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The Dynamics of Non-methane Hydrocarbons and Other Trace Gas Fluxes at a Subarctic Mire in Northern Sweden

Kristina Bäckstrand

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Geobiosphere Science Centre
Physical Geography and Ecosystems Analysis
Lund University
Sölvegatan 12
S-223 62 Lund
Sweden



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By Kristina Bäckstrand, 2004

Supervisor: Torben R. Christensen,
Geobiosphere Science Centre,
Physical Geography and Ecosystem analysis,
Lund University
Sweden

Abstract

In the context of climate change, it is important to understand how the terrestrial carbon cycle is interacting with the anthropogenic increase in atmospheric carbon dioxide (CO₂) concentration. Boreal and subarctic regions in the northern hemisphere are great carbon pools, as well as they are subject to predicted warming. These facts place them in the absolute frontline of ecosystems that are to be studied in the context of coupled climate models, where the terrestrial carbon cycle is included. In addition to CO₂ and methane (CH₄), which have been intensively studied regarding carbon cycle and climate, there are other biogenic volatile organic compounds (BVOC) emitted by vegetation that have shown to be of great importance. One group is called non-methane hydrocarbons (NMHCs). Their emissions is a part of the carbon flux in ecosystems, and have an indirect role in determining atmospheric concentration of some greenhouse gases as well as biogenic aerosols. A study of CO₂, CH₄ and NMHC flux dynamics has been conducted on the subarctic mire Stordalen in northern Sweden. The objective is to contribute to the existing knowledge about exchanges of CO₂ and CH₄, and primarily to add new knowledge of NMHC emissions from a subarctic ecosystem, which has not earlier been studied.

An automatic multichamber system was used to collect high temporal resolution data of CO₂ and total hydrocarbon (THC) fluxes from three different sub-ecosystems on the mire: a wet minerotrophic site, a wet intermediate ombro-minerotrophic site and a semiwet ombrotrophic site. Further, manual sampling of CH₄ fluxes was conducted approximately three times a week, from mid-June to late August. This gave the possibility to estimate the amount of NMHCs (THC flux -CH₄ flux). A temperature dependent respiration model was developed from night time CO₂ flux data, and gross primary production (GPP) could be estimated for each sub-ecosystem. Environmental variables as light, temperature, moisture and thaw depth are included in the correlations.

The results show a certain degree of temperature, light and GPP dependency for NMHC emissions from all of the different plant communities, however it is a great distinction between different plant specie. The largest emissions come from wet minerotrophic sub-ecosystems with vascular plants, compared to a mostly *Sphagnum* moss vegetated semiwet site, 2.8 mg/m²/hr and 0.9 mg/m²/hr respectively. The NMHC flux rates are however, likely to be underestimated. They are based on the molar weight of CH₄ (16 g/mol), while isoprene (C₅H₈), which is one of the lightest NMHCs, have a molar weight that is more then four times greater. The output of NMHC-carbon from the mire ecosystem was found to be close to 2 % from the wet minerotrophic site, in relationship to CO₂-C and CH₄-C. CH₄ emissions are higher from wet, compared to semiwet microsites. The water table position at a depth of 15-25 cm play an important role at the semiwet site, while water table variations within a depth of 0-10 cm do not affect the CH₄ emissions. Moreover, the presence of vascular plants and their ability to give qualitative substrates for CH₄ production through photosynthesis, as well as their capacity for plant mediated CH₄ transport, are most likely explaining the difference between the two sites. This is in addition to the actual moisture content, explained as being the main cause for high CH₄ emissions. Conclusively, research of BVOCs from northern latitude ecosystem like the subarctic mire Stordalen, should be a part in future studies of the terrestrial carbon cycle. Their part in the carbon budget at this site is shown to be significant.

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Introduction

Climate models predict, that as the anthropogenic emissions of carbon dioxide (CO₂) increase, due to fossil fuel burning and deforestation etc., the temperature on Earth will also increase. In arctic regions, climate change is predicted to be of great relevance, both concerning a rise in temperature and precipitation. Climate models to predict future climate change include many components of the climate system and more recently, the terrestrial carbon cycle as a part of the climate model, has obtained more attention. It is required in order to capture several important climate feedbacks on CO₂ concentration. Such as, the fertilisation of plant growth by CO₂, or increased CO₂ input to the atmosphere by increased decomposed plant material as a result of amplified temperatures. (Cox *et al.*, 2000)

The boreal and subarctic regions in the northern hemisphere are great carbon pools, which together with the predicted warming, place them in the absolute frontline of ecosystems that are to be studied in context of the terrestrial carbon cycle and climate models. About 30 % (200 Gt) of the total world pool of soil carbon is stored as peat in northern peatforming wetlands and tundra regions (Post, 1982 in: Joabsson *et al.*, 1999). Further, wetland is one of the most important sources of the temperature and moisture dependent greenhouse gas methane (CH₄). (IPCC, 2001)

In addition to CO₂ and CH₄, that have been intensively studied regarding carbon cycle and climate, there are other biogenic reactive carbon compounds emitted by vegetation. Biogenic volatile organic compounds (BVOC), where the most abundant species are non-methane hydrocarbons (NMHCs), must not be forgotten in a comprehensive climate model that includes the terrestrial carbon cycle. Their emissions significantly contribute to the carbon flux in ecosystems and have an indirect role in determining atmospheric concentration of greenhouse gases (e.g. CO₂ and CH₄) as well as biogenic aerosols. Conclusively, as related compounds like CO₂, CH₄ and aerosols all influence the radiative balance on Earth; a clear link between NMHC emissions, carbon cycles and climate models is detected. (IPCC, 2001)

As far as is known, there is no published work on NMHC emissions in the subarctic regions, although the great carbon pools in peat are potential reserves and previous research on more southern boreal wetlands have shown NMHC emissions of significance to the carbon budget (Janson & De Serves, 1998, Janson *et al.*, 1999 and

Klinger et al., 1994). This research report, presents a study of CO₂, CH₄ and NMHC flux dynamics on the subarctic mire Stordalen in northern Sweden (68° 22'N, 19° 03'E), which has been a subject of interest concerning biosphere-atmosphere interactions for about 30 years. The trace gases are examined in relation to each other as well as to various environmental variables. The research methodology is based on an automatic chamber system, which measures and gives a high temporal resolution data set of trace gas fluxes. Fieldwork was undertaken during the summer of 2003.

The research objective is to contribute to knowledge about the carbon cycle in general in a subarctic ecosystem. In detail, it is to try to describe the patterns, rates and causes of the various trace gas fluxes at four different sub-ecosystems on the mire and in particular, expand the currently limited knowledge of NMHC emissions in this region. Further, as there already are long-term records available of trace gas measurements on the site, this work aims to make already extensive records even more comprehensive. Finally, the findings may in future be useful as knowledge for modelling of the terrestrial carbon cycle, which in turn relates this research to climate models and future climate change predictions.

Literature review

The greenhouse effect and climate change

The reason why the temperature on Earth is as high as it is today is the so-called greenhouse effect. Short wave radiation from the sun reaches the Earth's atmosphere and most of the heat is absorbed by the surface of the Earth. Some of the radiation is however reflected back by either the atmosphere or the surface of the Earth. The solar radiation that is absorbed by the Earth heats the surface, which in turn will emit longwave infrared radiation (heat). Some of this heat will pass out through the atmosphere, but some of the heat is absorbed and re-emitted in the atmosphere by greenhouse gases (including water vapour and clouds) and aerosols. This results in heat that is trapped within the atmosphere, which in turn warms up Earth's surface. This mechanism is called *the natural greenhouse effect (Figure 1)*. (IPCC, 2001)

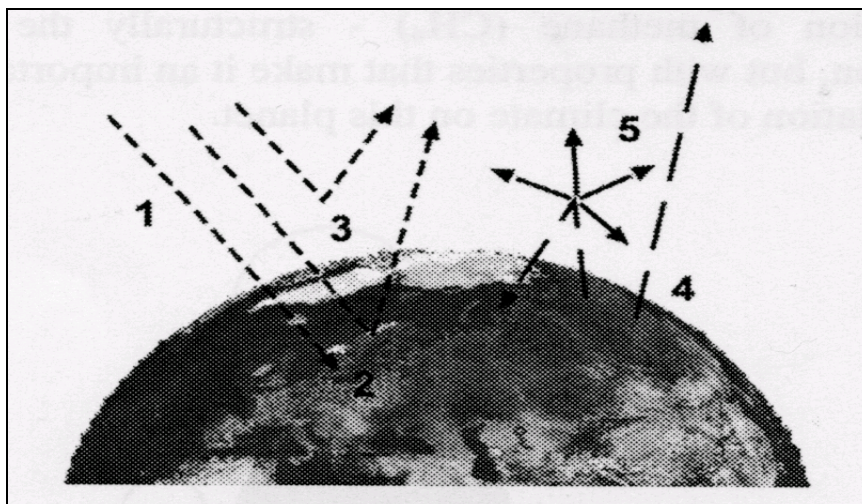


Figure 1, The greenhouse effect.

The figure explains the processes causing the greenhouse effect. 1) Solar radiation passes through the atmosphere. 2) Most of the radiation is absorbed by the Earth and heat up the surface. 3) Some of the incoming radiation is reflected by the Earth or its atmosphere. 4) Heat from the surface of Earth is emitted as longwave radiation. 5) Some of the heat passes out of Earth's atmosphere while some are absorbed and reflected back again by greenhouse gases. (From Joabsson, 2001)

Human activities, in particular those involving the combustion of fossil fuels for industrial or domestic usage, and biomass burning, produce greenhouse gases and aerosols which affect the composition of the atmosphere. We know that the concentration of CO₂ in the atmosphere has increased due to anthropogenic perturbation. Further, the concentration of the nitrogen oxides (NO and NO₂) and carbon monoxide (CO) are also evidently increasing. But in addition to the anthropogenic ones, there are several natural sources of importance for the atmospheric composition. For example wetlands, and animals such as livestock and termites, that emits CH₄ in highly significant amounts. The heating of the Earth that all these activities cause is called *the enhanced greenhouse effect*. (IPCC, 2001)

Accurate and detailed observations of climate and climate variability in the past, as well as climate models, are used to simulate and quantify the climate response to present and future human activities. It is expected that the climate on Earth will change during the coming century with the magnitude of change varying between regions. In the climate models, it is important to pay attention to the links between vegetation and the terrestrial energy, water and carbon cycles, and how these might change due to eco-physiological responses to elevated CO₂ and changes in land use. Further on, it has to be considered what feedbacks the changing ecosystems might have on the climate system itself. (IPCC, 2001)

Cox et al. (2000), account for the effect of climate/carbon feedbacks on CO₂ concentration and global-mean and land-mean temperatures (*Figure 2 & 3*). The results are from a fully coupled, three-dimensional carbon-climate model and indicate the significance of carbon-cycle feedbacks on the climate system. It is important though, to be aware of the uncertainties that modelling yet today implies and that this certain model might not be totally correct. The results do show however, that an extended knowledge about the carbon cycle of the Earth's ecosystems is essential and of fundamental importance in the process of developing predictive climate models.

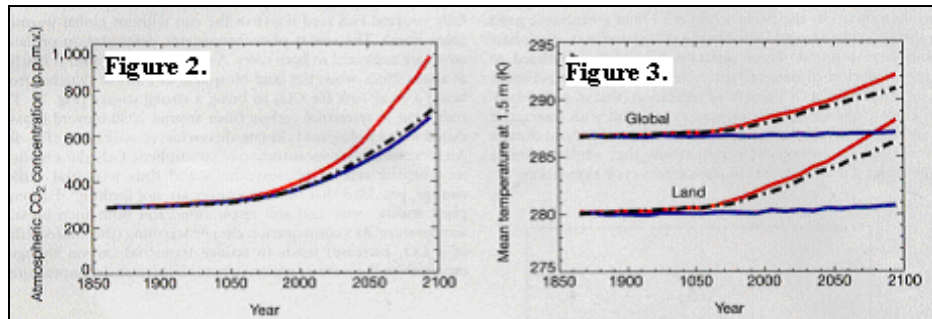


Figure 2 & 3, Simulated CO₂ concentration and global mean temperature rise. Figure 2 shows a global-mean CO₂ concentration and Figure 3 the global-mean and land-mean temperatures, from three different simulations. The red line indicate CO₂ rise from a fully coupled simulation with interactive CO₂ and vegetation dynamics, the dashed line is based on data from a standard global circulation model with fixed vegetation and the blue line shows a simulation which neglects direct CO₂ induced climate change. (From Cox et al. 2000)

The northern latitude ecosystems have been pointed out to be particularly sensitive to climate change where higher temperatures and increased precipitation are to be expected. But why, and in what way are these regions particularly sensitive? There is no doubt that human activities have significantly modified the carbon cycle over the past few hundred years. All carbon pools in all terrestrial ecological systems, including forests, agricultural- and range-lands, are being disturbed by human activities. And the fact is that the northern latitude peatforming wetlands and tundra regions are the most extensive carbon pool on Earth, holding approximately 200 Gt, or ~30 % of the world soil carbon (Post, 1982 in: Joabsson et al., 1999). This, combined with the substantial increases in temperature and precipitation predicted for these regions, put the northern high latitude ecosystems in the frontline of environmental research. (IPCC, 2001)

The northern latitudes as an organic carbon pool

The large amount of the organic carbon in the northern hemisphere is stored in forest biomass, wetlands and peat formations. Peatlands are formed at sites where the net productivity of vegetation is greater than its rate of decomposition, which will result in an accumulation of dead plant material that might be consistent for thousands of years. (Klinger *et al.*, 1994) The reason for the great amount of peat accumulation in the northern latitudes is largely cold ground and lower air temperatures. This decreases the decomposition rate of organic material and affects the evaporation at these sites, making the input of precipitation much greater than the evaporative losses. This results in an anoxic environment less capable of decomposing organic material. The presence of permafrost in northern latitudes reduces water infiltration during the frozen period, and acts as a moisture source during thaw season, which results in waterlogged soils. (Joabson, 2001) The same effect of waterlogging comes from the lack of slope, trapping moisture at certain places in the terrain (Svensson *et al.*, 1999).

The role of CO₂

The process of photosynthesis make the peatland a sink for the greenhouse gas CO₂, as long as the photosynthesis is greater than the respiration losses (Klinger *et al.*, 1994). Photosynthesis can be explained through the uptake of CO₂ by the plants, the capture of light energy that splits water molecules to produce high energy molecules and oxygen (O₂), after which the reduction of CO₂ to carbohydrates occurs: light energy + H₂O + CO₂ ↔ CH₂O + O₂.

The rate of photosynthesis and carbon binding in the plants can be explained as the rate of gross primary production (GPP). However, to determine the amount of net primary production (NPP), the amount of plant respiration has to be considered resulting in the following relationship: $NPP = GPP - \text{respiration}_{\text{plants}}$. Further, soil respiration affects NPP in an ecosystem so that the net ecosystem exchange (NEE) of CO₂ in this case, is determined by: $NEE = NPP - \text{respiration}_{\text{soil}}$. In other words, the final binding of CO₂, is dependent on the total fixation of carbon by the plants and how much carbon that is lost by plant and soil respiration. Respiration, is defined in the same way as the process of photosynthesis but the other way around, using oxygen

for the oxidation of carbohydrates, which result in the release of CO₂ to the atmosphere and is very much dependent on temperature. (*Schlesinger, 1991*)

The role of CH₄

Wet conditions and the accumulation of the plant material in the northern regions as described above, will most likely result in an anoxic sub-surface environment. Anoxic conditions favour reduction pathways in decomposition that will result in the production of new trace gases, among others: CH₄ (*Klinger et al., 1994*). CH₄ is of particular interest as it is a greenhouse gas 23 times more efficient than CO₂ in a 100 yr time span. Several studies have shown clear temperature dependence on CH₄ fluxes, which rank the emission of this greenhouse gas as highly important in climate change scenarios (*Crill et al., 1992*). Today's estimation of the CH₄ emission from northern wetlands is about 40 Tg/yr, which is at the most one third of the emissions for the total global wetlands ranging from about 115-237 Tg CH₄/yr (*IPCC, 2001*).

Factors controlling methanogenesis

CH₄ production is called methanogenesis. It occurs by the action of microbes in anaerobic conditions in the soil environment. The methanogenic bacteria are dependent on a limited number of organic substrates for their biosynthesis and energy production. Reduction of CO₂ in the presence of hydrogen can be one pathway to methanogenesis ($\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$), but also acetate may work as a substrate through acetate splitting ($\text{CH}_3\text{COOH} \rightarrow \text{CO}_2 + \text{CH}_4$). To determine the net CH₄ fluxes from wetlands, it is essential to estimate the degree of methane consumption (methanotrophy) by methanotrophic bacteria in addition to the methanogenesis. Methanotrophy occurs in the oxic surface layers in the soil and in the surroundings of plant roots where oxygen leaking occurs, resulting in CH₄ being oxidized to CO₂. (*Calow, 1999*)

The part of the CH₄ in the soil that avoids oxidation may be emitted at the surface and this is the gas flux that can be measured above ground. There are three known ways of CH₄ transport to the atmosphere: transport through vascular plants, diffusion through the soil profile and bubble ebullition. (*Joabson, 2001; Schlesinger, 1991*) See Figure 4 for a schematic description of methanogenesis, methanotrophy and pathways of CH₄ to atmosphere.

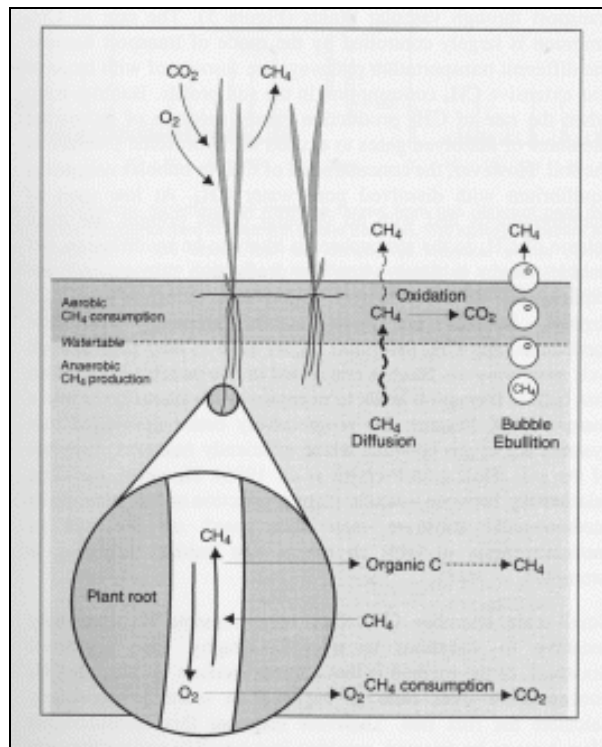


Figure 4, Methanogenesis, methanotrophy and pathways to the atmosphere.

The figure is a schematic description of how carbon compounds are provided by plants and later on can be utilized for methane production. Consumption of methane may be present deep in the soil if oxygen is leaking from roots or closer to surface at the anaerobic zone. There are three pathways of CH_4 to atmosphere: Diffusion through vascular plants, diffusion through soil and bubble ebullition. (From Joabsson, 2001)

Anoxic properties of the environment are absolutely necessary for methanogenesis and there is often a clear positive relationship between the height of the water table and CH_4 emissions. Further, fluxes are shown to increase with temperature and the supply of organic matter for most wetland ecosystems. The dependence on nutritional sources and light for methanogenesis has also been discussed. (Joabsson *et al.*, 1999; Schlesinger, 1991) Geomorphology and microtopography in northern ecosystems like wetlands are indirect effects of the distribution and discontinuity of permafrost. Morphological characteristics of a site interact with vegetation characteristics like density, type and distribution.

The temperature change and carbon sink/source relationship

In general, the peatlands are today seen as a sink of CO₂ through peat accumulation and a source of CH₄ due to anaerobic decomposition in existing favourable conditions. Actively discussed is what the implications of a temperature change might be on the carbon sink/source relationship, and how this might affect feedback mechanisms on climate in northern latitudes. Taking CO₂ and CH₄ into account, the discussion could briefly be something like follows. Warmer temperatures in the northern latitudes could possibly imply a longer growing season and more nutrients released in the ground (*Chapin et al., 1995*), which may result in more carbon fixed in growing plants. Warmer ground temperatures however, would also be likely to increase soil respiration, which releases CO₂ back to the atmosphere (*Lloyd & Taylor, 1994*). The carbon fixed in the plants may further work as a substrate for CH₄ production. Higher CH₄ emissions have also shown clear positive relationships with higher ground temperatures (*Christensen et al., 2003a; Crill et al., 1992; Klinger et al., 1994*). In addition, increased CH₄ emission from anoxic grounds derived from melted permafrost may be expected. However, increased temperatures could also lead to higher evaporation, lowering the water table in the ground, which would in turn result in lower CH₄ emission (*Klinger et al., 1994*). What has to be considered as well is how the specific species composition might come to change as a result of changed geomorphology, hydrology and soil properties. Vascular plants, mosses and other vegetation may all have different capabilities of binding carbon and respire CO₂, as well as having varying influences on the ground properties which influence CH₄ emission.

The importance of other reactive gases and aerosols

Although CO₂ and CH₄ fluxes have been the subject of interest for many years now concerning peat accumulation, carbon budget and climate, there are other reactive biogenic hydrocarbons that have received much less attention. In general, the group of various compounds may be called biogenic volatile organic compounds (BVOC). Although the interest for these reactive gases have been minor especially in the northern latitudes compared to Mediterranean and tropical regions, the importance of them is confirmed by the result from a few investigations of boreal wetlands (i.e. *Isidorov et al. (1985), Isidorov et al. (1994), Isidorov & Jdanova (2002), Janson &*

De Serves (1998), Janson et al. (1999) and Klinger et al. (1994)). Further, the significance of aerosols as a part of the radiative forcing on Earth shows great uncertainty, which in turn is related to the BVOC emissions since the amount of organic aerosols in the atmosphere is known to be affected by these emissions (*IPCC, 2001*).

