Carbon and Nitrogen Transformations in Alpine Ecosystems of the Eastern Alps, Austria

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(Oliver Koch)

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List of abbreviations

A_C	Substrate quality index for C mineralization
A_N	Substrate quality index for N mineralization
AMC	7-amino-4-methyl-coumarin
ANOVA	Analysis of variance
CFE	Chloroform fumigation-extraction
CH_{4aq}	Dissolved methane
C_{mic}	Microbial carbon
Cmin	C mineralization
C_{org}	Organic carbon
C_t	Total carbon
DOC	Dissolved organic carbon
GAI	Green area index of plants
Glob. rad.	Global radiation
GLUC	ß-glucosidase
LEU	Leucine aminopeptidase
MUB	4-methylumbelliferyl
NAG	*N*-acetyl-ß-glucosaminidase
NEC	Net ecosystem CO_2 exchange
NEC_{day}	Daily net ecosystem CO_2 exchange
$NEC_{daylight}$	Daily net ecosystem CO_2 exchange during daytime (*PAR*>0)
NEC_{light}	Net ecosystem CO_2 exchange during daytime (*PAR*>0)
NEC_{max}	Maximum NEC_{light}
Nmin	N mineralization
N_t	Total nitrogen
PAR	Photosynthetic active radiation
wfps	Water-filled pore space
wt	Water table
pb	green above-ground standing plant biomass
ppm	Parts per million
Q_{10}	Temperature quotient (Δ10°C)
R_{night}	Daily ecosystem respiration during nighttime (*PAR*=0)
R_{tot}	Ecosystem respiration during nighttime (*PAR*=0)
RTS	Relative temperature sensitivity
st_5	Soil temperature in 5 cm soil depth
st_{15}	Soil temperature in 15 cm soil depth
st_{35}	Soil temperature in 35 cm soil depth
TYRO	Tyrosine aminopeptidase
XYL	ß-xylosidase

Study sites:

meadow	alpine meadow (*Curvulo-Nardetum*)*:*
transitional	transient fen site (*Carici echinatae-Trichophoretum caespitosi*)
fen	fen site (*Carici echinatae-Trichophoretum caespitosi*)
wet fen	fen site (only *Carex nigra)*

1 Summary

This thesis investigated net CH_4 and net CO_2 emissions from sites in the alpine region of the Eastern Alps, Austria. Four mature alpine sites (one dry meadow and three fen sites following a natural water gradient) were selected and the influence of abiotic (radiation, temperature, soil water conditions) and biotic (above-ground standing plant biomass) environmental controls on diurnal and seasonal emission patterns were studied. For a better understanding of the response of soil C- and N pools to global warming, the temperature sensitivity of activities involved in C- and N cycling were determined.

The first part of the thesis dealt with net methane fluxes measured over a period of 24 months. During snow-free periods, average methane emissions of the fen sites ranged between 19 and 116 mg CH_4 m^{-2} d^{-1}. Mean emissions during snow periods were much lower, being 18 to 59% of annual fluxes. The alpine dry meadow functioned as a small methane sink during snow-free periods (-2.1 mg CH_4 m^{-2} d^{-1} (2003); -1.0 mg CH_4 m^{-2} d^{-1} (2004)). The diurnal and seasonal methane uptake of the dry meadow was positively related to soil temperature and negatively related to water-filled pore space (*wfps*). In the fen, the seasonal methane fluxes were related to soil temperature and groundwater table. The live above-ground standing plant biomass contributed to net methane fluxes only at those sites with higher water table positions. This study provided evidence that alpine fens acted as methane sources throughout the year, whereas an alpine meadow site acted as a net methane sink during snow-free periods.

In the second part of the thesis the CO_2 balance was estimated based on diurnal flux measurements and on the influence of photosynthetic active radiation (*PAR*), plant green area index (*GAI*), soil temperature and *wfps*. The daylight net ecosystem CO_2 emission rate was influenced by *PAR* and *GAI* throughout snow-free seasons. The seasonal net CO_2 emission rate at night was positively related to soil temperature, while low *wfps* reduced flux rates at the meadow and at the driest fen study site but reinforced carbon loss at the wetter fen sites. The daily average ecosystem net CO_2 gain during snow-free periods at the meadow was 3.5 g CO_2 m^{-2} d^{-1} and at the fen sites between 1.5 and 3.4 g CO_2 m^{-2} d^{-1}. The mean average daily CO_2 emission during snow periods was low, being -0.9 g CO_2 m^{-2} d^{-1} for the meadow and between -0.2 and -0.7 g CO_2 m^{-2} d^{-1} for all fen sites. All sites function as significant annual net carbon sinks, with a net carbon gain from 50 to 121 g C m^{-2} a^{-1} (averaged over both years), irrespective of water balance. The results indicate that alpine fen sites, that have built up a large carbon stock in the past, are not expected to gain a further carbon surplus compared with meadows under the current climate.

Temperature is important for regulating biological activities. The third part of the thesis focused on temperature sensitivity of soil C mineralization, N mineralization and potential

enzyme activities involved in the C- and N cycle (ß-glucosidase, ß-xylosidase, *N*-acetyl-ß-glucosaminidase, tyrosine aminopeptidase, leucine aminopeptidase) over a temperature range of 0-30°C. The objective was to calculate Q_{10} values and relative temperature sensitivities (*RTS*) and to quantify seasonal (summer, autumn, winter) and site-specific factors.

The Q_{10} values of C mineralization were significantly higher (average 2.0) than for N mineralization (average 1.7). The Q_{10} values of both activities were significantly negatively related to soil organic matter quality. In contrast, the chemical soil properties, microbial biomass and sampling date did not influence Q_{10} values. Analysis of *RTS* showed that the temperature sensitivity increased with decreasing temperature. The C- and N mineralization and potential aminopeptidase activities (tyrosine, leucine) showed an almost constant temperature dependence over 0-30°C. In contrast, ß-glucosidase, ß-xylosidase and *N*-acetyl-ß-glucosaminidase showed a distinctive increase in temperature sensitivity with decreasing temperature. Low temperature at the winter sampling date caused a greater increase in the *RTS* of all activities than in autumn and summer. Our results indicate a disproportion of the *RTS* for potential enzyme activities of the C- and N cycle and a disproportion of the *RTS* for easily degradable C compounds (ß-glucose, ß-xylose) compared with the C mineralization of soil organic matter. Thus, temperature may play an important role in regulating the decay of different soil organic matter fractions.

In conclusion, this study proved that climatic properties are important for net emissions of the climate-relevant trace gases, CO_2 and CH_4, derived from alpine ecosystems. Net N_2O fluxes were not found at any study site. Considering the small cover of wetlands in the alpine zone of Austria (0.14%) compared to alpine grassland (78.3%), and extrapolating our data to a regional scale (vegetation-free area excluded), this study expect a small net sink for CH_4 ($|0.14|$ g CH_4 m^{-2} a^{-1}) and a net sink for CO_2 ($|420|$ g CO_2 m^{-2} a^{-1}) under current climate conditions. This rough estimation requires more detailed investigations because the alpine environment is very patchy. The influence of temperature on soil activities of the C- and N cycle in our study showed an apparent decoupling of *RTS* for the investigated activities, which may alter the composition of soil organic matter in terms of quality and quantity under global warming.

2 Zusammenfassung

In der vorliegenden Arbeit wurden Netto-CH_4- und Netto-CO_2-Emissionen alpiner Standorte der österreichischen Ostalpen untersucht. Vier Standorte (ein Trockenrasen, drei Moorstandorte innerhalb eines natürlichen Wassergradienten) wurden ausgewählt und der Einfluss abiotischer (Strahlung, Temperatur, Bodenwassergehalt) und biotischer (oberirdische Pflanzenbiomasse) Umwelteinflüsse auf das tägliche und saisonale Emissionsmuster untersucht. Um den Einfluss der Temperatur auf die Kohlenstoff- und Stickstoff-Vorkommen im Boden zu untersuchen, wurden die Temperaturabhängigkeiten von C- und N-Umsätzen bestimmt.

Der erste Teil der Arbeit befasst sich mit Netto-Methanflüssen, gemessen über einen Zeitraum von 24 Monaten. Während der schneefreien Zeit wurden 19-116 mg CH_4 m^{-2} d^{-1} für die Moorstandorte ermittelt. Während der schneebedeckten Zeit waren diese Flüsse viel geringer und betrugen 18-59% der jährlichen Gesamtemissionen. Der Trockenrasen stellte während der schneefreien Zeit eine kleine Senke für Methan (-2.1 mg CH_4 m^{-2} d^{-1} (2003); -1.0 mg CH_4 m^{-2} d^{-1}(2004)) dar. Diese Netto-Methanaufnahme des Trockenrasens korrelierte positiv mit der Bodentemperatur und negativ mit dem wassergefüllten Porenvolumen des Bodens (*wfps*). Im Moor ließ sich eine Beziehung des saisonalen Methanflusses mit der Bodentemperatur und dem Grundwasserstand finden. Die oberirdische grüne Pflanzenbiomasse korrelierte nur mit dem Netto-Methanfluss der Moorstandorte mit hohen Grundwasserständen. Diese Untersuchung belegt, dass alpine Moore ganzjährige Methanquellen sind, während ein alpiner Trockenrasen eine Methansenke innerhalb der schneefreien Zeit darstellt.

Gegenstand des zweiten Teiles der Arbeit war die Berechnung einer CO_2-Bilanz basierend auf Tagesgängen von Gasflussmessungen. Berücksichtigt wurden dabei der Einfluss von photosynthetisch aktiver Strahlung (*PAR*), der grüne Pflanzenflächenindex (*GAI*), die Bodentemperatur und das *wfps.* Bei Tageslicht wurden die Netto-Emissionsraten innerhalb der schneefreien Zeit von *PAR* und *GAI* gesteuert. Die Netto-Emissionsraten während der Nachtzeit korrelierten positiv mit der Bodentemperatur. Niedrige *wfps*-Werte führten dabei zur Verringerung der Flussraten auf dem Trockenrasen und der trockenen Moorfläche, wohingegen die Kohlenstoffverluste auf den vernässten Moorstandorten zunahmen. Während der schneefreien Zeit betrug der durchschnittliche Netto-CO_2-Gewinn des Trockenrasens 3.5 g CO_2 m^{-2} d^{-1} und für die Moorstandorte 1.5 bis 3.4 g CO_2 m^{-2} d^{-1}. Die durchschnittliche Atmung der Standorte während der schneebedeckten Periode war niedrig: -0.9 g CO_2 m^{-2} d^{-1} für den Trockenrasen und -0.2 bis -0.7 g CO_2 m^{-2} d^{-1} für die Moorstandorte. Unabhängig vom Wasserhaushalt waren alle Standorte, gemittelt über beide Untersuchungsjahre, signifikante

Netto-C-Senken (50 bis 121 g C m^{-2} a^{-1}). Die Ergebnisse zeigen, dass bei heutigen Klimaverhältnissen alpine Moore mit ihrem großen Kohlenstoffvorrat keine weitere Kohlenstofffestlegung im Vergleich zu alpinen Trockenrasen erwarten lassen.

Die Temperatur stellt einen bedeutenden Faktor für die Regulierung biologischer Aktivitäten dar. Deshalb wurde in der dritten Untersuchung die Temperaturabhängigkeit der bodenbürtigen C-Mineralisation, N-Mineralisation und potentieller Enzymreaktionen des C- und N-Kreislaufes (ß-Glucosidase, ß-Xylosidase, *N*-acetyl-ß-Glucosaminidase, Tyrosin-Aminopeptidase, Leucin-Aminopeptidase) für einen Temperaturbereich von 0-30°C ermittelt. Das Ziel war es, Q_{10}-Werte und die relative Temperaturabhängigkeit (*RTS*) zu berechnen sowie den Einfluss verschiedener Jahreszeiten (Sommer, Herbst, Winter) und standortsspezifischer Faktoren zu ermitteln.

Die Q_{10}-Werte der C-Mineralisation (2.0) waren signifikant höher als die der N-Mineralisation (1.7). Die Q_{10}-Werte beider Aktivitäten korrelierten negativ mit der Substratqualität. Die chemischen Bodeneigenschaften, der mikrobielle Kohlenstoffgehalt und der Zeitpunkt der Probenahme zeigten keinen Einfluss auf die Q_{10}-Werte. Die berechneten *RTS*-Werte machten deutlich, dass die Temperaturabhängigkeit mit abnehmender Temperatur zunahm. Die C- und N-Mineralisation und die potentiellen Aminopeptidaseaktivitäten (Tyrosin, Leucin) wiesen eine fast konstante Temperaturabhängigkeit über den Temperatur-bereich von 0-30°C auf. Im Gegensatz dazu zeigten ß-Glucosidase, ß-Xylosidase und *N*-acetyl-ß-Glucosaminidase einen ausgeprägten Anstieg der Temperaturabhängigkeit mit abnehmender Temperatur. Die vorherrschende tiefe Temperatur der Probenahme im Winter verursachte einen stärkeren Anstieg der *RTS* als dies für die Probenahme im Herbst und Sommer der Fall war. Diese Ergebnisse deuten zum einen auf eine Disproportionalität der *RTS* von potentiellen C-Enzymaktivitäten und N-Enzymaktivitäten hin und zum anderen auf eine Disproportionalität der Mineralisation von leicht verfügbaren C-Verbindungen (ß-Glucose, ß-Xylose) im Vergleich zur C -Mineralisation der bodenbürtigen organischen Substanz in alpinen Böden. Daher könnte die Temperatur eine wichtige Rolle bei der Regulierung des Abbaus unterschiedlicher Fraktionen der organischen, bodenbürtigen Substanz darstellen.

Zusammenfassend lässt sich feststellen, dass klimatische Eigenschaften bedeutend für Netto-Emissionen der Klimagase CO_2 und CH_4 in alpinen Ökosystemen sind. Netto-N_2O-Flüsse ließen sich auf keinem Standort finden. Geht man von einer geringen Gesamtmoorfläche der alpinen Zone Österreichs (0.14%) im Vergleich zum alpinen Rasen (78.3%) aus und überträgt die Daten auf eine regionale Ebene (unter Ausschluss vegetationsfreier Flächen), so stellen die Alpen eine kleine CH_4-Senke (|0.14| g CH_4 m^{-2} a^{-1}) und CO_2-Senke (|420 g| CO_2 m^{-2} a^{-1}) bei heutigen Klimaverhältnissen dar.

Diese grobe Abschätzung bedarf jedoch weiterer Untersuchungen, da die alpine Zone sehr kleinräumige und vielseitige Landschaftsstrukturen aufweist. Der Einfluss der Temperatur auf die bodenbürtigen C- und N-Aktivitäten war unterschiedlich. Die ausgeprägte Entkopplung der *RTS* der untersuchten Aktivitäten könnte die Zusammensetzung der organischen Bodensubstanz hinsichtlich einer globalen Klimaerwärmung qualitativ und quantitativ verändern.

3 General introduction

Today, global climate change is a very important topic of interest for both the public and the scientific community. A global temperature rise is predicted associated with the increasing atmospheric concentration of trace gases like methane (CH_4), carbon dioxide (CO_2) and nitrous oxide (N_2O) [*IPCC*, 2001]. Since preindustrial time, the CO_2 concentration in the atmosphere has continuously increased from 280 to 367 ppm and is expected to further increase in a range of 478 to 1099 ppm by the year 2100; during this same period, CH_4 emissions have increased, but the current atmospheric concentration has stabilized at 1.75 ppm. The global climate change debate led for example to the "Kyoto Protocol" in 1997, which was ratified recently. The overall goal is to reduce climate-relevant trace gas emissions. However, the agreement has only marginally changed the increasing global emission trend. These climate-relevant gases function like glass panels of a greenhouse, absorbing long wave radiation reverberating from the Earth's surface. Thus, the heat energy remains in the atmosphere and a global temperature increase (range: 1.4 to 5.8°C) is predicted for the next 100 years [*IPCC*, 2001]. Global warming may well be unevenly distributed. A recent study predicted a more intensive increase of mean summer temperature for the European Alps than for temperate regions in Europe [*Heimann and Sept*, 2000].

There is a major discussion on whether agro-, forest- or natural ecosystems function as sinks or sources of climatic trace gases. Global Change may cause positive feedback mechanisms for the carbon balance of terrestrial ecosystems [*Schlesinger and Andrews*, 2000]. Moreover, cold-adapted alpine environments are expected to respond very sensitively to global warming. Soils are the basis of terrestrial ecosystems, and the contribution of soil nutrients within the overall ecosystem is much higher in northern- or high-elevation ecosystems than elsewhere [*Körner*, 1999]. Carbon and nitrogen are the largest nutrient pools in soils. Since these pools are linked, the influence of temperature on both carbon and nitrogen transformations is crucial with respect to global warming.

3.1 Methane and carbon dioxide cycle of ecosystems

3.1.1 Carbon pools and C cycle

Globally, about 1400 10^{15} g carbon is stored in soils [*Post et al.*, 1982], while wetlands contribute more than 30% of this total amount (455 to $700 \cdot 10^{15}$ g). This is the third highest contribution of global carbon stock after oceans ($38600 \cdot 10^{15}$ g) and sources of fossil fuels ($10000 \cdot 10^{15}$ g). Landscapes at northern latitudes and high elevations account for a significant percentage of the Earth's land surface and include arctic tundra, boreal forest, temperate forest, sub alpine forest, and alpine tundra [*Bouwman*, 1990], while alpine tundra covers about 8% of the terrestrial global surface (10.5 million km^2) [*Archibold*, 1995].

CO_2 and CH_4 are the most important components of the C cycle from ecosystems [e.g. *Conrad*, 1996]. The metabolic rate of these gases is dynamically coupled with the atmosphere. Soils function as sources or sinks for CO_2 and CH_4. However, the absolute values of the total budget and the percental contribution by soils should be accepted with caution, because the individual sources and sinks strengths are highly uncertain [*Conrad*, 1996]. The problem is that the fluxes generally show a high variability with respect to site and time. Especially in alpine regions, this landscape pattern is very patchy and characterized by a high variation in length of vegetation period, vegetation cover, water regime and climatic or microclimatic properties [*Bowman and Fisk*, 2001].

3.1.2 Methane cycle

Under anaerobic soil conditions the mineralization end product is mainly CH_4, which contributes about 1% of total carbon mineralization. Important intermediate products of the anaerobic pathway are acetate, carbon dioxide, hydrogen and various alcohols that are further reduced to methane [*Deppenmeier et al.*, 1996]. Methanogenic archaea are widespread and always associated with anaerobic bacteria because they are unable to use complex organic compounds. Furthermore, methane production competes with anaerobic bacteria using the same substrates but other potential electron acceptors (NO_3^-, Mn^{4+}, Fe^{3+}, SO_4^{2-}) than CO_2. Under aerobic soil conditions, methanothrophic bacteria using O_2 as an electron acceptor can oxidize CH_4. Methanotrophs in aerated soil layers of wetland are characterized by a much lower CH_4 affinity than methanotrophs found in upland soils, which exclusively utilize the atmospheric methane concentration (1.75 ppm) as an energy source [*Conrad*, 1996].

Methane flux from wetland soils to the atmosphere is the net result of anoxic methane production, methane oxidation in aerated soil layers and transport from belowground to the atmosphere [e.g. *Conrad*, 1996]. Methane transport is the result of diffusion through water,

aerated soil matrix or plant-mediated transport via the aerenchyme. For waterlogged soil conditions, plant-mediated methane transport may account for almost 100% of total net flux [*Kelker and Chanton*, 1997]. This is because methane diffusion in air is much higher than in water. Methane transport by diffusion in drained surface layers of wetlands is controlled by methanothrophic bacteria, which can oxidize most of methane produced before it reaches the atmosphere [*Hanson and Hanson*, 1996]. The main abiotic controls of methane flux from wetlands are water table position and temperature. The water table triggers the vertical distribution of anoxic methane production and methane oxidation and transport via water, air and plants. The influence of temperature on net methane emission depends on the vertical allocation of methane production (and/or competitive processes) and methane oxidation, because all processes generally depend on temperature. In addition, the temperature distribution within the vertical soil matrix may also control net methane flux.

In upland soils, methanotrophs exclusively utilize atmospheric methane concentration as energy source, leading to net sinks for methane in these ecosystems. Ammonium has been found to competitively inhibit atmospheric methane oxidation [*de Visscher and van Cleemput*, 2003]. The main controls of atmospheric net methane uptake are soil porosity and soil water content, which control gas diffusion into the atmosphere; this is followed by soil temperature, which seems to be less important [*Conrad*, 1996].

Wetlands are the largest natural source of methane flux to the atmosphere, and northern and high-elevation wetlands account for a third of this natural source [*IPCC*, 2001]. Climatic properties are important controls for seasonal methane flux. High-latitude and high-elevation ecosystems are characterized by short vegetation periods and long snow periods; however, net methane fluxes during snow periods comprise a significant part of the annual budget and should not be ignored [*Schmidt et al.*, 2001]. Alpine tundra serves as sources and sinks for atmospheric methane, depending on landscape patterns [*West et al.*, 1999]. However, our knowledge is limited to studies in the Rocky Mountains [*Chimner and Cooper*, 2002; *West et al.*, 1999; *Wickland et al.*, 2002] and the Tibetan Plateau [*Hirota et al.*, 2004], and no data are available for the European Alps. Because of the complexity of various controls for net methane flux and the patchy landscape in the alpine environment worldwide, seasonal investigations of net methane flux and abiotic and biotic controlling factors will improve our knowledge of the alpine environment with respect to the global budget.

3.1.2 Carbon dioxide cycle

Ecosystems exchange carbon dioxide with the atmosphere; this cycling is the major part of the C cycle for ecosystems. Carbon dioxide is sequestered by vegetation via photosynthesis, stored as carbon in the soil matrix, or released again to the atmosphere by total ecosystem respiration (plants, animals, microflora) [e.g. *Körner*, 1999]. Plant photosynthesis is greatly influenced by irradiation, the phenological status of the vegetation and length of the snow-free period. Total ecosystem respiration in the alpine environment mainly depends on temperature, plant biomass and soil water content [*Cernusca and Decker*, 1989].

The C budget of mature quasi-stable ecosystems is commonly balanced. In contrast, northern wetlands have built up a large carbon stock (270 to 370 Pg) since the last deglaciation by accumulating atmospheric carbon dioxide [*Turunen et al.*, 2002]. This is due to the slow decomposition rate favoured by water-logged anoxic conditions. The long-term rate of carbon accumulation in wetlands also depends on their age and water balance. The rate was lower for old than young boreal fens, and lower for drained than undrained fens [*Turunen et al.*, 2002]. The ecosystem carbon dynamics are sensitive to global change, leading to slower accumulation of carbon. First, global warming has the effect of reducing soil organic carbon by stimulating decomposition rates more than net ecosystem productivity [*Kirschbaum*, 2000]. Second, the water balance of ecosystems is likely to change. Soils may become drier during the vegetation period due to lower precipitation in summer and increasing evapo-transpiration. This may have a higher impact on wetlands than other ecosystems because the anoxic soil layers are reduced. Third, there is no evidence that an increasing atmospheric CO_2 concentration leads to a higher net ecosystem carbon gain via photosynthesis. Although leaf photosynthesis of plants is generally more efficient at higher CO_2 partial pressure, ecosystem net carbon gain was not affected by doubled CO_2 concentration in alpine tundra compared to ambient conditions [*Diemer and Körner*, 1998]. This means that we already live in a carbon-saturated environment and other factors are more important for limiting net plant productivity.

Our knowledge about the annual carbon balance under the present climate in high-elevation ecosystems (above tree line) is mainly limited to the productivity of the above-ground and below-ground plant biomass combined with data on ecosystem respiration. Annual or seasonal ecosystem net CO_2 flux data from the alpine tundra (above the tree line) or high-elevation wetlands are rare; studies are only available from the Rocky Mountains [*Welker et al.*, 1999; *Wickland et al.*, 2001], the Tibetan plateau [*Hirota et al.*, 2006; *Kato et al.*, 2004] and the Swiss Alps [*Diemer and Körner*, 1998]. Literature data show large differences for ecosystem respiration, ecosystem net carbon gain, contribution of CO_2 flux during snow periods and annual carbon balance. The high variability of data probably reflects

site-specific differences. Because of the patchy landscape pattern, more investigations are necessary to estimate the global carbon budget of alpine ecosystems.

3.2 Temperature effects on soil C- and N dynamics

All biochemical processes depend on temperature. The temperature dependence is of great interest for understanding temperature responses of nutrient cycling to global warming. The strong effect of temperature on decomposition has been quantified for many soils under different conditions (e.g. *Lloyed and Taylor*, 1994; *Kirschbaum*, 1995; *Kätterer et al.*, 1998; *Fierer et al.*, 2006). The temperature quotient (Q_{10}) gives the ratio of activities for a 10°C change and is often used in the literature. First-order exponential functions, yielding constant Q_{10} values, have been frequently applied. However, there is still no consensus about the relation of biochemical processes to temperature. Relative temperature sensitivity, which describes increasing temperature sensitivity with decreasing temperature using linear, power and Arrhenius-type functions, has been less used [*Kätterer et al.*, 1998]. Based on this relative temperature sensitivity (*RTS*), cold-adapted soils should be more sensitive to global warming than soils from warmer regions. However, a large range of temperature sensitivity of C mineralization has been reported in the literature. There is evidence that this variation is negatively related to substrate quality of the soil organic matter [*Fierer et al.*, *2006*]. Furthermore, the variability is due to climatic adaptation, whereby cold-adapted soils have a lower temperature sensitivity than soils from warmer regions [*Dutzler-Franz*, 1981; *Fierer et al.*, *2006*].

Net N mineralization appears to be less temperature sensitive than C mineralization (especially at low temperature) when using data of a wide range of incubation temperatures and different soils [*Kirschbaum*, 1995; *Kirschbaum*, 2000]. Since most ecosystems are N limited, a low temperature dependence of activities in the N cycle could also be an adaptation to maintain sufficient nutrient supply, especially during cold seasons. Since N mineralization depends on the C- to N ratio of substrate, the high variability is also linked to chemical soil properties. So far, no efforts have been made to relate the temperature sensitivity of gross N mineralization to substrate quality of soil organic matter. Moreover, no investigations are available about the climatic adaptation on the temperature sensitivity of soil N mineralization and the comparison of different N dynamics within a soil.

