denitrification and gaseous loss of N into the atmosphere as N_2O.

Figure 8.1 Mean annual NO/N_2O ratio estimated for British soils with AGEM.



8.7 SUGGESTIONS FOR FURTHER WORK.

Larger scale models reflect general trends in N_2O and NO emissions with the main controlling factors, in contrast to small scale models for measurement plots which better reflect the fluctuating character of N_2O and NO emissions with the inclusion of local controlling factors. An increasing complexity of models at small scales leads to more effective mechanistic solutions which better represent the dynamic nature of bacterial processes in soils e.g. SOILN and SUNDIAL. Their application is very restricted at national and regional scales due to the large requirements for input parameter data and too coarse a resolution of existing input data of global mechanistic models (0.5° x 0.5° in NBM or 1° x 1° in CASA models[2]). The development of models at both small and large scales is necessary to progress further into an integrated modelling system. As the relationships between N_2O or NO emissions and their controlling factors change with the scale of modelling in empirical approaches, any attempt to decrease the scale of the study would need to establish specific models for the new scales. An area that would need some investigation is establishing groups of factors controlling N_2O and NO emissions at hierarchical scales. The current work observed that N input, soil moisture and soil temperature are important controlling factors of N_2O emissions at plot and regional scales. For NO emissions N input and soil moisture were shown to be 'universal' controlling factors. The results of this study, however, are constrained by the limited data for the known factors controlling emissions (chapter two) provided in the published results of field measurements. More information from experimental studies, giving a full account of all soil environmental factors, would enable an assessment of the relationships established here. It would be beneficial to establish a comprehensive system of measurements, which would facilitate not only field scale modelling, but also an integrated modelling approach. Such an integrated system of N_2O and NO emission measurements could be achieved with a network of field measurement sites in Great Britain. A similar network of sites, where ammonia emissions are measured, has already been active (Sutton *et al.*, 1998). For measurements of N_2O emissions an application of micrometeorological methods would bring considerable benefits to the integrated system of modelling N_2O emissions, as it would greatly decrease the uncertainty of scaling from a measurement plot to a field scale, which is currently unknown. The development of more dynamic models of N_2O and NO emissions would require a new computer

[2] NBM and CASA models are described in detail in section 2.3, chapter two.

software solution, as ArcInfo used explicitly for modelling here is currently not suitable for dynamic models.

8.8 CONCLUSION.

This study has shown that regression analysis is a valid method able to describe the relationships between the amounts of emissions and their controlling factors. This simple approach also helped to discriminate the insignificant variables at the larger scale of this study. There are two main areas for which the approach presented here was assessed: (1) concept and definition of the models and (2) their application to predict N_2O and NO emissions from Great Britain. This paragraph summarises the advantages and limitations of the modelling methods proposed in this thesis.

Advantages and limitations of AGEM approach.

1. Model definition.

(a) advantages:

- Universal model for temperate climate (defined by the location of field studies used for definition of the model);
- Simple to apply and does not require many detailed parameters (as opposed to mechanistic models);
- Outlines major emission controlling factors at a regional scale;
- Good approach to predict mean emission rates at annual and seasonal scales at a resolution of 5 km grid.

(b) limitations:

- Uncertainty of the predictions introduced by restrictions of the regression method, which partly reduced the described variability of emissions (60 % for N_2O and >80 % for NO);
- Large uncertainty of predictions due to the dynamic and complex nature of the emission processes, which is impossible to reflect with this simple approach. This uncertainty increases when the model is applied to small scales (as observed by the validation against field measurements in Scotland).

2. Application for Great Britain.

(a) advantages:

- The predictions made by AGEM use more detailed agricultural data and spatially variable N input based on the published recommendations. Despite existing problems of data incompatibility, the predictions are more spatially variable than generalised extrapolating approaches;
- Outlines areas with the highest emission rates in Great Britain where some emission reducing measures would have to be implemented;
- The AGEM framework could be applied in future for similar modelling;
- Provides estimates for the national inventories of NO_x and greenhouse effect gases (N_2O) and future inputs for atmospheric models (e.g. HARM[3]);

(b) limitations:

- AGEMs were defined on the basis of mainly foreign studies due to a rather small data set of field measurements in Great Britain. This was confirmed by the model validation, which showed a tendency of AGEMs to overestimate emissions. The overestimate was probably due to a large proportion of agricultural soils and warmer environments in the N_2O and NO experimental data sets used to define the AGEMs;
- Great uncertainty was introduced by modelled soil moisture, and some errors are expected due to N input and soil temperature as those data sets were not readily available for this study.

In this study, two stages of modelling have been outlined. Firstly, N_2O and NO emission models were defined for temperate climates on the basis of field measurement data published in literature. Secondly, the defined models were applied to predict spatial distribution of the emissions from soils in Great Britain. The empirical approach was chosen to define the models because of its simplicity, compatibility with ArcInfo that was used to predict the emissions for Britain and relatively low requirements of input data that were available for Great Britain at the modelling scale. A mechanistic approach, although more suitable for simulating dynamic processes of N_2O and NO emissions, could not be applied because of its high requirements of input variables that were not available to this study. The principal aim of this research was to show that the regression method presents a valid modelling approach at large spatial scales.

At the scale of temperate climates, the regression model outlined the controlling variables of N_2O emissions as N input that varied according to main land use types and soil moisture. Soil temperature was not an important variable in the model. NO emissions in the regression analysis responded significantly to N input. Soil moisture was an important limiting factor, although its significance was relatively low. The reason might be a limited availability of field measurement data. The predicted emissions were spatially disaggregated at 5 km grid and presented on the first-of-its kind national maps of annual and seasonal N_2O and NO emissions from British soils.

This study proved that simple regression models can be used to observe relationships between N_2O and NO emissions and their controlling factors at large scales of temperate climates and applied to predict the spatial distribution of the emissions at the national scales. There are, however, considerable uncertainties of this approach that were shown by data analysis and model validation. Important reasons for the uncertainties lie in the restrictions of the regression method used to define the models and limited availability of field measurement data e.g. soil temperature. The uncertainties of predicted N_2O and NO emissions are also to a large extent the effect of uncertainties associated with input data of variables obtained for Great Britain (land use data and N input in particular).

Limited data availability and restrictions of the modelling approach determined the spatial and temporal scale of the predictions. The possible areas of future investigation include: (1) increasing temporal and spatial detail of modelling N_2O and NO emissions with an application of mechanistic approaches; (2) testing the predicted levels of N_2O and NO emissions from British soils with new measurement data at the scales corresponding with the AGEM models from other British locations; (3) further work on a definition of the AGEMs in order to reduce the uncertainty of the models; (4) integrating mechanistic and regression approaches at various spatial and temporal scales to present a more holistic view of complex processes of N cycle.

[3] The Hull Acid Rain Model described in Metcalfe *et al.*, 1995

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Map Appendix

LIST OF FIGURES.

Figure A1 Reference map

Figure A2 Seasonal changes of soil temperature at 30 cm depth.

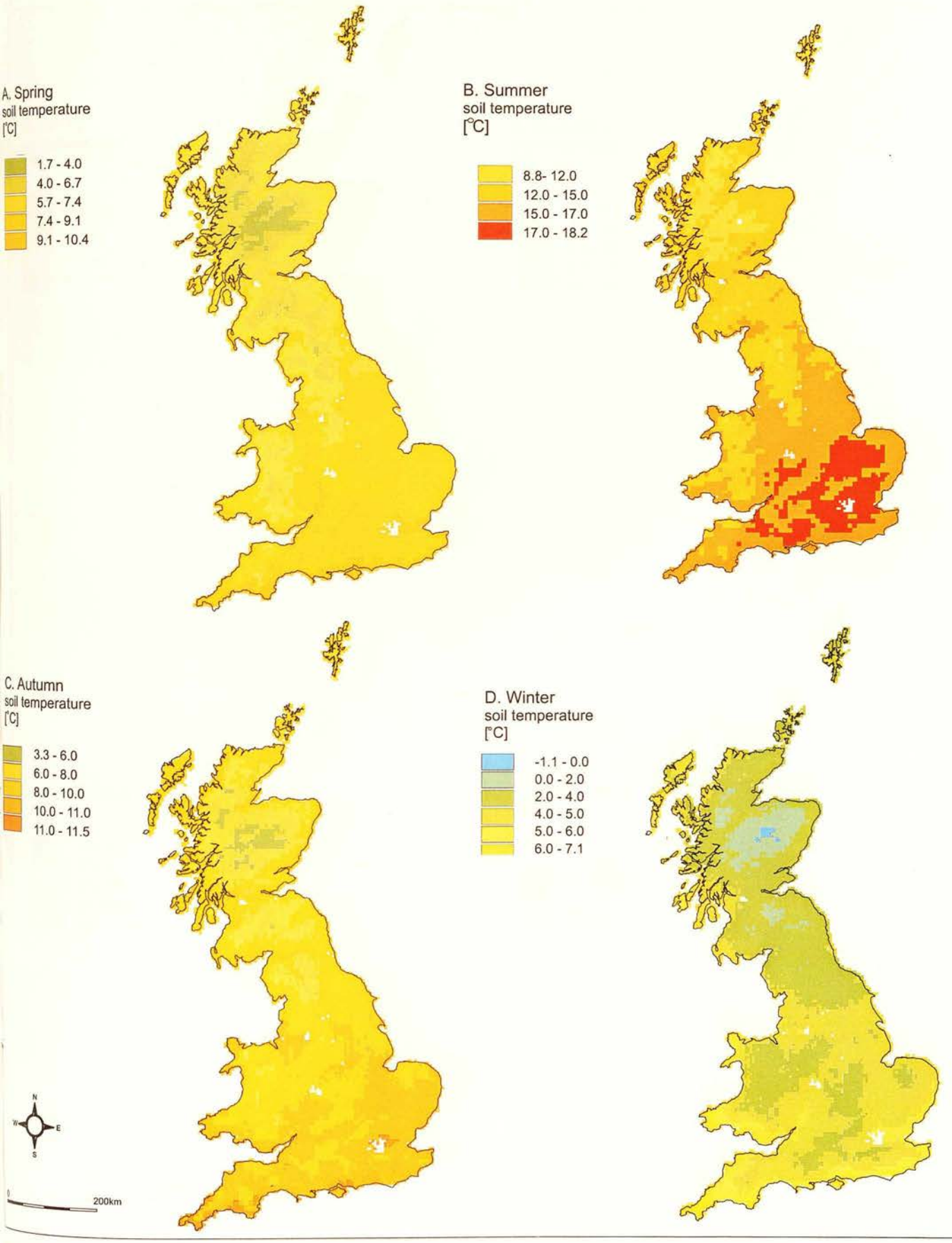


Figure A3 Seasonal changes of soil temperature at 5 cm depth.

