

**Nutrient stocks, acidity, processes of N transformation and
net uptake of methane in soils of a temperate deciduous
forest with different abundance of beech
(*Fagus sylvatica* L.)**

Dissertation

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Anja Guckland

geboren in Halberstadt

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1. Gutachter: Prof. Dr. Heiner Flessa

2. Gutachter: Prof. Dr. Edzo Veldkamp

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Contents

List of Tables	iv
List of Figures	vi
Zusammenfassung	ix
Abstract	xii
1 Introduction	1
1.1 Soil acidity, nutrient stocks and soil organic matter	1
1.2 Soil N cycle	2
1.3 Uptake of atmospheric methane	4
1.4 Objectives	5
1.5 References	7
2 Study area	12
3 Acidity, nutrient stocks and organic matter content	15
3.1 Abstract	15
3.2 Introduction	17
3.3 Materials and Methods	18
3.3.1 Study sites	18
3.3.2 Sampling design	22
3.3.3 Litter sampling and analyses	23
3.3.4 Soil sampling and analyses	24
3.3.5 Statistical analyses.....	25
3.4 Results	25
3.4.1 Production and composition of tree litter	25
3.4.2 Soil organic matter	28
3.4.3 Soil acidity and exchangeable cations.....	28
3.5 Discussion	35

3.5.1	Soil acidity and exchangeable cations.....	35
3.5.2	Effect of soil parent material	35
3.5.3	Effects related to tree species	36
3.5.4	Land use history	40
3.5.5	Soil organic matter	40
3.6	Conclusion.....	41
3.7	References	42
4	Soil N cycling and N₂O emission	45
4.1	Abstract.....	45
4.2	Introduction	46
4.3	Material and methods	47
4.3.1	Site description.....	47
4.3.2	Soil and litter sampling	48
4.3.3	Analysis of leaf litter, organic layer and mineral soil	48
4.3.4	Gross N transformation rates, microbial biomass and net N transformation rates	50
4.3.5	Calculation of mean residence time	52
4.3.6	N ₂ O fluxes, soil temperature, moisture content and extractable N	52
4.3.7	Statistical analyses.....	53
4.4	Results	53
4.4.1	Leaf litter, organic layer and mineral soil	53
4.4.2	Gross rates of N transformation, N pool sizes and mean residence time of N pools.....	55
4.4.3	Net rates of N-transformation	58
4.4.4	N ₂ O flux rates and soil factors	59
4.5	Discussion.....	61
4.5.1	Leaf litter quality and soil fertility increased with decreasing beech abundance.	61
4.5.2	Gross rates of N transformation increased with decreasing beech abundance	61
4.5.3	Net rates of soil N cycling did not reflect soil N availability.....	62
4.5.4	N ₂ O emissions increased with decreasing beech abundance	63
4.6	Conclusions	64

4.7	References	65
5	Controls of temporal and spatial variability of methane uptake	71
5.1	Abstract.....	71
5.2	Introduction	72
5.3	Material and methods	74
5.3.1	Study site.....	74
5.3.2	CH ₄ flux measurements and CH ₄ in soil air.....	76
5.3.3	Soil sampling and analysis	77
5.3.4	Modelling CH ₄ fluxes and statistical analysis.....	77
5.4	Results	78
5.4.1	Spatial and temporal variation of net CH ₄ uptake.....	78
5.4.2	Controls of CH ₄ uptake	80
5.4.3	Model results	84
5.5	Discussion.....	85
5.5.1	Annual CH ₄ uptake.....	85
5.5.2	Temporal variation of CH ₄ uptake	86
5.5.3	Spatial variation of CH ₄ uptake.....	89
5.5.4	Modelling CH ₄ uptake.....	90
5.6	Conclusions	91
5.7	References	92
6	Conclusions	99
6.1	Soil acidity, nutrient stocks and soil organic matter content	99
6.2	Stand and soil N cycling.....	100
6.3	Net uptake of atmospheric methane	100
6.4	General conclusion	101

List of Tables

Table 3-1: Number and percentage (in brackets) of trees and tree basal area of the most important tree genera of the study plots in the Hainich National Park and the Shannon-Weaver index (Hs; calculated from the total number of tree genera growing on the plots) on the basis of tree genus density and tree genus basal area. The plot codes abbreviate different diversity levels (DL1, DL2, DL3) of deciduous tree species and the replicate plots (a to c).	21
Table 3-2: Thickness of the loess cover, soil texture and soil bulk density of the replicated (a to c) plots with different diversity levels (DL1, DL2, DL3) of deciduous tree species.	22
Table 3-3: Soil area-related production of leaf litter with corresponding masses of C and N, leaf litter composition (C:N ratio, concentration of Ca, Mg, P, Mn) and ash alkalinity of leaf litter in stands with different diversity levels of deciduous tree species (DL1, DL2, DL3) (means and standard deviation, n = 3). Different letters indicate significant differences among stand types.	27
Table 3-4: C:N ratio in the organic surface layer and the mineral soil (mean and standard deviation, n = 3) in stands with different diversity levels of deciduous tree species (DL1, DL2, DL3). Different letters indicate significant differences among stand types within a given soil depth.	27
Table 3-5: Cation exchange capacity (CEC), exchangeable cations as percentage of total CEC and stocks of exchangeable Ca and Mg (means and standard deviation, n = 3) at different soil depths in stands with different diversity levels of deciduous tree species (DL1, DL2, DL3). Different letters indicate significant differences among stand types comparing the same soil depth.	30
Table 4-1: Soil properties in 0-5 cm and 5-10 cm mineral soil of the investigated stands with different beech abundance. Means (± 1 SE, n = 6) followed by a different letter indicate significant differences among stands (one-way ANOVA with Tukey HSD test at $P \leq 0.05$).	49
Table 4-2: Dry mass, nutrient concentrations and nutrient stocks in the leaf litter, organic layer and 0-5 cm mineral soil of the investigated stands with different abundance of beech. Means (± 1 SE) followed by a different letter indicate significant differences among stands (one-way ANOVA with Tukey HSD test at $P \leq 0.05$).	54

Table 4-3: Spearman rank correlation coefficients among gross rates of N transformations, N pool sizes and soil properties in 0-5 cm mineral soil (n = 18).	57
Table 5-1: Physical and chemical soil properties of the three stands (A, B, C) with different abundance of beech (means and standard deviations in brackets, n = 6). Different letters indicate significant differences between stands.	75
Table 5-2: Cumulative methane uptake (means and standard deviation in brackets, n = 6) of the soils of the three stands (A, B, C) with different abundance of beech and total precipitation during the growing and winter periods. Different lower case letters indicate significant differences between stands; different capital letters indicate significant differences between the selected periods for the same stand.	83
Table 5-3: Literature values of methane uptake rates in soils of temperate deciduous forests based on field measurements of at least one year.	87

List of Figures

- Figure 1-1:** Scheme of the major processes affecting pool sizes in forest soils. Processes in standard letters represent the internal N cycle; those written in *Italics* belong to the external N cycle (adapted from Hart et al., 1994 and Corre et al., 2003). 3
- Figure 2-1:** Mixed species stand at the Hainich National Park (Foto: I. Mölder)..... 12
- Figure 3-1:** Location of the study plots in the forested (in grey) area of the Hainich National Park. The replicate plots (a to d) are located in stands with different diversity levels of deciduous tree species (DL1, DL2, DL3). 20
- Figure 3-2:** Soil profile (Luvisol) next to the DL3c stand (A) and a transect with litter collectors and throughfall collectors at a pure beech stand (DL1b) (B). 23
- Figure 3-3:** Relationship between the quantity of exchangeable Ca or Mg (0 to 20 cm) and 1) Ca and Mg in leaf litter (left) and 2) the clay content in 20 to 30 cm (right). The different symbols represent stands with different levels of tree species diversity: \blacklozenge DL1, \bullet DL2, \blacksquare DL3..... 26
- Figure 3-4:** pH (H₂O) and base saturation at different soil depths in stands with different diversity levels of deciduous tree species (DL1, DL2, DL3). (Means and standard deviation, n = 3). Different letters specify significant differences among stands with different diversity level. 29
- Figure 3-5:** Measured versus estimated cation exchange capacity (CEC) of soil samples from the experimental plots ($R^2 = 0.93$). CEC was estimated from the humus content, clay content and pH using the following equation: $CEC \text{ (mmol}_c \text{ kg}^{-1}) = [\text{organic matter content (g kg}^{-1}) \times 2 \times f] + [\text{clay content (g kg}^{-1}) \times 0.534]$. The reduction factor f depends on soil pH as shown by “Bodenkundliche Kartieranleitung” (2005) and describes the decrease of CEC of soil organic matter with decreasing pH..... 30
- Figure 3-6:** Cation exchange capacity (CEC) of soil organic matter stocks down to a depth of 30 cm in stands with different diversity levels of deciduous tree species (DL 1, DL 2, DL 3) (means and standard deviation, n = 3). Different letters specify significant differences among stands with different diversity level..... 32
- Figure 3-7:** Relationship between the abundance of beech expressed as percentage of the total tree basal area and i) the C stocks of the organic surface layer, ii) the quantity of

- exchangeable Mg (0 to 20 cm) and iii) the quantity of exchangeable Ca (0 to 20 cm). The different symbols represent stands with different levels of tree species diversity: ♦DL1, ● DL2, ■ DL3. 33
- Figure 3-8:** Organic carbon stocks in the organic surface layer and at different depths in the mineral soil of stands with different diversity levels of deciduous tree species (DL1, DL2, DL3). (Means and standard deviation, n = 3). Different letters specify significant differences among the diversity levels within a given soil layer. 34
- Figure 4-1:** Gross rates of N transformation ($\text{mg N kg}^{-1} \text{ d}^{-1}$), N pools (mg N kg^{-1} , upper numbers in boxes) and mean residence time (d, lower numbers in boxes). For each parameter, means (± 1 SE, n = 6) followed by a different letter indicate significant differences among stands (Kruskal-Wallis H-test with multiple comparison extension at $P \leq 0.05$). NH_4^+ pool is given separately for November 2006 (first values) and April 2007 (second values) since for each stand these sampling periods differed (Paired-samples T-test at $P \leq 0.05$). 56
- Figure 4-2:** Regression analysis between annual gross N mineralization and nitrification rates using the mean values for each transect (n = 9; three transects per stand) (A) annual leaf litter-N input (gross N mineralization = $0.03x - 2.6$, $r^2 = 0.61$, $p = 0.007$; gross nitrification = $0.005x - 0.06$, $r^2 = 0.51$, $p = 0.018$) and (B) leaf litter C:N ratio (gross N mineralization = $-0.03x + 2.7$, $r^2=0.56$, $p = 0.012$; gross nitrification = $-0.01x + 0.4$, $r^2 = 0.46$, $p = 0.026$). 58
- Figure 4-3:** Net rates of N transformation in (A) November 2006 and (B) April 2007. 59
- Figure 4-4:** Seasonal changes of N_2O fluxes (means \pm SE, n = 6) measured in stands with different abundance of beech (A, B, C) during the experimental period of 2 years, and concentration of extractable NH_4^+ , NO_3^- and total soluble N ($\text{DON} + \text{NH}_4^+\text{-N} + \text{NO}_3^-\text{-N}$), water-filled pores space (WFPS) and temperature at a depth of 5 cm soil depth (means of all stands, n = 18). 60
- Figure 5-1:** Seasonal changes of a) CH_4 uptake rates (means and standard deviation, n = 6) measured in 3 stands (A, B, C) with different abundance of beech, b) soil water filled pore space (soil depth of 0-5 cm) in these stands (means, n = 6, standard deviations were generally smaller than the plotted symbols), c) soil temperature at a depth of 5 cm (means of all three stands), and d) daily precipitation from September 2005 till September 2007. 79

Figure 5-2 Relationship between the mean CH ₄ uptake rates measured at the 18 experimental subplots during the period May 2006 to November 2006 and the mean CH ₄ concentration in 5 cm soil depth.	81
Figure 5-3: Relationship between uptake rates of atmospheric CH ₄ and soil water filled pore space in a depth of 0 to 5 cm (data from all stands).....	82
Figure 5-4: Relationship between the annual uptake rates of atmospheric CH ₄ measured at the 18 experimental sub plots and the soil clay content in the depth 0 to 5 cm.....	82
Figure 5-5: Measured versus modelled (using the model of Potter et al., 1996) CH ₄ uptake rates for the two experimental years and all stands.....	84
Figure 5-6: Measured and modelled (using the model of Potter et al., 1996) time course of the mean CH ₄ uptake rates (calculated over all stands) in soils of the Hainich National Park during the experimental period of 2 years.....	85

Zusammenfassung

Baumarten können Bodeneigenschaften, Prozesse und zugehörige Bodenfunktionen beeinflussen. Während Unterschiede zwischen Nadelbäumen und Laubbäumen hinsichtlich ihrer Auswirkungen auf Bodeneigenschaften und Funktionen häufig untersucht wurden, ist der Einfluss verschiedener Laubbaumarten in Mischbeständen auf Bodenprozesse und die Biogeochemie von Ökosystemen weitgehend unbekannt. Deshalb wurde im Rahmen dieser Arbeit ein temperater Laubwald mit unterschiedlicher Buchenhäufigkeit und Baumartendiversität auf Acidität, Nährstoffvorräte und Gehalte der organischen Bodensubstanz sowie die Umsätze von Stickstoff (N) im Boden und die Senkenstärke des Waldbodens für atmosphärisches Methan (CH₄) untersucht. Ziel war es, die Hauptfaktoren der räumlichen Variabilität dieser Bodeneigenschaften und Prozesse in einem Laubmischwald zu bestimmen und den Einfluss der Buchenhäufigkeit zu klären. Aus diesem Grund wurden im Nationalpark Hainich/Thüringen Flächen mit i) Buche (*Fagus sylvatica* L.) (diversity level 1, DL1), mit ii) Buche, Esche (*Fraxinus excelsior* L.) und Linde (*Tilia cordata* Mill. and/or *T. platyphyllos* Scop.) (DL2) und mit iii) Buche, Esche, Linde, Ahorn (*Acer pseudoplatanus* L. and/or *A. platanoides* L.) und Hainbuche (*Carpinus betulus* L.) (DL3) ausgewählt. Alle Bestände haben eine langjährige Waldgeschichte und einen hohen Anteil von alten Bäumen. Sie unterliegen den gleichen klimatischen Bedingungen und stocken auf dem selben geologischen Ausgangssubstrat (Löss (60-120 cm) über Kalkstein). Der Bodentyp ist eine Parabraunerde, die im Winter Staunässe aufweist.

Auf diesen Flächen wurden Produktion und Zusammensetzung der Laubstreu sowie Bodenacidität, austauschbare Nährstoffe und die Menge und Verteilung der organischen Bodensubstanz in der organischen Auflage und im Mineralboden (0–30 cm) bestimmt. Drei Flächen (je 6 Plots) mit unterschiedlicher Buchenhäufigkeit wurden ausgewählt, um die N-Vorräte und N-Umsätze des Bestandes, Netto- und Bruttoreaten der N-Transformationen im Mineralboden und jährliche N-Verluste durch N₂O-Emissionen sowie die Beziehungen zwischen N-Pools und N-Flüssen zu analysieren. Auf diesen Flächen wurde ebenfalls die Senkenstärke des Waldbodens für CH₄ über zwei Jahre mit geschlossenen Hauben untersucht und es wurden die Hauptsteuergrößen für die räumliche und zeitliche Variabilität des Netto-CH₄-Umsatzes bestimmt.

Die Streuproduktion war in allen Beständen vergleichbar (3,2 bis 3,9 Mg Trockenmasse ha⁻¹ yr⁻¹), die Menge an mit der Streu eingetragendem Ca und Mg stieg

jedoch mit zunehmender Baumartendiversität und abnehmender Buchenhäufigkeit an (von 47 auf 88 kg Ca ha⁻¹ yr⁻¹; von 3,8 auf 7,9 kg Mg ha⁻¹ yr⁻¹). Die pH-Werte und die Basensättigung in den obersten 30 cm des Mineralbodens waren geringer unter Buche als in Mischbeständen (pH: 4,2–4,4 vs. 5,1–6,5; BS: 15–20% vs. 80–100%). Die Mengen an austauschbaren Al und Mn waren unter Buche am höchsten. Die Vorräte von Ca und Mg in den obersten 30 cm des Mineralbodens waren 12–15 bzw. 4–13-mal höher unter Mischbeständen als unter Buche. Die Akkumulation von organischem Kohlenstoff in der organischen Auflage war am höchsten unter Buche.

Mit abnehmender Buchenhäufigkeit stieg der jährliche N-Eintrag mit der Streu (21 bis 51 kg N ha⁻¹ yr⁻¹) und der N-Vorrat im Mineralboden (800–1500 kg N ha⁻¹). Die Umsatzrate des Streu-N ist höher in den Mischbeständen als in den Buchenbeständen, während die mittlere geschätzte Verweildauer von N in der organischen Auflage 2–4 bzw. 13 Jahre betrug. Die Nettoraten der N-Mineralisation und Nitrifikation unterschieden sich nicht zwischen den Beständen. Die Brutto-N-Mineralisation stieg von 2,4 auf 7,0 mg N kg⁻¹ d⁻¹ mit abnehmender Buchenhäufigkeit. Fünf bis vierzehn Prozent des produzierten NH₄⁺-N wurden nitrifiziert. Beide Prozesse waren eng korreliert mit der mikrobiellen Biomasse, welche wiederum mit dem N-Eintrag durch die Streu und deren C:N-Verhältniss, sowie mit dem N-Vorrat im oberen Mineralboden und der Basensättigung korrelierte.

Die N₂O-Emissionen waren in der Regel in allen Beständen gering. Eine Ausnahme bildete eine Frostperiode im Winter 2006 mit stark erhöhten Emissionen, die zu 46% bis 94% der jährlichen N₂O-Verluste beitrugen. Die mittleren kumulativen N₂O-Emissionen nahmen mit abnehmender der Buchenhäufigkeit zu. Sie waren auf der DL3-Fläche am höchsten (0,39±0,21 kg N₂O-N ha⁻¹ a⁻¹) und auf der DL1-Fläche am niedrigsten (0,10±0,11 kg N₂O-N ha⁻¹ a⁻¹).

Die jährliche CH₄-Aufnahme lag bei 2,0 bis 3,4 kg CH₄-C ha⁻¹. Die zeitliche Variation der CH₄-Aufnahme konnte zu einem großen Teil ($R^2 = 0,71$) mit der Änderung des Wassergehaltes in den obersten 5 cm des Mineralbodens erklärt werden. Unterschiede in der Jahresaufnahme zwischen den Flächen resultierten vorwiegend aus der räumlichen Variabilität des Tongehaltes in 0–5 cm ($R^2 = 0,50$). Während der Vegetationsperiode (Mai bis September) sank die CH₄-Aufnahme mit zunehmenden Niederschlägen. Geringe CH₄-Aufnahmeraten im Winter wurden zusätzlich durch Bodenfrost und Schneeeauflage reduziert. Es gab keinen Hinweis auf einen signifikanten Einfluss der Bodenacidität, der Nährstoffverfügbarkeit, der Mächtigkeit der Humusaufgabe oder der Buchenhäufigkeit auf die Nettoaufnahme von CH₄ in diesem Laubwald.

Die wichtigsten Faktoren, die die Variabilität der Bodenversauerung und der Nährstoffvorräte im Boden und in der organischen Auflage verursachten, waren der Tongehalt im Unterboden und die unterschiedliche Qualität der Laubstreu. Die Zusammensetzung und Qualität der Streu in den untersuchten Beständen wurde von der Buchenhäufigkeit beeinflusst, da die Nährstoffgehalte (z.B. N, Ca, Mg) der Laubstreu und deren biologische Verfügbarkeit unter Buche geringer waren als in Mischbeständen. Die Umverteilung von Nährstoffen mit der Laubstreu hat ein hohes Potential der Bodenversauerung entgegenzusteuern und die Basensättigung in diesen Lössböden über Kalkstein zu erhöhen. Baumartenspezifische Unterschiede in der Intensität des Kationenkreislaufes zwischen Boden und Baum waren ein Schlüsselfaktor, der zu den beobachteten Unterschieden in Bodenacidität und Nährstoffvorräten im Boden beitrug. Neben einer zunehmenden Basensättigung stiegen auch die N-Einträge mit der Streu und die Qualität der Streu mit abnehmender Buchenhäufigkeit. Diese Faktoren beeinflussten die Menge der mikrobiellen Biomasse und damit die Bruttoreaten der N-Transformation und die N-Verluste durch N₂O-Emissionen. Die Nettoaufnahme von CH₄ wurde nicht von der Buchenhäufigkeit beeinflusst. Für eine zuverlässige großräumige Abschätzung der CH₄-Senkenstärke dieses Laubwaldes sind detaillierte Informationen über die räumliche Verteilung der Tongehalte im obersten Mineralboden von großer Bedeutung. Aus den Ergebnissen lässt sich schlussfolgern, dass die Klimaveränderung mit dem Trend zu trockeneren Sommern und wärmeren Wintern in steigende CH₄-Aufnahmeraten in dieser Region resultieren wird.

Die Ergebnisse dieser Studie zeigen, dass zwei Faktoren die räumliche Variabilität der analysierten Bodeneigenschaften und Prozesse in dem untersuchten Laubmischwald bestimmen: 1. Die Buchenhäufigkeit und die damit verbundene geringere Umverteilung von Nährstoffen mit der Laubstreu und 2. die kleinräumige Variabilität des Tongehaltes im Ausgangsmaterial (d.h. in der Lössauflage). Die Trennung dieser beiden Faktoren war schwierig, da sich die räumlichen Muster von Buchenhäufigkeit und Tongehalt in dieser cross-site Studie in natürlichen Beständen überlagerten. Dennoch tragen die hier gewonnenen Ergebnisse zu einer verbesserten Kenntnis über den Einfluss der Buchenhäufigkeit in temperaten Laubmischwäldern auf Bodeneigenschaften und Bodenprozesse bei.

Abstract

Tree species can influence soil properties, processes and related soil functions. Whilst differences between conifers and deciduous tree species in affecting soils properties and functions have frequently been reported, the influence of different deciduous tree species in mixed stands on soil processes and ecosystem biogeochemistry is rarely understood. Therefore, a temperate deciduous forest with differing beech abundance and tree species diversity was investigated regarding acidity, nutrient stocks and organic matter content as well as nitrogen (N) transformations in the soil and the soil sink strength for atmospheric methane (CH₄). The aim was to analyze the key factors that determine the spatial variability of these soil properties and processes in a deciduous mixed forest and to elucidate the influence of beech abundance on soil properties and functions. For that purpose, stands were selected in the Hainich National Park in Central Germany with i) European Beech (*Fagus sylvatica* L.) as dominant tree species (diversity level 1, DL1), with ii) beech, ash (*Fraxinus excelsior* L.) and lime (*Tilia cordata* Mill. and/or *T. platyphyllos* Scop.) (DL2) and with iii) beech, ash, lime, hornbeam (*Carpinus betulus* L.) and maple (*Acer pseudoplatanus* L. and/or *A. platanoides* L.) (DL3). All stands had a long-term forest history and a high proportion of mature trees. They experienced similar climatic conditions, as they are found growing on the same geological substrates (loess (60-120 cm) which is underlain by limestone), and the soil type was a Luvisol which showed stagnic properties during winter.

In these stands the production and composition of the litterfall, soil acidity, exchangeable nutrients, and the amount and the distribution of soil organic matter in the humus layer and in the mineral soil (0-30 cm) were investigated. Three stands (each with 6 subplots) with different beech abundance were selected to analyze stand N stocks and N turnover, net and gross rates of N transformation in the mineral soil and N losses via N₂O emissions as well as the relationships amongst N pools and fluxes. The sink strength of the soil for atmospheric CH₄ was measured over two years in these stands with closed chambers and the main controls of the spatial and temporal variability of the net CH₄ exchange were determined.

Litter production was similar in all stands (3.2 to 3.9 Mg dry mass ha⁻¹ yr⁻¹). The amount of Ca and Mg input via litterfall increased with decreasing beech abundance and increasing tree species diversity (47 to 88 kg Ca ha⁻¹ yr⁻¹; 3.8 to 7.9 kg Mg ha⁻¹ yr⁻¹). The pH and base saturation in the upper 30 cm of the mineral soil were smaller under beech than in mixed stands (pH: 4.2-4.4 vs. 5.1-6.5, BS: 15-20% vs. 80-100%). The quantities of exchangeable Al

and Mn were highest under beech. The stocks of Ca and Mg in the upper 30 cm of the mineral soil were 12-15 and 4-13 times higher in mixed stands than in beech stands, respectively. The accumulation of organic carbon in the humus layer was highest in beech stands.

The annual N input via tree leaf litter (21 to 51 kg N ha⁻¹ yr⁻¹) and the N storage in the upper mineral soil (800-1500 kg N ha⁻¹) increased with decreasing beech abundance. Litter N turnover was faster in the mixed stands than beech stands, with the mean apparent residence time of N in the organic surface layer being 2-4 years and 13 years, respectively. Net rates were not different between stands. Gross N mineralization increased from 2.4 to 7.0 mg N kg⁻¹ d⁻¹ with decreasing beech abundance. Five to fourteen percent of the produced NH₄⁺-N was nitrified. Both processes were closely correlated with microbial biomass which in turn correlated with N input via leaf litter and litter C:N ratio as well as with the N stocks in the upper mineral soil and base saturation.

N₂O emission rates were generally low in all stands except for a frost period in 2006 with strongly increased emissions which accounted for 46% to 94% of the annual N₂O loss. The mean cumulative N₂O emission decreased with the abundance of beech. It was highest at the DL3 stand (0.39±0.21 kg N₂O-N ha⁻¹ a⁻¹) and lowest at the DL1 stand (0.10±0.11 kg N₂O-N ha⁻¹ a⁻¹).

The annual uptake of atmospheric CH₄ was between 2.0 and 3.4 kg CH₄-C ha⁻¹. The temporal variation of the CH₄ uptake could be explained to a large extent ($R^2 = 0.71$) by changes of the water content in the upper 5 cm of the mineral soil. Differences in the annual uptake between stands predominantly result from the spatial variability of the clay content in the 0-5 cm layer ($R^2 = 0.50$). During the growing period (May till November) CH₄ uptake increased with decreasing precipitation. There was no evidence for a significant impact of soil acidity, nutrient availability, the thickness of the humus layer or beech abundance on the net uptake of CH₄ in this deciduous forest.