Differences in the temperature sensitivity between C- and N dynamics may cause a decoupling of soil processes, leading to qualitative and/or quantitative changes of soil organic matter with respect to global warming. Extra-cellular soil enzymes are involved in these processes and catalyze the rate-limiting steps of decomposition and nutrient cycling

[*Sinsabaugh*, 1994]. In a recent study*, Trasar-Cepeda et al.* [2007] investigated the temperature sensitivity of a wide range of enzyme activities within a given soil; they reported differences in temperature sensitivity and temperature optimum. No comparison of temperature effects on enzyme activities and the overall mineralization of C- and N pools has yet been conducted.

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4 Outline of the thesis

Investigations about climate-relevant trace gas emissions from alpine regions are still rare. The objectives of this study were to quantify net CH_4 and net CO_2 fluxes from alpine sites in the Eastern Alps, Austria. The aim was to identify abiotic and biotic drivers influencing the diurnal and seasonal net fluxes of these climatically relevant trace gases in alpine environemnt. The third part of this thesis deals with the temperature sensitivity of different soil activities of the C- and N cycling in order to deepen our understanding of temperature effects on nutrient cycling in alpine soils.

Four study sites (2250 m a.s.l.) in the Eastern Alps, Austria, were selected for analysis: one alpine meadow site (used as pasture) and three fen sites following a natural water gradient. All study sites are characterized by different plant communities representing quasi-stable major ecosystem stages being developed for 5000 to 10000 years.

In the first and second part of this thesis, the diurnal and seasonal variation of net CH_4 and net CO_2 fluxes were measured in a field study using the “closed chamber method” over an entire period of 24 months. Net fluxes were related to potential drivers: soil temperature (in 5, 15, 35 cm), water-filled pore space (in 5 cm), water table position, radiation and above-ground standing plant biomass. Based on empirical models, we upscaled trace gas emissions to quantify diurnal and seasonal (snow-free, snow period) flux in order to gain information about the annual C budget in this alpine region.

In alpine environments, temperature is important for regulating biological processes. In the third part of the thesis, the temperature sensitivities (0-30°C) of activities in the C- and N cycle (C-, N mineralization and enzyme activities of the C- and N cycle) were determined for three seasons (summer, autumn, winter). It was hypothesized that (i) C mineralization has a higher temperature sensitivity than N mineralization, (ii) the temperature sensitivity of both activities depends on substrate quality of the soil organic matter, (iii) all activities of the winter sampling are less temperature dependent than during the vegetation period and (iv) that the relative temperature sensitivity of all activities increases with decreasing temperature.

5 Seasonal and diurnal net methane emissions from organic soils of the Eastern Alps, Austria: effects of soil temperature, water balance and plant biomass

5.1 Abstract

Although the contribution of methane emission to global change is well recognized, analyses of net methane emissions derived from alpine regions are rare. Therefore, three fen sites differing in water balance and plant community, as well as one dry meadow site, were used to study the importance of soil temperature, water table and plant biomass as controlling factors for net methane emission in the Eastern Alps, Europe during a period of 24 months. Average methane emissions during snow-free periods in the fen ranged between 19 and 116 mg CH_4 m^{-2} d^{-1}. Mean wintertime emissions were much lower and accounted for 18 to 59% of annual flux. The alpine dry meadow functions as a methane sink during snow-free periods, with mean flux of -2.1 mg CH_4 m^{-2} d^{-1} (2003) and -1.0 mg CH_4 m^{-2} d^{-1} (2004). Seasonal methane emissions of the fen were related to soil temperature and groundwater table. During the snow-free periods the water table was the main control for seasonal methane emission. The net methane flux related to water table was much higher for the distinctly drier year 2003 than for the wetter year 2004. Methane emissions differed diurnally at sites where the water table position was high or very low. The influence of total above-ground biomass on methane emission was apparent only for those sites with high water table positions. Seasonal and diurnal methane uptake of the dry meadow was related to soil temperature and water-filled pore space, whereas plant biomass did not significantly influence methane fluxes. Our studies gave evidence that fens in the Eastern Alps act as a source of methane throughout the whole year and that a dry meadow site act as net methane sink during snow-free periods.

5.2 Introduction

Methane is an important greenhouse gas and the atmospheric concentration has increased (0.8% a^{-1}) during the past few decades more than CO_2 (0.5% a^{-1}) [*Moisier et al.*, 1998]. Methane emission from wetlands accounts for roughly 70% of natural methane sources [*Khalil*, 2000]. Recent studies of methane sources have focused on high-latitude wetlands because they store about 30% of the global carbon pool in the soil [*Gorham*, 1991]. Methane emissions from alpine tundra regions are often compared with northern tundra ecosystems. Our knowledge of net methane emissions from alpine environments, however, is only limited to North America [*Chimner and Cooper*, 2003; *Mast et al.*, 1998; *West et al.*, 1999; *Wickland et al.*, 2001] and to recent investigations in the Tibetan Plateau [*Hirota et al.*, 2004]. Model estimations from ecosystems across the entire pan-arctic region (area north of 45°N) revealed a net methane flux of 51.0 Tg CH_4 a^{-1} including a small net gain for Austria of 0 to -1 g CH_4 m^{-2} a^{-1} [*Zhuang et al.*, 2004]. A wide range of mean daily net methane fluxes from various alpine dry or wet tundra (-0.77 mg CH_4 m^{-2} d^{-1} to 8.45 mg CH_4 m^{-2} d^{-1}) and alpine wetlands (33 mg CH_4 m^{-2} d^{-1} to 251 mg CH_4 m^{-2} d^{-1}) have been reported. However, there are no available data for net methane flux from alpine environments of the European Alps. Since alpine tundra covers an area of roughly 10.5 million km^2 globally [*Archibold*, 1995] and the variability of net methane fluxes from alpine ecosystems is high, more precise investigations are necessary to estimate the role of alpine environments for the global CH_4 budget.

In general, methane flux rates from wetlands are the net result of CH_4 production (anaerobic), CH_4 oxidation (aerobic) and CH_4 transport from belowground to the atmosphere [*Bubier and Moore*, 1994; *Conrad*, 1996]. The main controls for various methane-emitting environments are water table, temperature [*Bubier et al.*, 2005; *Rask et al.*, 2002] but also peat chemistry [*Yavitt et al.*, 2005]. In addition, plant community and plant biomass have been found to influence net methane emissions considerably [*Bellisario et al.*, 1999; *Schimel*, 1995].

Methane is released from soils either from ebullition of biogenic gas bubbles, diffusion or plant-mediated transport [e.g. *Bubier and Moore*, 1994]. The diffusion of methane is only important for aerated soil pores because diffusion in air is 10^4 times higher than in water [*Schachtschabel et al.*, 1998]. The role of plant communities may be important, since diffusion of methane via plants may account for 37 to 100% of total net methane flux in various moist tundra regions and wetlands [*Schimel*, 1995; *Kelker and Chanton*, 1997; *Hirota et al.*, 2004]. Diurnal variations of net methane emissions have been investigated for various methane-emitting environments [*Mikkelä et al.*, 1995; *Thomas et al.*, 1998]. Diurnal emission patterns have been related to radiation, plant biomass, soil temperature or redox potential. So far, only a few plant species or plant communities have been investigated.

Hence, the overall daily variation of methane emission remains poorly understood; but it often differs considerably between vegetation types and depends on total plant biomass and soil water conditions.

In well-drained soils, methanotrophs can utilize atmospheric CH_4 (1.75 ppm) for biomass production. These adapted "high affinity" methanotrophs are related, but not identical, to type II methanotrophs and are different from those ("low affinity" methanotrophs) of wetlands [*Conrad*, 1996]. Hence, unsaturated soils represent the only biological net sink for atmospheric methane, in contrast to wetlands [*Conrad*, 1996]. Alpine tundra ecosystems have been found to act as net sinks and sources for atmospheric methane depending on the moisture conditions and soil temperature [*Mast et al.*, 1998; *Wickland et al.*, 1999; *West et al.*, 1999].

The objectives of this study were to (I) quantify the seasonal variation of net methane emissions and (II) determine key factors controlling the diurnal and seasonal patterns of net methane emission derived from soils of the alpine zone in the European Alps. Four study sites (dry meadow and three sites in a fen) differing in vegetation type and water balance were selected and monitored over a period of two years.

5.3 Material and methods

5.3.1 Study area

This research was conducted in the Ötztal range (46°50´N, 11°03´E) in Tyrol, Austria, at an altitude of 2250 m a.s.l. The research area lies in the Rotmoos valley above the present tree line (Fig. 5.1B). The valley is flanked by the mountain Hohe Mut (2659 m a.s.l.) and the mountain Hangerer (3021 m a.s.l.) and is exposed south to northwest. According to *Hoinkes and Thöni* [1993], the principal basic material consists mainly of mica slate and silicate. The climate has a continental character with cool summers and cold, snowy winters. The snow-free period is about 4.5 months (June to mid-October) (M. Strobel, University of Innsbruck, personal communication) with a mean annual precipitation of 820 mm (1970-1996). The mean annual air temperature for 1997-1998 was -1.3°C [*Kaufmann*, 2001]. The study sites are located in the Rotmoos fen (Fig. 5.1C). The Rotmoos measures 8.5 ha, with an average peat depth of 1.5 m (range 0.5-2.9 m) [*Rybníček and Rybníčková*, 1977] (Fig. 5.1D). It is fed mainly by the water flowing down the hill slopes of the flanking mountains. The peat water drains into the glacial stream of the Rotmoosferner glacier. The oldest organic layer at the bottom of the peat is around 5200 years old [*Bortenschlager*, 1970]. During peat formation the Rotmoos was periodically overwhelmed with 15 layers (1-27 cm) of silt or sand sediments (or both). The deepest and oldest layer is

eolian while the others were glacial or colluvial [*Rybníček and Rybníčková*, 1977]. Nearly all sediment layers are located 2 m below the peat surface.

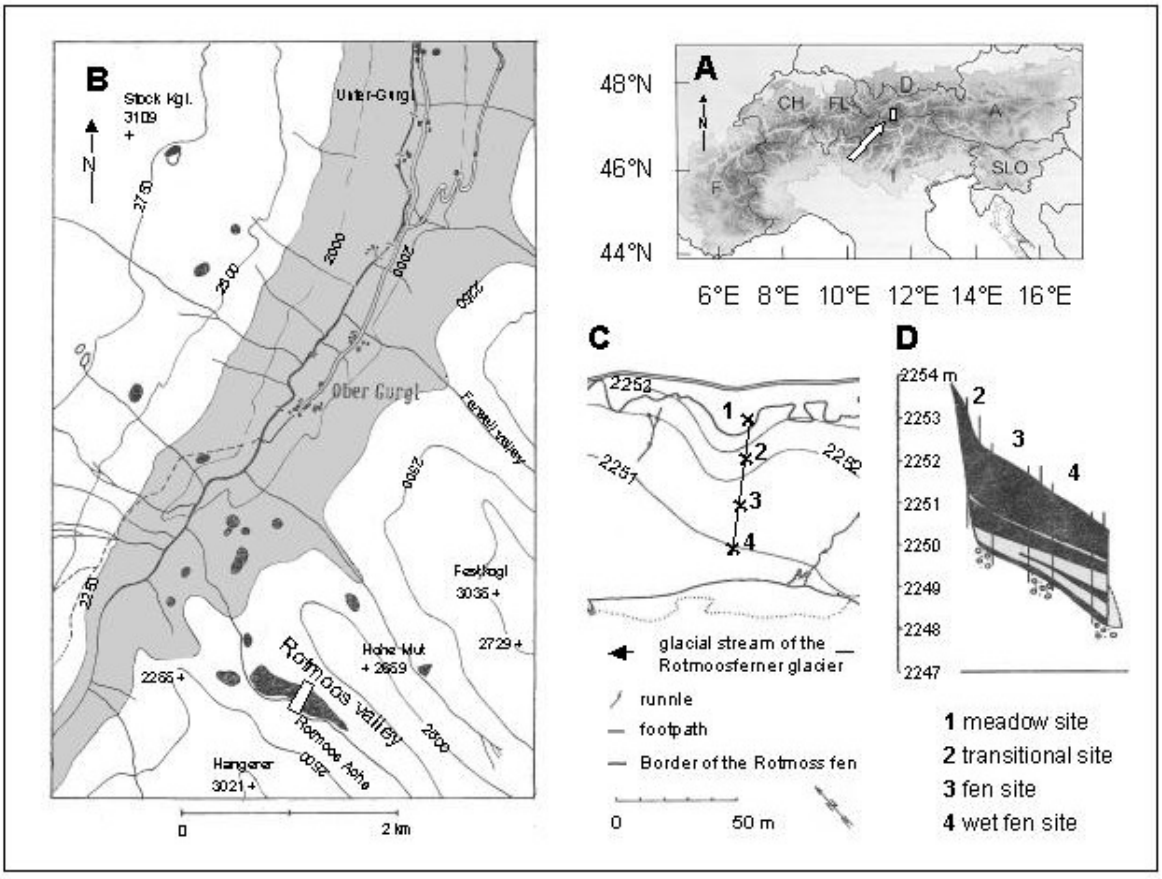

Figure 5.1: (A) Geographical position of the study area in the European Alps (A=Austria, CH=Switzerland, D=Germany, F=France, FL=Liechtenstein, I=Italy, SLO=Slovenia). (B) Distribution of alpine fens in the study area (black locations); the gray area in the map represents the potential tree area below 2250 m a.s.l. (C) Position of the study sites outside and within the Rotmoos fen. (D) Peat profile of the Rotmoos fen (only major sediment layers are illustrated) (Fig. 5.1B - 5.1D modified from Rybníček and Rybníčková, 1977).

5.3.2 Study sites

Four study sites were chosen (one alpine dry meadow and three sites in the Rotmoos fen). They differ in water balance and vegetation community. All sites have a southwest exposure and 1-4° slope. The study sites are traditionally used as a pasture for sheep and horses. At the dry meadow site, these domestic animals were more frequent compared to the fen sites. The first site is an alpine meadow (*meadow*), which was classified as a *Curvulo-Nardetum* (G.-H. Zeltner, University of Hohenheim, personal communication) and is relative rich in herbs. The soil (maximum depth 50 cm) is a Cambisol out of loamy sand over scree. The *meadow* is well-drained over the snow-free period, and 90% (10% small boulders) of the soil surface is covered by vegetation. The herbs here are *Alchemilla vulgaris* L.,

Anthoxanthum odoratum L., *Anthyllis vulneraria* L., *Campanula cochlearifolia* Lamk., *Campanula scheuchzeri* Vill., *Dianthus carthusianorum* L., *Euphrasia alpina* Lamk., *Euphrasia minima* Jacq. Ex. DC., *Gentiana ramosa* L., *Geum montanum* L., *Hippocrepis comosa* L., *Leonthodon helveticus* Mérat, *Ligusticum mutellina* (L.) Crantz, *Phyteuma hemisphaericum* L., *Potentilla aurea* L., *Rhinantus angustifolius* C.C. Gmelin, *Silene vulgaris* (Moench.) Garcke. Grass species are *Carex curvula* All., *Carex flava* L., *Carex sempervirens* Vill., *Deschampsia cespitosa* (L.) P.B., *Luzula campestris* (L.) DC., *Nardus stricta* L., *Poa alpina* L. The shrubs are *Calluna vulgaris* (L.) Hull, *Salix herbacea* L., *Rhododendron ferrugineum* L. and *Vaccinium myrtillus* L. The surface cover of each species was less than 5%, except for *Nardus stricta* (10%).

The second study site (*transitional*) is located in the transition area between *meadow* and the Rotmoos fen. The vegetation is described as a *Carici echinatae-Trichophoretum caespitosi* community [*Rybníček and Rybníčková*, 1977]. Additionally, a relative high cover of plant species belonging to *Curvulo-Nardetum* was observed. The surface of the *transitional* site is completely covered by vegetation, with the dominant species (and their cover) being, Herbs: *Bartsia alpina* L. (<5%), *Homogyne alpina* (L.) Cass. (<5%), *Leonthodon hispidus* L. (<5%), *Ligusticum mutellina* (5%), *Potentilla aurea* (10%), grass species: *Carex echinata* Murray (5%), *Eriophorum angustifolium* Honck. (20%), *Nardus stricta* (20%), *Trichophorum caespitosum* (L.) Hartman (30%), shrubs: *Calluna vulgaris* (<5%). The third site (*fen*) is located in the Rotmoos fen and is characterized by a typical *Carici echinatae-Trichophoretum caespitosi* plant community. The *fen* site has lower species richness than the *transitional* site. Dominant species and their cover (in parentheses) are *Carex echinata* (5%), *Carex nigra* (L.) Reichard (<5%), *Eriophorum angustifolium* (40%) and *Trichophorum caespitosum* (60%). The fourth study site (*wet fen*) is located in the centre of the Rotmoos fen and consists solely of *Carex nigra*, which covers 30% of the soil surface. This site can be temporarily flooded by groundwater. All soils of the Rotmoos fen (*transitional*, *fen* and *wet fen*) were classified as Rheic Histosols, with observed soil depths deeper than one meter (Fig. 5.1D).

5.3.3 Methane measurements

The methane flux rates were measured using the static closed chamber method. During the snow-free period, we used chambers consisting of a quadratic frame (40 cm x 40 cm x 30 cm) and a lid with an inserted septum. The chambers were equipped with a small battery-driven fan that allowed circulation of the enclosed air. The material was acrylic glass, highly porous for photosynthetic active radiation (89%). Three chambers per site were carefully inserted 3 cm into the soil at least 15 h before each measurement started. Because of moderate grazing (sheep and horses) the frames had to be removed between the

sampling days, but the exact location of each chamber was discernible throughout the snow-free periods. On each site, one chamber was provided with a common resistance thermometer 5 cm above ground level for estimating the temperature difference inside and outside the chamber. Three stainless steel pots (diameter 15.5 cm; 25.0 cm height) per site were used for gas measurements during the snow periods. After the snow was removed from an area of about 2 m x 2 m at each study site, the steel pots were placed gently on the soil surface and sealed with wet snow. After the gas sampling, the area was covered with snow again. Gas samples were collected using evacuated flasks (22.5 ml) with butyl-rubber septum. Prior to sampling, the flasks were evacuated 5 times and flushed with nitrogen in the laboratory. Gas samples were collected approximately every 3 weeks within the snow-free season 2003 (n=7) and once a month during the snow-free season 2004 (n=4). One tip of a double needle was inserted through the septum of the chamber lid and the other tip of the needle was inserted through a butyl-rubber septum of an evacuated flask. One sample drawing consists of four gas sub samples, which were drawn at 0, 6, 20 and 30 min after the chamber was closed. During snow-free periods, gas samples were taken every 3 h to account for diurnal changes, yielding eight independent samples per day. The sampling procedures (n=10 for each site) always started at noon and ended at 9:00 the following day. During the snow periods, one sample drawing (time intervals 0, 30, 60 and 90 min) at about noon was done in intervals of 1 to 3 months (n=11 for each site).

Methane concentrations were measured using a flame ionisation detector in a Perkin Elmer (PE Auto system and PE Headspace Sampler HS 40XL) gas chromatograph. Chromatographic separations were made using a 6 ft stainless steel column packed with Poropak Q (100/120 mesh). The oven of the column and the detector was maintained at 40°C (oven temperature) and the detector was operated at 350°C. The oven had to be heated to 120°C for 10 min after each gas sample to prevent water accumulation in the column. Nitrogen was used as carrier gas, with a gas flow rate of 45 ml min^{-1}. Gas standards (1.0, 5.0 and 10.0 ppm CH_4) were used for calibration. All single values were corrected for air temperature and air pressure using the ideal gas law. This procedure allowed an analytical precision of 40 nl l^{-1}.

The flux rates were calculated from the linear slope of the increase (or decrease) of the methane concentration versus the accumulation time in the chamber. Not-significant regressions were rejected. This occurred in 4% of the cases (almost exclusively during winter sampling) and was probably due to sporadic events like ebullition.

5.3.4 Hydrology

Groundwater tables were measured at every fen site (*transitional*, *fen*, *wet fen*) with horizontally slotted (width 0.3 mm) PVC wells (total length 100 cm). One tube was installed on each fen site with a standard bucket auger. The space between the tubes and the peat soil was filled with silica sand (grain size 1.2-1.7 mm) to avoid accumulation of mud. The top was sealed with a PVC cap to prevent the direct contact of the groundwater with precipitation. Water tables were determined at every gas sampling date (n=22). Soil moisture on the *meadow* site was measured hourly with a soil moisture sensor SMS3 (Cylobios, Austria) at 5 cm below the soil surface. For calibrating the soil moisture sensor, three undisturbed soil cores (100 cm^3) were taken from 0-5 cm soil depth at every sampling date during the snow-free periods. The volumetric water content (θ) was determined gravimetrically after drying at 105°C for 48 h. For the conversion of the volumetric water content to water-filled pore space (*wfps*), the maximum saturation water content [g cm^{-3}] for the soil depth was determined in the laboratory. Briefly, undisturbed soil cores (100 cm^3; n=5) were slowly saturated with degassed water over a 4-day period and weighed before and after drying at 105°C for 48 h. A density for water of 1 g cm^{-3} was assumed and *wfps* [%] was calculated by the proportion of water content to the maximum saturation water content. Moisture data for the winter period were not used because values were not reliable due to frozen water.

Groundwater samples for chemical analysis and for the determination of dissolved methane concentration were taken from the PVC tubes at 20 cm below the water table. One sample per site was taken at each sampling date. Before sampling, the water in the tubes was pumped out and the soil solution that drained into the tubes was sampled after reaching the prior water level. Groundwater samples were collected with a syringe. Evacuated flasks (22.5 ml) were immediately filled one third and the remaining vacuum was balanced later with pure N_2 in the laboratory. The methane concentration in the headspace was measured by the same GC procedure as described above and was related to the sampled water. The amount of water and the corresponding headspace volume was determined gravimetrically. Dissolved methane concentrations were corrected by the Bunsen solubility coefficient for methane. All water samples for chemical analysis were filtered (PET 45/25; Macherey-Nagel, Germany) and kept frozen until analysis. DOC was determined with a Dimatoc 100 TOC/TN-analyzer, Dimatec, Germany, and ammonium and nitrate were photometrically determined. The pH was measured potentiometrically.

5.3.5 Plant biomass

Above-ground standing plant biomass was determined for every sampling date during the snow-free periods in 2003 and 2004. The plant biomass was calculated from 25 x 25 cm soil surface areas. Five replicates for each site were collected after randomly positioned a frame on the soil surface. After sampling, the plant material was stored in plastic bags and frozen at -20°C until analysis. The green and non-green biomass was separated and oven dried at 60°C for 72 h before weighing. Only the green biomass was considered for above-ground standing biomass.

5.3.6 Climate data

The climate data used in this study were provided by R. Kaufmann (University of Innsbruck; personal communication). The weather station (2270 m a.s.l.) is located 2 km away from the study sites, with an altitude difference of about 20 m. Air temperature, global radiation, precipitation and relative humidity were recorded every 15 min. The soil temperature at every study site was recorded hourly at 5 cm below the soil surface using temperature loggers (UTL-1, Geotest AG, Switzerland). Since June 2003, temperature was additionally recorded at 15 cm, as well as at 35 cm below the soil surface at all fen sites (*transitional*, *fen*, *wet fen*).

5.3.7 Statistics

In the snow-free periods, the net methane flux values per day [mg CH_4 m^{-2} d^{-1}] were obtained by summarizing the diurnal measurements [mg CH_4 m^{-2} h^{-1}] of one day (n=8 per day). For the snow periods the single measurement per day was assumed to be constant during the day. The cumulative annual flux was roughly estimated by linear interpolation between the sampling dates during the snow-free season and the mean flux during the snow periods (which was not statistically different between sampling dates). The length of the snow-free periods was defined as the time-frame between an abrupt increase and decrease of soil temperature (5 cm soil depth). Water tables were linearly interpolated. All given errors are standard errors.

The methane flux values were logarithmically transformed to obtain homogeneity of variance (Levene´s test). Differences in the methane flux of *meadow* between the sampling dates were tested by univariate analysis of variance. For the fen sites (*transitional*, *fen*, *wet fen*), a simple two-factorial analysis of variance (time and site) was applied to quantify variations in methane emissions according to sampling time and study site. The ANOVA was calculated separately for each snow and snow-free period. Additionally, the effect of season and study

site on the plant biomass was quantified using simple two-factorial analysis of variance (time and site). Stepwise multiple linear regression analyses were applied to evaluate the relationship between methane flux rates and environmental properties. The data of the seasonal and diurnal measurements were separated. The water table (*transitional*, *fen*, *wet fen*), water-filled pore space (*meadow*), soil temperature (5 cm soil depth) and dissolved methane concentration in the groundwater were used in the regression model to explain seasonal net methane flux. For the diurnal net methane flux, water table (*transitional*, *fen*, *wet fen*), water-filled pore space (*meadow*), soil temperature (5, 15, 35 cm soil depth), global radiation and plant biomass were included in the model. Partial correlation analysis was applied to determine the contribution of each environmental factor to the variation of methane emissions, while holding the other remaining factors in the regression equation constant. All calculations were carried out using Statistica 6.0 (StatSoft. Inc., Tulsa, USA).

5.4 Results

5.4.1 Climatic properties

The annual mean air temperature was -0.4°C (2003) and -1.3°C (2004). The mean annual soil temperature (5 cm) ranged between 3.5°C (*wet fen*; 2004) and 4.6°C (*wet fen*; 2003) (Fig. 5.2). The average snow-free period was 149 days (May 9 to October 5) and 123 days (May 27 to October 4) for 2003 and 2004, respectively. Temperature and precipitation differed considerably for both snow-free periods. The mean air temperature was 8.9°C (2003) and 6.4°C (2004). Precipitation during snow-free period was 276 mm (2003) and 326 mm (2004). In contrast, the mean global radiation was more balanced, being 218 W m^{-2} and 207 W m^{-2} for 2003 and 2004, respectively. The mean soil temperature ranged from 10.4°C (*wet fen*; -35 cm) to 13.0°C (*transitional*; -5 cm) and 8.4°C (*wet fen*; -35 cm) to 10.9°C (*transitional*; -5 cm) for the snow-free periods 2003 and 2004, respectively. Soil temperature showed large diurnal differences during the snow-free periods. The maximum temperature in 5 cm soil depth occurred at about 14:00–15:00 (Central European time) and minimum temperature at about 5:00–6:00. The maximum and minimum temperatures in 15 cm soil depth were roughly four to six hours later than at 5 cm, and the amplitudes between diurnal minimum and maximum temperature were much more dampened with increasing soil depth. During the snow periods, mean soil temperature was almost constant and ranged between 0.1°C (*meadow*, *fen*, *wet fen*) and 0.2°C (*transitional*) (Fig. 5.2). Due to the insulation of the deep snow cover (maximum 235 cm), the absolute minimum soil temperature (hourly recordings) reached -0.5°C in the topsoil. Neither diurnal differences nor differences between study sites were observed during snow periods.