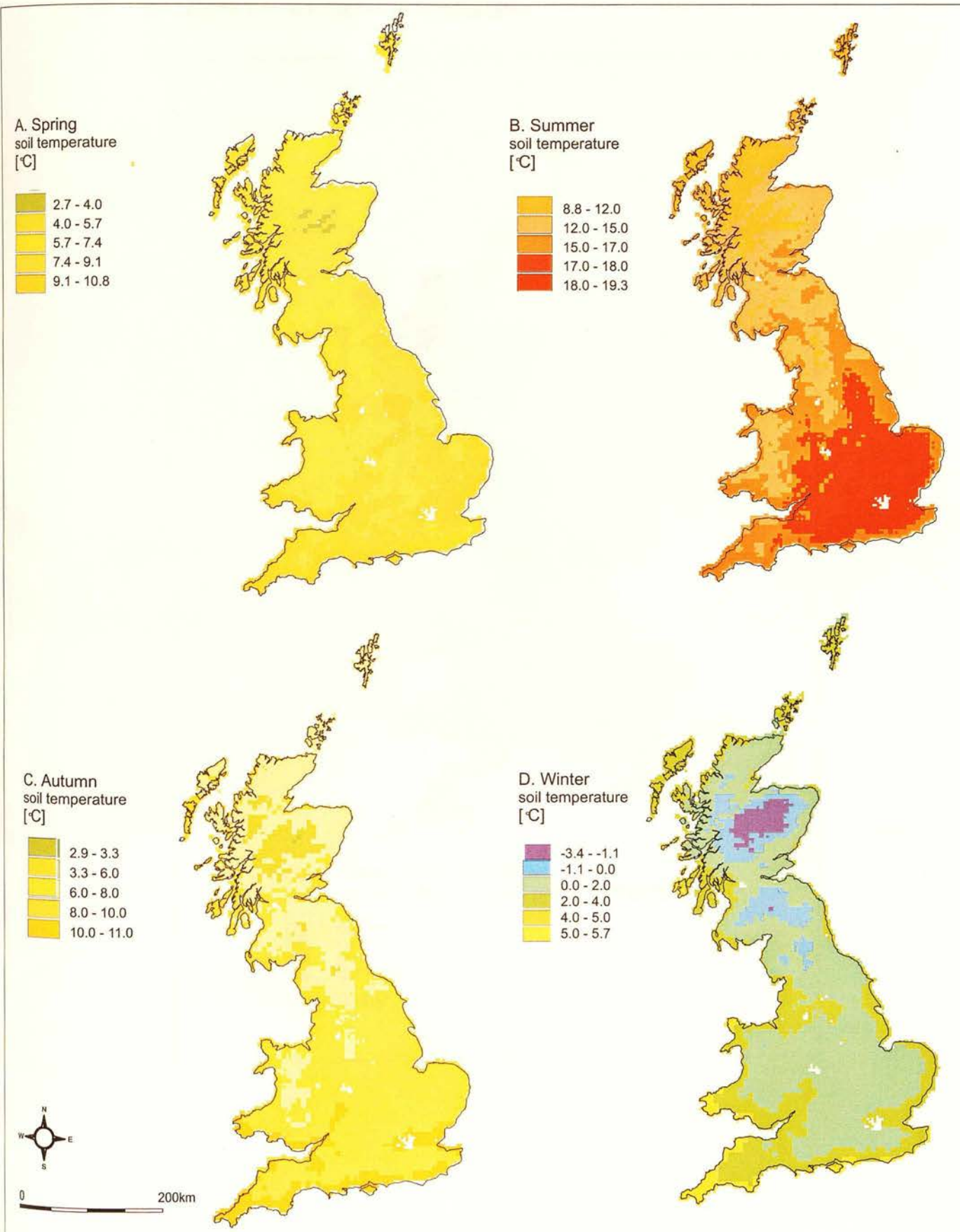
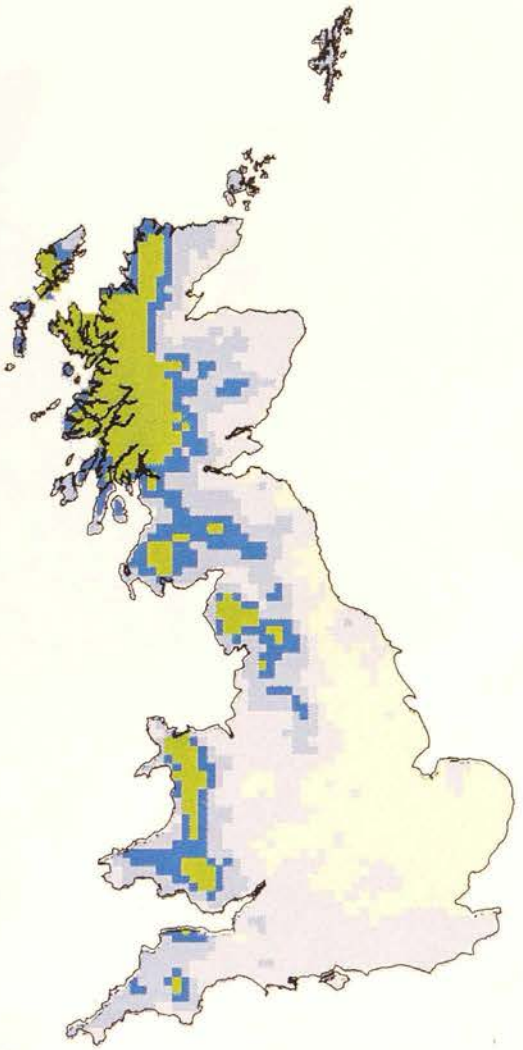


Figure A4 Rain zones in Great Britain.



Classes of rain zones in Great Britain
designated on the basis of annual precipitation [mm].

0 - 700
700 - 1000
1000 - 1400
1400 - 1800
1800 - 3700

1grid = 10 km^2

re A5 Seasonal variability of soil moisture in Great Britain as estimated by SPACTeach with initial moisture at FC.

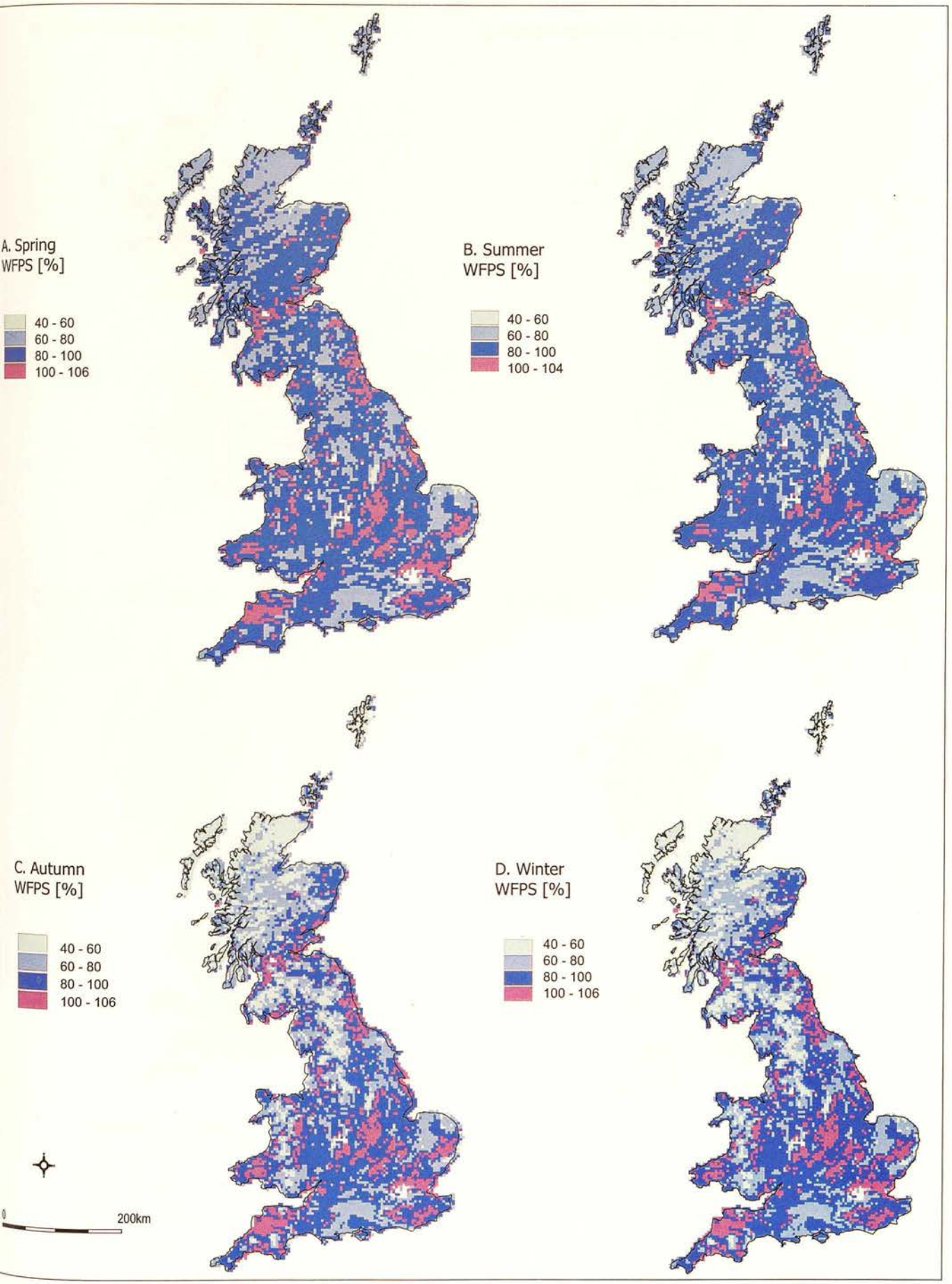
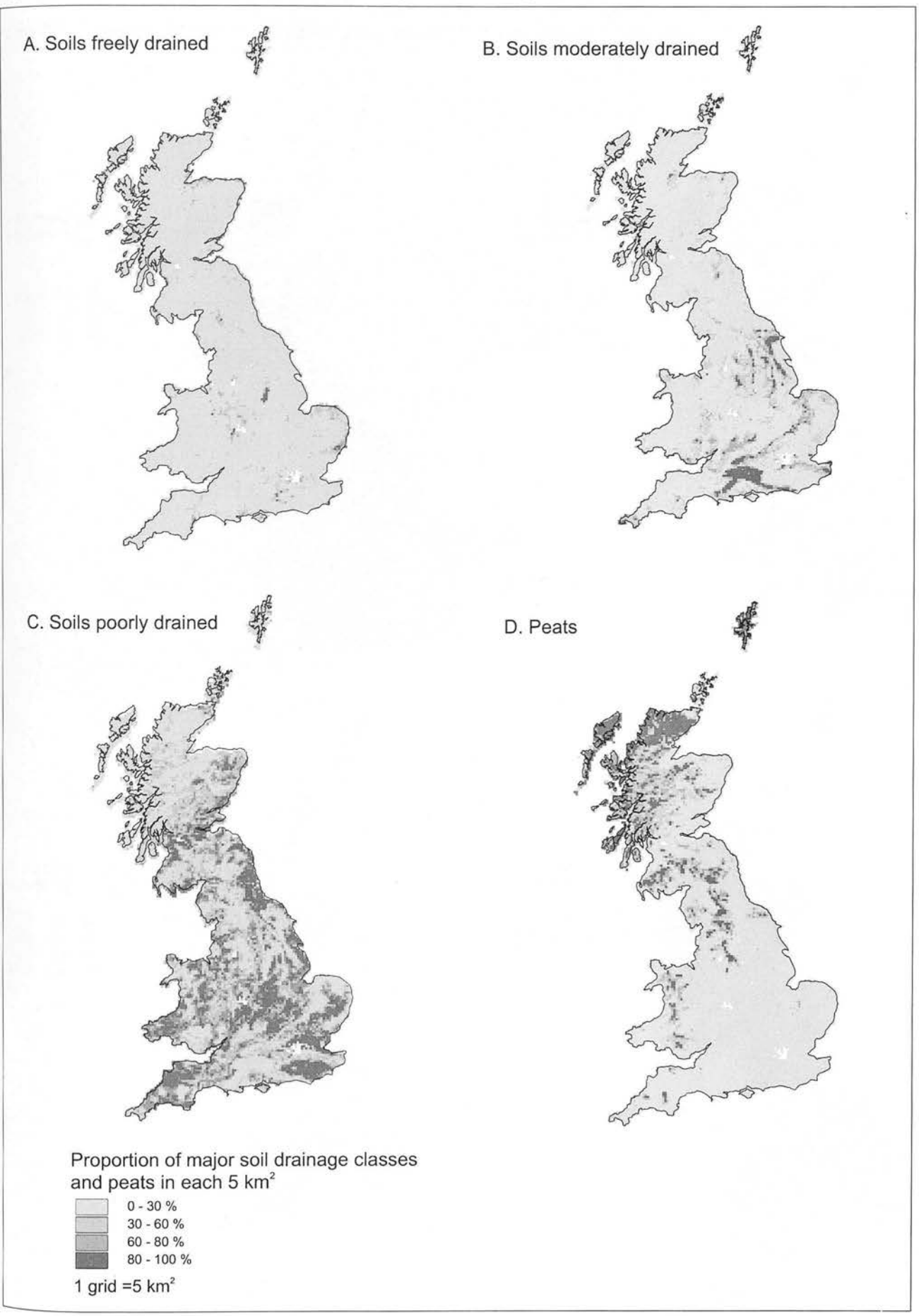


Figure A6 Distribution of the three main drainage classes and peats in Great Britain..



gure A7 Seasonal changes in WFPS in Great Britain estimated by SPACTeach with varied initial soil moisture.

