Characterisation of Soil Organic Matter under Intensively Used Grassland along an Alpine Elevation Gradient in South Tyrol, Italy.

master thesis

Cecilie Birgitte Foldal

Matriculation number: 0640086
Study program number: 458
Field of study: Organic Farming

Supervisors: Mag. Dr. Ika Djukic
D.I. Dr. Georg J. Lair
AO. Prof. Dr. Jürgen K. Friedel

Institute of Soil Research & Division of Organic Farming
University of Natural Resources and Life Sciences,
Vienna, October 2012

Acknowledgements

This work was supported by the project “Climate Change in South Tyrol” led by Ulrike Tappeiner at the Institute of Ecology, Innsbruck, Erich Tasser and Georg Niedrist at the European Academy (EURAC) in Bolzano.

I am very grateful for the support and advice I received from my supervisors Ika Djukic, Georg Lair and Jürgen Friedel during the work on this master thesis and also want to thank Axel Mentler, Michael Tatzber and Karin Wriessnig for their technical advice, as well as Ewald Brauner, Elisabeth Kopecky and Karin Hackl for their technical assistance in the lab.

And last but not least I want to thank Christoph, Anders and Oskar. Without your support and encouragement I wouldn’t have made it.

Content

Tables

Figures

Appendix

Abstract

Alpine grasslands are known to accumulate large amounts of soil organic matter (SOM) and present an important and active terrestrial carbon pool. Alpine ecosystems are also known to be especially vulnerable to climate changes. It is still unknown however, how the changing climatic condition will impact the stored soil organic carbon (SOC) in alpine grasslands. In this study four intensively used grassland sites in the South Tyrolean Alps along an elevation gradient from 1000 to 2000 m asl, having similar soil forming factors (i.e. geology, soil type, vegetation), were characterised in order to determine the quantity and properties of the SOM. Besides elemental analysis (i.e. organic C and total N content) we applied Simultaneous Thermal Analysis on bulk soil and Fourier Transform Infrared Spectrometry on extracted humic acids (1 M NaOH), taken from soils at depths down to 0 – 40 cm. We found that the soils in the 0 – 15 cm soil depth accumulated 0.48 kg/m^2 SOC per 100 m altitude in the sites. The highest SOM amount was observed in the upper layer (0 – 5 cm) and that the tendency decreased with increasing soil depth. Within the profile we could observe a decrease in labile organic compounds and an increase in more stabile pool with soil depth. However, the SOM was dominated (63 - 77%) by thermal labile compounds, resulting from high annual inputs of manure and low decomposition/mineralization rates of the organic matter in the study area. Labile aliphatic bounds and N-related compounds in the humic acids showed altitudinal variations at all soil depths whereas most other bands did not change with the elevation. The amount and composition of SOM was mainly controlled by the prevailing climatic conditions, soil properties (i.e. pH and C:N ratio) and land management practices. We found organic matter decomposition at all sites to be limited to an early (i.e. labile) stage.

Zusammenfassung

Alpines Grasland speichert hohe Mengen an organischer Bodensubstanz (SOM) und alpine Graslandböden stellen damit eine wichtige und aktive Kohlenstoffsenke dar. Zudem sind alpine Ökosysteme für Klimaveränderungen besonders sensibel. Es ist noch unbekannt, wie sich die verändernden klimatischen Bedingungen auf den gespeicherten organischen Bodenkohlenstoff (SOC) in den alpinen Böden auswirken werden. In der vorliegenden Studie werden vier intensiv genutzte Grünlandflächen der Südtiroler Alpen untersucht um Änderungen in Menge und Eigenschaften der organischen Substanz im Boden zu können. Die Standorte befinden sich entlang eines Höhengradienten von 1.000 bis 2.000 m über dem Meeresspiegel und weisen ähnliche bodenbildende Faktoren (z.B. Geologie, Bodentyp, Vegetation) auf. Die Analysen reichen von der Elementaranalyse und Simultane Thermoanalyse der entnommenen Bodenproben (0 – 40 cm Bodentiefe) bis zur Fourier-Transform Infrarot-Spektroskopie der extrahierten Huminsäuren (1M NaOH). Es stellte sich heraus, dass die Böden in 0 - 15 cm Bodentiefe 0,48 kg / m^2 SOC pro 100 Meter Höhenunterschied akkumulieren. Die höchste SOM Anreicherung wurde in der obersten Schicht (0 – 5 cm) beobachtet, mit abnehmender Tendenz bei zunehmender Bodentiefe. Innerhalb der Bodenprofile konnte eine Abnahme der labilen organischen Verbindungen zugunsten des stabilen Pools beobachtet werden. Die Hauptbestandteile der organischen Substanz stellten thermisch labile Verbindungen (63 - 77%) dar, die aus den jährlichen Gülle- bzw. Stallmistgaben und einer geringen Abbaurate des organischen Materials im Untersuchungsgebiet resultierten. Labile aliphatische- und N-Verbindungen in den Huminsäuren zeigten in alle Bodentiefen höhenstufenabhängige Veränderungen während die meisten anderen Banden sich mit der Seehöhe nicht änderten. Die Menge und Zusammensetzung der SOM war hauptsächlich durch die vorherrschenden klimatische Bedingungen, Bodeneigenschaften (z.B. pH-Wert, C:N-Verhältnis) und die Form der Landnutzung beeinflusst. An allen Standorten war der Abbaugrad der organischen Substanz auf eine frühe (labile) Stufe begrenzt.

1 Background and Objectives of the Study

This study is part of the project: “Climate Change in South Tyrol” and was conducted in cooperation with the European Academy (EURAC) Institute of Alpine Environment in Bolzano, the Institute of Ecology at the University in Innsbruck and the Institute of Soil Research at the University of Natural Resources and Life Sciences in Vienna. The main objectives of the project are to identify and quantify the impact of climate change (i.e. increasing mean temperatures and lower annual precipitation) on grassland productivity, water resources and water household and soil properties. As study area the Matcher-valley in South Tyrol, Italy, was chosen. The Matcher-valley is a dry inneralpine valley where the surrounding mountain chains are responsible for above average temperatures during the vegetation period and low precipitation throughout the year (NIEDRIST, 2009). Such dry conditions would be expected in further parts of the Alps in the future and this makes the study sites suitable to forecast future agricultural production conditions in inneralpine areas (NIEDRIST, 2011).

In general, mountain areas are very suitable for studying the long-term influences of climate on soil properties under natural conditions since ecosystem properties change within short distances. In this project there are two methodological approaches for simulating the climatic change.

a) Climosequence, reflecting the long term effects of climatic change as the chosen sites along an elevation gradient, shows severe changes in climatic properties of temperature and precipitation. The predicted factors that will alter with e.g. increasing temperatures (vegetation, snow cover, soil properties etc.) can be easily investigated in situ (BENISTON ET AL., 1997, HITZ ET AL., 2001, RUSTAD, 2006, DJUKIC ET AL., 2010).

b) Soil translocation, where undisturbed soil monoliths are transferred from one climatic zone to another in order to simulate a climate change and thereby investigate the short-term effects of climatic changes (REY ET AL., 2007, DJUKIC ET AL., 2010).

Only a few studies (e.g. LEIFELD ET AL., 2009, BUDGE ET AL., 2011, SINGH ET AL., 2011) have been done to analyze SOC stocks and qualities under managed grassland at high altitudes. The present study is based on the climosequence approach and is focused on the characterisation of SOM under intensively used grasslands.

The main objective of this work is to study the long-term influence of temperature (i.e. vegetation period) and long-term grassland management (i.e. irrigation, meadow vs. pasture) on the amount and properties of the SOM along an elevation gradient covering an increase of approximately 3° C per 500 m asl.

In the very dry inner-alpine study area we expect a relatively fast accumulation of SOM with increasing altitude due to less favourable climatic conditions for SOM decomposition (i.e. lower mean annual temperatures), Since the sites are all intensively used grasslands and fertilized regularly with cattle manure we assume a similar composition of SOM in the topsoils along the elevation gradient. With increasing soil depth we expect a progressed humification of SOM to more stable, aromatic compounds as the relative portion of older (more decomposed) SOM is increasing in deeper soil layers. Changes in SOM composition shall be observed with analysis of the bulk soil using thermogravic measurements and the characterisation of humic acids extracted with 1M NaOH with mid-infrared spectroscopy.

2 Introduction

As has been published in numerous accounts, worldwide the mean annual temperature (MAT) is increasing. Impacts from changing climates differ between the different regions and ecosystems of the world. In the Alp regions the changes have been especially pronounced over the last century, with a temperature increase twice as high as the global mean (IPCC, 2007). The climate in the Alps is known to be very complex and characterised by high interannual variability (BENISTON ET AL., 1997). The impact of the climatic change is expected to become more serious since a continued increase of annual temperature, more extreme weather patterns and reduced annual precipitation in the Alps are predicted (IPCC, 2007). Less snow cover and longer vegetation seasons as well as extended dry summers in the inneralpine regions shall further stress mountainous ecosystems (KÖRNER, 2003, p288).