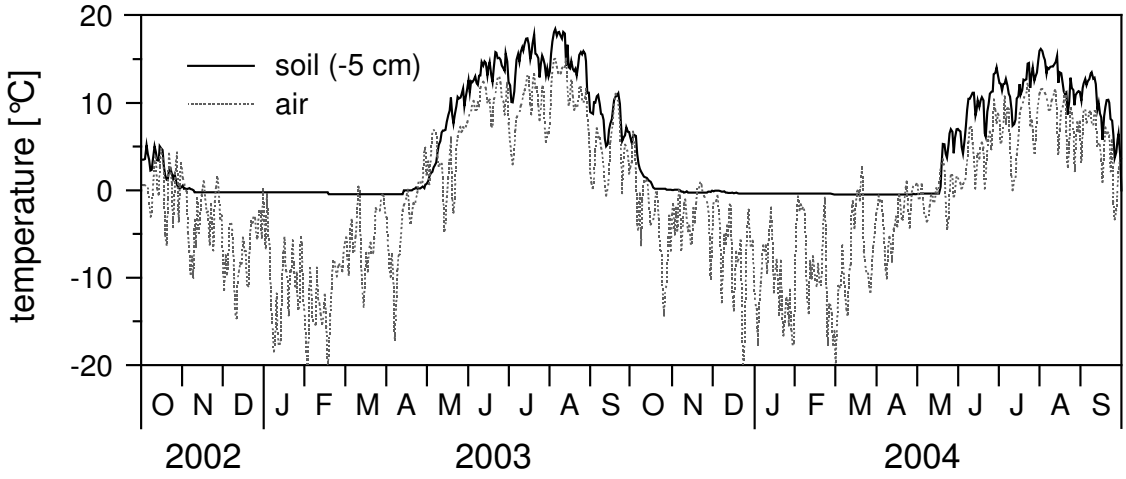

Figure 5.2: Time course of air temperature and soil temperature (5 cm depth) at the *transitional* site.

5.4.2 Hydrology

The interpolated average water table position for the entire study period increased in the order *transitional* (-32 cm) > *fen* (-9 cm) > *wet fen* (+1 cm) (Tab 5.1). The water table position for all fen sites remained almost constant during the winter (Fig. 5.3A). During the snow-free periods, the water tables of all fen sites decreased, reaching minimum values in August and then increasing again and remaining constant for the following winter period. The decline was much more pronounced during the snow-free period 2003 than for 2004. At *meadow*, the mean water-filled pore space (*wfps*) was much lower in 2003 (47%) than in 2004 (66%) throughout the snow-free season (Tab. 5.1). Four distinctive desiccation periods were observed in 2003, whereas *wfps* was much more balanced in 2004 (Fig. 5.3B).

Table 5.1: Mean values and interpolated values (interpol.) of water table (*wt*) at the *transitional* site (*trans*), the *fen* site (*fen*) and the *wet fen* site (*wet fen*) (as noted with the acronym:[a]); water-filled pore space (5 cm soil depth) (*wfps*) at the alpine *meadow* site (*meadow*) (as noted with the acronym:[b]) and the range of above-ground standing plant biomass (*pb*) for the entire study period and the snow-free periods 2003 and 2004.

	Hydrology and plant biomass										
	entire study period (731 days)			snow-free period 2003 (149 days)				snow-free period 2004 (123 days)			
	trans[a]	*fen*[a]	*wet fen*[a]	*trans*[a]	*fen*[a]	*wet fen*[a]	*meadow*[b]	*trans*[a]	*fen*[a]	*wet fen*[a]	*meadow*[b]
wt[a] [cm] *wfps*[b] [%]											
mean	-34	-12	-2	-53	-33	-19	47	-27	-8	-1	66
interpol.	-32	-9	+1	-51	-31	-16		-19	-5	+3	
pb [g m^{-2}]											
min				81	33	19	54	65	7	4	96
max				239	204	64	242	290	222	71	237

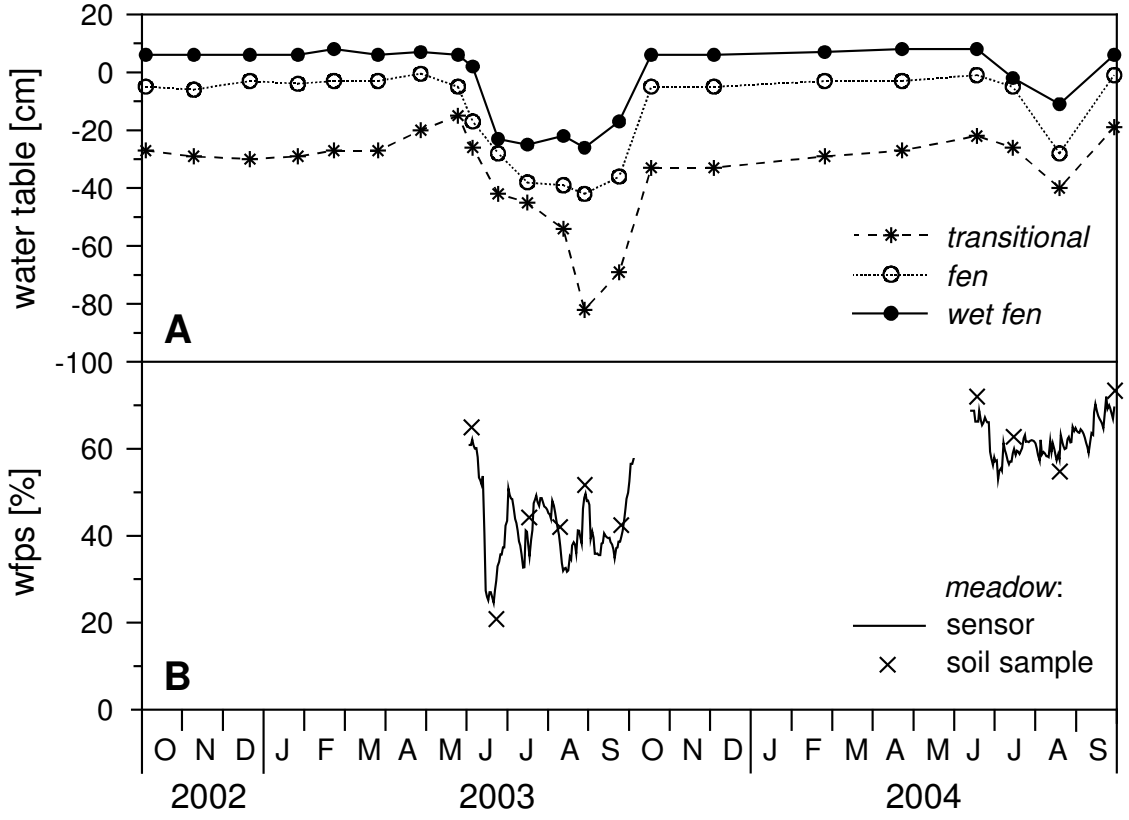

Figure 5.3: Time course of water table at the *transitional*, *fen* and *wet fen* site (A) and water-filled pore space (*wfps*) at the *meadow* site during the snow-free periods (B).

5.4.3 Groundwater chemistry of the fen sites (*transitional*, *fen*, *wet fen*)

The dissolved methane concentration in the groundwater was much higher during snow-free periods than in the winter (Fig. 5.4). The increase of methane concentration at the onset of both snow-free periods was more delayed for *transitional* than *fen* and *wet fen*. The ranges of dissolved methane for the entire study period were 1.6 to 1295.2 µg CH_4 l^{-1} (*transitional*), 4.9 to 1325.2 µg CH_4 l^{-1} (*fen*) and 4.3 to 1395.1 µg CH_4 l^{-1} (*wet fen*). The ammonium concentration ranged from 0 to 1.3 mg l^{-1}, DOC from 7.8 to 34.8 mg C l^{-1} and pH from 4.3 to 6.1 for all fen sites. Nitrate was not detectable (detection limit <0.2 mg/l) at any site. Except for the dissolved methane concentration, no clear effect of site or sampling date was found for any dissolved component.

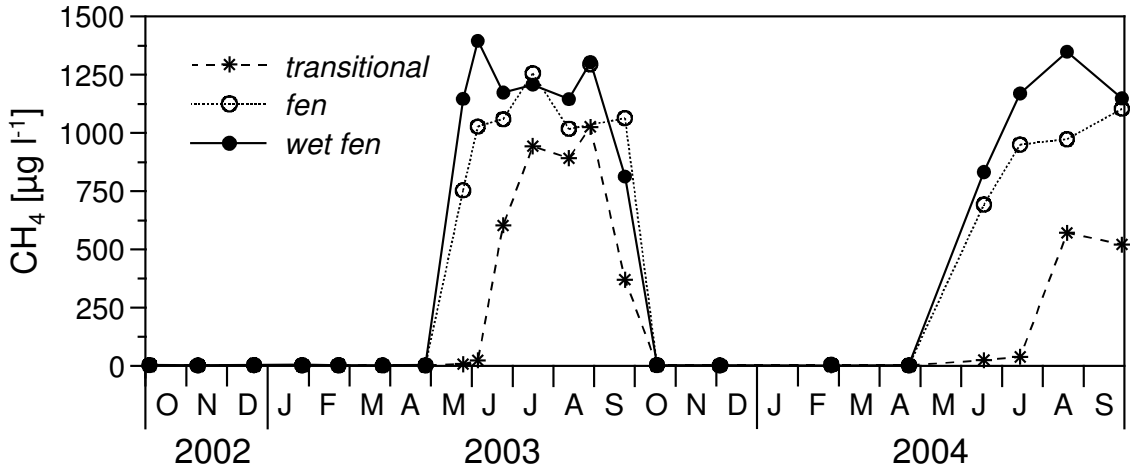

Figure 5.4: Time course of dissolved methane concentrations in groundwater (to maximum 1 m soil depth) at the *transitional*, *fen* and *wet fen* sites.

5.4.4 Plant biomass

The total green above-ground standing plant biomass was determined for the snow-free periods. Peak biomass was reached during 2003 in mid-July on *meadow*, *transitional* and *fen* and in late August on *wet fen*. The snow-free period in 2004 started about three weeks later and maximum biomass was reached in August at all study sites. Plant biomass at *wet fen* was much lower than at the other sites (Tab. 5.1). Significant differences for sampling date and study site for both snow-free periods were found (2003: $F_{(site)}$=83.55, P<0.001; $F_{(date)}$=49.25, P<0.001; $F_{(site\ x\ date)}$=34.9, P<0.001; 2004: $F_{(site)}$=74.55, P<0.001; $F_{(date)}$=34.05, P<0.001; $F_{(site\ x\ date)}$ =8.9, P<0.001).

5.4.5 Seasonal methane flux of the fen sites (*transitional, fen, wet fen*)

Seasonal methane emission was higher and more variable during the snow-free periods than during winter (Fig. 5.5A). For the snow periods the net methane flux was two orders of magnitude lower than during the snow-free periods. In winter, the mean methane emission was 14±11 mg CH_4 m^{-2} d^{-1} for *transitional*, 15±11 mg CH_4 m^{-2} d^{-1} for *fen* and 13±11 mg CH_4 m^{-2} d^{-1} for *wet fen*. No significant differences between study sites and sampling dates were found ($F_{(site)}$=0.42, P=0.659, $F_{(date)}$=0.45, P=0.897; $F_{(site\ x\ date)}$=0.39, P=0.984). In the snow-free periods, *transitional* had the lowest emission rate, followed by *fen* and *wet fen* (Tab. 5.2, Fig. 5.5A). Significant differences between sampling dates and study sites were found for the snow-free period 2003 ($F_{(site)}$=130.02, P<0.001, $F_{(date)}$=18.61, P<0.001; $F_{(site\ x\ date)}$=10.05, P<0.001), whereas only significant differences between study

sites were detected in 2004 ($F_{(site)}$=8.24, P=0.002, $F_{(date)}$=0.39 P=0.765, $F_{(site\ x\ date)}$=0.05, P=0.999). The cumulative annual methane flux for 2003 at *transitional* was 7 g CH_4 m^{-2} a^{-1} (snow period 47%), followed by 14 g CH_4 m^{-2} a^{-1} (snow period 31%) for *fen* and 15 g CH_4 m^{-2} a^{-1} (snow period 27 %) for *wet fen*. For 2004 the cumulative annual methane emission was 6 g CH_4 m^{-2} a^{-1} (snow period 59%) for *transitional*, 13 g CH_4 m^{-2} a^{-1} (snow period 29%) for *fen* and 17 g CH_4 m^{-2} a^{-1} (snow period 18%) for *wet fen*.

5.4.6 Seasonal methane flux of the dry alpine meadow (*meadow*)

The alpine meadow was a net sink for atmospheric methane during the snow-free periods, whereas no detectable methane emission or consumption was found for the snow periods (Fig. 5.5B). The net methane consumption during the two snow-free periods differed considerably, being higher in 2003 than in 2004 (Tab. 5.2). The net methane flux differed significantly between sampling dates in 2003 ($F_{(date)}$=6.28; P=0.004), but not in 2004 ($F_{(date)}$=1.24, P=0.38).

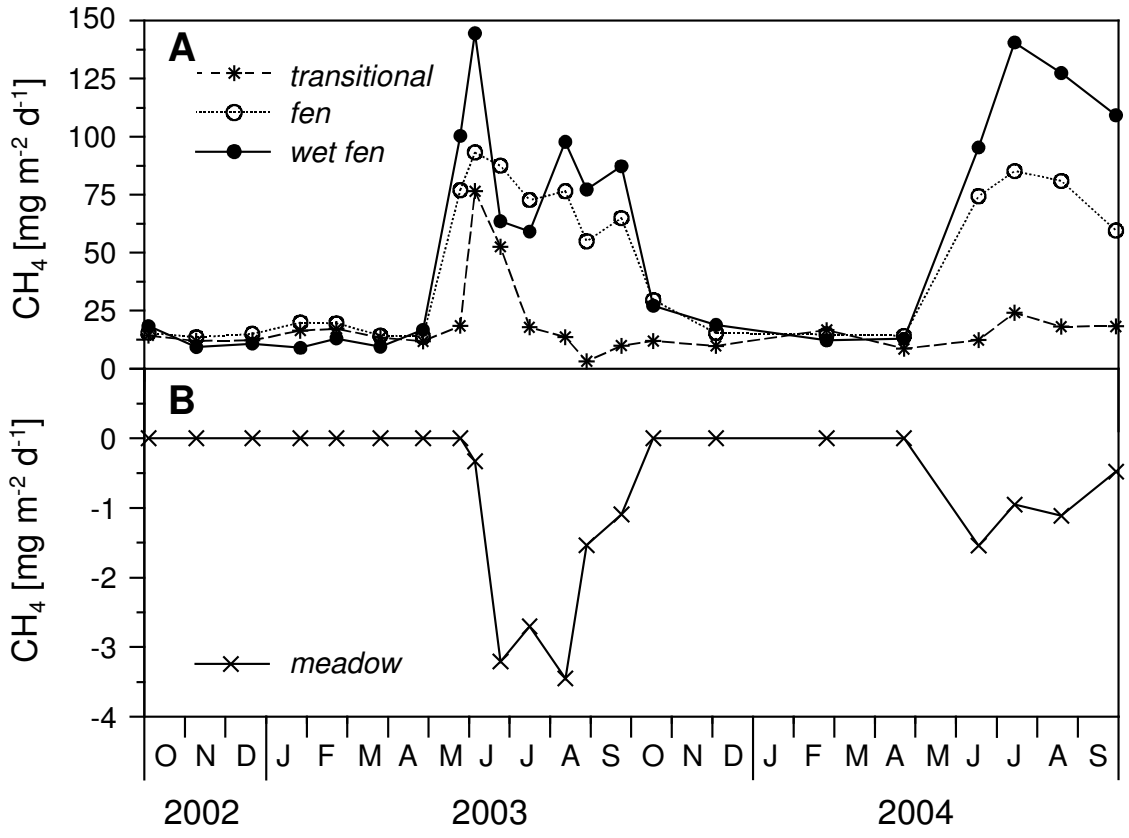

Figure 5.5: Time course of net methane emissions at the *transitional*, *fen* and *wet fen* sites (A) and the *meadow* site (B).

Table 5.2: Mean net CH_4 flux and standard error (se), mean of interpolated values (interpol.) and cumulative CH_4 flux (cum. flux) at the *transitional* site (*trans*), the *fen* site (*fen*), the *wet fen* site (*wet fen*) and the alpine *meadow* site (*meadow*).

	Seasonal net CH_4 flux										
	entire study period (731 days)			snow-free period 2003 (149 days)				snow-free period 2004 (123 days)			
	trans	*fen*	*wet fen*	*trans*	*fen*	*wet fen*	*meadow*	*trans*	*fen*	*wet fen*	*meadow*
net CH_4 flux [mg m^{-2} d^{-1}]											
mean	19	46	57	28	76	89	-2.1	19	83	116	-1.0
se	5	13	10	4	18	18	0.5	2	18	20	0.2
interpol.	17	36	43	24	67	78	-1.9	19	71	112	-0.8
cum. flux [g m^{-2}]	12	26	32	4	10	11	-0.3	2	9	14	-0.1

5.4.7 Controls of seasonal methane emission at the fen sites (*transitional*, *fen*, *wet fen*)

Multiple linear regression analysis identified water table and soil temperature as major controls of methane emission in alpine fen sites (Tab. 5.3B). The derived models explained 38% (*transitional*) to 76% (*wet fen*) of the seasonal variance. Seasonal methane emissions during the entire study period tended to be positively related to soil temperature and water table (Tab. 5.3A). The dissolved methane concentration had no influence on methane emission at any study site.

For the snow-free periods, the water table was the most important environmental control for within- and among-site variability of the seasonal net methane emission (Fig. 5.6). However, this relationship differed considerably, being much higher for the dryer snow-free period 2003 than for 2004.

Table 5.3: Partial regression coefficients (A) and multiple linear models (B) for daily net methane emission of the entire study period (n=22 for the *transitional*, *fen* and *wet fen* sites; n=10 for the alpine *meadow* site). Dependent variable: ln transformed methane flux [mg CH_4 m^{-2} d^{-1}] (ln flux) for *transitional*, *fen* and *wet fen* and methane uptake [mg CH_4 m^{-2} d^{-1}] (flux) for *meadow*. Independent variables: water table [cm] (*wt*) (at *transitional*, *fen*, *wet fen* as noted with the acronym:[a]) and ln-transformed dissolved methane concentration [µg CH_4 l^{-1}] (CH_{4aq}), water-filled pore space [%] (*wfps*) (at *meadow* as noted with the acronym:[b]) and soil temperature [°C] at 5 cm soil depth (st_5). Level of significance: P≤0.05 (*** P<0.001, ** P<0.01, * P≤0.05).

A	Partial regression coefficients (R) of the daily net methane flux				
	transitional[a]	*fen*[a]	*wet fen*[a]	*transitional*[a], *fen*[a], *wet fen*[a]	*meadow*[b]
wt[a] *wfps*[b]	0.59**	0.37	0.33	0.54*	0.57
st_5	0.52*	0.61**	0.53*	0.50*	-0.58
CH_{4aq}	-0.19	-0.17	0.20	-0.10	
B	Multiple linear models of the daily net methane flux				
transitional:	ln flux = 0.023 *wt* + 0.048 st_5 + 3.209				R = 0.61*
fen:	ln flux = 0.007 *wt* + 0.117 st_5 + 2.912				R = 0.87***
wet fen:	ln flux = 0.008 *wt* + 0.091 st_5 + 1.952				R = 0.82***
transitional, *fen*, *wet fen*:	ln flux = 0.022 *wt* + 0.107 st_5 + 2.624				R = 0.74**
meadow:	flux = 0.038 *wfps* - 0.167 st_5 - 1.658				R = 0.86**

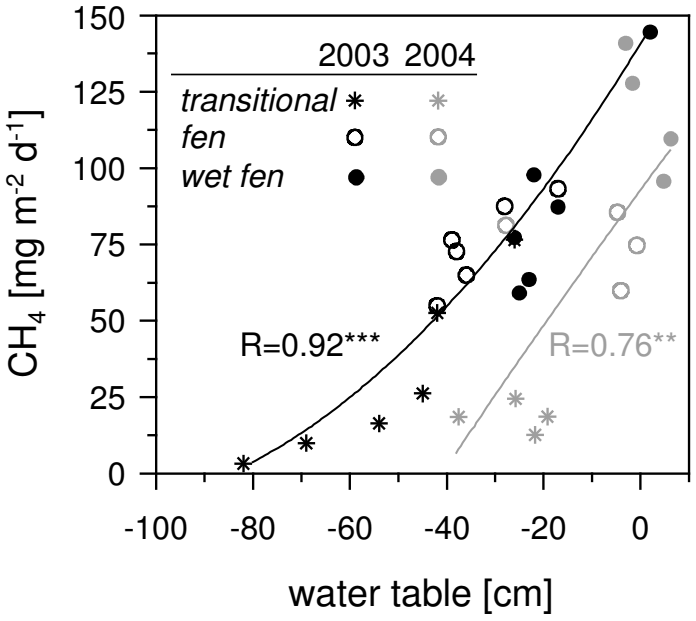

Figure 5.6: Relation between water table and daily net methane flux at the *transitional*, *fen* and *wet fen* sites for the snow-free period 2003 (n=18) and 2004 (n=12). Second polynomial function was used for both regressions (* P≤0.5, ** P<0.01, *** P<0.001).

5.4.8 Controls of seasonal methane emission at the alpine dry meadow (*meadow*)

Partial regression analysis showed that seasonal net methane emission was positively related to *wfps* and negatively related to soil temperature (Tab. 5.3A). The derived multiple regression model explained 74% of the seasonal variance (Tab. 5.3B). Nonetheless, the partial correlation coefficients were not significant for both variables.

5.4.9 Diurnal methane emission of the fen sites (*transitional, fen, wet fen*)

Diurnal changes in methane flux tended to be highest if the water table position was very high or very low. No clear changes were found at intermediate water table positions. For water-saturated soil conditions, methane flux was highest in the afternoon, whereas at low groundwater level the methane flux was highest at night (Fig. 5.7). The biggest difference between daily maximum and minimum methane emissions was found at water-saturated conditions at *wet fen*, with methane emissions twice as high in the afternoon as at night. For all study sites the average difference between the diurnal maximum and minimum methane flux was 155%.

The water table was the most powerful control of diurnal methane flux, followed by soil temperature (Tab. 5.4A). At *transitional*, methane emission was positively correlated with the temperature in 35 cm soil depth, whereas at *fen* and *wet fen* the influence of temperature was most significant in 15 cm soil depth. The above-ground plant biomass positively influenced *fen* and *wet fen*, but not *transitional*. Global radiation was not important for any study site. The empirical linear multiple regression model explained 61% (*fen*) to 69% (*transitional*) of the variance (Tab. 5.4B).

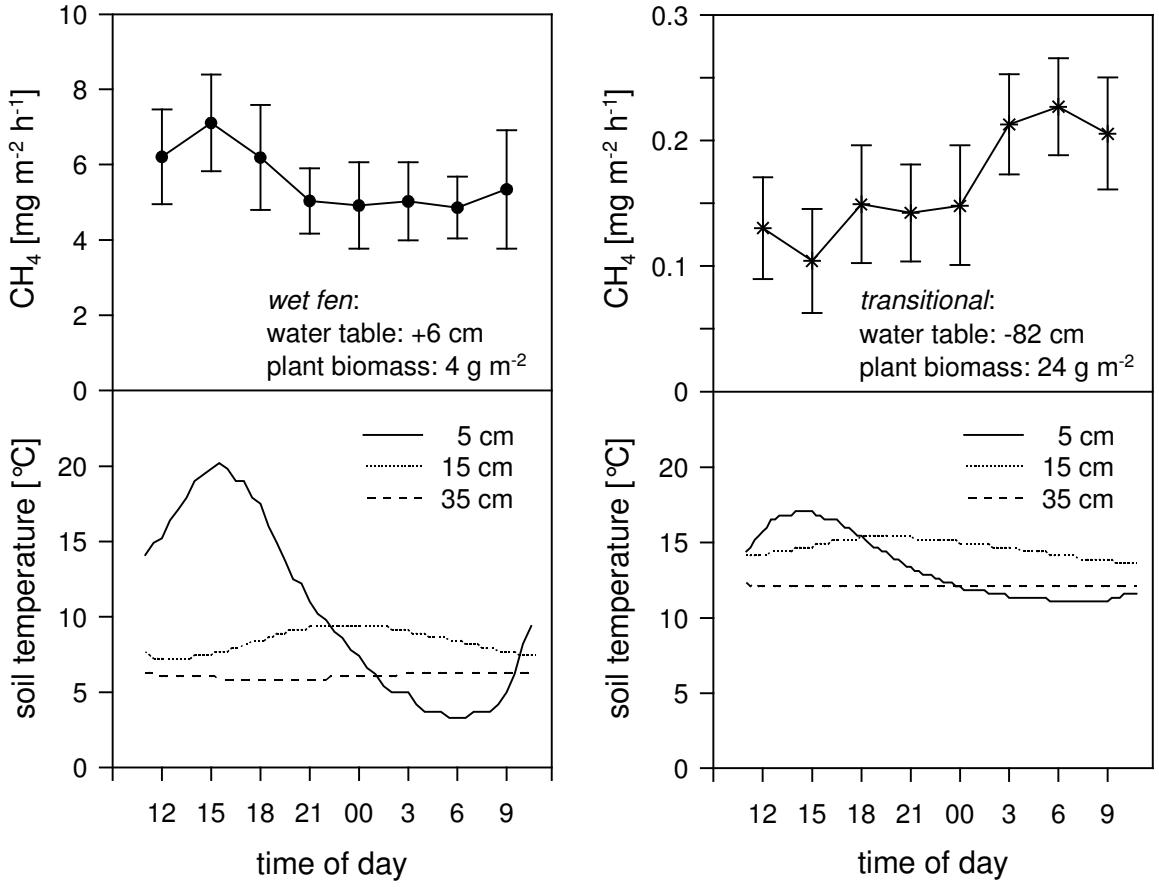

Figure 5.7: Time course of diurnal net methane emissions and soil temperature (5cm, 15cm, 35cm soil depth) at the *wet fen* site (17 June 2004) (A) and at the *transitional* site (28 August 2003) (B).