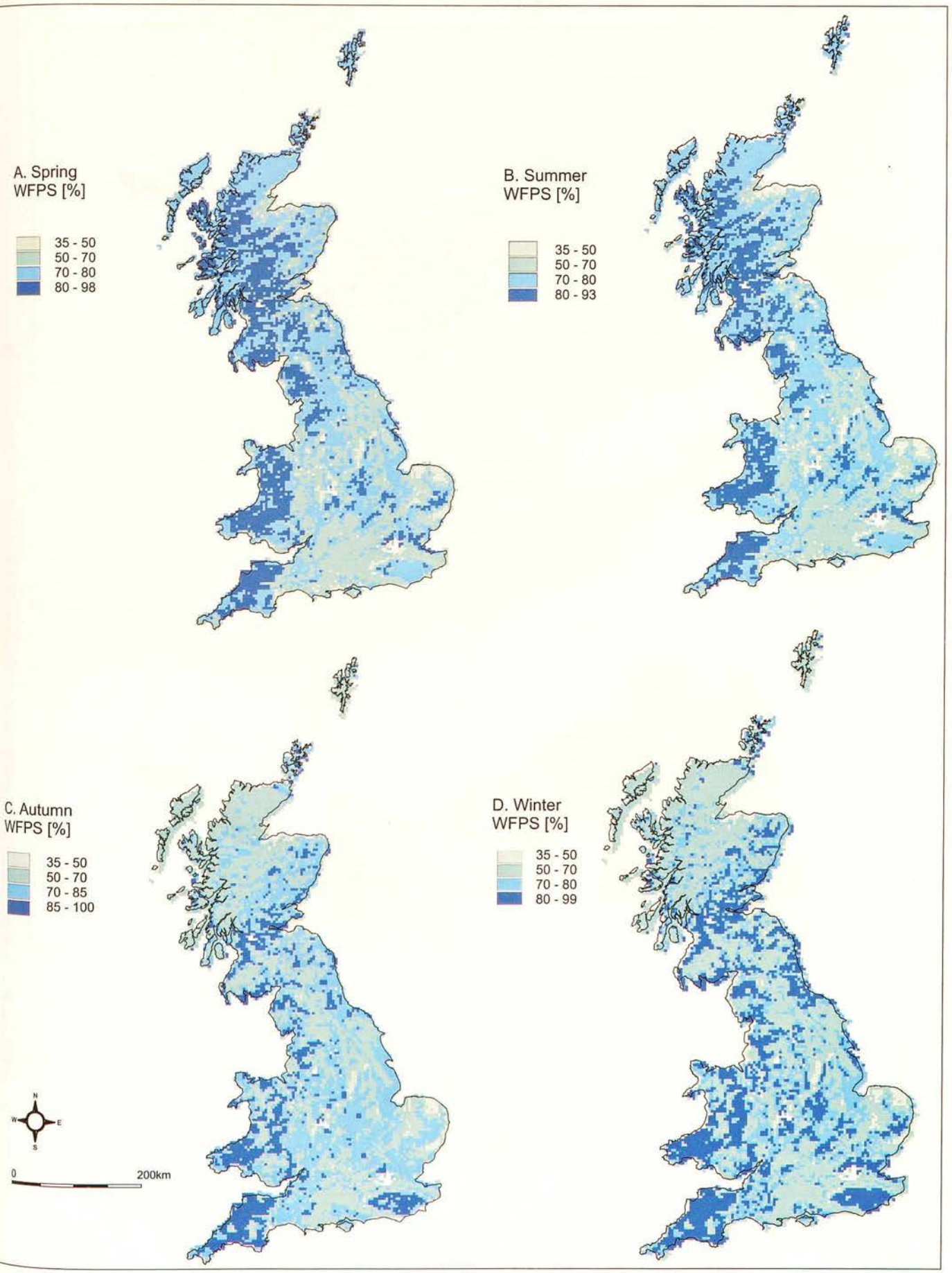


Figure A8 A comparison of estimated WFPS of British soils in winter with soil moisture at field capacity.

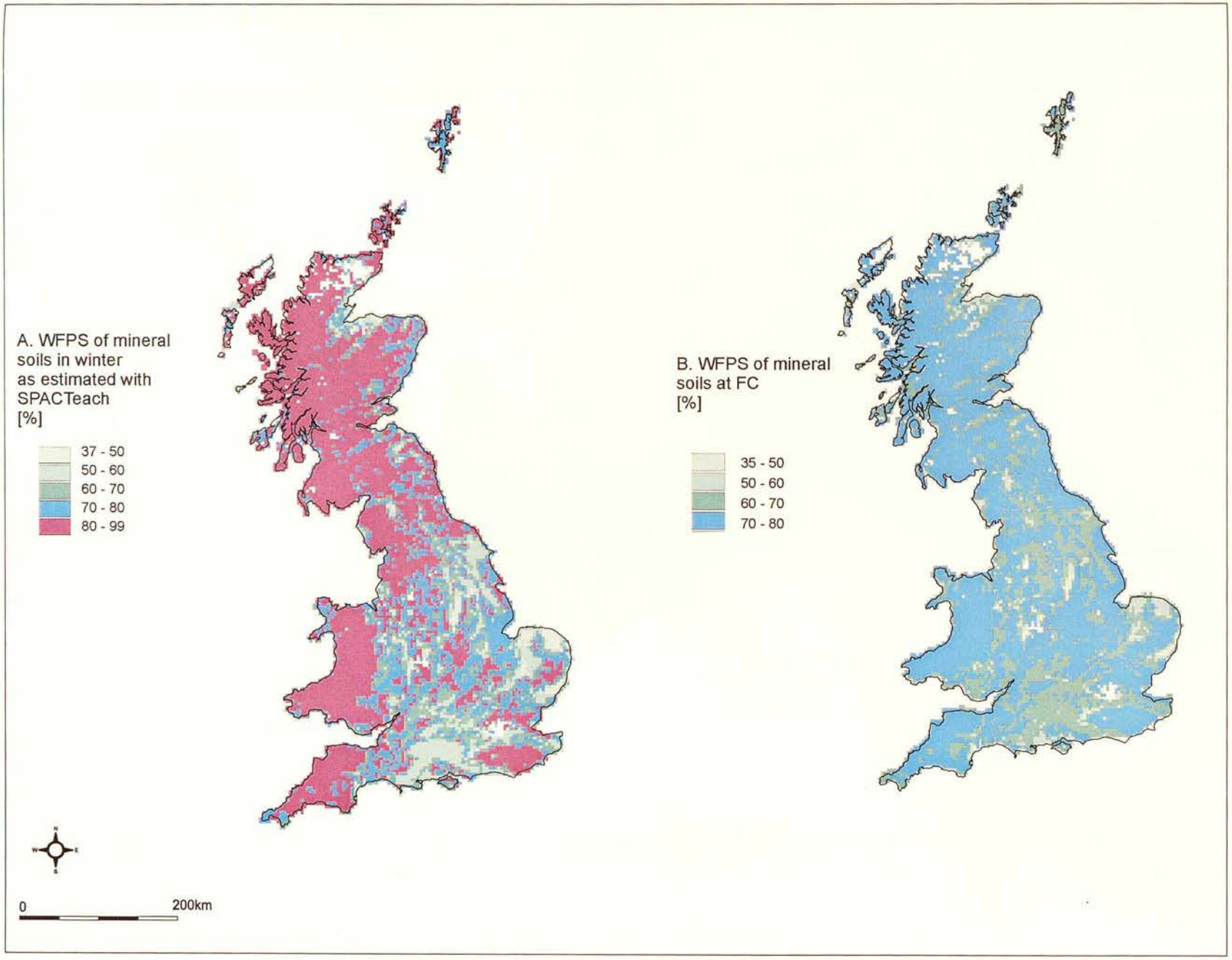


Figure A9 Regional mean mineral N fertiliser input according to guidelines of good fertiliser practice.

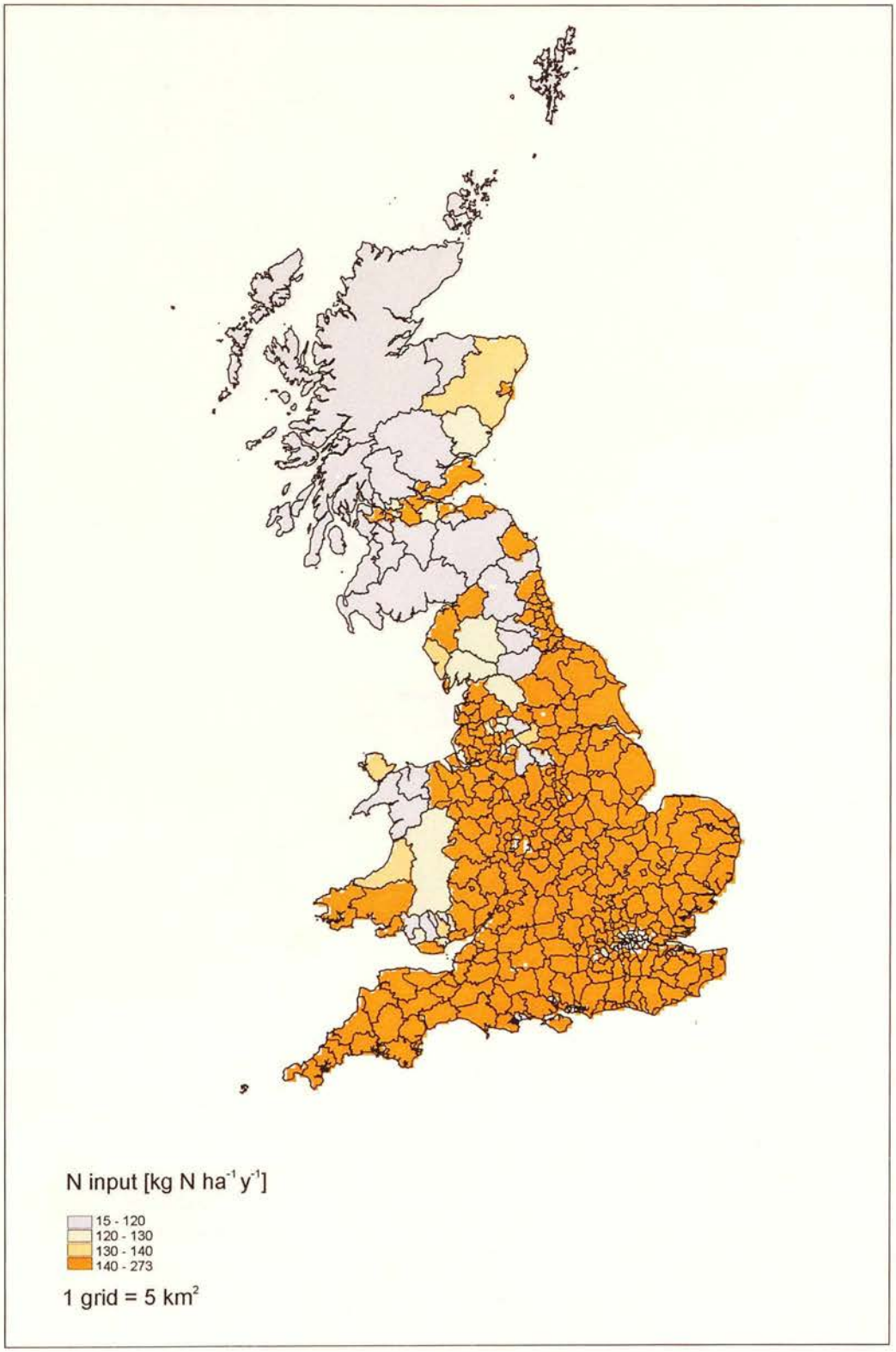


Figure A10 Dominant land use class in each 5 km^2 pixel.