Soil organic matter (SOM) deserves particular attention in this context because of its dominant influence on many physical, chemical, and biological properties of soil, upon which our societies and agroecosystems depend. SOM is a major determinant of, e.g., soil structure and water-holding capacity and represents an important nutrient reservoir for plants and microbes. In the global carbon cycle, SOM represents the largest component of the terrestrial carbon pool. More than four times the atmospheric carbon is bound in organic compounds above- and belowground (JANZEN, 2004).The stock of SOM at a given site is a function of the organic matter (OM) inputs and its rate of decomposition, on which in turn are related to climate, vegetation and geology (BRADLY and WEIL, 2008, p. 495). Land use and farming management practices also affect the quantity and quality of SOM (BOT & BONITES, 2005, GERZABEK ET AL., 2006, DEMYAN ET AL., 2012). The largest source of carbon is plant residues entering the soil, either as litter above- or as root tissue, sloughed root cells and root exudates belowground (GREGORICH & JANZEN, 1996). Within different ecosystems the allocation of organic carbon (OC) between above- and belowground varies. Based on data from IPCC, JANZEN (2004) showed that wetlands and boreal forest ecosystem stored the most OC and that more than 84% of this OC was soil organic carbon (SOC). Temperate grasslands can store as much as tropical rainforests but, whereas the allocation of OC in a tropical forest is about 50/50 above- and belowground, OC in temperate grass- and shrubland ecosystems is found to be 97% in the soil and only 3% in the aboveground biomass (ibid). Globally most SOC is accumulated belowground at sites of higher latitudes and/or altitudes (GAVAZOV, 2010, SJÖGERSTEN ET AL., 2011, p120).

SOM is a heterogeneous mixture of organic substances, originating from plants and microbial by-products and consists of approximately 50 % carbon (SCHEFFER & SCHACHTSCHABEL, 2008, p51, RASMUSSEN & WHITE, 2010). The different organic compounds exhibit a wide range of kinetic properties (DAVIDSON & JENSSENS, 2006). Based on the theory of BOSATTA & ÅGREN (1999), who defined the term “quality” as the chemical composition of the material and thereby how easily (i.e. in how many enzymatic steps) the organic material gets mineralized by the microbial biomass, the quality of SOM has been classified into labile, stabile and recalcitrant pools depending on their persistence and stability against decay at increasing temperatures (e.g. TRUMBORE ET AL., 1996, LOPEZ-CAPEL, ET AL., 2005, DAVIDSON & JENSSENS, 2006). Some studies found the labile pools (like e.g. unprotected soluble celluloses, hemicelluloses and microbial carbon) to be more sensitive to increasing temperatures (e.g. TRUMBORE ET AL., 1996). Others have concluded that the more stabile organic compounds (like e.g. lignin and aromatic compounds) are more sensitive, because of their inherent kinetics and demands for higher activation energies in order to decompose (e.g. KNORR ET AL., 2005, DAVIDSON & JANSSENS, 2006, HADDIX ET AL., 2010). However, studies also exist which show similar responses of stabile SOM fractions as labile pools to global warming by appropriate biotic and abiotic conditions (e.g. FANG ET AL., 2006, KLEBER, 2010). In their review LÜTZOW ET AL. (2006) found that "*the soil biotic community is able to disintegrate any OM of natural origin*" independently of quality characterisations. With varying conditions microbial communities shift according to changes of environment and/or food supply. Currently there is a general agreement that decomposition depends on ecosystem properties and that the actual environment is of primarily importance (SCHMIDT ET AL., 2011).

The complex nature of SOM, ranging from organic debris at different degrees of decomposition to individual organic molecules and humified macromolecules (all with different chemical and physical properties) leads to complex processes of decomposition and stabilisation.

Decomposition is the biotic and abiotic breakdown of dead plant, animal and microbial material through fragmentation, leaching and chemical degradation into CO_2 and inorganic nutrients (CHAPIN ET AL., 2002, p151) and is quantified by mass loss. At any step of decomposition CO_2 is released from microbial respiration and the ratio of carbon to nitrogen (C:N ratio) decreases. Already in 1979 SWIFT (In: CHAPIN ET AL., 2002, p159ff) listed three major factors that control decomposition and stabilization of organic compounds in the soil: physical environment (temperature, moisture, particle size distribution and soil structure), the quantity and quality of organic substrate available to decomposers and the characteristics of the microbial community. Berg & McClaugherty (2003, p13ff) divide the decomposition process into different stages and emphasize that at an early stage, when soluble, unprotected cellulose and hemicelluloses decomposes the process is highly influenced by climate and nutrient availability, whereas when proceeded by humification the progress is less dependent on abiotic factors.

KIRSCHBAUM (2006) sees the temperature dependence of SOM decomposition as the central link between climatic change and the global C cycle. It has been found that soil temperature is directly related to air temperature (ROUNSVELL ET AL., 1999) and that all biogeochemical reactions (e.g. plant growth, microbial activity) are regulated by temperature and water availability (SJÖGERSTEN ET AL., 2011, p119). At higher altitudes the inclination and thereby the exposition is of greater importance compared to sites in the lowlands (SCHEFFER & SCHACHTSCHABEL, 2008, p255). Under the extreme conditions at high altitudes the differences in relief and topography are decisive due to their effects on factors such as soil moisture and duration of snow cover. Less precipitation and reduced soil moisture decrease the activity of soil organisms and thereby limit SOM decomposition (CHAPIN ET AL., 2002, p159f, DAVIDSON & JANSSENS, 2006, GAVAZOV, 2010). The clay content of soil plays an important role through its stabilizing effect by adsorption. SOM can also be incorporated into soil aggregates (esp. micro aggregates) and may be protected against microbial decomposition by spatial inaccessibility (TRUMBORE ET AL., 1996).

In soil science one differs between the processes of mineralization and humification. At the end of the mineralization process components are released in their inorganic forms like CO_2, nitrate, phosphate and sulfate, while by humification different organic and inorganic compounds transform into new and more complex humic substances. Humic substances are part of SOM and can, at any level in the humification process, be subject to decomposition by mineralization or further humification.

CHAPIN ET AL. (2002, p169f)) listed five different steps which are considered to be important in the formation of humus (humic substances) (Figure 1):

1) Selective preservation: preferred decomposition of labile compounds in detritus, leaving behind partly decomposed stable compounds (e.g. waxes, suberin, chitin and microbial cell walls). These stable “leftovers” may transform into macromolecules with other organic and mineral compounds.
2) Microbial transformation: enzymatic breakdown of SOM produces water-soluble amino acids and sugars which can readily react with more stable compounds in humus formation (see 5)
3) Polyphenol formation: soluble phenolic compounds or polyphenols may also be important reactants, they derive either from microbial degradation of plant lignin or microbial synthesis of phenolic polymers or produced by the plants as defense mechanism or soluble phenolic compounds
4) Quinone formation: quinones are highly reactive polyphenolic compounds occurring as co-products by the polyphenol oxidation by fungi.
5) Abiotic condensation: where quinones spontaneously react with other soil compounds, preferentially amino groups but also recalcitrant compounds that accumulate in soils.

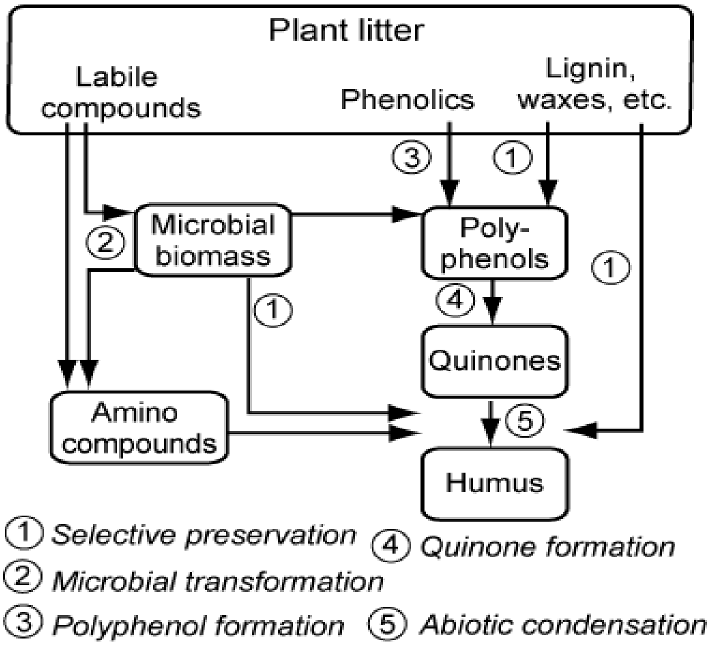


Figure 1: Principle pathways by the formation of humic substances. From CHAPIN ET AL., 2002

The effect of climatic changes on carbon fluxes continues to be discussed among scientists. It remains unclear whether the soil will act as a source or sink of carbon dioxide (CO_2) with increasing temperature. Depending on the response of decomposition rates and net primary production (NPP), one could expect either positive feedback from accelerated decay of SOM as temperature increases, or experience that higher CO_2 concentrations in the atmosphere at some point would make plants able to synthesise more organic biomass so that C gets sequestrated (KIRSCHBAUM, 2000, DAVIDSON & JANSSENS, 2006

The carbon cycle has a long equilibrium time and it is important to understand which parameters affect the C flows through agroecosystems in order to maintain soil productivity for the future (JANZEN, 2004).