5.4.10 Diurnal methane emission of the dry meadow (*meadow*)

Net methane emission at *meadow* showed no distinct diurnal pattern (data not shown). Multiple linear regression analysis identified temperature at 15 cm soil depth and *wfps* to be most important, explaining 52% of the methane uptake at *meadow* (Tab. 5.4A and 5.4B). The influence of soil temperature at 5 cm depth, global radiation and plant biomass was weak.

Table 5.4: Partial regression coefficients (A) and multiple linear models (B) for all diurnal measurements during the snow-free periods (n=73-80 for each site). Dependent variable: ln transformed net methane flux [mg CH_4 m^{-2} h^{-1}] (ln flux) for the *transitional*, *fen* and *wet fen* sites and methane uptake [mg CH_4 m^{-2} h^{-1}] (flux) for the *meadow* site. Independent variables: water table [cm] (*wt*) (at *transitional*, *fen* and *wet fen* as noted with the acronym:[a]), water-filled pore space (5 cm soil depth) [%] (*wfps*) (at *meadow* as noted with the acronym:[b]), soil temperature [°C] (soil depth: 5 cm (st_5), 15 cm (st_{15}), 35 cm (st_{35})), global radiation [W m^{-2}] (*glob. rad.*) and above-ground standing plant biomass [g m^{-2}] (*pb*). Level of significance: P≤0.05 (*** P<0.001, ** P<0.01, * P<0.05).

A	Partial regression coefficient (R) of the diurnal net methane flux				
	transitional[a]	*fen*[a]	*wet fen*[a]	*transitional*[a], *fen*[a], *wet fen*[a]	*meadow*[b]
wt[a] *wfps*[b]	0.72***	0.73***	0.80***	0.87***	0.21
st_5	0.01	-0.24*	0.30*	0.02	-0.13
st_{15}	0.06	0.61**	0.40*	0.01	-0.22
st_{35}	0.54**	-0.16	0.01	0.62***	
glob. rad.	-0.07	0.06	0.12	-0.06	-0.14
pb	0.19	0.28*	0.54**	-0.03	-0.10
B	Multiple linear models of the diurnal net methane flux				
transitional:	ln flux = 0.046 *wt* + 0.250 st_{35} + 0.425				R = 0.83***
fen:	ln flux = 0.015 *wt* - 0.012 st_5 + 0.074 st_{15} + 0.001 *pb*+ 0.619				R = 0.78***
wet fen:	ln flux = 0.033 *wt* + 0.017 st_5 + 0.052 st_{15} + 0.008 *pb*+ 0.618				R = 0.81***
transitional, *fen*, *wet fen*:	ln flux = 0.053 *wt* + 0.191 st_{35} + 0.014				R = 0.87***
meadow:	flux = 0.004 *wfps* - 0.234 st_{15} - 0.342				R = 0.72***

5.5 Discussion

5.5.1 Environmental controls of seasonal methane emission at the fen sites (*transitional, fen, wet fen*)

Seasonal methane flux was positively related to soil temperature and water table position. Several studies confirm the importance of water table and soil temperature. However, the influence for environmental properties can change seasonally or between study years [*Bubier et al.*, 2005; *Shannon and White*, 1994]. Q_{10} values derived from the multiple linear regression models in this study were 1.6 (*transitional*), 3.1 (*fen*) and 2.6 (*wet fen*) or 2.9 if all plots were pooled. These values fit to the lower range (1.6 to 11) of in situ data calculated by simple Arrhenius equations from various water-saturated environments [*Chapman and Thurlow*, 1996]. The water table was the main driver for net methane emissions during snow-free periods. The water table fluctuation during 2003 was much more pronounced than during 2004 and resulted in much higher net CH_4 emission related to the water table depth in 2003. Net methane flux was even observed at a water table position of -82 cm at the *transitional* site. *Chimner and Cooper* [2003] found a similar pattern on a drained alpine fen exposed to a large water table drop. A mean annual water table position of about -15 cm as a critical threshold factor for zero net flux was found for temperate soils [*Fiedler and Sommer*, 2000] and for several boreal ecosystems [*Rask et al.*, 2002]. However, the history of water table fluctuations may be crucial, leading to long- and short term effects for the microbial community composition and function [*Moore and Dalva*, 1993; *Shannon and White*,

1994]. During a three-year study, *Shannon and White* [1994] found long-term effects after a desiccation period during the summer: methane flux was influenced even for the subsequent snow-free period. Large fluctuations in the water table may cause long-term effects by disturbing the location of an effective methanotroph population. This is because the highest methanotrophic activity in wetland soils is often found around the mean standing water table position [*Conrad*, 1996]. In contrast, the spatial distribution of strictly anaerobic methanogens may be limited to deeper soil layers [*Chimner and Cooper*, 2003]. Besides the altering of the microbial community, temporarily aerated soils may also favour the formation of alternative electron acceptors (sulphate, nitrate, ferric iron), which play a greater role in overall anaerobic respiration than methanogenesis [*Conrad*, 1996; *Moore and Dalva*, 1993]. On the other hand, the water table may also imply short-term effects for flooded soils. Enhanced methane flux from a Canadian wetland ecosystem could be observed after the water table dropped below the soil surface probably due to the reduced resistance of methane transfer in air [*Bellisario et al.*, 1999]. Furthermore, a dropping water table from submerged soils uncovers plant parts responsible for plant-mediated CH_4 emissions [*Kelker and Chanton*, 1997]. In our study, methane fluxes related to the water table position were lower for the snow-free period 2004 than for 2003, indicating more long-term effects caused by the severe desiccation in 2003.

5.5.2 Environmental controls of diurnal methane emission at the fen sites (*transitional, fen, wet fen*)

Diurnal differences of methane emission were only apparent for low or high water tables. Low water tables increased methane flux during the night, whereas at high water tables methane flux peaked together with the temperature of the topsoil in the afternoon. Similar results were obtained for boreal wetlands in north Sweden, with higher night time flux for drained sites but smaller differences at high water tables [*Mikkelä et al.*, 1995]. The influence of temperature on diurnal methane emission differed with soil depth. The net flux at the driest fen site (*transitional*) was controlled more by temperature in deeper soil layers, whereas *fen* and *wet fen*, with higher water tables, were controlled more by temperature in shallower soil depths. The importance of soil temperature may be influenced by standing water table, because anearobic methane production is linked to water-saturated soil conditions. According to *Rask et al.* [2002], stronger positive correlations of net methane flux with temperature at certain soil depths indicate the main location of CH_4 formation; this agrees with our results. The negative relationship between net methane flux and the topsoil

temperature at the fen study site can be explained by the highest methane oxidation potential just above standing water table [*Conrad*, 1996].

Total above-ground plant biomass had no significant influence on diurnal methane emission for the driest fen site, *transitional*, but the influence increased with higher mean water table positions of *fen* and *wet fen*. The lack of influence for *transitional* may be attributed to the deeply aerated upper soil layer. Hence, the proportion of plant-mediated methane flux should be low and less important than at wetter ecosystems [*Kutzbach et al*., 2004]. The partial influence of total plant biomass was eight times higher for *wet fen* than for *fen*. This leads to the assumption that the *Carex nigra*-dominated *wet fen* has a more pronounced effect on plant-derived methane flux than the *Trichophorum caespitosum*-dominated *fen. Trichophorum caespitosum* has a relative shallow root system with no root aerenchyma and tolerates saturated but not flooded soil conditions [*Bragazza and Gerdol*, 1996]. In contrast, the *Carex* species and *Eriophorum angustifolia* have distinctive root aerenchyma down to about 80 cm and may therefore more important for methane transport via plants in the *fen* and *wet fen*. Evidence for species-specific methane transport is given by *Schimel* [1995], who showed that the plant-mediated methane transport of *Eriophorum angustifolia* was higher than that of *Carex aquatilis*. The greater influence of plant biomass on methane flux at *wet fen* compared to *fen* might also be attributed to passive methane transport by diffusion, as reported for different *Carex* species and several sedges [*Hirota et al*., 2004; *Kelker and Chanton*, 1997; *Kutzbach et al*., 2004].

Global radiation was not correlated with diurnal methane flux. Accordingly, methane flux seems not to be controlled by stomata conductivity. Field studies have shown different results in relation to radiation. *Hirota et al*. [2004] found no response of *Carex allivescers* V. Krez. to radiation, in contrast to the response of different sedges. In a laboratory experiment, *Thomas et al.* [1998] reported that plant-mediated methane transport from *Carex* species and *Eriophorum* species largely responded to light under constant temperature due to higher stomata conductance. The authors concluded that the diurnal temperature course might mask the stomata effect for in situ measurements. Since many alpine plants have their maximum diurnal stomatal conductivity in the afternoon [*Körner and Mayr*, 1981] together with the maximum diurnal soil temperature, this effect could explain the lack of a relationship between global radiation and net methane flux in our study.

5.5.3 Environmental controls of methane oxidation at the alpine meadow site (*meadow*)

The *meadow* site functions as a net sink for methane during snow-free periods. Diurnal and seasonal net methane emissions were negatively correlated with temperature and positively with water-filled pore space. Moreover, for diurnal net methane emissions, soil temperature in 15 cm soil depth was more important than in 5 cm. Similar results were reported by *West et al*. [1999] for alpine meadows in the Colorado Front Range. These results lead to the assumption that atmospheric methane oxidation in alpine environments is located in deeper soil layers as found for many other environments [*Conrad*, 1996]. The maximum atmospheric methane oxidation in the deeper soil layer can be explained by the higher inorganic nitrogen concentrations usually found in the topsoil, since ammonium is known to be a competitive inhibitor for methane oxidation [*de Visscher and van Cleemput*, 2003].

5.5.4 Magnitude of methane flux at the fen sites (*transitional, fen, wet fen*)

The range of the mean seasonal net CH_4 flux during the snow-free periods was 19 mg CH_4 m^{-2} d^{-1} (*transitional*, 2004) to 116 mg CH_4 m^{-2} d^{-1} (*wet fen*, 2003), with a maximum value of 145 mg CH_4 m^{-2} d^{-1} at waterlogged soil conditions at *wet fen*. Mean net methane emissions of the study sites in the Rotmoos fen were in the order *wet fen* > *fen* > *transitional*, with mean water table levels having the same order. The estimated annual flux rates corresponded to the lower range of flux values reported from alpine wetlands in the Rocky Mountains [*Chimner and Cooper*, 2003; *Mast et al*., 1998; *Wickland et al*., 1999] and in the Tibetan Plateau [*Hirota et al*., 2004]. The relatively low methane flux at *wet fen* may be partly due to the low plant productivity, because 4% of the daily net CO_2 assimilation is emitted as methane as found for Canadian submerged wetlands [*Bellisario et al*., 1999].

The range of the mean net methane flux during the snow periods was remarkably similar being 13 mg CH_4 m^{-2} d^{-1} (*wet fen*) to 15 mg CH_4 m^{-2} d^{-1} (*fen*) with no obtained seasonal differences. During the snow periods 2003/2004 the relatively constant soil temperature at all fen sites in 15 cm and in 35 cm depth (0.3°C and 1.0°C, respectively) and the high and constant water table levels may be responsible for similar net methane flux between study sites and the lack of seasonal differences. In contrast, *Mast et al*. [1998] found differences in methane flux rates for moist alpine (4.4 mg CH_4 m^{-2} d^{-1}) and water saturated soils (45.9 mg CH_4 m^{-2} d^{-1}) in the Rocky Mountains. Much lower net methane flux (minimum 1.6 mg CH_4 m^{-2} d^{-1}) was obtained for an alpine wetland by *Wickland et al*. [1999]. These differences of reported net methane flux during snow periods may be partly attributed to the different gas measurement methods. A comparison of the chamber method with the snow-

gradient method resulted in higher net methane flux values if chambers were used [*Alm et al.*, 1999].

The contribution of wintertime emission to annual methane flux ranged from 18% (*wet fen*) to 59% (*transitional*). These values fit to the broad range observed for alpine wetland ecosystems in the Rocky Mountains having similar length of snow-periods compared to our study site [*Mast et al.*, 1998; *Wickland et al.*, 1999].

5.5.5 Magnitude of methane oxidation at the alpine meadow site (*meadow*)

The average net methane uptake at *meadow* differed considerably for the two investigated snow-free periods, with much higher methane consumption for 2003 (-2.1 mg m^{-2} d^{-1}) than 2004 (-1.0 mg m^{-2} d^{-1}). In contrast to *Sommerfeld et al.* [1993], we found no methane flux at snow-covered soil conditions. Methane consumption during the snow-free periods was higher than mean values reported for several alpine tundra ecosystems (+8.5 to -0.8 mg CH_4 m^{-2} d^{-1}) [*Neff et al.*, 1994; *West et al.*, 1999; *Whalen and Reeburgh*, 1990]. However, the net oxidation rates in this study were comparable with the range observed from arctic tundra ecosystems [*Christensen*, 1993; *Whalen and Reeburgh*, 1992]. The higher rates found in our study may be also caused by higher soil fertility due to the traditional use of the study sites as pasture [*Kruse and Iversen*, 1995].

5.5.6 Global aspects of alpine methane flux

In the alpine zone of Austria (2000 m to 3800 m a.s.l.) wetlands cover about 0.14% (5.5 km^2), alpine grassland (*meadow*) about 78.3% (3150 km^2) and forested land about 21.7% (875 km^2) of the vegetation area [*Steiner*, 1992]. Within the Rotmoos fen, *transitional*, *fen* and *wet fen* represent roughly 10%, 85% and 5%, respectively. If we extrapolate our data to the alpine environment in Austria, we would expect, that alpine regions are a small net sink for methane (-0.14 g CH_4 m^{-2} a^{-1}) in areas with no forest sites. So far, there are no data from other alpine regions in Europe. This rough estimation agrees with findings from Niwot Ridge, Colorado Rocky Mountains, acting as a small net methane sink [*West et al.*, 1999]. *West et al.* [1999] estimated that the global alpine area (10.5 million km^2) might be responsible for -1 to +10 Tg CH_4 a^{-1}. Based on a model dealing with the entire pan-arctic region, the entire European Alps may act as a small net sink of methane (0 to -1 g CH_4 m^{-2} a^{-1}) [*Zhuang et al.*, 2004]. There are still high uncertainties about net methane fluxes from alpine regions and more investigations are necessary to estimate the role of alpine areas in the global methane budget.

5.6 Conclusions

Abiotic environmental properties were mainly responsible for regulating seasonal and diurnal net methane emissions of an alpine ecosystem. The influence of water table was found to be most important for seasonal within- and among-site variability. The effect of temperature on methane emission rates varied in the different soil depths presumably due to differences in the vertical distribution of methanogenes and methane oxidizers. Our results indicate that plant-mediated methane transport is only important for water saturated soil conditions, whereas at drier soil conditions diffusion through the soil matrix becomes more important. Methane fluxes during the winter period substantially contributed to the methane flux rate of a year and should be considered in future studies. We conclude that alpine wetlands act as a methane source, while well-drained alpine grassland could function as a net sink of methane in the Eastern Alps of Europe. More investigations of methane fluxes from alpine landscapes are necessary to evaluate the role of alpine areas in the global methane budget.

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6 Interannual ecosystem CO_2 dynamics in the alpine zone of the Eastern Alps, Austria

6.1 Abstract

Information about the annual carbon fluxes of fen and meadow ecosystems in alpine environment is rare. We studied the influence of photosynthetic active radiation (*PAR*), plant green area index (*GAI*), soil temperature and water filled pore space (*wfps*) on the net CO_2 emission at four alpine sites (one meadow and three fen sites), differing in water balance and plant community. Measurements over two years were made in the Eastern Alps, Austria, including two snow-free periods and two snow periods. During snow-free periods, net CO_2 gain during daylight periods (NEC_{light}, $PAR>0$) depended on *PAR* and *GAI.* The net CO_2 emission rate at night (R_{tot}, $PAR=0$) was positively related to soil temperature, while low *wfps* reduced the carbon loss via R_{tot} of the meadow and driest fen study site but reinforced carbon loss of the wetter fen sites. Daily average ecosystem net CO_2 gain (NEC_{day}) during snow-free periods (averaged over both years) at the meadow was 3.5 g CO_2 m^{-2} d^{-1} and ranged from 1.5 to 3.4 g CO_2 m^{-2} d^{-1} at the fen sites. The average mean daily wintertime CO_2 emission was low, being only -0.9 g CO_2 m^{-2} d^{-1} for meadow and between -0.2 and -0.7 g CO_2 m^{-2} d^{-1} for all fen sites. All sites function as significant annual net carbon sinks, with a net carbon gain from 50 to 121 g C m^{-2} a^{-1} (averaged over both years) irrespective of water balance. Our results indicate that alpine fen sites that have built up a large carbon stock in the past are not expected to gain a further carbon surplus compared with meadows under the current climate.

6.2 Introduction

Investigations dealing with the carbon balance of terrestrial ecosystems are important because changes in the global climate cause positive feedback mechanisms here [*Schlesinger and Andrews*, 2000]. Arctic and alpine ecosystems store much carbon and cover a large part of the global land surface [*Rastetter et al.*, 1991]. Therefore, investigations on CO_2 dynamics derived from alpine environments are necessary to understand global carbon cycling.

The C cycle of quasi-stable ecosystems over long time scales and large areas must be balanced [*Körner*, 1999]. In contrast, pristine peatlands are characterized by accumulation of atmospheric carbon because of the slow decomposition rate favoured by water-logged and anoxic conditions. The formation of present peatlands in the Eastern Alps, Austria, started at the last ice age (about 5000 years ago) [*Bortenschlager*, 1970]. However, the fate of these ecosystems under current climate conditions remains to be investigated.

In general, net ecosystem CO_2 exchange (*NEC*) is the result of gross photosynthesis (P_g) derived by green plants minus the total respiration of the overall ecosystem (R_{tot}), consisting of plants, soil fauna and soil microbes [e.g. *Rustad et al.*, 2000]. Atmospheric CO_2 is sequestered by vegetation via photosynthesis. Carbon is accumulated as organic carbon in the soil or respired again to the atmosphere. Photosynthesis in alpine plants is mainly influenced by irradiation, the phenological status of plants, the length of vegetation period and to a lesser extent by temperature [*Körner*, 1999]. Although the above-ground plant biomass is much smaller compared to lowland plant communities due to different C allocation, alpine plant species use more efficiently CO_2 for photosynthesis than lowland plants [*Körner*, 1999].

Total ecosystem respiration in alpine environment depends on temperature, soil water content and plant biomass [*Cernusca and Decker*, 1989]. Moreover, R_{tot} is more sensitive to temperature than photosynthesis [*Kirschbaum*, 2000] and may be crucial for the present ecosystem carbon balance if global temperature increases due to climate change. Although the productivity of alpine meadows is reasonably well understood, the seasonal and annual net CO_2 balance of alpine wetland ecosystems has been investigated on only a few occasions.

We therefore (i) determined plant community properties by harvesting the above- and below-ground biomass, (ii) empirically modelled the seasonal ecosystem CO_2 dynamics using meteorological data and the plant green area index (*GAI*) and (iii) roughly estimated the annual C budget of four alpine sites in the Eastern Alps, Austria. Four study plots along a soil moisture gradient (one dry meadow and three sites in a fen) were selected differing in vegetation community and water balance. Net CO_2 flux, plant biomass and climatic

properties (radiation, air temperature, precipitation, soil temperature and water filled pore space in 5 cm soil depth) were monitored over a two-year period.

6.3 Material and methods

6.3.1 Study sites

The study area is located in the Ötztal range (46°50´N, 11°03´E) in Tyrol, Austria. The study sites are located in the Rotmoos valley above the present tree line (2250 m a.s.l.) (Fig. 6.1). The valley is exposed south to northwest and flanked by the mountains Hohe Mut (2659 m a.s.l.) and Hangerer (3121 m a.s.l.). The climate is relatively continental with cold, snowy winters and cool summers with a mean snow-free period of about 4.5 months (June to mid-October) (M. Strobel, University of Innsbruck, personal communication). Mean annual precipitation amounts to 820 mm (1970-1996) and mean annual air temperature (1997-1998) is -1.3°C [*Kaufmann*, 2001].

Four study plots along a moisture transect were chosen (one alpine dry meadow and three plots in the Rotmoos fen); they differ in water balance and vegetation community. The dry study plot (*meadow*) was chosen in an alpine meadow site classified as a *Curvulo-Nardetum* (G.-H. Zeltner, University of Hohenheim, personal communication) (Tab. 6.1). Its soil is a Cambisol of loamy sandy silicates with a maximum observed soil depth of 50 cm. The *meadow* is well drained, and 90% of the soil surface is covered by vegetation (10% small boulders). The other three sites are located in the Rotmoos fen. The Rotmoos fen measures 8.5 ha and the average peat depth is 1.5 m (range 0.5-2.9 m) [*Rybníček and Rybníčková*, 1977]. The fen is mainly fed by surface water from runnels flowing down the hill slopes of the flanking mountains. Its soils are classified as Rheic Histosols. According to *Bortenschlager* [1970], the fen was periodically overwhelmed with 15 layers (1-27 cm) of silt or sand sediments (or both) mainly located in deeper than 2 m soil depth. One of the three fen sites (*transitional*) is located in the transition area between alpine dry meadow and the Rotmoos fen. According to *Rybníček and Rybníčková* [1977], the vegetation of the *transitional* site can be defined as a *Carici echinatae-Trichophoretum caespitosi* community. A relative high cover of plant species also belongs to *Curvulo-Nardetum* (Tab. 6.1). The second fen plot (*fen*) is located deeper in the Rotmoos fen and is characterized by a typical *Carici echinatae-Trichophoretum caespitosi* plant community [*Rybníček and Rybníčková*, 1977]. The species richness of the *fen* site is lower than the *transitional* site (Tab. 6.1). The wettest fen site (*wet fen*) is located in the center of the Rotmoos fen and consists solely of *Carex nigra* L. (Tab. 6.1). The vegetation cover was only 30% and this site can be temporarily flooded.

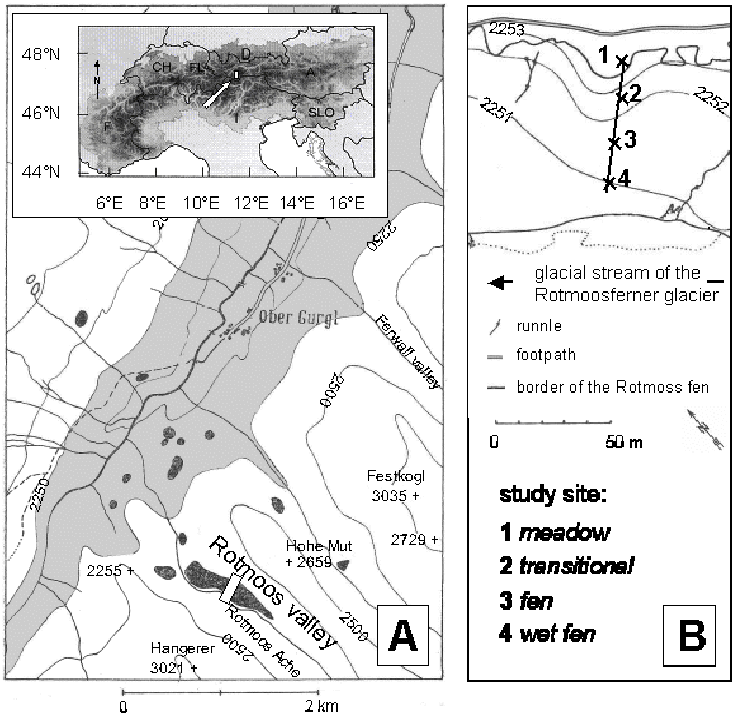

Figure 6.1: Map of the study area and study sites. (A) Overview of alpine fens in the study area (black areas) based on mapping by Rybníček and Rybníčková (1977); gray area in map represents the potential tree area (altitude below 2250 m a.s.l.); legend of the overview of the Alps: A=Austria, D=Germany, CH=Switzerland, F=France, FL= Liechtenstein, I=Italy, SLO=Slovenia. (B) Map section of the Rotmoos valley with locations of study sites.