The subsoil clay content and the litter quality were the most important factors, which determined the spatial variability of soil acidification and nutrients stocks in the upper mineral soil and the organic surface layer. Litter composition and quality in the analyzed stands were influenced by the abundance of beech since nutrient concentrations (e.g. N, Ca, Mg) in leaf litter and litter bioavailability were lower under beech than in mixed stands. The results show that the redistribution of nutrients with tree leaf litter has a high potential to counteract soil acidification and to increase the base saturation in these loess derived soils over limestone. Tree species related differences in the intensity of soil-tree cation cycling were a key factor,

which contributed to the observed differences in soil acidity and soil nutrient stocks. The increase in base saturation, leaf litter N input and litter quality with decreasing beech abundance influenced the amount of microbial biomass and, therefore, the gross rates of N transformation and N losses via N_2O emissions. The net uptake of atmospheric CH_4 was not influenced by the abundance of tree species. For a reliable larger scale estimate of the CH_4 sink strength in this mixed deciduous forest detailed information on the spatial distribution of the clay content in the upper mineral soil is necessary. The results suggest that climate change will result in increasing CH_4 uptake rates in this region because of the trend towards drier summers and warmer winters.

The results of this study show that there are two key factors which determined the spatial variability of the analyzed soil properties and processes in the investigated mixed deciduous forest: 1. The abundance of beech and the associated lower nutrient redistribution in its leaf litter, and 2. the small scale variability of the clay content in the parent material (i.e. in the loess cover). It was difficult to separate these two factors due to the interfering spatial pattern of beech abundance and clay content in this cross-site study within natural stands. Nevertheless, the results contribute to an improved knowledge on the influence of European beech abundance in deciduous mixed forests on soil properties and soil related processes.

1 Introduction

Quasi-monospecific forests where European beech (*Fagus sylvatica* L.) is occupying 80-100% of the canopy area (Ellenberg, 1996) form the natural forest vegetation of Central Europe. In limestone areas, the use and management of beech forests often resulted in an admixture of different proportions of other broad-leaved species and an increase in tree species diversity. Changes of tree species or even the admixture of species can have a pronounced influence on various chemical, physical, and biological soil properties. Nutrient cycling and soil properties under different tree species have been investigated regarding soil chemistry (Rothe et al., 2002, Augusto et al., 2002), soil biology (Saetre et al., 1999, Neirynek et al., 2000), carbon and nitrogen mineralization (e.g. Giardina et al., 2001, Corre et al., 2003, Inagaki et al., 2004, Geßler et al., 2005) and fluxes of nitrous oxide and methane (e.g. Dong et al., 1998, Borken & Beese, 2006, Butterbach-Bahl & Papen, 2002).

The effects of tree species on soil properties and functions were examined mostly in pure stands of hardwoods and conifers and mixtures of both. There is little information on the influence of different hardwood species in temperate forest on soil properties, nutrient turnover and functions of soils (Norden, 1994a, Finzi et al., 1998, Rothe and Binkley, 2001, Neirynek et al., 2000, Augusto et al., 2002). However, even deciduous tree species may differ in their effects on soil acidity, soil nutrient stocks, soil nitrogen (N) dynamics or net exchange of trace gases. The following sections provide a short introduction about soil properties (nutrient and organic carbon stocks, soil acidity) and processes (soil N cycling and nitrous oxide (N₂O) emission, net uptake of atmospheric methane) which were analyzed in this study. It is described how they are influenced by tree species.

1.1 Soil acidity, nutrient stocks and soil organic matter

Soil acidity is determined by the content of dissolved or solid acids, from which H⁺-ions dissociate and then form H₃O⁺-ions in the soil solution. Sources of H⁺-ions are oxidation of biomass and root respiration with resulting formation of carbonic acid and organic acids, the release from roots during cation assimilation, oxidation of NH₄⁺ and NH₃, oxidation of soluble Fe²⁺- and Mn²⁺- ions and of Fe-sulphides as well as input of acid precipitation. The identity, quality and quantity of plant and microbial biomass can influence soil acidity and therefore indirectly affect the cation exchange capacity (CEC) and the base saturation of soils.

These parameters, in turn, have a direct impact on the nutrient availability for plants and the balance of matter of landscapes. Further, the parent material of the soils plays an important role for soil acidity and CEC, since it provides the main source of inorganic nutrients, clay minerals and oxides as sorbents for exchangeable cations. Also organic matter can act as such a sorbent. Organic matter is formed from dead plants and animals and their conversion products. The organic matter can form an organic surface layer and is also mixed into the mineral soil.

These chemical soil properties as well as physical and biological properties of soils can be altered by plant species, since they differ in their nutrient uptake, root activity, canopy interception (Alriksson & Eriksson, 1998, Binkley & Giardina, 1998), biochemical composition (Zak et al., 2003), and redistribution of nutrients (Neirynek et al., 2000). It has been shown that the overstory composition can influence the soil nutrient status and acidity of the soil (Dijkstra et al., 2003, Binkley & Valentine, 1991, Reich et al., 2005). Raulund-Rasmussen and Vejre (1995) reported a tree species effect on the mass of organic carbon stored in the humus layer and in the mineral soil. This may be due to tree species related differences in the litter composition (Finzi et al., 1998).

1.2 Soil N cycle

The nitrogen (N) cycle in terrestrial ecosystems can be divided into an external and an internal one. The external N cycle comprises processes that add or remove N such as deposition, N fertilization, biological fixation, denitrification and leaching (Hart et al., 1994). The internal N cycle consist of the transfer of N between ecosystem pools by processes like mineralization, nitrification, plant assimilation and microbial immobilization. The processes of the internal N cycle are microbially mediated and they greatly influence outputs of N (Figure 1-1). The mineralization of organic N of plant detritus and dead microorganisms to the inorganic NH_4^+ provide the substrate for other processes of the internal N cycle. Oxidation of NH_4^+ by aerobe autotrophic microorganisms is the dominating nitrification process in soils. Heterotrophic organisms like certain bacteria or fungi can oxidize both NH_4^+ and organic N and they may be more important in acid forest soils, when autotrophic nitrification is restricted (Brumme and Beese, 1992). During nitrification and denitrification gaseous N forms are emitted to the atmosphere. The oxides of nitrogen, especially N_2O , belong to the most important radiatively active gases (ICCP, 2007). Additionally, the highly mobile NO_3^- can be leached from the soil and act as a ground water polluting compound.

The microbially mediated internal N cycle is influenced by several soil chemical properties (Bengtsson et al., 2003, Booth et al., 2005, Kooijman et al., 2008) since they affect the microbial biomass (Corre et al., 2003, Berg and Matzner, 1997). Additionally, plant diversity affects the amount of microbial biomass (Gaston and Spicer, 2004) and tree species influence the composition and activity of the soil fauna and microflora (Saetre et al., 1999, Neiryneck et al., 2000). Leaf litter chemistry has a direct effect on decomposition rates (e.g. Taylor et al., 1991, Prescott, 2002, Inagaki et al., 2004, Miyamoto and Hiura, 2008) and differences in litter quality between hardwoods and conifers influence stocks and transformation processes of N in soils (Jerabkova et al., 2006, Joshi et al., 2006, Inagaki et al., 2004). Gaseous losses of N (N_2O) are different in deciduous and coniferous forests (Ambus et al., 2006, Butterbach-Bahl et al., 2002). The admixture of broadleaf species to coniferous stands are reported to increase the litter N release, storage of inorganic N (Li and Han, 2008) and net rates of mineralization and nitrification due to improved litter quality (Ferrari, 1999). Different broadleaf species can also affect soil N dynamics since they differ in litter chemistry and in their effects on soil chemistry (Norden, 1994a and b).

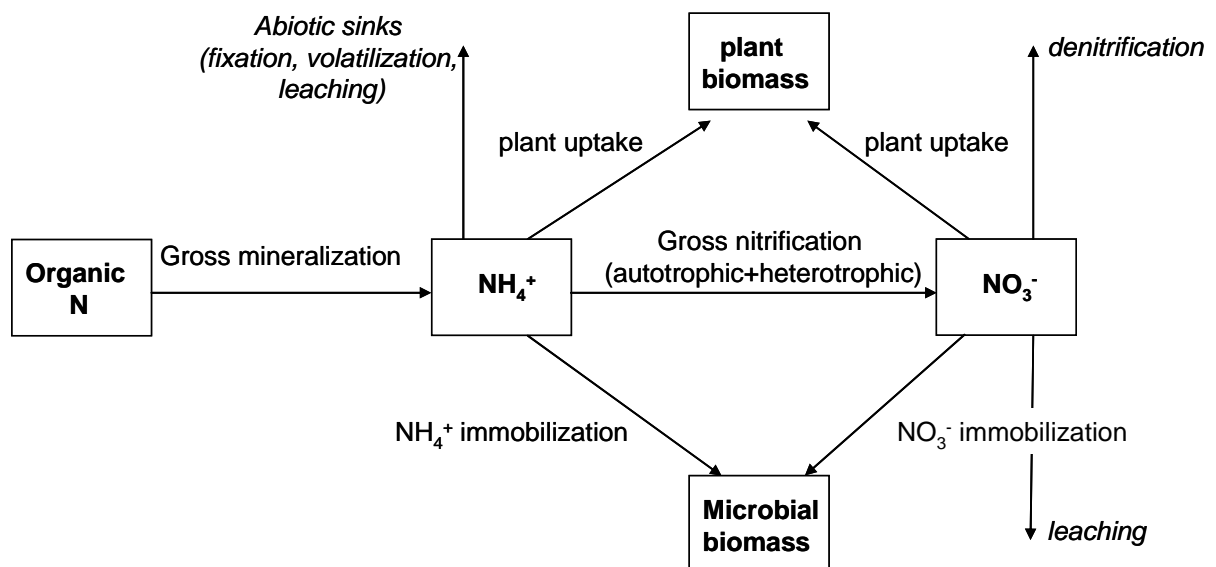


Figure 1-1: Scheme of the major processes affecting pool sizes in forest soils. Processes in standard letters represent the internal N cycle; those written in Italics belong to the external N cycle (adapted from Hart et al., 1994 and Corre et al., 2003).

Gross and net rates of microbially mediated N transformations are often unrelated due to different controls upon N production and consumption (Davidson et al., 1992). Thus, to investigate detailed effects of tree species on the microbially mediated internal N cycle gross

and net rates of N transformation have to be determined as it was recently done for mature coniferous forests (Davidson et al., 1992, Hart et al., 1994) and for pure deciduous stands (Verchot et al., 2001). However, there is a lack of information about the significance of different deciduous tree species for the spatial and temporal variability of soil internal N cycling in temperate mixed deciduous forests.

1.3 Uptake of atmospheric methane

Methane (CH₄) is a radiatively active trace gas, which has been increased in the atmosphere since the beginning of industrialization from 715 ppb to 1774 ppb in 2005 (IPCC, 2007). CH₄ is released to the atmosphere through biogenetic sources such as anoxic production in wetlands and rice agricultures or biomass burning as well as ruminant animals. In addition, the industrial mining of fossil fuel is an important anthropogenic CH₄ source (ICCP, 2007). The most important sinks are the reaction with the hydroxyl free radical (OH) in the troposphere (506 Tg yr⁻¹), the destruction in the stratosphere (40 Tg yr⁻¹) and the microbial oxidation in soil (30 Tg yr⁻¹) (ICCP, 2001). Thus, soils are the only biological sink for CH₄. Two groups of CH₄ oxidizing microorganisms exist in soils. The high affinity methanotrophs are well adapted to the low atmospheric CH₄ concentration (1.8 ppmv) and have a low threshold for CH₄ (Dunfield et al., 1999). Low affinity methanotrophs are active only at high CH₄ concentrations typical for landfill cover soils (Kightley et al., 1995) or oxic horizons of wetland soils (Segers, 1998).

Well aerated forest soils act as an important net sink for atmospheric CH₄ (Stuedler et al., 1989, Smith et al., 2000), whereas anoxic soils or soil layers are net sources of CH₄ (Davidson et al., 2004, Yavitt et al., 1990). Flux rates between soils and atmosphere are the sum of the oxidation of CH₄ through methanotrophic microorganisms under aerobic conditions and the production of CH₄ by methanogenic microorganisms in anaerobic soils or at anaerobic microsites within a soil.

The net sink strength of soils for atmospheric CH₄ is mainly influenced by factors that affect the gas diffusivity in soils, like soil moisture, soil bulk density and soil texture (e.g. Dörr et al., 1993, Bender and Conrad, 1993, McNamara et al., 2008). Land use change from forest to agriculture can reduce the soil sink strength by about two-thirds (Dobbie and Smith, 1996, Smith et al., 2000) and afforestation and reforestation increases soil CH₄ uptake (Saggar et al., 2008). Studies that compared the uptake of atmospheric CH₄ by soils under hardwood stands and adjacent coniferous stands attributed differences to the tree species effect on soil

acidity, soil bulk density, depth and structure of the organic layer and microbial activity in the upper mineral soil (Borken and Brumme, 1997, Borken et al., 2003, Butterbach-Bahl and Papen, 2002, Reay et al., 2005). Different broadleaved tree species in deciduous forest soils may also affect CH₄ uptake, since they also can differ in their effects on soil chemistry (Nordén, 1994a) and soil biology (Neiryneck et al., 2000, Cesarz et al., 2007).

1.4 Objectives

This study was performed within the DFG (Deutsche Forschungsgemeinschaft) Research Training Group (Graduiertenkolleg 1086) 'The role of biodiversity for biogeochemical cycles and biotic interactions in temperate deciduous forests'. Fourteen PhD students investigated the impact of deciduous tree species diversity on ecosystem functions in temperate forests.

Within this project, I analyzed the effect of beech abundance in a mixed deciduous forest on soil properties and carbon (C) and nitrogen (N) transformations in soils.

The objectives of this project were:

1. to identify and evaluate the main factors that contribute to the variability of soil acidification, soil nutrient status and the amount and distribution of soil organic matter in mixed stands of broad-leaved tree species with different abundance of beech. The role of beech abundance on soil chemical properties and nutrient availability in soils should be analyzed.
2. to determine N stocks and N cycling in stands with different abundance of beech at the stand level and within the soil. The main controls of net and gross rates of N transformations should be determined and the influence of beech abundance on these processes should be elucidated. In addition, emissions of N₂O emission should be quantified and relations between these emissions and soil internal gross N transformation rates and the beech abundance should be evaluated.
3. to determine the net CH₄ exchange rate of soils of broad-leaved mixed stands with different abundance of beech and to analyze the key factors that determine the seasonal, inter-annual and spatial variability of the CH₄ flux rates. Again, the role of beech abundance on soil net exchange of CH₄ should be analyzed.

Based on these three main objectives, three studies were conducted to answer the following hypotheses:

The first study aimed at the determination and comparison of soil acidification, the soil nutrient status and the amount and distribution of soil organic matter in stands with different abundance of beech. I hypothesized that the tree litter composition and small-scale variations in the soil parent material are the key factors influencing these soil properties.

In the second study I determined i) stand N stocks and cycling ii) net and gross rates of N transformation in the upper mineral soil and iii) annual N loss via N₂O emission. I analyzed the relationship of stand N cycling and N₂O losses to the gross rates of N mineralization and nitrification in the upper mineral soil.

I hypothesized that N cycling is greater in stands with low beech abundance due to differences in litter decomposition and degradability. I expected lower net- and gross-N mineralization and nitrification rates in beech dominated stands. The higher production and availability of mineral N will probably result in larger N₂O losses from sites with low abundance of beech.

With the third study the net CH₄ exchange and the key factors influencing the temporal and spatial variability of CH₄ flux rates in different stands were investigated. I hypothesized that the soils of the stands are a net sink for atmospheric CH₄ and that the seasonal dynamic of CH₄ uptake is predominantly controlled by the soil moisture regime. The spatial variability of CH₄ uptake is probably controlled by soil physical properties and by the abundance of beech. The influence of beech is expected to be due to its effect on soil acidity and humus accumulation in the organic surface layer.

1.5 References

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2 Study area

This observational study was conducted in the old-growth deciduous forest of the Hainich National Park in Central Germany. The forest is dominated by European Beech (*Fagus sylvatica* L.) and consists of up to 14 deciduous tree species. All stands had a high proportion of mature trees with an age of 100 to 150 yrs and a long-term forest history of at least 200 years. Historic forest utilization includes coppice-with-standards systems and selective cutting. The forest has not been managed since 1990; before that time, it had been used for military training since the 1960s. In December 1997, it became a National Park. The study area exhibits similar climatic conditions with annual precipitation of about 670 mm and annual mean temperature of 7.5°C (weather station Weberstedt/Hainich) and is situated at a slightly inclined plateau of Triassic limestone (Muschelkalk) covered by Pleistocene loess (60-120 cm).

Study plots that belong to three tree species different diversity levels (DL) have been established to compare i) monospecific stands of predominantly beech (DL 1), ii) three species stands with beech, ash (*Fraxinus excelsior* L.) and lime (*Tilia cordata* Mill. and/or *T. platyphyllos* Scop.) (DL 2) and iii) five species stands with beech, ash, lime, hornbeam (*Carpinus betulus* L.) and maple (*Acer pseudoplatanus* L. and/or *A. platanoides* L.) (DL 3).



Figure 2-1: Mixed species stand at the Hainich National Park (Foto: I. Mölder)

Three replications of each treatment have been established. The 2500 m² near-natural stands are characterized by a closed canopy and homogenous stand structure concerning basal area and DBH (breast height diameter). They represent a gradient of beech abundance and tree species diversity. The Shannon Index ranges from 0.2 in the monospecific stands to 1.8 in the five species stands. The soil type of all plots is a Luvisol formed on limestone with a loess cover of at least 60 cm, which shows stagnic properties in winter and spring and which is quite dry in summer.

3 Acidity, nutrient stocks and organic matter content*

3.1 Abstract

The production and composition of leaf litter, soil acidity, exchangeable nutrients, and the amount and distribution of soil organic matter were analyzed in a broad-leaved mixed forest on loess over limestone in Central Germany. The study aimed at determining the current variability of surface soil acidification and nutrient status, and at identifying and evaluating the main factors that contributed to the variability of these soil properties along a gradient of decreasing predominance of European beech (*Fagus sylvatica* L.) and increasing tree species diversity. Analyses were carried out in a) mature monospecific stands with a predominance of beech (DL1), b) mature stands dominated by three deciduous tree species (DL2: beech, ash (*Fraxinus excelsior* L.), lime (*Tilia cordata* Mill. and/or *T. platyphyllos* Scop.)), and c) mature stands dominated by five deciduous tree species (DL3: beech, ash, lime, hornbeam (*Carpinus betulus* L.), maple (*Acer pseudoplatanus* L. and/or *A. platanoides* L.)).

The production of leaf litter was similar in all stands (3.2 to 3.9 Mg dry matter ha⁻¹ yr⁻¹) but the total quantity of Ca and Mg deposited on the soil surface by leaf litter increased with increasing tree species diversity and decreasing abundance of beech (47 to 88 kg Ca ha⁻¹ yr⁻¹; 3.8 to 7.9 kg Mg ha⁻¹ yr⁻¹). The soil pH(H₂O) and base saturation (BS) measured at three soil depths down to 30 cm (0 - 10 cm, 10 - 20 cm, 20 - 30 cm) were lower in stands dominated by beech (pH = 4.2 to 4.4, BS = 15 to 20%) than in mixed stands (pH = 5.1 to 6.5, BS = 80 to 100%). The quantities of exchangeable Al and Mn increased with decreasing pH and were highest beneath beech. Total stocks of exchangeable Ca (0 - 30 cm) were 12 to 15 times larger in mixed stands (6660 to 9650 kg ha⁻¹) than in beech stands (620 kg ha⁻¹). Similar results were found for stocks of exchangeable Mg that were 4 to 13 times larger in mixed stands (270 to 864 kg ha⁻¹) than in beech stands (66 kg ha⁻¹). Subsoil clay content and differences in litter composition were identified as important factors that contributed to the observed variability of soil acidification and stocks of exchangeable Ca and Mg. Organic carbon accumulation in the humus layer was highest in beech stands (0.81 kg m⁻²) and lowest in stands with the highest level of tree species diversity and the lowest abundance of beech (0.27 kg m⁻²).

The results suggest that redistribution of nutrients via leaf litter has a high potential to increase base saturation in these loess-derived surface soils that are underlain by limestone.

* Guckland, A., Jacob, M., Flessa, H., Thomas, F.M., Leuschner, C. (2009) Acidity, nutrient stocks and organic matter content in soils of a temperate deciduous forest with different abundance of European beech (*Fagus sylvatica* L.). Journal of Plant Nutrition and Soil Science 172: 500-511.

Species-related differences of the intensity of soil-tree cation cycling can thus influence the rate of soil acidification and the stocks and distribution of nutrients.

3.2 Introduction

Natural forest vegetation in Central Europe is unique due to the widespread occurrence of quasi-monospecific beech forests (*Fagus sylvatica* L.) in which this single species is occupying 80 to 100% of the canopy area. Land use changes and forest management have greatly reduced the area coverage of these beech forests. Transformation to even-aged monospecific coniferous forests has even resulted in a substantial decrease of forest structural diversity. However, the conversion to mixed stands of beech with other broad-leaved or coniferous species increased structural and species diversity.

Changes of tree species can have a pronounced influence on various chemical, physical, and biological soil properties due to differences in nutrient uptake from soil, litter chemistry, root activity, canopy interception and growth (Alriksson and Eriksson, 1998, Binkley and Giardina, 1998). Several studies have shown that the composition of the forest overstory can influence soil nutrient status (Dijkstra, 2003, Berger et al., 2004), mineralization processes (Son and Lee, 1997), soil acidity (Binkley and Valentine, 1991, Reich et al., 2005) and mineral weathering (Augusto et al., 2000). In addition, tree species can influence the mass of organic carbon stored in the humus layer and in the mineral soil (Raulund-Rasmussen and Vejre, 1995), the composition and activity of soil fauna and microflora (Saetre et al., 1999, Neiryneck et al., 2000) and soil structure (Graham et al., 1995). Distinctive differences were found between conifers and hardwood species in affecting soil chemistry or ecosystem biogeochemistry (Rothe et al., 2002, Augusto et al., 2002), but even among hardwood species striking differences can occur (Norden, 1994). Comprehensive reviews on the impact of several common European and American tree species on soil properties were published by Augusto et al., (2002) and Binkley (1995).

Use and management of beech forests in limestone areas of Central Europe often resulted in an admixture of different proportions of other broad-leaved species and an increase of tree species diversity. One outstanding example of a temperate broad-leaved forest with large gradients in beech abundance and tree species diversity is found in the Hainich National Park in Central Germany. Here, different forest ownerships have generated a small-scale stand mosaic of species-poor, beech-dominated forest patches and stands with up to 14 deciduous tree species per hectare that are all growing under similar climate and on the same geological substrate (Triassic limestone (Muschelkalk) covered by loess). In 2005, a long-term study on

biogeochemical cycles and biotic interactions in stands with decreasing abundance of beech and associated increasing tree species diversity has been initiated in the Hainich National Park (<http://www.forest-diversity.uni-goettingen.de>). This study compares i) mature monospecific stands with predominance of European beech (*Fagus sylvatica* L.) to ii) mature stands dominated by three deciduous tree species (beech, ash (*Fraxinus excelsior* L.), lime (*Tilia cordata* Mill. and/or *T. platyphyllos* Scop.)) and to iii) mature stands dominated by five deciduous tree species (beech, ash, lime, hornbeam (*Carpinus betulus* L.), maple (*Acer pseudoplatanus* L. and/or *A. platanooides* L.)).

Here, we present and discuss results on soil properties in these stands. The objectives of our study were to determine soil acidification, soil nutrient status and the amount and distribution of soil organic matter in these stands with different abundance of beech and tree species diversity and to identify and evaluate the main factors that contributed to the variability of these soil properties. Special attention is given to the effects of tree litter composition and to the small-scale heterogeneity of soil parent material. We hypothesize that these are pivotal factors in governing the current variability of the surface soil acidity and nutrient status, and of the amount and distribution of soil organic matter.

We like to point out that such an observational study that compares soil properties in existing forest stands with different mixtures of tree species in general has strong limitations with regard to the analysis of putative causal relationships between tree species and soil properties or ecosystem functions because there are no exact replicates of treatments as it is the case in planted experimental stands. In addition, the natural variability of edaphic, climate and soil parent material properties or differences in land use history can introduce several covarying factors (Leuschner and Jungkunst, 2008). Despite these shortcomings, such observational studies are indispensable to gain an insight into long-term effects of tree species and species diversity on soil properties since planted large-scale biodiversity experiments with trees have been initiated just recently (Scherer-Lorenzen, 2005) and do not yet allow the analysis of long-term effects.

3.3 Materials and Methods

3.3.1 Study sites

The study was conducted in multiple aged stands of deciduous forest in the Hainich National Park, Thuringia, Germany, at an elevation of approximately 350 m a.s.l.. All stands had a high

proportion of mature trees with an age of 100 to 200 yrs and a long-term forest history of at least 200 years. Historic forest utilization includes coppice-with-standards systems and selective cutting. Details of stand characteristics are given in Table 3-1. The mean annual temperature is 7.5 °C and the mean annual precipitation is 670 mm. The geological substrate of the study sites is Triassic limestone covered by loess. The forest has not been managed since 1990; before that time, it had been used for military training since the 1960s. In December 1997, it became a National Park. In the northeastern part of the National Park, study plots that belong to three different diversity levels (DL) of tree species were selected: a) monospecies stands with European beech (*Fagus sylvatica* L.) as predominant tree species (diversity level 1, DL1), b) three-species stands with beech, ash (*Fraxinus excelsior* L.) and lime (*Tilia cordata* Mill. and *T. platyphyllos* Scop.) as predominant species (diversity level 2, DL2), and c) five-species stands with beech, ash, lime, hornbeam (*Carpinus betulus* L.) and maple (*Acer pseudoplatanus* L., *A. platanoides* L., *A. campestre* L.) as predominant species (diversity level 3, DL3). The mean abundance of beech decreased in the order DL1 > DL2 > DL3 (Table 3-1). Within a radius of approximately 4 km four replicate plots were selected for each stand type and numbered from a to d (Figure 3-1). The main species of the herbaceous layer that were found in all stands were *Anemone nemorosa*, *Hordelymus europaeus*, *Carex sylvatica*, *Deschampsia caespitosa*, and *Milium effusum*. *Anemone ranunculoides* and *Asarum europaeum* were found in stands of diversity level 2 and 3, and *Allium ursinum* was typical for stands of the highest diversity level (DL3) (Mölder and Schmidt, 2007).

