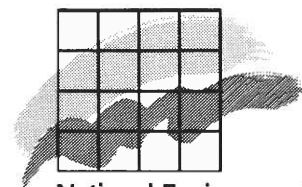


Danmarks Miljøundersøgelser  
Afd. for Flora- og Faunaøkologi  
Kalø, Grenåvej 12, 8410 Rønde

14 JAN. 1992

Ministry of  
the Environment



National Environmental  
Research Institute

# **Emission of methane and non-methane volatile organic compounds in Denmark**

## **Sources related to agriculture and natural ecosystems**

**NERI, Technical Report No. 19  
1991**

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**TITLE:** Emission of methane and non-methane volatile organic compounds in Denmark. Sources related to agriculture and natural ecosystems.

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**DIVISION:** Institut of Population Biology, University of Copenhagen

**PUBLISHER:** National Environmental Research Institute, DK

**YEAR OF PUBLICATION:** 1991

**TYPING:** Linda West

**ISBN:** 87-7772-020-2

**ISSN:** 0905-815x

**NUMBER OF PAGES:** 74

**KEYWORDS:** Methane, volatile organic compounds, emission, Denmark, natural sources, agriculture

**PLEASE QUOTE:** Priemé, A., Christensen, S. Emission of methane and non-methane volatile organic compounds in Denmark. Sources related to agriculture and natural ecosystems. National Environmental Research Institute. Report No. 19, 1991.

**FOR SALE AT:** National Environmental Research Institute  
Department of Emissions and Air Pollution  
Frederiksborgvej 399 DK-4000 Roskilde, Denmark  
Phone: +45 46 30 12 00

**PRICE INCL. 22% VAT:** Dkr. 100,00 (excl. freight)

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## Abstract

The present increase in concentration of atmospheric methane ( $\text{CH}_4$ ) of 0.9-1.2 %  $\text{yr}^{-1}$  has caused much concern since methane directly as well as indirectly contributes to the greenhouse effect. Non-methane volatile organic carbons (NMVOC) play important roles in tropospheric physiochemistry. The emissions in Denmark of methane and non-methane volatile organic carbons (NMVOC) from natural and agriculture-related sources have been estimated.

It was found that present emissions of methane from these sources are somewhat above unperturbed natural emissions. Livestock, freshwater marshes and meadows together with leakages from near-surface deposits of natural gases are the most significant contributors of methane. It seems unrealistic to reduce the present emission of methane to natural levels but measures already being taken will reduce the emission from livestock and perhaps also from freshwater marshes and meadows as well as from other aquatic systems. Further research in the potential of natural sources and sinks of methane is needed, if we are to understand the size and the dynamics of these sources. Forests apparently constitute the major source of biogenic NMVOC from Denmark, but much research is needed to reliably estimate biogenic NMVOC emissions from Denmark.

## Preface

### *Scope*

The much-debated greenhouse effect has caused concern among policy-makers as well as the public, since atmospheric concentrations of the so-called "greenhouse gases" are increasing and are expected to have profound effects on future global climate.

Second only to the well-known carbon dioxide ( $\text{CO}_2$ ), methane ( $\text{CH}_4$ ) is a highly important greenhouse gas. Also, the non-methane volatile organic compounds (NMVOC) contribute indirectly to the greenhouse effect through their reactions with greenhouse gases in the atmosphere.

### *Funding*

The Ozone and Climate Committee of the Nordic Council of Ministers has initiated a study to establish budgets of greenhouse gases in the Nordic countries. The present report is a background report for the Danish contribution to this study, which has been coordinated by the National Environmental Research Institute. The work on this report has been financed by the National Environmental Research Institute.

*Structure of the report*

The report reviews the studies on emissions of methane and NMVOC from agriculture and from natural ecosystems, and it attempts to establish emission rates from these sources in Denmark. The emission rates are discussed briefly. As far as possible it has been attempted to evaluate the human influence on the emission rates of natural ecosystems.

Also included in the report are introductory chapters on atmospheric and microbial dynamics of methane and NMVOC (Chapters 2 and 3).

*Acknowledgements*

Linda West turned the manuscript into a report and made it ready for printing. Jes Fenger inspired and encouraged. Many persons and institutions kindly assisted with valuable information and are quoted in the text.



# 1. Introduction

## 1.1. Methane

### *Increases in atmospheric methane*

At present the atmospheric concentration of methane ( $\text{CH}_4$ ) is increasing at 15-20 parts per billion volume (ppbv) or 0.9-1.2% per year (*Levine et al.*, 1985; *Rinsland et al.*, 1985; *Rasmussen, Khalil*, 1986; *Blake, Rowland*, 1988; *Dianov-Klokov, Yurganov*, 1989; *Dianov-Klokov et al.*, 1989; *Khalil, Rasmussen*, 1989, 1990a; *Brunke et al.*, 1990; *Rohde*, 1990).

Analysis of air bubbles trapped in polar ice cores suggest that the concentration of methane over the past few hundred years must have increased from a pre-industrial level of 650-1150 ppbv to the current concentration of about 1700 ppbv (*Khalil, Rasmussen*, 1982; *Rasmussen, Khalil*, 1984; *Ramanathan et al.*, 1985; *Stauffer et al.*, 1985; *Pearman et al.*, 1986; *Blake, Rowland*, 1988; *Etheridge et al.*, 1988; *Rohde*, 1990).

It is essential to note that the predominant rise of the atmospheric concentration of methane is observed during the last two centuries (*Craig, Chou*, 1982; *Khalil, Rasmussen*, 1982; *Rasmussen, Khalil*, 1984; *Pearman et al.*, 1986; *Pearman, Fraser*, 1988; *Graedel, Crutzen*, 1989), and that the increase in human population correlates well to the atmospheric increase of about  $1\% \text{ yr}^{-1}$  (*Pearman, Fraser*, 1988; *Harriss*, 1989; *Bouwman*, 1990) which may be indicative for the influence of anthropogenic activities as sources for the increased concentration.

### *Causes of the increase*

The increase is primarily due to increasing emissions (70%); a minor cause (30%) is the depletion of hydroxyl radicals ( $\text{OH}^\cdot$ ), which are responsible for the oxidation of atmospheric methane (*Khalil, Rasmussen*, 1985; *Levine et al.*, 1985; *Bolle et al.*, 1986). The increasing emission is caused primarily by increasing areas of rice cultivation, production of wastes, number of ruminants, biomass burning, and gas production (*Bolle et al.*, 1986; *Bouwman*, 1989). The hydroxyl depletion is caused by increasing methane and carbon monoxide ( $\text{CO}$ ) emissions (*Khalil, Rasmussen*, 1985; *Bouwman*, 1990).

### *Major global sources*

At present the major sources in the global methane budget are rice paddies ( $60\text{-}170 \text{ Tg CH}_4 \text{ yr}^{-1}$ ), wetlands ( $40\text{-}200 \text{ Tg CH}_4 \text{ yr}^{-1}$ ), landfill sites ( $30\text{-}70 \text{ Tg CH}_4 \text{ yr}^{-1}$ ), oceans/lakes/other biogenic ( $15\text{-}35 \text{ Tg CH}_4 \text{ yr}^{-1}$ ), ruminants ( $65\text{-}90 \text{ Tg CH}_4 \text{ yr}^{-1}$ ), termites ( $2\text{-}42 \text{ Tg CH}_4 \text{ yr}^{-1}$ ), exploitation of natural gas and coal mining ( $50\text{-}95 \text{ Tg CH}_4 \text{ yr}^{-1}$ ), and biomass burning ( $50\text{-}100 \text{ Tg CH}_4 \text{ yr}^{-1}$ ) (*Crutzen et al.*, 1986; *Bingemer, Crutzen*, 1987; *Cicerone, Oremland*, 1988; *Pearman, Fraser*, 1988; *Bouwman*, 1990) totalling  $310\text{-}800 \text{ Tg CH}_4 \text{ yr}^{-1}$ .



The global methane emission rates have been estimated by several authors besides the ones quoted above, e.g. *Seiler* (1984), *Bolle et al.* (1986), and *Bouwman* (1989), and often the rates of the individual sources reported differ by more than one order of magnitude which clearly reflects the large uncertainties in estimating emission rates.

### *Major sinks*

The major sinks for methane are reactions with hydroxyl radicals in the troposphere (260-420 Tg CH<sub>4</sub> yr<sup>-1</sup>), transport to the stratosphere (60 Tg CH<sub>4</sub> yr<sup>-1</sup>), and oxidation in dry soils (16-56 Tg CH<sub>4</sub> yr<sup>-1</sup>) (*Seiler*, 1984; *Bolle et al.*, 1986; *Cicerone, Oremland*, 1988; *Bouwman*, 1990; *Schütz et al.*, 1990) totalling 340-540 Tg CH<sub>4</sub> yr<sup>-1</sup>.

Estimation of regional and global emissions of methane are impeded by extreme spatial and temporal variations in measured fluxes and the currently used measurement techniques, often involving small flux-chambers, making the extrapolation of these fluxes a difficult task. Moreover, rates of emission from natural ecosystems are severely under-represented in existing data.

This study will only consider natural and agriculture-related sources and sinks of methane in Denmark. All methane production and consumption rates are given as total weight of methane and not as the carbon weight of methane.

## **1.2. Non-methane volatile organic compounds**

Non-methane volatile organic compounds (NMVOC) are emitted from plants, especially trees, and to a lesser extent from soils and sediments.

Generally speaking, NMVOC include hydrocarbons containing only hydrogen and carbon as well as species composed partly of oxygen, nitrogen, sulphur, halogens and other atoms (substituted hydrocarbons). A large fraction of the hydrocarbons in the atmosphere come from natural sources. The reactions with oxidants (especially ozone (O<sub>3</sub>), nitrate (NO<sub>3</sub><sup>-</sup>), and hydroxyl (OH) radicals) in the air constitute their most important sinks leading to the formation of substituted hydrocarbons.

### *Global emissions*

Total worldwide emissions of terpenes are 830 Tg yr<sup>-1</sup> (*Zimmerman et al.*, 1978) but no trend in global emission rates has been identified to date (*Ramanathan et al.*, 1987).

The importance of biogenic NMVOC relative to anthropogenic hydrocarbons varies between rural and urban atmospheres and the absolute mixing ratios of atmospheric biogenic NMVOC often vary with season (*Arnts, Meeks*, 1981; *Altshuller*, 1983; *Roberts et al.*, 1983; *Greenberg, Zimmerman*, 1984; *Sexton, Westberg*, 1984; *Zimmerman et al.*, 1988; *Hov*

*et al.*, 1989). Emission rates of NMVOC are higher in tropical than in cool temperate plant species and tropical forests like the Amazon are probably a globally important source of biogenic hydrocarbons. However, ambient levels of plant emitted hydrocarbons are similar in tropical and temperate forest atmospheres as the average atmospheric lifetime is shorter in the tropics.

This study will only consider natural sources of NMVOC in Denmark. All emission rates in this study are given in total weight per unit time.

## 2. Atmospheric dynamics

### 2.1. Atmospheric dynamics of methane

Methane plays important roles in the radiation budget of the Earth and also in atmospheric chemistry. A continued increase in the atmospheric burden of methane can be expected to have a significant impact on global climate.

#### *Atmospheric reactions*

Methane is not as inert in the atmosphere as e.g. nitrous oxide (N<sub>2</sub>O). Rather, it is oxidized through the reaction:

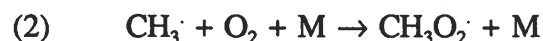


Perhaps 85 to 90% of the methane released from the Earth's surface is consumed by this reaction in the troposphere (*Levine et al.*, 1985; *Cicerone*, 1987; *Cicerone, Oremland*, 1988). The remaining 10 to 15% reaches the stratosphere where the abovementioned reaction is once again the main sink. Similar reactions with chlorine atoms (reaction (24), p. 13) and excited oxygen atoms, O('D), also occur (*Cicerone*, 1987; *Cicerone, Oremland*, 1988).

#### *Total atmospheric decomposition*

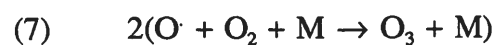
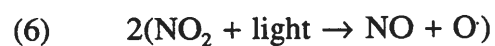
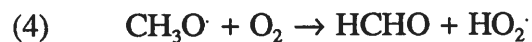
The total atmospheric decomposition of methane has been estimated to be about 320-480 Tg CH<sub>4</sub> yr<sup>-1</sup> (*Seiler*, 1984; *Bolle et al.*, 1986; *Cicerone, Oremland*, 1988; *Bouwman*, 1990).

The methyl radical (CH<sub>3</sub>·) formed in reaction (1) continues the methane oxidation chain, but the reaction sequences are different at high and low atmospheric NO<sub>x</sub> concentrations. For example, the methane oxidation chain can either produce or consume ozone (*Cicerone, Oremland*, 1988; *Bouwman*, 1990):



where  $M = N_2, O_2$  or any third body with which collisions stabilize the product.