Non-methane hydrocarbons (NMHC)

Biogenic volatile organic compounds (BVOC) is a term that includes organic atmospheric trace gases other than CO₂ and carbon monoxide (CO), which are produced within living organisms, and in some cases are emitted to the atmosphere. Within the BVOC group, there is a division of hydrocarbon gases that excludes CH₄ for which the term NMHC is commonly used. (*Kesselmeier & Staudt, 1999*) Although the hydrocarbons consist only of the elements hydrogen and carbon, there are an enormous amount of different compounds where the class of terpenes (also called isoprenoids) include the most abundant species (*Guenther, 2003; Kesselmeier & Staudt, 1999; Peñuelas & Llusà, 2001; Simeonidis et al. 1999*). Within the class of terpenes, there are hemiterpenes (compounds that contains 5 carbon atoms), monoterpenes (10 carbon atoms), sesquiterpenes (15 carbon atoms) and diterpenes (20 carbon atoms) (*Figure 5*). The hemiterpene isoprene (C₅H₈) is emitted in the highest rates globally. In addition to NMHC, other BVOCs include oxygenated compounds such as alcohols, aldehydes, ketones, acids, ethers, esters, alkanes, alkenes, arenas, sulfur compounds and nitrogen compounds. (*Guenther, 2003; Kesselmeier & Staudt, 1999*)

The global annual emission of biogenic NMHCs is estimated to range up to 1500 Tg C/yr, and terpenes are thought to constitute the biggest part of this (*Guenther, 2003; Peñuelas & Llusà, 2001*). However, there might be up to 300 % uncertainty according to some researchers (*Isidorov et al., 1994*) due to the diversity of ecological and climatic variables.

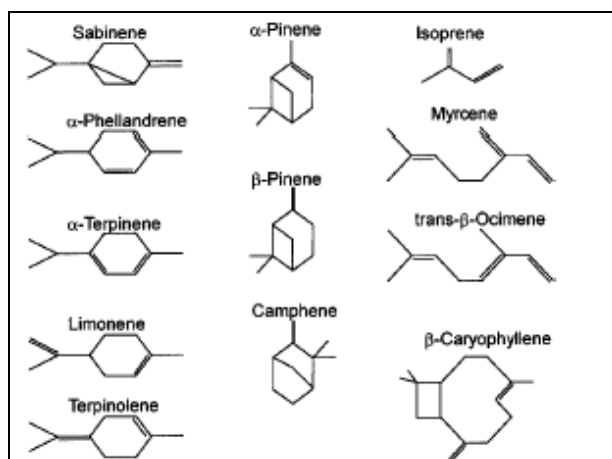


Figure 5, Molecular structures of some volatile hydrocarbons.

The figure is a schematic representation of the molecular structures of some volatile hydrocarbons : isoprene (C_5), some monoterpenes (C_{10}) and one of the semivolatile sesquiterpenes (C_{15}). (From Kesselmeier & Staudt, 1999)

Biogenic sources of NMHC

The principal biogenic source of NMHCs that is known today is the foliage (leaves and needles) from deciduous and coniferous forests. Shrubs and plants are presently expected to have less impact on the total amount emitted but should not be forgotten. (Guenther, 2001) There are great uncertainties about the biogenic sources and their significance since many plant communities in different ecological and climatic regimes are yet to be studied. Fluxes of isoprene have been identified to be as large from Sphagnum species on boreal wetlands as they have from a boreal spruce forest. These are recent results presented by Janson et al. (1999) and Janson & De Serves (1998), confirming the importance of further research in northern latitudes. In addition to leaves and needles as a source of NMHC, some quantity comes from stems, corticals and roots and a minor amount even comes from microorganisms and animals. NMHCs are also emitted by anthropogenic activities such as combustion and industrial processes. However, only a small part of the global total originates from human sources and evidently, these emissions are greatest in urban and industrial areas. (Guenther, 2001)

The biological role of NMHC

The biological role of NMHC synthesis and emission to plants is either i) a significant benefit to the organism (attracting pollinators, repel pests, signals of physiological changes, remove toxic compounds etc), ii) the loss of an unneeded metabolic product (that might be toxic), iii) unintentional losses (this may occur when an organism exchanges other gases like water vapour, oxygen, carbon dioxide and could possibly increase as a result of physical stress or damage to the plant). (*Guenther, 2001*)

The atmospheric importance of NMHC

NMHC are not important greenhouse gases themselves, but they are important precursors of greenhouse gases and particle production in the atmosphere. The atmospheric importance of NMHCs and other BVOCs can briefly be divided into three parts, as they influence i) the oxidative capacity of the atmosphere, ii) the formation of aerosols as well as their significant weight in iii) the carbon cycle. (*Kesselmeier et al., 2002; Peñuelas & Llusà, 2001*)

In more detail, what actually happens is that photo-oxidation of hydrocarbons in the atmosphere, in the presence of nitrogen oxides (NO_x) and hydroxyl radicals (OH), will produce tropospheric O₃, which at the moment is the third most important greenhouse gas after CO₂ and CH₄ (*IPCC, 2001*). Further on, as the reactive hydrocarbons are incorporated in the photo-chemical reactions, they are removed from the atmosphere through a transformation into CO, which ultimately will result in the production of CO₂. Further they are expected to increase the CH₄ oxidation rate. (*IPCC, 2001; Kesselmeier & Staudt, 1999; Kesselmeier et al., 2002; Simeonidis et al. 1999; Steiner et al., 2002*) BVOC also influence climate via their production of organic aerosols, which affect the radiative balance on the Earth (*Guenther, 2003; IPCC, 2001*). By covering inorganic particles with an organic layer, NMHCs have the possibility to make the particles more prone to absorb and scatter radiation as well as increasing their efficiency as cloud condensation nuclei (*Kulmala et al., 2001*). As mentioned earlier, there is great uncertainty concerning the role aerosols as a radiative forcer and so all processes affect aerosol formation must be more extensively studied, including the emission of BVOCs.

Isoprene is mainly an important component in tropospheric chemistry by producing tropospheric O₃, while monoterpenes play an important role concerning aerosol formation. (IPCC, 2001) See Figure 6 for a description of potential outcomes of emitted NMHC species.

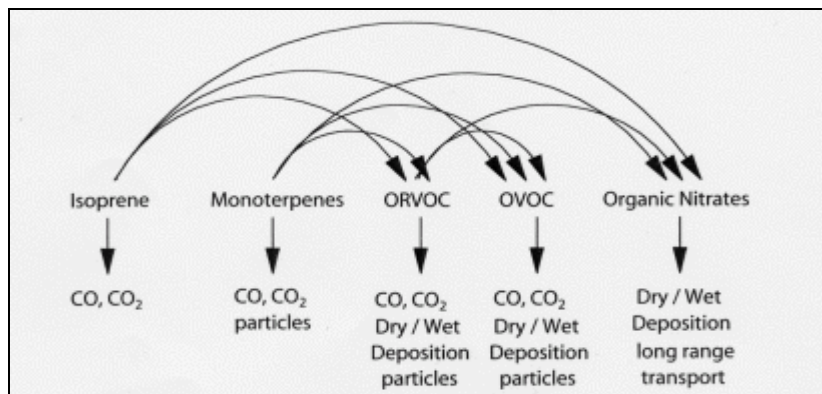


Figure 6, Potential outcomes of emitted NMHC species.

The figure shows how emitted NMHC species are processed in the atmosphere and potentially can end up in CO₂ again. Other species may end up in chemical reactions and come to belong to groups of other reactive and less reactive VOCs (ORVOC, OVOC) but they may also contribute to organic nitrates and aerosol production. This carbon might return to the carbon reservoir by dry or wet deposition but it may also oxidize to longer living species like CO, which together with less reactive VOC can be responsible for a carbon loss from the terrestrial biosphere. (From Kesselmeier, 2002)

Factors controlling NMHC emission

Besides the genetically predetermined biodiversity in vegetation emissions, the release of NMHC by a given plant species exhibits important temporal and spatial variations due to complex interactions between the organism and its environment, that are only partly understood (Kesselmeier & Staudt, 1999). The biosphere-atmosphere exchange of NMHC is very sensitive to the climate itself. In the time intervals of hours to days, temperature and light conditions have a great impact on the emission rates. The same relationship also occurs for seasonal long-term intervals. This explains why most of the presently known global total BVOC is thought to be emitted from tropical regions. At these latitudes, there are high temperatures and light regimes through out the year and the total biomass of trees and plants in the region is great. Northern latitudes however, have a clear seasonal cycle inhibiting the landscape to emit such large quantities. A pronounced difference in the temperature and light regime are present and result in significant higher emission rates during summer, compared to winter times. (Guenther, 2003)

In addition, the biogeochemistry of photosynthesis has to be considered. Kesselmeier et al. (2002) accounts for NMHCs in relation to plant carbon fixation and the terrestrial carbon budget. The conclusion of the study is that BVOC emissions are significant in relation to NPP. However, the already well-examined relationship of light, temperature and photosynthesis should be considered when interpreting these results, as should other factors controlling photosynthesis (i.e., soil water content, type of plants, soil nutrients etc).

Figure 7 accounts for factors controlling production and emissions of BVOCs. It is a complex net of interactions between different parts, which explain both temporal and spatial variations of the emissions. This demonstrates the importance of understanding how different plants in different ecosystems work, and how this might be modified by changes in climate and environment. However, when making conclusions about factors affecting NMHC emissions from what is known today, it is important to remember the huge amount of plant species and vegetations types in different ecological and climatic conditions that have not yet been examined.

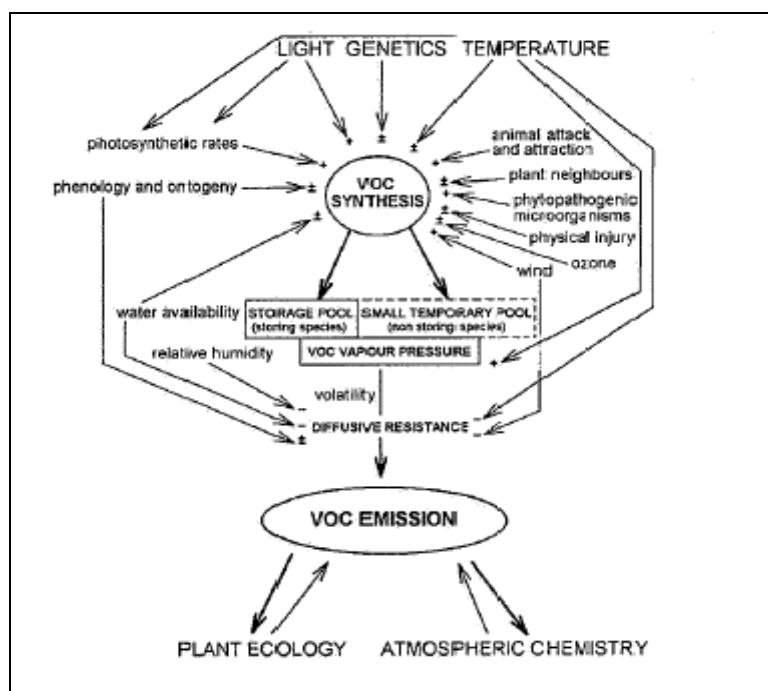


Figure 7, Factors controlling synthesis and emissions of BVOCs.

The schematic shows the most important steps in production and emission of VOCs, as well as the major and best known factors controlling the emissions. These are depicted in bold type, while other factors that are less known, have less effect and that might be of more temporary and local relevance, are not implemented in current standard algorithms to estimate emissions (+ enhancing effect, - decreasing effect). (From Peñuelas & Llusà, 2001)

Earth system interactions and global change

As expressed above, the emissions of NMHCs, are definitely to a certain degree, a component in the interactions between biosphere and atmosphere, but the question is how significant they might come to be in a global climate change scenario. To what extent are they a part of the global carbon cycle today, and where might this lead in the future? At present, estimations of the amount of photosynthetically fixed carbon that are emitted as BVOC to the atmosphere range around 2-4% of NPP, but there are cases where it is as high as 45-50 %. (*Kesselmeier et al., 2002*) The significance of NMHCs in the carbon cycle is a topic of debate among scientists. However, researchers in the subject point out the importance of these emissions and that they must be accounted for if we want to be able to predict future changes in the carbon balance of the Earth system (*Guenther, 2003*). Further, *Kesselmeier (2002)* also states that NMHCs must be studied simultaneously with CO₂ to be able to understand and quantify the role they play to the net carbon budget of an ecosystem and a biome as whole.

Considering the northern latitudes as the area of study for this research, the importance lies in the huge carbon pool of forest biomass and wetlands as well as the so far not examined plant communities and ecosystems. As discussed earlier, there is an uncertainty about what might happen with CO₂ and CH₄ fluxes in ecosystems of these regions facing a climate change scenario, currently acting as a sink of CO₂. The total amount of NMHC emitted and related tropospheric physicochemical processes are even more uncertain, although biogenic aerosol formation has been detected above boreal ecosystems and VOC emissions from Nordic wetlands and moss-vegetation are found to be in amounts of matter (*Janson & De Serves 1998; Janson et al. 1999; and Klinger et al. 1994*). Ultimately, fully coupled Earth System Models would be developed including NMHCs and other BVOCs so that the global carbon balance and vegetation dynamics could be modelled under different temperature and CO₂ scenarios.

Methods

Basically, the method of this research is built up of three parts: fieldwork, data processing and literature studies. Fieldwork was conducted throughout the summer growing season, from the 12th of June to the 30th of August 2003. After that, approximately 6 weeks have been spent on data processing. Very briefly, the methodology is based on keeping an automatic chamber system running, and from this system, collecting data of CO₂ and total hydrocarbon (THC, the total amount of hydrocarbon compounds including methane) from six different chambers. Further, manual air samples were collected and analysed in order to measure CH₄. By comparing THC to CH₄ fluxes, the amount of NMHC may be estimated. NMHC is correlated with environmental variables including temperature and photosynthetically active radiation (PAR). Also, correlations with estimated GPP are conducted. CO₂ and CH₄ dynamics are examined in terms of seasonal patterns, how they depend on each other and factors like temperatures, water table and active layer depth etc.

Detailed site description

The research was undertaken in the north of Sweden, 10 km east of Abisko on the subarctic mire Stordalen (68° 22'N, 19° 03'E) (*Figure 8*). The area around Abisko is characterized by environmental transitions like altitudinal gradients from 350 meters above sea level (masl), on which altitude Stordalen lies, up to 1200 masl in only a short distance. Further, there is a climatic gradient from the west coast of Norway towards continental Sweden, placing Abisko in a rainshadow on the eastern side of the Scandinavian mountain range. The Stordalen mire itself has an area of about 49 ha and is located close to a series of small lakes distributed between Lake Torneträsk and the road running from Kiruna, Sweden in the east to Narvik, Norway in the west. The climate at Stordalen is subarctic with a long-term mean annual temperature of -0.7°C and 299 mm accumulated precipitation.



Figure 8, Map of Sweden and the position of Stordalen.

This map show the position of Stordalen in the subarctic Sweden (legends should be considered being approximate. (From MSN Map& directions, 2003-11-30)

The soil of Stordalen mire is mainly histosol, which is an organic soil made up of plant parts and include peat. Beneath the ground surface there is underlying discontinuous permafrost. This discontinuous permafrost has an obvious influence on the geomorphology and microtopography on the mire, which in turn directly affects ecological characteristics, wetness and nutrient status. Several types of sub-ecosystems have developed on the mire as a result of the interaction between physical parameters and various plant communities. With the purpose of trying to describe and understand trace gas fluxes on a subarctic mire, it is essential to go in detail into the various sub-ecosystem types, since considerable differences in their flux patterns of CO_2 and CH_4 are expected. Further, the lack of NMHC studies on subarctic mire ecosystems today, confirm the demand for a study, which is as detailed as possible. And the fact that NMHC emissions are very much plant specie specific, points out the importance of trying to get hold of the small scale variations, to be able to make any conclusions about these fluxes for specific sub-ecosystems and plant communities.

The Stordalen mire is a mixed mire where ombrotrophic dry hummocks are in complex with minerotrophic wet lower areas. Three types of sub-ecosystems have been examined in this study using 6 chamber plots numbered Ch.2, 4, 6, 7, 8 and 9. The chamber technique is described under the heading Fieldwork. The three representative sub-ecosystems are categorized by moisture and nutrient properties: semi-wet ombrotrophic (Ch.2, 4 and 6), wet intermediate ombro-minerotrophic (Ch. 9) and wet minerotrophic (Ch.7 and 8).

The semiwet ombrotrophic site

The semiwet ombrotrophic site is situated in a lower hollow where the active layer reaches about 60 cm in late August. The site gets a certain degree of drainage water from the surrounding area, but since there is permafrost in the ground hindering the input of nutrients from underneath, it will still be classified as ombrotrophic. The water table through out the summer season oscillates around 15-20 cm depth and the plant community of this sub-ecosystem is characterized to a high degree by mosses, e.g. *Sphagnum fuscum* (rusty peat moss) and *Spagnum balticum* (baltic bog-moss). Further, a lower degree of vascular plants and lichens are present, mainly *Carex rotundata* (round sedge) and some occurrence of *Andromeda polifolia* (rosemarin) and *Eriophorum vaginatum* (haretail cottongrass).

The wet intermediate ombro-minerotrophic site

The position of the wet intermediate ombro-minerotrophic site is somewhere in between a lower hollow and a depression. Additionally, it is something like a south-north going drainage line coming through as well as it is close to a former hummock site, which most likely has sunk in the process of disappearing permafrost. If there is permafrost on this site, it lies more than 1 m beneath the ground surface from mid-July while the water table is on a depth varying between 10-20 cm. On this site, the vegetation consists of one tussock of *Eriophorum vaginatum* (haretail cottongrass).

The wet minerotrophic site

Chamber 7 and 8 constitute the wet minerotrophic sub-ecosystem, which is situated in a depression where there is no permafrost. The water table oscillates from being above the surface of the ground to a depth of 5 cm. Water and nutrients are drained from the surroundings as well as from the groundwater, hence making the site wet and minerotrophic. The plant characteristics for these kinds of depressions are a high degree of vascular plants, and in this case it is mostly *Eriophorum angustifolium* (common cottongrass). Also there are some moss species present that can tolerate the wet environment: *Sphagnum balticum* (baltic bog-moss) and *Sphagnum lindbergii* (brown-stemmed bog-moss).

Fieldwork

Auto chamber system

Trace gas exchanges have been a subject of interest on Stordalen mire since the 1970's. It started off with measurements by Bo Svensson using a metal can to measure CO₂ and CH₄ (Svensson, 1980), further developing the research methodology to be using static chamber techniques before establishing the recent automatic chamber system, today measuring CO₂ and THC. The automatic multichamber system, which is the foundation of the whole methodology of this project, was first set up on Stordalen in October 2001, with actual measurements starting in March 2002. The designer of the chamber system is mainly Patrick Crill (professor at the University of New Hampshire, USA and Stockholm University, Sweden), while the project is running in cooperation with the Department of physical geography and ecosystem analysis, Lund University, Sweden and primarily financed through the EU funded CARBOMONT project.

Design

The chambers are constructed out of transparent lexan with aluminium frames (*see Figure 9 for photo of chamber*). The bases are 38 cm * 38 cm and depending on the vegetation, chamber heights vary between 25-45 cm. Supporting the lexan bases, a pneumatically actuated lexan lid is joined, driven by a compressor. Each chamber was cut in to the ground approximately 5-10 cm deep in October 2001, half a year before

operational sampling started in 2002. The chambers are attached by high density polyethylene tubing to the associated control system, placed inside a shack not further away than approximately 20 m, in order minimize tubing length. The power essential to run the system is received from a residential house through the official power lines, from a distance of a couple of hundred meters.

Figure 9 is a visual explanation of the chamber design and associate control system, and works as a complement to this text to briefly describe the technique behind the system. The multichamber system gives spatial and high temporal frequency data with sampling every 3 hours over the diurnal cycle. Every 18 minutes, an individual chamber is selected and a diaphragm pump pulls out air from the chamber. During the first 8 minutes, no sampling occurs but the tubing is flushed to clear out the sample line of previous air artefacts. On the 9th minute, the lid closes for 5 minutes and air from the specific chamber is sampled and analysed concerning the concentration of CO₂ and THC. After 5 min of closure time, the chamber opens and this chamber will be “selected” for another 5 minutes. After that, a new chamber is selected and sample line flushed etc. The slope of the concentrations changes over time is later on used to calculate the actual fluxes and this is described under the heading Data processing. The trace gas concentrations were measured every 3 s and averaged every 15 s. The pressure recorded within the IRGA (Infrared Gas Analyser measuring CO₂) during a sample is a good indicator of possible tubing blockage or leaking, making it easier to look after the system. To avoid pressure changes during air sampling, there is a corresponding tube adding air to the chamber during closure time.

A brief explanation of how the IRGA and THC analyser operate is as follows. The IRGA, which may be called a CO₂/H₂O analyser, is based on the differences in absorption of IR passing through gas sampling cells. In a reference cell, there is a known concentration of either CO₂ or H₂O and an air sample from a selected chamber will be present in a sample cell. IR is transmitted to both cells, and the difference in absorption is proportional to the output voltage that is used to compute the CO₂ mole fraction in the air sample.

The THC analyser is used to measure the total concentration of hydrocarbons within the gaseous sample, which in this case is made by a flame ionisation detector (FID). There is a burner in the analyser with a flame sustained by flows of air and

pure hydrogen. When the gaseous sample comes into the burner, an electrostatic field cause the ions to migrate to respective electrodes and a precision electrometer amplifier measures the current between the electrodes. The current is directly proportional to the hydrocarbon concentration of the sample.