Table 6.1: Plant species and coverage [%] of the study sites.

	meadow	*transitional*	*fen*	*wet fen*
Herbs:				
Alchemilla vulgaris L.	<5			
Anthoxanthum odoratum L.	<5			
Anthyllis vulneraria L.	<5			
Bartsia alpina L.		<5		
Campanula cochlearifolia Lamk.	<5			
Campanula scheuchzeri Vill.	<5			
Dianthus carthusianorum L.	<5			
Euphrasia alpina Lamk.	<5			
Euphrasia minima Jacq. Ex. DC.	<5			
Gentiana ramosa L.	<5			
Geum montanum L.	<5			
Hippocrepis comosa L.	<5			
Homogyne alpina (L.) Cass.		<5		
Leonthodon helveticus Mérat	<5			
Ligusticum mutellina (L.) Crantz	<5	<5		
Phyteuma hemisphaericum L.	<5			
Potentilla aurea L.	<5	10		
Rhinantus angustifolius C.C. Gmelin	<5			
Silene vulgaris (Moench.) Garcke	<5			
Grass species:				
Carex curvula All.	<5			
Carex echinata Murray		5	<5	
Carex flava L.	<5			
Carex nig L.			<5	30
Carex sempervirens Vill.	<5			
Deschampsia cespitosa (L.) P.B.	<5			
Eriophorum angustifolium Honck.		20	40	
Luzula campestris (L.) DC.	<5			
Nardus stricta L.	10	10		
Poa alpina L.	<5			
Trichophorum caespitosum (L.) Hartman		30	60	
Shrubs:				
Calluna vulgaris (L.) Hull	<5	<5		
Salix herbacea L.	<5			
Vaccinium myrtillus L.	<5			

6.3.2 CO_2 measurements

The net CO_2 flux was determined by measuring CO_2 concentration changes using the "closed chamber" technique under depletion state. Plexiglas chambers with inserted septums in the lid (frame: 40 cm x 40 cm x 30 cm; lid 40 cm x 40 cm) were used during the snow-free periods. On average, *PAR* was reduced by 11% due to the plexiglas screen. Each chamber (n=12) was equipped with a small battery-driven fan that ensured an adequate circulation of the enclosed air. Per study plot, three frames fitting to the lids were carefully inserted 3 cm into the soil at least 15 h before each measurement. Because of grazing (sheep and horses) the frames had to be removed between the sampling days. On each plot, one chamber was provided with a common resistance thermometer 5 cm above the soil surface to estimate the temperature difference inside and outside the chambers. The maximum temperature in the chamber headspace during the time of measurements was on average 8.6°C (range 4.6 to 14.1°C depending on incident radiation) higher during daytime and 1.1°C (range 0.2 to 2.0°C) during nighttime compared to ambient conditions; theses values were similar for all study sites. Vapour pressure deficit (*vpd*) of the enclosed air was reduced compared to the ambient conditions. Gas samples were collected for analysis approximately every 3 weeks within the snow-free season 2003 (n=6) and every 4 weeks during the snow-free season 2004 (n=4). Gas samples were taken with double needles connecting the chamber with butyl-rubber septums of evacuated flasks. The flasks were evacuated and washed with nitrogen 5 times in the laboratory prior to sampling. One sample drawing consists of four sub-samples, which were drawn 0, 6, 20 and 30 min after the chamber was closed. For the measurements during daylight, we additionally drew a sub-sample after 10 min. Since we simultaneously measured CH_4, the chambers had to be closed for a minimum of 30 min. The sampling procedure was repeated every 3 hours (n=8); it started at noon and ended at 9:00 in the following day. During snow periods, gas samples were collected every 1 to 3 months (n=11 for each plot) using three stainless steel pots (diameter 15.5 cm; 25.0 cm height) per site. After the snow was removed from an area of about 2 x 2 m at each study plot, the steel pots were gently placed on the soil surface and sealed with wet snow. After gas sampling and removal of pots, the area was recovered with snow. One sample drawing was made at noon and consisted of four sub-samples, which were taken at 0, 30, 60 and 90 min.

In the laboratory, CO_2 concentrations of the collected air probes were measured using a flame ionisation detector in a Perkin Elmer (PE Auto system and PE Headspace Sampler HS 40XL) gas chromatograph. Chromatographic separations were made using a 6 ft stainless steel column packed with Poropak Q (100/120 mesh). The oven of the column was maintained at 40 °C and the detector was operated at 350°C. Nitrogen was used as a carrier gas (gas flow rate: 45 ml min^{-1}). Gas standards (200 ppm, 1000 ppm and 3000 ppm) were used for calibration and CO_2 flux was calculated according to *Livingston and*

Hutchinson [1995]. The CO_2 release during nighttime and snow periods was calculated from linear regressions. During daytime, the measured net CO_2 flux followed a first-order exponential decrease caused by declining CO_2 concentrations in the chambers. The first derivative of simple first-order exponential curve fits ($f_{(x)}=ae^{bx}$) was used to calculate the CO_2 flux. At high *PAR* and high above-ground standing plant biomass, the first three sub-samples of the sample drawings were used for calculations only, yielding better curve fittings. Regressions coefficients of the curve fits lower than $R^2=0.90$ were rejected. All rates are expressed on a ground surface basis.

6.3.3 Climate data

The climate data were provided by R. Kaufmann (University of Innsbruck, personal communication). The weather station (2270 m a.s.l.) is located 2 km away from the study sites. Air temperature [°C], global radiation [W m^{-2}], precipitation [mm] and relative humidity [%] were recorded two meters above ground every 15 min. *PAR* [µmol m^{-2} s^{-1}] was monitored directly at our study location every minute during diurnal gas measurements using a *PAR* quantum sensor and data hog2 (skye instruments, United Kingdom). *PAR* and global radiation at the weather station were significantly correlated ($R^2=0.96$; n=326; $p<0.001$). This linear function was used to convert the global radiation data from the weather station to *PAR*; it was in the range of the conversion factors of the typical light situations (cloudy, sunny conditions) given by *McCree* [1972]. Soil temperature and soil moisture were recorded hourly at every study site in 5 cm soil depth using temperature loggers (UTL-1; Geotest AG, Suisse) and soil moisture sensors (SMS3; Cylobios, Austria). For calibration of the soil moisture sensors, soil cores (100 cm^3; n=3) were taken from 0-5 cm soil depth at every sampling date and on every study site during the snow-free periods (n=10). Volumetric water content [θ] was determined gravimetrically after drying at 105°C for 48 h. Water filled pore space (*wfps*) [%] was calculated by the proportion of volumetric water content (θ) from the maximum saturation water content. Maximum saturation water content [g cm^{-3}] was determined in the laboratory. Soil cores (100 cm^3; n=5) were saturated with degassed water over a 4-day period and weighed before and after drying at 105°C for 48 h. Our determined *wfps* sometimes exceeded 100% (maximum 107%), probably because desiccation and rewetting events were not congruously taken in the calibration curve. Then we set these values to 100%. Recorded moisture data of snow periods were rejected because values were not reliable due to frozen water conditions.

6.3.4 Plant biomass and plant green area index (*GAI*)

Above-ground standing plant biomass [g m^{-2} ground area] and plant green area index (*GAI* [m^2 m^{-2}]) were determined for each study site during the snow-free periods in 2003 (n=6) and 2004 (n=4). Plant material was clipped from a 25 x 25 cm area (n=5 for each site) inside a frame randomly positioned on the soil surface. Standing green biomass and non-green biomass was separated visually and oven dried at 60°C for 72 h before weighing. Specific projected leaf surface area [g m^{-2} leaf area] of the entire plant community was determined with an ordinary flatbed scanner and the software rootedge (Version 2.3, Iowa State University, Inc.). *GAI* represents the projected area of green biomass per ground area [*Wohlfahrt et al.*, 2001].

Below-ground plant biomass was estimated when peak above-ground standing biomass was observed in 2003 by sampling the fine roots (diameter<2 mm) from 0-10 cm soil depth (n=5 for each site). A bucket auger (diameter=8 cm) was used. In the laboratory, live roots were visually separated from dead roots after being washed out with a sieve (mesh size 0.5 mm^2) according to *Leuschner et al.* [2004], and weighed after being dried at 60°C (72 h).

6.3.5 Calculations and statistics

Net CO_2 flux rate at daytime (*PAR*>0) during the snow-free periods represents the net ecosystem CO_2 exchange rate at daytime (NEC_{light} [mg CO_2 m^{-2} h^{-1}]). NEC_{light} was described by a modified response function [*Diemer and Körner*, 1998; *Küppers and Schulze*, 1985] based on *PAR* [µmol m^{-2} s^{-1}] and *GAI* (equation 6.1):

$$NEC_{light_{(PAR,GAI)}} = NEC_{\max} \cdot \left(1 - e^{-k \cdot (PAR - \Gamma)}\right) \cdot GAI \,, \quad (6.1)$$

where NEC_{max} is maximum NEC_{light} in full sunlight at a given *GAI*, Γ is the ecosystem light compensation point and *k* a coefficient affecting the curvature of the function. *PAR* values were reduced by 11% to account for the reduction of *PAR* by the chambers. Temperature (soil, air) and *wfps* did not significantly contribute when additionally added to the model function. High leaf temperature have a negative affect on net photosynthesis, resulting in about 30% lower CO_2 assimilation when leaf temperature is 5°C higher than optimum temperature at full sunlight [*Küppers and Schulze*, 1985]. The influence of the temperature difference of chambers compared to ambient temperature condition ($\Delta T°C_{cham\text{-}amb}$) on the function parameters used in equation (6.1) was tested by dividing NEC_{light} values

into $\Delta T℃_{(cham-amb)}$ categories. No significant effect of $\Delta T℃_{(cham-amb)}$ was detected for any function parameter.

The CO_2 flux rates during nighttime (*PAR*=0) of the snow-free period were used as an estimate for total ecosystem respiration (R_{tot} [mg CO_2 m^{-2} h^{-1}]). R_{tot} was described by a multiple linear regression model (equation 6.2):

(6.2) $$\ln R_{tot\,(st_5,wfps)} = b_1 + b_2 \cdot st_5 + b_3 \cdot wfps\,,$$

where st_5 [℃] represents soil temperature, and *wfps* [%] the water filled pore space in 5 cm soil depth. *GAI* did not significantly contribute when additionally added to the model function. Winter-time CO_2 flux was not included in the model because measurements were made after removal of the snow cover. In equations (6.1) and (6.2), we used the data of both snow-free periods to obtain better curve fittings. Here, R_{tot} (carbon loss) is presented as negative and NEC_{light} as positive values (if there was a positive net carbon gain for the ecosystem).

Calculations of the daily net ecosystem CO_2 flux during snow-free periods (NEC_{day} [g CO_2 m^{-2} d^{-1}]) were based on day-based integration on hourly data (*t* in hours) of NEC_{light} presented as $NEC_{daylight}$ [g CO_2 m^{-2} d^{-1}] and day-based integration on hourly data of R_{tot} presented as R_{night} [g CO_2 m^{-2} d^{-1}]:

(6.3) $$NEC_{daylight} = \int_{t1}^{t2} NEC_{light\,(t)} \cdot dt\,, \qquad PAR>0$$

(6.4) $$R_{night} = \int_{t1}^{t2} R_{tot\,(t)} \cdot dt\,, \qquad PAR=0$$

(6.5) $$NEC_{day} = NEC_{daylight} + R_{night}\,.$$

For seasonal ecosystem C fluxes, all day-based values were summed over the snow-free periods, expressed as g C m^{-2} $season^{-1}$:

(6.6) $$\sum NEC_{daylight} = \int_{d1}^{d2} NEC_{daylight} \cdot dt\,,$$

(6.7) $$\sum NEC_{day} = \int_{d1}^{d2} NEC_{day} \cdot dt\,,$$

(6.8) $$\sum R_{night} = \int_{d1}^{d2} R_{night} \cdot dt\,.$$

During snow periods we assumed that the measured CO_2 emission rate was constant over the entire day. Daily CO_2 flux during the snow period (R_w [g CO_2 m^{-2} d^{-1}]) was calculated taking the averaged hourly flux values for each site. Seasonal ecosystem C fluxes during winter [g C m^{-2} $season^{-1}$] are presented as:

(6.9) $$\sum R_w = \int_{d1}^{d2} R_w \cdot dt \, .$$

Annual ecosystem C balance (NEC_{year} [g C m^{-2} a^{-1}]) was calculated:

(6.10) $$NEC_{year} = \sum NEC_{day} + \sum R_w \, .$$

The lengths of snow periods were defined by the abrupt decrease and increase of top soil temperatures (daily values). *GAI* values of the sites were linearly interpolated between sampling dates. To fill the gaps of missing data from the beginning of the snow-free period until the first measurement, as well as between the last measurement during the snow-free period and the onset of the snow period, we assumed a constant *GAI*, taking its value at the nearest sampling date.

Effects of the study site and study years on peak above-ground standing biomass and below-ground biomass were tested by univariate analysis of variance followed by a Student-Newman-Keuls test. Additionally, a simple two-factorial analysis of variance (sampling date and study site) was applied to quantify differences of the seasonal course of *GAI*. Both study years were treated separately. The Student-Newman-Keuls multiple range test was used to calculate maximum critical range (LSD) using time or site as the main factor.

6.4 Results

6.4.1 Climatic properties and hydrology

The mean annual air temperature differed considerably between the two studied years, being -0.4°C (2003) and -1.3°C (2004), while mean annual soil temperatures (in 5 cm soil depth) at all study sites ranged between 3.5°C and 4.6°C for both years. The length of the snow-free period started 19 days earlier in 2003 (149 days) than in 2004 (123 days). During snow-free periods, the mean soil temperature was on average 2.2°C higher in 2003 than in 2004. Diurnal soil temperature varied according to time of day (data not shown). The maximum temperature span was reached on a clear day at mid season (2003), ranging from 6.2°C to 29.4°C. During snow periods, soil temperature was almost constant, with no diurnal change because of the insulation effect of a deep snow cover (maximum 235 cm). On average it was between 0°C and 0.1°C. Total precipitation during snow-free period was lower in 2003 (276 mm) than in 2004 (326 mm) (Fig. 6.2). Average water filled pore space (*wfps*) of both snow-free periods increased in the order *meadow* (46%) < *transitional* (59%) < *fen* (77%) < *wet fen* (81%) (Fig. 6.3). The year 2003 was much drier than 2004 at all sites. During snow-free periods, *wfps* decreased, reaching minimum values in August and early September; it increased again later in the season. In 2003, four distinctive desiccation periods were observed, whereas *wfps* was much more balanced during 2004. During the entire snow period, soils were water saturated for *fen* and *wet fen*. The soil of the *meadow* and the *transitional* site remained wet during snow periods.

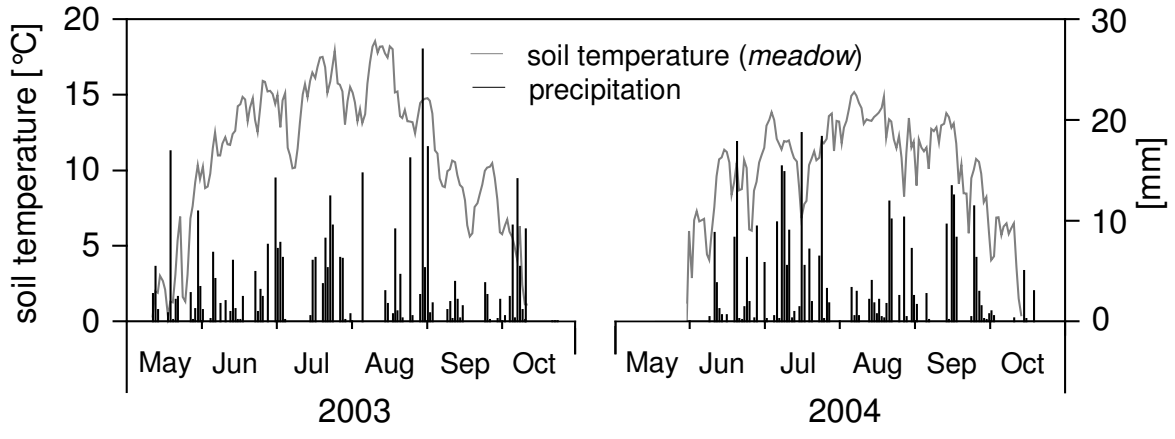

Figure 6.2: Time course of soil temperature in 5 cm soil depth (*meadow*) and precipitation during the snow-free periods.

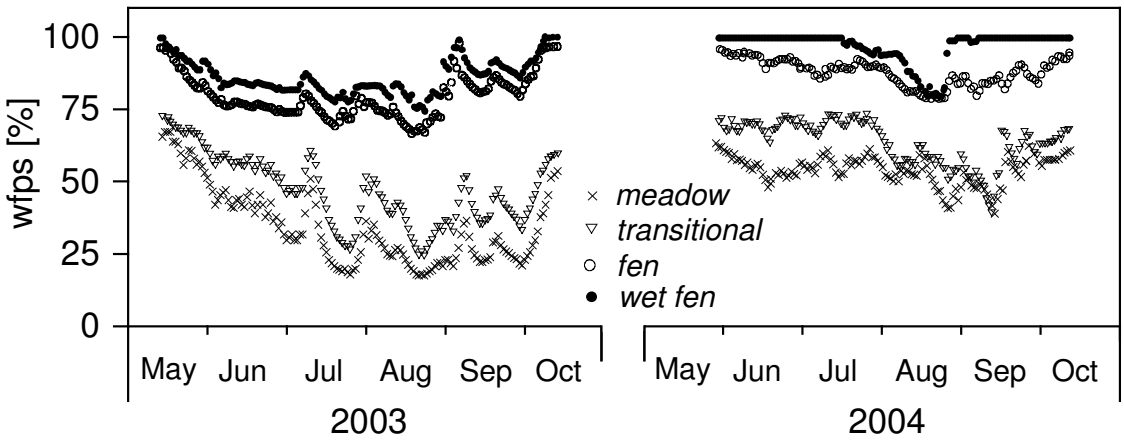

Figure 6.3: Time course of the water-filled pore space in 5 cm soil depth during the snow-free periods.

6.4.2 Vegetation properties

The green above-ground standing plant biomass was similar at the *meadow*, *transitional* and *fen* sites, but about three to four times lower at the *wet fen* site (Tab. 6.2). No significant differences between the study years were found at any study site. The ratio between green and non-green above-ground standing plant biomass (mainly necromass) was highest for *meadow* and lowest for *wet fen* (Tab. 6.2). In the wetter year 2004, this ratio increased for the fen sites. Highest root biomass (0-10 cm soil depth) was observed at *meadow* followed by *fen* and *transitional* (Tab. 6.2). Root biomass at *wet fen* was small, being three to four times lower than at the other sites. The plant green area index (*GAI*) peaked in July (2003) and August (2004) at all sites (Fig. 6.4). *Wet fen* had the lowest *GAI* throughout the snow-free periods, while all other sites had similar values. Maximum *GAI* for both study years were: *meadow* (4.3) > *transitional* (3.7) > *fen* (3.2) > *wet fen* (1.0).

Table 6.2: Above- and below-ground plant biomass at peak-standing plant biomass of the two investigated years 2003 and 2004. Different letters in the row indicate significant differences between study sites and years ($p \leq 0.05$).

site	*meadow*		*transitional*		*fen*		*wet fen*	
year	2003	2004	2003	2004	2003	2004	2003	2004
above-ground:								
green biomass [g m^{-2}]	242^{a}	237^{a}	239^{a}	280^{a}	204^{a}	222^{a}	64^{b}	71^{b}
green biomass/ non-green biomass	0.98^{a}	0.89^{a}	0.71^{ab}	0.83^{a}	0.66^{b}	0.85^{a}	0.53^{b}	0.74^{ab}
below-ground (0-10 cm):								
live biomass [g m^{-2}]:	349^{a}		273^{ab}		278^{ab}		95^{b}	

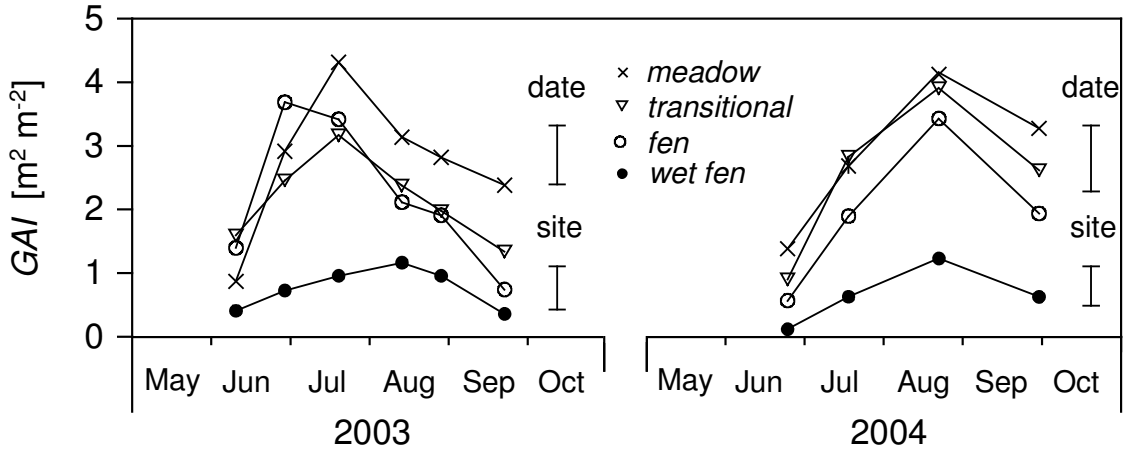

Figure 6.4: Time course of the plant green area index (*GAI*) during the snow-free periods. Error bars indicate the maximum critical range (LSD) for sampling date (date) and study site (site).

6.4.3 Controls of net ecosystem CO_2 exchange rate during daytime and total ecosystem respiration rate during nighttime

The net ecosystem CO_2 exchange rate during daytime (NEC_{light}) depended significantly on *PAR* and *GAI* (Tab. 6.3A). NEC_{max} derived from the models at a given *GAI* was highest at the *wet fen* site, and the ecosystem light compensation point (Γ) was highest for the *meadow*. At all sites, significant linear relationships (R^2=0.54 to 0.69; p<0.001) between NEC_{light} and *GAI* were found at high *PAR* (>800 µmol m^{-2} s^{-1}).

Total ecosystem respiration (R_{tot}) depended significantly on water filled pore space (*wfps*) and soil temperature (st_5) (Tab. 6.3B). The influence of *wfps* was different for the sites (see b_2 in Tab. 6.3B). R_{tot} was positively related to *wfps* at the drier sites (*meadow*, *transitional*), whereas R_{tot} increased with decreasing *wfps* at the wetter sites (*fen, wet fen*). The response of R_{tot} to a temperature difference of 10°C (Q_{10}) was calculated using the multiple linear model. The derived Q_{10} values were 3.0 (*meadow*), 3.5 (*fen*) and 3.9 (*transitional*, *wet fen*).

Table 6.3: (A) Parameters of the model functions to calculate net ecosystem carbon exchange rates during daytime (NEC_{light} [mg CO_2 m^{-2} h^{-1}]) and (B) total respiration rate (R_{tot} [mg CO_2 m^{-2} h^{-1}]); *PAR:* photosynthetic active radiation [µmol m^{-2} s^{-1}], *GAI:* plant green area index [m^2 m^{-2}], st_5*:* soil temperature in 5 cm depth [°C], *wfps:* water filled pore space [%]. All model function parameters and correlation coefficients were highly significant (p<0.001).

	meadow	*transitional*	*fen*	*wet fen*
A	$NEC_{light\,(PAR,GAI)} = NEC_{\max} \cdot \left(1 - e^{-k(PAR-T)}\right) \cdot GAI$ (n=36 for each study site)			
$NEC_{\max}$	233.72	250.78	228.04	324.44
k	0.0028	0.0027	0.0038	0.0044
T	128.91	109.13	106.86	93.03
R^2	0.71	0.67	0.60	0.59
B	$(-1)\ln R_{TOT\,(st_5,wfps)} = b_0 + b_1 st_5 + b_2 wfps$ (n=30 for each study site)			
b_0	4.05	3.52	4.94	6.94
b_1	0.17	0.14	0.12	0.14
b_2	0.007	0.005	-0.017	-0.045
R^2	0.80	0.81	0.88	0.86

6.4.4 Seasonal daily CO_2 fluxes

The calculated seasonal courses of NEC_{day} during snow-free periods increased until July (2003) or August (2004) and decreased towards the end of seasons (Fig. 6.5). The pattern follows the trend of *GAI and PAR*, resulting in a sharper increase and decrease of NEC_{day} in 2003 versus 2004. *Wet fen* had the overall lowest NEC_{day} values during both snow-free seasons compared to all other sites. Average NEC_{day} of both study years were in the order: *meadow* (4.56 g CO_2 m^{-2} d^{-1}) > *transitional* (4.00 g CO_2 m^{-2} d^{-1}) > *fen* (3.45 g CO_2 m^{-2} d^{-1}) > w*et fen* (1.77 g CO_2 m^{-2} d^{-1}).

Daily nighttime ecosystem respiration (R_{night}) increased (became more negative) from the beginning of the snow-free periods and peaked at all study sites in August (both study years) (Fig. 6.5B). R_{night} decreased again towards the end of snow-free periods. Average R_{night} values (both seasons) were *meadow* (-1.21 g CO_2 m^{-2} d^{-1}) > *transitional* (-0.89 g CO_2 m^{-2} d^{-1}) > *fen* (-0.74 g CO_2 m^{-2} d^{-1}) > *wet fen* (-0.36 g CO_2 m^{-2} d^{-1}).

R_w during snow periods was on average highest at *meadow* (-0.87 g CO_2 m^{-2} d^{-1}) followed by *transitional* (-0.65 g CO_2 m^{-2} d^{-1}), *fen* (-0.21 g CO_2 m^{-2} d^{-1}) and *wet fen* (-0.16 mg CO_2 m^{-2} d^{-1}). Significant differences were calculated between sites ($F_{(site)}$=5.81; p<0.009) but not between sampling dates ($F_{(date)}$=1.73; p=0.26).