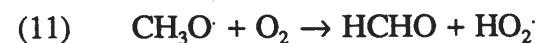
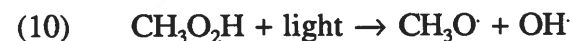
At high nitric oxide concentration (>10 ppt NO):



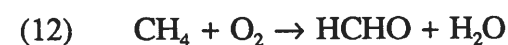
Net of reaction (1) - (7):



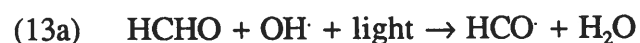
At low nitric oxide concentration (<10 ppt NO):



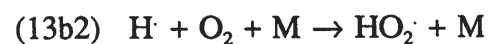
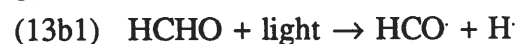
Net of reaction (1) - (2) + (9) - (11):



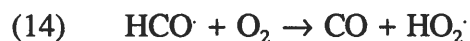
Subsequent oxidation of HCHO is the same for low and high NO concentrations:



or



Oxidation of HCO $\cdot$  is as follows:

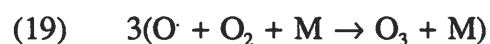
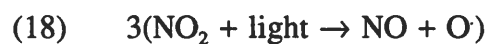
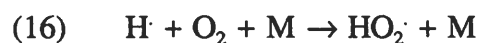


Hence, oxidation of methane constitutes an important source of atmospheric carbon monoxide, which is subsequently oxidized as follows:

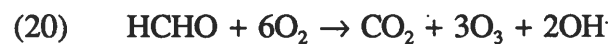


Again, depending on the concentration of nitric oxide the subsequent pathways are:

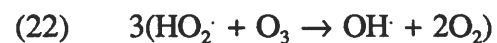
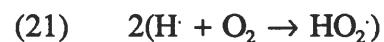
High nitric oxide concentration (>10 ppt NO):



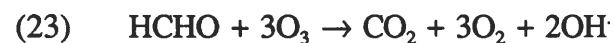
Net of reaction (13) - (19):



Low nitric oxide concentration (<10 ppt NO):



Net of reaction (13) - (15) + (21) - (22):



### *Implications of decomposition*

The important implications of the overall oxidation of methane via carbon monoxide to carbon dioxide are, that in the presence of sufficient nitric oxide, as in polluted or moderately dirty tropospheric air and in the entire stratosphere, there is a net production of 3.7 ozone molecules and 0.5 hydroxyl radicals for each methane molecule oxidized (*Cicerone, Oremland, 1988*); whereas in the absence of nitric oxide a net loss of 1.7 ozone molecules and 3.5 hydroxyl radicals may occur (*Bouwman, 1990*). *Cicerone and Oremland (1988)* estimated a loss of about two hydroxyl radicals per molecule methane oxidized in environments poor in nitric oxide. The global net result is a loss of hydroxyl radicals in clean atmospheres and a gain of ozone in polluted atmospheres.

Also, the reaction



is important in stratospheric chemistry, mostly because it sequesters ozone-destroying chlorine atoms into a temporary reservoir, hydrochloric acid (HCl), that is inactive toward ozone.

## **2.2. Atmospheric dynamics of NMVOC**

Because of their high reactivity and atmospheric lifetimes of only a few hours (*Altshuller, 1983*) biogenic NMVOC do not directly affect climate. They do, however, undergo many reactions with various atmospheric compounds. Their reaction with ozone can be a significant source of carbon monoxide (CO). *Zimmerman et al. (1978)* estimated that the oxidation of NMVOC from vegetation could account for 20-55% of global carbon monoxide production.

NMVOC are also involved in the formation of ozone, peroxy acetyl nitrate (PAN), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), and oxygenated secondary organic carbons (like formic, HCOOH and acetic acids, CH<sub>3</sub>COOH) which contribute to regional-scale air pollution as e.g. acid precipitation and may be harmful to crops and forests. Organic acids presumably originating from biogenic sources have been measured in many places around the world (*Keene, Galloway, 1984, 1986; Norton, 1985; Andreae et al., 1988; Arlander et al., 1990*).

Also, at high terpene emission rates and with high ambient concentrations of ozone, sulphur dioxide (SO<sub>2</sub>), and nitrogen dioxide (NO<sub>2</sub>), a significant impact on the sulphur dioxide/nitrogen dioxide oxidizing process could be expected (*Kotzias et al., 1990*).

The processes involved differ between rural unpolluted and urban sites (e.g. *Trainier et al.*, 1987), and between daytime and nighttime (*Zimmerman et al.*, 1988). Further the impact of NMVOC on the chemistry of ambient air will have a substantial height dependence as mixing ratios fall off rapidly with height due to their short lifetime and slow vertical transport near the surface (*Hov et al.*, 1983).

Due to the multitude of compounds involved and their high reactivity, the atmospheric reactions and dynamics of NMVOC are highly complex, and an overall picture is only starting to emerge (see e.g. *Tranier et al.*, 1987a, 1987b; *Jacob, Wofsy*, 1988; *Kotzias et al.*, 1990, and review by *Atkinson*, 1990).

### 2.3. Effects of atmospheric methane

Methane has strong infrared (IR) absorption bands in the 5 to 20 micrometer region - also called the atmospheric window (*Ramanathan et al.*, 1985; *Mitchell*, 1989) - and thus contributes to the greenhouse effect.

#### Ozone

In addition to its direct effects on the greenhouse effect, methane reacts photochemically to produce ozone, carbon dioxide and water vapor which also have a greenhouse effect. These indirect contributions are comparable to the direct effect of methane. This idea is based on the estimate that every emitted mole of methane results in the formation of 1 mole of carbon dioxide, about 0.7 mole of ozone, and a certain amount of water vapor (*Rohde*, 1990).

Besides being an effective greenhouse gas, ozone is an important component of the stratosphere. It serves as a shield against biologically harmful solar ultraviolet (UV) radiation, initiates key stratospheric chemical reactions, and transforms solar radiation into the mechanical energy of atmospheric winds and heat (*Cicerone*, 1987).

#### Stratospheric water vapor

*Blake and Rowland* (1988) estimated that the increase in the atmospheric methane concentration from the 1940's to present levels has caused an increase in total stratospheric water vapor over this period of about 28%. This increase in stratospheric water vapor may contribute to the formation of polar stratospheric clouds in the Antarctic (*Ramanathan*, 1988). Enhancement of the clouds has the possibility of adding a positive feedback to the ozone depletion observed over the Antarctic in recent years (*Blake, Rowland*, 1988).

Thus the climatic effects of methane may involve complex interactions among atmospheric chemistry, radiation, thermodynamics and dynamics.

### *Warming potential*

Because greenhouse gases have different lifetimes, the relative cumulative impact of each mole of gas may be quite different from its relative initial impact. Therefore, the relative warming potential of given greenhouse gas emissions must be considered, rather than the relative radiative forcing of changes in atmospheric concentrations. For example, methane has an instantaneous impact 40 times greater than carbon dioxide (about 0.65 and 0.015 W m<sup>-2</sup> ppm<sup>-1</sup>, respectively) but since carbon dioxide has a long atmospheric lifetime (120 years when considering a time period of 100 years, but see *Rohde* (1990) for a discussion of carbon dioxide lifetime) compared to the present 7-12 years lifetime of methane (*Khalil, Rasmussen*, 1985, 1990b; *Cicerone, Oremland*, 1988; *Rohde*, 1990) the cumulative impact (and global warming potential) of methane is only 3.7 times greater on a molar basis than for carbon dioxide (*Lashof, Ahuja*, 1990).

In the future, the atmospheric lifetime of methane will probably be somewhat longer than now as a result of an ever slower breakdown as hydroxyl radicals are depleted (*Khalil, Rasmussen*, 1985; *Stauffer et al.*, 1985; *Rohde*, 1990). This would increase the relative impact of methane.

It has been suggested that the rapid increase in atmospheric methane concentration may in part be caused by an increase of the carbon monoxide concentration which also depletes hydroxyl radicals during breakdown (*Khalil, Rasmussen*, 1985; *Stauffer et al.*, 1985). Photochemical calculations indicate that as a result of the increase of methane and carbon monoxide, levels of hydroxyl radicals may have decreased by about 25% since 1950 (*Levine et al.*, 1985).

The present contribution of methane to global warming relative to other greenhouse gases has been estimated to 9.2% (*Lashof, Ahuja*, 1990), 15% (*Rohde*, 1990), and 19% (*Bouwman*, 1990).

### *Future increases*

The atmospheric concentration of methane has been estimated to increase to 1900-1950 ppbv by year 2000 (*Khalil, Rasmussen*, 1985), to 2340 ppbv by year 2030 (*Ramanathan et al.*, 1987), to 2800 ppbv by year 2040 (*Mitchell*, 1989), to 2100-4000 ppbv by year 2050 (*Dickinson, Cicerone*, 1986), and to 3490-9910 ppbv by year 2100 (*Ramanathan et al.*, 1987).

Some authors have tried to estimate the effect on global climate by future increased methane levels. *Ramanathan et al.* (1985, 1987) estimated that an increase in atmospheric methane from 1980 values to 2030 will cause a global average temperature rise of 0.14-0.4°C.

### *Climatic feedbacks*

The total effect of the different greenhouse gases is expected to cause an increase in the average global temperature of 1.5 to 4.5°C some time around the middle of the next century (*Dickinson, Cicerone*, 1986; *Ramanathan et al.*, 1987; *Rohde*, 1990). When global warming occurs as a result of the greenhouse effect there is a potential for additional increases

of methane emissions from biogenic sources due to the effects of changes in soil and water temperature and of soil moisture status on microbial metabolism (see e.g. *Manabe, Wetherald, 1987*).

But the principal sink of atmospheric methane reaction with hydroxyl radicals might also increase with temperature for two reasons. Firstly the atmospheric concentration of hydroxyl radicals generally increases with that of water vapor, rising with temperature. Secondly, the rate constant for the reaction of methane with hydroxyl radicals also increases with temperature. But the concentration of hydroxyl radicals also depends strongly on the amounts of ozone and nitrous oxide present and the intensity of ultraviolet light. Without a knowledge of these relations, it is not possible to predict how atmospheric methane decomposition rates respond to temperature perturbations.

Melting of the upper layers of permafrost in the high Arctic could constitute a positive feedback mechanism adding more methane to the atmosphere. The combination of the response of wetlands and permafrost may add a significant amount of methane to the atmosphere (*Hameed, Cess, 1983; Harriss, 1989; Khalil, Rasmussen, 1989, Burke et al., 1990*).

Analysis of air bubbles in polar ice cores actually show that methane concentrations were lower during periods of global cooling indicating that the natural methane cycle may provide a positive feedback in any future global warming (*Raynaud et al., 1988; Stauffer et al., 1988; Houghton, Woodwell, 1989; Khalil, Rasmussen, 1989; Chappellaz et al., 1990; Nisbet, 1990*).

### **3. Methane and microbial processes**

#### *Methanogenesis*

Biological methane formation (methanogenesis) occurs in most anaerobic environments where organic matter undergoes decomposition: Swamps, aquatic sediments, waterlogged soils, the intestinal tracts of animals, landfills and anaerobic sewage digestors. It results from the activity of a highly specialized group of bacteria, the methanogens, that converts fermentation products (notably carbon dioxide (CO<sub>2</sub>), hydrogen (H<sub>2</sub>), formate (CHOO<sup>-</sup>), and acetate (CH<sub>3</sub>COO<sup>-</sup>)) formed by other anaerobes to methane or to methane and carbon dioxide.

#### **3.1. Microbial processes**

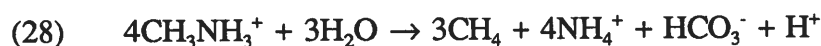
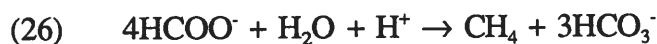
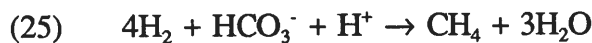
The ratio of carbon dioxide and methane produced depends on the degree of oxidation of the initial organic material. One of the main pathways in



methane formation in nature proceeds via acetate, which yields equal amounts of carbon dioxide and methane.

### *Main processes*

The main processes involved in methane formation are:



In nature hydrogen plus carbon dioxide (reaction 25) and acetate (reaction 29) are the major substrates for the methanogenic bacteria (*Archer, Harris, 1986*).

Because they can metabolize only a limited number of substrates, methanogens depend on other microbes for producing these substrates from organic matter.

### *Terminal decomposers*

The methanogens are terminal members of the anaerobic food chain. As organic matter in soils or aquatic sediments is decomposed by microbes the hydrogen acceptors (=oxidizing agents) used by the different microbes are used up one by one in a thermodynamically determined sequence of the following processes: Aerobic respiration, nitrate ( $\text{NO}_3^-$ ) reduction, general fermentations, sulphate ( $\text{SO}_4^{2-}$ ) reduction and at last methane fermentation by methanogens. Only after the disappearance of sulphate will methanogenesis take place.

In some environments, like sewage digestors and some sanitary landfills, methanogenesis occurs at a rate that makes collection of methane economically feasible.

### *Sulphate reducing bacteria*

In some environments, like marine sediments in which methanogenesis is not quantitatively important, a comparable role is played by the sulphate-reducing bacteria. The factors that determine which of the two groups will dominate are not well understood, but an affinity uptake system for acetate and hydrogen, that is higher in the sulphate-reducing bacteria than in methanogens, is thought to contribute (*Robinson, Tiedje, 1984*). The demonstration that methanogens are also capable of sulphate reduction

suggests that perhaps they contribute to mineralizations even when methanogenesis does not occur.

Methane escaping from anaerobic environments may be oxidized by a multitude of methanotrophic bacteria, which can derive carbon and energy from one-carbon compounds like methane.