The study sites are close to a meteorological station (meteomedia, station Weberstedt/Hainich; N 51° 06', E 10° 31'; 270 m a.s.l.). All plots had to fulfill the following criteria: level or only slightly inclined terrain (inclination < 5%) on eutrophic soils formed on limestone with a loess cover of at least 60 cm; near-natural stands without distinct anthropogenic impact on their structure during the last several decades; closed canopy; homogeneous stand structure among all plots. In each stand type, three plots (a, b, c) met all of the above-mentioned requirements. These were considered core plots, and an area of 54 m × 54 m around a previously designated central tree was fenced. Within this area, investigations were performed on the innermost 50 m × 50 m area, which is only walked on for measurement purposes. On each plot, all trees with a diameter at breast height (dbh) of at least 7 cm were recorded in spring 2005. To evaluate the tree species diversity we computed the Shannon-Weaver index (Hs). This index (Hs) was calculated for both density (number of stems with a dbh > 7 cm) and stem basal area per hectare: $H_s = -\sum p_i \ln p_i$, where $p_i =$

proportion of total density or of total basal area of tree genus *i*. H_s based on density and H_s based on basal area increased in the order $DL1 < DL2 < DL3$ (Table 3-1).

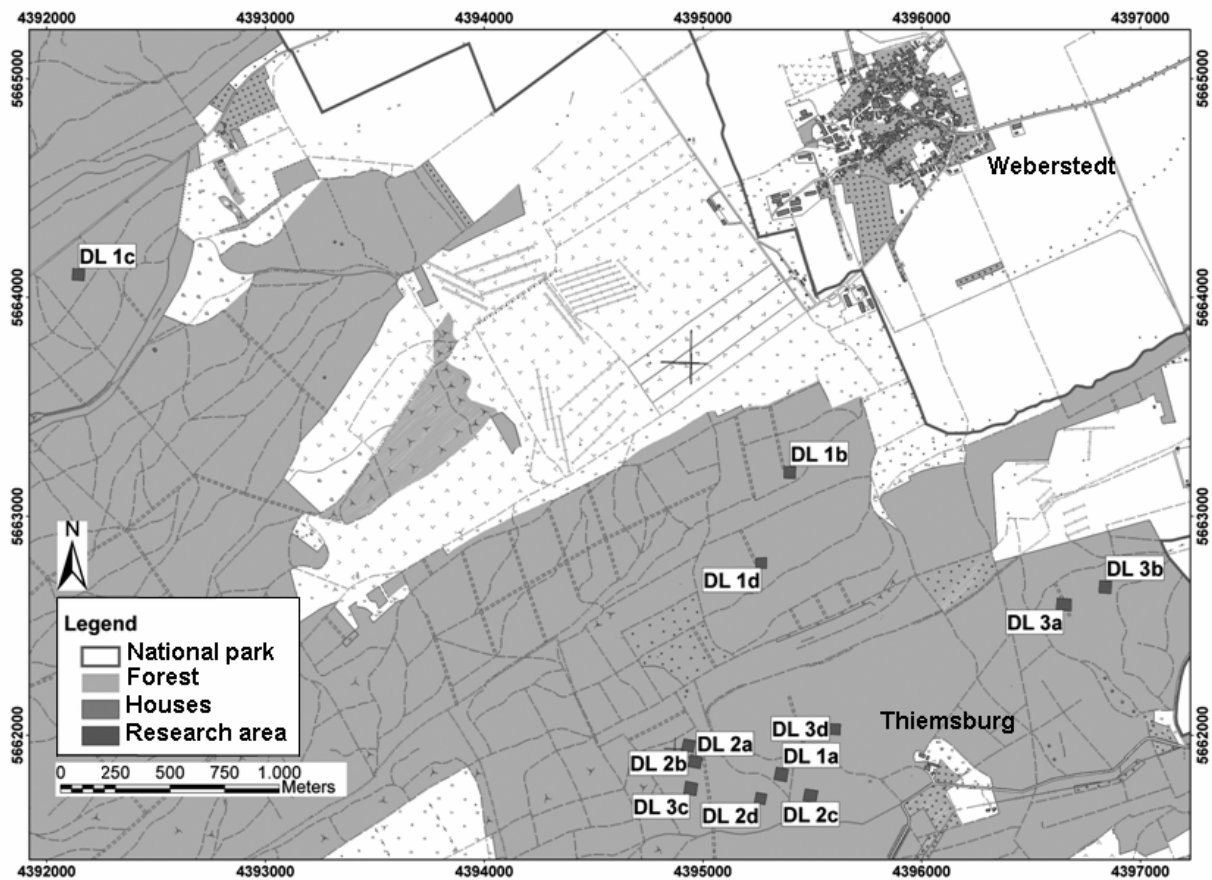


Figure 3-1: Location of the study plots in the forested (in grey) area of the Hainich National Park. The replicate plots (a to d) are located in stands with different diversity levels of deciduous tree species (DL1, DL2, DL3).

The soil type was a Luvisol developed from loess, which is underlain by limestone (FAO, 1998). Soil texture in the upper mineral soil (0 to 30 cm) of all plots was characterized by high silt content (mean silt content of $74 \pm 8\%$ (mean \pm standard deviation)) and low sand content ($< 5\%$) (silt loam to silt clay loam, Table 3-2). The thickness of the loess cover that was generally free of carbonates varied between 60 and 120 cm (Table 3-2); it was on average 72 cm on DL3 plots, 80 cm on DL2 plots and 87 cm on DL1 plots. The clay content in 20 to 30 cm differed depending on the thickness of the clay-depleted E horizon (A1 according to the German classification system) and the depth of the underlying Bt horizon. The mean clay content in 20 to 30 cm was higher in DL3 stands (30%) than in DL1 stands (15%) (Table 3-2) and it was in-between in DL2 stands (26%). Tree roots easily reached the calcareous subsoil

Table 3-1: Number and percentage (in brackets) of trees and tree basal area of the most important tree genera of the study plots in the Hainich National Park and the Shannon-Weaver index (H_s; calculated from the total number of tree genera growing on the plots) on the basis of tree genus density and tree genus basal area. The plot codes abbreviate different diversity levels (DL1, DL2, DL3) of deciduous tree species and the replicate plots (a to c).

Plot	Number of trees (ha ⁻¹)							Tree basal area (m ² ha ⁻¹)								
	Beech	Lime	Ash	Maple	Horn-beam	Oak	Sum	H _s	Beech	Lime	Ash	Maple	Horn-beam	Oak	Su	H _s
DL1a	400 (0.93)	12 (0.03)	8 (0.02)	8 (0.02)	0 (0)	0 (0)	428	0.31	43.5 (0.95)	1.3 (0.03)	0.9 (0.02)	0.3 (0.01)	0 (0)	0 (0)	46.0	0.27
DL1b	180 (0.83)	0 (0)	0 (0)	4 (0.02)	0 (0)	32 (1.15)	216	0.51	36.4 (0.88)	0 (0)	0 (0)	0.2 (0.01)	0 (0)	4.6 (0.11)	41.2	0.38
DL1c	220 (1.00)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	220	0	35.2 (1.00)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	35.2	0
DL2a	208 (0.48)	144 (0.33)	60 (0.14)	24 (0.06)	0 (0)	0 (0)	436	1.15	19.2 (0.59)	6.2 (0.19)	4.3 (0.13)	2.7 (0.08)	0 (0)	0 (0)	32.4	1.10
DL2b	316 (0.60)	20 (0.04)	176 (0.34)	12 (0.02)	0 (0)	0 (0)	524	0.98	24.9 (0.67)	0.7 (0.02)	9.3 (0.25)	2.4 (0.06)	0 (0)	0 (0)	37.3	1.01
DL2c	572 (0.74)	84 (0.11)	100 (0.13)	20 (0.03)	0 (0)	0 (0)	776	0.82	30.0 (0.67)	5.7 (0.13)	8.0 (0.18)	1.3 (0.03)	0 (0)	0 (0)	45.0	0.94
DL3a	12 (0.03)	264 (0.68)	28 (0.07)	32 (0.08)	36 (0.09)	16 (0.04)	388	1.16	3.3 (0.09)	19.2 (0.54)	3.4 (0.10)	2.1 (0.06)	3.6 (0.10)	4.0 (0.11)	35.6	1.45
DL3b	8 (0.02)	212 (0.65)	44 (0.13)	24 (0.07)	36 (0.11)	4 (0.01)	328	1.18	3.9 (0.12)	15.2 (0.48)	1.6 (0.05)	3.5 (0.11)	6.5 (0.20)	1.3 (0.04)	32.0	1.52
DL3c	196 (0.42)	160 (0.34)	76 (0.16)	20 (0.04)	16 (0.03)	0 (0)	468	1.28	16.6 (0.41)	6.0 (0.15)	12.8 (0.31)	3.6 (0.09)	1.8 (0.04)	0 (0)	40.8	1.36

horizons developed from limestone at each study plot. The two-layer soils (loess over limestone) showed stagnic properties during winter and spring, and they were dry during summer. The soil physical properties of the experimental plots are summarized in Table 3-2.

Table 3-2: Thickness of the loess cover, soil texture and soil bulk density of the replicated (a to c) plots with different diversity levels (DL1, DL2, 1DL3) of deciduous tree species.

Plot	Thickness of loess cover (cm)	Soil texture (sand/silt/clay) (%)			Bulk density (g cm ⁻³)		
		0-10 cm	10-20 cm	20-30 cm	0-10 cm	10-20 cm	20-30 cm
DL1a	120	4 / 78 / 18	3 / 82 / 15	4 / 80 / 16	0.9	1.1	1.4
DL1b	70	3 / 83 / 14	3 / 83 / 14	4 / 82 / 14	1.2	1.3	1.5
DL1c	75	3 / 82 / 15	2 / 83 / 15	2 / 83 / 15	1.3	1.3	1.4
DL2a	60	2 / 73 / 25	2 / 77 / 21	3 / 73 / 24	1.1	1.2	1.5
DL2b	60	3 / 64 / 33	2 / 68 / 30	2 / 63 / 35	1.0	1.3	1.4
DL2c	120	2 / 78 / 20	3 / 80 / 17	3 / 79 / 18	1.2	1.4	1.6
DL3a	75	3 / 74 / 23	2 / 74 / 24	2 / 74 / 24	1.0	1.2	1.3
DL3b	80	2 / 76 / 22	3 / 75 / 22	3 / 75 / 22	1.2	1.3	1.3
DL3c	60	2 / 66 / 32	3 / 65 / 32	2 / 53 / 45	1.2	1.3	1.4

3.3.2 Sampling design

For soil inventory and sampling within plots a grid of 12 m x 12 m (12 sampling points per plot) was established within a radius of 25 m around the central tree. In addition, a soil profile pit was dug adjacent to each plot. Further, on all plots randomly distributed sampling subplots have been established as follows: Three transects (30 m long and 3 m wide) were randomly distributed over each plot by randomly determining *a*) their starting point within a 2 m × 2 m grid and *b*) their angle to the x-axis of this grid. If the transects were not completely located within the

50 m × 50 m area of the plot or in the case of overlapping, they were shifted along the x- and the y-axis of the grid to the smallest possible extent. The minimum distance between two transects was 1 m. Along each transect, 31 points (including starting and end point) that were separated by distances of 1 m were marked. Five of these points were randomly selected for the installation of litter collectors, resulting in a total number of 15 litter collectors per plot.

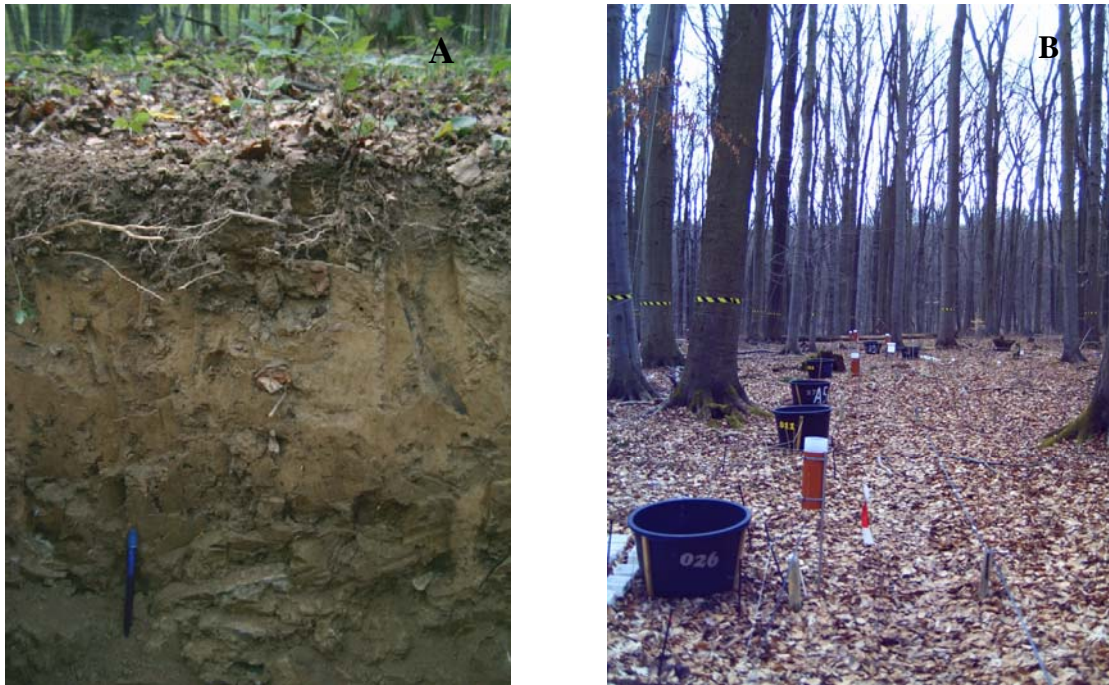


Figure 3-2: Soil profile (Luvisol) next to the DL3c stand (A) and a transect with litter collectors and throughfall collectors at a pure beech stand (DL1b) (B).

3.3.3 Litter sampling and analyses

For tree litter sampling, 35-L buckets with a surface of 0.29 m² were placed on wooden frames above the forest floor at randomly selected sampling points (see 3.3.2). From September to December 2005, the buckets were cleared at monthly intervals. The biomass of leaf litter was determined after drying at 60 °C. Leaf litter from all litter collectors of the same transect line (see 3.3.2) was mixed resulting in three mixed samples per plot. These mixed samples were ground and used to determine the mean quantity and the mean composition of leaf litter within a plot. Total carbon and nitrogen contents were determined by an automated C and N analyzer (Heraeus

Elementar Vario EL, Hanau, Germany). Concentrations of Ca, Mg, P and Mn in the litter were determined by ICP-AES (Spectro, Kleve, Germany) after pressure digestion with concentrated nitric acid. The ash alkalinity of leaf litter was determined by titration using the method described by Jungk (1968).

3.3.4 Soil sampling and analyses

In the winter of 2004/2005 soil cores with a diameter of 6.4 cm were taken from the upper 30 cm of the soil at all 12 sampling points per plot (see 3.3.2), and the thickness of the loess cover was determined using a soil auger. Additionally, samples of the organic surface layer were collected at each sampling point (sampled surface of 300 cm²). The soil cores were divided into three parts representing the soil depths of 0 to 10 cm, 10 to 20 cm and 20 to 30 cm. Samples were dried at 40 °C and passed through a 2-mm sieve.

Soil pH was measured in a suspension with distilled H₂O and 1M KCl (5 g of soil, 15 ml of H₂O or KCl solution). Organic carbon (SOC) and total nitrogen (Nt) contents of soil and forest floor samples were determined by an automated C and N analyzer (Heraeus Elementar Vario EL, Hanau, Germany) after grinding the samples (all samples were free of carbonates). Cation exchange capacity (CEC) of mineral soil samples was determined at three sampling points per plot. These points were randomly selected from the grid of 12 sampling points (depths of sampling: 0 - 10, 10 - 20, 20 - 30 cm). Soil samples were leached with 100 ml of 1M ammonium chloride (NH₄Cl) for 4 h as described by König and Fortmann (1996). Cations in the extract were quantified by atomic absorption spectroscopy, and exchangeable protons were calculated from pH of the NH₄Cl solution before and after percolation. The CEC was calculated as the equivalent sum of the exchangeable Na, K, Ca, Mg, Mn, Fe, Al and H ions. Base saturation was defined as the equivalent sum of base cations (Na, K, Ca and Mg) as percent of CEC. The soil texture was determined using the sieving and pipette method (Schlichting et al., 1995). The texture analysis was performed on all samples that were used for CEC determination. After drying at 105 °C, soil bulk density was determined gravimetrically from undisturbed soil cores (125 cm³, n = 3) taken from the adjacent soil profile pit.

3.3.5 Statistical analyses

To examine differences among the stands (DL1, DL2, DL3) with regard to i) the production and composition of tree leaf litter, ii) soil acidification and amount of exchangeable cations, iii) the stocks of soil organic carbon and total nitrogen, iv) the thickness of loess cover, and v) the clay content we performed an analysis of variance (ANOVA) followed by the Tukey test for all pairwise mean comparisons of diversity level effects. The assumptions of normality and homogeneity of variance were met in nearly all cases ($p > 0.05$; Shapiro-Wilk's test, Levene's test). Only in a few cases (base saturation, stocks of exchangeable Ca and Mg) the p-level of these assumptions were lower ($p > 0.01$). Differences among species mixtures were analyzed separately for each soil depth. Significant differences were evaluated at the $p < 0.05$ level.

Correlation (Pearson) and regression analyses were used to analyze the relationship between a) different soil properties, b) the Shannon index and soil properties, c) the relative abundance of beech and soil properties, d) litter Ca and Mg contents and soil properties, and e) the thickness of loess cover and soil properties.

3.4 Results

3.4.1 Production and composition of tree litter

There was no significant influence of the level of tree species diversity on tree basal area (Table 3-1) and leaf litter production (Table 3-3). The C:N ratio of litter decreased with increasing tree species diversity from 62 in DL1 stands to 49 in DL3 stands (Table 3-3). Total N input via leaf litter increased with increasing level of tree species diversity (from 26 to 40 kg ha⁻¹). Concentrations of Ca and Mg in leaf litter were nearly twice as high in DL3 stands than in DL1 stands (Table 3-3) and they were in between in DL2 stands. Thus, the total quantity of Ca and Mg deposited yearly on the soil surface by leaf litter increased in the order DL1 (47 kg Ca and 3.8 kg Mg ha⁻¹), DL2 (77 kg Ca and 5.8 kg Mg ha⁻¹), DL3 (88 kg Ca and 7.9 kg Mg ha⁻¹). There was a close linear relationship between the annual input of Ca and Mg via leaf litter and the stocks of exchangeable Ca and Mg in the upper 20 cm of the soils (Figure 3-3). The concentration of phosphorus in the tree litter was not affected by tree species diversity (Table 3-3). The concentration of Mn in leaf litter was three to five times higher in beech-dominated stands than in mixed stands (Table 3-3).

The ash alkalinity of freshly fallen leaf litter was higher in DL2 and DL3 stands than in beech-dominated stands (DL1) (Table 3-3).

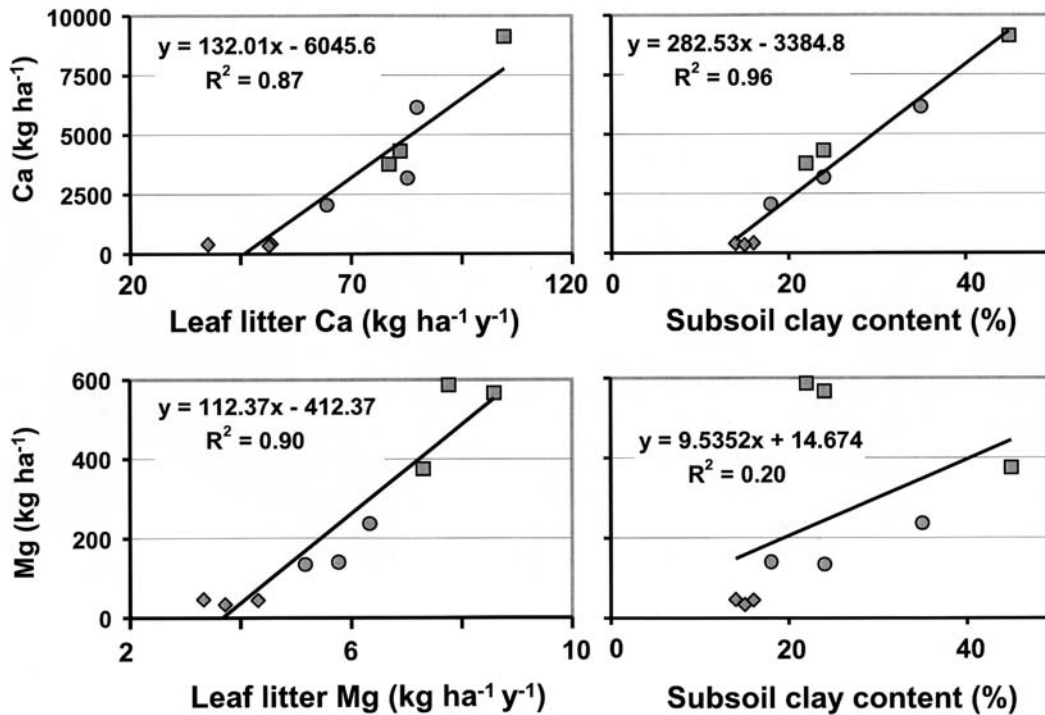


Figure 3-3: Relationship between the quantity of exchangeable Ca or Mg (0 to 20 cm) and 1) Ca and Mg in leaf litter (left) and 2) the clay content in 20 to 30 cm (right). The different symbols represent stands with different levels of tree species diversity: \blacklozenge DL1, \bullet DL2, \blacksquare DL3.

Table 3-3: Soil area-related production of leaf litter with corresponding masses of C and N, leaf litter composition (C:N ratio, concentration of Ca, Mg, P, Mn) and ash alkalinity of leaf litter in stands with different diversity levels of deciduous tree species (DL1, DL2, DL3) (means and standard deviation, n = 3). Different letters indicate significant differences among stand types.

Diversity level	Leaf litter production				Leaf litter composition					
	Dry matter	C	N	C:N	Ca	Mg	P	Mn	Ash alkalinity	
										mmol _c kg ⁻¹
DL1	3.2 ^a (0.22)	1.58 ^a (0.10)	0.026 ^a (0.004)	62.4 ^a (6.5)	14.28 ^a (1.94)	1.16 ^a (0.12)	0.43 ^a (0.13)	2.08 ^a (0.62)	2030 ^a (50)	
DL2	3.9 ^a (0.37)	1.91 ^a (0.18)	0.034 ^a (0.004)	57.4 ^{ab} (2.6)	19.74 ^b (1.56)	1.48 ^{ab} (0.15)	0.47 ^a (0.06)	0.67 ^b (0.05)	2230 ^b (70)	
DL3	3.9 ^a (0.59)	1.92 ^a (0.28)	0.040 ^a (0.009)	49.4 ^b (4.7)	22.44 ^b (0.98)	2.05 ^b (0.44)	0.55 ^a (0.07)	0.37 ^b (0.09)	2180 ^b (130)	

Table 3-4: C:N ratio in the organic surface layer and the mineral soil (mean and standard deviation, n = 3) in stands with different diversity levels of deciduous tree species (DL1, DL2, DL3). Different letters indicate significant differences among stand types within a given

Diversity level	C:N (mineral soil)		
	C:N (organic surface layer)	0-10 cm	10-20 cm
DL1	28.7 (1.5) ^a	17.2 (1.0) ^a	13.7 (1.0) ^a
DL2	31.1 (2.7) ^a	13.9 (0.7) ^b	11.8 (1.0) ^a
DL3	30.9 (3.8) ^a	14.5 (0.7) ^b	12.3 (0.5) ^a

3.4.2 Soil organic matter

Organic carbon stocks in the organic surface layer were higher in beech-dominated stands than in mixed stands (Figure 3-8). Samples of the organic surface layer exhibited a C:N ratio of approximately 30, and C:N did not differ among stands with different species diversity level (Table 3-4). There was mull type humus at all sites, but it exhibited distinct differences. The thin surface layer of mixed stands (DL2, DL3) consisted primarily of leaf litter from the previous year, whereas in beech-dominated stands (DL1) litter from several years accumulated and formed a permanent thin layer of partly decomposed tree remains. According to the German classification system, the humus type was L-Mull in DL2 and DL3 stands and F-Mull in DL1 stands (Bodenkundliche Kartieranleitung, 2005). The mean ratio of C stocks in the organic surface layer to annual C input via tree leaf litter was 5.2 for the beech-dominated sites, 1.8 for stands with diversity level DL2 and 1.6 for stands with the highest species diversity level (DL3). There was a positive relationship between forest floor C and the relative abundance of beech ($R^2 = 0.66$) (Figure 3-7).

Organic carbon stocks in the A horizon (0 to 10 cm) ranged from 2.9 to 3.7 kg m⁻² without significant differences among stand types (Figure 3-8). Below the A horizon (depths: 10 to 20 and 20 to 30 cm), organic matter contents were higher in mixed stands than in beech-dominated stands. However, the close relationship between SOC concentration and clay content ($R^2 = 0.87$ and 0.79 in 10 to 20 and 20 to 30 cm, respectively) indicates that these differences were mainly a result of the higher clay content in the subsoil of mixed stands. There was no difference among stand types if the carbon content was related to a unit clay fraction (total soil organic carbon g⁻¹ clay).

3.4.3 Soil acidity and exchangeable cations

Soil pH(H₂O) was lower in beech stands (DL1) than in DL2 or DL3 stands (Figure 3-4). It generally increased with soil depth; however, this increase was more pronounced in mixed stands than in beech-dominated stands. There was no significant relationship between the thickness of the loess cover and the pH of the surface soil (0-10 cm). However, pH of the surface soil tended to increase with increasing clay content of the subsoil (20-30 cm) ($R^2 = 0.41$).

The cation exchange capacity (CEC) of the soil varied considerably within the same stand type (Table 3-5). It was primarily related to the clay content ($R^2 = 0.89$), and its variability could be

explained to a large extent by differences in clay content, organic matter concentration and soil pH (Figure 3-5, $R^2 = 0.93$). The specific CEC of soil organic matter differed in stands with different tree species diversity. If we consider the well established positive relationship between soil pH and CEC to soil organic matter in temperate humid climates (Bodenkundliche Kartieranleitung, 2005), the mean total contribution of soil organic matter to CEC down to a depth of 30 cm was $2.6 \text{ mol}_c \text{ m}^{-2}$ in the beech-dominated soil (DL1); it was $6.9 \text{ mol}_c \text{ m}^{-2}$ in the soil of DL2 stands; and it was highest under stands with the highest level of tree species diversity (DL3; $9.9 \text{ mol}_c \text{ m}^{-2}$) (Figure 3-6).