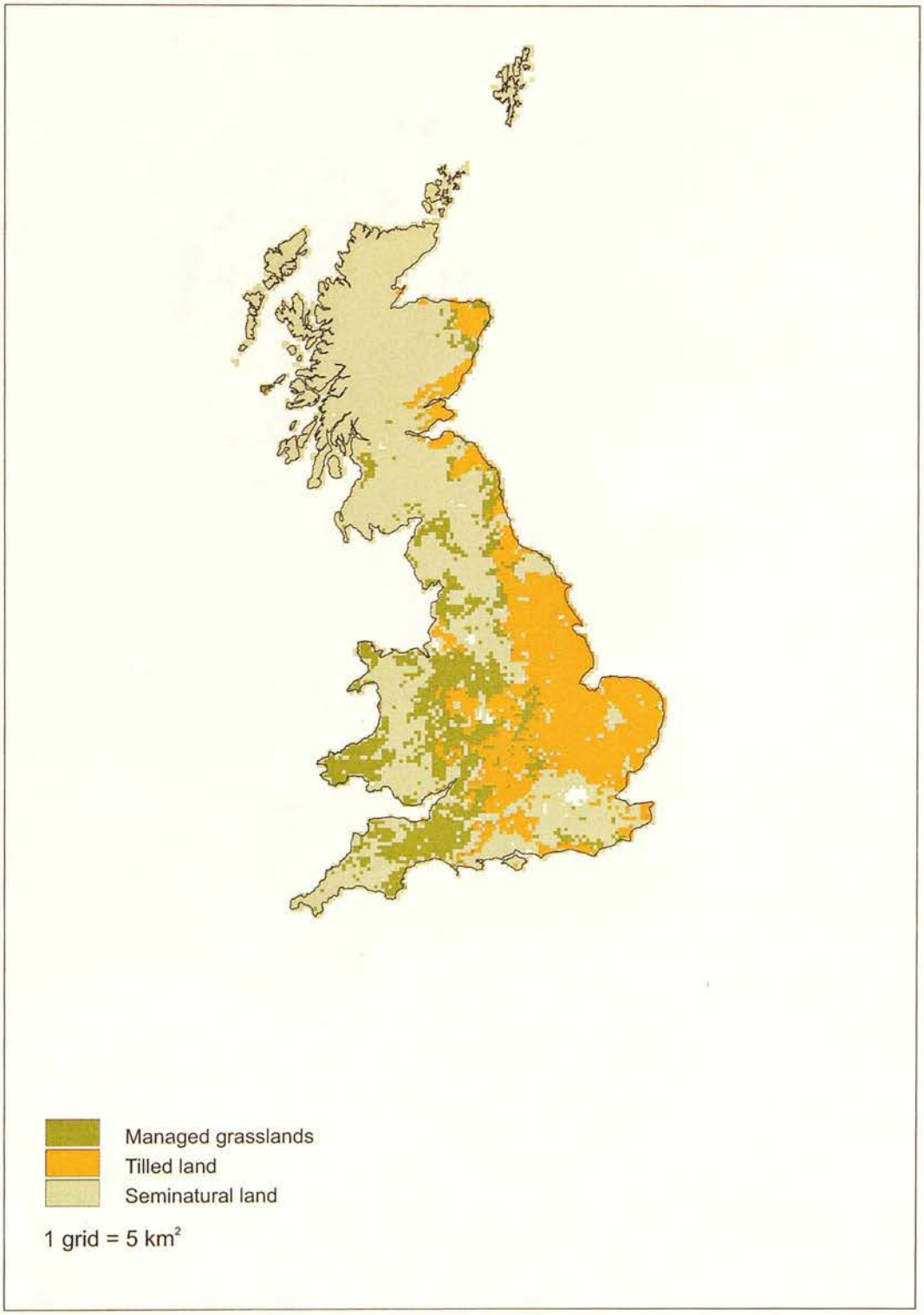


Figure A11 Mineral N fertiliser input to cereals in Great Britain.

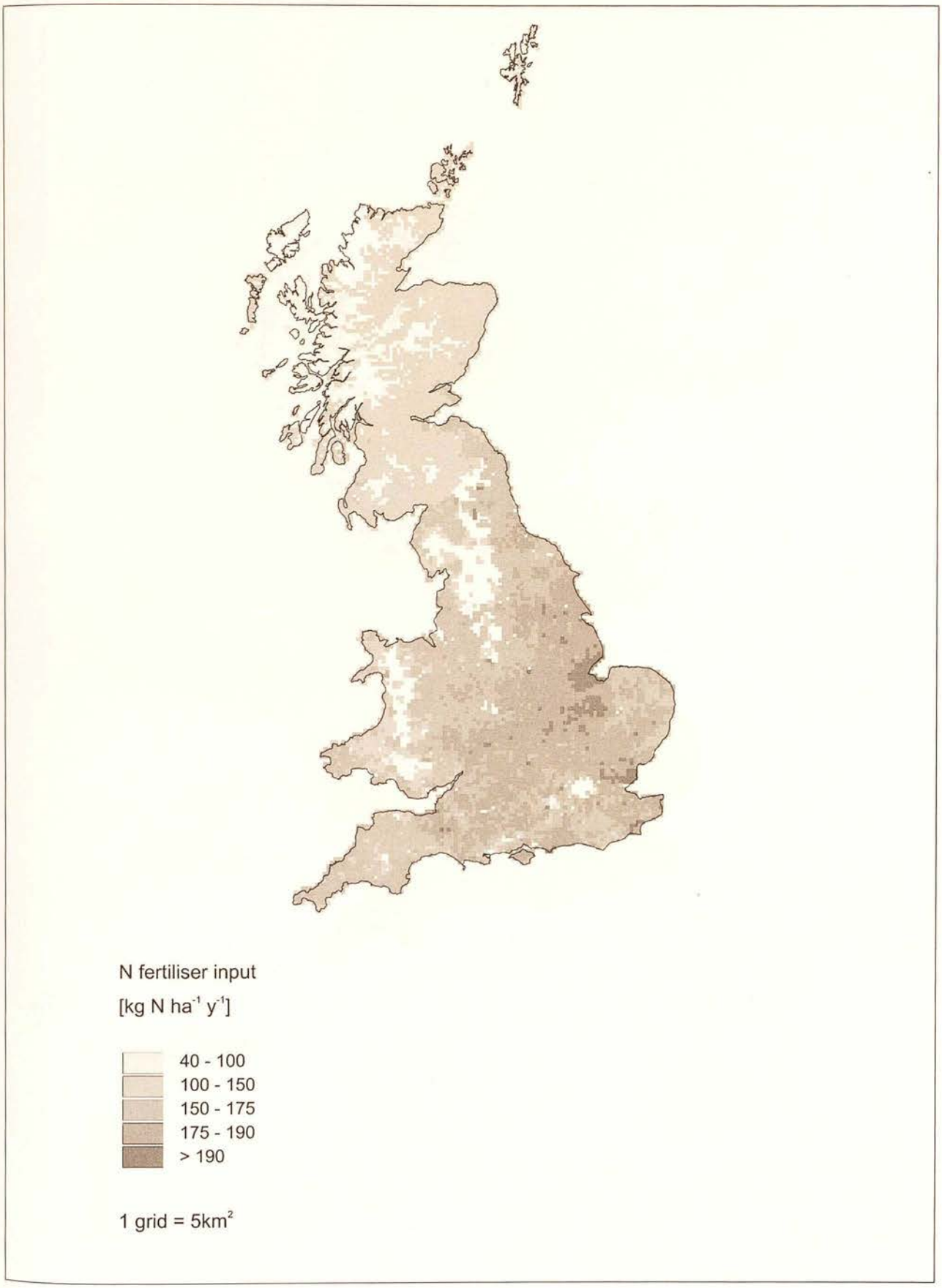


Figure A12 N_2O emissions from cereal crops in Great Britain.

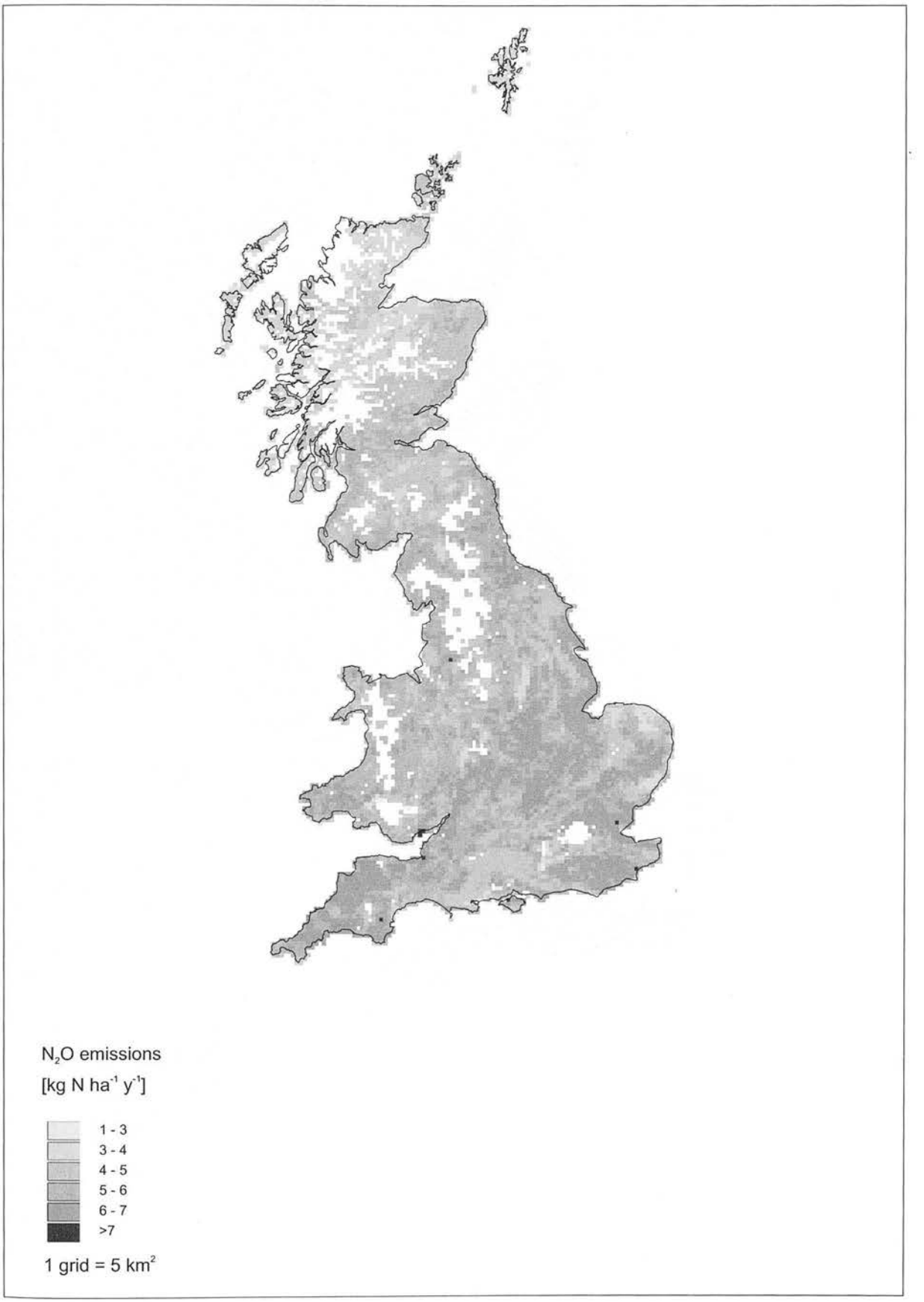


Figure A13 Mean annual soil moisture (WFPS) predicted by SPACTeach model with varied initial moisture level.