3 Material and Methods

3.1 Study Area

The study sites are located in the Matcher-valley in the province of South Tyrol, Northern Italy. Following an altitudinal transect from approximately 1000 to 2050 meter above sea level (m asl), four study sites were selected (Figure 2). The three lower sites are located at the entrance of the valley at 986 m asl (B1), 1480 m asl (B2) and 1919 m asl (B3) and are south-west exposed, while the fourth site (KW) is found further into the valley and exposed at 2043 m asl in south-east direction.

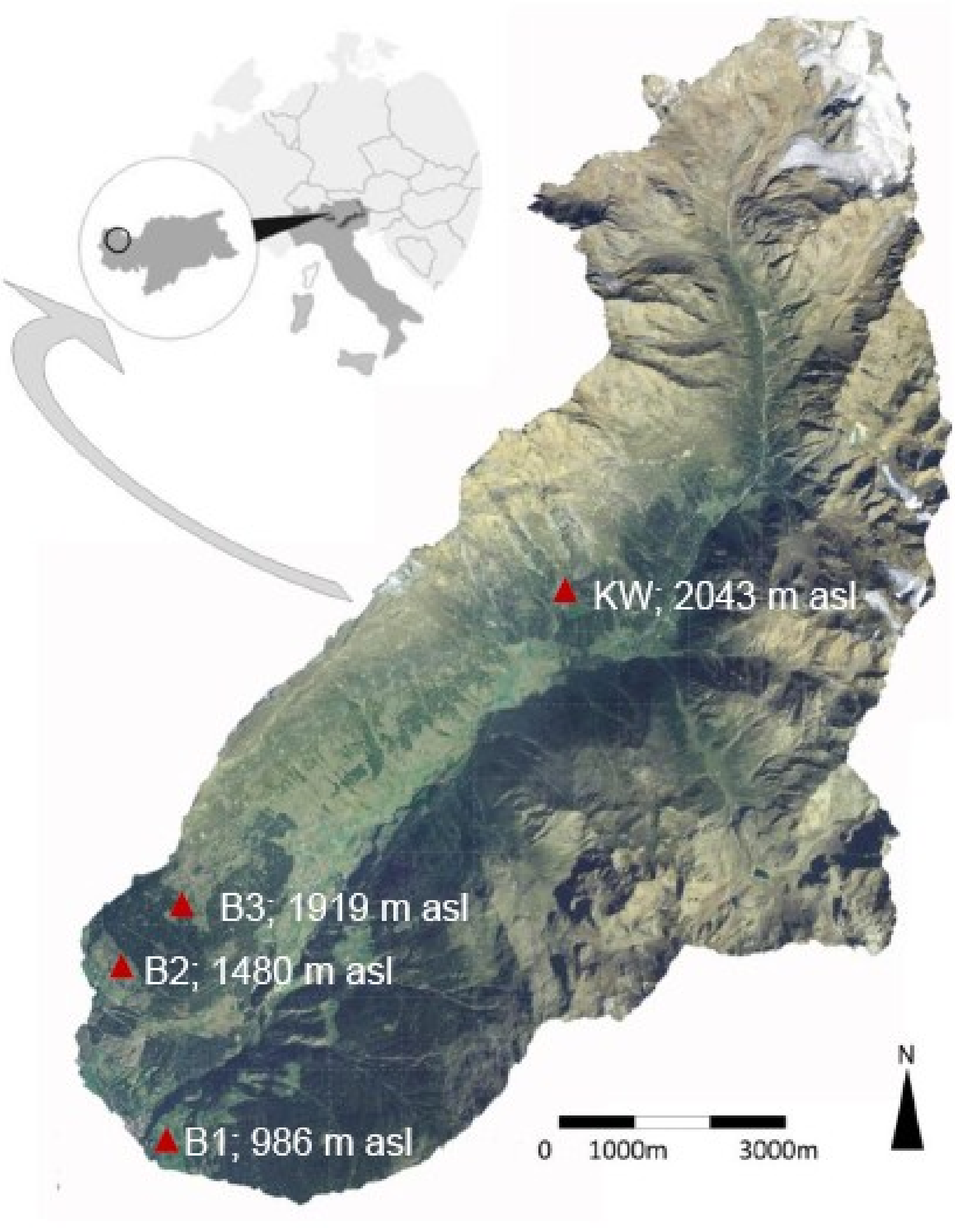


Figure 2: Map of the Matcher-valley with study sites marked with triangles. (Source; EURAC, Bolzano, 2010)

The mean annual temperature (MAT) decreases from 8.4°C to 2.7 °C whereas the mean annual precipitation (MAP) rises from 630 to 770 mm with increasing elevation. Due to a negative water balance during the vegetation period, the meadows at B1and B2 sites are irrigated (Table 1).

Table 1: Description of the study sites

Site	Altitude	Coordinates	Exposition	MAT	MAP	Land-use	Mowed	Fertilized
	m asl	WGS 84		°C	mm		times year^{-1}	
B1	986	46° 39' 66'' N 10° 35' 42'' E	SW	8.4	627 + 320a	meadow	3	2
B2	1480	46° 41' 17' N 10° 34' 79'' E	SSW	5.5	686 + 200a	meadow	2	2
B3	1919	46° 41' 48'' N 10° 35' 52'' E	SSW	2.7	772	pasture	0	1
KW	2043	46° 43' 66'' N 10° 40' 08'' E	SSO	n.g.	n.g.	meadow	1	1

MAT = mean annual temperature, MAP = mean annual precipitation, m asl = meter above sea level, WGS 84 = World Geodetic System 1984, a = additional irrigation, n.g. = data not given (Data from Demez, 2011).

The soils are classified as Cambisols (B1, B2) or leptic Cambisols (B3, KW; WBR 2006) developed on biotite mica schist. According to Hell (2010) bulk density is slightly decreasing along the elevation gradient from 1.2 g cm^{-1} at B1 to 0.9 g cm^{-1} at KW in the topsoil (0-10 cm), whereas the clay content ranges from 6.1 to 21.8 % between the sites, with the highest clay content found at B2. Texture is classified as loamy sand (lS) at B1, B3 and KW and sandy loam (sL) at B2. The soil profiles at sites B1 and B2 show disturbed layers caused by anthropogenic levelling for easier machine processing.

The study sites are all intensively used alpine grasslands (Table 1, Figure 3). Historical data indicate a long traditional use of the sites for hay production and pastures (Thanei, G., s.a.). The frequency of utilisation follow the duration of the vegetation period and decreases with increasing elevation, ranging from three to one grass cuts a year and of fertilisation twice to once a year, respectively (Table 1). Due to changes in climatic conditions and land-use, the grass communities and characteristic species differ between the sites along the selected altitude transect. For instance, the thermophile specie *Arrhenatherum elatius* at the lower-elevation site (B1) is replaced by *Trisetum flavescens* at the next higher site (B2). Both species are common in intensively used alpine meadows. In the pasture (B3) the plant community is rich in pasture-indicator- species such as *Nardus stricta* dominate, while in the meadow at the highest elevation site (KW) *Festuca rubra* and *Agrostis capillaries* are the predominant species. Furthermore, Demez (2011) found a pronounced higher amount of herbs (incl. legumes; more than 40%) at B1 and B2 compared to the intensively grazed site B3 (less than 5 % herbs incl. legumes) (for KW unfortunately no data available).

a) Site B1 (986 m asl; SW exposition) a meadow (3x mowed and 2x fertilized) with *Arrhenatherum elatius* - community.

b) Site B2 (1480 m asl; SSW exposition) a meadow (2x mowed, 2x fertilized) with *Trisetum flavensces*.

c) Site B3 (1919 m asl; SSW exposition) pasture (1x manure) with a typical *Siversio - Nardetum strictae community*. Experimental plots are located within the fence.

d) Site KW (2043 m asl; SE exposition) a *Festuco-Agrostietum* meadow (1x mowed and 1x fertilized).