### 3.2. Environmental factors controlling net methane-production

It is very difficult to predict the amount of methane produced in an environment as the shift of methane from product to substrate can occur by minute changes in highly variable parameters such as oxygen status and substrate availability. Also, so-called hotspots can be important in methane production (*Bridgham, Richardson, 1990*).

Moreover, it is not known whether the initiation of methane production is paralleled by the development of a population of methanogens, or requires only the activation of the population of methanogens already present in soils and sediments. In fact, very little seems to be known about numbers or even the existence of methanogens in oxic soils and sediments. But some methanogenic species can remain viable up to several weeks in dried oxic soils and has been found in well-drained forest and cultivated soils (*Mayer, Conrad, 1990*).

*Oxygen status -  
redox potential*

Methanogens are strict anaerobes and require highly reducing conditions ( $Eh < -200$  mV) to produce methane. A positive correlation exists between reduction potential (Eh) of soils and methane emission (*Cicerone et al., 1983; Bouwman, 1990*). High levels of available ferrous ions ( $Fe^{2+}$ ), high content of organic matter, low nitrate, manganese dioxide ( $MnO_2$ ) and oxygen, and high temperatures favor an Eh decrease (*Bouwman, 1990*).

*pH*

Apparently methane production proceeds best at pH 6-8. *DeLaune et al.* (1986) and *Phelps and Zeikus* (1984) found that methane production rates were pH-dependent with an optimum rate at neutral pH. *Williams, Crawford* (1984) have shown that the optimum pH for methanogenesis is 6.0 for peat soils with actual pH values of 3.8 to 4.3. But *Harriss et al.* (1985) observed no differences in methane production from peat at pH 3-4 and from peat at pH 6-7. *Williams and Crawford* (1985) isolated an acid tolerant strain of methanogens which was able to produce methane at pH 3.1.

*Substrate  
availability*

Methane fluxes may correlate with availability of oxidizable substrate (*DeLaune et al., 1986*), or peat depth and nutrient enrichment from e.g.

sewage effluent (*Harriss, Sebacher, 1981*), or organic fertilizer (*Schütz et al., 1989b; Yagi, Minami, 1990*).

The flux from rice fields shows peaks when organic matter is applied, when the rice plants are in their physiologically most active period and hence give off a good supply of easily decomposable substrate in the form of root exudates, shortly after inundation of the paddies due to mineralization of soil organic matter, and when the root system deteriorates after harvest (*Holzappel-Pschorn, Seiler, 1986; Holzappel-Pschorn et al., 1986; Schütz et al., 1989b*). Similar patterns have been observed in a temperate swamp (*Wilson et al., 1989*).

### *Nitrogen*

Nitrate or its reduction products can repress methane formation (*Bollag, Czlonkowski, 1973; Jakobsen et al., 1981; Westermann, Ahring, 1987*). The effect of nitrate is twofold. First it delays methane formation until the reduction of nitrate is complete and the redox potential is lowered sufficiently for further anaerobic reactions to proceed. Secondly, nitrate exerts a toxic effect on methanogenesis or competes for sites of the enzymes.

The application of urea and ammonium fertilizers repressed methane emission in rice fields (*Schütz et al., 1989b*), but increases in emission rates after application of N-fertilizers to rice fields have also been observed (*Cicerone, Shetter, 1981; Cicerone et al., 1983*). The effect of N-fertilizers also seems to depend heavily on the mode of application (*Schütz et al., 1989b*).

### *Sulphate concentration and sulphate bacteria*

Sulphate in e.g. sea water and sulphate reducing bacteria may interact with methanogenesis by competition with and by inhibition of methanogenesis in sediments (*Winfrey, Zeikus, 1977; Abram, Nedwell, 1978; Jakobsen et al., 1981; Jones et al., 1982; DeLaune et al., 1983; Robinson, Tiedje, 1984; Holzappel-Pschorn et al., 1985; Yavitt et al., 1987*).

In environments which contain abundant sulphate, methanogenesis usually takes place at depths beneath the zone of sulphate depletion (*Cicerone, Oremland, 1988*), or simultaneously as methanogenic bacteria then use alternative substrates like methionine ( $C_4H_8SCOONH_3$ ), methanol ( $CH_3OH$ ) and trimethylamine ( $(CH_3)_3N$ ) for growth (*Oremland, Polcin, 1982; Oremland et al., 1982*).

*Bartlett et al.* (1985, 1987) found methane and sulphate concentrations in a coastal salt marsh to be negatively correlated. The addition of ammonium sulphate ( $(NH_4)_2SO_4$ ) to a rice paddy reduced methane fluxes probably because methanogens were outcompeted by sulphate reducing bacteria (*Schütz et al., 1989b*). Methane emission from saline wetlands which contain considerable amounts of sulphate, are usually much lower than from freshwater wetlands.

### Water depth

The depth of the water layer over the soil or sediment may control methane fluxes from wetlands. Microbial methane oxidation in aerobic water columns deeper than 10 cm may occur (DeLaune *et al.*, 1983). Sebacher *et al.* (1986) found that emission rates positively related with water depth up to about 10 cm, and that water depths greater than 10 cm do not promote methane emission.

### Temperature

Diurnal and seasonal variation of methane emission is often correlated with temperature (Holzapfel-Pschorn, Seiler, 1986; Moore, Knowles, 1987, 1990; Schütz *et al.*, 1989b, 1990). Temperature influences methane production markedly (Svensson, 1984; Williams, Crawford, 1984; DeLaune *et al.*, 1986; Holzapfel-Pschorn, Seiler, 1986; Westermann, Ahring, 1987; Wieder *et al.*, 1990) with  $Q_{10}$  of 2-5 (Kelly, Chynoweth, 1981; Westermann, Ahring, 1987; Schütz *et al.*, 1990). Holzapfel-Pschorn, Seiler (1986) and Schütz *et al.* (1989b) found doubling of emission rates at a temperature increase of 20 to 25 °C. But the temperature response of methanogenic bacteria to temperatures is complex. Westermann *et al.* (1989) found a decrease in the temperature coefficient ( $Q_{10}$ ) in *Methanosarcina barkeri* and hence a decrease in the temperature dependency as a function of decreasing substrate concentration. This methanogen seems to compensate for decreasing temperature by modulation of its affinity to hydrogen and acetate. This imply that net methane production might be independent of temperature in natural ecosystems where substrates are usually found at subsaturating levels.

The temperature range for methanogens is quite broad. In northern areas methane fluxes may be higher than expected from studies in temperate regions. A possible explanation is the presence of low temperature adapted methanogens, a phenomenon reported by e.g. Svensson (1984). For lake sediments Zeikus and Winfrey (1976) found that the optimum temperature for methanogenesis was 35 to 42°C though the in situ temperature was only 23°C. In the same study the predominant methanogenic population was metabolically active at 4 to 45°C. Several thermophilic methanogens with temperature optima of up to 83°C have been isolated (Oremland, 1988).

Temperature also indirectly influences methanogenesis. Conrad *et al.* (1987) has shown that temperature limits hydrogen turnover to a greater extent than hydrogen-dependent methanogenesis resulting in the limitation of the methanogens by available hydrogen as substrate rather than by temperature itself.

### 3.3. Microbial consumption of methane

Methane can be oxidized by both aerobic and anaerobic bacteria. Aerobic methane oxidation has been well characterized, but the microbes and reactions involved in anaerobic oxidation have yet to be defined.

#### *Aerobic methane consumption*

Aerobic methane-oxidizing (methanotrophic) bacteria constitute a group of eubacteria which (with a single exception, see *Cicerone, Oremland, 1988*) grows only on methane and/or other one-carbon compounds.

All aerobic methanotrophs oxidize methane to carbon dioxide in the following way:



Methanotrophs need oxygen for growth. Often they are found at the interface between oxic and anoxic layers in water bodies and sediments where both methane and oxygen are available.

Aerobic methane oxidation is a dynamic process that is sensitive to changes in oxygen concentration (e.g. *Kuivila et al., 1988*). Shifts in oxygen concentration can occur rapidly because of changes in photosynthesis or respiration, leading to changes in methane emissions of several hundred percent (*King, 1990*).

#### *Effects of nitrogen*

Many methanotrophs can fix nitrogen. Under nitrogen-fixation, many species are sensitive to high oxygen tensions because of their unprotected nitrogenase enzyme (*Cicerone, Oremland, 1988*). During periods of nitrogen limitation in stratified lakes the methane oxidizers can therefore be confined to a microaerophilic zone within the thermocline with sufficient oxygen to oxidize methane but not with high oxygen concentrations inhibiting nitrogen fixation. At high nitrogen concentration methane oxidizers can be found throughout the water column (*Rudd et al., 1976*).

Recently, it has been observed that the marine ammonia oxidizer, *Nitrosococcus oceanus*, exhibits a kinetic response to methane as well as to its primary substrate ammonia (*Ward, 1990*). Methane acts as a substrate analogue for *N. oceanus*. In the presence of methane, ammonia oxidation is inhibited, and the amount of inhibition is related to the relative concentration of methane and ammonia (*Ward, 1990*).

Aerobic methanotrophs in e.g. aerobic soils can actually remove methane from the atmosphere and hence constitute a sink for methane (*Harriss et al., 1982; Keller et al., 1983, 1986; Seiler et al., 1984; Steudler et al., 1989*).

Also, the consumption of methane by these microbes significantly limits the flux of methane to the atmosphere from various ecosystems as they can consume part of the methane produced within the system.

*Anaerobic  
methane  
consumption*

This is a poorly understood and somewhat controversial process, but it appears to be an important sink in certain types of anaerobic environments (Alperin, Reeburgh, 1984). The organisms and the chemical pathways in anaerobic methane oxidation are not known (Cicerone, Oremland, 1988).

Most studies on anaerobic methane oxidation have been carried out in sulphate-containing systems, such as marine sediments and anoxic saline waters (e.g. Iversen, Blackburn, 1981; Devol, 1983; Lidstrøm, 1983; Iversen, Jørgensen, 1985). In a meromictic lake, at least 52% of the methane entering the water column from the sediments was consumed by anaerobic oxidation (Iversen *et al.*, 1987).

### 3.4. Processes of methane release to the atmosphere

Possible ways of release are (Bartlett *et al.*, 1988):

*Diffusion*

1) Usually this is the quantitatively most important way of release. Diffusional loss of methane across a water surface to the atmosphere is a function of the surface methane concentration, wind speed across the surface, water column stability and stratification, and methane supply to the surface (Sebacher *et al.*, 1983, Bartlett *et al.*, 1988; Crill *et al.*, 1988).

*Ebullition*

2) Methane loss as bubbles from sediments can be a significant mechanism sometimes accounting for more than one third or even of the entire flux to the atmosphere (Martens, 1984; Bartlett *et al.*, 1988, Crill *et al.*, 1988; Wilson *et al.*, 1989).

*Transport  
through plants*

3) Aquatic plants of marshy habitats typically have large lacunae for the storage and transport of gases like oxygen. Methane can also be transported through this system. The phenomenon of methane transport through plants have been reported for a variety of aquatic plants (Sebacher *et al.*, 1985; Bartlett *et al.*, 1988).

Methane emission through aquatic plants depends on factors like plant density and species, but the relationships are very complex. Up to 95% of the total methane emission from paddy fields is due to plant-mediated transport (Cicerone, Shetter, 1981; Seiler, 1984; Holzappel-Pschorn, Seiler, 1986; Holzappel-Pschorn *et al.*, 1986; Schütz *et al.*, 1989a).

Often a significant part of the methane released from anaerobic to aerobic environments through diffusion is oxidized by methan-oxidizing

bacteria, but usually most of the methane released through ebullition and through plants is not oxidized.

## 4. Methane emission from natural areas and animals

### 4.1. Freshwater systems

#### *Freshwater systems*

Due to the waterlogged conditions in sediments of freshwater systems the potential for methanogenesis is generally favourable, though the water column above the sediments in e.g. lakes and the sediments themselves can consume a significant part of the methane produced.

Most work on methane emission from freshwater systems has focused on ecosystems like tundras, riverine swamps and northern peatlands (e.g. *Harriss et al.*, 1985; *Sebacher et al.*, 1986; *Moore, Knowles*, 1987, 1990; *Wieder et al.*, 1990) which are not comparable to Danish freshwater systems. The literature only gives little information on methane fluxes from freshwater systems found in Denmark (see appendix 1).

#### *Temporal and spatial variation*

Generally, flux rates from wetland systems show extremely high temporal and spatial variation (e.g. *King, Wiebe*, 1978; *Harriss et al.*, 1982; *Svensson, Rosswall*, 1984; *Whalen, Reeburgh*, 1988; *Harvey et al.*, 1989; *Wilson et al.*, 1989; *Moore, Knowles*, 1990). Moreover, the input of organic matter can influence methane emission strongly (*Kelly, Chynoweth*, 1981). However, the factors that control emission from wetlands are uncertain, but probably very complex.

#### *Freshwater marshes*

Freshwater marshes include marshes and wet meadows. The latter typically situated near streams and fairly big lakes and are often grazed by livestock. Freshwater marshes does not include raised bogs which are treated separately (see later).

Especially in marsh-areas emission rates depend on the water column above the sediment which can consume a significant part of the methane produced in the sediments. *DeLaune et al.* (1983) found that in a Louisiana marsh, U.S.A., emission rates from sites with 100 cm of water column above the sediment were only 9% of the rates from sites with 10 cm of water.

