A REVIEW OF SOIL FACTORS AND PROCESSES THAT CONTROL FLUXES OF HEAT, MOISTURE AND GREENHOUSE GASES

N.H. Batjes and E.M. Bridges

ISRIC

Related Reports and Publications:

Batjes, N.H. (ed.), 1992. *World Inventory of Soil Emissions: Report of Working Group Discussions and Recommendations*. Proceedings of an international workshop organized in the framework of the Netherlands National Research Programme on Global Air Pollution and Climate Change (24-27 August 1992). WISE Report No. 1, ISRIC, Wageningen, 20 pp.

Batjes, N.H. and E.M. Bridges (eds), 1992. *World Inventory of Soil Emission Potentials*. Proceedings of an International Workshop organized in the framework of the Netherlands National Research Programme on Global Air Pollution and Climate Change (NOP). WISE Report No. 2, International Soil Reference and Information Centre, Wageningen, 122 pp. [ISBN 90-6672-049-2].

....

A REVIEW OF SOIL FACTORS AND PROCESSES THAT CONTROL

FLUXES OF HEAT, MOISTURE AND GREENHOUSE GASES

N.H. Batjes and E.M. Bridges

Preface

Terrestrial ecosystems are important sources and sinks of a number of radiatively-active gases, such as water vapour, carbon dioxide, methane, nitrous oxide and nitric oxide, and as such play an important role in the so-called 'greenhouse effect'. The soil conditions and chemical, physical and biological processes that control the production/absorption and emission of 'greenhouse gases' in terrestrial ecosystems are incompletely understood and only poorly quantified. As a contribution to increasing the understanding of these processes, and their inter-linkages, the International Soil Reference and Information Centre (ISRIC) initiated a project on 'Geographic Quantification of Soil Factors and Processes that Control Fluxes of Greenhouse Gases'. This 3-year project, which is currently referred to as 'World Inventory of Soil Emission Potentials' (WISE), is a follow-up to the International Conference on 'Soils and the Greenhouse Effect'. It is part of a wider research programme being carried out within the framework of the Netherlands National Research Programme on Global Air Pollution and Climate Change (NOP-MLK; Project No. 851039).

The WISE project has been divided into two phases. The first phase, September 1991 to September 1992, has been to assemble the relevant literature in a background study of the currently known chemical, physical and biological factors controlling the gaseous exchanges involved. This phase of the project culminated in a workshop, attended by an international panel of scientists working in the field, whose expertise and experience were drawn upon to refine the broad lines of the project outlined in the original research agreement. The executive summary and invited papers to the workshop have been issued as separate publications by ISRIC (Batjes, 1992; Batjes and Bridges, 1992b). This Technical Paper has been derived from the Background Document to the WISE workshop (Batjes and Bridges, 1992a).

The second phase of the WISE project which ends in September 1994, includes two main goals, the successful completion of the first of these will enable the second to be accomplished. A global soil data base with a grid size of 30' latitude by 30' longitude is to be compiled from the 'cleaned' digital version of the 1:5 M Soil Map of the World in close collaboration with staff of the Food and Agriculture Organisation's Land and Water Division (FAO - AGLS). These 'area' data will be linked to a soil profile data base. Once this is done, the framework will be in place for assembling and handling the data required to make an assessment of methane production from wetlands and/or irrigated rice soils to achieve a more accurate figure of global soil emissions of methane. This will require development of a scheme to model the different aspects of methane production and emission to the atmosphere.

i

Acknowledgements

Table of Contents

Chapter 1 Introduction

Chapter 2 Soil heat and moisture balance

Chapter 3 Methane

Chapter 4 Nitrous oxide

Chapter 5 Organic matter and carbon dioxide

List of Figures

List of Tables

List of Appendices

Chapter 1 Introduction

N.H. Batjes and E.M. Bridges

1.1 The greenhouse effect and climatic change

The gaseous composition of the atmosphere has changed markedly and rapidly during the last decades mainly through increased industrial emissions, fossil fuel combustion, widespread deforestation and related burning of biomass, as well as changes in land use and management practices. While most of these anthropogenic activities have resulted in increased emissions of naturally occurring radiatively-active trace gases (e.g., CO_2, CH_4, N_2O), popularly known as 'greenhouse gases', several industrial activities have produced new trace gases not occurring naturally in the atmosphere (Figure 1.1). These include the synthetic chlorofluorocarbons (CFCs) which in the lower atmosphere trap heat. In the upper part of the troposphere CFCs cause chemical reactions leading to the degradation of the ozone layer, which protects the Earth's surface from harmful solar radiation. While CO_2 is chemically inert in the atmosphere, this is not the case for CH_4, N_2O and CFCs. The role of the latter gases in the photochemistry of the atmosphere has recently been reviewed by Levine (1989) and Bouwman (1990a).
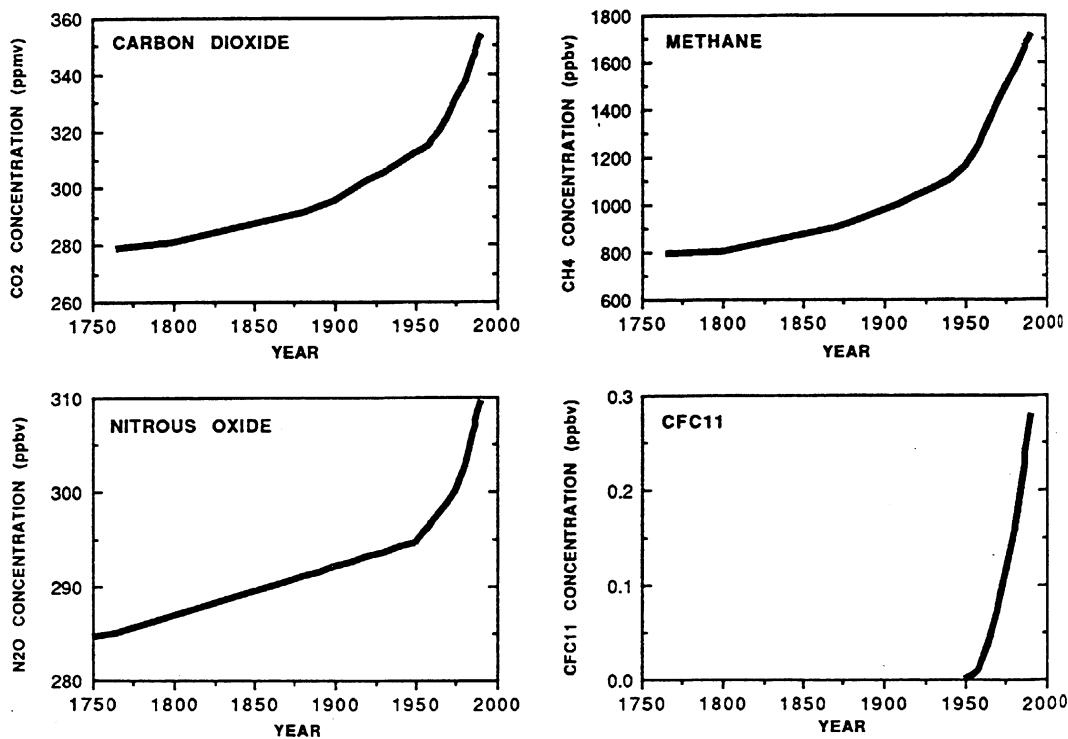
Figure 1.1.   Increases in atmospheric concentrations of CO_2, CH_4, N_2O and CFCs since the year 1750 (Source: IPCC, 1990 p. 16).

Biogenic trace gases contribute to the so-called 'greenhouse effect' or 'global warming' in that they are fairly transparent to the incoming shortwave solar radiation, but absorb and reflect longwave infrared radiation emitted from the warm surface of the Earth. Thereby part of the energy associated with the longwave radiation, reflected by the Earth's surface and lower atmosphere, is trapped within the atmosphere. This keeps the Earth's surface temperature at a higher average value than it would have been if the trace gas concentrations were low. Arrhenius (1896) calculated that water vapour and carbon dioxide concentrations in the atmosphere have caused the Earth's temperature to increase from an average of -18 $^{\circ}$C to +15 $^{\circ}$C, a net change of +33 $^{\circ}$C. If there were no trace gases, the long-wave radiation re-emitted from the Earth's surface would largely be lost into space resulting in a cold, inhospitable globe. Alternatively, increasing concentrations of radiatively-active trace gases in the atmosphere currently lead to an appreciable, *enhanced* warming of the globe (ORNL, 1990 p. 194). Additional warming will increase the concentration of water vapour, the main greenhouse gas, and this will further enhance the process of global warming. In contrast to CO_2, CH_4 and N_2O, the concentration of water vapour is determined internally within the climate system so that, on a global scale, it is not affected by human sources and sinks (IPCC, 1990).

The 'greenhouse effect' is apparent to many climatologists through the concurrent rise in temperature and atmospheric CO_2 levels (Idso, 1988). Between the 1760s and 1990s the atmospheric CO_2 concentration increased by about 74 ppmv, while in the same period mean global temperature increased by about 0.7-0.8 $^{\circ}$C (Esser, 1990). This would seem to suggest atmospheric CO_2 level and temperature are correlated, but as Esser (1990) observes 'correlations never establish causal relationships'. Similarly, Idso (1988) pointed out that the recent global warming is not necessarily caused by the increase of CO_2 or other greenhouse gases in the atmosphere. Idso stated that if 'the temperature trend is viewed in a broader historical context the warming could be nothing but the natural expression of the Earth's recovery after the Little Ice Age (1550-1850 A.D.)'. Alternatively, Hansen *et al.* (1990) studied the extent to which global warming might be moderated by variations in solar radiation and atmospheric dust (aerosols). They conclude that solar variability will not counteract global warming, and that despite uncertainties in the effects of dust, greenhouse gas emissions must be reduced if the climate and environment are to remain 'bearable' for biota. With reference to analyses of 1400 year old tree-ring records of Scots pine (*Pinus sylvestris* L.), Briffer *et al.* (1990) concluded that 'it will not be possible to detect a regional greenhouse effect (with 95 % confidence) until around 2020'. Similarly, the IPCC (1990) working group concluded that an 'unequivocal detection of the enhanced greenhouse effect from observations is not likely to occur for a decade or more'.

In spite of the various views on the subject, as portrayed in the above examples, most natural scientists agree that global climatic changes related to the greenhouse effect are liable to occur. As the possible consequences thereof are likely to have profound environmental and socio-economic repercussions, the controlling factors and processes need to be elucidated further. The desire to meet this need is reflected in the large array of studies that currently are devoted to understanding the possible influence of global climate warming on processes, and their dynamics, in the oceans, sea-ice caps, terrestrial ecosystems and atmosphere (Arnold *et al.*, 1990; Scharpenseel *et al.*, 1990; IGBP, 1990). For instance, there can be an associated release of pollutants previously believed to be held firmly in soils and sediments (e.g., Batjes and Bridges, 1991; Stigliani, 1988), widespread human-induced soil degradation (Oldeman *et al.*, 1991) and changes in land use and sea levels (e.g., Brouwer *et al.*, 1991; Parry, 1990), thereby ultimately limiting the carrying capacity of Earth for biota.

The above problems often transcend national boundaries. Policy makers increasingly recognize the need for internationally accepted, abatement measures to ensure a sustainable and equitable use of the environment. However, there still seems to be no consensus about how this objective should be achieved (e.g., 1992 United

Nations Conference on Environment and Development, UNCED). Well known international research programmes addressing global change include the International Geosphere-Biosphere Programme (IGBP, 1988, 1990) and World Climate Research Programme (WCRP). Closely related national programmes include the Terrestrial Initiative in Global Environmental Research (TIGER) of the United Kingdom, and the Netherlands National Research Programme on Global Air Pollution and Climate Change (NOP-MLK).

The atmospheric concentrations of trace gases such as methane and nitrous oxide are increasing more rapidly than is the case for CO_2 so that their relative importance in modifying climate is changing (Bolin *et al.*, 1986). Global concentration increases of greenhouse gases over the last 200 years, in per cent, are about 20 for CO_2, 8 for N_2O and over 200 for methane (Lorius, 1988). The heat absorption potential of these gases depends on factors such as their relative concentration in the atmosphere, infrared absorption profile and atmospheric life-time, and as a consequence it varies widely between them. An additional molecule of CH_4, for example, will trap about 32 times as much heat as an incremental CO_2 molecule would, while this is about 150 times that for a molecule of N_2O (Esser, 1990). After 20 years a molecule of CH_4 is 63 times more potent than a molecule of CO_2, decreasing to 21 times after 100 years and 9 times after 500 years (JEA/EPA, 1990 p. 2). In the case of man-made CFCs, differences are even more pronounced; an incremental molecule of CFC traps about 20,000 times more heat than a CO_2 molecule (Esser, 1990). Since the atmospheric life times of CO_2, CH_4, N_2O and CFCs are relatively long (Table 1.1), this means that increased atmospheric concentrations of these trace gases - and their atmospheric derivatives - may markedly affect climate and thereby biodiversity on Earth. It also means that abatement measures aimed at stabilizing or reducing atmospheric concentrations of the so-called 'long-lived' greenhouse gases (i.e., CO_2, N_2O, CFCs) can first have a noticeable effect on a time scale in the order of several decades to centuries, as opposed to within decades for methane. Stabilization of the concentrations of the 'long lived' trace gases at their present levels would require at least a 60 per cent reduction in their current anthropogenic emissions, whereas this would be 15 to 20 per cent for methane (Table 1.1). Controls of CFCs, HCFCs and nitrogen oxides have an adverse effect on methane concentrations, which make additional reductions of methane emissions necessary (Rotmans *et al.*, 1992).

Table 1.1. Atmospheric life time, pre-industrial and current concentrations, and yearly average increases in atmospheric concentrations of CO_2, CH_4, N_2O and CFCs, and reductions in anthropogenic emissions necessary to stabilize these concentrations at their current levels (Adapted from IPCC, 1990).

	CO_2	CH_4	N_2O	CFC-11	CFC-12
Atmospheric lifetime (yr)	50-200 yr	10 yr	150 yr	65 yr	130 yr
Pre-industrial conc. (1750-1800)	280 a	0.8 a	288 b	0 c	0 c
Present day levels (1990)	353 a	1.72 a	310 b	280 c	484 c
Current average yearly increase	0.5 %	0.9 %	0.25 %	4 %	4 %
Reduction in emissions required for stabilization at current levels	> 60 %	15-20 %	70-80 %	70-75 %	70-85 %

Note: Concentrations specified as: a = ppmv = parts per 10^6 by volume; b = ppbv = parts per 10^9 by volume; c = pptv = parts per 10^{12} by volume.

The accumulated greenhouse forcing for the periods 1850-1957 and 1958-1989 is 0.87 and 1.17 W m^{-2}, respectively (Figure 1.2). This forcing may increase to 4.6 W m^{-2} by the year 2025 if the 'business-as-usual' scenario of IPCC (1990 p. 45) is used, which clearly reflects the need for appropriate emission abatement measures now. During the period 1850-1957 CO_2 and CH_4 dominated, but since then there has been a clear increase in the importance of CFCs and N_2O on greenhouse forcing. Increased concentrations of tropospheric and stratospheric O_3 may be responsible for 10 % of the total forcing since pre-industrial times (IPCC *op cit.*). As CO_2, CH_4 and N_2O are to a large extent associated with sources in the biosphere it is important to evaluate the possible biotic and abiotic sources and sinks of these trace gases in the biosphere. In the present study we shall limit ourselves to terrestrial ecosystems.
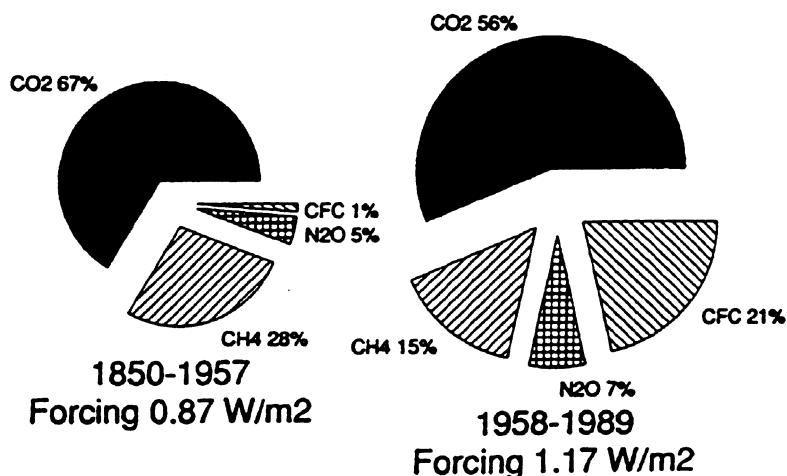
Figure 1.2. Accumulated greenhouse forcings for the periods 1850-1957 and 1958-1989 (Source: Matson and Ojima, 1990 p. 1).

1.2 Soil mapping and classification

Just over 100 years ago, soil science emerged as a separate scientific study in its own right. This was mainly the result of studies in Russia and the United States, although an early interest in soils was not confined to these countries, as for example, The Netherlands, Britain, Hungary, Germany and many other countries which were following their own more localized interests at this time. It was in Russia, particularly as a result of the work of Dokuchaev, that the *soil profile* with its different *horizons* was recognized as the unique expression of the soil forming processes which operate on the surface of the earth. Dokuchaev also identified, but did not quantify, a number of *soil forming factors* which provided the overall parameters for soil formation; these included climate, vegetation, relief and the age of the land.

Until the time of World War Two, subsequent workers attempted to provide soil maps, not only of their own countries, but also of the whole world. The first of these appeared at the end of the nineteenth century, when sufficient information had been gathered to enable the first soil maps of the world to be compiled. These were mostly in the category of derived maps. As little direct soil information was available for inclusion, they were mostly deductive maps using climate or vegetation as a surrogate for first-hand soil information. Such an approach led to the concept of 'Great Soil Groups' which dominated soil geography until the 1960s.

Throughout the first half of the twentieth century, soil knowledge increased greatly, both in understanding the formative processes which operated and also in the geographical distribution of different soil types. This took place as a result of the former colonial powers attempting to understand the environment and increase the productivity of their overseas possessions. The knowledge gained only partly confirmed the earlier concept of great soil groups, and so in 1960 at the instigation of the International Society of Soil Science, FAO in conjunction with Unesco, began the development of a new Soil Map of the World (FAO/Unesco, 1971-1981). This map, at a scale of 1:5 M, was intended to be a first appraisal of the world's soil resources, assembled on a uniform basis. It was meant to provide a scientific basis for the transfer of knowledge and experience between different areas with similar environments and to provide a generally accepted framework of soil classification throughout the world. Published between 1971 and 1981, the FAO-Unesco Soil Map of the World largely achieved these objectives, and in the last decade has come to be an invaluable document for soil scientists and others to use. Since the work on the compilation of this map was begun, much new information has become available, and parts of the original map are known to lack the desired accuracy. Consequently, a revised version of the classification was issued jointly by FAO and ISRIC in 1988, and proposals have been drawn up to revise certain areas of the Soil Map of the World. This has already occurred in East Africa, and it is hoped that funding will become available to deal with other areas, such as the Amazonian area of South America in the near future.

The FAO-Unesco Soil Map of the World has retained many of the traditional names given to soils, but has combined these with concepts of diagnostic horizons and properties which bring to the classification system an element of quantification and mutual exclusivity. (Officially, the system is a map legend not a classification, but it is widely used as a means of comparison of soils from different parts of the world). Differentiating criteria for diagnostic horizons and properties are the natural properties of the soil itself, defined in terms of measurable and observable properties. Certain 'clusters' of these properties have been selected for the definition of diagnostic horizons; many of these properties are relevant to soil use and have a value for practical applications. Hence, the units employed on the Soil Map of the World have a predictive value, not only for the use of the soil, but for many other purposes as well.

The twenty-eight soil units of the revised legend of the Soil Map of the World (FAO, 1988) may be separated into eight groups based on common geographical and evolutionary backgrounds:
  - Group 1 includes Fluvisols, Gleysols, Regosols and Leptosols, soils which are not associated with any specific zonal climatic conditions of formation.
  - Group 2 comprises soils the formation of which is strongly conditioned by the nature of the parent material. These are the Arenosols, Andosols and Vertisols.
  - Group 3 has only one soil unit, the Cambisols, representing a range of soil formation more strongly expressed in other soils.
  - Group 4 includes those soils which possess accumulations of salts, Calcisols, Gypsisols, Solonetzes and Solonchaks.
  - Group 5 has soils where an accumulation of base-saturated organic matter occurs; these are the Kastanozems, Chernozems, Phaeozems and Greyzems.
  - Group 6 includes soils with accumulations of clay or sesquioxides and organic matter in the subsurface horizons. These are the Luvisols, Planosols, Podzoluvisols and Podzols.
  - Group 7 is dominant in the tropics and sub-tropics, where weathering is intense, and includes Lixisols, Acrisols, Alisols, Nitisols, Ferralsols and Plinthosols.
  - Group 8 is confined to the Histosols which are organic soils.

1.3 Role of soils

Soils are an essential part of natural ecosystems, and are necessary for the growth of human food, animal fodder, fibre and timber crops. Until recently it was assumed that they could endlessly absorb contaminants, but it is now generally accepted that 'loading' by some chemical compounds has become such that it is disrupting the natural functions and productivity of soils. Currently, almost 12 % of World soils have been degraded by chemical deterioration. Additionally, 56 % of World soils have been degraded by water erosion, 28 % by wind erosion, and 4 % by physical degradation (for more details see Oldeman *et al.*, 1991). Since soils form the essential link between the inanimate geosphere and the living biosphere, it is of crucial importance that measures to protect soils from further physical and chemical deterioration be implemented rapidly. In recent years, it is also increasingly recognized that soils and their biota play a significant role in the so-called 'greenhouse effect'. In a recent discussion paper, Greenland (1991) wrote soil scientists must 'provide answers to questions such as what proportion of the greenhouse gases - CO_2, CH_4, N_2O, NO - entering the upper atmosphere are derived from the soil, how the amounts evolved are affected by land use, and how far soils act as a sink for those gases and for gases derived from other sources'. While many of these topics have been the subject of discussion during the international conference on 'Soils and the Greenhouse Effect' (Bouwman, 1990a), as well as other scientific meetings (Bolin *et al.*, 1986; Trabalka *et al.*, 1986; Matson and Ojima, 1990), there remain significant areas of uncertainty in our current knowledge. This applies, for instance, to the chemical, physical and biological processes which control the production and absorption of the respective trace gases in a particular ecosystem, the possible interactions between these processes, and their ultimate effect on the rates and magnitudes of the associated gas fluxes. Additional difficulties are associated with the measurement of trace gas fluxes in the field, and subsequent extrapolation or scaling-up of these values to regional and global scales through modelling (Bouwman, 1990a; Rosswall *et al.*, 1988). Geo-referenced data bases can provide the 'geographic' framework for scaling-up results of flux measurements and fundamental process studies to ecosystems at the global level (Bliss, 1990; IGBP, 1990; Matthews, 1990; Moore III *et al.*, 1989; Oldeman and Sombroek, 1990; Van Breemen and Feijtel, 1990). Hence the need for developing appropriately scaled and compatible data bases of the main environmental resources of relevance to studies of global change, including soils (Sombroek, 1985, 1990; Bouwman, 1990a; Oldeman and Sombroek, 1990).

1.4 Purpose of study

The present booklet originated as a background document for the WISE workshop, which took place in August 1992 (Batjes and Bridges, 1992a). It consists of 6 Chapters, 2 Appendices and a Glossary. Chapter 2 is a review of the physical controls of the balance of heat, water and gases in soils. In Chapter 3 the soil factors and processes that control the production/consumption and net emission of methane in terrestrial ecosystems are reviewed, nitrous oxide is discussed in Chapter 4, and soil organic matter and carbon dioxide in Chapter 5. In the present context, where it is required to compile a map and data base of the geographic quantification of the soil conditions and processes that regulate emissions of 'greenhouse gases' from soils, the predictive use of the Soil Map of the World becomes of significant importance. In the context of the WISE data base, the areas of soil units on the Soil Map of the World are to be used as a cartographic basis for the preparation of the ½ x ½ degree grid data base. For each rectangle of the grid, it is proposed to take the spatially dominant soil units as shown by the map; this is the 'area data'. To each area on the map will be attached, by appropriate descriptors, actual profile data from a representative pit. This is the 'soil point data'. The attributes proposed for consideration in the WISE data base are listed in Chapter 6. The way to proceed in developing the data base and possible methods to refine estimates of methane emissions from

wetland soils have been formulated during the WISE workshop (Wageningen, 24-27 August 1992; Batjes, 1992; Batjes and Bridges, 1992b). The WISE data base is being developed by ISRIC in close cooperation with the Land and Water Development Division of the Food and Agricultural Organization (FAO).

Chapter 2 Soil heat and moisture balance

E.M. Bridges

2.1   Introduction

2.1.1   Background

The current situation concerning the study of the interface between atmospheric and earth sciences is a challenging one. It is an area of study where considerable co-operation is necessary between disciplines to make progress. This will not necessarily be achieved easily, as within the broad generalisations of earth or atmospheric sciences, detailed chemical and physical studies are necessary to fully comprehend the factors and processes involved.

The role of soils in the total problem of the 'greenhouse gases' has tended to be regarded as a minor one and overlooked by atmospheric scientists, but publication of numerous papers, together with the conference proceedings *Soils and the Greenhouse Effect* (Bouwman, 1990a) has drawn the attention of a wider audience to the significance of gaseous emissions from soils. The importance of emissions of gases from soils has now been recognized in the reports of the Intergovernmental Panel on Climate Change (IPCC, 1990 and 1992). Reasonable estimates of the global budgets of CO_2, CH_4 and N_2O are available, but the magnitude of the sources and sinks of these gases, especially with respect to soils, are less well known.

Similarly, the budget of heat received from the sun and that radiated from the earth's surface is well known at a global scale. Recent remote sensing studies have highlighted the significance of emissions at different wavelengths of energy associated with different surfaces, including bare soils and various vegetation covers. Inseparable from the energy budget is the role of water and water vapour. Changes in physical state of water result in the release or absorption of heat into the soil and lower atmosphere.

Soils, with their specific chemical, physical and biological properties, are able to act both as sources and sinks for the major greenhouse gases. It is imperative, therefore, that an awareness is achieved of how the factors and processes which operate within soils influence gaseous emission and absorption in order to fully comprehend the way these processes operate. With this knowledge, it may be possible to influence or even control them should the need arise.

Any understanding of the role of soils in the greenhouse problem must be seen in a dynamic situation. In the long-term, changes of climate are significant for soils, but in the short-term changes in land use have a much greater impact. Drainage of wetlands and oxidation of their accumulated carbon content has been proceeding for many years, so has forest clearance with extensive burning of the residues. There is evidence that both these common practices have increased in the past decade.

Global warming also influences the level of the sea through glacial ice melting and thermal expansion. This may result in flooding of lowlands and an increased area of wetland subject to poor drainage, in which organic accumulation could take place and methanogenesis occur. In other circumstances, increased rainfall in some areas is another 'greenhouse' effect which could result in higher levels of the water table and the development of more extensive gley soils. Elsewhere, higher temperatures may result in increased oxidation of currently stable organic matter, but conversely could also lead to increased plant growth, provided water and nutrients are not limiting.

This review attempts to draw attention to the broad implications of the energy exchanges which occur at the surface of the earth and the movement of moisture which takes place between the soil and the atmosphere. Similar physical constraints must be considered when the potential of soils to absorb and emit gases is assessed. This account does not set out to be a comprehensive discussion of the physics of the soil-atmosphere interface, that is beyond the scope of the present context. However, most textbooks of soil physics contain background material about the physical relationships of heat and moisture exchange (Baver *et al.*, 1972; Hillel, 1980; Van Keulen and Wolf, 1986; Koorevaar *et al.*, 1983; Marshall and Holmes, 1988).

The objective of the WISE programme is to arrive at a geographical quantification of the soil conditions which lead to emissions or absorption of radiatively-active soil gases. The way in which these fluxes are encouraged or prevented by specific soil conditions or characteristics needs to be identified so that these features can be associated with particular soils or areas of the earth's surface. Only then can an adequate data base be constructed and a more accurate estimate of the significance of these gases be obtained.

In the longer term, many advantages are foreseen in the construction of a global soil data base. Global modellers in agriculture, soil science, and climatology all require more accurate knowledge about the soils of the World. A soil data base which will interface with modern systems of data management, such as SOTER (Van Engelen and Pulles, 1991) and Geographical Information Systems offers a new and exciting perspective in the study and management of the World's soils.

2.1.2   Structure of chapter

Information in this Chapter is brought together by first considering the simple physical properties of soils in Section 2.2. This is followed by a discussion of the energy balance of soils in Section 2.3 and the influence this has upon the movement of soil moisture and gases. The basic relationships of rainfall infiltration, percolation and evapotranspiration are given in Section 2.4, and finally a brief discussion of the diffusion of gases into and out of the soil is considered in Section 2.5. The significant factors which should be included in any data base concerning the movement of gases into and out of the soil are listed in Chapter 6.

2.2   **Physical properties of soils**

2.2.1   Soil composition and formation

Soil is composed of four main constituents: mineral and organic matter which together form the solid aggregates, and the pore spaces which are either filled with air or water. The combination of these four constituents, together with a wide range of living organisms, makes soils very varied entities. As is shown in Figure 2.1, the mineral matter of an average fertile topsoil comprises some 45 per cent of the volume of soil, organic matter up to about 5 per cent (except for organic soils) with the soil air and water occupying the other 50 per cent. The components of the soil solid phase, mineral and organic, the gaseous phase and the liquid phase, the soil solution (water), are convenient starting points for a discussion of the physical properties of soils.
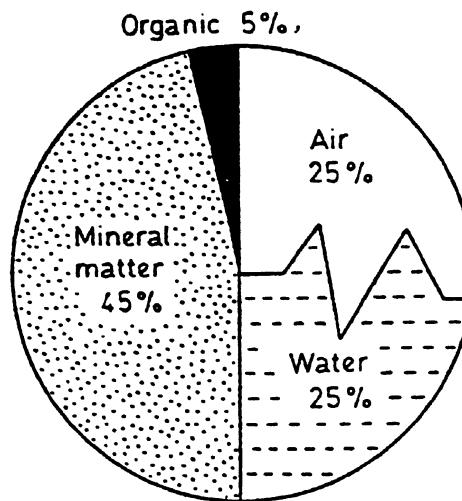
Figure 2.1.   Volumecomposition of a typical topsoil

This may be expressed empirically as:

$$V = S + M + G \tag{1}$$

where:

V = volume of total sample volume (cm^3)

S = volume of soil solids (cm^3)

M = volume of soil moisture (cm^3)

G = volume of soil air (cm^3)

The soil was described many years ago as the 'excited skin of the earth' and in the present context this is a very apt description because soils result from interactions of energy and matter which take place at the earth's surface. Soils lie at the interface between the lithosphere and the atmosphere and are subject to the influences of the factors of the climate and the biosphere, including mankind.

The soil forming factors of climate and organisms are the broad controls over the various processes which take place in soils and contribute to the development of soil profiles. The factors of soil formation were described by Jenny (1941) in his empirical formula:

$$S = f \, (c, \, o, \, r, \, p, \, t, \, ...) \tag{2}$$

where:

S = any soil feature

f = function of specified factors

c = climate

o = organisms

r = relief

p = parent material

t = time

..=   other factors as yet unidentified.

Many soil scientists have long recognized a latitudinal element in the geographical pattern of soils and this is the result of the distribution of solar energy received from the sun. Temperature and rainfall are both included in the climate factor of Jenny's equation. In recent years the effects of mankind have had such an overwhelming influence that an anthropogenic factor has been separated from the plant and animal organisms by some authors (Bidwell and Hole, 1965). Regionally, relief plays a part in soil formation in the range of altitude found in high mountain ranges, but it is also particularly important at the local level. Surface relief and the ground-water table interact in the development of many poorly drained soils. The parent material is very significant for it provides the mineral matter of which soils are formed and the time factor has to be taken into account for the degree of development and maturity of soils. Jenny's approach forms a useful qualitative assessment of soil formation and draws attention to the broad principles which control it. However, the approach has a number of difficulties in its application as the factors, supposedly independent variables, are not as independent as they might seem.

Soils have been described as an open system (Buol *et al.*, 1973) as they exist in a state of dynamic equilibrium (steady state) with flows of energy and matter entering and leaving the system. The gains and losses of the soil system are shown diagrammatically in Figure 2.2.

Seen from above, soils may look uniform and solid, but when a section is visible in a roadside cutting or in a soil inspection pit, the soil can be seen to have a sequence of layers of different colour, texture, structure and further investigation reveals other physical, chemical and biological characteristics as well. These layers of the soil are known as soil horizons and the complete sequence of horizons makes a soil profile.

Soils are identified by their profiles which have a variable number of horizons; these lie approximately parallel to the surface of the earth. Systems of soil classification utilize the different attributes of the horizons to characterize the profiles of soils and place them in logical groupings. This subject is relevant to the present study only in so far as certain chemical and physical attributes of soils may influence the processes which facilitate and control gaseous emissions from soils to the atmosphere. As some of the attributes of soils are utilized for the purposes of classification, in some cases, it is possible to use the classified soils to retrieve features which may be of help for identifying sources and sinks of radiatively-active gases. Their distribution can then be represented cartographically.

Soil horizons with their characteristic features owe their existence to a number of recognized processes of soil formation. These processes operate within the broad parameters set by the factors of soil formation. Soil forming processes may be described as complex 'bundles' of chemical, physical and biological reactions which take place, changing the geological parent material into a recognisable soil. As examples, simple descriptions of some of the more common soil forming processes of the cool humid climates are:

-    leaching which removes soluble constituents, cations of Ca, Mg, Na and K and acidifies soils;
-    podzolization in which clay minerals are broken down and iron, aluminium and organic matter are translocated into the lower horizons of the soil;
-    gleying the development of soil under water-saturated, anaerobic conditions which may be temporary or permanent;

-   organic accumulation including humus incorporation in mineral soils and peat formation in upland and lowland bogs.

The impact and intensity of these processes vary both in space and time, so the resultant pattern of soils on the earth's surface has great geographical variation.
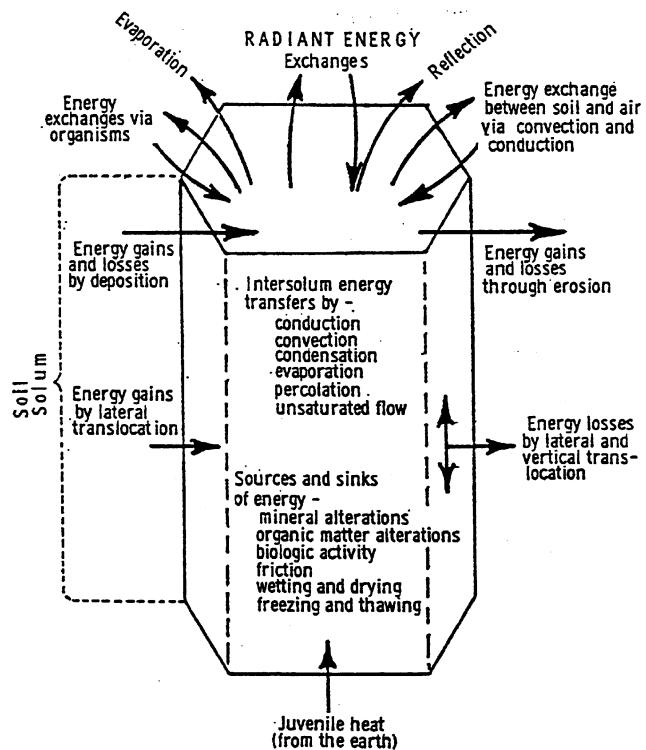
Figure 2.2.   Representation of a soil as an open system (After Buol *et al.*, 1973)

2.2.2   The solid phase of soils

The solid matter of which soils are composed is either mineral or organic material which is present in a wide variety of forms. The processes of soil formation gradually change these mineral and organic constituents into new materials with recognisable soil characteristics. Some new minerals are produced, and organic materials are humified, storing carbon which is eventually decomposed, releasing carbon dioxide and methane into the atmosphere.

The inorganic fraction of soils is composed of a wide range of mineral particles which are derived from the underlying parent material together with any aeolian additions which may have been blown in. The most characteristic feature of the mineral matter is its particle-size distribution, commonly referred to as the texture of the soil. Particle-size is not easily changed and so has been used by many soil scientists as a stable attribute of soils; it is also a good surrogate for many other physical characteristics of soils. Soil texture is assessed from the 'fine earth' which refers to the sand, silt and clay which passes a 2 mm round-hole sieve. Coarser materials, stones, are regarded as 'mineral skeleton' and although physically important for their bulk, do not

play a significant chemical role. Experienced soil surveyors can recognize at least 12 different textures from the various admixtures of sand silt and clay which occur (Figure 2.3).
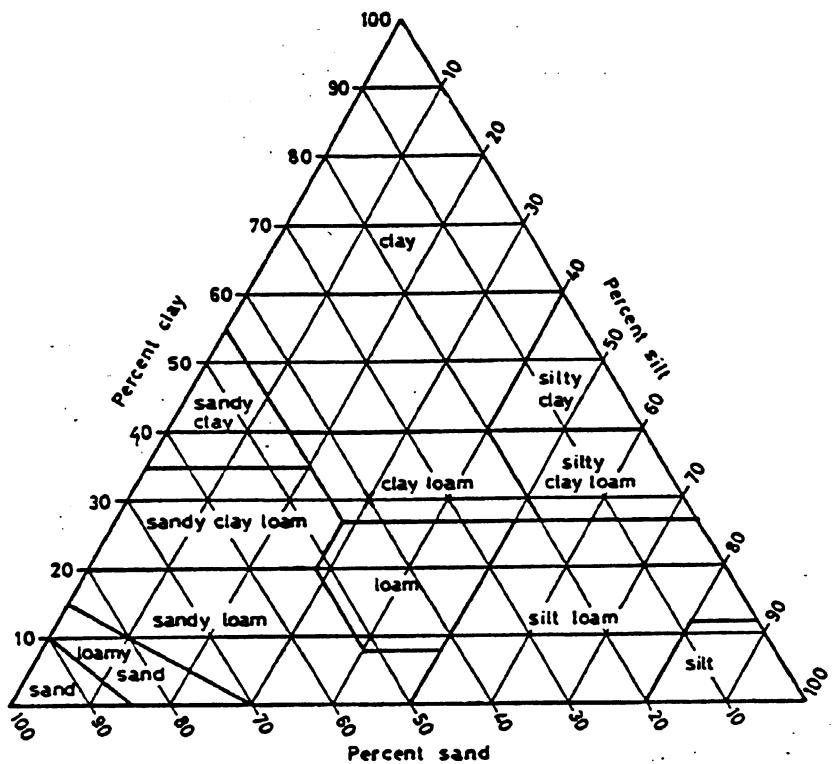
Figure 2.3.   Soil textural classes determined by percentages of sand, silt and clay present (Source: Hodgson, 1978)

Mineral constituents

The mineralogical composition of the particle-size groupings is also different. Usually, sands (2.00 mm - 0.02 μm) are composed of 95 or more per cent of quartz with subsidiary amounts of feldspars, micas, ferromagnesian minerals, iron oxides and other accessory minerals such as zircon, garnet and apatite. Silts (0.02 - 0.002 μm) also are dominated by quartz particles, but the accessory minerals tend to be present in greater quantities. The arbitrary lower limit of silt is taken as 0.002 μm and particles smaller than this are clays. The mineralogy of the clays is in marked contrast to that of the sands and silts, being composed mainly of secondary alumino-silicates, many of which have been formed within the soil. Below 0.001 μm clays assume colloidal properties which introduces further complexity into their behaviour both in physical and chemical terms.

Organic materials

Soil organic matter is a minor but significant component in most soils, normally amounting to less than about 5 per cent, but in the Histosols (organic soils) can be between 30 and 100 per cent of the total composition. Organic matter in freely drained mineral soils is derived from the oxidative breakdown products of plant material which are gradually humified and then subsequently mineralized; only in the saturated conditions

typical of the organic soils is the process of breakdown inhibited by the lack of oxygen and so accumulation of undecomposed, or partly decomposed, plant remains takes place.

The main source of organic matter within soils is the vegetation growing upon them. Leaf litter falls to the ground surface and begins to decay, roots die within the soil and as they decay further organic matter is added. The processes of breakdown are complex involving a succession of soil microfauna and fungi, each of which takes the process of decomposition a stage further. The final result is the production of humus, a dark-coloured, amorphous material containing a variety of organic components. Mixing of this material into the surface horizon is mainly the result of the activity of soil fauna, especially the earthworms.

Soil structure

The term soil structure is used by pedologists for the aggregation of the individual soil particles into larger aggregates, commonly referred to as peds. Peds are soil aggregates bounded by natural surfaces which become apparent when the soil is exposed in a soil pit or exposure. As the face of the soil dries, their clarity is usually enhanced. In the surface layer of agricultural soils, structures would normally result from cultivation practices and are therefore artifacts bounded by fractures, rather than with natural surfaces.

Soil structures are created by the succession of cycles of wetting and drying, the activity of plant roots and soil fauna. As soils dry, desiccation cracks develop, and once formed tend to perpetuate themselves as their surfaces become coated with organic breakdown products (mucilages and gums), as well as clay particles oriented parallel to the structure face.

Soil structures are usually described according to the type, which gives the shape and arrangement of peds; the class, which describes the size and the grade, which expresses the degree of cohesion of the aggregates (Figure 2.4). The degree of aggregation of soils is significant in terms of the soil's ability to transmit liquids and gases through the pore systems (Youngs and Leeds-Harrison, 1990; Ball *et al.*, 1988).
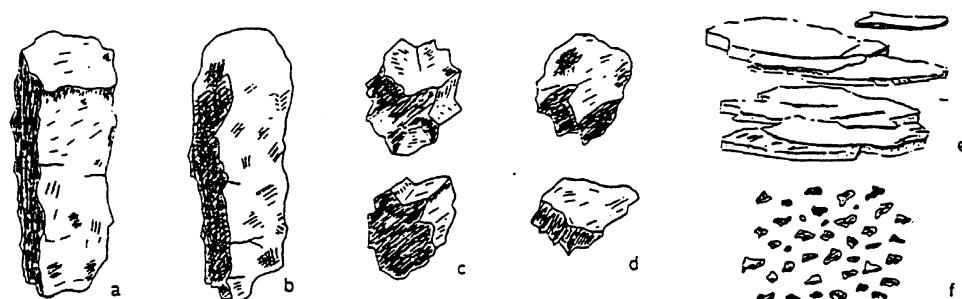
Figure 2.4.   Typical forms of soil structure (Soil structure formed by the aggregation of the sand, silt and clay particles: (a) prismatic; (b) columnar; (c) angular blocky; (e) platy; (f) crumb or granular)

2.2.3 The gaseous and liquid phases of soils

One soil feature which has often been neglected in the past has been the spaces between the structures, normally referred to as pores or voids. These are very important features of soils in the context of the present study as they provide preferential paths for the movement of liquids into soils, and gases between the soil and the atmosphere. Johnson *et al.* (1960), proposed classes of abundance, size, continuity, orientation, distribution and morphology for their description which have been adopted in some form by the soil surveys of many countries. The soil pores are either filled with the soil atmosphere or, if saturated, with the soil solution. However, when the soil is moistened the clays expand and pores become restricted and may even become completely closed.

The total pore space (TPS) of soil is the volume not occupied by soil solids; it may be obtained from the following equation:

$$TPS = (V_t - V_s) / V_t \tag{3}$$

where:

V_t = total sample volume (cm^3)
V_s = volume of solids (cm^3)

The value of the TPS of a soil is largely determined by the bulk density of the sample, the weight per unit volume. The content of organic matter has a significant influence upon the specific density of a soil (mineral matter 2.60 g cm^{-3}, organic matter 1.43 g cm^{-3}) and according to Driessen (1986b, p. 219) may be determined by:

$$SD = 1 / (0.38 + 0.57 \times C_m) \tag{4}$$

where:

C_m = carbon content of the matrix material (g g^{-1}).

The soil voids, the pores and fissures between the solid materials, contain the soil atmosphere and the soil solution. The soil atmosphere differs from the air above in two major respects; normally it is saturated with water vapour and the average content of carbon dioxide may be 10 to 100 times that of the air; it also may contain smaller quantities of other gases such as methane and nitrous oxides (see appropriate chapters). The continuity and width of soil pores is important for the diffusion of gases from the soil into the atmosphere.

In freely drained soils, the amount of the soil solution present depends upon the rainfall or irrigation the soil receives, and so it changes with wetting and drying cycles. The amount of water available for plants, the 'plant available' moisture, is that moisture which lies between the field capacity and wilting point for any particular soil. With poorly drained soils, there may be continual saturation of the soil with pores filled with water to the exclusion of air. The soil solution contains dissolved electrolytes, small quantities of dissolved gases and other water-soluble or water-dispersed compounds. Because the soil solution is the medium from which plants obtain their nutrients, the content and concentration of dissolved substances changes with the time of year, with microbial activity and the amount of rainfall received. When soil pores are filled or partly filled with water the rate of diffusion of gases may be greatly reduced.

2.2.4   Drainage

The drainage of the soil profile is described by the field scientist under the headings of excessively, freely, moderately, imperfectly, poorly and very poorly drained. Allocation of a soil to one or other of these categories is usually done on the basis of colour, particularly the intensity of the mottling and its distribution within the profile. It is assumed that these colour patterns are related to the average drainage conditions over a long period of time. However, the correlation of colours with poor drainage is only partially correct (Hodgson, 1978).

More often than not, these conditions of drainage may be related to the position of a soil on the landscape as Figure 2.5 demonstrates. It is in relief relationships such as these that the soils with poor and very poor drainage lie at the bottom of slopes whereas freely and excessively drained soils occur on the slope or the crest. Soils on the crest and slope will drain rapidly whereas those on the footslopes receive water from upslope and will remain wet for much longer periods. In such conditions, the period of saturated anaerobic conditions may be prolonged and lead to the possibility of methane production.
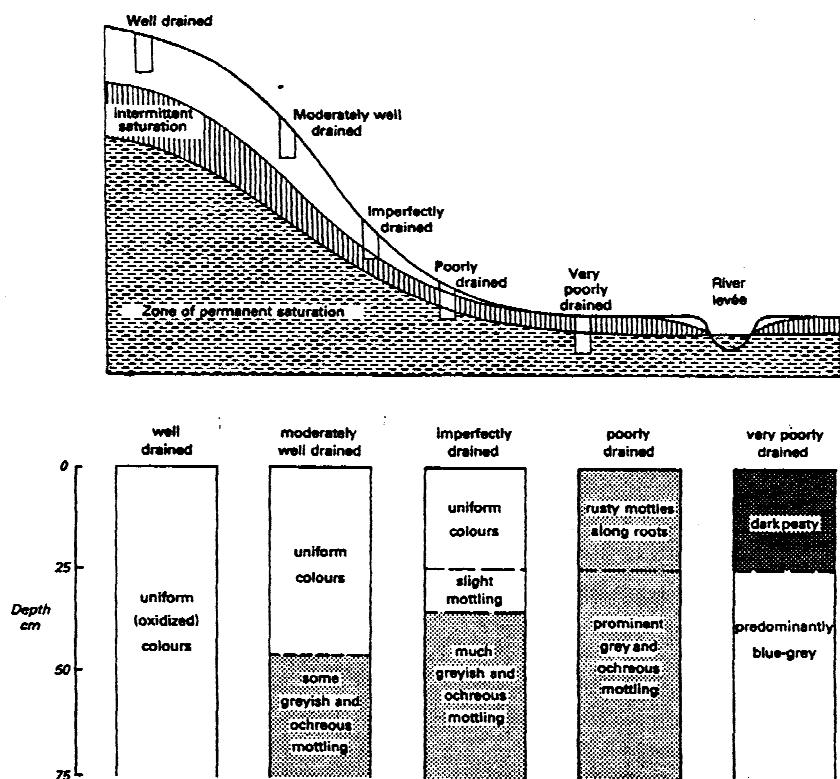
Figure 2.5.   A hydrological sequence of soils in a permeable parent material (From Avery, 1987)

A widespread case of human-induced poor soil drainage conditions is in paddy rice fields. Although paddy fields on some alluvial parent materials may be naturally poorly drained, many paddy fields are only puddled in the surface layers to reduce permeability during the period of growth of the rice plants. After growth of the crop has occurred, the fields are allowed to dry out and aerobic conditions return. Thus, the soils are under a constant cycle of aerobic and anaerobic conditions.

In addition, the paddy field usually has a green crop or weeds ploughed in before the field is flooded and the rice is planted, so microbial activity is encouraged during the period before planting. It is preferable to plant the rice after the first flush of decomposition has occurred when it can grow in a more favourable environment. During the flooded period the more important processes taking place include generation of carbon dioxide, methane, hydrogen and ammonia, as well as the reduction of nitrate, iron and manganese oxides, and sulphates (Ponnamperuma, 1964).

2.3   Factors controlling the energy balance of soils

2.3.1   Introduction

Virtually all of the heat energy utilized in the soil is acquired from the radiant energy of the sun. Theoretically, there is a small outflow of energy from the deeper layers of the earth, but in practice this may be discounted. Energy arrives at the outer part of the atmosphere as short-wave solar radiation centred on a waveband of 0.5 μm, and it has been estimated that only 0.002 % of the total radiation emitted by the sun is received by the earth. The amount of energy which is received at the outer reaches of the atmosphere, the solar constant, is $8.36 \, J \, m^{-2} \, yr^{-1}$ ($2.0 \, cal \, cm^{-2}$ minute or Langleys/minute) (Hillel, 1980). Reflection, scattering and absorption greatly reduces the amount of radiation which penetrates the atmosphere and eventually reaches the earth's surface. According to Phillipson (1966), in mid-latitudes this amounts to $1.96 \times 10^9 \, kJ$ ($4.7 \times 10^8 \, kcal \, m^{-2} \, yr^{-1}$).

A clear atmosphere is fairly transparent to incoming short-wave radiation and on a global scale this accounts for some 48 % of which 9 % is absorbed in passing through the atmosphere, 9 % is reflected back into space, and 6 % is down-scattered, leaving 24 % to reach the surface (Figure 2.6). Fifty-two per cent encounters clouds which absorb 10 per cent, another 25 % are reflected back into space leaving 17 % to pass through to the ground surface. On the average, 34 % is reflected back into space, 19 % is absorbed into the atmosphere and only 47 per cent, (24 + 17 + 6) is received at the earth's surface.
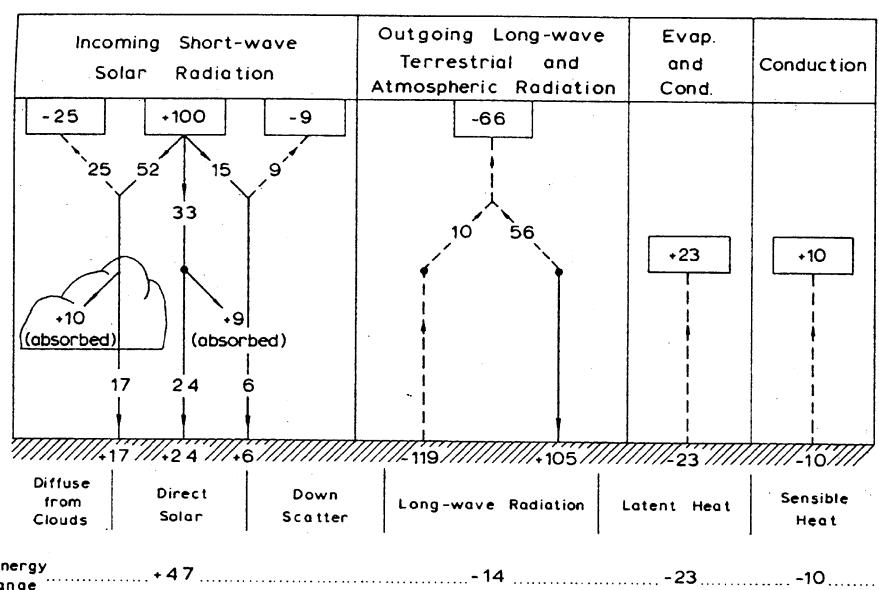
Figure 2.6.   The mean energy exchange between earth and atmosphere (After Watts, 1971)

In order to conform to the First Law of Thermodynamics, this receipt of energy must be balanced by losses otherwise the surface of the earth and the atmosphere would steadily increase in temperature. The balance of energy received and lost is completed by a net loss of 14 % from the energy circulating between the atmosphere and the earth, 23 % are lost through latent heat as water vapour is evaporated and condensed and conduction results in a loss of another 10 per cent (14 + 23 + 10 %), equalling those gained.

The net radiation received by the soil surface may be determined by a radiometer or, in theory, it can be estimated simply from meteorological data using the equation:

$$H = E + (Q_a + Q_s) \qquad\qquad (5)$$

in which:

E = heat used for evaporation of water from soil and crop

Q = heat lost to surroundings (Q_a to the air and Q_s to the soil).

The net effect of the greenhouse gases on the energy balance is that they absorb some of the incoming short-wave radiation and outgoing radiation. Of the outgoing emission of 390 W m^{-2}, only 8 per cent is lost to space, the rest being retained in the atmosphere. Without the presence of the greenhouse gases, the amount of outgoing radiation would be 236 W m^{-2}. Most of the retention, 154 W m^{-2}, is caused by water vapour (100 W m^{-2}) and carbon dioxide (50 W m^{-2}), which leaves only a small contribution from the remaining gases.

2.3.2 Radiant energy at the earth's surface

Energy is lost from the atmosphere and the soil surface in the form of longwave radiation, centred upon 10 μm, with a range of 4-40 μm. At this wavelength the energy is less penetrating and is reflected and absorbed by clouds, water vapour and other greenhouse gases in the atmosphere. Losses and gains of heat energy occur through evaporation, an endothermic process, and condensation, an exothermic process. In appropriate situations, changes of state between freezing and thawing also take up and release latent heat. Evaporation may take place from the bare soil surface alone, or from both soil and vegetation surfaces. This process requires energy, and so the flux of water vapour from either soil or vegetation surfaces is closely associated with transfers of latent heat. There is also a transfer downwards of sensible heat into the soil. In dry soils this is a slow and inefficient process as the points of contact between soil particles are small, but as the moisture content of the soil increases, the water is a better conductor of heat than the soil materials, and a maximum conduction value is reached when water saturates the soil. The lowest layers of the atmosphere are also warmed by contact with a warm soil. The amount of heat stored in the vegetation is negligible compared with storage in the soil (Tanner, 1960).

The balance between incoming and outgoing energy at the soil surface is described by Marshall and Holmes (1988) using the equation:

$$(1-\alpha)R_s = R_l + G + H + \lambda E \qquad\qquad (6)$$

where:

R_s = shortwave radiation

α = reflection of surface

R_l = longwave radiation

G = flux of heat to the ground

H = flux of heat to the air

λE = latent heat consumed by evaporation

This equation may be re-written:

$$R_n = S(1-\alpha) + L_n \tag{7}$$

where:

R_n = net radiation

α = reflection co-efficient

$S(1-\alpha)$ is the short wave radiation energy absorbed

L_n = net longwave radiation (L_i - L_o; L_i is inward, and L_o is outward longwave radiation)

The net radiation is an important parameter as it is the amount of energy available at the ground surface to drive the processes of soil formation, photosynthesis and crop growth, air heating and evapotranspiration. Figures for Rothamsted, England, indicate that 80 per cent of the incoming radiation is absorbed and 30 per cent re-radiated as long wave radiation (Gregory, 1988).

2.3.3   Albedo

Critical factors in the energy balance are the physical characteristics of the soil surface, for these influence the amount of solar energy which is available for conversion into heat. These factors are combined into the albedo, which may be defined as the ratio of the outgoing to incoming radiative flux (Bolle, 1990). The value of the albedo varies according to the angle of incidence, the higher the sun in the sky, the lower the albedo. Thus, as latitude increases towards the poles, the albedo becomes more significant as the angle of incidence becomes more acute. However, individual sites may offset this effect to some extent if the slope is sun-facing.

Where bare soils are concerned, 10-30 % of incident solar radiation is reflected; the albedo of some different soil materials in comparison with snow are:

dry soil   0.25 - 0.45
dry sand   0.30 - 0.40
moist soil   0.10 - 0.15
peat   0.05 - 0.15
snow   0.80 - 0.95

The structure of the vegetation also is a significant complicating factor as the angle of disposition of the leaves to incoming light influences the direction of reflection which occurs. A change in land use or deforestation would significantly change the albedo (Henderson-Sellers *et al.*, 1988).

Previously, it was stated that it was possible to determine the amount of net radiation (Penman, 1948). In practice, this is not a simple problem as it is difficult to partition λE, which is involved in both energy and water movement. Penman also showed that the radiation R_n and L_n can be calculated with sufficient accuracy from standard meteorological data. This he accomplished using the relationships:

$$R = R_T(a_1 + 0.62n/N) \tag{8}$$

and

$$Ln = \sigma T^4 (0.47 - 0.065\sqrt{e_d})(0.17 + 0.83n/N) \tag{9}$$

in which R is the incident short wave radiation and R_T is the incoming solar radiation if the atmosphere was completely transparent. This can be calculated from the solar constant, latitude and the time of the year. σ represents the Stefan-Boltzman constant (5.67×10^{-8} W m^{-2} K^{-4}) and T is the temperature of the absorbing surface and e_d the vapour pressure of water in air in mbar and a_l a constant dependent upon latitude (Gregory, 1988).

2.3.4 Soil temperature change

The rate at which soil temperature changes occur will depend upon the heat flux into and out of the soil. In turn, the flux of heat depends upon the temperature gradient and the soil's thermal capacity and conductivity. The position is complicated by the diurnal and annual rhythm and by the lack of homogeneity of soils. Heat energy received during the day is released during the night into the lower atmosphere. Seasonally, the shortwave energy provides a surplus during the spring and summer, a situation which is balanced by losses in autumn and winter.

The flux of sensible heat at the earth's surface may be described by the equation:

$$H = -K_H d(\rho C_p T)/dz, \tag{10}$$

where:

T	=	temperature at height z
K_H =		a transfer coefficient dependent upon the horizontal wind velocity, aerodynamic roughness of the land surface, height of measurement and stability of the atmosphere
ρ	=	density of the air
C_p	=	heat capacity at constant pressure.

As the density of the air and the heat capacity at constant pressure are substantially constant (Marshall and Holmes, 1988), the equation becomes:

$$H = -K_H \rho C_p dT/dz. \tag{11}$$

Heat flux into the soil is conductive, and the rate which a soil warms depends upon its heat capacity (specific heat $\times$ mass). As the specific heat (the calories required to raise one gram of a substance 1° C) is known for soil constituents (see Table 2.1), the heat capacity of soils may be calculated, according to Baver *et al.* (1972), from:

$$Cs = 0.46x_m + 0.60x_o + x_w \tag{12}$$

where:

Cs is the heat capacity of the soil, and
x_m, x_o and x_w are the volume fractions of the mineral and organic matter and water, respectively.

Table 2.1.   Specific heat and heat capacity of soil materials (Kohnke, 1982).

Material	Specific heat $J\ g^{-1}$ (cal g^{-1})	Heat capacity $J\ cm^{-3}$ (cal cm^{-3})
Humus	1.67 (0.4)	2.34 (0.56)
Water	4.18 (1.0)	4.18 (1.00)
Ice	2.09 (0.5)	1.92 (0.46)
Air	1.04 (0.25)	1.25 (0.30)
Clay	0.92 (0.22)	2.09 (0.50)
Quartz	0.79 (0.19)	2.09 (0.50)
$CaCO_3$	0.84 (0.20)	2.25 (0.54)

The thermal conductivity of a soil (its ability to transfer heat) is dependent upon its content of air and water, but also on its state of compaction. Thermal conductivity is greatest in wet compact soils (Moench and Evans, 1970). Thermal conductivities of common materials are: air 0.5×10^{-4}, dry soil $3\text{-}5 \times 10^{-4}$, snow 3.9×10^{-4}, moist soil $20\text{-}40 \times 10^{-4}$ and depending on temperature, water $13\text{-}14 \times 10^{-4}$ calories s^{-1} cm^{-2} per °C change in temperature.

The rate of change in temperature of a soil body at a given depth is the result of the flux of heat and the thermal capacity (the amount of heat required to change the temperature of a given mass of soil) by:

$$dT/dt = kd^2T/\rho cdz^2 \tag{13}$$

where:

ρ = soil density
c = specific heat capacity
k = thermal conductivity
$k/\rho c$ = thermal diffusivity

Dampening of the daily and annual temperature fluctuations in soil is controlled by thermal diffusivity. The observed decrease in amplitude with depth is described by the expression:

$$e^{-zw/2D} \tag{14}$$

where:

z = depth in cm
w = angular velocity of the daily/annual cycle (and equals $2\pi/t$ radians sec^{-1} where t
   is the number of seconds in a day or year)
D = the thermal diffusivity of the soil.

At a depth of $z = \sqrt{2D/W}$, the amplitude of the temperature wave is e^{-1} or 0.37 times the amplitude at the surface; this is referred to as the 'dampening depth'.
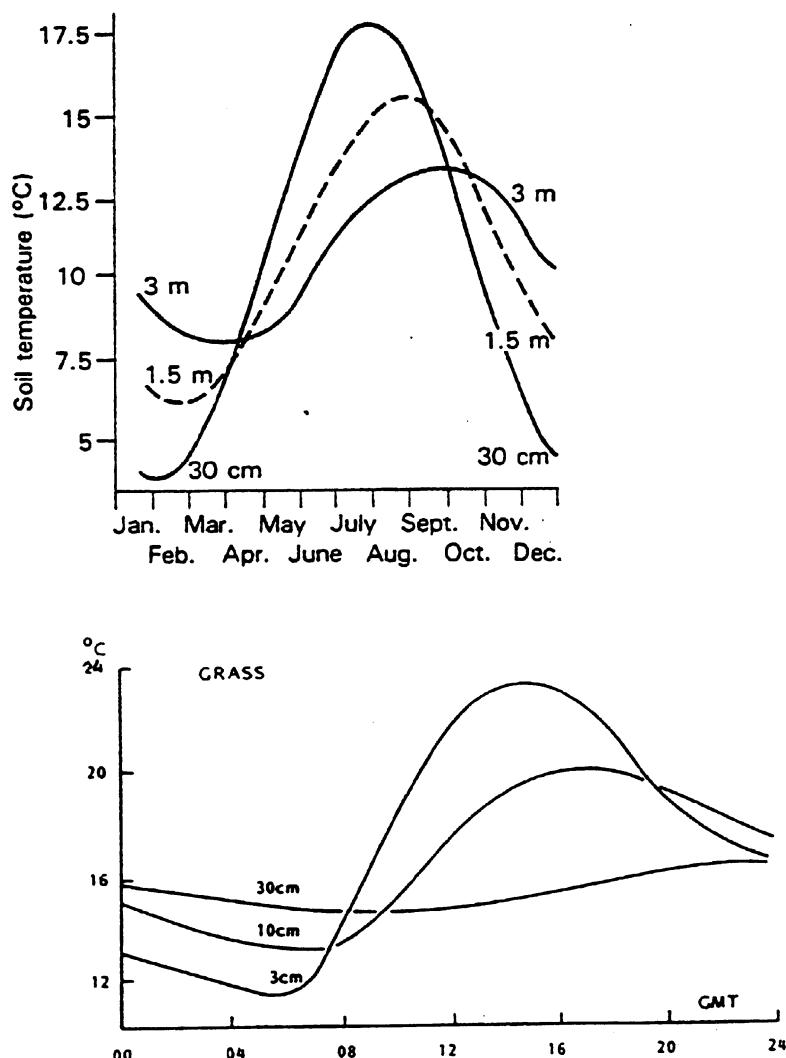
Figure 2.7.   (A) Annual variation of soil temperature with depth under short grass, Oxford (Payne and Gregory, 1988); (B)The daily range of soil temperature at three depths under grass at Berner's Heath, Thetford, 11 August, 1981 (Oliver *et al*, 1987).

In an unsaturated soil with a temperature gradient, water evaporates in the warmer horizons and diffuses, as water vapour, to cooler horizons where condensation occurs. This transfer of water vapour also transfers heat as it is absorbed in the process of evaporation and released in condensation.

The soil temperature is influenced by the presence of moisture, but this is not a straight-forward relationship as the surface dries first and this influences the albedo and also the rate of evaporation of water vapour. The dampening effect referred to previously means that in most soils there is little temperature variation below 10 cm caused by moisture content. Camillo (1989) has attempted to estimate the surface temperature of soils for remote sensing purposes from subsurface temperature values using Fourier series and Wolf and Rogowski (1991), in studying the distribution of heat flux and growing degree days, comment on the influence soil heat flux has on the mineralisation of carbon and nitrogen and the potential for pollution caused by the latter.

On the soil surface, the presence of vegetation, plant debris or mulches reduces the diurnal range of temperature fluctuation by the insulating effect of a layer of trapped, still air. Under a canopy of trees all shortwave radiation will be intercepted, leaving only reflected longwave radiation to reach the soil surface. Emitted longwave radiation from the soil surface will be absorbed and reflected by the canopy. Thus, above a crop or forest canopy, the air temperature will be lower than the surface soil temperature on a clear night, whereas over a bare soil the air temperature will be the same as that of the soil. During the day, air temperatures may be higher than soil surface temperatures as sensible heat is dissipated into the atmosphere. In winter, different forms of vegetation cover influence the impact of frost and the depth to which it penetrates. In tropical regions, shade trees or mulches are necessary to maintain equable soil temperatures and moisture content for active root growth (Horton, 1989).

2.3.5 Sensible and latent heat

The flux of sensible and latent heat from the soil or plant foliage involves the transfer of warm humid air into the lower layers of the atmosphere as a result of gradients of temperature and vapour pressure. When the soil surface is moist, most of the net radiation received is absorbed and used to evaporate water, but as the soil dries, an increasing amount of energy is dissipated as sensible heat to the air or to the deeper layers of the soil.

Values for these heat fluxes may be obtained by averaging values in the following equations:

$$C \quad = \quad -\rho c_p K_h \, \vartheta T/\vartheta z \tag{15}$$

and

$$\lambda E \quad = \quad \frac{-\rho c_p}{\gamma} K_v \vartheta e/\vartheta z \tag{16}$$

where:

ρ	=	density of air
c_p	=	specific heat capacity of air at constant pressure
λ	=	heat of vaporisation of water (2.453×10^6 J kg^{-1})
γ	=	psychromatic constant (ratio $\rho c_p / 0.622$)
p	=	total air pressure.

The ratio of sensible heat to latent heat transfer is the Bowen ratio σ, (see equation 9), and after some simplification for still air conditions, it can be written:

$$\sigma \quad = \quad g(T_o - T_a) / (e_o - e_a) \tag{17}$$

where:

T_o	=	mean air temperature
T_a	=	mean air temperature at height z above the surface
e_o	=	vapour pressure
e_a	=	vapour pressure at height z above the surface.

Comparisons with measurements from lysimeters show that there is good accordance with calculations using the Bowen ratio.

Returning to the energy balance equation (6), it may be re-written, omitting the symbols for energy retained by the surface and energy stored during photosynthesis, which are unnecessary for a bare soil:

$$R_n - G = C - \lambda E \tag{18}$$

where:

   R_n = net radiation
   G = heat energy conducted to warm materials below the surface
   C = energy used to warm the air
   λ = latent heat of vapourisation
   E = evaporation

Present-day analysis of these problems utilizes resistance nomenclature and in this format the two elements C and LE may be re-written as

$$C = \frac{\rho c \ (T - T_a)}{r_h} \tag{19}$$

and

$$\lambda E = \frac{\rho c_p}{\lambda} \ \frac{(e_{so} - e_a)}{r_v} \tag{20}$$

where:

   ρc_p = volumetric specific heat capacity of air
   T_o = surface temperature
   e_{so} = surface vapour pressure
   T_a = temperature at a reference height in the air
   e_a = vapour pressure at a reference height in the air
   r_h = resistance to sensible heat convection between the wet surface and the air at reference height.
   r_v = resistance to vapour transfer respectively between the wet surface and the air at reference height.

2.3.6   Relationships of heat and evaporation

The process of evaporation may be represented quantitatively with reference to the radiant heat energy received and the amount of sensible heat lost to the atmosphere or as latent heat to the soil. Berkhout and Van Keulen (1986) show how these factors are related. First concerning the relationship of heat loss caused by evaporation:

$$R_N = H + LE \tag{21}$$

where:

   R_N = net radiation
   H = sensible heat loss

E   = rate of water loss from the surface

LE = evaporative heat loss

Secondly the loss of sensible heat to the surrounding atmosphere and soil can be represented by:

$$H = h_u(T_s - T_a) \tag{22}$$

where:

H   = sensible heat loss

h_u = sensible heat transfer coefficient

T_s = temperature of the evaporating surface

T_a = temperature at standard screen height.

The sensible heat transfer coefficient h_u is dependent upon the turbulence of the atmosphere and may be expressed:

$$h_u = a_u(1 + b_u\bar{u}) \tag{23}$$

where:

$\bar{u}$ = mean wind velocity

a_u = empirical constant (circa 6.4×10^5 J m^{-2} d^{-1} °C^{-1})

b_u = empirical constant (circa 0.54 s m^{-1})

A water surface loses water vapour in proportion to the vapour pressure difference between the surface and the overlying air. This may be represented by:

$$E = k_u(e_s - e_a) \tag{24}$$

where:

E   = rate of water vapour loss

k_u = the vapour transfer coefficient

e_s = surface vapour pressure

e_a = vapour at screen height

Both the exchange of sensible and evaporative heat are controlled by processes of diffusion and turbulence in the atmosphere. These may be related by Bowen's ratio in which the psychrometer constant:

$$\gamma = h_u k_u^{-1} L^{-1} \tag{25}$$

has a value of approximately 0.66.

A wet soil surface or a grass-covered surface having sufficient water supplied to it, gives a Bowen ratio (σ) = 0 to 0.2; as the surface dries, σ becomes larger because the proportion of sensible heat increases. In arid conditions, the ratio becomes negative as energy is extracted from the air to evaporate water. Henning (1989) provides maps showing the world distribution of the Bowen ratio. It is relevant to note that Penman (1948)

developed an equation which described evaporation in terms of radiation, saturation deficit, temperature and diffusion resistances. He linearized the relationship between the saturated vapour pressure and the temperature of the air to estimate the vapour pressure difference between the saturated surface and the air (e_{so} - e_a) from temperature differences and saturation deficit (e_{sa} - e_a). This enabled him to propose the equation:

$$e_{so} - e_a = (e_{sa} - e_a) + \Delta(T_o - T_a) \qquad (26)$$

where:

Δ is the slope of the vapour pressure curve at $(T_o - T_a)/2$

after which (e_{so} - e_a) is eliminated using equation 15 to give the Penman equation:

$$\lambda E = \frac{\Delta (R_n - G) + (\rho c_p (e_{sa} - e_a)/r_h)}{\Delta + \gamma (r_v / r_h)} \qquad (27)$$

Subsequently, Monteith (1965, 1973) combined the energy balance and vapour heat transfers to give the Penman-Monteith version of the equation which is a widely used and physically realistic model (Oliver, 1983). It may be expressed for crops as:

$$\lambda E = \frac{\Delta R_n + (\rho c_p (e_{sa} - e_a)/r_h)}{\Delta + \gamma (r_v + r_c)/r_h} \qquad (28)$$

where:

r_h = the 'aerodynamic' resistance to the diffusion of water vapour from the surface to a level above the crop.

r_c = the 'surface' resistance to water vapour flow from within the leaf to the surface where evaporation takes place.

The canopy resistance, r_c, depends upon the amount of stomatal opening, except when the leaves are wet with dew, rain or irrigation water when it is close to zero. The value of r_c lies between 0.3 and 0.5 s cm^{-1} for many crops when well supplied with water and the leaves are dry (Gregory, 1988).

2.4   Factors controlling water in the soil system

2.4.1   Introduction

Brotherton (1990) referred to water vapour as the most significant greenhouse gas, but water droplets in the form of clouds also exert a great influence upon the absorption and reflectivity of the atmosphere. However, it must not be overlooked that changes in land use strongly influence the character of the land surface, and with it the albedo and physical characteristics controlling the movement of water between soil, vegetation and the atmosphere. For example, where tropical forests have been removed, evaporation is reduced, and a cloud cover does not form so readily.

It is clear that there is a continuum of movement of water through the soil-plant-atmosphere system. Within the soil, lateral movement of water is controlled by gravity and a gradient of matric potential, but in plants osmotic potential also strongly influences water movement. Analogies have been made of the flow being similar to that of an electric current so that the water flux equals the difference in water potential divided by the resistance to flow.

In unsaturated soils, water is held in thin films on soil particle or pore surfaces by forces which resist the downward pull of gravity. As the soil dries, it becomes held increasingly tightly by these forces. Thus to obtain water from the soil greater amounts of energy must be used to extract it; consequently, it is convenient to use energy relationships to describe the situation which prevails.

Most soil survey reports contain information upon soil moisture contents in the form of gravimetric measurements (W/W %), or if volume and bulk density were considered, upon a volumetric basis (V/V %). Another common method is to report soil moisture contents as a function of the pF, the negative pressure retaining water in the soil against the pull of a column of water, expressed on a logarithmic scale. Increasingly in recent years, soil moisture contents are being reported in terms of the energy differences resulting from the attractive forces between the soil solids and water in the soil, collectively referred to as matric potential (ψ). Undisturbed moisture contents may be determined using a neutron probe. Using the figures obtained by either method, the amount of available water capacity (AWC) for the profile may be calculated. Gregson *et al.* (1987), examine the relationship between the soil water content and the soil water potential, otherwise known as the soil moisture characteristic and indicate that it may be simply determined from one paired measurement of soil water content against matric potential.

2.4.2   Infiltration

Water enters the soil system as a result of rain, irrigation or seepage. Excluding the meteorological processes of raindrop formation and their fall through the atmosphere, entry of water into the soil is subject to two limiting factors; the infiltration capacity and the permeability of the soil. Both infiltration and permeability may vary in time because of the interaction of water with the soil, particularly the clay fraction.

Raindrops vary in size according to the intensity of a rainstorm. A light rain, the drops of which might typically be 1 mm in diameter has an impact velocity of 3.8 m s^{-1}, but in a heavy rainstorm, drop size may increase to 4.5 mm diameter and have a terminal velocity of 9.0 m s^{-1}. The greater size and rate of fall provides approximately 500 times the kinetic energy and 200 times the momentum of the smaller drops. Davies and Payne (1988) quote an example of a storm of 5 cm h^{-1} which dissipates energy at the rate of 5.6 kW ha^{-1}. A small increase to 7.5 cm h^{-1} raises the energy dissipated by a factor of 100 to 520 kW ha^{-1} (Sharma *et al.*, 1991).

Impact of raindrops upon a bare soil surface may cause disruption of surface structures into their constituent sand, silt, clay and organic components. Subsequently, these individual particles are transported a short distance away from where they originated and are deposited, blocking pores and reducing the rate of infiltration. Very permeable soils have infiltration rates up to 0.1 mm s^{-1} but soils of low permeability have rates of 10^{-4} mm s^{-1} which approximates to a range between 10 m d^{-1} and 10 mm d^{-1} (Payne, 1988). The rate of infiltration as measured under field conditions usually shows a steep decline following the application of water to the soil surface, and approaches the saturated hydraulic conductivity.

Clods produced by cultivation may also shatter on wetting as swelling of clays causes further disruption of an already fractured soil structure. Whether dispersed by impact or by disruption, the individual soil particles are then available for transport. This may be restricted to a few millimetres in which case redeposition may block pores and greatly reduce infiltration. This phenomenon is sometimes referred to as 'capping'. As this is most likely to occur during heavy rainstorms, the restriction of infiltration is serious as a greater proportion of the rainfall is diverted to overland flow and may cause erosion.

Below the surface horizon, wetting of the subsoil results in expansion of the clays which also restrict the size of pores. Closing of cracks is most marked in Vertisols with a large proportion of smectite-type clays. However, swelling also occurs to a lesser extent in other clays, reducing the permeability of saturated soils and leading to the formation of gley phenomena.

2.4.3   Water movement within soils

The concept of field capacity (water held in the soil after any excess has drained away following heavy rain or irrigation) represents an upper limit of plant available water in freely drained soils. The wilting point (the moisture content of the soil at which leaves of plants growing in the soil first reached a stage when they did not recover when placed in a saturated atmosphere without addition of water to the soil) represents the lower limit of available moisture. As all plants do not respond in the same way, these figures can only give an approximation of the plant available water in soils. In more recent years, suction figures of 5 kPa (-0.05 bar) and 1.5 MPa (-15 bar) have been used to define these limits (Gregory, 1988) but experimental work has shown wide variation of these limits in different soils.

Clay content accounts for most of the variation observed, but organic matter is also involved and is responsible for at least part of the water-holding capacity, particularly in coarse-textured soils. Loamy soils containing appreciable contents of silt can hold the greatest quantity of available water; however the concept of plant-available water is an equilibrium concept and cannot be an exact part of soil science (Gregory, 1988).

Water is present in the inter-connecting system of fissures and pores which surround and penetrate the peds of a soil. In the larger pores and fissures, water may flow freely under the influence of gravity, but in the finer pores the influence of capillarity is more significant. This led in the 1930s to a tripartite division of soil water into gravitational, capillary and structural components of soil water. Subsequently, these approximations of the soil water content have been superseded by moisture contents defined in terms of the matric suction.

Water moves through soils in response to differences in gravity, matric potential and temperature. In the case of gravity flow, it drains from the larger pores until the water films which remain become sufficiently thin for the tension holding the water to be greater than the pull of gravity. At this point, and particularly when the films of water become discontinuous, obvious flow of soil water ceases, but some movement still occurs in the finer pores. However, the pores of soils are not parallel-sided capillaries, so constrictions and bubbles of entrapped air may reduce the flow of water substantially before all the potentially available moisture has been moved.

Movement of water in response to a difference in matric potential implies that water is able to move in response to the tendency to equalize that potential. The rate of movement is proportional to the gradient of the potential and the hydraulic conductivity of the soil. The relationship is demonstrated by Darcy's Law:

$$\frac{dQ}{dt} = -K\frac{d\psi}{dl} \tag{29}$$

where:

dQ/dt is the flow rate across an area perpendicular to the direction of flow.

dψ/dl is the gradient of the potential expressed as a head of water.

K is the hydraulic conductivity of the soil.

Previously, it has been stated that the maximum values of hydraulic conductivity occur in a saturated soil where all pores are transmitting water. In unsaturated conditions it has proved practically convenient (although not physically correct) to treat water movement in soils as a diffusion process down a concentration gradient. If water diffusibility is defined as the product of conductivity and the rate of change of suction with water content, c, then the flow equation may be re-written:

dQ/dt = -Ddc/dl   (30)

which expresses the movement of water as a diffusion coefficient (the product of water diffusivity and the gradient of water concentration).

Darcy's equation has to be modified for flow through unsaturated soils both for vertical as well as horizontal movements as is demonstrated by Marshall and Holmes (1988). Further complications are introduced by the (generally) isotropic nature of soil profiles. However, Vereecken *et al.* (1989) describe how it is possible to obtain a measure of the hydraulic conductivity from easily measured soil properties.

Thirdly water movement may occur in soils under the influence of a temperature gradient. A gradient in temperature will cause water to move through the soils in the vapour phase. It moves from hot regions to cold regions of the soil. Heating of the soil surface during daytime causes water to migrate as vapour into lower horizons as well as evaporate into the atmosphere. At night time the soil surface cools below that of the subsurface horizons and a reverse movement of water vapour can be observed in Australia (Rose, 1968, quoted by Payne, 1988).

Vapour movement also occurs in soils subject to freezing. Water is effectively removed from circulation in the soil when it is converted to ice. As freezing occurs, water and water vapour are drawn from other areas of the soil and added to the ice body. Where temperatures fall slowly the tension which holds water to clays prevents it from freezing, but it is gradually overcome and so the water moves to the growing ice mass.

2.4.4   Subsoil water movement

The net movement of moisture in humid climates is downwards under gravity, but in arid or seasonally arid climates the matric suction (ψ) may be greater and water is drawn upwards from the groundwater. This movement is normally referred to as the capillary rise; the water being drawn upwards to the point where gravity and the soil matric suction are in balance. The upper limit of the capillary fringe is referred to as the piezometric surface, the level of which may be measured in dip wells, except for those situations when the piezometric surface is above soil level.

The vertical distance of capillary movement for different matric potentials and soil texture classes have been prepared by Rijtema and are reproduced by Driessen (1986). He presents equations for low- and high- suction ranges to calculate capillary rise:

$$CR = \frac{k_0 \cdot (e^{-\alpha \cdot \psi} - e^{-\alpha \cdot (z_t - RD)})}{e^{-\alpha \cdot (z_t - RD)} - 1}, \; if \; \psi \leq \psi_{max} \tag{31}$$

and

$$CR = k\psi \cdot \left(\frac{\psi}{\Delta(z_t - RD)} - 1\right) \tag{32}$$

where

ψ is the mean suction in the increment $\Delta(z_t - RD)$, and

$k\psi$ is the hydraulic conductivity expressed in terms of a texture-specific suction limit and a texture-specific constant.