Figure 3: Study sites (Photos: Lair, G., 2011).

3.2 *Soil Sampling and Soil Analyses*

At each study site, soil samples were collected in October 2010, from three pits approximately 15 to 20 m apart. The samples were taken at depth intervals of: 0-5, 5-10, 10-15, 15-25 and 25-40 cm. Subsequently, the soil was air dried, sieved to 2 mm and stored at room temperature until analyses.

Particle size distribution of fine earth (<2 mm) was gained by wet-sieving after soil dispersion with $Na_4P_2O_7$ and sedimentation of particles less than 40 µm. Bulk density was measured by taking undisturbed soil samples with cylinders of defined volume (HELL, 2012). The potential soil pH was determined with two replicates according to ÖNORM 1083 in a proportion of 1 part soil to 5 parts of 0.01M $CaCl_2$. The contents of organic carbon (OC) and total nitrogen (Nt) were measured by dry combustion at 1050°C using a Carlo-Erba Total Analyzer. Soil pH-value and the contents of OC and Nt content were measured by the soil survey staff at the Institute of Soil Research at the University of Natural Resources and Life Sciences (BOKU) in Vienna.

3.3 Characterization of SOM by Simultaneous Thermal Analysis

Data from thermal analysis of bulk soil are directly related to SOM composition (GRISI ET AL., 1997) and provides information of the biochemical stability of OC compounds (PLANTE ET AL., 2009). By this method, the mass loss as a function of temperature (Thermogravimetry, TG) as well as the endo– and exothermic heat flow from or to the bulk soil samples by the Differential Scanning Calorimetry (DSC) is measured. Measurements were performed at the Institute of Applied Geology at BOKU using Netzsch STA 409 PG/PC.

Prior to the measurements bulk soil < 2 mm was ground and homogenized in a mill (RETSCH MM 200; 25 s^{-1}; 4 minutes) and pre-calibrated at 65°C for moisture content. Approximately 50.00 mg of soil was weighed into the Pt-Rh sample carrier and heated from 25 to 600°C at a linear rate of 5°C min^{-1} under an air flow of 50 ml min^{-1}, with 15 ml min^{-1} N_2 as a protective gas. An identical and empty crucible was used for reference. The Netzsch software (Netzsch Proteus – Thermal Analysis, Version 4.1.2) was used for the analyses of the recorded TG and DSC signals.

According to DELL'ABATE ET AL. (2002) and PLANTE ET AL. (2011) the TG weight losses between 190 and 600°C are associated with the thermal decomposition of SOM (EXOtot) and can be divided into labile SOM (EXO1; 190 – 380°C), stable SOM (EXO2; 380 – 475°C) and more stable SOM (EXO3; 475 – 600°C). According to the review of PLANTE ET AL. (2009) EXO1 is ascribed as the decomposition of carbohydrates and aliphatic compounds, whereas EXO 2 is related to aromatic compounds like lignin and other polyphenols. EXO3 “includes polycondensed aromatic carbon” like black carbon (DE LA ROSA., 2008). The fractionation enabled comparison of the SOM pools at the sites and in the profiles.

3.4 Characterization of SOM by Chemical Fractionation and Fourier Transform Infrared Spectroscopy

Extracted humic acids (HA) are related to the dynamic and labile part of SOM (TATZBER ET AL. 2009, TATZBER ET AL., 2011) and respond within decades to climatic conditions and land use.

3.4.1 Extraction of Humic Acids and Standard Analyses

The extractions of the humic acids (HA) were done according to the method of TATZBER ET AL. (2007). 25 g of air-dried soil (sieved to <2 mm) was weighed into 250 ml bottles and filled up with 1M NaOH to the 200 ml mark. The samples were shaken on a horizontal shaker over night and centrifuged for 30 minutes at 24000 x *g* (Beckman 2J-HS with Fiberlite® F14 6x215 top) and the supernatant collected and stored cool (4°C). The extraction with 1M NaOH was repeated two times, with the centrifugation setting also for the next separation steps. In order to separate fulvic and humic acid fractions in the extract, 16 ml of 35% HCl was added and centrifuged for 20 minutes. The HAs were collected as precipitates and the fulvic acids (FA) remained in solution. To remove any clay minerals, the extracted HAs were dissolved by 20 ml of 1M NaOH, refilled with deionised water up to volume of 200 ml and centrifuged for 40 minutes (TATZBER ET AL., 2009). The solute HAs were refilled in new bottles and the samples were washed in 3 steps by gradually adding decreasing concentrations of NaOH and HCl and centrifuged for 20 minutes. The collected HAs were freeze-dried and stored in a desiccator until analyses.

In order to determine the mineral and salt compounds in the extracted HAs, between 20 and 40 mg of organic acids were burned in a muffle oven (Nabertherm) according to ÖNORM EN 13039, with one hour of heating up and six hours maintaining at 550°C. The yield, the OC and Nt contents of the extracted HAs were corrected by the ash content in all calculations. Ash content also provides an indication of how successful the extraction process has been. Any values below 5% indicate an excellently purified extract (TATZBER, 2012).

The amount (mass %) of OC and Nt in the HA's were determined by dry combustion in a Carlo Erba elemental analyzer 1500 according to ÖNORM L 1080.

A preliminary study performed during this research, where some selected soil-samples (5 – 10 cm depth) treated prior with 1 M NaOH for HAs extraction were additionally analysed by STA, showed a pronounced reduction of organic matter in the labile pool (EXO1). The relative proportion of EXO1 decreased from 73.1% to 56.2% of EXOtot (mean of all sites, 5 – 10cm). For EXO 2 there were relatively minor changes, whereas the EXO3 part increased proportional to the EXO1 (Table 6). This confirms that NaOH-extracts mainly contain HA from the labile SOM pool (EXO1) in our studied soils.

3.4.2 Fourier-Transform Infrared Spectroscopy (FT-IR)

Infrared spectroscopy is based on the interactions between infrared radiation and matter. By measuring transmitted and absorbed radiation, any vibrations caused by stretching and bending of molecular bonds can be detected. These vibrations are characteristic for particular functional groups and can be used for the identification of molecules (HESSE ET AL., 2005, p34). FT-IR bands located from 4000 cm^{-1} to 1500 cm^{-1} include vibrations that are typical for functional groups (e.g. aromatic groups at 3050 or aliphatic stretch at 2920 and 2850 cm^{-1}) within a molecule. The spectra below 1500 cm^{-1} is called the fingerprint region and involves vibrations of molecular bonds which are characteristic for the entire molecule or large parts of it. For many functional groups the spectra in the fingerprint region may be weak and overlapping and therefore harder to identify (HESSE ET AL., 2005, p42).

Freeze-dried HA (0.7 ±0.03 mg) were weighed in with 200 mg KBr (FT-IR grade) in an agate capsid and mixed for 30 seconds in a swing mill (Pirker Elmer S10 Vibration Mill). The mixture was filled into an evacuable die and pellets were prepared using a hydraulic press at 12 bar. The FT-IR spectra of the pellets were immediately recorded in the BRUKER TENSOR 27 FT-IR spectrometer in the mid-infrared area from 400 – 4000 cm^{-1}, with 64 scans per sample and a resolution of 4 cm^{-1}. The measurements were corrected against 201 mg pure KBr-pellets with ambient air as background.

The band evaluations for all samples followed after a base line correction. Start and end points of the 18 different bands were the same for all samples (Table 2). Calculated peak areas were normalized to the OC content of the extracted HAs, and the results were given in absorbance per wavenumber unit, [A cm^{-1} (mg OC)$^{-1}$].

Table 2: Assignments of mid-infrared bands in the humic acids (according to TATZBER ET AL., 2007)

Location (cm^{-1})	Basepoints of the integrated bands (cm^{-1})	Assignment
3050	3105 - 3025	Aromatic groups
2920	2990 - 2883	Aliphatic stretch
2850	2860 - 2828	Aliphatic stretch
1700	1767 - 1703	Carbonyl vibrations of carboxylgroups, partly also carbonylgroups of esters
1650	1685 - 1575	C=O of amide, contributions of nitrates and nitrites
1550	1553 - 1529	COO- , -C-NO_2 and C=C
1500	1529 - 1494	N-bounds of amide and C=C
1450	1472 - 1443	Aliphatic C-H
1420	1432 - 1403	C=N of primary amide, contribution also possible from groups like COO^-
1360	1381 - 1357	-CO-CH3 and vibrations of nitrate
1315	1346 - 1311	Sulfone groups
1270	1298 - 1252	Nitrate, also possible =C-O-C groups, P=O-vibration and P-O of phenolic groups
1210	1240 - 1191	C-O and OH of COOH, C-O of aryl ethers and phenols, also P-O bounds and tertiary alcohols possible
1120	1138 - 1110	C-OH of aliphatic OH-groups, sulfones
1075	1097 - 1065	C-O of alcohols and C-O of aliphatic ethers
1020	1053 - 945	C-O of polysaccharide and influence of Si-O from silicates
900	926 - 903	$R_2C=CH_2$ groups
794	849 - 799	Benzene rings, R_2C=CRH groups, and nitrates

3.5 Statistical Analysis

The data were calculated as arithmetic means of 3 replicates with a standard derivation and significant differences tested by one-way analysis of variance (ANOVA). The Duncan's test was used for comparison of means at a significance level of $p= 0.05$.