Combined with the lack of data from wet meadows and the scattered reports from marsh areas (all of them are from USA), see appendix 1), the influence of water table and probably also of variations in organic input

to the marshes makes the task of estimating methane fluxes from these areas highly uncertain. During drought, marsh areas might even turn into sinks of atmospheric methane as it has been observed in swamps (Harriss *et al.*, 1982).

From appendix 1 an average emission rate of 1200 kg ha<sup>-1</sup> yr<sup>-1</sup> is applied to Danish freshwater marshes and wet meadows which cover 47 500 ha (Danmarks Statistik *et al.*, 1990) and 120 000 ha (Skov- og Naturstyrelsen, 1988), respectively. This results in a total emission of about 200 kt yr<sup>-1</sup> from Danish freshwater marshes, but this estimate can only be regarded as tentative due to the factors mentioned above.

Results from a Danish freshwater meadow (Christensen, 1991) indicate that these systems can also act as sinks for methane. The measurements were, however, carried out at the margin of the freshwater meadow which, depending on water table, include a high proportion of measurement sites with a fairly low soil moisture content. Much work is needed to clarify the potential of Danish freshwater marshes and meadows as sources of methane.

#### *Future trends*

Until recently the area of freshwater marshes and meadows in Denmark has been decreasing due to drainage. This decrease has now stopped and an increase can be anticipated as regulated streams are being turned back to their natural state and farmers are giving up cultivation of drained land.

The input of organic material in the discharge from municipal sewage and from drainage to these systems may stimulate methane production. A reduction in emission rates can be anticipated as organic input rates are being lowered according to a major national environmental plan. However, it is not known if the reduction in methane emission rates because of decreased carbon input is outweighed by the increase in methane emission from an increased area of wetlands.

#### *Raised bogs*

Reported fluxes from raised bogs vary considerably (appendix 1) but an average value of 360 kg ha<sup>-1</sup> yr<sup>-1</sup> seems appropriate for Danish bogs. Untouched and ecologically viable raised bogs in Denmark cover only 2500 ha (Danmarks Statistik *et al.*, 1990), which results in a total emission from raised bogs of 0.9 kt yr<sup>-1</sup>.

#### *Swamps*

Permanently waterlogged stands of especially alder (*Alnus glutinosa*) have a high potential for methane emission (see e.g. Westermann, Ahring, 1987). A report from a mixed temperate *Tsuga*, *Betula* and *Populus* swamp in Canada gives emission rates of 12-42 kg ha<sup>-1</sup> yr<sup>-1</sup> (Moore, Knowles, 1990) which could be applied to Danish alder stands (see appendix 1). But no data on the area covered by waterlogged forests in Denmark could be found. Probably this area is rather small and hence the



total emission is insignificant compared to other sources like freshwater marshes.

### *Lakes*

The emission of methane from lakes depends on a complex array of different factors. In lakes bubble ebullition is often the dominant means of escape for methane to the atmosphere (*Cicerone, Shetter, 1983; Ormerod, 1983*).

The water column and aerobic zones of sediments often consume most of the methane produced in the sediments (*Lidstrøm, Somers, 1984; Heyer, Babenzien, 1985; Iversen et al., 1987; Kuivila et al., 1988; Frenzel et al., 1990*). The consumption in the water column not only depends on the oxygen concentration in the water but also on the extent of stratification (*Jones et al., 1982; Ward et al., 1989*). In a stratified lake methane might escape from the sediment to the anoxic hypolimnion and stay in the hypolimnion until the lake turns over (*Ormerod, 1983*). When the lake circulates, the accumulated methane becomes distributed throughout the now aerobic water masses and is oxidized by aerobic methanotrophic bacteria (*Ormerod, 1983*). Up to 95% of the annual methane oxidation might occur during and just after overturn (*Rudd et al., 1976; Kuivila et al., 1988*). Anaerobic methane oxidation might also consume methane in lake sediments and deep anoxic waters (e.g. *Iversen et al., 1987*).

### *Organic input*

Methane flux to the atmosphere from lakes is to some degree related to the amount of organic input. *Kelly and Chynoweth (1981)* found that emission rates from five lakes were linearly related to organic input. But other workers found that the percentage of organic input which is regenerated in anoxic sediments as methane is variable (*Ford, Naiman, 1988; Kuivila et al., 1988*) and until further research has been carried out it seems wise not to deduce methane fluxes to the atmosphere from the amount of organic input to lakes.

Despite the importance of methane oxidation in lakes the few reports on methane emissions from temperate lakes gives somewhat surprisingly high emission rates (see appendix 1). If the average of these emission rates of  $390 \text{ kg ha}^{-1} \text{ yr}^{-1}$  is applied to the 47 000 ha of Danish lakes (*Danmarks Statistik et al., 1990*) it results in a total emission of  $18 \text{ kt yr}^{-1}$  from lakes. As for freshwater marshes the emission rates from lakes might decrease as measures are taken to lower the eutrophication of lakes.

### *Streams*

The only work on emission of methane from streams has been done in Canada (*Ford, Naiman, 1988*). The average emission rate of  $1.3 \text{ kg ha}^{-1} \text{ yr}^{-1}$  from these streams and rivers can be applied to Danish streams.

Assuming an average width of 1.5 meter, the 40,000 km of Danish streams (*Danmarks Statistik et al.*, 1990) emit a total of less than 0.01 kt yr<sup>-1</sup>.

## 4.2. Coastal and marine areas

### *Coastal and marine areas*

In contrast to freshwater sediments, methane production in marine sediments is generally rather low, probably because of the inhibition of methanogenesis by high sulphate content and/or the competition from sulphate reducing bacteria (*Abram, Nedwell*, 1978; *Jakobsen et al.*, 1981; *Mountfort, Asher*, 1981; *Senior et al.*, 1982; *DeLaune et al.*, 1983; *Nedwell*, 1984; *Bartlett et al.*, 1987).

However, some results indicate that relatively high emissions of methane from salt marshes can occur at salinities up to approximately 1.3‰ (*Bartlett et al.*, 1987) which can be of importance for Danish conditions as brackish water from the Baltic Sea dominate in the waters south of the Belts.

Methane fluxes in saline environments may correlate with nutrient enrichment, but the relationship is not simple (*Cicerone, Shetter*, 1981; *Mountfort, Asher*, 1981; *Bartlett et al.*, 1987).

### *Methane oxidation*

Anaerobic as well as aerobic methane oxidation in the sediments or water columns often consume most of the methane produced in the sediments (*Devol*, 1983; *Lidstrøm*, 1983; *Iversen, Jørgensen*, 1985; *Ward et al.*, 1989). Hence, the depth of the water column above the sediment influences the emission rate from saline environments. *DeLaune et al.* (1983) found for a salt marsh that emission rates from a water column of 100 cm above the sediment was 30% of the emission rates from a water column of 10 cm. The corresponding figure for a brackish marsh was 7%. As for freshwater lakes, stratification in saline waters during summer can influence methane emission significantly (*Ward et al.*, 1989).

Most of the emission from saline environments to the atmosphere is through ebullition (*Martens*, 1984) but wetland plants also appear to affect the emission rates since they can serve as conduits passing gas from the sediments to the atmosphere (*Bartlett et al.*, 1987).

Methane loss from the sediments by advective transport (dissolved in porewaters and carried away in tidal creeks), can be of importance in marsh areas though only little attention has been paid this means of emission. *Bartlett et al.* (1985, 1987) estimated that this mechanism might be as important as diffusional losses across the sediment-air interface.

*Salt and  
brackish  
marshes  
and meadows*

Methane emission rates cover a range of more than two orders of magnitude (appendix 2). Excluding the two highest and the lowest value given for salt marshes results in average emission rates of 25 kg ha<sup>-1</sup> yr<sup>-1</sup> and 450 kg ha<sup>-1</sup> yr<sup>-1</sup> for salt and brackish marshes, respectively. 42 000 ha of Denmark are covered by salt and brackish marshes and meadows (*Danmarks Statistik et al.*, 1990) but no figure could be found on the relative distribution of brackish to salt marshes, but assuming that half of it is brackish and the rest salt, results in a total emission of about 10 kt yr<sup>-1</sup>.

*Coastal areas*

The many fjords, estuaries and other shallow brackish or salt water areas in Denmark hold a potential for methane emission (see *Martens*, 1984; *de Angelis, Lilley*, 1987). Emission rates from these areas are assumed to show extreme temporal and spatial variability and the very limited data in appendix 2 only offer little help. Moreover, no geodetic data exist covering these areas (*Plato*, 1991). In summary it is not possible, at present, to estimate the total emission of methane from these areas.

*Oceans*

Emission rates from open seas are generally very low, ranging from 0.013 to 0.16 kg ha<sup>-1</sup> yr<sup>-1</sup> (see appendix 2). As the sea surrounding Denmark is generally very productive and nutrient-rich compared to a global average the higher value is probably the most realistic. Using the value of 0.16 kg ha<sup>-1</sup> yr<sup>-1</sup> on the 10 400 000 ha of marine area within Danish territorial limits (*Skov- og Naturstyrelsen*, 1988) results in a total emission of 1.7 kt yr<sup>-1</sup> from the open sea surrounding Denmark.

### **4.3. Domestic animals and humans**

*Enteric  
fermentation*

Methane is produced by enteric fermentation in the digestive tract of ruminants, other herbivorous fauna and humans.

Gases produced during rumen fermentation are mostly vented to the atmosphere through belching and typically contain 30-40% methane (*Church*, 1979; *Cicerone, Oremland*, 1988). The methane production varies between 3 and 10% of total energy intake for ruminants and 0.25 to 3% for other animals (*Bouwman*, 1990). But cows may loose up to 15% of the feed energy as methane (*Ørskov, Ryle*, 1990).

The rate of methane release from ruminants is dependent on e.g. the amount and quality of the ingested diet and the weight of the animal itself. Generally, the higher the quality of the diet, e.g. low cellulose content, the lower is the fractional release of methane (*Crutzen et al.*, 1986; *Cicerone, Oremland*, 1988).

About 82% of the methane formed in the rumen is thought to be formed from hydrogen reduction of carbon dioxide, while the rest is

derived from formate (*Oremland, 1988*). As some hydrogen is used in the rumen while digesting unsaturated fatty acids the amount of these fatty acids in the diet influences the fractional release of methane.

Also, rumen modifiers like the antibiotics rumensin and monensin significantly decrease the production of methane in the rumen (*Wolin, 1981; Dobson, Dobson, 1988*) though the effects of these compounds have not as yet been fully elucidated. When rumen modifiers are applied the relative production of propionic acid in the rumen increases while the relative production of the methane producing butyric and acetic acids decreases (*Kirchgessner, 1982; De Jong, 1989*). Rumensin and monensin are now used as modifiers of rumen fermentation processes in beef cattle which, however, only constitutes a minor part of the cattle in Denmark.

### Cattle

The methane production in cattle can be estimated by stoichiometric calculations, when the amount of fermented carbohydrates is known (e.g. *Hvelplund, 1983*), or by experiments where single animals are placed in closed chambers (e.g. *Blaxter, Clapperton, 1965*).

Several attempts have been made to establish a relation between food intake and methane production in cattle, but the relationship is complex. Factors like feeding level relative to maintenance and food quality (digestibility of the diet) seems to influence strongly on methane production in cattle.

### Relation to gross energy intake

*Blaxter and Clapperton, (1965)* in analysing numerous data on methane production by cows found that methane loss declined by 1-1.5% of gross energy intake as feeding level was raised from maintenance level to twice maintenance. The decline was greater for diets with a high digestibility than for low digestibility diets. *Blaxter and Clapperton (1965)* also found that at maintenance level methane production increased from 7.5% to 9% when the digestibility of the feed was raised from 65% to 95%. The methane production (6.5-7%) were independent of the digestibility at a feeding level of twice maintenance and decreased from 6% to 5% at three times maintenance when digestibility changed from 60% to 90%.

The non-digestible part of the gross energy intake in cattle does not contribute to methane production. However, methane production seems to correlate well with gross energy intake anyway (*Blaxter, 1962; Blaxter, Clapperton, 1965; Crutzen et al., 1986*). The correlation differs with digestibility of the diet, with feeding level, and with age-class.

The digestibility of the diet varies according to food type but an estimated average for the diet given to Danish cattle is 80% of gross energy intake (calculated from information provided by *Thøgersen (1991)*, though digestible energy as percentage of gross energy intake is often depressed when feeding level is raised in ruminants (*Church, 1979*).

The feeding level for dairy cows in highly productive stages is 3 to 3.5 times maintenance (*Crutzen et al.*, 1986). With a daily gross energy intake of 270 MJ *Thøgersen* (1991) the methane production deduced from (*Blaxter, Clapperton*, 1965) is 5.5% of gross energy intake or 98 kg per animal per year (as the energy content of methane is 55.65 MJ kg<sup>-1</sup> (*Crutzen et al.*, 1986)).

#### *Stoichiometric calculations*

*Hvelplund* (1983) has estimated methane production in Danish dairy cows from stoichiometric calculations of the fermentation processes. He found methane production to be 136-143 kg per year according to the composition of the diet. As he bases his calculations on dairy cows with a 12% higher gross energy intake than an average danish dairy cow according to *Thøgersen* (1991) his methane production rates can be adjusted to 121-127 kg per animal per year.