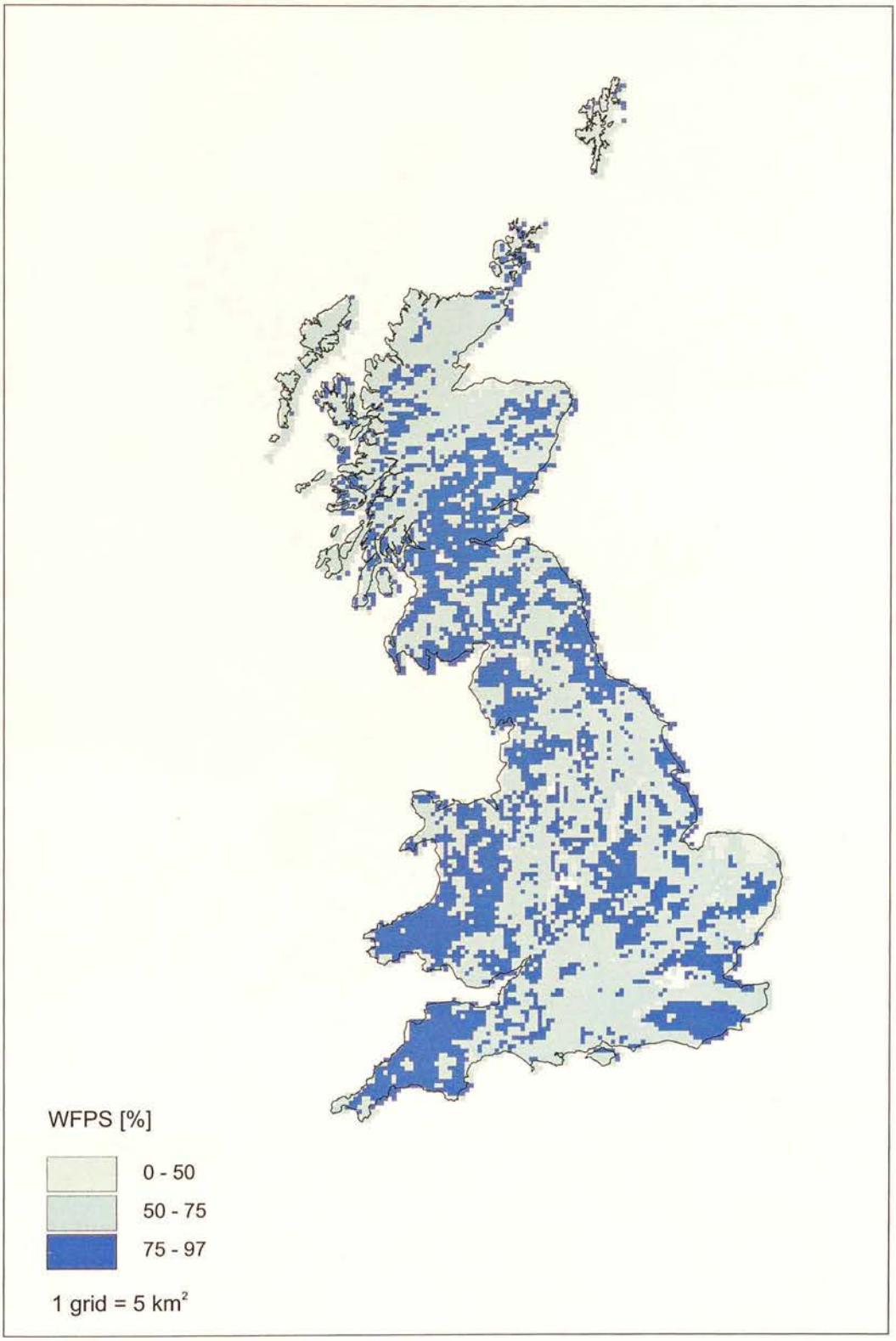


Figure A14 Mineral N fertiliser input to non-cereal tillage crops in Great Britain.

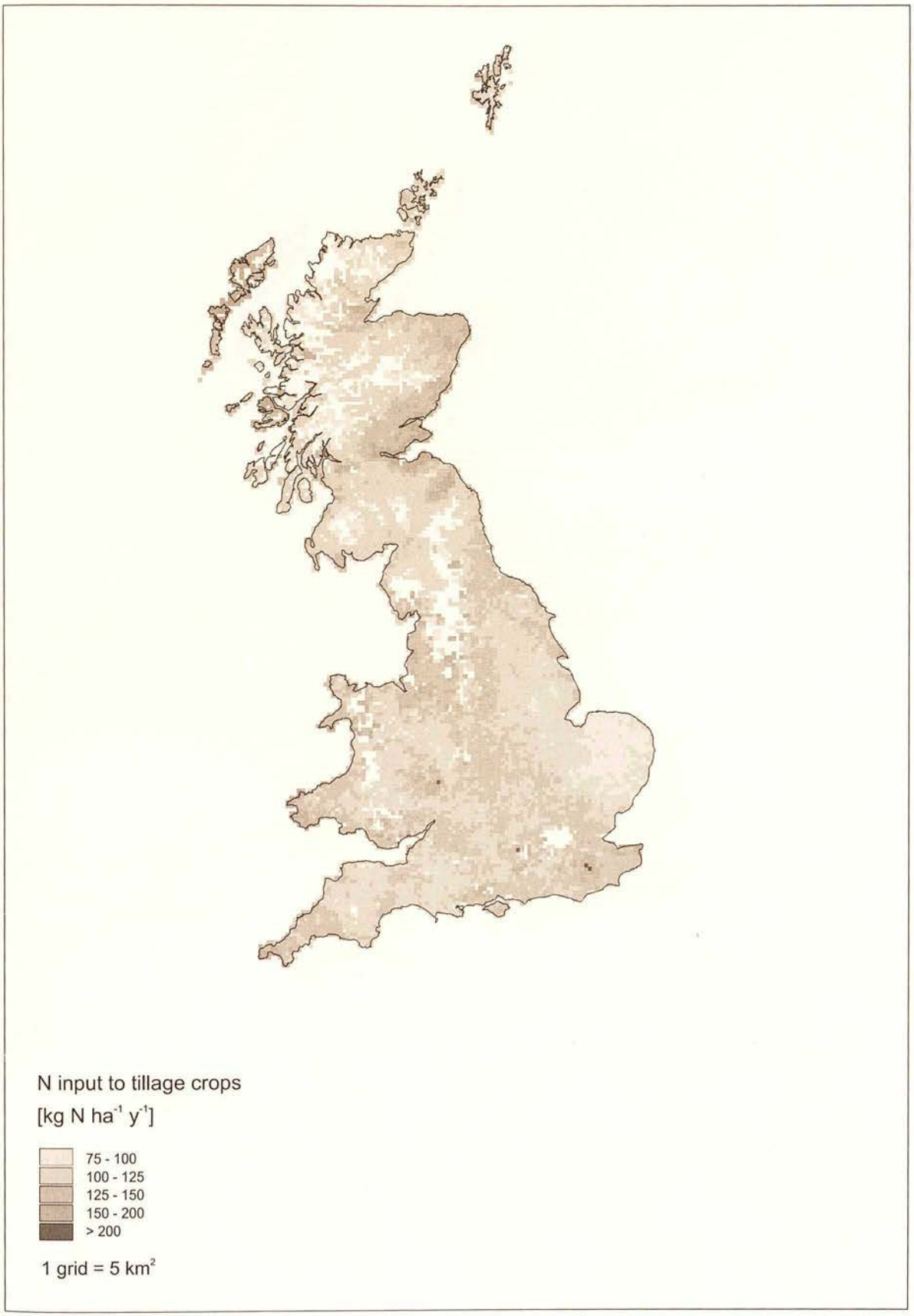


Figure A15 N_2O emissions from non-cereal tillage crops in Great Britain.

Figure A16 Livestock distribution in Great Britain

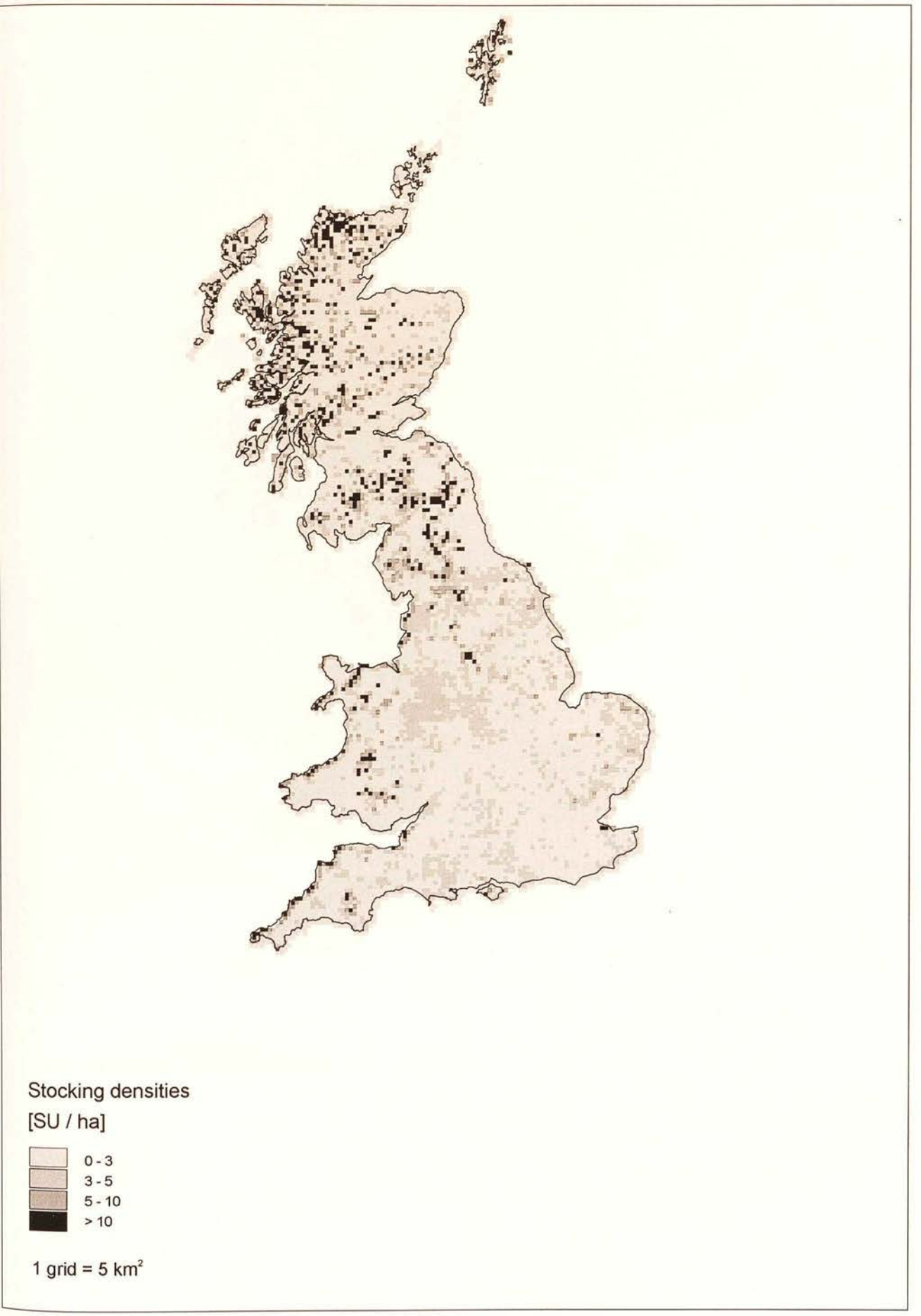


Figure A17 Distribution of mineral N fertiliser input to grasslands in Great Britain estimated with fertiliser recommendations.