With the value of the matric suction lower than the value of the pull of gravity, soil water movement is downwards as percolation. This water, moving down in response to gravity is that water which has escaped evaporation, and absorption by roots. It may eventually reach the water table and rejoin the wider circulation of water in the hydrological cycle.

2.5   Gaseous movement in soils

2.5.1   Introduction

The movement of oxygen, carbon dioxide, water vapour and other gases between soils and the atmosphere takes place through the continuous pore spaces extending from the deeper horizons to the soil surface. In a simple situation, diffusion occurs as a result of differences in specific gas concentrations, but when the movement of soil gases is considered there are several complicating factors. Pores are of variable width and water may be trapped by constrictions in otherwise broad pores. Changes in atmospheric pressure and temperature cause expansion and contraction in the volume of the soil atmosphere resulting in displacement to the atmosphere. Some ventilation may occur through the gustiness of the wind and rainwater seeping downwards can displace air below the wetting front (Grismer, 1988). However, since the earlier years of the 20th century, diffusion has been seen as the most significant process involved in soil gaseous movements and this position is still supported at the present day (Van Bavel, 1952; Payne and Gregory, 1988).

2.5.2 Diffusion

The relationship between the rate of diffusion of a gas in soil (D) to that of a gas in the open atmosphere (D_o) can be represented, as a first approximation, by the expression $D/D_o = 0.6S$, where S is the proportion of the soil volume occupied by air. Currie (1960 and, 1965) modified this statement to improve the representation of the soil structure and moisture content (a) to $D/D_o = aS$. By the introduction of a tortuosity and a shape factor into the equation the differences in rates of diffusion between well- and poorly-structured soils were more accurately quantified. The same author's experiences investigating within-crumb and between-crumb rates of diffusion came to the conclusion that the within-crumb diffusion rate is about one-fifth of that between the crumbs.

Different gases will diffuse at different rates through different media. Oxygen, for example, will diffuse more rapidly through a 1 m column of air than through a 1 mm water film. Although the physical fluxes can be measured, they are complicated by microbial activity, both for generating and absorbing gases. However, the significance of structure and an adequately drained soil for gaseous movement is evident. The position is further complicated in that there may be small areas of anaerobic conditions in an otherwise freely drained soil. This condition is often revealed by the presence of a mottled colour pattern, and the waters of which may contain virtually no oxygen, only carbon dioxide and nitrogen.

The oxygen demand of soils is stated by Payne and Gregory (1988) to be unusually large, compared with the amount of oxygen present in the soil. They claim that if a soil using 7 g m^{-2} d^{-1} was sealed, and all the use of oxygen took place in the upper 25 cm and the soil air contains 20 per cent by volume oxygen, the soil's oxygen supply would only last about 2 days. The same authors refer to the crusting phenomenon encountered in certain soils, commenting that research has shown that, even in these soils, there are sufficient cracks and holes, which together with air turbulence, are sufficient to maintain a satisfactory oxygen concentration gradient. However, if the surface horizon is saturated gaseous diffusion is effectively restricted (Rasmuson *et al.*, 1990).

The flux of carbon dioxide to the atmosphere was found by Monteith to be 1.5 g m^{-2} during winter and 6.7 g m^{-2} d^{-1} in summer (quoted by Payne and Gregory, 1988). Carbon dioxide is, of course, soluble in water (31 times greater than oxygen) an observation which Greenwood (1970) uses to predict that the CO_2 content of air in the soil should not rise above 1 per cent, other than in anaerobic pockets. Diffusion coefficients for oxygen and carbon dioxide in water and air at 25 °C are given by Marshall and Holmes (1988):

	oxygen (m^2 s^{-1})	carbon dioxide (m^2 s^{-1})
air	2.26×10^{-5}	1.81×10^{-5}
water	2.60×10^{-9}	2.04×10^{-9}

2.5.3   Quantitative relationships

Diffusion of gases occurs in response to a concentration gradient is demonstrated by Fick's law:

$$q = D_o dC/dx \qquad (33)$$

where:

q = the gas flux per unit area of cross-section
C = its concentration
x = a space co-ordinate normal to the section

This may be simplified to:

$$q = D'_o dp/dx \qquad (34)$$

as the partial pressure (p) of a gas in the mixture of gases is proportional to its concentration C.

In the soil the tortuosity of the pores reduces the effective cross-section of the pathways for diffusion and the following equation has been put forward to account for the movement of a gas through a soil:

$$q_s \quad = \quad D_o b e_a dC/dx \qquad (35)$$

where:

q_s = gas flux
b = impedance factor
D_o = diffusion coefficient for specific gases
e_a = air filled porosity

If D is the diffusion coefficient for a gas diffusing through a soil, then:

$$D/D_o = b e_a \qquad (36)$$

The value of 0.66 was adopted by Penman (1940) for the impedance factor b, but subsequently other investigators, including Currie and Rose (1985), have refined the approach to account for tortuosity and the presence of water in pores, partially closing the pathways (Bruchler *et al.*, 1989). For a moist soil Currie proposed:

$$D/D_o = (e_a/e)^4 e^m \qquad (37)$$

in which m is approximately 1.5 in sands. Currie (1984) subsequently concluded that no single relationship between D/D_o and e_a would fit the results obtained.

Soil microbial activity and rooting systems are capable of absorbing free oxygen. Concentrations of oxygen in the soil solution are normally some 50 to 100-fold greater than in the cytoplasm of cells, so an adequate gradient exists to maintain diffusion into the living tissue. A feedback situation exists with carbon dioxide concentrations because oxygen demand decreases as the carbon dioxide concentration increases. The demand

for oxygen from actively growing crop roots (and the microbial population) is between 7 and 35 g m^{-2} d^{-1} during the summer period of temperate climates, declining to one tenth of this rate during winter. Even though soil contains up to 3 g m^{-3} of water, roots can suffer from anaerobic conditions. When this occurs ethylene is generated, inhibiting many plants, but stimulating growth of rice plant roots.

Diffusion of oxygen into the soil is particularly significant for methane oxidation in freely drained soils. Tiedje *et al.* (1984) report that denitrification increases rapidly when oxygen concentration falls below 2 per cent and the water-filled pore space exceeds 60 per cent. Rates of gaseous diffusion from soil to atmosphere or vice versa, depends upon the difference between concentration in the free atmosphere and in the soil atmosphere, the length of the diffusion path and the diffusion co-efficient of the gases concerned. Collin and Rasmuson (1988) compare gas diffusion models for unsaturated porous media; Rasmuson (1990) extends this work into the transport of hydrolysable gases in soils. Payne and Gregory (1988) state that diffusion is much less dependant upon the shape of air-filled pores than is the hydraulic conductivity, and it is approximately proportional to the soil volume consisting of air. Hodgson and Macleod (1989) use the oxygen flux density to estimate the air-filled porosity of a vertisol.

2.6   Conclusions

The factors which contribute to the evolution and emission of greenhouse gases from soils result from the interaction of the traditional factors of soil formation advocated by Jenny some 50 years ago. Then, as now, these factors set the broad parameters of soil formation. However, it is recognized in this review, that underlying virtually all of the processes of soil formation are basic physical interactions which are critical not only for soil genesis, but also for the generation of gases by some soils and the absorption of gases by others. The flux of heat into and out of the soil and its effect on the flux of water vapour and gases between the soil and the atmosphere has been an area of particular scientific interest for soil physicists. The aim of this chapter has been to draw attention to the underlying physical relationships which control or influence the generation, movement and emission of gases from soils.

Essentially, the study of soil physics is concerned with the description, measurement and prediction (and possibly control) of the processes of transport of heat, gases and solutes through the soil (Koorevaar *et al.*, 1983). Soil is the zone of intimate interpenetration of the atmosphere and the geosphere; it is a most interesting area of environmental study, shared by ecologists, and both atmospheric and soil scientists. It is the zone in which soil-related greenhouse gases are generated, and must pass through before reaching the open atmosphere. It is important that a greater understanding should be acquired of the processes which control the production of soil gases, their absorption and emission.

The heat flux at the soil surface is one of the most fundamental processes. It influences the development of the soil profile and controls the speed of reactions which take place. This includes all the dynamic activity associated with life on the earth's surface, whether it is the physico-chemical process of weathering or the biological activity of seed germination, root and shoot growth or microbial activity, and gaseous emission and absorption.

Soils and vegetation are the reactive part of the earth's surface which is involved closely in the absorption and exchange of energy received from the sun. This energy is the driving force behind most of the physical, chemical and biological processes which occur on the earth's surface. Water, which can exist in solid, liquid and gaseous phases at the temperatures experienced on the earth's surface, requires energy when changing

its state. Water is also necessary for many of the chemical and biological processes to operate, so its presence is of critical importance.

Movement of heat in soils occurs by conduction in the solid and liquid phases and by convection in the gaseous and liquid phases. Conduction transmits thermal energy from particle to particle and is a relatively slow process, especially in dry soils. Convection in the soil air or soil solution within soil pores is a more rapid process of heat transport and is associated with gains and losses of heat through the latent heat of evaporation/condensation and freeze/thaw processes.

The gaseous phase in soils generally decreases in amount with depth in the soil profile, mainly as a result of the loosening effects of soil fauna and roots. In air-filled pores, the process of diffusion is dominant in the exchange of gases between the soil air and the atmosphere, but displacement by water also plays an important part.

Throughout the last 100 years, there has been considerable emphasis on the study of water movement, and numerical models have been developed to account for its behaviour as it passes through the porous medium of the soil, either in a saturated or unsaturated state. As has been shown, water movement can be described by the hydraulic potential gradient, the volume and the rate of movement expressed as a flux density.

The factors and processes involved in soil formation which regulate the conditions in which emissions and absorption of heat take place and greenhouse gases are generated offer mankind points where some manipulation of the system can take place to limit or reduce the amount of these gases migrating into the atmosphere.

Chapter 3 Methane

N.H. Batjes

3.1   Introduction

3.1.1   Background

Methane, one of the major 'greenhouse gases', strongly influences the photochemistry of the atmosphere (Cicerone and Oremland, 1988). Based on present calculations, it accounts for about 15 % of the current increase in commitment to global warming (JEA/EPA, 1990). Methane's strong ability to absorb infrared radiation and its relatively short atmospheric lifetime (8-12 years), combined with the fact that a large fraction of the atmospheric CH_4 originates from paddy soils, makes CH_4 control an important opportunity for addressing global climate change. The latter especially since a 60 % increase in rice production, from 480 10^6 ton in 1989 to 780 10^6 ton by the year 2020 and corresponding increase in 'harvested' area, would be needed to nourish the projected increased population (IRRI as quoted by Braatz and Hogan, 1991).

Ice core measurements are the exclusive source of information on the concentrations and trends of methane before the middle of the 20th century. Measurements on ice cores at Byrd Station and Dye3, both in Antarctica, show that atmospheric methane concentration was only about 350 ppbv about 20,000 year B.P. ($\approx$ last glaciation), in comparison with a mean pre-industrial level of about 650 ppbv, and a present mean value of 1650 ppbv (Stauffer *et al*., 1988). Average atmospheric CH_4 concentrations are lower in the southern hemisphere, possibly due to less anthropogenic input. Short-term temporal and spatial variability is common and influenced by geographic location, seasonality, mixing patterns, and diurnal cycles (Khalil and Rasmussen, 1983; Blake and Rowland, 1988).

Atmospheric methane concentrations have increased at an average rate of 16.6 ± 0.4 ppbv yr^{-1} or 1.02 ± 0.02 % over a period of 8 years (Khalil and Rasmussen, 1990). According to these researchers the trend has not been constant but has varied between 12 ± 2 and 23 ± 2 ppbv yr^{-1} over 2 years after seasonal changes were observed. Rasmussen and Khalil (1981) and Khalil and Rasmussen (1983) reported annual global increases of nearly 2 % and 1.3 % yr^{-1}, respectively. The current increase is about 1.1 % per year according to Khalil and Rasmussen (1987), while Steele *et al*. (1987) reported an increase of slightly less than 0.8 % yr^{-1} for atmospheric methane. The observed increase is presumably due to more extensive and intensive use of paddy fields, increased number of ruminants, biomass burning, escape of methane from coal mines, and leakage of natural gas wells and distribution systems. Most methane budgets show that irrigated rice fields and ruminant cattle are the largest biogenic sources of methane on a global scale. Quantification of the individual contributions of the various sources and sinks, however, remains a challenge (Bouwman, 1990a; Crützen, 1991; see Appendix I). Until the reasons for the observed increases in atmospheric methane are better understood, it will be difficult to project future increases with any degree of certainty, but a 20-50 % increase during the next 50 yr seems plausible (Bolin *et al*., 1986).

The major removal processes of methane in the atmosphere are reviewed, amongst others, by Cicerone and Oremland (1988) and Bouwman (1990a). In addition to being an additive factor to global warming phenomena, methane is destroyed in the atmosphere by oxidation with free hydroxyl radicals, with an estimated loss of 420 ± 80 Tg yr^{-1} (Crützen, 1991), with the production of carbon monoxide and hydrogen. Methane is also a source of stratospheric water vapour. Alternatively, elevated levels of methane may help to protect the stratospheric ozone layer from destruction by halo-carbons and $O(^1D)$, corresponding with a

CH_4 loss of 10 ± 5 Tg yr^{-1} (Crützen, 1991). Additional atmospheric losses include the uptake of 30 ± 15 Tg yr^{-1} by soil sinks. The total atmospheric sink of methane is thus estimated to be 460 ± 100 Tg yr^{-1}. With an annual increase in the atmospheric loading of about 54 ± 5 Tg, the total methane source thus is 504 ± 105 Tg yr^{-1} (Crützen, 1991). In the preceding analysis, Crützen (1991) took into account the fact that the rate at which methane reacts with hydroxyl radicals may have been overestimated by up to 25 per cent in the past (Vaghjiani and Ravishankara, 1991).

While oceans account only for about 15 ± 12 Tg CH_4 yr^{-1}, which is less than 5 per cent of the total budget (Seiler, 1984; Bolle *et al.*, 1986; Cicerone and Oremland, 1988), soils are an important source of atmospheric methane. This methane is produced mainly by microbial degradation of organic substrates in rice paddies (100 ± 50 Tg yr^{-1}), natural wetlands (100 ± 50 Tg yr^{-1}), and landfills (50 ± 20 Tg yr^{-1}) which together account for about half of the total CH_4 emission of 496 ± 251 Tg yr^{-1}. Non-soil related sources of atmospheric methane include ruminants (85 ± 15 Tg yr^{-1}), burning of biomass (80 ± 20 Tg yr^{-1}), and leakage related to activities such as natural gas winning and coal mining (233 ± 60 Tg yr^{-1}) (Schütz *et al.*, 1990). Biogas generators do not contribute markedly to the global atmospheric methane budget ($\ll 1$ Tg yr^{-1}; Khalil *et al.*, 1991). The most recent estimates of the various sources and sinks of CH_4, as computed by IPCC (1992), are presented in Appendix I.

Taking into consideration the fact that the atmospheric methane concentration is increasing at a much higher rate that the atmospheric CO_2 concentration, and that an incremental molecule of CH_4 may trap about 32 times as much heat as an incremental molecule of CO_2 (e.g., Dickinson and Cicerone, 1986), methane is likely to become an even more important contributor to the greenhouse effect in the future (see ORNL, 1990), unless appropriate abatement measures are rapidly implemented. Several causes for the current increase in atmospheric methane concentrations are recognized by Papen and Rennenberg (1990):

   a.   The current increase in global methane sources (e.g., increase in harvested paddy rice acreage);
   b.   A reduction in methane sink strength;
   c.   A reduction in both sink strength and an increase in source strength.

3.1.2   Structure of chapter

Three main processes determine the net emission of greenhouse gases to the atmosphere, namely production, consumption and transfer processes. In Section 3.2 the biotically mediated processes of methane formation and consumption are reviewed. Possible transfer processes of CH_4 from terrestrial ecosystems to the atmosphere are discussed in Section 3.3. Following examples of temporal and spatial variations in measured methane fluxes (Section 3.4), and data on global methane fluxes from selected terrestrial environments (Section 3.5), the presently recognized abiotic process controlling factors are discussed in Section 3.6. In Section 3.7 methodological approaches used by three research groups to calculate global CH_4 emissions using global data bases are discussed together with the possibilities for process-based simulation of methane production. In the final Section, the usefulness and possible shortcomings of a global soil data base, of the type to be developed for WISE (see Chapter 6), within the framework of global studies of environmental change is discussed.

3.2 Methanogenesis and methane consumption

3.2.1 General

The balance between the microbial processes of methanogenesis and methane consumption controls to a great extent whether a certain terrestrial ecosystem will function as a sink or source of atmospheric CH_4. The main biological processes leading to methane production and consumption are reviewed in the present Section. A discussion of methane emissions caused by animals, termites, biomass burning, landfills and natural gas/coal consumption is beyond the scope of this study (see for instance the review by Bouwman 1990a and the three-dimensional model synthesis of the global methane cycle by Fung *et al.*, 1991).

3.2.2 Methanogenesis

Methanogenesis, the biological formation of methane, is a geochemically important process that occurs in all anaerobic environments in which organic matter undergoes decomposition: lakes, wetlands, paddy fields, as well as the digestive tracts of ruminants and termites. Methane of apparently biogenic origin has also been detected in several anaerobic, hyper-saline environments such as the Great Salt Lake, as well as in thermophilic environments (see review by Oremland, 1988). Vogel *et al.* (1988) prepared an extensive review of the biochemistry of methane formation for the past 80 years.

The biogenic CH_4 results from the metabolising activity of a small and highly specific bacterial group, which are terminal members of the food chain in their environment. These strictly anaerobic bacteria convert fermentation products formed by other microorganisms, notably CO_2, H_2, and esters and salts of methanoic acid (HCOOH) into CH_4, but other substrates may be used as well (Koyama, 1963; Cicerone and Oremland, 1988; Oremland, 1988; Stainer *et al.*, 1976; Neue and Roger, 1992). Neue and Scharpenseel (1984) prepared a generalized scheme for the degradation of organic matter to methane in anaerobic environments. In this report we shall exemplify some of the possible reactions with reference to the type of methanogens involved (adapted after Papen and Rennenberg, 1990):

a) H_2 reduction of CO_2 by obligate chemoautotrophic methanogens:

$$CO_2 + 4\,H_2 \quad ---> \quad CH_4 + 2\,H_2O$$
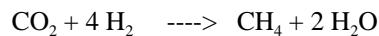
b)   Several strains of methanogens can also use HCOOH or CO as a substrate for producing methane in addition to CO_2 and H_2 (Papen and Rennenberg, 1990):

$$4\,HCOOH ---> CH_4 + 3\,CO_2 + 2H_2O$$

$$4\,CO + 2\,H_2O ---> \quad CH_4 + 3\,CO_2$$
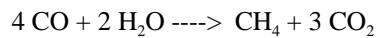
c)   Methane can also be produced by methylotrophic methanogens which use methyl-group containing substrates such as methanol, acetate and trimethylamine (Papen and Rennenberg, 1990):

$$4\,CH_3OH ---> 3\,CH_4 + CO_2 + 2\,H_2O$$

$$CH_3COOH ---> CH_4 + CO_2$$

$$4 \ (CH_3)_3\text{-}N + 6 \ H_2O \ \text{----}> 9 \ CH_4 + 3 \ CO_2 + 4 \ NH_3$$
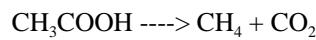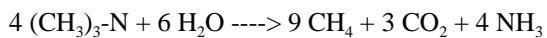
Methane was mainly produced from H_2 - CO_2 (30-50 %) and from acetate in the radio-tracer studies of Schütz *et al.* (1989b). Takai and Wada (1990) recognize the decarboxylation of acetic acid (CH_3COOH) as being the most important biochemical pathway of methane formation in waterlogged paddy soils. Yavitt *et al.* (1987) observed that methane production proceeded primarily through the CO_2-reduction pathway in deep peat (30-45 cm) and that the rate was controlled, in part, by the availability of H_2. Addition of glucose and H_2 - CO_2 to peat stimulated methanogenesis in the experiment of Williams and Crawford (1984), whereas addition of acetate inhibited methanogenesis.

3.2.3 Methane consumption

Some aerobic terrestrial ecosystems function as sinks for methane (Seiler *et al.*, 1984; Steudler *et al.*, 1986; Schütz *et al.*, 1990). In the study of Oremland and Culbertson (1992), methanotrophs consumed more than 90 % of the methane potentially available. Some of the microorganisms responsible for the oxidation of methane are strictly *aerobic*, obligate methylo- or methano-trophic Eubacteria. These microorganisms can use methane as a substrate as well as other C_1-compounds such as methanol. Papen and Rennenberg (1990) exemplified the reactions as follows:

$$CH_4 + NADH + H^+ + O_2 \ \text{--}(1)\text{-->} \ CH_3OH + NADH + H^+ + H_2O$$

$$CH_3OH + PQQ \ \text{--}(2)\text{-->} \ CH_2O + PQQH_2$$

$$CH_2O + NAD^+ + H_2O \ \text{--}(3)\text{-->} \ HCOOH + NADH + H^+$$

$$HCOOH + NAD^+ \ \text{--}(4)\text{-->} \ CO_2 + NADH + H^+$$
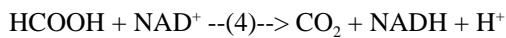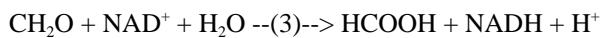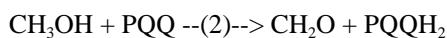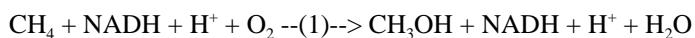
With: 1) methane-monooxygenase; 2) methanol-dehydrogenase; 3) formaldehyde-dehydrogenase; 4) formate-dehydrogenase; PQQ= methotaxin.

Some aerobic chemoautotrophic NH_4^+-oxidizers can use CH_4 in addition to ammonium as a substrate (Papen and Rennenberg, 1990):

$$CH_4 + O_2 + XH_2 \ \text{--}(1)\text{-->} \ CH_3OH + H_2O + X$$
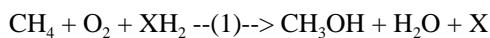
With: 1): ammonia-monooxygenase; X, XH_2: coenzyme and co-substrate in the reduced and oxidized form, respectively.

Addition of ammonium as NH_4Cl to intact soil cores decreased the aerobic CH_4 flux in the experiment of Conrad and Rothfuss (1991), suggesting that oxidation of methane was apparently inhibited by the addition of ammonium. Possibly, the supplied ammonium stimulated nitrification in favour of CH_4 oxidation and/or it may have constrained the availability of oxygen (Conrad and Rothfuss, 1991). The role of methane-oxidizing bacteria in the methane budget can be revealed by using methylfluoride, which is a specific inhibitor of oxidation of CH_4 by methane-monooxygenase (Oremland and Culbertson, 1992).

There is experimental evidence that methane-oxidation could occur in some anaerobic sediments (Alperin and Reeburgh, 1985; Yavitt et al., 1990; Kimura, 1992). Since sulphate is the only apparent oxidant present in sufficient quantity to cause a significant removal of methane under these conditions, it is possible that sulphate reducers consume methane under anaerobic conditions (Yavitt et al., 1990). Bartlett et al. (1987) observed that methane and sulphate concentrations are inversely related. This supports the competition of CH_4-producing and sulphate reducing bacteria for acetate and H_2-substrates as observed by Kimura et al. (1991). The anaerobic, sulphate dependent, oxidation of methane still has to be elucidated further (Oremland, 1988, pp. 647-650). Papen and Rennenberg (1990) exemplified the possible reaction as follows:

$$CH_4 + SO_4^{2-} ---> HCO_3^- + HS^- + H_2O.$$

3.3   Processes regulating the transfer of CH_4 to the atmosphere

3.3.1   Ebullition

Several researchers recognize ebullition of gasses entrapped in sediments and peats as being possibly a common form of methane release to the atmosphere. Factors which might influence the ebullition process, include wind speed, water temperature, solar radiation, water level, local water table and atmospheric pressure (Mattson and Likens, 1990).

In the study of Bartlett et al. (1988) some 49-64 % of the total methane flux was attributed to ebullition, while Crill et al. (1988) reported values of up to 70 per cent. Ebullition accounted for 34 % of the total methane flux recorded during the study period in a Virginian Swamp, although ebullition occurred in less than 20 % of the measurements (Wilson et al., 1989). During the observation period the average bubble flux was 34 10^{-3} g CH_4 m^{-2} d^{-1} and the average diffusive flux 66 10^{-3} g CH_4 m^{-2} d^{-1}. In an Amazonian floodplain ebullition was the dominant mechanism of methane emission, accounting for 85 % of the total release (Devol et al., 1988).

Submergence can seriously reduce the rate of gas exchange between the soil and the atmosphere, as a result of which methane, as well as other gases, may be entrapped in the soil. The continuing production of these gases causes the pressure to increase, sometimes causing a 'vesicular structure' in sediments (Moormann and van Breemen, 1978), so that these gases may be released as bubbles to the atmosphere (Ponnamperuma, 1984). The rate of methane ebullition from paddy soils can vary, amongst others, with the fertilizer treatment. In a Typic Albaqualf from the Crowley Rice Research Station, Louisiana, the entrapment of methane in KNO_3-treated microplots was significantly lower ($P < 0.05$) at all sampling dates than for urea treated plots (Lindau et al., 1990). It should be noted, however, that no rice plants were grown in the experiment of Lindau et al. (op cit.). Rice plants may reduce the entrapment of methane gases in flooded soils (see Section 3.3.3; Figure 3.1).
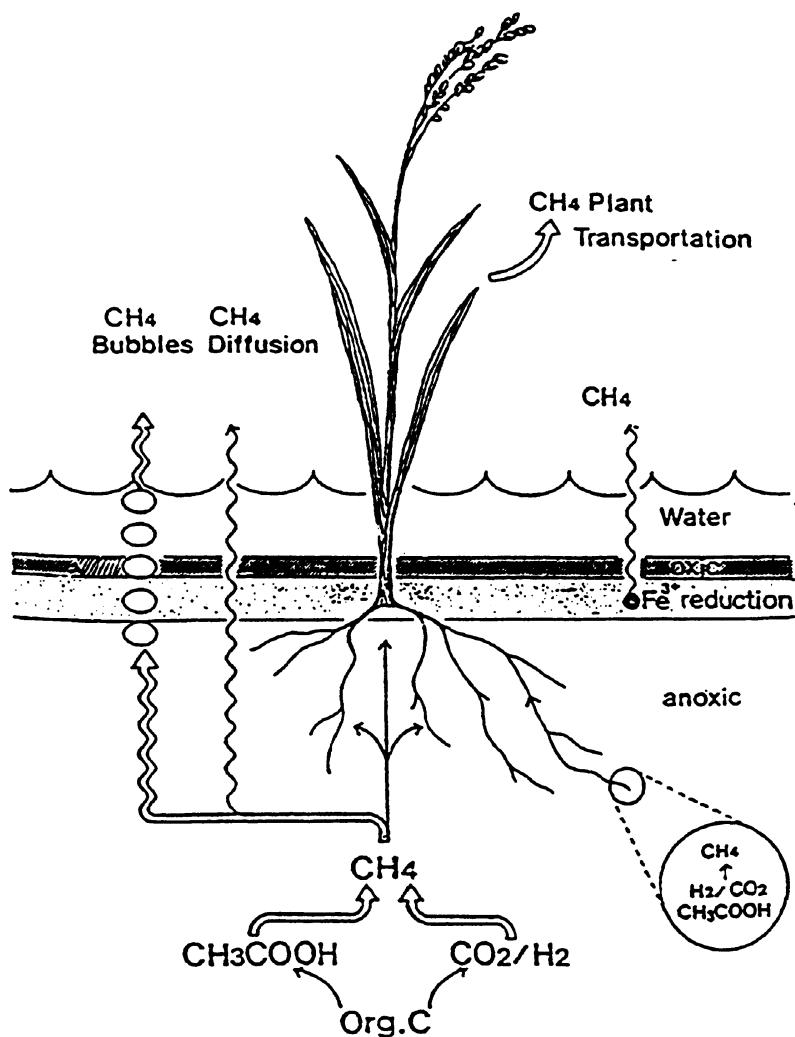
Figure 3.1.   Schematic representation of methane production and its release in a rice paddy (After Takai and Wada, 1990)

Holzapfel-Pschorn *et al.* (1986) found that gas bubbles entrapped in unvegetated soils had significantly higher CH_4 mixing ratios than in soils planted in rice. In addition the CH_4 mixing ratio of gas bubbles emitted from the inundated soil were significantly lower than those recorded in bubbles taken directly from the submerged soil. This could be an indication of active oxidation of CH_4 in the oxidized surface layer of the submerged soil or in the oxidized zones within the rhizosphere.

Methane emissions from fields without rice plants amounted to about 50 % of those observed in fields planted with rice. During the measurements, the emissions from the un-planted field were almost exclusively due to ebullition (Schütz *et al.*, 1989). In Japan, Takai and Wada (1990) observed that methane ebullition is important during the early stage of flooding (June-July), when rice plants are small, whereas vascular transport becomes more important as the rice plants grow (August-October).

Sporadic methane bubble releases from the sediments of a 11 m deep lake, which has thick organic sediments and becomes anaerobic below 9 m depth by mid-summer, were correlated with changes in local air pressure (Mattson and Likens, 1990). Low air-pressure events usually associated with storm systems induced ebullition (18 % increase per millibar drop in air pressure, corresponding with 0.14 mmol CH_4 m^{-2} d^{-1}), whereas high pressure inhibited ebullition. Although the methane ebullition rates were erratic during the 1987 observation period, with an average rate of 0.76 and a maximum of 4.26 mmol m^{-2} d^{-1} at the deepest site, the proportion of methane in the bubbles was relatively constant (70 ± 7 %). The CH_4 flux rates may not be a simple linear function of atmospheric pressure changes. According to Mattson and Likens (1990) there may be an hysteresis effect on ebullition which is related to the porosity of the sediments.

Bartlett *et al*. (1988) observed high concentrations of dissolved CH_4 in root mats of floating meadows suggesting *in situ* methanogenesis with restricted flow when water can become deficient in dissolved oxygen. Another possible explantation is that methane may be entrapped by the mats and subsequently released as bubbles (Bartlett *et al*., 1988).

3.3.2   Diffusion

The diffusion of gases in water is about 10^4 times slower than in air, so that the exchange of gases almost stops when soils are waterlogged. The actual diffusion of methane from rice fields is a function of the methane supply to the floodwater, the actual CH_4 concentration in the floodwater, and the prevailing wind speed (Sebacher *et al*., 1983). Bartlett *et al*. (1985) found that the methane concentration gradient between sediments and water was a factor controlling rates of diffusive methane flux in a Virginian swamp. In the incubation experiment of Conrad and Rothfuss (1991) about 80 % of the potential diffusive CH_4 flux through the water was oxidized in the thin oxic surface layer. Microbial methane oxidation in the thin aerobic top zone of anaerobic soils, may thus remove a large part of the bacterially formed CH_4. Similarly, Whalen and Reeburgh (1990) found that the subsurface CH_4 oxidizing activity is important in controlling upward CH_4 fluxes in tundras at sites where vascular plants are absent, particularly when the CH_4 evolves by dry diffusion rather than by ebullition.

Consumption of atmospheric CH_4 by soils depends on transport to zones of consuming activity. Transport in waterlogged tundra soils is by aqueous molecular diffusion. Waterlogged tundra soils have a methane consumption maximum centred near the water table (the aerobic/anaerobic boundary), sustained by upward diffusion of dissolved CH_4. By contrast, transport in dry tundra soils is by gas-phase diffusion so that porous low-resistance tundra soils do not limit the supply of methane (Whalen and Reeburgh, 1990).

3.3.3   Vascular transport

In a number of aquatic plants as well as rice methane can be transported through the aerenchyma (De Bont *et al*., 1978; Cicerone and Shetter, 1981; Seiler, 1984; Sebacher *et al*., 1985; Inubushi *et al*., 1989, Wilson *et al*., 1989). This transport process could circumvent CH_4 oxidation by methanotrophs (De Bont *et al*., 1978; Sebacher *et al*., 1985). Holzapfel-Pschorn *et al*. (1986) found that during the growing season of a rice crop 67 % of the CH_4 produced was oxidized, and only 23 % actually emitted to the atmosphere. The percentage of methane that was oxidized in the paddy soils studied by Sass *et al*. (1990) ranged from 24-68 % and 19-22 % throughout the growing season, respectively.

In the study of Seiler *et al*. (1984) over 95 % of the total CH_4 release from paddy soils to the atmosphere was through diffusive transport through the aerenchyma of rice plants, while transport by bubbles or diffusion through the paddy water were of minor importance. Similarly, Holzapfel-Pschorn (1986) observed that 80 % of the observed methane transport of 6 weeks old rice plants was by diffusion through the stems of these plants. The presence of rice plants also enhanced the escape of CH_4 to the atmosphere in the study of De Bont *et al*. (1978). Schütz *et al*. (1989b) observed that as the rice plants grew not only the contribution of plant mediated CH_4 emission increased but also the percentage of produced CH_4 that was reoxidized, and hence not emitted. Takai and Wada (1990) found that planting of rice suppresses methane formation due to the aeration caused by the diffusion of oxygen from the rice rhizosphere. In this context Ueckert *et al*. (1990) found a clear correlation between the aerenchyma size of *Leptochloa fusca* L. Kunth (Kallangra grass) and the oxygen concentration in the rhizosphere after 24 hours of incubation. They noted also that it is the percentage of root porosity rather than the absolute volume of the aerenchyma which is important for root aeration, and thereby possibly for the rate of methane oxidation in the rhizosphere.

Inubushi *et al*. (1990a) observed that the amount of CH_4 emitted through rice plants varied between 3 soil types, being the highest in the soil type with the highest methane production. In the absence of rice plants about 35 % of the CH_4 produced was emitted, but the actual production of methane was much lower than for soils planted in rice (Holzapfel-Pschorn *et al*., 1986). Emissions via the plant constituted more than 90 per cent of the total emissions. The flux rate was controlled by the rate of CH_4 production in the soil and was not curtailed by limitations of the diffusion processes from the soil into the root system or through the aerenchyma of the rice plant (Holzapfel-Pschorn *et al*., 1986).

Inubushi *et al*. (1990a) injected water saturated with CH_4 into the rhizosphere, causing an immediate increase in the amount of CH_4 transported through the rice plants which they saw as an indication that roots of rice plants may take up methane along with water. Nouchi *et al*. (1990), however, observed no clear correlation between changes in transpiration rate and change in CH_4 emission rate. They also observed that methane was mainly released at the culm, an aggregation of leaf sheaths, but not from the leaf blade. Based on these findings, Nouchi *et al*. (1990) proposed that CH_4 dissolved in the soil water surrounding the rice roots diffuses into the cell-wall water of the root cells, gasifies the root cortex, and then is mostly released through the micropores in the leaf culm. Nouchi *et al*. (1990) also found that the rate of emission of methane through rice plants is proportional to the methane concentration in the culture solution. Sass *et al*. (1990) found that soil pore methane and plant stem gas concentration are related to the distribution in the soil of methane production as well as root biomass. In one of the rice fields studied by Sass *et al*. (1990) the methane emission was strongly related to the above ground biomass.

The resistance to gas diffusion through rice plants is likely to vary with the growth stage, as well as with the cultivar (e.g., floating rice *versus* short straw high yielding cultivars). Rice plants at the ripening stage, for instance, released about 20 times as much CH_4 than 2 week old seedlings in one study (De Bont *et al*., 1978). Inubushi *et al*. (1990b) found that methane fluxes through rice plants reached maximum values at the heading stage. In this experiment, the maximum emission could be reduced to 40-70 % by a percolation treatment equivalent to 51 mm water per 2 weeks.

Schütz *et al*. (1989b) observed that the percent of methane emitted on an hourly basis from a paddy field by a rice plant can vary between 0-97 % over a growing season. The diffusion of CH_4 through the aerenchyma of rice plants is likely to vary on a daily basis as a result of effects of fluctuating environmental conditions on the rate of photosynthesis/respiration (Bouwman, 1990a p. 84). Indeed, Raskin and Kende (1985) have related the rate and direction of air movement in rice plants to photosynthesis. It is thus possible that less

oxygen is transported to the root system at night, so that methane oxidation would be reduced. With respect to algal mats King (1990) observed that shifts from light to dark on methane emissions are best explained as a result of changes in the availability of oxygen. Seiler *et al*. (1984), however, found no correlation between light intensity and CH_4 release in their experiment, which they saw as an indication that the CH_4 release is independent of the photosynthesis and/or width of the stomata of rice plants.

3.3.4   Other processes

Another transport process that could be of importance for methane transport in waterlogged soils is advection. In the glacial peatlands of Lake Agassiz, Minnesota, it was not clear whether gas transport through the peat is mostly by diffusion (Clymo, 1984) or by ground water advection (Siegel, 1983). Studies have recently been initiated to assess the relative importance of these processes in the Lake Agassiz peatlands (see Siegel and Glaser, 1991).

3.4   Temporal and spatial variation in CH_4 emissions

3.4.1   Temporal variability

Generally, methane emissions in a given location show strong diurnal and seasonal variations the pattern of which changes from year to year (e.g., Schütz *et al*., 1989b). Cicerone *et al*. (1983), however, did not find significant diurnal variations in CH_4 emissions in a Californian paddy during their experiments. Holzapfel-Pschorn and Seiler (1986), however, found a strong dependence of time of day on CH_4 emissions in an Italian paddy. Both Cicerone *et al*. (1983) and Holzapfel-Pschorn and Seiler (1986) observed two seasonal peaks in emissions, although the magnitude and times of occurrence of these peaks varied between the sites studied. With respect to the Italian paddy (Holzapfel-Pschorn and Seiler, 1986), the seasonal emissions peaks were attributed to mineralization of organic matter prior to flooding and the subsequent release of organic root exudates, respectively. Similarly, in a temperate swamp high methane fluxes were observed during autumn, corresponding with the period of maximum leaf fall (Wilson *et al*., 1989). Methane emissions may also vary markedly with the water regime or with temperature variations in the upper decimeter of paddy soils (e.g., Seiler *et al*., 1984). The CO_2, acetate and formate which is produced during biomass burning, upon dissolving in the standing water of wetlands, may serve as the substrate for methanogenesis which would explain post-burn enhancement of methane emissions (Levine *et al.*, 1990).

The seasonal variation in methane fluxes from a Japanese paddy field as modified by applications of straw, compost and mineral fertilizers and the irrigation/drainage regime is shown in Figure 3.2. The seasonal variation of methane fluxes from paddy fields to the atmosphere is mainly related to the variation in methane production in these fields (Yagi *et al.*, 1990; Yagi and Minami, 1991). The CH_4-emission rates varied both with the soil type and application of organic matter. Sass *et al*. (1990) reported a 3-fold emission difference between two rice fields on different soil types in Texas, even though the soils were treated in the same way and located in close proximity of each other. This may mean that if methane emission measurements for paddy soils are to make sense, comparative measurements must be made in the major soils representative of the major rice producing areas of the globe, particularly in Asia.
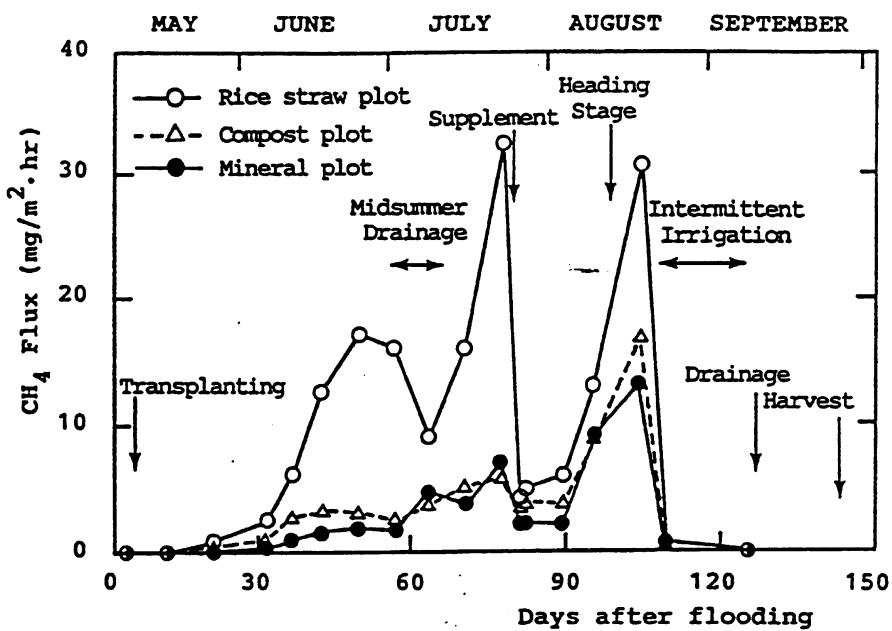
Figure 3.2.   Seasonal variation in the methane fluxes from the alluvial Ryugasaki paddy field as influenced by mineral and organic amendments and the drainage regime (Source: Yagi *et al.*, 1990)

Schütz *et al.* (1990) observed two maxima in CH_4 production corresponding with the early vegetative period of the rice crop (i.e. end of April - end of June) grown in Hangzhou Province in the People's Republic of China. During the early vegetative period, maximum CH_4 emissions, occurred at noon and during the night, while the CH_4 emissions peaked only in the night during the late vegetation period. It is possible that less oxygen may be transported to the root system of rice plants at night so that the methane oxidation would be reduced, resulting in higher net emissions (Raskin and Kende, 1985).

After the heading stage, Inubushi *et al.* (1990a) injected the rhizosphere of rice plants with various solutions to clarify the effects of several substances on the transfer of methane through rice plants. The amount of CH_4 transferred through the rice plants varied diurnally and also with the age of the rice plant, ranging from 0.5 to 23 mg CH_4-C hr^{-1} m^{-2}. In this study, the maximum emissions were observed late in the afternoon, and at the heading stage.

Seasonal variations in methane emissions may also be influenced by thawing of permafrost. In acid peats in subarctic mires, methane formation was restricted to the upper horizon of the peat, and there was no correlation between the depth of the permafrost and methane fluxes (Svensson and Rosswall, 1984). Maximum concentrations of methane occurred in the layer below the layer of maximum production. According to Svensson and Rosswall (1984) this may be due to the freezing proper, which starts at the surface and proceeds downwards to the permafrost with subsequent entrapment of gases. This would also explain the peaks in methane emissions recorded for subarctic fens during the spring melt (Moore and Knowles, 1987). Similarly, Harris *et al.* (1982) reported high levels of methane release in early spring in the Great Dismal Swamp. According to Wilson *et al.* (1989) the increase in methane flux in spring most likely reflects the mineralisation of organic materials accumulated in the soil during the winter, when microbial activity is low. As the temperature rises, this organic matter is rapidly decomposed by fermentation bacteria which produce the substrates required for methanogenesis.

Seasonal variation in methane emissions in the People's Republic of China showed three maxima during the early rice growing period, the first at tillering, the second during the reproduction phase, and the third at flowering. High average methane emission rates were observed at the very beginning of the late rice growing period and also during tillering (Schütz *et al.*, 1990). Holzapfel-Pschorn and Seiler (1986) also reported an increased release of methane during the flowering stage of rice. Similarly, Wilson *et al.* (1989) observed high rates of release of methane during the flowering stage of *Petlandra virginica L.* (arrow-arum) in a temperate swamp.

Seasonal variations in CH_4 fluxes have also been attributed to other plant-related effects. Methane emission in two Japanese paddy soils was controlled not only by the soil conditions but also by the growth stage of the rice plant (Inubushi *et al.*, 1990b). In China, Schütz *et al.* (1991) found that within 'regions' daily CH_4 emissions are more than 3 times greater for 'late' than for 'early' maturing rice cultivars. The temporal and spatial distribution of CH_4 production is related to rice root biomass (Sass *et al.*, 1990), which may be seen as cultivar and soil dependent property. This shows the importance of considering the actual length of the growing cycle, in addition to the cropped acreage and cultivar type, when calculating CH_4 emissions from paddy fields. Besides these cultivar effects, diurnal variations and seasonal variations in methane fluxes may also be influenced by meteorological factors such as the atmospheric pressure (see Mattson and Likens, 1990). Precipitation, through its effect on the soil aeration status, may also influence the net flux of greenhouse gases from soils. In a catena under native short-steppe grassland, Mosier *et al.* (1991) found the N_2O flux for all 3 sites considered was highest immediately following precipitation. Under very dry conditions, both the CH_4 uptake and CO_2 emissions declined and remained low until soil water content increased (Mosier *et al.*, 1991).

3.4.2 Spatial variability

The spatial and temporal variability in methane emission, strictly speaking, should not be discussed as separate entities since they are inherently linked. Wilson *et al.* (1989) studied methane flux measurements at 4 sites in a freshwater temperate swamp over a 13 month period, finding that methane emissions were highly variable between sites and over time at any one site. Laboratory incubations of soils cores showed that methanogenesis is highest near the soil surface in the rice row and decreases with depth and distance from the rice plant (Sass *et al.*, 1990), so that plant density may form a possible source of spatial variation in CH_4 emissions from paddy fields.

A high spatial and temporal variability in methane flux was observed in the field study of Bartlett *et al.* (1985; 100 measurements over a 2 year period), ranging from -2.4 to 21.3 mg CH_4 m^{-2} d^{-1}. Estimates of annual methane emission within a creek system were 0.42 g CH_4 m^{-2} for a salt meadow, 1.3 g CH_4 m^{-2} for short *Spartina alterniflora,* and 1.2 g CH_4 m^{-2} d^{-1} for tall creek *S. alterniflora.*

Barlett *et al.* (1988) performed 186 methane measurements, over a 3-monthly period, in primary Amazon floodplain environments of open water lakes, flooded forests and floating grass mats. They found that emissions of methane were lowest over open water, increasing for flooded forests and floating grass mats (27 ± 5, 192 ± 27, and 230 ± 72 mg CH_4 m^{-2} d^{-1}, respectively).

Bartlett *et al.* (1988) also reported a large spatial variability in average methane emission through ebullition for Amazonian floodplain, with estimated losses of 168 ± 32 mg CH_4 m^{-2} d^{-1} for flooded forest, 346 ± 128 mg CH_4 m^{-2} d^{-1} for floating grasses, and 173 ± 5 mg CH_4 m^{-2} d^{-1} for open water. On the average this

corresponded with a 49, 54 and 64 % methane loss through ebullition for open water, flooded forest and floating grass mats, respectively. Similarly, Devol *et al.* (1988) observed that water surfaces covered by macrophytes in an Amazonian floodplain had the highest CH_4 emission (590 mg CH_4 m^{-2} d^{-1}), while emissions from flooded forest were 110 mg CH m^{-2} d^{-1}, and 120 mg CH_4 m^{-2} d^{-1} for open lakes during the observation period in an Amazonian floodplain. These findings illustrate that this variability in source strength, both in space and time, will be a crucial issue in making low spatial resolution estimates of methane emissions for 'complex' ecosystems.

In the study of Harris and Sebacher (1981) the variability of methane flux within two cypress swamps was greater than the differences in average flux between the undisturbed swamps studied. They hypothesized that nutrient enrichment and organic soil enrichment are important variables influencing methane flux in these cypress swamps. This means that pollution of wetlands by fertilizers, acid rain or waste effluents may substantially change the CH_4 emissions, making estimates of global CH_4 source strength from freshwater swamps difficult (Harris and Sebacher, 1981).

Whalen and Rheeburg (1988) studied the spatial variability in methane fluxes for a tundra ecosystem which included *Eriophorum* tussocks, inter-tussock depressions, moss-covered areas, and *Carex* stands. They observed a high diel, seasonal, intra site and between site variability. *Eriophorum* tussocks and *Carex* were the main contributors to the release of CH_4 to the atmosphere (8.05 ± 2.50 and 4.88 ±0.73 g CH_4 m^{-2} d^{-1}, respectively), with the fluxes from moss sites and inter-tussock depressions being much lower (0.47 ± 0.16 and 0.62 ±0.28 g CH_4 m^{-2} d^{-1}, respectively). Over 90 % of the mean annual methane flux from *Eriophorum*, inter-tussock depressions and *Carex* sites occurred between thaw and freeze up, while 40 % of the CH_4 flux for mosses occurred in winter (Whalen and Rheeburg, 1988).

Bartlett *et al.* (1989) found that the unit area methane flux to the atmosphere from a water saturated Everglades environment, measured *in situ*, varied over more than an order of magnitude (4.2 - 81.9 mg CH_4 m^{-2} d^{-1}), depending on which habitat component was sampled. In this study the observed physical characteristics of the surface - water and soil depth and temperature - were not quantitatively associated with the variability in flux rates. However, the distribution of the vegetation community types provided an empirical indicator of flux, permitting an inventory of CH_4 emission to be based on a mapping exercise of regional patterns of vegetation. Bartlett *et al.* (1989) could thus use high-resolution, orbital remote sensing to reduce the uncertainty in the CH_4 emission inventory of the Everglades by directing *in situ* sampling exercises to important habitats, and by providing a means for calculating an area-weighted, mean flux for the area as a whole. The study of Bartlett *et al.* (1989) thus shows that spatial variability in measured methane flux within a major wetland ecosystem can introduce uncertainty when extrapolating these values to large areas, even if the extent of the major ecosystem is known. Whiting *et al.* (1991) found a direct relationship between spatial variability in plant biomass, net ecosystem production, and methane emissions in a natural *Cladium* spp. wetland.

Svensson (1986) found that the most important factor involved in the regulation of methane formation in acid tundra mires, from a spatial point of view, was the peat moisture content. Similarly, Moore *et al.* (1990) observed that although methane flux was weakly correlated with either peat temperature at 0.1 m depth or water table position within each site a strong association of flux and these variables occurred. This is an indication of the value of 'ecological' attributes in identifying the pattern of CH_4 fluxes.

3.5   Global CH_4 emissions from various environments

3.5.1   Rice paddies

Methane emission and consumption are highly sensitive to a wide range of biotic and abiotic factors. Estimates of global CH_4 emissions from paddy soils that are based on laboratory experiments therefore cannot adequately reflect the wide diversity of environmental and agricultural conditions observed in the field (Moormann and van Breemen, 1978; De Datta, 1981; Hackman, 1979; Kawaguchi and Kyuma, 1977; Ponnamperuma, 1984; Watanabe and Roger, 1985; Neue, 1989 and many others). The total global acreage of rice is about 143 10^6 ha of which about 51 % is irrigated, 27 % rainfed, 8 % consists of deep-water rice and about 14 % of upland rice (see Braatz and Hogan, 1991). In this context, it may be noted that terms such as 'upland' rice may not be appropriate to characterize rice land ecologies. Moormann and Van Breemen (1978) proposed to replace the commonly used crop-oriented terminology with land-oriented terms. In this proposal, they consider the hydrological situation, the natural source of water supply for rice land, as well as the possible man-induced changes in the natural microtopography and water regime (Moormann and Van Breemen, 1978). Neue and Roger (1992) proposed a scheme to discriminate between irrigated-, rainfed- and deep-water rice ecologies in a recent estimate of methane source strength.

Koyama (1963) extrapolated the results of one incubation experiment to the global rice acreage, which give a predicted a CH_4 emission from paddy soils of 190 Tg CH_4 yr^{-1} *anno* 1960. Similarly, Ehhalt (1974) and Ehhalt and Schmidt (1978) used laboratory flux measurements to arrive at their global CH_4 emissions of 220 to 280 Tg yr^{-1} for paddy soils. Based on the first field measurements, recorded in a short-term trial in a Californian rice paddy, the total CH_4 emission was estimated to be 59 Tg CH_4 yr^{-1} (Seiler, 1984). Using semi-continuous field measurements of CH_4 fluxes from Spanish and Californian rice paddies, Seiler (1984) and Holzapfel-Pschorn and Seiler (1986) arrived at global estimates of 30 to 75 Tg CH_4 yr^{-1} and 70 to 170 Tg CH_4 yr^{-1}, respectively. The lower figures obtained, using the results for the Spanish paddy (Seiler, 1984), were later attributed to the possible presence of sulphates originating from Mediterranean inflow. This 'justification' clearly illustrates that extrapolation of a limited number of CH_4 measurements to the global level can easily be fraught with errors.

Bolle *et al*. (1986) estimated the global emissions of CH_4 from rice paddies to be 70 to 170 Tg yr^{-1}. Cicerone and Oremland (1988), reported similar ranges with a central estimate of 110 Tg yr^{-1}. Seiler (1989) arrived at 70 to 110 Tg yr^{-1} using preliminary field measurements in the Peoples Republic of China, one of the major rice growing areas in the world. Seiler (1989) accounted for varying lengths of growing periods as well as for varying seasonal effects. Schütz *et al*. (1990) estimated the emissions of CH_4 from paddy fields to be 100 $\pm$ 50 Tg yr^{-1} of the total CH_4 emission of 496 $\pm$ 251 Tg yr^{-1}. Around the same time, Neue *et al*. (1990) arrived at an annual global emission of CH_4 from wetland rice of 25 to 60 Tg based on their finding that only 80 10^6 ha of paddy soils are potential sources of methane production (see Section 3.7.1). This is much less than the preliminary estimate of about 100 Tg CH_4 yr^{-1} for the Far East alone which was obtained using CH_4 emissions from rice paddies in Hangzhou area in the Peoples Republic of China; the actual measurements were for a period of 1.5 years and covered 3 growing/vegetation periods (Wang *et al*., 1990, quoted by Schütz *et al*., 1990). The review of Bouwman (1990a) estimates the total release of methane from rice paddies at 51 to 111 Tg yr^{-1}.

The preceding global methane emissions from paddy soils range from 25 to 170 Tg CH_4 yr^{-1}, that is they differ by a factor of about 7. The reported differences in calculated global fluxes are the consequence of the large hourly, daily and seasonal variation in measured CH_4 emissions, uncertainty about the relative importance of the respective process controlling factors, and the subsequent extrapolation of results generally obtained for short-term measurements to areas for which they are not necessarily representative (see Section

3.7). In this respect it may be observed that of the about 146 10^6 hectares of paddy harvested annually in the 1990's over 90 % occur in Asia, one of the areas with relatively few CH_4 emissions measurements so far.

3.5.2   Natural wetlands

The major natural wetlands of the world are in boreal, low Arctic and tropical ecosystems. Similar to CH_4 emission measurements for paddy soils, the temporal and spatial variability in recorded CH_4 emissions from natural wetland ecosystems is large. A comprehensive review on CH_4 emissions from swamps, marshes, fens, tundras, and a number of saltwater environments, all broadly described in terms of type of 'vegetation' and geographical location, can be found in Bouwman (1990a p. 93-94). Again the interpretation of the factors that may control methane fluxes in these ecosystems is complicated by the extreme diversity in climatological, vegetational as well as soil conditions in these environments (e.g., Kyuma, 1985; Zoltai and Pollet, 1983). Soil water content, temperature and other seasonal climatological factors as well as vegetation and land use are all potentially critical factors in determining whether natural wetlands function as a source or as a sink of atmospheric CH_4.

Matthews and Fung (1987) arrived at a total of 110 Tg CH_4 yr^{-1} using methane emissions considered representative for 5 broadly defined categories of natural wetlands, with corrections for the effects of latitude ($\approx$ the CH_4 production period). Schütz et $al.$ (1990) obtained CH_4 emissions from natural wetlands of 100 $\pm$ 50 Tg yr^{-1}. These figures are higher than the 25 to 70 Tg CH_4 yr^{-1} that Bolle et $al.$ (1986) reported for natural wetlands.

3.5.3   Methane consumption in terrestrial ecosystems

Under aerobic conditions, some soils may act as a sink of atmospheric CH_4. Based on the few available data on CH_4 uptake, the global sink strength of soils may be as high as 23 to 56 Tg (Schütz et $al.$, 1990). According to Seiler et $al.$ (1984) the global methane consumption must be at least 20 Tg yr^{-1}, while Seiler and Conrad (1987) estimate the global CH_4 consumption by soils as 32 $\pm$ 16 Tg yr^{-1}. As the role of large potential areas of CH_4 uptake are unknown (e.g., savannas, deserts, tundras) these figures remain highly speculative. The latter even more so since the present temporal increase of CH_4 mixing ratios in the atmosphere, may cause an increase of the sink strength with time (Schütz et $al.$, 1990).

Tussock and low-shrub tundra, with 35-50 % vascular plant cover, are expected to show larger CH_4 consumption than wet meadow tundras with 80-90 % vascular plant cover (Whalen and Reeburgh, 1990). Harriss et $al.$ (1982) found that a fresh water peat under waterlogged conditions was a net source of CH_4 to the atmosphere with seasonal variations in emission rates of < 0.001 to 0.02 g CH_4 m^{-2} d^{-1}. During conditions of drought, however, these swamps consumed atmospheric methane at rates of < 0.001 to 0.005 g CH_4 m^{-2} d^{-1}. Evidence of methane oxidation under anaerobic conditions in peat has been observed by Yavitt et $al.$ (1990).

The CH_4 uptake at the surface of soils in semi-arid climates ranged from 3 10^{-4} to 24 10^{-4} g CH_4 m^{-2} h^{-1} (Seiler et $al.$, 1984). A CH_4 consumption of 0.13 mg CH_4-C m^{-2} h^{-1} in hardwood plots in temperate forests and of 0.11 mg CH_4-C m^{-2} h^{-1} in pine plots has been reported by Steudler et $al.$ (1986). Using these values, the estimated global consumption by temperate forests amounts to 0.6 to 9.31 Tg CH_4-C yr^{-1} (Steudler et $al.$, 1986). Methane uptake in subtropical broad-leafed savannah amounted to 52 CH_4 m^{-2} h^{-1} (Seiler et $al.$, 1984).

Steudler *et al*. (1989) predicted that tropical forests consume from 1.26 to 2.53 Tg CH_4-C yr^{-1} on the basis of a literature survey. Hao *et al*. (1988), however, found no methane consumption in their experiment with tropical forest soils. Keller *et al*. (1983) found methane uptake rates of 6-24 10^{-6} g CH_4 m^{-2} h^{-1} in tropical forests. Whalen and Reeburgh (1990) observed uptake rates of 0-112 10^{-6} g CH_4 m^{-2} h^{-1} in tundra soils. Methane uptake in a Colorado semi-arid grassland ranged from 6 to 61 10^{-6} g CH_4 m^{-2} h^{-1} (Mosier *et al*., 1991). If Mosier *et al*.'s (1991) measurements are representative for CH_4 uptake by semi-arid grasslands globally, then 0.5 to 5.6 Tg of CH_4 are removed from the atmosphere in these grasslands each year.

The study of Mosier *et al*. (1991) shows that recent changes in land use or management, such as cultivation of grassland, have decreased the CH_4 uptake, and increased the N_2O efflux to the atmosphere. This means that remedial measures for CH_4 may affect N_2O production.

3.6 Abiotic regulating factors of methane production and consumption

3.6.1 General

Methane production and consumption are biologically mediated processes. Therefore, any factors affecting the physical, chemical and biological characteristics of the terrestrial environment will influence the net CH_4 production. The soil related controlling factors of methane production include: organic substrate supply, temperature, texture, mineralogy, Eh/pH buffer systems, hydrologic conditions, and salinity. Soil and floodwater properties will interact with the meteorological regime by temperature, changes in reflectivity, heat capacity, thermal conductivity, incoming water temperature and water flow (Neue *et al*., 1990). In view of the variety of soils (see FAO/Unesco, 1971-1981) and agro-ecological conditions occurring at the international level, it is difficult to establish unambiguous relationships between the various factors controlling net methane emissions. In this Section the abiotic flux controlling factors are discussed in separate paragraphs for convenience's sake, although it is recognized that many interactions do occur. Wilson *et al*. (1989) justly wrote that 'because methane flux is a function of a variety of processes and release mechanisms, which may vary seasonally and among sites, simple correlation with factors such as temperature provide, of necessity, only approximations of the true dynamics of methane flux'.

3.6.2 Effects of Temperature

Temperature plays an important role in the rate of activity of soil microorganisms, including those involved in methane production (see Zeikus and Winfrey, 1976) and consumption. Wahlen and Reeburgh (1990) observed microbially mediated CH_4-oxidation in Alaskan tundra soils at a temperature of about 7 °C; this population was capable of oxidizing methane at concentrations 10 times lower than the ambient atmospheric methane concentration. Alternatively, Sebacher *et al*. (1986) recorded significant CH_4 emissions in tundra areas where the peat temperature was 2-4 °C and permafrost occurred a 25 cm below the surface. Svensson (1984) reported a temperature coefficient (Q_{10}) of 5.5-8.0 for the temperature interval from 2-10 °C. Yagi *et al*. (1990), however, found very little methanogenesis at 5 °C and 15 °C in Japanese paddy fields. Wilson *et al*. (1989) observed major changes in methane fluxes between 10 and 16 °C in a temperate swamp. Svensson (1984) found evidence for the possible existence of strains of low-temperature adopted methanogens, and also reported different temperature optima for acetate (20 °C) and H_2-utilizing (28 °C) methanogens in peat.

Pacey and De Gier (1986) found that methane production drastically decreases below 10-15 $^{\circ}$C and generally ceases above 60 $^{\circ}$C. Thermophilic environments, such as hot springs, however can be sites of active methanogenesis (Oremland, 1988). According to Neue and Scharpenseel (1984) most methanogenic bacteria display optimum rates of CH_4 production around 30 $^{\circ}$C. Inubushi et al. (1990a) found that a high temperature enhances CH_4 formation, especially above 30 $^{\circ}$C. Additionally, they observed that fluctuations in air temperature, during incubation experiments, enhanced the formation of CH_4. Temperature changes from 20 to 30 $^{\circ}$C or from 30 to 40 $^{\circ}$C during incubation had a larger effect on methane production than constant temperature of 30 $^{\circ}$C or 40 $^{\circ}$C, respectively. Based on these findings, Inubushi et al. (1990a) concluded that we must be careful when estimating the amount of CH_4 formed in paddy fields where temperatures vary widely. Svensson and Rosswall (1984) observed that the correlation of methane emissions with temperature probably not only reflects the immediate response of methanogens, but also an effect on the methane diffusion rate which increases with soil temperature.

CH_4 emissions from an Italian rice field increased exponentially with rising temperatures. Holzapfel-Pschorn and Seiler (1986) found almost a doubling of methane emission rates when the soil temperature rose from 20 to 25 $^{\circ}$C, corresponding with a Q_{10} of about 4. Similarly, incubation under N_2-atmosphere of paddy soil samples from 12 Agricultural Experimental Stations in Japan and 4 sites in Louisiana at 35 $^{\circ}$C led to substantially higher production of methane than at 25 $^{\circ}$C, although there were large differences between CH_4 production by the various soils studied (Yagi et al., 1990). In other experiments, however, methane emissions are poorly correlated with temperature (Sebacher et al., 1986; Cicerone et al., 1983). For example, the seasonal variation in methane emissions in a rice paddy at Vercelli, Italy, was not clearly related to soil temperature. However, the diel changes in CH_4 fluxes were significantly correlated with the diel changes of the temperature at a particular soil depth (Schütz et al., 1990b). Similarly, methane production in a Mississippi deltaic peat was related to temperature in the 0-40 cm depth zone, but it was relatively constant below a depth of 40 cm (DeLaune et al., 1986).

There are several possible explanations for the temperature dependency of methane production and consumption. Yamane and Sato (1967), for instance, observed that with increasing temperatures (10-35 $^{\circ}$C) organic acids persisted for a shorter time and that more methane was produced. The studies of Svensson (1984) and Yavitt et al. (1987) indicate that methane production will not respond to an increase in temperature if one or more of the other environmental factors is limiting production. Yavitt et al. (1988), for instance, found that low temperature constrained the potential for methane production from peat in winter, while the chemical status of the peat substrate appeared to control the CH_4 production in summer.

Sebacher et al. (1986) showed that the total CH_4 flux from tundras are of the same magnitude as those from wetlands located in 'more' temperate regions, even though temperatures are much lower. Svensson (1986) observed that the CH_4 production in cold areas, in casu the Antarctica moss carpets ($\approx$ 2 $^{\circ}$C) and subarctic mires in Sweden, are comparable to those found in 'warmer' areas such as Florida and Italy. Similarly, the literature review of Bouwman (1990a) shows that although high temperatures seem to stimulate CH_4 formation, annual methane emissions estimated from field measurements are in the same order of magnitude (1-200 g m^{-2} yr^{-1}) for tropical, cool temperate and subarctic environments.

3.6.3 Effects of soil pH

Different opinions have been expressed in the literature on the effects of soil pH on methanogenesis. Svensson (1986), for instance, found that differences in pH values between wetlands seem to have little effect

on methane emissions to the atmosphere. It would seem that methanogenesis is favoured by neutral or slightly above neutral pH, with the exact optimum pH influenced by the type of soil (Minami, 1989) and strain of methanogens. According to Williams and Crawford (1985) methanogens adopted to acidic conditions may produce methane at a similar rate as the methanogens inhabiting neutral areas in terms of pH. One of the methanogenic strains studied by Williams and Crawford (1985) was able to form methane from CO_2 - H_2 (4:1) at rates that were similar over a range of pH values. Moore and Knowles (1987), however, observed differences in methane fluxes between a fen (pH of 4.9; 28 mg CH_4 m^{-2} d^{-1}) and a bog (pH of 3.7; 0.7 mg CH_4 m^{-2} d^{-1}) which appeared to be related to the acidity of the environments and their microbial characteristics. DeLaune *et al.* (1986) found that the CH_4 production rate in Mississippi river deltaic peat is pH dependent, with an optimum rate of methanogenesis at pH 7.7. In a laboratory experiment by Williams and Crawford (1984), the optimum pH for methanogenesis was found to be 6.0 for peat soils with initial field pH values of 3.8 to 4.3. According to Pacey and de Gier (1986) the optimal pH for methane production is between 6.8 and 7.2, and methane generation is not inhibited unless the pH drops below 6.0. Harris *et al.* (1985), however, observed no differences between ombrotrophic peat (pH of 3-4) and minerotrophic peat (pH of 6 to 7) in methane production, while Svensson and Rosswall (1984) reported higher CH_4 production in minerotrophic peats.

Yavitt *et al.* (1987) studied the combined effect of pH adjustment and acetate amendment. In the experiment where the pH was modified in presence of acetate, they found that the untreated peat incubated at a pH of 3.1 showed lower methane production than at a pH of 4.5. The methane production did not increase markedly either when the pH was increased to 6.4.

Ponnamperuma (1984) discusses the effect of flooding on the soil pH. In surface soils with an initial pH of 5 to 6, the increase in alkalinity (HCO_3^-) associated with the reduction of ferric oxide to aqueous Fe^{2+} will cause an increase in pH, normally from 6.5 to 7.0. In calcareous soils, however, the mobility of Fe^{2+} is generally lower, and less balancing HCO_3^- ions are formed. Under these conditions, the acidifying effect of the accumulated CO_2 is dominating, causing a fall in pH to 6.5 - 7.0. Strongly alkaline soils with pH over 9 that are low in inorganic matter content, however, will show little reduction upon flooding. The pH of these soils tends to remain around 8.5, unless the soils are amended with organic matter (Moormann and van Breemen, 1978).

3.6.4   Effects of organic substrates

The degradation and mineralization of organic substrates in flooded rice soils are promoted by several actions (Neue *et al.*, 1990):

a.   Thorough puddling of the soil before planting of the soils;
b.   Soil temperature of the puddled layer of 30-35 $^{\circ}$C;
c.   Neutral to alkaline pH of flooded soils;
d.   High soil/water ratio associated with a low bulk density (0.2-0.8 g cm^{-3}) of the puddled layer;
e.   Shallow depth of the floodwater standing on the paddy;
f.   High and well balanced nutrient supply.
g.   Permanent supply of energy rich photosynthetic aquatic and benthic biomass;
h.   High diversity of micro- and macro-organisms;
i.   Supply of oxygen into the reduced root layer by rice roots, excretion and diurnal supersaturation of the floodwater with oxygen.

Yagi *et al*. (1990) found no close correlation between methane production rates and total carbon contents in soils. They observed that these results suggest that other factors controlling methane production were important, such as the balance of bacterial population and oxidizing capacity of the soil. Alternatively, it may indicate that total carbon contents alone are not a good indicator for the availability of organic substrates for biogenic methane production. Bridgham and Richardson (1992), for instance, reported that poor substrate quality of a highly decomposed, humified peat limited both CO_2 and CH_4 production rate in a southern USA peatland, even though the peat was 95 % organic matter. This shows organic substrate quality must be considered also. Inubushi *et al*. (1990a) reported that the mineralizable-N content was most significantly related to the amount of CH_4 produced. Yagi and Minami (1990) found a positive correlation between the annual emission rate of CH_4 and the contents of readily mineralizable carbon in pre-cultivated paddy soils. Based on these findings, Inubushi *et al*. (1990a) concluded that CH_4 is derived mainly from the easily decomposable fraction of soil organic matter through decarboxylation of acetic acid and reduction of CO_2. The observed enhancing effect of organic matter application on CH_4 formation was also seen as evidence for this consideration.

CH_4 emissions from an Italian rice field increased considerably in the early stages of growth after application of organic matter (Schütz *et al*., 1989). Incorporation of rice straw in a Japanese paddy field caused a significant increase in CH_4 emissions, whereas addition of compost did not (Yagi and Minami, 1990). Inubushi *et al*. (1990a) found that CH_4 formation in incubation experiments of paddy soils was enhanced by the application of rice straw, wheat straw, glucose, alanine and Na-acetate. Except for paddies with high percolation rates or aeration periods, a rapid decay of organic substrate and fats turnover is always associated with high CH_4 production (Neue *et al*., 1990). Inubushi *et al*. (1990b) found that the total amount of methane emitted during the cropping season of a rice crop decreased by about 40-98 % due to percolation (equivalent to 51 mm water per 2 weeks). Williams and Crawford (1984) observed an inhibition of methanogens by acetate, and concluded that CH_4 and other C-derivatives which may accumulate in peats at some depth can become inhibitory to methanogens. Similarly, DeLaune *et al*. (1987) observed that the accumulation of metabolic end-products in a peat matrix appeared to be important in limiting methanogenesis in a peat from the Mississippi delta. Yavitt *et al*. (1987) reported that acetate became a toxin for methanogens when the pH of an acid *Sphagnum*-derived peat was lowered from the original pH value of 4.5 to 3.1. According to Yavitt *et al*. (1987), the undissociated forms of organic acids can permeate the cytoplasmic membranes of microorganisms and acidify the cytoplasm. At a pH of 6.4, however, the addition of acetate stimulated the methane production over that in the unamended peat (pH of 4.5) 2.2 and 1.6 fold for the 0-5 cm and 20-25 cm depth zone, respectively. Yavitt *et al*. (1987) presumed that in other studies where addition of acetate enhanced methane production, as was the case in the study of Svensson (1984), the pH of the environment must have been greater than the pK of acetic acid.

Seiler *et al*. (1984) observed seasonal peaks in CH_4 fluxes that may be associated with an increase in soil organic matter content. The peaks were observed after the incorporation of crop residues prior to flooding, and following the release of soil organic matter as root exudates and litter at the heading and flowering stages of rice. Holzapfel-Pschorn and Seiler (1986) reported peaks in CH_4 fluxes shortly after inundation of a paddy and an upland soil, which they attributed to mineralization of the organic matter. A second peak was observed in planted field in the physiologically most active period of rice growth. This peak was attributed to the supply of organic materials in the form of root exudates. Swarup (1989) observed that the second peak may also be related to the drop in Eh of the soil, which was lowest after 30 days of crop growth. Such a drop in Eh, however, may also be seen as the expression of a microbial population explosion caused by the increase in readily decomposable organic materials under anaerobic conditions. The amount of CH_4 formed in paddy

soils is positively correlated with several soil parameters such as the content of organic-C and water soluble organic-C, and mineralizable-N (Inubushi *et al.*, 1990a; Kimura, 1992).

Application of rice straw at a rate of 12 tons per hectare enhanced the rate of methane emission by a factor 2 as compared with the control plot, while higher applications did not result in any additional increases (Schütz *et al.*, 1989a). Incorporation of rice straw 1 or 2 months before submerging the paddy soil reduced subsequent methane emissions to 15-50 % of the amounts recorded when straw was incorporated at the time of flooding (Inubushi *et al.*, 1990b). Application of rice straw to paddy fields significantly increased the CH_4 fluxes in all sites studied by Yagi *et al.* (1990). The annual emission rate from the paddy plots supplied with 6000 kg ha^{-1} of rice straw and a mineral fertilizer increased by a factor 2-3 as compared with the rates observed at the sites which only received the mineral fertilizer. The methane fluxes measured by Yagi *et al.* (1990) differed between 3 paddy soils amended with rice straw, with annual emissions of 44.8, 27.0, 9.8, and 1.1 g CH_4 m^{-2} yr^{-1} for the 'peaty', 'alluvial', 'humic Andosol' and 'light coloured andosol' respectively. The interpretation of this type of results, in terms of possible effects of soil conditions on methane fluxes, would be facilitated to some extent if the soils were fully characterized and classified according to a widely accepted system (e.g., FAO/Unesco, 1971-1981; FAO, 1988).

Kimura *et al.* (1991) observed that the decomposition of soil organic matter, and thereby the potential CO_2 and CH_4 production, is primarily determined by the soil chemical properties and the temperature, and not by the agricultural practices. According to this study, the agricultural management, such as mid-summer drainage and intermittent irrigation, may only influence the CO_2/CH_4 ratio.

In conclusion, it appears that the nature (e.g., C/N quotient), volume, timing and mode of application/incorporation of organic substrates to waterlogged soils may both affect CH_4 production and consumption.

3.6.5   Effects of nutrient status and mineral fertilizers

Svensson (1986) observed that nutrient availability and H-mediated interactions between nitrogen fixing cyanobacteria and methanogenic bacteria may influence CH_4 fluxes in an acid tundra mire. Cicerone and Shetter (1983) found CH_4 fluxes to be related to peat depth and nutrient enrichment through upward seepage.

Mosier *et al.* (1991), in studies in the Colorado short-grass steppe with nitrogen-fertilized and wheat-growing prairie soils from spring to late autumn 1990, found that nitrogen fertilization and cultivation can both decrease CH_4 uptake and increase N_2O production. Similarly, nitrogen fertilization applied as urea decreased the CH_4 uptake in a Colorado short-steppe (Mosier *et al.*, 1991). Steudler *et al.* (1989) reported similar observations for temperate forest soils. In the annually fertilized sites, annual N-urea applications caused the CH_4 uptake to decrease by an average of 41 % ($P < 0.01$). Methane uptake by the midslope site decreased from 6.3 to 4.1 g C ha^{-1}d^{-1} as a result of applying 45 g m^{-2} urea-N in 1981 ($P < 0.01$). A similar application to a more fertile swale soil in 1982 did not alter the CH_4 uptake, which averaged 3.6 g CH_4 ha^{-1}d^{-1}. The data suggested that a high N-turnover, whether native or due to fertilization, suppresses CH_4 uptake (Mosier *et al.*, 1991).

Cicerone and Shetter (1983) reported a 5-fold increase in methane emissions in a Californian rice field upon the application of $(NH_4)_2SO_4$. Schütz *et al.* (1989), however, recorded reduced CH_4 fluxes after addition of $(NH_4)_2SO_4$ or urea to rice paddies. In the case of ammonium sulphate the decrease was attributed to the

presence of sulphates. Due to the nature of the reduction sequence in waterlogged soils, addition of fertilizers including compounds such as nitrates or sulphates may suppress methanogenesis (see Section 3.6.8). According to Jacobsen *et al.* (1981) this may be due to a two-fold effect: a) nitrate delays the formation of methane through its effect on the redox conditions, b) nitrate may have a toxic effect on methanogenesis.

Preliminary results reported by Schütz *et al.* (1990) showed that the application of the mineral fertilizers KCl and K_2SO_4 as well as various organic manures (i.e. animal excreta, rape seed cake), as commonly used in the Hangzhou area, did not significantly affect the CH_4 emission rates. Lindau *et al.* (1991) reported a significant urea-fertilizer effect in a flooded Louisiana rice field. The observed CH_4 emissions were highly variable during the observation period, with maximum methane emissions from the 0, 100, 200, 200 and 200 kg urea-N treatments amounting to 6.0, 8.9, 9.8 and 11.2 kg CH_4 ha^{-1} dm^{-1}, respectively. The effect of fertilizer application may also be influenced by the mode of application. Deep incorporation in contrast to surface application of urea increased total the CH_4 emission by 19 % on a crop-season basis in an Italian paddy (Schütz *et al.*, 1989a). Alternatively, in the Philippines, Denier van der Gon *et al.* (1992) found the mode of urea application did not affect the pattern and emission levels of methane.

A tabular review of methane emissions from various types of wetland rice fields, subjected to different fertilizer and/or organic amendments, has been prepared by Bouwman (1991).

The above quoted studies indicate that the relationship between CH_4 flux and mineral fertilizer amendment is complex and depends on crop factors, soil factors as well as cultivation practices such as rate, timing, mode of application and type of fertilizers in relation to water management practices.

3.6.6   Effects of redox conditions

Takai and Kimura (1966) recognize two stages in the reduction of submerged soils. During the first stage, facultative or obligate anaerobes, consume O_2 or reduce NO_3^-, Mn^{4+} and Fe^{3+}. In the subsequent stage, obligate anaerobes reduce sulphate and form methane. Takai (1961) found that the CO_2/CH_4 ratio in Japanese rice fields depends on the 'oxidizing capacity', expressed by the amount of O_2, NO_3^-, Mn^{4+} and Fe^{3+} (see also Kimura, 1992). Figure 3.3 shows the critical redox potential at which oxidized inorganic redox systems begin to undergo reduction in flooded soils. The sequence of the reduction processes occurring in anaerobic soil can be described with the Nernst equation (e.g., Novozamsky *et al.*, 1978).
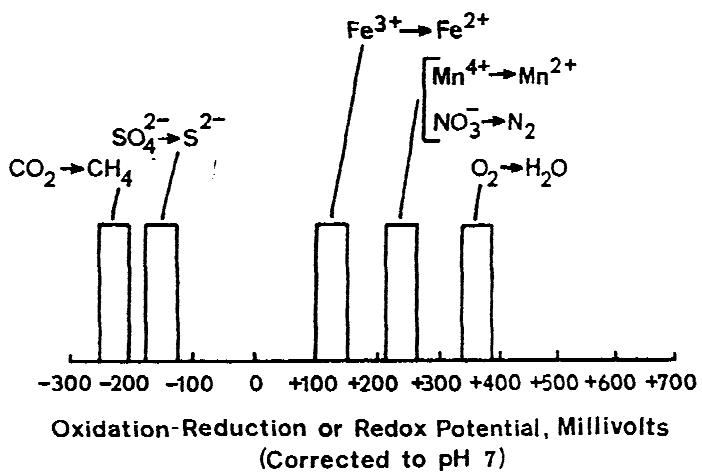
Figure 3.3. Schematic representation of the critical redox potential at which oxidized inorganic redox systems begin to undergo reduction in flooded soils (After Patrick, 1981)

In soils with high contents of iron and organic matter the Eh falls to -50 mV and may then slowly decline over a period of a month to -200 mV. Soils low in active-iron with high organic matter contents attain Eh values of -200 to -300 mV within 2 weeks after submergence (Ponnamperuma, 1972 and 1981). Flooded rice soils may have Eh values as low as -250 to -300 mV (Patrick, 1981), while redox potentials (corrected to pH 7) of -150 mV to -190 mV are needed for methane formation (Neue *et al*., 1990). Lindau *et al*. (1991) observed no methane formation above -100 mV, while Jacobsen *et al*. (1981) only observed a small amount of CH_4 formation at a redox potential of -120 mV.

Yagi *et al*. (1990) observed strong seasonal variations in CH_4 fluxes in field experiments. The CH_4 emissions began to increase as the Eh decreased, nearly a month after flooding of the paddies. The fluxes increased as the rice plant grew. Considerable decreases in CH_4 fluxes were recorded during the period of mid-summer drainage (increase in Eh) and shortly after top-dressing the rice plants. Methane emissions were not detected or very low during dry soil conditions in a Louisiana rice field, corresponding with the pre-flood period and time prior to harvest (Lindau *et al*., 1991). After drainage and aeration the redox potential rapidly rises from negative to positive values of 300 to 600 mV typical for aerated soils (Moormann and Van Breemen, 1978). Methane oxidation may thus increase when the soil is temporarily drained. Methane production, however, may continue for as long as the interior of clods remain reduced and adequate organic substrates are present in these aggregates.