Correlations between variables were calculated with the Spearman correlation coefficient. Significance was assumed at $p < 0.05$ (*) and $p < 0.01$ (**).

For testing any potential of differentiation between the sites, two standardized canonical discriminant functions based on the evaluated FT-IR bands (Table 2) were calculated. The use of Wilks' Lambda enabled the stepwise selection of variables in order to assess the dominating molecular functional groups behind the separation.

These statistical analyses were performed using SPSS V. 15.0.1 (SPSS Inc, Chicago, 2006). Diagrams were drawn by SigmaPlot Version 11.0 (Systat Software Inc, Germany, 2008).

Linear regression and the coefficient of determination were preformed in Excel (Microsoft Office, 2007).

4 Results and Discussion

4.1 Soil Properties

4.1.1 Bulk Soil Analysis

Table 3: Soil properties of bulk soil and humic acids (HA). Numbers are given as mean values with standard derivation in parentheses (n=3).

Site	**Depth**	**pH**	**OC**	**C : N**	**OC**	**HA**	**HA**
m asl	cm	$CaCl_2$	%		kg m^{-2}	OC %	Nt %
B1	0 – 5	6.1 (0.1)	4.5 (0.1)	12.4 (0.4)	2.7 (0.07)	52.7 (0.05)	5.27 (0.03)
986	5 – 10	5.8 (0.1)	3.4 (0.2)	12.6 (0.3)	2.1 (0.13)	51.1 (0.01)	5.11 (0.01)
	10 – 15	5.9 (0.1)	2.9 (0.2)	13.2 (1.5)	1.8 (0.15)	52.4 (0.03)	5.38 (0.03)
	15 – 25	6.0 (0.1)	2.2 (0.2)	12.0 (0.3)	3.1 (0.29)	53.1 (0.05)	5.61 (0.01)
	25 – 40	6.2 (0.2)	1.7 (0.1)	12.7 (1.4)	3.6 (0.15)	51.4 (0.03)	5.92 (0.01)
B2	0 – 5	5.4 (0.3)	9.8 (0.8)	11.4 (0.2)	4.5 (0.37)	53.4 (0.05)	5.17 (0.02)
1480	5 – 10	5.0 (0.3)	5.8 (0.8)	11.8 (0.7)	2.7 (0.35)	52.8 (0.02)	5.46 (0.03)
	10 – 15	5.0 (0.2)	4.5 (1.0)	11.9 (0.7)	2.1 (0.48)	48.9 (0.07)	5.38 (0.02)
	15 – 25	5.1 (0.1)	4.8 (2.7)	12.1 (1.9)	6.1 (3.49)	52.0 (0.02)	5.67 (0.02)
	25 – 40	5.2 (0.1)	3.8 (1.6)	12.5 (0.8)	7.4 (2.98)	51.6 (0.02)	5.60 (0.03)
B3	0 – 5	4.3 (0.2)	11.9 (2.2)	12.7 (0.3)	5.2 (0.97)	49.9 (0.00)	5.04 (0.03)
1919	5 – 10	4.0 (0.1)	7.2 (0.8)	12.7 (0.5)	3.2 (0.34)	53.7 (0.06)	5.27 (0.03)
	10 – 15	4.1 (0.0)	6.0 (0.7)	13.5 (0.6)	2.6 (0.30)	52.7 (0.04)	5.31 (0.03)
	15 – 25	4.3 (0.1)	4.5 (0.5)	14.4 (0.6)	5.4 (0.59)	53.7 (0.02)	5.08 (0.03)
	25 – 40	4.4 (0.2)	2.7 (0.2)	16.2 (1.6)	4.9 (0.43)	54.2 (0.05)	4.99 (0.03)
KW	0 – 5	4.3 (0.2)	12.7 (2.4)	11.7 (0.6)	5.5 (1.06)	54.0 (0.05)	5.26 (0.02)
2043	5 – 10	3.9 (0.1)	6.4 (1.5)	13.5 (1.6)	2.8 (0.64)	55.0 (0.00)	5.04 (0.03)
	10 – 15	4.0 (0.1)	3.2 (0.6)	16.4 (1.3)	1.4 (0.27)	54.8 (0.05)	4.72 (0.00)
	15 – 25	4.2 (0.1)	2.2 (0.1)	18.6 (1.1)	2.6 (0.10)	57.7 (0.06)	4.24 (0.03)
	25 – 40	4.3 (0.1)	1.8 (0.2)	21.6 (2.3)	2.6 (0.10)	57.5 (0.05)	3.63 (0.00)

The studied soils are generally acidic. Along the elevation gradient the pH value significantly decreased from 6.0 to 4.1 (mean; 0 – 40 cm) with the highest values at B1 and the lowest values at KW (Table 3). At all sites the pH values are influenced by the intermediate rock as parent material as well as prevailing climatic conditions. Lower MAT and higher precipitation (especially at the high elevation sites (B3 and KW)) slows down decomposition and force the leaching of fulvic acids complexed with leachable basic cations in the soil. Further the accumulation of organic acids with altitude lowers soil pH value (BRADY & WEIL, 2008, p359f).

Within the profiles, soil pH decreased from bottom up to 5 cm depth and was highest in the topsoil 0 – 5 cm (Table 3). The regular application of farmyard manure, which ensures an input of basic cations and anions, seems to have a strong influence on the pH value in the top soil layers. This is in accordance with GERZABEK ET AL. (1997) in a long-term fertilization field experiment in Sweden. A bottom-up decline of the soil pH is reflecting acidification by root respiration and root exudates, as well as the acidifying effect of the OM and leaching of basic ions. The slightly higher values at the bottom of the profiles probably arise from the buffering of bedrock.

For optimal plant growth, favourable pH values in grassland soils ranges from 5 to 6.5 (BUCHGRABER & GINDL, 2009, p26) meaning that our high-elevation sites (i.e. B3, KW), with pH values below 5, exhibit a lower bioavailability of anions and basic cations as nutrients for plant growth. Lower pH values also decelerate SOM decomposition and mineralisation and usually cause a lower degree of humification (DJUKIC ET AL., 2010).

Along the elevation gradient the OC concentration increased from 4.5 to 12.7% in 0 – 5 cm topsoil (Table 3). Among the studied sites with similar exposition (B1 to B3) the mean concentration of OC down to 40 cm soil depth more than doubled. Our findings are in accordance with other studies where it has been reported that shorter vegetation periods (i.e. lower mean temperatures) limit the turnover of organic material, resulting in accumulation of SOC along elevation gradients (TRUMBORE ET AL., 1996, SJÖGERSTEN ET AL., 2011, p119).

Within the profile the OC was concentrated in the uppermost layers and decreased continuously with the depth at all sites (Table 3). In the soil profile OC gets translocated by bio- and cryoturbation and by leaching of dissolved OC through coarse pores. Root architecture also affects the vertical OC distribution in the soil. The direct inputs by the plants, like root residues and root exudates, represent a large proportion of SOC (JOBBÁGY & JACKSON, 2000, RASSE ET AL., 2005, ERICH ET AL., 2012) and explain the highest concentration of OC in the main rooting zone in grasslands (0 – 10 cm; KÖRNER, 2003, p150). Furthermore, annual application of farmyard manure enriches also SOM amounts in the topsoil of our study sites.