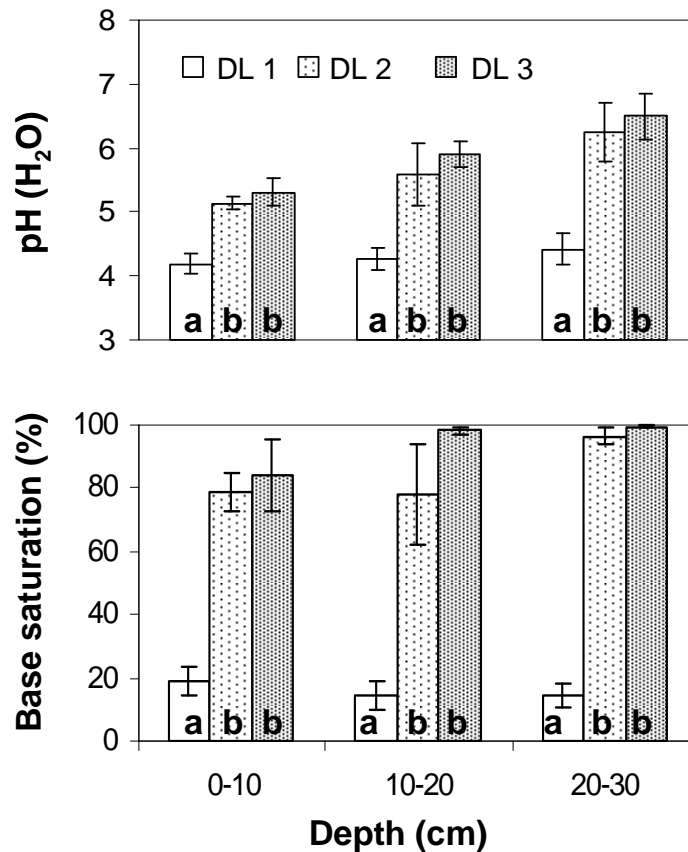


Figure 3-4: pH (H₂O) and base saturation at different soil depths in stands with different diversity levels of deciduous tree species (DL1, DL2, DL3). (Means and standard deviation, $n = 3$). Different letters specify significant differences among stands with different diversity level.

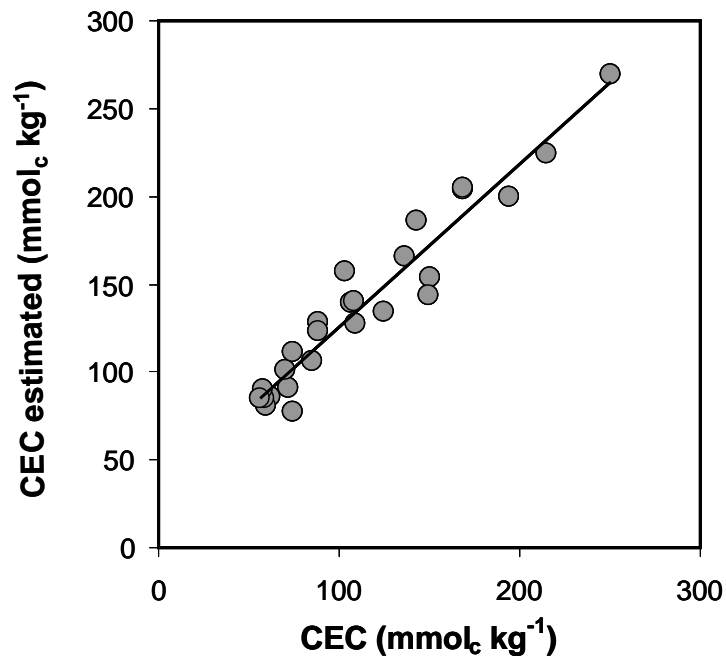


Figure 3-5: Measured versus estimated cation exchange capacity (CEC) of soil samples from experimental plots ($R^2=0.93$). CEC was estimated from the humus content, clay content and pH using the following equation: $\text{CEC (mmol}_c \text{ kg}^{-1}) = [\text{organic matter content (g kg}^{-1}) \times 2f] + [\text{clay content (g kg}^{-1}) \times 0.534]$. The reduction factor f depends on soil pH as shown by “Bodenkundliche Kartieranleitung” (2005) and describes the decrease of CEC of soil organic matter with decreasing pH.

Table 3-5: Cation exchange capacity (CEC), exchangeable cations as percentage of total CEC and stocks of exchangeable Ca and Mg (means and standard deviation, $n = 3$) at different soil depths in stands with different diversity levels of deciduous tree species (DL1, DL2, DL3). Different letters indicate significant differences among stand types comparing the same soil depth

Soil depth (cm)	Diversity level	CEC (mmol kg ⁻¹) ^c	Contribution to CEC (%)										Exchangeable Ca (Mg ha ⁻¹)	Exchangeable Mg (Mg ha ⁻¹)
			H	Na	K	Ca	Mg	Fe	Mn	Al				
0-10	DL1	72.7 ^a (12.6)	5.8 ^a (1.6)	0.4 ^a (0.2)	2.4 ^a (0.6)	14.2 ^a (6.4)	2.5 ^a (0.8)	0.8 ^a (0.8)	4.1 ^a (1.5)	69.8 ^a (7.9)	0.23 ^a (0.05)	0.024 ^a (0.004)		
	DL2	119.9 ^a (42.6)	2.0 ^b (1.4)	0.3 ^a (0.1)	2.6 ^a (0.5)	62.9 ^b (26.8)	6.0 ^{ab} (1.6)	0.1 ^a (0.1)	4.1 ^a (1.2)	22.8 ^b (25.5)	1.86 ^a (0.85)	0.098 ^b (0.022)		
	DL3	152.6 ^a (55.8)	0.8 ^b (1.3)	0.4 ^a (0.2)	2.5 ^a (0.5)	68.2 ^b (19.0)	13.1 ^b (5.7)	0.2 ^a (0.3)	2.6 ^b (1.1)	12.1 ^b (17.1)	2.47 ^a (1.84)	0.210 ^c (0.019)		
10-20	DL1	60.2 ^a (1.6)	5.2 ^a (1.1)	0.4 ^a (0.3)	2.0 ^a (0.6)	10.1 ^a (9.4)	1.9 ^a (1.5)	0.3 ^a (0.2)	2.7 ^a (0.9)	77.2 ^a (10.4)	0.16 ^a (0.07)	0.018 ^a (0.007)		
	DL2	100.5 ^{ab} (38.0)	3.0 ^b (2.0)	0.4 ^a (0.1)	2.0 ^a (0.6)	64.8 ^b (30.7)	4.3 ^a (1.5)	0.0 ^b (0.1)	2.9 ^a (1.1)	23.9 ^b (29.2)	1.93 ^{ab} (1.27)	0.072 ^{ab} (0.031)		
	DL3	156.7 ^b (35.4)	0.0 ^b (0.0)	0.4 ^a (0.2)	1.9 ^a (0.3)	81.8 ^b (6.5)	14.1 ^b (6.4)	0.0 ^b (0.0)	1.1 ^b (0.7)	0.7 ^b (1.5)	3.27 ^b (1.12)	0.299 ^b (0.105)		
20-30	DL1	62.9 ^a (10.0)	5.8 ^a (2.4)	0.5 ^a (0.2)	2.1 ^a (0.5)	11.4 ^a (8.7)	2.1 ^a (1.3)	0.4 ^a (0.7)	3.3 ^a (1.8)	74.4 ^a (11.8)	0.23 ^a (0.13)	0.024 ^a (0.012)		
	DL2	117.2 ^a (47.8)	1.9 ^b (1.8)	0.4 ^a (0.1)	2.5 ^a (0.7)	80.5 ^b (24.6)	4.9 ^a (1.3)	0.0 ^a (0.0)	1.7 ^{ab} (1.0)	9.7 ^b (23.6)	2.87 ^a (1.33)	0.100 ^{ab} (0.028)		
	DL3	169.5 ^a (72.8)	0.0 ^b (0.0)	0.4 ^a (0.2)	2.4 ^a (0.9)	81.3 ^b (7.8)	15.3 ^b (7.7)	0.0 ^a (0.0)	0.6 ^b (0.3)	0.0 ^b (0.0)	3.91 ^a (2.28)	0.355 ^b (0.110)		

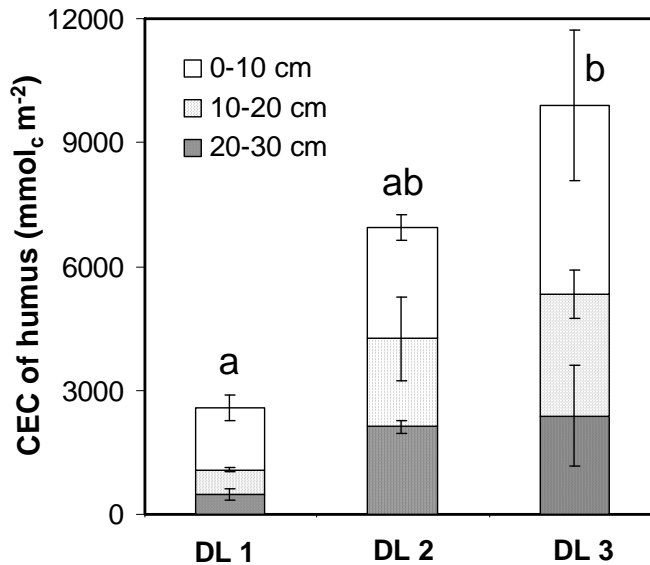


Figure 3-6: Cation exchange capacity (CEC) of soil organic matter stocks down to a depth of 30 cm in stands with different diversity levels of deciduous tree species (DL 1, DL 2, DL 3) (means and standard deviation, $n = 3$). Different letters specify significant differences among stands with different diversity level.

Base saturation in the upper 30 cm of the mineral soil was much lower in DL 1 stands (< 20%) than in mixed stands with several deciduous tree species (DL2, DL3 > 75%) (Figure 3-4). Exchangeable Al percentage in soil was highest under beech (DL1) in all soil horizon and lowest in mixed stands with the highest level of species diversity (DL2, DL3) (Table 3-5). Exchangeable Al was generally low in soil samples with $\text{pH} > 5$. In contrast, at $\text{pH} < 5$ it strongly increased with decreasing pH. Exchangeable Mn percentage was also higher under beech than in the soil of DL3 stands, and it also increased with decreasing soil pH. Total quantities of exchangeable Ca in the A horizon (0 to 10 cm) were about ten times higher in mixed stands (1860 to 2470 kg ha⁻¹) than under beech (230 kg ha⁻¹) (Table 3-5). Differences among stands were even more pronounced if exchangeable Ca stocks were calculated for the upper 30 cm of soil: it was 620 kg Ca ha⁻¹ for DL1 stands, 6660 kg Ca ha⁻¹ for DL 2 stands and 9650 kg Ca ha⁻¹ for DL3 stands. Similar results were found for exchangeable Mg. The stocks of exchangeable Mg were smallest under beech (DL1) and largest in mixed stands with the highest species diversity level (DL3).

Calculated for the soil layer 0 to 30 cm it amounted to 66 kg ha⁻¹ for DL1, 270 kg ha⁻¹ for DL2 and 864 kg ha⁻¹ for DL3 (Table 3-5). Stocks of exchangeable Mg were particularly high in the soils of the DL3a and DL3b stands where abundance of beech was lowest and where Mg concentration of leaf litters was highest (2.3 mg g⁻¹).

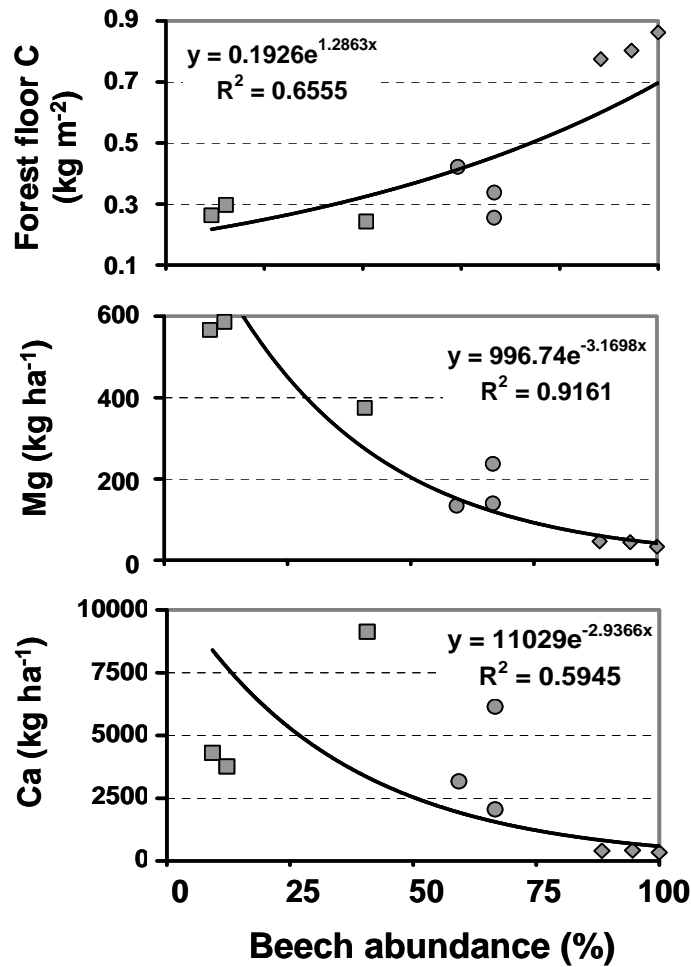


Figure 3-7: Relationship between the abundance of beech expressed as percentage of the total tree basal area and i) the C stocks of the organic surface layer, ii) the quantity of exchangeable Mg (0 to 20 cm) and iii) the quantity of exchangeable Ca (0 to 20 cm). The different symbols represent stands with different levels of tree species diversity: ◆DL1, ● DL2, ■ DL3.

Correlation analyses indicates a close relationship between stocks of exchangeable base cations and the abundance of beech expressed as percentage of the total basal area ($R^2 = 0.92$ and 0.59 for Mg and Ca, respectively) (Figure 3-7). However, we also found a close relationship between the subsoil (20-30 cm) clay content and the stock of exchangeable Ca in the upper 20 cm of the soil ($R^2 = 0.96$, Figure 3-3). In contrast, there was no close relation between the subsoil (20-30 cm) clay content and the content of exchangeable Mg (Figure 3-3). Stocks of exchangeable Ca and Mg in the upper 20 cm were not related to the thickness of the loess cover.

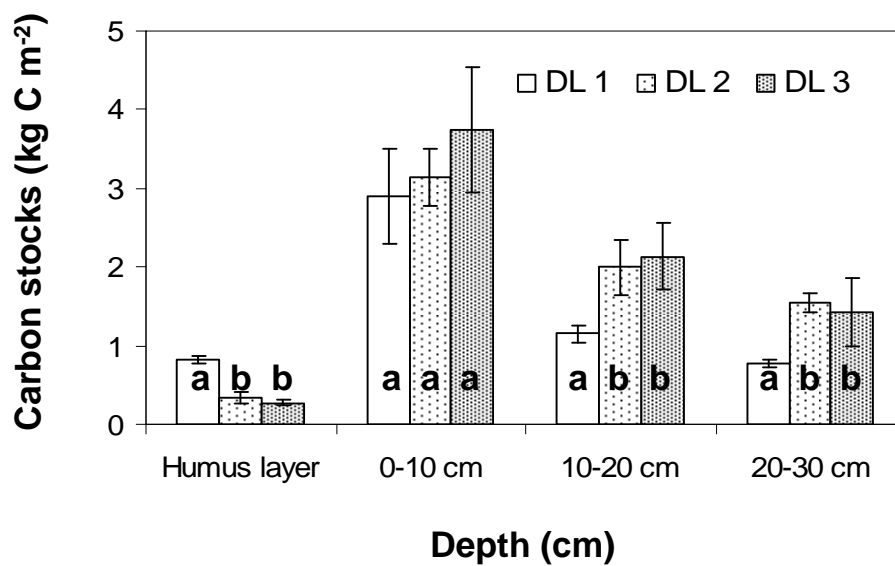


Figure 3-8: Organic carbon stocks in the organic surface layer and at different depths in the mineral soil of stands with different diversity levels of deciduous tree species (DL1, DL2, DL3). (Means and standard deviation, $n = 3$). Different letters specify significant differences among the diversity levels within a given soil layer.

3.5 Discussion

3.5.1 Soil acidity and exchangeable cations

There were large differences in soil pH, base saturation and quantity of exchangeable cations among the stands with different diversity levels of deciduous tree species. Differences were significant between beech-dominated stands (DL1) and mixed stands (DL2, DL3), and small or absent if mixed stands with different diversity level were compared. Several factors could have contributed to the result that soil acidification was greater and base saturation was lower in DL1 stands than in mixed ones (DL2 and DL3): a) differences in the mineral composition of the parent material, in particular variations in the content and composition of the clay fraction among stand types, b) effects related to the presence of different tree species, in particular effects induced by litter composition and decomposition, the accumulation of inorganic cations in excess of anions in tree biomass and forest floor, and species dependent differences in acid deposition, and c) differences in the historical land use, in particular if it involved export of biomass and nutrients.

Due to these manifold factors that might have contributed to the observed differences in soil chemistry and that even interact in their potential effects on soil nutrient status; it is not possible to quantify exactly the effects of single factors in our observational study. However, our results help to assess the potential importance of at least some of these factors.

3.5.2 Effect of soil parent material

Soil parent material is a main factor determining nutrient uptake of trees, litter composition and soil acidification (Sariyildiz and Anderson, 2005, Meier et al., 2005). Although we put much effort into the selection of stands with similar parent material and only sites on limestone with a significant loess cover were included (see 3.3.1), differences in soil parent material, such as thickness of the loess layer, differences in clay content or clay mineralogy might have influenced the degree of soil acidification in the analyzed stands. We found no evidence of a significant influence of the thickness of the loess cover (60 to 120 cm) on nutrient stocks or acidity of the surface soil. This is in line with the field observation that tree roots reached the calcareous subsoil in all stands. The results indicate that the loess layer did not act as a significant barrier that

hampers nutrient uptake from the calcareous bedrock. The close relationship between clay content and CEC suggests that mineral composition of the clay fraction was similar in all soil samples even if the clay content differed considerably. Thus, differences in soil chemistry cannot be explained by a different mineralogy of the clay fraction. The observed CEC of the clay fraction ($0.534 \text{ mmol}_c \text{ g}^{-1}$, regression equation in the title of Figure 3-5) is typical for loess-derived soils in Central and Northern Germany (Renger, 1965).

Our results suggest that the subsoil (20-30 cm) clay content was a decisive factor that determined the variability of the exchangeable Ca content in the surface soil. The highly significant relationship between these soil properties indicates that an increasing subsoil clay content reduced soil acidification and losses of exchangeable base cations probably by providing increasing subsoil nutrient stocks and acid neutralization capacity. However, differences in clay content were relatively small if compared with the observed large variability of exchangeable Ca and Mg stocks in the upper 20 cm that were 12 and 15 times higher in DL3 stands than DL1 stands. In addition, differences in subsoil clay content only partly explained the variability of exchangeable Mg in the surface soil. The results suggest that the subsoil clay content was an important but not the only factor that contributed to the observed differences of soil acidification and stocks of exchangeable nutrients.

3.5.3 Effects related to tree species

The evaluation of tree species effects is hampered by the fact that clay content was higher in mixed stands (DL2, DL3) than in beech stands (DL1) and that both factors (i.e. soil texture and tree species) have probably contributed to the observed differences in soil chemistry. Nevertheless, the results on nutrient recycling via leaf litter provide insight into the potential of the investigated species mixtures to influence soil acidity and stocks of exchangeable cations.

The quantity of litterfall was similar in all stands, but annual deposition of Ca, Mg and alkalinity to the soil surface via leaf litter increased with increasing species diversity and decreasing abundance of beech. Calculated for a period of 50 yrs total Ca and Mg deposition via leaf litter of trees was by $2057 \text{ kg Ca ha}^{-1}$ and $205 \text{ kg Mg ha}^{-1}$ higher in DL3 stands than DL1 stands. This is in the same order of magnitude as the observed differences of exchangeable Ca and Mg in the Ah horizon of these stands and shows the great potential of tree litter composition to influence stocks of exchangeable cations in the upper soil horizon. The close relationships between litter Ca and

Mg and stocks of exchangeable Ca and Mg in the surface soil (0-20 cm) supports this conclusion even if the results raise the question about the cause-effect chain. Are stocks of exchangeable Ca and Mg large because of high Ca and Mg inputs via leaf litter or are litter concentrations high because of the high nutrient availability? Both factors are closely linked and cannot be separated. However, long-term changes of the surface soil nutrient status are strongly influenced by the ability of different tree species to improve or maintain soil productivity via nutrient uptake and redistribution (Neiryneck et al., 2000). Differences in subsoil clay content have probably contributed to the higher litter Ca and Mg concentrations in mixed stands than beech stands. However, the effect of clay content on litter composition was probably minor because we found no relationship between subsoil clay content and litter Ca and Mg within mixed stands. Moreover, the mixed stands with relatively low subsoil clay content (DL2c, DL3b) also showed much higher leaf litter Ca and Mg contents than beech stands. The results suggest that the differences in litter Ca and Mg were largely driven by species-specific differences in litter quality. This conclusion is also supported by first results on leaf litter composition of different tree species in the mixed stands DL2 and DL3 that indicate lowest Ca and Mg concentrations in beech and oak litter (personal communication, M. Jacob).

Our results support the observation that litter quality of different species and the associated nutrient recycling through the soil-tree system can have significant implications for the pattern of soil fertility and soil acidity in mixed stands (Norden, 1994, Finzi et al., 1998a, Rothe and Binkley, 2001). The striking differences between beech-dominated stands (DL1) and mixed stands (DL2, DL3) suggest that the presence and abundance of beech contributed to the observed differences in soil acidity and availability of Ca and Mg. This assumption is supported by the significant negative correlation between the percentage of beech expressed as proportion of tree basal area and the stocks of exchangeable Ca and Mg and the positive relationship between the abundance of beech and the accumulated soil acidity in the form of exchangeable Al. Several studies have reported distinct differences among deciduous tree species in their ability to acidify the upper mineral soil in terms of a decrease of exchangeable base cation pools and increase of exchangeable Al. In deciduous forests in Sweden, *Tilia cordata* acidified the soil the least, whereas sites covered by *Fagus sylvatica* exhibited considerably lower pH values and base saturation (Norden, 1994). Similar results were reported by Finzi et al., (1998a) and Neiryneck et al., (2000), who found much lower pH and base saturation beneath canopies of *Fagus* species than under *Tilia*, *Fraxinus* and *Acer* species. In these studies, the largest differences in soil

acidification occurred beneath *Acer saccharum* and *Fagus grandifolia*, and *Tilia platyphyllos* and *Fagus sylvatica*, respectively. Augusto et al., (2002) summarized effects of tree species on soil fertility in European temperate forests and concluded that the acidifying ability of *Fagus sylvatica* and *Quercus* species was higher than that of all other deciduous tree species. The ability of tree species to change chemical soil properties related to acidity and exchangeable cations was shown to be largely mediated by litter Ca and Mg concentrations and litter ash alkalinity (Noble and Randall, 1999, Dijkstra, 2003, Reich et al., 2005), which fits to our results on litter quality and soil acidity in stands of different diversity levels. Differences among tree species growing under similar soil and climate conditions in nutrient uptake and leaf litter chemistry are considered as intrinsic species-specific traits, and several mechanisms of enhanced nutrient acquisition that are primarily related to growth and activity of roots or mycorrhiza have been described (Washburn and Arthur, 2003, Reich et al., 2005). The redistribution of Ca, Mg and alkalinity in the soil profile by different tree species through nutrient uptake, litter deposition and mineralization and the induced changes in soil chemistry depend on the nutrient availability and buffer capacity in different soil depths (Noble and Randall, 1999, Augusto et al., 2002, Meier et al., 2005). At our experimental plots, this process of “biological pumping” had a highly beneficial effect since it enabled the translocation of base cations and alkalinity from the alkaline subsoil (limestone) to the surface parent material (loess), which has a rather low buffer capacity and thus tends to form strongly acid forest soils. This ameliorating effect obviously differed due to the abundance of different tree species. It counteracted the accumulation of acidic cations such as Al^{3+} , Mn^{2+} and Fe^{3+} at the exchange complex and, thus, reduced the replacement of exchangeable "base" cations, in particular Ca^{2+} .

Even if it was not possible in our study to clearly separate effects of clay content and tree species mixtures, the results show that differences in litter composition in the analyzed stands have a high potential to change the soil nutrient status. Thus, we consider tree litter composition as an important factor that contributed to the observed differences of base saturation and acidification of the surface soil.

Decomposition of litter can contribute to soil acidification by the production of organic acids or by providing substrate for nitrification (if nitrate is leached) (Finzi et al., 1998a). There is no evidence that these processes were important at our sites since high organic acid production occurs if litter decomposition is slow and a thick forest floor developed (this was not the case at

our sites), and first results on N mineralization indicated that nitrification was very low in all stands (data not shown).

Soil acidity and stocks of exchangeable "base" cations in different stands can also be influenced by the accumulation of inorganic cations in excess of anions in tree biomass (Bredemeier et al., 1990, Norden, 1994). The internal net proton production by this process in different German forests was between 0.3 and 1 $\text{kmol}_c \text{ ha}^{-1} \text{ yr}^{-1}$ (Bredemeier et al., 1990). The higher values were associated with high contents of "base" cations in tree biomass. Norden (1994) reported similar results for deciduous forests in South Sweden and showed that differences between deciduous tree species (*Fagus*, *Quercus*, *Tilia*, *Acer*) growing at the same site were small. If these results are considered, it is unlikely that this process can explain the large difference of stored acidity in the analyzed soils. Even if we consider soil acidity solely in the form of exchangeable Al in the upper 20 cm, it was much higher in beech-dominated stands (DL1: 109 $\text{kmol}_c \text{ ha}^{-1}$) than in stands with higher tree species diversity (DL2: 61 $\text{kmol}_c \text{ ha}^{-1}$; DL3: 22 $\text{kmol}_c \text{ ha}^{-1}$).

Deposition effects may also be important since the capacity of tree species to intercept atmospheric deposition is known to influence soil acidity and nutrient leaching (Augusto et al., 2002). Crown surface properties of the trees determine deposition rates, and it is well documented that interception is higher in stands of coniferous species than in stands of deciduous species because of the higher leaf area index and, in most cases, persistent foliage (Augusto et al., 2002). There are only a few studies that have determined the influence of different deciduous tree species on atmospheric deposition (review by Augusto et al., 2002). Norden (1991) analyzed acid deposition and throughfall fluxes for five deciduous tree species (*Fagus sylvatica*, *Quercus robur*, *Carpinus betulus*, *Tilia cordata*, *Acer platanoides*) in South Sweden and found only small differences of the total acid input: the mean (\pm standard deviation) acid input calculated over all species was 2.0 (± 0.2) $\text{kmol}_c \text{ ha}^{-1} \text{ yr}^{-1}$. Thus, there is no evidence of large species-related differences of atmospheric deposition that could explain the different acidification in the analyzed soils.