Environmental variables used in this research, measured in conjunction with the actual fluxes, are ground temperature, air temperature and PAR. Temperature was measured by two thermocouples in each chamber, one positioned close to the ground surface while the second one was placed to measure ambient air. A PAR sensor was located on the roof of the shack that contains the control system.

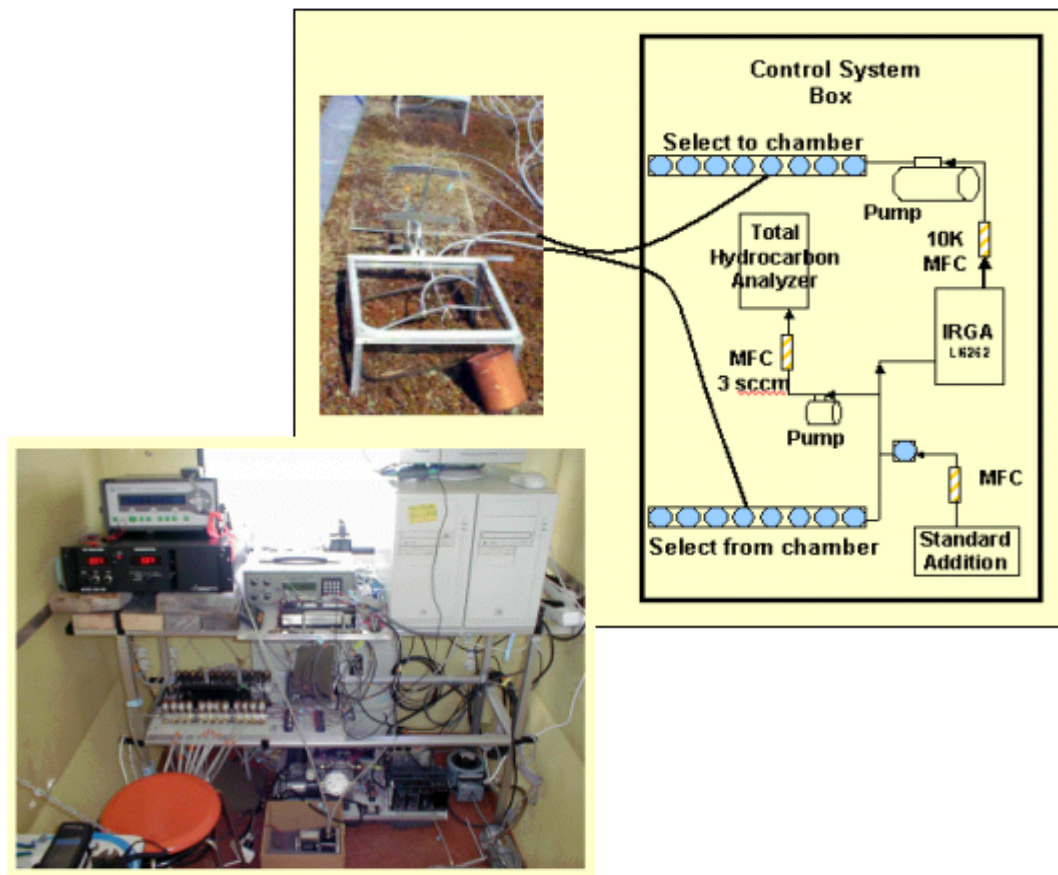


Figure 9. Photo of chamber and control system.

The figure is a visual explanation of the chamber design and associate control system. Chambers are selected, lids closes and air samples are taken from the chambers through the white tubing and then analysed by the THC analyser and IRGA (CO₂) separately. Gas concentrations together with for example temperature data are measured and data saved in the associate computer control system to be downloaded and used in data processing.

An automatic chamber system like this requires frequent maintenance to make sure that it is reliable. It is an automatic system, which may give comprehensive loads of data when running, but it is very much relying on complicated techniques and it has to be looked after. This is why continuous maintenance is important, including among other things: power checks, calibration of gas analysers, tests of leakage and blockage on the tubing, system pressure checks, verification of lightened flame in the FID in the THC analyser and drainage of compressor.

Grab sampling and GC analysis

To be able to estimate the rate of NMHC fluxes in the different sub-ecosystems, manual grab samples of air were collected during selected chamber closure and later analysed in a gas chromatograph (GC), with the purpose to decide CH₄ fluxes and compare them to the corresponding THC fluxes recorded by the control system.

The time resolution of sampling over the season has been continuously 3 days a week, from the 16th of June to the 29th of August, with a few exceptions. In total, 27 days of grab sampling were completed. The time of sampling was most frequently the 12 o'clock cycle but at some days grab samples were taken before 12 and after 15.

Grab sampling in field

In the control system, there is a sample port that has to be open when grab sampling occurs. From the sample port, it is possible to take out air samples by using plastic syringes. Syringes with a volume of 10 ml were used for this research. When a chamber has been selected by the control system and air flushes the tubing, it is possible to take grab samples from that chamber. In this case, a total of 6 syringes were used for each of the selected chambers. The first sample was taken 1 minute before chamber closure. After that, the next 5 were taken while the chamber was closed starting 30 seconds from closing and with 1 minute between each sample after that. Syringes were numbered and time recorded when each syringe was taken so that the true concentration change in the chamber during closure time could be presented.

GC analysis

Within a time span of 6 hours, the air samples in the syringes were analysed at the laboratory, in a GC equipped with a FID. CH₄ from a tube with known mole concentration was used as a reference gas. Further on, the FID works in the same way as with the analysis of THC: molecules of different gases are separated, a detector determines the amount of molecules of a certain gas (in this case CH₄), which is printed as a curve with an area that is direct proportional to the gas concentration of that sample.

Other fieldwork

Respiration measurements during the day

As the CO₂ fluxes recorded by the automatic chamber system are NEE, we need a number of respiration measurements to determine the actual GPP. During one day in July, more precisely the 12th of July, respiration measurements were conducted, however more respiration measurements are required to obtain reliable data and to be able to describe a variation. By covering the chambers with black material and keeping all light out, any photosynthesis was inhibited and so only respiration was measured during the 5 minutes. This flux data was stored in raw data files by the chamber control system in the same way as all concentration data is recorded.

Measurements of water level and thaw depth

Data of water table and thaw depth in close vicinity of the chambers at the different sub-ecosystems were recorded through out the field season. Water table was measured by digging a hole with a depth of about 30 cm and an area of about 15 cm * 15 cm, at each locality. The distance from the surface of the ground to the water level is the depth of the water table below ground surface. The thaw depth, or the active layer was measured by pushing a steel rod with a diameter of about 1 cm, as far down in the ground as possible. This was also conducted close to the chambers at the sub-ecosystems and both water table and active layer measurements were conducted at the time of grab sampling, i.e. 3 days a week.

Photo documentation

Photos of the chambers and the development of the plant communities in the different eco-systems were taken a few times through out the summer season and they are used to support the numeric data analyses.

Data processing

In addition to the actual fieldwork, a lot of the research project consists of data processing. First the flux calculations from the automatic chamber system, secondly determination of the CH₄ fluxes from the manual samples and finally the NMHC fluxes. Further on, respiration models for all the different chambers have been developed based on CO₂ flux and ground temperature at night, which also give the possibility to model the GPP. The actual respiration fluxes measured on the 12th of July are also calculated and compared to the respiration model.

Flux calculations

The data received from the automatic chamber control system are raw data files containing gas concentrations at specific times for a specific chamber. These are added into a flux calculation program that calculates the final fluxes of CO₂ and THC during the time a particular chamber was closed. The fluxes are estimated by using the ideal gas law $PV=nRT$ where P= pressure, V=volume, n= number of moles, T=temperature, and R=8.31 J/(mol·K) the ideal gas constant. In the case of CO₂ fluxes and THC fluxes, it looks like this:

$$\text{CO}_2 = \text{rate } \mu\text{l}/\text{lmin} * P/R * 1/T * V_c/A_c * 1000 \text{ l}/\text{m}^3 * 1 \text{ min}/60 \text{ sec} = \mu\text{mol}/\text{m}^2/\text{s}$$

and

$$\text{THC} = \text{rate ppm}/\text{min} * (P/R * 16\text{g}/\text{mol}) * 1/T * V_c/A_c * 1000\text{mg}/\text{g} * 1440\text{min}/\text{d} = \text{mg}/\text{m}^2/\text{d}$$

where

rate = the concentration measured over time

P = the pressure assumed to be 1 atm

R = the gas constant 0,08206 $\mu\text{l atm}/\text{deg } \mu\text{mol}$ (used for CO₂ flux) or

R = the gas constant 0,00008206 $\text{m}^3 \text{ atm}/\text{deg}/\text{mol}$ (used for CH₄)

16 g/mol = molar weight of CH₄ (although THC have a different molar weight than CH₄)

V_c = total volume of a specific chamber (m³)

A_c = area that the chamber covers 0,16 m² (for all chambers)

T= 273,15 deg K which is set to average air temperature

Figure 10 is an example of the data that are provided when adding the raw data files to the flux calculation program. The fluxes showed are the total flux during the time of chamber closure. The r^2 of CO₂ and THC is the regression value of the concentration measurements over time, i.e. the ppm values that the flux calculations are based upon. Additionally, averaged ground and air temperatures are given, as well as PAR.

Date	chmbr	CO2press	T_107	FIDpress	ppmCO2/min	CO2_r2	ppmCH4/min	CH4_r2	avgPAR	avgTair	avgTgrnd	CO2 flux	THC flux
10.06.22:58	7	-6999	16,86	91,4	2,250896607	0,994442968	0,121272055	0,991506	294,4818	3,665455	3,507364	0,58756512	43,76177823
10.06.23:14	8	-6999	16,97	91,6	2,196351453	0,991881395	0,09112793	0,966009	292,5364	4,172091	4,115909	0,55372944	31,76004082
10.06.23:32	9	98	16,03	91,2	3,472708014	0,801944977	0,00709087	0,251487	289,5545	-1,968364	6,553909	0,875515921	2,471320383
10.06.23:50	10	97,2	15,97	91,8	0,239995623	0,711751783	-0,013163731	0,436061	281,6455	-6999	-6999	0	0
11.06.00:08	1	97,9	15,9	91,5	1,989130638	0,969776923	0,02509077	0,599302	288,6455	3,991273	4,486818	0,252092779	4,395870112
11.06.00:26	2	98,2	16,2	91,4	1,77455827	0,990952565	0,021854703	0,58851	287,0455	4,276091	5,009636	0,268524573	4,571644469
11.06.00:44	3	98,1	16	91,4	2,774600915	0,943260916	0,017091251	0,620448	284,2455	3,897818	4,364909	0,369175675	3,143693254
11.06.01:02	4	-6999	15,87	91,4	2,872711313	0,998746204	0,079562179	0,967705	285,3091	3,960091	4,256182	0,429890036	16,45909034
11.06.01:20	5	98,3	15,7	91,7	5,581787219	0,999445151	0,018145354	0,558571	285,1	3,746091	3,457364	0,80416472	3,613856845
11.06.01:38	6	98,2	16,11	91,6	3,083737371	0,998594099	0,060473164	0,916086	287,2364	3,458455	3,939545	0,338796771	9,184559589
11.06.01:56	7	98,4	15,95	91,6	2,263652624	0,989082706	0,117961476	0,974763	291,8455	2,864364	3,044182	0,596115673	42,56713517
11.06.02:14	8	98,4	15,42	92,1	1,978170859	0,991737141	0,09534736	0,983756	291,3909	3,455091	3,481545	0,498723208	33,23060276
11.06.02:32	9	97,8	15,35	91,3	2,254504149	0,759880074	0,014763554	0,450443	292,1	-2,476727	5,984727	0,588390509	5,145415792
11.06.02:50	10	97,2	15,23	91,6	0,272725783	0,701367801	-0,016873065	0,344679	294,2182	-6999	-6999	0	0
11.06.03:08	1	97,8	15,74	91	1,458192332	0,988456835	0,017891267	0,561254	300,1727	3,496545	3,811273	0,184804231	3,134526552
11.06.03:26	2	98,2	15,58	91,7	1,701830459	0,982970913	0,040836658	0,965797	310,2182	3,657727	4,472727	0,257519466	8,542357321

Figure 10. Example of data table from flux calculation program.

This table shows data that are provided when adding raw data files from the chamber control system into a flux calculation program.

Concerning the manual CH₄ fluxes, the same equation is used as described above. The mixing ratio ppm/min is determined based on the GC responses for each of the syringes over time. Appendix II contains a compilation of how the CH₄ fluxes are calculated.

A notation should be made that solely CO₂, THC and CH₄ fluxes where the r^2 value of the mixing ratio was equal or greater than 0,95 are used in any correlations and presented results. Further, all data sets have been filtered on suspected error data.

In those cases when the actual carbon part in NMHC (NMHC - C) has been estimated in terms of mg/m²/hr, the NMHC flux rate (THC flux - CH₄ flux), which is based on the molar weight of CH₄, has been multiplied with (68 g*mol⁻¹/16 g*mol⁻¹) in order to get a flux rate which is influenced by the molar weight of isoprene (C₅H₈) rather than CH₄. Further on, to account for the carbon part in this flux, the data are multiplied with (60/68), i.e. the molecule of isoprene is also here the base for the calculation. The isoprene molecule is one of the absolutely smallest non-methane hydrocarbon molecules and in the literature and earlier studies found to be of high significance.

At the semiwet site, where each chamber looks very similar concerning nutrient status, moisture and plant community, data from the three chambers 2, 4 and 6 are often averaged. Standard error is shown in the diagrams as error bars for those times when at least two out of three chambers had valid data present.

Trend lines, equations and correlation values for some analyses in the result section are viewed even though these might not be statistically significant. Instead, they are used and motivated in this case just to show the fact of insignificance.

It should also be noted that solely daytime fluxes are considered and used in the analyses with exception from one night-time correlation of CH₄ and respiration.

Calculations of respiration measurements during the day

No flux calculation program was used to determine the respiration on the 12th of July. It was made manually, using the same CO₂ flux equation as above. The rate ppm/min was determined by looking at the actual recordings of concentrations during the 5 minutes the chamber was closed and covered with black material.

Development of a respiration model

Respiration and GPP for each chamber was estimated by developing a ground temperature dependent respiration model for each chamber, and in the case of the semiwet site an average of Ch.2, 4 and 6 has been used. CO₂ data used are from midnight, in early June and from late July to late August, when PAR is below 50 ($\mu\text{mol/s/m}^2$) and hence the CO₂ concentration change is assumed to be the actual respiration at that temperature recorded. An exponential regression was used to model respiration as a function of temperature (Lloyd & Taylor, 1994).

GPP and respiration

By putting ground temperature data from specific chambers into corresponding respiration model equation, respiration was estimated and there after GPP, from the relationship $\text{NEE} = \text{GPP} - \text{Respiration}$. Respiration and GPP are determined for the same days as grab sampling was conducted, so that these data can be correlated with CH₄ and NMHC data.

Results

The results are presented in three different sections. NMHC fluxes are first described and analysed, followed later by CO₂ and CH₄ fluxes. Finally, an estimation of outgoing carbon in the form of CO₂, CH₄ and NMHC from each sub-ecosystem respectively is described.

NMHC fluxes

The significance of NMHC fluxes compared to THC and CH₄ fluxes are shown. This is followed by the seasonal pattern of NMHC fluxes and their dependency on temperature, PAR and GPP.

The significance of measured NMHC fluxes

A comparison of THC fluxes from auto chambers and corresponding CH₄ fluxes from grab samples is conducted and the result is showed in Figure 11. Saying that the method used to estimate the fluxes is approved, the CH₄/THC picture for the entire 6 chambers shows approximately 88 % CH₄ out of 100% THC, i.e., 12% NMHC with a correlation value $r = 0,99$ (Figure 11).

When looking more into the detail of the CH₄/THC relationship for different chambers, the picture changes (Figure 12 & 13). The semiwet site (Figure 12), with mostly *Sphagnum* mosses and some degree of *Carex rotundata*, has a smaller range of flux values, where the largest THC fluxes reach approximately 1,8 mg/m²/hr. However, the percentage rate of NMHCs out of total 100 % THC may be as high as 35 % with a correlation value $r = 0,74$. The situation concerning the wet minerotrophic and intermediate ombro-minerotrophic site (Figure 13) with a high amount of vascular plants (*Eriophorum angustifolium* and *Eriophorum vaginatum*) gives a strong correlation with r around 0,95-0,98 and NMHC ranges between 7-10 % of THC. The largest fluxes of THC reach 16 mg/m²/hr.

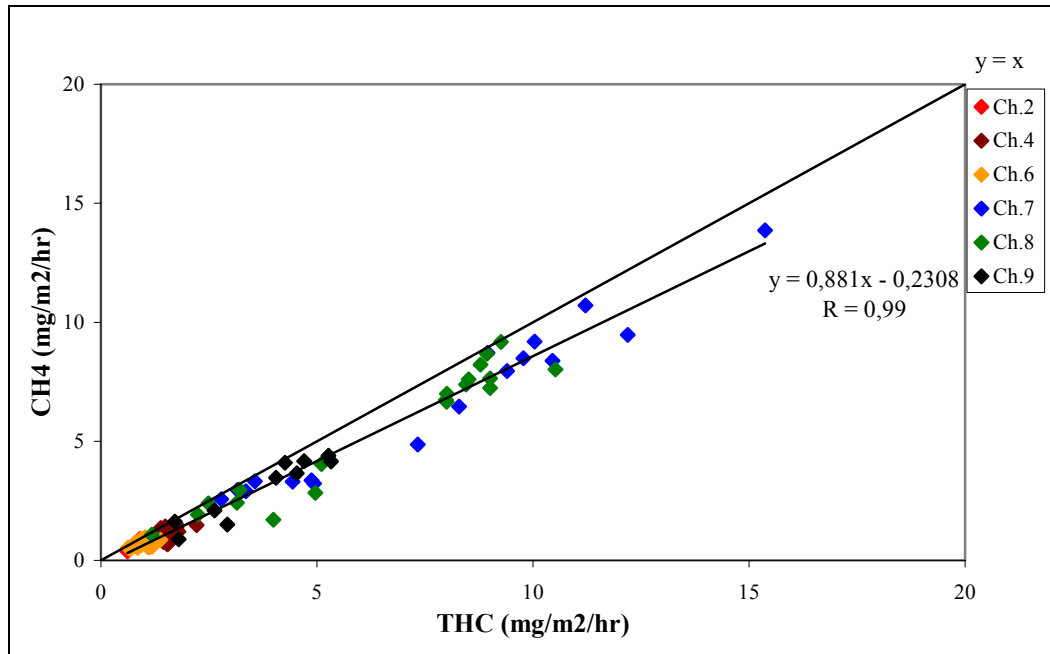


Figure 11, The relationship of CH₄ and THC fluxes for wet and semiwet chambers. The diagram shows the relationship of CH₄ and THC fluxes for wet and semiwet chambers based on data from the whole field season. The estimation concerning NMHC fluxes result in approximately 12 % NMHC out of total 100 % THC.

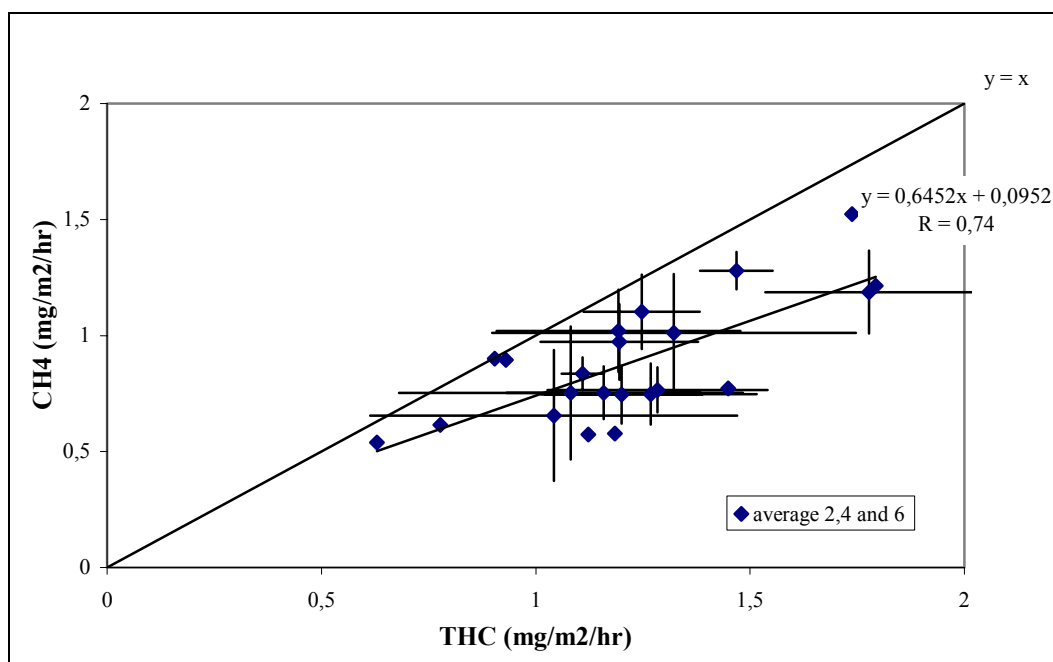


Figure 12, Detailed relationship of CH₄ and THC fluxes for semiwet chambers. The diagram shows the relationship of CH₄ and THC fluxes for semiwet chambers. The amount of NMHC fluxes might be as high as 35 % out of total 100 % THC from this site, mostly vegetated by *Sphagnum* moss species.