Figure A18 Estimated N input of organic N from animal excreta to agricultural soils..

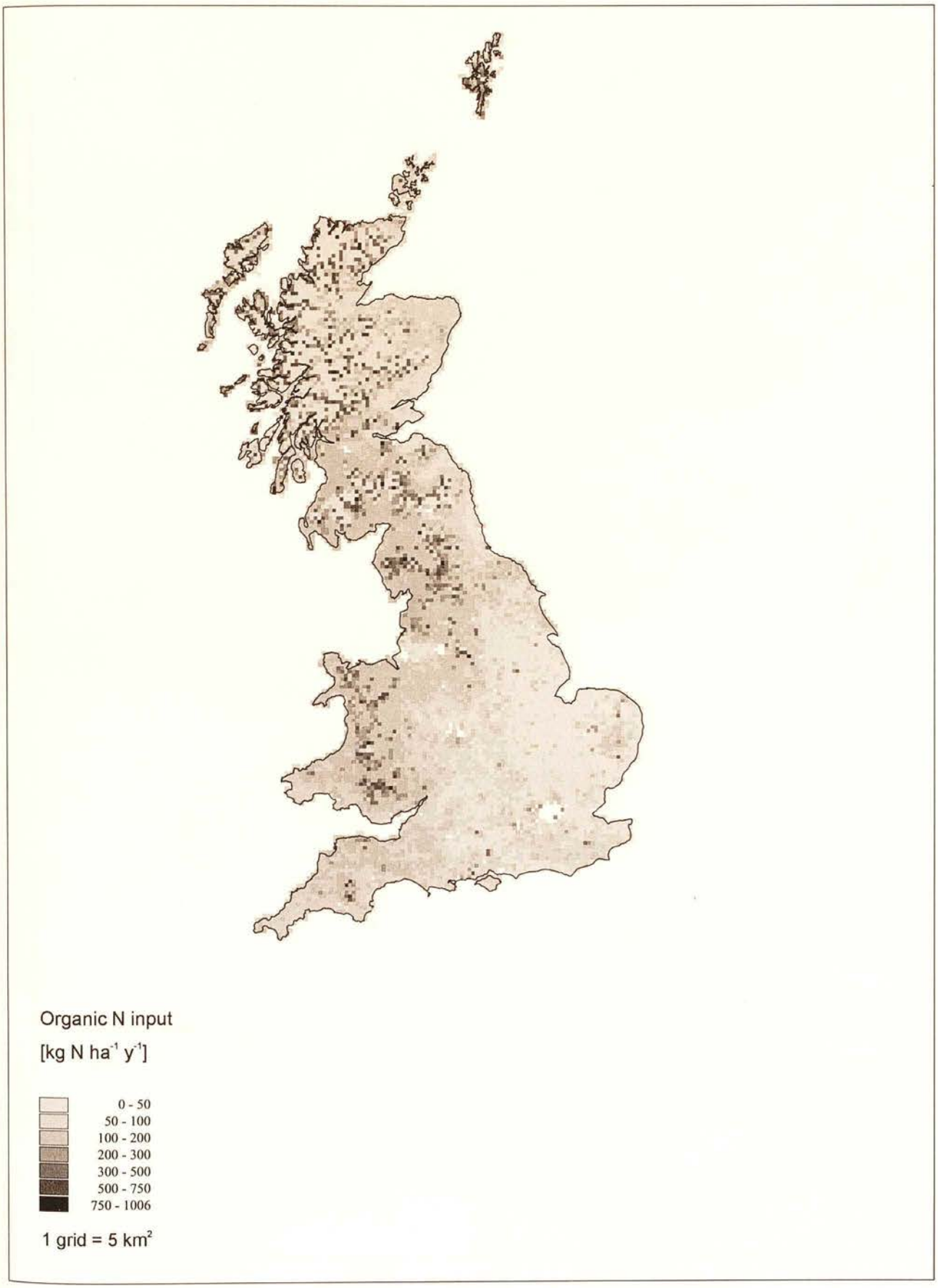


Figure A19 N_2O emissions from agricultural soils predicted by model (6.1).

Figure A20 Total mineral and organic N inputs to agricultural soils.

Figure A21 Mean annual atmospheric N deposition.

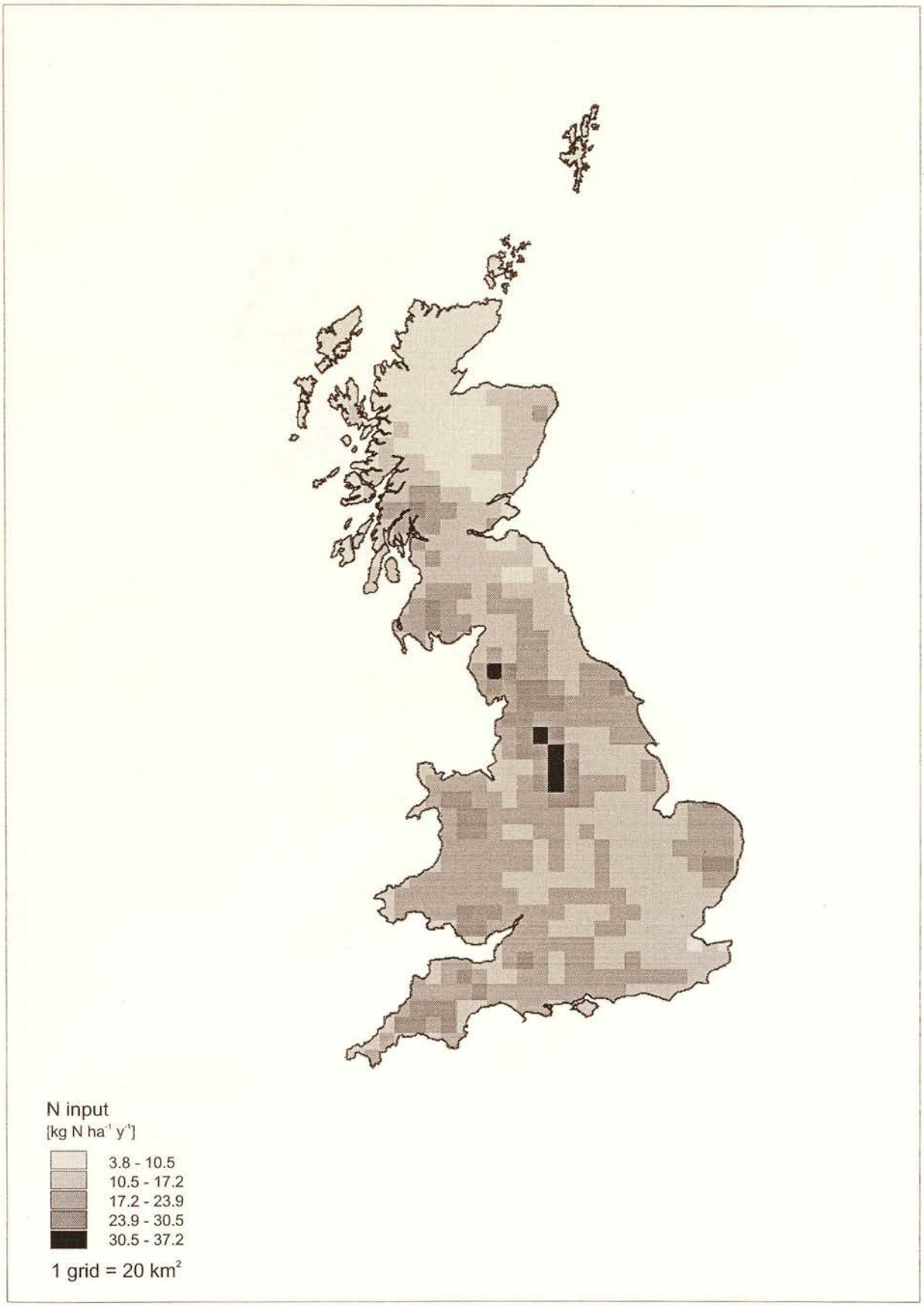


Figure A22 N_2O emissions caused by atmospheric N deposition.

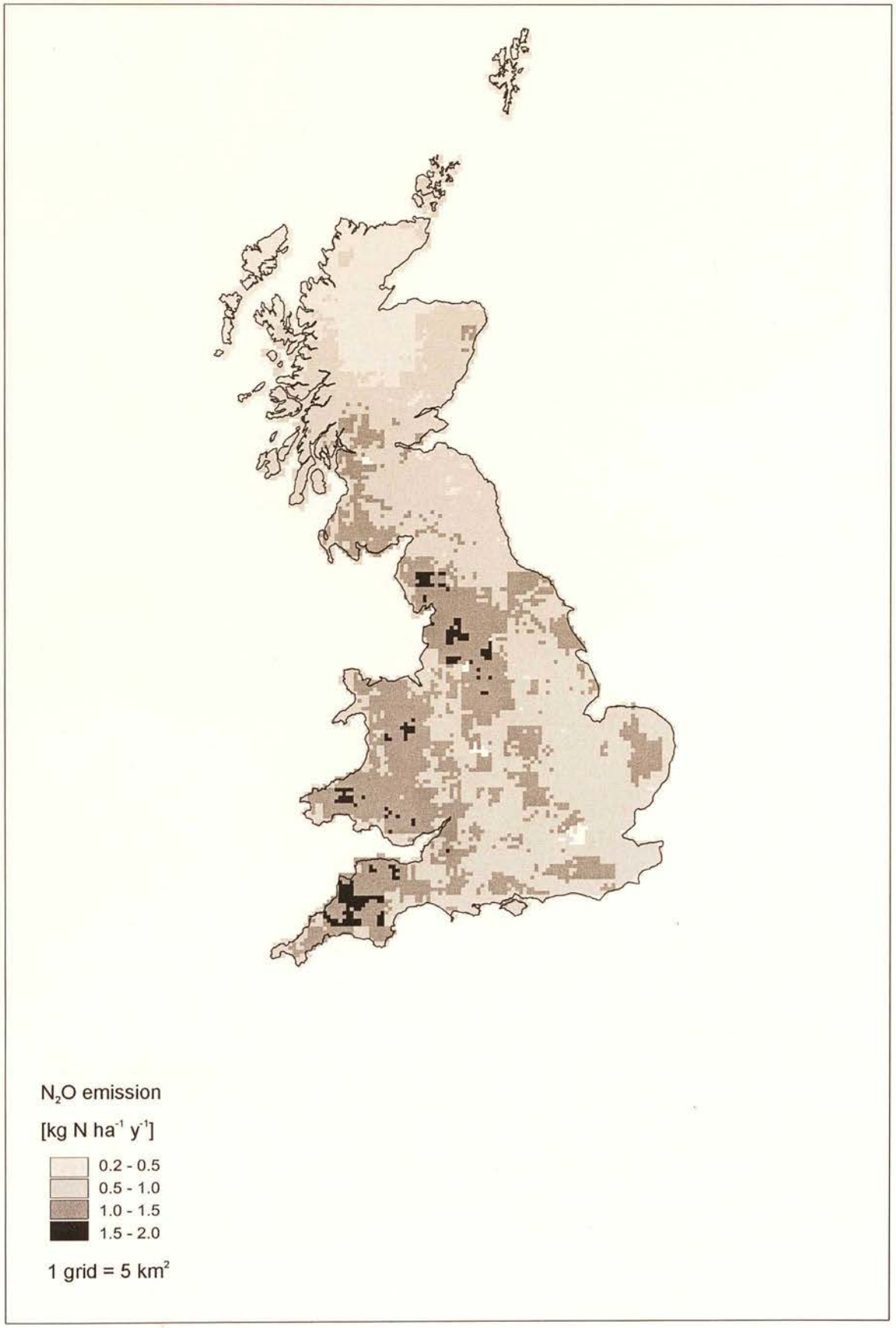


Figure A23 N_2O emissions from British soils predicted with model (6.1).