The C:N ratio in all studied soil layers ranged from ~ 11 to 22, with a narrow mean value of 13.7 (±2.6) (Table 3), which is consistent with the values for grasslands (ranging from 6 to 15) mentioned in SCHEFFER & SCHACHTSCHABEL (2008, p306). This indicates a fast mineralisation or transformation of the organic matter by microbial activity in grassland soils. There were no significant differences of C:N between the studied sites in the upper soil layers (0 – 15 cm), whereas the samples from the subsoil at the higher altitude (B3, 25 – 40 cm and KW, 15 – 40 cm) showed a significantly wider ratio ($p < 0.01$) (Table 3) reflecting a lower microbial activity with the soil depth. Along the elevation gradient, the different grass communities at the four study sites (Figure 3) show differences in the root biomass and architecture which may also explain part of the differences between the sites. For instance, the main grass *Nardus stricta* in the B3 pasture is known to have quite deep ligneous roots. On the other hand, the *Festuca rubra* in the KW-meadow is characterised by a lot of thin roots mainly in the topsoil (KARRER, 2011). According to JOBBÀGY & JACKSON (2000) the wider C:N ratio in the subsoil at KW could be an imprint of previous more lignin-rich vegetation, since OM in the subsoil can “*persist for centuries or millennia*” (ibid). In addition it must be considered that the turnover of OM in the subsoil, caused by unfavourable climatic conditions (e.g. low temperatures), is even slower than in the upper layers (ibid).

In our study we experienced an increase in the OC stocks (0 – 15 cm) along the elevation gradient from 6.6 to 11.1 kg m^{-2} (MAT 8.4 – 2.7 °C); MAP 627 – 772 mm) with highest amount at B3 (Table 3). This was lower than found by GARCIA-PAUSAS ET AL. (2007) under high altitude grasslands in the Pyrenees (~6 to 30 kg m^{-2}; to bedrock; MAT -0.7 to 5.0°C; MAP 1400 – 1900 mm), but higher than stated by LEIFELD ET AL. (2009) in a comparable study in the Swiss Apls (~ 7 to 8 kg m^{-2}; 0-15 cm depths; MAT 0.9 to 8.9°C; MAP 880 – 1230 mm). The Pyrenees are influenced by the Atlantic and experience a higher MAP than the inneralpine Matcher-valley. This enables an increase of biomass growth during the short vegetation period. It is known that decomposition rates change faster than biomass growth with decreasing temperatures and thereby cause OC to accumulate (LÜTZOW & KÖGEL-KNABER, 2009). The meadows in the Swiss Alps experienced similar land-use and climatic conditions as our sites. We explain the higher OC accumulation at our study sites by the exposition. The studied sites in the Swiss Alps were exposed to W / NW (ZIMMERMANN, 2012) and thereby experience slightly better conditions for decomposition due to higher soil moisture compared to the dry soil conditions of the SW exposed sites in the Matcher-valley.

A clear relationship between the amount of SOC (kg m^{-2}) and the elevation gradient at the studied sites with similar exposition and slope (B1, B2, B3) is presented in Figure 4a. Along the studied elevation gradient the content of SOC in the upper 0 – 15 cm soil depth increased by 0.48 kg m^{-2} per 100 m altitude (Figure 4a). This is a more severe incline than the mid-European average calculated by SJÖGERSTEN ET AL. (2011, p121ff), with 0.31 kg m^{-2} per 100 m altitude. Consequently the SOM stocks in the study area are expected to respond sensitively to changes in temperature, moisture, land-use and farming practices

The same clear correlation is seen in Figure 4b, when the mean annual temperature (MAT) and mean annual water-supply (MAW = MAP + irrigation) at the production sites are considered. The amount of OC rose with decreasing MAT (R^2=0.997) and decreasing MAW (R^2=0.919), reflecting low SOM decomposition at high elevation sites due to short vegetation periods.

.

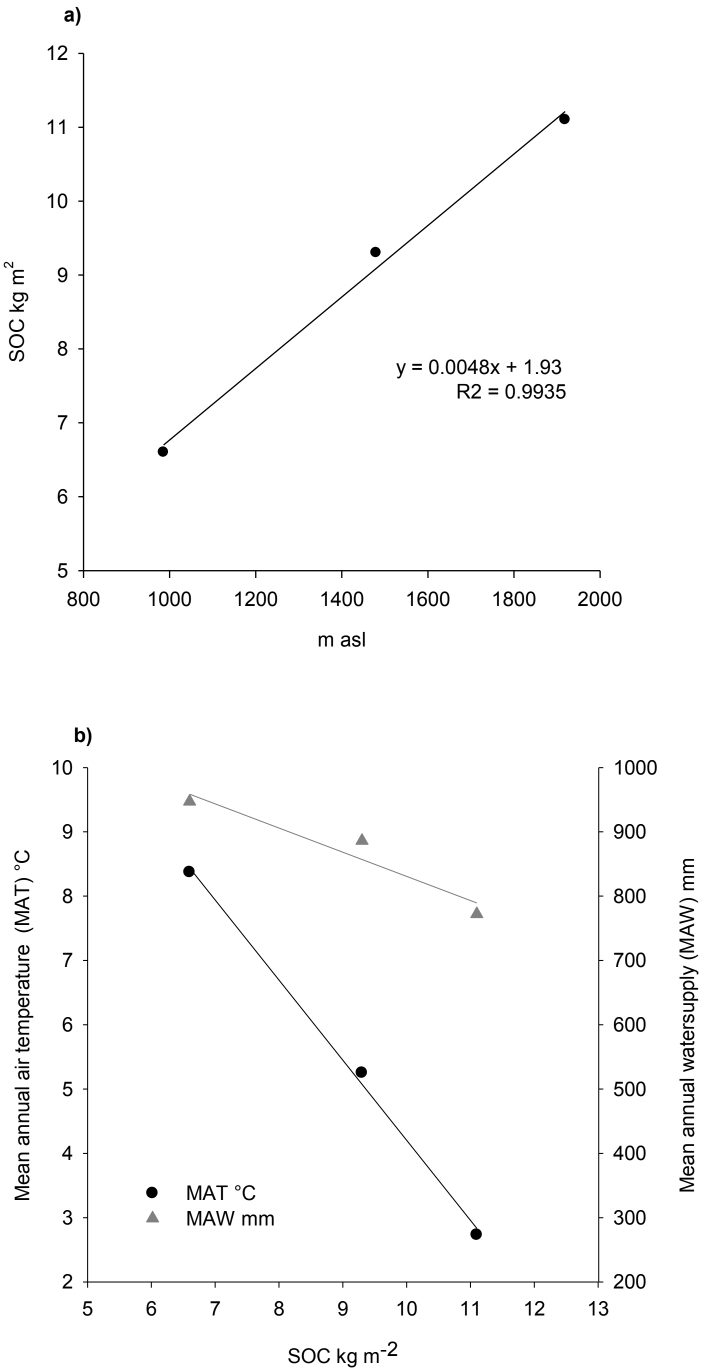


Figure 4: Correlation between SOC stocks (kg m^{-2} in 0-15 cm) and the elevation gradient (986 – 1919 m asl; a) and mean annual air temperature (MAT, °C) as well as mean annual water-supply (MAW) (b)

According to modelled data, the central parts of the alpine regions will experience an increasing MAT with dry summers, mild winters and precipitation mostly as rain (ZEBISCH ET AL., s.a.). In the modelled future the climatic conditions at B2 could be similar to current B1 and B3 similar to current B2. This will enable an increase of production level due to longer vegetation periods.

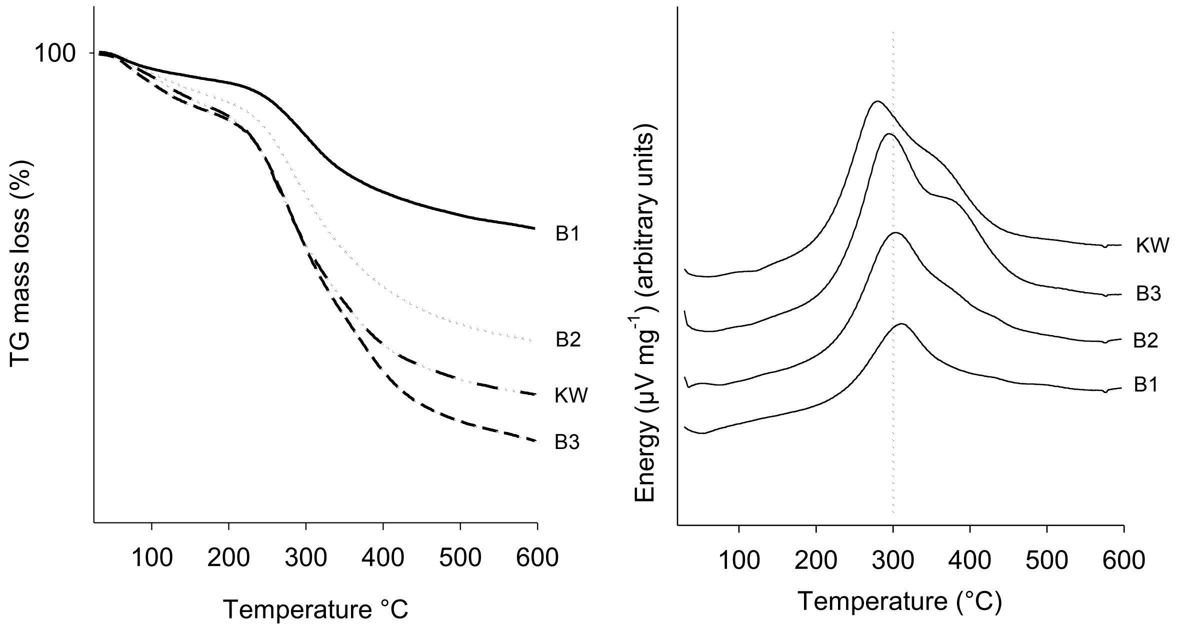
From our data we can roughly estimate a loss of 2.4 kg OC m^{-2} (0 – 15 cm soil depth) at B2 and B3 respectively when the mean annual temperature would rise by 3°C with unchanged precipitation (+ irrigation) values. Potential SOC losses by respiration during mineralisation could be compensated by soil formation at higher altitudes. In glacier forefield, where soils are in an early stage of soil development, SOC accumulation is estimated between 3 and 11 g m^{-2} a^{-1} (MAT 0 – 5 °C; MAP 2400mm) (DÜMIG ET AL, 2011). In the Marchfield, (Eastern Austria), characterised by only 550 mm precipitation and an average MAT of 9°C, mean SOC accumulation rate within the first 120 years is estimated in topsoil between 15 and 20 g m^{-2} a^{-1} leading to the formation of chernozem (compare ZEHETNER ET AL., 2009). If in our dry study area 15 g OC m^{-2} could be stored per year it would take at least 160 years to store the released carbon from the lower site B3 in mineral soil at higher elevations, where soil starts to form.