3.6.7   Effects of depth of water table

The depth of the water table may influence methane production in different ways. Methane fluxes from tundras (Sebacher *et al*., 1986) and swamp sites (Harriss *et al*., 1982) are positively correlated with the level of the water table (see also Section 3.6.6). Moore and Knowles (1987) found that methane evolution in Canadian peatland soils decreased in a log-relationship as the water table was lowered; the molar ratios of CO_2/CH_4 increased from 4-173 under inundated conditions to >2500 when the water table was at a depth of 70 cm. Wilson *et al*. (1989), however, found that the water depth was poorly correlated with the methane flux in a temperate swamp. Similarly, Lindau *et al*. (1991) found no relationship between floodwater depth in a flooded rice paddy (5-10 cm) and CH_4 emission. In the study of Harriss and Sebacher (1981) soil-water

temperature and water depth did not exhibit any relationship to methane flux. Sebacher *et al*. (1986), however, found that CH_4 emissions increased with water depth up to a depth of about 10 cm, but thereafter the emissions decreased. According to DeBont *et al*. (1978) and DeLaune *et al*. (1983) microbial oxidation of CH_4 may occur in aerobic water columns deeper than 10 cm, possibly due to transport of oxygen to the rhizosphere through the aerenchyma of vascular plants. Inubushi *et al*. (1990a) found that methanogenic activity was higher at 5-10 cm than at 0-2 cm depth in a submerged paddy soil, which was sampled at different depths after harvest, although the overall activity was generally low. Inubushi *et al*. (1990a) attributed this to the fact that in the upper part of the solum, which included the oxidized layer, more CH_4 is oxidized than in the lower part during rice cultivation, and that most of the organic substrates in the soil are depleted at harvest time.

Moore and Knowles (1989) found that CH_4 evolution decreased in a log-relationship as the water table was lowered in a laboratory column filled with peat. Similarly, twenty per cent of the stations studied during a high-latitude transect, all with a lowered water table, had zero or negative CH_4 fluxes possibly as a result of methane oxidation (Whalen and Reeburgh, 1990). Thus lowering of the water table in tundras as a result of a warmer, drier climate will decrease methane fluxes and could cause these areas to provide a negative feedback for atmospheric methane. Alternatively, oxidation of peat following a drop in the watertable may form a substantial source of atmospheric CO_2, another important greenhouse gas (Moore and Knowles, 1987).

3.6.8   Effects of sulphates and salts

Bartlett *et al*. (1985, 1987) found that methane concentrations and sulphate concentrations are negatively correlated. Similarly, DeLaune *et al.* (1983) found that CH_4 emission was inversely related to salinity and sulphate concentration, with CH_4 emissions increasing and salinity and sulphate decreasing with distance from the ocean. Sulphate depletion in a Humic Fluvisol, developed under marine influence, lead to intensive methanogenesis (Giani and Giani, 1990).
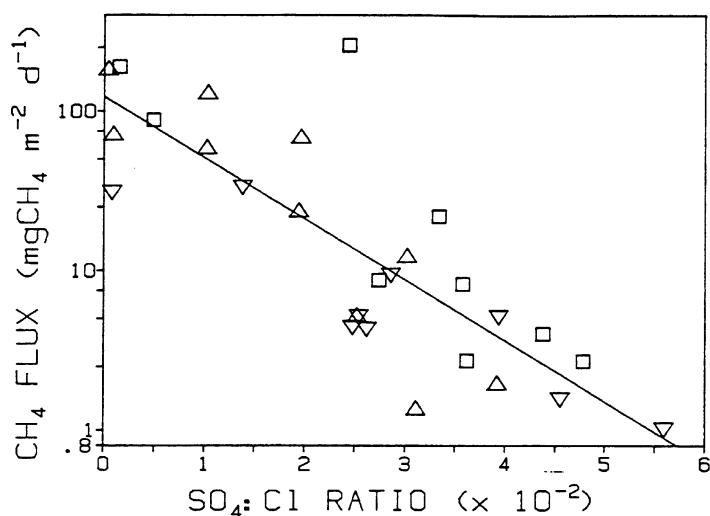
Figure 3.4.   Average SO_4^{2-} /Cl⁻ ratios in the top 15 cm of marsh soils and methane emissions across the air-soil interface (r= -0.824, P < 0.1; After Bartlett *et al.*, 1987)

Sulphate and sulphides may be toxic to methanogens (Jacobsen *et al.*, 1981). A concentration of 10 m*M* sulphate is considered inhibitory for methane production (DeLaune *et al.*, 1983). In incubation experiments, the formation of CH_4 is suppressed by the application of Na2SO4, possibly because methane forming bacteria may be overcome by sulphate reducing bacteria in competing for hydrogen (Inubushi *et al.*, 1990a). The partial pressure of hydrogen utilized by sulphate reducing bacteria is lower than the one required by methane forming bacteria (Schönheit *et al.*, 1982). Hori *et al.* (1990) found that sulphate reducing bacteria and methane forming bacteria compete for acetic acid in submerged paddy soils. Such a competition for acetic acid has also been found in peat soils (Yavitt *et al.*, 1987) and in sediments (Ward and Winfrey, 1985). Sulphate depletion allows methanogenic bacteria to use acetate and H_2/CO_2 as substrates (Mountfort *et al.*, 1980; Winfrey *et al.*, 1981), otherwise the acetate and H_2 is used by sulphate reducers (Kristjansson *et al.*, 1982; Winfrey *et al.*, 1981; Kimura *et al.*, 1991). According to Thauer *et al.* (1977) the presence of sulphate prevents methane formation, due to the competition between sulphate-reducing and methanogenic bacteria for hydrogen and acetate, because sulphate-reduction produces more energy per mole H_2 or acetate than CH_4-formation. Bartlett *et al.* (1987) found a strong correlation between SO_4^{2-}/Cl^- ratios and CH_4 release to the atmosphere across a salt marsh (Figure 3.4), and saw this as an indication that the activity of sulphate reducers is a primary control of CH_4 flux. Oremland *et al.* (1982), however, have suggested that competition with sulphate reducing bacteria may not be important in salt marsh sediments due to the utilization of 'non-competitive' substrates such as methanol and methylated amines. Zaiss (1981) reported that the inhibitory effect of sulphates on methane production in freshwater sediments can be reversed by addition of acetate or H_2. Kimura *et al.* (1991) observed that in some soils there may be a competitive use of root exudates by methane-producing and sulphate-reducing bacteria.

Lawongse and Wada (1988) found that addition of NaCl and Na2SO4 suppressed denitrification and Fe^{3+} reduction, and enhanced the accumulation of various organic acids such as acetic acid, propionic, lactic, and p-hydroxy-phenylacetic acids. On the basis of these observations they concluded that CH_4 formation and sulphate reduction are more strongly suppressed with salts than the biochemical reactions responsible for the formation of these organic acids. Alternatively, a possible explanation could be that rice varieties differ in their susceptibility to salinity. Moormann and Van Breemen (1978) wrote that at a given salinity level, rice plants are more sensitive to NaCl at high light intensities and low relative humidity, and consequently can withstand a given level of salinity better during the wet than during the dry season. This may be seen as an additional complicating factor in interpreting the effect of NaCl concentrations on CH_4 emissions.

In the study of Saenjan and Wada (1990) the suppressive effects of NaCl on CO_2 and CH_4 formation varied widely depending on the type of organic acids present (i.e. acetic, propionic, lactic, p-hydroxy-phenylacetic, ± Na2SO4), becoming more evident with increasing NaCl concentration. Among the two main pathways of CH_4-formation, the reduction of CO_2 is less susceptible to NaCl than the decomposition of acetic acid (Saenjan and Wada, 1990). In the control plot examined without addition of organic acids, CH_4-formation was slightly more susceptible to NaCl than to SO_4^{2-} reduction (Saenjan and Wada, 1990).

3.6.9   Effects of 'topographic position'

Many paddy fields and natural wetlands occur in 'depressed' topographic positions and hydrological settings that favour the supply of bases as well as organic detritus from surrounding sites. The topographical and related hydrological situation may thus influence the nutrient status and thereby indirectly affect the production and emission of CH_4.

G70Only a few measurements of trace gas fluxes have been made along toposequences. Moore *et al.* (1990) found that topography and water table elevation were important controls on methane emission in subarctic fens. Mosier *et al.* (1991) measured the CH_4 uptake along a toposequence - sandy loam upland (mid slope) versus sand clay loam lowland (swale) - in a short-grass steppe in Colorado to assess whether the landscape position affected the uptake of CH_4. The methane uptake rates in the unfertilized grassland averaged 3.6, 5.8 and 6.3 g C ha^{-1} d^{-1} in the swales, CAFS (control annual fertilized) and midslope sites, respectively, between March and December 1990. Methane uptake was significantly less in the swale ($P < 0.001$) than at the CAFS and midslope sites. The midslope and CAFS soils were similar in texture and total N-content, whereas the swale soil had finer texture and higher total-N content. The soil nitrate and ammonium contents were similar. Annual in situ mineralisation at the midslope, however, was substantially lower than in the swale (41 compared to 55 kg N ha^{-1}yr^{-1}), suggesting that it was the N-turnover (mineralization and nitrification), rather than the mineral N-content, which directly influenced the CH_4 uptake (Mosier *et al.*, 1991).

3.6.10   Effects of soil type

Since soil conditions generally are poorly described in CH_4 emission studies, little experimental evidence is available on the possible effects of texture and mineralogy on methane production and emission. Soil texture and mineralogy, through their effect on puddling, can affect percolation rates and thereby the net emission of CH_4 in waterlogged paddy soils (Neue *et al.*, 1990). Heavy clay soils may crack upon drying, facilitating the emission of entrapped methane while in slowly cracking soils there may be more time for methane to be oxidized. Table 3.1 shows methane emissions for three Japanese paddy fields, reflecting differences in mean fluxes between these soils (Inubushi *et al.*, 1990a). Similarly, Yagi and Minami (1990) found a relationship between CH_4 emissions from paddies and soil type, the emissions decreasing in the sequence 'peaty soils', 'alluvial soils' and 'andosols'. With respect to Japanese paddy fields, Kimura *et al.* (1991) reported a significant correlation between the CO_2/CH_4 ratio and the content of free iron and the amount of NH_4^+ produced during incubation.

Asami and Takai (1970) added amorphous iron oxide to anaerobically incubated soils, which depressed the formation of volatile fatty acids and methane. Similarly, the content of free Fe-oxide was negatively correlated with the amount of CH_4 produced, except for 2 of the 13 Japanese paddy soils investigated. Takai and Wada (1990) postulate that the content of bio-active iron may be the most important controlling factor in methane production.

Table 3.1.   Differences in CH_4 emission from 3 Japanese paddy fields (After Inubushi *et al.*, 1990a).

Cropping pattern	Japanese soil type	CH_4 emission[*] range resp. mean	
With rice plants	Gley soil	1.9 - 22.7	12.7
	Gray lowland soil	0.1 - 15.8	5.2
	Brown lowland soil	0.5 - 3.3	1.8
Without rice plants	Gley soil	0.2 - 5.1	1.9
	Gray lowland soil	0.02 - 0.2	0.06
	Brown lowland soil	0.3 - 1.4	0.9

Note: Methane emissions specified in mg CH_4-C h^{-1} m^{-2}.

The following soil conditions are considered adverse to CH_4 production (Neue *et al.*, 1990):

- Electrical conductivity (EC) greater than 4 mS cm^{-1} while flooded.
- Low soil pH (acidic or allitic reactions)
- Ferritic, gibbsitic, ferruginous or oxidic mineralogy.
- More than 40 % of kaolinitic or halloysitic clay minerals
- Less than 18 % of clay in the fine earth fraction if the water regime is epiaquic.
- Occasional drying of the soil during the cultivation period.

This type of soil conditions usually occurs within the order of Oxisols, most of the Ultisols and some of the Aridisols, Entisols and Inceptisols of Soil Taxonomy (USDA, 1987). Methane production is often favoured in rice soils formed on Entisols, Histosols, Inceptisols, Alfisols, Vertisols and Mollisols (Neue *et al.*, 1990). Denier van der Gon *et al.* (1992) showed soils can be ranked according to their methane-producing capacity and Bachelet and Neue (1992) assigned a coefficient to each FAO soil unit according to its hypothetical methane emission capacity.

Neue and Roger (1992) present a table of linear correlations between selected physico-chemical soil properties and methane production. Negative correlations were found with Eh, electrical conductivity (EC), chloride and sulphate content and C/N ratio, and a positive correlation with pH. These results clearly reflect the uncertainties that remain in assessing the relative importance of various soil factors on methane production. The minimum set of soil properties needed for reliable modelling of methane production in soils still has to be determined, but it will certainly include organic carbon content, C/N ratio, per cent clay, mineralogy, active-Fe, Eh/pH-buffer systems and salinity (Neue *et al.*, 1990; Denier van der Gon *et al.*, 1992; see also Section 3.7.2).

These considerations indicate the usefulness of developing a soil data base to show where potentially suited areas of CH_4 production and emission occur (see Chapter 6). The interest for this type of data bases has been expressed by several research groups (e.g. Sombroek, 1990; Braatz and Hogan, 1991).

3.7 Modelling CH_4 emissions from paddy soils and natural wetlands

3.7.1 Empirical models

Three global modelling exercises of CH_4 emissions are discussed in this Section, namely those of Matthews and Fung (1987), Aselmann and Crützen (1990) and Neue *et al.* (1990). In this report we use the term 'empirical model' for approaches in which the total emission of methane from rice paddies or natural wetlands is basically calculated as follows:

$$Emission_{CH4} = Sum (A_i . R_i . t_i)$$

where:

A_i the harvested area of rice (or area of natural wetland);
R_i the average release of methane from the individual areas over the respective release periods as measured in the field;
t_i the average length of the respective vegetation periods.

Natural wetlands

Matthews and Fung (1987) combined three data bases in their study of global CH_4 emissions from natural wetlands: 1) the vegetation data base of Unesco (1973), 2) the Soil Map of the World (FAO/Unesco, 1971-1981, as digitized by Zobler, 1986), and 3) the Operational Navigational Charts to estimate the fractional inundation on a 1 x 1 degree grid basis. The integration of these data bases produced 3233 grids of 1 x 1 degree, which comprise 130 vegetation types covering 100 units of the FAO/Unesco Soil Map of the World with fractional inundation ranging from 1 to 100 per cent. Since only few methane measurements, from well defined ecosystems, are available presently, Matthews and Fung (1987) reduced the information on wetlands to 5 broad functional groups: forested bog, non-forested bog, forested swamp, non-forested swamp, and alluvial formations. Methane fluxes, considered representative for each of these groups, were subsequently used to compute global CH_4 emissions from natural wetlands. The 'representative' fluxes ranged from 0.03 g CH_4 m^{-2} d^{-1} for the alluvial formations, to 0.2 g CH_4 m^{-2} d^{-1} for forested and non-forested bogs. Based on the above assumptions and methodology Matthews and Fung (1987) arrived at emissions of 110 Tg CH_4 yr^{-1} from natural wetlands. With respect to the study of Matthews and Fung (1987), Wilson *et al*. (1989) noted that latitudinally averaged methane productive seasons may induce considerable error terms, at least in temperate regions, since the seasonal changes in methane flux may be closely linked to the growing dynamics of the respective vascular plant communities (see also Section 3.4.2).

Aselmann and Crützen (1990) developed a global data set on the geographic distribution and seasonability of freshwater wetlands and rice paddies using a 2.5 degrees latitude by 5 degrees longitude grid. The data set was complied from wetland monographs, surveys and maps, while information on the seasonality was derived from climatic records and hydrological data of major catchment areas. The natural wetlands were grouped into six broad categories, termed: bogs, fens, swamps, marshes, flood-plains and shallow lakes. In the initial approach, published net primary production (NPP) data were used to develop latitude dependent mean NPP values for each of the six categories of natural wetlands. When the average CH_4/NPP ratio (on a carbon basis) of 2-7 % is applied to the averaged NPP values of the six wetland categories a total emission of 50-360 Tg CH_4 yr^{-1} is obtained, which is far too large a range to be consistent with the overall CH_4 budget. Aselmann and Crützen (1990) therefore concluded that use of the CH_4/NPP ratio seems inappropriate to obtain reasonable CH_4 emission estimates. In a subsequent effort, they extrapolated geometric means of measured CH_4 fluxes to the six categories of wetlands and obtained global emissions of 60-140 Tg yr^{-1} for natural wetlands.

Although Matthews and Fung (1987) and Aselmann and Crützen (1990) calculated the global acreage of natural wetlands as 5.3 10^{12} m^2 and 5.7 10^{12} m^2 respectively, it is interesting to note that the geographical distribution of these wetlands varies due to differences in the methodologies used (see Bouwman, 1990a). Additionally, the definitions used for the various wetland categories (e.g., bogs, fens) do not seem to be standardized internationally. An important contribution to refining global estimates of CH_4 fluxes from wetland soils would be the production of a global data base showing the extent of hydromorphic soils using actual soil survey information (see Section 3.7.4). There is also a clear need for more 'representative' methane emission measurements from well defined categories of wetlands and paddies (IGBP, 1991; Matthews *et al.*, 1991). Bouwman's (1990a p. 93-94) tabular review of the variability and range in CH_4 fluxes from broadly defined categories of swamps, marshes, bogs, tundras and salt water environments illustrates this point. This brings us to a general problem encountered in global data bases. The key attributes of the spatial units (grids or polygons) of necessity are characterized using point observations (e.g., for soils, fluxes, rainfall), which by definition are limited in space and time. Interpolation or extrapolation of this information to larger areas remains a sensitive and unresolved issue of discussion (Nielsen and Bouma, 1985; Bouma and Bregt, 1988).

Rice paddies

Estimates of global methane emissions from rice paddies also differ considerably between different studies. Matthews and Fung (1987), for instance, arrived at a figure of 40-160 Tg yr^{-1} for rice paddy-fields. According to Neue *et al*. (1990), however, only 80 x 10^6 million ha of harvested wetland rice lands are potential sources of CH_4 formation, corresponding with a global emission from wetland rice of only 25-60 Tg. Neue *et al*. (1990) discriminated the global rice area harvested in 1988 with respect to major rice ecologies (irrigated, rainfed, deep-water and upland) and considered four groups of soil related controlling factors (temperature; texture and mineralogy; Eh/pH buffer systems; salinity) in their analysis. Subsequently, they assumed an average CH_4 emission of 200-500 mg CH_4 m^{-2} during an average growing season of 130 days. This assumption of an average growing period of 130 days for rice globally and the use of one single flux range for all rice ecologies should be seen as a first apprximation. For instance, there is a considerable acreage of floating rice, which grows with increasing water depths. It is likely that in the deep-water areas (floating rice) the release of methane may be lower than that observed in well managed, shallowly irrigated (about 10 cm) rice paddy-fields. A large amount of soil-entrapped methane that would be oxidized in undisturbed soils may escape to the atmosphere due to cultural practices such as soil disturbances due to wet tillage, transplanting, fertilizer application, weeding, pest control and harvesting (Neue and Roger, 1992).

Bachelet and Neue (1992) reviewed 3 procedures and replicated three possible techniques to estimate global methane emission from rice paddy-fields. Field and laboratory experiments of Denier van der Gon *et al.* (1992) support the approach of Bachelet and Neue (1992) that soils can be grouped according to their methane producing potential. Denier van der Gon *et al.* (1992) propose a possible way to extrapolate methane emission data from field experiments which considers climate, soil type, carbon input, cultural practices and total rice crop biomass. Important factors which also should be included, but still are poorly quantified at the global level, are: rice varietal differences, water regimes and application of organic amendments of manure (Denier van der Gon *et al.*, 1992). In India, Parashar *et al.* (1991) found methane emission from different paddy varieties grown under similar soil conditions can vary by an order of magnitude.

3.7.2   Process-based models

There is a need for process-based models of CH_4 production, as well as a general recognition that the present understanding of the controlling factors and processes is not yet sufficient for such activities (Van Breemen and Feijtel, 1990; IGBP, 1991). In order to develop process-related models of methane production additional research will be needed on the following (JEA/EPA, 1990):

a)   The biogeochemistry of methane production, both in paddy-fields and natural wetlands, including methanogenesis, methanotrophs, and regulating factors;

b)   The effects of climate, soil, water management, cultivars, fertilizer applications and cultural practices on CH_4 fluxes;

c)   Variation in CH_4 fluxes between sites in time;

d)   Effects of techniques to reduce CH_4 emissions on emissions of N_2O;

e)   Field-level measurements to assess spatial variability, and simulation models to synthesize the process-level and field-level data. Mosier (1990) reviewed the techniques which can be used to measure trace gas fluxes in terrestrial ecosystems. Possible procedures for 'scaling- up' field measurements to larger spatial areas have been discussed a.o. by IGBP-IGAC (1991).

Whereas process-related simulation for CH_4 emissions from natural wetlands should be seen as a very distant goal, proposals for developing process-related models for methane emissions by rice paddies have recently been initiated. Braatz and Hogan (1991) discuss how such a process based model could be structured. They propose to develop three major, interactive modules describing the soil redox processes, the development of the rice plant, and the 'physical and microbial' dynamics. Braatz and Hogan (1991) formulate the minimum data requirements of these models as follows:

a) Daily climate data (solar radiation, elevation, rainfall, irradiation, maximum and minimum temperature).

b) Experimental site data (latitude, longitude, planting date, rice variety)

c) Soil and fertilizer data (soil nitrate, ammonium, iron, manganese, organic carbon, oxidation state, bulk density, pH, crop residue, C/N ratio; timing, type, amount and depth of incorporation of mineral or organic fertilizers; initial concentration and addition of sulphate; root exudation and die-back coefficients; gas transport properties; changes in redox potential at 2, 5 and 10 cm depth with time; floodwater depth; percolation rate; depth of perched water table; soil disturbances)

d) Emission data, including hourly CH_4 (and N_2O) emissions.

Only a limited number of the soil data requirements listed under item c) are collected on a routine basis during routine soil surveys (see Msanya, 1987), which makes it difficult to include them in a global soil data base. Additionally, the description of soil conditions in most greenhouse gas related studies is rather basic (e.g., acid clay). This means that a coordinated effort must be made to collect the 'basic' data sets according to uniform procedures at all the present/new experimental sites in order to develop, test and validate the proposed process-based CH_4 models. During the WISE workshop, ISRIC expressed its willingness to carry out soil analyses, according to the standardized LABEX-procedures (Van Reeuwijk, 1992), at long-term 'seasonal' measurements sites, but this would require additional funding.

3.7.3   Stochastic models

Deterministic versions of process-based models by definition will produce results pertaining to single events. However, since the environmental and land use factors are always subject to spatial and temporal variability there will be a degree of stochastic uncertainty in the results of deterministic models. Future developments should consider the possibility of combining a stochastic and deterministic approach in one single CH_4-model; this should be seen as a long-term objective.

3.7.4   Required global digital data bases

Matthews (1990) discusses the design and development of global digital data bases and their integration in studies of terrestrial sources and sinks on greenhouse gases, proposing a sequential approach. First, primary data bases on major surface characteristics are prepared. These data bases are subsequently integrated to produce secondary sets of source categories (e.g., soils, vegetation, hydrology). Finally, these secondary data bases are combined with measured flux to produce tertiary data sets on emissions. The basic data bases required in estimating biogenic sources/sinks of methane include vegetation, soils, land use, seasonal inundation, temperature and precipitation (see review by Matthews, 1990). A review of global land data bases has been prepared by Bouwman (1990a p. 36) and Sombroek (1990). IIASA has recently completed a ½ x ½ degree resolution global data base of mean monthly values of temperature,

precipitation, and cloudiness (Leemans and Cramer, 1991). Matthews *et al.* (1991) developed a data base on the geographic and seasonal distribution of rice cultivation on a global scale.

Soil scientists can infer a wealth of information on soil conditions from the FAO/Unesco terminology (see Sombroek, 1990 p. 228). Groenendijk (1990), for instance, compiled a ½ x ½ degree resolution soil data set to estimate the water-holding capacity of soils in Europe using soil maps at a scale of 1:1 M to 1:5 M. For each grid cell the three spatially dominant soil units were specified, together with information on topsoil texture, stoniness and dominant slope. A different approach has been proposed for developing the WISE data base(see Chapter 6).

3.8   Conclusions

This Chapter shows that there are many microbial, climatic, hydrological, soil, crop and management factors that control the production, consumption and transfer of methane in terrestrial ecosystems in different ways. Some of these factors work additively whereas other have antagonistic effects on CH_4 production and emission, but other forms of interactions are possible as well. At this moment it is still proves difficult to establish to what degree the respective process controlling factors will quantitatively affect the production and emission of CH_4 in a certain terrestrial ecosystem at a particular moment in time. This is why proposals for developing process-related CH_4-models have only recently been formulated, initially with respect to rice paddy-fields. The preliminary data requirements of these models in terms of soil conditions, as formulated by Braatz and Hogan (1991), already exceed the level of information held in most existing high resolution soil survey reports, so that new data collection activities should be initiated at the level of the experimental site.

Refined estimates of global CH_4 production can already be obtained by extrapolating seasonally averaged, field measured CH_4 emission rates considered representative for well described natural wetlands or irrigated rice ecosystems to the corresponding global 'ecosystem'. Such a refined extrapolation will not only require additional CH_4-flux data but also knowledge of the geographic and seasonal distribution of the various types of natural and man-made wetlands (Matthews *et al.*, 1991) as well as more detailed and up to date information about the distribution and main characteristics of potential methane producing soils. An 'attribute-oriented' soil data base would be useful in the context of these activities. Such a data base could also be used in other studies on global change, such as revised estimates of N_2O-emissions from soils, climate-vegetation succession models and to assess the vulnerability of soils to chemical pollution.

Chapter 4 Nitrous oxide

N.H. Batjes

4.1   Introduction

4.1.1   Background

The transfer of nitrogen between the surface of the earth and the atmosphere is dominated by ammonia (NH_3), nitrous oxide (N_2O), nitric oxide (NO), nitrogen dioxide (NO_2), and dinitrogen (N_2). Different societal values have been attributed to the various categories of N-losses. These values strongly determine the type of abatement that will be prioritised. Initially, the interest for the biological, environmental and management practices that influence gaseous N-losses was mainly from the perspective of increasing the efficiency of N-fertilizers. In the last decades, however, it has been recognized that the use of N-fertilizers to sustain the production of food, fodder, fibre and timber may also affect the global environment. For instance, through leaching of nitrates to the ground water, thereby affecting its quality for consumption, or through gaseous N-emissions which may contribute to acid deposition (Chadwick and Kuylenstierna, 1990; Klemedtsson and Svensson, 1988; RIVM, 1991; Van Breemen, 1990) and increased atmospheric concentrations of N_2O (e.g., Bouwman, 1990a).

Nitrous oxide contributes to the 'greenhouse effect' in that it absorbs radiation in the infrared band. On a molecule per molecule basis, the relative potential for thermal adsorption of N_2O is 150 times that of CO_2 (Bouwman 1990a p. 2). N_2O has an atmospheric life time of $\approx$ 100-200 years, which is much greater than that of either NH_3 or NO_x. It has been estimated that N_2O may account for 5-10 % of the 'greenhouse' effect (Bolin *et al*., 1986). Although N_2O is chemically inert in the troposphere it plays an important role in the depletion of stratospheric ozone. In the stratosphere, N_2O is destroyed almost exclusively by photolysis and reaction with $O(^1D)$, forming NO which plays a major role in regulating the concentration and distribution of ozone (O_3) (Crützen, 1987). Besides being involved in photochemical reactions, the atmospheric NO_x concentration also influences the oxidation of methane and CO. Nitric oxide (NO), however, does not absorb infrared radiation. The chemistry of the relevant atmospheric processes has recently been reviewed by Bouwman (1990a, Chapter 2.2).

Ice core data for N_2O indicate pre-industrial concentrations of around 285 ppbv (part per billion volume), while present levels are around 310 ppbv (Khalil and Rasmussen, 1988). This is equivalent to about 1500 Tg N (Bolle *et al*., 1986). Prinn *et al*. (1990) deduced a 10-year average global nitrous oxide emission rate of 20.5 ± 2.4 Tg N_2O yr^{-1}, with significant year-to-year variations in emissions possibly associated with year-to-year variations in tropical land emissions. The current average annual increase in atmospheric concentration of N_2O is about 0.2-0.3 % (Weiss, 1981; Bolin *et al*., 1986; Prinn *et al.*, 1990). The average N_2O concentration in the northern hemisphere is persistently 0.75 ± 0.16 ppbv higher than in the southern hemisphere (Prinn *et al.*, 1990).

Although over 20 % of the total global N_2O emissions and 50 % of the total ($N_2O + N_2$) emissions may be due to natural terrestrial emissions (Bowden, 1986), the observed increase is essentially due to the increased use of N-fertilizers and combustion processes (Bolin *et al*., 1986). According to Bouwman (1990a p. 2), however, about 90 % of the increase in atmospheric concentrations of N_2O is of biotic origin. At present rates, atmospheric concentrations of 350 to 400 ppbv of N_2O are predicted towards the year 2050 (Bolin *et al*., 1986).

Table 4.1.   Estimated sources and sinks of nitrous oxide (Source: IPCC, 1992).

Natural sources	Tg N$_2$O-N yr^{-1}
Oceans	1.4-2.6
Tropical soils	
- Wet forests	2.2-3.7
- Dry savannas	0.5-2.0
Temperate soils	
- Forest	0.05-2.0
- Grasslands	?
Anthropogenic sources	
Cultivated soils	0.03-3.0
Biomass burning	0.2-1.0
Stationary combustion	0.1-0.3
Mobile sources	0.2-0.6
Adipic acid production	0.4-0.6
Nitric acid production	0.1-0.3
Sinks	
Removal by soils	?
Photolysis in atmosphere	7-13
Atmospheric increase	3-4.5

A number of budgets for atmospheric N$_2$O have been prepared, each of which presents somewhat different values for the various sources and sinks (Seiler and Conrad, 1987; Prinn *et al.*, 1990). The budget of Seiler and Conrad (1987) shows the relative importance of N$_2$O emissions from 'natural' soils (6 ± 3 Tg yr^{-1}) and fertilized soils (2 ± 1 Tg yr^{-1}), as compared to oceans (1.5 ± 1 Tg yr^{-1}). More recently, global estimates of 7 Tg N$_2$O-N yr^{-1} have been presented for undisturbed terrestrial ecosystems (Bouwman *et al.*, 1992), and of 2.3 to 3.7 Tg N$_2$O-N yr^{-1} for cultivated lands (Bouwman, 1990a). Contaminated aquifers may release from 0.8 to 1.7 Tg N$_2$O-N per year (Lashof and Tirpak, 1990 p. 85). N$_2$O production from all potential sources is likely in the order of 13 ± 1.5 Tg N$_2$O-N yr^{-1} (Prinn *et al.*, 1991). Recently, Thiemens and Trogler (1991) indicated N$_2$O associated with global production of adipic acid in the preparation of nylon may account for nearly 10 % of the increase observed for atmospheric N$_2$O. Efforts should continue to identify sources and possible sinks as yet not identified. Other possible sources of nitrous oxide may include treatment of sewage water, land 'disturbance' and inland and coastal waters (e.g. Bouwman and Van der Hoek, 1991) and riparian zones (Davidson and Swank, 1990). Degassing of nitrous oxide dissolved in soil solution is considered to be insignificant for global atmospheric budgets (Davidson and Swank, 1990). The most recent overview of estimated sources and sinks of nitrous oxide, as prepared for discussion by IPCC (1992), is presented in Table 4.1.

While the estimated source strengths remain uncertain, emissions from soils appear to dominate the N$_2$O budget (IPCC, 1992). The main biogenic sources of N$_2$O, NO$_x$ and N$_2$ from soils are the microbial processes

of denitrification and nitrification. Fossil fuel combustion and biomass burning have been considered to be significant global sources of N_2O and NO_x, but the recent discovery of an artefact producing increased levels of N_2O in combustion gas samples collected in grab-bottles before sampling (Muzio and Kramlich, 1988, cited by Cofer *et al.*, 1991) has resulted in downgrading the importance of these two sources in the global N_2O budget. According to Cofer *et al.* (1991) biomass burning contributes to no more than $\approx$ 7 % of the global source of N_2O. The most important nitrogen gas emitted from biomass burning now appears to be molecular nitrogen, with the largest contribution coming from flaming combustion (Kuhlbusch *et al.*, 1991). Pyro-denitrification associated with burning of biomass equals about 12-28 Tg of biomass N, which corresponds to about 9-20 % of the estimated global rate of terrestrial nitrogen fixation. This illustrates that biomass burning is not only of relevance for the atmospheric chemistry and greenhouse effect, but also for the biogeochemistry of savanna and agricultural ecosystems (Lobert *et al.*, 1990). Global patterns of soil nitrogen have been discussed by Post *et al.* (1985).

4.1.2   Structure of chapter

In Section 4.2 the important microbial processes of N_2O formation in soils, mainly nitrification and denitrification, are discussed. Examples of the spatial and temporal variability inherent in N_2O emissions from soil are presented in Section 4.3. Subsequently, the effects of environmental and management factors in controlling the production and consumption of N_2O in terrestrial ecosystems and the rate determining factors are discussed. Examples of N_2O emissions from agricultural lands and undisturbed lands are given in Section 4.5. Possible methods for modelling gaseous N-emissions are discussed in Section 4.6. General conclusions as to the current possibility to model global N_2O emissions from soils are made in Section 4.7.

4.2   Processes of N_2O formation in soils

4.2.1   Introduction

Soils are important sources of atmospheric N_2O. A wide range of processes may produce this N_2O, as well as minor amounts of NO_x, but not all of these seem to be fully understood. The main biological processes of N_2O formation in soils are shown in Figure 4.1. They include nitrification, denitrification - the dissimilatory reduction of nitrate to ammonium - and the assimilatory reduction of nitrate wherein N is incorporated in the cell biomass. Additionally, some NO_x and N_2O may be released due to chemo-denitrification (see Section 4.2.6) and 'pyro-denitrification' (Lobert *et al.*, 1990). Of these processes, nitrification and denitrification are the most important with respect to N_2O production. In order to predict N_2O emissions from soils it is necessary to differentiate between these two processes, as discussed by Klemedtsson *et al.* (1988b) and Klemedtsson and Hannson (1990).
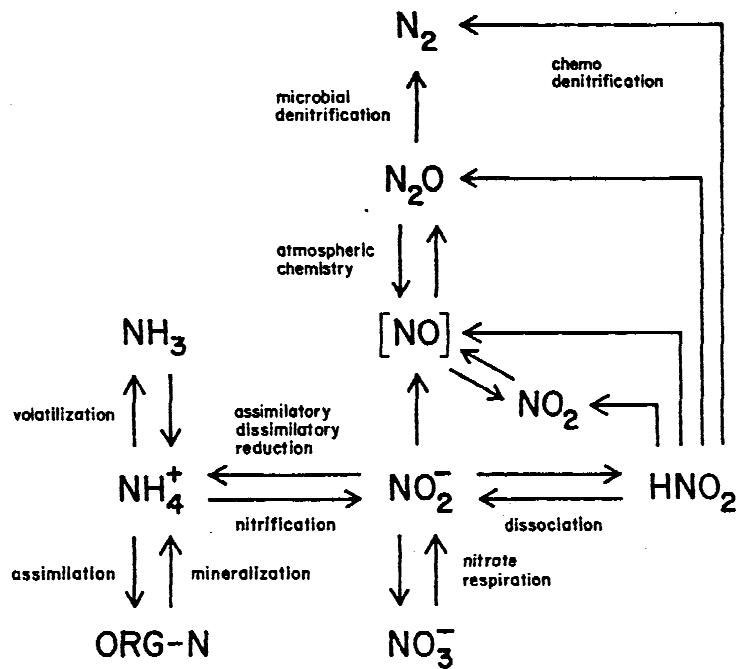
Figure 4.1. Schematic representation of the components of the nitrogen cycle (Compounds in the upper section of the flow diagram are the main nitrogenous gases emitted by ecosystems. Brackets around NO indicate that the occurrence of this intermediate product in biological denitrification remains uncertain) (Source: Bowden, 1986)

The main biological and abiological processes mediating N_2O production and consumption in soils are reviewed below. For more information on the subject reference is made to the reviews of Bowden (1986), Sahrawat and Keeney (1986), Tiedje (1988), Stouthamer (1988) and Beauchamp *et al.* (1989) amongst others.

4.2.2   Denitrification

In both nitrification and denitrification, energy from chemical reactions are used to drive various growth processes rather than to incorporate nitrogen into the cells themselves. Production of N_2O and molecular N_2 by microbial denitrification occurs when bacteria capable of denitrification colonize a location where oxygen is absent and water, nitrate and decomposable organic compounds are present. Microbial denitrification is the process in which nitrate (NO_3^-), nitrite (NO_2^-) and nitrous oxide (N_2O) serve as 'alternative' electron acceptors to O_2 for essentially aerobic bacteria at low O_2 concentrations, with the result that ultimately molecular N_2 can be produced (Delwiche, 1981; Knowles, 1982). The reaction sequence for denitrification may be exemplified as follows:

$$NO_3^- \longrightarrow NO_2^- \longrightarrow [NO] \longrightarrow N_2O \longrightarrow N_2$$

In this reductive pathway, nitric oxide [NO] may occur as an intermediate between NO_2^- and N_2O but it's existence has not been assessed unambiguously (Firestone, 1982; Poth and Focht, 1985; Bowden, 1986). Munch (1989), however, found that NO was a natural product of denitrification for *Bacillus polymyxa*. Later, Munch (1991) showed that the formation of NO_x in soil is related directly to the composition of the denitrifier population, and only indirectly to physicochemical soil properties. In the study of Munch (1989) the nitrate concentration influenced only the rate of denitrification, but not the N_2O/N_2 ratio of each organism. Secondly, the amounts of nitrite formed transitorily were found to be specific for the organisms involved. These amounts of nitrite influenced neither the emission of N_2O, nor the ratio of N_2O/N_2 or of N_2O/consumption of nitrate. Thirdly, the N_2O formation depended primarily on the microbial soil population, and thereafter on the nitrate concentration in correlation with the type of denitrifiers. Munch and Ottow (1986) also observed that the intensity and composition of denitrification gases (NO, N_2O and N_2) differed considerably from organism to organism and from soil to soil. This is also apparent form the study of Abou-Seada and Ottow (1988) which included the denitrifiers *Aeromonas 'denitrificans', Azospirillum lipoferum* DSM 1843, and *Bacillus licheniformis* ATCC 14580, and soil material from the Ah-horizon of a Gleyi-Eutric Fluvisol, Orthic Luvisol, Calcaric Fluvisol and Eutric Cambisol. Gas production in this study was measured by gas chromatography in regular intervals. With *A. 'denitrificans'* NO was released from the Calcaric Fluvisol and Orthic Luvisol, whereas *B. licheniformis* did not produce NO in any of the soil materials tested. N_2O was liberated by *A 'denitrificans'* in all soils tested, but *A. lipoferum* produced it only in the Fluvisol and *B. licheniformis* exclusively in the Eutric Cambisol. Alternatively, Germon and Jacques (1990) hypothesize that in a homogeneous pedologic area the denitrifying microflora could behave similarly, and that the natural N_2O production could be a constant proportion of denitrified N in spite of different pH values. This study was for naturally acid loamy soils for which the pH was increased by agricultural practices. The need to confirm this kind of results for other experimental conditions and soils was indicated by Germon and Jacques (1990). Soil conditions and agricultural practices that seem to influence the relative amount of N_2O/N_2 are reviewed in Section 4.4. Hauck (1986) and Mosier *et al.* (1990) have reviewed techniques for measuring denitrification in the field.

Most denitrifying bacteria are aerobic heterotrophs, belonging to taxonomically diverse genera such as *Pseudomonas, Alcaligenes* and *Azospirillum*. However, some autotrophic organisms such as *Paracoccus denitrificans, Rhodopseudomonas sphaeroides* and *Thiobacillus denitrificans* are also capable of denitrification. A review of known denitrifying bacteria strains is given by Beauchamp *et al.* (1989 p. 115). Not all the denitrifying bacteria can carry out the complete pathway of denitrification (Knowles, 1982), because they lack the relevant reductase(s), however they partially contribute to the process of microbial denitrification. Possible explanations for a partial denitrification have been proposed by Ingraham (1981):

a) Although intermediary products such as NO_2^-, NO and N_2O may be present, the initial nitrate may be lacking.
b) The environmental conditions may not be conducive to one or more of the reaction steps.
c) The different reductases, responsible for the denitrification process may differ in induction rates.
d) Genetically deficient strains may not be capable of synthesising the complete set of required reductions. Alternatively, the enzyme N_2O reductase can reduce an extraneous source of N_2O as it is a free obligatory intermediate in denitrification (Smith *et al.*, 1983).

Mosier (1990) discussed methods for measuring denitrification in the field and their limitations. A commonly used procedure is the 'cover box' method in which a soil is perfused with acetylene (C_2H_2), to prevent any reduction of N_2O to N_2, and the N_2O released from the soil is trapped under an inverted box cover and measured by gas chromatography. Keeney (1988) found that acetylene does not inhibit N_2O production from

the heterotrophic nitrifiers of the species *Arthrobacter* (and nitrapyrin does not inhibit heterotrophic nitrification). Consequently, the N_2O produced by heterotrophic nitrifiers will probably be included in estimates of N_2O production from denitrification (Klemedtsson and Hansson, 1990).

4.2.3 Autotrophic nitrification

Both autotrophic and heterotrophic nitrification occur (see review of Tiedje, 1988). Autotrophic nitrification is an aerobic biological process whereby NH_4^+ is converted to NO_3^-. This oxidation process is essentially carried out in two stages:

a) $NH_4^+ + 3/2\ O_2\ ---->\ NO_2^- + 2H^+ + H_2O + E$

b) $NO_2^- + 1/2\ O_2\ ---->\ NO_3^- + E$
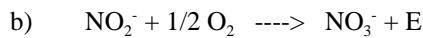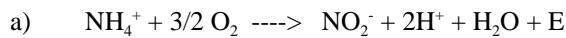
In soils, the oxidation of ammonium to nitrite (stage a) is mainly performed by *Nitrosomonas*, while the oxidation of nitrite to nitrate (stage b) is dominantly performed by *Nitrobacter*. The process of N_2O production via nitrification of ammonium to nitrite is not clearly understood (see Sahrawat and Keeney, 1986). According to Papen and Rennenberg (1990) N_2O could be formed during stage a) of the chemoautotrophic nitrification process as follows:

$$NH_4^+\ ---->\ NH_2OH\ ---->\ [HNO]\ ---->\ NO\ ---->NO_2^-$$
$$|$$
$$N_2O$$
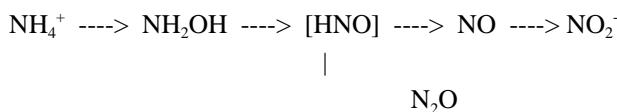
The presence of the nitroxyl radical (HNO) would explain the possibility for N_2O production during nitrification since, especially under anaerobic conditions, there would be a spontaneous (chemical) decomposition of [HNO] to N_2O (Anderson, 1976 as quoted by Rosswall, 1981). Yoshida and Alexander (1970), however, showed that *Nitrosomonas europea* produces N_2O during the oxidation of NH_4^+ or NH_2OH to nitrite. Bremner and Blackmer (1978) also found that N_2O is formed during nitrification. According to researchers cited by Bouwman (1990a p. 121) the NO/N_2O production ratio for nitrifying bacteria is in the order of 1-5, and about 0.01 for denitrifying bacteria. Little seems to be known about the absolute production levels. In the experiment of Klemedtsson *et al*. (1988a) nitrifiers produced up to 16.5 times more N_2O than denitrifiers during a 6-day laboratory experiment after addition of 40 µg NH_4^+-N and 40 µg NO_3^--N g^{-1} dry soil at 60 % of the soil's water holding capacity.

In the field, N_2O production via nitrification is mainly controlled by the oxygen status of the soil, a readily available supply of nitrifiable nitrogen, by the moisture content and by temperature (*cf* Bowden, 1986). Since the nitrification pathway requires aerobic conditions it is likely that a low partial oxygen pressure during the nitrification process may enhance the formation of N_2O (Johansson and Galbally, 1984), as later explained by Poth and Focht (1985). Anderson and Levine (1986) showed that at low O_2 levels, the nitrite formed during stage a) may be reduced to N_2O before it is reduced to nitrate through step b). Bacteria that oxidize NO_2^- to NO_3^-, corresponding with stage b) of the autotrophic nitrification process, are not able to form N_2O (Umarov, 1990). Application of nitrifiable forms of N-fertilizer (urea, ammonia or $(NH_4)_2SO_4$) often greatly increase the N_2O emission (Bremner and Blackmer, 1978). Similarly, Bremner and Blackmer (1981) concluded that N_2O emission associated with nitrification was related to the nitrifiable-N content, and not

influenced by the addition of NO_3^--N. Application of the nitrification inhibitor nitrapyrin to soil supplied with urea or NH_4^+-N fertilizers greatly retarded emission of N_2O from well aerated soils.

The chemoautotrophic *Nitrosomonas* and *Nitrobacter* metabolize about 35 and 100 times as much nitrogen, respectively, as the carbon dioxide they fix, which means that a few microorganisms can process a large amount of nitrogen (Sprent, 1990). This type of nitrification is therefore quite rapid, especially in well aerated soils. Autotrophic nitrifiers probably are the major producers of N_2O in freely aerated soils, both under natural conditions (Parton *et al*., 1988) as well as under agriculture (e.g., Klemedttson *et al*., 1988). Umarov (1990), however, thinks the role of autotrophic nitrifiers in producing N_2O is insignificant in the biosphere (see Section 4.2.4).

4.2.4   Heterotrophic nitrification

Heterotrophic nitrification is the oxidation of NH_3/NH_4^+ or the oxidation of organic-N containing compounds to NO_2^- and/or NO_3^- under aerobic conditions in the presence of carbon substrates (*cf* Papen and Rennenberg, 1990). The role of the carbon substrates is to serve both as carbon and energy sources. For heterotrophic nitrification to occur, the content of nitrogen must exceed the amount of nitrogen necessary for normal growth (Umarov, 1990). Papen and Rennenberg (1990) proposed the following reaction sequence:

$$R\text{-}NH_2/NH_4^+ \longrightarrow NH_2OH \longrightarrow [NOH] \longrightarrow NO \longrightarrow NO_2^- \longrightarrow (NO_2?) \longrightarrow NO_3^-$$
$$|$$
$$N_2O$$
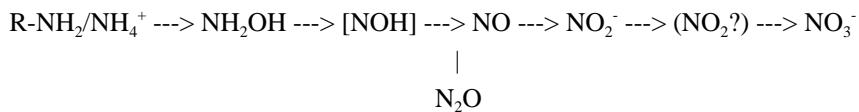
The importance of biological NO_x production during field nitrification is unknown (Bowden, 1986). Papen *et al*. (1989) showed that in cultures of *Alcaligenes faecalis*, a heterotrophic nitrifying bacteria, N_2O, NO and traces of NO_2 were formed besides NO_2^- and NO_3^-. Since a broad spectrum of different bacteria and fungi are able to catalyze heterotrophic nitrification, this process could possibly account for important nitrogenous trace gas emissions from soils according to Papen and Rennenberg (1990). Focht and Verstraete (1977), however, believed that the importance of heterotrophic nitrification in agricultural soils is low. Similarly, Bowden (1986) observed that although the potential for N_2O production during heterotrophic denitrification exists, there is little evidence yet that the relevant microorganisms do so in the field. Alternatively, Umarov (1990) postulated the role of autotrophic nitrifiers in forming N_2O in the biosphere is insignificant. He observed that although the activity of heterotrophic nitrifiers is generally about 10^3 to 10^4 times slower than that of autotrophic nitrifiers, the former are very important in view of the large ecological versatility of the microorganisms involved and the great number of nitrogen compounds they can oxidize. Additionally, Umarov (1990) observed that heterotrophic nitrification is not markedly inhibited by acidification of soils contrary to autotrophic nitrifiers. This could mean that the role of heterotrophic nitrifiers is likely to increase with increasing 'environmental pollution', associated with acid deposition, while the role of autotrophic nitrifiers will decrease.

4.2.5   Other biological processes

Small amounts of N_2O may be formed in soils by nitrate respiration by non-denitrifying bacteria (Smith and Zimmerman, 1981) which are able to reduce nitrate to ammonia (Stouthamer, 1988, p. 258). Burth and Ottow (1982) also observed N_2O release by non-denitrifying nitrate reducers. Tiedje *et al*. (1982) found that nitrate respiring, non-denitrifying bacteria may produce significant amounts of N_2O under anaerobic conditions in ecosystems high in organic matter content. All the nitrate respiring (i.e. NO_3^- reduction to NO_2^- or NH_4^+) bacteria tested by Bleaky and Tiedje (1982) produced N_2O, but could not reduce it further. In addition, they isolated one assimilatory nitrate reducing bacterium (*Azotobacter vinelandii*) and numerous yeasts and fungi (e.g., *Aspergillus* and *Fusarium*) that produced N_2O. In acid forest ecosystems yeasts and fungi may prove important producers of N_2O (Robertson and Tiedje, 1987). Bollag and Tung (1972) reported that fungi can form N_2O during the reduction of NO_2^-. Malinowsky and Ottow (1991) found that *Fusarium* strain 50 released N_2O from nitrite (but not from nitrate) both under aerobic as well as completely anaerobic conditions; this process was inducible by nitrite. N_2 could not be detected in the above experiment.

The non-respiratory N_2O production, typically produces N_2O and not N_2 as the product of N-oxide reduction. The mechanism for this type of N_2O production is not yet known. Neither has it been shown whether the non-denitrifying sources of nitrous oxide are of environmental significance, the difficulty being that experimental methods do not permit to separate these sources of N_2O unequivocally from the respiratory denitrifier sources (see review of Tiedje, 1988).

Unlike the assimilatory pathway, dissimilatory nitrate reduction is an anaerobic process not inhibited by ammonium accumulation. Although it occurs in the same environment as denitrification, dissimilatory nitrate reduction to ammonium differs in 3 main features: a) the microflora is fermentative (strictly or facultative anaerobic); b) the mechanism requires more reducing power and c) it is a poor producer of energy (Tiedje, 1988). The dissimilative nitrate reduction to ammonium in soils is further discussed by Correa and Germon (1991).

Some free-living Rhizobia may play an important role as denitrifiers in fertile environments (see review by O'Hara and Daniel, 1985). Smith and Smith (1986) studied the denitrification by two strains of *Bradyrhizobium japonicum*. The rhizobia grew in anaerobic batch cultures, depleting NO_3^- and producing N_2O in the presence of C_2H_2. Denitrification rates of whole detached nodules were unaffected by the presence of O_2, though the rates were limited by the external NO_3^--concentration. Denitrification by intact, nodulated soybean plants under aerobic conditions was also observed by Smith and Smith (1986). The estimated range of N-denitrified to N-fixed ranged from 0 to 0.3, depending on assay conditions.

Gaseous losses of nitrogen from plants are discussed by Farquhar & McKenny (1979). It has been reported that N_2O evolved at the soil surface can be taken up by maize through foliar uptake (Lensi and Chalamet, 1981) and by rice plants (Minzoni *et al*., 1988); N_2O metabolization by plants would be an unusual biochemical process, as microbial N_2O reduction requires a low oxygen availability. Cervelli and Rolston (1983) reported that the herbicide atrazine caused a decrease in the N_2/N_2O ratio of gases evolved from denitrification.

4.2.6 Chemodenitrification

Chemodenitrification refers to nitrogen gas producing reactions that are catalyzed by abiologic agents. Chalk and Smith (1983) prepared a review of chemo-denitrification. Based on the subsequent review of Tiedje (1988) the predominant product of chemodenitrification is usually NO, but N_2 and N_2O may be produced as well.

Chemodenitrification is not considered to be an important process at the global level, but it may occur locally in nitrite containing acid (pH < 5) or frozen soils. The required high contents of nitrite and low pH values may coexist in cropped soils after the application of an alkaline hydrolysing fertilizer or prills. The NO_2^- which accumulates within the 'fertilized' band will diffuse from the band in response to a concentration gradient, so that compounds such as CH_3ONO can be formed by chemical reaction (Magalhaes and Chalk, 1983). Alternatively, chemodenitrification of nitrite in presence of organic matter or Fe^{2+} may lead to N_2O production measured as biological denitrification in enclosures (Chalamet and Bardin, 1977; Morgaghan and Buresh, 1977). Similarly, Christianson and Cho (1983) observed that chemical denitrification occurs in frozen soils by soluble organic matter-NO_2^- reactions. Cofer *et al.* (1991) postulate that heating of soils during large fires may cause significant releases of biogenically produced N_2O.

4.3 Temporal and spatial variability in N_2O emissions

4.3.1 General

Numerous environmental and agricultural factors influence the biological processes of soil microorganisms responsible for N_2O-emissions from soils (Table 4.2), in addition to the type and composition of the microbial population (Munch and Ottow, 1986; Munch, 1991). The environmental factors include soil temperature, soil moisture content and soil aeration status, as influenced by the structure, texture, porosity and precipitation/irrigation, and by the soil reaction (pH), organic matter content and soil type. Agricultural and management practices that may affect N_2O emissions from soils include the fertilizer regime (e.g., type, rate, application technique, timing), cultivation practices (e.g., tillage, irrigation and drainage) and the crop assortment. All of these vary widely at the local, regional and global level as climate and soil conditions are highly variable in space and time (Nielsen and Bouma, 1985; Bouma and Bregt, 1988; Mausbach and Wilding, 1991). In conjunction with the wide range in biological processes involved in the production of N_2O this explains why field-measured N_2O fluxes often vary markedly both in space and time. The latter is particularly the case when the N_2O is essentially produced by denitrification, since nitrification generally is a fairly constant process across ecosystems (Firestone and Davidson, 1989). Nitrifier denitrification (Poth and Focht, 1985) and respiratory denitrification, however, probably are not 'constant' in time.

Table 4.2.   Key-factors affecting N_2O emissions from soils (Adapted after Eichner, 1990).

Management practices	Environmental factors
Fertilizer type	Temperature
Application rate	Precipitation
Application technique	Soil moisture content
Timing of application	Organic C content
Tillage practices	Oxygen availability
Use of other chemicals	Porosity
Crop rotation	pH
Irrigation	Freeze and thaw cycle
Residual N and C from crops and fertilizer	Microorganisms

The interpretation of the effects of the various biological and abiological controlling factors on N_2O fluxes is further complicated by the limitations that are inherent to the respective gas measurement techniques (see discussion by Mosier, 1990). Based on their field experiments, Matthias *et al*. (1980) concluded that the accuracy of the mean N_2O flux for a given area is much more dependent on the number of flux measurements than on the accuracy of any particular flux measurement. Rolston *et al*. (1979) concluded that the accuracy of field measurements of N_2O emissions is more limited by sampling problems resulting from spatial and diurnal variability in these emissions than by analytical problems associated with assessments of N_2O fluxes. Additionally, the spatial and temporal variability in measured fluxes in a given area can vary from one year to the other over comparable measurement periods (e.g., Goodroad and Keeney, 1984b). Therefore it is often difficult to quantify accurately the gaseous N-losses and their relative composition from soils, unless long-term and 'highly-resolved' determinations of fluxes are used (Lotfield *et al.*, 1992).

The interpretation of field emission data would be facilitated if experiments specify the underlying biological processes and nature of the biological population. Knowledge of the fact whether N_2O emissions are produced through nitrification or denitrification would contribute to understanding the abiotic and management factors affecting N_2O emissions from soil systems at the site level. Determination of the reaction source, however, is not always possible in regional and global assessments of N_2O emissions as this aspect is difficult to consider at the macro-scale (Eichner, 1990). Bouwman *et al.* (1992), however, accounted for the 'reaction source' in a global modelling study of N_2O emissions from natural soils. Scaling-up of site measurements to the ecosystem or global level remains an important topic of discussion and investigation (IGBP, 1990; Roswall *et al.*, 1988).

4.3.2   Temporal variability

When assessing the soil-derived N_2O (and NO_x) emissions in a particular region it is necessary to have adequate information about the spatial and temporal variability in these emissions. Consequently, many researchers have studied the spatial and temporal variability of N_2O emissions from soils. In Sections 4.2 and 4.3 selected examples are used to illustrate the dimensions of this variability.

Diurnal variability

The recommended or adopted period of measurement during the day varies markedly from one experiment to the other, often because of logistic reasons. Ryden *et al.* (1978), for instance, suggested that N_2O measurements should be performed during the mid morning hours or mid- to late afternoon to 'avoid' <sic> the N_2O flux they observed in the early afternoon during their experiment. Mosier *et al.* (1991) measured N_2O fluxes in closed chambers in a Colorado grassland at mid-morning, and generally weekly at each of the considered sites. The experiment of Blackmer *et al.* (1982), however, showed that reasonably accurate estimates of N_2O fluxes cannot be obtained by measuring the rate of N_2O emission during a relatively short period of the day. Peaks in N_2O emissions which are known to be associated with marked rainfall events or changes in soil temperature over the day may be missed altogether in such experiments.

Blackmer *et al.* (1982) studied the diurnal variability of emissions of nitrous oxide from Iowa soils using the chamber technique of Matthias *et al.* (1980) to measure the N_2O emission rates on fertilized and unfertilized sites at intervals of 1 or 2 hours for periods ranging from 1 to 5 days. These experiments revealed large coefficients of variation in N_2O emission within 24 hour periods, ranging from 12 to 66 % with an average of 38 per cent. As much as 90 % of the diurnal variability in N_2O emission could be attributed to diurnal N_2O emission patterns related to changes in soil temperature in this study. Alternatively, the wind speed was found to influence the diurnal patterns in N_2O emissions from soils in some studies (Ryden *et al.*, 1978) but not in others (Blackmer *et al.*, 1982). Possible causes for the diurnal variability in N_2O emissions in the experiment of Ryden *et al.* (1978) were given as the effect of an increase in temperature on the activity of denitrifying bacteria, as well as on the rate of N_2O diffusion in soil. Alternatively, changes in the soil aeration status following rainfall on the nitrifier and denitrifier activity may also influence the N_2O emissions.

Denmead *et al.* (1979), when studying N_2O emissions from a grass sward in Australia, observed a clearly defined diurnal pattern with maximum rates occurring in the afternoon and minimum rates near sunrise when the temperature of the topsoil was lowest. During the measurement period Denmead *et al.* (1979) found little phase difference between the diurnal variability in topsoil temperature and N_2O emissions in this sward. Alternatively, Blackmer *et al.* (1982) found that the diurnal variability in N_2O emission is often markedly out of phase with the diurnal variability in the temperature of the topsoil.

Seasonal variability

The N_2O emissions at any given location vary with the measurement period as well as the time of measurement. In the study of Thompson *et al.* (1983) the average coefficient of variation for denitrification was 98 % for the winter and 180 % for the spring experiments. These values became respectively 43 % and 75 % when these researchers only considered mean fluxes exceeding 0.10 kg N ha^{-1} d^{-1}.

Crop type and crop development may also influence N_2O emissions. Mosier *et al.* (1986), for instance, measured N_2O and N_2 emissions from irrigated fields to assess the magnitude of N loss by denitrification. The relevant soils were supplied with 200 kg N ha^{-1} as 99 atom percent ^{15}N ammonium-sulphate. The vertical N_2O and N_2 fluxes were measured periodically by sampling, using a cover method, and analyzing N_2O by gas chromatography and N_2 by mass spectrometry. During the cropping seasons under consideration (1982 and 1983) the maximum N_2O emissions occurred in May for Barley and in July for corn. Both the emissions for barley and corn increased with increasing soil-water content. During 1982, total volatile-N loss of (N_2O + N_2) from the moderately well drained clay loam soil was about 2.5 % of the applied fertilizer N, and about 70 % of the total consisted of N_2O. In case of the barley field, about 1 % of the applied fertilizer-N was emitted with about equal amounts of each gas.

In the study of Bremner *et al*. (1980) 67 % of the N_2O produced was evolved in summer with little production occurring in winter. Christensen and Tiedje (1990), however, observed a marked N_2O-flux at thaw in an 'acid sandy loam soil' between January (1 ºC) and March (4 ºC) which could be due to an increased microbial activity under warmer conditions. The temperature effect observed in the field could be duplicated in laboratory experiments, during which thawing soil cores at controlled temperature, nitrate and moisture contents yielded a large flush of N_2O in comparison to unfrozen soils. Similarly, Cate and Keeney (1987) observed a large increase in N_2O in soil air when the temperature increased to 0-1 ºC after a frozen period. According to Christensen and Tiedje (1990) the spring peak in N_2O maybe due to respiratory denitrification. The carbon source mediating the process could be the microorganisms killed by the freezing or detritus that became available by the freezing-thawing process. Alternatively, emissions in autumn may be associated with falling of leaves and partial dying-back of roots.

4.3.3   Spatial variability

Numerous researchers have studied the spatial variability of N_2O emissions from soils. Often these studies were implemented to assess the effect of different water and fertilizer practices on N_2O emissions. The latter mainly to improve the efficiency of N-fertilizer use by reducing emissions of gaseous N-products as well as to decipher the global behaviour of N_2O emission from soils.

Rolston *et al*. (1979) studied the spatial and diurnal variability of N_2O emission within small, apparently uniform, soil plots (generally 20 by 20 m), finding coefficients of variation (CV) of 31 to 168 per cent. Similarly, Parsons *et al*. (1991) found that nitrogen gas evolution was highly variable on a spatial scale, with replicate measurements showing CVs between 74 and 268 per cent. They found that the denitrifying enzyme activity in the 2 soils studied, ranged from 0.1 to 119 ng N_2O-N g^{-1} soil min^{-1} and varied spatially and temporally, but did not exhibit the same seasonal pattern as N-gas loss. Alternatively, the coefficients of variation ranged from 161 to 508 % for the ($N_2O + N_2$) fluxes, and 282 to 379 % for the N_2O fluxes, in a study of the structure and magnitude of the spatial variability of N-fluxes along 12 transects of a well drained alluvial Yolo loam (Typic Xerorthent) (Folorunso and Rolston, 1984). In this study the measured N_2O and ($N_2O + N_2$ fluxes) - acetylene inhibition technique, closed chambers - were ln-normally distributed. Subsequent statistical analyses based on autocorrelograms and partial autocorrelograms showed that in only one out of the 12 transects studied the ($N_2O + N_2$) and N_2O fluxes revealed any spatial dependence indicative of an autoregressive process. Consequently, the denitrification flux values for this field site can be considered to be spatially independent. Folorunso and Rolston (1984) calculated that from 156 to 4177 ($N_2O + N_2$) flux measurements and 350 N_2O flux measurements are needed to estimate the 'true' mean flux within 10 % of the estimated mean on a 3 by 36 m experimental plot. The possible implications for obtaining representative flux measurements for large fields as well as for scaling-up these results in global studies are evident.

In a subsequent study with Yolo loam soils Folorunso and Rolston (1985) found that the cyclic nature of the soil-water content in the surface soil appeared to be the primary cause of cycling of the denitrification gas flux at a period of 4 to 5 m. Cycling of water-soluble organic C at periods different from that of water content also caused some periodic behaviour in denitrification gas fluxes. The study of Folorunso and Rolston (1985)

shows that spectral[1] and coherency techniques, contrary to standard correlation or regression methods, provided evidence of significant causal effects on denitrification.

The spectral and coherence analysis of Grundmann *et al*. (1988) indicated that denitrification flux in an irrigated Typic Xerorthent, amended with chopped alfalfa and nitrate, did not cycle at the frequency of imposed soil-water content due to several interacting factors. In this study variations in soil-water content were responsible for much of the variability of other parameters (especially nitrate) which subsequently affected denitrification flux through the development of anaerobic sites, reduction in the gas transfer to the soil surface by diffusion, and nitrate leaching.

The high spatial variability of field-measured denitrification gas fluxes is connected to the problem of definition of denitrification sites in relation to substrate sources and O_2-concentration. In aggregated, unsaturated soils anaerobiosis, and hence denitrification, is mainly confined to micro-aggregates corresponding with the so-called hot-spots of Parkin (1987) or associated with earthworm casts (Svensson *et al*., 1986; Knight *et al*., 1989). Leffelaar (1986) showed that denitrification from a single aggregate can be predicted with success only when the spatial and temporal distribution of denitrifiers, water, oxygen, decomposable organic compounds and nitrate can be measured or calculated. Smith (1980) observed that, in principle, denitrification losses from aggregated field soils can be predicted when denitrification losses from individual aggregates and their size distribution are known. Sextone *et al*. (1985), however, noted that not-all aggregates with anaerobic sites necessarily display denitrification. Possible reasons for this have been listed as the absence of denitrifiers and/or substrates, NO_3^- and/or carbon inside the aggregates. Additionally, soil gas diffusion, as related to both the development of anaerobic sites and diffusive transport of produced gases to the soil surface should be considered in a model if the predictive capability and understanding of the mechanisms causing the large spatial variability of denitrification gas fluxes are to be elucidated further (Grundmann *et al*., 1988). Benckiser *et al*. (1987) observed that to increase the understanding of the microbiology and biochemistry of the denitrification process under natural conditions, more emphasis should be given to field studies of physical processes like N_2O-diffusion and N_2O-retention in the soil. Similarly, Chalamet (1990) observed that the high spatial variability in N_2O fluxes could well be related to the oxygen diffusion coefficients (D) which vary markedly with the environmental conditions, decreasing in the general sequence: air (D$\approx$ 1.8 10^{-1} m^2 s^{-1}) $\gg$ gas phase of soil (D$\approx$ 10^{-3} m^2 s^{-1}) > free water and mud (D$\approx$ 10^{-5} m^2 s^{-1}) $\gg$ inter-aggregates (D$\approx$ 8.5 10^{-6} m^2 s^{-1}) > sediments (D$\approx$ 10^{-7} m^2 s^{-1}).

As was observed earlier, the spatial variability of N_2O emissions associated with nitrification is generally less than that reported for denitrification (Firestone and Davidson, 1989). This is essentially due to the fact that contrary to denitrification, nitrification is widely distributed and not related to the presence of 'anaerobic microsites'.

---

[1]   Spectral or harmonic analysis is a statistical tool for transforming data from the time or spatial domain to the frequency domain; it is essentially a partitioning of the total variance of a set of samples from a stochastic process to assess which of the frequencies have the greatest significant variances associated with them (Folorunso & Rolston 1985).

4.4 Environmental and agricultural controls of N$_2$O production

4.4.1 Introduction

All microbial processes in nature, including nitrification and denitrification, are sensitive to changes in the environmental and agricultural regulating factors. Inherently, these factors are highly variable in space and time (see Section 4.3). Additionally, important regulating factors of water, temperature, plants and organic matter can have both synergistic and antagonistic effects on the status of other regulating factors. In this context reference can already be made to several examples. Koskinen and Keeney (1982), for instance, observed that it is difficult to evaluate whether the effect of pH on denitrification, and thereby the N$_2$O fraction, is due to the pH *per se* or to an interaction of other factors such as the availability of nitrite. Higher rates of denitrification and denitrifying enzyme activity in a Kentucky toposequence, were related to topography and physical characteristics of the soil through the indirect effect of topography on soil moisture conditions (Parsons *et al.*, 1991). Weier and Doran (1987) found that fertile Brigalow soils of eastern Australia had the potential to denitrify but that this was limited by soil water content and available carbon. Alternatively, the existence of a biological regulation of nitrification by *protozoa* has recently been reported (Griffiths, 1989).

The above discussion already shows that in N$_2$O production and emissions studies it is important that the N$_2$O measurements are accompanied by data on the main regulating factors of available carbon, nitrate concentration, O$_2$-concentration or water content, as well as agricultural practices. This would help to explain the vatiations of denitrification and nitrification measured in the field. In the following sections some of the possible effects of soil and management factors on emissions of N$_2$O from soils are reviewed, using general headings for convenience's sake.

4.4.2 Effects associated with the soil moisture/aeration status

The moisture and aeration status of a soil is closely related to its physical properties, as determined mainly by soil texture, mineralogy, stoniness, organic matter content and structure and by the rainfall/irrigation regime and the crop or vegetation cover (see Chapter 2). Plants consume oxygen by root respiration and use water thereby decreasing the amount of water held in the pore spaces. Fluctuations in water-filled pore space in turn influence: a) the rate of N$_2$O diffusion in the soil, b) the amount of N$_2$O dissolved in the soil water, c) the rate of N$_2$O production by soil microorganisms, d) the rate of reduction of N$_2$O to N$_2$ by soil microorganisms, and e) the amplitude in the diurnal change in temperature that occurs at any given depth in the soil (Blackmer *et al.*, 1982). Alternatively, plants take up nitrate which may reduce the availability of nitrate for denitrification.

Generally, the release of N$_2$O to the atmosphere is enhanced by alternating dry-wet cycles (Letey *et al.*, 1981). The wetting enhances mineralisation of organic matter with resultant pulses in nitrification, and creates (local) anaerobic conditions that favour denitrification. Under these conditions, the production of N$_2$O may exceed the reduction of N$_2$O to N$_2$; generally the peaks in N$_2$O decrease with subsequent rainfall events. Cady and Bartholomew (1960) found that the higher the water content in Norfolk soils, the more rapid was the conversion of N$_2$O to N$_2$. According to Letey *et al.* (1980a), the enzyme dissimilatory nitrate reductase develops rapidly and the enzyme dissimilatory N$_2$O-reductase develops only after a period of time following the creation of anaerobic conditions. The net effect, however, would be a somewhat lower total N$_2$O production (Colbourn and Harper, 1987). As the soil dries, the fraction of N$_2$O may increase; the higher O$_2$

status inhibits the reduction of N_2O to N_2 (Letey *et al.*, 1981; Focht, 1974). Groffman and Tiedje (1988) reported an hysteresis effect as a result of which respiration and denitrification gradually decrease, without peaking, when soils dry. Several explanations have been given for the fact that oxygen represses microbial denitrification. Oxygen may either repress nitrate reductase (Knowles, 1982), interfere with the thermodynamics (Thauer *et al.*, 1977) or inhibit nitrate uptake in cells (Hernandez and Rowe, 1987). It is likely that plants with well developed aerenchyma cells, which allow transport of oxygen to the root surface, will give less support to denitrification than non-vascular plants (Prade and Trolldenier, 1990a). Upon depletion of O_2 in soil, facultative anaerobic denitrifiers must adapt their enzyme system to the shift from aerobic to anaerobic conditions (Tiedje, 1988).
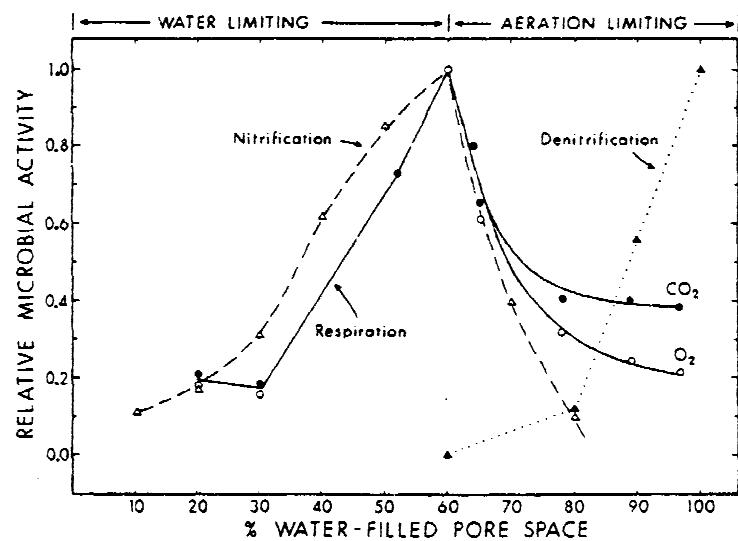
Figure 4.2.   Relationship between water-filled pore space and relative amount of microbial nitrification, denitrification, and respiration (O_2-uptake) and CO_2-production (Source: Linn and Doran, 1984 p. 1271)

Denitrification increases markedly when the oxygen concentration drops below 2 % (Tiedje *et al.*, 1984). In many soil types, a water filled pore space (WFPS) of over 60 % seems to facilitate the development of anaerobic conditions favourable to denitrification (Knowles, 1982; Linn and Doran, 1984; Prade and Trolldenier, 1990b; Parsons *et al.*, 1991; see also Figure 4.2). Similarly, Eaton and Patriquin (1989) observed only small amounts of N_2O at 60 % of field capacity, but as the moisture content was raised the production of N_2O increased. This general relationship is affected by other factors as well, such as temperature (see Table 4.3). Additionally, water may stimulate denitrification by temporarily reducing the oxygen diffusion into the soil as well as by increasing the solubility of organic C and nitrate (Bowden, 1986). Prolonged waterlogging can limit denitrification if it also restricts nitrification which produces the nitrate for denitrification; these conditions prevail for instance in well managed, permanently flooded paddy soils. The foregoing illustrates that we can not expect a simple relationship between soil water content and the amplitude of the daily pattern in the rate of N_2O emissions, associated with denitrification, from soils.

The maximum activity of nitrification is generally around 60-80 % of field capacity. Nitrifiers start to denitrify NO_2^- when oxygen becomes limiting, producing N_2O (Tiedje, 1988). It is possible that denitrifiers may use N_2O as an alternative electron acceptor under conditions where nitrate production through nitrification is blocked. The N_2O produced during nitrification is more likely to evolve to the atmosphere than

N_2O produced by denitrification. Since soil pores are generally 'open' during nitrification, gaseous diffusion to the soil surface should be possible. Alternatively, there will be less soil water in which the N_2O may dissolve. As such nitrification generally is a fairly constant process, compered with denitrification (Byrnes *et al*., 1990; Davidson and Firestone, 1989). As has been indicated earlier, this does not apply to denitrification where N_2O emissions often occur as short-termed, episodic events associated with the initial stages of development of anaerobism in soils.

Soil oxygen concentrations in permeable soils are related to the proximity of drains and the depth of the water table, so that a spatial relationship between denitrification and drainage may be expected. Colbourn and Harper (1987) found that drainage limited denitrification to about 65 % of the losses from undrained soils, with denitrification occurring between a depth of 10 and 50 cm. The emissions from the undrained soil were in the range 1-12 g N ha^{-1} h^{-1}, while those from drained soil amounted to 0.6-6.0 g N ha^{-1} h^{-1}, giving estimated total losses of (N_2O + N) of 14 $\pm$ 2 and 9 $\pm$ 1 kg N ha^{-1}, respectively. These researchers also reported that drainage changed the fraction of N_2O in the total denitrification product. During December, emissions from the drained soil (1.8 $\pm$ 0.6 g N ha^{-1} h^{-1}) were composed entirely of N_2O, whereas in undrained soil (2.7 $\pm$ 1.1 g N ha^{-1} h^{-1}) losses were almost entirely in the form of nitrogen gas; the fraction of N_2O in the total loss was 0.02. In February, denitrification declined due to colder conditions and the emission of N_2O from drained soils declined relative to nitrogen gas so that the fraction of N_2O was 0.03 for both drainage treatments. The delayed onset of N_2O reduction in the drained soil was related to the concentration of O_2 and NO_3^-. Fertilizer application in the spring gave rise to maximum rates of emission of 5-12 g N ha^{-1} h^{-1} with the balance shifting towards N_2O production; the fraction of N_2O became 0.2-0.8 in April and May (Colbourn and Harper, 1987).

Emissions of nitrous oxide often show a marked response to rainfall events or small additions of water (Mosier *et al*., 1981, 1986, 1991; Denmead *et al.*, 1979; Rolston *et al*., 1982; Sextone *et al*., 1985), especially after N-fertilizer application (Brams *et al*., 1990). Mulvaney and Kurtz (1984), for instance, simulated the effect of wetting-drying cycles on gaseous N-losses using soil cores enriched with ^{15}N-labelled fertilizers, and found that the N-evolution peaked 2 to 9 days after precipitation. Christensen (1990) reported that the mean denitrification in a 'sandy loam soil' (pH 3.8) increased markedly during a week that followed 1-2 days of heavy thunderstorms. In this study only 4 out of 30 permanent points in a 5 x 6 grid, with 1 m spacing, were responsible for much of the increase in mean N_2O rates. Following the heavy rainfall, plants started to decompose in 3 spots in the field. The relevant spots were part of the 4 locations where denitrification 'hot spots' occurred. In the study of Mosier *et al*. (1986) the ratios of N_2/N_2O varied from 0 to 60 with an average of 10.3 upon water applications causing the topsoils to be close to or wetter than field capacity; the proportion of N_2 was highest during intense emission periods and fell to zero, or below the N_2 detection limit, as the soil dried.

Differences between the N_2O concentrations in 'soil air' and measured fluxes from the soil surface are commonly observed. According to Stegeman and Cammenga (1990) this can be due to:
-    Reduction of N_2O to N_2 by microbes;
-    The low diffusion coefficients of N_2O in soils;
-    Physical adsorption of N_2O at the soil matrix;

Denitrification rates vary with the size and composition of soil aggregates. With reference to wet-sieved aggregates, Elliot (1986) suggested that the availability of C-substrate increases with the size of the aggregates. The pretreatment of the sample - i.e. wet-sieving or dry sieving, temperature and time of drying - also affects the N_2O evolution from soil aggregates. Seech and Beauchamp (1988) found that N_2O

production generally increased with increasing aggregate size in water-sieved aggregates, in marked contrast to dry-sieved aggregates.

Release of N_2O held by physical adsorption might be responsible for emmisions of N_2O when dry surface soils, as commonly observed on a warm and dry summer, are wetted (Stegeman and Cammenga, 1990). Emissions of N_2O are also stimulated by alternating drying and wetting cycles (Letey *et al.*, 1981). Letey *et al.* (1980c) found that the fraction of nitrogenous gases diffusing from a soil core increased as the soil air-filled porosity increased and the adsorption coefficient between the soil and gas decreases. Benckiser *et al.* (1987) suggest that N_2O may be adsorbed at the soil matrix, especially under relatively dry conditions in soils with high organic matter content. Similarly, Chalamet and Chauchard (1976) observed N_2O was only absorbed in large amounts on clay if the water content was below that of air-dry soil. Stegeman and Cammenga (1990) found that oven-dried soil samples form a strong adsorbing medium for N_2O, with the sorbed gas mass being related to the clay content over the 8-30 % range. Drying of soils may 'activate' clay minerals when water is removed by heating; this assumption is supported by the non-sorbing behaviour of quartz sand under the same conditions (Stegeman and Cammenga, 1990). In air-dried samples (1-3 % moisture content), however, the relationships could no longer be observed (Stegeman and Cammenga, 1990). Adsorption of N_2 and N_2O occurs on surface soils during dry afternoons as the water molecules evaporate (Kemper *et al.*, 1985).

4.4.3   Effects associated with changes in temperature

Interpretation of the relationship between temperature and the nitrifier-denitrifier rate is complicated by interactions between microbial activity, water filled pore space, solubility of oxygen and availability of organic substrates. Blackmer *et al.* (1982), for instance, showed that when the concentration of N_2O in a surface soil is similar to the concentration of N_2O in the atmosphere, temperature induced changes in the solubility of N_2O in soil water should not produce significant diurnal patterns in the rate of N_2O emission from soil. Alternatively, Thompson *et al.* (1983) found that variations in the rate of denitrification observed in each of 3 slurry treatments reflected the variation in soil temperature. In the study of Parsons *et al.* (1991), however, denitrification measured as N_2O production under C_2H_2, was not positively correlated with soil temperature over the 2 to 26 °C temperature range at either site of a toposequence. In this study, an inverse relationship between temperature and water filled pore space was observed. Alternatively, Powlson *et al.* (1988) showed that denitrifying organisms can adapt to the local climate. Brams *et al.* (1990) observed that a warmer soil temperature was not a sufficient condition to enhance the emission of N_2O, but that it was necessary to allow the soil microbial population to respond to other 'perturbations' such as fertilization or rainfall, and particularly a combination of the two.

Blackmer *et al.* (1982) observed that a 17 °C decrease in the 0-2 cm depth layer at a shaded site corresponded with a 17-fold decrease in N_2O emission from the shaded site as compared to the unshaded site. In a subsequent laboratory study of the same soil, however, Blackmer *et al.* (1982) found that a 20 °C change in temperature corresponded only with a 4.5-fold change in the rate of N_2O production.

The optimum temperature for nitrification lies in the range 30 to 35 °C, while temperatures below 5 °C and above 40 °C are generally considered limiting (Alexander, 1977). Appreciable nitrification of slurry-NH_4^+ has been reported at temperatures below 6 °C (Thompson and Pain, 1989). The lower limit for denitrification to occur is commonly given as 2.7 to 10 °C (Firestone, 1984). Eaton and Patriquin (1989) observed no N_2O production below 15 °C in infertile soils of lowbush blueberry (*Vaccinium Angustifolium*). Parson *et al.*

(1991) observed that in 11 of the 12 cores of a soil under uncultivated mixed bluegrass N_2O evolved at a rate ≥ 0.95 10-6 g N m^{-2} h^{-1} when temperature was 2 °C. A Q_{10} for microbial denitrification of 1.4 to 1.6 has been reported by Focht and Verstraete (1977). The lower limit for N_2O production to occur varies with the soil-environmental as well as biological characteristics of the microbial population. Bailey (1976), for instance, reported that denitrification can occur at low temperatures in the absence of O_2 and in the presence of a readily available source of C. Generally, a decrease in temperature will reduce the denitrification activity and increase the N_2O/N_2 ratio in the denitrification products (Keeney *et al.*, 1979). Bailey and Beauchamp (1973) found that the rate of NO_3^- reductase in the denitrification process was more affected by a low temperature than the NO_2^- reductase step. The percentage of N_2/N_2O was not greatly affected by temperature changes in the study of Focht (1974); soil aeration and pH were shown to be the two factors causing the greatest variability in N_2O production through denitrification.