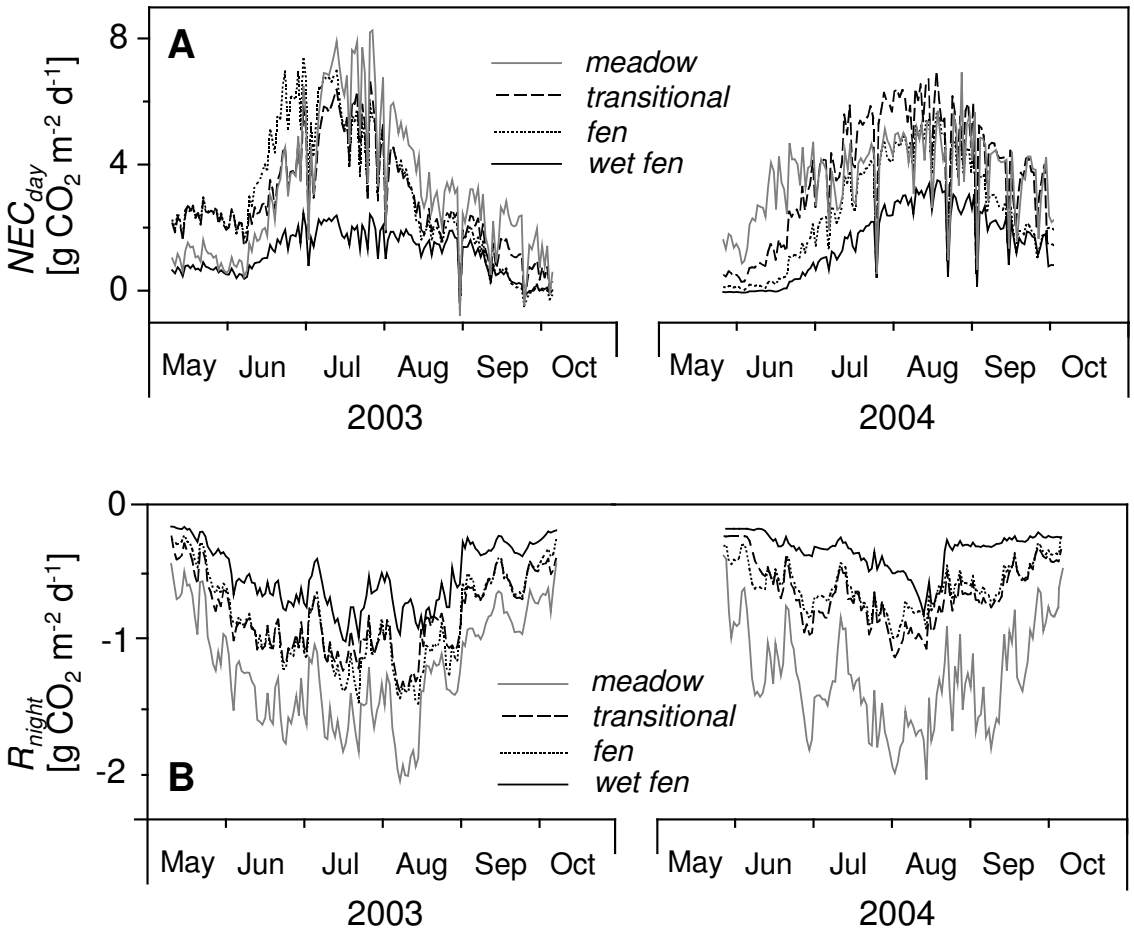

Figure 6.5: Time course of the seasonal NEC_{day} (A) and R_{night} (B) during the snow-free periods.

6.4.5 Cumulative C fluxes and annual C balance

All study sites function as net annual carbon sinks during snow-free seasons (ΣNEC_{day}). ΣNEC_{day} was highest at *meadow* for both study years (Tab. 6.4). However, ΣNEC_{day} at *transitional* and *fen* was almost as high as for *meadow*, while *wet fen* had the lowest values, being about two to almost three times lower than for all other sites. ΣR_w was highest for *meadow*, while *transitional*, *fen* and *wet fen* have ΣR_w values being about two to five times lower compared to *meadow*. The annual C balance (ΣNEC_{year}) is the sum of ΣNEC_{day} and ΣR_w. All sites were net annual carbon sinks, ranging from 96 to 125 g C m^{-2} a^{-1} for *meadow*, *transitional* and *fen* (average of both years). *Wet fen* had the lowest net annual carbon gain about two times lower than all other sites.

Table 6.4: Cumulative CO_2 fluxes (ΣNEC_{day} [g C m^{-2} $period^{-1}$], ΣR_w [g C m^{-2} $period^{-1}$]) and annual C balances [g C m^{-2} a^{-1}] of the two investigated study years 2003 and 2004.

site	*meadow*		*transitional*		*fen*		*wet fen*	
year	2003	2004	2003	2004	2003	2004	2003	2004
ΣNEC_{day}	171	167	141	155	146	110	67	64
ΣR_w	-51	-58	-27	-30	-12	-14	-9	-11
NEC_{year}	120	109	114	125	134	96	58	53

6.5 Discussion

6.5.1 Environmental controls of net ecosystem CO_2 exchange rate at daytime (NEC_{light})

The ecosystem light compensation point (Γ) was higher for *meadow* (129 µmol m^{-2} s^{-1}) than for all fen sites (109 µmol m^{-2} s^{-1} to 103 µmol m^{-2} s^{-1}). Similar Γ values (70 to 130 µmol m^{-2} s^{-1}) were reported for ungrazed vegetation near the treeline in the central Caucasus [*Trappeiner and Cernusca*, 1996]. *Diemer and Körner* [1998] found Γ values ranging between 80 and 110 µmol m^{-2} s^{-1} for mid-season, but increasing towards the end of vegetation period for alpine grassland dominated by *Carex curvula* (Swiss Alps). In contrast, zero net ecosystem CO_2 exchange rates were found for a higher range of *PAR* (250 to 400 µmol m^{-2} s^{-1}) at an alpine meadow in the Tibetan Plateau [*Kato et al.*, 2004] with a similar amount of above-ground plant biomass as in our study. Taking the derived model from *Hirota et al.* [2006] yielded remarkably low Γ values (<1 µmol m^{-2} s^{-1}) for several wetlands in the Tibetan plateau. However, our calculated parameters include a considerably dry snow-free season. Γ values from a boreal nutrient-poor fen were generally higher than our data, but much lower for a wet vegetation period (147 µmol m^{-2} s^{-1}) than a dry vegetation period (281 µmol m^{-2} s^{-1}) [*Bubier et al.*, 2003]. In general, low ecosystem light compensation point favours the net carbon gain of an ecosystem. In our study, the lower Γ values of all fen sites compared to the *meadow* may be an adaptation of these ecosystems, which have built up a large pool of soil organic matter.

In this study, net CO_2 flux measured at high radiation (*PAR*>800 µmol m^{-2} s^{-1}) was linearly related to *GAI,* confirming the importance of plant structure at different developmental stages. Similarly, a linear interpolated leaf area index has been used in seasonal gross ecosystem CO_2 exchange models for boreal organic soils [*Maljanen et al.*, 2004]. The calculated NEC_{max} for maximum observed *GAI* was highest for *meadow (*1.01 g CO_2 m^{-2} h^{-1}) followed by *transitional* (0.93 g CO_2 m^{-2} h^{-1}), *fen* (0.75 g CO_2 m^{-2} h^{-1}) and *wet fen* (0.39 g CO_2 m^{-2} h^{-1}). Higher values were reported at mid season for alpine meadows:

1.5 g CO_2 m^{-2} h^{-1} derived by single measurement in the Swiss Alps at full sunlight [*Diemer*, 1994] or for an alpine meadow in the Tibetan plateau (1.58 g CO_2 m^{-2} h^{-1}) [*Kato et al.*, 2004]. In contrast, a lower maximum NEC_{light} value (0.7 g CO_2 m^{-2} h^{-1}) over the entire growing season was found in a dry alpine tundra ecosystem, namely Niwot Ridge, Colorado [*Welker et al.*, 1999]. The seasonal NEC_{max} for the fen sites in our study (0.4 to 0.9 g CO_2 m^{-2} h^{-1}) were comparable with the range of seasonal NEC_{max} values (0.18 g CO_2 m^{-2} h^{-1} to 0.71 g CO_2 m^{-2} h^{-1}) of different wetlands in the Tibetan plateau [*Hirota et al.*, 2006]. Lower NEC_{max} values might be due to grazing. Remarkably reduced CO_2 uptake was observed for a grazed sub-alpine meadow [*Rogiers et al.*, 2005] during vegetation period and for alpine wetlands [*Hirota et al.*, 2005] in comparison to control sites. Moreover, *Gilmanov et al.* [2007] reported reduced maximal net ecosystem carbon gain and reduced light-use efficiency (defined as the ratio of gross ecosystem carbon gain to incident *PAR*) after hay-mowing events or grazing for several European grassland sites (temperate to sub-alpine).

6.5.2 Environmental controls of total ecosystem respiration rate (R_{tot})

During snow-free periods, the ecosystem respiration rate (R_{tot}) was related to soil temperature and *wfps* in 5 cm depth. Q_{10} values were lowest at the *meadow* site (3.0) compared to the fen sites (3.4 (*fen*) and 3.9 (*transitional*, *wet fen*)). Our Q_{10} values (corrected for soil moisture) fit to values calculated for other alpine ecosystems. *Cao et al.* [2004] found Q_{10} values based on soil temperature in 0-10 cm being 2.75 and 3.22 in a heavily grazed alpine meadow and lightly grazed alpine meadow, respectively. Q_{10} values for the entire snow-free season in alpine wetlands at the Tibetan plateau ranged from 2.7 to 5.1 [*Hirota et al.*, 2006]. An average Q_{10} of 3.5 was found for sub-alpine wetlands in the Rocky Mountains [*Wickland et al.*, 2001]. However, the wide range of temperature sensitivity found for ecosystem respiration is difficult to compare and probably reflects several variables: Q_{10} values were found to be higher for a lower temperature range and/or for a higher ratio of root to soil respiration [*Kirschbaum*, 2000], but do also highly depend on the quality of soil organic matter [*Fierer et al.*, 2006]. Moreover, soil respiration is exponentially related to temperature in contrast to respiration of above-ground plant biomass, which was linearly related to temperature in an alpine meadow [*Cernusca et al.*, 1978]. Beside soil temperature, *wfps* was the second important control of R_{tot}. The influence, however, differed depending on study site. In the *meadow* and the driest fen site (*transitional*), R_{tot} was positively related to *wfps*. Since we used the sign convention of R_{tot} having negative values, this means that the absolute value of R_{tot} decreased with decreasing *wfps*, which is an indication of water stress. This is remarkable because most alpine environments are expected to be not water limited

[*Körner*, 1999]. Incubation experiments yielded an optimum of 40 to 50% water holding capacity for soil respiration in forest and mineral soils [*Bowden et al.*, 1998]. In our experiments, however, *meadow* and *transitional* were exposed to very low *wfps* in 5 cm soil depth, especially during the snow-free period in 2003. These results identify topsoil as the major source for soil-derived CO_2 emissions and explain the greater carbon loss via R_{tot} with decreasing *wfps* in topsoil even at one of the fen sites (*transitional*). The influence of *wfps* on R_{tot} was negative for the *fen* and *wet fen.* Accordingly, the absolute value of R_{tot} increased if *wfps* decreased. The positive influence of *wfps* can be explained by the shift of anoxic to oxic soil conditions at low *wfps* because aerobic respiration is the main source of CO_2 emission [e.g. *Conrad*, 1996]. Also, water-logging may prevent CO_2 diffusion in the soil matrix, resulting in lower soil CO_2 emission. Our results are in agreement with several studies for alpine [*Hirota et al.*, 2006] or boreal wetland ecosystems [e.g. *Alm et al.*, 1997; *Bubier et al.*, 2003].

6.5.3 Magnitude of seasonal CO_2 fluxes

In quasi-stable ecosystems, the gross annual primary production is positively correlated with total ecosystem respiration, while low annual temperatures negatively influence both processes [*Gilmanov et al.*, 2007]. The magnitude of NEC_{day} and the duration of snow-free periods are the main factors for the ecosystem net carbon gain; here, R_{night} is the carbon loss of NEC_{day} during nighttime. At *meadow*, the averages (both snow-free periods) of modelled NEC_{day} and R_{night} were 3.50 g CO_2 m^{-2} d^{-1} and -1.11 g CO_2 m^{-2} d^{-1}, respectively. In comparison with the *meadow* site, a high range of CO_2 fluxes have been reported from alpine meadow ecosystems. For example, *Diemer and Körner* [1998] found a higher average NEC_{day} (8.41 g CO_2 m^{-2} d^{-1}) and a similar average R_{night} (-1.18 g CO_2 m^{-2} d^{-1}) for a Swiss alpine meadow dominated by *Carex curvula.* A much lower average NEC_{day} (0.17 g CO_2 m^{-2} d^{-1}) was calculated for an alpine dry tundra ecosystem at Niwot Ridge, Colorado [*Welker et al.*, 1999], even thought maximum R_{tot} during nighttime was comparable with our data. *Kato et al.* [2004] reported an average NEC_{day} of 4.3 g CO_2 m^{-2} d^{-1}, yet the maximum R_{night} (-9.2 g CO_2 m^{-2} d^{-1}) was more than four times higher than our data. Lower R_{night} values are likely a result of grazing: *Cao et al.* [2004] found 30% lower total ecosystem respiration for heavily grazed than for lightly grazed meadows in the Tibetan plateau.

At our fen sites, average NEC_{day} and R_{night} values (both study years) were lower than at *meadow*, ranging from 1.58 to 3.38 g CO_2 m^{-2} d^{-1} and -0.26 to -0.66 g CO_2 m^{-2} d^{-1}, respectively. Similar NEC_{day} values (0.53 to 3.26 g CO_2 m^{-2} d^{-1}) were found for various wetlands in the Tibetan plateau [*Hirota et al.*, 2006]. Those authors reported day-based total

ecosystem respiration for the entire day and found average values ranging from -1.43 to -4.00 g CO_2 m^{-2} d^{-1}. If we extrapolate our measured R_{tot} values during nighttime for the entire days taking model (6.2), we obtain lower average values (-1.05 to -1.93 g CO_2 m^{-2} d^{-1}). According to *Atkin et al.* [1997], however, artificial darkening (a common practice in many studies) of light-exposed leaves overestimates dark respiration compared to dark-acclimatized leaves and therefore overestimates total ecosystem respiration flux rates. Average R_w at *meadow* (-0.87 g CO_2 m^{-2} d^{-1}) falls into the range of R_w (-0.32 g C m^{-2} d^{-1} to -1.16 g CO_2 m^{-2} d^{-1}; 0 to -5°C soil temperature) that was found at Niwot Ridge, Rocky Mountains, Colorado [*Brooks et al.*, 1993]. Similar R_w values (-0.93 mg CO_2 m^{-2} d^{-1} at 0°C) were found in an alpine meadow ecosystem in the Tibetan plateau [*Kato et al.*, 2005] and in an alpine meadow in Austria (-1.06 g C m^{-2} d^{-1}) [*Cernusca et al.*, 1978]. Other studies reported higher R_w values from alpine and sub-alpine meadows, like for Wyoming (-0.64 to -2.38 g CO_2 m^{-2} d^{-1}; *Sommerfeld et al.* [1993]), Rocky Mountains National Park (-1.86 g CO_2 m^{-2} d^{-1}; *Mast et al.* [1998]) and for a meadow in the Swiss Alps (-2.28 g CO_2 m^{-2} d^{-1}; *Diemer and Körner* [1998]). Average R_w at our fen sites were lower (-0.16 to -0.65 g CO_2 m^{-2} d^{-1}) than for the *meadow* site, following the mean water gradient of the study sites. In comparison, *Mast et al.* [1998] found higher R_w values: -1.86 g CO_2 m^{-2} d^{-1} and -0.64 g CO_2 m^{-2} d^{-1} for moist and saturated alpine soils, respectively. The wide variation of reported flux values for similar temperature may reflect site-specific biological activity. Moreover, differences between the snow gas gradient method and chamber method after snow removal were reported by *Alm et al.* [1999]. Due to the long duration of snow periods in alpine regions, however, even small differences in R_w are significant for the ecosystem annual carbon budget. The ΣR_w correspond to 30-35% and 9-19% of ΣNEC_{day} for the *meadow* and all fen sites, respectively (see Appendix 1). *Sommerfeld et al.* [1993] calculated a contribution of ΣR_w to yearly above-ground net primary production of 20 to 50% for alpine and sub-alpine meadows, and *Brooks et al.* [1996] reported 20% for an alpine meadow in the Rocky Mountains. *Diemer and Körner* [1998] found a much higher contribution of ΣR_w to ΣNEC_{day} (73%) for an alpine meadow; note, however, that ΣR_w was calculated taking a value more than twice as high and with a snow period about one month longer than in our study. Hence, assuming the same wintertime respiration for snow period duration, the ratio ΣR_w to ΣNEC_{day} for the *meadow* site would shift to values (about 85%) similar to those found by *Diemer and Körner* [1998]. The fen sites appeared to be more robust to severe changes in the length of annual snow cover because ΣR_w to ΣNEC_{day} contributed less. Low ratios indicate that ecosystems are not in equilibrium and accumulate significant amounts of carbon [*Diemer and Körner*, 1998]. However, dissolved organic carbon may be transported in the aquifer, leading to significant carbon loss

from ecosystems; in our study, all fen sites are fed by water running down the hill slopes. *Alm et al.* [1997] also point to the role of leaching: they estimated an annual carbon loss of about 8 g C m^{-2} from dissolved organic matter leached from boreal fens in Finland.

6.5.4 Annual C balance in alpine ecosystems and global aspects

All of our sites proved to be significant annual carbon sinks (53-138 g C m^{-2} a^{-1}) for atmospheric CO_2. Beside *wet fen*, all other sites had similar values. Within the Rotmoos fen, *wet fen* cover was only roughly 5%. The cover of *transitional* and *fen* was estimated to be 10% and 85%, respectively. Thus, the Rotmoos fen has built up a huge amount of carbon per surface area in the past, but we expect no further carbon surplus compared to *meadow* under the current climate. Recent annual C balance data from alpine regions showed no consistent pattern. For example, *Diemer and Körner* [1998] found a lower annual carbon gain (20.4 g C m^{-2} a^{-1}) for a Swiss alpine meadow dominated by *Carex curvula*, while *Welker et al.* [1999] found a small carbon gain (7 g C m^{-2}) for the growing season in an alpine tundra ecosystem in Niwot Ridge, Colorado; because of the long annual winter period (7 months), the latter site is likely a net annual carbon source. Much greater differences in the annual C balance (-171 to 75 g C m^{-2} a^{-1}) derived from European sub-alpine meadows managed by grazing or cut herbage (no further manure application or mineral N input) were found by *Gilmanov et al.* [2007]. For sub-alpine fen sites, *Chimner and Cooper* [2003] calculated an average carbon gain of 24 g C m^{-2} a^{-1} (range: -142 to 180 g C m^{-2} a^{-1}) in the southern Rocky Mountains, while *Wickland et al.* [2001] found, for a wetland in the same area, a net annual carbon loss (-106.8 to -115.2 g C m^{-2} a^{-1}). A global C model predicted an annual carbon gain of 0 to 10 g C m^{-2} a^{-1} for the European Alps [*Zhuang et al.*, 2003], but the authors used only data from the North American continent. Great uncertainties still exist about net CO_2 fluxes from alpine ecosystems and the influence of management for those sites. These must be tackled before determining the role of alpine areas in the global C budget.

6.6 Conclusions

This study on the C balance of alpine ecosystems shows that net annual carbon gain was not related to the site's water balance under current climatic conditions. During snow periods, only a small part of the carbon gain during the vegetation period was respired. However, the high range of alpine wintertime CO_2 emission rates found in the literature is crucial for annual carbon loss during long snow periods. Due to the large variability of seasonal and annual net CO_2 fluxes from different alpine ecosystems, more investigations are necessary to evaluate

the role of alpine areas in the global carbon budget under present und future climate conditions.

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6.8 References

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Appendix

Appendix 6.1: Cumulative CO_2 fluxes ($\Sigma NEC_{daylight}$ [g C m^{-2} $period^{-1}$], ΣR_{night} [g C m^{-2} $period^{-1}$]) and selected ratios of cumulative CO_2 fluxes ($|\Sigma R_{night}/\Sigma NEC_{daylight}|$, $|\Sigma R_w/\Sigma NEC_{day}|$).

site	*meadow*		*transitional*		*fen*		*wet fen*	
year	2003	2004	2003	2004	2003	2004	2003	2004
seasonal C fluxes:								
$\Sigma NEC_{daylight}$	218	210	176	186	180	131	84	74
ΣR_{night}	-47	-43	-35	-31	-34	-21	-17	-10
ratio between C fluxes [%]:								
$\lvert \Sigma R_{night} / \Sigma NEC_{daylight} \rvert$	22	20	20	17	19	16	20	14
$\lvert \Sigma R_w / \Sigma NEC_{day} \rvert$	30	35	19	19	9	13	13	17

7 Temperature sensitivity of microbial respiration, nitrogen mineralization and potential soil enzyme activities in organic alpine soils

7.1 Abstract

Investigations focusing on the temperature sensitivity of microbial activity and nutrient turnover in soils improve our understanding of potential effects of global warming. This study investigates the temperature sensitivity of C mineralization, N mineralization and potential enzyme activities involved in the C- and N cycle (tyrosine aminopeptidase, leucine aminopeptidase, ß-glucosidase, ß-xylosidase, *N*-acetyl-ß-glucosidase). Four different study sites in the Austrian alpine zone were selected and soils were sampled in three seasons (summer, autumn, winter). A simple first-order exponential equation was used to calculate constant Q_{10} values for the C- and N mineralization over the investigated temperature range (0-30°C). The Q_{10} values of the C mineralization (average 2.0) for all study sites were significantly higher than for the N mineralization (average 1.7). The Q_{10} values of both activities were significantly negatively related to a soil organic matter quality index calculated by the ratios of respiration to the organic soil carbon and mineralized N to the total soil nitrogen. The chemical soil properties or microbial biomass did not affect the Q_{10} values of C- and N mineralization. Moreover, the Q_{10} values showed no distinct pattern according to sampling date, indicating that the substrate quality and other factors are more important. Using a flexible model function, the analysis of relative temperature sensitivity (*RTS*) showed that the temperature sensitivity of activities increased with decreasing temperature. The C- and N mineralization and potential aminopeptidase activities (tyrosine, leucine) showed an almost constant temperature dependance over 0-30°C. In contrast, ß-glucosidase, ß-xylosidase and *N*-acetyl-ß-glucosaminidase showed a distinctive increase in temperature sensitivity with decreasing temperature. Low temperature at winter sampling date caused a greater increase in the *RTS* of all microbial activities than for autumn and summer sampling date. Our results indicate (I) a disproportion of the *RTS* for potential enzyme activities of the C- and N cycle and (II) a disproportion of the *RTS* for easily degradable C compounds (ß-glucose, ß-xylose) compared with the C mineralization of soil organic matter. Thus, temperature may play an important role in regulating the decay of different soil organic matter fractions due to differences in the relative temperature sensitivities of enzyme activities.

7.2 Introduction

Alpine soils store a large pool of soil organic matter [*Körner*, 1999]. The alpine zone is adapted to a cool environment characterized by a long seasonal snow cover and a short vegetation period. A recent study predicted an increase of mean summer temperature between 3-5°C for the next 100 years, being more intensive for the European Alps than for temperate regions in Europe [*Heimann and Sept*, 2000]. The strong influence of temperature on carbon mineralization has been reviewed for different conditions [e.g. *Kirschbaum*, 1995; *Kirschbaum*, 2000; *Lloyed and Taylor*, 1994]. The hypothesis that respiration depends more on temperature than net photosynthesis is crucial for the ecosystem C balance [*Kirschbaum*, 2000]. This makes investigations on the temperature sensitivity of C mineralization very important. The temperature quotient (Q_{10}) describes the ratio of activity for a 10°C (or 10 K) change of temperature. However, there is still no consensus about the form of the relationship between temperature and decomposition [*Kätterer et al.*, 1998]. The temperature quotient (Q_{10}) is often calculated by simple first-order exponential functions yielding a constant Q_{10} over the investigated temperature range. Q_{10} values of soil respiration are influenced by substrate quality [*Fierer et al.*, 2006; *Mikan et al.*, 2002]. On the other hand, flexible exponential functions implying an increasing temperature sensitivity at low temperatures have been found to best describe the temperature response for C- or N mineralization over a wide temperature range [*Kirschbaum*, 1995; *Lloyed and Taylor*, 1994].

The temperature sensitivity of N mineralization is more difficult to investigate because of methodological problems in distinguishing between different soil N turnover processes. In general, the temperature sensitivity of net N mineralization appeared to be slightly lower than of C mineralization for a wide range of investigated soils [*Kirschbaum*, 1995]. *Kirschbaum* [1995], however, pointed out that the high individual range of reported values precludes a final conclusion. *Magit et al.* [2001] found that the decay of plant residues at low temperatures resulted in a higher proportion of mineralized nitrogen compared with C mineralization. The net N mineralization is a result of the mineralization-immobilization turnover (MIT). There was no relationship between net N mineralization rate of various humus samples and incubation temperatures below 15°C [*Niklińska et al.*, 1999]. The ^{15}N pool dilution technique showed a higher temperature sensitivity of gross N immobilization versus gross N mineralization for soils being treated with green manure [*Andersen and Jensen*, 2001]. This temperature-dependent decoupling of MIT may be crucial in understanding the temperature dependency of N cycling of easily degradable substrates like plant residues in agro-ecosystems. However, little information is available about the temperature sensitivity of C- and N processes in organic soils in alpine regions. Additionally, the temperature sensitivity of soil microbial activities in the alpine environment may change seasonally as an adaptation to seasonal changes in microbial biomass [*Lipson et al.*, 2002].

Extracellular enzymes are important because they catalyze the rate-limited steps of decomposition and nutrient cycling [*Sinsabaugh*, 1994]. Surprisingly, there are very few published data about temperature sensitivities of a wider range of potential enzyme activities within a given soil [*Trasar-Cepeda et al.*, 2007]. In general, potential enzyme activities have been found to depend less on temperature compared to the C mineralization with Q_{10} values < 2 [*Browman and Tabatabai*, 1978; *Tabatabai*, 1982].

This study investigates the C- and N mineralization as well as the potential activity of soil enzymes involved in C- and N cycling over a temperature range of 0-30°C. We tested the hypothesis that (I) the Q_{10} value of C mineralization is higher than that of N mineralization, (II) Q_{10} values of C- and N mineralization are lower in winter than in summer as an adaptation of the microbial biomass, (III) the relative temperature sensitivity (*RTS*) of C- and N mineralization as well as enzyme activity increases with decreasing temperature, and (IV) the quality of soil organic matter influences the temperature sensitivity of C- and N mineralization. Four alpine study sites were selected (one meadow and three fen plots), and soil samples were taken in three seasons (summer, autumn and winter).

7.3 Material and methods

2.3.1 Study sites description

The study sites are located in the Rotmoos valley of the Ötztal range (46°50´N, 11°03´E) in Tyrol (Austria) above the present tree line (2250 m a.s.l.). The snow-free period is about 4.5 months (June to mid-October) (M. Strobel, University of Innsbruck, personal communication), mean annual precipitation is 820 mm (1970-1996) and mean annual air temperature (1997-1998) is -1.3°C [*Kaufmann*, 2001].