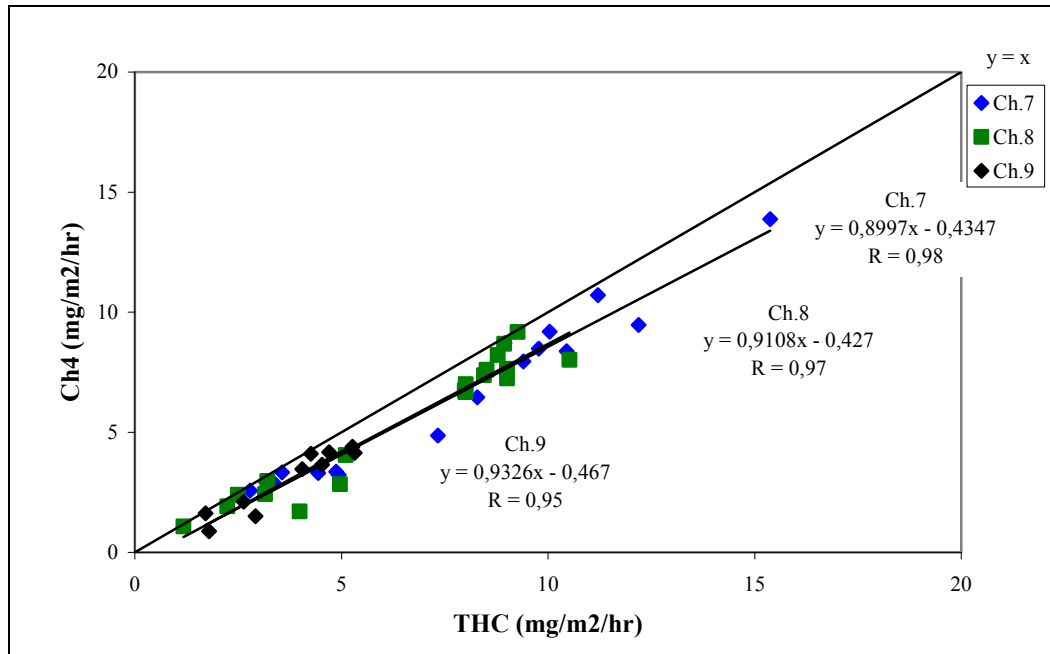


Figure 13, Detailed relationship of CH₄ and THC fluxes for wet chambers.
The diagram shows the relationship of CH₄ and THC fluxes for wet chambers. The estimation concerning NMHC fluxes result in approximately 10 % for Ch.7, 9 % for Ch.8 and 7 % for Ch.9, out of total 100 % THC.

Seasonal NMHC fluxes and their dependency on temperature, PAR and GPP

NMHC fluxes over the season

By subtracting the manually measured CH₄ fluxes from the THC fluxes recorded by the auto chambers, we are able to look at the presumed NMHC fluxes by the time of CH₄ grab sampling (Figure 14 and 15). Looking at the actual rates of NMHC from the different sub-ecosystems, it is an unstructured pattern of high and low fluxes randomly over the season and a distinctive daily variation. At some parts of the record, high and low rates of fluxes follow each other, but mostly there is no clear connection between the chambers. The data is too vague to determine whether there is an increasing or decreasing trend over the season, but it looks like a decreasing trend for the wet intermediate ombro-minerotrophic site, representing a tussock of *Eriophorum vaginatum*. The wet minerotrophic site, with *Eriophorum angustifolium*, has high emissions through out the summer with exception for the daily variations, while the semiwet site with *Sphagnum* mosses and *Carex rotundata* have much lower emissions. The differences in flux patterns between the two types of field sites are the rates, i.e. ranging up to 0,9 mg/m²/hr for the semi-wet and up to 2,8 mg/m²/hr for the wet site.

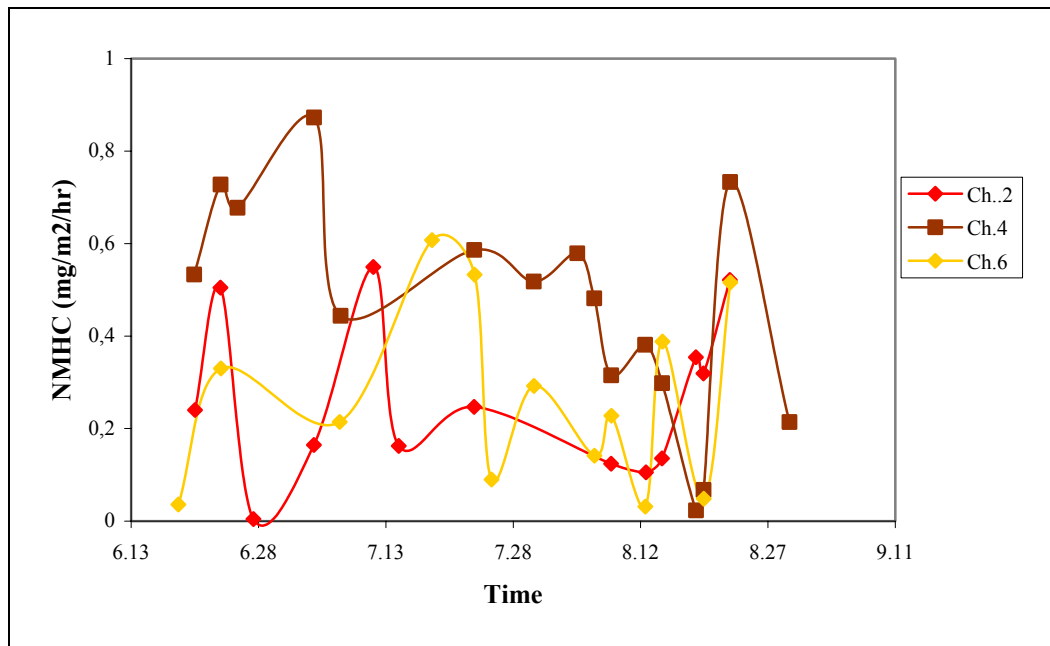


Figure 14, NMHC fluxes over time for semiwet chambers.
Diagram shows NMHC fluxes over time for Ch. 2, 4 and 6 and how they seem to decrease over the season.

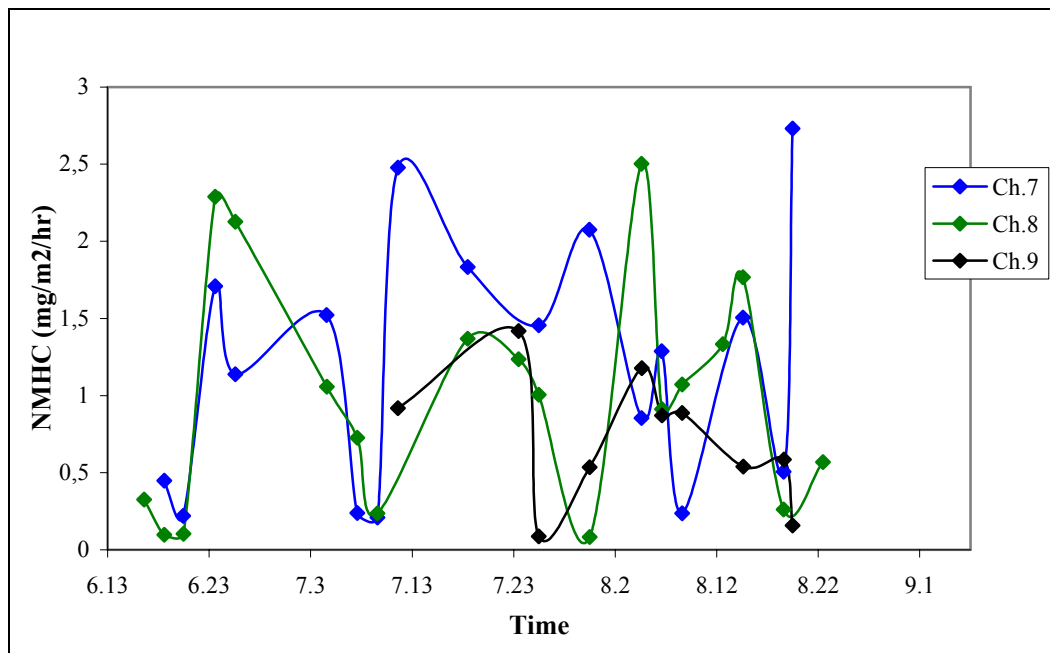


Figure 15, NMHC fluxes over time for wet chambers.
Diagram shows NMHC fluxes over time for Ch. 7, 8 and 9. Ch. 9 seems to have fluxes that decrease over time, which is not the case for Ch. 7 and 8.

Looking at the NMHC expressed as a percentage of the total THC, there is a somewhat decreasing trend for all the chambers further into the growing season (Figure 16 and 17). Evidently, the percentage of CH₄ is therefore increasing throughout the growing season. In this case of NMHC expressed as a percentage of THC, the patterns for the two different ecosystems are more similar.

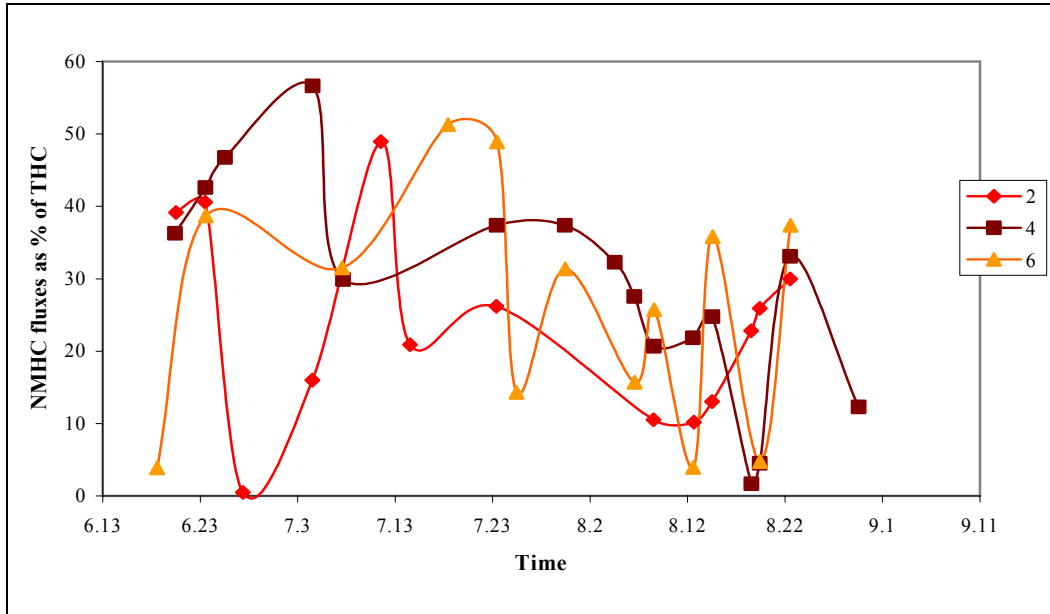


Figure 16, Percentage rate of NMHC in relation to THC for semiwet chambers.
The diagram shows how the percentage rate of NMHC in relation to the total THC is decreasing over the summer season for Ch.2, 4 and 6.

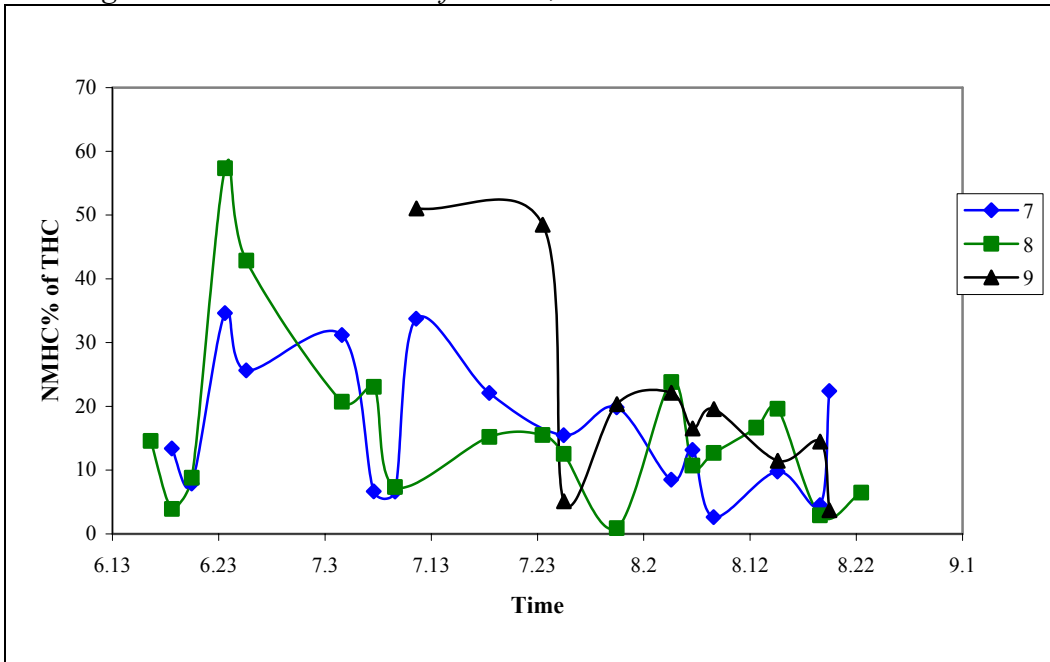


Figure 17, Percentage rate of NMHC in relation to THC for wet chambers.
The diagram shows how the percentage rate of NMHC in relation to the total THC is decreasing over the summer season for Ch.7, 8 and 9.

The effect of temperature and PAR on NMHC fluxes

Correlations of NMHC fluxes versus air temperature and PAR, for all the earlier mentioned chambers are conducted and presented in Figure 18-21. Recorded data from the semiwet sub-ecosystem with high abundance of *Sphagnum* mosses and some *Carex rotundata* result in a clear temperature dependency (Figure 18), which also is the case for the wet minerotrophic site with *Eriophorum angustifolium* (Figure 19). However, the wet and less nutrient rich site with *Eriophorum vaginatum* (Figure 19), shows more uncertain r^2 values, even if the rate of NMHC fluxes seems to increase with temperature as much as on the semiwet site.

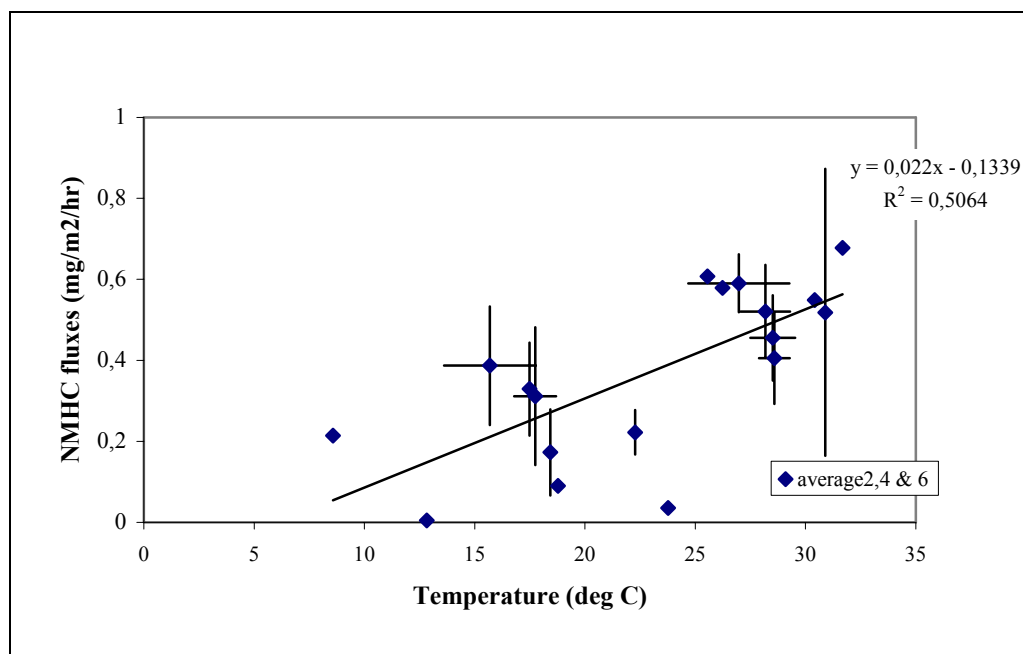


Figure 18, The temperature dependency for NMHC fluxes from semiwet chambers. The relationship between NMHC fluxes and temperature are described in the picture, showing the result as an average for Ch.2, 4 and 6 with standard error bars. The r^2 correlation value is 0,51, which shows a temperature dependency on NMHC fluxes for the semiwet sub-ecosystem.

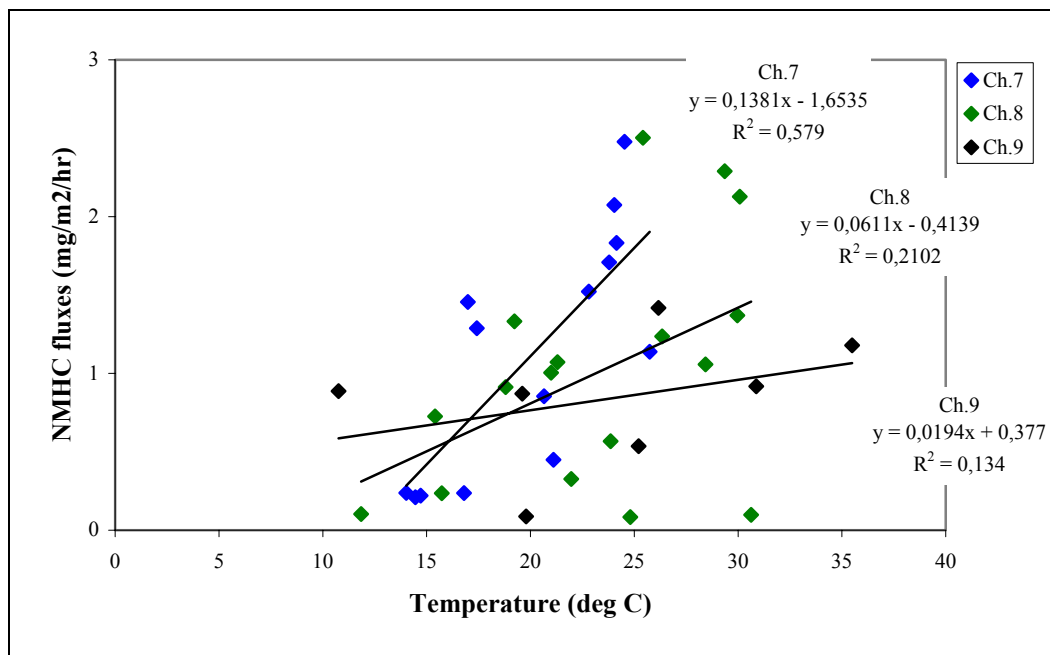


Figure 19, The temperature dependency for NMHC fluxes from wet chambers. The relationship between NMHC fluxes and temperature are described in the picture, showing the result for Ch.7, 8 and 9. The r^2 correlation value is approximately 0,58 and 0,21 for Ch.7 and Ch.8 respectively, while Ch.9 show more uncertainty with an r^2 value of 0,13.

The effect of PAR on NMHC fluxes that is found in this research is described below. The relationship is shown to be similar to the temperature dependency where wet minerotrophic sub-ecosystems seem to be affected the most. The analysis also shows a result where there is a negative relationship for Ch.9. (Figure 20 and 21), however the r^2 value is too low to make any final conclusions about the analysis.

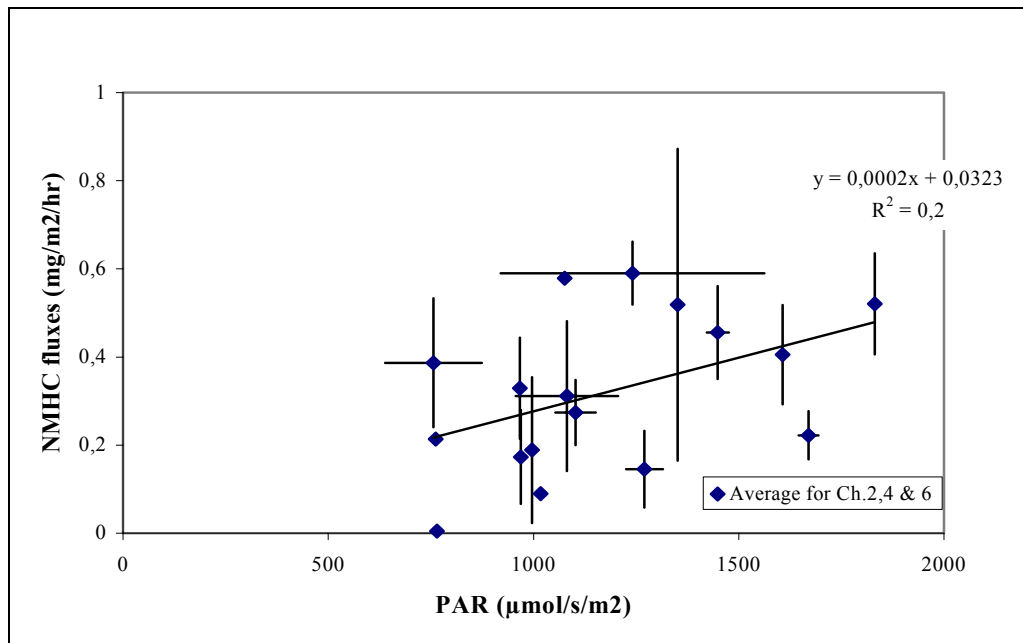


Figure 20, The PAR dependency for NMHC fluxes from semiwet chambers. This figure explains the effect of PAR on NMHC fluxes from the semiwet ombrotrophic sub-ecosystem, as an average for Ch.2, 4 and 6. Error bars show standard error.