Table 4.3. Daily denitrification losses from previously air-dried soil (upper 30 cm) incubated with and without acetylene at different temperatures and water contents[1,2] (Source: Benckiser *et al.*, 1986).

Soil temperature (°C)	N_2O-evolution[4] at water contents (% v/v) of:			
	22	26	32	35
5	-	-	-	12. 9 ± 3.1 (0.4)[3]
8	-	-	3.1 ± 0.4	60 ± 20.4 (1.9)
13	-	-	60.4 ± 17.8	281.3 ± 27.6 (4.5)
20	-	8.0 ± 7.1	232.4 ± 92.0	861.3 ± 121.8 (10.3)

Note: 1) means of 4 replicates; 2) All replicates were adjusted to 33 μg NO_3^--N g^{-1} soil; 3) Numbers in parentheses are the N_2/N_2O-ratios at water contents of 35 % v/v (about 90 % WHC); 4) in ng N_2O-N g^{-1}d^{-1}.

Christensen (1990) found that at low moisture contents, corresponding with < 100 % of field capacity, the N_2/N_2O ratio was not affected significantly by changes in temperature over the range 2 to 25 °C. The averaged N_2/N_2O ratio was 1.5 to 2.5 for the temperature range 20-25 °C and 2-10 °C, respectively. At soil moisture contents of 100-175 % of field capacity, however, the N_2/N_2O ratio increased with temperature over the range 2-25 °C. In this case, the increase amounted to 2.5 to 5.5 for the temperature range of 20-25 °C as compared to the 2-10 °C interval (Christensen, 1990). Below 2-10 °C, however, the N_2/N_2O ratio apparently was not affected by the soil moisture content, whereas above 20-25 °C the N_2/N_2O ratio increased with increasing soil moisture contents. Similarly, the study of Benckiser *et al.* (1986) indicates that it is mostly N_2 that forms during denitrification as the temperature increases (Table 4.3).

Goodroad and Keeney (1984b) observed that although soil temperature was near freezing N_2O emissions were as high during the spring thaw as they were during the rest of the year. Similarly, Thompson *et al.* (1983) observed that denitrification continued in slurry application experiment, particularly in the injected treatment, despite frozen conditions at the soil surface. The results of Thompson *et al.* (1983) support the view that large amounts of readily decomposable carbon may enhance denitrification at temperatures near to freezing. Similarly, Benckiser *et al.* (1986) observed a mean rate of N_2O-evolution of 0.04 kg N ha^{-1} during 48 h measurement directly after thawing (5-8 °C). Eggington and Smith (1986a, b), in an experiment with grassland observed that most of the N_2O loss occurred immediately after thaw. It is likely that the spring flush

in microbial growth responsible for the decay of organic detritus accumulated during the winter may have increased the competition for oxygen sufficiently to enhance the potential for denitrification (Brams *et al.*, 1990).

4.4.4   Effects associated with soil pH

Soil pH clearly influences the rate of denitrification as well as the distribution of gaseous end products. Knowles (1981) found that the optimal pH range for denitrification is 7.0 to 8.0. Below a pH of 6.0 the rate of denitrification is often times found to decrease with a further drop in pH (Wijler and Delwiche, 1954; Van Cleemput *et al.*, 1976; Eaton and Patriquin, 1989). Van Cleemput *et al.* (1976), however, also observed significant denitrification in strongly acid soils. N_2O may be the dominant gas evolved in acid infertile forest soils (Mellilo *et al.*, 1983; Eaton and Patriquin, 1989). In the study of Eaton and Patriquin (1989) raising the pH resulted in increased rates of denitrification as well as more conversion of N_2O to N_2. This could be due to the greater sensitivity of the nitrous oxide reductase enzyme to low pH or proton activity (Alexander, 1977; Knowles, 1981). N_2 became the dominant N-gas evolved from denitrification at a pH of 6.9 in the incubation study of Koskinen and Keeney (1982) and above a pH of about 6.0 in the experiment of Eaton and Patriquin (1989). The highest amounts of NO was recorded at a pH of 4.6 to 5.4 in the later study. Similarly, Bollag *et al.* (1973) also reported that more NO and N_2O are produced under acid conditions. Chemodenitrification of nitrite may also play a role in the gaseous N-product evolution, particularly under acid conditions (see Section 4.2.6).

The mineralisation rate of organic-C rather than the pH *per se* may control the rate of denitrification in C-limited systems (Koskinen and Keeney, 1982). At 100×10^{-6} g NO_3^--N added per gram of soil, the overall rate of denitrification correlated with the rates of C-mineralisation (CO_2 evolution) but were not consistently related to pH or to total organic C. Based on these findings, Koskinen and Keeney (1982) wondered whether pH should be used as a variable in predictive models of denitrification as proposed by Focht (1974).

Goodroad and Keeney (1984a) reported that nitrification of NH_4^+-fertilizer increased with increase in soil pH over the range 4.7 to 6.7, when temperature ranged from 10 to 30 ºC and the water content from 10 to 30 % v/v.

4.4.5   Effects associated with chemical status

In well aerated soils nitrification should not be a limiting factor unless the inorganic-N levels are low. In the latter case the denitrification rate will depend strongly upon the mineralization-nitrification kinetics (Chalamet, 1990). According to Ryden (1981) a lower limit of 1µg NO_3^--N g^{-1} soil is needed for denitrification to occur. Eaton and Patriquin (1989), however, found that the N_2O production from waterlogged soils without added nitrate was positively correlated with the percentage of organic matter and the nitrate concentration of the soils at the time of sampling (initial pH of 4.0-5.5). No N_2O production was detected from samples containing less than 5 µg N g^{-1} soil. Of the cores with NO_3^--concentrations below the detection limit of 0.25 µg NO_3^--N g^{-1} dry soil, 65 % of the Maury and 88 % of the Lanton soil evolved measurable amounts of N_2O in an uncultivated mixed bluegrass (Parsons *et al.*, 1991). This is in line with Murray *et al.*'s (1989) observation that denitrifying bacteria possess high affinity kinetic systems for NO_3^--utilization (Michaelis-Menten constant or $K_M < 10$ µ*M*), which would allow denitrifiers to use NO_3^- at concentrations lower than the above detection limit. Such very low concentrations are not likely to occur

rapidly in agricultural soils. Abbeel *et al.* (1989), for instance, noted that even after 7 months after application of manure the NO_3^--concentration was still higher than 7.5 µg NO_3^--N g^{-1} soil. Possible sinks for nitrate in soils include run-off, plant uptake, dissimilatory reduction to NH_4^+, adsorbtion in strongly weathered soils (anion-exchange capacity; AEC), percolation losses, immobilization by microbes and denitrification.

Table 4.4. Emission of nitrous oxide from flooded swamp forests amended with 10 g N m^{-2} of ammonium sulphate and KNO_3, respectively (DeLaune *et al.*, 1990).

Sampling date (days)	N_2O evolved (mg $m^{-2}min^{-1}$)	
	NO_3^--N source	NH_4^+-N source
0	ND	ND
2	49	ND
5	61	ND
8	14	ND
15	ND	12
21	ND	26
27	ND	26

Note: ND stands for not-detectable.

The rates of N_2O production in Pigeon Hill soils increased linearly up to the maximum of NO_3^- added (300 µg N g^{-1} soil), while no N_2O was detected in soil samples containing less than 5.0 µg NO_3^--N g^{-1} soil in the study of Eaton and Patriquin (1989). These findings support the earlier findings of Knowles (1982) that denitrification follows 1st-order kinetics up to 40-60 µg NO_3^--N g^{-1} soil, and zero order kinetics at higher NO_3^--levels. This means that high amounts of nitrate do not automatically lead to a relative increase (per unit of respired nitrate) in N_2O (and NO). High nitrate concentrations may be toxic for the enzyme N_2O reductase (Tiedje *et al.*, 1984; Knowles, 1982).

DeLaune *et al.* (1990) studied the effects of N-application on N_2O evolution from flooded swamp forests. Two sources of nitrogen were used, ammonium sulphate and KNO_3. Nitrous oxide emissions was recorded on the second day following application of 10 g m^{-2} NO_3^--N, and lasted for about 2 weeks. According to DeLaune *et al.* (1990) this corresponded with the period needed for all the NO_3^--N to be denitrified. In case of the application of 10 g N m^{-2} as NH_4^+, however, it took about 15 days before N_2O was evolved from an adjacent plot. This time lag can be explained by the time that is needed for the ammonium source to be nitrified (Table 4.4).

Prade and Trolldenier (1990 a and b) observed that denitrification was increased either by low K-nutrition or by infection with the common root fungus *Gaerimannomyces graminis var tritici* (Ggt). The highest denitrification rate in the rhizosphere of wheat plants was found for a combination of both K-deficiency and Ggt-attack. Compared with healthy plants with high K-supply, the effect of either K-deficiency or Ggt-attack approximately doubled denitrification. Based on these observations, Prade and Trolldenier (1990), conclude that laboratory experiments with young healthy plants may underestimate the rhizosphere effect on denitrification. In the field, however, roots are generally attacked to a varying degree by pathogens, causing 'leakage' of readily accessible organic substrates, thereby increasing indirectly the number of organisms in

the rhizosphere. This may have a considerable influence on microbial processes in the root zone, and the fraction of N_2O evolved.

Munch (1989) showed that the composition of denitrification gases (N_2O, NO and N_2) was exclusively caused by the species of the active organisms involved in the study; the nitrate concentration only influenced the denitrification rate, but not the N_2O/N_2 ratio of each organism. Similarly, Abou-Seada and Ottow (1988) concluded that, apparently, the production of NO and N_2O as products of incomplete denitrification at relatively high nitrate concentrations is determined primarily by the organism in question and only secondarily by the chemical properties of the soil.

4.4.6 Effects associated with available carbon

The main role of carbon in soils is to function as an energy source, an electron donor and to provide bacterial growth structure. According to the review article of Haider *et al*. (1990) suitable carbon sources for denitrifiers consist of aliphatic or sugar components. (Note: Aliphatics are organic compounds containing open chains of carbon compounds, as distinct from the closed rings of carbon atoms of the aromatic compounds). Additional easily available C-compounds are excreted by plant roots and consist of aliphatic acids, sugars, low molecular weight polysaccharides and amino compounds. Beauchamp *et al*. (1989) have extensively discussed the role of carbon sources for denitrification.

Addition of organic matter to soil through slurry application or manuring will greatly enhance microbial O_2 consumption, so that oxygen deficiency may occur within this localized zone even at low soil moisture contents. Additionally, it will greatly influence the nitrate contents through mineralization or immobilization (e.g., straw with high C/N ratio). Redox and soil pH may be decreased due to high C turnover in the localized region, whereas temperature, except for some extreme cases, seems to be little affected by organic matter addition (Von Rheinbaben, 1990).

Parkin (1987) found that so-called 'hot spots' of high denitrification activity in soils were associated with particulate organic C material. In the 4 cores that displayed stable 'hot spots', from 25 to 85 % of the total denitrification activities of the intact soil cores were associated with the particulate organic matter, which represented from 0.4 to 0.08 % of the total soil mass of the cores. The specific denitrification rates of the isolated hot spots were several orders of magnitude higher than the denitrification rate of inorganic soil material (Table 4.5). Similarly, Knight *et al*. (1989) showed that earthworm casts are an enhanced pedological site for denitrification under field conditions. They also noted that inorganic fertilizers increased the rate of denitrification. In lysimeters studies, however, the activity of earthworms reduced the denitrifying rates of soil applied with dung (Knight *et al*., 1989). This again illustrates the care that must be used when interpreting any results in isolation. This aspect is also illustrated by the studies of Guenzi *et al*. (1978) and Mosier *et al*. (1986) who found decreased denitrification losses in planted soils through plant competition for available nitrate and to possibly drier conditions in rooted soil. It is possible that the presence of crops affects the N_2/N_2O ratio differently than in unplanted similar soils (Haider *et al*., 1990).

Table 4.5. Specific rates of denitrification and CO_2 production for soil particulate organic material and inorganic soil material (Source: Parkin, 1987)

Material	Weight (g)	Denitrification (10^{-6} g N_2O-N $g^{-1}d^{-1}$)	CO_2 production (10^{-6} g CO_2-C $g^{-1}d^{-1}$)
Beetle carapace	0.008	2520	45,000
Plant root	0.068	510	1,950
Plant root	0.137	21,400	3,640
Pigweed leaf	0.080	55,400	3,640
Plant root	0.398	8,100	6,780
Soil	5.6	12.7	198
Soil	3.6	n.d	98
Soil	7.6	0.5	36
Soil	5.1	18.4	n.d
Soil	7.1	6.3	n.d
Soil	7.7	14.3	n.d
Soil	9.3	4.8	n.d

Note: All incubations were conducted under aerobic conditions (about 18-kPa O_2); Particulate organic fractions were picked clean of all visible soil material and the particulate organic matter was removed from the soil fraction; n.d. stands for undetectable rates.

Future research should be directed at improving the characterization of the C and nitrate pool available for denitrification in a dynamic field environment. The use of average values of C and N in bulk soil is an oversimplification of actual substrate levels at sites of denitrification. Any improvement in predicting denitrification will (also) depend upon increased understanding and characterization of the locations of denitrification activity with soil depth, time and spatial allocation (Grundmann *et al*., 1988). Corré *et al*. (1990) measured denitrification rates in soil layers between 15 and 90 cm depth, and found that more than 50 % of the denitrification in the upper 90 cm of the soil appeared to be concentrated in the top 15 cm. Although the 'deeper' soil layers may contribute to denitrification, it is likely that part of the nitrous oxide formed may not diffuse to the surface.

4.4.7   Other effects

Germon and Jacques (1990) studied the natural N_2O production and denitrification rates from 16 different parcels from the same pedological unit, showing great variation in fluxes. In this experiment, the physical soil properties were more relevant to determine the denitrification rate than chemical parameters such as carbon availability. The denitrification rate appeared to be correlated with bulk density, which can be seen as a surrogate for soil porosity. According to Von Rheinbaben (1990) the only means of reducing N-loss through denitrification by agricultural methods is to provide a favourable soil structure, i.e. to avoid soil compaction and plough pans in particular. Under very wet and anaerobic conditions N_2O diffusion may be reduced, forming a possible restriction to gaseous emission (Sahrawat and Keeney, 1986). Alternatively, various researchers have indicated that N_2O may be consumed in wet soils (Letey *et al*., 1981; Ryden, 1981; Smith *et al*., 1983; Terry *et al*., 1981).

The effects of salinity on ammonia and nitrification vary depending on the N-source, the amounts and types of salts added (Na_2SO_4, NaCl and $CaCl_2$), and the soil types used. The percentage inhibition of nitrification ranged from 8 to 83 % among the soils studied, as well as with the type of salts added; in most cases, Na_2SO_4 was less inhibitory to nitrification than the chloride salt (McClung and Frankenberger, 1985). Inhibition of nitrification at ECe values of 20 dS m^{-1} (NaCl) were as high as 75 and 83 per cent when $(NH_4)_2SO_4$ and urea were applied to the soils, respectively (McClung and Frankenberger, 1985). N_2O evolution from salt, brackish and fresh water swamps amounted to 31, 48, 55 mg N_2O-N m^{-2} g^{-1}, respectively in the study by DeLaune *et al*. (1990).

Mosier *et al*. (1991) found that N-fertilization and cultivation can both decrease methane uptake and increase N_2O production in wheat growing prairie soils, thereby contributing to the increasing atmospheric concentrations of these greenhouse gases. The inverse relationship between N_2O flux and CH_4 uptake was apparent without nitrogen fertilization. The influence of N- fertilization, however, was most evident in moist soils, whereas its influence on CH_4 uptake was most marked as soils began to dry after rain (Mosier *et al*., 1991).

4.5 N_2O evolution from various terrestrial ecosystems

4.5.1   Agricultural systems

Upland crops

Reviews of N_2O evolution from agricultural soils have been prepared by Sahrawat and Keeney (1986), Freney and Simpson (1983) and Bouwman (1990a) amongst others. Recently, Eichner (1990) prepared a review of direct measurements of fertilizer derived N_2O emissions from 104 fields in temperate regions (excluding rice), receiving less than 250 kg N ha^{-1}, as reported in the agricultural and scientific literature for the period 1979-1987. This review was used to estimate worldwide emissions of fertilizer-derived N_2O emissions from soils. The review of Eichner (1990) did not reveal any trend between emissions and a particular soil type or agricultural system (keeping in mind that the latter are often poorly described in the N_2O emissions literature). Using the fraction of fertilizer evolved as N_2O for five main N-fertilizers (Table 4.6) and fertilizer-use statistics, Eichner (1990) estimated that from 0.1 to 1.0 Tg N_2O-N was released during the respective 'sampling periods', with a median of 0.2 Tg N_2O-N. If emissions after the 'sampling period', the amounts of fertilizers lost in drainage water and groundwater are taken into account, then the estimated range becomes 0.2 to 2.1 Tg N_2O-N yr^{-1} *anno* 1984. Assuming a global use of 100 Tg N-fertilizer by the year 2000, global fertilizer-N derived N_2O emissions to the atmosphere should not exceed 3 Tg N_2O-N in the year 2000 (Eichner *op cit*.). Different values have been proposed by other researchers, partly as a result of different assumptions pertaining to the N-fertilizer consumption rates and the fraction of N-fertilizer released as N_2O (Table 4.7). Bolle *et al*. (1986), for instance, assumed the average N_2O emission from nitrate-fertilizers, ammonia and urea, and anhydrous ammonia to be 0.04, 0.15-0.19 and 5 per cent, respectively. It should be noted that few studies have attempted to differentiate fertilizer induced emissions of N_2O resulting from nitrification from those resulting from denitrification. The N_2O efflux during nitrification of N-fertilizers, although variable, is generally less than 1 per cent (Byrnes *et al*., 1990). During the seminar on 'Nitrogen in organic wastes applied to soils' participants wondered about the magnitude of N_2O production during nitrification of slurry and the loss of ammonia from plants. It appeared that more research is required before the magnitude of these two gaseous loss mechanisms can be elucidated (*cf* Hansen and Henriksen, 1989). Aulakh *et al*. (1984) caution against the use of any single ratio of N_2O to N_2 in the estimation of N_2O liberated from agricultural soils, since these can vary widely with time.

Table 4.6.   Percentage of fertilizer evolved N$_2$O (After Eichner, 1990).

Fertilizer type	No. of experiments	Range (%)	Median (%)	Average (%)
Anhydrous ammonium	9	0.86 - 6.84	1.63	2.70
Ammonium type, amm. chloride, amm. sulfate	17	0.02 - 0.90	0.12	0.25
Ammonium nitrate	8	0.04 - 1.71	.12/.40	0.44
K-, Ca- and Na- nitrate	13	0.001- 0.50	0.03	0.07
Urea	6	0.07 - 0.18	0.11	0.11

Note: Irrespective of length of sampling period, soil system, location and other variables; paddies not included.

The solubility of N$_2$O is greater in acidic than in alkaline solutions. Minami and Ohsawa (1990) reported losses of N$_2$O from drainage water from agricultural land. This N$_2$O may originate from: a) nitrification in the drainage water, b) denitrification in the sediments, and c) N$_2$O dissolved in the drainage water. Bowden and Borman (1986) reported a N$_2$O efflux from drainage water originating from a clear-cut hardwood forest watershed. It is possible that the cutting of trees reduces the demand for nitrogen and water, while at the same time exposing the soil to more insolation. The higher moisture, nitrogen and temperature would favour microbial mineralisation so that more NH$_4^+$ may be produced and be subjected to nitrifier-denitrifiers.

Table 4.7.   Estimates of annual emissions from fertilizer derived N$_2$O or agricultural lands.

Author	Emission range (Tg N$_2$O-N yr^{-1})
Crützen (1983, cited by Bolle *et al*., 1986)	< 3
Seiler (1986; cited by Bolle *et al*., 1986)	0.6 - 2.3
McElroy and Woofsy (1985)	0.2 - 0.6
Bouwman (1990a)	2.3 - 3.7
Eichner (1990)	0.1 - 1.0[*]

Note: The data of Eichner (1990) refer to 'fertilizer induced' emissions only.

Wetland rice

The root rhizosphere and oxidized surface layer of flooded rice soils are zones of active nitrification-denitrification, and hence a possible source of N$_2$O production. Ammonium volatilization, however, appears to be a much greater source of N-loss from paddy fields than nitrification-denitrification (Buresh *et al*., 1991). Ammoniacal-N can be converted to nitrate by nitrification in floodwater and oxidized soil zones. This NO$_3^-$ can then move into the reduced soil zones where it is readily denitrified to N$_2$O and N$_2$ (e.g., Reddy and Patrick, 1986). Alternatively, translocation of oxygen through the aerenchyma of vascular plants into flooded soil would tend to increase the area prone to nitrate formation. This nitrate in turn could move into the reduced zone where it can be denitrified (DeLaune *et al*., 1990).

Buresh *et al*. (1991) observed a greater flux of $(N_2 + N_2O)$-^{15}N with chambers placed over rather than between rice plants, which indicated that quantification of ^{15}N gases evolved must take into account the transport of gases through rice plants. Similarly, Reddy *et al*. (1987) and Mosier *et al*. (1990b) demonstrated that N gases formed in flooded soil by denitrification can be transported to the atmosphere through rice plants. Freney *et al*. (1990) studied the distribution of gaseous N_2, between the atmosphere, floodwater and pore water of the soil in a flooded rice field after addition of ^{15}N-labelled urea into the floodwater. Of the urea added, 0.02 % was lost as N_2O to the atmosphere, 0.9 % as NH_3, and 3.6 % as N_2 during the 7 days of the measurement period.

Alternating aerobic-anaerobic cycles in paddy soils are likely to promote N_2O emissions to the atmosphere, whereas under continuously flooded conditions most of the N_2O formed will be reduced to N_2. This may be exemplified by the study of DeLaune *et al*. (1990) in which the evolution of N_2O from Louisiana Gulf wetlands increased as the length of the anaerobic-aerobic cycle was increased from 7-7 to 14-14 days. Although it is generally accepted that some oxygen intensifies the emission of nitrous oxide in the course of denitrification (Firestone *et al*., 1979), it should be noted that different types of denitrifying microorganisms have their maximum N_2O production at an organism-specific O_2 concentration (Abou-Seada and Ottow, 1985). Alternatively, changing rice management practices to reduce methane emissions from paddies might lead to increased emissions of trace gases such as N_2O.

Leguminous crops

Nitrogen-fixing leguminous plants merit attention, particularly in savannas and tropical forests (Bouwman, 1990a). N_2O emissions from leguminous crops range from 0.34 to 4.6 kg N_2O-N ha^{-1} yr^{-1}; these figures are based on a review by Eichner (1990) and include natural emissions, emissions associated with cultivation and emissions from N-fixed by the legume crop. Estimated N_2O emissions from fields of cultivated leguminous crops are in the range of 23 to 315 Gg N_2O-N per year according to Eichner (1990).

4.5.2   Natural ecosystems

N_2O emissions from fertilized crop systems are not necessarily greater than for a fertilized non-cropped system (Eichner, 1990). Bouwman *et al*. (1990) estimate global N_2O emission from natural terrestrial ecosystems to be 7 ± 3 Tg N_2O-N yr^{-1}. Bowden (1986) reviewed the N losses resulting from denitrification and N_2O emission from terrestrial, non-agricultural ecosystems. The measured N_2O emissions ranged from 0-20 kg N ha^{-1} yr^{-1} with most measurement being lower than 1 to 2 kg N ha^{-1} yr^{-1}. With respect to NO_x, the review of Bowden (1986) arrived at annual emissions of 1 to 2 kg N ha^{-1} yr^{-1}, with NO apparently being the more important than NO_2 as a component of NO_x. Table 4.8 presents ranges for global emissions of volatile N-compounds from undisturbed terrestrial ecosystems of the world as prepared by Bowden (1986).

Due to the anaerobic nature of wetlands and paddies the formation of NO and N_2O is quite small (Seiler and Conrad, 1987). Similarly, DeLaune *et al*. (1990) reported low N_2O emissions from Louisiana Gulf Coast marshes. The latter was mainly attributed to the low natural nitrate content. Run-off, containing nitrate from agricultural areas, thus could greatly enhance the emissions from these areas.

Table 4.8.   Ranges for global emissions of volatile N-compounds from selected undisturbed terrestrial ecosystems of the world (After Bowden, 1986 p. 268).

Ecosystem	Area (10⁹ ha)	Global emission rate (Tg N yr⁻¹)				
		NH_3	$(N_2O + N_2)$	N_2O	NO_x	Total
Temp. hardwood	1.55	tr	tr-15.5	tr-1.5	1.5	1.5-15.5
Temperate conifer	0.50	tr	tr	tr-1.0	1.0	1.0-2.0
Tropical forests	2.45	nd	7.1	7.1	nd	7.4-9.8
Prairie/grassland	2.40	0-24	tr	tr-4.8	3-24	4.8-48.0
Arid lands/desert	4.20	4.2	0-80	nd	nd	4.2-84.0
Tundra/Boreal	2.00	0	tr	tr	nd	tr
Wetlands/Marsh	0.20	nd	6-130	tr-20	nd	6.0-130
Total	13.30^x	4-28	13-323	7-16	5-26	20-280

Note: 'tr' indicates global emission rates < 10 x 12 Tg N yr⁻¹; 'nd' indicates no data were available; 'x' does not include cultivated land (1.4 x 10⁹ ha) or lakes (0.12 x 10⁹ ha).

4.6   Modelling of gaseous N-losses

4.6.1   General

The foregoing Sections have shown that many factors influence the emission of gaseous-N from soils in various ways. The understanding of these relationships can be increased by building models. Modelling is an iterative process, which involves numerous repetitions of the following steps (Hutson and Wagenet, 1991):

a)   Site evaluation
b)   Identification of important processes
c)   Model configuration to include these main processes
d)   Preparation of input data files, using available information or initial estimates
e)   Measurement of missing values
f)   Tests model runs
g)   Evaluation of model output
h)   Adjustment of input parameters and repetition of simulation procedure.

Models can be used to test hypotheses concerning the various chemical, physical and biological processes that underlie intricate processes such as crop growth and production (e.g. Van Keulen and Wolf, 1986), the evolution of methane from paddy fields (e.g. Braatz and Hogan, 1991), the turnover of organic matter in soil (e.g. Jenkinson, 1990), and losses of soil-N from terrestrial ecosystems. If there is a good fit between model results and *independently* obtained measurement results, models may be used to test hypotheses with confidence (Hutson and Wagenet, 1991; Jenkinson, 1990).

Volume 7 of the Journal Soil Use and Management (1991) was devoted to the differing current approaches to modelling nitrate leaching. Rolston *et al.* (1984) simulated denitrification losses from soils supplied with nitrogen fertilizer. A theoretical model of the fate of nitrogen applied to paddy fields, using a NH_4-^{15}N tracer technique and an estimation of the rate of N uptake by rice plants, has recently been elaborated by Yamamuro (1991). Jayaweera and Mikkelsen (1990) discuss a computer model of ammonia volatilization in flooded soil systems. Groot *et al.* (1991) present the results of a workshop held to compare various N-simulation models, with special reference to the turnover of nitrogen in soil-crop systems. It would seem few attempts of modelling global emissions of N_2O from soils seem to have been undertaken so far (see Section 6.2).

Basically, models can be grouped into empirical, deterministic, and stochastic models, as well as combination of several components of these into one single model. In the following sections selected examples of these different approaches in modelling N-losses are given.

4.6.2 Empirical models

Site level

Empirical models are generally based on statistical analyses so that there is no understanding of the processes (black box) underlying the relationship. With respect to denitrification regression models often have poor overall predictive ability; this may be seen as an indication of their limited suitability to adequately represent the high degree of spatial variability of denitrification rate *in situ* (e.g., Parkin and Robinson, 1989). The study of Parsons *et al*. (1991) shows that regression equations derived from the mean value data are better predictors of the observed mean denitrification rate (r^2 of 74 to 91 %) than the regression equations which were obtained using the entire set of measurements (r^2 of 11 to 27 %). According to Parsons *et al*. (1991) this suggests that the measured characteristics of the bulk soils (CO_2, moisture content, NO_3^-, temperature, most probable number counts of bacteria (MPN), denitrifying enzyme activity (DEA)) are better indicators of long-term spatial variability than of small-scale spatial variability. The inclusion of MPN and DEA in the model did not substantially improve the predictive power of the regression equations, and explained little of the total variation in denitrification rate.

Global level

Much attention is being paid to localized environmental effects, such as the occurrence of so-called hot spots, on N_2O emissions from soil. Bouwman *et al*. (1992) argue that the importance of these high-frequency, 'small scale' events has not yet been established in the framework of global assessments of N_2O emissions, and stressed the need for integrating their effects. According to Eichner (1990), determination of the reaction source is not considered important for regional and global assessments of N_2O emissions. Bouwman *et al*. (1992), however, considered whether N_2O essentially evolves from respiratory denitrification or nitrification in their global modelling study.

Bouwman (1990b) made an analysis of the conditions controlling the N_2O emissions using global data bases of vegetation/land use, soil type, soil moisture regime and temperature. He observed that the scalars on the basis of which the analysis was made are tentative and the flux classes highly uncertain. The study reveals that extrapolation of single flux estimates to global areas cannot give reliable results on a regional or global scale. Stratification of ecosystems, on the basis of soil, vegetation and climatic conditions, should provide more insight in the variation within source regions of N_2O (Bouwman, 1990b).

In a follow up study Bouwman *et al*. (1992), used global data bases on climate, soils and vegetation in combination with current N_2O emission data from selected natural ecosystems. The main regulating factors of nitrous oxide emission considered in this empirical model are the effect of temperature on the decomposition of organic matter, and the effect of soil water availability and oxygen availability. The latter are considered using monthly time steps. Soil fertility and C plus N availability, the other regulating factors in the model, are assessed as being constant over the year. Using an expert-judgement derived scheme of scalars, Bouwman *et al*. (1992) estimated the global pre-agricultural N_2O emission at 7 Tg N_2O-N yr^{-1}, with

a confidence interval (range of $\pm$ standard deviation) of 3.1 to 13.4 Tg yr^{-1}. According to this study, the tropical region between 30ºN and 30ºS contributes to 5.6 Tg yr^{-1} (range: 2.8 - 9.4 Tg yr^{-1}), while emission for the zone >30ºN and >30ºS is 1.4 Tg N$_2$O-N yr^{-1} (range: 0.3 - 4.1 Tg yr^{-1}). The prominence of tropical and subtropical forests for global nitrous oxide emissions is also apparent from the data presented by Lashof and Tirpak (1990; 6 ± 3 Tg N$_2$O-N yr^{-1}). According to Bouwman *et al.* (1992) the role of wetlands in the global N$_2$O budget remains uncertain. Burning of the peat of wetlands, for instance, may cause large emissions of N$_2$O at the local level (Levine *et al.*, 1990). In other wetland soils, nitrification may temporarily be inhibited due to high groundwater tables which may retard or preclude denitrification (Bouwman *et al.*, 1992 and Section 4.4.5).

4.6.3   Deterministic simulation

Betlach and Tiedje (1981) and Cho and Mills (1979) proposed denitrification models for homogeneous soil systems without transport processes. In both, the N-reduction is modelled with Michaelis-Menten kinetics. These models have neglected processes that influence denitrification at the aggregate level, such as the formation of anaerobic microsites, sequential reduction of nitrate to N$_2$, 'immobile' zones of water, transient solute diffusion between aerobic and anaerobic regions, and changes in C-availability and enzyme activity with time; McConnaughey and Bouldin (1985a) proposed a model that includes these processes. The qualitative behaviour of gaseous N evolution as a function of nitrate levels, gaseous oxygen concentration, and depth of saturation predicted by the model agreed with data presented in the literature (McConnaughey and Bouldin, 1985b).

Arah and Smith (1989) presented a model which calculates steady-state denitrification as a function of what they termed 'more readily' measured soil parameters. These were soil moisture characteristics, the probability distribution of aggregate size and oxygen reduction potential, the nitrate concentration and the moisture tension. A possible use of the model would be to predict the fraction of N$_2$O formed/emitted during the denitrification process.

Few models consider microbial growth. Leffelaar and Wessel (1988), for instance, proposed a denitrification model in which this aspect is included. Yet this model apparently does not consider transport processes. Leffelaar and Wessel (1990) simulate microbial growth in a soil layer, considered spatially uniform in all phases, in which no transport processes occurred. Aspects of microbial growth modelled included the reductive pathway NO$_3^-$ ---> NO$_2^-$ ---> N$_2$O ---> N$_2$ with reference growth and maintenance of biomass at the expense of glucose carbon, and the concomitant reduction of nitrate to molecular nitrogen, via nitrite and nitrate. The state variables included in the model are bacteria, glucose carbon, CO$_2$, O$_2$, NO$_3^-$-N, NO$_2^-$-N, N$_2$O-N, N$_2$-N, assimilated N, mineralized carbon and nitrogen from dead biomass, and immobilized carbon and nitrogen in resistant organic matter. The simulation model proved to give a reasonable description of the denitrification process in laboratory incubation vessels. A major difficulty, however, was that no coherent data sets exist to parametrize the model (Leffelaar and Wessel, 1988). This 'hunger for data' versus actual availability of data may be seen as a common problem encountered in deterministic modelling (Hutson and Wagenet, 1991). Consequently, more attention should be paid to the gathering/compiling of coherent and readily available data sets for simulation purposes. The foregoing also suggests there is only limited scope, at present, to elaborate deterministic models of N$_2$O production for applications at regional or global level (Van Breemen and Feijtel, 1990).

4.6.4 Stochastic models

Parkin and Robinson (1989; see Rolston, 1990) proposed a stochastic model of denitrification dependent only upon two driving variables, potential denitrification enzyme activity and carbon dioxide evolution. The stochastic nature of the denitrification enzyme activity and carbon dioxide evolution were described by measured probability density functions for a field site, which formed the basis for a Monte Carlo simulation model to calculate a probability density function for denitrification rate.

Alternatively, White and Mageson (1991) showed that a stochastic transfer function model (TFM) based on the probability function nitrate travel-times worked satisfactorily when the nitrate originates from a pulse input of soluble fertilizer to the soil surface. However, a TFM based on the probability density function of a surface applied tracer proved less satisfactory for simulating losses of indigenous soil nitrate. Among the problems encountered by White and Magneson (1991) were the difficulty of estimating mean nitrate content in field soils because of its high spatial variability, accounting for denitrification during leaching, and the uncertain reproducibility of the soil's transport characteristics.

4.7   Conclusions

This review shows that many biological, environmental as well as management factors determine the production, transfer and subsequent emission of N_2O and NO_x from soils. Although much research has been carried out on the possible interrelationships between the respective controlling factors and processes, models of N_2O evolution for particular ecosystems still remain in the early stages of development. Empirical models of N_2O emissions from natural terrestrial ecosystems at the global level have just recently been initiated. Although the soil characteristics of the type recorded on low resolution soil maps such as produced by FAO/Unesco (1971-1981) do not appear to be the main determinants of gaseous N_2O emissions from terrestrial ecosystems at the global level, a refined ½ x ½ degree grid global soil data base would be useful in the context of these modelling exercises (see Chapter 6). Ancillary data bases on climate, land use/vegetation cover, and fertilizer use (type, application), however, will probably have the 'most' weight in determining the ultimate emissions.

Although extrapolation of field measured N_2O fluxes from the local to the global scale using book-keeping methods appear straight forward, the results will be fraught with uncertainty (e.g., Bouwman, 1990a). An important task seems to be the elaboration of procedures that account for 'site' temporal and spatial variability so that local flux measurements can be scaled up to the global level. Stratification of ecosystems would provide a better insight into the variation in source regions of N_2O (Bouwman, 1990b), thereby providing a more solid basis for applying book-keeping methods.

There is a need to establish a network of measurement stations across the various continents, each site covering the representative range of crops, soil types and management practices typical of the region (IGBP, 1990). At each of these site, time series of N_2O and NO_x, as well as other 'greenhouse' gases, should be supplemented with accurate descriptions of the prevailing agro-environmental conditions. Eventually, this increased data set may provide the knowledge required to develop process based models that describe the production, transfer and evolution of N_2O from well defined ecosystems.

Chapter 5 Organic matter and carbon dioxide
N.H. Batjes

5.1 Introduction

5.1.1 Background

Increasing concentrations of radiatively-active trace gases - particularly carbon dioxide, methane, nitrous oxide and chlorofluorocarbons (CFCs) - in the atmosphere are likely to severely affect the global climate in the near future (Bolle *et al.*, 1986; Lashof and Tirpak, 1990; IPCC, 1990). A historical review of the associated, so-called 'greenhouse effect' has been prepared by Scharpenseel and Becker-Heidman (1990). In the present Chapter, the role of carbon dioxide (CO_2) in the global carbon budget will be reviewed with special reference to the role of terrestrial biota and soils. Carbon dioxide is chemically inert in the atmosphere, but being a radiatively-active gas it influences the Earth's radiation budget and so affects the climate and chemistry of the atmosphere (Levine, 1989; Bouwman, 1990a).

Atmospheric levels of carbon dioxide (CO_2), as derived from ice-core measurements, have increased from around 280 ppmv in the middle of the 18th century to around 300 ppmv in 1920 and 320 ppmv in the 1960s (ORNL, 1990; Neftel *et al.*, 1985). CO_2 records from direct chemical measurements in the 19th century have been reviewed by Fraser *et al.* (1986). Direct measurements of atmospheric CO_2 at the Mauna Loa Observatory, Hawaii, indicate present levels of 348 (Lashof and Tirpak, 1990) to 352 ppmv (Keeling *et al.*, 1989); the current increase is in the order of 0.5 % yr^{-1}. By mass of carbon this would correspond to an atmospheric burden in the order of 720-740 Pg C (Lashof and Tirpak, 1990; Moore III *et al.*, 1989). At any given latitude, atmospheric carbon dioxide levels exhibit a seasonal variation of several ppmv which has been attributed to climatically mediated changes in CO_2-uptake by photosynthesis (Woodwell, 1984b; Levine, 1989). CO_2 currently contributes to about 50 % of the total 'greenhouse' forcing (Scharpenseel and Becker-Heidman, 1990; Lashof and Tirpak, 1990). The average atmospheric lifetime of CO_2 is about 50-200 yr (IPCC, 1990).

Analysis of past CO_2 observations using the Maximum Entropy Method suggest that the atmospheric CO_2 content will increase to 405 ppmv by the year 2024 (Mannerma and Karras, 1989), while Mitchell (1989) quotes an estimated CO_2 concentration of 475 ppmv for the year 2035. According to model calculations of Walker and Kasting (1992) atmospheric carbon dioxide levels could be sustained indefinitely below 500 ppmv if fossil fuel combustion rates were immediately reduced from their current value by a factor of 25, and further forest clearance were halted. If this 'scenario' is not met and the consumption of fossil fuel continues unabated, peak CO_2 concentrations of 1000-2000 ppmv are probable in the next few centuries according to the model of Walker and Kasting (1992).

According to conservative scenarios the world in the year 2030, on average, could be 1-2 °C warmer and sea levels 14-24 cm higher than today so that important agricultural regions in coastal lowlands and deltas could be threatened by flooding, erosion and salt intrusion (Warrick and Barrow, 1990). In other studies, mean increases in temperature of 2-4 °C have been coined as being most likely to occur (Lashof and Tirpak, 1990), with possibly even more severe environmental and socio-economic repercussions.

Most advanced Global Circulation Models (GCMs) predict greater temperature increases at high latitudes, especially during the winter, because of more stable temperature stratification and ice-snow feedbacks. Such

changes in climate, and possible related effects on duration of the growing period in any given location, may ultimately affect the latitudinal and altitudinal distribution of ecosystems, as well as ecosystem diversity, and thereby the carbon dynamics in these systems. Possible changes in soil properties and land use as a result of the anticipated climate change have been discussed by Arnold *et al.* (1991), Brouwer *et al.* (1991) and Scharpenseel *et al.* (1991). Grotch (1988) and Essex (1991) recently reviewed what kind of information can be derived from GCMs. An authoritative review of the accuracy of GCM-based climate models is presented in IPCC (1990, Chapter 4).
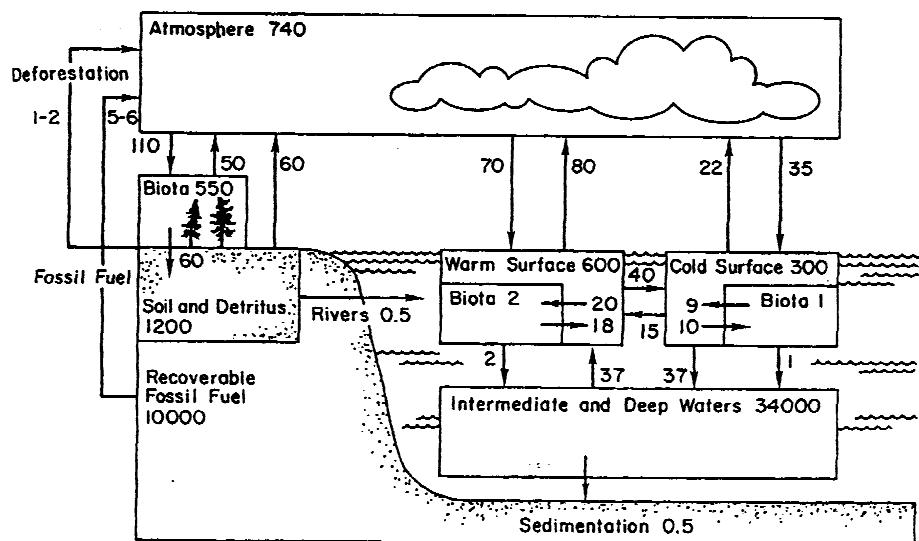
Figure 5.1.   Estimates of main sources and sinks of the global carbon cycle (in Pg CO_2-C yr^{-1}; source: Moore III *et al.*, 1989)

The major pools and sinks of organic carbon and magnitude of the main global fluxes are depicted in Figure 5.1. Other research groups have presented somewhat different values in view of the prevailing uncertainties in estimating the contributions of the different sources and sinks of CO_2 at the global level, and differences in adopted methodological approaches (Bolin, 1981 and 1986; Trabalka and Reichle, 1986; Bouwman, 1990a; Esser, 1990 a and b; Goudriaan and Ketner, 1984; IPCC, 1990; Sarmiento and Sundquist, 1992). Table 5.1 lists the estimated annual sources and sinks of CO_2 as presented by Houghton and Woodwell (1989). It indicates a current net gain of atmospheric CO_2 of about 3 Pg C per year, corresponding with about 50 % of current total emissions. Sarmiento and Sundquist (1992) estimated the inferred terrestrial uptake of CO_2 to be 1.8 ± 0.4 and 2.0-4.7 Pg C yr^{-1} using data of IPCC (1990) and Tans *et al.* (1990), respectively (Table 5.2).

Table 5.1.   Indicative annual carbon fluxes (Source: Houghton and Woodwell, 1989).

Processes	Removal of CO_2-C from the atmosphere (Pg C yr^{-1})	Emissions of C into atmosphere as CO_2 (Pg C yr^{-1})
Photosynthesis	100	-
Respiration by plants	-	50
Soil respiration	-	50
Fossil fuel burning	-	5
Deforestation	-	2
Physicochemical processes at the sea surface	104	100
	----	----
Total	204	207

Table 5.2.   Budgets for anthropogenic perturbation of carbon dioxide (Source: Sarmiento and Sundquist, 1992 p. 590).

	Average perturbation (Pg C yr^{-1})	
	IPCC (1990)	Tans *et al.* (1990)
Sources:		
Fossil fuels	5.4 ± 0.5	5.3
Deforestation	1.6 ± 1.0	0.0 - 3.2
Total	7.0 ± 1.2	5.3 - 8.5
Sinks:		
Atmosphere	3.2 ± 0.1	3.0
Oceans (steady state models)	1.6 ± 0.8	0.3 - 0.8
Total	5.2 ± 0.8	3.3 - 3.8
Imbalance (inferred terrestrial uptake)	1.8 ± 0.4	2.0 - 4.7

Processes that are fundamental to the long-term geochemical carbon cycle include (Berner, 1991):

a)   The uptake of CO_2 from the atmosphere and its transformation into dissolved HCO_3^- during the weathering of silicate rocks, with part of this HCO_3^- subsequently precipitating in the oceans as carbonate minerals;

b)   The thermal breakdown of carbonate minerals via metamorphism and magmatism, upon burial to great depths, with the resulting CO_2 being transported back to the atmosphere-ocean system (e.g., Barnes *et al.*, 1984);

c)   The burial of organic matter in sediments, its decomposition on the continents, and its thermal breakdown via diagenesis, metamorphism, and magmatism followed by oxidation of reduced gases to CO_2.

It is mainly through the process of photosynthesis that CO_2, the oxidized form of carbon, is converted to the reduced state in which it occurs in organic compounds and that the reduced form of oxygen (H_2O) is oxidized to molecular oxygen (O_2). Although some autotrophs can reduce CO_2 to organic material while oxidizing compounds other than H_2O (e.g., NO_3^-, NO_2^-, H_2, Fe^{3+} and reduced forms of sulphur), the contribution of these processes to the total fixation of CO_2 is of minor importance (Stainer *et al.*, 1976). The CO_2 emissions related to burning of fossil fuels, cement manufacturing and changes in land use have increased markedly during the last century due to the demands of the rapidly growing world population for food, timber and fuel, as well as unnecessary wastage. Basically, there would be three main approaches to slowing down the current release of carbon dioxide (Mintzer, 1985):

a) Improving the efficiency of energy supply and use;
b) Shifting the current fuel use away from coal towards less CO_2 intensive fuels; and
c) Reducing the rate of carbon dioxide emissions from biotic sources.

The balance of all the processes which determine modifications in atmospheric CO_2 concentration with time (dCO_2/dt) can be expressed as follows (Goreau, 1990):

$$d(CO_2)/dt = C + D + R + S + O - P - I - B$$
with:

Main sources:
C, the contribution of fossil fuel combustion to atmospheric CO_2 levels;
D, the CO_2 emissions associated with deforestation;
R, the autotrophic respiration of terrestrial plants;
S, the heterotrophic respiration from decomposers such as bacteria, fungi and animals;
O, the CO_2 flux from oceans to the atmosphere;

Main sinks:
P, the CO_2 fixed by terrestrial photosynthesis;
I, the CO_2 flux from the atmosphere to oceans;
B, the incorporation of carbon in organic and inorganic forms in sediments and soils.

The terrestrial biosphere absorbs about 100-120 Pg C yr^{-1} of CO_2 from the atmosphere via gross primary production. About the same amount is released to the atmosphere via autotrophic respiration and heterotrophic decomposition processes (Table 5.1). Average terrestrial net primary productivity (NPP) is in the order of 55 Pg C yr^{-1} and the annual global CO_2 flux from soils is estimated to average 68 ± 4 Pg C yr^{-1} (Raich and Schlesinger, 1992). The net release of carbon associated with deforestation and biomass burning is estimated to account for about 10-40 % of the annual anthropogenic CO_2 emissions to the atmosphere (Burke and Lashof, 1990; Hileman, 1990). Uncertainties in these estimates result from limited data on the types, amounts and acreages of biomass burned and highly variable emissions per unit of biomass burned. Estimates of biomass in trees and total carbon in live plants per unit area at an equatorial scale of 1:30 M on a ½ by ½ degree grid have been presented by Olson *et al.* (1983). Global biomass burning not only contributes to CO_2 emissions but also to about 10-20 % of annual emissions of methane, 20-40 % of carbon monoxide (CO), 5-15 % of N_2O, and 10-35 % of NO_x (Burke and Lashof, 1990). For additional information on the contribution of terrestrial ecosystems to emissions of the latter greenhouse gases, reference is made to Bouwman (1990a).

The total amount of recoverable fossil fuel, most of which is coal, is probably in the range 4000 to 6000 Pg C. Between the year 1860 and 1964 an estimated 183 ± 15 Pg C have been emitted to the atmosphere by fossil fuel combustion alone (Bolin, 1986b). In 1989 the global emissions of CO_2 associated with fossil fuel burning, gas flaring and cement manufacturing amounted to 5.97 Pg C (CDIAC, 1992); this figure could well be of the same order of magnitude as the one associated with a possible, small change in soil respiration flux associated with the anticipated warming of Earth. The year 1989 marks the sixth consecutive year that the 'industrial' CO_2 emissions have increased (CDIAC, 1992). By the year 2050 this may change to 2-20 Pg C yr^{-1}, depending on the 'adopted' abatement strategies (Keepin et $al.$, 1986).

Carbon stored in deep oceans amounts to about 39,000 Pg C. About 90-100 Pg C yr^{-1} is exchanged annually between the atmosphere and the ocean, resulting in a net oceanic uptake of 1-3 Pg C yr^{-1} (Lashof and Tirpak, 1990; IPCC, 1990). A clear overview of the uptake of CO_2 by the oceans is included in IPCC (1990, Section 1.2).

At present, coral reefs worldwide act as a sink for 111 Tg C yr^{-1} (1 Tg = 10^{12} g C), corresponding with about 2 % of present anthropogenic output (Kinsey and Hopley, 1991). Recent best-estimates for global river organic carbon fluxes are 0.2 Pg C yr^{-1} for dissolved organic carbon and 0.2-0.3 Pg C yr^{-1} for particulate organic carbon, with a range of 0.3 to 0.5 Pg C yr^{-1} for total organic carbon (Sarmiento and Sundquist, 1992 p. 590).

Some 800 Pg C is probably stored in calcic horizons, popularly known as caliches or calcretes, which occur in the world's deserts. The natural carbon flux from the atmosphere to inorganic carbon in arid soils is estimated to be about 1-2 Pg C yr^{-1} (Schlesinger, 1985 and 1986). Vast amounts of carbon are stored in sediments worldwide, and these amounts are relatively stable. The role of weathering in the CO_2 balance of soils, however, cannot be neglected as it may remove from 0.16 to 0.27 Pg C yr^{-1} of atmospheric CO_2 as HCO_3^- (Van Breemen and Feijtel, 1990). Bohn (1990) recently discussed the possible changes in inorganic carbon content in soil upon climate change (see also Sombroek, 1990).

Estimates for the amounts of carbon stored in land biota and world soils are 700-1700 and 1000-3000 Pg C, respectively (see Section 5.5.1). This means that changes in the carbon contents in land biota and soils may have important repercussions for atmospheric C-levels. The principal, technical means of reducing biotic emissions would be to limit the rate of tropical deforestation and to make biomass use more efficient. In this Chapter the focus of the discussion will be on the factors and processes that control the storage/release of CO_2 in terrestrial ecosystems. The present Chapter of necessity is selective in view of the vast 'dimension' of this aspect of the carbon cycle.

5.1.2   Structure of chapter

In Section 5.2 the functions and turnover of organic matter and its fractions in soil are reviewed. The main abiotic and biotic factors that regulate the stability and decomposition of organic matter in soils are reviewed in Section 5.3. Examples of CO_2 evolution associated with 'soil respiration' and changes in land use are presented in Section 5.4, which also includes a discussion of the possible 'fertilization effect' associated with increasing atmospheric CO_2 levels. In Section 5.5 estimates of world soil carbon pools are discussed with reference to some modelling approaches. Possible limitations inherent in using available soil data for estimating the size of soil carbon pools worldwide are formulated in Section 5.5, and concluding remarks from Section 5.6.

5.2 Organic matter in soil

5.2.1 Properties

The favourable effects of organic matter on the physical and chemical properties of soils and on biological activity, and by implication in sustaining soil productivity, have been discussed at length in many handbooks (Russell, 1980 and 1988; Neue and Scharpenseel, 1984 and many others). The organic constituents of tropical soils do not possess any special qualities that set them apart from those of temperate regions (e.g., Theng *et al.*, 1989). Organic matter has a stabilizing effect on soil structure (see Section 5.3.4), improves the moisture holding and release characteristics of soil, and protects soils against erosion. Decaying organic matter slowly releases nutrients (e.g., N, P, S, K) essential for plant and microbial growth. Some organic constituents in humic substances may stimulate plant growth under conditions of adequate mineral nutrition (Chen and Aviad, 1990). Soil organic matter is also an important determinant of the cation exchange capacity of soils, particularly in coarse textured soils and so called 'low activity' clay soils. It also plays an important role in retention of non-ionic organic compounds and pesticides in soil (Chiou, 1990). The generally dark colour of organic matter in topsoils can increase the absorption of solar energy. As a result, crop growth on bare soils rich in organic matter may start somewhat earlier in cool climates. Upon deforestation or a shift in land use the above favourable properties may be altered to a varying extent as a result of accelerated decomposition of a fraction of the organic matter present in soil. The related decrease in soil organic matter content commonly leads to structural soil degradation, causing increased compaction and decreased soil hydraulic properties (Spaans, 1989, 1990), clay mobilization (Wielemaker and Landsu, 1991), increased erosion hazard, and/or enhanced losses of soil acting herbicides adsorbed to soil organic matter (Harrod *et al.*, 1991; Vaidyanathan and Eagel, 1991).

5.2.2 Definitions of soil organic matter

Organic matter levels in soil are essentially regulated by net primary production, the distribution of photosynthates into 'roots' and 'shoots', and the rate at which these various organic residues decompose. Plant residues that fall on the soil as 'fresh' litter are gradually altered through physical fragmentation, fauna/microflora interactions, mineralisation and humus formation. The different types of organic matter in litter have recently been reviewed by Eijsackers and Zehnder (1990). Litter is not considered to be a part of soil organic matter as it essentially lies on the soil's surface. As such it is not considered in the calculation of soil organic carbon pools (Buringh, 1984; Bouwman, 1990a).

Many research groups have studied the characteristics, fractions and dynamics of organic matter in soil (Kononova, 1966; Greenland and Hayes, 1978; Stevenson, 1982; Frimmel and Christman, 1988; Coleman *et al.*, 1989; Mortvedt and Buxton, 1987; Shawney and Brown, 1989; Russell, 1980). In the following paragraphs the definitions of 'soil organic matter' as formulated by Russell (1980), Schnitzer (1991), Theng *et al.* (1989) and Stevenson (1982) are discussed to illustrate the necessity for a standardization of terms.

According to Russell (1980) the 'soil organic matter consists of a whole series of products which range from undecayed plant and animal tissues through ephemeral products of decomposition to fairly stable amorphous brown to black material bearing no trace of the anatomical structure of the material from which it was derived'. It is this latter, amorphous material that Russell (1980) terms humus. Similarly, Schnitzer (1991) defines soil organic matter as the sum total of all organic carbon-containing substances in soils which consist

of 'a mixture of plant and animal residues in various stages of decomposition, of substances synthesized microbiologically and/or chemically from the breakdown products, and of the bodies of live and dead microorganisms and small animals and their decomposing products'. The same author divides soil organic matter into non-humic and humic substances. Non-humic substances still display recognizable chemical characteristics, are relatively easily degraded in soils, and have short life-spans. Conversely, humic substances no longer exhibit specific chemical and physical characteristics and are more resistant to microbiological and biological degradation.

Theng *et al.* (1989) use a somewhat different definition of soil organic matter which they divide into a 'living' and 'non-living' component. The 'living' component (on average < 4 % of total soil organic C) is divided into plant roots, macroorganisms or fauna, and microorganisms (5-10, 15-30 and 60-80 per cent, respectively). The 'non-living' component consists of 'macro-organic materials' and 'humus'. The 'macro-organic' fraction largely consists of plant residues in varying stages of decomposition that can not pass through a sieve with 0.25 mm mesh. It is considered to be similar to the 'light fraction' obtained by flotation on liquids with a density of 1.6 to 2.0 g cm^{-3}. In the terminology of Theng *et al.* (1989) 'humus' is what remains after physical separation of the 'light fraction'. It consists of non-humic substances, which are well defined classes of organic compounds, and humic substances.

Stevenson (1982) uses a narrower and possibly more widely applied definition (by modellers) of soil organic matter: 'the organic constituents of soil - excluding undecayed plant and animal tissue -, their partial decomposition products and the soil biomass'. According this definition soil organic matter includes: a) identifiable high-molecular weight organic materials such as polysaccharides and protein; b) simpler substances such as sugars, amino acids, and other small molecules; and c) humic substances. In this sense soil organic matter resembles humus which is commonly defined as the structureless component of the soil organic fraction (see also Russell, 1980). This humus is primarily derived from the higher plants and formed during the microbial decomposition of original plant materials and of new substrates synthesized by soil micro-organisms.

Fractions

Humic substances form 'a category of naturally occurring biogenic, heterogeneous organic substances that can generally be characterized as being yellow to black in colour, of high molecular weight, and refractory' (Aiken *et al.*, 1985a). Humic substances cannot be classified into any discrete categories of compounds such as polysaccharides or proteins (MacCarthy *et al.*, 1990c; Stott and Martin, 1990; Theng *et al.*, 1989). Each humic component in each environment (soil, stream water and ocean water) is unique and possesses an individuality that is characteristic of the particular component in any particular environment (Malcolm and MacCarthy, 1991).

By convention the 'fractions' of humic substances are operationally divided into humic acid, fulvic acid and humin. The fraction of humic substances that is not soluble in water under strongly acidic conditions (pH < 2) but is soluble at higher pH values is termed humic acids. Fulvic acids are the components of humic substances that are soluble irrespective of the pH conditions in aqueous solutions. Humin corresponds with the fraction of humic substances that is not soluble in water at any pH value (Aiken *et al.*, 1985a). These definitions do not imply any distinct functional boundary between humic acid, fulvic acid and humin (as fractions) in terms of their physico-chemical properties in relation to their biological degradability.

Modelling of pedogenetic processes and soil acidification demand data on functional attributes such as pKs, density of dissociable groups, and complex formation constants (Theng *et al.*, 1989). Alternatively, soil organic matter is often divided into a so-called 'light' and 'heavy' fraction when modelling the dynamics of organic matter turnover in soil. These fractions are considered to correspond with the 'labile' and 'stable' compartments, respectively. The fractions are commonly separated physically by sieving and flotation.

The 'light fraction', as defined by Anderson and Ingram (1989) in the Tropical Soil Biology and Fertility (TSBF) Manual , is physically bounded by a mesh size of 2 mm - the upper limit for the USDA 'fine earth' fraction - and 0.25 mm, and separated from the soil by flotation on water. It is considered to consist of microbial biomass and partially humified/cellular organic matter with a rapid turnover (1-5 yr). Independent studies, however, have shown the 'light fraction' (< 1.6 g cm^{-3}) may include significant amounts of recalcitrant charcoal which should be removed (Skjemstad *et al.*, 1990). For obvious practical reasons the 'heavy fraction' of TSBF is defined as corresponding with the fraction not retained by a 0.25 mm sieve. The corresponding organic matter is considered to be physically protected or to consist of organic matter which is resistant to decomposition with 'slow' (20-40 yr) to 'passive' (200-1500 yr) turnover times (Anderson and Ingram, 1989).

As is already reflected by the findings of Skjemstad *et al.* (1990) there still is a need for developing fractionation schemes that 'truly' reflect the dynamic character of soil organic matter for use on a wide range of soils (e.g., Theng *et al.*, 1989; Bonde, 1991). Experimental work suggests it may be necessary to combine physical fractionation with biologically based techniques such as long-term incubation (Bonde, 1991). Mechanical procedures such as sieving or sonic vibration of soil samples before incubation, however, may introduce artifacts that affect the observed mineralisation of the respective fractions (Houot *et al.*, 1991; Feller *et al.*, 1991; Balesdent *et al.*, 1991). Fractionation schemes that truly reflect the biological diversity of organic matter in soil are needed (Van Veen, 1986); adequate methods to experimentally establish the partitioning of soil organic matter over the different pools conceptualized in modelling studies are still lacking (Verberne *et al.*, 1990).

Residence time

With the introduction of radioisotopic dating techniques it became possible to calculate the mean age of carbon in soil (for discussion see Harkness *et al.*, 1991). The calculated ^{14}C age of humus in five pasture soils from the midwestern USA was 200-400 yr (Simonson, 1959). Half-lives of 1700 to 2200 yr were reported by Paul *et al.* (1964) for humus in selected Canadian soils. The mean calculated age of humus in some soils of the Rothamsted classical experiments was 1240 yr (Jenkinson and Rayner, 1977). Topsoil (0-23 cm), sampled in 1881 from unmanured plots of the Broadbalk continuous wheat experiment, contained 27.5 t ha^{-1} of organic carbon with a measured ^{14}C age (recomputed to 1881) of 1330 years (Jenkinson, 1990). The mean residence time of the various humus fractions of a Chernozem increases in the sequence humic acid $\approx$ humin > fulvic acid with mean values of 495 ± 60 yr, 1140 ± 50 yr and 1235 ± 60 yr, respectively (Campbell *et al.*, 1967 a, b). Alternatively, Zehnder (1982) reported the 'mobile' humus fraction, which includes humic and fulvic acids, has a mean residence time of 250-800 yr whereas humins are often older than 2000 yr. Marked differences exist in the mean residence time of the 'acid hydrolysable' and 'non-hydrolysable' components of both the humic acid and humin fractions (Campbell *et al.*, *op cit.*). The oldest organic fraction in two soils of the Jura mountains, France, corresponded with the non-hydrolysable material of clay-sized humin (Balesdent, 1987). Mean residence times of 2000 to 5000 yr have been reported for soils rich in allophane

(Wada and Aomine, 1975), reflecting the importance of mineralogy in preserving organic materials in soil (see Section 5.3.3).

The $^{14}C/^{12}C$ ratio of the upper part of the litter of Brazilian Tabuleiros soils was shown to be in equilibrium with atmospheric CO_2 levels, indicating a turnover time of less than 1 year (Lobo *et al.*, 1990). The lower part of the litter had a turnover time of 17 ± 1 yr, whereas in the A1-horizon (0-24 cm) the mean turnover time was 100 ± 15 yr (Lobo *et al.*, 1990). Harrison *et al.* (1990) studied the turnover time of organic matter in various soil layers in an oak-ash-birch forest of Meathop Wood, Cumbria, with radiocarbon dating. The calculated turnover times increased with depth from the litter layer from about 2 yr for the litter, 18 yr for soil organic matter in the '0-5 cm', 40 yr for the '5-10 cm', 100 yr for the '10-15 cm', 500 yr for the '15-25 cm', and 600 yr for the '25-50 cm' layer, respectively. Raich and Schlesinger (1992) estimated that, when reasonable estimates about root respiration are made, the global mean residence time of soil organic matter is about 32 years.

Turnover of microbial biomass

The microbial biomass forms a relatively small and labile fraction of the soil organic matter complex. Yet, its turnover is a rate determining process in the cycling of organic matter and nutrients (Van Veen, 1986). Available techniques for measuring microbial biomass have been reviewed and discussed by Bonde (1991) amongst others.

The microbial biomass may be influenced by the type of vegetation present. Microbial C - determined with the fumigation extraction method - for selected soils under conifers, deciduous forest and arable use was 1.19, 1.13, and 1.04 % of total C, respectively (Martikainen and Palojärvi, 1990). Microbial biomass amounted to 2.9-4.1 % (Bonde, 1991) and 1.8-3.2 % (Houot *et al.*, 1991) of total carbon in selected temperate agro-ecosystems. Similar values have been reported for a tropical Acrorthox (i.e., 1.8-4.8 % of total carbon; Bonde, 1991). Van Veen *et al.* (1985) postulated that soils have characteristic capacities to preserve both organic matter and microorganisms. Preservation of the microorganisms could be the result of protection against degradation and/or amelioration of harsh environmental conditions. Van Veen and co-workers assumed that biomass which is formed in excess of the soil's preservation capacity will die at a relatively high rate.

Paul and Voroney (1983) used simulation modelling to estimate the turnover time of microbial biomass C, finding mean values of 0.24 yr for a site in Brazil and 2.5 yr in England. Similarly, Houot *et al.* (1991) measured a turnover time of 1.4-1.8 yr for microbial biomass C in a field incubation in France, while Bonde (1991) reported a turnover time of about 0.13-0.17 yr at his EMBRAPA site in Brazil. These data point at a more rapid degree of microbial breakdown in the humid tropical sites as compared to the temperate European sites which have been examined.

Recalcitrant carbon

Not all the components of the physically defined 'active' fraction of soil are as easily decomposable as the terminology would imply. Measurement of $D^{13}C$ values with depth in Australian krasnozems, for instance, showed that charcoal was a serious contaminant in the light fraction (< 1.6 g cm^{-3}) of all samples (Skjemstad *et al.*, 1990). Sanford *et al.* (1985) calculated that the uppermost 1 m of selected 'terra firme' forest soils from

Venezuela contain 4.6 ± 1.8, 6.9 ± 3.6 and 13.9 ± 6.6 Mg ha^{-1} of charcoal (the ratio of C to charcoal was not specified). The age of the charcoal fragments ranged from 250 ± 50 yr to 6260 ± 110 yr B.P., the oldest mean age being recorded for the 60-70 cm layer of the soils under consideration. Jenkinson (1990) showed it is necessary to consider biologically inert carbon in the Rothamsted model; arbitrarily, the corresponding value was set at 300 g C m^{-2} for all freely draining soils of the world. The fact that fossil charcoal in soil can still be related to the occurrence of paleo-wildfire (Jones and Chaloner, 1991) may illustrate the degree of persistence of some charcoal compounds.

The importance of past and present charcoal formation during biomass burning in present global carbon budgets remains a source of uncertainty (Bolin, 1986b). Based on several assumptions Esser (1990a) suggests that charcoal formation since 1860 may have amounted to as much as 8 Pg C in grasslands and savannas, and 1.5 Pg C in coniferous forests. Seiler and Crützen (1980) reported that charcoal or inert carbon, resulting from biomass burning, may amount to 0.5 to 1.7 Pg C. This amount is significant, reflecting the need for further efforts to define the relevant processes in simulation models such as the Osnabruck Biosphere Model (Esser, 1990 a and b) or the model of Goudriaan (1990).

5.2.3   Modelling organic matter turnover in soil

Interest in the spatial distribution and nature of organic matter in soil has existed for a long time. In 1882 Dockuchaev compiled a systematic map of organic matter content in the Chernozem areas in Russia. Jenny (1941) was one of the first to model the turnover of organic matter in soil. Since then many conceptual and mathematical models have been developed to describe the dynamics of organic matter in soil. In most of these one to several pools of organic matter are considered. These compartments are kinetically defined with different and specific turnover rates (see reviews of Jenkinson, 1990; Bouwman, 1990a). Alternatively, Janssen (1984) presented a model in which the decomposition rate is made variable in time ($k = 2.82*(a + t)^{-1.6}$, with a the apparent age of the organic material added).

Jenkinson (1990) essentially groups organic carbon turnover models according to whether they are: a) single homogenous compartment models; b) two compartment models; c) multi-compartmental models; and d) non-compartment decay models. Models b) to c) conceptualize a small pool of organic matter with a rapid turnover time, and one or more pools of greater size and slower turnover rates. The decay processes of the respective pools commonly is described using first-order, logarithmic decay functions. The model of Jenkinson (1977) may be considered as an example of a two compartment model. In this model, each C compartment (X and Y) decomposes according to a first order process at different and distinct rates (k1 and k2, respectively):

$$C = X.e^{-k1.t} + Y.e^{-k2.t}$$

Alternatively, Houot *et al.* (1991) described the kinetics of released CO_2 as a combination of first-order kinetics and zero order kinetics:

$$CO_2\text{-}C = C1.(1 - e^{-k1.t}) + k2.t$$

After about 30 days the kinetics of C mineralization became nearly constant which is represented by the second term of the equation (k2*t). Houot *et al.* (1991) observed similar rates (k2) of CO_2 accumulation in cultivated or bare soils which had been amended with organic materials. Similarly, Melillo *et al.* (1989)

presented a two-phase breakdown model for organic matter with a first phase of rapid mass loss and a much slower second phase. Well known examples of multi-compartment models include CENTURY (Parton *et al.*, 1987, 1989) and ROTHAMSTED (Jenkinson, 1990). The principles of the latter model, which considers 5 compartments, are discussed briefly (Figure 5.2).
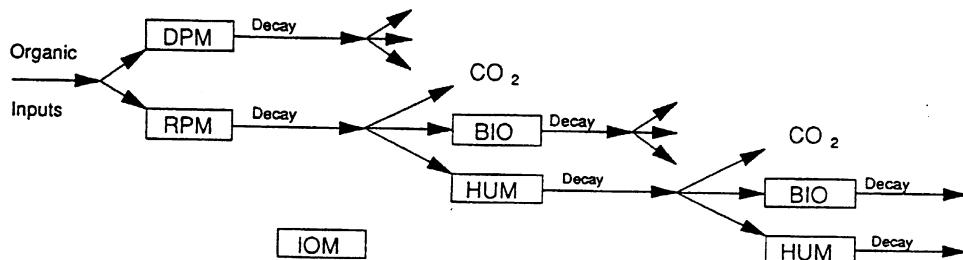
Figure 5.2.   Schematic representation of the ROTHAMSTED model (Source: Jenkinson, 1990; see text for definition of abbreviations)

The ROTHAMSTED model uses a monthly time step. Inputs of crop residues are first alloted into decomposable (DPM) and resistant (RPM) plant material. Both the DPM and RPM are considered to decompose to carbon dioxide, which is lost from the system by evolution, microbial biomass (BIO) and humified organic matter (HUM). A uniform BIO/HUM conversion ratio is assumed during substrate decomposition for all soils. During decomposition of HUM, more CO_2, microbial biomass (BIO) and fresh humus (HUM) are formed, again in the same proportion. A small organic component is considered to be inert to biological attack (IOM). The monthly decay is derived from the expression $1 - e^{-abckt}$. In this expression *a* is a temperature rate modifying factor, *b* a moisture rate modifying factor, and *c* a plant retainment factor. Additional information on the ROTHAMSTED model may be found in Jenkinson (1990).

Agren and Bosatta (1988, 1991) and Moran *et al.* (1990) have challenged the concept/use of discrete pools of soil organic matter in models. They visualize the decomposition as a continuum that starts with the addition of organic matter and leads to the formation of refractory humic substances. This means they view soil organic matter heterogeneity as a continuously varying quality variable, where the substrate degrades in quality due to microbial action. As the mathematical modelling of this approach is considered difficult, as compared to compartment-based models, it has not been applied to long runs of data from agricultural trials (see Jenkinson, 1990). Alternatively, it may be cumbersome to derive the degradation rate constants (k) for the respective carbon pools in multi-compartmental models. Van Breemen and Feijtel (1990), for instance, consider distinct and different k-factors for litter - depending on whether it consists of leaves, branches or stems -, roots, soluble organic C, and soil organic C at different depths in the soil. These k-factors are adjusted for actual conditions of moisture and temperature using a 'conversion graph'. This may require calibration for specific situations, thereby posing a high demand in terms of field observations. Attempts to describe more precisely the turnover of organic matter in soil are increasingly focusing attention on the key role of biota (see review of Ladd, 1986; Van Veen, 1986). There is also a need to consider more the spatial distribution of soil organic matter and its decomposers in soil (Van Veen, 1986; Verberne *et al.*, 1990).

An important bottleneck in 'refining' models is that it remains difficult to physically or chemically isolate the 'conceptual' soil organic matter pools that are considered in the respective types of models (see Section 5.2.2).

5.3   Factors affecting the organic matter status of soils

5.3.1   Introduction

The primary environmental determinants of plant growth in any location are solar radiation, temperature and length of the growing period (e.g., Van Keulen and Wolf, 1986). Photosynthesis, through its effect on net primary production, strongly determines the size of the input of organic matter into the soil. As the increase in microbial decay rate (Q_{10}) generally exceeds the increase in plant growth associated with a similar rise in temperature - provided water and nutrients are not limiting - there often is a negative relationship between temperature and soil organic matter content. If the soil forming factors of parent material, topography, vegetation and time are held constant, organic carbon in soil is further expected to increase with increasing precipitation (Jenny, 1941). Because of the many possible interactions between the different abiotic and biotic regulators of organic matter formation and decomposition it often proves difficult to assess unambiguously how the various controls will affect the dynamics of organic matter in any given soil. Process-based modelling provides a tool for increasing the conceptual knowledge of these relationships. Major environmental controls of organic matter decomposition in soil are moisture status, soil temperature, oxygen supply, soil fertility, clay content and mineralogy (Alexander, 1977; Eijsackers and Zehnder, 1990; Anderson and Flanagan, 1990). Biotic controls include the type of flora and fauna, as well as possible modifications therein resulting from the influence of man (e.g., cultivation, irrigation, atmospheric pollution).

5.3.2   Effects of climate

The distribution of rainfall and temperature over the year determine the period during which soil moisture and soil temperature conditions are favourable for plant growth as well as for the activities of micro-, meso- and macro-fauna. In the humid tropics this may be the whole year as opposed, for instance, to temperate regions where cold conditions may slow down or stop biotic growth in some seasons. Basically, under non-limiting conditions of temperature and nutrient supply, the breakdown of organic matter in soil will be slowed down when soils are either too dry or too wet. As a result arid soils generally have lower organic matter contents than soils from wetter regions where organic matter tends to accumulate (e.g., USDA, 1975; Kimble *et al.*, 1990). The latter happens particularly under cool temperatures, anaerobic conditions and high water tables commonly associated with depressions in the landscape as topography influences soil organic matter through the effects of slope and drainage. Colberg (1988) reviewed the anaerobic microbial decomposition of cellulose, oligolignols and monoaromatic lignin derivatives. Figure 5.3 shows a framework for relating the direct interaction of climatic factors (rainfall, temperature etc.) on organic matter dynamics in soil.

Kadeba (1978) observed that mean annual rainfall and, particularly the number of rainy days, were the major factors governing the amounts and distribution of soil C and N in some savanna soils of northern Nigeria. During the dry season, similar soils tend to dry out earlier and more completely in the open than under shade. Consequently, the decay of organic matter can continue longer in the shade, although at lower temperatures (Jenkinson and Ayanaba, 1977). Similarly, Dabin (1980) attributes to the reduced humidity during the dry season in savanna the fact that the ratio of 'litter/addition of organic materials to soil' is higher under savanna than under forest, which restricts the decomposition of the litter. Dabin (1980) reported transformation coefficients are 0.1 under forest and 0.2 under savanna.
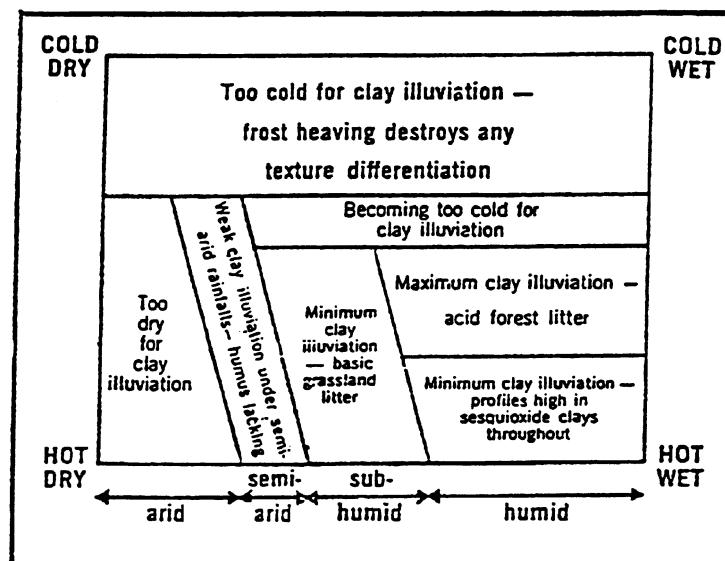
The effect of climate on texture differentiation in soils.
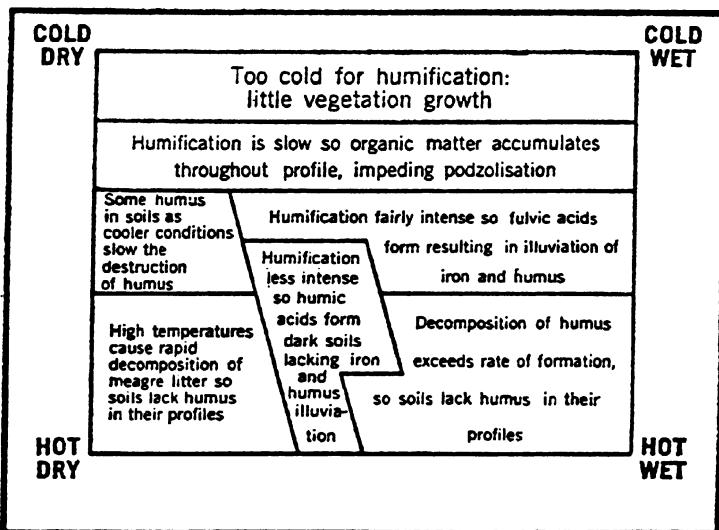
The role of organic matter in soil formation in response to climate.

Figure 5.3.   A framework for relating the direct interactions of climatic factors with the three processes that determine the characteristics and dynamics of soils (Source: Walker and Graetz, 1988 p. 17)
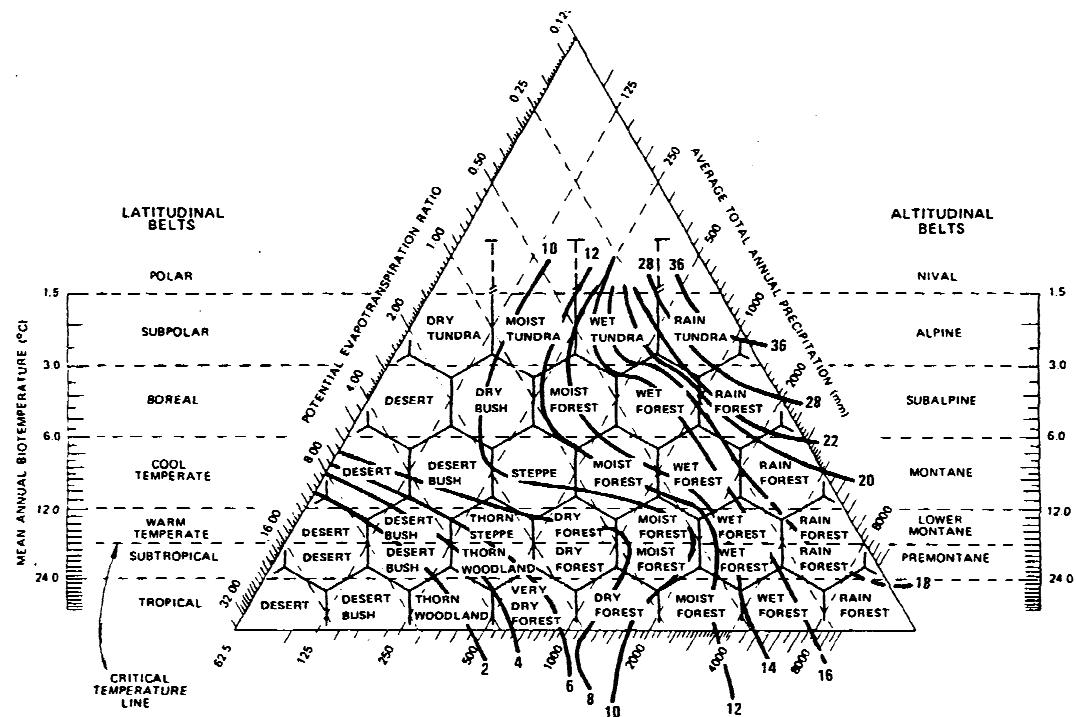
Figure 5.4.   Contours of soil carbon density (kg m⁻³) plotted in Holdridge's scheme for world life zone classification
(Source: Post *et al.*, 1985)

Post *et al.* (1985, Figure 5.4) grouped 3100 soil profiles on a climate basis using the Holdridge life zone classification system. They showed soil carbon density generally increases with rising precipitation, and also that soil carbon density increases with decreasing temperature for any particular level of precipitation. Kimble *et al.* (1990) studied 2715 profiles, classified according to the Keys to Soil Taxonomy (USDA, 1987), and found that both within 'iso' and 'non-iso' soil temperature regimes there is a decrease in carbon as the mean soil temperature rises.

McDaniel and Munn (1985) grouped 143 Mollisols and Aridisols from Wyoming and Montana into cryic, frigid and mesic temperature regimes, and found that texture was only significantly correlated to organic C content in the mesic (warmest) soils (0-40 cm depth zone). Sims and Nielsen (1986) found that clay content had much less influence on organic matter accumulation in cool soils of Montana than in warmer soils of the southern Great Plains of the USA. Similarly, clay content was selected earlier in the stepwise multiple-regression fitting-process for the tropical areas than for the 'cooler' areas of Australia (Spain *et al.*, 1983). Similar observations were made by Lepsch *et al.* (1991) in a study of 99 paired native-vegetation/row-cropped sites in well drained, clayey 'low activity clay' soils from udic, ustic and perudic regions of St. Paolo State. In these 'tropical' climatic zones, the organic C content in the 0-20 cm layer was found to be better related to clay+silt content than to any other soil or climatic parameter. A practical implication of the above findings is that empirical relationships between clay content and organic C content, or degradation constants (k-factors), should only be applied in the regions and for the site conditions for which they were originally developed.