Four study sites were chosen along a natural moisture transect (one alpine dry meadow and three sites in the Rotmoos fen); they differed in water balance and plant community. The first site is a well-drained alpine dry meadow (*meadow*) classified as a Curvulo-Nardetum (G.-H. Zeltner, University of Hohenheim, personal communication). The other three sites are located in the Rotmoos fen. The fen is mainly fed by surface water from runnels flowing down the hill slopes of the flanking mountains. The first site in the Rotmoos fen (*transitional*) is a Carici echinatae-Trichophoretum caespitosi community [*Rybníček and Rybníčková*, 1977]. This *transitional* site is located closer to the *meadow* site than the other fen sites and contains a high cover of plant species belonging also to the Curvulo-Nardetum. The second fen site (*fen*) is located deeper in the Rotmoos fen and is characterized by a typical Carici echinatae-Trichophoretum caespitosi plant community [*Rybníček and Rybníčková*, 1977]. The species richness was lower than at the *transitional* site. The third fen site (*wet fen*) is located in the centre of the Rotmoos fen and consists solely of *Carex nigra* L.

with a sparse vegetation cover compared to all other study sites. This site can be temporarily flooded by ground water.

7.3.2 Soil sampling, chemical soil properties and microbial biomass (C_{mic})

All soils represent mature alpine stages and have been developed since the last ice age (5000-10000 years ago) [*Bortenschlager*, 1970]. The parent material of the *meadow* soil consists of loamy sandy silicates and granite with a maximum soil depth of 50 cm. The substrate is silty sand and the soil is classified as an acid Cambisol. All soils in the fen are rheic Histosols with soil depths deeper than 1 m. The sites were randomly sampled in 0-5 cm soil depth (n=5 for each study site) at three sampling dates: the first sampling date was in autumn (a: October 3, 2002), the second date in summer (s: July 5, 2003) and third date in winter (w: February 2 2004) under a snow cover of about 180 cm. The mean daily soil temperature in 5 cm depth for ± 2 weeks around the sampling date was similar for all study sites. The overall order was: s (14.2°C) > a (3.9°C) > w (0.0°C). The samples were carefully homogenised by hand and the roots were sorted out. The homogenised soil was stored frozen (-20°C) in plastic bags until analysis. The chemical soil properties ($pH_{(CaCl_2)}$, C_{org}, N_t) and microbial carbon (C_{mic}) were determined for every sampling date. The $pH_{(CaCl_2)}$ was potentiometrically determined using 5 g soil and 10 ml 0.01 M $CaCl_2$ solution. The total carbon (C_t) and total nitrogen (N_t) were determined on air-dried soil by dry combustion at 1200°C using a LECO CNS 2000 element analyser with infrared and thermal conductivity detector. Since all soils were acidic, C_t was considered as soil organic carbon (C_{org}). C_{mic} was determined from field-moist soil samples with the chloroform fumigation-extraction (CFE) method. The soil samples (1 g, n=3) were fumigated for one day in chloroform vapour, followed by extraction (0.5 M K_2SO_4), filtration and analysis of the dissolved organic carbon (DOC) by flow injection analysis (Dimatoc 100 TOC/TN-analyzer, Dimatec, Germany). The DOC of blanks (n=3) was extracted from each soil sample without fumigation. C_{mic} was calculated by the difference between fumigated samples and the blanks with the recovery factor of 0.45 proposed for peat soils [*Sparling et al.*, 1990]. The chemical properties and C_{mic} of the autumn samples are listed in Tab. 7.1. There were no significant differences between the sampling dates for any soil property at any study site ($F_{(date)} \leq 2.9$; $p \geq 0.06$; two-way ANOVA).

Table 7.1: Chemical soil properties and C_{mic} of the study sites (autumn sampling). Different letters in the column indicate significant differences of the means between study sites. Values in parentheses are standard errors.

	$pH_{(CaCl_2)}$	C_{org} [%]	N_t [%]	$C_{org}\ N_t^{-1}$ [% $\%^{-1}$]	$C_{mic}\ C_{org}^{-1}$ [mg g C^{-1}]
meadow	3.9 (0.1) [a]	17.0 (1.9) [a]	1.0 (0.1) [a]	17.1 (1.6) [a]	42.8 (6.2) [a]
transitional	4.3 (0.1) [a]	28.2 (1.8) [b]	1.6 (0.1) [b]	17.2 (0.7) [a]	23.3 (4.1) [b]
fen	4.3 (0.1) [a]	30.8 (2.2) [b]	1.5 (0.1) [b]	21.1 (0.8) [b]	17.2 (3.8) [b]
wet fen	4.0 (0.1) [a]	35.1 (1.3) [b]	1.6 (0.1) [b]	22.0 (0.9) [b]	18.9 (5.2) [b]

7.3.3 Temperature incubation experiment

C mineralization, N mineralization and enzyme activities involved in C- and N cycling were measured in all soil samples over a temperature range of 0-30°C (5°C steps). Two incubators (Heraeus BK 600) and a climate chamber (SBS C120) were used to regulate the temperature with a precision (±1°C) that prevented any sample in any analysis from freezing during the incubation time at 0°C.

7.3.3.1 C mineralization

The frozen soil samples were allowed to thaw at 4°C for 10 days before the incubation experiment started. The water content of the soil samples was not adjusted prior the incubation experiment to avoid disturbance and/or adaptation to surrounding temperature during time of adjustment. However, the water content of the soils was not expected to limit soil respiration; all samples corresponded to a range of 79 to 98% maximum water holding capacity. Temperature sensitivity was determined by measuring the activity response of a soil sample to the different temperature steps. Soil samples (10 g) were incubated in air-tight flasks and the CO_2 evolved was trapped in 2 ml of NaOH (1 M) and titrated by HCL (0.1 M) after treated with 0.5 ml saturated $BaCl_2$. Blanks (n=3) were run in the same procedure for each incubation temperature. The soil samples were allowed to adapt to the incubation temperature in open flasks for at least 2 hours before the measurement started. The incubation time varied depending on incubation temperature, starting with 9 days at 0°C and ending with 1 day at 30°C (in total 25 days). During the experiment, soil moisture was kept constant. A preliminary experiment showed that soil respiration was constant for all study sites after 7 days and that cumulative CO_2 evolution (at 20°C) for all study sites was linear (R^2>0.98) for at least 6 weeks (data not shown). We therefore conclude that the temperature sensitivity during the total incubation time is not affected by decreasing respiration rates due to changes in the substrate quality of the soil organic matter.

7.3.3.2 N mineralization

The N mineralization was measured under water-logged anaerobic conditions according to *Keeney* [1982] and *Kandeler* [1996]. Thus, 3 sub-samples (5 g) of each soil sample were mixed with 15 ml deionized water and incubated for 4 days. The N-NH_4^+ produced was measured colorimetrically (Berthelot colour reaction) at 660 nm after being extracted with KCL (2 M) and filtered (N-free filters). Blanks were run in triplicates for each soil sample (immediately extracted and measured without incubation). The N mineralization activity was determined as the difference between samples and blanks (zero-order reaction). A preliminary study was conducted to investigate the effect of incubation time (2, 4, 6, 8 and 12 days) on NH_4^+ production at different incubation temperatures (0°C, 15°C and 30°C) for the summer soil samples. For all soils and all incubation temperatures, the NH_4^+ production was constant for at least 4 days. After this period, values fell or were even slightly negative (probably indicating N immobilization) (data not shown). Water-logging of soil samples may not immediately result in anaerobic soil conditions, especially at low incubation temperatures with their usually low activity. N mineralization may therefore be underestimated because ammonium is oxidized during incubation. The potential nitrification activity of the study soils was tested according to *Berg and Rosswall* [1985] and no significant nitrification activity was detected. Thus, ammonium oxidation is not important for these acidic alpine soils and does not influence the N mineralization rates in our study.

7.3.3.3 Enzyme activity

Hydrolytic enzymes involved in C- and N processes were investigated using a fluorimetric microplate assay [*Marx et al.*, 2001]. The activities of ß-glucosidase (GLUC; E.C. 3.2.1.21), ß-xylosidase (XYL; E.C. 3.2.2.37) and *N*-acetyl-ß-glucosaminidase (NAG; E.C. 3.2.1.30) were measured using 4-methylumbelliferyl (MUB)-ß-1,4-glucoside, MUB-ß-xylopyranoside and MUB-*N*-acetyl-ß-1,4-glucosaminide, respectively. The activity of leucine aminopeptidase (LEU; E.C. 3.4.11.1) and tyrosine aminopeptidase (TYRO; E.C. 3.4.11) were measured using L-leucine-7-amino-4-methyl-coumarin and L-tyrosine-7-amido-4-methyl-coumarin, respectively. The enzyme activity was determined as the hydrolytic cleavage of 4-methylumbelliferone (MUB) and 7-amido-methylcoumarin (AMC) from MUB- and AMC-labelled substrate, respectively. Before measuring the enzyme activities, suspensions (soil:water=1:100) were prepared from each soil sample using low-energy sonication (50 J s^{-1} output energy for 2 min according to *Stemmer et al.* [1998]) and 20 µl were transferred into vials of a 96-well microplate. 80 µl of buffer (100 mM 2-[N-morpholino]ethanesulfonic acid buffer (pH 6.1) for MUB substrate or TRIZMA buffer

(pH 7.8) for AMC substrate and 100 µl of substrat (1 mM) were added to each sample and incubated at the respective temperature using incubators or the climate chamber. All solutions and soil suspensions were prepared with autoclaved deionized water. Impurities of the solutions and/or the stability of the substrates were proved with blanks (samples without soil suspension). All temperature steps were conducted with each soil solution within 12 h.

The release of MUB or AMC was measured using an automated luminescense spectrophotometer (FL_x 800 microplate, Bio-Tex Instruments, Inc.; emission 446 nm, extinction 377 nm) at 20 to 40 min intervals for at least 2 h (depending on incubation temperature). After each measurement (~1 min) the microplates were immediately returned to the incubators or the climate chamber. The produced fluorescense was converted into amounts of MUB or AMC with soil-specific standards to correct for possible quenching effects of the soil matrix on the fluorescense intensity.

7.3.4 Temperature models

Two different temperature models were used to calculate the temperature sensitivity of the investigated activities. The first model is a simple first-order exponential equation 7.1:

(7.1) $f_{(T)} = A \cdot e^{(BT)}$; *T*: temperature [°C],

A is the exponential constant, or activity at 0°C, and B the exponential parameter of the equation.

The second model is a flexible exponential equation 7.2 [*Lloyed and Taylor*, 1994]:

(7.2) $f_{(T)} = A_1 \cdot e^{(-B_1/(T-T_0))}$; *T*: temperature [K],

A_1 is the exponential constant, while B_1 (loosely related to the activation energy) and T_0 are the exponential parameters [see *Kirschbaum*, 2000; *Lloyed and Taylor*, 1994]. This function implies a temperature sensitivity decreasing with increasing temperature and was found to be safely applicable for soil respiration at a temperature range of –10°C to almost 40°C

[*Lloyed and Taylor*, 1994]. The relative temperature sensitivity (*RTS*) was calculated according to equation 7.3:

$$(7.3) \quad RTS_{(T)} = \left(\frac{1}{f_{(T)}} \cdot \frac{df_{(T)}}{dT}\right) = \frac{B_1}{(T - T_0)^2},$$

Equation 7.3 is a derivation function of equation 7.2 and allows the temperature sensitivity to be calculated for a given temperature [*Lloyed and Taylor*, 1994].

Equation 7.1 was used to calculate constant Q_{10} values of the C- and N mineralization. Q_{10} values of the potential enzyme activities were not calculated because the hydrolytic cleavage of MUB- or AMC substrates may bias the activation energy and therefore the temperature dependency [*Fey and Conrad*, 2003]. Hence, the mutated activation energy of the artificial substrates influences the absolute temperature sensitivity (according to the Arrhenius theory) and is therefore not useful in interpreting these values.

Equation 7.2 was used to calculate the *RTS* of the activities (C mineralization, N mineralization, potential enzyme activities) for two different temperature frames (Δ5°C). We select the temperature frames 0-5°C: $RTS_{(0\text{-}5)}$ and 13-18°C: $RTS_{(13\text{-}18)}$, which incorporated the average mean daily soil temperatures (±2 weeks) at the three sampling dates for all study sites. Since at a given temperature *RTS* depends on the activation energy, the ratio $RTS_{(0\text{-}5)}/RTS_{(13\text{-}18)}$ was calculated. This procedure allows comparing the *RTS* of all investigated activities. Hence, a higher $RTS_{(0\text{-}5)}/RTS_{(13\text{-}18)}$ ratio indicates a greater increase of the *RTS* with decreasing temperature than a lower $RTS_{(0\text{-}5)}/RTS_{(13\text{-}18)}$.

7.3.5 Data handling and statistics

All results are calculated on an oven-dry weight basis (105°C, 2 days). The C mineralization (µg $C\text{-}CO_2$ g^{-1} C day^{-1}) was calculated on a C_{org} basis. This relation is an index for substrate quality [e.g. *Fierer et al.*, 2006; *Mikan et al.*, 2002]. Higher respiration rates related to the C_{org} indicate a better substrate quality. The N mineralization (µg $N\text{-}NH_4^+$ g^{-1} N day^{-1}) was calculated on a N_t basis. The potential enzyme activities (nmol MUB g^{-1} min^{-1} or nmol AMC g^{-1} min^{-1}) were related to the bulk soil. The Q_{10} values were linearly correlated with the chemical soil properties ($pH_{(CaCl_2)}$, C_{org}, N_t, C_{org} N_t^{-1}), C_{mic} and the exponential constant *A* derived by equation 7.1 (A_C: exponential constant A of

C mineralization; A_N: exponential constant A of N mineralization) in order to investigate the influence of these parameters on the temperature sensitivity. An a priori inverse auto-correlation between A and Q_{10} values (as demonstrated by *Reichstein et al.* [2005] when only one individual data set was used) did not exist because our A- and Q_{10} values are derived from more individual data sets (n=60 for each activity). Normal distribution of the data was tested by the Kolmogorow-Smirnoff-goodness-of-fit test, and homogeneity of variances was tested by Levene´s test. Differences of the Q_{10} values (C-, N mineralization) and the $RTS_{(0\text{-}5)}/RTS_{(13\text{-}18)}$ ratios (C-, N mineralization and enzymes (GLUC, XYL, NAG, TYRO, LEU)) were tested by a simple two-factorial analysis of variance (factor 1: sampling date (F_{date}); factor 2: study site (F_{site})). Differences of the mean Q_{10} values between the C- and N mineralization were tested with a mixed linear model using the restricted maximum likelihood (REML) measure. The model contains a fixed three-factorial design (factor 1, element of mineralization (C or N): $F_{element}$; factor 2: F_{date} and factor 3: F_{site}) combined with a repeated random subject term (date x site x replicate (within the site x date interaction)). This random interaction term accounts for the correlation of both activities within soil samples. Differences of the $RTS_{(0\text{-}5)}/RTS_{(13\text{-}18)}$ between activities (C-, N mineralization and enzymes (GLUC, XYL, NAG, TYRO, LEU)) were tested with the same mixed linear model design (factor 1: activity ($F_{activity}$); factor 2: F_{date}; factor 3: F_{site} and the repeated interaction of date x site x replicate (within the site x date interaction)). All values in the figures and tables are means (± standard error). For ease of interpretation, all temperatures in the figures are given in the Celsius scale.

7.4 Results

7.4.1 Q_{10} of the C- and N mineralization

The simple first-order exponential equation was used to calculate constant Q_{10} values for the entire investigated temperature range (0-30°C) (Tab. 7.2). The predicting ability (R^2) of the fitted model for the individual field replicates was 0.85 to 0.99 (C mineralization) and 0.78 to 0.96 (N mineralization).

The mean (±SE) Q_{10} value of the C mineralization for all field replicates, study sites and sampling dates was 2.0 (±0.04). There was only a small significant difference for sampling date (F_{date}=4.3, p=0.019; two-way ANOVA), with a higher mean Q_{10} value in autumn (2.1) than in summer (1.9) and winter (2.0). The mean (±SE) Q_{10} value of the N mineralization for all field replicates, sampling date and study sites was 1.7 (±0.03). Significant differences were found for sampling date (F_{date}=7.1, p=0.002; two-way ANOVA), with a higher mean Q_{10} value in winter (1.8) than in summer (1.6) and autumn (1.6). The study site (F_{site}) or the factor

interaction F_{site} x F_{date} were not significant for C mineralization ($p \geq 0.113$) and N mineralization ($p \geq 0.211$).

The mixed model identified an overall (all sampling dates and study sites) higher mean Q_{10} value for C mineralization than for N mineralization ($F_{element}=37.8$, $p<0.001$). However, there was also a small significant $F_{element}$ x F_{date} interaction ($F_{element\ x\ date}=5.2$, $p=0.007$), mirroring the different results of the C- and N mineralization for F_{date} in the two-way ANOVA. In addition, a small significant difference was found for sampling date ($F_{date}=5.8$, $p=0.004$), with a lower mean Q_{10} value in summer (1.7) than in autumn (1.9) and winter (1.9). The factor study site ($F_{(site)}$) and all other factor interactions were not significant ($p \geq 0.112$).

Table 7.2: Model parameters of the simple first-order exponential function (equation 7.1) for C- and N mineralization. Units: A_C [µg C-CO_2 g^{-1} C day^{-1}], A_N [µg N-NH_4^+ g^{-1} N day^{-1}], B [$°C^{-1}$]. Values are means (± standard errors).

	simple first-order model : $f_{(T)}=A\cdot e^{(BT)}$; T [°C]							
	C mineralization				N mineralization			
	A_C	B	Q_{10}	R^2	A_N	B	Q_{10}	R^2
summer:								
meadow	49.3 (9.1)	0.059 (0.004)	1.8 (0.1)	0.87-0.94	73.6 (10.1)	0.048 (0.003)	1.6 (0.1)	0.83-0.95
transitional	36.3 (6.2)	0.054 (0.006)	1.7 (0.1)	0.91-0.98	82.3 (9.3)	0.039 (0.004)	1.5 (0.1)	0.86-0.93
fen	34.1 (7.3)	0.063 (0.004)	1.9 (0.1)	0.85-0.93	94.7 (8.2)	0.044 (0.004)	1.5 (0.1)	0.82-0.92
wet fen	22.9 (6.7)	0.068 (0.005)	2.0 (0.1)	0.87-0.98	51.5 (11.6)	0.053 (0.005)	1.7 (0.1)	0.83-0.91
autumn:								
meadow	53.0 (9.9)	0.073 (0.004)	2.1 (0.1)	0.88-0.99	103.6 (14.3)	0.041 (0.005)	1.5 (0.1)	0.84-0.96
transitional	27.4 (5.1)	0.076 (0.005)	2.1 (0.1)	0.91-0.97	55.0 (6.1)	0.054 (0.004)	1.7 (0.1)	0.84-0.94
fen	34.1 (7.1)	0.070 (0.005)	2.0 (0.1)	0.88-0.96	75.7 (5.3)	0.041 (0.005)	1.5 (0.1)	0.81-0.91
wet fen	24.4 (4.1)	0.081 (0.004)	2.3 (0.1)	0.89-0.97	87.0 (8.4)	0.043 (0.003)	1.5 (0.1)	0.78-0.90
winter:								
meadow	95.3 (16.1)	0.056 (0.005)	1.7 (0.1)	0.89-0.95	144.6 (17.3)	0.047 (0.003)	1.6 (0.1)	0.84-0.95
transitional	17.4 (3.9)	0.078 (0.004)	2.2 (0.1)	0.87-0.97	58.4 (7.5)	0.061 (0.004)	1.8 (0.1)	0.85-0.94
fen	48.5 (5.1)	0.057 (0.005)	1.8 (0.1)	0.89-0.96	64.0 (8.3)	0.061 (0.004)	1.8 (0.1)	0.80-0.90
wet fen	20.2 (4.2)	0.076 (0.004)	2.1 (0.1)	0.88-0.97	38.8 (5.4)	0.056 (0.004)	1.7 (0.1)	0.78-0.92

The correlation of the Q_{10} values with the exponential constant A (index for substrate quality) was examined to investigate the influence of substrate quality on the temperature sensitivity of C- and N mineralization. The index for substrate quality of the C mineralization (A_C) and N mineralization (A_N) was inversely related to the corresponding Q_{10} values (Fig. 7.1). The regressions explained 44% (C mineralization) and 54% (N mineralization) of the variability of Q_{10} values. The slopes of the linear regressions and the y-axis intercepts were almost similar, being slightly lower for the C- than for N mineralization. There were no significant correlations between Q_{10} values and all other independent soil properties ($pH_{(CaCl_2)}$, C_{org}, N_t, C_{org} N_t^{-1} and C_{mic} ($p>0.115$)).

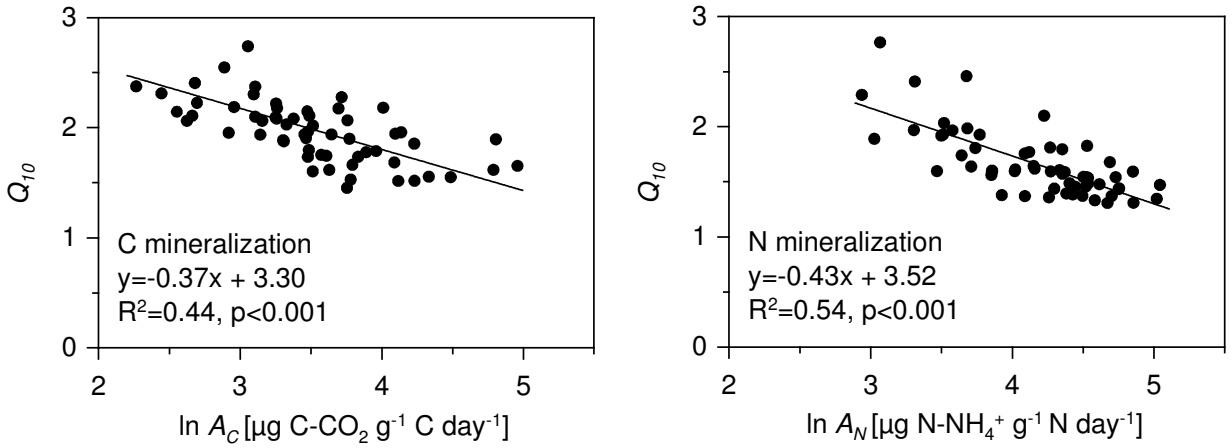

Figure 7.1: Relationship between Q_{10} values and the exponential constant A (index of soil organic matter quality). Q_{10} values, A of C mineralization (A_C) and N mineralization (A_N) were obtained from a simple first-order exponential equation (equation 7.1).

7.4.2 Substrate quality index of the C- and N mineralization

The substrate quality index of the C mineralization (A_C) was related to the substrate quality index of the N mineralization (A_N) (Fig. 7.2). If both soil-derived activities were in quasi- equilibrium with the available soil substrate (C_{org}, N_t), we would expect a 1:1 dialog. A significant linear relationship between A_C and A_N was found, being almost parallel to the 1:1 line. The regression line, however, did not go through the origin. If the regression line was forced to go through the origin, the relationship between A_C and A_N was not significant. Thus, both activities were much better described by including a constant y-axis intercept term (41.6) in the regression equation. This leads to the assumption that the different methods employed here to study C- and N mineralization may use different pools of soil organic matter and are not directly related.

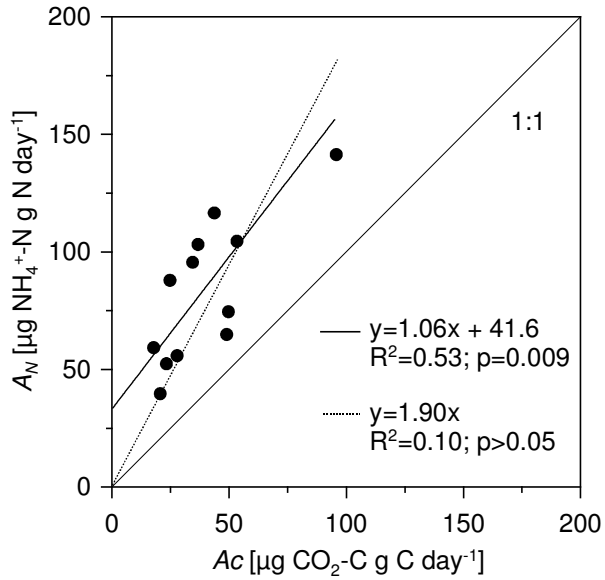

Figure 7.2: 1:1 dialog between the exponential constant A (index of soil organic matter quality) of C mineralization (A_C) and N mineralization (A_N); obtained from a simple first-order exponential equation (equation 7.1). Solid line is the linear regression line between C- and N mineralization; dashed line represents the linear regression through origin.

7.4.3 Relative temperature sensitivity (*RTS*) of the C- and N mineralization and enzyme activities (TYRO, LEU, GLUC, XYL, NAG)

The flexible temperature dependance model [*Lloyed and Taylor*, 1994] was used to determine the relative temperature sensitivity (*RTS*) of all activities (Tab. 7.3, Tab. 7.4). The equation follows the hypothesis that temperature sensitivity increases with decreasing temperature. The predicting ability (R^2) of the fitted flexible model for the individual field replicates of all activities (all sampling dates and study sites) were between 0.78 to 0.96. Its predicting ability was similar to the simple first-order exponential equation model for C- and N mineralization (Tab. 7.2, Tab. 7.3). *RTS* values (C- and N mineralization, enzyme activities) were plotted against temperature in Fig. 7.3. The C- and N mineralization and the aminopeptidases (TYRO, LEU) showed almost no increase of the *RTS* with decreasing temperature. In contrast, GLUC, XYL and NAG more closely followed the flexible model, with much higher *RTS* values at low than at higher temperatures. This relative trend of the curves was generally observed for all study sites and all sampling dates (data not shown).