From the work of *Hvelplund* (1983), adjusted according to *Thøgersen* (1991) and *Blaxter, Clapperton* (1965) an estimated emission of 110 kg per year per dairy cow is found appropriate for Denmark.

As calves younger than 6 months are fed primarily on milk and other highly digestible feed they only produce a negligible amount of methane (*Blaxter*, 1962; *Crutzen et al.*, 1986).

As the quality of the feed changes during animal growth from highly digestible to mixtures including more roughage a mean methane production of 6.5% of gross energy intake is adopted for cattle from 6 to 24 months old (in accordance with *Crutzen et al.*, 1986).

For heifers and bulls more than two years old 7% of the gross energy intake is lost as methane (*Crutzen et al.*, 1986).

#### *Sheep*

Gross energy intake for sheep is strongly influenced by ambient temperature, wool length and exercise. Adult sheep in Germany have a daily gross energy intake of 30-40 MJ, while immatures are fed 20-25 MJ per day (*Crutzen et al.*, 1986). Applying a mean methane production of 6% of gross energy intake (see *Crutzen et al.*, 1986) gives production rates of about 14 and 9 kg methane per animal per year for adult and immature sheep, respectively.

#### *Pigs*

The gross energy intake for pigs has been adopted from *Tybirk* (1991) and the percentage of energy intake lost as methane in pigs has been adopted from *Crutzen et al.* (1986). It is noted that pigs for slaughter usually only have a lifetime of about six months so the methane emission per animal per year (see table 1) is a theoretical value.

### *Horses*

Methane yields for horses are between those for pigs and ruminants. They equal 3-4% of the intake of digestible energy (*Kirchgessner, 1982*). The daily energy demand for horses depend on body weight and work load. The daily energy demand for horses with a mean body weight of 400 kg, executing medium work loads for 2 hours a day is about 84 MJ of digestible energy (calculated from *Kirchgessner, 1982*). If 3.5% of the intake of digestible energy is released as methane the mean annual methane production is 19 kg per animal per year.

### *Humans*

Only about one-third of the adult population actually harbours methanogenic bacteria (*Wolin, 1981; Oremland, 1988*). The methane produced in the large intestine is partly transported via the bloodstream to the lungs, where it is respired, and partly expelled as flatus (*Crutzen et al., 1986*).

From the information given by *Crutzen et al. (1986)* an average methane production of 0.07 kg per year per individual has been calculated.

This estimate is highly uncertain but this uncertainty does not influence total methane emission from Denmark much as emissions from humans are negligible in the total budget.

### *Total emission from enteric fermentation*

Table 1 summarizes the methane losses from the different subclasses of livestock and humans in Denmark. The numbers of livestock and humans are from *Danmarks Statistik (1989, 1990)*. Table 1 gives a total emission of methane directly from livestock and humans in Denmark of 137 kt yr<sup>-1</sup>.

Since 1980 a significant reduction in livestock numbers has taken place. As Denmark still has an over-production of e.g. dairy products according to EEC quotas, this reduction is assumed to continue for the years to come with a corresponding annual decrease in methane emission directly from livestock of 4.7 kt yr<sup>-1</sup> (table 1).

### *Manure*

Manure from livestock also contributes to methane emission especially when kept under anaerobic conditions in e.g. liquid-manure tanks.

About 75% of the manure from Danish farms is stored as liquid manure (*Energistyrelsen, 1991*) which is usually kept anaerobic in tanks, whereas the storage of solid manure imply that some of the decomposition during storage is aerobic.

In 1988 the potential methane production from dejections from cattle, pigs and poultry was 690 mill. m<sup>3</sup> per year or 490 kt yr<sup>-1</sup> (*Energistyrelsen, 1990*). Not all this manure is kept anaerobic and no reports on methane emission rates from storage tanks have been found in the literature.

Accordingly, it is only possible to give a very rough estimate on methane emission from livestock dejections. Two estimates made by The National Energy Agency (*Energistyrelsen, 1991*) assume that methane production is 10-20% and 40%, respectively, of the potential production from

dejections in Denmark. Assuming that 25% of the potential methane production is converted to methane results in an estimated emission from dejections of about 125 kt yr<sup>-1</sup>. This estimate is, however, highly uncertain.

*De Reydellet* (1990) quotes a french report that assumes an emission factor from pig dejections of 11 kg per animal per year. Applying this emission factor to Denmark results in an emission from pigs of about 100 kt per year. This value is much higher than the emission obtained from the above estimate as pigs 29% of total manure from Danish farms which equals a methane emission of 35 kt yr<sup>-1</sup>.

Until year 2000 total manure production in Denmark is expected to fall by about 1% annually (*Energistyrelsen*, 1990) which corresponds to an annually decline in methane emission from manure of about 1.25 kt yr<sup>-1</sup>.

Table 1. Emission of methane directly from livestock and humans in Denmark in 1989. (See text for further explanation).

Subclass	Numbers (*1000)	Gross energy intake (MJ d <sup>-1</sup> )	Methane loss (% of energy intake)	Emission per animal <sup>1</sup> (kg CH <sub>4</sub> yr <sup>-1</sup> )	Emission per subclass (t CH <sub>4</sub> yr <sup>-1</sup> )	Annual change in numbers (*1000)	Annual change in emission <sup>-1</sup> (kt CH <sub>4</sub> yr <sup>-1</sup> )
<b>Cattle:</b>							
Bull and steer calves, <½ yr	213	83	0	0	0		
Bull and steer calves, ½-1 yr	193	83	6.5	35	6755		
Bulls and bullocks, 1-2 yr	57	130	6.5	55	3135		
Bulls and bullocks, >2 yr	9	104	7.0	48	432		
Heifer calves, <½ yr	222	52	0	0	0		
Heifer calves, ½-1 yr	211	52	6.5	22	4642		
Heifers, 1-2 yr	383	88	6.5	38	14554		
Heifers, >2 yr	102	125	7.0	57	5814		
Cows and heifers having calved	831	(271)	(5.5)	110	91410		
<b>CATTLE, total</b>	<b>2221</b>	<b>-</b>	<b>-</b>	<b>57</b>	<b>126742</b>	<b>-82.2</b>	<b>-4691</b>
<b>Sheep:</b>							
Breeding ewes	69	35	6.0	14	966		
Immatures and rams	75	22	6.0	9	675		
<b>SHEEP, total</b>	<b>144</b>	<b>-</b>	<b>-</b>	<b>11</b>	<b>1641</b>	<b>9.8</b>	<b>112</b>
<b>Pigs:</b>							
Breeding sows	840	55	0.6	2.2	1848		
Pigs for slaughter	8139	18	0.6	0.7	5697		
Boars, barren sows, others	211	25	0.6	1.0	211		
<b>PIGS, total</b>	<b>9190</b>	<b>-</b>	<b>-</b>	<b>0.8</b>	<b>7756</b>	<b>-85.2</b>	<b>-68</b>
<b>HORSES</b>	<b>35</b>	<b>84*</b>	<b>3.5</b>	<b>19</b>	<b>675</b>	<b>-1.6</b>	<b>-31</b>
<b>HUMANS</b>	<b>5130</b>	<b>-</b>	<b>-</b>	<b>0.07</b>	<b>359</b>	<b>1</b>	<b>0.07</b>
<b>TOTAL</b>	<b>-</b>	<b>-</b>	<b>-</b>	<b>-</b>	<b>137173</b>	<b>-</b>	<b>-4678</b>

\*) The energy intake for horses refers to digestible energy.



## 4.4. Groundwater

### *Groundwater*

Groundwater can contain high levels of methane. In Denmark, *Terraqua ApS* (1986) has found methane concentrations of up to 22 mg methane per liter groundwater.

The methane in Danish groundwater probably originates from the anaerobic degradation of interglacial and postglacial deposits of organic material (*Terraqua ApS*, 1986).

It is not known how much of this methane will eventually be released to the atmosphere through 1) springs and streams that are groundwater outlets, 2) through marine environments where groundwater discharges, and 3) as a result of the use of groundwater on the land surface for municipal and agricultural purposes. Alternatively, the methane is biologically oxidized, especially during the process of manipulated oxidation with atmospheric oxygen in order to precipitate iron and manganese in the water.

The average methane concentration in analysis from 292 groundwater drillings in southern Denmark were about 1.8 mg l<sup>-1</sup> (*Terraqua ApS*, 1986). If this value is used as an average for Denmark which uses a total of 1.3 · 10<sup>9</sup> m<sup>3</sup> of groundwater per year (*Danmarks Statistik et al.*, 1990) about 2.3 kt yr<sup>-1</sup> of groundwater methane are either released or oxidized.

## 4.5. Leakage from near-surface deposits of natural gases

### *Near-surface deposits*

A probably very important, but little known, source of methane in Denmark is the leakage from natural deposits of natural gases located very near the surface of marine sediments or just below the ground surface on land. No attempts have ever been made to measure the fluxes to the atmosphere from these leakages in Denmark.

In Kattegat just off Frederikshavn in the northern-most part of Jutland methane bubbles up from the sea-floor about 10-12 meters below sea-level from an area covering at least 20-40 km<sup>2</sup>. Flux rates from the sea-floor of up to 1 l CH<sub>4</sub> m<sup>-2</sup> h<sup>-1</sup> has been measured but a rate of 0.5 l m<sup>-2</sup> h<sup>-1</sup> seems like a realistic estimate of the flux from the sea-floor (*Iversen*, 1991). However, it is not known how much methane is being oxidized in the water column before reaching the atmosphere. Bacterial oxidation has little influence on the methane content of rising bubbles (*Cicerone, Orem-land*, 1988) and on calm days methane can be seen bubbling to the sea-surface in the area (*Iversen*, personal communication) but the situation might be quite different on windy days.

Assuming that 25% of the methane emitted from the sea-floor is oxidized in the water column, the flux to the atmosphere from the area off Frederikshavn is 60 000 kg ha<sup>-1</sup> yr<sup>-1</sup>. This results in a total emission to the atmosphere of 120-240 kt yr<sup>-1</sup> from the whole area.

On the beeches near Frederikshavn methane can be seen bubbling up and on land 20 · 10<sup>6</sup> m<sup>3</sup> of gas were extracted near Frederikshavn during World War II from deposits of natural gas situated very close to the ground surface (sometimes as close as 50 cm from the surface) (*Iversen, 1991*).

Nothing is known about the size of the emission from the land-based deposits, and the fact that methane also bubbles up from the shoreline indicates, that these leakages could constitute a very large source of atmospheric methane.

Very recently, an unconfirmed report indicates that similar leakages have been located off Hirtshals in northern Jutland at 30 meters below sea level (*Iversen, 1991*).

#### 4.6. Uptake by natural areas

##### *Atmospheric sink*

In contrast to wetlands, predominantly dry and aerated soils generally act as sinks for atmospheric methane. Though production of methane may occur in anaerobic micro-niches of otherwise aerated soils, and dry soils may temporarily become waterlogged and hence methane producing, it is assumed that dry soils act predominantly as sinks for methane.

Only very little work has been done on methane uptake by soils and most of it has been carried out in tropical regions (*Keller et al., 1983, 1986; Seiler et al., 1984; Goreau, de Mello, 1986*) or in temperate forests (see appendix 3). Methane consumption has also been observed in swamp soils during drought conditions (*Harriss et al., 1982*), in peat exposed to aerobic conditions (*Yavitt et al., 1990a*), in tundra soil (*King et al., 1989; Whalen, Reeburgh, 1990*), and in temperate grasslands and cultivated land (*Born et al., 1990*).

##### *Forests*

The limited data presented in appendix 3 can not justify separate values for methane uptake by different forest types or forests on different soils. From the uptake rates in appendix 3 an uptake rate of 5 kg CH<sub>4</sub> ha<sup>-1</sup> yr<sup>-1</sup> is found appropriate for Danish forest soils.

At the latest forest survey in 1976 Denmark had 406 000 ha of forests (*Danmarks Statistik, 1983*). Since 1976 about 1500 ha has been planted with forest each year (*Skov- og Naturstyrelsen, 1990*) giving an estimated total forest area of about 427 000 ha in 1990. This suggests an uptake of methane by forest soils of 2.0 kt yr<sup>-1</sup>.

The Danish Ministry of the Environment has put as a goal that the total forested area in Denmark will be doubled within the next 80-100 years (*Skov- og Naturstyrelsen*, 1988). It is of course uncertain how much forest will actually be planted during the next decades. Estimates ranging from 50 000 to 500 000 ha have been offered but 5000 ha per year seems a realistic figure (*Skov- og Naturstyrelsen*, 1990). The present 1,500 ha of newly planted forest per year corresponds to an annual increase in sink strength of forest soils of 0.01 kt yr<sup>-1</sup>.

#### *Cultivated land*

Only one estimate on methane uptake by temperate cultivated and dry grassland soils has been found in the literature: 0.02-2 kg CH<sub>4</sub> ha<sup>-1</sup> yr<sup>-1</sup> (*Born et al.*, 1990). This value and results of *Christensen* (1991) indicate lower uptake rates of methane for cultivated soils than for forest soils. Partly, this could be due to the widespread use of N-fertilizers in agriculture as e.g. *Steudler et al.* (1989) found that methane uptake by forest soils decreased significantly by nitrogen additions. But the intensively managed agricultural systems in Western Europe might also reduce the proportions of methanotrophic bacteria in cultivated soil and hence the sink strength compared to relatively undisturbed forest soils.