A similar increase in temperature - under otherwise non-limiting conditions - will affect the activity of plants and microorganisms to a different degree. On average, net primary production increases with temperature with a Q_{10} of 1.0-1.5 (Harvey, 1989; Kohlmaier et $al.$, 1990), while soil respiration increases with an average Q_{10} of 2.0-2.4 (Harvey, 1989; Raich and Schlesinger, 1992). Kohlmaier et $al.$ (1990) report a somewhat wider range for mean Q_{10} values (1.3-4.0) for heterotrophic soil respiration. Inherently, the size of the Q_{10} ratios will vary with the temperature range under consideration (e.g., from 0 to 10 $^{\circ}$C or from 20 to 30 $^{\circ}$C) and will be biota specific. Nevertheless, the above figures suggest that an increase in mean soil temperature, as associated with an enhanced global warming, is likely to form a positive feedback to the greenhouse effect.

5.3.3   Effects of soil mineralogy and fertility

The inherent fertility of soils, as determined by the nature of the parent material/rock, is one of the regulators of net primary production and thereby of the possible input of organic matter in soils under pristine conditions. The organic matter content of soil depends to an important degree upon the phosphorus content of the parent material and the degree of weathering (Walkers and Syers, 1976). When the other regulating factors are not limiting, soils formed on basic rocks will tend to have a higher content of organic matter than acid soils (under freely drained conditions). In Nigerian savannas, a good correlation was observed between organic C and percent clay in soils developed from basaltic rocks, while no such relationship was found for soils developed from acid rocks (Kadeba, 1978). The effect of parent material is also illustrated by the low organic C levels in the Nebraska Sand Hills and some sandy areas of Minnesota and Wisconsin (Franzmeier et $al.$, 1985). Schimel et $al.$ (1985) observed microbial biomass and mineralization did not vary with the slope position, whereas parent material (sandstone, siltstone and shale) had a significant effect upon organic matter transformations. Surface accumulation of organic matter in forest rendzinas over limestone, for instance, can be explained by inhibition of humification processes by active calcium carbonate. Similarly, the stability of soil organic matter in man-made 'Terra Preto dos Indios' is due to large additions of organic materials rich in Ca, P and N. Stimulation of microbial activity by these inputs leads to an accelerated mineralization of organic substances less resistant to degradation (e.g., polysaccharides, proteins) and thus to a relative enrichment of the stable humus fraction rich in aromatic compounds (Zech et $al.$, 1990).

The parent rock/material also has an effect on stabilizing organic matter in soil in that it determines to a great extent the type of clay minerals that will be formed upon weathering. The formation of interlayer clay-organic complexes, for instance, requires a smectitic clay mineralogy, an accumulation of organic matter associated with low microbial activity, and a highly acid soil reaction (Theng et $al.$, 1986). Nayak et $al.$ (1990) propose that a decreasing content of acidic groups in humic substances promotes their fixation by montmorillonite because of a lowering of the inter-particle repulsive forces as well as a reduction in hydratation energies; the net energy available for breaking down the clay-humus bonds would consequently be reduced. In absence of montmorillonite and calcium carbonate, and under conditions of good drainage and aeration, soil humus is less condensed and less stabile so that it can easily be destroyed by small alterations of the environment (Volkoff and Cerri, 1980). Boudot et $al.$ (1990) observed the gross mineralization rates of both N and C were inversely related to the content of amorphous-Al and materials rich in allophane, reflecting a good protection of organic matter by these materials. Conversely, the mineralization of deceased micro-organisms and newly formed metabolites did not seem to be affected by the mineralogical composition of the allophanic soil samples (Boudot et $al.$, 1990). Generally, the stabilizing effect of clay size particles on organic matter decreases in the following order: allophane > amorphous or poorly crystalline Al-silicates > smectite > illite > kaolinite (Van Breemen and Feijtel, 1990).

Possible changes in soil weathering rates associated with a potential doubling of atmospheric CO_2 concentration and associated temperature increases have been discussed by Sombroek (1990). The CO_2 sink associated with weathering is generally much lower in areas with silicate rocks than in calcareous areas (Van Breemen and Feijtel, 1990). The size of this sink will gradually decrease as the area affected by acid deposition increases. Consequently, the possible effects of acid deposition on organic matter dynamics should be studied as a lowered soil pH and associated nutrient losses may have an adverse effect on biotic diversity, biomass growth, and organic matter decomposition in soil.

Soil acidity slows down the decomposition of organic matter under tropical conditions although the differences between acid soils and neutrals soil become less marked with time (2 yr incubation period; Ayanaba and Jenkinson, 1990). Jenkinson (1977) found similar results for acidic and neutral soils under temperate conditions, in which decomposition was markedly slower in the acidic soil during the first year or two. For tropical regions, Dabin (1980) showed that the decomposition of organic matter is always important in well drained media, even when soils are acid. Only an increase in the length of the dry season increased the fraction of non-decomposed organic matter, and at the same time caused a decrease in total C. In Brazil, the geographic distribution of soil organic matter under natural vegetation was shown to be principally determined by three factors: temperature (external), soil acidity and soil drainage (Volkoff and Cerri, 1988). In the acid soils studied, the differentiation is first according to drainage, and thereafter according to temperature if the soil remains well drained. No effect of rainfall regime on soil organic matter contents was observed in the study of Volkoff and Cerri (1988).

5.3.4 Effects of soil structure

The higher stability of soil aggregates in pasture soils as compared to arable soils reflects the effect of higher levels of indigenous organic matter in producing more stable aggregates (Swift, 1991). The physical protection of organic matter in soil varies with the degree of aggregation of the soil particles (soil structure) and the clay mineralogy (Sorensen, 1975; Mendoca *et al.*, 1991 and many others). Organic substances in aggregates can increase the cohesion of clay fractions through H-bridges, covalent linkages, physical linkages by Van der Waal's forces, and complexation with metallic ions. Volkoff *et al.* (1984), for example, explained organic carbon accumulation by the formation of organo-mineral complexes stable with aluminium. Part of the humified organic matter in clayey Oxisols may be locked-up in organo-Fe complexes (Santos *et al.*, 1989). The organic material in interlayer-clay complexes is resistant to H_2O_2 (peroxide) and pyrophosphate extraction, and thermally stable up to 400 ºC (Theng *et al.*, 1986).

Encrustation of plant debris is an important feature of many stable aggregates and a major mechanism responsible for protecting the enclosed plant debris (Waters and Oades, 1991). Cell walls, humified hyphae, and other decomposed organic materials, easily identified in large pore spaces, are important in binding the clay particles in micro-aggregates of some Oxisols (Santos *et al.*, 1989). The positive effect of soil organic matter in forming and stabilizing soil aggregates is not caused by the soil organic matter as a whole but to specific components. The polysaccharides and soil humic substances are particularly important in this respect (Swift, 1991). Tisdall and Oades (1980) proposed a hierarchical conceptual model for soil aggregate structure in which various binding agents operate at different stages in the structural organization of aggregates. They grouped the organic binding agents into 3 functional groups: a) transient binding agents, consisting mainly of polysaccharides, which are readily decomposed by microorganisms; b) temporary binding agents such as thin roots and fungal hyphae; and c) persistent organic binding agents such as resistant aromatic components associated with polyvalent metal cations, and strongly sorbed polymers. Several subsequent and independent

studies have confirmed that the nature and stability of organic matter in aggregates may change with the size of the aggregates. Macro-aggregates of Red-Yellow latosols, for instance, contain more fulvic acids and less humic acids than the micro-aggregates (Mendoca *et al.*, 1991). In an Australian krasnozem, the organic matter within micro-aggregates (< 0.2 mm) contained up to 32 % more 'old' carbon than the remaining soil material 83 years after conversion from forest to pasture (Skjemstad *et al.*, 1990). Van Veen and Paul (1981) observed soil organic matter is strongly complexed by inorganic colloids in so-called 'water-stable' aggregates, in that it is oxidized with more difficulty by H_2O_2 than the organic matter of aggregates with low water stability. Similarly, Mendonca *et al.* (1991) found that the resistance of organic matter to oxidation is related to the soil structure, changing between the classes of aggregates (i.e., > 4, 4-2, 2-0.2 and 0.2-0.05 mm) and depth (*sensu* A1 and A3 horizons). The quantities of organic matter, Fe, Al, P and humic substances also varied between classes of aggregates and were influenced by soil cultivation. The macro- and micro-aggregates differed in organic matter-Fe complexation, which was shown to be influenced by the kind of organic matter present (Mendoca *et al.*, 1991).

The calculated turnover rates for organic matter in the 'heavy' soil fraction (> 1.6 g cm^{-3}) from the 0-7.5, 7.5-15 and 60-80 cm depth zone of a krasnozem soil was 60, 75 and 276 years, respectively, while it was 75, 108 and 348 years for organic matter within micro-aggregates from the same horizons (Skjemstad *et al.*, 1990). Martin *et al.* (1990) found the turnover of organic carbon of coarse debris (> 250μm) was greater than the mineralization of the clay-associated fractions (< 20μm). Similarly, Elliot (1986), with reference to wet-sieved aggregates, suggested that C substrate availability to organisms increases with increasing aggregate size. Alternatively, Piccolo and Mbagwu (1990) observed a close relationship between aggregate stability and presence of high molecular humic substances (from pig slurry, cattle slurry and sewage slurry). Waters and Oades (1991) used scanning electron microscopy to confirm soil aggregates are not random assemblages of smaller particles, but that soil particles are stabilized in increasingly larger units by different organic binding agents.

Van Veen and Kuikman (1990) recently discussed the importance of spatial arrangement in soil on the availability of substrates to microorganisms. Upon cultivation the soil structure is disrupted and the aggregates are broken apart as a result of which a larger surface area is exposed to microbial attack (e.g., Waters and Oades, 1991). Disruption of soils results in an increase in mineralization of both carbon and nitrogen, and it apparently reduces the protection of part of the originally physically protected soil organic matter against microbial attack (Gregorich *et al.*, 1989).

5.3.5   Effects of texture

In many studies the content of organic matter in soil has been shown to be related to the textural composition. The general pattern appears to be that organic carbon is better protected from decomposition in fine textured (clayey) soils than in coarse-textured (sandy) soils (Kononova, 1966; Korteleven, 1963; Dabin, 1980; Schimel *et al.*, 1985 a, b; Spain *et al.*, 1983; Feller, 1991; many others), although clay mineralogy and soil structure are also of importance in this respect (Sections 5.3.3 and 5.3.4). The low physical protection of soil organic matter in sandy savanna soils from Côte d'Ivoire, for instance, has been attributed to the low (5-6 %) clay content of mainly kaolinite minerals (Martin *et al.*, 1990). Korteleven (1963) attributed the lower mineralization of soil organic matter in clay soils, as compared to sandy soils, to a physical protection of soil organic matter and microbial biomass.

The C and N contents are correlated with the size of the silt and clay fractions (r=0.92 and r=0.91, respectively) in virgin soils of the semi-arid pampas, Argentina. These correlations disappear upon a change in land use to agricultural management and pasture (Buschiazzo *et al.*, 1991). Bauer and Black (1981) reported more pronounced losses of both C and N in sandy soils than in medium to fine textured soils. Alternatively, over a 1-2 year period, soil texture had relatively little influence on the decay of organic matter in the soils studied by Ayanaba and Jenkinson (1990). A relative enrichment in organic carbon was observed only in the fine silt and clay fractions in the long-term experiment described by Houot *et al.* (1991). Incorporation of straw into soil often maintains a high carbon content in the coarse fraction (Christensen and Sorensen, 1985; Houot *et al.*, 1991).

Feller (1991) studied the relative variation of soil organic matter within different size fractions as influenced by three cropping systems (i.e., clearing-cultivation succession; cultivation-fallow/pasture succession; cultivation plus organic amendments). For coarse textured soils, the main variations (plus or minus) in relation to the different cropping systems concerned mainly the 'plant debris' (> 20 μm) followed by the 'organo-silt' (2-20 μm) fraction, but the 'organo-clay' (0-2 μm) fraction was little affected. For fine textured soils, the main variations (+ or -) concerned the 'plant debris' and the 'organo-clay' fractions. With respect to soil organic matter dynamics and biochemical processes the results of Feller (1991) indicate the major role of plant debris in sandy soils, and the importance of the 'organo-clay' compartment in clayey soils.

The 'protection' of organic matter by clay minerals has been considered in models. Verberne *et al.* (1990), for instance, divide the 'active' organic matter into a physically protected component (POM) and a non-protected component (NOM) as a function of the clay + silt content, using a higher degree of protection for fine textured soils. The labile fraction, which includes root exudates and products of the microbial activity, was allocated to the fine clay fraction and the latter to the coarse clay fraction. Anderson and Paul (1984), however, found both labile and stabilized organic matter in the clay fraction. Similarly, Bonde (1991) found active, slow and passive soil organic matter was present in all particle-size classes, but in varying proportions. Balesdent *et al.* (1988) observed the clay fraction included both the most stable C, and some labile C, whereas clay associated with fine silt had a turnover that suggested slow replacement of the whole fraction. These findings suggest that mechanical separation of particle-size classes and subsequent analysis of soil organic matter content may not be sufficient to estimate the active, slow and passive fractions. This may make it difficult to determine soil organic matter fractions, as needed for models, through physical separation alone (Bonde, 1991).

Feller *et al.* (1991) used the sonic vibration and sodic resins method to study the distribution of organic C in 19 tropical soils. The mean C/N quotient of the 0-2 μm, 2-20 μm and 20-2000 μm fraction were 10.5 ± 1.5, 16.5 ± 3.2 and 20.8 ± 4.4, respectively, decreasing from the coarse to the fine fractions. No significant differences in C/N quotient were found for the 0-0.2 and 0.2-2.0 μm fractions (clay). The C/N quotient of the 2-20 μm fraction is considered indicative for the presence of organic debris. In relative terms the 20-2000, 2-20 and 0-2 μm fractions represented 25, 26 and 47 % of the total C in the soils under consideration. Balesdent *et al.* (1991) found the organic C concentration in coarse clay was always higher than for the fine clay fraction; regressions of the quantities of organic C in the clay fractions *versus* the respective mass of these fractions yielded slopes of 32 ± 9 mg C g^{-1} coarse clay (0.2-2 μm) and 13 ± 5 mg C g^{-1} fine clay (< 0.2 μm). Similarly, Feller *et al.* (1991) observed that the organic C content of coarse clay fractions was significantly higher than the organic C content of the fine clay fraction. A possible explanation for the above phenomenon has not yet been proposed by the respective researchers.

Schnitzer *et al.* (1988) studied the organic matter associated with the fine clay fraction separated from the Ae horizon of a Typic Haplorthod. About half of the clay-associated organic matter consisted of humic materials; the other half was composed mainly of long chain aliphatics. The study indicated that long-chain aliphatics have low mobilities in soils and that it is fulvic acid that is capable of penetrating clay interlayers. Schnitzer *et al.* (1988) postulate that if aliphatics are present in clay interlayers, they have most likely been transported there by fulvic acids or other humic materials within which they are captured and that act as vehicles for the transport of hydrophobic materials within soil profiles.

Nelson *et al.* (1991) studied the relationship between soil properties and dissolved organic carbon (DOC) in Australian streams. The concentration of DOC in these streams was shown to depend on the clay content of the soils in the catchment area and the flow path of water through the soils. Some of the organic carbon transported by rivers will be deposited in alluvial or marine deposits or be degraded in the sea.

5.3.6   Effects of organisms

Ladd (1986) reviewed methods for following the turnover of organic matter in soils, and stressed the need for describing more precisely the key role of biota. The main role of organic carbon in soils is to function as an energy source, electron donor and to provide organisms with the carbon needed for growt. Beauchamp *et al.* (1989) reviewed the importance of carbon sources for microbes, with special reference to denitrifiers. Selected examples of how different organisms may affect the decomposition of organic matter in soil are presented below. Tinker and Ineson (1991) discuss possible effects of climate change upon the micro-organism species involved in the decomposition of organic matter.

Beck's (1989) measurement of microbial biomass and activity in a beech forest showed the role of saprophagous soil fauna in decomposing litter consisted in controlling the resource utilization by fungi. The soil fauna caused hyphal growth to utilize the litter as the primary food resource, whereas in the absence of soil fauna fungi consumed their own decaying hyphal mass. In the study under consideration the main role of soil fauna consisted in controlling the kind and speed of litter decomposition by interaction with the microflora, especially by controlling microfloral growth.

Interactions between different types of organisms are also possible. Bacterial feeding nematodes, for instance, affect the decomposition of organic matter in various ways (Freckman, 1988): a) by feeding on microbes and regulating the rate at which organic compounds are degraded into inorganic forms; b) by dispersing microbes throughout the soil and water; c) by feeding on saprophytic and plant pathogenic bacteria, and by influencing the composition of the microbial community; d) by serving as prey and a source of nutrient for fauna and microflora, such as soil nematophagous fungi; and e) by affecting the distribution and function of plant symbionts.

Absence of soil animals and restricted microbial decomposition in an acid soil was responsible for the formation of mor type humus (Hopkins *et al.*, 1990). In case of mull soils under beech forest, a greater number of species, greater faunal biomass (≈ 15 g dry mass m^{-2}), dominance of macrofauna and microfauna, and a greater trophic diversity with a preponderance of saprophagous animals has been reported (Schaeffer and Schauermann, 1990). Alternatively, moder soils under beech forests have a smaller number of species, smaller faunal biomass (≈ 5 g dry mass m^{-2}) and more mesofaunal microphytophagous animals. Mull forming fauna penetrate deeper into soil than moder forming soil fauna (Schaefer and Schauermann, 1990).

The rapid turnover of soil organic matter in especially the upper 10 cm of savanna soils from Côte d'Ivoire has been attributed to the intense activity of earthworms in this layer (Martin *et al.*, 1990). Differences exist between various earthworm species. *Lumbricus rubellus*, for instance, stimulated microbial respiration by 15 % in a coniferous forest soil whereas *Denrobaena octaedra*, stimulated it only slightly (Haimi and Hutha, 1990). Alternatively, termites play a major role in decomposing litter in savannas. In semi-arid bushland from Northern Kenya, they consumed 50 % of the grass litter and 4 % of the woody litter from the original plant litter substrates. The termites were estimated to consume about 298 g m^{-2} of litter per year, corresponding with about 61 % of the estimated annual net primary production (Bagine, 1989). Additionally, termites are an important source of methane (see Chapter 3).

Respiration by the fauna responsible for decomposition causes a net increase in CO_2 levels in the soil rhizosphere. As a result the concentration of CO_2 dissolved in soil solution may increase ($H_2O + CO_2 \to H^+ + HCO_3^-$). Upon reaching open-water surfaces, the CO_2 dissolved in aqueous solution will equilibrate with the atmospheric CO_2 levels; the surplus of CO_2 will be released to the atmosphere by degassing. Draining of waterlogged areas to improve timber production can lead to increased CO_2 emissions (Eriksson, 1991). Alternatively, in case of peat soils, drainage may also increase the oxidation rate releasing an additional amount of CO_2.

5.3.7   Effects of vegetation

Vegetation is the main source of organic matter input into soil. In forest ecosystems most of the fresh organic residues are in the litter layer, but under pasture they are predominantly in the dense root mats. Both the quantity, nature, and spatial distribution of these fresh organic residues may have an effect on organic matter in soil. Different results have been reported in different studies.

Different rates of decomposition were recorded for different components of vascular plants in a Georgian wetland (Moran *et al.*, 1989). Additionally, changes in rates of decomposition of each component changed over time, so that the specific rate of decay of each fraction decreased as decomposition proceeded. The kinetics of decomposition were best described by a decaying coefficient model which treats plant detritus as a single component but allows for a decreasing specific decomposition rate as material ages (Moran *et al.*, 1989). This model accommodates changes in quality of plant detritus which result from the preferential decomposition of more labile components (e.g., non-lignocellulose material and holocellulose) and the relative accumulation of more refractory components (e.g., lignin) observed with time. Bosatta and Agren (1991) also consider initial litter quality as a parameter in distinguishing different organic materials. Jenkinson *et al.* (1991) use different 'decomposable plant material' over 'resistant plant material' (DPM/RPM) ratios for forests (0.25), tropical woodland and savanna (0.43), deserts, tundra and cool temperature steppe (0.5), and for cultivated land and temperate thorn steppe (0.67) in the ROTHAMSTED model.

Hopkins *et al.* (1988) observed no significant effects of grass species on the turnover of organic matter in some grassland soils. Similarly, Krosshavn *et al.* (1990) found no correlation between the vegetational background and chemical structure of terrestrial humus. Changes in amounts and nature of photosynthates added to freely drained soils will not change the composition of the organic matter; the latter is controlled by the microbial biomass and interactions of the biomass and its decomposition products with the soil matrix (Oades *et al.*, 1988). Conversely, other studies show how the chemical composition of plant debris influences the rate of decomposition of organic matter in soil. Weakly acidic to neutral pH values for organic materials

stimulated soil respiration under spruce while a low pH value (< 2.1) inhibited it (Wilhelmi and Rothe, 1990). Besides the pH, the relative proportions of compounds such as cellulose, hemicellulose and lignin are important in that they determine the recalcitrance of organic material to breakdown (Alexander, 1977; Moran *et al.*, 1989). The degree of recalcitrance of certain of these components can be modified by the drainage conditions, the effect increasing with anaerobiosis (see Colberg, 1988).

In the modelling study of Pastor and Post (1986) patterns of soil organic matter are related to differences in initial organic matter levels and differences between successional species, especially in the amounts of woody litter produced (Aspen and Pin cherry). Decomposition of young *Calluna vulgaris* was shown to be slower than that of young grass material; in this case the plant species affected organic matter accumulation (Hopkins *et al.*, 1988). The rate of litter decomposition was inversely related to lignin content and the lignin/N ratio of litter in a study comprising a mixed terra firma forest, a tall Amazonian catinga and a low bana (campina) forest on podzolized sands (Cuevas and Medina, 1988). Alternatively, Cepeda-Pizarro and Whitford (1990) observed differences between decomposition of litter from the locally dominant species and Creosote bush leaf litter in some instances, but these differences could not be attributed to differences in lignin content nor C/N ratio.

The regeneration form of certain plants such as *Protea* has an influence on the 'root:shoot' ratio (Smith and Higgins, 1990), and thereby on soil organic matter evolution. *Eragrostis curvula* pastures were more effective in restoring the organic matter and N levels in sandy, but not in loamy soils (Haplic Phaeozems and Kastanozems) with respect to the original undisturbed semi-arid pampas. This could be due to a better efficiency of roots of *E. curvula,* as compared to the autochthonous grass species, to produce humifiable residues in coarse textured soils than in fine textured soils (Buschiazzo *et al.*, 1991). Skjemstad *et al.* (1990) observed that of two grasses, *Pennisetum clandestinum* gave more input of organic matter into the 7.5-15.0 cm layer of a krasnozem than *Paspalum dilatatum*. In the other layers considered, however, both grasses performed equally. Schiffman and Johnson (1989) reported old field plantations of *Pinus taeda* store more carbon than natural forests of *P. virginiana* by 42 Mg ha^{-1} ($\approx$ 22 %), with most of the gain being in the phytomass. Regeneration or succession may thus influence how the biomass is distributed and later degraded in soil. This points at the importance of considering sample site vegetation and cultivation history in studies of soil organic matter.

Growing roots are a significant source of readily accessible C for microbial biomass and render an additional fraction of soil organic carbon available to microbial utilization (Lynch, 1990). Consequently, growing plant roots often have a priming effect on the breakdown of soil organic matter (Helal and Sauerbeck, 1986; Lynch, 1990). Alternatively, in 'drier' climates plant roots may compete for moisture with the decomposing organisms.

Bazzaz and Williams (1991) studied changes in atmospheric CO_2 levels with height in a mixed deciduous forest in New England, USA, and found the CO_2 concentrations in the forest may be quite different from those in bulk air. Consequently, seedlings, saplings and mature trees may experience different CO_2 environments for which they may exhibit different responses in photosynthesis, growth and water use. Graham *et al.* (1990) discuss the potential effects of changed climate and elevated CO_2 on key ecological processes for each level of biotic organization (i.e., the biosphere, the biome, the ecosystem, and the tree). Patterson and Flint (1990) recently prepared a review of the possible effects of increasing atmospheric CO_2 levels and climate change for plant communities in natural and managed ecosystems. Increasing atmospheric CO_2 to twice ambient levels, the usual assumption in General Circulation Models (GCMs), will generally increase biomass production although the magnitude of growth simulation will vary greatly with species,

photosynthetic pathway (more for C_3 and less for C_4 plants), growth stage, and water and nutrient status. Weeds and other plants with broad ecological amplitudes are likely to prosper at the expense of endemic species or species already in marginal habitats. This will have repercussions for the incorporation of organic detritus in soils, the breakdown of organic matter and development of new steady-state conditions for soil organic carbon pools as the process of global climate change evolves. The study of Aerts *et al.* (1988), for instance, showed *Erica tetralix* will probably be replaced by *Molinia caerula* in a wet heathland when available nutrient levels increase as a result of atmospheric deposition of e.g. Nitrogen, which in turn will lead to an increased flow of carbon and nutrients into the soil system. Alternatively, Wookey and Ineson (1991) showed that realistic concentrations of 'dry deposited' SO_2, a well known atmospheric pollutant, can induce marked chemical and biological changes in forest litter. Some organic carbon may also be deposited with polluted rainfall, especially in forest areas (Bartels, 1990). This again shows the need for long-term impact studies of the formation of soil organic matter and organic carbon and nutrient cycling, particularly in forest ecosystems prone to atmospheric pollution.

5.3.8   Effects of land use changes or succession

Introduction

Over long periods of time carbon storage in soils can vary as a result of climatic-, geologic- and soil- changes, while over short time periods vegetation disturbances or succession, and land use conversion mainly affect storage (Zinke *et al.*, 1986). Upon cultivation, soil carbon contents may decline because of a variety of processes, including the removal of topsoil by mechanical clearing, disruption of aggregates and increased oxidation of organic matter or increased accessibility of organic matter to decomposing organisms. According to Buringh (1984), the estimated average loss of soil carbon after conversion of forest to cropland is 48 per cent, of forest to grassland 28 per cent, and of forest to mixed cropland and grassland 35 % over a 1 m depth interval. Other values have been proposed by different researchers in view of the occurring uncertainties (see Bouwman, 1990a). From the magnitude of the above changes it is apparent that changes from forest to agricultural use especially will have a marked effect on soil C pool size and thereby CO_2 evolution to the atmosphere.

There is an abundant literature quantifying C-losses associated to cultivation (Mann, 1986; Bouwman, 1990a). Of necessity, these reviews are based on data from earlier studies. Few of these investigations consider the kind of sampling density and intensity required to reveal significant changes in soil organic-C upon a change in land use practices. Nor are they necessarily based on similar analytical procedures for assessing soil carbon contents. Several methodological aspects of relevance to the quantification of global carbon pools and possible changes therein are discussed in Section 5.5.4. In this part of the report selected examples of how changes in land use or succession may influence soil organic matter pools are discussed.

Time to achieve steady state conditions

In any undisturbed soil, the organic matter content will stabilize at an equilibrium level characteristic of the 'permanent' soil characteristics and land use or vegetation cover. When soils are first placed under cultivation the organic matter content usually declines. Thereafter, a prolonged period of constant management is required to reach a new equilibrium. In the long-term Deherain field experiment, for instance, which started in 1875 with a wheat-sugar beat rotation to compare the effects of organic amendments and mineral

fertilizers, soil organic matter has presently reached equilibrium and the various pools are constant (Houot *et al.*, 1991). It takes at least 10-30 years before a new organic carbon equilibrium is reached in soil (Buringh, 1984). Brown and Lugo (1990) found that the time for recovery of soil C and N during succession was similar in the three subtropical life zones under consideration, being about 40-50 yr for C and 15-20 yr for N, respectively. They observed that the rate of recovery of soil C was more rapid in the wet and moist life zone, whereas N seemingly recovered faster in the dry life zone (Brown and Lugo, 1990). About 30 yr was needed for soil organic matter to be stabilized in the tidal marsh environment studied by Hsieh and Weber (1984). The dynamics of soil organic matter evolution and turnover in soil can be studied using a range of mathematical models (see Section 5.2.3).

Conversion of forest to arable land or pasture

Forests contain from 20 to 100 times more organic C per unit area than agricultural land so that conversion of forest to cropland or pasture generally reduces the amount of organic carbon on land (Houghton, 1990). Detwiler (1986) reports that cultivation reduced the carbon content by 40 % 5 years after clearing whereas the use of the same tropical soils for pasture reduced it by about 20 per cent. Generally, the carbon content of soils used by shifting cultivators returns to the level found under primary forest about 35 years after abandonment (Detwiler, 1986). With increasing population density, however, the length of the 'restoration cycle' rapidly drops below this recommended level. On an all India basis, for example, the total area affected by shifting cultivation has increased by about 81 % (from 2,710 to 4,912 million ha) during the period 1956 to 1984/85. During the same time period the annual area under shifting cultivation increased from about 0.542 to 1.000 million ha ($\approx$ 84 %), reflecting the severity of the problem. Kaul (1991) estimated that over 151 million tons of forest biomass (dry weight) was burnt annually in India during the period 1985-1987, the major contribution being from tree biomass (88 %), burning of litter (8 %) and grasses (3.5 %). This corresponds with some 68 Tg of carbon evolved as CO_2.

Sanchez *et al.* (1983) studied the changes in soil properties during the first 8 years after clearing of a 17 yr old secondary forest (slashed, burned, then crops for 8 yr $\pm$ fertilization) in Peru. The rate of organic carbon decomposition averaged 25 % during the first year and then levelled off; no significant differences due to fertility treatment were detected during the study period.

Choné *et al.* (1991) studied the effects of burning and deforestation on soil organic matter in the topsoil of two managed Oxisols in Manau (< 2 mm fraction; treatments: natural forest, before and after slash and burning, and under pasture established for 1, 2 and 8 years). Under natural forest, the organic carbon content reached maximal values of 28 t ha^{-1} in the 0-3 cm layer, 62 t ha^{-1} in the 3-20 cm layer, and decreased rapidly with depth. Burning removed about 4 t ha^{-1} of organic carbon, chiefly from the 0-3 cm soil layer, but this loss was recovered after one year of pasture (Choné *et al.*, 1991). Decreases of about 8 t ha^{-1} after 1 year and 28 t ha^{-1} after 2 years were observed in the 3-20 cm layers, probably because the humification of grass root residues did not balance the decomposition of pre-existing soil organic matter from natural forest. After 8 years of pasture, however, the initial organic carbon content of surface soil had been almost entirely restored, including the 3-20 cm layer. The introduction of graminaceous vegetation in succession to forest may stimulate microorganisms during the initial years as a result of which they also decompose residues and even humified material from the original forest (Choné *et al.*, 1991). Clear-felling of tropical rainforest soils and subsequent cropping with pastures caused an initial decrease in microbial biomass, followed by an increase in 1-2 yr old pastures and a subsequent decrease in 8-yr old pastures (Bonde, 1991).

Brown and Lugo (1990), in a study encompassing mature and secondary forests and agricultural sites in three subtropical life zones of the US Virgin Islands and Puerto Rico, observed that conversion of forests to pasture resulted in less soil C and N loss than conversion to crops. Choné et al. (1991) observed that the entry of new organic C derived from pasture (upon clearing of natural forest) proceeded mainly from the soil surface, suggesting that the contribution of aerial parts of pasture was higher than that of root deposits during the initial period. After 8 yr of pasture, however, there was a great contribution of carbon from both the aerial parts and root deposits of the pasture, and soil carbon content was then again close to that observed under natural forest.

Conversion of grassland and cropland to forest

Martin et al. (1990) studied the medium term dynamics of organic matter in sandy savanna soils from Latimo, Côte D'Ivoire, looking at the change in the $^{13}C/^{12}C$ ratio induced by vegetation changes from C_4 to C_3 photosynthetic plants. After 25 years of protection from fire, a soil previously covered by C_4 grassland vegetation had been progressively colonized by C_3 woody plants. Although the total C content did not differ markedly, 52-70 % of the original C_4 carbon was turned over when the vegetation cover was changed.

Schiffman and Johnson (1991) found that natural reforestation of old agricultural fields over a 50-70 yr period increased carbon storage from about 55,000 to 185,000 kg ha^{-1} ($\approx$ + 235 %). Carbon in the phytomass accounted for 76 % of the increase, the forest floor for 13 per cent, and surface soil for 10 per cent. The contemporary practice of converting natural *P. virginiana* forest to *P. taeda* plantations, however, yielded only a small gain in carbon, most of which is stored in phytomass scheduled for harvesting and not in detritus.

Conversion of natural grassland soils to crop land

The review of Schlesinger (1986) indicates that the loss of carbon from soil profiles on cultivation is about 30 % over a 20-50 yr period. Tiessen et al. (1982) studied the losses of C, N and P when three prairie soils of different texture were cultivated. In this study, the concentrations of organic carbon were reduced to about 35 % in clay and silt soils after 60 to 70 years of cultivation. Reductions in N concentrations ranged from 18 to 34 % and were influenced by the presence or absence of leguminous crops. Phosphorus losses were reduced by 12 per cent, all of which were accounted for by losses from the organic fraction. During a similar period of cultivation a lighter sandy soil had greater losses of C, N and P of 46, 46 and 29 per cent, respectively, with P losses occurring both in the organic and inorganic fractions. The average soil organic matter content under Dutch grasslands was shown to be 2 to 5 times higher than that of 'cropland' and to increase with clay and silt content (Korteleven, 1963).

Annual tillage in an experiment changed the dominant plant species from grasses to annual herbs as a result of which carbon storage in the surface 15 cm of soil was reduced by 24 % (679 g C m^{-2}), 76 % of which was due to a reduction in root biomass (Richter et al., 1990). Relatively small changes were found in mineral soil organic C from annual tillage, i.e., about 1 mg C g^{-1} soil (Richter et al., 1990). Bauer and Black (1981) found that average organic C and total N contents were significantly higher under wheat stubble mulch than conventional tillage management.

Under irrigation the pool size of organic carbon in soils of arid regions will tend to increase. The potential for changes in the storage of inorganic carbon in soil carbonates when arid lands are irrigated has been discussed by Schlesinger (1986 p. 206). Generally, irrigation will result in dissolution of a part of the carbonates present. Nettleton *et al.* (1990) provide a full discussion of the occurrence of calcium carbonate in soils.

Effects of cultivation upon the distribution of organic matter in arable land

In a long-term experiment, addition of lower organic inputs (roots, crop residues, farmyard manure) caused the total soil organic carbon to decrease, and this mostly associated with the silt and clay fractions (Houot *et al.*, 1991). In the long-term study of Hang *et al.* (1988) cultivation caused a relative shift of organic matter from the sand and the silt fractions towards the fine clay fractions in Iowa soils with similar climate, parent material, time and slope. Two years of growing *Digitaria decumbens* in a Vertisol from Martinique markedly increased the C and N contents; fractionation of the organic matter indicated that this increase occurred mainly in the >50 μm fraction (plant residues) and < 5 μm fraction (organo-mineral) (Chotte, 1988). Similarly, Feller (1988) observed the fractions most affected by different cropping systems (grassland, fallow and crop rotation) on selected Vertisols and Ferallitic soils mainly were the 5-200 μm (plant residues) and organo-mineral (< 5 μm) fractions.

The effects of land use on soil carbon content generally become negligible somewhere between a depth of 10-60 cm, the wide range being attributed to differences in life zones, soil type and land use (Detwiler, 1986). Other studies have presented evidence for loss of soil carbon during cultivation up to a soil depth of 50 to 100 cm (Brown and Lugo, 1990). Mann (1985) reported an average 40 % difference in carbon concentration (0-15 cm) between all cultivated and uncultivated loess derived Alfisols and Mollisols in a study of the changes in soil carbon following cultivation. The carbon content of the total profile data was 28 % lower in cultivated as compared to the uncultivated Udalfs studied, and 11 % greater in cultivated *versus* uncultivated Udolls (only one soil series). After 60 years of cultivation, total soil organic C, N, and P had declined by 55-63 % in the surface 15 cm in the study of Bowman *et al.* (1990), with about half of this loss occurring in the first 3 years of cultivation. In comparison the labile fractions of the organic C and N declined by 67-75 % after 60 years, but over 80 % of the labile C loss and more than 60 % of the labile N loss occurred during the first 3 years of cultivation. Half of the total P decline came from the organic pool, representing about a 60 % decrease in the organic P levels in the first 3 years.

The organic matter content in soil can also increase under cultivation, provided large amounts of organic material of good quality are added. An extreme example are the Anthropogenic soils which have received large amounts of farm-refuse over a prolonged period of time. As an example, the 'Terra Preto do Indios' in Brazil may be cited (Sombroek, 1966). Similarly, soils of the Rothamsted Classical experiments, which have received 35 t ha^{-1} farm yard manure (FYM) each year since their start in the 1840s and 1850s, now have about 3.5 % C compared to 1 % C initially (Johnston, 1991). Between, 1942-1967 annual applications of 37.5 t ha^{-1} of FYM to the sand loam at Woburn increased organic carbon from 0.87 to 1.64 % C; doubling the FYM input gave an increase to 2.26 % C. The soil humus content began to decline rapidly when the FYM treatment was no longer applied; in the first 5 years, soils which had received the single and double FYM lost 0.17 and 0.41 % C, respectively (Johnston, 1991).

Effects of forest harvesting

Activity of logging machinery in the study of Johnson *et al.* (1991) resulted in the redistribution of organic matter within the solum; the thickness of the O horizon decreased while the O horizon mass and organic matter content increased (from 8.7-12.2 kg m^{-2} and from 5.4-5.7 kg m^{-2}, respectively). One fourth of the post-harvest soils exhibited an Ap horizon which was not present prior to harvesting, and was made up of material from the O, E and Bh horizons. Compaction during logging resulted in a 5-15 % increased bulk density in the upper 20 cm of the mineral soil (This means that use of uniform soil sampling intervals for studying changes in soil C may not be truly indicative of carbon changes in cases where the bulk density has changed). The total pool of organic C in the solum did not change following harvesting. Losses of organic matter via streamwater and respiration were approximately balanced by inputs from decaying roots and leaf litter (Johnson *et al.*, 1991).

Huntington and Ryan (1990) quantitatively assessed the C and N pools before and after whole-tree harvesting (0 resp. 3 yr after) in a 65 yr old second growth northern broadleaf forest at Hubbard Brook. The aim of the study was to assess whether cutting would reduce or redistribute the C and N pools within soil compartments. Logging operations resulted in immediate disturbance which displaced or buried the original forest floor over 24 % of the watershed. Mechanical disturbance contributed to an increase in variability of soil N and C pool-size estimates, and made it more difficult to distinguish forest-floor/mineral soil boundary in the field.

Five main processes essentially explain changes in organic matter pools, bulk density and horizonation following whole tree harvesting (Johnson *et al.*, 1991):
   a)   leaching loss of organic matter from the solum to streams;
   b)   respiration;
   c)   decay of root biomass;
   d)   physical disturbance and mixing induced by logging machinery; and
   e)   accelerated decomposition and translocation of organic matter from the O horizon to the upper mineral soil.

Effects of fire/burning

Inherently, the intensity of fire will be related to the nature and amount of biomass burned as well as moisture and wind conditions. Zinke *et al.* (1978) observed that during a fire temperature may surpass 600 ºC at 1-2 cm above the soil, whereas at a depth of 3 cm soil temperature did not surpass 70 ºC except under concentrated piles of fuel (cited in Detwiler, 1986). Ghuman and Lal (1989) measured soil temperature at several depths following biomass burning in windrows following clearing of a primary rainforest in southern Nigeria. During burning the maximum soil temperatures rose to 218, 150, 104 and 70 ºC at 1, 5, 10, and 20 cm depths, respectively.

No general tendencies can be identified for fire-induced changes in the content and composition of organic matter in soil. The processes for the incorporation and denaturalization of the humic fraction greatly depend on the soil geochemistry, as well as on such external factors as the type of vegetation and morphology of the soil epipedon (Almendos *et al.*, 1990). Burning clearly affected the content of organic carbon in the 0-3 cm layer in the study of Choné *et al.* (1991). Hernani *et al.* (1987a), however, observed the total organic C content above and below a depth of 4 cm did not decrease significantly as a result of burning. Similarly, Greene *et al.* (1990) found no significant effect of fire 'treatments' on the total organic carbon content of the

0-1 cm layer in a semi-arid eucalypt woodland. The fire reduced the percentage of water-stable aggregates (> 2 mm), but increased the percentage of aggregates (< 0.25 mm) in the 0-1 cm layer relative to the unburnt control (Greene *et al.*, 1990). As was indicated earlier, part of the biomass consumed by fire may remain in soil as recalcitrant charcoal (Skjemstad *et al.*, 1990). Slow burning of standing trees is also a possible mechanism for producing 'wood-ash stone', composed mainly of calcite, in nutrient poor acidic soil parent materials (Humphrey *et al.*, 1987).

Jones *et al.* (1990) studied how soil organic matter and biological factors respond to burning regime. Surface soils (0-15 cm) were sampled from plots burned annually, biennially and triennially in winter, as well as in plots protected from fire for 34 years. The organic C content was 25 % higher in the protected plot than in the burned plots, where there was a gradual decrease in carbon with increasing fire frequency. Total N followed the same trend, as did the N mineralization potential. Nitrogen mineralization showed a much greater sensitivity than total N to burning frequency. Burning may severely reduce the amount of microbial biomass present in the surface layer (Cerri *et al.*, 1985). Jones *et al.* (1990), for instance, observed microbial biomass was double on their unburned plot relative to the burned plots (0.008 % as compared to 0.004 %). Santos and Grisi (1979) observed that while the microbial activity under undisturbed tropical rain forest decreased with soil depth, it increased with soil depth in burned areas, reflecting the possible effect of burning on soil fertility and soil dynamics.

Burning of vegetation often has a short-term positive effect on soil biological processes. It can cause the release of nutrients by direct oxidation during the fire, and often leads to an increase in temperature due to removal of shading and blackening of the surface. Burning also may cause an increase in surface pH through the formation of oxides of bases and an increase in moisture content of the surface soil because of cessation of transpiration, so that microbial activity increases (Post, 1990).

The flaming stage of biomass burning produces higher oxidized products, while methane is mainly formed during smouldering combustion (Lobert *et al.*, 1990; Kuhlbusch *et al.*, 1990). The CO/CO_2 emission ratio is as a good indicator for the extent of smouldering combustion. Post (1990 p. 20) expressed the ratio of CH_4/CO_2 emission resulting from biomass burning as a function of the temperature index CO_2/CO with $Y = a.X^b$. In this expression Y is the CH_4/CO_2 ratio, X the molar CO_2/CO ratio with $a = 0.1187$ and $b = -1.17$ fitted by the least squares technique.

Effects of fire and/or drainage in peatlands

In case of peatlands, the intensity of fire and the amount of organic matter that is oxidized depend not only on current weather but also on the antecedent weather and its effect on the water table (Post, 1990). Large reserves of carbon exist in soils and peats of the boreal and tundra ecosystems which are estimated to contain 350 Pg C (Post *et al.*, 1985). Estimates of peat stored in bogs range from 180 Pg to 280 Pg C (Gorham, 1988). These ecosystems are thought to be small net sinks of atmospheric carbon ($\approx$ 0.1-0.3 Pg C yr^{-1}) since the last glacial retreat (Miller, 1981; Gorham, 1988), reflecting the imbalance of organic matter production over decomposition. Alternatively, Kling *et al.* (1991) observe that the above estimates of the carbon balance are only for the 'terrestrial' part of the ecosystems. Their measurements of the partial CO_2 pressure (pCO_2) in 20 aquatic ecosystems across arctic Alaska, in most cases, showed that CO_2 was released to the atmosphere. This CO_2 probably originated in terrestrial environments; erosion of particulate carbon plus ground water transport of dissolved carbon from tundra soils contribute to the CO_2 flux from surface water

to the atmosphere. If this system is representative for that of other tundra areas, Kling *et al.* (1991) believe current estimates of the arctic terrestrial sink for atmospheric CO_2 may be 20 % too high.

DeLaune *et al.* (1990) modelled the processes governing marsh formation. Due to natural accretion, Histosols may absorb about 0.2 Pg C yr^{-1} (Buringh, 1984). This value was obtained by assuming an average accretion of 0.5 to 1 mm yr^{-1}, an average bulk density of 0.25 g cm^{-3} and an average carbon content of 50 per cent, in conjunction with the extent of Histosols delineated on the FAO/Unesco soil map. This type of estimate could be refined on a geo-referenced basis using the future WISE data base.

The net release of CO_2 from wetlands upon drainage amounts to 0.15-0.18 Pg C yr^{-1} according to Armentao and Menges (1986). According to Schlesinger (1986) drainage and cultivation may release 0.03 Pg C yr^{-1} from organic soils of the world, transforming peatlands areas from a sink to a source of atmospheric CO_2. Additional releases of about 1.6 to 3.1 Pg C yr^{-1} of CO_2 and somewhat greater than 0.22 Pg C yr^{-1} of CH_4 to the atmosphere may occur as a result of the climate change scenarios modelled by Post (1990). These figures reflect the potential significance of climate change impacts, particularly from the boreal and tundra regions (Post, 1990; Malmer, 1992).

Carbon losses associated with erosion

The importance of organic matter in protecting soils from water and wind erosion is well known. Organic matter essentially affects the soil's susceptibility towards 'on site' erosion, as opposed to 'off-site erosion', through its effects on surface aggregate stability, surface sealing and crusting, and soil porosity (see Gabriels and Michiels, 1991). As water erosion sorts soil particles by size and weight, the smallest and lightest particles are moved furthest. Since these are the 'active' fractions from a biological point of view, it is likely that superficial organic materials in depositional areas are easily decomposable (Voroney *et al.*, 1981; Tiessen and Stewart, 1983; Anderson *et al.*, 1981).

Voroney *et al.* (1981) modelled soil organic C dynamics and found that organic C levels decreased rapidly when water erosion was included as an output of the model. Similarly, Tiessen *et al.* (1982) reported that organic matter levels in untilled grasslands continued to decline after 90 years because of erosion. Erosion caused an extra loss of organic C of at least 7 per cent after a 100 year cultivation period in the simulation study of Bouwman (1990c). Erosion runoff experiments in Ontario have shown that 20 yr of continuous maize production has caused soil organic matter content to decrease by up to 20 per cent (Voroney, 1988).

Selected studies of organic C losses associated with erosion illustrate the possible magnitude of the problem. In Western Nigeria, C losses from bare-fallow Alfisol plots with slopes of 1, 5, and 10 % varied from 54 to 3080 kg ha^{-1} (Lal as cited by Gabriels and Michiels, 1991). Hernani *et al.* (1987b) studied C losses from Yellow Latosol (Ultic Haplorthox) plots with a 14 % slope. The annual losses of organic matter varied with management practices, amounting to 497, 32, 7.2 kg ha^{-1} for 'total clearing by bulldozer', 'total burning', 'all forest material left on site (mounding)' as compared to only 0.9 kg ha^{-1} for the intact forest plots. Using rainfall simulators, Lowrance and Williams (1988) found that continuous fallow plots had significantly higher C concentrations in runoff and higher sediment concentrations. The highest C content measured in runoff was 5.83 % from a four-row peanut plot. Total loads of C and sediment and total runoff were about twice as high as for their bare bedded plots. About 1 % of the total soil C, from the 0-29 cm zone, could be moved annually from the continuous fallow plots in the experiment of Lowrance and Williams (1988). The total amount of C transported depended on surface runoff, and the C content of the eroded sediments was

related to the crop residue cover (Lowrance and Williams, 1988). Bouwman (1990a) calculated a possible C loss of 0.15 to 0.30 ton C ha^{-1} by assuming a total soil loss in the range 5-10 t ha^{-1} and average soil organic carbon content of 3 % in the eroded materials.

Assessing changes in soil organic matter following succession with the $D^{13}C$ technique[2]

Plants differ in their capability to take up atmospheric CO_2 during the process of photosynthesis (Smith and Epstein, 1971; Bazzaz and Fajer, 1991). Plants with a Calvin cycle (abbreviated as C_3 plants) are more discriminative against the natural radioisotope ^{13}C than those with a Hatch-Slack cycle (C_4). This means that changes in climax vegetation from either C_4 to C_3 plants or from C_3 to C_4 plants provide a natural labelling of organic matter. Many researchers have used radioisotopic labelling to study the dynamics of organic matter incorporation into soil, both in time and with depth. For instance, where forest is cleared to grassland (i.e., C_3 to C_4 vegetation; Cerri *et al.*, 1985; Balesdent *et al.*, 1977; Bonde, 1991; Choné *et al.*, 1991; Skjemstad *et al.*, 1990) or where a climax grassland vegetation is reafforested (i.e., C_4 to C_3; Balesdent *et al.*, 1988; Martin *et al.*, 1990). Mean $D^{13}C$ values of C_3 plants are in the order of -26 to -27 $^o/_{oo}$ while this is about -12 $^o/_{oo}$ for C_4 plants (Balesdent *et al.*, 1988; Choné *et al.*, 1991). Martin *et al.* (1990) reported mean $D^{13}C$ values of -12.9 to -15.8 $^o/_{oo}$ for savanna soils and of -27.5 to -23.5 $^o/_{oo}$ for forest soils. Lobo *et al.* (1988) consider $D^{13}C$ values of -33.1 and -26.7 $^o/_{oo}$ as being representative of organic matter derived from a forest vegetation.

$D^{13}C$ values of 'under-canopy' leaves in a tropical rain forest were always more negative than those from the 'upper-canopy' (i.e., -32.9 to -36.0 *versus* -28.8 to -32.6 $^o/_{oo}$, respectively), and this difference varied with the tree species. Leaves, stems and roots of the same plants show small differences in $D^{13}C$ values (Medina *et al.*, 1986). In adult trees maximum differences in $D^{13}C$ between upper-canopy leaves and bark from the main trunk at 1.5 m height ranged from 0.7 $^o/_{oo}$ in *Micrandra sprucei* to 3.1 $^o/_{oo}$ in *Eperuara purpurea*. Such differences will be reflected in the $D^{13}C$ of litter that falls on the ground. The ^{13}C isotopic composition of organic matter in soil is not constant with depth. In the litter layer of well drained acid soils Volkoff and Cerri (1988) observed a slight enrichment in ^{13}C. Two scenarios are however possible for the deeper layers depending on whether the soil is under forest or savanna. In the case of forest there is a progressive enrichment in ^{13}C with depth (Volkoff *et al.*, 1978; Bonde *et al.*, 1991), whereas under savanna the opposite pattern is observed (Volkoff and Cerri, 1987). Bonde *et al.* (1991) found $D^{13}C$ values in the forest soils under consideration ranged from less than -28 $^o/_{oo}$ in the topsoil to about -26 $^o/_{oo}$ in the deepest layers. Similarly, Bertram (1985) reports a linear enrichment of ^{13}C of about 2 $^o/_{oo}$ from the soil surface down to the bottom of the aerated layer of undisturbed forest soils from Scandinavia and Germany. This effect has been attributed to carbon isotope fractionation during the microbial degradation of soil organic matter. Microbes would preferentially 'consume' the isotopically lighter material, because it is energetically easier to 'decompose' its bondings, so that the residual organic matter becomes enriched in ^{13}C (Bertram, 1985). The decrease in $D^{13}C$ values from fresh under-canopy litter to decomposing litter and soil organic matter may also be related to changes in the chemical composition during the decomposition process (Medina *et al.*, 1986). Natelhoffer and Fry (1988) found no evidence for selective preservation of ^{13}C depleted litter components, such as lignin, during long-term decomposition of organic matter in surface soils of oak forests (*Quercus* spp.).

Atmospheric CO_2 levels vary with height within a forest which may affect photosynthesis (Bazzaz and Fajer, 1991). Medina *et al.* (1986) report lower $D^{13}C$ values of the shade flora under a tropical rain forest may primarily result from the assimilation of CO_2 depleted in $D^{13}C$ which originates from soil respiration; the

---

[2] $D^{13}C$ (in %o) = 1000 %o x [($^{13}C/^{12}C)_{sample}$ - ($^{13}C/^{12}C)_{PDB}$)] / ($^{13}C/^{12}C)_{PDB}$; with PDB the standard.

study of Medina *et al.* (1986) did not specify whether the shade flora was of the C_3 or C_4 type. The $D^{13}C$ of soil CO_2 also varies as a function of soil depth due to differences in the $D^{13}C$ of the organic substrate undergoing decomposition and the mixing with CO_2 from the overlying atmosphere (Amundson and Davidson, 1990).

Choné *et al.* (1991) studied changes in the $^{13}C/^{12}C$ ratio of soil organic matter to determine the respective contribution of the organic carbon originating from forest (Cf) and from pasture (Cp). One year after clearing the forest, the proportion of forest derived C was already 5 % in the whole 0-20 cm layer. After 2 years it was 20 per cent, whereas about 40 % of the C originating from forest had disappeared. After a period of 8 years, the proportion of Cp was close to 40 per cent. No further decrease of Cf was observed between 2 and 8 yr of permanent pasture. Following forest clearing and 1 year of pasture, the variation in $D^{13}C$ did not exceed 1 $^o/_{oo}$. Subsequently, the $D^{13}C$ value of the 0-3 cm layer increased from -23 $^o/_{oo}$ after 2 years of pasture to -17.5 $^o/_{oo}$ after 8 yr of pasture. The $D^{13}C$ values in the 0-10 cm layer were -26 and -24 $^o/_{oo}$ after 2 and 8 yr pasture, respectively (Choné *et al.*, 1991).

A difficulty in applying the $D^{13}C$ technique in soil comparative studies of organic matter dynamics in a particular soil (series) is to ensure that the 'disturbed' soils were similar to the reference soils at time zero (in terms of original soil carbon content between different sites under forest) (Choné *et al.*, 1991).

Discussion

One of the conclusions that may be derived from the above review is that the amount of carbon stored in a soil at a certain moment in time, for instance as corresponding with the time of sampling in routine soil surveys, need not be in equilibrium depending on whether the site was under climax vegetation or recently disturbed by management practices. In cases where commonly accepted standards have been followed (FAO/ISRIC, 1990) little or no information will be recorded about the 'recent past' land use. This may be seen as a possible source of uncertainty when such data sets are used in a soil data base (e.g., WISE) to assess the size of current soil carbon pools, and the anticipated changes therein upon specified changes in land use (e.g., natural forest to crop land). Additional remarks as to possible sources of uncertainty associated with the use of routinely collected soil carbon data are made in Section 5.5.4.

5.4   CO$_2$ emissions from selected terrestrial ecosystems

5.4.1   Introduction

Two main forms of biotic processes influence the evolution of carbon dioxide from soil: CO_2 release through 'soil respiration' (Section 5.4.2) and CO_2 releases essentially associated with large scale deforestation (Section 5.4.3). The physical, chemical and biological processes regulating the production of CO_2 in, and evolution of CO_2 from terrestrial ecosystems are highly variable in space and time. The importance of macroclimate on soil microbial biomass and basal respiration (CO_2-evolution) has been discussed by Insam (1990). In a diffusion dominated soil, the partial pressure or concentration of CO_2 in the soil atmosphere varies as a function of soil depth and is dependent on the microbial production rate and gas diffusivity (Amundson and Davidson, 1990). Mean rates of soil respiration in different types of vegetation range from $60 \pm 6 \text{ g C m}^{-2} \text{ yr}^{-1}$ for tundras up to $1260 \text{ g C m}^{-2} \text{ yr}^{-1}$ for tropical moist forests (Raich and Schlesinger, 1992). Inorganic reactions involving CO_2 will influence the CO_2 concentration in soil and natural waters. Such processes include the natural precipitation of CO_2 in soils as carbonates, CO_2 release by irrigation with

alkaline and CO_2-rich water, the removal of $CaCO_3$ by dissolution and accumulation of HCO_3^- as a result of irrigation, and the release of CO_2 by upwelling of CO_2 rich waters (Bohn, 1990; Nettleton *et al.*, 1991). Consequently, CO_2 concentrations within the soil and just above the soil-plant surface vary widely both between and within different ecosystems. Worldwide, soil CO_2 concentrations vary from 0.04 to 13.0 % by volume in the upper several metres of freely drained soil (Amundson and Davidson, 1990). In poorly drained soils higher CO_2 levels may be anticipated as diffusion will be limited.

5.4.2 CO_2 evolution associated with 'soil respiration'

Definition

Carbon dioxide (naturally) evolved from intact soil or 'soil respiration' consists of CO_2 derived from microbial respiration, faunal respiration, autotrophic root respiration, and in some cases abiotic oxidation of organic matter. The contribution of soil fauna to the CO_2 flux generally is much less than that of the microbial population, often accounting for only a few percent of the total carbon mineralized. Holt (1987), for instance, estimated C respired from a population of termite mounds (101 kg ha^{-1} yr^{-1}) amounted to some 3 % of the total C respired (3400 kg ha^{-1} yr^{-1}). On average from 30 to 70 % of the CO_2 evolved by soil respiration may be due to root respiration (Schlesinger, 1977), but the contribution of root respiration is difficult to measure in the field (Smucker and Safir, 1986). Holt *et al.* (1990) determined that, in an Australian tropical semi-arid woodland, root respiration accounted for about 39 % of the CO_2 released by soil respiration (1500 *versus* 3800 kg C ha^{-1} yr^{-1}). In this tropical area soil moisture was found to have a major effect on soil respiration, while temperature was of lesser importance. Most respiratory activity in the soil was confined to the relatively short wet season, with respiration rates being much lower during the dry season. Whether soil respiration rates during the day surpass those during the night depends upon the interactive effects of temperature and water on soil biological activity (Grahammer *et al.*, 1991) and possibly root respiration through photosynthesis. This example already indicates 'soil respiration' related CO_2 evolution rates from any particular soil will be highly variable both in space and time. A possible additional source of variability in measured CO_2 fluxes resides in the method of determination adopted.

Measurement methods

Mosier (1990) reviewed the techniques available for measuring trace gas fluxes from soil. Soil respiration is often determined by recording the efflux of CO_2 from the soil surface; on an annual basis this efflux will be about equal to the soil respiration rate provided significant losses of inorganic C, for instance through leaching or deposition, do not occur (Raich and Schlesinger, 1992). Commonly applied methods for measuring soil respiration include the use of CO_2 absorbents such as NaOH, and direct measurements such as infrared gas analysis and gas chromatography. For additional information on these techniques reference is made, amongst others, to Raich *et al.* (1989), Shelton and Parkin (1989), Sparling and West (1990), Sakamoito and Yoshida (1988), Rochette *et al.* (1991), Freijer and Bouten (1991), Gardini *et al.* (1991).

Raich *et al.* (1990) compared the 'soda-lime' method for measuring CO_2 evolution in forest soils with a static chamber technique using gas chromatography analysis of CO_2-concentration changes during short-term incubations. The CO_2 efflux rates were variable within sites and showed no spatial autocorrelation. Neither were there any consistent differences between the two methods, indicating that either one of the two methods may be used over the range of mean daily CO_2 efflux rates encountered (1.7-11.4 g m^{-2} d^{-1}). The 'soda-lime'

technique cannot give any information on diel variations in CO_2 effluxes. The short-term incubation technique, however, can be used to simultaneously monitor several trace gases and to assess diel trends in flux rates (Raich *et al.*, 1991).

Sakamoto and Yoshida (1988) measured *in situ* soil respiration rates by a dynamic method in which CO_2 was directly measured by an infrared gas analyzer. They observed the rate of soil respiration increased with increasing air flow-rate. The CO_2 diffusion rate, however, was approximately constant regardless of the air flow-rate and was almost equal to that under natural conditions (without a chamber). Based on these findings Sakamoto and Yoshida suggest that the process of mass flow by air flow contributed to soil respiration. In a comparison with soil respiration measured with a static technique (use of alkali NaOH solution to entrap CO_2), the soil respiration rate as measured by the static method was 58 per cent of that determined by the dynamic method at an air flow of $1\,l\,min^{-1}$. The observed difference in values between the static and dynamic method may be due to the decrease in the rate of CO_2 diffusion and mass flow in the static method. Sparling and West (1990) recommended the gas chromatography method to measure soil respiration should be restricted to soils at field capacity or below and with a pH of less than 6.5. CO_2 retention was shown to increase markedly in solutions above pH 6.5.

Freijer and Bouten (1991) evaluated three widely used methods for measuring the total CO_2 evolution from soil:

1) The 'dynamic CO_2 absorption method' has the potential to absorb all CO_2 emanating at the soil surface, and was shown to have only a small impact on the CO_2 concentration-depth gradient and the efflux of CO_2. The method proved accurate, simple and of low cost, and consequently suitable for the study of temporal and spatial dynamics of CO_2 evolution from soil.

2) The 'static CO_2 absorption method' was shown to underestimate the evolution of CO_2 from soil, because the absorption velocity is too low, due to slow diffusion processes;

3) The 'chamber technique' records increasing CO_2 concentration with time under a closed cover. The accumulation of CO_2, however, alters the gradient, does not yield the exact surface efflux, because the effect of increasing storage in soil is not incorporated.

In view of the different measurement techniques used, a significant part of the inter-site variability in soil respiration rates may partly be due to methodological differences. This makes the comparison and interpretation of published soil respiration data cumbersome (Raich and Schlesinger, 1992). Mean rates of soil respiration with different types of vegetation, as derived from an analysis of the literature by Raich and Schlesinger (1992), are presented in Table 5.3 indicating the importance of mean annual temperature and mean annual precipitation at the global level. Additionally, there is a close correlation between mean annual NPP of different vegetation biomes and their mean annual soil respiration rates; on the average, soil respiration rates are 24% higher than mean annual NPP. Priority areas for additional research on soil respiration rates are the arid, semi-arid and tropical regions for which there only relatively few measurements available (Raich and Schlesinger, 1992).

Table 5.3.   Mean rates of soil respiration with different types of vegetation (Source: Raich and Schlesinger, 1992).

Vegetation type	Soil respiration ($gC\ m^{-2}yr^{-1}$; Mean $\pm$ SE)	n
Tundra	60 - 6	11
Boreal forest and woodlands	322 - 31	16
Temperate grasslands	442 - 78	9
Temperate coniferous forests	681 - 95	23
Temperate deciduous forests*	647 - 51	29
Mediterranean woodlands and heath	713 - 88	13
Croplands, fields, etc.	544 - 80	26
Desert scrub	224 - 38	3
Tropical savannas and grasslands	629 - 53	9
Tropical dry forests	673 - 134	4
Tropical moist forests	1260 - 57	10
Northern bogs and mires	94 - 16	12
Marshes	413 - 76	6

Note: * = including mixed broad-leaved and needle-leaved forests. SE is the standard error, and *n* the number of observations.

Spatial and temporal variability

In the following paragraphs the results of several studies of CO_2 evolution associated with soil respiration are presented and the important predictor variables tentatively are identified.

Random CO_2 evolution measurements over the growing season of a wheat crop indicated the number of samples required to estimate soil respiration of a one hectare area within 10 % (p= 0.05) of its mean value decreased from 190 at the time of seeding to 30 at the end of the cropping season. The maximum soil respiration during the growing season corresponded with the period of maximum growth of the maize and wheat crops, reflecting the possible importance of root respiration (Rochette *et al.*, 1991). Beyer (1991) found that while in a sandy Podzol 5 replicate measurements gave adequate results of CO_2 flux associated with soil respiration, with an error probability of 10 per cent, in their loamy Luvisols it was necessary to use 10 replicates to specify the same degree of difference.

Rochette *et al.* (1991) studied the spatial and temporal variability of soil respiration using chamber measurements of CO_2 evolution on bare soil and soil under maize and wheat crops. Semi-variograms indicated no definite structure of spatial autocorrelation on bare soil when measurements were made along transects. The spatial variability was found to occur at a scale smaller than 15 cm. Under dry conditions, soil respiration under the maize crop was significantly higher than in the interrow. When wet, soil respiration in the interrow compacted by the tractor wheel was significantly lower than on non-compacted soil and no significant difference was found between rows and interrows. Rochette *et al.* (1991) attribute these observations to the contribution of plant roots to soil respiration measured in dry conditions. In wetter soil, the role of microorganisms was dominant except in the compacted interrow where a lower air-filled pore

space caused lower respiration. Similarly, in the study of Groffman and Tiedje (1991), CO_2 production rates were positively related to air-filled pore space in well drained loams but negatively related to air filled porosity in poorly drained loams. Doran *et al.* (1990), with respect to 18 US benchmark soils, found soil respiration to be parabolically related to water filled pore space (WFPS). Maximum evolutions were observed for 54, 61 and 78 % WFPS, for medium to fine textured soils, coarse textured and highly weathered soils, respectively. Less available moisture or aeration in soil, which results in a decreased microbial activity, may explain the 'conserving' effect of living roots on soil organic matter (Dormaar, 1990).

Seasonal changes in CO_2-evolution rate and soil temperature were exponentially correlated in two Japanese forest soils, with Q_{10} values of 1.93 and 2.33, respectively (Sakai, 1990). Naganawa *et al.* (1989) measured soil respiration with portable infrared gas analyzers by measuring CO_2 concentration in small chambers placed in an experimental field at Shimane University (103 plots, 1081 data). The soil respiration rate had a geometrical mean of 11.4 mmol h^{-1} m^{-2}, with a range from about 0 to 80. In this experiment, the evolution of CO_2 was strongly enhanced by temperature ($r^2 = 0.76$; $Q_{10} = 2.2$; temperature range 4 - 40 ºC), and weakly by the soil moisture level and input of organic matter. Wilhelmi and Rothe (1990) measured CO_2 evolution under spruce, and found an optimal biological activity at 20-35 ºC and water contents ranging from 40 to 60 per cent. Alternatively, Carlyle and Than (1988) found temperature had little effect on soil respiration at low soil moisture levels. Maximum soil surface temperature and soil moisture content proved to be the most reliable predictors of CO_2 evolution for all treatments in Weber's (1990) study with aspen. Rochette *et al.* (1991) observed a peak in soil respiration after a 2 hour rainfall event, when soil was at field capacity. Soil respiration was 9 times higher than its level prior to the shower and gradually decreased with time. Similarly, fluxes in N_2O from soil are often associated with rainfall events (see Chapter 4).

Aiken *et al.* (1991) measured the soil CO_2 efflux in a wheat field at two different dates with differing soil water contents, and soil plus vegetation CO_2 efflux in three grassland sites in order to characterize the positional trend, spatial correlation and random variation in these effluxes. The alkali absorption method was used to measure the CO_2 efflux using static chambers positioned in a 3 m grid within a 18 by 18 m square. Statistical analyses indicated the assumption of spatial homogeneity (first-order stationary) was not justified for CO_2 efflux for 4 of the 5 data sets. Positional trends accounted for 16 to 48 % of the total variability in CO_2 efflux in these cases. Aiken *et al.* (1991) detected no spatial correlation, although ignoring positional trends may well have resulted in the opposite conclusion. Spatial structure in CO_2 evolution was affected by the soil water content under wheat.

Yang *et al.* (1989) studied soil respiration from 4 meadows with *Kobresia humilis, Dasiphora fruticosa* a shrub, *Elymus mutans* and forbs meadows in the Hepei alpine environment, China. Soil respiration varied according to vegetation types and also diurnally, with the highest soil respiration occurring during day time. Soil respiration also decreased gradually with soil depth (depths of sampling of 0-10, 10-20, 20-40 and 40-60 cm). Under the 4 vegetation types considered, soil respiration was correlated with the number and activity of microorganisms, the enzyme activities and soil temperature. Additionally, significant correlations were found between soil respiration and total N, pH, CEC, organic matter, available K and hydrolysable N content (Yang *et al.*, 1989).

In Ontario, Weber (1990) studied the respiration of forest soils under stands of 20 yr old aspen (*Populus tremuloides* and *P. grandidentata*) which had been subjected to cutting or burning treatments either before or after the 1984 spring leaf-flush. Soil respiration was measured *in situ* as CO_2 evolution using the 'soda lime' technique. The CO_2 evolution varied seasonally from a maximum of about 7000 mg CO_2 m^{-2} d^{-1} in midsummer for the control, minima of just over 2000 mg CO_2 m^{-2} d^{-1} in spring and autumn reflecting a

possible temperature effect. Similarly, Insam (1990) found a significant relationship between basal microbial respiration and climate. Soils from warmer climates exhibited a mean basal respiration of 0.3 mg CO_2 g^{-1} soil per hour as compared to 0.1 mg CO_2 g^{-1} soil per hour for cooler climates.

When plant residues are added to soil much of the C is rapidly oxidized to carbon dioxide. For crop residues, typically 70 % of the carbon is converted to CO_2 in 1 year (MacCarthy *et al.*, 1990b). Carbon added in the form of water-soluble compounds that can be assimilated by microbes, is mineralized even more rapidly, with as much as 90 % evolved as CO_2 in 1 yr (Stott and Martin, 1990). Polysaccharides and proteins in soils are also readily mineralized in a period of 6 to 12 months. The remainder of this non-aromatic C is incorporated into the soil organic matter and microbial biomass (MacCarthy *et al.*, 1990b). Bremner *et al.* (1991) studied the effects of grinding, addition of fertilizer N, and the absence of soil on C mineralization from agricultural plant residues with an elevated C/N ratio (wheat straw, lentil straw and lentil green manure with a C/N ratio of 80, 36 and 9, respectively). In the initial stage the CO_2 evolution was much faster for the lentil green manure than from the lentil or wheat straw, but by 98 days similar amounts of CO_2 had evolved from all residues incubated in soil with no added N. Incubation of plant residues in the absence of soil had little effect on CO_2 evolution from the lentil green manure or lentil straw, but strongly reduced CO_2 evolution from the wheat straw. Grinding did not affect carbon dioxide evolution from the lentil green manure but did increase the CO_2 evolution from the lentil straw without added N and from the wheat straw. The addition of N increased the rate of CO_2 evolution from ground wheat straw between days 4 and 14 of the experiment but not from unground wheat straw, and only slightly increased the rate of CO_2 evolution from lentil straw during the initial decomposition. Over the study period of 98 days, the added N reduced the amounts of CO_2 evolved from both lentil and wheat straw, due to reduced rates of CO_2 evolution after about 17 days. Bremer *et al.* (1991) attributed the lack of an N response during the early stages of decomposition to the low C/N ratio of the soluble straw component and to microbial adaptations to an N deficiency, while the inhibitory effect of N on CO_2 evolution during the later stages of decomposition may be attributed to effects of high mineral N concentrations on lignocellulolytic microorganisms and enzymes.

In Brazil, Zech *et al.* (1990) studied the CO_2 evolution from Ah horizons of a 'Terra Preta do Indios', a man-made 'kitchen-midden' Humox, and a Haplorthox, respectively. Both soils had similar clay + silt content and were formed from similar 'Beltera clay' parent material. The CO_2 production during incubation from the Ah-horizon of the Terra Preta was significantly lower than that of the Haplorthox even though the Ah of the Terra Preta contained 92 g C kg^{-1} and the Ah of the Haplorthox 30 g C kg^{-1} (Zech *et al.*, 1990). This reflects the higher stability of the soil organic matter in the Terra Preta (see also Section 5.3.4).

Based on a recent study, Raich and Schlesinger (1992) conclude that conversion of native vegetation appears to increase soil respiration. Similarly, fertilization generally seems to increases soil respiration rates. Additional direct measurements and comparisons of soil respiration from 'untreated' *versus* 'treated' sites are needed to fully elucidate the nature and importance of the respective controls of soil respiration. The rate at which carbon dioxide is meitted from soil to the atmosphere is dependent on its rate of production in the soil, soil characteristics (e.g. texture, structure, moisture content, organic carbon content), concentration gradients between CO_2 in soil pore space and in the atmosphere immediatelt above the ground, as well as wind speed.

Soil CO_2 levels

It is unlikely that increased concentrations of atmospheric carbon dioxide will directly modify the CO_2 concentration in the soil pores, as the latter levels are much higher than the former (IGBP, 1992 p. 65). Kursar (1989) observed substantial microspatial variation for soil respiration and soil CO_2 concentration in a study of soil gas exchange in freely drained soils in lowland moist forest in Panama. During the rainy season, the soil CO_2 levels at 40 cm below the surface amounted to 2.3-4.6 % and were shown to be correlated with rainfall during the preceding two weeks. Temporal changes in soil CO_2 were rapid, large and displayed similar trends between sampling points. The soil CO_2 levels in acid forest soils in Shenandoah National Park, Virginia, fluctuated annually by two orders of magnitude, showing a strong correlation with soil temperature (Castelle and Galloway, 1990). In coarse textured Nevada desert soils, soil CO_2 appeared to be more dependent on temperature than moisture during the winter and spring, whereas it appeared to be dependent on moisture in the summer and autumn (Terhune and Harden, 1991).

Dyer and Brook (1991) studied the spatial and temporal variations in soil CO_2 concentration in a Georgian temperate forest soil during the 'non-growing' season over the 1985-1986 period. The soil CO_2 levels varied with soil depth, varied spatially at constant depth, and varied temporally with changing environmental conditions. Variations with depth in the upper 140 cm of the soil were of greater magnitude than temporal variations, and spatial differences at 30 cm depth were of lesser magnitude. Mean soil CO_2 content was higher in evergreen forest (0.21 %) than in deciduous and mixed forest (0.16 %). Dyer and Brook (1991) observed no trends in soil CO_2 along hillslopes or with changes in soil texture, bulk density, moisture content, or temperature. Higher soil CO_2 levels were recorded near trees, possibly reflecting increased root densities and/or more numerous pockets of microbial activity. At a depth of 30 cm, the mean daily temperature range in the month before measurement and the actual evapotranspiration in the week before measurement (AET) explained 76 % of the variation in mean soil CO_2 levels. In a profile, where soil CO_2 levels was measured at five depths, 66 % of the variability in CO_2 was explained by soil depth, AET, and the average daily temperature range in two months before measurement.

5.4.3 CO_2 evolution associated with deforestation and afforestation

Deforestation as a cause of CO_2 emission

For many centuries human activities associated with agricultural expansion and urbanization have caused wide scale changes in natural ecosystems. During the last century the major component of the associated (biogenic) carbon loss resulted mainly from the cultivation of virgin grasslands, while more recently it derives mainly from deforestation. Tropical forest resource assessments have been prepared by FAO/UNEP (1981). The alarming rate of current deforestation in many tropical regions is apparent from the recent reviews of Woodwell *et al.* (1983, 1984a, 1986), Hall *et al.* (1988), Detwiler and Hall (1988), Myers (1989) and Bouwman (1990a) amongst others. Estimations of the extent and rates of loss of forests over the globe vary widely, in part because of different definitions and methodologies. The importance of remote sensing in monitoring changes in forested area has been discussed, for example, by Woodwell (1984a), Bouwman (1990a), Estes and Consentino (1989) and Veldkamp *et al.* (1992).

The amount of forest remaining in the humid tropics is now in the order of 8 million km^2 or roughly half of what once existed according to bioclimatic data. Around 100,000 km^2 are being severely disrupted each year by heavy logging and intensive slash-and-burn practices. About 2.5 % of the biome is being removed each

year in terms of viable forest cover with full biomass and ecological complexity (Myers, 1989). As a 'regional' example, the recent deforestation history of eastern rainforest in Eastern Madagascar may be quoted. In 1985 there remained 3.8 Mha of rain forest, corresponding with about half of the 7.6 Mha remaining in 1950, and with about 34 % of the estimated original extent of 11.3 Mha of rain forest in eastern Madagascar (Green and Sussman, 1990). Current deforestation rates of 20 to 30 % per year are accepted for the states of Amazonas, Mato Grosso, Pará and Rondônia where most of the deforestation takes place in Brazil (Setzer and Pereira, 1991). The latter deforestation and burning processes in the Amazon region started in the early 1970s with the official policy to develop the region (Setzer and Pereira, 1991). This reflects current deforestation rates are essentially related to the ever increasing land pressure and related unfavourable socio-economic conditions of the local population. Consequently, there is an urgent need for sustainable agricultural policies to reduce current deforestation rates in the humid tropics (Sanchez *et al.*, 1990).

Deforestation and changes in land use during the period 1860-1984 have been estimated to cause losses of 150 ± 50 Pg C (Bolin *et al.*, 1986), with current releases being in the range 1-2 Pg C yr^{-1} (Bolin, 1986b; Bouwman and Sombroek, 1990) to 2-5 Pg C yr^{-1} (Houghton *et al.*, 1985; Crützen and Andreae, 1990). Detwiler and Hall (1988) estimate the current CO_2 release from non-tropical forest regions *anno* 1980 to be at the most 0.1 Pg C and for tropical forests to be 0.42 - 1.60 Pg C. Of the latter amount, 0.1-0.3 Pg C were attributed to decreases in soil organic matter content, while decay and burning may have accounted for 0.3 to 1.3 Pg C (Detwiler and Hall, 1988). The mean annual carbon release associated with fire in moist tropical forests is estimated to be 30 g m^{-2} yr^{-1}, in contrast to 150 g m^{-2} yr^{-1} for seasonally dry savannas and scrubland. Fires in closed tropical and subtropical forest release about 0.5 Pg C yr^{-1}, whereas for temperate forests this is some 0.1 Pg C yr^{-1}. Tropical woodlands and savannas, on average, are estimated to contribute 1.5 Pg C yr^{-1} (Olson, 1981 as quoted by Mooney *et al.*, 1987). The preceding estimates of C loss vary amongst other in view of the uncertainties in acreage deforested, type of forest removed (biomass), land uses to which these forests are cleared, and differing definitions of biomes (see Bouwman, 1990a).

Afforestation as a possible means of sequestering atmospheric CO_2

Afforestation of bare land or redundant arable land has been proposed as a good measure for (temporarily) sequestering atmospheric CO_2 in growing trees and for reducing the greenhouse effect. However, there are several arguments why this need not be so. Putting previously bare land under vegetation would lower atmospheric carbon dioxide levels by only 1.5 ppmv for each 10^{12} m^2 of land additionally covered (Goudriaan, 1989). Alternatively, to produce annually the amount of fuelwood equivalent to the world use of fossil fuel-energy *anno* 1980 (15 Pg stemwood) would require 10 to 37 10^{12} m^2 of managed forest of the type described by Houghton (1990). Wolf and Janssen (1991) modelled that a (proposed) doubling of forest area in the Netherlands would just offset carbon losses associated with other changes in land use, and that it would not result in additional fixation of carbon in soil. Reforestation withdraws carbon from the atmosphere for only as long as the forests are gaining biomass; after maturity forests are approximately in balance with respect to carbon (Houghton, 1990).

Many authors have discussed the possibility of planting trees to reduce the build-up of carbon dioxide in the atmosphere (Kimball *et al.*, 1990; Grantham, 1990; Houghton, 1990; Bekkering, 1992). These studies do not always consider where these vast areas of trees could be planted. Alternatively, Houghton (1990) considered only those areas where trees had been grown in the past (prior to deforestation and currently not under cropland or urban use) as being climatically and edaphically suitable for forests. In planning studies at the global level, environmentally suitable areas for forestry can be derived from physical land evaluation, using

for instance ½ x ½ degree grid data bases on climate (e.g., Leemans and Cramer, 1991) and soils, combined with generalized information on the environmental requirements of important tree species (see FAO, 1984). The assessment must also take into consideration the need for land other than as viewed from the perspective of the global carbon cycle (e.g., food, fibre, timber, housing). Schlesinger (1990) observes that as the human population continues to grow exponentially, contributions of potential vegetation shifts (e.g., arable land to forest) and the 'CO$_2$-fertilization effect' (see Section 5.4.4) to create an enhanced carbon sink on land may become largely academic. Alternatively, large scale changes in natural ecosystems to accommodate vast acreages of forest may have some 'unanticipated' effects. Expansion of commercial forestry in Finland, for instance, is leading to the replacement of most of the region's natural forests with uniform plantations. Instead of moderating the greenhouse effect, the associated draining of vast areas of Finnish peatlands for forestry has resulted in huge increases in CO$_2$ emissions (Isomaki, 1991). Alternatively, draining of these peat areas reduces the emission of methane, another critical greenhouse gas.

Mattson and Swank (1989) observed no statistically significant difference in CO$_2$ efflux between two types of residue treatment on forest clear-cuts in the southern Appalachian (the logging residue was removed on one 'clearcut' and left in place on the other). The CO$_2$ evolution from the clearcuts were 33 % lower than those from the control watershed (uncut). The lower CO$_2$ effluxes from the two clearcuts were associated with higher soil temperatures, smaller live root masses, and larger forest-floor masses. Mattson and Swank (1988) observed no long-term changes in soil carbon pools following forest cutting and natural regeneration (5-8 yr period). Cutting of these Appalachian forests followed by regeneration does not seem to result in large net transfers of carbon to the atmosphere (Mattson and Swank, 1989), contrary to what has been generally assumed. Similarly, modelling studies by Emanuel *et al.* (1984) have shown that due to establishment of ground vegetation following forest clearing the net carbon flux from the terrestrial biotic system to the atmosphere is less than the release due to clearing, in some instances.