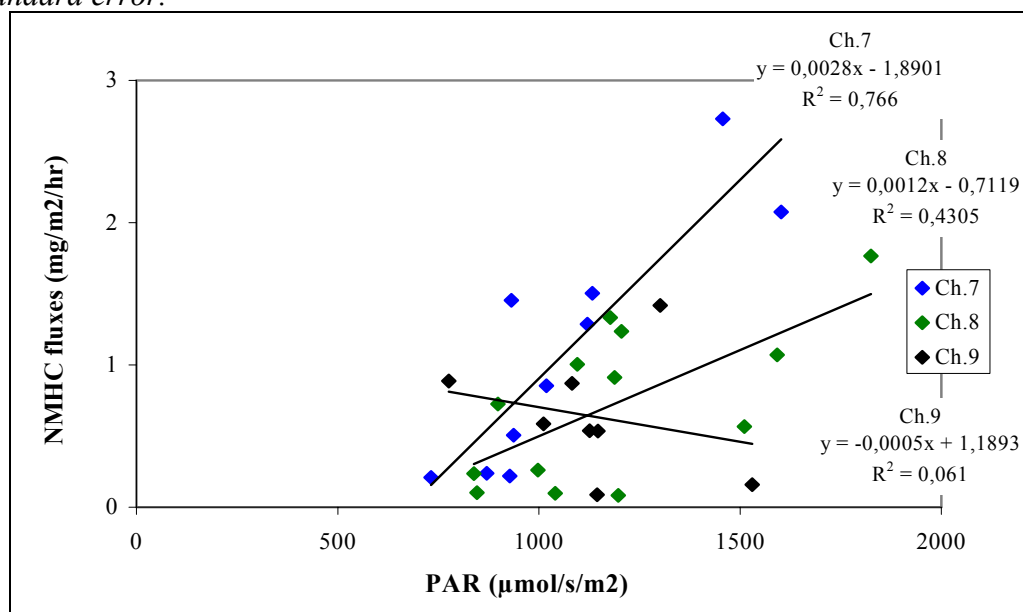


Figure 21, The PAR dependency for NMHC fluxes from wet chambers. This figure explains the effect of PAR on recorded NMHC fluxes on the wet minerotrophic and the wet intermediate ombro-minerotrophic sub-ecosystems.

The effect of GPP on NMHC fluxes

As accounted for in the literature review, GPP might be correlated with NMHC fluxes for some plant species. This relationship is here examined as an average for Ch.2, 4 and 6 as well as for Ch.7, 8 and 9 separately (*Figure 22 and 23*). There is a slightly increasing trend of NMHC fluxes with increasing GPP, however the r^2 values are low. The semiwet sub-ecosystem with mainly *Sphagnum* mosses and a lower degree of *Carex rotundata* seems to have the highest GPP dependency, however the actual values of NMHC fluxes and GPP are much higher at the wet ecosystems. The actual rates of GPP come to just lower than $4 \mu\text{mol}/\text{m}^2/\text{s}$ at the semiwet ombrotrophic site but as high as $15 \mu\text{mol}/\text{m}^2/\text{s}$ on the more wet and nutrient rich sites. GPP is a simulated value and based on a respiration model for each chamber, which is implied in the process of determining the parts of GPP and respiration from NEE (*see Methods and Respiration model under Result*). GPP is given a negative value since it is an uptake of CO_2 from the atmosphere, and an input to the biosphere.

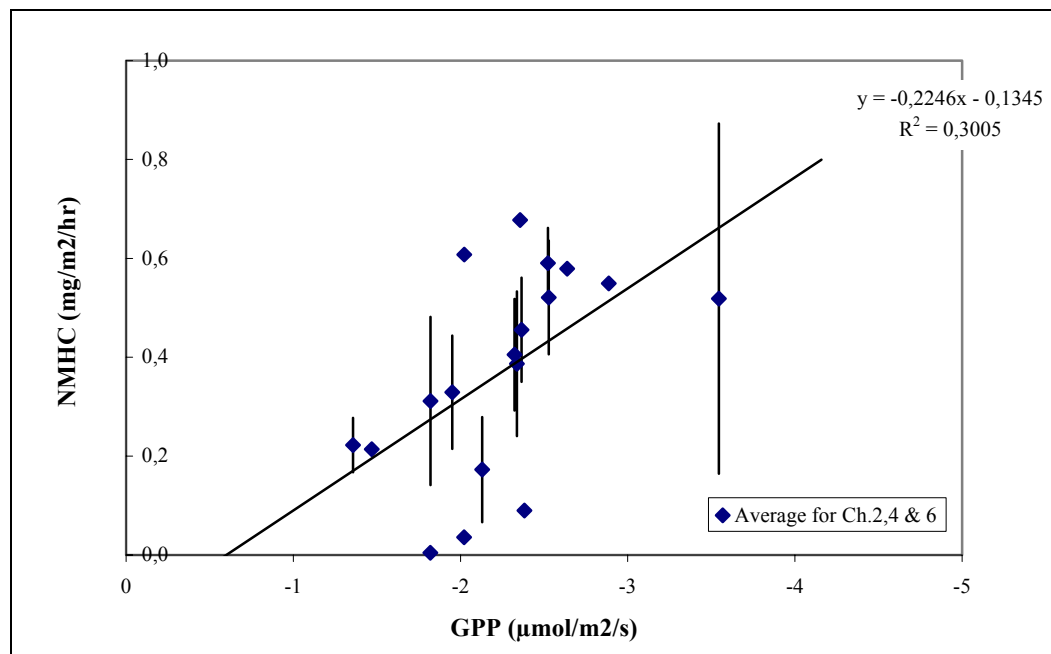


Figure 22, The effect of GPP on NMHC fluxes from semiwet chambers.
This diagram describes a positive relationship between NMHC fluxes and GPP as an average for Ch.2, 4 and 6. Error bars show standard error.

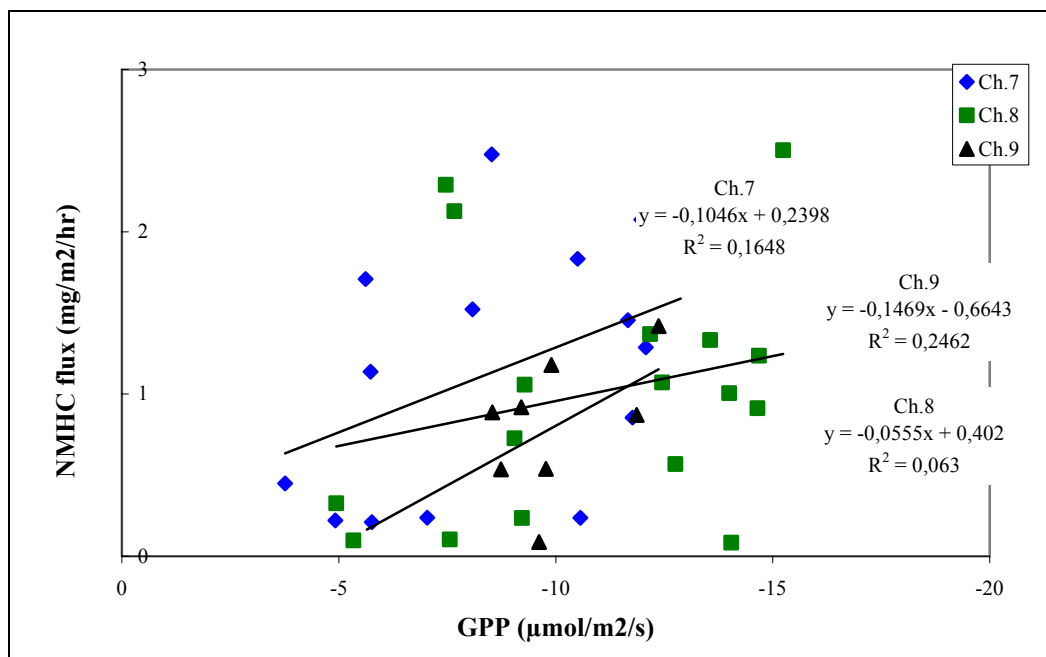


Figure 23, The effect of GPP on NMHC fluxes from wet chambers.
This diagram describes a positive relationship between NMHC fluxes and GPP for Ch.7, 8 and 9, however the r^2 values show uncertainty.

The amount of NMHC-C compared to GPP-C and NEE-C

BVOC emissions and their rates compared to GPP are interesting with regard to the terrestrial carbon budget and the amount of photosynthetically fixed carbon that is lost in form of BVOC emissions. Further, BVOC in relation to the net ecosystem carbon exchange is obviously of an even greater fraction. Here, the average seasonal GPP and NEE from the different sub-ecosystems are presented in terms of $\text{mg/m}^2/\text{hr}$ as well as percentage and compared to the rates of NMHC. As noted in Methods, isoprene (C_5H_8) with a molar weight of 68g/mol is the base for determining the NMHC flux and corresponding carbon part of the total NMHC. Percentages of photosynthetically fixed carbon are lost in the rates of 0,7 - 1,3 % (Table 1). In terms of percentage of NEE, the loss through NMHCs is estimated to be between 1,5 - 2,7 %, where the smallest loss is from the wet intermediate ombro-minerotrophic site with (1,5 %) and the larger losses are from the semiwet ombrotrophic and wet minerotrophic sites respectively (2,7%) as seen in Table 2. It should be noted that this is a comparison between NMHC, GPP and NEE respectively, and any other carbon compounds like for example methane are excluded. Further, GPP and NEE have positive values in the tables below, however they are accounted for as a negative values since they both represent a loss of carbon from the atmosphere, at this certain ecosystem.

Table 1. The amount of carbon in form of NMHC compared to carbon in form of GPP

	Semiwet ombrotrophic	Wet minerotrophic	Wet intermediate ombro-minerotrophic
GPP (mg/m ² /hr)	101,0	401,0	379,0
NMHC (mg/m ² /hr)	1,3	4,1	2,7
Total (mg/m ² /hr)	102,3	405,1	381,7
GPP %	98,7	99,0	99,3
NMHC%	1,3	1,0	0,7
Total %	100,0	100,0	100,0

Table 2. The amount of carbon in form of NMHC compared to carbon in form of NEE

	Semiwet ombrotrophic	Wet minerotrophic	Wet intermediate ombro-minerotrophic
NEE - C (mg/m ² /hr)	47,0	151,0	182,0
NMHC - C (mg/m ² /hr)	1,3	4,1	2,7
Total - C (mg/m ² /hr)	48,3	155,1	184,7
NEE - C %	97,3	97,3	98,5
NMHC - C %	2,7	2,7	1,5
Total - C %	100,0	100,0	100,0

CO₂ fluxes

In this result section concerning CO₂ fluxes, it is described how a respiration model was developed and what it looks like for each chamber system. There after, the simulated respiration data is compared to data from one day of actual respiration measurements in field to give an estimation of how good the respiration model fits with reality. Further, daytime NEE, GPP and respiration for all chamber systems are illustrated in separate diagrams.

Respiration model

Respiration and GPP for each chamber was estimated by the ground temperature dependent relationships shown below in Figure 24 and 25. These equations are used to produce the diagrams that show NEE, GPP and respiration over the season (*Figure 26-28*).

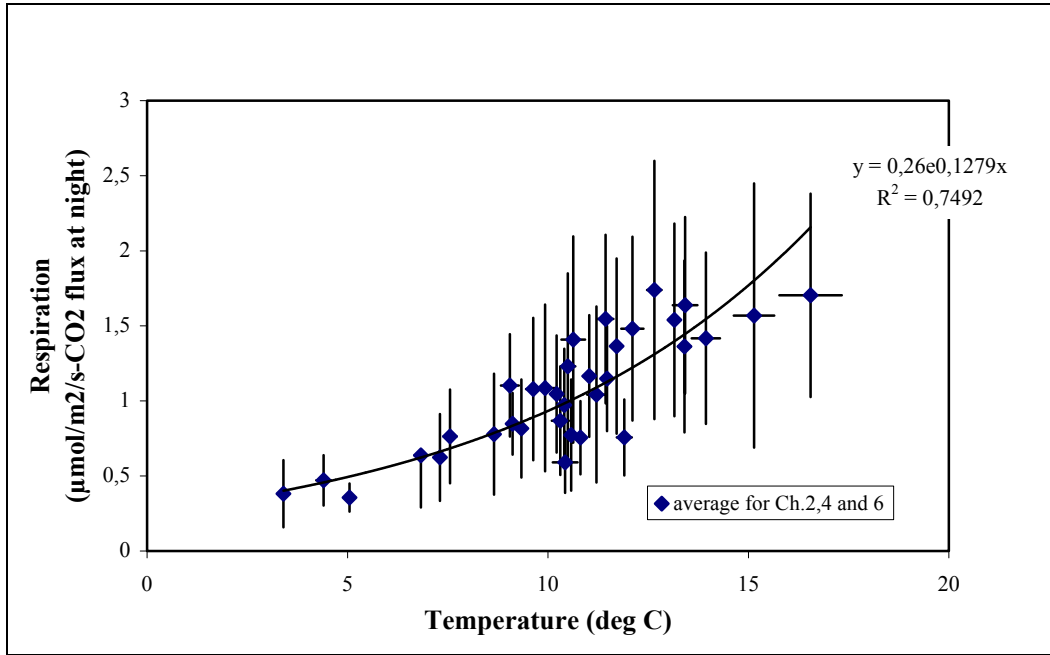


Figure 24, Respiration models for Ch. 2, 4 and 6.

This diagram shows the relationship between respiration and temperature that is present at night and from which a respiration model is developed. This model is developed as an average for Ch. 2, 4 and 6 and error bars show standard error.

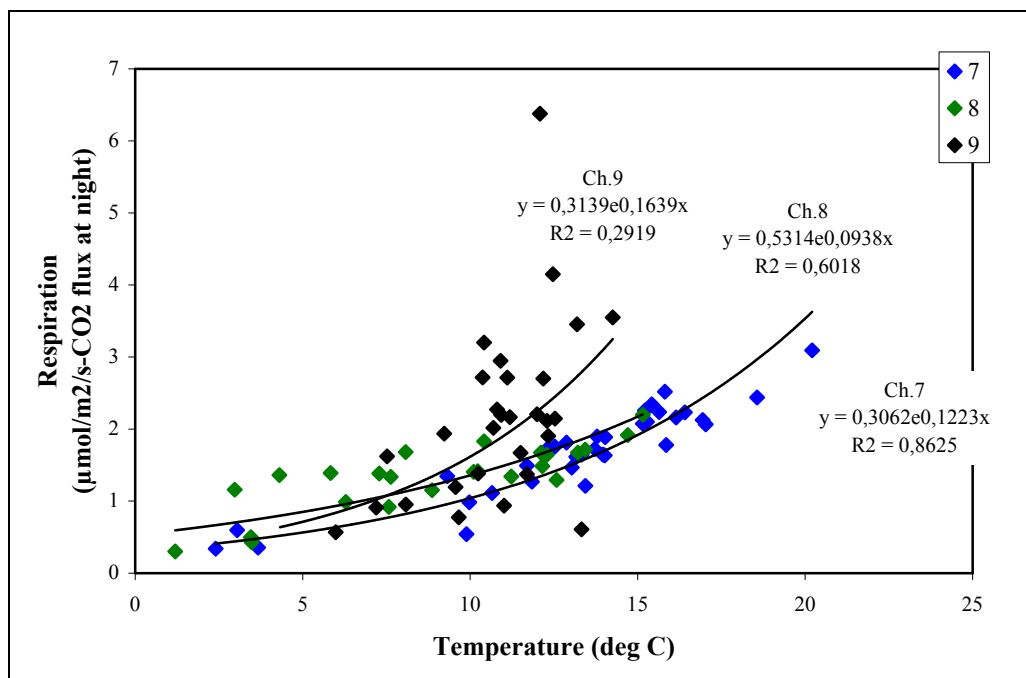


Figure 25, Respiration models for Ch. 7, 8 and 9.

This diagram shows the relationship between respiration and temperature that is present at night and from which a respiration model is developed for Ch. 7, 8 and 9.

One day of respiration measurements was conducted. Comparing these actual respiration measurements with modelled respiration at corresponding times give the result as in Table 3. The table shows the actual respiration on the 12th of July and the modelled respiration. The data from the respiration model overestimate respiration compared to the data from measurements on the 12th of July. However, it should be noted that on the 12th of July, the weather was cloudy and some rain occurred, which of course decreases respiration to a great amount, compared to what might have been found on a hot sunny day.

Table 3, Actual respiration measurements compared to modelled respiration at corresponding times.

Chamber	Actual respiration measurements during the 12th of July		Respiration model
	umol/m2/s		umol/m2/s
2	1,50		4,31
4	1,17		4,31
6	0,95		4,31
7	1,17		5,83
8	1,53		9,84
9	3,64		5,22

NEE, GPP and respiration patterns

The following diagrams (*Figure 26-28*) show daytime CO₂ fluxes. NEE that is recorded at the selected times of grab sampling through out the growing season, and modelled respiration is illustrated as well as used to estimate GPP. All of the sub-ecosystems have a negative NEE which conclude that the net exchange of CO₂ implies a greater uptake of CO₂ by the sub-ecosystems than release to the atmosphere by respiration (*Figure 26*). This net uptake begins to increase from the start of July and possibly, a decrease is present from late August. The semiwet site with *Sphagnum* mosses and *Carex rotundata* have the lowest NEE, compared to the more wet nutrient rich sites.

Concerning respiration, there is a similar seasonal pattern to that of NEE, where respiration processes seem to peak in late July and after that slowly decrease again. The soil and plants at the nutrient rich and wet sub-ecosystem have a higher respiration than the ombrotrophic semiwet site (*Figure 27*).

Sphagnum mosses and *Carex rotundata* at the semiwet site show low GPP compared to *Eriophorum angustifolium* and *Eriophorum vaginatum* (Figure 28). This suggests that the photosynthetic activity is lower on the ombrotrophic site, with a small amount of vascular plants, than on the minerotrophic site with a high amount of vascular plants. GPP seems to increase steadily from the middle of July for both the wet minerotrophic and the wet intermediate ombro-minerotrophic site and CO₂ uptake reaches 10-15 μmol/m²/s. The most intensive growing season for the *Eriophorum angustifolium* in Ch. 7 and 8 and *Eriophorum vaginatum* in Ch.9 seem to have last for about a month before a decrease of GPP is seen from the middle of August. No clear seasonal trends can be detected at the ombrotrophic semiwet site.

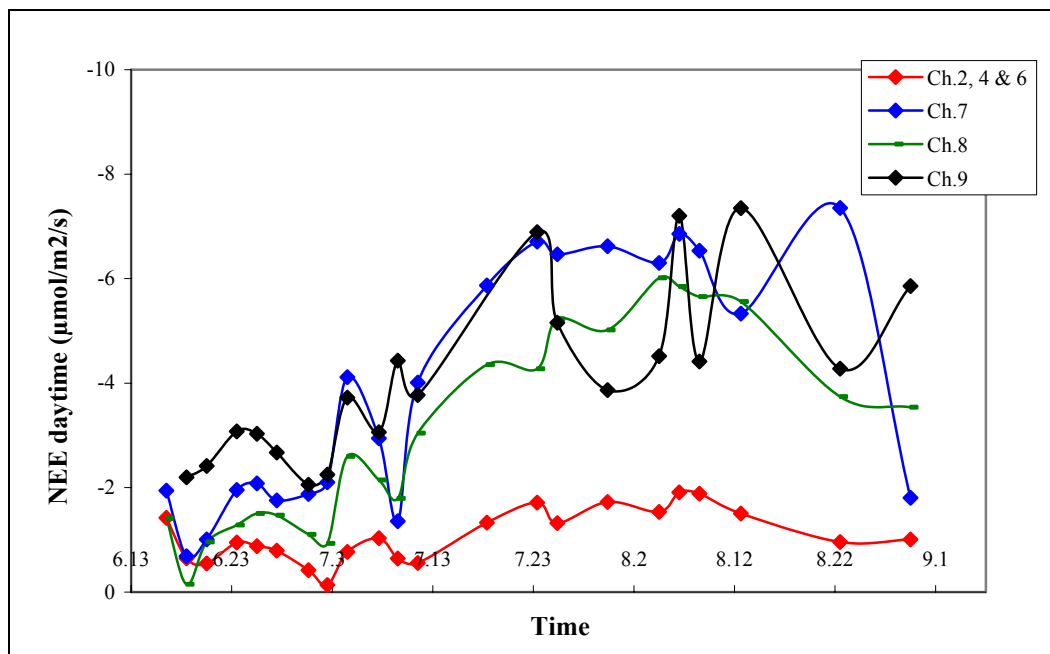


Figure 26, NEE for each of the chamber systems over the season.

The diagram shows that NEE implies an uptake of CO₂ by these sub-ecosystems during the summer growing season, rather than being a source of CO₂ to the atmosphere. This fact is strongest for the more wet and nutrient rich sites compared to the drier and less nutrient rich one.