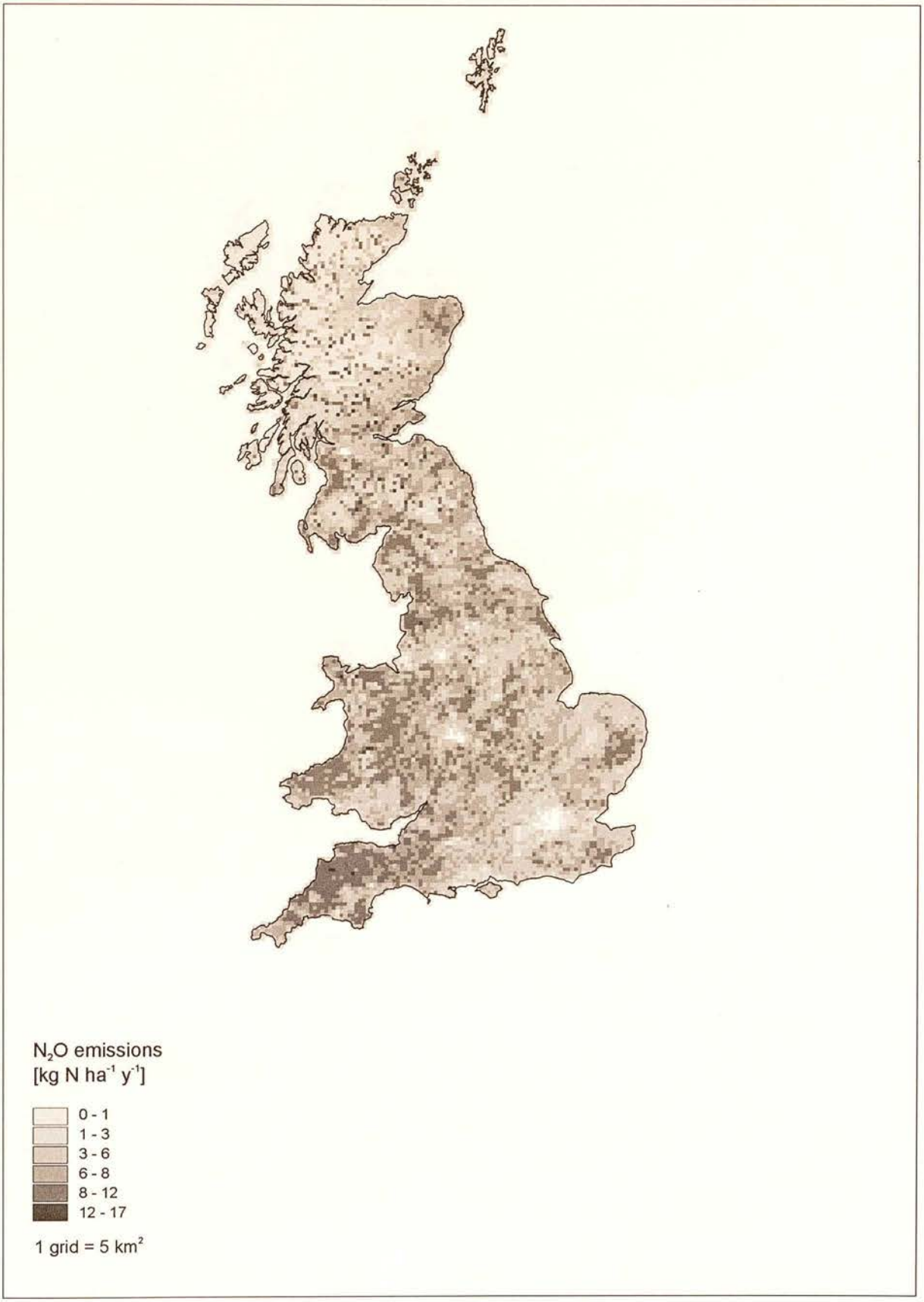


Figure A24 N_2O emissions from British soils estimated with model (6.2)

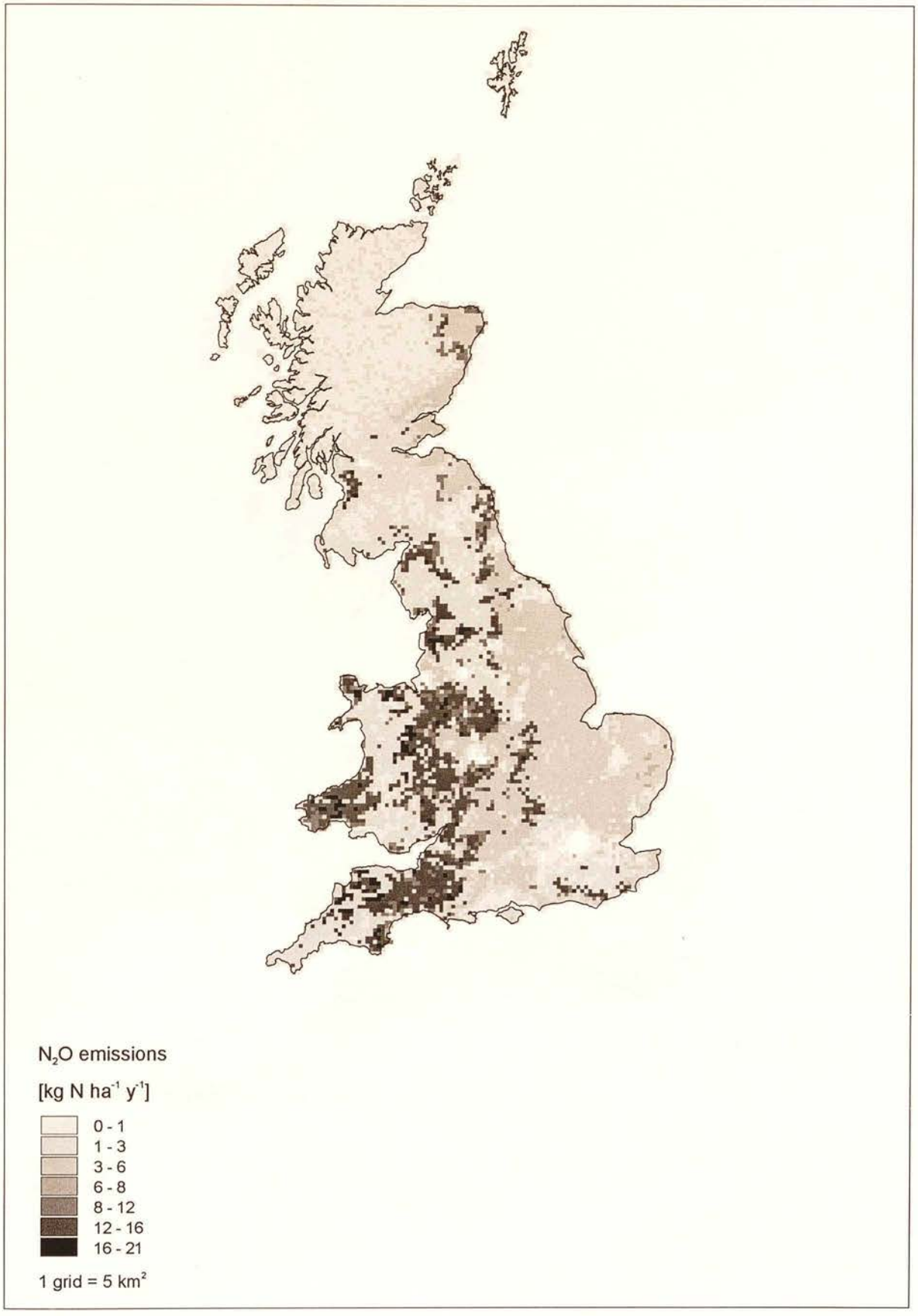


Figure A25 N_2O emissions estimated for agricultural land in 1997.

N_2O emissions from agricultural soils

[kg N ha^{-1} y^{-1}]

- 0 - 1
- 1 - 3
- 3 - 5
- 5 - 8
- 8 - 10
- > 10

1 grid = 5 km^2

Figure A26 Change in N_2O emissions from agricultural soils between 1988 and 1997.

Figure A27 Seasonal N fertiliser input estimated by AGEM from fertiliser recommendations.

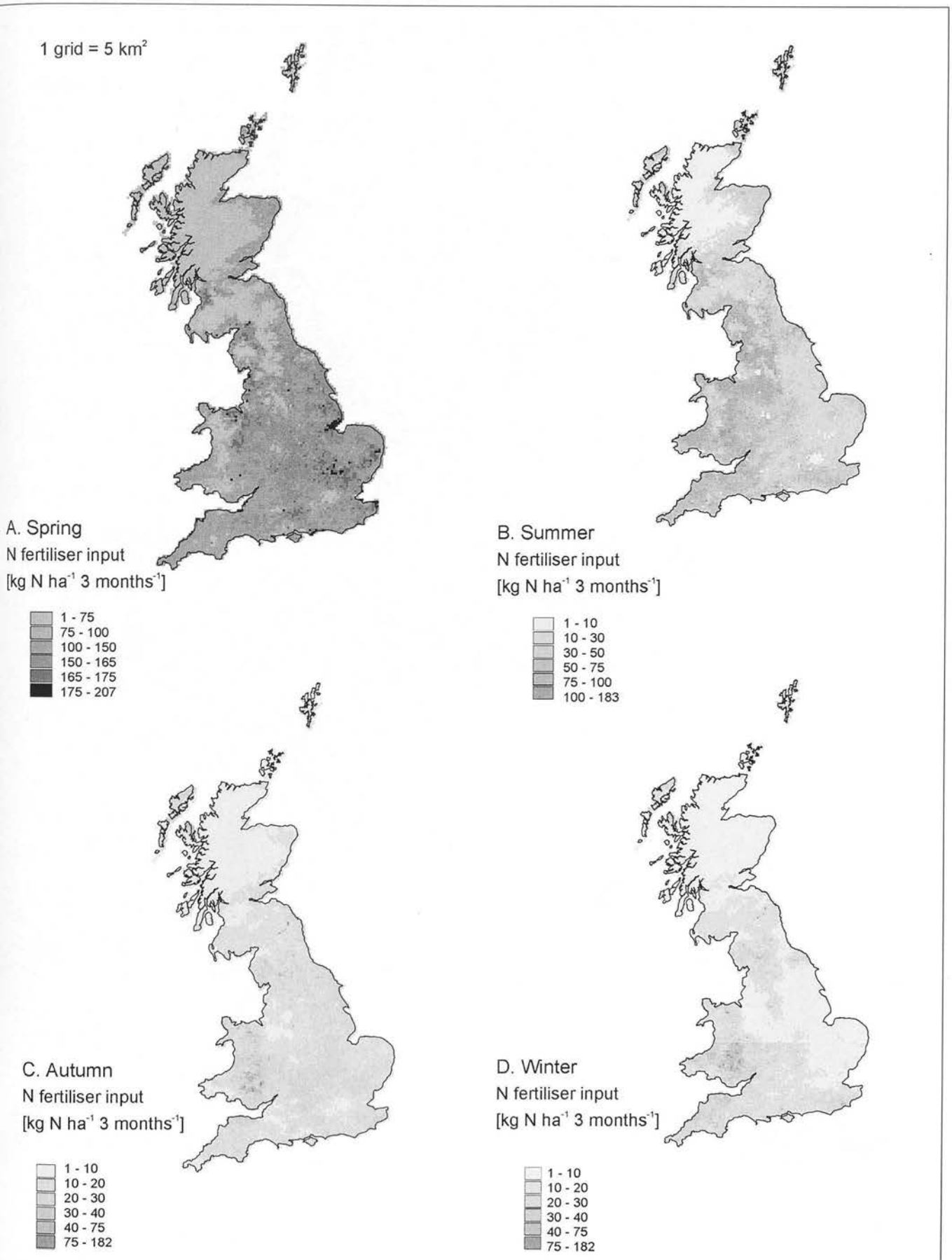


Figure A28 Seasonal distribution of N_2O emissions from British soils as predicted by model (6.1).