Effects of massive forest burning on local climate; the Amazon as an example

The repercussions of biomass burning in Brazil's Amazon Basin during the dry season of 1987 were analyzed by Setzer and Pereira (1991) using satellite imagery. As a conservative estimate 350,000 independent fires were identified, corresponding possibly to about 20 million ha of different types of burned vegetation. Estimates of the emissions emanating from these dry season fires, in million of tons, were 1700 for CO$_2$, 94 for CO, 6 for total particulate matter, 9 for ozone (secondary reactions), 10 for CH$_4$, 1 for NO$_x$ and 0.1 for CH$_3$Cl. The emissions essentially influenced the lower troposphere, although some smoke clouds reached up to 4 km before starting to disperse horizontally. The relevant emissions caused severe atmospheric pollution effects on a synoptic scale, with possible global implications (Setzer and Pereira, 1991). This aspect is also illustrated by the work of Shukla *et al.* (1990) who coupled numerical models of global atmosphere and biosphere to assess the effects of Amazonian deforestation on regional and global climate. When tropical forests were replaced by degraded pastures, the model indicated there would be a significant increase in surface temperature and a decrease in evapotranspiration and precipitation over the Amazon basin. The simulation runs showed the length of the dry season would increase. This would make it difficult to re-establish forests as potential captors of atmospheric CO$_2$ after extensive deforestation (Shukla *et al.*, 1990). Additionally, clearing of primary forest for other uses often is associated with a significant loss of nutrients. This may form an additional limitation for widespread reafforestation, particularly where the inherent fertility of the mineral soil is low. Under conditions of reduced nutrient supply and reduced rainfall the potential positive effects of the enhanced atmospheric concentrations of CO$_2$ may not materialize (see Section 5.4.4). Henderson-Sellers *et al.* (1988), with reference to climate models, discussed important processes associated

with tropical deforestation such as a possible increase in surface albedo, a decrease in length of the surface-roughness, and changes in the soil properties.

5.4.4   Possible consequences of the CO_2-fertilization effect

Many researchers studied how crops respond to a possible doubling of carbon dioxide (Idso, 1989; Cure and Acock, 1986; Kimball *et al.*, 1990; Lekkerkerk *et al.*, 1990; Kuikman *et al.*, 1991). The increase in atmospheric CO_2 concentration, however, is but one of the aspects of the projected enhanced greenhouse effect (e.g. Hume and Cattle, 1990). There are three ways in which the 'greenhouse effect' can be important for agriculture (Warrick, 1986a; Parry, 1990; Parry *et al.*, 1990). Increased atmospheric concentrations of CO_2 can have a direct effect on the growth rate of certain crops, plants and weeds (the so-called CO_2-fertilization effect). Secondly, CO_2 induced changes may alter the ambient temperature, rainfall and incoming sunshine (e.g., through changes in cloud cover) and thereby modify plant and animal productivity. Thirdly, there may be adverse effects associated with anticipated sea level changes, such as an increased intrusion of salinization in agriculturally important low lying areas (see Szabolcs, 1991).

Shugart *et al.* (1986) and Maini (1988) recently discussed how global change could affect forests, for instance by ultimately shifting the current latitudinal and altitudinal zoning of many forest types (particularly in the middle latitudes) as well as the latitudinal and altitudinal tree-lines, and by influencing growth and biomass production. Schlesinger (1990b) indicates that if the terrestrial biosphere is indeed to act as a carbon sink under future elevated levels of CO_2, this would be more likely to be the result of changes in the distribution and biomass of terrestrial vegetation than of changes in the accumulation of soil organic matter. A limitation of climate models is that they cannot yet provide estimates of the regional climate changes (e.g., length and time of occurrence of growing period) which are essential to assess the possible impacts on agriculture (see Hume and Cattle, 1990).

There remain widely differing views on the possible repercussions of enhanced atmospheric CO_2 concentrations and related changes in climate on net primary production, and by implication on phytomass and soil carbon reserves, amongst the different research groups (see Kimball *et al.*, 1990). Basically, increased atmospheric levels of carbon dioxide may affect plant growth in three ways (Bazzaz and Fajer, 1992; Esser, 1990; Kimball *et al.*, 1990; Goudriaan and Unsworth, 1990). First through a direct effect of the partial CO_2-pressure in the plant cell on the enzyme kinetics of RUBP carboxylase, which directly affects the quantum efficiency of photosynthesis (RUBP is a five-carbon sugar called ribulose phosphate). Increased CO_2 levels also have an indirect effect on plant transpiration through the stomatal resistance. The intercellular partial pressure of CO_2 will rise with increasing atmospheric CO_2 levels to which plants may respond by closing the stomata (increasing the stomatal resistance) to maintain the internal CO_2 partial pressure constant. Closing of the stomata would reduce the transpiration.

Idso (1991) in a challenging paper terms the increasing levels of atmospheric CO_2 as 'probably the best thing that could ever happen to the biosphere' as it could lead to its 'rebirth'. About 5 to 10 % of the actual rate of increase of agricultural productivity worldwide can be ascribed to the fertilizing effect of rising atmospheric CO_2 levels (Goudriaan and Unsworth, 1990). The positive direct effect of CO_2 on plant growth is often smaller when crops are poorly fertilized, but it is fully retained when water shortage limits productivity (Goudriaan and Unsworth, 1990). Bazzaz and Fajer (1992) explain why the possible beneficial effects of enhanced atmospheric CO_2 levels on plant growth, the so-called 'CO_2-fertilization' effect, are likely to be overstated. Often, these studies do not consider possible associated regional changes in mean air

temperature or precipitation and related shifts in 'climate' zones. The modelling study of Adams *et al.* (1990) indicates the size of the terrestrial carbon reserve would seem to be responding more to climate factors than to the level of atmospheric CO_2 *per se*. Another important aspect is that most of the projections claiming advantageous growth under increased levels of atmospheric CO_2 are based on studies of vegetative growth. Sinha *et al.* (1988), however, indicate that a warming of 2 °C above a mean temperature of 22 °C promotes sterility in rice and will reduce the yield by 25 % or more, although the temperature increase *per se* has little effect on photosynthesis.

Mooney *et al.* (1987) argued that it is uncertain whether any possible increase in carbon fixation resulting from increased atmospheric CO_2 concentration will also cause increased decomposition. This could be a crucial point, because it is the change in net carbon storage, and not photosynthesis, that controls feedback from carbon dioxide absorption by plants, to further alter atmospheric concentration. Decomposition could simply increase with increasing productivity. Yet when nutrients are limiting, plant tissues will display higher ratios of C to nutrients when CO_2 levels are elevated. This change in plant chemistry could alter (reduce) the rate of decomposition of plant materials and related nutrient release, which possibly will reduce production on the long-term in natural systems and by implication possible future inputs of organic residues into soil (see appropriate Chapters). Alternatively, Lekkerkerk *et al.* (1990) suggest that under elevated CO_2 levels in air the decomposition rate of organic matter may decrease due to competition between plants and microbes for limiting nutrients and water possibly leading to increased soil organic matter contents. Alternatively, the temperature increase associated with the enhanced greenhouse effect could cause decomposition to increase faster than net primary productivity (NPP).

5.5   Modelling changes in terrestrial carbon pools and sinks

5.5.1   Introduction

Changes between the Last Glacial Maximum and present times

About 18 Kyr ago, at the time of the Last Glacial Maximum, about 968 Pg C was stored in vegetation (346 Pg C) and soils (625 Pg C) based on an analysis of palynological, pedological and sedimentological data. The present carbon reserve, as calculated by Adams *et al.* (1990b), is 924 Pg C for vegetation, 1115 Pg C for soils and 280 Pg C for peat, amounting to a total of 2319 Pg C. The corresponding, calculated increase in terrestrial carbon since the Last Galcial Maximum is 1351 Pg C (Adams *et al.*, 1990b). This is much more than the change of 30 to -50 Pg C which Prentice and Fung (1990) computed for the mass transfer of terrestrial biosphere carbon to the atmosphere. With respect to the preceding studies, Schlesinger (1990) observed they are 'only' based on changes in the distribution of vegetation in response to past and future climates. As such these studies do not consider the possible stimulation of photosynthesis and carbon storage as a response to higher CO_2 concentrations in the atmosphere today. Esser (1987) calculated that between 1860 and 1981 the NPP of the terrestrial biosphere has increased from 43.1 to 48.6 Pg C yr^{-1} due to the CO_2-fertilization effect. It should be noted the latter figure includes a considerable reduction associated with a lower NPP of agricultural areas, as compared to the original vegetation, of which the acreage expanded markedly during the period 1860-1981 (Esser, 1987). The major carbon 'components' of major vegetation zones of the world, as presented by Tinker and Ineson (1991), are summarized in Table 5.4.

According to the calculations of Adams *et al.* (1990b), the size of the soil carbon pool has increased by 490 Pg C since the Last Galcial Maximum. Buringh (1984) calculated about 537 Pg C of soil organic carbon has

been lost since prehistoric times, corresponding with about 27 % of the amount present prior to the spread of civilization in the last 2000 yr (from 2014 to 1477 Pg C). Alternatively, Schlesinger (1984) computed the cumulative transfer of carbon to the atmosphere since prehistoric times only may have amounted to 40 Pg C. These figures reflect the uncertainty in these calculations.

Table 5.4.   Current estimates of plant biomass, litter input, soil organic matter and microbial biomass of major global vegetation types (Source: Tinker and Ineson, 1990 p. 79)

Subject	Tropical forest	Temperate forest	Boreal forest	Savanna	Temperate grassland	Tundra
Area (10^{12} m^2)	24.5	12.5	12.0	15	9	8
Plant biomass (g C m^{-2})	18,000	14,000	9,000	1,800	1,440	250
Litter input (g C m^{-2})	710	368	250	360	667	75
Soil C (g m^{-2})	13,000	9,000	15,000	5,400	23,000	22,000
Soil N (g m^{-2})	816	640	1,100	333	2,100	1,125
Microb. biomass C (")	50	110	35	60	215	20
Microb. biomass N (")	2	14	2.5	8.7	51	1
Microbial turnover (yr)	0.07	0.30	0.14	0.17	0.32	0.27

Before 1980 the biosphere was a net carbon source (to atmosphere), releasing about 30 to 40 Pg C during the period $\approx$ 1860-1980 (Esser, 1990; Goudriaan, 1989). In the mid 1980s the inferred terrestrial storage of carbon was 2.0-3.4 Pg C yr^{-1} which would indicate soils and the terrestrial vegetation are already acting as a sink for atmospheric CO_2; the atmosphere does not contain as much of the fossil fuel CO_2 as it should according to model calculations (Tans *et al.*, 1990; Walker and Kasting, 1992). Similarly, according to Esser (1990), the terrestrial biosphere formed a net sink for atmospheric carbon of 0.6 Pg C yr^{-1} in 1980. Deforestation, afforestation and changes in agricultural use resulted in CO_2 emissions of 0.8 Pg C yr^{-1}, but these losses were compensated by the fertilization effect ($\approx$ 1.25 Pg C yr^{-1}) with the litter and soil organic carbon binding an additional 0.2 Pg C yr^{-1} due to so-called 'secondary effects' (Esser, 1990). The current maximum potential sink in soils is not likely to exceed 0.4 Pg C yr^{-1} according to Schlesinger (1990b). Alternatively, Tinker and Ineson (1991) estimate the current net release of C from soils and plants to be around 1 Pg C yr^{-1}.

The reviews of Schlesinger (1986) and Bouwman (1990a p. 62) and Table 5.5 illustrate that estimates for current soil carbon pools vary widely. Computations by the various authors are based on different calculation techniques, i.e. based on soil groups, vegetation groups and life zone classes, and based on different data sets and variable assumptions (see discussion in Bouwman, 1990a). This results in a fairly wide uncertainty in estimates of the size of terrestrial carbon pools. This aspect may be illustrated by the study of Zinke *et al.* (1984) who used two different computation procedures. In the first, soil profiles were classified into Holdridge life zones using appropriate life zone areas. Based on this approach, the global soil pool was estimated to be 1,309 Pg for C and 92 Pg for N, respectively. In an alternative approach, the average organic carbon and nitrogen densities from 1 degree latitude bands were multiplied by the earth's surface area in the relevant bands. The total pools so obtained were 1,728 Pg C and 117 Pg N, respectively (Zinke *et al.*, 1984).

Table 5.5.   Estimates of global organic carbon pools in soils (Pg C).

Method	Source	Carbon pool	Cumulative loss	Annual release
Vegetation	Bolin (1977)*	700	10-40a	0.3
	Schlesinger (1977)*	1456	--	0.85
	Bolin *et al.* (1986)*	1672	--	1 - 2
	Atjay *et al.* (1979)*	1635	--	--
	Houghton *et al.* (1983)*	--	45-76b	0.87
	Zinke *et al.* (1984)	1309 or 1728		
Soil	Bohn (1976)*	3000	--	--
	Atjay *et al.* (1979)*	2070	--	--
	Post *et al.* (1985)	1272	--	--
	Schlesinger (1984b)*	1515	36a	0.8
	Buringh (1984)	1477	537b	1.5-5.4
	Bohn (1982)	2200		
	Kimble *et al.* (1990)	1061		
	Bouwman (1990a)	1600-1800		
	Adams *et al.* (1990b)	1115	-490c	
Modelling	Meentemeyer *et al.* ('81)*	1457		
	Goudriaanand Ketner ('84)*	1400		

Note: For sources indicated with * see Bouwman (1990a); a refers to C losses since prehistoric times, b to losses since the mid 1980s, and c to losses since the Last Glacial maximum.

Post *et al.* (1985) estimated the size of the world organic soil carbon pool at 1272 Pg C by associating Holdridge life zone classification with estimates of the area of major ecosystem complexes, relying on the correspondence of life zones with vegetation associations. Soil carbon was calculated for each life zone using the relevant mean soil carbon densities. Bohn (1982) estimated the total mass of organic C in mineral and organic soils at 2200 Pg C, of which 1800 Pg C occur in mineral soils. Kimble *et al.* (1990) estimated the organic carbon content in soils of the world to a depth of 1 m - using about 2700 pits classified according to the Keys to Soil Taxonomy (USDA, 1987) - and the spatial extent of the relevant orders (Histosols excluded) at 1061 Pg C, of which an estimated 496 Pg C occur in tropical soils. Present reserves of C in peat have been variously estimated at around 202 or 377 Pg C (*cf* Adams *et al.*, 1990 p. 713).

In a similar manner to Buringh (1984), Bouwman (1990a) compiled 'generalized' soil carbon profiles for the major soil units of the Soil Map of the World (FAO/Unesco, 1971-1981). He assumed a bulk density of 1.5 g cm^{-3} for all soils and a maximum thickness of 1 m, and combined this information with the area for the respective major soil units and land cover types, showing the global soil C pool to be in the order of 1600-1800 Pg C. The estimates of Bouwman (1990a) exclude C stored in organic soils. Bouwman (1990a) used general conversion keys (e.g., soil carbon in the upper 1 m decreases by 40-60 per cent when forest or grassland is converted to cropland) to estimate the possible effect of broad categories of land use change on soil carbon pools. Inherently, results may vary widely depending on the data and type of assumptions used (e.g., land use affects the soil organic matter content to a depth of 40 cm or 100 cm).

Current estimates of world soil carbon pools - both for mineral and organic soils - could be improved greatly by presenting organic carbon data for regionally representative major soils of the world together with such

essential data as soil horizon depth, bulk density and stone content, combined with quantitative estimates of the geographic extent of the various major soil units (see Chapter 6).

Possible explanations for the so-called 'missing carbon'

From the beginning of the 20th century, significant changes in land use have occurred over large areas in the mid-latitudes. These changes include extensive reforestation, which may lead to higher woody biomass and possibly carbon storage in soil. During the period these forests are in a mid-successional stage they may form an important potential sink for atmospheric carbon (see appropriate Sections). Especially because current N-eutrophication associated with pollution, and enhanced levels of atmospheric CO_2 could lead to a higher NPP. Based on these considerations, Matson and Ojima (1990) proposed that changes in the so-called 'chemical climate' may amplify the possible sink strength for atmospheric CO_2. Alternatively, it can be argued that acid deposition and ozone accumulation, being a source for forest decline, could adversely affect potential storage of atmospheric carbon dioxide in tree biomass. The possible antagonisms and synergisms as portrayed above make it difficult to understand the causative factors as well as their relative importance; there is a need for 'manipulative' experiments (Matson and Ojima *op cit.*).

It still proves cumbersome to balance the global carbon budget. The estimated emissions are larger than the sum of atmospheric increase plus the model-computed CO_2-uptake by the oceans. This suggests there exists an important, unidentified 'missing carbon' sink. In part, the 'missing carbon' has been attributed to a 'CO_2-fertilization effect', associated with increased atmospheric CO_2 levels on plant growth. It has been argued that this contribution may outweigh the effect of forest clearing (Walker and Kasting, 1992), but the views on this matter still differ appreciably between the various research groups (see Section 5.4.3). The actual increase in amplitudes of seasonal variations in atmospheric carbon dioxide levels, as reported by Bacastraw *et al.* (1985) and Houghton (1987), may be seen as 'independent' evidence of a possible atmospheric CO_2-fertilization effect. Alternatively, discrepancies in estimates of the still unknown, large terrestrial sink for CO_2 may in part be due to the net flux of carbon to the oceans by rivers and rain; these figures must be added to the synoptic air-to-sea CO_2 flux to obtain the total oceanic uptake of anthropogenic CO_2 (for more details see Sarmiento and Sundquist, 1992).

Detwiler and Hall (1988) have reduced the discrepancy in the carbon budget to a maximum of 2.8 Pg C of 'missing carbon' in 1980. Tans *et al.* (1990) calculated there must be a terrestrial sink for atmospheric CO_2 at temperate latitudes to balance the global carbon budget and to match the N-S gradient of atmospheric CO_2. The mechanism of this sink, with a size of 2.0 to 3.4 Pg C yr^{-1}, is unknown. It depends on the sources in the tropical and boreal and tundra ecosystems (see Tans *et al.*, 1990). In a recent study of the inter-hemispheric transport of carbon dioxide, Broeckner and Peng (1992) challenged the findings of Tans *et al.* (1990). It would appear that the N-S gradient of atmospheric CO_2 has changed sign in recent times. Watson (1992), with reference to the findings of Broeckner and Peng (1992), finds it very plausible that Tans *et al.* (1990) may have underestimated the northern ocean sink. As a result, Tans *et al.* (1990) may have had to assume an unrealistically large vegetation sink to balance the global carbon dioxide budget according to Watson (1992). An increased CO_2-fertilization effect of the terrestrial biosphere must be accompanied by a smaller exchange rate between the deep seas and the mixed surface layer (Goudriaan, 1992).

5.5.2   Examples of book-keeping methods

The role of terrestrial biota in the CO_2 balance has been estimated with 'book-keeping' methods (Bolin, 1986a; Detwiler and Hall, 1988) and with 'dynamic' models (see discussion below). Commonly used book-keeping methods for calculating CO_2 emissions associated with mainly deforestation have been reviewed by Bouwman (1990a p. 74-76).

The net release of carbon from a certain soil-vegetation type varies depending on whether the area was cleared for permanent agriculture, pasture, shifting cultivation or timber. In most book-keeping methods, the carbon released upon clearing one hectare of forest (primary or secondary) for specified types of land use is computed by multiplying the estimated release per unit surface area by the land area converted yearly to each land use in the region under consideration. The general data requirements for this type of book-keeping methods are:

a) Carbon content of soil to a given depth (at equilibrium) before clearing;

b) Estimated average changes in soil carbon content over the considered depth range under each land use (see Houghton, 1986);

c) Area of forest converted to the respective uses each year. This type of information can increasingly be derived from remote sensing/GIS based studies of changes in vegetation or land use (Bouwman, 1990a; Woodwell, 1984b; Estes and Cosentino, 1989).

Alternatively, book-keeping methods have been used to estimate the possible effect of enhanced global warming on 'biological' activity. Bertram (1991), for instance, calculated the additional release of CO_2 associated with temperature increase since 1880. To this end he used a 'representative' Q_{10} value for soil respiration in combination with past temperature increase in a global model. According to these calculations the amount of soil-borne CO_2 associated with the increase in mean air temperature could be of the same order of magnitude as the CO_2 evolved from the burning of fossil fuels, and about 2/3 of the observed increase in atmospheric CO_2 may come from soil respiration and not from industrial pollution (Bertram, 1991). If average soil respiration is 68 Pg C yr^{-1} and the average Q_{10} for metabolic activity is 2.4, then the increase in soil respiration associated with a uniform global warming of 0.3 ^{o}C at the end of the next decade could increase soil respiration by almost 2 Pg C yr^{-1} (Raich and Schlesinger, 1992). This may be seen as a substantial, positive feedback to the greenhouse effect. Alternatively, Carlyle and Than (1988) studied the effects of soil moisture and soil temperature in two models (GRESP and BRESP) to predict soil respiration. Both models overestimated respiration at low moisture levels, because the Q_{10} quotient had initially been given a fixed value in both models (Carlyle and Than, 1988). Inclusion of a moisture dependent Q_{10} term in a revised version of GRESP, however, gave an excellent fit with measured respiration (r^2= 0.85).

A common shortcoming of the above mentioned 'book-keeping' methods is that they do not account for the CO_2-fertilization effect (Esser, 1990). This 'limitation' also applies to the equilibrium model which Wolf and Janssen (1991) propose to calculate the effect on net CO_2 emissions associated with rates of tropical deforestation, as well as those associated with a 'possible' shift of climate zones with their characteristic vegetation.

5.5.3   Examples of dynamic models

The interest for developing CO_2-simulation models continues to increase. An example of a well known dynamic model is OBM, the Osnabruck Biosphere Model (Esser, 1987). In this model, carbon transfer rates and transfer coefficients, respectively, are calculated on a grid basis from environmental variables such as mean annual temperature, average annual precipitation, CO_2 concentration of the atmosphere, soil fertility,

related vegetation formation, and land use category. The relevant equations are based on theoretical considerations and have been calibrated against ecological field data or data from physiological experiments. For a complete description of the assumptions and procedures of OBM and its data requirements reference is made to Esser (1987, 1990). For descriptions of other dynamic global C models see for instance Goudriaan and Ketner (1984), Goudriaan (1987, 1989, 1992) and Walker and Kasting (1992). Examples of terrestrial-biosphere models include those developed by King *et al.* (1989) and Schimel *et al.* (1990).

Schimel *et al.* (1990), with reference to the CENTURY model, discussed the steps required to develop ecosystem models for regional extrapolation. First, driving variables for the processes of interest need to be identified. Then, relationships between the driving variables and rates of the processes have to be quantified. Subsequently, the geography of the driving variables must be assessed. This information may then serve to develop regional simulation models. Schimel *et al.* (1990) indicate that if the environmental variables have been identified, much of the spatial variability in rates of processes can be simulated. These researchers consider the above approach a suitable mechanism for extrapolation from process measurements typically conducted in the laboratory or in small scale fields to the regional level.

Jenkinson *et al.* (1991) extended the ROTHAMSTED simulation model to the global scale to predict how much CO_2 will be liberated from the world soil organic matter pool for a given rise in temperature. Jenkinson *et al.* (1991) calculated that if world temperature would rise by 0.03 ºC annually, the most probable increase according to IPCC (1990), the additional release of CO_2 from soil organic matter over the next 60 years will be 61 Pg C. This corresponds with about 19 % of the CO_2 that will be released by combustion of fossil fuel during the next 60 years under the assumption that present fuel use remains at the current level (Jenkinson, 1990). Jenkinson *et al.* (1991) set the clay content for all soils at 20 per cent, a recognized (yet not necessary) source of error.

Van Breemen and Feijtel (1990) discuss a procedure to model the CO_2 balance of soil units from the FAO/Unesco Soil Map of the World. Besides soil data, information is needed on climate and land use as these essentially determine the net primary production and hence the inputs of fresh organic matter into the soil. According to Van Breemen and Feijtel (1990) the following soil factors should ideally be considered in such an exercise: depth of soil profile, textural make-up; nature of the clay fraction (incl. percentage of allophane); presence or absence of calcium carbonate; weatherability of silicate minerals; soil drainage class. Van Breemen and Feijtel outline, in general terms, how information on the specified soil factors could be derived from the 'qualitative' terminology of the FAO/Unesco Soil Map of the World. These data have been proposed for inclusion as attributes in the WISE soil data base, but then (ideally) as quantitative attributes (see Chapter 6). With good geographic data on land use and changes in land use together with geo-referenced soil data, process-oriented models should ultimately replace the more common book-keeping methods to estimate changes in CO_2 fluxes from soils (Van Breemen and Feijtel, 1990). Several possible sources of uncertainty in current soil data sets - of importance for studies of changes in carbon pools - are discussed in Section 5.5.4.

5.5.4   Uncertainty in soil carbon data

Several sources of uncertainty may be encountered when modelling changes in the organic carbon content of soils upon a predefined change in land use. The following discussion mainly concerns the soil attribute data. Information will be also be required on the type and extent of the various types of land use and changes

therein, which form an additional source of uncertainty. These aspects have been discussed in detail by Bouwman (1990a).

Sampling intensity and density

Huntington *et al.* (1988) assessed whether an intensive sampling programme can provide estimates of soil C and N pool size with sufficiently small confidence limits that changes of 20 % of the means can be detected. To this avail 60 plots were selected out of a total of 360 from a 25 x 25 m grid, located in a northern hardwood forest ecosystem. Huntington *et al.* (1988) stratified the plots into six elevation bands to ensure adequate representations of the elevation gradient, soil mapping units, topography and tree species. The number of plots per band was weighted by the proportion of the watershed represented by the elevation band. The location of pits within plots was also randomly selected. Sampling was according to depth strata as this was considered more repeatable than per genetic horizon (0-10, 10-20, and 20 cm to bottom of B horizon). Mann (1986) found that a 30 cm sampling depth provided a less variable estimate ($r^2 = 0.9$) of changes in carbon than a sampling depth of 15 cm ($r^2 = 0.6$). This indicates that a judicious selection of sampling depth will be needed to adequately reflect changes in soil C content upon changes in land use (see under sampling methodology).

Huntington *et al.* (1988) calculated the minimum detectable changes (defined as 1.96 times the standard error) in total C pool sizes for the forest floor and 0-10 cm depth stratum were 5.9 and 2.4 Mg C ha^{-1}, respectively. Based on these findings they concluded that large scale disturbances, such as harvesting of timber, may produce statistically measurable changes within a period of 5 to 20 yr. In practice, however, few studies of soil organic matter content modifications following a change in land use have considered the kind of sampling intensity as used by Huntington *et al.* (1988).

Sampling methodology

Besides the sampling density/scheme the technique of analysis can be important in identifying changes in soil carbon pools. Jones *et al.* (1990), for instance, found that while changes between burned and unburned sites were sufficiently marked after a period of 34 years to be detectable by total analysis, differences between annual, biennial and triennial burnings were more subtle requiring the measurement of mineralization rates and microbial biomass, a more sensitive technique. In order to determine the effects of land use on soil C, the soil sampling scheme must distinguish clearly between effects on plant roots from those on mineral-soil organic matter (Richter *et al.*, 1990). In view of the nature of the frequency distribution of soil carbon data in Australian Great Soil Groups, Spain *et al.* (1983) considered it preferable to present summaries of these data in terms of medians and interquartiles instead of averages. Out of necessity, however, many studies of soil C changes induced by modifications in land use practices do only consider single pit (e.g., in 'paired' studies) or average carbon data.

During routine soil surveys, soil samples are taken according to the horizonation which reflects the pedogenesis. These depth 'layers' do not necessarily coincide with the depth zone that will be affected by a change in land use. As land use practices may influence horizonation and soil bulk density in any soil, similar soil depth ranges 'before' and 'after' cultivation need not correspond with similar volumes of soil, making the comparison for changes in organic carbon content cumbersome. An additional problem is that bulk density data are seldom provided on a routine basis in many soil survey reports (e.g. Msanya, 1987;

FAO/Unesco, 1971-1981). In case of missing data, Post *et al.* (1982) calculated bulk density using a regression function of the following form: bd = bo + b1xd + b2xlog(cf), with bd the bulk density, d the depth to the centre of the horizon, and cf the mass fraction of organic carbon. Post *et al.* (1982) assumed bulk density does not vary greatly with depth in soils from the same vegetation type. The fact that this need not be so is apparent from the low coefficients of determination (r^2= 0.18 to 0.52) which reflect the poor predictive capability of the proposed regression function. Soil structure/porosity, soil texture/mineralogy and soil carbon content are important determinants of bulk density which ideally should be considered when developing pedotransfer functions for bulk density. Additionally, the volume of coarse fragments should be considered in calculations of carbon density.

Analytical methods

The way according to which soil organic matter and soil organic carbon content are determined in the laboratory also has repercussions on the estimates of soil organic C-reserves. With respect to the commonly used Walkley-Black method, Allison (1965) recommends using a conversion factor of 1.33 to account for incomplete oxidation unless more accurate methods - e.g., dry combustion, an estimator of actual organic C - are available for comparison. Similarly, in their study of organic matter in surface soils from Australia, Spain *et al.* (1983) scaled all the Walkley-Black data by this arbitrary (but widely used) average factor to convert them to a level comparable with that obtained by dry combustion. A correction factor > 1 indicates the presence of organic compounds that are resistant to chemical digestion but which are readily broken down by high temperature dry combustion, while a correction factor of < 1 possibly indicates the presence of ferrous iron in the samples (Allison, 1965). Recent statistical analyses by Grewal *et al.* (1991), for 40 samples from 8 New Zealand soils with a wide range in texture (20-56 %) and organic matter content (2-16 %), suggest an average conversion factor of 1.25 irrespective of the position in surface or subsurface horizon. Recomputation of the individual conversion ratios for the respective horizons, however, indicates a fairly wide range between the individual conversion factors of about 1.1 - 1.6, corresponding with individual recoveries in the range 62 to 85 per cent. Similarly, in the original study of Walkley and Black (1934) the individual recoveries ranged from 60 to 80 per cent.

In the 8 soils studied by Grewal *et al.* (1991) there was no clear tendency in the recovery ratio to either decrease or increase consistently with soil depth. Alternatively, Edwards and Todd-Ross (1983) used correction factors for 'high temperature dry combustion / Walkley and Black' of 1.08, 0.90 and 1.38 for the 0-15, 15-30 and 30-45 cm depth zones, respectively. Basically, the higher correction factor for the 30-45 cm zone, as compared to the 0-15 and 15-40 cm zone reflects the fact the ratio of relatively inert organic compounds to readily decomposable compounds should increase with depth from the readily decomposable litter and root detritus near the surface. In the soil studied by Edwards and Ross-Todd (1983) the 30-45 cm layer was almost devoid of roots. Richter *et al.* (1990 p. 79) used the 'uncorrected' Walkley and Black values when studying the effect of annual tillage on soil organic carbon levels; according to these researchers the correction factors vary too widely. Tiurin (as quoted in the Transactions of the, 1930 International Congress of Soil Science, p. 124) suggested a comparison of the titration value with the amount of CO_2 actually liberated by oxidation might be used to characterise the type of organic matter present.

The organic matter (OM) content has frequently been estimated by loss-on-ignition and organic C content by using a 'C/OM' ratio. Considerable error is expected when a single C/OM ratio is used, because the ratio varies depending upon soil type and soil depth (Nelson and Sommers, 1982). The review of Nelson and Sommers (1982) showed a range of 0.40 to 0.59 for the C/OM ratio. Schlesinger (1977) criticized his own

use of the commonly adopted 'standard' correction factor of 58 % (1/1.724) for converting from soil organic matter to carbon because there should be a qualitative change in the nature of organic matter with depth. This aspect may be illustrated by the study of Huntington *et al.* (1989). These researchers observed the carbon concentration decreases more rapidly with depth than the organic matter concentration, resulting in a decrease in C/OM ratio from 0.56 in the Oi + Oe horizon of the forest floor to 0.44 in the Bs2 horizon of a forested Spodosol. In an earlier study, Huntington *et al.* (1988) measured a conversion factor of 0.55 ± 0.02 (kg/kg) for 'C/OM loss on ignition' for forest floor samples in their study, while 0.45 ± 0.09 was found for the mineral soil. Similarly, the C/OM ratio commonly changes with the nature of the vegetation present. Wolf and Janssen (1991), for instance, used different C concentrations for crop residues, tree litter, manure and soil organic matter (average C/OM ratios of 0.45, 0.48, 0.50 and 0.58, respectively) in their modelling study.

Although the above discussion shows the use of 'standard' conversion factors for 'incomplete oxidation (1.33)' and 'C/OM conversion (58 %)' irrespective of the vegetation/crop cover, type of humus and soil depth need not be justified, it will often be necessary to use these conversion factors in studies at the global level as there are no other valid alternatives. Procedures for estimating soil organic matter content from remote sensing remain in the early stages of development (see Henderson *et al.*, 1989).

Type of data sources

Numerical data for soil profiles considered representative of major soil units (*sensu* FAO/Unesco, 1971-1981) will be included as 'point data' in the WISE data base (see Chapter 6). From a scientific point of view the use of point data may conflict with the spatial resolution (and related level of abstraction) required in a 1:5 million scale, ½ by ½ degree grid mapping exercise. Alternatively, actual soil carbon data as a function of depth will be needed for each major soil unit if quantitative estimates of global carbon pools are to be refined.

Most data on the 'worldwide organic soil carbon and nitrogen data' of Zinke *et al.* (1991) tape originate from profiles under natural vegetation. Thereby, they form a baseline for evaluation of effects of disturbance and modification to natural vegetation on soil carbon equilibrium in regional and global studies. Soil carbon data derived from routine soil survey reports, however, need not correspond with 'steady state' conditions. Although soil pit descriptions will mostly present information on current land use often they do not specify the past land use history. Nor do they indicate at which moment in time eventual changes in land use, and related modifications in soil organic matter dynamics, may have occurred nor do they tell us anything about the nature of these changes. Nevertheless, the available numerical data should be stored in WISE as they provide the best (and only) alternative available today for geo-referenced quantitative studies of e.g., soil carbon at the global level. Similarly, of necessity Kimble *et al.* (1990) did not consider differences in 'cropping systems and native vegetation' in their study of organic carbon in tropical and temperate soils. The alternative of compiling 'synthetic carbon profiles' for the major soil units, as has been done by Bouwman (1990a), is not considered the most suitable alternative for application in a geo-referenced soil data base. The use synthetic soil profiles has been shown to be unpractical in the World Soils and Terrain Digital Data base (Van Engelen and Pulles, 1991).

5.6   Conclusions

The understanding of the global carbon cycle markedly has improved in recent years, an now permits the development and testing of dynamic models (Bolin, 1986a; Esser, 1990; Goudriaan, 1989), yet there remain several sources of uncertainty. While the CO_2 emissions associated with fossil fuel burning, ocean-atmosphere transport and wide scale deforestation/biomass burning are fairly well understood and quantified in the global budget some of the carbon is still 'missing' if the budget is to be balanced. These uncertainties to a large degree seem to be related to the still poorly understood role of terrestrial biota and soils in the turnover of carbon.

Quantification of the past and present global exchange of atmospheric CO_2 associated with growth of terrestrial plants and soil respiration remains difficult in view of the ubiquitous, and spatially and temporarily diverse nature of the underlying physical, chemical and biological processes. The greatest challenge to the projections of General Circulation Models may well come from the realm of biology as these elaborate models essentially operate within the confines of physics and physical chemistry (Idso, 1991). So far, they account little for the complex functioning of the living world.

An important topic of discussion relates to how the fertilization effect of enhanced levels of atmospheric CO_2, and other atmospheric pollutants, will affect the carbon flow in terrestrial ecosystems through its effect on photosynthesis, the distribution of photosynthates over aerial and subaerial parts, the 'quality' of these photosynthates, their decay in litter and soil, and ultimately the effect on soil organic mater reserves. How will the biological processes be influenced, for instance, by acid deposition or alternatively eutrophication associated with agricultural, urban and industrial activities? What will be the nature of the carbon feedback from different ecosystems, also seen in the perspective that the latitudinal and altitudinal boundaries of ecosystems are likely to shift as a result of possible regional and seasonal changes in temperature and rainfall associated with global warming? Can the present biota 'cope' with the anticipated, relatively rapid nature of the predicted climate change? And how will this affect future biotic diversity? Or what will be the consequences of the increasing human population and related increased demands for arable and urban land for the size of the terrestrial carbon pool? These are but a few of the sources of uncertainty that still need to be resolved to better understand the effects of biota on soil carbon reserves in terms of sequestering of atmospheric CO_2. Within the framework of the related modelling activities there would be a clear need for up to date and geo-referenced information on selected 'key properties' (e.g., organic C; C/N ratio; texture; bulk density) of the FAO soil units of the world. This type of data will be included in the WISE data base. As such, it could be used to refine the still widely varying estimates of current soil carbon pools, show how the soil carbon reserves are geographically distributed on a global terrestrial grid, and provide critical input for e.g. vegetation-succession models.

Chapter 6 The WISE data base: general considerations on a possible structure and attribute data

N.H. Batjes

6.1 Introduction

6.1.1 Background

Since the early days of pedology soil surveys have been carried out in the various countries of the world according to different field and laboratory methodologies, classification systems and mapping approaches (Brady, 1984; Duchaufour, 1982; FAO, 1988; Fitzpatrick, 1983; USDA, 1975). Integration of this wealth of information on soil conditions into global soil maps is an intricate procedure, necessitating intensive correlation activities based on well described and uniform procedures. Well known examples of global soil maps include the 1:5 M scale Soil Map of the World (SMW; FAO/Unesco, 1971-1981), the 1:15 M scale map produced by Glazovskaya and Friedland (1982) and the 1:50 M scale map published by the United States Department of Agriculture in collaboration with the Soil Conservation Service (USDA/SCS, 1972). Of these 'world soil maps', the one developed by FAO/Unesco is most widely used internationally.

The first applications of SMW mainly concerned the compilation of a World Map of Desertification (FAO/Unesco/WMO, 1977), crop yield forecasting within equivalent agro-ecological zones (FAO, 1978-1981) and an assessment of the carrying capacity of land (FAO/UNFPA/IIASA, 1982). Since then there has been a gradual shift towards environmental issues such as erosion, pollution and emissions of greenhouse gases. Most modelling studies of processes of global change involving soils are based on either 1 x 1 or ½ x ½ degree resolution data bases, digitized from the printed Soil Map of the World, which only retained information about the spatially dominant soil unit of each grid cell (e.g. Gildea and Moore, 1985; Zobler, 1986). This means a wealth of the original information on associated- and included soil units has been lost for interpretative purposes during the griding process.

Since the time of production of SMW new information on map unit boundaries and map unit composition has been obtained for many areas of the world, including the Amazon basin of South America, large sections of Africa (Endale and Hakkeling, 1987) and the European Communities (Tavernier, 1985). New national soil surveys since the 1970s have also lead to the preparation of a Revised Legend (FAO, 1988), which has already been used in a 1:25 M global soil resources mapping activity (FAO, 1991a) and at a scale of 1:1 M for part of Northern Africa. For some parts of the world, the topographical base map of SMW needs to be updated (Van Velthuizen, 1992).

Sombroek (1985) prepared a discussion paper on the possible establishment of an 'International Soil and Land Resources Information Base'. This led to a proposal for developing a 1:1 M, digital World Soils and Terrain Data base (SOTER), which was officially endorsed during the 13th International Soil Congress at Hamburg (ISSS, 1986a, 1986b). Since then ISRIC has coordinated the SOTER development activities (see Van Engelen and Pulles, 1991). Pending world coverage in SOTER, which is scheduled to take from 10 to 20 years in view of the large scientific and logistic magnitude of the task, there remains a pressing demand for 'up to date' information on soil boundaries and soil attributes in a widely accessible digital format (Bliss, 1990; Matthews, 1990; Moore *et al.*, 1989; Oldeman and Sombroek, 1990). This prompted the International Soil Reference and Information Centre (ISRIC) to implement a project on 'World Inventory of Soil Emission Potentials' (WISE) which is complementary to the activities of SOTER and ISIS, ISRIC's Soil (Pedon)

Information System. A key objective of WISE is to develop, within a time-frame of 2 years, a 30 minutes longitude by 30 minutes latitude world soil data set that is linked to a pedon data base. The geographical distribution of soils within each grid cell will be derived from the cleaned digital version of SMW, prepared by FAO-AGLS in 1992.

Upon its completion, the WISE data base would form an essential 'data layer' of a global Geographical Information System on natural resources. Other critical data layers in such a GIS include climate, geology, hydrology and land use/cover (Moore *et al.*, 1989; Oldeman and Sombroek, 1990). Ideally, a link to non-biophysical attributes, such as population density, should be provided also. Ultimately, these data base development activities should result in an 'integrated' global GIS. Such a system will provide scientists with a comprehensive data set to model possible consequences of different scenario's of environmental change, providing a better basis for policy makers to identify recommended policy options.

6.1.2   Structure of chapter

A possible procedure for developing the WISE data base is presented in this Chapter. Implications of the 1:5 M map scale and use of 30' x 30' grid cells for the spatial and attribute data that can be considered are made in Section 6.2. A proposed structure and tentative list of key-attributes are presented in Section 6.3 and Appendix II. This set of key-attributes is based on the findings of Chapters 2 to 5, with due attention for the availability, comparability and compatibility of the respective data sets at the international level. In Section 6.4, technical constraints that may be encountered when developing global soil data bases are discussed. The general way to proceed in developing the data base, as recommended by the WISE workshop, is presented in the final Section.

6.2   Implications of scale of mapping for the spatial and attribute data

6.2.1   Spatial attributes

A proposed application of the WISE data base within the context of the Netherlands National Research Programme on Global Air Pollution and Climate Change (NOP) is to refine estimates of soil-borne methane emissions. The WISE data base thus must provide as good as possible an indication of the geographical distribution of potential methane-producing soils, particularly peat soils and hydromorphic soils, and quantify their process controlling soil factors (i.e. be 'attribute-oriented').

Smallest mappable area

The basic cartographic requirement for delineating a map unit at any scale is that it should have a minimum area of 0.25 cm^2 on the map. On a 1:5 M scale map this corresponds with 625 km^2 or 25 by 25 km in the field whereas at a scale of 1:50,000 this would be 0.25 by 0.25 km. This has clear consequences for the soil patterns that can be visualized on a map at a particular scale. Using different maps from a section of Côte d' Ivoire, Van Diepen (1985) showed that the proportion of hydromorphic soils was estimated to be 0% at 1:5 M scale (FAO/Unesco, 1971-1981), 3 % at 1:2 M scale, 9 % at 1:0.5 M scale, 11 % at a scale of 1:200,000, and 17-29 % for 1:50,000 scale maps. This example shows that a 1:5 M scale soil map, such as SMW, can only give a rough indication of the extent of hydromorphic soil units. At the considered scale, the hydromorphic soil units often have been mapped as 'inclusions'. By its nature, small scale mapping

necessitates a marked degree of data integration with respect to both the spatial and attribute data, the aim being to simplify the geographical distribution of soils to a regionally representative pattern of spatially dominant soil units.

Soil Map of the World map unit composition

The mapping units or 'vector-units' of the Soil Map of the World are associations consisting of a spatially dominant soil unit with or without associated and included soil units. By definition the associated soil units cover at least 20 % of the area of an association, while included soil units cover less than 20%. The map units are further defined by the textural class(es) of the upper 30 cm of the dominant component soil unit. Slope classes refer to those which dominate in the area of a soil association. Where data on texture or slope classes are lacking, they are omitted from the map unit codes (FAO/Unesco, 1981 p. 5). In this case, the slope and texture classes of component soil units are derived from the 'Composition Rules' (FAO, 1991b). Where relevant, phases are indicated on the map as overprints on the colour of the association (FAO/Unesco, 1974). Phases are used to indicate where hard or indurated layers occur at shallow depth or to show stoniness, alkalinity or salinity. Phases do not relate to any soil unit in particular, but are subdivisions of map units based on characteristics which are significant for the use or management of land. When the phase is present in the map unit symbol it applies to the dominant soil unit, all associated and included soil units being considered unaffected (FAO, 1991b).

A broad analysis of the relative area covered by the dominant soil unit of associations on the 1:1 M scale map of the European Communities (EC) showed that most dominant soil units cover only 40-80 % of the area of a soil association (Reinds *et al.*, 1992). Summed, the dominant soil units cover about 60 % of the total EC-area.

The properties of some of the associated and included soil units may be similar to those of the spatially dominant soil unit of an association, but the opposite may be true also. This is rather crucial information in studies in which the focus essentially is on 'problem' soils, such as methane-producing hydromorphic soils, which often are not the most extensive soil units. Conversely, in yield forecasting at the macro-level there is less need for information on the associated and included soil units because an indication of the overall production potential of a map unit is generally needed.

The above discussion shows that the composition and heterogeneity of each association of SMW deserves careful consideration when compiling the spatial information (i.e. composition of the 30' x 30' grid cells) for the WISE data base. The most 'simple' association consists of one single soil unit, while the most intricate one comprises 3 associated soil units and 4 included soil units (FAO, 1991b). Overlaying a 30' x 30' lattice over the printed SMW shows that, on average, each grid cell may consist of 1 to 5 different soil associations. The relative extents of the dominant, associated and included soil units of these associations can be derived from the map unit symbols, using the 'Composition Rules' (FAO, 1991b).

In the case of the 1:1 M map of the European Communities, Van Lanen *et al.* (1992) of necessity assumed that the attribute data and 'management' conclusions for the spatially dominant component soil unit of an association apply to the whole area of this association, that is also to its associated and included soil units. Similarly, in a study of the 'flat wetlands of the World', Van Dam and Van Diepen (1982) made an inventory of the map units of SMW as if they were homogeneous and would consist only of the dominant soil unit. This type of assumption is not considered appropriate in the context of the WISE project.

A 'complicating' factor in WISE is that the data base needs to present information on the typology and relative extents of all potential methane-producing soils, as derivable from SMW. These hydromorphic soils often have been mapped as associated- and included soil units. Consequently, the WISE workshop recommended that the area-data on the hydromorphic soil units (type and relative extent within a 30' x 30' cell) be stored in WISE, taking into account both the dominant, associated and included soil units (see Batjes, 1992). A procedure to calculate the relative extent of the component soil units within a 30' x 30' grid cell is being elaborated.

It remains to be ascertained in how far the original information on topsoil texture, slope classes and phases shown on SMW can be retained in a scientifically sound manner during the compilation of the WISE grid-map. For instance, in the case of a dominant soil unit with compound topsoil texture and slope classes, the relative area of each component soil unit that is covered by the respective texture and slope classes is difficult to infer with confidence (Reinds *et al.*, 1992; see also Verheye, 1987). The latter even more so when both the dominant-, associated- and included soil units have to be considered. A commonly used assumption has been that each 'texture-slope' subunit covers equal parts of the area of the soil association. Indiscriminate application of this 'rule' to the topsoil, slope class and phases may easily lead to the creation of large and unmanageable files with 'derived-data' of low reliability, and hence limited practical significance. Reinds *et al.* (1992), for instance, showed that the derived-data for topsoil and slope cannot be applied to about 40 percent of the EC-area.

6.2.2   Linking of spatial and attribute data

There is a marked demand for quantitative data or techniques for land use planning and environmental research (Driessen, 1986a; Gardiner, 1987; IGBP, 1990; Bouma and Bregt, 1989; Bouwman, 1990a; Van Lanen and Bregt, 1989; Braatz and Hogan, 1991; Groenendijk, 1990; Reinds *et al.*, 1992; IGBP-DIS meeting at Silsoe, October 1992). For the WISE data base to provide this kind of information, it will be necessary that soil profile data be linked into the area-data of the 30' x 30' grid cells. The assumption will be that the respective soil units of a 30' x 30' grid differ markedly in their attributes, whereas 'individual' soil units are considered to be homogeneous in their properties.

Most soil units on the printed SMW have been characterized using one single soil profile (see e.g. FAO/Unesco, 1971-1981, Vol. V p. 91). This means that the attributes of these profiles are considered to be 'representative' for the component-soils of this soil unit, irrespective of its geographical location. In practice, this assumption may not be appropriate. Although soils of a particular FAO soil unit by definition have common diagnostic horizons and properties - which reflect the result of similar processes of soil formation - they will, by nature, differ in some of their properties from one region to the other. A dark, cracking and swelling clay soil (Pellic Vertisol) from Spain, for instance, will be similar yet not identical to a Pellic Vertisol from Belize. Soil profiles considered representative for a particular soil unit therefore, ideally, should be presented on a region-by-region basis with reference to the local climate, relief, geology and possibly land use. The WISE data base thus should include a data file of soil profiles considered representative for each soil unit in the various regions of the globe (e.g. stratified by climate and parent material). The relevant soil profiles should be selected by regional soil correlators using standardized procedures. As the number of soil profiles available per soil unit in a given region increases, the range in measured characteristics of this soil unit can be quantified better (e.g. median value, extremes and 90%-confidence intervals). A complicating factor in this respect is that cross-border correlation of analytical

results may be cumbersome (see Section 6.3.3.). Since WISE is a short-term project, a pragmatic approach must be adopted when collecting a set of regionally representative soil profiles.

6.2.3 Updating the Soil Map of the World

Both the boundaries and composition of map units shown on SMW are now known to be out-of-date for several areas of the globe. Out of 158 countries, 68 per cent now have complete national soil maps at a scale of 1:1 M or larger, while 32 % are still updating their maps. In terms of acreage covered, this corresponds with about 30 % of the world, excluding Antarctica, having been updated (FAO, 1991a).

During the initial SMW map compilation activity, much of the information on landforms and lithology has been discarded. In any full-scale update of SMW, the latter should be reflected in the map symbols and/or in the data base (see Van Velthuizen, 1992). During such an overall recompilation activity, in which physiographic and soil boundaries are to be redrawn to match current knowledge, the criteria of the Revised Legend (FAO, 1988) can readily be introduced. This 'ideal-case' scenario extends beyond the possibilities of finance and time of the WISE project and rather falls into the activities of SOTER. The initial focus in the WISE project thus should be on better quantification of the soil attribute data for the various FAO soil units.

Application of the Revised Legend (FAO, 1988), which includes several new classification concepts, to the current SMW may lead to interpretation problems, as straight conversions are not always possible without having reference to the original data sources. During the initial correlation of the legends and maps from various countries of the world to group soils using the original Legend (FAO/Unesco, 1974), the same map unit symbols may have been given to map units with somewhat different contents. This may make it difficult to apply the Revised Legend to the component soils of map units for areas for which no new soil data have been gathered. Consequently, the original Legend of SMW must be retained in the WISE data base.

6.3 The WISE data base

6.3.1 General

An important consideration in developing any soil data base is: what kind of data do users need to derive from it, how can this information be derived, and how should it be presented to the user? The first question is difficult to answer because all possible applications of a 30' by 30' data base for global environmental research cannot be anticipated. Often, sensitivity analyses will have to show which are the relevant soil factors at a particular scale (parameterization of models). Conversely, WISE can only present information on those soil characteristics that are widely available from 'routine' soil surveys.

As a first approximation, information on the range of characteristics of a soil unit can be derived from its classification using expert-based decision-rules (see Sombroek, 1990; Van Breemen and Feijtel, 1990; Reinds et al., 1992; Verheye, 1987). This essentially qualitative information may be used to rate process-controlling soil-factors as 'scalars' (e.g. Bouwman et al., 1992). For WISE to have maximum applicability, it will need to be supported by a suite of soil profile data in digital format.

Figure 6.1.   Schematic representation of the proposed WISE data base

6.3.2   Proposed data base structure for WISE

The proposed data base for WISE would include (Figure 6.1):

-        File 1: Information on individual 30' x 30' grid cells and their component FAO soil units, corresponding with the area-data.
-        File 2: A file with the range in characteristics of the topsoil and subsoil of the respective FAO soil units. Initially, this file would be derived using a limited number of soil profiles.
-        File 3: A file of 'actual' soil profile data for the respective FAO soil units, with attached a subfile listing the analytical methods (see Appendix II).

6.3.3   Acquisition of soil profile data

WISE is dependent upon existing soil profile data, which will have to be retrieved from national data bases or survey reports. It will not always be possible to obtain complete data sets for each profile. Very few soil survey reports present data on physical soil characteristics such as bulk density, water holding characteristics and saturated hydraulic conductivity according to a survey of 146 soil resources inventories from 46 countries (Msanya, 1987). Similarly, few of the 40 representative pits listed in the explanatory booklets to the 1:1 M scale soil map of the European Communities (EC) and 1:5 M Soil Map of the World include data on water holding capacity and bulk density. With respect to potential methane-production, it may be cumbersome to infer information on critical soil factors, such as the free-iron content and redox buffering capacity, and particularly information on their seasonal dynamics. Similarly, it may prove difficult to obtain/derive data on the albedo and surface roughness, variables which play an important role in the surface heat balance, from routinely collected soil data. Albedo, for instance, is strongly influenced by slope direction (aspect), altitude and land use practices/vegetation cover besides topsoil colour and topsoil moisture content. An additional

problem in estimating albedo is relating measurements made in limited segments of the spectrum to the complete band width that has to be considered (Townshend, 1992 p. 18).

Besides information about the type of FAO soil unit, its estimated relative extent within a 30' x 30' grid cell, the aspect, slope, drainage class, parent material, land use and average depth of soil at the site, the WISE workshop proposed that File 2 should also include bulk density, structure, particle size class, stoniness class, water holding capacity, total organic carbon, type of organic matter (C/N ratio), soil reaction (pH), cation exchange capacity and content of $CaCO_3$ for both the topsoil and subsoil (Batjes, 1992).

The proposed list of attributes for File 3, as shown in Appendix II, was drafted with reference to Chapters 2 to 5, the list of attributes published for representative soil profiles in the 1:1 M Soil Map of the European Communities (Tavernier, 1985) and 1:5 M Soil Map of the World (FAO/Unesco, 1971-1981), and ISIS and SOTER (Van Waveren, 1987; Van Engelen and Pulles, 1991). This list will be fine-tuned as the soil profile collection programme and data base development proceeds.

The pedon data will be stored and manipulated with a database management system derived from ISIS (Van Waveren and Bos, 1988). Earlier, ISIS formed the basis for developing SDB, the Soil Data Base system of FAO/ISRIC (1989). The procedures of ISIS, which are written in the dBase III$^+$ programming language, are being adapted to handle the attribute data selected for WISE. of WISE.

6.4   Discussion

Given WISE's dependence upon existing soil data sources, the accuracy of the spatial and attribute data will be largely predetermined and vary within and between the 'source materials'. Each country, for instance, has its own methods of soil sampling and soil analyses. The results of these analyses are not necessarily comparable without adequate correlation (FAO/Unesco, 1971-1981, Volume V p. 91; Gardiner, 1987; Pleijsier, 1989; Van Reeuwijk, 1983). To a large extent this 'correlation' problem can be circumvented when the representative profiles are derived from a system such as ISIS (Van Waveren, 1987; Van Waveren and Bos, 1988). This reference pedon data base on FAO soil units contains only soil profiles whose characteristics have been determined according to uniform and standardized analytical procedures in one laboratory (Van Reeuwijk, 1992), with subsequent 'quality control' based on a scheme of cross-checks. As the ISIS data base mainly focuses on soils from tropical regions, it will be necessary to obtain soil profiles for other regions from national soil survey organizations (e.g., Soil Conservation Service at Lincoln, Nebraska; ORSTOM, France), either in a digital or manuscript form. The need for international cooperation in this respect has been highlighted during an IGBP-DIS/GCTE workshop on Global Soil Data Bases in Silsoe (October 1992).

The use of a limited number of 'representative' soil profiles in a 1:5 M mapping exercise encompasses a simplification of real-life spatial and temporal variability in soil characteristics. However, there seem to be no valid alternatives for developing small scale soil data bases (Van Engelen and Pulles, 1991). The uncertainties associated with spatial and temporal variability of soil properties at different scales (Bouma and Bregt, 1989; Mausbach and Wilding, 1991; Bregt, 1992), and the development and parametrization of procedures for 'scaling-up' site gas flux data to the macro-level in a Geographical Information System are still inadequately understood (Burrough, 1989; Roswall *et al.*, 1988; Walker and Graetz, 1988). There remains a clear need for coordinated efforts to refine global estimates of trace gas fluxes into the atmosphere (Figure 6.2). To enhance the usefulness of published site and trace gas flux measurement data, these should

be measured according to standardized methods with quality control, and be supplemented with detailed information on so-called key site-attribute data (e.g., climate, land use, soils, land management practices). The site attribute data should be described using internationally accepted and well defined terms to permit international correlation of research findings.
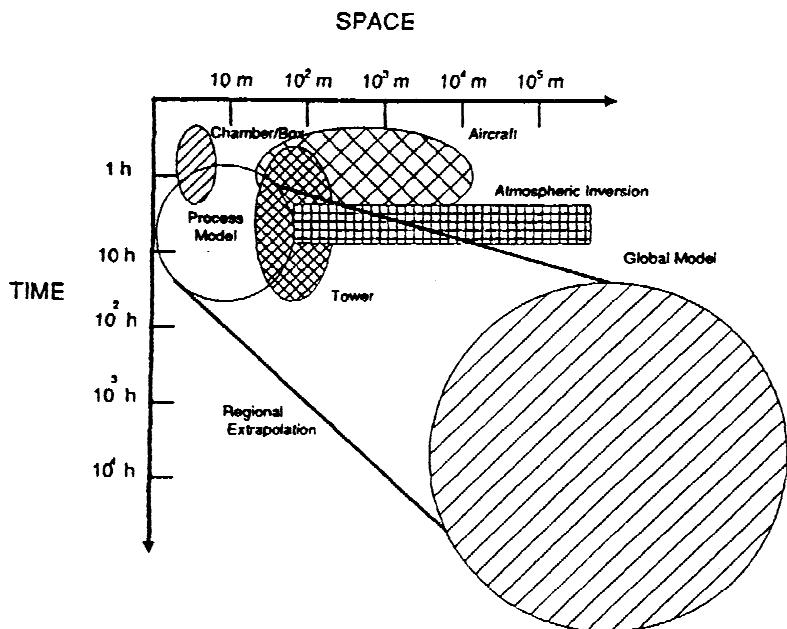
SPACE

Figure 6.2   Visualization of the importance of time and space in the 'scaling up' of biogenic gas fluxes from the site-level to the macro-level (Source: IGBP, 1990 p. 60)

Descriptive terms such as 'acid clay' and 'forest soil', for instance, are commonly encountered in articles on trace gas fluxes from terrestrial ecosystems. These terms form a very meagre basis for trying to decipher the role of the respective soil factors on the production (or consumption), transfer and emission of individual trace gases from a particular terrestrial ecosystem. Soil profiles at all measurement sites should be described according to uniform and internationally accepted standards, such as the 'Guidelines for Soil Description' (FAO/ISRIC, 1990), and classified according to the FAO Legend and the national system of soil classification.

The aspect of data compatibility between WISE and 'auxiliary' global data bases deserves careful consideration to ensure its wide applicability in studies of environmental change. The common absence of information about the accuracy of 'traditional' and digital versions of cartographic products and their associated attribute data can lead to difficulties in spatial analyses, as the data will have to be taken at 'face value' despite obvious errors inherent in assuming homogeneity (Goodchild, 1988). This problem will be compounded in GIS-applications where maps with different accuracy attributes are combined to produce new output (Smith *et al.*, 1987).

Logistic and computer-technical aspects of importance when building and managing large data bases for global science have been discussed, amongst others, by Mounsey (1988) and Buchman *et al.* (1990).

6.5   Conclusion

The cleaned, digital version of the Soil Map of the World forms the best common denominator for defining the geographic distribution of major soil units at the global level. In its present form, it permits a qualitative evaluation of the nature, geographical extent and 'management aspects' of world soils. The aim of WISE is to develop a soil profile data base which is linked to a 30' x 30' grid version of the cleaned-version of the Soil Map of the World. Such a data base would form an improvement on existing soil data bases derived from the original, printed version of SMW (e.g. Zobler, 1986). An important and unresolved point of discussion relates to the identification of the data sets modellers would require for their respective studies in relation to the basic soil data sets that can be presented in a digital data base linked to a 1:5 M scale map.

The 'cleaned' digitized version of SMW provides the best available geographical basis for developing the WISE data base. The data base development activities, as recommended by the WISE workshop, include:
 (1)   Rasterization of the cleaned SMW vector-map to a 30' x 30' grid, and computerized generation of files specifying the typology and relative extents of the component soil units of the grid cells.
 (2)   Improving the knowledge about soil attributes for each FAO soil unit, initially by inferring them from algorithms based on a limited number of soil profiles.
 (3)   Providing statistically reliable information on data shown within the map units, with reference to a gradually increasing number of regionally representative soil profiles (e.g. stratified by climate and parent material), keeping in mind the possibility of data acquisition at the global level.
 (4)   Revision of grid-information as sections of SMW are being updated. (These areas are to be flagged in the WISE data base).

The aspect of variable quality and 'spatial relevance' of soil data is recognized as being a 'sensitive' issue in any soil database compilation activity. Since WISE is a short-term project, a pragmatic approach must be adopted when collecting a set of regionally representative soil profiles.

Once the WISE data base is complete (stages 2 and 3), a procedure to refine estimates of potential methane production in natural and man-made wetland soils can be tested. A possible way to proceed has been formulated during the WISE workshop. However, much innovative work still has to be carried out with respect to model development, parametrization and calibration.

The primary responsibility for keeping the Soil Map of the World up-to-date resides with its *auctor intellectualis,* the Food and Agricultural Organization. A complete updating activity will require financing for a long-term programme. FAO has prepared a proposal to update SMW at a scale of 1:5 M which is to include: use of a new standard topographic base (ONC series), use of geomorphological entries at the first level for differentiating mapping units, and differentiation of soils according to the Revised Legend (Van Velthuizen, 1992). In view of similarities with the aims and procedures of the SOTER programme, the methodology of which has recently been endorsed by FAO, ISRIC, ISSS and UNEP, cooperation of FAO with ISRIC also would be very beneficial with respect to this 'full-scale' updating activity of soil information at the global level.

References

Abbeel, R. van den, A. Claes and K. Vlassak, 1989. Gaseous nitrogen losses from slurry manured land. In: *Nitrogen in organic wastes applied to soils* (eds A. Hansen and K. Henriksen). Academic Press, London. p. 213-244.

Abou-Seada, M.N.I. and J.C.G. Ottow, 1985. Effect of increasing oxygen concentration on total denitrification and nitrous oxide release from soil by different bacteria. *Biology and Fertility of Soils* **1**: 31-38.

Abou-Seada, M.N.I. and J.C.G. Ottow, 1988. Effect of soil properties on the quantity and quality of denitrification with different bacteria (In German with English summary). *Zeitschrift für Planzenernährung und Bodenkunde* **151**: 109-115.

Adams, J.M., H. Faure, L. Faure-Denard, J.M. McGlade and F.I. Woodward, 1990b. Increases in terrestrial carbon storage from the Last Glacial maximum to the present. *Nature* **348**: 711-714.

Adams, R.M., C. Rosenzwieg *et al.*, 1990a. Global climate change and US agriculture. *Nature* **345**: 219-224.

Aerts, R., N. Berendse, M. Klerk and C. Bakker, 1988. Root production and root turnover in two dominant species of wet heathlands. *Oecologia* **81**: 374-378.

Agren, G.I. and E. Bosatta, 1987. Theoretical analysis of the long-term dynamics of carbon and nitrogen in soils. *Ecology* **68**: 1181-1189.

Aiken, G.R., D.M. McKnight, R.L. Wershaw and P. MacCarthy, 1985a. An introduction to humic substances in soil, sediments and water. In: *Humic substances in soil, sediment, and water* (eds G.R. Aiken, D.M. McKnight and R.L. Wershaw). John Wiley, New York. p. 1-9.

Aiken, R.M., M.D. Jawson. K. Grahammer and A.D. Polymenopoulos, 1991. Positional, spatially correlated and random components of variability in carbon dioxide efflux. *Journal of Environmental Quality* **20**: 301-308.

Alexander, M., 1977. *Introduction to soil microbiology* (2nd Edition). John Wiley and Sons, New York.

Allison, L.E., 1965. Organic carbon. In: *Methods of soil analysis, part 2: Chemical and microbiological properties* (C.A. Black et al.). Agronomy 9:771-1572, American Society of Agronomy, Madison, Wisconsin.

Almendos, G., F.J. Gonzalez-Vila and F. Martin, 1990. Fire-induced transformations of soil organic matter from an oak forest: An experimental approach to the effects of fire on humic substances. *Soil Science* **149**: 158-168.

Alperin, M.J. and W.S. Reeburgh, 1985. Inhibition experiments on anaerobic methane oxidation. *Applied and Environmental Microbiology* **50**: 940-945.

Amundson, R.G. and E.A. Davidson, 1990. Carbon dioxide and nitrogenous gases in the soil atmosphere. *Journal of Geochemical Exploration* **38**: 13-41.

Anderson, J.M. and J.S. Ingram (eds), 1989. *Tropical soil biology and fertility: A handbook of methods.* C.A.B. International, Wallingford.

Anderson, D.W., S. Saggar, J.R. Bettany and J.W.B.Stewart, 1981. Particle size fractions and their use in studies of soil organic matter. I. The nature and distribution of forms of carbon, nitrogen, and sulphur. *Soil Science Society of America Journal* **45**: 767-772.

Anderson, D.W. and E.A. Paul, 1984. Organo-mineral complexes and their study by radiocarbon dating. *Soil Science Society of America Journal* **48**: 298-301.

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

Anderson, J.M. and P.W. Flanagan, 1990. Biological processes regulating organic matter decomposition in tropical soils. In: *Dynamics of soil organic matter in tropical ecosystems* (eds D.C. Coleman, J.M. Oades and G. Uehara), NifTAL Project, University of Hawaii Press, Honolulu. p. 97-123.

Arah, J.R.M. and K.A. Smith, 1989. Steady-state denitrification in aggregated soils: a mathematical model. *Journal of Soil Science* **40**: 139-149.

Armentanao, T.V. and E.S. Menges, 1986. Patterns of change in the carbon balance of organic soil in wetlands of the temperate zone. *Journal of Ecology* **74**: 755-774.

Arnold, R.W., I. Szabolcs and V.O. Targulian, 1990. *Global soil change: Report of an IIASA-ISSS-UNEP task force on the role of soil in global change.* International Institute for Applied Systems Analysis, Laxenburg.

Arrhenius, S. 1896. On the influence of carbonic acid in the air upon the temperature of the ground. *The Philosophical Magazine*, Series 5, volume **41**, No. 251. (Reprinted in Tisglow 1992, **3**: 3-26)

Asami, T. and Y. Takai, 1970. Relation between reduction of free iron oxides and formation of gases in a paddy soil (in Japanese with English summary). *Journal of Science of Soil Manure* **41**: 48-55.

Aselmann, I. and P.J. Crützen, 1990. A global inventory of wetland distribution and seasonality, net primary productivity, and estimated methane emissions. In: *Soils and the greenhouse effect* (ed. A.F. Bouwman). John Wiley and Sons, Chichester. p. 441-449.

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

Ayanaba, A. and D.S. Jenkinson, 1990. Decomposition of Carbon-14 labelled rye grass and maize under tropical conditions. *Soil Science Society of America Journal* **54**: 112-115.

Bacastraw, R.B., C.D. Keeling and T.P. Whorf, 1985. Seasonal amplitude increase in atmospheric CO_2 concentration. *Journal of Geophysical Research* **90**: 10529-10540.

Bachelet, D. and H.U. Neue, 1992. Methane emissions from wetland rice areas of Asia. *Chemosphere* (in press)

Bagine, R.K.N., 1989. Plant litter consumption by termites in an arid environment of northern Kenya. *Sociobiology* **15**: 113-124.

Bailey, L.D., 1976. Effect of temperature and roots on denitrification in a soil. *Canadian Journal of Soil Science* **56**: 79-87

Bailey, L.D. and E.G. Beauchamp, 1973. Effects of temperature on NO_3^- and NO_2^- reduction, nitrogenous gas production, and redox potential in a saturated soil. *Canadian Journal of Soil Science* **53**: 213-218.

Balesdent, J., 1987. The turnover of soil organic fractions estimated by radiocarbon dating. *Science of Total Environment* **62**: 405-408.

Balesdent, J., G.H. Wagner and A. Mariotti, 1988. Soil organic matter turnover in long-term field experiments as revealed by Carbon-13 natural abundance. *Soil Science Society of America Journal* **52**: 118-124.

Balesdent, J., J.-P. Petraud and C. Feller, 1991. Effets des ultrasons sur la distribution granulometrique des matieres organiques des soils. *Science du Sol* **29**: 95-106.

Ball, B.C., M.F. O'Sullivan and R. Hunter, 1988. Gas diffusion, fluvial flow and derived pore continuity indices in relation to vehicle traffic and tillage. *Journal of Soil Science* **39**: 327-339.

Barnes, I., W.P. Irvin and D.E. White, 1984. *Map showing world distribution of CO_2 and major zones of seismicity.* Misc. Investigation Series Map I-1528, Dept. of the Interiors, U.S. Geological Survey.

Bartels, U., 1990. Organic Carbon deposited by rainfall into spruce and beech forests in North Rhine-Westfalia (In German with English summary). *Zeitschrift für Planzenernährung und Bodenkunde* **153**: 125-127.

Bartlett, K.B., R.C. Harriss and D.I. Sebacher, 1985. Methane flux from coastal salt marshes. *Journal of Geophysical Research* **90**: 5710-5720.

Bartlett, K.B., D.S. Bartlett, R.C. Harriss and D.I. Sebacher, 1987. Methane emissions along a salt marsh salinity gradient. *Biogeochemistry* **4**: 183-202.

Bartlett, K.B., P.M. Crill, D.I. Sebacher, R.C. Harriss, J.O. Wilson and J.M. Melack, 1988. Methane fluxes from the central Amazonian floodplain. *Journal of Geophysical Research* **93**: 1571-1582.

Bartlett, D.S., K.B. Bartlett, J.M. Hartman, R.C. Harriss, D.I. Sebacher, R. Pelletier-Travis, D.A. Dow and D.P. Brannon, 1989. Methane emissions from the Florida Everglades: Patterns of variability in a regional wetland ecosystem. *Global Biogeochemical Cycles* **3**: 364-374.

Batjes, N.H. (ed.), 1992. *World Inventory of Soil Emissions: Report of working group discussions and recommendations.* Proceedings of an international workshop organized in the framework of the Netherlands national Research Programme on Global Air Pollution and Climate Change (24-27 August 1992). WISE Report No. 1, International Soil Reference and Information Centre, Wageningen.

Batjes, N.H. and Bridges, E.M. (eds), 1991. *Mapping of soil and terrain vulnerability to specified chemical compounds in Europe at a scale of 1:5 M.* Proceedings of an International Workshop organised in the framework of the Chemical Time Bomb Projects of the Netherlands Ministry of Housing, Physical Planning and Environment and the International Institute for Applied Systems Analysis (Wageningen, 20-23 March 1991). Chemical Time Bombs Project and International Soil Reference and Information Centre, Wageningen.

Batjes, N.H. and E.M. Bridges, 1992a. World inventory of soil emissions: Indentification and geographic quantification of soil factors and soil processes that control fluxes of CO^2, CH^4 and N^2O, and the heat and moisture balance (Background paper for discussion). Working Paper and Preprint No. 92/4, International Soil Reference and Information Centre, Wageningen.

Batjes, N.H. and E.M. Bridges (eds), 1992b. *World inventory of soil emission potentials.* Proceedings of an International Workshop organized in the framework of the Netherlands National Research Programme on Global Air Pollution and Climate Change (NOP). WISE Report No. 2, International Soil Reference and Information Centre, Wageningen.

Bauer, A. and A.L. Black, 1981. Soil carbon, nitrogen and bulk density comparisons in two cropland tillage systems after 25 years and in virgin grasslands. *Soil Science Society of America Journal* **45**: 1166-1170.

Baver, L.D., W.H. Gardner and W.R. Gardner, 1972. *Soil Physics*, Fourth Edition, John Wiley, New York.

Bazzaz, F.A. and E.D. Fajer, 1992. Plant life in a CO_2 rich world. *Scientific American* **266**: 18-24.

Bazzaz, F.A. and W.E. Williams, 1991. Atmospheric CO_2 concentrations within mixed forest: Implications for seedling growth. *Ecology* **72**: 12-16.

Beauchamp, E.A. and A.G. Seech, 1990. Denitrification with dry- and wet-sieved soil aggregates. *Mitteilungen der Deutschen Bodenkundlichen Gesellschaft* **60**: 83-88.

Beauchamp, E., J.T. Trevors and J.W. Paul, 1989. Carbon sources for denitrification. In: *Advances in Soil Science*, Volume 10 (ed. B.A. Stewart). Springer Verlag, New York. p. 113-142.

Beck, L., 1989. Beech forest soil as habitat. I. Soil fauna and litter decomposition - an overview (In German with English summary). *Verhandlungen Gesellschaft für Okologie* **17**: 47-54.

Bekkering, T.D., 1992. Using tropical forests to fix atmospheric carbon: the potential in theory and practice. *Ambio* **21**: 414-419.

Benckiser, G., K. Haider and D. Sauerbeck, 1986. Field measurements of gaseous nitrogen losses from an Alfisol planted with sugar beets (in English). *Zeitschrift für Planzenernährung und Bodenkunde* **149**: 250-261.

Benckiser, G., G. Gaus, K.M. Syring, K. Haider and D. Sauerbeck, 1987. Denitrification losses for an Inceptisol treated with mineral fertilizer or sewage sludge. *Zeitschrift für Planzenernährung und Bodenkunde* **150**: 241-248.

Berkhout, J.A.A. and van Keulen, H., 1986. Potential Evapotranspiration In: *Modelling of Agricultural Production: Weather, Soils and Crops* (eds H. Van Keulen and J. Wolf), Pudoc, Wageningen.

Berner, A.R., 1991. A model for atmospheric CO_2 over Phanerozoic time. *American Journal of Science* **291**: 339-376.

Bertram, H.G., 1985. Verlauf der stabilen Kohlenstoffisotope in natürlich gewachsenen Profilen: Stratigraphisches Hilfmittel und Modellgrundlange. *Mitteilungen der Deutschen Bodenkundlichen Gesellschaft* **43**: 531-536.

Bertram, H.G., 1991. Carbon dioxide and climate: Climatic impact of soil-borne CO_2. In: *Diversity of environmental biogeochemistry* (ed. J. Berthelin). Elsevier, Amsterdam. p. 392-395.

Betlach, R.M. and J.M. Tiedje, 1981. Kinetic explanation for accumulation of nitrite, nitric oxide, and nitrous oxide during bacterial denitrification. *Applied and Environmental Microbiology* **42**: 1074-1084.

Beyer, L., 1991. Intersite characterization and variability of soil respiration in different arable and forest soils. *Biology and Fertility of Soils* **12**: 121-126.

Bidwell, O.W. and F.R. Hole, 1965. Man as a factor in soil formation. *Soil Science* **99**: 65-72.

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

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

Blake, D.R. and F.S. Rowland, 1988. Continuing worldwide increase in tropospheric methane. *Science* **239**: 1129-1131.

Bliss, N.B., 1990. A hierarchy of soil data bases for calibrating models of global climate change. In: *Soils and the greenhouse effect* (ed. A.F. Bouwman). John Wiley and Sons, Chichester. p. 523-529.

Bohn, H.L., 1982. Estimates of organic carbon in world soils: II. 1982. *Soil Science Society of America Journal* **46**: 1118-1119.

Bohn, H.L., 1990. Considerations for modelling carbon interaction between soil and atmosphere. In: *Soils and the greenhouse effect* (ed. A.F. Bouwman). John Wiley and Sons, Chichester. p. 391-394.

Bolin, B. (ed), 1981. *Carbon cycle modelling*. SCOPE 16, John Wiley and Sons, Chichester.

Bolin, B., 1986a. Requirements of a satisfactory model of the global carbon cycle and current status of modelling. In: *The changing carbon cycle: A global analysis* (eds. J.R. Trabalka and D.E. Reichle). Springer Verlag, New York. p. 403-424.

Bolin, B., 1986b. How much CO_2 will remain in the atmosphere? The carbon cycle and projections for the future. In: *The greenhouse effect, climatic change and ecosystems* (eds Bolin, B., B.R. Döös, J. Jäger and R.A. Warrick). SCOPE 29, John Wiley and Sons, Chichester. p. 93-155

Bolin, B., J. Jäger and B.R. Döös, 1986. The Greenhouse effect, climatic change, and ecosystems. A synthesis of present knowledge. In: *The greenhouse effect, climatic change and ecosystems* (eds B. Bolin, B.R. Döös and J. Jäger). SCOPE 29, John Wiley and Sons. p. 1-32.

Bolin, B., B.R. Böös, J. Jäger and R.A. Warrick (eds), 1986. *The greenhouse effect, climatic change and ecosystems*. SCOPE 29, John Wiley and Sons, Chichester.

Bollag, J.M. and G. Tung, 1972. Nitrous oxide release by soil fungi. *Soil Biology and Biochemistry* **4**: 271-276.

Bollag, J.M., S. Drzymal and L.T. Kardos, 1973. Biological versus chemical nitrite decomposition in soil. *Soil Science* **116**: 44-50.

Bolle, H.J., 1990. The effect of land use change on net radiation and its partitioning into heat fluxes. In: Bouwman A.F. (Editor), *Soils and the Greenhouse Effect*, John Wiley, Chichester. p. 329-342.

Bolle, H.J., W. Seiler and B. Bolin, 1986. Other greenhouse gases and aerosols: assessing their role for atmospheric radiative transfer. In: *The greenhouse effect climatic change and ecosystems* (eds B. Bolin, B.R. Döös, B.A. Warrick and D. Jager). SCOPE 29, John Wiley and Sons, New York. p. 157-203.

Bonde, T.A., 1991. *Size and dynamics of active soil organic matter fraction as influenced by soil management*. Linköping Studies in Arts and Science 63, Linköping University.

Bonde, T.A., T. Rosswall and R.L. Victoria, 1991. The dynamics of soil organic matter and soil microbial biomass following clear-felling and cropping of a tropical rainforest in the central Amazon. *Soil Science Society of America Journal* (submitted).

Bosatta, E. and G.I. Agren, 1991. Theoretic analysis of carbon and nutrient interactions in soils under energy limited conditions. *Soil Science Society of America Journal* **55**: 728-733.

Boudot, J.P., B.A. Bel Hadj and T. Choné, 1990. Dependence of carbon and nitrogen mineralization rates upon amorphous metallic constituents and allophanes in highland soils. *Geoderma* **42**: 245-260.

Bouma, J. and A.K. Bregt (eds), 1989. *Land qualities in space and time*. Pudoc, Wageningen.

Bouwman, A.F. (ed.), 1990a. *Soils and the greenhouse effect*. John Wiley and Sons, Chichester.

Bouwman, A.F., 1990b. Analysis of global nitrous oxide emissions from terrestrial, natural and agro-ecosystems. *Transactions 14th International Congress of Soil Science*, Kyoto **II**: 261-266

Bouwman, A.F., 1990c. Modelling soil organic matter decomposition and rainfall erosion in two tropical soils after forest clearing for permanent agriculture. *Land Degradation and Rehabilitation* **1**: 125-140.

Bouwman, A.F., 1991. Agronomic aspects of wetland rice cultivation and associated methane emissions. *Biogeochemistry* **15**: 65-88

Bouwman, A.F. and W.G. Sombroek, 1990. Inputs to climatic change by soils and agriculture related activities: Present status and possible future trends. In: *Soils on a warmer Earth* (eds H.W. Scharpenseel, H.W., M. Schomaker and A. Ayoub). Developments in *Soil Science* 20, Elsevier, Amsterdam. p. 15-30.

Bouwman, A.F. and K.W. Van der Hoek, 1991. *Analysis of soil and water borne emissions of nitrous oxide and methane in the Netherlands*. Report 736301010, National Institute of Public Health and Environmental Protection, Bilthoven.

Bouwman, A.F., I. Fung, E. Matthews and J. John, 1992. Global analysis of the potential for N_2O production in natural soils. (Submitted to *Global Biogeochemical Cycles*)

Bowden, W.A., 1986. Gaseous nitrogen emissions from undistubed terrestrial ecosystems: An assessment of their impacts on local and global nitrogen budgets. *Biogeochemistry* **2**: 249-279.

Bowden, W.B. and F.H. Boorman, 1986. Transport of nitrous oxide in soil water after forest clear cutting. *Science* **233**: 867-869.

Bowman, R.A., J.D. Reeder and R.W. Lober, 1990. Changes in soil properties in a Central Plains rangeland soil after 3, 20 and 60 years of cultivation. *Soil Science* **150**: 851-85..

Braatz, B.V. and K.B. Hogan, 1991. *Sustainable rice productivity and methane reduction research plan*. US Environmental Protection Agency, Office of Air and Radiation, Washington DC.

Brady, N.C., 1984. *The nature and properties of soils (Ninth edition)*. MacMillan Publishing Company, New York.