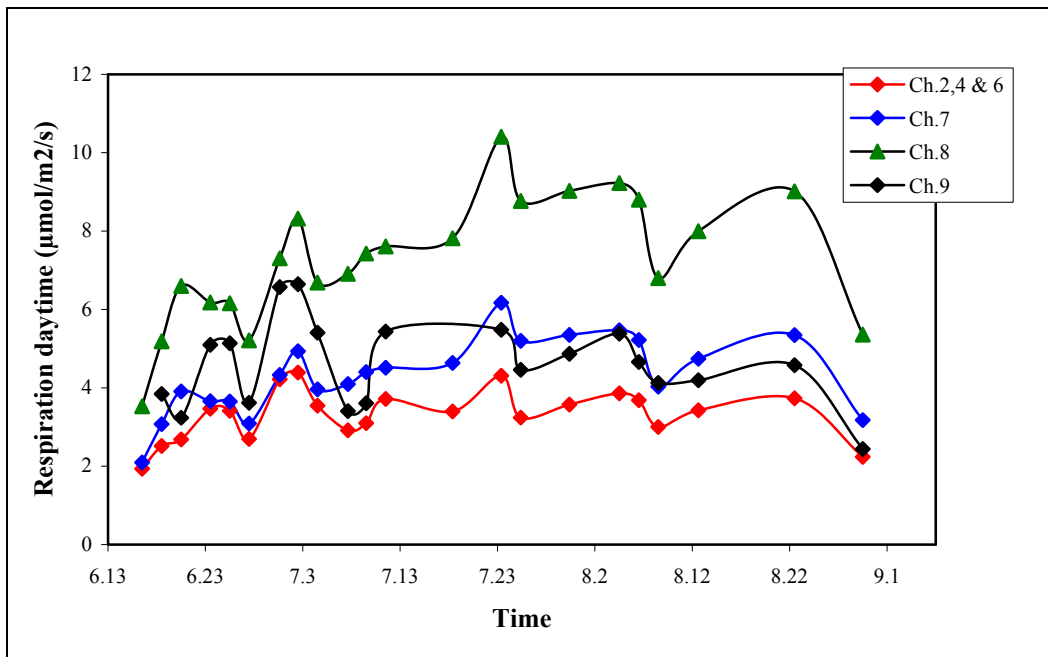


Figure 27, Respiration for each of the chambers over the season.
In the diagram, it is illustrated how modelled respiration shows that respiration processes increase from the beginning in the summer with a peak in late July, thereafter decreasing again. The soil and plants at the nutrient rich and wet sub-ecosystem have a higher respiration than the ombrotrophic semiwet site.

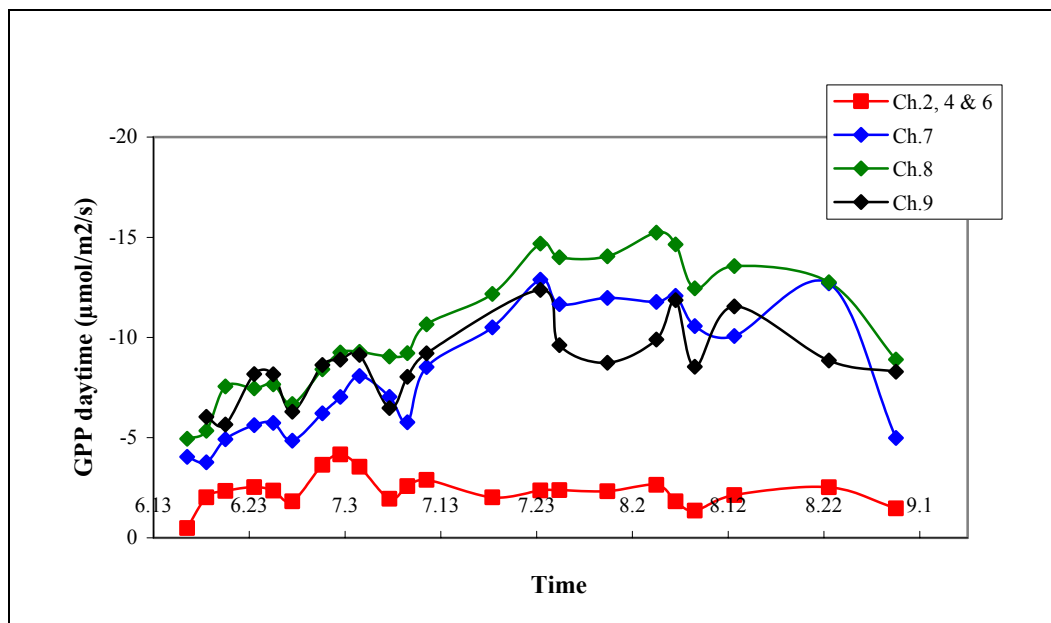


Figure 28, GPP for each of the chambers over the season.
The diagram shows daytime GPP for all of the chambers through out the growing season, where the more wet and nutrient rich sites are the most productive ones, followed by the semiwet ombrotrophic chambers.

CH₄ fluxes

This result section accounts for the seasonal patterns of CH₄ fluxes with a discussion about the seasonal variation of water table and thaw depth. Further on, the relationships between respiration - CH₄ and GPP - CH₄ are examined. Finally, ground processes are studied as the effect of water table on respiration/CH₄ ratio.

CH₄ fluxes over the season

Looking at the CH₄ fluxes over the summer season, there is a steady increase from mid July for the wet chambers Ch.7, 8 and 9 (Figure 29). These sub-ecosystems have thaw depths deeper than 1 m from mid July and water table close to ground surface, i.e. 5-10 cm during most of the summer (Figure 30 and 31). The flux rates reach 10-15 mg/m²/hr from Ch.7 at the wet minerotrophic site and about 5 mg/m²/hr at the wet intermediate ombro-minerotrophic site. Concerning the semiwet chambers Ch.2, 4 and 6, where the thaw depth is not deeper than 50 cm any time during the summer and the water table vary between 15-25 cm, there is evidently low CH₄ fluxes. The flux rates vary around 0,5-1,5 mg/m²/hr through out the summer with now significant increase.

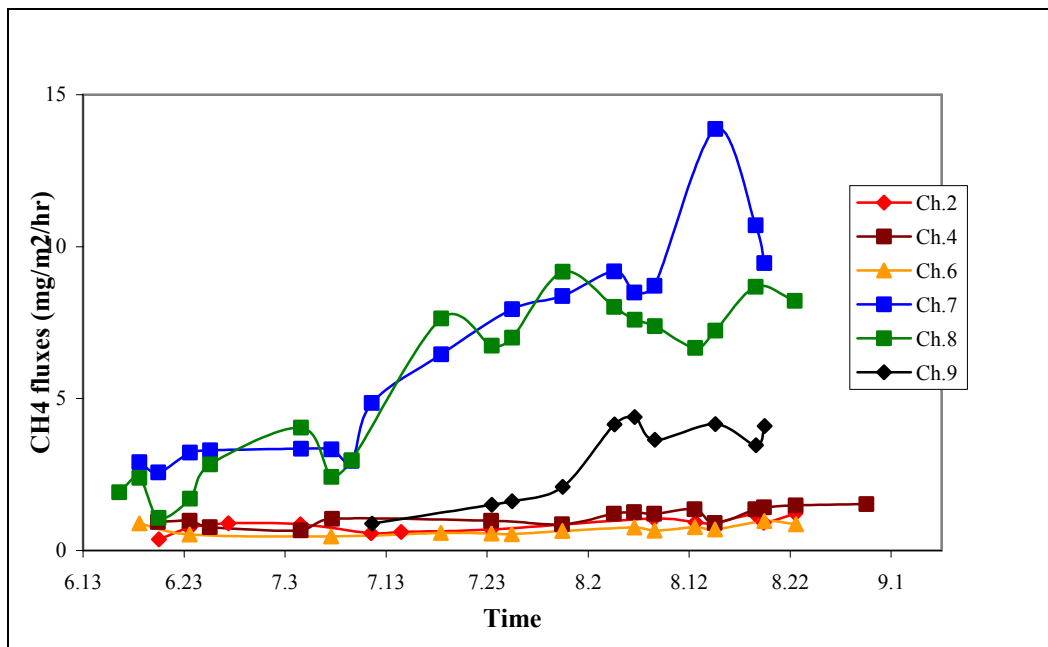


Figure 29, CH₄ patterns over the season for semiwet and wet sub-ecosystems. This diagram shows CH₄ flux patterns for wet and semiwet sub-ecosystems where there is a significant increase in the emissions for wet sub-ecosystems while only a small increase concerning the semiwet site.

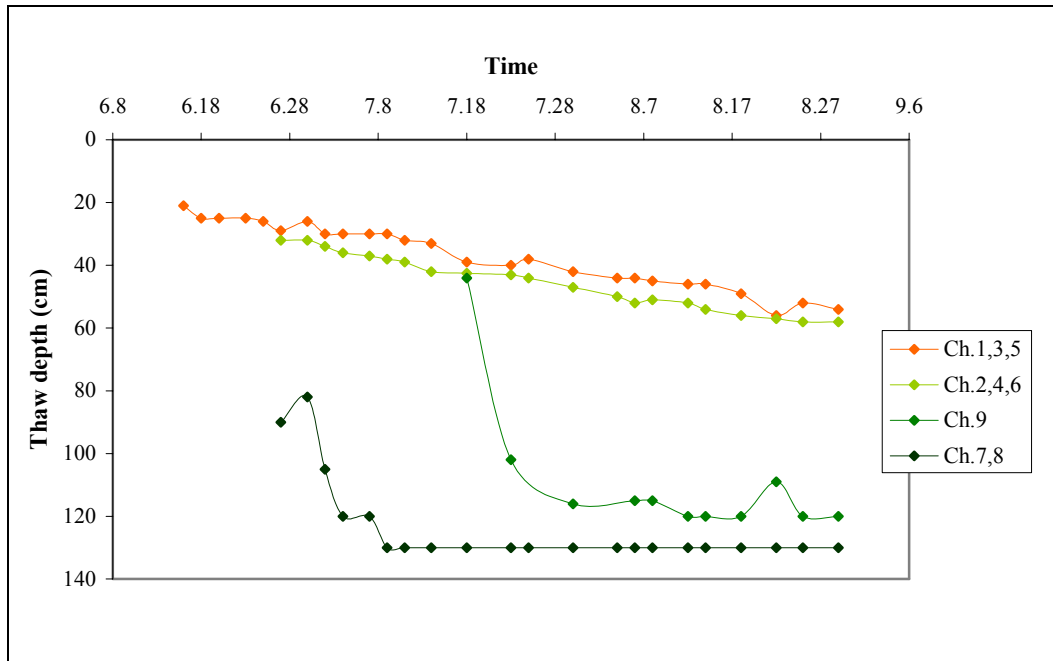


Figure 30, Thaw depth over the season for the different sub-ecosystems.
Recorded thaw depths at different sub-ecosystems are illustrated in the diagram. (It should be noted that the maximum thaw depth by Ch.7 and 8 actually is the maximum length of the stick measuring thaw depth, and so there might be frozen ground far beneath this depth.)

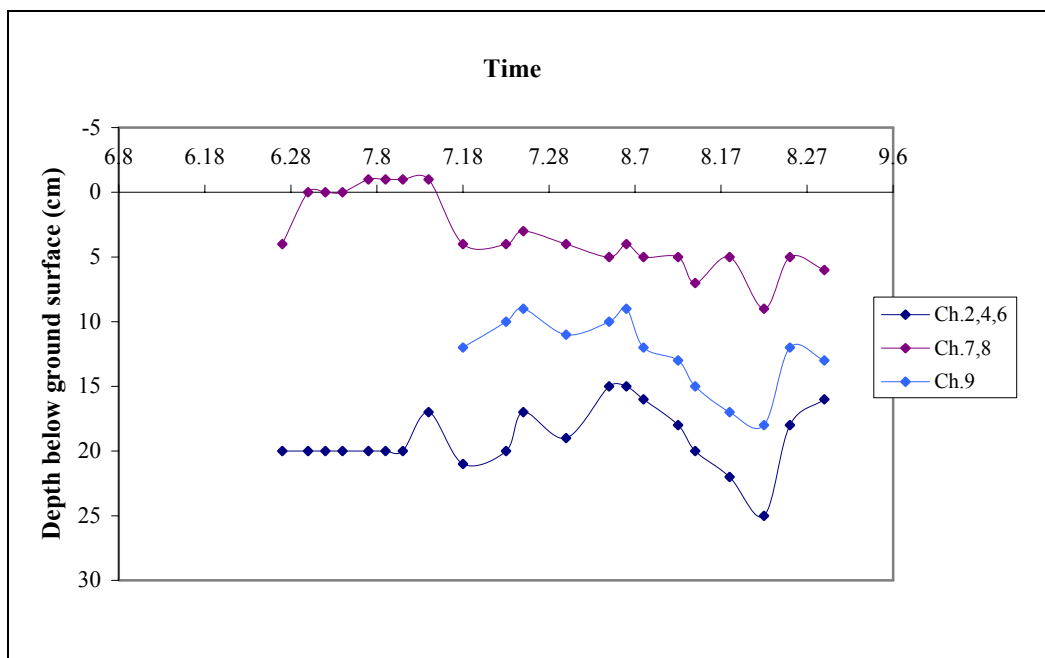


Figure 31, Water table over the season for the different sub-ecosystems.
Recorded water table at different sub-ecosystems is illustrated in the diagram.

CH₄ and respiration

CH₄ emissions could be expected to have a positive relationship with respiration at night times, when PAR values are low and no photosynthesis occurs. The processes of respiration and methanogenesis can both be considered to be ways of decomposition and so it might be interesting to study how they interact. This is shown in Figure 32 and 33, with varying correlation values for the different sub-ecosystems. Concerning the midnight correlation, THC fluxes have to be used instead of CH₄ fluxes, since no grab sampling and GC analysis were made at this time. Although, NMHC fluxes are suspected to be very low during night as a result of low PAR and temperature, so THC fluxes can be suspected to mostly represent CH₄ (*Janson & De Serves, 1998*). CO₂ fluxes at this time with no sunlight are assumed to be respiration data. When using only night-time data, other factors affecting CH₄ emissions and respiration (for example photosynthetic processes, PAR and higher temperatures) can be eliminated from the correlation.

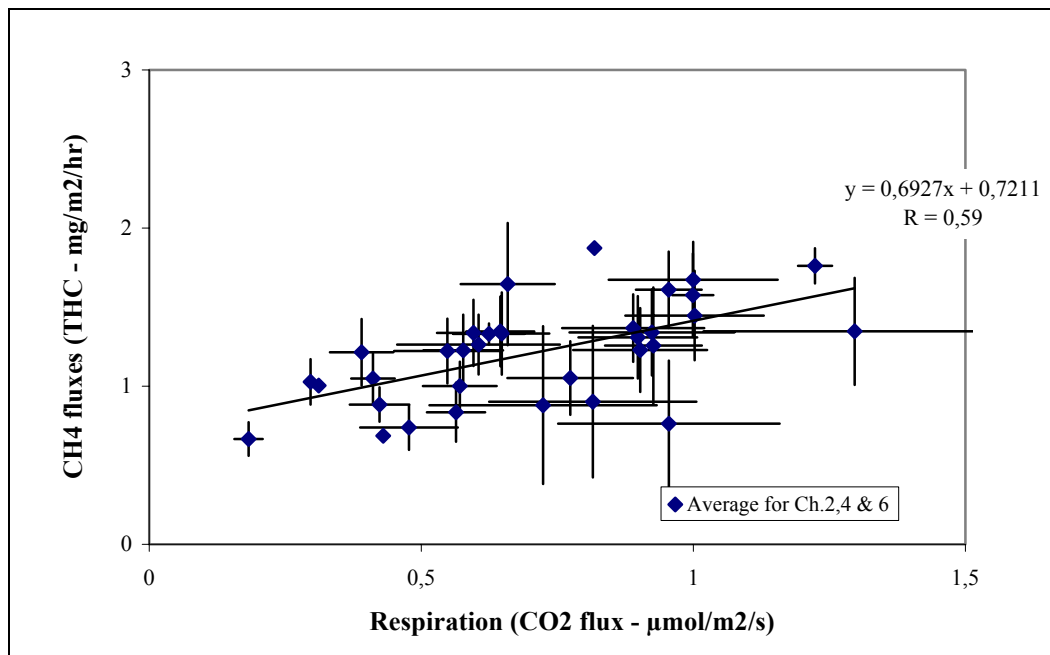


Figure 32, CH₄ fluxes and respiration at night for the semiwet sub-ecosystem.
The correlation shows how CH₄ fluxes have a positive relationship with respiration at night time, as an average for Ch.2, 4 and 6. Error bars show standard error.

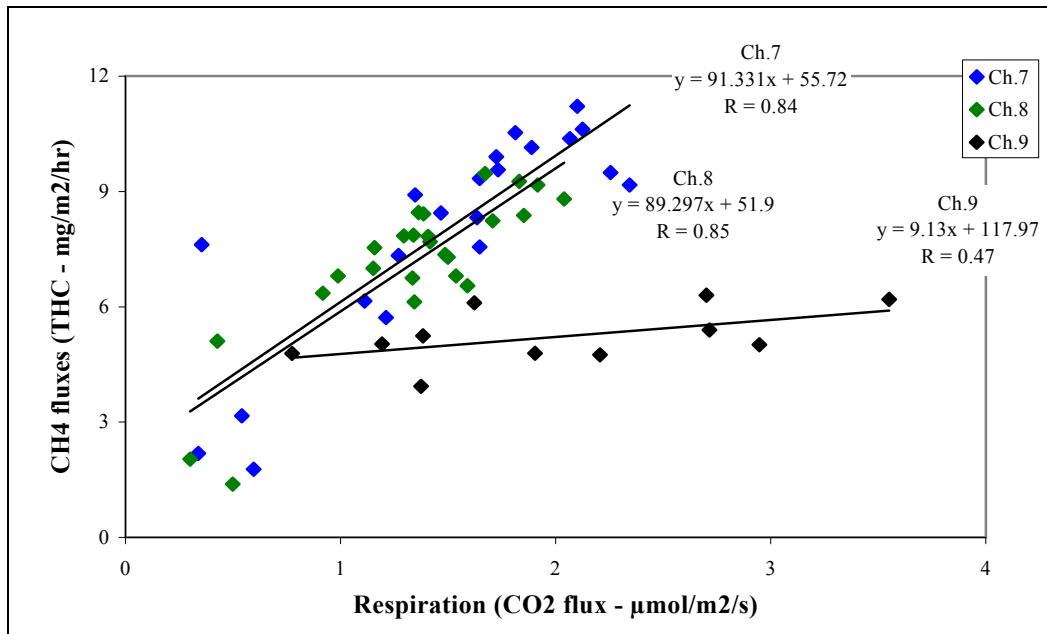


Figure 33, CH₄ fluxes and respiration at night for the wet sub-ecosystem.
The correlation shows how CH₄ fluxes have a positive relationship with respiration at nighttime, for Ch.7, 8 and 9.

The relationship between GPP and CH₄ fluxes

To find out if there is a simple relationship between GPP and CH₄ production, the following correlations were conducted. The result is that there is a clear positive relationship at the wet minerotrophic sub-ecosystem, but no detected relationship at the less nutrient rich sites as illustrated in Figure 34.

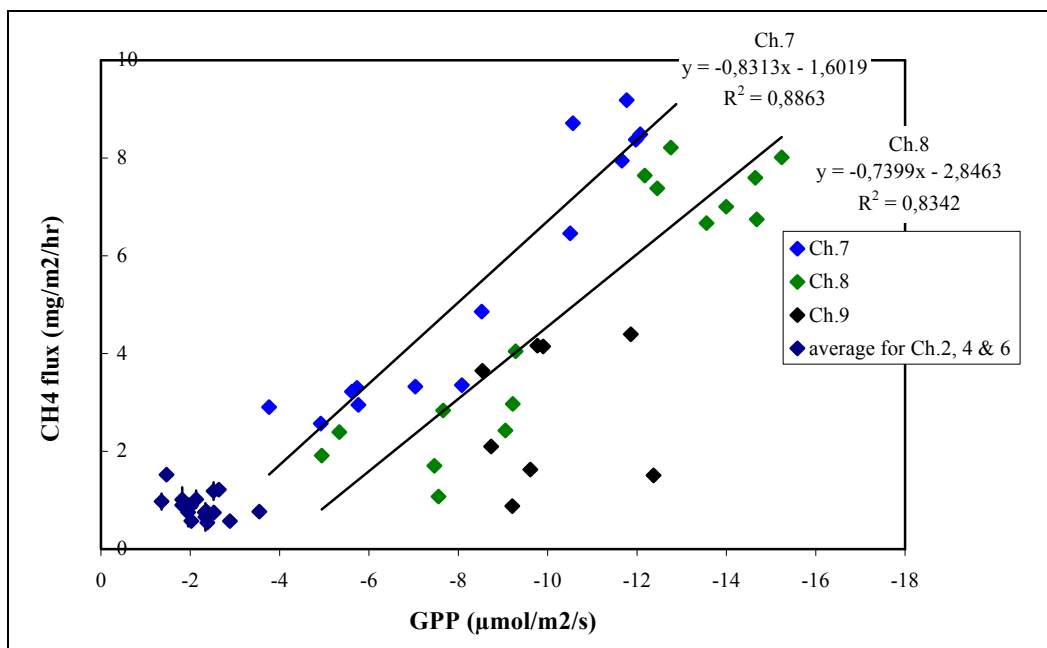


Figure 34, GPP and CH₄ fluxes for wet and semiwet sub-ecosystems.
The diagram shows a correlation of how CH₄ fluxes might be dependent on GPP. Error bars show standard error for the averaged Ch.2, 4 and 6.

The effect of water table on respiration/CH₄ ratio – ground processes

The ratio of respiration/CH₄ fluxes can be expected to decrease when the water level in the ground comes closer to the surface. I.e., the more wet it is, the more CH₄ will be produced and emitted, and the less respiration in the ground will occur and the smaller the ratio will be. On the semiwet site, it is clear how this ratio is varying with water level (*Figure 35*). The range of depth where the water table is shifting around at this site has evidently a great impact on the CH₄ fluxes. In contrast, on the wet sites, the water table is all the time close to the surface and the effect of the respiration/CH₄ ratio as dependent on water table could not be shown.