3.5.4 Land use history

The forest history, in particular if it involved biomass and nutrient export as charcoal production, litter raking or grazing can significantly increase soil acidification and decrease base saturation (Hüttl and Schaaf, 1995). The present composition and diversity of tree species in the Hainich National Park is strongly determined by former forest use and management. It indicates that former management of the investigated stands differed. Although historical documents provide no evidence of different biomass export from our experimental sites or former agricultural use, we cannot exclude the possibility that present soil conditions might be influenced by historical land use since such effects can persist for very long periods. We consider historical land use as the main factor of uncertainty that might have contributed to the observed differences in base saturation and acidification of the surface soil.

3.5.5 Soil organic matter

There was a striking effect of tree species on C and N stocks in the forest floor. The larger C and N accumulation in the organic surface layer of beech-dominated stands (DL1) compared to DL2 and DL3 stands was not due to higher litter production, but to lower decay rates in the DL1 stands. This can be explained by the relatively high recalcitrance of beech litter that was found to depend on the lower nutrient concentrations and on the higher lignin to N ratio compared with litter of *Acer* and *Fraxinus* species (Melillo et al., 1982, Finzi et al., 1998b). In addition, litter decomposition probably was hampered by the lower soil pH. Our findings are in accordance with the results of other studies that showed that the organic surface layer generally is thicker beneath beech than beneath other hardwood species with the exception of oak (Finzi et al., 1998b, Neiryneck et al., 2000). Neiryneck et al. (2000) concluded that *Fagus* and *Quercus* belong to mullmoder-forming species, whereas *Tilia*, *Acer* and *Fraxinus* are mull-forming trees. The results suggest that the abundance of beech was the key factor that determined the mass of the organic surface layer at our experimental sites. This conclusion is supported by the significant positive correlation between the percentage of beech expressed as the proportion of tree basal area and the quantity of C stocks in the organic surface layer. Similar forest floor C stocks under beech were reported for other limestone areas in Central Europe (Leuschner et al., 2006). Differences in the C to N ratio were found for leaf litter of different stands but not for forest floor samples. This

might be explained by the accumulation of more decomposed tree remains under beech that have very likely a narrower C:N ratio compared with the fresh litter material in mixed stands.

Differences in the organic carbon content of the mineral soil (comparing the same soil depth) resulted mainly from differences in the clay content and there was no evidence of a significant effect of the tree species diversity.

The results show that the quality of soil organic matter in terms of its ability to bind and store exchangeable cations was lower in beech-dominated stands than in stands with higher portions of lime, ash and maple. This was due to the strong effect of pH on the surface charge of soil organic matter and, thus, on the factors that contributed to the variability of soil acidification (see 3.5.1).

3.6 Conclusion

We found distinct differences in surface soil acidification, stocks of exchangeable base cations and carbon accumulation in the humus layer in temperate broad-leaved mixed forest stands on loess over limestone. Subsoil clay content and differences in litter composition were identified as important factors that contributed to the variability of these soil properties. The redistribution of Mg, Ca and alkalinity via tree litter has a high potential to increase base saturation in these loess-derived surface soils that are underlain by limestone. Our results suggest that this process of “biological pumping” of base cations increased with decreasing abundance of beech. In addition, beech abundance influenced litter decomposition rate and nutrient accumulation in the organic surface layer. Thus, the conversion of quasi-monospecific beech forests to mixed stands of beech with other broad-leaved species appeared to increase the intensity of soil-tree cation cycling and as a consequence it can influence the rate of soil acidification and nutrient stocks in the surface soil. The results suggest that at sites that allow production of broadleaf tree species with nutrient-rich, easily decomposable foliage the establishment and promotion of these species is an important silvicultural tool to counteract natural or anthropogenic soil acidification and to maintain soil productivity.

However, the significance of our results is impaired by the interfering effects of soil texture and tree species composition, and in addition, by the uncertainty associated with the historical land use. A follow-up study will be conducted in clusters of single tree species within the selected stands to reduce these factors of uncertainty and to constrain the effects of tree species composition on soil properties.

3.7 References

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4 Soil N cycling and N₂O emission*

4.1 Abstract

The admixture of other broadleaf species into beech forests in Central Europe leads to an increase of tree species diversity, which may alter soil biochemical processes. This study was aimed at 1) assessing differences in gross rates of soil N cycling among deciduous stands of different beech (*Fagus sylvatica* L.) abundance in a limestone area, 2) analyzing the relationships between gross rates of soil N cycling and forest stand N cycling, and 3) quantifying N₂O emission and determining its relationship with gross rates of soil N cycling. We used ¹⁵N pool dilution techniques for soil N transformation measurement and chamber method for N₂O flux measurement.

Gross rates of mineral N production in the 0-5 cm mineral soil increased across stands of decreasing beech abundance. These rates were correlated with microbial biomass which, in turn, was influenced by substrate quantity, quality and soil fertility. Leaf litter-N, C:N ratio and base saturation in the mineral soil increased with decreasing beech abundance. Soil mineral N production and assimilation by microbes were tightly coupled, resulting in low N₂O emissions. Annual N₂O emissions were correlated with gross nitrification rates. Our results suggest that soil N availability may increase through the admixture of broadleaf species into beech forests.

* Guckland A, Corre MD, Flessa H. Soil N cycling and N₂O emission increase with decreasing beech abundance in a mixed deciduous forest (submitted).

4.2 Introduction

Natural forest vegetation in Central Europe is unique due to the widespread occurrence of quasi-monospecific beech forests in which this single species occupies 80 to 100% of the canopy area. In limestone areas of Central Europe, the use and management of beech forests often resulted in an admixture of different proportions of other broadleaf species and an increase of tree species diversity. Changes in tree species or even the admixture of species can have a pronounced influence on various chemical, physical, and biological soil properties due to species-specific differences in nutrient uptake, litter chemistry, root activity, canopy interception and growth (Alriksson and Eriksson, 1998, Binkley and Giardina, 1998). The composition of the forest overstory was shown to influence the understory vegetation (Mölder et al., 2008), soil nutrient status (Dijkstra, 2003, Guckland et al., 2009), mineralization processes (Raulund-Rasmussen and Vejre, 1995, Son and Lee, 1997), soil acidity (Binkley and Valentine, 1991, Reich et al., 2005), composition and activity of soil fauna and microflora (Saetre et al., 1999, Neirynek et al., 2000, Cesarz et al., 2007), and soil structure (Graham et al., 1995).

Soil nitrogen dynamics is directly affected by litter quality (e.g. Taylor et al., 1991, Prescott, 2002, Inagaki et al., 2004, Miyamoto and Hiura, 2008) and soil conditions (Bengtsson et al., 2003, Booth et al., 2005, Kooijman et al., 2008). Distinctive differences were found between conifers and hardwood species with regard to their effects on stocks, distribution and mineralization rates of soil N (Jerabkova et al., 2006, Joshi et al., 2006, Inagaki et al., 2004). In addition, N₂O emissions were significantly higher in deciduous than in coniferous forests (Ambus et al., 2006, Butterbach-Bahl et al., 2002). Even within deciduous forests, differences in broadleaf species affect soil N dynamics through their differences in litter chemistry and their effects on soil chemistry. The dominance of broadleaf species in hemlock-hardwood stands was shown to increase the rate of net mineralization and nitrification as a result of improved litter quality (Ferrari, 1999). Species-related differences in litterfall fluxes of elements (Ca, Mg, K, P and N) and in soil acidification were observed under canopies of different deciduous species (Nordén, 1994a, 1994b). Soil biology, especially earthworm biomass, was also influenced by deciduous tree species (Neirynek et al., 2000, Cesarz et al., 2007). In general, beech litter was found to decompose more slowly than the litter of other Central European deciduous tree species (Wise and Schäfer, 1994).

From our previous study in a broadleaf mixed forest with beech, ash (*Fraxinus excelsior* L.), lime (*Tilia cordata* Mill. and/or *T. platyphyllos* Scop.), hornbeam (*Carpinus betulus* L.), and maple (*Acer pseudoplatanus* L. and/or *A. platanoides* L.), we found that surface soil acidity, C and N accumulation in the humus layer, and leaf litter C:N ratio increased with increasing abundance of beech (Guckland et al., 2009). Differences in the redistribution of nutrients and alkalinity via leaf litter were identified as important factors that contributed to this beech effect. These results suggest that the abundance of beech might also affect processes of soil N transformation in deciduous mixed forests and thus in N availability to plants and microbes. In the present study, we report on the soil N dynamics in this broadleaf mixed forest. Three stands with different beech abundance were studied. We hypothesized that soil N transformation rates and thus N₂O losses increase with decreasing beech abundance. Our objectives were i) to assess differences in gross rates of soil N cycling among stands of different beech abundance, ii) to analyze the relationships between gross rates of soil N cycling and forest stand N cycling, and iii) to quantify N₂O emission and assess its relationship with gross rates of soil N cycling. To our knowledge, this study is the first to investigate differences in soil N cycling across a range of beech abundance in a European mixed deciduous forest.

4.3 Material and methods

4.3.1 Site description

The study was conducted in mature stands of deciduous forest in the Hainich National Park, Thuringia, Germany. The site has an elevation of 350 m a.s.l.. The mean annual temperature is 7.5 °C and the mean annual precipitation is 670 mm. The geological substrate is Triassic limestone covered with 60-70 cm loess. The soil type is a Stagnic Luvisol (FAO classification) with some of the characteristics given in Table 4-1. The soil exhibits stagnic properties during winter and spring but is quite dry during summer. The forest has a history of at least 200 years. This has not been managed since 1990; before that time it had been used for military training since the 1960s. In 1997, it became a national park. Different forest ownerships have generated a small-scale stand mosaic of species-poor, beech-dominated forest patches and stands with up to 14 deciduous tree species per hectare that are all growing under similar climatic conditions on the

same geological substrate. Our study is a part of a long-term project on biogeochemical cycles and biotic interactions in stands with decreasing abundance of beech and conversely with increasing tree species diversity. Three stands were selected with decreasing beech abundance (expressed as percentage of total tree basal area, Table 4-1): stand A is dominated by beech, stand B is a three-species stand with beech, ash and lime as predominant species, and stand C is covered with beech, ash, lime, hornbeam and maple as predominant species.

4.3.2 Soil and litter sampling

In each stand, three transects were randomly selected and on each transect two plots (5 m x 5 m each) were established, totalling to 6 plots per stand. Measurements of soil N cycling, N₂O emissions and soil properties were conducted on these plots. The distance between plots in one stand ranged from 10 to 50 m. Gross and net rates of N transformation were determined in November 2006 and April 2007 using intact soil cores from the upper 5 cm of the mineral soil. Five soil cores (diameter of 8 cm, height of 5 cm) were taken with stainless-steel cylinders on each plot, with approximately 1 cm distance between cores. The cores were transported to the laboratory and stored at 4 °C overnight prior to measurements the following day. Additional soil cores from 0 to 5 cm and 5 to 10 cm were taken at each plot for general physical and chemical characteristics. Leaf litter was collected starting from September 2005 to December 2005 at monthly intervals, described in detail by Guckland et al. (2009). Five litter collectors (surface area of 0.29 m²) were randomly distributed along each of the three transects per plot. In addition, we sampled 12 points out of a 12 m x 12 m grid per stand for measurements of total N and organic C in the organic layer.

4.3.3 Analysis of leaf litter, organic layer and mineral soil

Leaf litter dry matter was determined gravimetrically after drying to constant mass at 60 °C. Leaf litter from all litter collectors of the same transect was combined resulting in three pooled samples per stand. These pooled samples were ground and analyzed for total C and N using CNS Elemental Analyzer (Elementar Vario EL, Hanau, Germany) and base cations (Ca and Mg) by

Table 4-1: Soil properties in 0-5 cm and 5-10 cm mineral soil of the investigated stands with different beech abundance. Means (± 1 SE, n = 6) followed by a different letter indicate significant differences among stands (one-way ANOVA with Tukey HSD test at $P \leq 0.05$).

Stand	Beech abundance (% of tree basal area)	0 - 5 cm mineral soil				5 - 10 cm mineral soil			
		pH	Base saturation (%)	Texture (Clay/Silt/Sand) (%)	Bulk density (g cm ⁻³)	pH	Base saturation (%)	Texture (Clay/Silt/Sand) (%)	Texture (Clay/Silt/Sand) (%)
A	89	4.5 (0.1) ^b	48 (1) ^b	15 ^c / 82 / 3	0.8 (0.03)	4.3 (0.02) ^b	19 (1) ^b	14 ^c / 83 / 3	
B	59	5.4 (0.2) ^a	91 (4.1) ^a	23 ^b / 75 / 2	0.9 (0.02)	5.0 (0.2) ^a	77 (7) ^a	23 ^b / 74 / 3	
C	42	5.7 (0.2) ^a	97 (4.7) ^a	31 ^a / 66 / 3	1.0 (0.03)	5.8 (0.3) ^a	97 (1) ^a	31 ^a / 65 / 4	

pressure digestion in concentrated HNO₃ (König and Fortmann, 1996) followed by analysis of the digests using Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES; Spectro Analytical Instruments, Kleve, Germany). For the organic layer and mineral soil, total organic C and N from ground samples were determined as mentioned above. Soil pH was measured in a suspension with distilled H₂O (5 g of soil to 15 mL of H₂O).

Cation exchange capacity (CEC) of the mineral soil was determined by percolating 2-mm sieved soil samples with 100 ml of 1M NH₄Cl for 4 h (König and Fortmann, 1996) and measuring cations in percolates using ICP-AES. Base saturation was calculated as percentage base cations (Na, K, Ca and Mg) of the CEC. Soil texture was determined using the sieving and pipette method (Schlichting et al., 1995). Soil bulk density was determined by soil core method.

4.3.4 Gross N transformation rates, microbial biomass and net N transformation rates

We used the ¹⁵N pool dilution technique and calculation procedures as described in details by Davidson et al. (1991) and Hart et al. (1994). Two intact cores of each plot were injected with (¹⁵NH₄)₂SO₄ solution (for gross N mineralization and NH₄⁺ consumption rates) and another two cores were injected with K¹⁵NO₃ solution (for gross nitrification and NO₃⁻ consumption rates). Each soil core received five 1-mL injections, containing 25 µg N mL⁻¹ with 95% ¹⁵N enrichment. One core of each labeled pair was broken up immediately, mixed in a plastic bag, and a subsample was extracted with 0.5 mol L⁻¹ K₂SO₄ solution (1:5 dry soil mass to solution ratio) ten minutes after ¹⁵N injection (T₀). Mineral N extraction was done by shaking the samples for 1 hour and filtering them through K₂SO₄-prewashed filter papers. The T₀ cores were used to correct for the reactions that occur immediately after addition of ¹⁵NH₄⁺ and ¹⁵NO₃⁻. The other core of the ¹⁵NH₄⁺-labeled pair was incubated for 1 day at 10 °C (T₁). For the ¹⁵NO₃⁻-labelled cores, a test conducted prior to measurement showed no detectable change in the NO₃⁻ concentration and ¹⁵NO₃⁻ after 1 day of incubation, and hence we incubated these cores for 2 days at 10 °C (T₁). The T₁ cores were then extracted with 0.5 mol L⁻¹ K₂SO₄ as described above. Microbial assimilation of NH₄⁺ was calculated as the difference between gross NH₄⁺ consumption and gross nitrification rates (Davidson et al., 1991). Microbial assimilation of NO₃⁻ was determined by the appearance of ¹⁵N in the CHCl₃-labile microbial biomass, using the nonlinear model described by

Davidson et al. (1991). About 25 g soil of the T₁ ¹⁵NO₃⁻-labeled samples were fumigated with CHCl₃ for 5 days and then extracted with 0.5 mol L⁻¹ K₂SO₄ as described above.

Part of the extracts was used for analysis of NH₄⁺ and NO₃⁻ concentrations using continuous flow injection colorimetry (Cenco/Skalar Instruments, Breda, Netherlands). NH₄⁺ was determined by Berthelot reaction method (Skalar Method 155-000) and NO₃⁻ by copper-cadmium reduction method (NH₄Cl buffer but without ethylenediamine tetraacetic acid; Skalar Method 461-000). The rest of the extracts was used for ¹⁵N analysis by diffusion of NH₄⁺ (from the ¹⁵NH₄⁺-labeled cores) and of NO₃⁻ (from the ¹⁵NO₃⁻-labeled cores). For the fumigated T₁ ¹⁵NO₃⁻-labeled samples, part of the extract was used for persulfate digestion for determination of ¹⁵N enrichment in extractable organic N pool (Corre et al., 2007), needed for the calculation of microbial assimilation of NO₃⁻. The same diffusion procedure and blank correction were followed as described in our earlier works (Corre et al., 2003, Corre and Lamersdorf, 2004, Corre et al., 2007). ¹⁵N was analyzed using isotope ratio mass spectrometry (Finigan MAT, Bremen, Germany).

Microbial biomass C and N were determined from the T₁ CHCl₃-fumigated and the corresponding unfumigated samples. Organic C content of the K₂SO₄ extracts was analyzed by UV-enhanced persulfate oxidation using a Dohrmann DC-80 carbon analyzer with an infrared detector (Rosemount Analytical Division, Santa Clara, California, USA). The organic N content of the extracts was determined by persulfate digestion (Corre et al., 2007), followed by colorimetric analysis of NO₃⁻ (as above). Microbial biomass C and N were calculated as the difference in extractable organic C and persulfate-N between the fumigated and unfumigated soils divided by $k_C = 0.45$ and $k_N = 0.68$ for 5-day fumigated samples (Brookes et al., 1985).

The remaining one soil core was used to estimate net N mineralization and net nitrification rates. The soil in the core was cut vertically into two parts. One part was removed from the core (T₀) and the half that remained in the core was incubated for 14 days at 10°C (T₁). The T₀ and T₁ soil samples were extracted with 0.5 mol L⁻¹ K₂SO₄ solution and the extracts were analyzed for NH₄⁺ and NO₃⁻ contents as described above. Net N mineralization and nitrification rates were calculated as the difference between T₁- and T₀-NH₄⁺ and NO₃⁻ concentrations, respectively.

4.3.5 Calculation of mean residence time

The mean residence time (MRT) specifies the average length of time an N atom resides in a given pool; a low MRT indicates a rapid turnover of the N pool. The calculation of MRT (N pool ÷ flux rate) assumes that the N pool is at steady state and that the flux is equal to the rate of input to that pool. MRT was calculated for the following N pools: a) total N in the organic layer using leaf litter-N as input flux rate, b) NH₄⁺ and NO₃⁻ pools in the 0-5 cm mineral soil using gross N mineralization and gross nitrification as input flux rates, respectively, and c) microbial biomass N using NH₄⁺ + NO₃⁻ assimilation as input flux rate.

4.3.6 N₂O fluxes, soil temperature, moisture content and extractable N

N₂O fluxes were measured biweekly from September 2005 to September 2007. On each plot, one permanent chamber base (0.04 m² area, 0.15 m height, and inserted into the soil to 0.10 m depth) was installed three weeks before the start of measurements. Soil N₂O fluxes were measured using vented static chambers (total volume 9.25 L). The cover was kept on the chamber base for one hour during which four gas samples were taken (0, 20, 40 and 60 minutes after closure) and stored in pre-evacuated glass containers with teflon-coated stopcock. Gas samples were analyzed using a gas chromatograph (GC 6000, Carlo Erba Instruments/Thermo Fisher Scientific, Milan, Italy) equipped with an electron capture detector and an autosampler system (Loftfield et al., 1997). Gas fluxes were calculated from linear regression of concentrations versus time for each chamber, corrected with measured air temperature and air pressure (Ruser et al., 1998). Zero fluxes (no change in concentration) were included. The annual N-oxide losses were approximated by applying the trapezoid rule on time intervals between measured flux rates, assuming constant flux rates per day.

Simultaneous to N₂O flux measurements, soil temperature (at 5-cm depth) was measured and soil samples were taken from 0-5 cm mineral soil (except from January to March 2006 when the ground was covered by snow) for measurements of soil moisture content and extractable N. Soil moisture content was determined gravimetrically by oven-drying at 105°C for one day and expressed as water-filled pore space (WFPS) using the measured bulk density and assuming a particle density of 2.65 g cm⁻³ for mineral soil. Extractable N was determined from the soils extracted with 0.5 mol L⁻¹ K₂SO₄ and the extracts analyzed for NH₄⁺, NO₃⁻ (as above) and total N

by continuous flow injection colorimetry (UV-persulfate oxidation followed by hydrazine sulfate reduction; Skalar Method 473-000).

4.3.7 Statistical analyses

For soil N transformation rates, differences between the two sampling dates (November 2006 and April 2007) for each stand were tested using Paired-samples T test. If there were no significant differences between sampling dates, we used the means of both sampling dates for further analyses; if otherwise, analysis was conducted separately for each sampling date. We used Kruskal-Wallis H test with multiple comparison extension to assess differences among stands (A, B, and C) when assumptions of normality and homogeneity of variance were not met. For parameters that showed normal distribution and homogenous variance, differences among stands were evaluated using one-way analysis of variance with Tukey HSD test. Spearman rank correlation was used to test relationships among soil N-cycling parameters and controlling factors. Regression analysis was conducted to relate gross rates of mineral N production in the soil to annual leaf litter-N input and C:N ratio using the mean values per transect. All tests were considered significant at $p \leq 0.05$.

4.4 Results

4.4.1 Leaf litter, organic layer and mineral soil

The annual leaf litter input, concentrations and stocks of Ca, Mg and N, and leaf litter quality (C:N ratio) increased with decreasing beech abundance. This was paralleled by decreasing mass, total N stocks and turnover time of total N pool in the organic layer (Table 4-1). Similarly, soil pH, base saturation (Table 4-1), concentrations and stocks of Ca, Mg and total N increased while C:N ratio decreased (Table 4-2) in the upper mineral soil with decreasing beech abundance. Clay content correlated with soil pH ($r = 0.82$, $p < 0.01$, $n = 18$), base saturation ($r = 0.85$, $p < 0.01$, $n = 18$) and total N ($r = 0.87$, $p < 0.01$, $n = 18$) in 0-5 cm mineral soil.

Table 4-2: Dry mass, nutrient concentrations and nutrient stocks in the leaf litter, organic layer and 0-5 cm mineral soil of the investigated stands with different abundance of beech. Means (± 1 SE) followed by a different letter indicate significant differences among stands (one-way ANOVA with Tukey HSD test at

Stand/ % beech	Dry mass (Mg ha ⁻¹)	Ca		Mg		Total N (Mg N ha ⁻¹)	C:N ratio	N turnover time [#] (year)
		(kg Mg ⁻¹)	(kg ha ⁻¹)	(kg Mg ⁻¹)	(kg ha ⁻¹)			
Annual leaf litterfall* (n=3)								
A / 89	3.0 ^b (0.1)	12.1 ^c (0.3)	36.2 ^c (1.0)	1.1 ^c (0.05)	3.6 ^c (0.2)	7.0 ^c (0.1)	0.021 ^c (0.001)	70 ^a (0.9)
B / 59	4.0 ^a (0.3)	21.3 ^b (0.5)	85.1 ^b (2.3)	1.33 ^b (0.04)	5.3 ^b (0.2)	8.9 ^b (0.3)	0.036 ^b (0.003)	55 ^b (2.0)
C / 42	4.7 ^a (0.1)	22.7 ^a (0.4)	106.9 ^a (2.0)	1.59 ^a (0.06)	7.5 ^a (0.3)	10.9 ^a (0.3)	0.051 ^a (0.004)	45 ^c (1.0)
Organic layer (n=12)								
A / 89	25.4 ^a (2.2)	n.d.	n.d.	n.d.	n.d.	10.8 ^b (1.1)	0.28 ^a (0.02)	29 (1.1)
B / 59	12.6 ^b (0.9)	n.d.	n.d.	n.d.	n.d.	11.6 ^{ab} (1.3)	0.15 ^b (0.01)	29 (1.2)
C / 42	7.4 ^c (0.6)	n.d.	n.d.	n.d.	n.d.	12.5 ^a (1.6)	0.09 ^b (0.01)	27 (0.6)
0-5 cm mineral soil (n=6)								
A / 89	461 ^a (39)	0.66 ^c (0.1)	0.3 ^c (0.03)	0.05 ^c (0.01)	0.02 ^c (0.01)	1.7 ^b (0.1)	0.8 ^b (0.01)	18 ^a (0.8)
B / 59	411 ^{ab} (39)	2.09 ^b (0.3)	0.9 ^b (0.17)	0.11 ^b (0.02)	0.05 ^b (0.01)	2.4 ^{ab} (0.1)	1.1 ^{ab} (0.04)	14 ^b (0.3)
C / 42	432 ^b (22)	4.54 ^a (0.7)	1.9 ^a (0.26)	0.18 ^a (0.02)	0.08 ^a (0.00)	3.8 ^a (0.4)	1.5 ^a (0.11)	14 ^b (0.3)

* Data collected by M. Jacob, Department of Plant Ecology, University of Göttingen.

N turnover time was calculated by dividing mean N pool with the mean annual leaf litter-N input, assuming a steady state condition.

4.4.2 Gross rates of N transformation, N pool sizes and mean residence time of N pools

Gross rates of soil N transformation and N pools (except for NH₄⁺) did not differ between sampling dates in all stands. Gross N mineralization rates in the 0-5 cm mineral soil increased with decreasing beech abundance (Figure 4-1). These values result in annual gross N mineralization rates of 450, 700 and 1030 kg N ha⁻¹ yr⁻¹ for stands A, B and C, respectively, assuming constant rates throughout the year. Gross NH₄⁺ assimilation rates were comparable and correlated with gross N mineralization rates (Figure 4-1, Table 4-3). Gross nitrification rates were 5-14% of gross N mineralization rates, and also increased with decreasing beech abundance (Figure 4-1). Gross nitrification rates were correlated with gross N mineralization rates, while microbial assimilation rates of NO₃⁻ were correlated with and as high as gross nitrification rates (Figure 4-1, Table 4-3). All N transformation processes were positively correlated with microbial N which, in turn, was positively correlated with total N, total C, pH and base saturation across stands (Table 4-3). Annual gross rates of N mineralization and nitrification were correlated with N input via leaf litter and leaf litter C:N ratio (Figure 4-2).