Brams, E.A., G.L. Hutchinson, W.P. Anthony and G.P. Livingston, 1990. Seasonal nitrous oxide emissions from an intensively managed, humid, subtropical grass pasture. In: *Soils and the greenhouse effect* (ed. A.F. Bouwman). John Wiley and Sons, Chichester. p. 481-487.

Bregt, A.K., 1992. *Processing of soil survey data.* Doctoral thesis, Agricultural University, Wageningen.

Bremer, E., W. Van Houtum and C. van Kessel, 1991. Carbon dioxide evolution from wheat and lentil residues as affected by grinding, added nitrogen, and the absence of soil. *Biology and Fertility of Soils* **11**: 221-227.

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

Bremner, J.M. and A.M. Blackmer, 1981. Terrestrial nitrification as a source of atmospheric nitrous oxide. In: *Denitrification, nitrification and atmospheric nitrous oxide* (eds C.C. Delwiche). Wiley and Sons, New York. p. 151-170.

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

Bridgham, S.D. and C.J. Richardson, 1992. Mechanisms controlling soil respiration (CO_2 and CH_4) in Southern peatlands. *Soil Biology and Biochemistry* **24**: 1089-1099.

Briffer, K.B., T.S. Bartholin, D. Eckstein, P.D. Jones, W. Karlen, F.M. Schweingruber and P. Zettenberg, 1990. A 1400 year tree-ring record of summer temperature in Fennoscandia. *Nature* **346**: 434-439.

Broeckner, W.S. and T.-H. Peng, 1992. Inter-hemispheric transport of carbon dioxide by ocean circulation. *Nature* **356**: 587-589.

Brotherton, F.P., 1990. Concluding remarks. In: Bouwman, A.F. (Editor), *Soils and the Greenhouse Effect*, John Wiley, Chichester. p. 355-361.

Brouwer, F.M., A.J. Thomas and M.J. Chadwick (eds), 1991. *Land use changes in Europe: Processes of change, environmental transformations and future trends*. Volume 18, The GeoJournal Library, Kluwer Academic Publishers, Dordrecht.

Brown, S. and A.E. Lugo, 1990. Effects of forest clearing and succession on the carbon and nitrogen content of soils in Puerto Rico and US Virgin Islands. *Plant and Soil* **124**: 53-64.

Bruchler, L., Ball, B.C. and Renault, P., 1989. Laboratory estimation of gas diffusion co-efficient and effective porosity in soils. *Soil Science* **147**: 1-10

Buchman, A., O. Günther, T.R. Smith and Y.F. Wang (eds), 1990. *Design and implementation of large spatial data bases*. Lecture notes in Computer Science No. 409, Springer Verlag, Berlin.

Buol, S.W., F.D. Hole and R.J. McCracken, 1973. *Soil Genesis and Classification*. Iowa State University Press, Ames.

Buresh, R.J., S.K. de Datta, M.I. Samson, S. Phongpan, P. Snitwongse, A.M. Fagi and R. Tejasarwana, 1991. Dinitrogen and nitrous oxide flux from urea basally applied to puddled rice soils. *Soil Science Society of America Journal* **55**: 268-273.

Buringh, P., 1984. Organic carbon in soils of the world. In: *The role of terrestrial vegetation in the global carbon cycle. Measurement by remote sensing* (ed. G.M. Woodwell). SCOPE 23, Wiley and Sons, New York. p. 91-109.

Burke, L.M. and D.A. Lashof, 1990. Greenhouse gas emissions related to agriculture and land use policies. In: *Impact of carbon dioxide, trace gases, and climate change on global agriculture*. (eds B.A. Kimball, N.J. Rosenberg and L.H. Allen Jr). ASA Special Publication No. 53, ASA/CSSA/SSSA. p. 27-43.

Burrough, P.A., 1986. *Principles of geographical information systems.* Oxford University Press.

Burrough, P.A., 1989. Modelling land qualities in space and time: The role of geographical information systems. In: *Land qualities in space and time* (eds J. Bouma and A.K. Bregt). Pudoc, Wageningen. p. 45-59.

Buschiazzo, D.E., A.R. Quiroga and K. Starr, 1991. Patterns of organic matter accumulation in soils of the semi-arid Argentinean Pampas. *Zeitschrift für Planzenernährung und Bodenkunde* **154**: 437-441.

Byrnes, B.H., C.B. Christianson, L.S. Holt and E.R. Austin, 1990. Nitrous oxide emissions from the nitrification of nitrogen fertilization. In: *Soils and the greenhouse effect* (ed. A.F. Bouwman). John Wiley and Sons, Chichester. p. 489-495.

Cady, F.B. and W.V. Bartholomew, 1960. Sequential products of anaerobic denitrification in Norfolk soils. *Soil Science Society of America Proceedings* **24**: 477-482.

Camilo, P., 1989. Estimating soil surface temperatures from profile temperature and flux measurements. *Soil Science* **148**: 233-249.

Campbell, C.A., E.A. Paul, D.A. Rennie and K.J. McCallum, 1967a. Factors affecting the accuracy of the carbon dating method in soil humus studies. *Soil Science* **104**: 181-185.

Campbell, C.A., E.A. Paul, D.A. Rennie and K.J. McCallum, 1967b. Dynamics of soil humus utilizing C dating techniques. *Soil Science* **104**: 217-224.

Carlyle, J.C. and U.B.A. Than, 1988. Abiotic controls of soil respiration beneath an eighteen year old Pinus radiata stand in south-eastern Australia. *Journal of Ecology* **76**: 654-662.

Castelle, A.J. and J.N. Galloway, 1990. Carbon dioxide dynamics in acid forest soils in Shenandoah National Park, Virginia. *Soil Science Society of America Journal* **54**: 252-257.

Cate, Jr. R.. and D.R. Keeney, 1987. Nitrous oxide production throughout the year from fertilized and manured maize. *Journal of Environmental Quality* **16**: 443-447.

CDIAC, 1992. *CDIAC communications No. 16*, Carbon Dioxide Information Analysis Centre, Oak Ridge National Laboratory, Oak Ridge.

Cepeda-Pizarro, J.G. and W.G. Whitford, 1990. Decomposition patterns of surface litter of six plant species along a Chihuahuan desert watershed. *American Midland Naturalist* **123**: 319-330. (In: Soils and Fertilizers 1990, 53, p. 1514).

Cerri, C.C., B. Volkoff and B.P. Eduardo, 1985. Effect of deforestation on the microbial biomass of a Yellow Latosol from Amazonia, Brazil (In Portuguese with English summary). *Revista Brasiliera de Cienca do Solo* **9**: 1-4.

Cervelli, S. and D.E. Rolston, 1983. Influence of atrazine on denitrification in soil columns. *Journal of Environmental Quality* **12**: 482-486.

Chadwick, M.J. and J.C.I. Kuylenstierna, 1990. *The relative sensitivity of ecosystems in Europe to acidic depositions*. A preliminary assessment of the sensitivity of aquatic and terrestrial ecosystems. Stockholm Environmental Institute, Stockholm, Sweden.

Chalamet, A., 1990. Source and sink mechanisms related to denitrification measurement. *Mitteilungen der Deutschen Bodenkundlichen Gesellschaft* **60**: 65-72

Chalamet, A. and J. Chauchard, 1976. Sorption des oxides d'azote sur les sols. Etude par sorption concurentielle de l'influence de l' humidité sur la retention de N_2O. *Ann. Chem.* **6**: 303-308. (quoted by Benckiser *et al.*, 1987)

Chalamet, A. and R. Bardin, 1977. Action des ions ferreux sur la réduction de l'acide nitreux dans les sols hydromorphes. *Soil Biology and Biochemistry* **9**: 281-285.

Chalk, P.M. and C.J. Smith, 1983. Chemodenitrification. In: *Gaseous loss of nitrogen from plant-soil systems*. Developments in plant and soil science. Vol. 9. Martinus Nijhoff, The Hague. p. 65-89.

Chen, Y. and T. Aviad, 1990. Effects of humic substances on plant growth. In: *Humic substances in soil and crop sciences* (eds MacCarthy P., C.E. Clapp, R.L. Malcolm and P.R. Bloom, 1990a). Selected readings, SSSA/ASA, Madison. p. 161-186.

Chiou, C.T., 1990. Roles of organic matter, minerals, and moisture in sorption of non-ionic compounds and pesticides by soil. In: *Humic substances in soil and crop sciences* (eds MacCarthy P., C.E. Clapp, R.L. Malcolm and P.R. Bloom, 1990a). Selected readings, SSSA/ASA, Madison. p. 111-161.

Cho, C.M. and J.G. Mills, 1979. Kinetics formulation of the denitrification process in soil. *Canadian Journal of Soil Science* **52**: 249-257.

Choné, T., F. Andreux, J.C. Correa, B. Volkoff and C.C. Cerri, 1991. Changes in organic matter on an Oxisol from the Central Amazonian forest during eight years as pasture determined by 13C isotopic composition. In: *Diversity of environmental biogeochemistry* (ed. J. Berthelin). Elsevier, Amsterdam. p. 397-405.

Chotte, J.L., 1988. Importance de l'activite rhizospherique dans la dynamique de reconstruction du stock organique des soils (Vertisol, Martinique). *Cahiers ORSTOM, Série Pédologie* **24**: 345-346.

Christensen, S., 1990. Effects of plants on denitrification. *Mitteilungen der Deutschen Bodenkundlichen Gesellschaft* **60**: 95-100.

Christensen, S. and J.M. Tiedje, 1990. Brief and vigorous N_2O production by soil at spring thaw. *Journal of Soil Science* **41**: 1-4.

Christensen, B.T. and L.H. Sorensen, 1985. The distribution of native and labelled carbon between soil particle fractions isolated from two long-term incubation experiments. *Journal of Soil Science* **36**: 219-229.

Christianson, C.B. and C.M. Cho, 1983. Chemical denitrification in frozen soils. *Soil Science Society of America Journal* **47**: 38-42.

Cicerone, R.J. and R.S. Oremland, 1988. Biogeochemical aspects of atmospheric methane. *Global Biogeochemical Cycles* **2**: 299-327.

Cicerone, R.J. and J.D. Shetter, 1981. Sources of atmospheric methane: Measurements in rice paddies and a discussion. *Journal of Geophysical Research* **86**: 7203-7209.

Cicerone, R.J. and J.D. Shetter, 1983. Seasonal variation of methane flux from a California rice paddy. *Journal of Geophysical Research* **88**: 11022-11024.

Cicerone, R.J., J.D. Shetter and C.C. Delwiche, 1983. Seasonal variations of methane flux from a California rice paddy. *Journal of Geophysical Research* **88**: 11022-11024.

Clymo, R.S., 1984. The limits of peat growth. *Philosophical Transactions Royal Society London* **B303**: 605-654.

Cofer III, W.R., J.S. Levine, E.L. Winstead and B.J. Stock, 1991. New estimates of nitrous oxide emissions from biomass burning. *Nature* **349**: 689-691.

Colberg, P.J., 1988. Anaerobic microbial degradation of cellulose, lignin, oligolignols, and monoaromatic lignin derivatives. In: *Biology of anaerobic microorganisms* (ed. A.J.B. Zehnder). Wiley Interscience, New York. p. 333-372.

Colbourn, P. and I.W. Harper, 1987. Denitrification in drained and undrained arable clay soils. *Journal of Soil Science* **38**: 531-539.

Cole, C.V., J.W.B.Stewart, H.W. Hunt and W.J. Parton, 1986. Cycling of carbon, nitrogen, sulphur and phosphorus: Controls and interactions. *Transactions 13th International Congress of Soil Science*, Hamburg. p. 636-643.

Coleman, D.C., J.M. Oades and G. Uehara, 1989. *Dynamics of soil organic matter in tropical ecosystems*. NifTAL Project, University of Hawaii Press, Honolulu.

Collin, M. and A. Rasmuson, 1988. A comparison of gas diffusivity models for unsaturated porous media. *Soil Science Society of America Journal* **52**: 1559-1565.

Conrad, R. and F. Rothfuss, 1991. Methane oxidation in the soil surface layer of a flooded rice field and the effect of ammonium. *Biology and Fertility of Soil* **12**: 28-32.

Correa, E.F. and J.C. Germon, 1991. Dissimilative nitrate reduction to ammonium in different soils in waterlogged conditions. In: *Diversity of environmental biogeochemistry* (ed. J. Berthelin), Elsevier, Amsterdam. p. 295-308.

Corré, W.J., W. Dijkman and W.M. Kieskamp, 1990. Denitrification in the topsoil of production grassland. *Mitteilungen der Deutschen Bodenkundlichen Gesellschaft* **60**: 183-188.

Crill, P.M., K.B. Bartlett, R.C. Harriss, E. Gorham, E.S. Verry, D.I. Sebacher, L. Madzar and W. Sanner, 1988a. Methane flux from Minnesota peatlands. *Global Biogeochemical Cycles* **2**: 371-384.

Crill, P.M., K.B. Bartlett, J.O. Wilson, D.I. Sebacher, R.C. Harriss, J.M. Melack, S. MacIntyre, L. Lesack and L. Smith-Morill, 1988b. Tropospheric methane from an Amazonian floodplain lake. *Journal of Geophysical Research* **93**: 1564-1570.

Crützen, P.J., 1987. The role of the tropics in atmospheric chemistry. In: *The geophysiology of Amazonia: Vegetation and climate interactions* (ed. R.E. Dickinson), John Wiley and Sons, New York.

Crützen, P.J., 1991. Methane's sinks and sources. *Nature* **350**: 380-381.

Crützen, P.J. and M.O. Andreae, 1990. *Science* **250**: 1669-1678.

Cuevas, E. and E. Medina, 1988. Nutrient dynamics within Amazonian forests. II. Fine root growth, nutrient availability and leaf litter composition. *Oecologia* **76**: 222-235.

Cure, J.D. and B. Acock, 1986. Crop responses to carbon dioxide doubling: a literature survey. *Agricultural and Forest Meteorology* **38**: 127-145.

Currie, J.A., 1960. Gaseous diffusion in porous media. Part 1. A non-steady state method. *British Journal of Applied Physics* **11**: 314-317.

Currie, J.A., 1965. Diffusion within microstructure: a structural parameter for soils. *Journal of Soil Science* **16: 279-289.*

Currie, J.A., 1984. Gas diffusion through soil crumbs: the effects of wetting and swelling. *Journal of Soil Science* **34**: 217-232.

Currie, J.A. and Rose, D.A., 1985. Gas diffusion in structured materials: the effect of tri-modal pore size distribution. *Journal of Soil Science* **36**: 487-493.

Dabin, B., 1980. Les matières organiques dans les sols tropicaux normalement drainés. *Cahiers ORSTOM, Série Pédologique* **XVIII**: 193-196.

Davidson, E.A. and M.K. Firestone, 1988. Measurement of nitrous oxide dissolved in soil solution. *Soil Science Society of America Journal* **52**: 1201-1203.

Davidson, E.A. and W.T. Swank, 1990. Nitrous oxide dissolved in soil solution - An insignificant pathway of nitrogen loss from a southern hardwood forest. *Water Resources Research* **26**: 1687-1690.

Davies, D.B. and D. Payne, 1988. Management of soil physical properties. In: Wild, A. (Editor), *Russell's Soil Conditions and Plant Growth*, Longman Scientific and Technical, Harlow.

De Bont, J.A.M., K.K. Lee and D.F. Bouldin, 1978. Bacterial oxidation of methane in a rice paddy. *Ecological Bulletin* **26**: 91-96.

De Datta, S.K., 1981. *Principles and practices of rice production*. John Wiley and Sons, New York.

DeLaune, R.D., W.H. Patrick Jr. and N. van Breemen, 1990b. Processes governing marsh formation in a rapidly subsiding coastal environment. *Catena* **17**: 277-288.

DeLaune, R.D., W.H. Patrick Jr., C.W. Lindau and C.J.Smith, 1990a. Nitrous oxide and methane emission from Gulf Coast wetlands. In: *Soils and the greenhouse effect* (ed. A.F.Bouwman). John Wiley and Sons, Chichester. p. 497-502.

DeLaune, R.D., C.J. Smith and W.H. Patrick Jr., 1983. Methane release from Gulf coast wetlands. *Tellus* **35B**: 8-15.

DeLaune, R.D., C.J. Smith and W.H. Patrick Jr., 1986. Methane production in Mississippi River deltaic peat plain. *Organic Geochemistry* **9**: 193-197.

Delwiche, C.C. (ed.), 1981. *Denitrification, nitrification, and atmospheric nitrous oxide*. John Wiley and Sons, New York.

Denmead, O.T., J.R. Freeney and J.R. Simpson, 1979. Nitrous oxide emissions during denitrification in a flooded field. *Soil Science Society of America Journal* **43**: 726-728.

Denier van der Gon, H.A.C., H.U. Neue, R.S. Lantin, R. Wassmann, M.C.R. Alberto, J.B. Aduna and M.J.P. Tan, 1992. Controlling factors of methane emission from rice fields. In: *World Inventory of Soil Emission Potentials* (eds N.H. Batjes and E.M. Bridges), Proceedings of an International Workshop organized in the framework of the Netherlands National Research Programme on Global Air Pollution and Climate Change (NOP). WISE Report No. 2, International Soil Reference and Information Centre, Wageningen.

Detwiler, R.P., 1986. Land use change and the global carbon cycle: The role of tropical soils. *Biogeochemistry* **2**: 67-93.

Detwiler, R.P. and C.A.S. Hall, 1988. Tropical forests and the global carbon cycle. *Science* **239**: 42-47.

Devol, A.H., J.E. Richey, W.A. Clark and S.L. King, 1988. Methane emissions to the troposphere from the Amazon Floodplain. *Journal of Geophysical Research* **93**: 1583-1592.

De Vries, D.A., 1950. Some remarks on gaseous diffusion in soils. *Transactions of the 4th International Congress of Soil Science* **II**: 41-43.

Dickinson, R.E. and R.J. Cicerone, 1986. Future global warming from atmospheric trace gases. *Nature* **319**: 109-114.

Dokuchaev, V.V. 1882. *Systematic map of Chernozem areas in Russia* (1:4.2 million). (Map reference SU-9d in ISRIC's historical map collection).

Doormaar, J.F., 1990. Effect of active roots on the decomposition of soil organic materials. *Biology and Fertility of Soils* **10**: 121-126.

Doran, J.W., L.N. Mielke and J.F. Power, 1990. Microbial activity as regulated by water filled pore space. In: *Transactions 14th International Congress of Soil Science*, Kyoto. **I**: 94-99.

Driessen, P.M., 1986a. *Soil data, a matter of concern*. Annual Report, International Soil Museum (now International Soil Reference and Information Centre), Wageningen. p. 43-47.

Driessen, P.M., 1986b. Soil data. In: *Modelling of Agricultural Production: Weather, Soils and Crops* (eds H. van Keulen and J. Wolf), Pudoc, Wageningen.

Duchaufour, P., 1982. *Pedology: Pedogenesis and classification* (translated by T.R. Panton). George Allen and Unwin, Boston.

Dyer, J.M. and G.A. Brook, 1991. Spatial and temporal variations in temperate forest soil carbon dioxide during the non-growing season. *Earth Surface Processes and Landforms* **16**: 411-426 (Quoted in: *Soil and Fertilizers* 1991, **54**: 1678).

Eaton, L.J. and D.G. Patriquin, 1989. Denitrification in lowland blueberry soils. *Canadian Journal of Soil Science* **69**: 302-312.

Edwards, N.T. and B.M. Ross-Todd, 1983. Soil carbon dynamics in a mixed deciduous forest following clear-cutting with and without residue removal. *Soil Science Society of America Journal* **47**: 1014-1021.

Eggington, G.M. and K.A. Smith, 1986a. Nitrous oxide emission from a grassland soil fertilized with slurry and calcium nitrate. *Journal of Soil Science* **37**: 59-67.

Eggington, G.M. and K.A. Smith, 1986b. Losses of nitrogen by denitrification from a grassland soil fertilized with cattle slurry and calcium nitrate. *Journal of Soil Science* **37**: 69-80.

Ehhalt, D.H., 1974. The atmospheric cycle of methane. *Tellus* **26**: 58-70.

Ehhalt, D.H. and U. Schmidt, 1978. Sources and sinks of atmospheric methane. *Pageoph.* **116**: 452-464.

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

Eijsackers, H. and A.J.B. Zehnder, 1990. Litter decomposition: A Russian matriochka doll. *Biogeochemistry* **11**: 153-174.

Elliot, E.T., 1986. Aggregate structure and carbon, nitrogen and phosphorus in native and cultivated soils. *Soil Science Society of America Journal* **50**: 627-683.

Emanuel, W.R., G.G. Killough, W.M. Post and H.H. Shugart, 1984. Modelling terrestrial ecosystems in the global carbon cycle with shifts in carbon storage capacity by land use change. *Ecologia* **65**: 970-983.

Endale, D.M. and R.T.A. Hakkeling, 1987. *Irrigation suitability of the soils of Eastern and North-Eastern Africa at 1:1 M scale*. Annual Report 1987, International Soil Reference and Information Centre, Wageningen, p. 9-18.

Eriksson, H., 1991. Sources and sinks of CO_2 in Sweden. *Ambio* **20**: 146-150.

Esser, G., 1987. Sensitivity of global carbon pools and fluxes to human and potential climatic effects. *Tellus* **39B**: 245-260.

Esser, G., 1990. Osnabrück Biosphere Model: Construction, structure, results. In: *Facets of Modern Ecology* (eds G. Esser and Overdieck). Elsevier, Amsterdam. p. 3-30 (In press)

Essex, C., 1991. What do climate models tell us about global warming? *Pure and Applied Geophysics* **135**: 125-133.

Estes, J.E. and M.J. Cosentino, 1989. Remote sensing of vegetation. In: *Global ecology: Towards a science of the biosphere* (eds M.B. Rambler, L. Margalis and R. Fester). Academic Press Inc., Boston. p. 75-111.

FAO, 1978-1981. *Reports on the Agro-ecological Zones Project*. Vols. 1-4. World Soil Resopurces Report 48/1 to 48/4, Food and Agricultural Organization, Rome.

FAO, 1984. *Land evaluation for forestry*. Forestry Paper No. 48. Food and Agricultural Organization, Rome.

FAO, 1988. *Soil Map of the World, Revised Legend*. World Resources report 60. FAO, Rome (Reprinted as Technical Paper 20. International Soil Reference and Information Centre, Wageningen 1989).

FAO, 1991a. *World Soil Resources: An explanatory note on the FAO World Soil Resources Map (1:25 M)*. World Soil Resources Report No. 66, Food and Agricultural Organization, Rome.

FAO, 1991b. *The digitized Soil Map of the World. Notes - Volume 1: Africa (release 1.0)*. World Soil Resources Report No. 67/1, Food and Agricultural Organization, Rome.

FAO/ISRIC, 1989. *FAO-ISRIC soil data base*. World Soil Resources Report 64, Food and Agricultural Organization, Rome.

FAO/ISRIC, 1990. *Guidelines for soil description (3rd Edition, revised)*. Food and Agricultural Organization, Rome.

FAO/UNEP, 1981. *Tropical forest resources assessment project. Forest resources of: Tropical America; Tropical Africa; Tropical Asia*. Food and Agricultural Organization, Rome.

FAO/Unesco, 1974. *Soil Map of the World (1:5 M)*. Volume 1 - Legend. Food and Agricultural Organization, Rome.

FAO/Unesco, 1971-1981. *Soil Map of the World, 1:5 M*. Volumes 1 to 10, United Nations Educational, Scientific and Cultural Organization, Paris.

FAO/Unesco/WMO, 1977. *World map of desertification* (1: 25 M). Conference Document No. A/CONF/74/2, Food and Agricultural Organization, Rome.

FAO/UNFPA/IIASA, 1982. *Potential population supporting capacities of lands in the developing world*. Technical Report of Project FPA/INT/13, Food and Agricultural Organization, Rome.

Farquhar, G.D., R. Wetselaar and B. Weir, 1983. Gaseous nitrogen losses from plants. In: *Gaseous loss of nitrogen from plant-soil systems* (eds J.R. Freney and J.R. Simpson). Martinus Nijhoff, The Hague. p. 159-194.

Feller, C., 1988. Effet de differents systemes de culture sur les stocks organiques de sols argileux tropicaux des Petites Antilles. *Cahiers ORSTOM, Serie Pedologie* **24**: 341-343.

Feller, C., 1991. Organic inputs, soil organic matter and functional soil organic compartments in some tropical agrosystems: Examples for low activity clay soils. In: *Dynamics of organic matter in relation to the sustainability of agricultural systems*. Abstract book of International Symposium held at Leuven, Belgium, Nov. 3-6, 1991.

Feller, C., G. Burtin, G. Bedard and J. Balesdent, 1991. Utilisation des resines et des ultrasons dans le fractionement granulometrique de la matiere organique des sols. Intéret et limites. *Science du Sol* **29**: 77-93.

Firestone, M.K., 1984. Biological denitrification. In: *Nitrogen in agricultural soils* (ed. F.J. Stevensson). Agronomy Monograph 22, ASA/CSSA/SSSA, Madison. p. 289-326.

Firestone, M.K. and E.A. Davidson, 1989. Microbiological basis of NO and NO_2 production and consumption in soil. In: *Exchange of trace gases between terrestrial ecosystems and the atmosphere* (eds. M.O. Andreae and D.S. Schimel). Dahlem Workshop Report, John Wiley and Sons, Chichester. p. 7-21.

Firestone, M.K., M.S. Smith, R.B. Firestone and J.M. Tiedje, 1979. The influence of nitrate, nitrite and oxygen on the composition of the gaseous products of denitrification. *Soil Science Society of America Journal* **43**: 1140-1144.

Fitzpatrick, E.A., 1983. *Soils: Their formation, classification and distribution*. Longman, London.

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

Focht, D.D. and W. Verstraete, 1977. Biochemical ecology of nitrification and denitrification. In: *Advances in microbial ecology*, Vol. 1 (ed M. Alexander). Plenum Press, New York. p. 135-214.

Folorunso, O.A. and D.E. Rolston, 1984. Spatial variability of field-measured denitrification of gas fluxes. *Soil Science Society of America Journal* **48**: 1214-1219.

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

Franzmeier, D.P., G.D. Lemme and R.J. Miles, 1985. Organic carbon in soils of North Central United States. *Soil Science Society of America Journal* **49**: 702-708.

Fraser, P.J., W.P. Elliot and L.S. Waterman, 1986. Atmospheric CO_2 record from direct chemical measurements during the 19th century. In: *The changing carbon cycle: A global perspective* (eds J.R. Trabalka and D.E. Reichle). Springer Verlag, New York. p. 66-88.

Freckman, D.W., 1988. Bacterivorous nematodes and organic matter decomposition. *Agriculture, Ecosystems and Environment* **24**: 195-217.

Freijer, J.I. and W. Bouten, 1991. A comparison of field methods for measuring soil carbon dioxide evolution: experiments and simulation. *Plant and Soil* **135**: 133-142.

Freney, J.R. and J.R. Simpson (eds), 1983. *Gaseous loss of nitrogen from plant-soil systems*. Martinus Nijhoff, The Hague.

Freney, J.R., A.R. Mosier and S.L. Chapman, 1990. Labelled dinitrogen emission from flooded rice fertilized with ^{15}N-urea. *Mitteilungen der Deutschen Bodenkundlichen Gesellschaft* **60**: 109-114.

Frimmel, F.H. and R.F. Christman (eds), 1988. *Humic substances and their role in the environment.* Wiley Interscience, New York.

Fung, I, J. John, J. Lerner, E. Matthews, M. Prather, L.P. Steele and P.J. Fraser, 1991. Three-dimensional model synthesis of the global methane cycle. *Journal of Geophysical Research* 96: 13,033-13,065.

Gabriels, D. and P. Michiels, 1991. Soil organic matter and water erosion processes. In: *Advances in soil organic matter research* (ed. W.S. Wilson). Special Publication No. 90, The Royal Society of Chemistry, Cambridge. p. 141-152.

Gardiner, M.J., 1987. Compilation of soil analytical data for the EC. In: *Agriculture: Computerization of soil land use data* (eds R.J.A. Jones and B. Biagi). Proceedings of a symposium in the Community project for coordination of agricultural research (20-22 May 1987, Pisa). Commission of the European Communities, Luxembourg.

Gardini, F., L.V. Antisari, M.E. Guerzoni and P. Sequi, 1991. A simple gas chromatography approach to evaluate CO_2 release, N_2O evolution, and O2 uptake from soil. *Biology and Fertility of Soils* **12**: 1-4.

Germon, J.C. and D. Jacques, 1990. Denitrifying activity measurement by soil core method. Effect of depth and characterization of NO_2/N_2 ratio in different soils. *Mitteilungen der Deutschen Bodenkundlichen Gesellschaft* **60**: 51-58.

Ghuman, B.S. and R. Lal, 1989. Soil temperature effects of biomass burning in windrows after clearing a tropical rainforest. *Field Crops Research* **22**: 1-10.

Giani, L. and D. Giani, 1990. Characteristics of a marshland built up from marine and peat material. *Geoderma* **47**: 151-157.

Gildae, M.P. and B. Moore, 1985. *FAO global soil data base (½' x ½') degree latitude, longitude.* University of New Hampshire, Science and Engineering Department, Complex Systems Research Centre, Durham.

Glazovskaya, M.A. and V.M. Friedland, 1982. *Soil Map of the World* (1:15 M). GUGK, Moscow.

Goodchild, M.F., 1988. The use and accuracy of global data bases. In: *Building data bases for global science* (ed. H. Mounsey). Proceedings of the First Meeting of the International Geographical Union Global Data base Planning project. Taylor and Francis, London. p. 41-48.

Goodroad, L.L. and D.R. Keeney, 1984a. Nitrous oxide production in aerobic soils under varying pH, temperature and water content. *Soil Biology and Biochemistry* **16**: 39-44.

Goodroad, L.L. and D.R.Keeney, 1984b. Nitrous oxide emission from forest, marsh and prairie ecosystems. *Journal of Environmental Quality* **13**: 448-452.

Goreau, T.J., 1990. Balancing atmospheric carbon dioxide. *Ambio* **19**: 230-236.

Gorham, E., 1988. Biotic impoverishment in northern peatlands. In: *Biotic impoverishment* (ed. G.M. Woodwell). Cambridge University Press, Cambridge.

Goudriaan, J., 1987. The biosphere as a driving force in the global carbon cycle. *Netherlands Journal of Agricultural Science* **35**: 177-187.

Goudriaan, J., 1989. Modelling biospheric control of carbon fluxes between atmosphere, ocean and land in view of climatic change. In: *Climate and geosciences* (eds A. Berger, S. Schneider and J. Cl. Duplessy). Kluwer Academic Publisher, Dordrecht. p. 481-499.

Goudriaan, J., 1990. Atmospheric CO_2, global carbon flux and the biosphere. In: *Theoretical production ecology: Reflections and prospects* (eds R. Rabbinge, J. Goudriaan, H. van Keulen, F.W.T. Penning de Vries and H.H. van Laan). Simulation Monographs 34, Pudoc, Wageningen.

Goudriaan, J., 1992. Biosphere structure, carbon sequestering potential and the atmospheric ^{14}C carbon record. *Journal of Experimental Botany* **43**: 1111-1149.

Goudriaan, J. and D. Ketner, 1984. A simulation study for the global carbon cycle, including man's impact on the biosphere. *Climatic Change* **6**: 167-192.

Goudriaan, J. and M.H. Unsworth, 1990. Implications of increasing carbon dioxide and climate change for agricultural productivity and water resources. In: *Impact of carbon dioxide, trace gases, and climate change on global agriculture*. (eds B.A. Kimball, N.J. Rosenberg and L.H. Allen Jr). ASA Special Publication No. 53, ASA/CSSA/SSSA. p. 111-130.

Graham, R.L., M.G.Turner and V.H. Dale, 1990. How increasing CO_2 and climate change affect forests. BioScience **40**: 575-587.

Grahammer, K., M.D. Jawson and J. Skopp, 1991. Day and night soil respiration from a grassland. *Soil Biology and Biochemistry* **23**: 77-81.

Granham, R.L., 1989. Approaches to correcting the global greenhouse drift by managing tropical ecosystems. *Tropical Ecology* **30**: 157-174.

Green, G.M. and R.W. Sussman, 1990. Deforestation history of the eastern rainforest of Madagascar from satellite images. *Science* **248**: 212-215.

Greene, R.S.B., C.J. Chartres and K.C. Hodgkinson, 1990. The effects of fire on the soil in a degraded semi-arid woodland. I. Cryptogram cover and physical and micromorphological properties. *Australian Journal of Soil Research* **28**: 755-777.

Greenland, D.J., 1991. The contributions of soil science to society - past, present, and future. *Soil Science* **151**: 19-23.

Greenland, D.J. and M.H.B. Hayes (eds), 1978. *The chemistry of soil constituents.* Wiley Interscience, New York.

Greenwood, D.J., 1970. Distribution of carbon dioxide in the aqueous phase of aerobic soils. *Journal of Soil Science* **21**: 314-329.

Gregorich, E.G., R.G. Kachanoski and R.P. Voroney, 1989. Carbon mineralization in soil size fractions after various amounts of aggregate disruption. *Journal of Soil Science* **40**: 649-659.

Gregory, P.J., 1988. Water and Crop Growth. In: Wild, A. (Editor) *Russell's Soil Conditions and Crop Growth,* Longman Scientific and Technical, Harlow.

Gregson, K., D.J. Hector and M. McGowan, 1987. A one-parameter model for the soil-water characteristic. *Journal of Soil Science* **38**: 483-486.

Grewal, K.S., G.D. Buchan and R.R. Sherlock, 1991. A comparison of three methods of organic carbon determination in some New Zealand Soils. *Journal of Soil Science* **42**: 251-257.

Griffiths, B.S., 1989. The effect of protozoan grazing on nitrification - implications for the application of organic wastes to soils. In: *Nitrogen in inorganic wastes applied to soils* (eds. J.A.A. Hansen and K. Henriksen). Academic Press, London.

Grismer, M.E., 1988. Vapour transport during solution displacement in soils. *Soil Science* **146**: 215-220.

Groenendijk, H., 1990. Compilation of a soil data set for Europe. In: *Soils and the greenhouse effect* (ed. A.F. Bouwman). John Wiley and Sons, Chichester. p. 535-539.

Grofmann, P.M. and J.M. Tiedje, 1989. Denitrification in northern temperate forest soils: Relationships between denitrification and environmental factors at the landscape scale. *Soil Biology and Biochemistry* **21**: 621-626.

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

Groot, J.J.R., P. de Willigen and E.J. Verberne (eds), 1991. *Nitrogen turnover in the soil-crop system*. Developments in Plant and *Soil Science*s No. 44, Kluwer Academic Publisher, Dordrecht.

Grotch, S.L., 1988. *Regional intercomparison of General Circulation Model predictions and historical climate data*. DOE/NBB-0084, TR041, US Department of Energy, Washington D.C.

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

Guenzi, W.D., W.E. Beard, F.S. Watanabe, S.R. Olsen and L.K. Porter, 1978. Nitrification and denitirification in cattle manure-ammended soil. *Journal of Environmental Quality* **7**: 196-202.

Hackman, Ch. W., 1979. Rice field ecology in northeastern Thailand. The effect of wet and dry season on a cultivated aquatic ecosystem. *Monographiae Biologicae* **34**: W. Junk Publisher, The Hague.

Haider, K., O. Heinemeyer and A.R. Mosier, 1990. Direct and indirect effects of plants on denitrification. *Mitteilungen der Deutschen Bodenkundlichen Gesellschaft* **60**: 101-108.

Haimi, J. and V. Hutha, 1990. Effects of earthworms on decomposition process in raw humus forest soils: A microcosm study. *Biology and Fertility of Soils* **10**: 178-183.

Hall, C.A.S., S. Brown, F.M. O'Hara Jr., P.B. Bogdonoff, D. Barshaw, E. Kaufman and S. Underhill, 1988. *Bibliography on tropical rainforests and the global carbon cycle. Vol. 1. An introduction to the literature.* ORNL/CDIA-24/V1, Oak Ridge National Laboratory. Oak Ridge, Tennessee.

Hansen, J.A.A. and K. Henriksen (eds), 1989. *Nitrogen in inorganic wastes applied to soils*. Academic Press, London.

Hansen, J.E. and A.A. Lacis, 1990. Sand and dust versus greenhouse gases: An assessment of their relative roles in global climate change. *Nature* **346**: 713-718.

Hao, W.M., D. Scharffe and P.J. Crützen, 1988. Production of N_2O, CH_4 and CO_2 from soils in the tropical savanna during the dry season. *Journal of Atmospheric Chemistry* **7**: 93-105.

Harkness, D.D., A.F. Harrison and P.J. Bacon, 1991. The potential of bomb-14C measurement for estimating soil organic matter turnover. In: *Advances in soil organic matter research* (ed. W.S. Wilson). Special Publication No. 90, The Royal Society of Chemistry, Cambridge. p. 238-251.

Harrison, A.F., D.D. Harkness and P.J. Bacon, 1990. The use of bomb-14C for studying organic matter and N and P dynamics in a woodland soil. In: *Nutrient cycling in terrestrial ecosystems: Field methods, application and interpretation* (ed. A.F. Harrison, P. Ineson and O.W. Heal). Elsevier Applied Sci., Barking

Harriss, R.C. and D.I. Sebacher, 1981. Methane flux in forested freshwater swamps of the southeastern United States. *Geophysical Research Letters* **9**: 1002-1004.

Harriss, R.C., D.I. Sebacher and F.P. Day, 1982. Methane flux in the Great Dismal Swamp. *Nature* **297**: 673-674.

Harriss, R.C., E. Gorham, D.I. Sebacher, K.B. Bartlett and P.A. Flebbe, 1985. Methane flux from northern peatlands. *Nature* **315**: 652-654.

Harrod, T.R., A.D. Carter and J.M. Hollis, 1991. The role of soil organic matter in pesticide movement via run-off, soil erosion, and leaching. In: *Advances in soil organic matter research* (ed. W.S. Wilson). Special Publication No. 90, The Royal Society of Chemistry, Cambridge. p. 129-138.

Harvey, L.D.D., 1989a. Effect of model structure on the response of terrestrial biosphere models to CO_2 and temperature increases. *Global Biogeochemical Cycles* **3**: 137-153.

Harvey, L.D.D., 1989b. Managing atmospheric CO_2. *Climatic Change* **15**: 343-381.

Hauck, R.D., 1986. Field measurements of denitrification - an overview. In: *Field measurement of dinitrogen fixation and denitrification* (eds R.D. Hauck and R.W. Weaver). Special Publication SSSA, Madison W.I.. p. 59-72.

Helal, H.M. and D. Sauerbeck, 1986. Effect of plant roots on carbon metabolism of soil microbial biomass (In English). *Zeitschrift für Planzenernährung und Bodenkunde* **149**: 181-188.

Henderson, T.L., A. Szilagyi, M.F. Baumgardner, C.C. T. Che and D.A. Landgrebe, 1989. Spectral band selection for classification of soil organic matter content. *Soil Science Society of America Journal* **53**: 1778-1784.

Henderson-Sellers, A., R.E. Dickinson and M.F. Wilson, 1988. Tropical deforestation: Important processes for climate models. *Climatic Change* **13**: 43-67.

Henning, D., 1989. *Atlas of the Surface Heat Balance of the Continents*. Gebruder Borntreager, Berlin.

Hernandez, D. and J.J. Rowe, 1987. Oxygen regulation of nitrate uptake in denitrifying *Pseudomonas aeruginosa*. *Applied and Environmental Microbiology* **53**: 745-750.

Hernani, L.C., E. Sakai, I. Ishimura and I.F. Lepsch, 1987a. Effects of land clearing of secondary forest on a Yellow Latosol of the Ribeira Valley, State of Sao Paolo, Brazil. I. Dynamics of physical and chemical attributes and corn production (In Portuguese, with English summary). *Revista Brasiliera do Cienca do Solo* **11**: 205-213.

Hernani, L.C., E. Sakai, F. Lombardi Neto and I.F. Lepsch, 1987b. Effects of land clearing of secondary forest on a Yellow Latosol of the Ribeira Valley, State of Sao Paolo, Brazil. II. Erosion losses (In Portuguese, with English summary). *Revista Brasiliera do Cienca do Solo* **11**: 215-219.

Hillel, D., 1980. *Applications of Soil Physics*. Academic Press, New York.

Hileman, B., 1990. Biomass burning: Environment hurt more than thought. *Chemical and Engineering News* **68**: 4-5.

Hodgson, A.S. and D.A. MacLeod, 1989. Use of oxygen flux density to estimate critical air-filled porosity of a vertisol. *Soil Science Society of America Journal* **53**: 355-361

Hodgson, J.M., 1978. *Soil Sampling and Soil Description*. Clarendon Press, Oxford.

Holt, J.A., 1987. Carbon mineralization in semi-arid northeastern Australia: the role of termites. *Journal of Tropical Ecology* **3**: 255-263.

Holt, J.A., M.J. Hodgen and D. Lamb, 1990. Soil respiration in the seasonally dry tropics near Townsville, North Queensland. *Australian Journal of Soil Research* **28**: 737-745.

Holzapfel-Pschorn, A. and W. Seiler, 1986. Methane emissions during a cultivation period from an Italian rice paddy. *Journal of Geophysical Research* **91**: 11803-11814.

Holzapfel-Pschorn, A., R. Conrad and W. Seiler, 1986. Effects of vegetation on the emissions of methane from submerged rice paddy soil. *Plant and Soil* **92**: 223-233.

Hopkins, D.W. and R.S. Shiel, 1991. Spectroscopic characterization of organic matter from soil with mor and mull humus forms. In: *Advances in soil organic matter research* (ed. W.S. Wilson). Special Publication No. 90, The Royal Society of Chemistry, Cambridge. p. 71-78.

Hopkins, D.W., R.S. Shiel and A.G. O'Donnel, 1988. The influence of sward species composition on the rate of organic matter decomposition in grassland soil. *Journal of Soil Science* **39**: 385-392.

Hopkins, D.W., D.M. Ibrahim, A.G. O'Donell and R.S. Shiled, 1990. Decomposition of cellulose, soil organic matter and plant litter in a temperate grassland soil. *Plant and Soil* **124**: 79-85.

Hori, K., K. Inubushi, S. Matsumoto and H. Wada, 1990. Methane formation in the submerged paddy soil as viewed from the angle of sequential occurrence of reduction reactions and organic matter decomposition. In: *Transactions 14th International Congress of Soil Science*, Kyoto **II**: 255-260.

Horton, R., 1989. Canopy shading effects on soils heat and water flow. *Soil Science Society of America Journal* **53**: 699-679.

Houghton, R.A., 1986. Estimating changes in the carbon content of terrestrial ecosystems from historical data. In: *The changing carbon cycle: A global analysis* (eds J.R. Trabalka and D.E. Reichle). Springer-Verlag, New York. p. 175-193.

Houghton, R.A., 1987. Biotic changes consistent with the increased seasonal amplitude of atmospheric CO_2 concentration. *Journal of Geophysical Research* **92**: 4233-4230.

Houghton, R.A., 1990. The future role of tropical forests in affecting the carbon dioxide concentration of the atmosphere. *Ambio* **19**: 204-209.

Houghton, R.A., R.D. Boone, J.M. Melillo, C.A. Palm, G.M. Woodwell, N. Meyers, B. Moore and L. Skole, 1985. Net flux of carbon dioxide from tropical forests in 1980. *Nature* **316**: 617-620.

Houghton, R., J. Hobbie and J.M. Melillo *et al.*, 1983. Changes in the carbon content of terrestrial biota between 1860-1980: A net release of CO_2 to the atmosphere. *Ecological Monograph* **53**: 235-262.

Houghton, R.A. and G.M. Woodwell, 1989. Global climatic change. *Scientific American* **260**: 36-44.

Houot, S., R. Chaussod, C. Hounemenou, E. Barriusos and S. Bourgeoius, 1991. Differences induced in the soil in the soil organic matter characteristics and microbial activity by various management practices in long-term field experiments. In: *Diversity of environmental biogeochemistry* (ed. J. Berthelin). Elsevier, Amsterdam. p. 435-443.

Hsieh, Y.P. and O.J. Weber, 1984. Net aerial primary production and dynamics of soil organic matter formation in a tidal marsh ecosystem. *Soil Science Society of America Journal* **486**: 65-72.

Hume, C.J. and H. Cattle, 1990. The greenhouse effect - Meteorological mechanisms and models. *Outlook on Agriculture* **19**: 17-23.

Humphrey, G.S., P.A. Hunt and Buchanan, 1987. Wood-ash stone near Sydney, N.S.W.; A carbonate pedological feature in an acidic soil. *Australian Journal of Soil Research* **25**: 115-124

Huntington, T.G. and D.F. Ryan, 1990. Whole-tree harvesting effects on soil nitrogen and carbon. *Forest Ecology and Management* **31**: 193-204.

Huntington, T.G., D.F. Ryan and S.P. Hamburg, 1988. Estimating soil nitrogen and carbon pools in a northern hardwood forest ecosystem. *Soil Science Society of America Journal* **52**: 1162-1167.

Huntington, T.G., C.E. Johnson, A.H. Johnson, T.C. Siccama and D.F. Ryan, 1989. Carbon, organic matter and bulk density relationships in a forested spodosol. *Soil Science* **148**: 380-386.

Hutson, J.L. and R.J. Wagenet, 1991. Simulating nitrogen dynamics in soils using a deterministic model. *Soil Use and Management* **7**: 74-78.

Idso, S.B., 1988. Greenhouse warming or little ice age demise: A critical problem for climatology. *Theoretical and Applied Climatology* **39**: 54-56.

Idso, S.B., 1989. Carbon dioxide, soil moisture, and future crop production. *Soil Science* **147**: 305-307.

Idso, S.B., 1991. Carbon dioxide and the fate of the Earth. *Global Environmental Change* **1**: 178-182.

IGBP, 1988. *The International Geosphere-Biosphere Programme: A report from the first meeting of the sceintific advisory council for the IGBP*. Report No. 7.2, International Geosphere-Biosphere Programme, Stockholm.

IGBP, 1990a. *Global Change: The initial core projects*. Report No. 12, International Geosphere and Biosphere Programme, Stockholm.

IGBP, 1990b. *Terrestrial biosphere exchange with global atmospheric chemistry* (eds P.A. Matson and D.S. Ojima). Global Change Report No. 13, International Geosphere-Biosphere Programme, Stockholm.

IGBP-IGAC, 1991. *Report of initial planning meeting of IGAC-IGBP Activity 7.2: Exchanges of N_2O, CH_4 and CO between terrestrial ecosystems and the atmosphere in mid-latitudes*. Report of open-meeting held at NCAR, Boulder, Colorado (23-26 September 1991).

Ingraham, J.L., 1981. Microbiology and genetics of denitrifiers. In: *Denitrification, nitrification, and atmospheric nitrous oxide* (ed. C.C. Delwiche). John Wiley and Sons, New York. p. 45-65.

Insam, H., 1990. Are the soil microbial biomass and basal respiration governed by the climatic regime? *Soil Biology and Biochemistry* **22**: 525-532.

Inubushi, K., K. Hori, S. Matsumoto, M. Umebayashi and H. Wada, 1989. Methane emission from a flooded paddy soil to the atmosphere through rice plants (In Japanese, with English summary). *Japanese Journal Soil Science and Plant Nutrition* **60**: 318-324.

Inubushi, K., M. Umebayashi and H. Wada, 1990a. Methane emission from paddy fields. In: *Transactions 14th International Congress of Soil Science*, Kyoto **II**: 249-254.

Inubushi, K., Y. Muramatsu, D. Taja and M. Umebayashi, 1990b. Control of methane emission from paddy soil. In: *Transactions 14th International Congress of Soil Science*, Kyoto **II**: 431-432.

IPCC, 1990. *Climate Change* (Eds Houghton, J.T., Jenkins, G.J. and Ephraums, J.J.), Cambridge University Press, Cambridge.

IPCC, 1992. *Climate Change 1992: The supplementary report to the IPCC Scientific Assessment* (Eds J.T. Houghton, B.A. Callander and S.K. Varney) Supplementary Report, Cambridge University Press, Cambridge.

Isomaki, R., 1991. Paper, pollution and global warming: unsustainable forestry in Finland. *The Ecologist* **21**: 14-17.

ISSS, 1986a. *Proceedings of an international workshop on the structure of a digital Soil Resource Map annex Data base* (20-24 January 1986, ISRIC, Wageningen). M.F. Baumgardner and L.R.Oldeman (eds), SOTER Report No. 1, International Society of Soil Science, Wageningen.

ISSS, 1986b. *Project proposal 'World Soils and Terrain Digital Data base at a scale of 1:1 M (SOTER)'*. M.F. Baumgardner (ed.), International Society of Soil Science, Wageningen.

Jacobsen, P., W.H. Patrick Jr. and B.G. Williams, 1981. Sulphide and methane formation in soils and sediments. *Soil Science* **132**: 279-287.

Janssen, B.H., 1984. A simple method for calculating decomposition and accumulation of 'young' soil organic matter. *Plant and Soil* **76**: 297-304.

Jayaweera, G.R. and D.S. Mikkelsen, 1990. Ammonia volatilization from flooded soil systems: A computer model. I. Theoretical aspects. *Soil Science Society of America Journal* **54**: 1447-1455.

JEA/EPA, 1990. *Methane emissions and opportunities for control*. Workshop results of Intergovernmental Panel on Climate Change. Coordinated by Japan Environmental Agency and United States Environmental Protection Agency.

Jenkinson, D.S., 1977. Studies on the decomposition of plant material in soil. V. The effects of plant cover and soil type on the loss of carbon from 14C-labelled rye-grass decomposing under field conditions. *Journal of Soil Science* **28**: 417-423

Jenkinson, D.S., 1990. The turnover of organic carbon and nitrogen in soil. *Philosophical Transactions Royal Society London* **B 329**: 361-368.

Jenkinson, D.S. and A. Ayanaba, 1977. Decomposition of carbon-14 labelled plant material under tropical conditions. *Soil Science Society of America Journal* **41**: 912-915.

Jenkinson, D.S. and J.H. Rayner, 1977. The turnover of soil organic matter in some of the Rothamsted classical experiments. *Soil Science* **123**: 298-305.

Jenkinson, D.S., D.E. Adams and A. Wild, 1991. Model estimates of CO_2 emissions from soil in response to global warming. *Nature* **351**: 304-306.

Jenny, H., 1941. *Factors of Soil Formation*. McGraw-Hill, New York.

Johansson, C. and I.E. Galbally, 1984. Production of nitric oxide in loam under aerobic and anaerobic conditions. *Applied and Environmental Microbiology* **47**: 1284-1289.

Johnson, W.M., J.E. McClelland, S.B. McCaleb, R. Ulrich, W.G. Harper, and T.B. Hutchings, 1960. Classification and description of soil pores. *Soil Science* **89**: 319-321.

Johnson, C.E., A.H. Johnson, T.G. Huntington and T.G. Siccama, 1991. Whole-tree clear-cutting effects on soil horizons and organic matter pools. *Soil Science Society of America Journal* **55**: 497-502.

Johnston, A.E., 1991. Soil fertility and soil organic matter. In: *Advances in soil organic matter research* (ed. W.S. Wilson). Special Publication No. 90, The Royal Society of Chemistry, Cambridge. p. 299-314.

Jones, C.L., N.L. Smoithers, M.C. Scholes and R.J. Scholes, 1990. The effect of fire frequency on the organic components of a basaltic soil in the Kruger National Park. *South African Journal of Plant and Soils* **7**: 236-238.

Jones, T.P. and W.G. Chaloner, 1991. Fossil charcoal, its recognition and paleo-atmospheric significance. *Global and Planetary Change* **97**: 39-50.

Kadeba, O., 1978. Organic matter status of some savanna soils of northern Nigeria. *Soil Science* **125**: 122-127.

Kaul, O.N., 1991. Forest biomass burning in India. *Tisglow* **2**: 2-17.

Kawaguchi, K. and K. Kyuma, 1977. *Paddy soils in tropical Asia, their material, nature and fertility*. Univ. Press of Hawaii, Honolulu.

Keeling, C.D., R.B. Bacastow, A.F. Carter, S.C. Piper, T.P. Whorf, M. Heimann, W.G. Mook and H. Roeloffzen, 1989. A three-dimensional model of atmospheric CO_2 transport based on observed winds: 1. Analysis and observational data. In: Aspects of climate variability in the Pacific and Western Americas (ed. D.H. Peterson). *Geophysical Monograph* **55**: 165-235.

Keeney, D.R., 1986. Critique of the acetylene blockage technique for field measurement of denitrification. In: *Field measurement of dinitrogen fixation and denitrification* (eds R.D. Hauck and R.W. Weaver). Special Publication No. 18, *Soil Science* Society of America, Madison. p. 103-115.

Keeney, D.R., I.R. Fillery, and G.P. Marx, 1979. Effect of temperature on gaseous N-products of denitrification. *Soil Science Society of America Journal* **43**: 1124-1128.

Keepin, W., I. Mintzer and L. Kristoferson, 1986. Emission of CO_2 into the atmosphere. In: *The greenhouse effect, climatic change and ecosystems* (eds Bolin, B., B.R. Böös, J. Jäger and R.A. Warrick). SCOPE 29, John Wiley and Sons, Chichester. p. 35-91.

Keller, M., S.C. Wofsy, T.J. Goreau, W.A. Kaplan and M.B. McElroy, 1983. Production of nitrous oxide and consumption of methane by forest soils. *Geophysical Research Letters* **10**: 1156-1159.

Kemper, W.D., Roseneau, R. and S. Nelson, 1985. Gas displacement and aggregate stability in soils. *Soil Science Society of America Journal* **49**: 25-28.

Khalil, M.A.K. and R.A. Rasmussen, 1983. Sources, sinks and seasonal cycles of atmospheric methane. *Journal of Geophysical Research* **88**: 5131-5144.

Khalil, M.A.K. and R.A. Rasmussen, 1987. Atmospheric methane: Trends over the last 10,000 years. *Atmospheric Environment* **21**: 2445-2452.

Khalil, M.A.K. and R.A. Rasmussen, 1988. Nitrous oxide: Trends and global mass balance over the last 3000 years. *Annals of Glaciology* **10**: 73-79

Khalil, M.A.K. and R.A. Rasmussen, 1990. Atmospheric methane: Recent global trends. *Environmental Science and Technology* **24**: 549-553.

Khalil, M.A.K., R.A. Rasmussen, M.X. Wang and L. Ren, 1990. Emission of trace gases from Chinese rice fields and biogas generators: CH_4, N_2O, CO, CO_2, chlorocarbons and hydrocarbons. *Chemosphere* **20**: 207-226.

Kimball, B.A., N.J. Rosenberg and L.H. Allen Jr., 1990. *Impact of carbon dioxide, trace gases, and climate change on global agriculture*. ASA Special Publication No. 53. ASA/CSSA/SSSA, Madison.

Kimble, J.M., H. Eswaran and T. Cook, 1990. Organic carbon on a volume basis in tropical and temperate soils. In: *Transactions of the 14th International Congress of Soil Science*, Kyoto **V**: 248-253

Kimura, M., 1992. Methane emissions from paddy soils in Japan and Thailand. In: *World Inventory of Soil Emission Potentials* (eds N.H. Batjes and E.M. Bridges). Proceedings of an international workshop organized in the framework of the Netherlands National Research Programme on Global Air Pollution and Climate Change (24-27 August 1992). WISE Report No. 2, International Soil Reference and Information Centre, Wageningen

Kimura, M., H. Ando and H. Haraguchi, 1991. Estimation of potential CO_2 and CH_4 production in Japanese paddy fields. *Environmental Science* **4**: 15-25.

Kimura, M., H. Murakami and H. Wada, 1991. CO_2, H_2 and CH_4 production in rice rhizosphere. *Soil Science Plant Nutrition* **37**: 55-60.

King, A.W., R.V. O'Neill and D.L. deAngelis, 1989. Using ecosystem models to predict regional CO_2 exchange between the atmosphere and the terrestrial biosphere. *Global Biogeochemical Cycles* **3**: 337-361.

King, G.M., 1990. Regulation by light of methane emissions from a wetland. *Nature* **345**: 513-514.

Kinsey, D.W. and D. Hopley, 1991. The significance of coral reefs as global carbon sinks - response to Greenhouse. *Global and Planetary Change* **89**: 363-377.

Klemedtsson, L. and G.I. Hansson, 1990. Methods to separate N_2O produced from denitrification and denitrification. *Mitteilungen der Deutschen Bodenkundlichen Gesellschaft* **60**: 19-24.

Klemedtsson, L. and B.H. Svensson, 1988. Effect of acid deposition, denitrification and N_2O-emission from forest soils. In: *Critical loads for sulphur and nitrogen* (Eds I. Nilsson and P. Grennfelt). Report of a workshop held at Skokloster, Sweden, 19-24 March 1988. Organized by UN-ECE and the Nordic Council of Ministers.

Klemedtsson, L., B.H. Svensson and T. Rosswall, 1988a. Relationships between soil moisture content and nitrous oxide production during nitrification and denitrification. *Biology and Fertility of Soils* **6**: 106-111.

Klemedtsson, L., B.H. Svensson and T. Roswall, 1988b. A method of selective inhibition to distinguish between nitrification and denitrification as sources of nitrous oxide in soil. *Biology and Fertility of Soils* **6**: 112-119.

Kling, G.W., G.W. Kipphut and M.C. Miller, 1991. Arctic lakes and streams as gas conduits to the atmosphere: Implications for tundra carbon budgets. *Science* **251**: 298-301.

Knight, D., P.W. Elliot and J.M. Andersen, 1989. Effects of earthworms upon transformations and movement of nitrogen from organic matter applied to agricultural soils. In: J.A.A. Hansen and K. Henriksen (eds). *Nitrogen in inorganic wastes applied to soils*. Academic Press, London. Academic Press, London. p. 59-80.

Knowles, R., 1981. Denitrification. In: *Terrestrial nitrogen cycles* (eds F.E. Clark and T. Roswall). Ecol. Bulletin (Stockholm) No. 33, p. 315-329

Knowles, R., 1982. Denitrification. *Microbiology Review* **46**: 43-70.

Kohlmaier, G.H., A. Janecek and J. Kindermann, 1990. Positive and negative feedback loops within the vegetation/soil system in response to a CO_2 greenhouse warming. In: *Soils and the greenhouse effect* (ed. Bouwman, A.F. 1990), John Wiley and Sons, Chichester. p. 415-422.

Kohnke, H., 1982. *Soil Physics*. Tata McGraw-Hill, New Delhi.

Kononova, V. 1966. *Soil organic matter: Its nature, its role in soil formation and in soil fertility*. 2nd English Edition, Pergammon Press Ltd., London.

Koorevaar, P., G. Menelik and C. Dirksen, C., 1983. *Elements of Soil Physics*. Developments in *Soil Science*, 13. Elsevier, Amsterdam.

Korteleven, J., 1963. *Quantitative aspects of humus build-up and humus degradation* (In Dutch). Verslagen Landbouwkundig Onderzoekingen 69/1, 109 p.

Koskinen, W.C. and D.R. Keeney, 1982. Effect of pH on the rate of gaseous products of denitrification in a silt loam soil. *Soil Science Society of America Journal* **46**: 1165-1167.

Koyama, T., 1963. Gaseous metabolism in lake sediments and paddy soils and the production of atmospheric methane and hydrogen. *Journal of Geophysical Research* **68**: 3971-3973.

Kristjansson, J.K., P. Schönheit and R.K. Thauer, 1982. Different Ks values for hydrogen of methanogenic bacteria and sulphate reducing bacteria: An explanation for the apparent inhibition of methanogenesis by sulphate. *Arch. Microbiology* **131**: 278-282.

Krosshavn, M., J.O. Bjorgum, J. Krane and E. Steinnes, 1990. Chemical structure of terrestrial humus materials formed from different vegetation characterized by soil-state 13C NMR with CP-MAS technique. *Journal of Soil Science* **41**: 371-377.

Kuhlbusch, T.A., J.M. Lobert, P.J. Crützen and P. Warneck, 1991. Molecular nitrogen emissions from denitrification during biomass burning. *Nature* **351**: 135-137.

Kuikman, P.J., L.J.A. Lekkerkerk and J.A. van Veen, 1991. Carbon dynamics of a soil planted with wheat under an elevated CO_2 concentration. In: *Advances in soil organic matter research* (ed. W.S. Wilson). Special Publication No. 90, The Royal Society of Chemistry, Cambridge. p. 267-274.

Kursar, T.A., 1989. Evaluation of soil respiration and soil CO_2 concentrations in a lowland moist forest in Panama. *Plant and Soil* **113**: 21-29.

Kyuma, K., 1985. Fundamental characteristics of wetland soils. In: *Wetland soils: Characterization, classification and utilization*. International Rice Research Institute, Los Banos.

Ladd, J.N., 1986. Techniques for following the turnover of organic matter in soil. In: *Transactions of the 13th International Congress of Soil Science*, Hamburg. p. 599-608.

Lashof, D.A. and D.A. Tirpak (eds), 1990. *Policy options for stabilizing global climate*. Hemisphere Publishing Company, New York.

Lawongse, P. and H. Wada, 1988. Effects of salts on microbial metabolism in submerged soils. *Proceedings of the First International Symposium on Paddy Soil Fertility*. Chiengmai (Thailand). p. 601-613.

Leemans, R. and W.P. Cramer, 1991. *The IIASA data base for mean monthly values of temperature, precipitation, and cloudiness on a global grid*. Research Report RR-91-18, IIASA, Laxenburg.

Leffelaar, P.A., 1986. Dynamics of partial anaerobiosis, denitrification, and water in a soil aggregate: Experimental. *Soil Science* **142**: 352-366.

Leffelaar, P.A. and W.W. Wessel, 1990. Denitrification in a homogeneous, closed system: Experiment and simulation. *Soil Science* **146**: 335-349.

Lekkerkerk, L.J.A., S.C. van de Geijn and J.A. van Veen, 1990. Effects of elevated atmospheric CO_2 levels on the carbon economy of a soil planted with wheat. In: *Soils and the greenhouse effect* (ed. A.F. Bouwman), John Wiley and Sons, Chichester. p. 423-429.

Lensi, R. and A. Chalamet, 1981. Absorption de l'oxyde nitreux par les parties aériennes de mais. *Plant and Soil* **59**: 91-98.

Lepsch, I.F., J.R.F. Menk and J.B. de Oliveira, 1991. A comparison of carbon storage and base status between cropped and native vegetation soils in Sao Paolo State, Brazil. *Journal of Soil Science* (Submitted)

Letey, J., A. Hadas, N. Valoras and D.D. Focht, 1980b. Effect of precipitation treatments on the ratio of N_2O/N_2 evolution. *Journal of Environmental Quality* **9**: 232-235.

Letey, J., W.A. Jury, A. Hadas and N. Valoras, 1980c. Gas diffusion as a factor in laboratory incubation studies on denitrification. *Journal of Environmental Quality* **9**: 223-227.

Letey, J., N. Valoras and D.D. Vocht, 1980a. Effect of air-filled porosity,nitrate concentration, and time on the ratio of N_2O/N_2 evolution during denitrification. *Journal of Environmental Quality* **9**: 227-231.

Letey, J., N. Valoras, D.D. Focht and J.C. Ryden, 1981. Nitrous oxide production and reduction during denitrification as affected by redox potential. *Soil Science Society of America Journal* **45**: 727-730.

Levine, J.S., 1989. Photochemistry of biogenic gases. In: *Global ecology: Towards a science of the biosphere* (eds M.B. Ramble, L. Margulis and R. Fester). Academic Press Inc., Boston. p. 51-74.

Levine, J.S., W.R. Cofer III, D.I. Sebacher, R.P. Rhinehart, E.L. Winstead, S. Sebacher, C.R. Hinkle, P.A. Schmalzer and A.K.M. Koller Jr., 1990. The effects of fire on biogenic emissions of methane and nitric oxide from wetlands. *Journal of Geophysical Research* **95**: 1853-1864.

Lindau, C.W., P.K. Bollich, R.D. DeLaune, W.H. Patrick and V.J. Law, 1991. Effect of urea fertilizer and environmental factors on CH_4 emissions from a Louisiana rice field. *Plant and Soil* **136**: 195-203.

Lindau, C.W., W.H. Patrick, R.D. DeLaune and K.R. Reddy, 1990. Rate of accumulation and emission of N2, N_2O and CH_4 fluxes from a flooded rice soil. *Plant and Soil* **129**: 269-276.

Linn, D.M. and J.W. Doran, 1984. Effect of water-filled pore space on carbon dioxide and nitrous oxide production in tilled and non-tilled soils. *Soil Science Society America Journal* **48**: 1267-1272.

Lobert, J.M., D.M. Scharffe, W.H. Hao and P.J. Crützen, 1990. Importance of biomass burning in the atmospheric budgets of nitrogen-containing gases. *Nature* **346**: 552-554.

Lobo, P.F.S., D.S. Barrera, L.F. Silva and J.M. Flexor, 1980. Carbon isotopes on the profile of characteristic soils of the south of the state of Bahia, Brazil (In Portuguese with English summary). *Revista Brasiliera do Cienco do Solo* **4**: 79-82.

Lorius, C.J., 1988. Polar ice cores and climate. In: *Climate and Geo-Sciences: A challenge for science and society in the 21st century* (eds. A. Berger, S. Schneider and J.Cl. Duplessy). Kluwer Academic Publisher, Dordrecht. p. 77-103.

Lotfield, N.S., R. Brumme and F. Beese, 1992. Automated monitoring of nitrous oxide flux and carbon dioxide flux from forest soils. *Soil Science Society of America Journal* **56**: 1147-1150.

Lowrance, R. and R.G. Williams, 1988. Carbon movement in runoff and erosion under simulated rainfall conditions. *Soil Science Society of America Journal* **52**: 1445-1448.

Lynch, J.M., 1990. *The rhizosphere.* Wiley Interscience, Chichester.

MacCarthy, P., C.E. Clapp, R.L. Malcolm and P.R. Bloom (eds), 1990a. *Humic substances in soil and crop sciences*. Selected readings. SSSA/ASA, Madison.

MacCarthy, P., R.L. Malcolm, C.E. Clapp and P.R. Bloom, 1990b. An introduction to soil humic substances. In: *Humic substances in soil and crop sciences* (eds MacCarthy *et al.*, 1990a) . Selected readings. SSSA/ASA, Madison. p. 1-12.

MacCarthy, P., P.R. Bloom, C.E. Clapp and R.L. Malcolm, 1990c. Humic substances in soil and crop sciences: An overview. In: *Humic substances in soil and crop sciences* (eds MacCarthy *et al.*, 1990a), Selected readings. SSSA/ASA, Madison. p. 261-271.

Magalhaes, A.T.M. and P.M. Chalk, 1987. Factors affecting the formation of methyl nitrite in soils. *Journal of Soil Science* **38**: 701-709.

Maini, J.S., 1988. Forest and atmospheric change. In: *The changing atmosphere*. WMO No. 710, Geneva. p., 193-209.

Malcolm, R.L. and P. MacCarthy, 1991. The individuality of humic substances in diverse environments. In: *Advances in soil organic matter research* (ed. W.S. Wilson). Special Publication No. 90, The Royal Society of Chemistry, Cambridge. p. 22-34.

Malinowsky, P. and J.C.G. Ottow, 1991. Ecological conditions and physiological mechanism of N_2O-formation from nitrite by *Fusarium solani*. In: *Diversity of environmental biogeochemistry* (ed. J. Berthelin). Elsevier, Amsterdam. p. 287-294.

Malmer, N., 1992. Peat accumulation and the global carbon cycle. In: *Greenhouse impact on cold-climate ecosystems and landscapes* (eds M. Boer and E. Coster). Catena Supplement 22, Catena Verlag, Cremlingen-Destedt. p. 97-110.

Mann, L.K., 1985. A regional comparison of carbon in cultivated and uncultivated Alfisols and Mollisols in the central United States. *Geoderma* **36**: 41-253.

Mann, L.K., 1986. Changes in soil carbon storage after cultivation. *Soil Science* **142**: 279-288.

Mannerma, J. and M. Karras, 1989. Use of the Maximum Entropy Method to predict atmospheric CO_2 content. *Geophysica* **25**: 37-46.

Marshall, T.J. and J.W. Holmes, 1988. *Soil Physics.* Cambridge University Press, Cambridge.

Martikainen, P.J. and A. Palojarvi, 1990. Evaluation of the fumigation extraction method for the determination of microbial C and N in a range of forest soils. *Soil Biology and Biochemistry* **22**: 797-802.

Martin, A., A. Mariotti, J. Balesdent, P. Lavelle and R. Vuattoux, 1990. Estimate of organic matter turnover rate in a savanna soil by 13C natural abundance measurements. *Soil Biology and Biochemistry* **4**: 517-523.

Matson, P.A. and D.S. Ojima, 1990. *Terrestrial biosphere exchange with global atmospheric chemistry*. Global Change Report No. 13, International Geosphere-Biosphere Programme, Stockholm.

Matthews, E., 1990. Global data bases for evaluation trace gas sources and sinks. In: *Soils and the greenhouse effect* (ed. A.F. Bouwman). John Wiley and Sons, Chichester. p. 311-325.

Matthews, E. and I. Fung, 1987. Methane emissions from natural wetlands: Global distribution, area, and environmental characteristics. *Global Biogeochemical Cycles* **1**: 61-86.

Matthews, E., I. Fung and J. Lerner, 1991. Methane emission from rice cultivation: Geographic and seasonal distribution of cultivated areas and emission. *Global Biogeochemical Cycles* **5**: 3-24.

Matthias, A.D., A.M. Blackmer and J.M. Bremner, 1980. A simple chamber technique for field measurement of emissions of nitrous oxide from soils. *Journal of Environmental Quality* **9**: 251-256.

Mattson, K.G. and W.T. Swank, 1989. Soil and detrital carbon dynamics following forest cutting in the southern Appalachians. *Biology and Fertility of Soils* **7**: 247-253.

Mattson, M.D. and G.E. Likens, 1990. Air pressure and methane fluxes. *Nature* **347**: 718-719.

Mausbach, M.J. and L.P. Wilding (eds, 1991. *Spatial variability of soils and landforms*. SSSA Special Publication No. 28, Soil Science Society of America, Inc., Madison, Wisconsin.

McClung, G. and W.T. Frankenberger Jr., 1985. Soil nitrogen transformations as affected by salinity. *Soil Science* **139**: 405-411.

McConnaughey, P.K. and D.R. Bouldin, 1985a. Transient microsite models of denitrification: I. Model development. *Soil Science Society of America Journal* **49**: 886-891.

McConnaughey, P.K. and D.R. Bouldin, 1985b. Transient microsite model of denitrification: II. Model results. *Soil Science Society of America Journal* **49**: 891-895.

McDaniel, P.A. and L.C. Munn, 1985. Effect of temperature on the relationship between organic carbon and texture in Mollisols and Aridisols. *Soil Science Society of America Journal* **49**: 1486-1489.

Medina, E., G. Montes, E. Cuevas and Z. Rokzandic, 1986. Profiles of CO_2 concentration and D13Cvalues in tropical rain forests of the upper Rio Negro Basin, Venezuela. *Journal of Tropical Ecology* **2**: 207-217.

Melillo, J.M., J.D. Aber, A.E. Linkins, A. Ricca, B. Fry and K.J. Nadelhoffer, 1989. Carbon and nitrogen dynamics along the decay continuum: Plant litter to soil organic matter. *Plant and Soil* **115**: 189-198.

Melillo, J.M., J.D. Aber, P.A. Steulder and J.P. Schimel, 1983. Denitrification potentials in a successional sequence of northern hardwood forest stands. In: *Environmental Biogeochemistry* (ed. R. Halberg). Ecological Bulletin 35, Stocholm. p. 217-228.

Mendonca, E. deS, W. Moura Filho and L.M. Costa, 1991. Organic matter and chemical characteristics of aggregates from a Red-Yellow Latosol under natural forest, Rubber plant, and grass in Brazil. In: *Advances in soil organic matter research* (ed. W.S. Wilson). Special Publication No. 90, The Royal Society of Chemistry, Cambridge. p. 185-195.

Miller, P.C. (ed.), 1981. Carbon balance in northern ecosystems and potential effect of carbon dioxide induced climate change. *Report of a workshop held at San Diego (March 7-9, 1980). CONF-8003118*, US Department of Energy, Washington D.C.

Minami, K. and A. Ohsawa, 1990. Emission of nitrous oxide dissolved in drainage waters from agricultural land. In: *Soils and the greenhouse effect* (ed. A.F. Bouwman). John Wiley and Sons, Chichester. p. 503-509.

Mintzer, I., 1985. Our changing atmosphere: Energy policies, air pollution and global warming. In: *The changing Atmosphere*. WMO No. 710, Geneva. p. 117-138.

Minzoni, F., C. Bonetto and H.L. Golterman, 1988. The nitrogen cycle in shallow-water systems of rice fields. Part I: The denitrification process. *Hydrobiologia* **159**: 189-202.

Mitchell, J.F.B., 1989. The 'greenhouse' effect and climatic change. *Rev. Geophysica* **27**: 115-139.

Moench, A.F. and D.D. Evans, 1970. Thermal conductivity and diffusivity of soil using a cylindrical heat source. *Soil Science Society of America Proceedings* **34**: 377-381.

Monteith, J.L., 1965. Evaporation and environment. *Symposium of the Society for Experimental Biology* **19**: 205.

Monteith, J.L., 1973. *Principles of Environmental Physics*. Edward Arnold, London.

Mooney, H.A., P.M. Vitousek and P.A. Matson, 1987. Exchange of materials between terrestrial ecosystems and the atmosphere. *Science* **238**: 928-932.

Moore III, B., M.P. Gildea, C.J. Vorosmarty, D.L. Skole, J.M. Mellilo, B.J. Peterson, E.B. Rastetter and P.A. Steudler, 1989. Biogeochemical cycles. In: *Global ecology: Towards a science of the biosphere* (eds M.B. Ramble, L. Margulis and R. Fester), Academic Press Inc., Boston. p. 113-141.

Moore, T.R. and R. Knowles, 1987. Methane and carbon dioxide evolution from subarctic fens. *Canadian Journal of Soil Science* **67**: 77-81.

Moore, T.R. and R. Knowles, 1989. The influence of water table levels on methane and carbon dioxide emissions from peatland soils. *Canadian Journal of Soil Science* **69**: 33-38.

Moore, T.R., N. Roulet and R. Knowles, 1990. Spatial and temporal variations of methane flux from subarctic/northern boreal fens. *Global Biogeochemical Cycles* **4**: 29-46.

Moormann, F.R. and N. van Breemen, 1978. *Rice: soil, water, land*. International Rice Research Institute, Los Banos.

Moran, M.A., R. Benner and R.E. Hodson, 1989. Kinetics of microbial degradation of vascular plant material in two wetland ecosystems. *Oecologia* **79**: 158-167.

Morgaghan, J.T. and R.J. Buresh, 1977. Chemical reduction of nitrite and nitrous oxide by ferrous iron. *Soil Science Society of America Journal* **41**: 47-50.

Mortvedt, J.J. and D.R. Buxton (eds), 1987. *Soil fertility and organic matter as critical components of production systems*. SSSA Special Publication No. 19, SSSA/ASA, Madison.

Mosier, A.R., 1990. Gas flux measurement techniques with special reference to techniques suitable for measurements over large ecologically uniform areas. In: *Soils and the Greenhouse Effect* (ed. A.F. Bouwman). John Wiley and Sons, London. p. 289-301.

Mosier, A.R., W.D. Guenzi and E.E. Schweizer, 1986. Soil losses of dinitrogen and nitrous oxide from irrigated crops in Northeastern Colorado. *Soil Science Society of America Journal* **50,** 344-348.

Mosier, A.R. and G.L. Hutchinson, 1981. Nitrous oxide emissions from cropped fields. *Journal of Environmental Quality* **10**: 169-173.

Mosier, A.R., S.K. Mohanty, A. Bhadrachalam and S. Chakravorti, 1990a. Influence of rice plants on the evolution of N_2 and N_2O from the soil to the atmosphere. *Mitteilungen der Deutschen Bodenkundlichen Gesellschaft* **60**: 115-120.

Mosier, A.R., S.K. Mohanty, A. Bhadrachalam and S. Chakravorti, 1990b. Evolution of N_2 and N_2O from the soil to the atmosphere through rice plants. *Biology and Fertility of Soils* **9**: 61-67.

Mosier, A.R., D.S. Schimel, D. Valentine, K. Bronson and W. Parton, 1991. Methane and nitrous oxide fluxes in native, fertilized and native grasslands. *Nature* **350**: 330-332.

Mosier, A.R., M. Stillwell, N.J. Parton and R.G. Woodmansee, 1981. Nitrous oxide emissions from a native shortgrass prairie. *Soil Science Society of America Journal* **45**: 617-619.

Mountfort, D.O., R.A. Asher, E.L. Mays and J.M. Tiedje, 1980. Carbon and electron flow in mud and sandflat intertidal sediments at Delaware Inlet, Nelson, New Zealand. *Applied and Environmental Microbiology* **39**: 686-694.

Mounsey, H. (ed.), 1988. *Building data bases for global science*. Taylor and Francis, London.

Msanya, B.M., 1987. *Soil resources inventories: Characterization, quality and evaluation of their adequacy for specific land use*. PhD. Thesis, Faculty of Sciences, State University of Ghent.

Mulvaney, R.L. and L.T. Kurtz, 1984. Evolution of dinitrogen and nitrous oxide from nitrogen-15 fertilized soil cores subjected to wetting and drying cycles. *Soil Science Society of America Journal* **48**: 596-602.

Munch, J.C., 1989. Organism specific denitrification in samples of an Udifluvent with different nitrate concentrations. *Zeitschrift für Planzenernährung und Bodenkunde* **152**: 395-400.

Munch, J.C., 1991. Nitrous oxide emissions from soil as determined by the composition of denitrifying microbial population. In: *Diversity of environmental biogeochemistry* (ed. J. Berthelin), Elsevier, Amsterdam. p. 308-315.

Munch, J.C. and J.C.G. Ottow, 1986. Nature des produits gazeux formés dans les sols à partir de differentes microflores dénitrifiantes. *Science du Sol* **24**: 337-350.

Murray, R.E., L.L. Parsons and M.S. Smith, 1989. Kinetics of nitrate utilization by mixed populations of denitrifying bacteria. *Applied and Environmental Microbiology* **55**: 717-721.

Muzio, L.C. and J.C. Kramlich, 1988. Artefacts in the measurement of N_2O combustion sources. *Geophysical Research Letters* **15**: 1369-1372.

Myers, N., 1989. Tropical deforestation and climatic change. *Climate and Geo-Sciences* (A. Berger et al.), Kluwer Academic Publishers. p. 341-353.

Naganawa, T., K. Kyuma, H. Yamamoto, Y. Yamamoto, H. Yokoi and K. Tatsuyama, 1989. Measurement of soil respiration in the field: Influence of temperature, moisture levels, and application of sewage sludge compost and agro-chemicals. *Soil Science and Plant Nutrition* **35**: 509-516 (Quoted in Soils and Fertilizers 119, 54 p. 161).

Natelhoffer, K.J. and B. Fry, 1988. Controls on natural nitrogen-15 and carbon-13 abundances in forest soil organic matter. *Soil Science Society of America Journal* **52**: 1633-1640.

Nayak, D.C., Varadachari and K. Gosh, 1990. Influence of organic acidic functional groups of humic substances in complexation with clay minerals. *Soil Science* **149**: 268-271.

Neftel, A., E. Moor, H. Oeschger and B. Stauffer, 1985. Evidence from polar ice cores for the increase in atmospheric CO_2 in the past two centuries. *Nature* **313**: 45-47.

Nelson, D.L. and L.E. Sommers, 1982. Total carbon, organic carbon, and organic matter. In: *Methods of soil analysis* (ed. A.L. Page). Agronomy **9**: 539-579.

Nelson, P.N., J.M. Oades and E. Cotsaris, 1991. The influence of soils on organic matter in water. In: *Advances in soil organic matter research* (ed. W.S. Wilson). Special Publication No. 90, The Royal Society of Chemistry, Cambridge. p. 115-120.

Nettleton, W.D. (ed.), 1991. *Occurrence, characteristics, and genesis of carbonate, gypsum and silica accumulation in soils.* SSSA Special Publication No. 26, SSSA/ASA, Madison.

Neue, H., 1989. Rice growing soils: Constraints, utilization and research needs. In: *Classification and management of rice growing soils.* FFTC Book Series, Food and Fertilizer Technology Centre for the ASPAC Region, Taiwan.

Neue, H.U. and P.A. Roger, 1992. *Rice agriculture: factors controlling emissions.* NATO-book Series (In press)

Neue, H.U. and W.W. Scharpenseel, 1984. Gaseous products of decomposition of organic matter in submerged soils. In: *Organic matter and rice.* International Rice Research Institute, Los Banos. p. 311-328.

Neue, H.U., P. Becker-Heidmann and H.W. Scharpenseel, 1990. Organic matter dynamics, soil properties, and cultural practices in rice lands and their relationships to methane production. In: *Soils and the greenhouse effect* (ed. A.F. Bouwman). John Wiley and Sons, Chichester. p. 457-466.