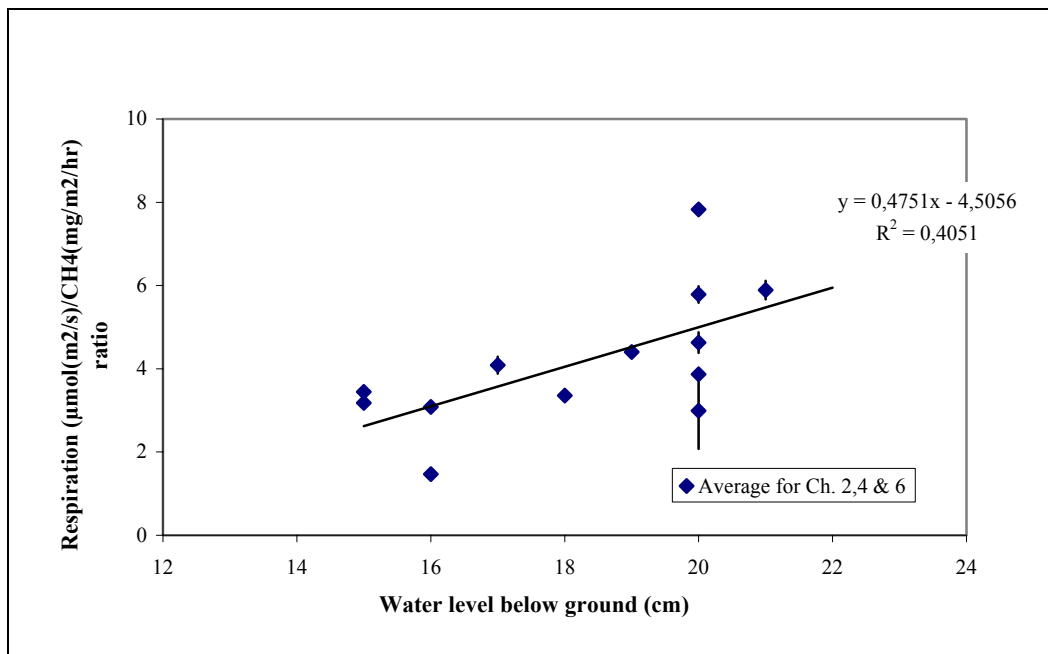


Figure 35, The effect of water table on the respiration/CH₄ ratio at the semiwet site. Ground processes of respiration and CH₄ fluxes as a function of water table are illustrated in the diagram, as an average for Ch.2, 4 and 6. Error bars show standard error.

Final output of carbon from the different sub-ecosystems

Estimated final output of carbon from the three different sub-ecosystems in form of CO₂-C, CH₄-C and NMHC-C is described in Figure 37, as a daytime average for the whole season (days when grab sampling of CH₄ occurred). Carbon output through respiration is modelled to be highest from the wet minerotrophic ecosystem in mg/m²/hr, secondly the wet intermediate ombro-minerotrophic and the least carbon is lost through respiration from the semiwet ombrotrophic site. Further, CH₄-C emission rates are the highest from the wet minerotrophic site where *Eriophorum angustifolium* is growing and a bit less from the wet but less nutrient rich site with a tussock of *Eriophorum vaginatum*. The semiwet ombrotrophic *Sphagnum* moss vegetated site with some *Carex rotundata* has obviously lower rates of CH₄-C going out from the system. When it comes to the carbon as a part of NMHC, the same relationship is present as for CH₄. In terms of percentages, NMHC-C accounts for approximately 1,6 % of total carbon output from the wet ecosystem, but less from the other wet and the semiwet sub-ecosystems (1,33 % and 0,88 % respectively).

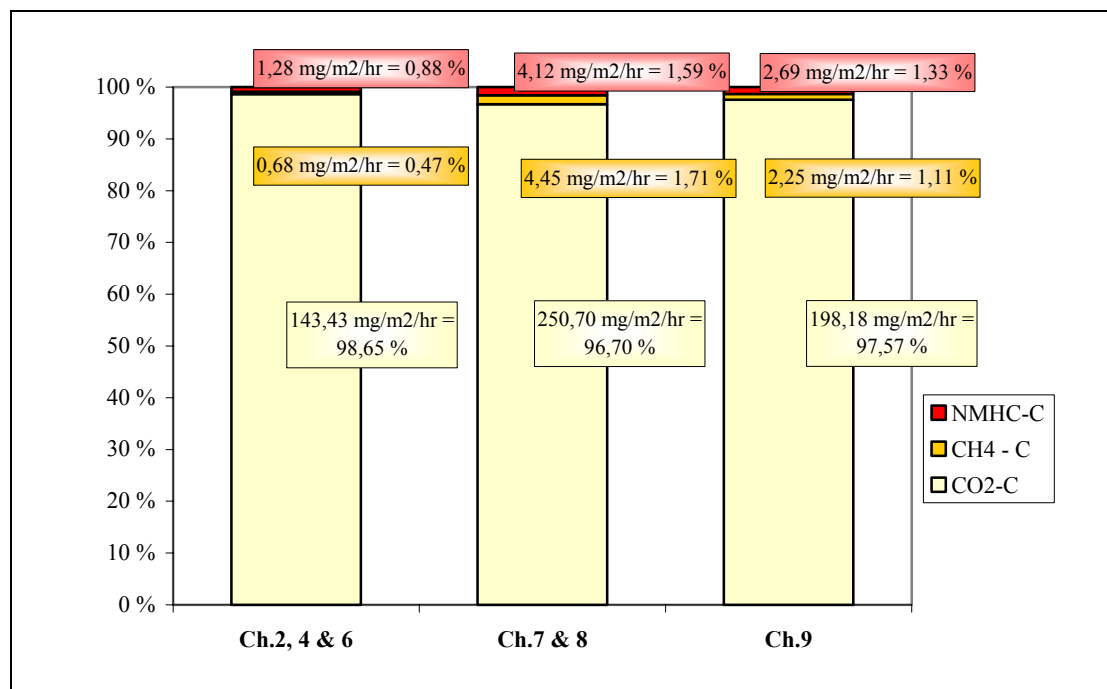


Figure 37. The final output of carbon from the different sub-ecosystems in form of CO₂, CH₄ and NMHC.

Carbon in mg/m²/hr that is lost via respiration processes is greatest from the wet minerotrophic site with a lot of *Eriophorum angustifolium* growing there, and less from the *Eriophorum vaginatum* tussock as well as the *Spagnum* mosses and *Carex rotundata*. This relationship is also true concerning CH₄-C output as well NMHC-C output

Discussion

NMHC

The analysis for determining the percentage amount of NMHC out of 100 % THC gave a result of on average 12 % NMHC for all three of the sub-ecosystems included (Figure 11). When dividing the data into a detailed study for each sub-ecosystem, NMHCs are recorded by all wet chamber systems to account for 7-10 % of THC (Figure 11), while at the semiwet site, 35 % is accounted for (Figure 12). There is evidently a chance that the NMHC fluxes in this study are underestimated, since the THC fluxes are calculated based on a molar weight of CH₄ (16 g/mol) while all NMHCs have greater molar weights than this. For example, isoprene, which is one of the lightest NMHCs (a molar weight of 68 g/mol) are also known to be the most abundant.

Estimating the percentage of NMHC based on the slope or the mixing ratio from the different gas concentrations of THC and CH₄, will give a result that is not affected by different molar weights, since the actual fluxes in mg/m²/hr are not calculated. The result of this comparison is 10 % NMHC, which means that 90 % of the THC flux could possibly be calculated with a molar weight of 16 g/mol and advisably 10 % with the molar weight of 68g/mol, or higher. This is a suggestion for further analysis and has not been conducted in this research.

The hourly fluxes of total NMHC recorded at Stordalen are fully comparable to other studies conducted on boreal wetlands in Sweden and Finland by Janson & De Serves (1998) and Janson et al. (1999), as well as studies in Canada by Klinger et al. (1994). Although, the main factor that must be held in mind in this discussion is the uncertainty associated with the unknown NMHC species composition in this research. No qualitative species examination of the NMHCs sampled was made, and therefore no determinations about what species are emitted, and in what quantities, can be made. Janson & De Serves (1998), Janson et al. (1999) and Klinger et al. (1994) found however, that isoprene dominated the fluxes of light hydrocarbons at all their study sites of wet and dry parts of minerotrophic peatlands. Isidorov et al. (1994) also points out that isoprene is one of the main components of BVOCs from moss species. The highest emissions recorded by Janson & De Serves (1998) were from a wet minerotrophic *Sphagnum* site where the water table was within 5 cm from surface and they measured fluxes of 2 mg/m²/hr. Emissions of 0,8 mg/m²/hr were recorded by

Janson et al. (1999) from another wet *Sphagnum* peatland in Scandinavia, while Klinger et al. (1994) measured highest fluxes of 0,66 mg/m²/hr for isoprene and concluded that bogs contains a great abundance of NMHC emitters. These data should be evaluated with corresponding data from Stordalen, where the moss dominated site with some *Carex rotundata* had maximum rates of NMHC ranging up to 0,9 mg/m²/hr and the vascular plant sub-ecosystems had emissions of up to 2,8 mg/m²/hr (Figure 14 and 15). However, these values most likely underestimated as mentioned before, since they are calculated with the low molar weight of 16 g/mol. Multiplying the above mentioned flux rates of NMHCs with 68/16 (g/mol) will give an estimation of the maximum seasonal fluxes to be in the order of 3,8 and 11,9 mg/m²/hr respectively for semiwet and wet site. These data are obviously higher than the previous mentioned and they might still be underestimated considering that isoprene is a light hydrocarbon.

Janson & De Serves (1998) found clear seasonal variations with high emissions later on during the summer growing season. They explained this as a result of either less isoprene emitting biomass in early June than July and August, or the fact that the seasonal photosynthetic capacity of the moss had just begun to develop in early June. These patterns were however not found in this research, where the emission rates seemed to decrease or stay steady through out the summer. This might have something to do with phenological processes going on in these certain species, which have been shown to affect emissions and peak emissions in the phase of plant development in the early growing season (Peñuelas, & Llusà, 2001). At Stordalen, the emissions from the *Sphagnum* moss species and the small amounts of *Carex rotundata* seem to decrease over the season, as do the emissions from the *Eriophorum vaginatum* tussock, which might be related to the common plant species.

Even though the actual flux rates are different at the wet and the semiwet sub-ecosystems, the NMHC expressed as a percentage of the total THC are similar. There is to some extent a decreasing trend of this relationship over the season explaining that the CH₄ part of THC seems to take over the further time gets into the growing season (Figure 16 and 17).

The present temperature and PAR dependency, for the semiwet *Sphagnum* moss site with some *Carex rotundata*, at Stordalen, is comparable with the temperature dependency that was discovered for NMHC emissions by Janson & De

Serves (1998) in similar habitats (*Figure 18-21*). Much of the emissions can, at that site, be explained by temperature and light, and all emissions show strong diurnal variations with high midday values and zero or near zero values at night. Looking at temperature and PAR versus NMHC flux for Ch.7 and 8, the NMHC emissions of *Eriophorum angustifolium* seem to have a similar temperature and PAR dependency compared to emissions of *Eriophorum vaginatum* (Ch.9). The distinct differences in plant species might be the explanation for this result, assuming that the different plant species emit different NMHC species compositions, where some might be temperature and/or PAR dependent and some not. Given the fact, that in this study, there is no qualitative data on the NMHC species emitted, there will be an obvious risk for different species dependent on separate variables, to reduce the total explained variance, in this case by temperature and PAR. Also, when looking at the temperature and PAR dependency separately, one should take into account the fact that there is most of the time, an obvious indirect relationship between PAR and temperature.

With regard to the carbon budget of the terrestrial biosphere, BVOC emissions are seen as a loss of photosynthetically fixed carbon. The significance of this loss for the regional and global carbon cycle, is, however controversial (*Kesselmeier et al., 2002*). Results presented by Kesselmeier et al. (2002) show clear seasonal correlations of GPP and carbon loss, in the form of BVOC from deciduous trees. Similar correlations of GPP and NMHC emissions were also conducted with data recorded at Stordalen (*Figure 22 and 23*). These results show a consistent positive relationship for all sub-ecosystems. However, the correlation values are low. Here, it is also important to consider the indirect relationships between GPP and PAR, and even more important, temperature, since GPP is estimated based on NEE and the temperature dependent respiration model.

The amount of carbon in form of NMHC compared to carbon as NPP, is most often ranging between 2-4%, but might be as high as 50 % for some plant species under special conditions (*Kesselmeier et al., 2002*). With average seasonal data from this research, NMHC-C constitutes between 0,7 – 1,3 % of GPP-C when the NMHC-C is calculated from the isoprene molecule. In addition to isoprene, there are several much heavier NMHC species. Monoterpenes for example, with 10 carbon atoms, giving them a molar weight at least the double that of isoprene. If the heavier NMHCs dominate, the contribution of NMHC to the total C budget would be greater.

CO₂ and CH₄

The temperature dependent respiration models developed from night-time CO₂ flux data from Stordalen, and ground temperatures from corresponding times, show a tendency to overestimate, when their outputs are compared the actual respiration measurements recorded during the day in July (*Figure 24, 25 and Table 3*). This fact might be true only for the respiration data collected at this certain moment though, since the 12th of July was a cloudy and colder day with some precipitation occurring. More respiration measurements during the field season are essential to show how reliable the respiration model actually is, even though the r^2 values on the temperature dependent respiration model are good for all chambers, except from Ch.9.

CH₄ emissions from the wet sites with vascular *Eriophorum angustifolium* and *Eriophorum vaginatum* illustrate a clear seasonal increasing trend, with the minerotrophic site showing the highest emission rates (up to 15 mg/m²/hr) (*Figure 29*). On the contrary, the *Sphagnum* moss vegetated semiwet site shows almost no increase at all and consistently low emission rates (up to 1,5 mg/m²/hr). There might be several possible explanations for this.

At the wet sites, thaw depth is more than 1 m over the main part of the season suggesting that there is no hinderence of nutrient supply from below, or of plant root development, by permafrost (*Figure 30*). Further, abundant water supply might be a factor that together with the one just mentioned, gives a clear difference in increased biomass further into the summer, as well as the evident factor that the vascular plants do have a more seasonal growth form variation than bryophytes. The high water table through out the season at the wet site makes the aerobic zone for CH₄ oxidation in the upper surface minimal, compared to a wider aerobic zone at the semiwet site (*Figure 31*).

Photographs for Ch.7 and 8 (Appendix I) show an obvious change in biomass, but also, an obvious increase in GPP for all the wet sites as described in the results section (*Figure 28*). Further, there is a clear positive relationship between GPP and CH₄ for Ch.7 and 8 (*Figure 34*). It is concluded that higher photosynthetic rates lead to more allocation of carbon to the root zone and further on higher acetate formations, which shows that acetate originates from recently fixed carbon. These studies were conducted by Ström et al. (2003) at an arctic wet tundra ecosystem. The author writes that it is reasonable to assume that the acetate originating from the recently fixed

carbon will result in CH₄ emissions from the ecosystem and indirectly relating the rate of photosynthesis to the rate of methanogenesis. Joabsson & Christensen (2001) and Klinger et al. (1994) demonstrate a similar finding of how photosynthetic assimilation of carbon may be related to CH₄ emission, although the implication of the two somewhat different time scales that the processes are occurring at, is pointed out by Klinger et al. (1994).

In view of the three different pathways of CH₄, from anoxic environments in the ground to the atmosphere to allow for CH₄ emissions to occur, there are two different factors of great importance: height of water table and possibility for plant-mediated CH₄ transport (Bubier, 1995; Bubier et al., 1995; Christensen et al., 2003b; Joabsson & Christensen, 2001; Klinger et al., 1994 and Ström et al., 2003). These facts support the results demonstrated in this report (Figure 29). The highest CH₄ emissions are from the wet minerotrophic site where the water table is within 0-10 cm, then from wet intermediate ombro-minerotrophic site with a water table within 10-15 and the lowest emissions from the semiwet sub-ecosystem where water table is within 15-25 cm. Further, it is the vascular plant sub-ecosystems where potential plant-mediated CH₄ transport may occur, that show greatest CH₄ emissions. CH₄ emissions in areas dominated by bryophytes have been shown to be more sensitive to water table depth (Bubier, 1995) since, bryophytes have no vascular structures that can transport CH₄ from methanogenic soils to the atmosphere, bypassing aerated soils and therefore avoiding oxidation in the ground and increasing CH₄ emissions. Possibly, the vascular plant specie growing at this site, *Carex rotundata*, might have its roots positioned very close to ground surface, hence decreasing the amount of CH₄ emitted. This might also be the case as a result of the plant specie being less capable of transporting CH₄ from ground to above ground within the cell structures. Further, *Eriophorum* species have been shown to be particularly efficient as CH₄ transporters, which also is comparable with results from this study (Joabsson & Christensen, 2001 and Ström et al., 2003).

The processes of methanogenesis and aerobic respiration are both pathways of decomposition, and there is interaction between them. An analysis of this kind was conducted for night-time data since this exclude light and higher daytime temperatures from disturbing the correlation, and the result showed that there were a positive relationship between CH₄ emissions and respiration (Figure 32 and 33).

However, there is some uncertainty associated with this analysis. To obtain CH₄ fluxes at night, THC data from the automatic chamber system had to be used since no grab sampling occurred at this time. For all sites, this gives assumed CH₄ values of in fact 1/3 higher rates than any CH₄ fluxes during the day. These fact point out the need of 24 hour measurements that are absent in this study, except from for the fluxes of CO₂ and THC. No analysis of the THC diurnal pattern are presented here but may certainly be important and could be included in further analyses of the collected data. Indeed, there is a possibility that the THC fluxes at night contain a certain degree of emitted NMHC even though there have rarely been any results showing NMHC emissions at night, especially not in the rates that would be needed in this case (the highest recorded emissions during the day would be necessary for each sub-ecosystem).

The effect of water table on the respiration/CH₄ ratio is also discussed in close connection to earlier mentioned plants-hydrology-CH₄ emission relationship. The effect of the water table is given through the variation of the width of the aerobic zone, in the upper part of the soil profile, where CH₄ oxidation is prone to occur. The results here show that there is a clear water table dependency for the respiration/CH₄ ratio at the semiwet site with mosses where water table ranges around 15-25 cm depth (*Figure 35*), which is not at all the case for the two wet sites with vascular plants. This is most likely due to the fact that mosses are more sensitive to water table since they have no vascular structures as also described in Bubier (1995). Also, since the water table is below the depth at which methanogenesis is found to be most prone to occur, more exact by the maximum root density (*Joabsson & Christensen, 2001*) the actual amount of produced CH₄ that is emitted is highly depending on depth of water table. At the wet sub-ecosystem, the water table is all the time as close to the ground surface so that it does not affect the respiration/CH₄ ratio. Further on, the high amount of vascular plants at these sites implies no great effect of water table, most likely explained by the possibility of plant mediated CH₄ transport, which more over could be expected to increase with the amount of biomass.

One problem with the chamber techniques used today to measure the CH₄ emissions is the difficulty in registering episodic fluxes as bubble ebullition, which in earlier studies on peat monoliths from different sites around Sweden have shown to account for 17-52 % of total CH₄ emission (*Christensen et al., 2003b*).

The final output of carbon in form of the different compounds CO₂, CH₄ and NMHC shows that the carbon loss through respiration processes is with no exception the greatest from all the three different sub-ecosystems studied (Figure 37). Thereafter, CH₄-C and NMHC-C account for the highest percentage from of total output from the wet minerotrophic site and decreasing from wet intermediate ombro-minerotrophic to semiwet. The specific fluxes of respiration should be taken as rough estimates since they are totally dependent on the respiration models accounted for earlier. Similarly, the NMHC-C could likely be underestimated if heavier NMHCs dominate. In spite of this, the relationship between CO₂-C, CH₄-C and NMHC-C may however still be the same but another technique that identifies NMHCs and determines the more exact respiration is required. CH₄-C and CO₂-C output data from Stordalen in 1974 and 1995, from different microsites, are presented in Svensson et al., (1999). These results have been compared with the results from the summer season of 2003. The conclusion from Svensson et al. (1999) contains a statement of that the respiration rates have increased during the 20 years. This fact is further strengthened by the respiration data from the field season of 2003 at the three correspondent microsites. This increasing trend is most clear at the wet minerotrophic site where average respiration-C output has developed from 21 mg C /m²/hr in 1974 via 41,2 mg C /m²/hr in 1995 to 250 mg/m²/hr almost 10 years later in 2003. The somewhat different methodologies used should be considered as well as the actual time span of fieldwork, which has been shown to be the shortest for 2003. More over, as mentioned before, the respiration data for 2003 are approximations from a temperature dependent respiration model, which has shown a tendency of overestimation and this, should be noted.

Conclusion

Evidently, a subarctic mire like Stordalen is important for future research of BVOCs. It has been shown in this study that NMHCs account for a significant part of total THC, i.e. at the least 10 % on average from the three kinds of sub-ecosystems studied. Further on, the possibility of underestimated flux rates has to be considered. Here, the flux rates are based on the molar weight of CH₄, while isoprene, one of the lightest and most abundant NMHCs, would make the fluxes more than four times greater. Additionally, this relationship will change if heavier NMHCs are dominating the emissions. Given that NMHC-C may be in the rate of approximately 1.5 - 2.7 % of NEE or more, they do constitute an important part of the net ecosystem carbon exchange. The part of the total output of carbon that NMHC-C represents is further reaching close to 2 % at one site.

The highest NMHC emissions are from the wet sites with vascular plants, compared to *Sphagnum* mosses and *Carex rotundata* species at a semiwet site. A certain temperature, light and GPP dependency exist for all the sub-ecosystems, except from that the wet intermediate ombro-minerotrophic site with *Eriophorum vaginatum* had no correlation at all with light. The most important here, is that it is a clear difference of variable dependency between the different plant species, in the different environments. More over, the uncertainty of NMHC species composition adds an obvious risk for that different NMHC species, dependent on separate variables, reduces the total explained variance in the correlations presented. It can be concluded that vascular plants, like *Eriophorum angustifolium* and *Eriophorum vaginatum*, growing at wet nutrient rich sites, emit more NMHC than *Sphagnum* moss species and *Carex rotundata* at a drier less nutrient rich site. However it has not been determined what kind of NMHCs are emitted from each site.