NH₄⁺ concentrations were lower in November 2006 than in April 2007, and in April 2007 NH₄⁺ levels increased with decreasing beech abundance. NO₃⁻ concentrations and microbial biomass N also increased with decreasing beech abundance. The NH₄⁺ pool MRT was about 1 day, NO₃ pool MRT was 2-5 days, and microbial N MRT was 2-3 weeks; these did not differ among stands (Figure 4-1).

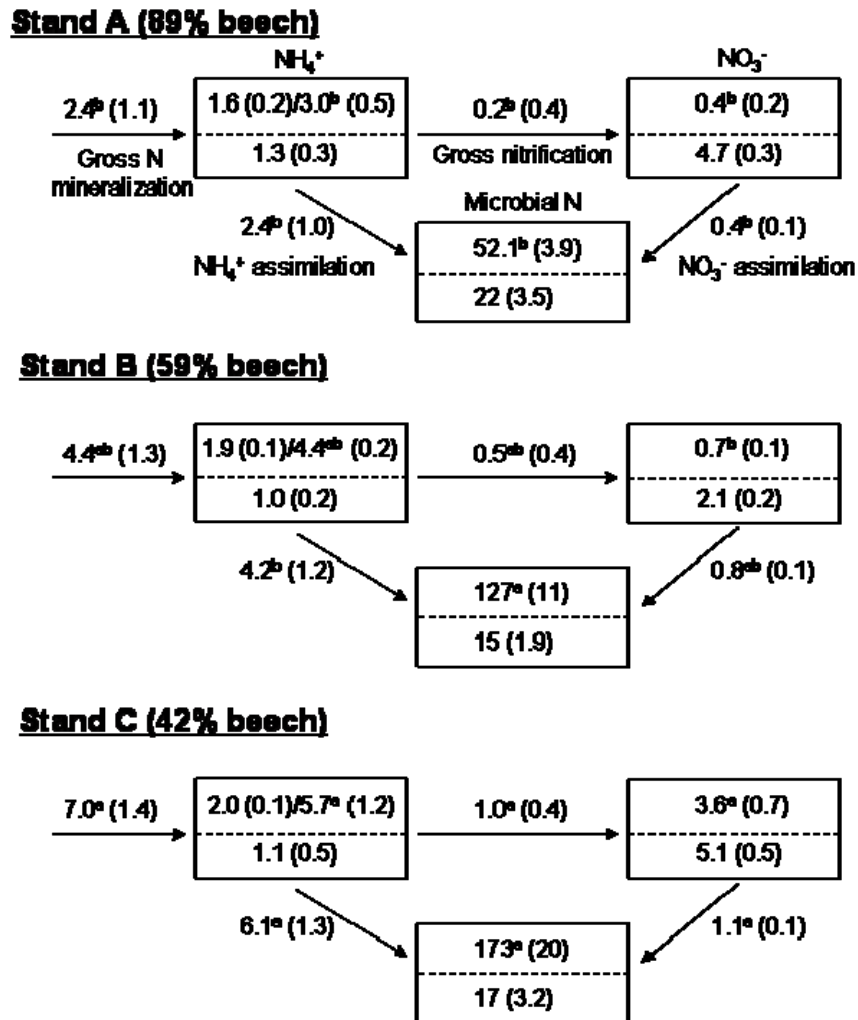


Figure 4-1: Gross rates of N transformation ($\text{mg N kg}^{-1} \text{ d}^{-1}$), N pools (mg N kg^{-1} , upper numbers in boxes) and mean residence time (d, lower numbers in boxes). For each parameter, means (± 1 SE, $n = 6$) followed by a different letter indicate significant differences among stands (Kruskal-Wallis H-test with multiple comparison extension at $P \leq 0.05$). NH_4^+ pool is given separately for November 2006 (first values) and April 2007 (second values) since for each stand these sampling periods differed (Paired-samples T-test at $P \leq 0.05$)

Table 4-3: Spearman rank correlation coefficients among gross rates of N transformations, N pool sizes and soil properties in 0-5 cm mineral soil (n = 18).

	NH ₄ ⁺ assimilation	Gross nitrification	NO ₃ ⁻ assimilation	NH ₄ ⁺ Nov 2006	NH ₄ ⁺ Apr 2007	NO ₃ ⁻	Microbial N	Total N	Total organic C	Soil pH	Base saturation
	mg N kg ⁻¹ d ⁻¹			mg N kg ⁻¹			mg C kg ⁻¹			%	
Gross N mineralization (mg N kg ⁻¹ d ⁻¹)	0.89**	0.50*	0.66**	0.14	0.11	0.67**	0.61**	0.72**	0.59*	0.60**	0.60**
NH ₄ ⁺ assimilation (mg N kg ⁻¹ d ⁻¹)		0.42	0.77**	0.02	0.13	0.55*	0.63**	0.62**	0.55*	0.54*	0.51*
Gross nitrification (mg N kg ⁻¹ d ⁻¹)			0.63**	-0.10	0.62**	0.74**	0.81**	0.68**	0.71**	0.62**	0.62**
NO ₃ ⁻ assimilation (mg N kg ⁻¹ d ⁻¹)				0.56*	0.55*	0.73**	0.81**	0.81**	0.85**	0.64**	0.68**
NH ₄ ⁺ Nov 2006 (mg N kg ⁻¹)					0.28	0.19	0.19	0.41	0.19	-0.51*	0.42
NH ₄ ⁺ Apr 2007 (mg N kg ⁻¹)						0.54*	0.60**	0.45	0.51*	-0.46	0.40
NO ₃ ⁻ (mg N kg ⁻¹)							0.68**	0.78**	0.87**	0.65**	0.72**
Microbial N (mg N kg ⁻¹)								0.85**	0.77**	0.73**	0.72**
Total N (mg N kg ⁻¹)									0.89*	0.74**	0.79**
Total organic C (mg C kg ⁻¹)										0.61**	0.67**
Soil pH											0.97**

* Correlation for NH₄⁺ pool was conducted separately for the corresponding months because NH₄⁺ levels differed between these sampling periods (Figure 4-1).

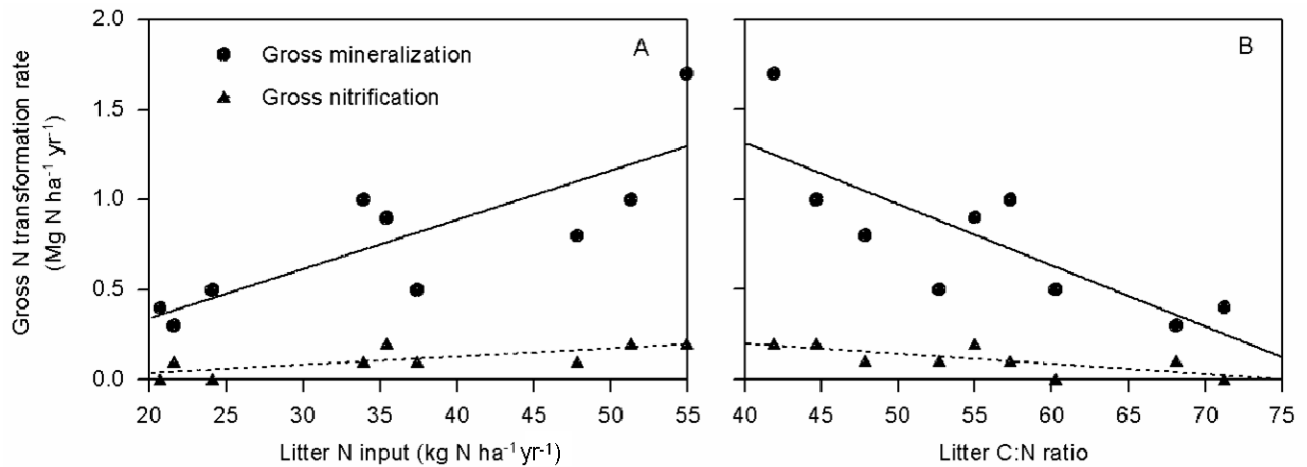


Figure 4-2: Regression analysis between annual gross N mineralization and nitrification rates using the mean values for each transect ($n = 9$; three transects per stand) (A) annual leaf litter-N input (gross N mineralization = $0.03x - 2.6$, $r^2 = 0.61$, $p = 0.007$; gross nitrification = $0.005x - 0.06$, $r^2 = 0.51$, $p = 0.018$) and (B) leaf litter C:N ratio (gross N mineralization = $-0.03x + 2.7$, $r^2 = 0.56$, $p = 0.012$; gross nitrification = $-0.01x + 0.4$, $r^2 = 0.46$, $p = 0.026$).

4.4.3 Net rates of N-transformation

The net N release differed between the two sampling dates (Figure 4-3). In November 2006, negative values of net N mineralization and nitrification rates (except for stand B, although this was not different from zero; One-sample T test at $p = 0.35$) were observed in the 0-5 cm mineral soil, implying that microbial N assimilation exceeded mineral N production. In April 2007, we observed positive values of net rates of N transformation in all stands (Figure 4-3). Net N mineralization and nitrification rates were negatively correlated with microbial C:N ratio ($r = -0.47$, $p < 0.05$, $n = 36$, and $r = -0.42$, $p < 0.05$, $n = 36$, respectively). The mean microbial C:N ratio across stands was significantly higher in November (9.2 ± 0.8) than in April (7.8 ± 0.4).

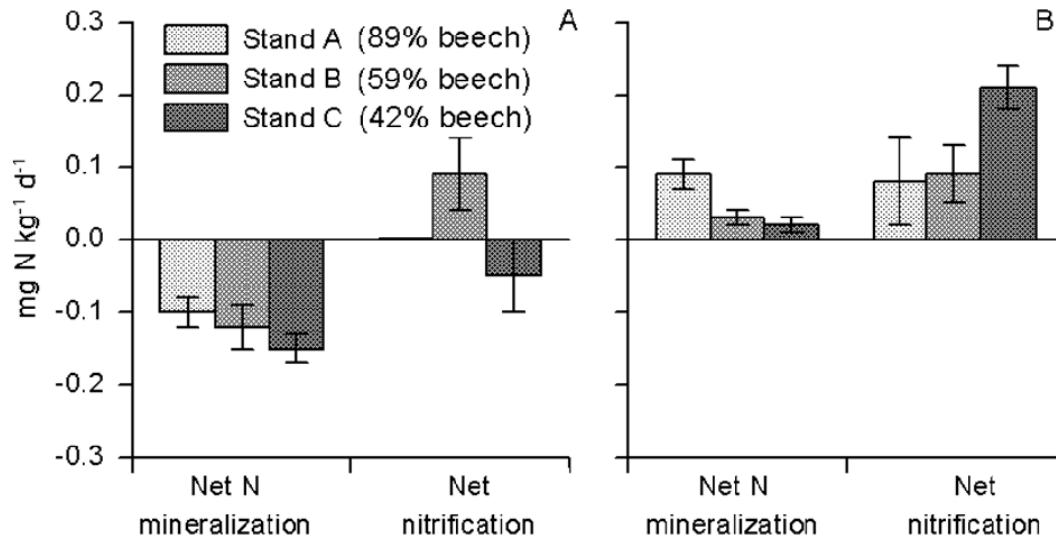


Figure 4-3: Net rates of N transformation in (A) November 2006 and (B) April 2007.

4.4.4 N₂O flux rates and soil factors

The emission rates of N₂O ranged from -31.4 to 167.8 $\mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$ but most (75%) of the measured fluxes did not differ from zero (Figure 4-4A). The highest N₂O emissions occurred between February and March 2006 when there was intermittent freezing and thawing of the soil. These emissions accounted 90%, 94% and 46% of the total emissions during the first year in stands A, B and C, respectively. Annual N₂O emissions increased with decreasing beech abundance (0.11 ± 0.11 , 0.19 ± 0.16 , and 0.40 ± 0.23 kg N₂O-N ha⁻¹ yr⁻¹ in stands A, B, and C respectively; $p = 0.02$). Annual N₂O emissions correlated with mean gross nitrification rates ($r = 0.62$, $p < 0.01$, $n = 18$). Peak emissions during freezing and thawing were correlated with mean microbial biomass N ($r = 0.61$, $p < 0.01$, $n = 18$). Soil extractable N was dominated by organic N (ranging from 8-14 mg N kg⁻¹ across stands) and constituted less NH₄⁺ (3.4-4.0 mg N kg⁻¹) and NO₃⁻ (0.9-2.0 mg N kg⁻¹); these did not differ among stands and exhibited no seasonal variability (Figure 4-4B). We found no correlations between N₂O flux rates and extractable N, WFPS (Figure 4-4C) or soil temperature (Figure 4-4D).

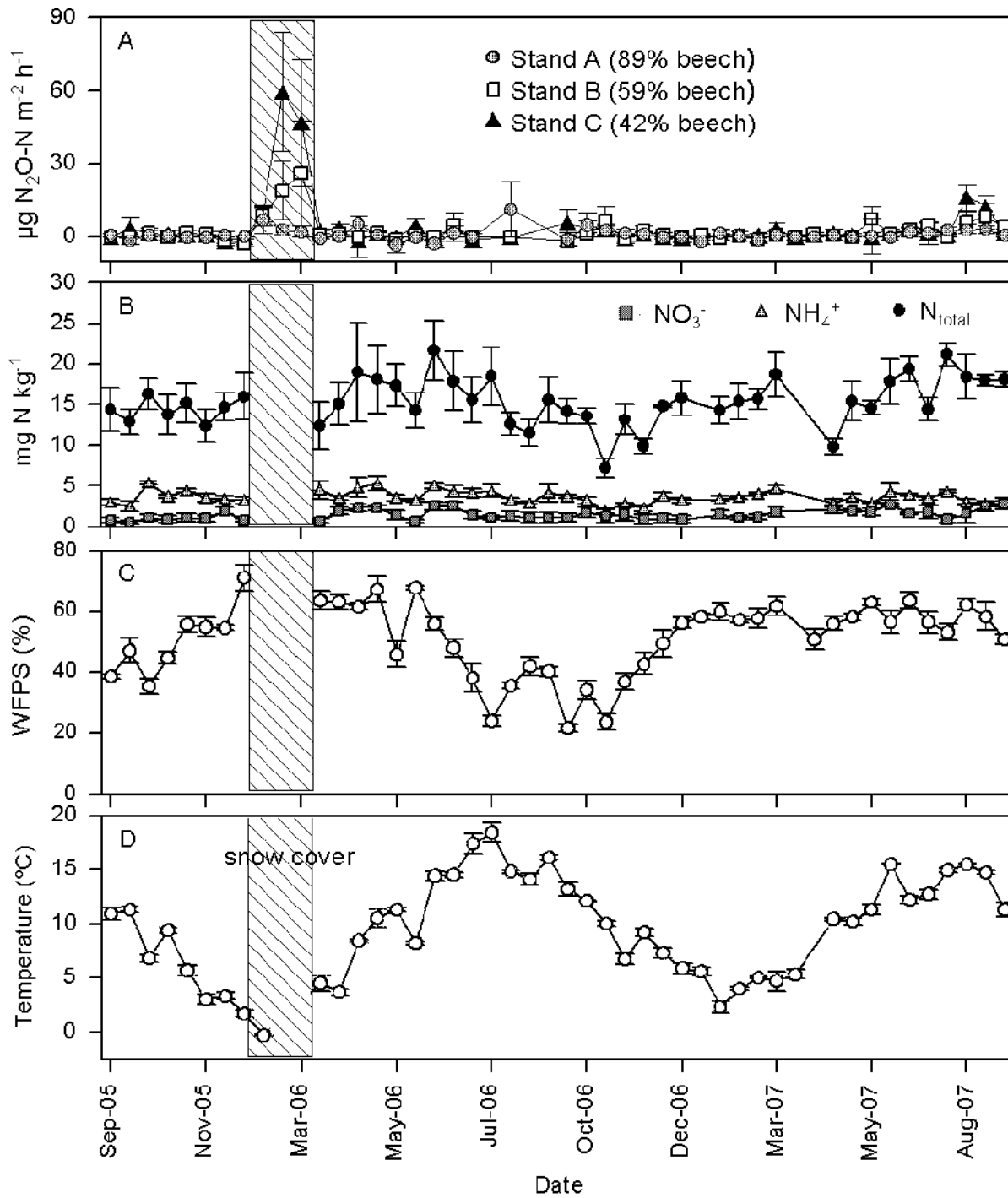


Figure 4-4: Seasonal changes of N₂O fluxes (means \pm SE, n = 6) measured in stands with different abundance of beech (A, B, C) during the experimental period of 2 years, and concentration of extractable NH_4^+ , NO_3^- and total soluble N (DON + NH_4^+ -N + NO_3^- -N), water-filled pores space (WFPS) and temperature at a depth of 5 cm soil depth (means of all stands, n = 18).

4.5 Discussion

4.5.1 Leaf litter quality and soil fertility increased with decreasing beech abundance

The increasing leaf litter N input and decreasing organic layer mass and N turnover time suggest increasing litter decomposition across stands with decreasing beech abundance. The faster turnover of litter N in the mixed stands (stands B and C) than in the beech stand (stand A) can be explained by differences in litter quality. The higher recalcitrance of beech litter is probably due to the lower nutrient contents, higher C:N ratio (Table 4-2) and higher lignin:N ratio (M. Jacob, unpublished data) compared to litter of the other deciduous tree species. Lignin:N ratio is known to be a key factor determining dynamics of litter decomposition (Taylor et al., 1991, Scott and Binkley, 1997, Goh and Totua, 2004). Our findings supported other studies that showed beech litter decomposition to be slower than litter of other broadleaf tree species with the exception of oak (Wise and Schaefer, 1994, Finzi et al., 1998, Neiryneck et al., 2000). The increased leaf litter quality with decreasing beech abundance was also paralleled by increased soil fertility (i.e., low acidity, high base saturation, large stocks of Ca, Mg and N, and low C:N ratio) in the upper mineral soil. In a related study, we have shown that the abundance of beech and tree species-related differences in magnitude of soil-tree nutrient cycling have contributed to the differences in surface soil acidification and base cation stocks (Guckland et al., 2009). In this study, the influence of soil texture on the soil-tree nutrient cycling feedback could not be separated. The correlation of clay content with measures of soil fertility suggests that the moderate clay contents in the mixed stands with high leaf litter quality may also have augmented the retention of nutrients released from litter decomposition. In view of these beech-related feedbacks on litter quality and soil biochemical conditions, we investigated how the microbially-mediated soil N transformation rates differ across sites of different beech abundance.

4.5.2 Gross rates of N transformation increased with decreasing beech abundance

The gross N mineralization rates measured in this study were comparable to the rates measured in other beech forests on Lithic Dystrichrept soils (Verchot et al., 2001, Geßler et al., 2005) and other deciduous forests on Dystric Cambisol soils (Bengtsson et al., 2003). Corre et al. (2003) reported lower gross NH₄⁺ transformation rates in a Dystric Cambisol mineral soil under beech in

Central Germany that has a more acidic soil and lower base cation stocks than our study site. Median gross rates of N mineralization in a mixed beech-oak stand on a Dystric Cambisol soil in Sweden were 2-6 folds higher than ours (Bengtson et al., 2006). Their large spatial variability was explained by tree species impact and variations in soil moisture and temperature.

Our study showed that the increasing gross N transformation rates with decreasing beech abundance were correlated with microbial N (Figure 4-1, Table 4-3). In turn, microbial N was correlated with measures of soil fertility (Table 4-3), suggesting the indirect influence of soil biochemical conditions on gross N transformation rates. The high leaf litter quality and improved soil fertility supported larger microbial biomass in the mixed stands than in the beech stand (Figure 4-1). The link between microbial biomass and gross N transformation rates is attributed to the role of microbial biomass size in driving the cycling of nutrients in the soil (Knops et al., 2002). In addition, the correlations among annual gross N mineralization and nitrification rates with annual leaf litter N input and leaf litter C:N ratio across stands (Figure 2) also suggest the influence of substrate quantity and quality on gross rates of mineral N production. Thus, the increasing N availability (measured by gross N transformation rates) with decreasing beech abundance were influenced both by the increases in microbial biomass size and substrate availability.

Microbial assimilation of NH₄⁺ was a larger fate of produced NH₄⁺ than nitrification (Figure 1). A similar NH₄⁺-dominated soil N cycle was also reported by Bengtsson et al. (2003) and Corre et al. (2007) for different deciduous and spruce forests. Our results showed that nitrifiers were poor competitors for NH₄⁺ and the produced NO₃⁻ was largely assimilated by microbial biomass. Despite longer MRT of NO₃⁻ than of NH₄⁺ pool (Figure 1), NO₃⁻ concentrations were lower than NH₄⁺ concentrations (Figure 1 and 4). The closely-coupled NH₄⁺ cycling, low rates and closely-coupled NO₃⁻ cycling, and fast turn over of microbial biomass indicated efficient retention of mineral N in the soil.

4.5.3 Net rates of soil N cycling did not reflect soil N availability

Net N transformation rates are the net result of the production and consumption of NH₄⁺ and NO₃⁻. The net assimilation of mineral N by microbial biomass (i.e., negative rates of net N mineralization and nitrification) observed in November 2006 was possibly due to a flash of C

inputs from litterfall, setting high demand for microbial assimilation of N. Support for this comes from the high microbial C:N ratio in autumn, indicating high assimilation of C, and from the negative correlations between microbial C:N ratios and net N mineralization and nitrification rates. Low or absence of net release of mineral N in forest soils following litter fall in autumn was also observed in other beech stands (Gasche et al., 2002, Geßler et al., 2005). The net production (positive rates) of mineral N in April 2007 suggests low microbial consumption relative to production of mineral N. This was supported by the higher NH₄⁺ concentrations in spring than in autumn (Figure 1) and the high proportion of net nitrification to net N mineralization rates in the mixed stands with high NH₄⁺ levels (Figure 3). Studies have shown that microbial production and consumption of mineral N do not vary commensurately across seasons, which may result in unrelated net and gross rates of N transformation processes (Davidson et al., 1992, Corre et al., 2002). Our results suggest that the net N cycling rates were influenced by microbial consumption as driven by flashes of C input and did not reflect the patterns of soil N availability across stands.

4.5.4 N₂O emissions increased with decreasing beech abundance

Annual N₂O emissions from the different stands were generally low, which reflect the efficient retention of N through the closely-coupled soil N cycling in our sites. These values were comparable to the estimated N₂O emission from deciduous forest soils in Germany with an average of 0.37 kg N₂O-N ha⁻¹ yr⁻¹ (Schulte-Bisping et al., 2003). Studies have shown that emissions were smaller in coniferous stands than in broadleaf stands (Butterbach-Bahl et al., 1998, Butterbach-Bahl et al., 2002, Borken and Beese, 2006), which were suggested to be caused by smaller gross rates of N mineralization and nitrification in coniferous than broadleaf stands (Ambus et al., 2006). There is little information on the influence of different deciduous tree species on N₂O emission. Our results showed that increasing annual N₂O emissions with decreasing beech abundance were related to the increasing N availability, as attested by the correlation between annual N₂O emission and gross nitrification rates and microbial biomass.

It should be stressed that the observed differences in N₂O emissions among stands originated from a short pulse of activity during intermittent freezing and thawing. The contribution of freeze-thaw N₂O emissions to annual N₂O loss supported previous findings in agricultural and

forest ecosystems that frost periods are of crucial importance in estimating annual N₂O emissions from temperate terrestrial ecosystems (Flessa et al., 1995, Papen and Butterbach-Bahl, 1999, Teepe et al., 2000). Our results suggest that the magnitude of freeze-thaw N₂O emissions might be influenced by the microbial biomass size, which increased with decreasing abundance of beech. This claim is supported by the results of Papen and Butterbach-Bahl (1999) who showed that increased N₂O emissions from forest soils during frost periods were fuelled by easily degradable substrate derived from dead microbial biomass. Sterilization experiments showed that N₂O emissions during freeze-thaw cycles originate from microbial N transformation (Röver et al., 1998), and Teepe et al., (2001) pointed out that N₂O production in frozen soil layers may originate from denitrification in thin liquid water films surrounding the soil matrix.

4.6 Conclusions

This study has shown that abundance of beech in mixed deciduous forests can have a pronounced effect on the stand and soil N cycling. Across stands of decreasing beech abundance, leaf litter-N input, leaf litter quality, turnover time of total N pool in the organic layer, soil fertility and microbial biomass increased, which the latter in turn resulted to a positive feedback of N cycling in the mineral soil. These effects of beech abundance may have also been augmented by the moderate clay contents in stands with low beech abundance. Gross N transformation rates in the mineral soil increased with decreasing beech abundance. The produced NH₄⁺ was largely assimilated by the microbial biomass. Both NH₄⁺ and NO₃⁻ cycling were closely-coupled and resulted to an efficient retention of mineral N in the soil. This efficient N retention was reflected by the generally low N₂O emissions. Annual N₂O emissions were mainly contributed by the freeze-thaw event emissions, which were correlated with the amount of microbial biomass. Finally, net N cycling rates did not reflect the trends of gross N cycling rates because microbial production of mineral N did not vary commensurately with microbial consumption of mineral N across stands and seasons. Our results suggest that increasing the tree species diversity in beech stands growing on limestone areas by the admixture of valuable broadleaf tree species may enhance rates of N cycling in the stand and within the soil.

4.7 References

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5 Controls of temporal and spatial variability of methane uptake*

5.1 Abstract

Aerated forest soils are a significant sink for atmospheric methane (CH₄). Soil properties, local climate and tree species can affect the soil CH₄ sink. A two-year field study was conducted in a deciduous mixed forest in the Hainich National Park in Germany to quantify the sink strength of this forest for atmospheric CH₄ and to determine the key factors that control the seasonal, annual and spatial variability of CH₄ uptake by soils in this forest. Net exchange of CH₄ was measured using closed chambers on 18 plots in three stands exhibiting different beech (*Fagus sylvatica* L.) abundance and which differed in soil acidity, soil texture, and organic layer thickness. The annual CH₄ uptake ranged from 2.0 to 3.4 kg CH₄-C ha⁻¹. The variation of CH₄ uptake over time could be explained to a large extent ($R^2 = 0.71$) by changes in soil moisture in the upper 5 cm of the mineral soil. Differences of the annual CH₄ uptake between sites were primarily caused by the spatial variability of the soil clay content at a depth of 0 to 5 cm ($R^2 = 0.5$). The CH₄ uptake during the main growing period (May to September) increased considerably with decreasing precipitation rate. Low CH₄ uptake activity during winter was further reduced by periods with soil frost and snow cover. There was no evidence of a significant effect of soil acidity, soil nutrient availability, thickness of the humus layer or the abundance of beech on net CH₄ uptake in soils in this deciduous forest. The results show that detailed information on the spatial distribution of the clay content in the upper mineral soil is necessary for a reliable larger scale estimate of the CH₄ sink strength in this mixed deciduous forest. The results suggest that climate change will result in increasing CH₄ uptake rates in this region because of the trend to drier summers and warmer winters.