Applying an uptake rate of 1 kg CH<sub>4</sub> ha<sup>-1</sup> yr<sup>-1</sup> to the 2 555 000 ha of cultivated land (including grasslands in rotation) (*Danmarks Statistik*, 1990) gives a consumption of methane of 2.6 kt yr<sup>-1</sup>.

Since 1980 the total area of cultivated land has decreased by about 14 500 ha annually (*Danmarks Statistik*, 1990) of which 10 000 ha yr<sup>-1</sup> has been used for infrastructure and municipal development (*Skov- og Naturstyrelsen*, 1988). It might be expected that in the coming years even more farmland will be taken over by other uses as farmers are inclined to leave marginal lands out of production.

A decline of 14,500 ha yr<sup>-1</sup> corresponds to an annual decline in methane uptake by cultivated land of 0.02 kt yr<sup>-1</sup>.

#### *Other terrestrial systems*

About 70 000 ha of Denmark are covered by heathland and moors, while another 7600 ha are covered by natural commons situated on well-drained soils (*Danmarks Statistik et al.*, 1990).

Results by *Christensen* (1991) from a natural common situated on old dune sand indicate an uptake rate by these areas of about 1 kg ha<sup>-1</sup> yr<sup>-1</sup> (appendix 3). This uptake rate results in a total uptake of 0.1 kt yr<sup>-1</sup> by heathlands, moors and commons.

## 5. Emission of NMVOC from natural areas

### 5.1. Vegetation

Plants produce and emit a vast array of volatile organic compounds, of which especially isoprene ( $C_5H_8$ ) and terpenes ( $C_{10}H_{16}$ ) are of interest. E.g. more than 70 compounds emitted by conifers have been found (*Isidorov et al.*, 1985). NMVOC's from plants are emitted through leaves.

#### *Terpenes*

Terpenes are emitted by a multitude of plant species (e.g. *Altshuller*, 1983). Although very numerous, the emitted terpenes studied are often limited to the following: Alpha-pinene, beta-pinene, camphene, delta-3-carene, limonene, myrcene, and phellandrene, of which alpha-pinene is usually considered the most important (*Tingey et al.*, 1980; *Hov et al.*, 1983; *Yokouchi et al.*, 1983; *Ciccioli et al.*, 1984; *Evans et al.*, 1985; *Isidorov et al.*, 1985; *Riba et al.*, 1987; *Petersson*, 1988).

Total concentration of all terpenes found in forests usually range between 0.3 and 7.5 ppbv (*Hov et al.*, 1983; *Roberts et al.*, 1983; *Greenberg, Zimmerman*, 1984; *Riba et al.*, 1987). Although the tree canopy is considered to be a more important source of terpenes than the herbaceous vegetation, the average level of concentration at 13 meter above the ground has been found to be only a little lower than the value obtained at 1.7 meter in a Canadian maple forest (*Clement et al.*, 1990).

Terpene emission is controlled by the chemical potential gradient between leaf and surrounding air (*Tingey et al.*, 1979, 1980; *Evans et al.*, 1985). The gradient is controlled by the vapor pressure of the individual terpenes. Emission rates increase exponentially with temperature, but light does not influence on emission rates (*Tingey et al.*, 1980).

Terpenes often show maximum concentration at night and minimum concentration during the day due to restricted vertical mixing of surrounding air masses at night and thus lower decomposition rates in the air (*Yokouchi et al.*, 1983; *Riba et al.*, 1987; *Clement et al.*, 1990).

#### *Isoprene*

Also isoprene is produced and emitted by many plant species (e.g. *Evans et al.*, 1982, 1985). Its biosynthesis is associated with photorespiration and intermediates of the glycolate pathway (*Jones, Rasmussen*, 1975; *Tingey et al.*, 1981) and thus its emission is closely related to light levels and biosynthetic rates. Like terpenes isoprene emission increase exponentially with temperature, but isoprene emission also increase with light intensity after reaching a threshold value (*Rasmussen, Jones*, 1973; *Tingey et al.*, 1979, 1980, 1981; *Jakob, Wofsy*, 1988).

Emission rates of isoprene differ widely between plant species, which are commonly grouped into three groups: High-isoprene emitters, low

*Estimating  
NMVOC  
emission from  
vegetation*

isoprene emitters and non-isoprene emitters. In Denmark only the following plant groups are recorded as high-isoprene emitters: Oaks (*Quercus* sp., *Fagaceae*), Willows (*Salix* sp., *Salicaceae*), and poplars (*Populus* sp., *Salicaceae*). No significant low-isoprene emitters are found in Denmark.

Unlike terpenes, isoprene concentrations are often low in the morning hours and increase throughout the day as temperature increases (*Tranier et al.*, 1987b; *Zimmerman et al.*, 1988).

Emission of terpenes and isoprene represents a loss of fixed carbon to plants on the order of 0.1-2% of photosynthetic uptakes (*Zimmerman et al.*, 1978, 1988; *Tingey et al.*, 1979, 1980; *Mooney et al.*, 1987).

NMVOC flux measurements have been made for fewer than 100 plant species (*Zimmerman et al.*, 1988). Emission rates and composition vary considerably between plant species even within genera (*Roberts et al.*, 1983; *Yokouchi et al.*, 1983; *Ciccioli et al.*, 1984; *Evans et al.*, 1985; *Isidorov et al.*, 1985; *Riba et al.*, 1987; *Petersson*, 1988).

Emission rates from plants have been determined in the field using 1) vegetation enclosure techniques in which the sample is enclosed by a bag; 2) micrometeorological gradient or energy balance methods where NMVOC concentration gradients are measured together with temperature and wind speed profiles; and 3) tracer techniques involving SF<sub>6</sub> tracer release and measurement of the downwind concentration profiles of SF<sub>6</sub> and natural hydrocarbons. *Lamb et al.* (1985, 1986, 1987) found a good agreement between results obtained with the different techniques.

Apart from field measurements, laboratory studies of emission rates have been performed under controlled conditions. Measurements have been made in gas-exchange chambers with controlled light intensity, leaf and air temperature, dew point, humidity, and carbon dioxide concentrations (e.g. the work of *Tingey et al.*, 1979, 1980, 1981).

Measured emission rates vary greatly because of fluctuations in environmental conditions such as temperature and time of the day, etc. This is the main reason why emission factors used in national emission inventories often vary considerably from one literature source to the next. Most investigations have been done in the U.S. (see *Lamb et al.*, 1987 for a review). Some other work is from Europe and Japan (see *Veldt*, 1988). However, there is no reason to suspect significant differences between European and U.S. emissions.

*Lamb et al.* (1987) lumped U.S. data and drew best fit lines through them. *Veldt* (1988) used these plus European and Japanese data to calculate temperature dependent emission factors for Dutch conditions. These emission factors have been adopted for this inventory (see table 2), and in principle the calculation procedure developed by *Veldt* (1988) is followed in this inventory.

Deciduous trees.

High isoprene emitters:

Isoprene: Deduced from fig. 7 in Veldt (1988).

Terpenes + unknown compounds:  $\ln E = 0.072t - 0.89$

Non-isoprene emitters:

Total NMVOC :  $\ln E = 0.069t - 1.43$

Coniferous trees.

Total NMVOC:  $\ln E = 0.15t - 3.21$

Crops.

Isoprene:  $\ln E = 0.0088t + 0.14$

Terpenes + unknown compounds:  $\ln E = 0.071t - 13.76$

Grasslands.

Total NMVOC:  $\ln E = 0.076t + 2.38$

$E =$  emission ( $\mu\text{g g}^{-1} \text{h}^{-1}$  - for crops and grasslands:  $\mu\text{g m}^{-2} \text{h}^{-1}$ ),  
 $t =$  temperature (°C).

*Table 2.* Emission rate temperature coefficients. Calculated or adopted from *Veldt* (1988).

Due to the multitude of compounds involved and to the uncertainties in measuring these compounds, NMVOC's from vegetation have been divided into only three groups: Isoprene, terpenes and unknown compounds.

*Controlling factors*

In order to estimate the emission of NMVOC's from vegetation in Denmark the following factors have to be considered:

*Vegetation type*

Plant species can be grouped into the following types:

A) Deciduous trees - high isoprene emitters.

The main Danish species involved are oaks, willows and poplars. Isoprene emissions are taken to be zero at night and are, of course, also absent when the trees are bare. These species also emit unknown compounds.

B) Deciduous trees - non-isoprene emitters.

All Danish deciduous tree species except high isoprene emitters are included in this category. A default composition of emitted NMVOC is chosen as 5% terpenes and 95% unknown compounds (*Veldt*, 1988), though the composition is likely to depend on e.g. temperature and time of the year. Very little work has been carried out on emission rates from this plant group.

C) Coniferous trees.

*Veldt* (1988) lumped measurement data from ten reports. Due to wide variations in reported measurement data and to differences in measured compounds (often only alpha-pinene has been measured and total emission of terpenes extrapolated from alpha-pinene emission rates) the emission from conifers can only be estimated at a high degree of uncertainty. A default composition of NMVOC is adopted from *Veldt* (1988) as 65% terpenes and 35% unknown compounds.

Some spruce species (*Picea* sp.) also emit isoprene (*Evans et al.*, 1982, 1985) and sitka spruce (*Picea sitchensis*) and perhaps also other spruce species might more appropriately be categorized as low isoprene emitters. Except for sitka spruce none of the spruce species commonly grown in Denmark have been investigated for isoprene emission rates.

D) Crops.

Little is known about NMVOC emission from agricultural crops. Emission rates are low compared to forested areas (*Veldt*, 1988) and consequently little is known about their composition because of analytical difficulties. A default value for the composition of non-isoprene NMVOC is taken as 62,5% terpenes and 37,5% unknown compounds (in accordance with *Veldt*, 1988). Isoprene emission is treated separately.

E) Grasslands.

The remarks applied to cropland can also be applied to grasslands. Default values for the composition of NMVOC are 0% isoprene, 20% terpenes, and 80% unknown compounds (*Veldt*, 1988).

*Emitting  
period*

Trees are assumed to emit NMVOC's during the whole vegetated period. Information about this period for deciduous species in Denmark has been provided by *Skovbrugsinstituttet* (1991).

*Vegetation  
cover*

*Danmarks Statistik* (1979) gives information on the area covered by oak, non-isoprene deciduous trees and coniferous trees at the last forest inventory in Denmark in 1976. These data have been extrapolated to 1990 conditions as 1500 ha of forest has been planted per year since 1976 (*Skov- og Naturstyrelsen*, 1990). The data on willow and poplars have been provided by *Skov- og Parkteknisk Institut* (personal communication), but these data only include forested area - an unknown area covered by willows and poplars are found near marshy areas and along roads, respectively.

The area covered by crops and grasslands has been taken from *Danmarks Statistik* (1990).

*Biomass  
factor*

Emission rates for trees are traditionally given in weight NMVOC per dry weight leaf per time unit. In order to transfer these rates to area rates a biomass factor (dry weight leaf per area unit) has to be incorporated. Biomass factors for Danish oak, beech (*Fagus sylvatica*, *Fagaceae*) and several different Danish and German coniferous species has been provided by *Skovbrugsinstituttet* (1991).

The biomass factors for oak and beech have been applied to the whole group of high- and non-isoprene emitting deciduous trees, respectively, as oaks and beeches make up the majority of the area covered by these two emitter-groups (see table 2). The biomass factors for the major coniferous species grown in Denmark have been applied to the area covered by these tree species and a weighed average of 1150 g dry weight m<sup>-2</sup> for Danish coniferous forests has been calculated.

As leaf biomass in deciduous trees declines by 10% during the growing season (*Skovbrugsinstituttet*, 1991) a comparable biomass decline has been incorporated when estimating the emission rates from deciduous trees.

The biomass factors provided by *Skovbrugsinstituttet* (1991) apply to mature stands. However, Danish oak, beech and conifer stands only reach full leaf biomass after 20-30 years, 15-20 years and some years, respectively, and very old stands also have a lower leaf biomass (*Skovbrugsinstituttet*, 1991).

In Denmark premature and very old stands of oaks, beeches and conifers make up about 30-40%, 15-20% and 10-15%, respectively, of the area covered by these groups (*Danmarks Statistik*, 1979). Biomass factors have been lowered by 10% for high isoprene emitters and by 5% for non-isoprene emitters and conifers in order to take young and very old stands into account.

*Ambient  
temperature*

Temperature influences emission rates strongly. Emission rate temperature coefficients have been calculated or adopted from the rates used in a Dutch inventory by *Veldt* (1988) (see table 2).

Temperatures have been divided into night and day temperatures. The means of daily minimum and maximum temperature, respectively (*Danmarks Meteorologiske Institut*, 1991) are used to represent temperature conditions during night and during days in March to October. During November to February the average of mean daily maximum and mean daily temperature is used to represent temperature conditions to estimate emission of terpenes and unknown compounds. This average is also used to represent temperature conditions for estimating isoprene emissions (see *Lamb et al.*, 1987).



*Veldt* (1988) used mean temperature during light hours to estimate emission of terpenes and unknown compounds, but as leaves and needles exposed to direct sunlight are heated well above ambient temperatures the mean of daily maximum temperature probably represents temperature conditions in a better way for most of the year.

*Solar radiation*

Only isoprene emission is controlled by solar radiation. However, at temperatures below 21°C isoprene emission rates are virtually the same for solar radiation fluxes between 200 and 800  $\mu\text{E m}^{-2} \text{s}^{-1}$ . These conditions are prevailing during the isoprene emitting period in Denmark except for single days and consequently no influence of solar radiation are taken into account.