Nielsen, D.R. and J. Bouma (eds), 1985. *Soil spatial variability.* Proceedings Workshop ISSS and SSSA, Las Vegas. Pudoc, Wageningen.

Nouchi, I., S. Mariko and K. Aoki, 1990. Mechanism of methane transport from the rhizosphere to the atmosphere through rice plant. *Plant Physiology* **94**: 59-66.

Novozamsky, I., J. Beek and G.H. Bolt, 1978. Chemical equilibria. In: *Soil chemistry. A. Basic elements* (eds. G.H. Bolt and M.G.M. Bruggenwert). Elsevier Scientific Publ. Co., Amsterdam. p. 13-42.

Oades, J.M., A.G. Waters, A.M. Vasallo, M.A. Wilson and P.G. Jones, 1988. Influence of management on the composition of organic matter in a red-brown earth as shown by 13C Nuclear Magnetic Resonance. *Australian Journal of Soil Research* **26**: 289-299.

O'Hara, G.W. and R.M. Daniel, 1985. Rhizobial denitrification: A review. *Soil Biology and Biochemistry* **17**: 1-9.

Oldeman, L.R. and W.G. Sombroek, 1990. Use of the SOTER data base to model global change. *Transactions 14th International Congress of Soil Science* **V**: 136-141

Oldeman, L.R., R.T.A. Hakkeling and W.G. Sombroek, 1991. *World map of the status of human-induced soil degradation. An explanatory note (Second revised edition).* International Soil Reference and Information Centre, Wageningen / United Nations Environment Programme, Nairobi. Published in cooperation with the Winand Staring Centre, International Society of Soil Science, Food and Agricultural Organization of the United Nations, and International Institute for Aerospace Survey and Earth Sciences.

Oliver, H.R., 1983. The availability of evaporation data in space and time for use in water balance computations. In: *New Approaches in Water Balance Computations.* Proceedings of the Hamburg Workshop, August 1983. IAIIS Publication No. 148.

Oliver, S.A., H.R. Oliver, J.S. Wallace and A.M. Roberts, 1987. Soil heat flux and temperature variation with vegetation, soil type and climate. *Agricultural and Forest Meteorology* **39**: 257-269.

Olson, J.S., 1981. Carbon balance in relation to fire regimes. In: *Fire regimes and ecosystem properties* (eds. H.A. Mooney, T.M. Bonnickson, N.L. Christensen, J.E. Lotan and W.E. Reiners). GTR WO-26, Forest Service, U.S. Department of Agriculture, Washington D.C.

Olson, J.S., J.A. Watts and L.J. Allison, 1983. *Carbon in live vegetation of major world ecosystems.* DOE/NBB-0037. Carbon Dioxide Research Division, Washington DC.

Oremland, R.M., 1988. Biogeochemistry of methanogenic bacteria. In: *Biology of anaerobic microorganisms* (ed. A.J.B. Zehnder). John Wiley and Sons, New York. p. 641-706.

Oremland, R.S. and C.W. Culbertson, 1992. Importance of methane-oxidizing bacteria in the methane budget as revealed by the use of a specific inhibitor. *Nature* **356**: 421-423.

Oremland, R.M., L.M. Marsh and S. Polcin, 1982. Methane production and simultaneous sulphate reduction in anoxic, marsh sediments. *Nature* **296**: 143-145.

ORNL, 1990. *TRENDS '90: A compendium of data on global change* (eds. T.A. Boden, K. Kanciruk and M.P. Farell). Carbon Dioxide Information Centre, Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Pacey, J.G. and J.P. De Gier, 1986. The factors influencing landfill gas production. In: *Energy from landfill gas.* Proceedings of a conference jointly sponsored by the United Kingdom Department of Energy and the United States Department of Energy (October 1986). p. 51-59.

Papen, H. and H. Rennenberg, 1990. Microbial processes involved in emissions of radiatively important trace gases. In: *Transactions 14th International Congress of Soil Scienc, Kyoto* **II**: 232-237.

Parashar, D.C., J. Rai, Prabhat K. Gupta and N. Singh, 1991. Parameters affecting methane emission from paddy fields. *Indian Journal of Radio and Space Physics* **20**: 12-17

Parkin, T.B., 1987. Soil microsites as a source of denitrification variability. *Soil Science Society of America Journal* **51**: 1194-1199.

Parkin, T.B. and J.A. Robinson, 1989. Stochastic models of soil denitrification. *Applied and Environmental Microbiology* **55**: 72-77.

Parry, M.L., 1990. *Climate change and world agriculture.* Earthscan Publications Limited (in association with International Institute for Applied Systems Analysis and United Nations Environment Programme), London.

Parry, M.L., J.H. Porter and T.R. Carter, 1990. Climatic change and its implications for agriculture. *Outlook on Agriculture* **19**: 9-15.

Parsons, L.L., R.E. Murray and M.S. Smith, 1991. Soil denitrification dynamics: Spatial and temporal variations of enzyme activity, populations and nitrogen gas loss. *Soil Science Society of America Journal* **55**: 90-95.

Parton, W.J., A.R. Mosier and D.S. Schimel, 1988. Rates and pathways of nitrous oxide production in a short grass steppe. *Biogeochemistry* **6**: 45-58.

Parton, W.J., R.L. Sanford, P.A. Sanchez and J.W.B. Stewart, 1989. Modelling soil organic matter dynamics in tropical soils. In: *Dynamics of soil organic matter in tropical ecosystems* (eds Coleman, D.C., J.M. Oades and G. Uehara). NifTAL Project, University of Hawaii Press, Honolulu.

Parton, W.J., D.S. Schimel, C.V. Cole and D.S. Ojima, 1987. Analysis of factors controlling soil organic matter levels in Great Plains grasslands. *Soil Science Society of America Journal* **51**: 1173-1179.

Pastor, J. and W.M. Post, 1986. Influence of climate, soil moisture, and succession on forest carbon and nitrogen cycles. *Biogeochemistry* **2**: 3-27.

Patrick, W.H. Jr, 1981. The role of inorganic redox systems in controlling reduction in paddy soils. In: *Proceedings of the Symposium on Paddy Soils.* Institute of Soil Science, Academia Sinica, Science Press, Beijing. p. 107-117.

Patterson, D.T. and E.P. Flint, 1990. Implications of increasing carbon dioxide and climate change for plant communities and competition in natural and managed ecosystems. In: Kimball et al. (1990), p. 83-110.

Paul, E.A., C.A. Campbell, D.A. Rennie and M.D. McCullum, 1964. Investigations of the dynamics of soil humus using carbon dating techniques. *Transaction of 8th International Congress of Soil Science* **3**: 201-208

Payne, D., 1988. The behaviour of water in soil. In: Wild A. (Ed.), *Russell's Soil Conditions and Plant Growth,* Longman Scientific and Technical, Harlow.

Payne, D. and P.J. Gregory, 1988. The soil atmosphere. In: Wild A. (Ed.), *Russell's Soil Conditions and Plant Growth,* Longman Scientific and Technical, Harlow.

Penman, H.L., 1940. Gas and vapour movements in the soil. 1. The diffusion of vapours through porous solids. *Journal of Agricultural Science* **30**: 437-62.

Penman, H.L., 1948. Natural evaporation from open water, bare soil and grass. *Proceedings of the Royal Society, London* **A 193**: 120-146.

Phillipson, J., 1966. *Ecological Energetics.* Arnold, London.

Piccolo, A. and J.S.C. Mbagwu, 1990. Effects of different organic waste amendments on soil microaggregate stability and molecular size of humic substances. *Plant and Soil* **123**: 27-37.

Pleijsier, K., 1989. Variability in soil data. In: *Land qualities in space and time* (eds J. Bouma and A.K. Bregt). Pudoc, Wageningen.

Ponnamperuma, F.N., 1972. The chemistry of submerged soils. *Advances in Agronomy* **24**: 29-96.

Ponnamperuma, F.N., 1981. Some aspects of the physical chemistry of paddy soils. In: *Proceedings of the Symposium on Paddy Soils*. Institute of Soil Science, Academia Sinica, Science Press, Beijing (Springer Verlag, Berlin). p. 59-94.

Ponnamperuma, F.N., 1984. Effects of flooding on soils. In: *Flooding and plant growth* (ed. T.T. Kozlowski). Academic Press Inc. p. 9-43.

Post, W.M., 1990. Report of a workshop on climate feedbacks and the role of peatlands, tundras and boreal ecosystems in the global carbon cycle. *Environmental Sciences Division Publ. No. 3289*, Oak Ridge National Laboratory, Tennessee.

Post, W.M., W.R. Emanuel, P.J. Zinke and A.G. Stangenberger, 1982. Soil carbon pools and world life zones. *Nature* **298**: 156-159.

Post, W.M., J. Pastor, P.J. Zinke and A.G. Stangenberger, 1985. Global patterns of soil nitrogen. *Nature* **317**: 613-616.

Poth, M. and D.D. Focht, 1985. ^{15}N kinetic analysis of N_2O production by Nitrosomonas europea: An examination of nitrifier denitrification. *Applied and Environmental Microbiology* **49**: 1134-11141.

Powlson, D.S., P.G. Saffinga and M. Kragt-Cottaar, 1988. Denitrification at suboptimal temperature in soils from different climate zones. *Soil Biology and Biochemistry* **20**: 719-723.

Prade, K. and G. Trolldenier, 1990a. Incidence of Geamannomyces graminis var. tritici and K deficiency increase rhizospheric denitrification. *Plant and Soil* **124**: 141-142.

Prade, K. and G. Trolldenier, 1990b. Denitrification in the rhizosphere of rice and wheat seedlings as influenced by the K-status of plants. *Mitteilungen der Deutschen Bodenkundlichen Gesellschaft* **60**: 121-126.

Prentice, K.C. and I.Y. Fung, 1990. The sensitivity of terrestrial carbon storage to climate change. *Nature* **346**: 48-51.

Prinn, R., D. Cunold, R. Rasmussen, P. Simmonds, F. Aleya, A. Crawford, P. Fraser and R. Rosen, 1990. Atmospheric emissions and trends of nitrous oxide deduced from 10 years of ALE-GAGE data. *Journal of Geophysical Research* **95**: 18369-18385.

Raich, J.W., R.D. Bowden and P.A. Steudler, 1990. Comparison of two static chamber techniques for determining carbon dioxide efflux from forest soils. *Soil Science Society of America Journal* **54**: 1754-1757.

Raich, J.W. and W.H. Schlesinger, 1992. The global carbon dioxide flux in soil respiration and its relationship to vegetation. *Tellus* (in press).

Raskin, I. and H. Kende, 1985. Mechanic aeration in rice. *Science* **228**: 327-329.

Rasmuson A., T. Gimmi and H. Fluhler, 1990. Modelling reactive gas uptake transport and transformation in aggregated soils. *Soil Science Society of America Proceedings* **54**: 1206-1213.

Rasmussen, R.A. and M.A.K. Khalil, 1981. Atmospheric methane (CH_4): Trends and seasonal cycles. *Journal of Geophysical Research* **86**: 9826-9832.

Reddy, K.R. and W.H. Patrick Jr., 1986. Denitrification losses in flooded rice fields. In: *Nitrogen economy of flooded rice soils* (eds S.K. De Datta and W.H. Patrick Jr.). Martinus Nijhoff, Dordrecht. p. 99-116.

Reddy, K.R., W.H. Patrick Jr. and C.W. Lindau, 1987. Fertilizer nitrogen losses in the root zone of rice. In: *Agronomy abstracts*. American Society of Agronomy, Madison. p. 191.

Reinds, G.J., G.H.J. de Koning and J.D. Bulens, 1992. *Crop production potential or rural areas within the European Communities: Part III - Soils, climate and administrative regions*. Working Document 67, Netherlands Scientific Council for Government Policy, The Hague.

Richter, D.D., L.I. Babbar, M.A. Huston and M. Jaeger, 1990. Effects of annual tillage on organic carbon in a fine-textured Udalfs: The importance of root dynamics to soil carbon storage. *Soil Science* **149**: 78-83.

RIVM, 1991. *Sustainable use of groundwater: Problems and threats in the European Communities*. National Institute of Public Health and Environmental Protection (RIVM) and Institute for Inland Water Management and Waste Water Treatment (RIZA). RIVM-RIZA project 600025. RIVM, Bilthoven.

Robertson, G.P. and J.M. Tiedje, 1987. Nitrous oxide sources in aerobic soils: nitrification, denitrification and other biological processes. *Soil Biology and Biochemistry* **19**: 187-193.

Rochette, P., R.L. Desjardins and E. Pattey, 1991. Spatial and temporal variability of soil respiration in agricultural fields. *Canadian Journal of Soil Science* **71**: 189-196.

Rolston, D.E., 1990. Modelling of denitrification: Approaches, successes and problems. *Mitteilungen der Deutschen Bodenkundlichen Gesellschaft* **60**: 397-402.

Rolston, D.E. and F.E. Broadbent, 1977. *Field measurement of denitrification*. U.S. Environmental Protection Agency Report EPA A-600/2-77-233, Washington D.C.

Rolston, D.E., P.S.C. Rao, J.M. Davidson and R.E. Jessup, 1984. Simulation of denitrification losses of nitrate fertilizer applied to uncropped, cropped and manure-amended field plots. *Soil Science* **137**: 270-279.

Rolston, D.E., A.N. Sharpley, D.W. Toy and T.E. Broadbent, 1982. Field measurement of denitrification III: Rates during irrigation cycles. *Soil Science Society of America Journal* **46**: 289-296.

Rosswall, T., 1981. The biogeochemical nitrogen cycle. In: *Some perspectives of the major biogeochemical cycles* (ed. G.E. Likens). SCOPE 17, John Wiley and Sons, Chichester etc. p. 25-49.

Rosswall, T., R.G. Woodmansee and P.G. Risser, 1988. *Scales and global change: Spatial and temporal variability in biospheric and geospheric processes.* SCOPE 35, John Wiley and Sons, Chichester.

Rotmans, J., M.G.J. Van den Elzen, R.J. Swart and H. Van der Woerd, 1992. Stabilizing atmospheric concentrations: Towards international methane control. *Ambio* **6**: 404-413.

Russell, E.W., 1980. *Soil conditions and plant growth (10th edition).* Longman, London.
[Revised by A. Wild (ed.), 1988. *Russell's soil conditions and plant growth (11th edition).* Longman, London].

Ryden, J.C., 1981. N_2O exchange between a grassland soil and the atmosphere. *Nature* **292**: 235-237.

Ryden, J.C., L.J. Lund and D.D. Focht, 1978. Direct in field measurement of nitrous oxide flux from soils. *Soil Science Society of America Journal* **42**: 731-737.

Saenjan, P. and H. Wada, 1990. Effects of salts on methane formation and sulphate reduction in submerged soil. In: *Transactions 14th International Congress of Soil Science*, Kyoto **II**: 244-247.

Sahrawat, K.L. and D.R. Keeney, 1986. Nitrous oxide emission from soils. In: *Advances in Soil Science*, Volume 4 (ed. B.A. Stewart). Springer Verlag, New York. p. 103-148.

Sakai, M., 1990. Carbon cycles of the soil-root system in two types of forest soil in Japan. In: *Transactions 14th International Congress of Soil Science*, Kyoto **II**: 413.

Sakamoto, K. and T. Yoshida, 1988. In situ measurement of soil respiration rate by a dynamic method. *Soil Science and Plant Nutrition* **34**:, 195-202.

Sanchez, P.A., C.A. Palm and T.J. Smyth, 1990. Approaches to mitigate tropical deforestation by sustainable soil management practices. *Soils on a warmer Earth (effects of expected climate change on soil processes, with emphasis on the tropics and sub-tropics).* Developments in *Soil Science* 20, Elsevier, Amsterdam. p. 211-220.

Sanchez, P.A., J.H. Villachica and D.E. Bandy, 1983. Soil fertility after clearing a tropical rainforest in Peru. *Soil Science Society of America Journal* **47**: 1171-1178.

Sanford, R.L., J. Saldarriaga, K.E. Clark, C. Uhe and R. Herrera, 1985. Amazon rainforest fires. *Science* **227**: 53-55.

Santos, O.M. and B.M. Grisi, 1979. Cellulose and leaf litter decomposition in a tropical rain forest in southern Bahia, Brazil: Comparative study in undisturbed and burned areas (In Portuguese with English summary). *Revista Brasiliera do Cienco do Solo* **3**: 149-153.

Santos, M.C.D., A.R. Mermut and M.R. Ribeiro, 1989. Submicroscopy of clay microaggregates in an Oxisol from Pernambuco, Brazil. *Soil Science Society of America Journal* **53**: 1895-1901.

Sarmiento, J.L. and E.T. Sundquist, 1992. Revised budget for the oceanic uptake of anthropogenic carbon dioxide. *Nature* **356**: 589-592.

Sass, R.L., F.M. Fisher, P.A. Harcombe and F.T. Turner, 1990. Methane production and emission in agricultural wetlands. *Global Biogeochemical Cycles* **4**: 47-68.

Schaefer, M. and J. Schauermann, 1990. The soil fauna of beech forests: comparison between a mull and moder soil. *Pedobiologia* **34**: 299-314.

Scharpenseel, H.W., M. Schomaker and A. Ayoub (eds), 1990. *Soils on a warmer Earth: Effects of expected climate change on soil processes, with emphasis on the tropics and sub-tropics.* Developments in *Soil Science* 20, Elsevier, Amsterdam.

Scharpenseel, H.W. and P. Becker-Heidmann, 1990. Overview of the greenhouse effect: Global change syndrome; general outlook. In: *Soils on a warmer Earth (effects of expected climate change on soil processes, with emphasis on the tropics and sub-tropics).* Developments in Soil Science 20, Elsevier, Amsterdam. p. 1-14.

Schiffman, P.M. and W.C. Johnson, 1989. Phytomass and detrital carbon storage during forest regrowth in the southeastern U.S. Piedmont. *Canadian Journal of Forest Research* **19**: 97-98.

Schimel, W.H., D.C. Coleman and K.A. Horton, 1985a. Soil organic matter dynamics in paired rangeland and cropland toposequences in North Dakota. *Geoderma* **36**: 201-214.

Schimel, W.H., M.A. Stilwell and R.G. Woodmanse, 1985b. *Biogeochemistry* of C, N, and P in a soil catena of the short grass steppe. *Ecology* **66**: 276-288.

Schimel, D.S., W.J. Parton, T.G.F. Kittel, D.S. Ojima and C.V. Cole, 1990. Grassland biogeochemistry: Links to atmospheric processes. *Climatic Change* **16**: 13-25.

Schlesinger, W.H., 1977. Carbon balance in terrestrial detritus. *Annual Review of Ecology and Systematics* **8**: 51-81.

Schlesinger, W.H., 1985. The formation of caliche in soils of Mojave desert, California. *Geochemica et Cosmochemica Acta* **49**: 57-66.

Schlesinger, W.H., 1984. Soil organic matter: A source of atmospheric CO_2. In: *The role of terrestrial vegetation in the global carbon cycle* (eds. G.W. Woodwell), SCOPE Vol. 23, John Wiley and Sons, New York.

Schlesinger, W.H., 1986. Changes in soil carbon storage and associated properties with disturbance and recovery. In: *The changing carbon cycle: A global analysis* (eds J.R. Trabalka and D.E. Reichle), Springer-Verlag, New York. p. 175-193.

Schlesinger, W.H., 1990a. Vegetation an unlikely answer. *Nature* **348**: 679

Schlesinger, W.H., 1990b. Evidence from chronosequence studies for a low carbon-storage potential of soils. *Nature* **348**: 232-234.

Schnitzer, M., 1991. Soil organic matter - the next 75 years. *Soil Science* **151**: 41-58.

Schnitzer, M., J.A. Ripmeester and H. Kodama, 1988. Characterization of the organic matter associated with a soil clay. *Soil Science* **145**: 488-49..

Schönheit, P., J.K. Kristjansson and R.K. Thauer, 1982. Kinetic mechanism for the ability of sulphate reducers to out-compete methanogens for acetate. *Arch. Microbiology* **132**: 285-288.

Schütz, H., P. Schröder and H. Renneberg, 1991. Role of plants in regulating the methane flux to the atmosphere. In: *Trace gas emission from plants* (eds. T.D. Sharkey, E.A. Holland and H.A. Mooney). Academic Press, New York.

Schütz, H., W. Seiler and R. Conrad, 1990b. Influence of soil temperature on methane emission from rice paddy fields. *Biogeochemistry* **11**: 77-95.

Schütz, H., W. Seiler and R. Conrad, 1989b'. Processes involved in formation and emission of methane in rice paddies. *Biogeochemistry* **7**:33-53.

Schütz, H., W. Seiler and H. Rennenberg, 1990a. Soil and land use related sources and sinks of methane (CH_4) in the context of the global methane budget. In: *Soils and the greenhouse effect* (ed. A.F. Bouwman). John Wiley and Sons, Chichester. p. 269-285.

Schütz, H., A. Holzapfel-Pschorn, R. Conrad, H. Rennenberg and W. Seiler, 1989a. A three year continuous record on the influence of day time, season and fertilizer treatment on methane emission rates from an Italian rice paddy field. *Journal of Geophysical Research* **4**: 16405-16416.

Sebacher, D.I., R.C. Harriss and K.B. Bartlett, 1983. Methane flux across the air-water interface: Air velocity effects. *Tellus* **35B**: 103-109.

Sebacher, D.I., R.C. Harriss and K.B. Bartlett, 1985. Methane emissions to the atmosphere through aquatic plants. *Journal of Environmental Quality* **14**: 40-46.

Sebacher, D.I., R.C. Harris, K.B. Bartlett, S.M. Sebacher and S.S. Grice, 1986. Atmospheric methane sources: Alaskan tundra bogs, an alpine fen, and a subarctic boreal marsh. *Tellus* **38B**: 1-10.

Seech, A.G. and E.A. Beauchamp, 1990. Denitrification in soil aggregates of different sizes. *Soil Science Society of America Journal* **52**: 1616-1621.

Seiler, W., 1984. Contribution of biological processes to the global budget of CH_4 in the atmosphere. In: *Current perspectives in microbial ecology* (eds M.J. Klug and C.A. Reddy), American Society for Microbiology, Washington D.C. p. 468-477.

Seiler, W., 1989. Role of rice cultivation in global emissions of trace gases. *Proceedings of the Workshop on Greenhouse Gas Emissions from Agricultural Systems of the IPCC Response Strategies Working Group* (December 12-14, 1989), Washington D.C.

Seiler, W. and R. Conrad, 1987. Contribution of tropical ecosystems to the global budgets of trace gases, especially CH_4, H_2, CO and N_2O. In: *Geophysiology of Amazonia. Vegetation and climate interactions* (eds. R.E. Dickinson). John Wiley and Sons, New York. p. 133-160.

Seiler, W. and P.J. Crützen, 1980. Estimates of gross and net fluxes of carbon between the biosphere and the atmosphere from biomass burning. *Climatic Change* **2**: 207-247.

Seiler, W., A. Holzapfel-Pschorn, R. Conrad and D. Scharffe, 1984. Methane emissions from rice paddies. *Journal of Atmospheric Chemistry* **1**: 241-268.

Setzer, A.W. and M.C. Pereira, 1991. Amazonia biomass burnings in 1987 and an estimate of their tropospheric emissions. *Ambio* **20**: 19-22.

Sextone, A.J., T.B. Parkin and J.M. Tiedje, 1985. Temporal response of soil denitrification rates to rainfall and irrigation. *Soil Science Society of America Journal* **49**: 99-103.

Sharma, P.P., S.C. Gupta and W.J. Rawb, 1991. Soil detachment by single raindrops of varying kinetic energy. *Soil Science Society of America Proceedings* **55**: 301-307.

Shelton, D.R. and T.B. Parkin, 1989. A semi-automated instrument for measuring total and radio-labelled carbon dioxide evolution from soil. *Journal of Environmental Quality* **18**: 550-554.

Shugart, H.H., M. Ya. Antonovsky, P.G. Jarvis and A.P. Sandford, 1986. CO_2, climatic change and forest ecosystems. Assessing the response of global forests to the direct effects of increasing CO_2 and climatic change. In: *The greenhouse effect, climatic change and ecosystems* (eds Bolin, B., B.R. Böös, J. Jäger and R.A. Warrick). SCOPE 29, John Wiley and Sons, Chichester. p. 475-521.

Shukla, J., C. Nobre and P. Sellers, 1990. Amazon deforestation and climate change. *Science* **247**: 1322-1325.

Siegel, D.I., 1983. Ground water and the evolution of patterned mires, Glacial Lake Agassiz peatlands, northern Minnesota. *Journal of Ecology* **71**: 913-921.

Siegel, D.I. and P.H. Glaser, 1991. *Mechanisms controlling the production and transport of methane, carbon dioxide, and dissolved solutes within a large boreal peat basin*. DOE Research Summary No. 11, Carbon Dioxide Information Analysis Centre, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Simonson, R.W., 1959. Outline of generalized theory of soil genesis. *Soil Science Society of America Proceedings* **23**: 152-156

Sims, Z.R. and G.A. Nielsen, 1986. Organic carbon in Montana soils as related to clay content and climate. *Soil Science Society of America Journal* **50**: 1269-1271.

Sinha, S.K., N.H. Rao and M.S. Swaminathan, 1988. Food security in the changing global climate. In: *The changing atmosphere*. WMO Report No. 710, World Meteorological Organization, Geneva. p.167-192.

Skjemstad, J.O., R.P. LeFeuvre and R.E. Prebble, 1990. Turnover of soil organic matter under pasture determined by C natural abundance. *Australian Journal of Soil Research* **28**: 267-276.

Smith, B.N. and S. Epstein, 1971. Two categories of 13C/12C ratios for higher plants. *Plant Physiology* **47**: 380-384.

Smith, C.J., F.M. Wright and W.H. Patrick Jr., 1983. The effect of soil redox potential and pH on the reduction and production of nitrous oxide. *Journal of Environmental Quality* **12**: 186-188.

Smith, G.B. and M.S. Smith, 1986. Symbiotic and free-living denitrification by *Bradyrhizobium japonicum*. *Soil Science Society of America Journal* **50**: 349-354.

Smith, K.A., 1980. A model of the extent of anaerobic zones in aggregated soils and its potential to estimate of denitrification. *Journal of Soil Science* **31**: 263-277.

Smith, M.S. and K. Zimmerman, 1981. Nitrous oxide production by non-denitrifying soil nitrate reducers. *Soil Science Society of America Journal* **45**: 865-871.

Smith, R.E. and K.B. Higgins, 1990. The root systems of three species of *Protea* shrubs in the Jonkershoek Valley, Cape Province. *South African Journal of Plant and Soil* **7**: 238-240.

Smith, T.R., S. Menna, J.L. Star and J.E. Ester, 1987. Requirements and principles for the implementation and construction of large scale geographic information systems. *International Journal of Geographical Information Systems* **1**: 13-31.

Smucker, A.J.M. and G.R. Safir, 1986. Root and soil microbial interactions which influence the availability of photo-assimilate carbon in the rhizosphere. In: *Microfloral and faunal interactions in natural and agro-ecosystems* (eds. M.J. Mittchell and J.P. Nakas). Nijhoff and Junk Publisher, Dordrecht. p. 203-244.

Sombroek, W.G., 1966. *Amazon soils*. PhD thesis, Agricultural University Wageningen., Pudoc, Wageningen.

Sombroek, W.G., 1985. *Establishment of an International; Soil and Land Resources Information Base.* Discussion paper for the ISSS Working Group on Digital Mapping of Global Soil Resources. International Soil Reference and Information Centre, Wageningen.

Sombroek, W.G., 1990a. Soils on a warmer earth: The tropical regions. In: *Soils on a warmer earth* (eds H.W. Scharpenseel, M. Schomaker and A. Ayoub). Elsevier, Amsterdam. p. 157-174.s

Sombroek, W.G., 1990b. Geographic quantification of soils and changes in their properties. In: *Soils and the greenhouse effect* (ed. A.F. Bouwman). John Wiley and Sons, Chichester. p. 225-244.

Sørensen, L.H., 1975. The influence of clay on the rate of decay of amino acid metabolites synthesised in soils during decomposition of cellulose. *Soil Biology and Biochemistry* **7**: 171-177.

Spaans, E.J.A., G.A.M. Baltissen, J. Bouma, R. Miedema, A.L.E. Lansu, D. Schoonderbeek and W.G. Wielemaker, 1989. Changes in physical properties of young and old volcanic surface soils in Costa Rica after clearing of tropical rain forest. *Hydrological Processes* **3**: 383-392.

Spaans, E.J.A., J. Bouma, A. Lansu and W.G. Wielemaker, 1990. Measuring soil hydraulic properties after clearing of tropical rain forest in a Costa Rican soil. *Tropical Agriculture (Trinidad)* **67**: 61-65.

Spain, A.V., R.F. Isbell and M.E. Probert, 1983. Soil organic matter. In: *Soils: An Australian viewpoint*, CSIRO, Melbourne/Academic Press, London. p. 552-563.

Sparling, G.P. and A.W. West, 1990. A comparison of gas chromatography and differential respirometer methods to measure soil respiration and to estimate the soil microbial biomass. *Pedobiologia* **34**: 103-112.

Sprent, J.I., 1990. The biology of nitrogen transformations. *Soil Use and Management* **6**: 74-77.

Stainer, R.Y., E.A. Adelberg and J.I. Ingraham, 1976. *General microbiology (4th edition)*. The MacMillan Press Ltd., London.

Stauffer, B., E. Lochbronner, H. Oeschger and J. Schwander, 1988. Methane concentration in the glacial atmosphere was only half that of the preindustrial Holocene. *Nature* **332**: 812-814.

Steele, L.P., P.J. Fraser, R.A. Rasmussen, M.A.K. Khalil, T.J. Conway, A.J. Crawford, R.U. Gamuron, K.A. Masaric and K.W. Thoning, 1987. The global distribution of methane in the troposphere. *Journal of Atmospheric Research* **5**: 127-171.

Stegeman, D. and H.K. Cammenga, 1990. Investigation on adsorption and diffusion of nitrous oxide in soil matrices. *Mitteilungen der Deutschen Bodenkundlichen Gesellschaft* **60**: 73-82.

Steudler, P.A., R.D. Bowden, J.M. Mellilo and J.D. Aber, 1989. Influence of nitrogen fertilization on methane uptake in temperate forest soils. *Nature* **341**: 314-316.

Stevenson, F.J., 1982. *Humus chemistry: Genesis, compositions, reactions*. Wiley Interscience, New York.

Stigliani, W.M., 1988. Changes in valued 'capacities' of soils and sediments as indicators of non-linear and time-delayed environmental effects. *Environmental Monitoring and Assessment* **10**: 245-307.

Stott, D.E. and J.P. Martin, 1990. Synthesis and degradation of natural and synthetic humic materials in soils. In: MacCarthy et al. (eds), *Humic substances in soil and crop sciences*. Selected readings. SSSA/ASA, Madison. p. 37-63.

Stouthamer, A.H., 1988. Dissimilatory reduction of oxidised nitrogen compounds. In: *Biology of anaerobic microorganisms* (ed. A.J.B. Zehnder). John Wiley and Sons, New York. p.245-303.

Svensson, B.H., 1984. Different temperature optima in methane formation when enrichments from acid peat are supplemented with acetate or hydrogen. *Applied Environmental Microbiology* **48**: 389-394.

Svensson, B.H., 1986. Methane as a part of the carbon mineralization in an acid tundra mire. In: *Perspectives in Microbial Ecology, Proceedings of the 4th International Symposium on Microbial Ecology* (eds F. Megusar and M. Ganter). Sloven Society for Microbiology, Ljubljana. p.611-616.

Svensson, B.H. and R. Rosswall, 1984. In situ methane production from acid peat in plant communities with different moisture regimes in a subarctic mire. *Oikos* **43**: 341-350.

Svensson, B.H., U. Boström and L. Klemedtsson, 1986. Potential for higher rates of denitrification in earthworm casts than in the surrounding soil. *Biology and Fertility of Soils* **2**: 147-149.

Swarup, A., 1989. Influence of organic matter and flooding on the chemical and electrochemical properties of sodic soil and rice growth. *Plant and Soil* **106**: 135-141.

Swift, R.S., 1991. Effects of humic substances and polysaccharides on soil aggregation. In: *Advances in soil organic matter research* (ed. W.S. Wilson). Special Publication No. 90, The Royal Society of Chemistry, Cambridge. p. 153-162.

Szabolcs, I., 1991. Salinization potential of European soils. In: *Land use changes in Europe: Processes of change, environmental transformation and future patterns* (eds. F.M. Brouwer, E.J. Thomas and M.J. Chadwick). GeoJournal Library Vol. 18, Kluwer Academic Publisher, Dordrecht.

Takai, Y., 1961. Reduction of microbial metabolism in paddy soils (in Japanese). *Nogyo Gijitsu (Agricultural Technology)*, **19**: 122-126.

Takai, Y. and T. Kamura, 1966. The mechanism of reduction in waterlogged paddy soil. *Folia Microbiology* **11**: 304-313.

Takai, Y. and E. Wada, 1990. Methane formation in waterlogged paddy soils and its controlling factors. In: *Soils on a warmer Earth* (eds H.W. Scharpenseel, H.W., M. Schomaker and A. Ayoub). Developments in *Soil Science* 20, Elsevier, Amsterdam. p. 101-107.

Tanner, C.B., 1960. Energy balance approach to evapotranspiration from crops. *Soil Science Society of America Proceedings* **24**: 1-9.

Tans, P.P., I.Y. Fung and T. Takahashi, 1990. Observational constraints on the global atmospheric CO_2 budget. *Science* **247**: 1431-1438.

Tavernier, R. (ed.), 1985. *Soil map of the European Communities 1:1 M*. Directorate General for Agriculture, Coordination of Agricultural Research. Office for Official Publications of the European Communities, Luxembourg.

Thauer, R.K., K. Jungermann and K. Decker, 1977. Energy conservation in chemotrophic anaerobic bacteria. *Bacteriol. Rev.* **41**: 100-180.

Terhune, C.L. and J.W. Harden, 1991. Seasonal variations of carbon dioxide concentrations in the stony, coarse textured desert soils of southern Nevada, USA. *Soil Science* **151**: 417-429.

Terry, R.E., R.L. Tate III and J.M. Duxburg, 1981. The effect of flooding on nitrous oxide emissions from an organic soil. *Soil Science* **132**: 228-232.

Thauer, R.K., K. Jungermann and K. Decker, 1977. Energy conservation in chemotrophic anaerobic bacteria. *Bacteriol. Rev.* **41**: 100-180.

Theng, B.K.G., G.J. Churchman and R.H. Newman, 1986. The occurrence of inter-layer clay-organic complexes in two New Zealand soils. *Soil Science* **142**: 262-26..

Theng, B.K.G., K.R. Tate and P. Sollins, 1989. Constituents of organic matter in temperate and tropical soils. In: *Dynamics of organic matter in tropical soils* (eds. D.C. Coleman, J.M. Oades and G. Uehara). NifTAL Project, University of Hawaii. p. 5-32.

Thiemens, M.H. and W.C. Trogler, 1991. Nylon production: An unknown source of atmospheric N₂O. *Science* **251**: 932-934.

Thompson, R.B. and B.F. Pain, 1989. Denitrification from cattle slurry applied to grassland. In: *Nitrogen in organic wastes applied to soils* (eds J.A. Hansen and K. Henriksen). Academic Press, London. p. 247-260.

Tiedje, J.M., 1988. Ecology of denitrification and dissimilatory nitrate reduction to ammonium. In: *Biology of anaerobic soils* (ed. Zehnder). John Wiley and Sons, New York. p. 179-244.

Tiedje, J.M., A.J. Sexstone, T.B. Parkin, N.P. Revsbeck and D.R. Shelton, 1984. Anaerobic process in soil. *Plant and Soil* **76**: 197-212.

Tiessen, H. and J.W.B. Stewart, 1983. Particle size fractions and their use in studies of soil organic matter. II. Cultivation effects on organic matter composition in size fractions. *Soil Science Society of America Journal* **47**: 509-514.

Tiessen, H., J.W.B. Stewart and J.R. Bettany, 1982. Cultivation effects on the amounts and concentration of carbon nitrogen, and phosphorus in grassland soils. *Agronomy Journal* **74**: 831-834.

Tinker, P.B. and P. Ineson, 1990. Soil organic matter and biology in relation to climatic change. In: *Soils on a warmer Earth* (eds H.W. Scharpenseel, H.W., M. Schomaker and A. Ayoub). Developments in *Soil Science* 20, Elsevier, Amsterdam. p. 71-87

Tisdall, J.M. and J.M. Oades, 1980. The effect of crop rotation on aggregation in red-brown earth. *Australian Journal of Soil Research* **18**: 423-433.

Townshend, J.R.G. (ed.), 1992. *Improved global data for land applications: a proposal for a high resolution data set.* Global Change Report No. 20, International Geosphere-Biosphere Programme, Stockholm.

Trabalka, J.R. and D.E. Reichle (eds), 1986. *The changing carbon cycle: A global analysis.* Springer-Verlag, New York.

Ueckert, J., T. Hureck, I. Fendrik and E.G. Nieman, 1990. Radial diffusion from roots of rice (*Oryza sativa* L.) and Kallandra grass (*Leptochloa fusca* L. Kunth), and effects of inoculation with *Azospirillum brasilense. Plant and Soil* **122**: 59-65.

Umarov, M.M., 1990. Biotic sources of nitrous oxide in the context of the global budget of nitrous oxide. In: *Soils and the greenhouse effect* (ed. A.F. Bouwman). John Wiley and Sons, Chichester. p. 263-268.

Unesco, 1973. *International classification and mapping of vegetation.* United Nations Scientific, Educational and Cultural Organization, Paris.

USDA, 1975. *Soil Taxonomy: A basic system of soil classification for making and interpreting soil surveys.* Agricultural Handbook 436, Soil Conservation Service, US Department of Agriculture, Washington D.C.

USDA, 1987. *Keys to Soil Taxonomy.* SMSS Technical Monograph 6, Ithaca, New York.

USDA/SCS, 1972. *Soils of the world: Distribution of orders and principal suborders (1:50 M).* Soil Geography Unit, Soil Conservation Service, Hyattsville.

Vaghjiani, G.L. and A.R. Ravishankara, 1991. New measurements of the rate coefficient for the reaction of OH with methane. *Nature* **350**: 406-408.

Vaidyanathan, L.V. and D.J. Eagel, 1991. The influence of organic matter and clay on adsorption of atrazine by top soils. In: *Advances in soil organic matter research* (ed. W.S. Wilson). Special Publication No. 90, The Royal Society of Chemistry, Cambridge. p. 381-391.

Van Bavel, C.H.M., 1952, Gaseous diffusion and porosity in porous media. *Soil Science* **73**: 91-104.

Van Breemen, N., 1990. Impact of anthropogenic atmospheric pollution on soils, with special relevance to tropical and subtropical soils, and possible consequences of the greenhouse effect. In: *Soils on a warmer earth* (eds. H.W. Scharpenseel, M. Schomaker and A. Ayoub). Developments in *Soil Science* 20, Elsevier, Amsterdam. p. 137-144.

Van Breemen, N. and T.C.J. Feijtel, 1990. Soil processes and properties involved in the production of greenhouse gases, with special relevance to soil taxonomic systems. In: *Soils and the greenhouse effect* (ed. A.F. Bouwman). John Wiley and Sons, Chichester. p. 195-223.

Van Cleemput, O., W.J. Patrick Jr. and R. McIllhenny, 1976. Nitrate decomposition in flooded soil under different pH and redox conditions. *Soil Science Society of America Journal* **40**: 55-60.

Van Dam, A.J. and C.A. Van Diepen, 1982. *The soils of the wetlands of the world: Their distribution and agricultuiral potential.* Paper prepared for the Symposium on 'Polders of the World' (4-10 October 1982, Lelystad, the Netherlands). International Soil Museum (currently International Soil Reference and Information Centre), Wageningen.

Van Diepen, C.A., 1985. Wetland soils of the world, their characterization and distribution in the FAO/Unesco approach. In: *Wetlands soils: Characterization, classification and utilization.* Proceedings of an IRRI Workshop. International Rice Research Institute, Los Banos. p. 361-374.

Van Engelen, V.W.P. and Pulles, J.H.M., 1991. *The SOTER Manual: Procedures for small scale digital map and data base compilation of soil and terrain conditions*. Working Paper and Preprint 91/3, International Soil Reference and Information Centre, Wageningen.

Van Keulen, H. and J. Wolf (eds), 1986. *Modelling of agricultural production: Weather, soils and crops.* Simulation Monographs. Pudoc, Wageningen.

Van Lanen, H.A.J. and A.K. Bregt, 1989. Application of computerized EC soil map and climate data. *Proceedings of a workshop in the Community Programme for Coordination on Agriculture (15-16 November, Wageningen)*. Commission of the European Communities, Brussels.

Van Lanen, H.A.J., C.M.A. Hendriks and J.D. Bulens, 1992. *Crop production potential or rural areas within the European Communities: Part V - Qualitative suitability assessment for forestry and fruit crops*. Working Document 69, Netherlands Scientific Council for Government Policy, The Hague.

Van Reeuwijk, L.P., 1983. *On the way to improve international soil classification and correlation: The variability of analytical data*. Annual Report, International Soil Museum (now International Soil Reference and Information Centre), Wageningen.

Van Reeuwijk, L.P., 1992. *Procedures for soil analysis (3rd edition)*. Technical Paper No. 19, International Soil Reference and Information Centre, Wageningen.

Van Veen, J.A., 1986. The use of simulation models of the turnover of soil organic matter: An intermediate report. *Transactions of the 13th International Congress of Soil Science*, Hamburg. p. 626-635.

Van Veen, J.A. and E.A. Paul, 1981. Organic carbon dynamics in grassland soils. I. Background information and computer simulation. *Canadian Journal of Soil Science* **61**: 185-201.

Van Veen, J.A. and P.J. Kuikman, 1990. Soil structural aspects of decomposition of organic matter by micro-organisms. *Biogeochemistry* **11**: 213-233.

Van Veen, J.A., J.N. Ladd and M. Amato, 1985. The turnover of carbon and nitrogen through he microbial biomass in a sandy-loam and a clay soil incubated with [14C(U)]-glucose and [15N]-(NH4)2SO4 under different moisture regimes. *Soil Biology and Biochemistry* **17**: 747-756.

Van Velthuizen, H.T., 1992. *Updating the World Soil Resources Data base.* Project proposal prepared for FAO *(unpublished)*.

Van Waveren, E., 1987. *Guidelines for the description and coding of soil data.* Technical Paper No. 14, International Soil Reference and Information Centre, Wageningen.

Van Waveren, E. and A.B. Bos, 1988. *ISRIC Soil Information System; User manual, Technical manual*. Technical Paper No. 15, International Soil Reference and Information Centre, Wageningen.

Veldkamp, E., A.M. Weitz, C.G. Staritsky and E.J. Huising, 1992. Deforestation types in the Atlantic zone of Costa Rica: A case study. *Land Degradation and Rehabilitation* **3**: 71-84.

Verberne, E.L.J., J. Hassink, P. de Willigen, J.J.R. Groot and J.A. van Veen, 1990. Modelling organic matter dynamics in different soils. *Netherlands Journal of Agricultural Science* **38**: 221-238.

Vereecken, H., J. Maes and J. Feyen, 1989. Estimating unsaturated hydraulic conductivity from easily measured soil properties. *Soil Science* **149**: 1-12.

Verheye, W.H., 1987. The new EC soil map as a computer data base for land use planning in the European Communities. In: *Agriculture: Computerization of soil land use data* (eds R.J.A. Jones and B. Biagi). Proceedings of a symposium in the Community project for coordination of agricultural research (20-22 May 1987, Pisa). Commission of the European Communities, Luxembourg.

Vogel, G.D., J.K. Keltjens and C. Van de Drift, 1988. Biochemistry of methane formation. In: *Biology* of anaerobic microorganisms (ed. A.J.B. Zehnder). John Wiley and Sons, Chichester. p. 707-700.

Volkoff, B. and C.C. Cerri, 1980. Humus comparison of a Solonchak, a Rendzina and a Lithosolic soil from semi-arid region of Rio Grande do Norte. *Revista Brasiliera do Cienco do Sol* **4**: 49-56.

Volkoff, B. and C.C. Cerri, 1987. Carbon isotopic fractionation in subtropical Brazilian grassland soils. Comparison with tropical forest soils. *Plant and Soil* **102**: 27-31.

Volkoff, B. and C.C. Cerri, 1988. L'humus des sols du Brésil. Nature et relations avec l'environment. *Cahiers ORSTOM, Série Pédologie* **XXIV**: 83-95.

Volkoff, B., C.C. Cerri and A.J. Melfi, 1984. Humus and mineralogy of superficial horizons of three soils from upland grass fields of Minas Gerais, Parana and Santa Catarina States, Brazil. *Revista Brasiliera do Cienco do Solo* **8**: 277-283.

Volkoff, B., J.M. Flexor, L. Santa Isabel and M. Santa Isabel, 1978. Characterization of the humus of Dystric Latosols of Bahia (In Portuguese with English summary). *Revista Brasiliera do Cienco do Solo* **2**: 59-63.

Von Rheinbaben, W., 1990. Nitrogen losses from agricultural soils through denitrification - a critical evaluation. Zeitschrift für Pflanzenernahrung und Bodenkunde **153**: 157-166.

Voroney, R.P., 1988. Loss of organic matter in Ontario. *Highlights of Agricultural Research in Ontario* **11**: 25-29 (As quoted in Soils and Fertilizers 1991, 55 p. 135).

Voroney, R.P., J.A. Van Veen and E.A. Paul, 1981. Organic C dynamics in grassland soils. 2. Model validation and simulation of the long-term effects of cultivation and rainfall erosion. *Canadian Journal of Soil Science* **61**: 211-224.

Wada, K. and S. Aomine, 1975. Soil development during the quaternary. *Soil Science* **116**: 170-177.

Wahlen, S.C. and W.S. Reeburgh, 1990. Consumption of atmospheric methane by tundra soils. *Nature* **346**: 160-162.

Walker, J.C.G. and J.F. Kasting, 1992. Effects of fuel and forest conservation on future levels of atmospheric carbon dioxide. *Paleogeography, Paleoclimatology, Paleoecology (Global Planetary Change Section)* **97**: 151-189.

Walker, B.H. and R.D. Graetz (eds), 1988. *Effects of atmospheric and climate change on terrestrial ecosystems*. Global Change Report No. 5, International Geosphere-Biosphere Programme, Stockholm.

Walker, T.W. and J.K. Syers, 1976. The fate of phosphorus during pedogenesis. *Geoderma* **15**: 1-19.

Walkley, A. and I.A. Black, 1934. An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method. *Soil Science* **34**: 29-38.

Wang, T.S.C., P.M. Huang, C-H. Chou and J-H. Chen, 1986. The role of soil minerals in the abiotic polymerization of phenolic compounds and formation of humic substances. In: *Interactions of soil minerals with natural organics and microbes* (eds. P.M. Huang and M. Schnitzer). SSSA Special Publication 17, Soil Science Society of America, Madison, Wisconsin.

Ward, D.M. and R.M. Winfrey, 1985. Interactions between methanogenic and sulphate-reducing bacteria in sediments. *Advances in Aquatic Microbiology* **3**: 141-179.

Warrick, R.A. and E.M. Barrow, 1990. Climate and sea level change: A perspective. *Outlook on agriculture* **19**: 5-8.

Warrick, R.A. and R. Gifford with M.L. Parry, 1986a. CO_2, climatic change and agriculture. In: *The greenhouse effect climatic change and ecosystems* (eds B. Bolin, B.R. Döos, R.A. Warrick and J. Jager). SCOPE 29, John Wiley and Sons, New York. p. 393-473.

Warrick, R.A., H.H. Shugart, M. Ja. Antonovsky, J.R. Tarrant and C.J. Tucker, 1986b. The effects of increased CO_2 and climatic change on terrestrial ecosystems. Global perspectives, aims and issues. In: *The greenhouse effect, climatic change and ecosystems* (eds Bolin, B., B.R. Böös, J. Jäger and R.A. Warrick). SCOPE 29, John Wiley and Sons, Chichester. p. 363-392.

Watanabe, I. and P.A. Roger, 1985. Ecology of flooded rice fields. In: *Wetland soils: Characterization, classification and utilization*. International Rice Research Institute, Los Banos.

Waters, A.G. and J.M. Oades, 1991. Organic matter in water-stable aggregates. In: *Advances in soil organic matter research* (ed. W.S. Wilson). Special Publication No. 90, The Royal Society of Chemistry, Cambridge. p. 163-174.

Watson, A., 1992. Conveying that sinking feeling. *Nature* **356**: 561-562.

Watts, D., 1971. *Principles of Biogeography.* McGraw-Hill, London.

Webb, R.S., C.E. Rosenzweig and E.R. Levine, 1991. *A Global data set of soil particle size properties*. NASA Technical Memorandum No. 4286, National Aeronautics and Space Administration, Washington D.C.

Weber, M.G., 1990. Forest soil respiration and burning in immature aspen ecosystems. *Forest Ecology and Management* **31**: 1-14.

Weier, K.L. and J.W. Doran, 1987. The potential for biological denitrification in a Brigalow clay soil under different management systems. In: *Nitrogen cycling in agricultural systems of temperate Australia* (eds. P.E. Bacon, J. Evans, P.R. Storrier and A.C. Taylor), Wagga Wagga. p. 327-339.

Weiss, R.F., 1981. The temporal and spatial distribution of nitrous oxide. *Journal of Geophysical Research* **86**: 7185-7195.

White, R.E. and G.N. Mageson, 1991. A stochastic empirical approach to modelling nitrate leaching. *Soil Use and Management* **7**: 85-93.

Whiting, G.J., J.P. Chanton, D.S. Batlett and J.D. Happel, 1991. Relationships between methane emissions, biomass, and CO_2 exchange in a subtropical grassland. *Journal of Geophysical Research* **96**: 13067-13071.

Wielemaker, W.G.and A.L.E. Lansu, 1991. Land use changes affecting classification of a Costa Rican soil. *Soil Science Society of America Journal* 55: 1621-1624

Wijler, J. and C.C. Delwiche, 1954. Investigations on the denitrification process in soils. *Plant and Soil* **5**: 155-169.

Wilhelmi, V. and G.M. Rothe, 1990.The effects of acid rain, soil temperature and humidity on C-mineralisation rates in organic soil layers under spruce. *Plant and Soil* **121**: 197-202.

Williams, R.J. and R.L. Crawford, 1984. Methane production in Minnesota peatlands. *Applied and Environmental Microbiology* **47**: 1266-1271.

Wilson, W.S. (ed.), 1991. *Advances on soil organic matter research: The impact on agriculture and the environment*. Special Publication No. 90, The Royal Society of Chemistry, Cambridge.

Wilson, J.O., P.M. Crill, K.B. Bartlett, D.I. Sebacher, P.C. Harris and R.L. Sass, 1989. Seasonal variation of methane emission from a temperate swamp. *Biogeochemistry* **8**: 55-71.

Winfrey, M.R., D.G. Marty, A.J.M. Bianchi and D.M. Ward, 1981. Vertical distribution of sulphate reduction, methane production and bacteria in marine sediments. *Geomicrobiology Journal* **2**: 341-362.

Wolf, J. and L.H.J.M. Janssen, 1991. Effects of changing land use in the Netherlands on net carbon fixation. *Netherlands Journal of Agricultural Science* **39**: 237-246.

Wolf, J.K. and B.B. Rogowski, 1991. Spatial distribution of soil heat flux and growing degree days. *Soil Science Society of America Proceedings* **55**: 747-657.

Woodwell, G.M., 1984a. *The role of terrestrial vegetation in the global carbon cycle.: Measurement by remote sensing.* SCOPE 23, John Wiley and Sons, Chichester.

Woodwell, G.M., 1984b. The carbon dioxide problem. In: *The role of terrestrial of terrestrial vegetation in the global carbon cycle: Measurement by remote sensing* (ed. G.M. Woodwell). SCOPE 23, John Wiley and Sons, Chichester. p. 3-17.

Woodwell, G.M., R.A. Houghton, T.A. Stone, A.B. Park, 1986. Changes in the area of forests in Rondonia, Amazon Basin, measured by satellite imagery. In: *The changing carbon cycle: a global analysis* (eds. J.R. Trabalka and D.E. Reichle). Springer Verlag, New York. p 242-257.

Woodwell, G.M. and 6 other authors, 1983. Global deforestation: Contribution to atmospheric carbon dioxide. *Science* **222**: 1081-1086.

Wookey, P.A. and P. Ineson, 1991. Chemical changes in decomposing forest litter in response to atmospheric sulphur dioxide. *Journal of Soil Science* **42**: 615-628.

Yagi, K. and K. Minami, 1990. Effects of organic matter application on CH_4 emissions from Japanese paddy fields. In: *Soils and the greenhouse effect* (ed. A.F. Bouwman). John Wiley and Sons, New York. p. 467-473.

Yagi, K. and K. Minami, 1991. Emission and production of methane in the paddy fields of Japan. *Japanese Agricultural Research Quarterly* **25**: 165-171

Yagi, K., K. Minami, G.A. Breitenbeck and H. Takayama, 1990. Emission and production of methane from paddy fields. In: *Transactions 14th International Congress of Soil Science*, Kyoto **II**: 238-243.

Yamamuro, S., 1991. A theoretical approach to the fate of nitrogen in paddy field by using a NH_4-^{15}N tracer technique and an estimate of the rate of N uptake by rice plant (In Japanese with extended English summary). *Bulletin of the Kyushu National Agricultural Experimental Station, Chikugo, Fukuoka*. p 1-64.

Yamane, I. and K. Sato, 1967. Effect of temperature on the decomposition of organic substances in flooded soil. *Soil Science and Plant Nutrition* **13**: 94-100.

Yang, T., W.B. Jiang, X-C. Sun, Y.G. Du and Y.Y. Li, 1989. Studies on respiration of soils under different vegetation types in alpine meadows. *Acta Pedologica Sinica* **26**: 188-192. (Quoted in *Soils and Fertilizers*, 1990, **53**: 758).

Yavitt, J.B., G.E. Lang and M. Downey, 1988. Potential methane production and methane oxidation rates in peatland ecosystems of the Appalachian mountains, United States. *Global Biogeochemical Cycles* **2**: 253-268.

Yavitt, J.B., G.E. Lang and R.K. Wieder, 1987. Control of carbon mineralization to CH_4 and CO_2 in anaerobic *Sphagnum*-derived peat from Big Run Bog, West Virginia. *Biogeochemistry* **4**: 141-157.

Yavitt, J.B., D.M. Downey, E. Lancaster and G.E. Lang, 1990. Methane consumption in decomposing *Sphagnum* derived peat. *Soil Biology and Fertility* **22**: 441-447.

Yoshida, T.M. and M. Alexander, 1970. Nitrous oxide formation by Nitrosomonas europea and heterotrophic microorganisms. *Soil Science Society of America Journal* **34**: 880-882.

Youngs, E.G. and P.B. Leeds-Harrison, 1990. Aspects of transport processes in aggregated soils. *Journal of Soil Science* **41**: 665-675.

Zaiss, U., 1981. Seasonal studies of methanogenesis and desulfurication in sediments of the river Saar. *Zentralblatt für Bakteriologie, Mikrobiologie und Hygiene, Abt. I. Originale* **C-2**: 76-89.

Zech, W., L. Haumaier and R. Hempfling, 1990. Ecological aspects of soil organic matter in tropical soils. In: MacCarthy et al., 1990a (eds), *Humic substances in soil and crop sciences*. Selected readings. SSSA/ASA, Madison. p. 187-202.

Zehnder, A.J.B., 1982. The carbon cycle. In: *The handbook of environmental chemistry*, Vol. 1B (ed. O. Hutzinger). Springer Verlag, Berlin. p. 83-110.

Zeikus, J.G. and M.R. Winfrey, 1976. Temperature limitations of methanogenesis in aquatic sediments. *Applied and Environmental Microbioly* **31**: 99-107.

Zinke, P.J., A.G. Stangenberger, W.M. Post, W.R. Emmanuel and J.S. Olson, 1984. *Worldwide organic soil carbon and nitrogen data*. ORNL/TM-8857, Oak Ridge National Laboratory. Oak Ridge, Tennessee.

Zobler, L., 1986. *A world soil file for global climate*. NASA Technical Memorandum 87-802.

Zoltai, S.C. and F.C. Pollet, 1983. Wetlands in Canada: Their classification, distribution and use. In: *Ecosystems of the World (4B). Mires: Swamps, Bog, Fen and Moor* (ed. A.J.P. Gore), Elsevier, Amsterdam. p. 245-268.

Appendices

Appendix I: Estimated sources and sinks of methane (In Tg CH_4 per year; Source: IPCC 1992).

Sources	
Natural	
- Wetlands	115 (100-200)
- Termites	20 (10-50)
- Oceans	10 (5-20)
- Freshwater	5 (1-25)
- CH_4 hydrate	0 (0-5)
Anthropogenic	
- Coal mining, natural gas and petroleum industry	100 (70-120)
- Rice paddies	60 (20-100)
- Enteric fermentation	80 (65-100)
- Animal wastes	25 (20-30)
- Domestic sewage treatment	25 (?-?)
- Landfills	30 (20-70)
- Biomass burning	40 (20-80)
Sinks	
Reaction with OH	420 (340-500)
Removal by soils	30 (15-45)
Removal in stratosphere	10 (?-?)
Atmospheric increase	37 (34-40)

Appendix II: Preliminary structure and list of attributes for the WISE soil data base

a) <u>File 1</u>:
  Description: Geo-referenced, individual 30' x 30' grids, characterized in terms of their component FAO soil units.

  Attribute data: GRID-ID (Eastings and Northings of upper left hand corner of grid cell)
                    Probable reliability of data in grid (H, M, L)
                    Regional update in WISE (Y, N)
                    Date of update (month/year)
                    - First spatially dominant major soil unit or sea, glacier etc. where appropriate [SOIL-code]; relative area within grid; identifier of representative profile (PROF-ID);
                    - Second spatially dominant major soil unit [SOIL-code]; percentage of grid area; reference number of representative profile (PROF-ID);
                    - as above, tentatively up to the first approximate 60%-70% of the grid cell's area. (Note the area of each 30' x 30' grid cell decreases according to a cosine function of latitude from the equator towards the poles, with an average area of about 55 x 55 km at the equator).

b) <u>File 2</u>:
  Description: Characteristics for the 'topsoil' and 'subsoil' of FAO soil units as derived from simple algorithms and expert-judgement; this file is to provide an overall indication of the range in characteristics.

  Attributes: SOIL-code
                    'Derived' values for e.g. texture, bulk density, pH-H_2O, water holding capacity for the topsoil and subsoil, respectively.

c) <u>File 3</u>:
  Description: Selected, readily 'available' attribute data for representative soil profiles (PROF-ID) of the respective FAO soil units (SOIL-code).

  Attribute data: GRID-ID
                    SOIL-code
                    PROF-ID

                    a) 'Site characteristics' file; ideally the data specified should be representative for the whole soil unit in so far this is possible at the considered scale of mapping with the available data sources; specified using the ISIS and SOTER coding conventions:
                        -   Latitude (° ' ")
                        -   Longitude (° ' ")
                        -   Elevation
                        -   Country
                        -   Laboratory ID (provides a key to the analytical procedures)
                        -   Date of sampling date (month/year)
                        -   Code for national data base/source of data (references in extra data file).
                        -   Landform
                        -   Landscape position

- Aspect
- Slope class
- Parent material
- Drainage class
- Average depth of groundwater table (mean lowest and highest)
- Average depth to rock, etc.
- Vegetation or land use (at time of profile description/sampling)

b) 'Soil layer' data file; listings of selected key soil
   characteristics per major horizon (to be specified as
   numerical values):
   - PROF-ID
   - HORIZON-number
   - FAO horizon codes
   - Top of master horizon i, average depth (below surface)
   - Bottom of master horizon i, average depth
   - Munsell colour code (dry and moist)
   - Organic carbon content
   - Total N content
   - Extractable P content
   - pH-water
   - pH-KCl
   - Electical conductivity
   - Calcium carbonate content
   - Gypsum content
   - Cation exchange capacity (measured at pH 7 in NH_4AOc)
   - Exchangeable Ca^{2+}, Mg^{2+}, K^+ and Na^+ (measured at pH 7 in NH_4AOc)
   - Exchangeable acidity (measured at field pH; **O**ptional, i.e. to be stored only
     when actually measured data are available)
   - Base saturation (%)
   - Coarse fragments (volume %)
   - clay%
   - sand%
   - silt%
   - FAO texture
   - Structure type
   - Soil moisture content at field capacity (O)
   - Soil moisture content at permanent wilting point (O)
   - Bulk density (O)

c) A file providing a detailed key to the analytical methods.

Glossary

The glossary was compiled from the following sources:

[1] ORNL, 1990. *Glossary: Carbon dioxide and climate*. Environmental Sciences Division Publication No. 3532, The Carbon Dioxide Information Analysis Centre, Oak Ridge National Laboratory.
[2] SSSA, 1979. *Glossary of soil science terms*. Soil Science Society of America, Madison, Wisconsin.
[3] Rambler, M.B., L. Margulis and R. Fester (eds), 1989. *Global ecology: Towards a science of the biosphere*. Academic Press, Inc., Boston. p. 149-169.
[4] Burrough, P.A., 1986. *Principles of Geographical Information Systems for land resources assessment*. Monographs on Soil and Land Resources Survey No. 12, Clarendon Press, Oxford. p. 177-183.
[5] IPCC, 1990. *Climate change: The IPCC scientific assessment*. Edited by J.T. Houghton, G.J. Jenkins and J.J. Ephraums. WMO/UNEP, Cambridge University Press, Cambridge.
[6] Abercombe, M., C.J. Hickman and M.L. Johnson, 1973. *A dictionary of biology (6th edition)*. Penguin books, Harmondsworth.
[7] Reinhardt, R.D., 1992. *Geographic Information Systems (GIS) - A global perspective*. Global Environmental Change Report, Cutter Information Corporation, Arlington.
[8] Brady, N,C., 1984. *The nature and properties of soils* (Ninth edition). MacMillan Publishing Company, New York.

Aerobic: (i) Having molecular oxygen as part of the environment; (ii) growing only in the presence of molecular oxygen, as aerobic organisms; (iii) occurring only in the presence of molecular oxygen (say of certain chemical or biochemical processes, such as aerobic decomposition) [8].

Albedo: The fraction of the total solar radiation incident on a body that is reflected by it [1].

Ammonification: The biochemical process whereby ammoniacal nitrogen is released from nitrogen-containing organic compounds [8].

Anaerobic: (i) Without molecular oxygen; (ii) living or functioning in the absence of air or free oxygen [8]. Sometimes, also called 'anoxic'.

Assimilation: The incorporation of inorganic or organic substances into cell constituents [1].

Atmosphere: The mixture of gases that surrounds a planet (e.g., on the Earth the atmosphere is composed of approximately 79 per cent nitrogen (N_2) and 21 percent oxygen (O_2), with smaller quantities of argon, carbon dioxide, water vapour, hydrogen, methane, sulphur oxides, and other gases) [3].

Attribute: Non-graphic information associated with a point, line, or area element in a GIS [4].

Autocorrelation, autocovariance: Statistical concepts expressing the degree to which the value of an attribute at spatially adjacent points covaries with the distance separating the points [4].

Autotroph: An organism capable of utilizing carbon dioxide or carbonates as a sole source of carbon and obtaining energy for carbon reduction and biosynthetic processes from radiant energy (photo-autotroph) or oxidation of inorganic substances (chemo-autotroph) [2]. Contrast with heterotrophic.

Autotrophic nitrification: Oxidation of ammonium to nitrate through the combined action of two chemoautotrophic organisms, one forming nitrite from ammonium and the other oxidizing nitrite to nitrate [2].

Auxiliary storage: Addressable memory devices outside the main memory of the computer such as disks and tape units [4].

Biogeochemical cycle: The chemical interactions among the atmosphere, biosphere, hydrosphere, and lithosphere [1].

Biomass: The total dry organic matter or stored energy content of living organisms that is present at a specific time in a defined unit (community, ecosystem, crop, etc.) of the Earth's surface [1].

Biome: A large, easily recognized community unit (ecological region) formed by the interaction of regional climates with regional biota and substrates. In a given the life form of the climax vegetation is uniform. Thus, the climax vegetation of the grassland biome is grass, although the dominant species of grass may vary in different parts of the biome [2].

Biosphere: The portion of the Earth and its atmosphere that can support life. The part (reservoir) of the global carbon cycle that includes living organisms (plants and animals) and life-derived organic matter (litter, detritus). The terrestrial biosphere includes the living biota (plants and animals) and the litter and soil organic matter on land, and the marine biosphere includes the biota and detritus in the oceans [1].

Biota: All living organisms of an area; the sum of all living things on Earth [3].

C_3 plants: Plants (e.g. soybean, wheat and cotton) whose carbon-fixation products have three carbon atoms per molecule. Compared with C_4 plants, C_3 plants show a greater increase in photosynthesis with a doubling of CO_2 concentration and less decrease in stomatal conductance, which results in an increase in leaf-level water-use efficiency [1].

C_4 plants: Plants (e.g. maize and sorghum) whose carbon fixation products have four carbon atoms per molecule. Compared with C_3 plants, C_4 plants show little photosynthetic response to increased CO_2 concentrations above 340 ppm but show a decrease in stomatal conductance, which results in an increase in photosynthetic water-use efficiency [1].

Caliche: A layer near the surface, more or less cemented by secondary carbonates of calcium or magnesium precipitated from the soil solution. It may occur as a soft thin soil horizon, as a hard thick bed just beneath the solum, or as a surface layer exposed by erosion.

Carbon budget: The balance of the exchanges (inputs and losses) of carbon between the carbon reservoirs or between one specific loop (e.g., atmosphere - biosphere) of the carbon cycle. An examination of the carbon budget of a pool or reservoir can provide information about whether the pool or reservoir is functioning as a sink or source for CO_2 [1].

Carbon cycle: The sequence of transformations whereby carbon dioxide is fixed in living organisms by photosynthesis or by chemosynthesis, liberated by respiration and by the death and decomposition of the fixing organism, used by heterotrophic species, and ultimately returned to its original state [2].
All reservoirs and fluxes of carbon; usually thought of as a series of the four main reservoirs of carbon inter-connected by pathways of exchange. The four reservoirs, regions of the Earth, in which carbon behaves in a systematic manner, are the atmosphere, terrestrial biosphere (usually includes fresh water systems), oceans, and sediments (includes fossil fuels). Each of these pools may be subdivided into smaller pools ranging in size from individual communities or ecosystems to the total of all living organisms (biota). Carbon exchange from reservoir to reservoir by various chemical, physical, geological, and biological processes [1].

Carbon density: The amount of carbon per unit area for a given ecosystem or vegetation type, based on climatic conditions, topography, vegetation cover type and amount, soils, and maturity of the vegetation stands [1].

Carbon dioxide fertilization: Enhancement of plant growth or of the net primary production by CO_2 enrichment that could occur in natural or agricultural systems as a result of an increase in the atmospheric concentration of CO_2 [1].

Carbon flux: The rate of exchange of carbon between pools [1].

Carbon isotope ratio: Ratio of carbon-12 to either of the other, less common, carbon isotopes, carbon-13 or carbon-14 [1].

Carbon-nitrogen (C/N) ratio: The ratio of the weight of organic carbon to the weight of total nitrogen (mineral plus organic forms) in soil or organic material [2].

Carbon pool: The reservoir containing carbon as a principal element in the geochemical cycle [1].

Carbon sink: A pool (reservoir) that absorbs or takes up released carbon from another part of the carbon cycle. For example, if the net exchange between the biosphere and the atmosphere is towards the atmosphere, the biosphere is the source, and the atmosphere is the sink [1].

Chemodenitrification: Non-biological processes leading to the production of gaseous forms of nitrogen (molecular nitrogen or an oxide of nitrogen) [2].

Chemotropy: Nutritional mode of organisms that obtain their energy from inorganic compounds [3].

Chlorofluorocarbons (CFCs): A family of inert nontoxic and easily liquified chemicals used in refrigerators, air conditioners, packaging, and insulation and as solvents or aerosol propellants. Because they are not destroyed in the lower atmosphere, they drift into the upper atmosphere where their chlorine components destroy ozone [1].

Classification, soil: The systematic arrangement of soils into groups or categories on the basis of their characteristics. Broad groupings are made on the basis of general characteristics and subdivisions on the basis of more detailed differences in specific properties [2].

Clear cutting: A forest-management technique that involves harvesting all the trees in one area at one time [1].

Climate change: The long-term fluctuations in temperature, precipitation, wind, and all other aspects of the Earth's climate. External processes, such as the Earth's orbital parameters (eccentricity, precession, and inclination), lithosphere motions, and volcanic activity, are factors of climate. Internal variations of the climate system also produce fluctuations of sufficient magnitude and variability through the feedback processes interrelating the components of the climate system [1].

Conduction: The transfer of heat by physical contact between two or more objects [8].

Convection: The transfer of heat through a gas or solution because of molecular movement [8].

Data base: A collection of interrelated information, usually stored on some form of mass-storage system such as magnetic tape or disk. A GIS data base includes data about the position and the attributes of geographical features that have been coded as points, lines, areas, pixels or grid cells [4].

Data base management system (DBMS): A set of computer programs for organizing the information in a data base. Typically, a DBMS contains routines for data input, verification, storage, retrieval, and combination [4].

Data set: A collection of logically related items arranged in a prescribed manner [7].

Decomposer: Small detritivores, usually bacteria and fungi, that consume such substances as cellulose and nitrogenous waste products. Their metabolic processes release inorganic nutrients, which are then available for re-use by plants and other organisms [3].

Denitrification: An anaerobic respiratory process characteristic of facultative aerobic bacteria growing under oxygen-depleted conditions (denitrifying bacteria). The reduction of nitrate to nitrite or to gaseous products such as nitrogen, nitrous oxide, and nitric oxygen [3].

Diffusion: The transport of matter as a result of the movement of the constituent particles. The intermingling of two gases or liquids in contact with each other takes place by diffusion [8].

Dissimilation: The release from cells of inorganic or organic substances formed by metabolism [2].

Ecosystem: The interacting system of a biological community and its non living environmental surroundings [1].
A community of organisms and the surroundings in which they live [2].
A visibly recognizable unit in nature, bounded by an ecotone and comprised of communities in which the biologically important chemical elements (C, N, S, P, and so on) are cycled; these elements cycle more rapidly within an ecosystem than between ecosystems [3].

Ecotone: Ecosystem boundary, transition zone between one ecosystem and another (e.g., field or forest edge, shoreline) [3].

Extrapolation: The act of extending the results of spatial sampling to points outside the area surveyed - not recommended [4].

General circulation models: Hydrodynamic models of the atmosphere on a grid or spectral resolution that determine the surface pressure and the vertical distributions of velocity, temperature, density, and water vapour as functions of time

from the mass conservation and hydrostatic laws, the first law of thermodynamics, Newton's second law of motion, the equation of state, and the conservation law for water vapour. Abbreviated as GCM [1].

Global Warming Potential (GWP): Index which allows a comparison of the climate effects of the emissions of greenhouse gases. The GWP depends on the position and strength of the absorption bands of the gas, its lifetime in the atmosphere, its molecular weight and the time period over which the climate effects are of concern [5].

Greenhouse effect: A popular term used to describe the roles of water vapour, carbon dioxide, and other trace gases in keeping the Earth's surface warmer than it would be otherwise. The 'radiatively-active' gases are relatively transparent to incoming shortwave radiation, but are relatively opaque to outgoing long-wave radiation. The latter radiation, which would otherwise escape to space, is trapped by these gases within the lower levels of the atmosphere. The subsequent reradiation of some of the energy back to the surface maintains surface temperatures higher that they would be if the gases were absent. There is concern that increasing concentrations of greenhouse gases, including carbon dioxide, methane and manmade chlorofluorocarbons, may enhance the greenhouse effect and cause global warming [1].

Grid: A cellular-based data structure composed of pixels or cells of equal size arranged in columns and rows [7].

Grid map: A map in which the information is carried in the form of grid cells. See Raster [4].

Heterotroph: An organism capable of deriving energy for life processes from the oxidation of organic compounds [2].

Heterotrophic nitrification: Biochemical oxidation of reduced forms of nitrogen (e.g., ammonium) to nitrate by heterotrophic microorganisms [2].

Hierarchical data base structure: A method of arranging computer files or other information so that the units of data storage are connected in a hierarchically defined pathway. From above to below, relations are one-to-many [4].

Holdridge life zones: A climate classification system that can be derived from basic monthly temperature and precipitation. The 3 indicators upon which the system is based are: biotemperature (based on length of growing season and temperature during the growing season), mean annual precipitation, and a potential evapotranspiration ratio that links biotemperature with annual precipitation and defines different humidity provinces.

Hydrologic cycle: The process of evaporation, vertical and horizontal transport of vapour, condensation, precipitation, and the flow of water from continents to oceans. It is a major factor in determining climate through its influence on surface vegetation, the clouds, snow and ice, and soil moisture [1].

Hydrosphere: The Earth's waters, as distinguished from its rocks (lithosphere), it living things (biota), and its air (atmosphere) [3].

Humic substances: Any fraction or substance in or separated from humus [2].

Humification: The conversion of organic residues through biological activity, microbial synthesis, and chemical reactions to humus [2].

Humus: The relatively resistant, usually dark-brown to black, fraction of soil organic matter, peats, or composts, which is formed during the biological decomposition of organic residues. Usually constitutes the major fraction of the soil organic matter [2].

Hydrologic cycle: The fate of water from the time of precipitation until the water has been returned to the atmosphere by evaporation and is again ready to be precipitated [2].

Latent heat: Energy transferred from the Earth's surface to the atmosphere through the evaporation and condensation processes [1].

Layer: A logical separation of mapped information according to theme [4] in GIS.

Map generalization: The process of reducing detail on a map as a consequence of reducing the map scale. The process can be semi-automated for certain kinds of data, such as topographical features, but requires more insight for thematic maps [4].

Mapping unit: A set of areas drawn on a mp to represent a well-defined feature or set of features. Mapping units are described by the map legend [4].

Map resolution: The precision with which the location and shape of map features are depicted for a given map scale [7].

Map scale: An expression of a unit of measure on a map and the equivalent measure on the Earth's surface, often expressed as a representative fraction of distance [7]. For instance, 1:5,000,000, or one unit (e.g. cm) on the map equals 5,000,000 units on the Earth's surface.

Mesobiota: See mesofauna [2].

Mesofauna: Nematodes, oligochaete worms, smaller insect larvae, and microarthropods [2].

Metabolism: The sum of all enzyme-mediated chemical conversion pathways characteristic of all autotrophic entities, cells, and organisms (e.g., the means by which energy and organic compounds are made available for use by microorganisms) [3].

Microbiota: Microflora and protozoa [2].

Modelling: An investigative technique that uses a mathematical or physical representation of a system or theory that counts for all or some of its known properties. Models are often used to test the effects of changes in system components on the overall performance of the system [1].

Net Primary Production: The part of the gross primary production (total product of photosynthesis) that remains stored in the producer organisms (primarily green plants) after deducting the amount used during the process of autotrophic respiration. Abbreviated as NPP [1].

Nitrate assimilation: Uptake of nitrogen by living organisms and conversion to cell substrates (e.g., protein) [2].

Nitrification: The oxidation of ammonia (in solution as a salt) to nitrite, often followed by the oxidation of nitrite to nitrate. An aerobic respiratory process characteristic of chemolithotrophs (nitrosofying and nitrifying bacteria) [3].

Nitrogen cycle: The sequence of chemical and biological changes undergone by nitrogen as it moves from the atmosphere into water, soil, and living organisms, and upon death of these organisms (plants and animals) is recycled through part or all of the entire process.

Nitrogen fixation: Metabolic process characteristic of some bacteria: incorporation of atmospheric nitrogen (N_2) into organic nitrogen compounds; requires nitrogenase [3].

NPP: Net Primary Production.

Ozone layer: A region in the upper stratosphere containing high concentrations of ozone (O_3), which protects the Earth's surface from harmful solar radiation [3].

Peat: Unconsolidated soil material consisting largely of un-decomposed, or only slightly decomposed, organic matter accumulated under conditions of excessive drainage [2].

Photosynthesis: Metabolic process involving the production of organic compounds from carbon dioxide and a hydrogen donor (e.g., hydrogen sulphide or water) by using light energy capture by chlorophyll [3].

Pore space: Total pore space not occupied by soil particles in a bulk volume of soils [2].

Producer: An autotrophic organism, usually a photosynthesizer, that contributes to the net primary productivity of a community [3].

Profile, soil: A vertical section of the soil through all its horizons and extending into the parent material [2].

Q_{10}: Temperature coefficient. The increase in rate of a process (expressed as a multiple of initial rate) produced by raising temperature of 10 ºC [6].

Radiatively-active gases: Gases that absorb incoming solar radiation or outgoing infrared radiation, thus affecting the vertical temperature profile of the atmosphere. Most frequently being cited as being radiatively-active gases are water vapour, CO_2, CH_4, N_2O, chlorofluorocarbons, and ozone [1].

Radiation flux: Amount of radiation impinging on a given surface per unit time [3].

Relational data base: A method of structuring data in the form of sets of records or 'tuples' so that relations between different entities can be used for data access and information [4].

Residence time: The size of any specific reservoir or pool of mass (e.g., carbon) divided by the total flux of mass into or out of that pool [1].

Resolution: The smallest spacing between two display elements; the smallest size of feature that can be mapped or sampled [4].

Respiration: A biochemical process by which living organisms take up oxygen from the environment and breakdown organic matter - in plants, the organic matter in photosynthate produced during daylight hours -, releasing both carbon dioxide and energy [1, 3]. The terminal electron acceptor is inorganic and may be oxygen or (in anaerobic organisms) nitrate, sulphate, or nitrite [3].

Rhizosphere: The zone of soil in which microorganisms are affected by living plant roots [2].

Semivariogram: A figure relating the variance of the difference in value of an attribute at pairs of sample points to separation distance [4].

Sensible heat: The excess radiative energy that has passed from the Earth's surface to the atmosphere through advection, conduction and convection processes [1].

Shortwave radiation: The radiation received from the sun and emitted in the spectral wavelengths less than 4 μm. It is also termed 'solar radiation' [1].

Soil: (i) The unconsolidated mineral material on the immediate surface of the earth that serves as a natural medium for the growth of land plants. (ii) The unconsolidated mineral matter on the surface of the earth that has been subjected to and influenced by genetic and environmental factors of: parent material, climate (including moisture and temperature effects), macro- and microorganisms, and topography, all acting over a period of time and producing a product - soil - that differs from the material from which it is derived in many physical, chemical, biological and morphological properties, and characteristics [2].

Soil association: A mapping unit used on general soil maps, in which two or more defined taxonomic units occurring together are combined because the purpose for which it is being made does not require delineation of the individual soils [2].

Soil organic matter: The organic fraction of the soil. Includes plant, animal and microbial residues, fresh and at all stages of decomposition, and the relatively resistant soil humus [2].

Spatial data: Information concerning location, shape and relationships among geographic features, usually stored as coordinates within a topological function [7].

Stomata: A minute opening bordered by guard cells in the epidermis of leaves and stems through which gases pass [3].

Stratosphere: The region of the upper atmosphere extending from the tropopause (8-15 km altitude) to about 50 km. The thermal structure is determined by its radiation balance and is generally very stable with low humidity [1]. Characterized by relatively uniform temperatures (about -75 °C) and horizontal winds (e.g., jet stream). The base of the stratosphere makes an upper limit to the general turbulence and convective activity of the troposphere [3].

Surface albedo: The fraction of solar radiation incident on the Earth's surface that is reflected by it. Reflectivity varies with the ground cover, and during the winter month it varies greatly with the amount of snow cover (depth and areal extent). Roughness of terrain, moisture content, solar angle, and angular and spectral distribution of ground-level irradiations are other factors affecting surface albedo [1].

Trace gas: A minor constituent of the atmosphere. The most important trace gases contributing to the greenhouse effect are water vapour, CO_2, O_3, CH_4, NH_3, NO, NO_2, N_2O, ethylene, sulphur dioxide, dichlorofluormethane or Freon 12, trichlorofluoromethane of Freon 11, methyl chloride, carbon monoxide, and carbon tetrachloride [1].

Topology: The way in which geographical elements are linked together [4].

Tropopause: The boundary between the troposphere and the stratosphere (about 8 km in polar regions and about 15 km in tropical regions), usually characterized by an abrupt change of lapse rate. The regions above the troposphere have higher atmospheric stability than those below. The tropopause marks the vertical limit of most clouds and storms [1].

Troposphere: The inner layer of the atmosphere below about 15 km, within which there is normally a steady decrease of temperature with increasing altitude. Nearly all clouds form and weather conditions manifest themselves within this region, and its thermal structure is caused primarily by the heating of the Earth's surface by solar radiation, followed by heat transfer by turbulent mixing and convection [1].

Vector: A quantity having both magnitude and direction [4].