Table 7.3: Model parameters of the flexible temperature dependance function (equation 7.2) for C- and N mineralization. Units: A_1 [µg C-CO_2 g^{-1} C day^{-1}] (C mineralization) and [µg N-NH_4^+ g^{-1} N day^{-1}] (N mineralization) and B_1, T_0 [K]. Values are means (± standard errors).

	flexible model [*Lloyd and Taylor*, 1994]: $f_{(T)} = A_1 \cdot e^{(-B_1/(T-T_0))}$; T [K]							
	C mineralization				N mineralization			
	A_1	B_1	T_0	R^2	A_1	B_1	T_0	R^2
summer:								
meadow	3.12 10^8 (4.23 10^7)	3853 (582)	56 (9)	0.88-0.94	8.92 10^6 (1.12 10^6)	2553 (306)	88 (13)	0.84-0.95
transitional	5.68 10^8 (5.24 10^7)	4216 (564)	46 (12)	0.91-0.98	6.78 10^5 (7.58 10^4)	1720 (196)	114 (15)	0.85-0.93
fen	2.24 10^7 (2.80 10^6)	3284 (539)	63 (6)	0.85-0.93	3.24 10^5 (4.35 10^4)	1357 (171)	137 (19)	0.82-0.92
wet fen	8.46 10^6 (6.18 10^5)	2841 (432)	87 (14)	0.87-0.97	6.17 10^4 (5.68 10^3)	1167 (132)	143 (17)	0.85-0.91
autumn:								
meadow	4.27 10^7 (5.14 10^6)	2887 (349)	87 (16)	0.87-0.98	2.89 10^5 (3.96 10^4)	1207 (140)	149 (24)	0.84-0.97
transitional	2.84 10^6 (3.18 10^5)	2353 (326)	99 (13)	0.91-0.97	5.88 10^6 (8.35 10^5)	2667 (253)	79 (11)	0.84-0.94
fen	4.46 10^7 (6.42 10^6)	3221 (432)	73 (10)	0.87-0.96	6.48 10^5 (8.22 10^4)	1494 (186)	137 (26)	0.81-0.92
wet fen	3.13 10^6 (2.53 10^5)	2479 (335)	96 (18)	0.89-0.98	1.38 10^5 (2.26 10^4)	1124 (152)	151 (20)	0.78-0.90
winter:								
meadow	2.70 10^7 (3.72 10^6)	2955 (345)	64 (9)	0.89-0.95	7.94 10^4 (9.69 10^3)	814 (67)	172 (17)	0.83-0.96
transitional	1.03 10^5 (9.93 10^3)	1367 (132)	148 (21)	0.86-0.97	4.27 10^4 (4.02 10^3)	889 (99)	167 (26)	0.85-0.94
fen	2.96 10^7 (4.27 10^6)	3278 (423)	53 (8)	0.90-0.96	1.35 10^4 (1.67 10^3)	710 (103)	174 (31)	0.80-0.90
wet fen	1.08 10^6 (1.63 10^5)	2162 (301)	111 (13)	0.88-0.97	2.31 10^4 (3.20 10^3)	950 (169)	162 (19)	0.77-0.91

Table 7.4: Model parameters of the potential enzyme activities using the flexible temperature dependance function (equation 7.2). Units: A_1 [nmol MUB g^{-1} min^{-1}] (ß-glucosidase, ß-xylosidase, *N*-acetyl-ß-glucosaminidase); [nmol AMC g^{-1} min^{-1}] (tyrosine aminopeptidase, leucine aminopeptidase) and B_1, T_0 [K]. Values are means (± standard errors).

	flexible model [*Lloyd and Taylor*, 1994]: $f_{(T)}=A_1 \cdot e^{(-B_1/(T-T_0))}$; T [K]								
	ß-glucosidase			ß-xylosidase			*N*-acetyl-ß-glucosaminidase		
	A_1	B_1	T_0	A_1	B_1	T_0	A_1	B_1	T_0
summer:									
meadow	2.68 10^4 (2.63 10^3)	814 (102)	204 (32)	4.44 10^5 (5.36 10^4)	1291 (126)	179(24)	4.71 10^4 (5.7310^4)	1108 (131)	179 (25)
transitional	6.07 10^4 (5.73 10^3)	990 (103)	195 (25)	2.17 10^5 (2.35 10^4)	1159 (134)	182 (16)	9.31 10^4 (1.03 10^5)	1203 (115)	176 (16)
fen	4.36 10^4 (3.19 10^3)	812 (162)	199 (32)	2.12 10^6 (3.83 10^5)	1684 (212)	163 (23)	1.13 10^4 (1.52 10^4)	988 (135)	184 (25)
wet fen	5.93 10^3 (7.98 10^2)	605 (76)	209 (19)	5.43 10^4 (4.84 10^3)	833 (116)	197 (24)	5.76 10^6 (7.20 10^5)	1776 (215)	155 (21)
autumn:									
meadow	1.41 10^4 (6.97 10^3)	673 (59)	212 (32)	8.86 10^5 (3.91 10^5)	1482 (184)	174 (28)	2.27 10^6 (8.32 10^5)	1578 (199)	168 (25)
transitional	9.83 10^3 (5.51 10^2)	581 (78)	215 (35)	3.25 10^5 (6.23 10^4)	1250 (134)	178 (26)	7.23 10^6 (2.74 10^6)	1830 (204)	159 (20)
fen	2.14 10^5 (1.94 10^4)	1019 (121)	195 (38)	1.96 10^6 (3.73 10^5)	1596 (301)	169 (29)	4.65 10^6 (2.93 10^6)	1992 (267)	148 (26)
wet fen	3.26 10^4 (3.73 10^3)	786 (98)	206 (36)	3.83 10^5 (9.21 10^4)	1132 (125)	186 (31)	6.63 10^5 (6.34 10^5)	1627 (165)	161 (24)
winter:									
meadow	1.27 10^4 (1.52 10^3)	638 (71)	211 (39)	2.17 10^5 (3.21 10^4)	1073 (96)	187 (19)	8.68 10^6 (2.23 10^5)	1489 (168)	168 (20)
transitional	1.03 10^4 (3.45 10^3)	674 (78)	206 (32)	5.51 10^4 (7.23 10^4)	1371 (165)	171 (28)	2.69 10^5 (9.34 10^4)	1298 (168)	179 (26)
fen	7.34 10^4 (7.24 10^3)	1005 (124)	195 (26)	3.23 10^5 (5.3210^4)	1194 (187)	184 (36)	2.65 10^6 (7.31 10^5)	1783 (362)	158 (33)
wet fen	6.54 10^3 (6.24 10^2)	590 (56)	214 (25)	1.27 10^6 (1.9410^5)	1475 (243)	173 (28)	1.93 10^5 (5.34 10^4)	1273 (154)	171 (25)

	Tyrosine aminopeptidase			Leucine aminopeptidase		
summer:	A_1	B_1	T_0	A_1	B_1	T_0
meadow	8.34 10^6 (1.03 10^5)	2950 (523)	86 (10)	7.54 10^6 (5.20 10^5)	2965 (368)	81 (13)
transitional	9.62 10^6 (2.39 10^5)	2765 (341)	98 (13)	3.44 10^7 (6.43 10^6)	3083 (403)	91 (9)
fen	7.58 10^6 (1.74 10^5)	2703 (503)	103 (21)	4.87 10^6 (8.21 10^5)	2960 (389	99 (16)
wet fen	7.11 10^7 (9.21 10^6)	3359 (322)	83 (11)	2.49 10^6 (9.21 10^5)	2241 (421)	113 (22)
autumn:						
meadow	4.07 10^6 (4.72 10^5)	2292 (298)	121 (19)	7.37 10^5 (5.32 10^4)	1770 (268)	139 (16)
transitional	9.42 10^6 (3.5310^5)	2584 (268)	106 (14)	9.12 10^4 (8.11 10^3)	1380 (223)	151 (27)
fen	6.95 10^8 (4.55 10^7)	3896 (532)	83 (15)	6.52 10^6 (9.21 10^5)	2410 (435)	114 (30)
wet fen	2.46 10^4 (3.93 10^3)	1664 (265)	157 (28)	3.29 10^6 (7.30 10^5)	2678 (343)	131 (22)
winter:						
meadow	1.12 10^5 (1.45 10^4)	1437 (165)	153 (15)	7.17 10^5 (5.23 10^4)	2119 (408)	109 (17)
transitional	5.26 10^6 (3.61 10^5)	2416 (321)	113 (12)	2.09 10^7 (5.1210^6)	2930 (355)	92 (13)
fen	1.12 10^4 (1.54 10^3)	1016 (186)	179 (17)	8.11 10^5 (7.87 10^4)	1674 (304)	147 (21)
wet fen	6.15 10^4 (6.7710^3)	1367 (156)	146 (19)	5.06 10^6 (4.48 10^5)	2193 (412)	123 (14)

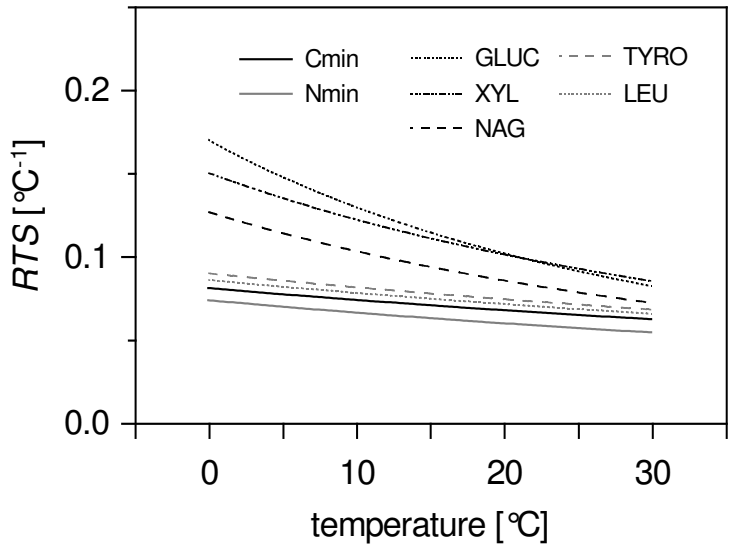

Figure 7.3: The relative temperature sensitivity (*RTS*) of the investigated soil microbial activities as a function of temperature (equation 7.3) (study site: *meadow*, sampling date: summer): C mineralization (Cmin), N mineralization (Nmin), enzyme activities: Tyrosine aminopeptidase (TYRO), leucine aminopeptidase (LEU), ß-glucosidase (GLUC), ß-xylosidase (XYL), *N*-acetyl-ß-glucosaminidase (NAG).

The ratio of $RTS_{(0\text{-}5)}/RTS_{(13\text{-}18)}$ was used to demonstrate differences of the relative temperature sensitivity between microbial activities, sampling dates and study sites, independent of different activation energies of the microbial activities (Fig. 7.4). There were no statistical differences of the $RTS_{(0\text{-}5)}/RTS_{(13\text{-}18)}$ of any studied activity (C- and N mineralization, GLUC, XYL, NAG, TYRO, LEU) for sampling date ($2.98 \geq F_{date} \geq 1.14$; $0.0605 \geq p \leq 0.8675$), study site ($2.0 \geq F_{site} \geq 0.07$; $0.120 \geq p \leq 0.977$) and sampling date x study site ($0.9 \geq F_{date \times site} \geq 0.2$, $0.484 \geq p \leq 0.975$) (two-way ANOVA).

The mixed three-factorial model was used to identify differences between the $RTS_{(0\text{-}5)}/RTS_{(13\text{-}18)}$ of the studied activities. Differences were significant between the activities ($F_{activity}=9.2$, $p \leq 0.001$). The ratios (all sampling dates and study sites) were in the ascending order: C mineralization (1.08), TYRO (1.11), LEU (1.13), N mineralization (1.14), XYL (1.20), NAG (1.22) and GLUC (1.25). The factor sampling date was significant ($F_{date}=6.6$; $p \leq 0.002$), with the overall lowest $RTS_{(0\text{-}5)}/RTS_{(13\text{-}18)}$ value (all study sites and activities) in autumn (1.12), followed by summer (1.16) and winter (1.20). The study site was not important ($F_{site}=1.4$; $p \leq 0.231$) and all factor interactions were also not significant ($0.7 \geq F \geq 0.03$; $0.755 \geq p \leq 0.100$).

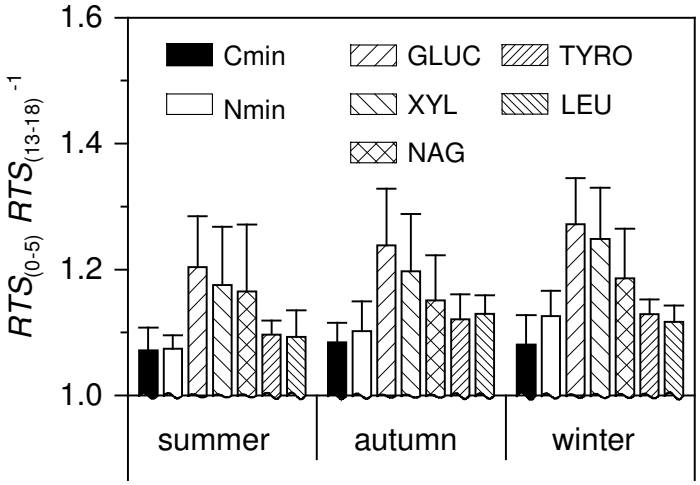

Figure 7.4: The ratio of the relative temperature sensitivity ($RTS_{(0\text{-}5)}/RTS_{(13\text{-}18)}$) for all soil activities (study site: *meadow*): C mineralization (Cmin), N mineralization (Nmin), enzyme activities: Tyrosine aminopeptidase (TYRO), leucine aminopeptidase (LEU), ß-glucosidase (GLUC), ß-xylosidase (XYL), *N*-acetyl-ß-glucosaminidase (NAG). Bars represent the mean, whiskers indicate standard error.

7.5 Discussion

7.5.1 Temperature sensitivity of the C- and N mineralization

7.5.1.1 Constant versus flexible temperature response

The temperature sensitivity of activities may vary depending on the investigated temperature range. In our study, there was no significant increase in the relative temperature sensitivity of C- and N mineralization with decreasing temperature at any study site and sampling date within the investigated temperature range (0 to 30°C). The predicting ability (R^2) of both models (simple exponential equation and flexible model according to *Lloyed and Taylor* [1994]) was similar for a given data set. This result indicated that the temperature sensitivity of C- and N mineralization is adequately explained by a constant temperature response. *Mikan et al.* [2002] found similar correlation coefficients of both models for six arctic tundra soils, although the temperature range (+0.5 to 14°C) was considerably smaller than in our study. A constant relation of basal respiration to temperature was also reported for larger temperature ranges in alpine [*Reichstein et al.*, 2000], antarctic [*Hopkins et al.*, 2006; *Smith*, 2003], temperate [*Pietikäinen et al.*, 2005] and mediterranean [*Fierer et al.*, 2003] regions in recent studies. In contrast, a considerable increase of the relative temperature sensitivity with decreasing temperature for C mineralization was found by *Kirschbaum* [1995] and *Lloyed and Taylor* [1994]. Calculating the temperature response from published data of several decomposition studies, *Kirschbaum* [1995] found a temperature sensitivity about three times higher at 0°C than at 20°C. Using 15 data sets from field experiments, *Lloyed and Taylor* [1994] detected a relative temperature increase about two times higher at 0°C than at 20°C. In contrast, a study has even reported an increasing temperature sensitivity of C mineralizaiton with increasing temperature for cold-adapted arctic soils [*Nadelhoffer et al.*, 1991].

The temperature sensitivity of net N mineralization has also been found to be constant over a wide temperature range and different soils [*Kladivko and Keeney*, 1987 (temperature range: 10 to 30°C); *Stanford et al.*, 1973 (temperature range: 5 to 35°C)]. In contrast, *Kirschbaum* [1995] reported that net N mineralization and denitrification appeared to have an overall lower temperature response with decreasing temperature than C mineralization. However, he concluded that the high variability in the published data prohibits any final conclusion. For net N mineralization, a lower increase of the relative temperature sensitivity at lower temperature may be influenced by nitrification and/or denitrification losses; these probably have different temperature responses than ammonification. Since potential nitrification rates were below the detection limit, we suggest that nitrification and/or denitrification did not influence net N mineralization in our study. There is evidence, however, that the mineralization immobilization turnover (MIT) may bias the temperature dependency.

Niklińska et al. [1999] found no relationship in the net N mineralization rate of seven European humus samples with incubation temperatures below 15°C compared to higher incubation temperatures. They concluded that, at lower temperatures, net N immobilization is more dominant than net N mineralization. In agricultural soils incorporated with green manure, gross N immobilization showed a higher temperature dependency than gross N mineralization using the ^{15}N pool dilution technique [*Andersen and Jensen*, 2001]. Thus, the relative temperature sensitivity of net N mineralization may depend on the MIT, suggesting an increasing temperature response at lower incubation temperatures. In accordance with the classical C- to N-concept, there was no net immobilization (at any incubation temperature) for our investigated soils (C- to N-ratios between 17 and 22% $\%^{-1}$). Our method, however, does not distinguish between N immobilization and gross N mineralization. Based on the constant temperature dependance we found over a wide temperature range, N immobilization may not be a major N flux during the short incubation period. This is also supported by *Wang et al.* [2001], who found lower N immobilization under water-logged conditions than under aerobic conditions for 20 different soils.

7.5.1.2 Q_{10} values of the C- and N mineralization

Incubation experiments have been criticized as underestimating temperature sensitivity because the quality of soil organic matter pools changes during incubation [*Kirschbaum*, 1995]. Accordingly, *Reichstein et al.* [2000] suggested to calculate Q_{10} values from rate constants derived from longer incubation periods rather than from instantaneously derived activities at different temperature intervals. There is not much evidence that respiration was affected by changes in soil organic matter quality during incubation: the respiration rate over six weeks (at 20°C) was fairly constant in a preliminary experiment. The incubation experiment for the temperature response of C mineralization was carried out by increasing incubation temperature stepwise. Temperature sensitivity did not decrease with increasing temperature, which can also be interpreted to reflect constant substrate quality throughout the incubation. A highly uniform organic matter pool is supported for cold-adapted organic arctic soils [*Weintraub and Schimel*, 2003] and for humus layers from boreal regions [*Niklińska et al.*, 1999]. Hence, the available C_{org} pool seems to be relatively large and uniform in cold-adapted environments.

The methodologies for calculating Q_{10} values can vary significantly, and direct comparisons require caution [*Fierer et al.*, 2005]. Therefore, we only compared absolute Q_{10} values derived by simple first-order exponential models (constant Q_{10} values). The average Q_{10} value of C mineralization for all study sites and all sampling dates was 2.0 (range 1.5-2.7). The range of Q_{10} values of soil respiration fit into the range of reported temperature

sensitivities (Q_{10}=1.2 to 3.9) from different alpine soils [*Duzler-Franz*, 1981]. *Schinner and Gstraunthaler* [1981] found a low Q_{10} value (1.5; 5-15°C) for an alpine meadow site in Austria, whereas higher values were reported for sub-alpine organic layers (2.5) and soils (2.8) between 5 to 25°C in the Swiss Alps [*Reichstein et al.*, 2000] and from 8 alpine soils (>3000 m a.s.l.) of the north American continent (Q_{10}=2.5 to 3.8) [*Fierer et al.*, 2006]. Very high temperature dependancies (Q_{10}=4.6 to 9.4) were reported for arctic tundra soils [*Mikan et al.*, 2002], while *Smith* [2003] found a median Q_{10} value of 2.0 (range 1.8 to 2.5) for 100 sites representing 21 habitats on a sub-antarctic island.

The average Q_{10} value of the N mineralization under water-logged conditions in this study was 1.7 (range 1.3-2.8) for all soils. Our results are in line with *Stanford et al.* [1973] and *Kladivko and Keeney* [1987], who found an average of 2.0 for a temperature range of 5 to 35°C (11 different soils) and 10 to 35°C (one soil). Both studies were carried out under aerobic conditions. There might be differences in the Q_{10} of aerobic and water-logged conditions. However, *Kladivko and Keeney* [1987] found no water-temperature interaction using a wide range of water potentials (-0.1 to -3.0 bar). Thus, there is no expectation that water-logged conditions yield lower temperature sensitivities than aerobic incubations.

7.5.2 Seasonal pattern in temperature sensitivity of soil-derived activities

Our data showed no distinct seasonal pattern. The Q_{10} values of C mineralization were slightly lower in summer than in autumn and winter. The Q_{10} values of N mineralization were highest in winter, but the differences between seasons were generally small. During the relative long incubation time (25 days) of the C mineralization experiment, soils may have adapted to the corresponding incubation temperature. However, a 4-day incubation might reveal no evidence for an adaptation of N mineralization rates. The *RTS* increase with decreasing temperature was greatest in winter for all investigated activities (C-, N mineralization, enzyme activities). Little information is available about the seasonal adaptation of the temperature response of soil activities. *Fierer et al.* [2006] found that 17% of the variability in Q_{10} values of C mineralization (77 soil samples) was positively correlated to the mean monthly soil temperature but not to the mean annual temperatures at the study sites - even though soils may have adapted to the surrounding temperature after being sampled and transported to laboratory. Similarly, a seasonal adaptation of potential respiration (substrate: potassium glutamate) occurred in an alpine meadow of the Rocky Mountains [*Lipson et al.*, 2002]. Those authors found lower temperature sensitivity in winter than in summer. Also, the temperature response of oxygen consumption was seasonally affected in coastal sediment, being higher in summer than in winter [*Thamdrup et al.*, 1998]. In contrast, *Niklińska et al.* [1999] found increasing Q_{10} values of respiration from humus

samples as mean annual temperatures at the study sites dropped. The relatively low differences we found in the temperature response for the C- and N mineralization over the year indicates that the soil activities are well adapted to enable nutrient cycling in this cold environment.

7.5.3 Effect of substrate quality on the temperature sensitivity of the C- and N mineralization

The Q_{10} values of C- and N mineralization were inversely related to substrate quality indices. Other studies also report an inverse relationship between Q_{10} values of C mineralization and the substrate quality index [e.g. *Fierer et al.*, 2005, *Fierer et al.*, 2006, *Mikan et al.*, 2002]. This supports the substrate quality-to-temperature sensitivity hypothesis, which implies higher activation energy for lower substrate quality. According to *Bosatta and Ågren* [1999], the carbon quality of the soil organic matter can be defined as the total number of enzymatic steps required to mineralize carbon to the end product CO_2. Hence, more enzymatic steps lead to higher activation energy for the C mineralization and greater temperature sensitivity. In contrast, no substrate quality-to-temperature sensitivity relationship was found in mineral soils [*Kätterer et al.*, 1998, *Reichstein et al.*, 2005]. Soil mineral particles can stabilize organic carbon through adsorption to surfaces, potentially resulting in different temperature sensitivities [*Mikan et al.*, 2002]. Therefore, organic soils may better reflect the temperature sensitivity of biological processes than mineral soils.

The nitrogen quality of soil organic matter was defined following the same concept. The relationship (slope and y-axis intercept of the regression line) between the substrate quality index and the Q_{10} were similar for C- and N mineralization. This suggests similar temperature sensitivity for both processes under equal substrate quality conditions. Assuming a generally constant C- to N-ratio in soils over longer time periods, we would expect a similar quality index for both activities. However, the index was higher for N- than C mineralization, pointing to differences in the use of soil organic matter pools. For C mineralization, soils were allowed to equilibrate until the respiration rate was constant (after the hyper-labile substrate pool was respired). According to *Boone* [1990], N transformations measured under water-logged conditions partly use easily degradable substrates from aerobic soil organisms killed by the anaerobic test conditions. This may help explain the higher substrate quality indices of N mineralization (A_N) than C mineralization (A_C) in our study.

It has been shown that the temperature sensitivity depend on the substrate quality index rather than on any other soil chemical property or microbial biomass. Similarly, *Fierer et al.* [2006] found Q_{10} values of C mineralization to be unrelated to soil chemical properties or microbial biomass (C_{mic}). Accepting that substrate quality is the key factor in the temperature

sensitivity of soil-derived processes, the turnover of more recalcitrant components should more strongly depend on temperature. In the framework of the global warming issue, this could alter the composition of the soil organic matter in peat soils.

7.5.4 Relative temperature sensitivity (*RTS*) of the enzyme activities

Extracellular enzymes are important because they catalyze the rate-limiting steps of decomposition and nutrient cycling [*Sinsabaugh*, 1994]. Our study revealed significant differences in the relative temperature sensitivity (*RTS*) between aminopeptidases (LEU, TYRO) and enzymes involved in the C cycle (GLUC, XYL, NAG). The greater increase of the *RTS* for GLUC, XYL and NAG at lower temperature compared to the aminopeptidases (TYRO, LEU) and C- and N mineralization suggest that temperature is an important factor regulating the use of different substrates. *Hopkins et al.* [2006] found a much higher temperature response for glucose-activated respiration at a lower temperature range (Q_{10}=3.3 to 6.9; temperature range: -0.5 to 20°C) versus an upper temperature range (Q_{10}=2.0 to 3.6; temperature range: 9 to 20°C) for five different antarctic soils. In contrast, the temperature sensitivity of C mineralization of these soils was constant over the entire temperature range, having lower Q_{10} values (1.2 to 3.3). The almost constant *RTS* for TYRO and LEU in our study suggests that polypeptide decay is more favoured at lower temperatures. Similarly, N mineralization is disproportionally high (versus C mineralization) in easily degradable green manures at low temperatures in cool temperate agro-ecosystems [*Magid et al.*, 2001]. However, soils from different climate regions may behave differently. *Trasar-Cepeda et al.* [2007] found much smaller *RTS* differences for a range of investigated enzymes of the C, N and S cycles in mediterranean soils in NW Spain. In our study, the disproportional *RTS* pattern for different enzymes of the N and C cycle may be characteristic for alpine ecosystems and allow a sufficient supply of nitrogen during the cold season in these N-limited cold environments.

7.6 Conclusions

This study revealed a temperature sensitivity of C- and N mineralization in the lower range of reported values from the literature. The relative low temperature response may be an adaptation to a cold environment in order to maintain nutrient cycling during the cold winter periods. No distinct seasonal adaptation was evident, but the within- and among-site variability in the temperature response was inversely related to substrate quality. However, the wide range of temperature responses for C- and N mineralization reported in the literature cannot be explained by substrate quality alone. This calls for future investigations to better understand the temperature sensitivity of soil-derived processes. The degradation of easily available C polymers was more strongly inhibited by low temperature than the decay of peptides by peptidases. Moreover, a surplus of easily available N compounds versus C compounds at lower temperature may be important for ecosystem functioning in cold-adapted and N-limited environments. Our results underline the key role of temperature in regulating the substrate use from different fractions of soil organic matter.

7.7 Acknowledgements

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8 Curriculum vitae

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