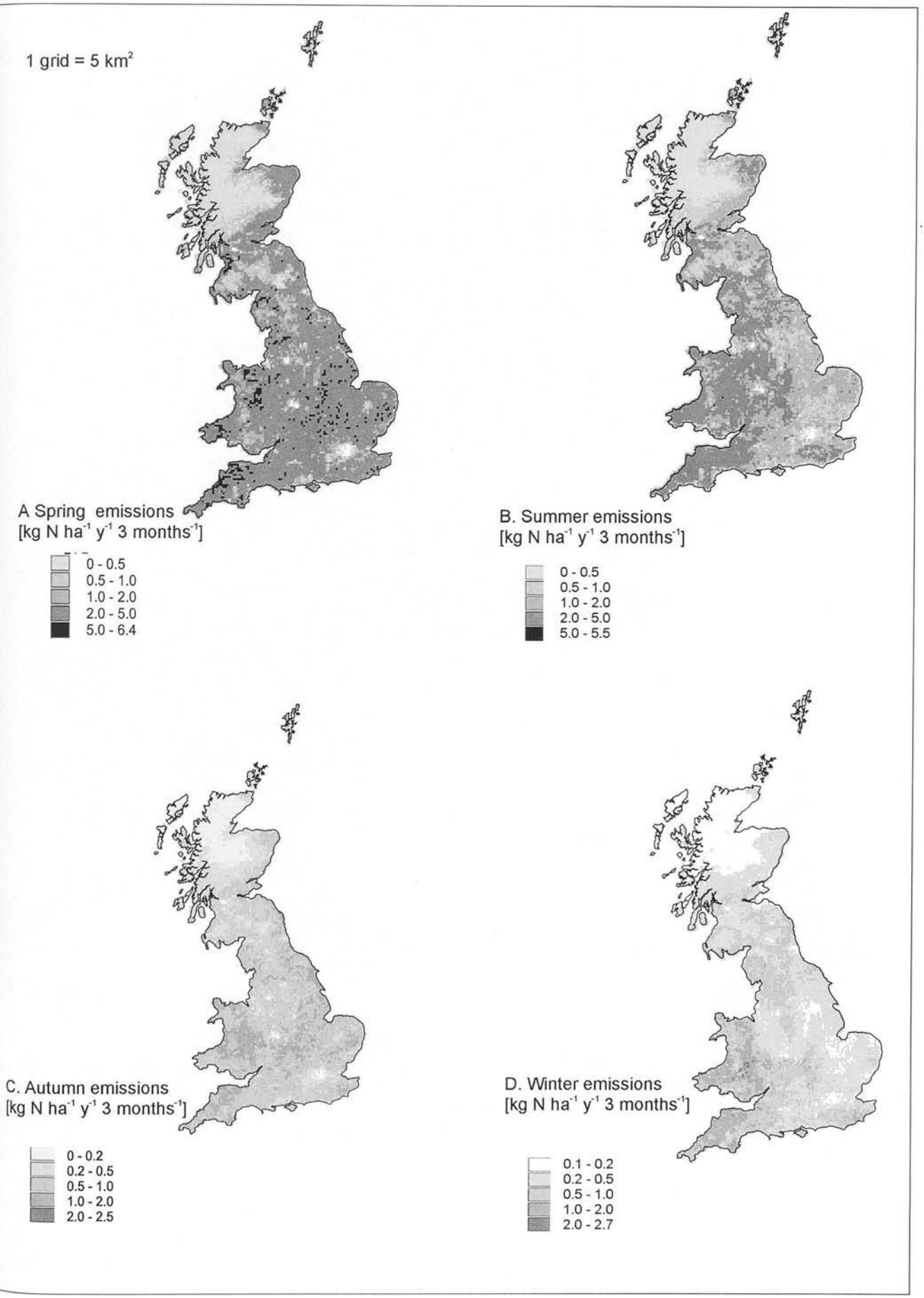


Figure A29. Seasonal distribution of N_2O emissions from British soils as predicted by model (6.2).

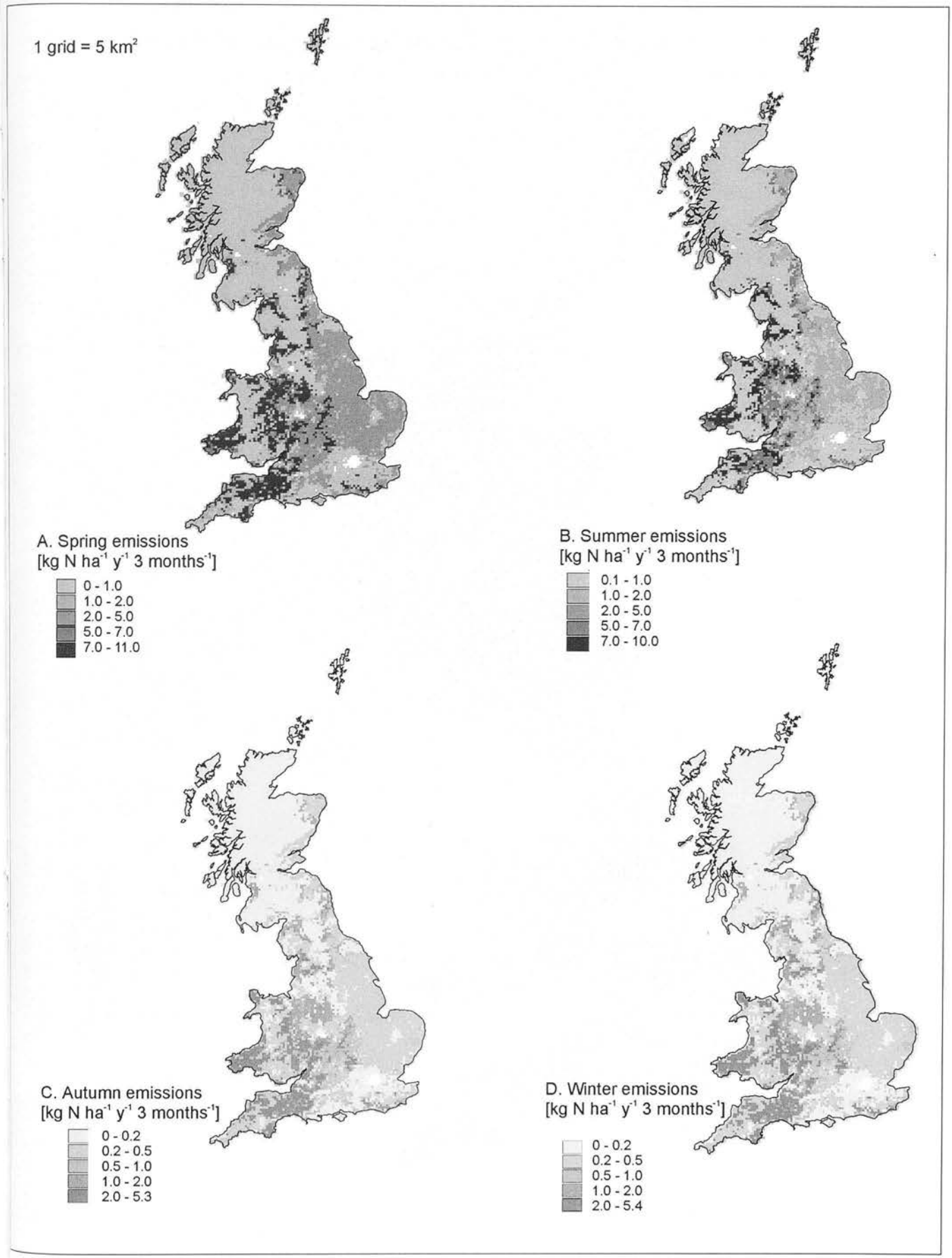


Figure A30 Annual NO emissions from soils in Great Britian predicted by model (7.5).

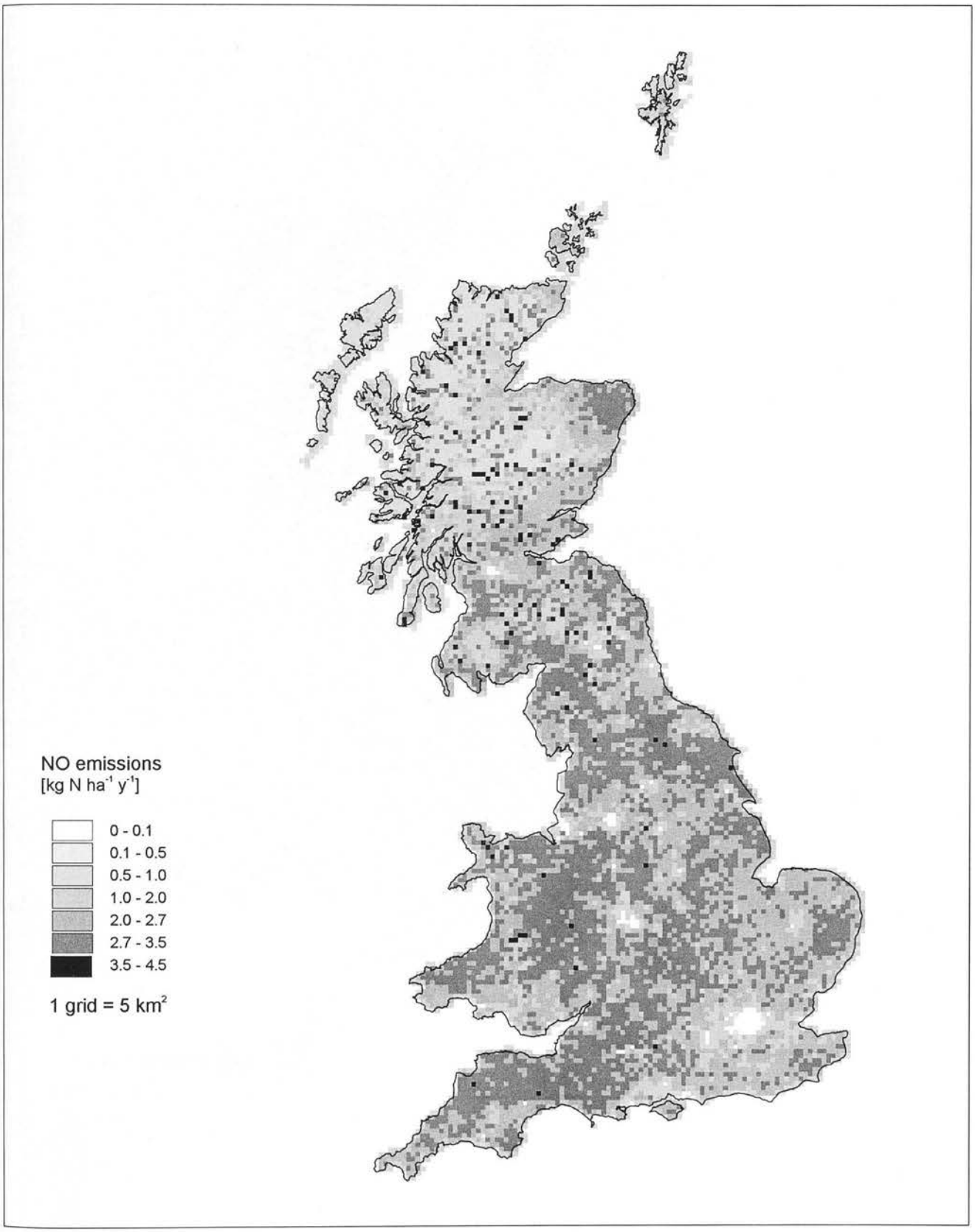


Figure A31 Annual NO emissions from British soils estimated with model (7.8).

Figure A32 Seasonal distribution of NO emissions as predicted by model (7.8).