4.1.2 Organic Carbon and Total Nitrogen in Humic Acids

Amount of extracted HAs (Appendix; Table 7) correlated positive with the content of OC of the bulk soil ($r = 0.695$, $p < 0.01$, $n = 60$). The concentration of OC and total nitrogen of the HAs did not alter significantly among the soil samples (Table 3). The concentration of OC ranged from ~ 49 to 58% and the proportion of total nitrogen ranged from ~ 3.6 to 5.9% (mean = 5.4%; all sites; 0 – 40cm). These values are in consistence with previous studies (e.g. TATZBER ET AL., 2009, TATZBER ET AL, 2011). High content of N in the HAs is an indicator of proceeded humification, as for instance N – compounds react readily with quinone to form more complex aromatic ring structures (CHAPIN ET AL., 2002, p166).

4.2 Characterization of Soil Organic Carbon Pools

4.2.1 Simultaneous Thermal Analysis of Bulk Soil



a) Mass loss of the samples as a function of temperature along the studied elevation gradient (5 – 10 cm).

b) Differential scanning calorimetry (DSC) showing the endo- and exothermic heat flow in the samples along the studied elevation gradient (5 – 10 cm).

Figure 5: Thermograms and DSC diagram from the soil depth of 5 – 10 cm as an example for all soil layers.

The resulting thermograms (Figure 5a) from the STA measurements show a rapid mass loss associated with a strong exothermic reaction between 190 and 380°C (EXO1) and a more gradual weight loss for the organic pools oxidised at temperatures above 380°C (EXO2 & EXO3). The high proportion of labile compounds (EXO1) at all sites reflects a constant input of fresh organic matter through litter and farmyard manure. This has also been found at other grasslands sites (LOPEZ-CAPEL ET AL., 2005). In a long term fertilisation study in Switzerland, LEIFELD ET AL. (2006) found a significantly higher concentration of labile organic compounds under plots fertilized with manure, compared to treatments with limited or no fertilization.

The exo- and endothermic heat flows recorded by the DSC (Figure 5b) showed a small endothermic peak in all samples between 100 – 190°C due to hydration, followed by a strong exothermic reaction resulting from thermal decomposition and combustion of SOM. These findings, with one main exothermic peak, are similar to the results from other thermal analyses of bulk soils under grassland (GRISI ET AL.,1997, LOPEZ-CAPEL ET AL., 2005, PLANTE ET AL., 2011), where the one major peak often is overlapping and masking any subsequent peaks which might follow at higher temperatures (ANTISARI ET AL., 2010).

Table 4: Thermogravimethric mass losses (%) of the exothermic peaks at 190 – 600 °C (EXOtot), 190 – 380 °C (EXO1), 380 – 475 °C (EXO2), 475 – 600 °C (EXO3), as well as differential scanning caloriemetry (DSC) temperature (°C) of exothermic peak of soil from the depth layers along the elevation gradient.

Site m asl	Depth cm	EXOtot g kg^{-1}	EXO1 %	EXO2 %	EXO3 %	DSC peak °C
B1	0 – 5	93.1	70.7	18.0	11.4	314
986	5 – 10	63.0	71.0	17.3	11.7	312
	10 – 15	53.3	70.9	16.7	12.4	311
	15 – 25	52.3	66.2	17.8	15.9	310
	25 – 40	43.2	63.9	18.5	17.6	313
B2	0 – 5	187.5	72.5	19.0	8.5	310
1480	5 – 10	105.2	72.2	17.8	10.0	305
	10 – 15	93.3	70.5	18.3	11.1	301
	15 – 25	97.9	70.3	18.4	11.3	298
	25 – 40	58.2	66.0	20.1	14.1	297
B3	0 – 5	226.2	73.1	20.3	6.6	305
1919	5 – 10	142.2	72.0	19.6	8.4	296
	10 – 15	117.9	70.8	19.7	9.5	297
	15 – 25	95.5	68.5	20.7	10.8	298
	25 – 40	61.9	63.5	21.5	15.0	308
KW	0 – 5	245.0	77.1	17.4	5.4	291
2043	5 – 10	123.4	77.1	15.3	7.5	280
	10 – 15	74.0	73.1	17.6	9.5	279
	15 – 25	58.5	67.9	20.5	11.8	289
	25 – 40	49.4	64.0	23.7	12.1	297 and 422

The content of SOM (EXOtot; 190 – 600°C) increased from 93.1 to 245.0 g kg^{-1} in 0 – 5 cm topsoil along the elevating gradient, with the highest concentration at the high-elevation site (KW; Table 4). A significant difference in the amount of SOM (EXOtot) was found between all sites and within the soil profiles for all different depths ($p<0.001$). This correlated highly to the concentration of soil OC ($r = 0.917$, $p < 0.01$, $n = 60$) and Nt ($r = 0.882$, $p < 0.01$, $n = 60$). According to PLANTE ET AL. (2011) these high correlation values show, that any reactions of mineral compounds during the measurements (e.g. dehydroxylation of clay minerals around 500°C or α-β inversion of quartz at ~575°C) only played a minor role in the thermal analysis of our samples, and that the method thereby is a simple tool to characterise SOM in bulk soil.

The relative values of labile organic compounds EXO1 ranging from rates of ~ 63 to 77%, showed a dominance of labile organic components in all studied soils.

Within the soil profiles, EXO1 portion in the two top soil layers was significantly higher ($p<0.01$; Table 4) and correlated highly negatively with depth ($r = -0.802$, $p < 0.01$, $n = 60$). The more stable SOM, degrading from 475 – 600°C (EXO3), increased inversely to the portion of EXO1 within the soil profiles. This reflects an increasing humification with soil depth. The stable SOM pool (EXO2), consisting of organic compounds decomposing at 380 – 475°C (e.g. lignin) showed an increasing but not significant trend from 5 – 40 cm soil depth, underlying the trend to a higher degree of humification with soil depth. The top 0 – 5 cm in all soils appeared to be influenced mainly by manure and management practices, as enriched by the higher portions of EXO2 as the underlying layers (Table 4). This is especially pronounced in the pasture B3. B3, besides having an annual application of farmyard manure, also contains the more lignin-rich *Nardus Stricta* vegetation community which influences the composition of SOM at the studied site.

The mean exothermic peak temperatures (0 – 40 cm) clearly decrease from the sites at B1 and B2 to the high-elevation sites B3 and KW (Table 3; also shown in Figure 5b). A lower DSC peak in the sample can be explained by higher disproportion between free SOM and the mineral soil matrix. Insufficient free mineral surface for the interaction and stabilization of the organic compounds result in a lower thermal stability of the SOM (GERZABEK ET AL., 2006). Also, BALDOCK & SKJEMSTAD (2000) concluded that after the saturation of the protective mineral surface, excessive OM will remain readily available for decomposition.