* A. Guckland, H. Flessa, J. Prenzel (2009) Controls of temporal and spatial variability of methane uptake in soils of a temperate deciduous forest. *Soil Biology and Biochemistry* 41: 1659-1667.

5.2 Introduction

Methane is a radiatively active trace gas, which has increased in the atmosphere since the beginning of industrialization from 715 ppb to 1774 ppb in 2005 (IPCC, 2007). This increase is caused mainly by anthropogenic emissions originating from rice agriculture, biomass burning, ruminant animals, landfills, and several industrial sources, in particular fossil fuel mining and distribution (IPCC 2007). Most CH₄ is removed from the atmosphere by reaction with the hydroxyl free radical (OH). Aerated soils represent the only net biological sink for atmospheric CH₄. Methanotrophic bacteria in aerated soils remove about 10 to 44 Tg of atmospheric CH₄ per year and contribute up to 10% of the global CH₄ sink (IPCC, 2001, Lowe, 2006).

Several studies have revealed that land use exerts a strong influence on soil uptake of atmospheric CH₄. Conversion of forest soils to agriculture reduced CH₄ uptake rates by about two-thirds (Smith et al., 2000). Differences of net uptake of atmospheric CH₄ were attributed mainly to factors influencing gas diffusivity in soils such as soil moisture, soil bulk density, and soil texture (Adamsen and King, 1993, Dörr et al., 1993, Bender and Conrad, 1993, Dobbie and Smith, 1996, Borken et al., 2000, Smith et al., 2000, Price et al., 2003, Teepe et al., 2004, Ball et al., 1997, Tate et al., 2007, McNamara et al., 2008). In addition, nitrogen availability (Steudler et al., 1989, Mosier et al., 1991, Brumme and Borken, 1999, Kravchenko et al., 2002, Wang and Ineson, 2002, Reay and Nedwell, 2004), soil acidity (Dunfield et al., 1993, Brumme and Borken, 1999, Borken et al., 2003), temperature (Dobbie and Smith, 1996, Priemé and Christensen, 1997, Borken et al., 2000, Price et al., 2003), and the structure and activity of methanotrophic populations (Borken et al., 2003) were identified as further factors influencing the uptake rate of atmospheric CH₄ in soils.

Large variations exist in annual CH₄ uptake rates in soils of temperate forest ecosystems (<0.1 to ~20 kg CH₄ ha⁻¹ yr⁻¹) (Smith et al., 2000, Ishizuka et al., 2000, Brumme et al., 2005). Tree species can have a pronounced influence on various chemical, physical and biological soil properties (Augusto et al., 2002, Binkley, 1995) that may affect CH₄ uptake. Several studies have revealed that CH₄ uptake rates are higher in soils of hardwood stands (e.g. beech, oak) than in those of adjacent coniferous stands (e.g. spruce, pine) (Borken and Brumme 1997, Borken et al., 2003, Butterbach-Bahl and Papen, 2002, Reay et al., 2005). Even admixture of spruce to beech forests was found to reduce CH₄ uptake (Borken and Beese, 2006). These species effects were explained by a combination of different factors including depth and structure of the organic layer,

which can act as a diffusion barrier for atmospheric CH₄, lower pH under spruce, and differences in soil bulk density and microbial activity in the upper mineral soil. Borken et al. (2003) pointed out that the activity or populations of methanotrophs are probably lower under spruce and pine than under beech.

Effects of tree species on CH₄ uptake may also occur in deciduous forests with different broad-leaved tree species since even these species can differ in their effects on soil chemistry (Norden, 1994, Guckland et al., 2009) and soil biology (Neiryneck et al., 2000, Cesarz et al., 2007). However, up to date there is a paucity of information about the significance of different deciduous tree species for the spatial and temporal variability of CH₄ uptake in forest soils.

In a recent study in a broad-leaved mixed forest with beech (*Fagus sylvatica* L.), ash (*Fraxinus excelsior* L.), lime (*Tilia cordata* Mill. and/or *T. platyphyllos* Scop.), hornbeam (*Carpinus betulus* L.), and maple (*Acer pseudoplatanus* L. and/or *A. platanoides* L.) it was shown that surface soil acidity and carbon accumulation in the humus layer increased with increasing abundance of European beech (Guckland et al., 2009). Differences in the redistribution of nutrients and alkalinity via leaf litter were identified as important factors that contributed to this beech effect. These results suggest that the abundance of beech might also affect the uptake of atmospheric CH₄.

In the present paper, we report on a two-year field study on net methane exchange in this broad-leaved mixed forest. This is the first study on soil CH₄ fluxes in this area.

Our objectives were to determine the net CH₄ exchange rate of this broad-leaved mixed forest and to analyze the key factors that determine the seasonal, inter-annual and spatial variability of the CH₄ flux rates. A simple model (Potter et al., 1996) was tested for its ability to capture the annual soil CH₄ sink and to predict temporal changes of CH₄ flux rates.

We hypothesize that the investigated stands are a net sink for atmospheric CH₄. The temporal variation of CH₄ uptake is expected to be controlled mainly by soil and climate factors that change gas diffusivity in soil. Besides spatial variability of soil physical properties, the abundance of beech might influence the annual sink strength for atmospheric CH₄ as a result of its effect on soil acidity and organic matter accumulation in the humus layer.

5.3 Material and methods

5.3.1 Study site

The study was performed in mature stands of deciduous forest in the Hainich National Park, Thuringia, Germany. The study sites are located at an elevation of approximately 350 m a.s.l.. The mean annual temperature is 7.5 °C and the mean annual precipitation is 670 mm. The geological substrate of all experimental sites is Triassic limestone covered by loess. All stands had a long-term forest history of at least 200 years. The forest has not been managed since 1990; previous to that it had been used for military training since the 1960s. In 1997, it became a National Park. Different forest ownerships have generated a small-scale stand mosaic of species-poor, beech-dominated forest patches and stands with up to 14 deciduous tree species per hectare that are all growing under similar climatic conditions and on the same geological substrate. In 2005, a long-term study on biogeochemical cycles and biotic interactions was started in selected stands with decreasing abundance of beech and associated increasing tree species diversity (<http://www.forest-diversity.uni-goettingen.de>) and fenced monitoring areas (54 x 54 m) have been established in these stands (Guckland et al., 2009). We used three of these fenced monitoring areas in different stand types to establish 18 sub plots for a two-year study on soil CH₄ exchange. Stand A was a single-species stand covered with European beech (*Fagus sylvatica* L.) as the predominant tree specie. Stand B was a three-species stand with beech, ash (*Fraxinus excelsior* L.) and lime (*Tilia cordata* Mill. and/or *T. platyphyllos* Scop.) as predominant species, and stand C was covered with beech, ash, lime, hornbeam (*Carpinus betulus* L.) and maple (*Acer pseudoplatanus* L. and/or *A. platanoides* L.) as predominant species. The abundance of beech (expressed as percentage of total tree basal area) decreased in the order stand A (88%) > stand B (59%) > stand C (41%) (Table 5-1). Six sub plots each were randomly distributed in the selected monitoring areas (Guckland et al., 2009). The soil type was a Luvisol (FAO, 1998) developed in a loess cover of 60 to 70 cm over limestone. The two layer soils exhibited stagnic properties during winter and spring, but they were quite dry during summer. Physical and chemical soil properties and the abundance of beech in the analyzed stands are summarized in Table 5-1. The texture of the upper mineral soil (0 to 10 cm) was dominated by the silt fraction (65% - 83%), and clay contents varied between 13% and 31%. Base saturation (BS) and soil pH were lowest under beech (stand A) and organic carbon stocks in the humus layer decreased with decreasing proportion of beech (Table 5-1).

Table 5-1: Physical and chemical soil properties of the three stands (A, B, C) with different abundance of beech (means and standard deviations in brackets, n = 6). Different letters indicate significant differences between stands.

Stand	Thickness of loess cover (cm)	Soil texture (clay/silt/sand)		Bulk density (g cm ⁻³)		pH	Base saturation (%)	Organic Carbon (kg m ⁻²)		Proportion of Beech*	
		0-5 cm	5-10 cm	0-5 cm	5-10 cm			Humus layer [§]	0-5 cm		5-10 cm
Stand A	70	15 / 82 / 3	13 / 83 / 3	0.9 (0.2)	1.2 (0.1)	4.5 (0.2) ^a	48 (12) ^a	0.77 (0.21) ^c	1.5 (0.3) ^a	0.8 (0.1) ^a	88
Stand B	60	23 / 75 / 2	22 / 74 / 3	0.8 (0.2)	1.0 (0.2)	5.4 (0.4) ^b	91 (10) ^b	0.42 (0.11) ^b	1.3 (0.4) ^a	1.0 (0.2) ^a	59
Stand C	60	31 / 66 / 3	31 / 65 / 4	0.9 (0.2)	1.0 (0.1)	5.7 (0.6) ^c	97 (2) ^b	0.24 (0.07) ^a	2.0 (0.5) ^b	1.7 (0.5) ^b	41

*abundance of beech in terms of percentage of total tree basal area

[§] see chapter 3 (n = 12)

5.3.2 CH₄ flux measurements and CH₄ in soil air

Net fluxes of CH₄ were measured biweekly using dark, closed chambers from September 2005 till September 2007. Each chamber had a volume of 9.25 L and covered a surface of 405 cm². The chambers were equipped with two vent tubes, one to ensure pressure equilibration and another one for gas sampling. For flux determination, chambers were tightly fixed onto base collars made of PVC (height of 15 cm), which had been carefully cut into the soil to a depth of 10 cm three weeks before the measurements started. These collars constituted the permanent sub plots for CH₄ flux determination. The chamber remained on the collar for 60 minutes. Using evacuated (<1 mbar) glass vials fitted with Teflon locks, we took four gas samples of the chamber atmosphere at equal sampling intervals of 20 min (after 0, 20, 40 and 60 min). Gas samples were analyzed using a gas chromatograph (Carlo Erba Instruments, GC 6000,) equipped with a flame ionization detector (FID) and an autosampler system that allowed automated CH₄ analysis of our sampling vials and of additional calibration gases. The setup and function of the gas chromatographic system was described in detail by Loftfield et al. (1997). The CH₄ flux rate was calculated from the slope of the temporal change in CH₄ concentration in the closed chamber according to equation 2.

$$F_C = k_{CH_4} (273/T) (V/A) (\Delta c/\Delta t) \quad (2)$$

where F_C is the flux rate of CH₄ ($\mu\text{g CH}_4\text{-C m}^{-2} \text{ h}^{-1}$), k_{CH_4} ($0.536 \mu\text{g C } \mu\text{L}^{-1}$) is the unit conversion factor for calculating CH₄ flux rates, T is the temperature ($^{\circ}\text{K}$) of the air, V is the volume (liter) of the air within the chamber, A is the area (m^2) of the soil covered by the chamber, and $\Delta c/\Delta t$ is the rate of change in CH₄ concentration ($\mu\text{L L}^{-1} \text{ h}^{-1}$).

Fluxes with a slope correlation coefficient of the linear concentration decrease of $R^2 > 0.95$ were accepted for further analysis. At a few dates during the winter, when soils were wet or even partly frozen, concentration gradients over time in single covers were insignificant because fluxes were close to zero. These fluxes were assumed to be equal to zero. The minimum detectable flux was approximately $3 \mu\text{g CH}_4\text{-C m}^{-2} \text{ h}^{-1}$. Flux rates were expressed as means with standard deviation. Cumulative CH₄ fluxes were calculated by assuming constant flux rates between two consecutive measurement dates.

Parallel to each flux measurement the air and soil (at a depth of 5 cm) temperature was measured and soil samples were taken from the depths 0 to 5 and 5 to 10 cm (except for the period January to March 2006 when the surface soil was frozen). Soil moisture content was determined gravimetrically after drying at 105° C for 24 hours. The water-filled pore space (WFPS) was calculated as follows: $WFPS = [(gravimetric\ water\ content \times soil\ bulk\ density) / total\ soil\ porosity]$ where the soil porosity = $[1 - soil\ bulk\ density / 2.65]$, 2.65 being the assumed particle density of the soil in ($g\ cm^{-3}$).

From May to November 2006 CH₄ concentration in soil air was determined parallel to the CH₄ flux determination to test the relation between surface fluxes and soil air concentrations. Stainless steel needles (diameter of 0.2 mm) fitted with luer-lock cocks, were inserted into the mineral soil to a depth of 5 cm and 10 cm. Soil air (6 ml) was sampled with glass syringes which were connected with the luer-lock cocks after flushing the sampling needle and syringe with soil air. The syringe needle was closed directly after sampling and analysis of CH₄ concentration was performed within 24 hours by manual injection of the sample in a gas chromatograph (GC-FID).

5.3.3 Soil sampling and analysis

After termination of the field measurements undisturbed soil cores (depth: 0 to 5 cm and 5 to 10 cm) were taken directly from inside the 18 base frames that formed the sub plots for chamber measurements. These samples were used to determine soil bulk density, soil texture using the sieving and pipette method (Schlichting et al., 1995), organic carbon and total nitrogen by an automated C and N analyzer (Heraeus Elementar Vario EL, Hanau, Germany), soil pH in a suspension with distilled H₂O (5 g soil in 15 ml H₂O), and the cation exchange capacity (CEC) following the procedure described by König and Fortmann (1996).

The CEC was calculated as the equivalent sum of the exchangeable Na, K, Ca, Mg, Mn, Fe, Al and H ions. Base saturation was defined as the equivalent sum of base cations (Na, K, Ca and Mg) as percent of CEC.

5.3.4 Modelling CH₄ fluxes and statistical analysis

We tested a simple model of Potter et al. (1996) for its ability to estimate the size of the annual CH₄ uptake and to predict seasonal and inter-annual changes of CH₄ uptake. Potter's model

assumes that soil gas diffusivity is the primary control of atmospheric CH₄ uptake and that diffusivity is driven by soil physical properties and soil water content. Data on soil texture and soil moisture at field capacity are used to compute gas diffusivity in inter- and intra-aggregate pore spaces of differently textured soils. The CH₄ concentration gradient in soil which drives CH₄ diffusion is assumed to be constant (0.04 ppmv cm⁻¹). Changes in soil moisture are normally predicted from rainfall, potential evapotranspiration and a term that describes the soil drying rate as a function of soil moisture (Potter et al., 1996). We used our measured soil moisture contents in 0 to 5 cm to run the model. Potter's model approach assumes that soil CH₄ uptake is negligible when soil temperatures are below the freezing point of water.

Correlation (Pearson) and regression analysis were used to compare modeled and measured CH₄ fluxes and to analyze the relationships between measured fluxes and soil and environmental factors. Differences among stands with regard to soil properties, CH₄ fluxes and soil CH₄ concentrations were tested for significance by one way analysis of variance followed by the Tukey's test if assumptions of normality and homogeneity of variances were met. This was not the case for the base saturation and the C stocks in the organic layer. For these factors, we employed the Kuskal-Wallis-ANOVA.

5.4 Results

5.4.1 Spatial and temporal variation of net CH₄ uptake

All soils were net sinks for atmospheric CH₄ (Figure 5-1). Measured CH₄ uptake rates ranged from 0 to 78 μg CH₄-C m⁻² h⁻¹. We found no evidence for a period with significant net-emission of CH₄. This is in accordance with our observation that CH₄ concentration in soil air was always below the atmospheric level. All stands showed the same distinct seasonal variation of CH₄ uptake activity. Highest uptake rates occurred in midsummer and early autumn, and CH₄ flux rates were lowest during the winter months (from January to the end of March) (Figure 5-1). Except for the cold and wet winter months when all sites showed low CH₄ uptake activity, uptake rates were higher in the soil of stand A (beech dominated) than in the soil of the other two stands (stand B and C). The mean CH₄ uptake rates during the main growing period from May to September (calculated over both experimental years) were 37 μg CH₄-C m⁻² h⁻¹ in stand A, 29 μg CH₄-C m⁻² h⁻¹ in stand B, and 26 μg CH₄-C m⁻² h⁻¹ in stand C.

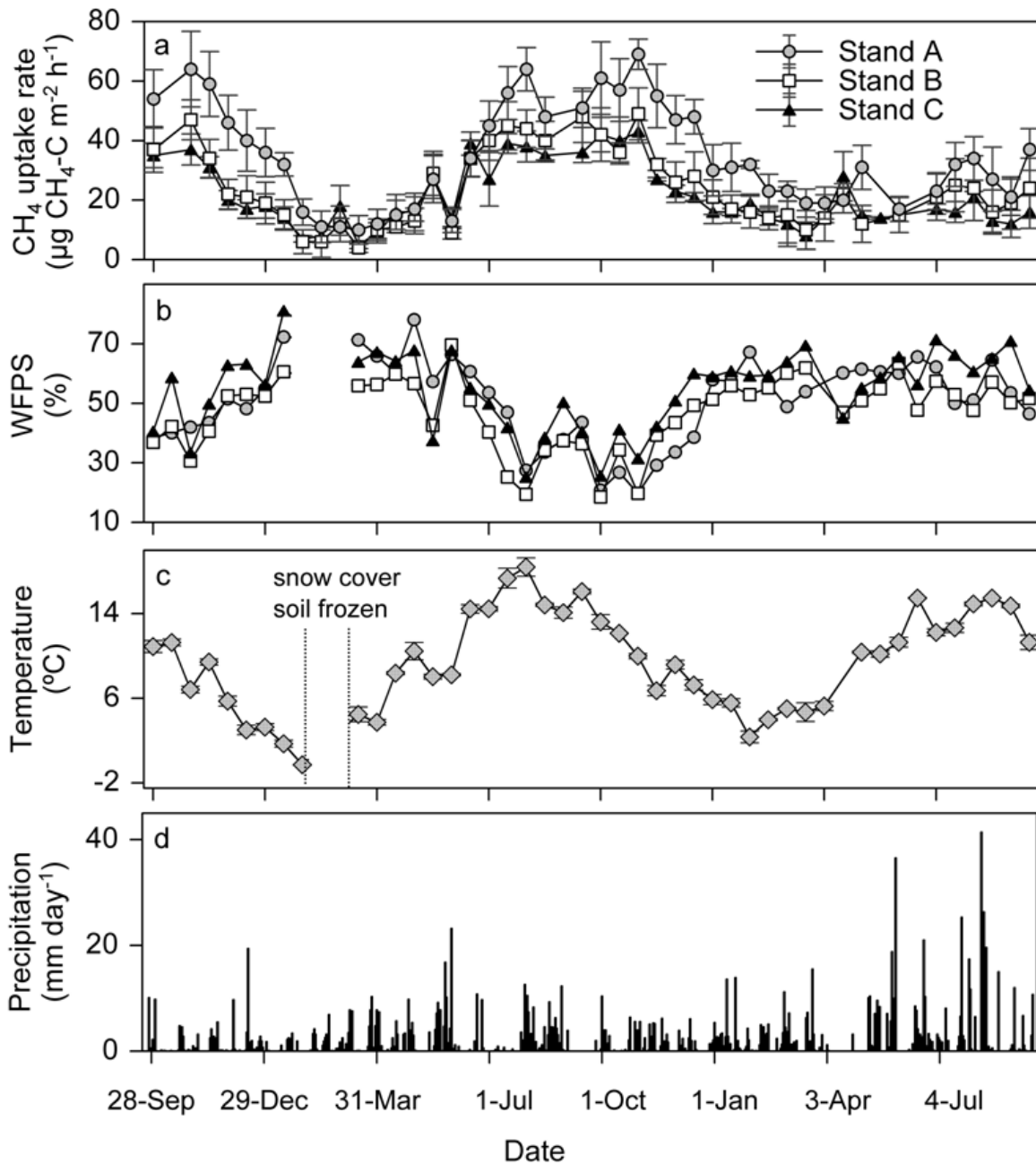


Figure 5-1: Seasonal changes of a) CH₄ uptake rates (means and standard deviation, $n = 6$) measured in 3 stands (A, B, C) with different abundance of beech, b) soil water filled pore space (soil depth of 0-5 cm) in these stands (means, $n = 6$, standard deviations were generally smaller than the plotted symbols), c) soil temperature at a depth of 5 cm (means of all three stands), and d) daily precipitation from September 2005 till September 2007.

The total annual CH₄ uptake was significantly higher in stand A (3.3 and 3.4 kg CH₄-C ha⁻¹ yr⁻¹) than in stand B (2.4 and 2.3 kg CH₄-C ha⁻¹ yr⁻¹) or stand C (2.4 and 2.0 kg CH₄-C ha⁻¹ yr⁻¹) (Table 5-2). The inter-annual variation of CH₄ uptake was low if annual fluxes were compared (2 to 15%). However, significant inter-annual differences occurred in all stands if winter and summer periods were analyzed separately (Table 5-2). Winter fluxes were lower and summer fluxes were higher in the first year than in the second year (Table 5-2).

Concentration of CH₄ in soil air was always lower than the atmospheric concentration. It varied between 0.96 and 1.63 μl L⁻¹ at a depth of 5 cm and between 0.72 and 1.44 μl L⁻¹ at a depth of 10 cm (data not shown). Lowest CH₄ concentrations in soil air were measured when soils were relatively dry and net CH₄ uptake rates measured at the soil surface were highest. The mean CH₄ concentration measured at a depth of 5 cm was lowest in soil of stand A (1.21 μl L⁻¹) and highest in soil of stand C (1.46 μl L⁻¹), stand B exhibited an intermediate value (1.39 μl L⁻¹). The same order was found at a depth of 10 cm, whereas mean CH₄ concentrations were 15% (stand A), 12% (stand B) and 27% lower than at 5 cm. The maximum CH₄ concentration gradient of 0.16 ppm_v cm⁻¹ was detected in the soil (0 to 5 cm) of stand A during summer at low WFPS. The mean concentration gradient over all plots was 0.09 ppm_v cm⁻¹. There was a close correlation between the mean CH₄ uptake rate measured at the soil surface and the mean CH₄ concentration in soil air at a depth of 5 cm ($R^2 = 0.50$) (Figure 5-2), whereas the relation with the CH₄ concentration in 10 cm depth was weak ($R^2 = 0.02$; data not shown).

5.4.2 Controls of CH₄ uptake

The measured CH₄ uptake rates were significantly influenced by soil moisture. Uptake of CH₄ was negatively correlated with the water-filled pore space (WFPS) in upper mineral soil (depth: 0 to 5 cm), and a linear regression explained 71% of the variability between CH₄ uptake and WFPS (Figure 5-3). The effect of soil temperature at a depth of 5 cm on CH₄ uptake was minor ($R^2 = 0.17$, $p < 0.001$). Multiple linear regression analysis including WFPS (0 to 5 cm) and soil temperature at a depth of 5 cm as independent factors slightly increased the degree of explanation to $R^2 = 0.78$. We did not find clear differences in soil temperature or soil moisture between the sampled stands (Figure 5-1). The inter-annual variation of CH₄ uptake during the main growing period and during winter appeared to be mainly related to differences in precipitation and temperature, respectively.

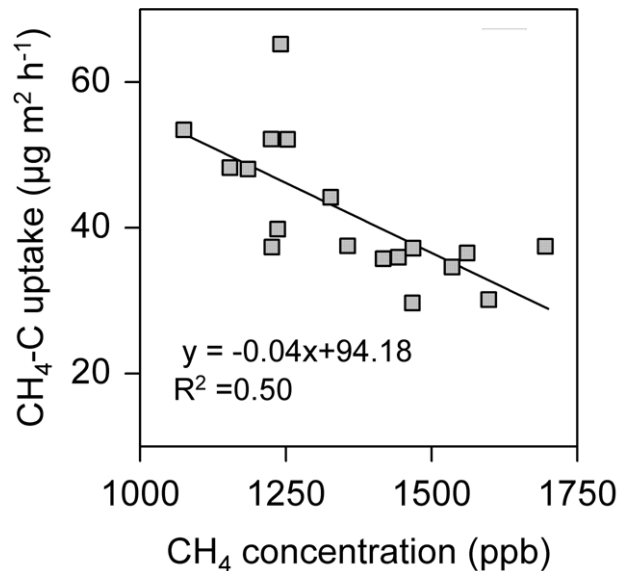


Figure 5-2: Relationship between the mean CH₄ uptake rates measured at the 18 experimental subplots during the period May 2006 to November 2006 and the mean CH₄ concentration in 5 cm soil depth.

Precipitation during the main growing period (May to September) was about 80% higher in 2007 than 2006, whereas CH₄ uptake was significantly reduced in all stands during the season 2007 (Table 5-2). Winter fluxes (November to May) were significantly lower in 2005/06 than 2006/07 (Table 5-2). These periods showed distinct differences in temperature and snowfall. The winter 2005/06 was cold with a long frost period and snow cover, whereas the following winter 2006/07 was considerably warmer: there was less snow, and soil was never frozen to a depth of 5 cm. Differences in the cumulative CH₄ uptake over 2 years at the 18 sub plots could be explained to a large extent by small scale variability of soil texture in the upper mineral soil. There was a significant negative correlation between the clay content at a depth of 0 to 5 cm and the CH₄ uptake ($R^2 = 0.5$) (Figure 5-4). There were negative correlations of CH₄ uptake with pH ($R^2 = 0.42$) and base saturation ($R^2 = 0.54$) at a depth of 0 to 5 cm. However, these factors were strongly intercorrelated with clay content in this depth ($R^2 = 0.70$ and $R^2 = 0.56$, respectively, $p < 0.01$).

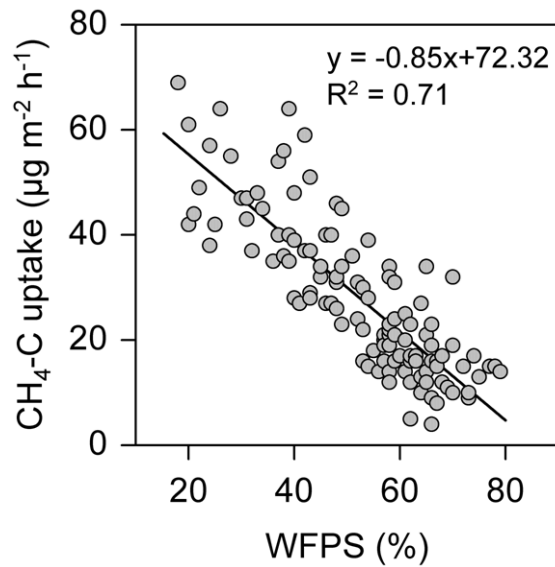


Figure 5-3: Relationship between uptake rates of atmospheric CH₄ and soil water filled pore space in a depth of 0 to 5 cm (data from all stands).