*Altitude*

As all landscapes in Denmark are situated below 175 m.a.s.l. the effect of altitude is assumed to be negligible and hence not taken into account.

*Other factors*

It is very likely that other factors like humidity (see *Lamb et al.*, 1985) influence on emission rates but since ambient temperature and light incidence are the only factors about which something is known, standardization of emission factors is restricted to these until more data become available.

The emission rates for forests are probably too low as they do not include emission from herbs and bushes, many of which are significant NMVOC emitters (*Evans et al.*, 1982; *Isidorov et al.*, 1985).

Table 3 summarizes the basic data for estimating natural NMVOC emission in Denmark while climatic data are compiled in table 4. In appendix 4 the calculation procedure for estimating NMVOC emission from vegetation is presented.

*Table 3.* Basic data for estimating natural NMVOC emissions in Denmark.  
For further explanation see text.

Plant group	Deciduous trees		Conifers	Crops	Grassland
	High isoprene	Non-isoprene			
Plant Species	Quercus spp. Populus spp. Salix spp.	All spp. except high isoprene emitters	All spp.	All spp.	All
Default composition of emitted NMVOC (%)					
Isoprene		0	0	-	0
Terpenes		5	65	62.6	20
Unknown		95	35	37.5	80
Influence of temperature	See table 1				
Influence of radiation	No influence taken into account				
Biomass factor (g dry wgt m <sup>-2</sup> )	250	280	1150	-	-
Emitting period	pri May- ult Oct	pri May- ult Oct	All year	pri May- ult Oct	All year
Area (ha*1000)	Quercus: 26 Populus: 0.2 Salix: 0.15	118	283	2227	547

Notes:

Row 5: Biomass factors are further adjusted according to season and after incorporating the area covered by young and very old stands (see text and table 4).

Table 4. Climatic data for Denmark used to estimate NMVOC from vegetation.

	$\bar{T}_{24hmax}$	$\bar{T}_{24hmin}$	$(\bar{T}_{24h} + \bar{T}_{24hmax})/2$	$\bar{T}_{eff}$ (day)	Average radiation flux ( $\mu E m^{-2} s^{-1}$ )	Day-hours	Night-hours
J	2.0	-2.4	1.0	1.0	116	7.8	16.2
F	2.2	-3.0	1.0	1.0	241	9.8	14.2
M	5.0	-1.3	3.4	5.0	438	11.9	12.1
A	10.2	2.4	8.2	10.2	624	14.0	10.0
M	15.7	6.3	13.4	15.7	696	16.2	7.8
J	19.0	9.7	16.7	19.0	779	17.4	6.6
J	21.1	12.2	18.8	21.1	698	16.9	7.1
A	20.6	12.2	18.4	20.6	664	15.0	9.0
S	17.2	9.7	15.2	17.2	501	12.7	11.3
O	12.0	5.9	10.4	12.0	317	10.3	13.7
N	7.2	2.6	6.1	6.1	173	8.1	15.9
D	4.1	0.1	3.2	3.2	113	7.1	16.9

**Notes:**

Column 1, 2, 6, 7: Average for Denmark for a 30 year period (Danmarks Meteorologisk Institut, 1991).

Column 3: Calculated from Danmarks Meteorologiske Institut (1989). This average best represents temperature conditions for estimating isoprene emissions according to Lamb et al. (1987).

Column 4: Values used for estimating emissions of terpenes and unknown compounds.

Column 5: Average for 1966-1975 from Højbakkegård, Zealand, which is considered typical for Danish conditions (Danmarks Meteorologiske Institut, 1991).

## 5.2. Soils and aquatic sediments

The literature on NMVOC emission from soils and aquatic sediments is limited to a few laboratory studies and a few reports on concentrations of these compounds *in situ*.

### Soils

Several species of NMVOC are produced by a multitude of microorganisms in soils (Goodlass, Smith, 1978), but only ethylene ( $C_2H_4$ ) is produced in significant quantities.

Ethylene can occur in anaerobic soils at concentrations sufficient to modify root growth, and concentrations up to 10-15 ppm has been observed in soil atmospheres (Dowdell et al., 1972; Smith, Dowdell, 1974; Lill, McWha, 1976).

Ethylene production is controlled by oxygen concentration, temperature (apparent  $Q_{10}$  is very high as often seen for anaerobic processes in a mixed aerobic/anaerobic system), and the availability of substrates (Smith, Dowdell, 1974). As ethylene is only produced in significant rates at temperatures exceeding 15-20°C and at high soil moisture contents (Sextone, Mains, 1990) the production rates observed under laboratory

conditions (*Lindberg et al.*, 1979; *Sexstone, Mains*, 1990) indicate that Danish soils produce ethylene at a rate far below  $0.1 \text{ kt yr}^{-1}$ .

#### *Aquatic sediments*

NMVOC's like ethane ( $\text{C}_2\text{H}_6$ ) and propane ( $\text{C}_3\text{H}_8$ ) are found in many anoxic aquatic environments and are probably produced by bacteria (*Hunt et al.*, 1980; *Oremland*, 1981; *Vogel et al.*, 1982; *Wiesenburg et al.*, 1985). The *in situ* concentrations reported in these works indicate that emission of NMVOC from aquatic systems is quite small, though no emission rate for Denmark can be estimated at present.

### **5.3. Leakage from near-surface deposits of natural gases**

At some localities in and around Northern Jutland natural gases are leaking from natural deposits very near the surface of marine sediments or just below the ground surface on land (*Iversen*, 1991) (also see chapter 4.5). However, the leaking gases contain only trace amounts of NMVOC like ethylene and ethane (*Iversen*, 1991). The emission of NMVOC from these deposits is hence considered as negligible.

## **6. Discussion**

### **6.1. Methane emission**

#### *Overview of methane emissions*

The estimated emission of methane in Denmark from the various natural and agriculture-related sources is summarized in table 5. The total emission amounts to about 610 kt per year. This emission plus the emission from other sources (which is not the scope of this study) has to be compared to the atmospheric decomposition of methane. For a total global atmospheric decomposition of  $340\text{-}540 \text{ Tg yr}^{-1}$  (see "Introduction") the decomposition "above" Danish land plus sea territory would be  $95\text{-}150 \text{ kt yr}^{-1}$ . Clearly, on an area basis Denmark must rank high among global contributors of atmospheric methane.

#### *Other investigations*

The EEC has within the CORINAIR project also tried to estimate methane emissions in Denmark. Their total emission from natural and agriculture-related sources is  $675 \text{ kt yr}^{-1}$ . However, the CORINAIR estimate does not include emission by leakage from near-surface deposits of natural gases. On the other hand, their estimate is rather rough and e.g. operates with

fairly high emission rates from e.g. forest soils. The CORINAIR emission rates are European averages that may not be applicable for Danish conditions.

The estimated ranges in table 5 indicate that a high degree of uncertainty is connected to most of the emission rates. However, the estimated emissions indicate that cattle, freshwater marshes and wet meadows, and leakage from deposits of natural gases are the main sources of methane in Denmark.

Even if livestock and other anthropogenic influences are taken out of the total emission, the emission from natural and agriculture-related sources is well above the atmospheric sink strength over Danish territory. This is in accordance with the fact that Danish aquatic systems are quite productive by global standards.

### *Future trends*

Summarizing the estimated annual changes in emission from the different sources (table 5) indicates that a minor annual decrease (tentatively estimated as  $6 \text{ kt yr}^{-1}$ ) in total emission will take place in the years to come. This decrease equals about 1% of the total emission from the sources included in this study.

However, due to the high concentration of livestock, and perhaps also the wide-spread eutrophication of aquatic ecosystems, the total Danish sources are so much more active than the natural steady state situation that Denmark for years will continue as a contributor to the increasing atmospheric concentration of methane.

Table 5. Estimated annual emission and uptake of methane from natural and agriculture-related sources and sinks in Denmark.

	Estimated annual emission (kt CH <sub>4</sub> )	Estimated range (kt CH <sub>4</sub> )	Estimated annual change (kt CH <sub>4</sub> yr <sup>-1</sup> )
<b>Sources of methane:</b>			
Freshwater marshes	200	50-800	?
Raised bogs	1	tr-4	ns
Swamps	?	?	ns
Lakes	18	2-40	ns
Streams	tr	tr	ns
Groundwater	2.3	tr-10	ns
<b>Freshwater systems, total</b>	<b>220</b>	<b>50-850</b>	<b>?</b>
Salt & brackish marshes	10	1-50	ns
Coastal areas	?	?	?
Open sea	2	0.1-10	ns
<b>Coastal &amp; marine areas, total</b>	<b>&gt;12</b>	<b>1- &gt;60</b>	<b>?</b>
Cattle	127	100-150	-5
Other animals, humans	10	5-15	-0.02
Dejections	125	25-350	-1.25
<b>Animals, total</b>	<b>262</b>	<b>130-515</b>	<b>-6</b>
<b>Leakage from gas deposits</b>	<b>&gt;120</b>	<b>60-?</b>	<b>ns</b>
<b>TOTAL EMISSION</b>	<b>615</b>	<b>240- &gt; 1500</b>	<b>-6/?</b>
<b>Sinks for methane:</b>			
Forests	2	1-10	ns
Cultivated land	3	1-10	ns
Other terrestrial systems	0.1	0.2-5	ns
<b>TOTAL UPTAKE</b>	<b>5</b>	<b>2-25</b>	<b>ns</b>
<b>SUM</b>	<b>610</b>	<b>215- &gt;1500</b>	<b>-6/?</b>

ns= the change is probably insignificant relative to the total emission from Denmark.

tr= trace amounts.

?= the figure can not be estimated at the present.

It is unrealistic to reduce the emission of methane to natural levels as livestock is an important part of Danish agriculture. But measures already being taken to reduce the population of cattle in Denmark, and perhaps also the measures taken to reduce the eutrophication of aquatic ecosystems, may reduce the total emission in Denmark significantly in the coming years.

Table 5 indicates that several gaps exist in our knowledge of methane emission from Denmark. Further research has to address these gaps if we are to understand the size and the dynamics of the different sources. Especially, the emission from freshwater marshes, lakes, coastal areas, dejections, and from near-surface deposits of natural gases should be monitored. Other areas to address are the potential of dry soils to act as sinks for atmospheric methane, and the potential of the open sea as a source of methane.

## 6.2. NMVOC emission

### Overview of NMVOC emissions

The estimated total emission of NMVOC in Denmark from the different natural sources is summarized in table 6. The total emission amounts to about 11 kt yr<sup>-1</sup>. Terpenes and unknown compounds from forests dominate total emission.

Table 6. Emission of NMVOC from natural sources in Denmark. Rates are given in t yr<sup>-1</sup>.

	Forests	Crop- + grasslands	Soils	All sources
Isoprene	344	61	-	405
Terpenes	5115	741	-	5856
Ethylene	-	-	<100	<100
Unknown	3849	1234	-	5083
Total NMVOC	9308	2036	<100	11400

Several attempts have been made to estimate natural NMVOC emission from European countries, some of them including Denmark (*Veldt*, 1988; *Lübker*, *de Tilly*, 1989; *Lübker*, *Schöpp*, 1989; *Molnar*, 1990). Though these attempts differ in model formulation and input data like forest coverage, biomass factors, and temperature data they are essentially based

on the same few reports on measurements of emission from different plant species, most of which are North American.

Within the OECD-MAP Inventory *Lübker and de Tilly* (1989) estimated NMVOC emission from natural sources in Denmark to be 46.8 kt yr<sup>-1</sup> in 1980. *Lübker and Schöpp* (1989) estimated NMVOC emission from Danish forests to be 6 kt yr<sup>-1</sup>, but only operates with a forested area of 239 000 ha. Extrapolating this estimate to a forest area of 427 000 ha results in a NMVOC emission from Danish forests of about 11 kt yr<sup>-1</sup>.

However, all these estimates (including this inventory) are highly uncertain as even slight differences in e.g. temperature gradients during the day influence emission rates strongly (*Lübker, Schöpp*, 1989). Also, biomass factors, emission rate temperature coefficients etc., are based on limited and/or extrapolated data. In conclusion comparison of the results of this study with other inventories is of limited value.

*Lamb et al.* (1987) estimated the overall uncertainty to be approximately a factor of three for their inventory of U.S. biogenic hydrocarbons emissions. However, during this study it has become clear that the uncertainty is probably more likely to be about a factor of 10. Until more research has been carried out on emission rates from more plant species under differing environmental conditions natural NMVOC emission can only be tentatively estimated.

## 7. Conclusion

### *Methane*

The estimated emission of methane from Denmark of 610 kt yr<sup>-1</sup> indicates that livestock, freshwater marshes, and leakage from deposits of natural gases are the major natural and agriculture-related sources. Due to the high concentration of livestock the present total Danish source strength of methane is elevated much above natural unperturbed steady-state source strength. It seems unrealistic to reduce present total emission of methane to natural levels. But the emission of methane caused by livestock and perhaps also from aquatic ecosystems will probably be reduced through measures already being taken. It is important that future research will address the gaps in our understanding of methane emissions in Denmark.

### *NMVOC*

The tentatively estimated emission of 11 kt yr<sup>-1</sup> of non-methane volatile organic carbons indicate that forests are the major source. More research is needed to make future estimates of NMVOC emission rates more reliable.