CH₄ emissions have been identified to be of much higher rates from wet sub-ecosystems where vascular plants are present compared to a semiwet site, which is vegetated by *Sphagnum* moss species and *Carex rotundata*. The variation of the water table position at a depth of 15-25 cm play an important role at the semiwet site, while a variation of the water table within 0-10 cm from the surface do not play any affect. More over, the presence of vascular plants and their ability to give qualitative

substrates for CH₄ production through photosynthesis as well as their capacity for plant mediated CH₄ transport are most likely explaining the difference.

Finally, future research of BVOCs and models of the terrestrial carbon cycle should include BVOC emissions from northern latitude ecosystems like the subarctic mire Stordalen, as they have been identified to be an important part of the total carbon budget of the mire.

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Appendix

Appendix I – Photo documentation

Photo documentation

Photos of the chambers and the plant development were taken a few times through out the season. Below is the documentation from 30th of June and 28th of August (Photograph 1-9).

The wet minerotrophic sub-ecosystem with *Eriophorum angustifolium* detects the most obvious change looking at the amount of biomass on the photographs, where also the NEE data show great values during the middle of the summer period; a net CO₂ uptake of approximately 4-8 $\mu\text{mol}/\text{m}^2/\text{s}$ for the entire sub-ecosystem in each chamber as shown in Figure 35-36.

Concerning the *Eriophorum vaginatum* in Ch.9, there has evidently been a high NEP during the summer season with a net uptake of 4-7 $\mu\text{mol}/\text{m}^2/\text{s}$, referring to Figure 37. Although, in the case of comparing the two photographs it is difficult to see any obvious difference in biomass.

For the dry ombrotrophic site, there is no clear change in the amount of biomass that is detectable in the photographs, and it is the same situation concerning the semiwet ombrotrophic site with moss species and the *Carex* species. Also, these sub-ecosystems have a relatively low NEE, mostly ranging between 0-2 $\mu\text{mol}/\text{m}^2/\text{s}$ exclusively from Ch.5 where the uptake is as great as 4 $\mu\text{mol}/\text{m}^2/\text{s}$ in late July and early August (*Figure 31-34*). For some of the plant species, the most intensive growing season has definitely passed while others still seem to have photosynthetic activity present. The *Carex* species at the semiwet ombrotrophic site are definitely out of season in late August.



Photograph 1, Chamber 1 at the dry ombrotrophic site.



Photograph 2, Chamber 3 at the dry ombrotrophic site.



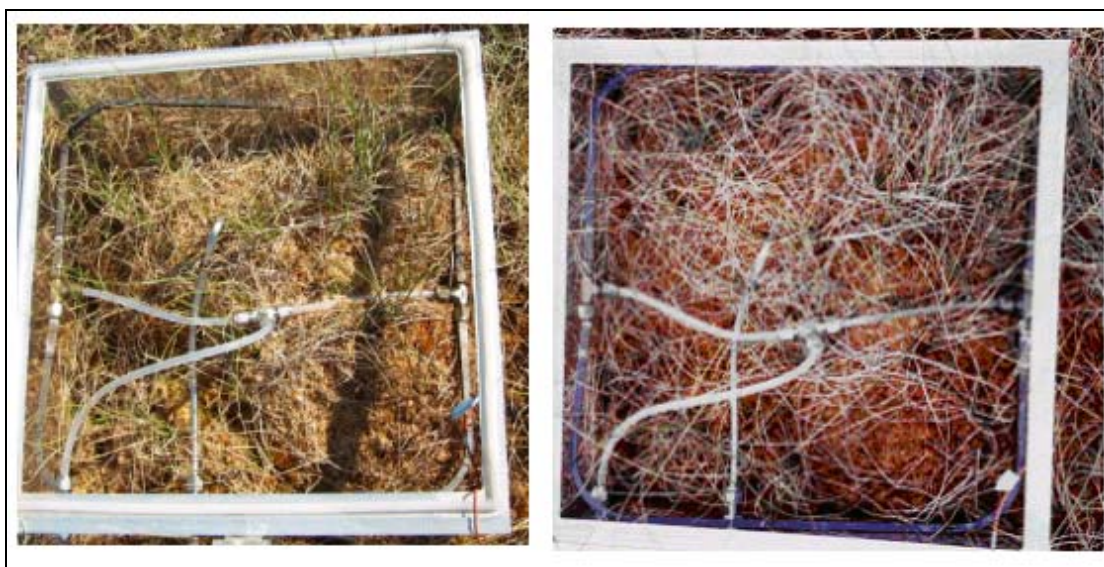
Photograph 3, Chamber 5 at the dry ombrotrophic site.



Photograph 4, Chamber 2 at the semiwet ombrotrophic site.



Photograph 5, Chamber 4 at the semiwet ombrotrophic site.



Photograph 6, Chamber 6 at the semiwet ombrotrophic site.



Photograph 7, Chamber 7 at the wet minerotrophic site.



Photograph 8, Chamber 8 at the wet minerotrophic site.



Photograph 9, Chamber 9 at the wet intermediate ombro-minerotrophic site.

Appendix II - Manual CH₄ calculations

This appendix shows how the manual CH₄ calculations have been conducted. The example is from the 4th of July 2003. Reference gas used is CH₄ with a ppmv of 1,96. The red numbers in the figures are linked to explaining text.

1. 10 standardisation runs with the reference gas were made before and after the actual samples were analysed.
2. The two lowest and highest responses were deleted.
3. Averaged response was calculated
4. Standard deviation of all the response times was calculated
5. % standard deviation of the mean response was calculated
6. The response factor in ppm/min was calculated by dividing the reference gas concentration with the average response
7. Syringe are samples were run in the GC and response area recorded
8. Concentration of CH₄ (ppmv) was calculated for each moment a sample was taken (response area from GC/response factor)
9. Mixing ratio and r² for the same was calculated (ppmv/min)
10. CH₄ flux in mg/m²/d was calculated using following equation:

$$\text{CH}_4 \text{ flux} = \text{rate ppm/min} * (\text{P/R} * 16\text{g/mol}) * 1/\text{T} * \text{Vc/Ac} * 1000 \text{ mg/g} * 1440\text{min/d}$$

where

rate = the concentrations measured over time

P = the pressure assumed to be 1 atm

R = the gas constant 0,00008206 m³ atm/deg/mol (used for CH₄)

16 g/mol = molar weight of CH₄ (although THC may have a molar weight different to CH₄)

Vc = total volume of a specific chamber

Ac = area that the chamber covers 0,16 m² (for all chambers)

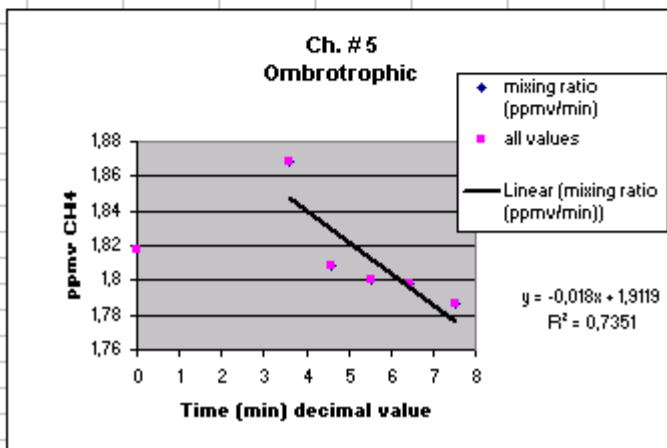
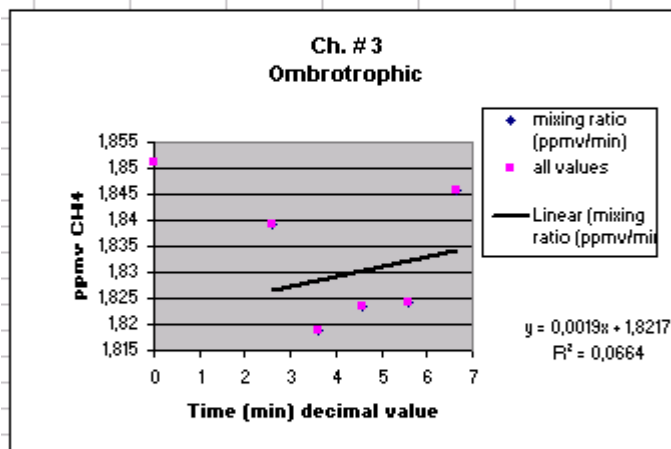
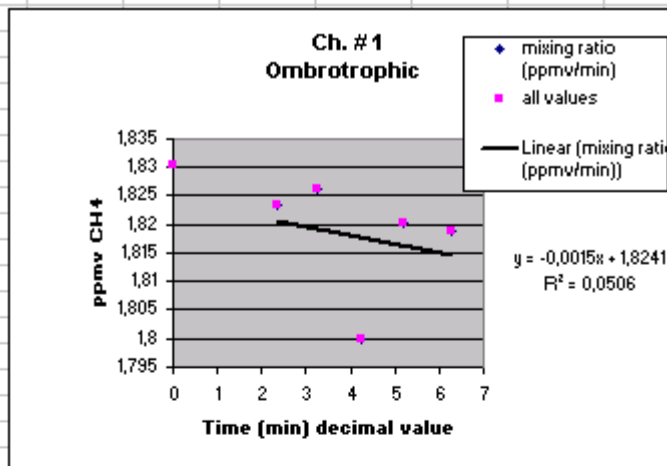
T= 273,15 deg K which is set to average air temperature

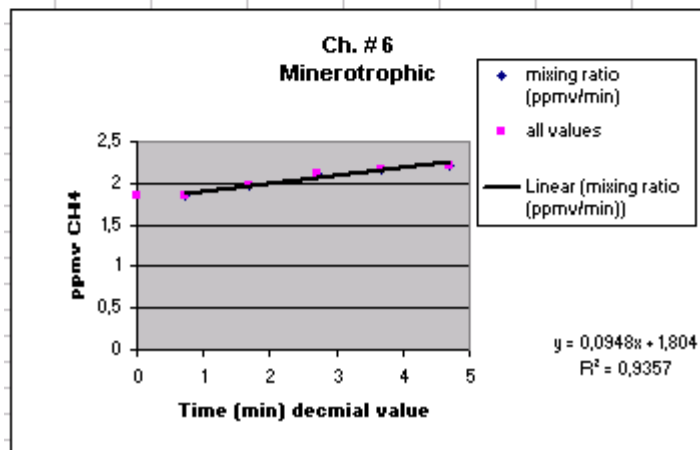
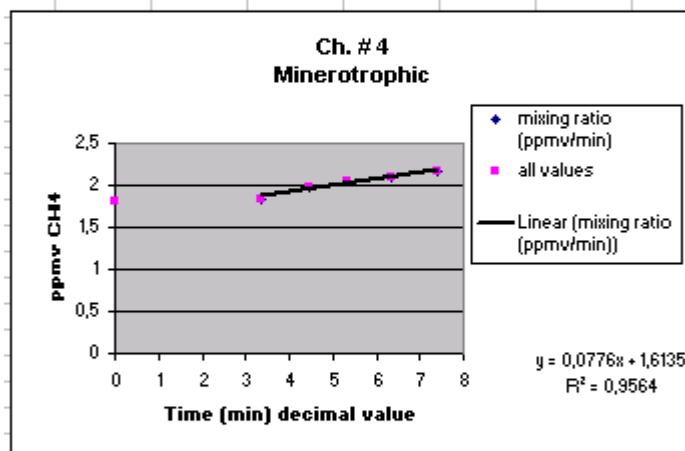
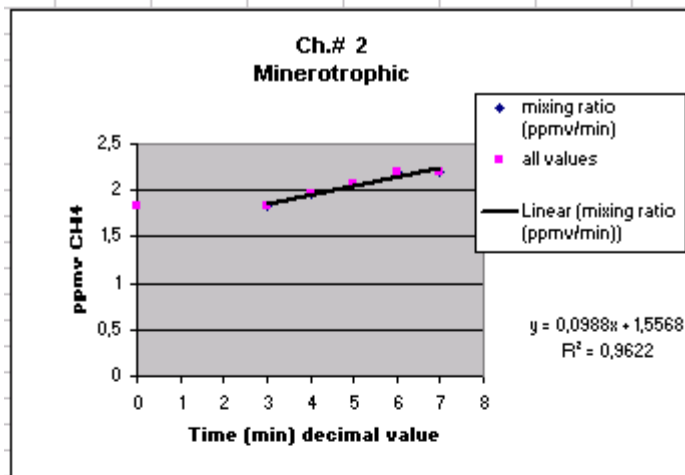
11. Finally, the fluxes are shown in the diagrams in the end of this Appendix 1.

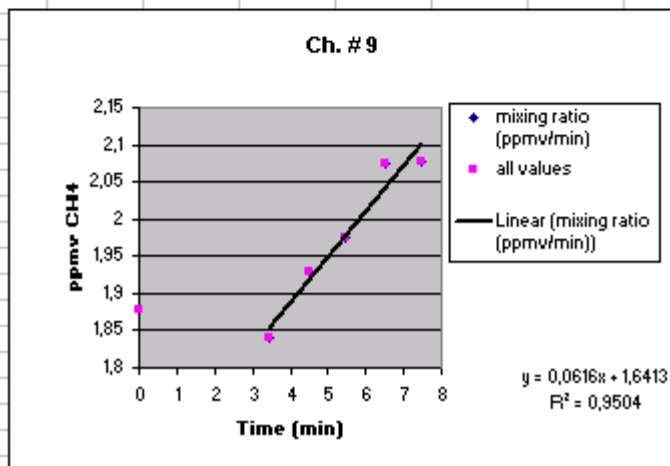
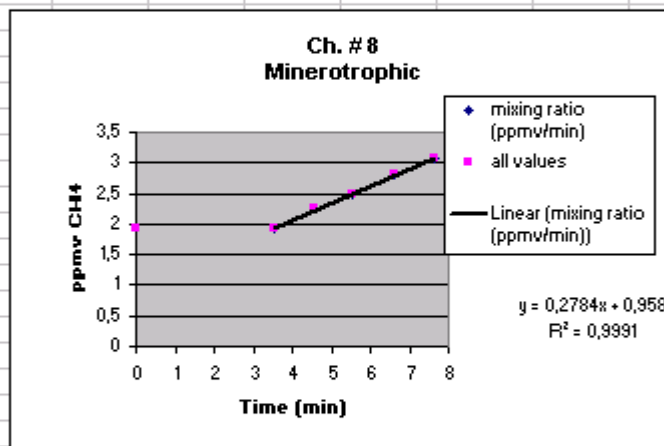
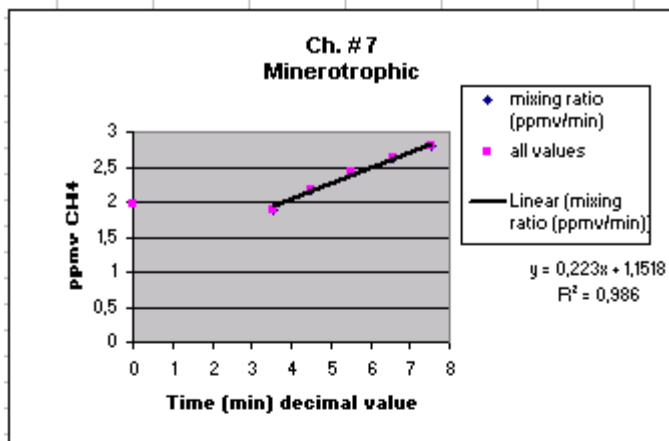
20030704		Reference gas	
	Respos	ppmv CH4	
			10995,625 Average response (av. of all stds)
First run Std		1,96	145,3450492 stdev of response (stdev of all stds)
			1,321844363 % std dev of the mean respons
			((stdev of mean respons/av. Respos) * 100)
	10791		0,000178253 ppm/unit Response factor (stds conc./av.respons)
	10791		
	10849		
	10857		
	10849		
	10939		
	10869		
	10955		
Last run Std		1,96	
	11135		
	11158		
	11162		
	11127		
	11089		
	11172		
	11106		
	11081		

The Dynamics of Non-methane Hydrocarbons &
Other Trace Gas Fluxes at a Subarctic Mire in Northern Sweden

Ch#	Syr#	Time	Respon	8		Time	Time relative to first sample	Secs	Mins (decimal value)	10 CH4flux mg/m2/day	
				7 ppmv CH4 (area*resp factor)	9 Mixing (ppmv/min) vs time (SLOPE)						r2 CH4
1	8-6-0	11:44:45	10269	1,830477122		11:44:45	00:00	0	0,00	-0,26	
	8-6-1	11:47:06	10229	1,823347013	-0,001503802	0,05058	11:47:06	02:21	141	2,35	
	8-6-2	11:48:01	10245	1,826199056			11:48:01	03:16	196	3,27	
	8-6-3	11:48:59	10098	1,799995907			11:48:59	04:14	254	4,23	
	8-6-4	11:49:56	10212	1,820316717			11:49:56	05:11	311	5,18	
	8-6-5	11:50:56	10203	1,818712442			11:50:56	06:11	376	6,27	
				0							
2	15-1-0	12:24:57	10279	1,832259649			12:24:57	00:00	0	0,00	20,70
	15-1-1	12:27:57	10273	1,831190132	0,098836976	0,96223	12:27:57	03:00	180	3,00	
	15-1-2	12:28:57	10991	1,959175581			12:28:57	04:00	240	4,00	
	15-1-3	12:29:56	11577	2,063631672			12:29:56	04:59	299	4,98	
	15-1-4	12:30:57	12283	2,189478088			12:30:57	06:00	360	6,00	
	15-1-5	12:31:56	12389	2,208372876			12:31:56	06:59	419	6,98	
				0							
3	8-5-0	12:43:21	10384	1,850976184			12:43:21	00:00	0	0,00	0,35
	8-5-1	12:45:58	10319	1,839389757	0,00188366	0,06636	12:45:58	02:37	157	2,62	
	8-5-2	12:46:57	10204	1,818890695			12:46:57	03:36	216	3,60	
	8-5-3	12:47:56	10229	1,823347013			12:47:56	04:35	275	4,58	
	8-5-4	12:48:57	10234	1,824238277			12:48:57	05:36	336	5,60	
	8-5-5	12:49:59	10355	1,845806855			12:49:59	06:38	398	6,63	
				0							
4	8-4-0	13:00:39	10146	1,808552038			13:00:39	00:00	0	0,00	16,05
	8-4-1	13:03:59	10326	1,840637526	0,077584149	0,9564	13:03:59	03:20	200	3,33	
	8-4-2	13:05:06	11126	1,983239698			13:05:06	04:27	267	4,45	
	8-4-3	13:05:59	11524	2,054184278			13:05:59	05:20	320	5,33	
	8-4-4	13:06:59	11813	2,105699312			13:06:59	06:20	380	6,33	
	8-4-5	13:08:02	12150	2,165770477			13:08:02	07:23	443	7,38	
				0							
5	15-4-0	13:18:28	10196	1,817464673			13:18:28	00:00	0	0,00	-3,58
	15-4-1	13:22:03	10480	1,868088444	-0,017999818	0,73514	13:22:03	03:35	215	3,58	
	15-4-2	13:23:04	10145	1,808373785			13:23:04	04:36	276	4,60	
	15-4-3	13:24:01	10097	1,799817655			13:24:01	05:33	333	5,55	
	15-4-4	13:24:55	10089	1,798391633			13:24:55	06:27	387	6,45	
	15-4-5	13:25:59	10020	1,786092196			13:25:59	07:31	451	7,52	
				0							
6	15-5-0	13:39:17	10435	1,860067072			13:39:17	00:00	0	0,00	14,37
	15-5-1	13:40:01	10318	1,839211505	0,094791895	0,93572	13:40:01	00:44	44	0,73	
	15-5-2	13:40:58	11034	1,966840448			13:40:58	01:41	101	1,68	
	15-5-3	13:41:59	11898	2,120850793			13:41:59	02:42	162	2,70	
	15-5-4	13:42:57	12093	2,155610072			13:42:57	03:40	220	3,67	
	15-5-5	13:43:59	12429	2,215502984			13:43:59	04:42	282	4,70	
				0							
7	8-2-0	13:54:26	11082	1,975396578			13:54:26	00:00	0	0,00	80,50
	8-2-1	13:57:59	10659	1,89999568	0,222959408	0,98602	13:57:59	03:33	213	3,55	
	8-2-2	13:58:57	12213	2,177000398			13:58:57	04:31	271	4,52	
	8-2-3	13:59:57	13616	2,427088956			13:59:57	05:31	331	5,52	
	8-2-4	14:01:00	14823	2,642239982			14:01:00	06:34	394	6,57	
	8-2-5	14:01:59	15644	2,78858546			14:01:59	07:33	453	7,55	
				0							
8	8-3-0	14:12:25	10813	1,927446598			14:12:25	00:00	0	0,00	97,12
	8-3-1	14:15:58	10846	1,933328938	0,278394681	0,99914	14:15:58	03:33	213	3,55	
	8-3-2	14:17:00	12654	2,255609845			14:17:00	04:35	275	4,58	
	8-3-3	14:17:58	14005	2,496429262			14:17:58	05:33	333	5,55	
	8-3-4	14:19:03	15737	2,805162963			14:19:03	06:38	398	6,63	
	8-3-5	14:20:02	17255	3,075750583			14:20:02	07:37	457	7,62	
				0							
9	15-3-0	14:30:29	10542	1,879140113			14:30:29	00:00	0	0,00	21,49
	15-3-1	14:33:56	10319	1,839389757	0,061617516	0,95039	14:33:56	03:27	207	3,45	
	15-3-2	14:34:59	10830	1,930476894			14:34:59	04:30	270	4,50	
	15-3-3	14:35:58	11079	1,97486182			14:35:58	05:29	329	5,48	
	15-3-4	14:36:59	11633	2,073613824			14:36:59	06:30	390	6,50	
	15-3-5	14:37:58	11654	2,077357131			14:37:58	07:29	449	7,48	







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