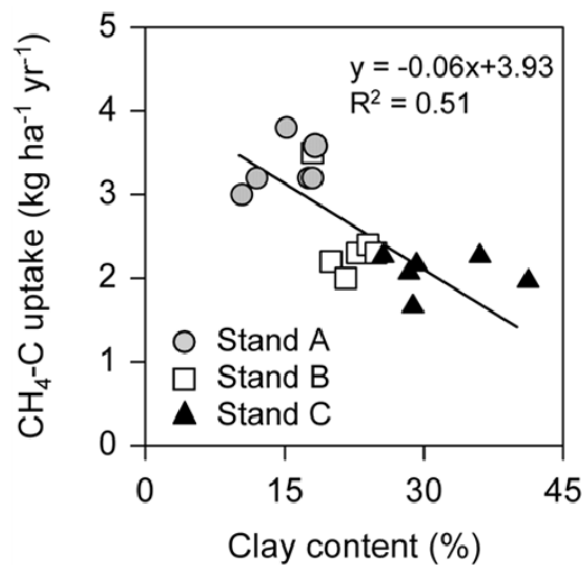


Figure 5-4: Relationship between the annual uptake rates of atmospheric CH₄ measured at the 18 experimental sub plots and the soil clay content in the depth 0 to 5 cm.

Table 5-2: Cumulative methane uptake (means and standard deviation in brackets, $n = 6$) of the soils of the three stands (A, B, C) with different abundance of beech and total precipitation during the growing and winter periods. Different lower case letters indicate significant differences between stands; different capital letters indicate significant differences between the selected periods for the same stand.

Season	Period	Methane uptake			Precipitation
		Stand A	Stand B	Stand C	
Year		(kg CH ₄ -C ha ⁻¹ period ⁻¹)			(mm)
	21 Sep 2005 – 20 Sep 2006 (365 d)	3.29 (0.41) ^{bA}	2.42 (0.46) ^{aA}	2.39 (0.19) ^{aB}	516
	21 Sep 2006 – 20 Sep 2007 (365 d)	3.35 (0.38) ^{bA}	2.28 (0.81) ^{aA}	2.04 (0.16) ^{aA}	735
Winter	2 Nov 2005 – 3 May 2006 (183 d)	1.24 (0.14) ^{bA}	0.71 (0.20) ^{aA}	0.76 (0.07) ^{aA}	240
	2 Nov 2006 – 7 May 2007 (186 d)	1.78 (0.26) ^{bB}	1.20 (0.44) ^{aB}	1.04 (0.14) ^{aB}	253
Summer	4 May 2006 – 20 Sep 2006 (141 d)	1.51 (0.25) ^{bB}	1.29 (0.22) ^{abB}	1.14 (0.12) ^{aB}	236
	8 May 2007 – 20 Sep 2007 (136 d)	0.94 (0.19) ^{bA}	0.63 (0.31) ^{abA}	0.59 (0.12) ^{aA}	430

5.4.3 Model results

Figure 5-5 shows the modeled CH₄ uptake rates from Potter's model versus the measured flux rates (mean uptake rates of each stand measured at single sampling dates during the two-year experimental period). The model was able to predict the general magnitude of the CH₄ uptake rates in soils of the Hainich National Park. The modeled mean CH₄ uptake rate over all experimental plots and the experimental period of two years was 12% higher than the calculated value from the measured flux rates (27 $\mu\text{g CH}_4\text{-C m}^{-2} \text{ h}^{-1}$). The model was also able to capture the general seasonal change of CH₄ uptake activity with higher uptake rates during the summer and lower rates during the winter (Figure 5-6). However, it was not able to reproduce the relatively small differences of CH₄ uptake between the analyzed stands.

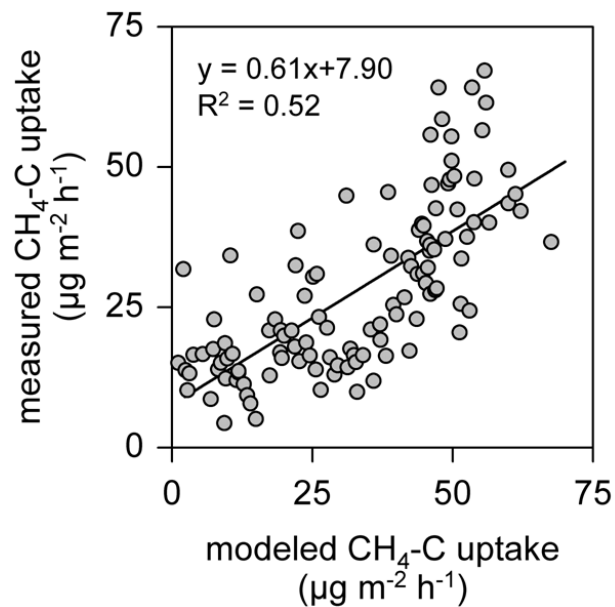


Figure 5-5: Measured versus modeled (using the model of Potter et al., 1996) CH₄ uptake rates for the two experimental years and all stands.

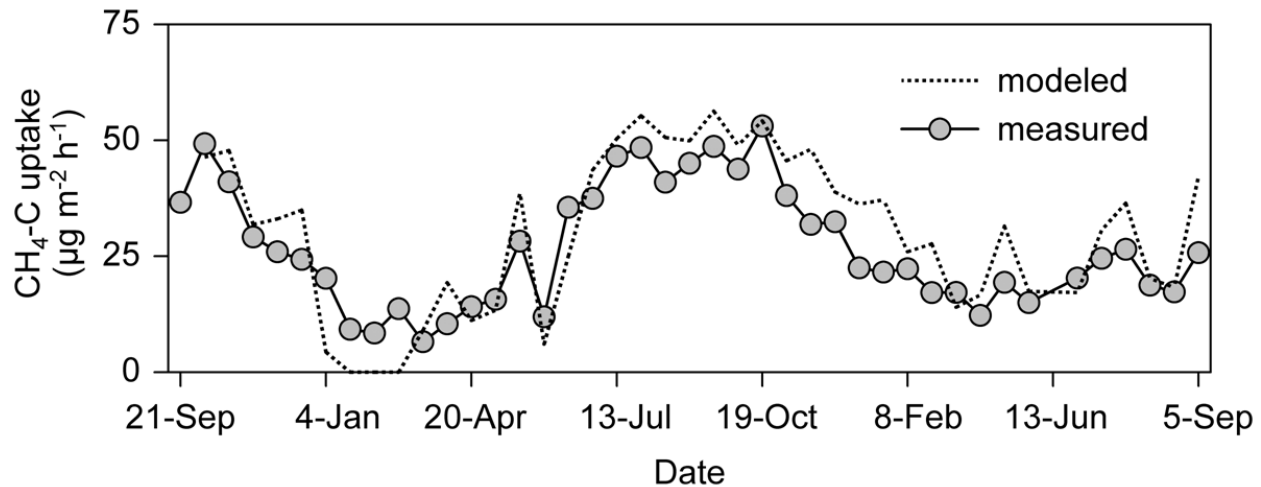


Figure 5-6: Measured and modeled (using the model of Potter et al., 1996) time course of the mean CH₄ uptake rates (calculated over all stands) in soils of the Hainich National Park during the experimental period of 2 years.

5.5 Discussion

5.5.1 Annual CH₄ uptake

The annual CH₄-C uptake rates of soils in the Hainich National Park (2.0 to 3.4 kg CH₄-C ha⁻¹ yr⁻¹) are within the range reported from other deciduous forests stands in the temperate zone (0.4 to 14.8 kg CH₄-C ha⁻¹ yr⁻¹, Table 5-3). Unfortunately, the available year-round data on CH₄ uptake in temperate deciduous forests originate from only 4 countries (Table 5-3). This clearly constrains the generalization and extrapolation of these results. In particular, there are no results from warmer and drier regions of the temperate zone. Most of the reported annual fluxes are below 6 kg CH₄-C ha⁻¹ yr⁻¹. In Europe, only two deciduous forest sites with coarse-textured sandy soils showed slightly higher uptake rates of 6.4 and 7.7 kg CH₄-C ha⁻¹ yr⁻¹ (Dobbie and Smith, 1996, Dong et al., 1998). It is surprising that considerably higher CH₄ uptake (10.4 to 14.8 kg CH₄-C ha⁻¹ yr⁻¹) was reported for deciduous forest soils in the Northeast of the U.S. (New England) (Table 5-3). The reason for this distinct regional difference in CH₄ uptake activity is not yet fully understood. Boriken et al. (2006) who analyzed CH₄ uptake in European forest soils and also in these “high activity” U.S. soils

suggested that good drainage and high gas diffusivity might explain the higher CH₄ uptake. The low soil bulk density and high stone content of these U.S. soils probably maintain high gas diffusivity even in rainy periods (Brumme and Borken, 1999). High nitrogen deposition rates in Europe (Bergström and Jansson, 2006) and differences in soil N availability are other factors that might have contributed to the lower CH₄ uptake in European soils (Ojima et al., 1993, Goldman et al., 1995, Klemmedtsson and Klemmedtsson, 1997, Butterbach-Bahl et al., 1998, Brumme and Borken, 1999). Smith et al. (2000) summarized results on CH₄ uptake in Northern European soils. They found that most of the flux rates reported for temperate forests in Europe are between 0.6 and 9 kg CH₄-C ha⁻¹ yr⁻¹. However, there was no differentiation between deciduous and coniferous stands. Brumme et al., (2005) pointed out that estimates of the annual CH₄ sink strength of forests ecosystems can be improved by stratifying forests by biome (boreal, temperate, tropical) and soil texture. Based on a literature review they reported a mean CH₄ uptake for medium and fine textured, temperate forest soils (including coniferous, deciduous and mixed stands) of 1.7 kg CH₄-C ha⁻¹ yr⁻¹, which is slightly lower than the flux rates measured in the Hainich National Park.

Del Grosso et al. (2000) concluded that annual CH₄ uptake rates in deciduous forest soils are generally higher and also more variable than those measured in coniferous stands. Their model to simulate CH₄ uptake in coniferous stands did not reliably predict CH₄ uptake in soils of deciduous stands. They proposed a separate subroutine to estimate CH₄ uptake in deciduous forest soils in which a direct linear effect of soil bulk density on potential CH₄ uptake is assumed.

5.5.2 Temporal variation of CH₄ uptake

Soil moisture content was the key factor which determined the time course of CH₄ uptake rates in the studied soils of the Hainich National Park. Our results are in accordance with the general observation that soil moisture is the primary environmental control on CH₄ uptake in soils because it regulates methane flux into the soil through diffusion (Borken et al., 2006, Ball et al., 1997, Adamsen and King, 1993, Butterbach-Bahl and Papen, 2002, Smith et al., 2000). We found a close linear relationship between soil moisture expressed as WFPS and the net-uptake of atmospheric CH₄, and there was no evidence for a limitation of CH₄ uptake at low soil moisture. A linear response of CH₄ uptake to soil moisture content was found in several studies

Table: 5-3: Literature values of methane uptake rates in soils of temperate deciduous forests based on field measurements of at least one year.

Reference	Country	Tree species	Precipitation (mm yr ⁻¹)	Mean air temperature (°C)	Soil pH	Soil texture class or clay/silt/sand (%)	CH ₄ -C uptake (kg ha ⁻¹ yr ⁻¹)
Ambus & Christensen, 1995	Denmark	Beech			5.4 - 5.8	Sandy loam	0.4
Borken et al., 2003	Germany	Beech	1038	7.2	3.8	19/54/27	2.2 - 3.8
Borken et al., 2006	USA	Mixed deciduous	1050	8.5		Sandy loam	11.7
Born et al., 1990	Germany	Beech, Oak, Maple			8.0	Loamy	2.3
		Mixed deciduous			5.0	clay	3.0
Brumme & Borken, 1999	Germany	Beech	680	7.8	5.2	38/59/3	1.9
	Germany	Beech, Oak	650	8.5	5.1	32/18/50	1.0
	Germany	Beech	750	8.0	4.3	17/1/32	0.6
	Germany	Beech	1090	6.4	3.9	17/57/26	0.08
Butterbach-Bahl et al., 2002	Germany	Beech	888	8.56	3.8	Sandy loam	2.8
Butterbach-Bahl & Papen, 2002	Germany	Beech	800	7.3	3.4		3.7 - 5.4
Crill, 1991	USA	Mixed deciduous-conifer	1098	8.3			4.3 - 4.6
Dobbie & Smith, 1996	UK	Mixed deciduous	723	6.9		Loamy sand	7.1
Dong et al., 1998	Germany	Beech, Oak	540	8.6	3.1 - 3.9	Sand	6.4
Goldman et al., 1995	USA	Oak	1030 - 1080	8.5 - 12.5	4.4 - 4.9	Coarse-loamy	10.4 - 14.8
Teepe et al., 2004	Germany	Beech	700	7.8	5.0	31/64/5	1.5
This study	Germany	Beech, mixed deciduous	516 - 735	7.5	4.5 - 5.7	Silty loam	2.0 - 3.4

(Koschorreck and Conrad, 1993, Dobbie and Smith, 1996, Bradford et al., 2001, Price et al., 2003), but the slope of this relationship can vary considerably (Borken et al., 2003). In general, the response function to moisture changes should not be extrapolated to drier conditions because CH₄ uptake activity can decrease rapidly if water stress restricts activity of methanotrophs (Del Grosso et al., 2000). The low temperature response of CH₄ uptake can be explained by strong substrate limitation of CH₄ oxidizing micro-organisms. This is particularly true for fine-textured soils where diffusive gas exchange is slow (Born et al., 1990, Crill, 1991, Koschorreck and Conrad, 1993, Smith et al., 2000, Butterbach-Bahl and Papen, 2002). Our results show that uptake of atmospheric CH₄ in soils of the Hainich National Park is controlled primarily by gas diffusivity and that the enzymatic control (temperature) plays a minor role.

Our results indicate that differences in precipitation during the growing season induce significant inter-annual variation of CH₄ uptake. The reduction of the precipitation rate during the main growing period (May to September) from 430 mm to 236 mm caused an increase in CH₄ uptake by 61 to 105%. Similar results were reported by Borken et al. (2003) for beech and spruce stands in Lower Saxony, Germany. Manipulation experiments with artificial summer drought also confirmed that the precipitation rate during summer strongly affects the annual soil CH₄ sink as a result of its effect on soil moisture and gas diffusivity (Borken et al., 2000). During winter, frost periods and snow cover can reduce the already low CH₄ uptake activity.

At our sites duration of snow cover and freezing of the upper mineral soil were probably the main reasons for the 27% to 40% decrease in CH₄ uptake during the first winter compared with the winter of the second experimental year. Borken et al. (2006) described similar winter effects with a reduction of methane uptake rates after the first snowfall from 4.5 to 0.6 mg CH₄ m⁻² d⁻¹ and very low fluxes when the soil was frozen. Both, snow cover and the formation of ice in soil pores can act as a barrier for gas diffusion and thus restrict supply of atmospheric CH₄ to methanotrophs. However, it is noteworthy that low CH₄ uptake activity persisted even in periods with a compact snow cover and soil frost. This is in accordance with observations made by Sommerfeld et al. (1993) and Flessa et al. (2008), who observed significant net-uptake of atmospheric CH₄ through a snow layer and during strong frost periods. Our results may contribute to understanding the implications of climate change for soil net CH₄ exchange in this region. Climate change is expected to decrease summer precipitation (by approximately 15%) and winter frost periods in this area considerably (Enke et al., 2005, Schindler et al., 2007,

Hundecha and Bárdossy, 2008). Our results suggest that both changes will result in an increase of soil CH₄ uptake.

5.5.3 Spatial variation of CH₄ uptake

The main factor which determined spatial variability of CH₄ uptake was soil texture and in particular the clay content in the upper mineral soil layer (0 to 5 cm). A soil texture effect on CH₄ uptake in soils has been observed in several studies and explained with generally lower soil moisture contents and higher gas diffusivity in coarse-textured soils (Dörr et al., 1993, Striegl, 1993, Boeckx et al., 1997, Verchot et al., 2000). Saari et al. (1997) found positive interactions of methane uptake rates with coarse particles (> 2mm) and also with fine particles (< 0.06 mm) in a moraine soil in northern Europe. The coarse particles enhanced soil gas diffusivity and allowed rapid CH₄ diffusion into the soil, which was also observed by Bender & Conrad (1993), whereas high methane oxidation activity of the finest soil particles was explained by methanotrophs requirement of surface adhesion for metabolic activity (Schnell & King, 1995). We have not found any significant differences in total soil moisture at a depth of 0 to 5 cm between stands despite the detected differences in clay content. Soil bulk density and water retention curves (U. Talkner, personal communication) in these stands indicated that total porosity and the proportion of macropores in 0 to 5 cm were similar in all soils and stands. However, the proportion of micropores increased and the proportion of mesopores decreased with increasing clay content. Koschorrek and Conrad (1993) found that CH₄ diffusion from the atmosphere into the soil via macropores was more rapid than microbial CH₄ oxidation. They concluded that CH₄ diffusion from air-filled macropores to the CH₄ oxidizing microorganisms was limiting CH₄ uptake. Since methanotrophic activity is highest in the finest soil fraction, the proportion of micropores, which is closely related to the clay content, can constrain CH₄ uptake particularly in periods with low moisture contents (during summer). This may explain why we found a clear effect of clay content on CH₄ uptake without observing significant differences in total soil moisture.

The close correlation between the CH₄ uptake rate and CH₄ concentration at a depth of 5 cm or soil properties in the upper 5 cm of the mineral soil is in accordance with the observation of several studies that the activity of “high affinity” methanotrophs, which oxidize atmospheric CH₄, is located mainly in the uppermost centimeters of the mineral soil. (Butterbach-Bahl et al., 1998, Butterbach-Bahl and Papen, 2002, Jäckel, 2004, Reay et al., 2005).

The beech stand (stand A) was the site with the slowest litter decomposition, and litter accumulation in the humus layer was approximately two to three times higher under beech than in the mixed stands of deciduous tree species. In addition, soil acidity in the upper mineral soil was considerably higher and stocks of exchangeable base cations were lower under beech than in the mixed stands. Guckland et al. (2009) found that the abundance of beech and tree-species related differences in the redistribution of nutrients via leaf litter contributed to the current chemical soil conditions. Since the litter layer can reduce soil CH₄ uptake by acting as a diffusion barrier (Dong et al., 1998, Brumme and Borken, 1999) and since soil acidity and reduced nutrient availability can also constrain CH₄ uptake activity of soils (Saari et al., 1997, Brumme and Borken, 1999, Borken et al., 2003), we were interested to see whether the observed differences in soil chemistry and humus layer thickness were important factors which determined variability of CH₄ uptake in this deciduous forest. Our results do not allow the exact quantification of the effects of these factors on CH₄ uptake, but they show that their influence was insignificant compared with the clay effect. We found a negative correlation between these soil properties and the soil CH₄ uptake because soil pH and base saturation increased with the clay content. Based on the results of Guckland et al. (2009) we can conclude that the abundance of beech influenced the thickness of the humus layer, soil acidity and nutrient availability in this mixed deciduous forest but there is no evidence that there is a strong effect of beech abundance on the net uptake of atmospheric CH₄.

5.5.4 Modelling CH₄ uptake

The model of Potter et al. (1996) assumes that CH₄ uptake by soils is limited by diffusion of atmospheric CH₄ into the soil. It predicted the size of the mean annual CH₄ uptake satisfactorily and was able to capture the general seasonal change of CH₄ uptake, even though it is based on several simplifications, which do not exist in soils: e.g. a constant linear concentration gradient of CH₄ in soil air or a constant homogeneously distributed mean soil moisture during the monthly time steps. In addition, this approach neglects several other factors, which might also affect soil CH₄ uptake at several sites, e.g. soil pH, thickness of the humus layer, temperature or CH₄ production in soil deeper soil layers or anoxic microsites. The good performance of the model at our experimental site supports the conclusion that CH₄ uptake was primarily controlled by gas diffusivity in the upper mineral soil and that all other potential controls were of minor

importance. We expect that Potter's model will be less accurate for soils with high porosity where the importance of gas diffusivity for CH₄ uptake is lower.

5.6 Conclusions

Soils of the Hainich National park were a net-sink for atmospheric CH₄ with an annual uptake rate of 2.0 to 3.4 kg CH₄-C ha⁻¹. The temporal variability of CH₄ uptake was mainly driven by moisture changes in the upper mineral soil. Differences in CH₄ uptake between stands could be explained to a large extent by differences in clay content in the surface soil. Despite the influence of beech abundance on humus layer formation and soil acidity, we found no evidence for an effect of beech on the size of CH₄ uptake. For reliable larger scale estimates of CH₄ uptake in the Hainich National Forest, detailed information on the distribution of soil clay content in the upper mineral soil is necessary. Forest stratification based on the abundance of different deciduous tree species is not necessary. The inter-annual variation of CH₄ uptake suggest that climate change will result in increasing CH₄ uptake rates in this region because of the trend to drier summers and warmer winters.

5.7 References

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6 Conclusions

The background of this thesis is the conversion of quasi-monospecific beech forests (*Fagus sylvatica* L.) growing in limestone areas to mixed stands with different broad-leaved species.

The long-term consequences of changing the beech abundance by admixture of valuable broad-leaved species on soil properties and soil related processes are not sufficiently investigated. Therefore, mature mixed stands of deciduous trees along a beech gradient were investigated, which are growing under similar climate and on the same geological substrate (loess over limestone). The dominating tree species which were mixed with beech were ash (*Fraxinus excelsior* L.), lime (*Tilia cordata* Mill. and/or *T. platyphyllos* Scop.), hornbeam (*Carpinus betulus* L.), and maple (*Acer pseudoplatanus* L. and/or *A. platanoides* L.)

I analyzed i) soil acidity, soil nutrient status, the amount and distribution of soil organic matter, ii) the soil N cycle, and iii) the fluxes of the greenhouse gas methane (CH₄) in these stands with the aim to determine the main controls of the spatial variability of these soil properties and processes and to elucidate the role of beech abundance as a possible factor, which contributes to this variability.

In this chapter, the main results of the different experiments were integrated and the most relevant conclusions are presented.

6.1 Soil acidity, nutrient stocks and soil organic matter content

Striking differences in soil pH, base saturation and quantity of exchangeable cations between beech-dominated stands and mixed species stands could partly be explained by the subsoil clay content. Nevertheless, the results suggest that beech abundance contributed the observed variability in nutrient availability and soil acidity. The leaf litter Ca and Mg contents were largely driven by species-specific differences in litter quality. The redistribution of Mg, Ca and alkalinity via tree litter had a high potential to ameliorate the surface soil. This process of “biological pumping” enables the translocation of base cations and alkalinity from the alkaline subsoil to the surface soil and increases its base saturation. The results suggest that this process increased with decreasing beech abundance, even if it was not possible to clearly separate the effects of subsoil clay content and beech abundance. Species-related differences in litter composition and the redistribution of nutrients via litter had a high potential to change acidity and the soil nutrient

status in the analyzed stands. The larger accumulation of C and N in the organic surface layer of the beech-dominated stands resulted mainly from the lower decay rate of beech litter due to its higher recalcitrance. The uncertainty associated with the historical land use and the interfering effects of soil texture and tree species composition affect the significance of these results.

6.2 Stand and soil N cycling

The abundance of beech influenced the annual N input via leaf litter, leaf litter quality, the turnover time of litter N, soil fertility and microbial biomass and led to an increase of the soil internal N cycle. These effects of beech abundance may have also been augmented by the moderate clay contents in stands with low beech abundance. Both NH_4^+ and NO_3^- cycling were closely-coupled and resulted to an efficient retention of mineral N in the soil through the microbial biomass. This efficient retention of mineral N is reflected by generally low N losses. Emission rates of N_2O were generally low in all stands with the exception of a severe frost period. Frost-induced emissions accounted for up to 94% of the annual N_2O loss and were correlated with the amount of microbial biomass.

The net rates of N mineralization and nitrification were not an adequate measure to reveal effects of beech abundance on soil N cycling because microbial production of mineral N did not vary commensurately with microbial consumption of mineral N across stands and seasons.

The results suggest that increasing the tree species diversity in beech stands growing in limestone areas by the admixture of valuable broad-leaved tree species enhances the rate of N cycling in the stand and within the soil.

6.3 Net uptake of atmospheric methane

The soils of the Hainich National park were a net-sink for atmospheric CH_4 with an annual uptake rate of 2.0 to 3.4 kg $\text{CH}_4\text{-C ha}^{-1}$. The seasonal dynamics of CH_4 uptake was mainly driven by moisture changes in the upper mineral soil. The inter-annual variations of CH_4 uptake during the summer and winter half year were mainly due to differences in precipitation and soil frost, which restricted diffusion of CH_4 into the soil. The observed spatial variability of CH_4 uptake could be largely explained by differences in the clay content of the upper mineral soil layer (0 to 5 cm). There was no evidence of the influence of beech abundance on the amount of CH_4

oxidised in these soils, although beech influenced the thickness of the humus layer and soil acidity.

6.4 General conclusion

The results indicate that the conversion of quasi-monospecific beech forests to mixed stands of beech with different valuable broad-leaved tree species increased the intensity of soil-tree cation cycling and the redistribution of alkalinity, and important nutrients (e.g. Ca, Mg, N) via litter fall. As a consequence, it reduced the degree of soil acidity and increased soil nutrient stocks in the upper mineral soil. High subsoil clay contents enforced this effect. In addition, admixture of valuable broad-leaved tree species to beech stands increased the size and rate of N cycling between soil and vegetation and also within the soil. The results suggest that at fertile sites that allow production of valuable broad-leaved tree species, the admixture and promotion of these species in beech stands is an important silvicultural tool to counteract natural or anthropogenic soil acidification and to maintain soil productivity.

In contrast, beech abundance did not influence the net uptake of atmospheric CH₄. The results show that detailed information on the spatial distribution of the soil clay content in the upper mineral soil layer is needed for a reliable larger scale estimate of the soil CH₄ uptake in the Hainich National Park. The inter-annual variation of CH₄ uptake suggest that climate change will result in increasing CH₄ uptake rates in this region because of the trend to drier summers and warmer winters.

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Curriculum vitae

Personal Details

Name: Anja Guckland

Date of birth: March 7, 1979

Place of birth: Halberstadt, Germany

Nationality: German

Education

1991 - 1997 Gymnasium Martineum Halberstadt
High School Graduation: Allgemeine Hochschulreife

1998 - 2005 Study of Geography, Georg-August-University Göttingen, Germany
Degree obtained: Diplom Geograph

2005 - 2009 PhD study „Forstwissenschaften und Waldökologie“, Georg-August-
University Göttingen, Germany