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# Appendices

Appendix 1. Freshwater systems.

Appendix 2. Saltwater systems.

Appendix 3. Methane uptake rates by soils in temperate regions.

Appendix 4. Calculation procedure for estimating NMVOC emission from vegetation.

Appendix 1. Freshwater systems.

Ecosystem	Location	Emission rate (kg CH <sub>4</sub> ha <sup>-1</sup> yr <sup>-1</sup> )	Reference	Remarks
Meadow	Denmark (Viby Sj.)	-0.35	Christensen (unpubl.)	At margin of marshy meadow
Meadow	USA (Minnesota)	2420	Harriss et al. (1985)	Sedge
Marsh	USA (Louisiana)	2130	DeLaune et al. (1983)	pH 6.3, salinity 0.04%, watertable 10 cm, Panicum sp.
Marsh	USA (Louisiana)	187	DeLaune et al. (1983)	pH 6.3, salinity 0.04%, water table 100 cm, Panicum sp.
Marsh	USA (Virginia)	182	Bartlett et al. (1987)	Spartina cynosuroides
Marsh	USA (Virginia)	812	Bartlett et al. (1985)	Open water site
Marshes	Global average	500-1460	Aselmann, Crutzen (1989)	Deduced from studies on NPP
Bog	USA (Minnesota)	570	Harriss et al. (1985)	
Bog	USA (Minnesota)	170	Harriss et al. (1985)	
Bog	USA (Minnesota)	710	Harriss et al. (1985)	
Doomed bog	Canada (S. Quebec)	1	Moore, Knowles (1990)	pH 2.8-3.3
Fen + bog	USA (Minnesota)	1530	Harriss et al. (1985)	
Fen	USA (Minnesota)	10	Harriss et al. (1985)	Shoreline fen
Fen	USA (Minnesota)	600	Harriss et al. (1985)	
Lake	USA (California)	470	Cicerone, Shetter (1981)	
Lake	USA (Louisiana)	179	DeLaune et al. (1983)	
Lake	USA (Michigan)	210	Kelly, Chynoweth (1981)	Small, surrounded by farmland, sed. rate 530 kgC ha <sup>-1</sup> yr <sup>-1</sup>
Lake	USA (Michigan)	905	Kelly, Chynoweth (1981)	Small, forested watershed, sed. rate 1270 kgC ha <sup>-1</sup> yr <sup>-1</sup>
Lakes	Global average	62-325	Aselmann, Crutzen (1989)	Deduced from studies of NPP
River	USA (Oregon)	9-58	de Angelis, Lilley (1987)	
Stream	Canada	1.6	Ford, Naiman (1988)	Width 20 m, depth 0.5-3 m, BOM 166 gC m <sup>-2</sup>
Stream	Canada	0.6	Ford, Naiman (1988)	Width 15 m, depth 2 m, BOM 228 gC m <sup>-2</sup>
Stream	Canada	2.7	Ford, Naiman (1988)	Width 1-2 m, depth 0.25 m, BOM 158 gC m <sup>-2</sup>
Stream	Canada	0.4	Ford, Naiman (1988)	Width 0.5-1 m, depth <0.1 m, BOM 484 gC m <sup>-2</sup>

Appendix 2. Saltwater systems.

Ecosystem	Location	Emission rate (kg CH <sub>4</sub> ha <sup>-1</sup> yr <sup>-1</sup> )	Reference	Remarks
Brackish marsh	USA (Louisiana)	970	DeLaune et al. (1983)	Salinity 0.18%, watertable 10 cm, Spartina patens
Brackish marsh	USA (Louisiana)	64	DeLaune et al. (1983)	Salinity 0.18%, watertable 100 cm, Spartina patens
Brackish marsh	USA (Virginia)	182	Bartlett et al. (1987)	Salinity 0.26%, Spartina cynosuroides
Brackish marsh	USA (Virginia)	224	Bartlett et al. (1987)	Salinity 0.55%, Spartina cynosuroides
Brackish marsh	USA (Virginia)	56	Bartlett et al. (1987)	Salinity 0.88%, mixed Spartina sp.
Salt meadow	USA (Virginia)	4.3	Bartlett et al. (1985)	Salinity 2.6%
Salt marsh	USA (Virginia)	13	Bartlett et al. (1985)	Salinity 2.6%, short Spartina alterniflora
Salt marsh	USA (Virginia)	12	Bartlett et al. (1985)	Salinity 2.6%, tall Spartina alterniflora
Salt marsh	USA (Louisiana)	57	DeLaune et al. (1983)	Salinity 1.8%, watertable 10 cm, Spartina alterniflora
Salt marsh	USA (Louisiana)	17	DeLaune et al. (1983)	Salinity 1.8%, watertable 100 cm, Spartina alterniflora
Salt marsh	USA (Georgia)	4	King, Wiebe (1978)	Tall Spartina sp.
Salt marsh	USA (Georgia)	58	King, Wiebe (1978)	Mid-marsh
Salt marsh	USA (Georgia)	531	King, Wiebe (1978)	Short Spartina sp.
Salt marsh	USA (California)	2.8	Cicerone, Shetter (1981)	Watertable 15 cm
Salt marsh	U.K	4.8	Senior et al. (1982)	Pan
Salt marsh	U.K	0.6-1.1	Senior et al. (1982)	Creek
Salt lagoon	USA (North Carolina)	912	Martens (1984)	Extremely high rates of organic degradation
Estuary	USA (Oregon)	10.6	de Angelis, Lilley (1987)	Salinity 0.2-3.4%
Ocean	Black Sea	0.16	Reeburgh et al. (1990)	Salinity 1.7-1.8%, the Black Sea is an anoxic basin
Ocean	Caribbean Sea (USA)	0.013	Ward et al. (1987)	
Ocean	Off SW Canada	0.13	Ward et al. (1989)	

Appendix 3. Methane uptake rates by soils in temperate regions.

Ecosystem	Location	Uptake rate (kg CH <sub>4</sub> ha <sup>-1</sup> yr <sup>-1</sup> )	Reference	Remarks
Hardwood forest	USA (Massachusetts)	6-13	Stuedler et al (1989)	
Hardwood forest	USA (New England)	0.4-1.4	Keller et al (1983)	Only measured during growing season
Hardwood forest	USA (Virginia)	7.3	Yavitt et al. (1990b)	
Deciduous forest	Germany	4	Born et al. (1990)	pH 5.0, clay soil
Beech forest	Denmark (Gribskov)	0.27	Christensen (unpubl.)	
Beech-oak-maple forest	Germany	3	Born et al. (1990)	pH 8.0, loamy soil
Beech-spruce forest	Germany	13	Born et al. (1990)	pH 7.7, sandy soil
Beech-spruce forest	Germany	13	Born et al. (1990)	pH 3.5, sandy soil
Spruce forest	Germany	0.9	Born et al. (1990)	pH 5.0, clay soil
Spruce forest	Denmark (Strødam)	1.42	Christensen (unpubl.)	
Spruce forest	USA (Virginia)	3.7	Yavitt et al. (1990b)	
Pine forest	USA (Massachusetts)	8-15	Stuedler et al (1989)	
Grassland	Germany	0.02-2	Born et al. (1990)	
Natural common	Denmark (N. Zealand)	0.62	Christensen (unpubl.)	Situated on old dune sand
Cultivated land	Denmark (Viby Sj.)	0.45	Christensen (unpubl.)	Crop: Barley
Cultivated land	Germany	0.02-2	Born et al. (1990)	

Appendix 4. Calculation procedure for estimating NMVOC emission from vegetation.

A) High-isoprene emitters.

Isoprene:

	(emission factor)	(Biomass factor)	(Area)	(Days)	(Dayhours)	(Conversion factors) <sup>-12</sup>	(Emission)	
M	2.35	225	26350	25	16.2	$10000 \times 10^{-12}$	56	
J	2.40	220		30	17.4		73	
J	2.45	215		31	16.9		73	
A	2.45	210		31	15.0		63	
S	2.35	205		30	12.7		48	
O	2.30	200		25	10.3		31	
	( $\mu\text{g g}^{-1} \text{h}^{-1}$ )	( $\text{g ha}^{-1}$ )	(ha)	(d)	( $\text{h d}^{-1}$ )	( $\text{m}^2 \text{ha}^{-1}$ )	( $\text{t ug}^{-1}$ )	$344 \text{ t yr}^{-1}$

Unknown compounds:

Day:

M	1.26	225	26350	25	16.2	$10000 \times 10^{-12}$	30
J	1.59	220		30	17.4		48
J	1.85	215		31	16.9		55
A	1.78	210		31	15.0		46
S	1.40	205		30	12.7		29
O	0.96	200		25	10.3		13

Night:

M	0.65	225		25	7.8		8
J	0.83	220		30	6.6		10
J	0.99	215		31	7.1		12
A	0.99	210		31	9.0		15
S	0.83	205		30	11.3		15
O	0.63	200		25	13.7		11
							$292 \text{ t yr}^{-1}$

B) Non-isoprene emitting deciduous trees.

Day:

M	0.71	265	118000	25	16.2	$10000 \times 10^{-12}$	90
J	0.89	260		30	17.4		143
J	1.02	255		31	16.9		161
A	0.99	250		31	15.0		136
S	0.78	245		30	12.7		86
O	0.55	240		25	10.3		40

Night:

M	0.37	265		25	7.8		23
J	0.47	260		30	6.6		29
J	0.55	255		31	7.1		36
A	0.55	250		31	9.0		45
S	0.47	245		30	11.3		46
O	0.36	240		25	13.7		35
							$870 \text{ t yr}^{-1}$

or:  $44 \text{ t yr}^{-1}$  terpenes +  $826 \text{ t yr}^{-1}$  unknown compounds.

C) Coniferous trees.

Day:													
J	0.05	x	1100	x	283000	x	31	x	7.8	x	10000x10 <sup>-12</sup>	=	38
F	0.05						28.25		9.8				43
M	0.09						31		11.9				103
A	0.19						30		14.0				249
M	0.45						31		16.2				703
J	0.75						30		17.4				1219
J	1.03						31		16.9				1680
A	0.96						31		15.0				1390
S	0.57						30		12.7				676
O	0.26						31		10.3				258
N	0.10						30		8.1				76
D	0.07						31		7.1				48
Night:													
J	0.03						31		16.2				47
F	0.03						28.25		14.2				37
M	0.03						31		12.1				35
A	0.06						30		10.0				56
M	0.11						31		7.8				83
J	0.18						30		6.6				111
J	0.26						31		7.1				178
A	0.26						31		9.0				226
S	0.18						30		11.3				190
O	0.10						31		13.7				132
N	0.06						30		15.9				89
D	0.04						31		16.9				65
													7802 t yr <sup>-1</sup>
or: 5071 t yr <sup>-1</sup> terpenes + 2731 t yr <sup>-1</sup> unknown compounds.													

D) Crops.

Isoprene:													
M	1.32	x	2227000	x	31	x	16.2	x	10000x10 <sup>-12</sup>	=	15		
J	1.35				30		17.4				16		
J	1.38				31		16.9				16		
A	1.37				31		15.0				14		
	(ug m <sup>-2</sup> h <sup>-1</sup> )		(ha)		(d)		(h d <sup>-1</sup> )		(m <sup>2</sup> ha <sup>-1</sup> )		(t ug <sup>-1</sup> )		61 t yr <sup>-1</sup>

Terpenes and unknown compounds:

Day:						
M	11.33			31	16.2	127
J	14.30			30	17.4	166
J	16.59			31	16.9	194
A	16.01			31	15.0	166
Night:						
M	5.83			31	7.8	31
J	7.41			30	6.6	33
J	8.84			31	7.1	43
A	8.84			31	9.0	55
						815 t yr <sup>-1</sup>
or: 509 t yr <sup>-1</sup> terpenes + 306 t yr <sup>-1</sup> unknown compounds.						



E) Grasslands.

Day:

J	11.69	x	547000	x	31	x	7.8	x	$10000 \times 10^{-12}$	=	15
F	11.69				28.25		9.8				18
M	15.85				31		11.9				32
A	23.56				30		14.0				54
M	35.81				31		16.2				98
J	46.04				30		17.4				131
J	54.02				31		16.9				155
A	52.01				31		15.0				132
S	40.14				30		12.7				84
O	27.02				31		10.3				47
N	17.24				30		8.1				23
D	13.82				31		7.1				17

Night:

J	9.02				31		16.2				25
F	8.62				28.25		14.2				19
M	9.81				31		12.1				20
A	13.01				30		10.0				21
M	17.50				31		7.8				23
J	22.68				30		6.6				25
J	27.43				31		7.1				33
A	27.43				31		9.0				42
S	22.68				30		11.3				42
O	16.98				31		13.7				39
N	13.21				30		15.9				34
D	10.92				31		16.9				<u>31</u>

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or:  $232 \text{ t yr}^{-1}$  terpenes +  $928 \text{ t yr}^{-1}$  unknown compounds.

## National Environmental Research Institute

The National Environmental Research Institute - NERI - is a research institute of the Ministry of the Environment. Neri's tasks are primarily to do research, collect data and give advice on problems related to the environment and nature.

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### Publications:

NERI publishes professional reports, technical instructions, reprints of scientific and professional articles, a magazine of game biology and the Annual Report.

Included in the annual report is a review of the publications from the year in question. The annual reports and an up-to-date review of the year's publications are available on application to NERI.