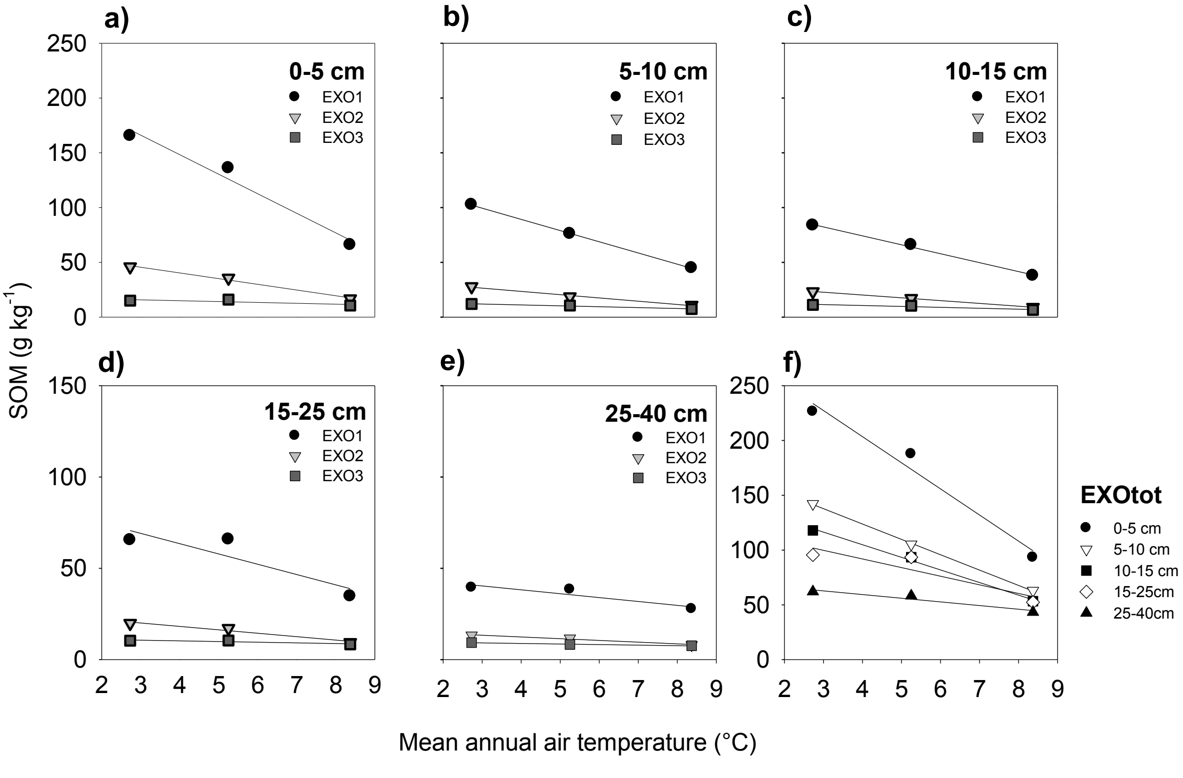


Figure 6: Amount of SOM (g kg^{-1}) in EXO1 (190 – 380°C), EXO2 (380 – 475°C) and EXO3 (475 – 600°C) as well as in EXOtot along the elevation gradient (986 to 1919 m asl) in the studied depths (0-40cm). Note different scaling of SOM in the figures.

Figure 7 shows the decline of SOM (g kg^{-1}) plotted against the MAT at the studied sites B1, B2 and B3. Figures 7 a) to e) show the SOM content divided into the three pools EXO1, EXO2 and EXO3 in the various soils. We can see that the labile pools (EXO1) decline strongly with increasing MAT, the stable organic compounds (EXO2) respond less, and the more stable ones (EXO3) only differ marginally between the sites along the climatic gradient. Similar trends were observed in all soil depths layers.

The highest SOM amount (EXOtot) was observed in the upper layer (0 – 5 cm) and decreased within the profile (Figure 7 f).

EXOtot is strongly correlated to OC contents as previous described, thereby trends similar to those presented in Figure 7 could also be found when the MAW is used instead of MAT. This demonstrates that both climatic parameters, temperature and moisture (precipitation + irrigation) (compare Figure 4b), are equally main factors for SOM accumulation and storage.

We have seen that the labile SOM compounds accumulate to a greater extent at higher altitudes (i.e. B3 and KW around 2000 m asl), than the more stable organic compounds. For each 1°C decrease of MAT, the EXO1 increased from B1 to B3 (altitudinal difference approximately 1000 m), by 65.2 g kg^{-1}, whereas EXO2 increased by 17.8 g kg^{-1} and EXO3 by 7.3 g kg^{-1}. These findings underline the importance of the labile SOM pool (EXO1) in grasslands at higher altitudes.

4.3 Analysis by Fourier Transform Infrared Spectroscopy on Humic Acids

4.3.1 Alternation of the Functional Groups along the Elevation Gradient

A discriminate analysis of the 18 FT-IR bands (n=3; Table 2) of the extracted HAs from the various soil depth layers showed a clear division between the sites (Figure 7). Function one (explaining 83.9% of variance) was dominated by the peaks at 1270 > 2850 > 1210 and 3050 cm^{-1}.

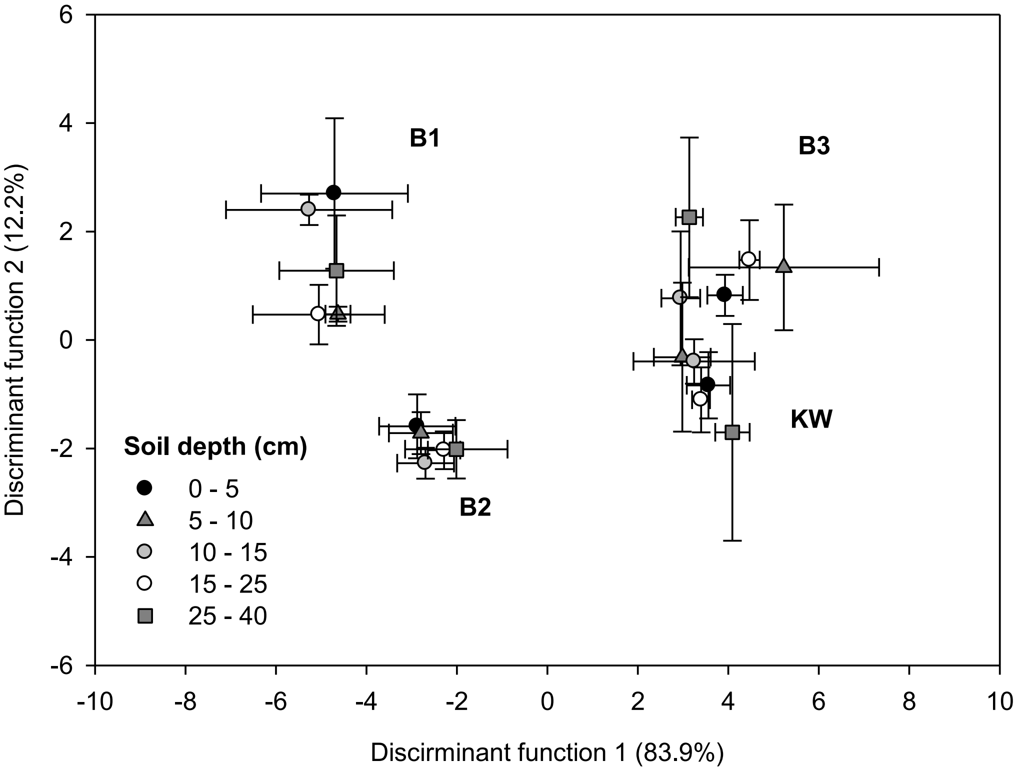


Figure 7: First two discriminate functions calculated from 20 FT-IR bands along the studied elevation gradient (986 - 2043 m asl) and soil profile (0 – 40 cm). Symbols are arithmetic means (n=3) and error bars indicate ± standard deviation.

The discriminant function 1 correlated highly negatively with soil pH ($r = -0.820$, $p < 0.01$, $n = 60$) and positively with C:N ratio ($r = 0.497$, $p < 0.01$, $n = 60$), and may as such be interpreted as parameters of the decomposition conditions. The sites with higher MAT, higher pH and lower C:N ratio (sites B1, B2; Table 3) are found on the left-hand side in the diagram of Figure 7 (negative DF 1), while the sites with lower MAT, lower pH and higher C:N ratio (sites B3, KW; Table 3) are found on the right-hand (positive DF1). Function 2 explained 12.2 % of the variance and was dominated by the peaks at 1420 > 1210 > 1270 and 3050 cm^{-1}, however, no correlation could be noted with the presented data. Possibly correlations exist with other site characteristics e.g. nutrient availability, clay fraction, or data from actual soil moisture in the studied soils.

In all studied soil layers the FT-IR spectra showed a similar number of absorption bands. In Figure 8 the spectra for soil layers 5 – 10 cm are presented as an example. Several of the absorptions bands showed marked changes with elevation of the site (Figure 9).

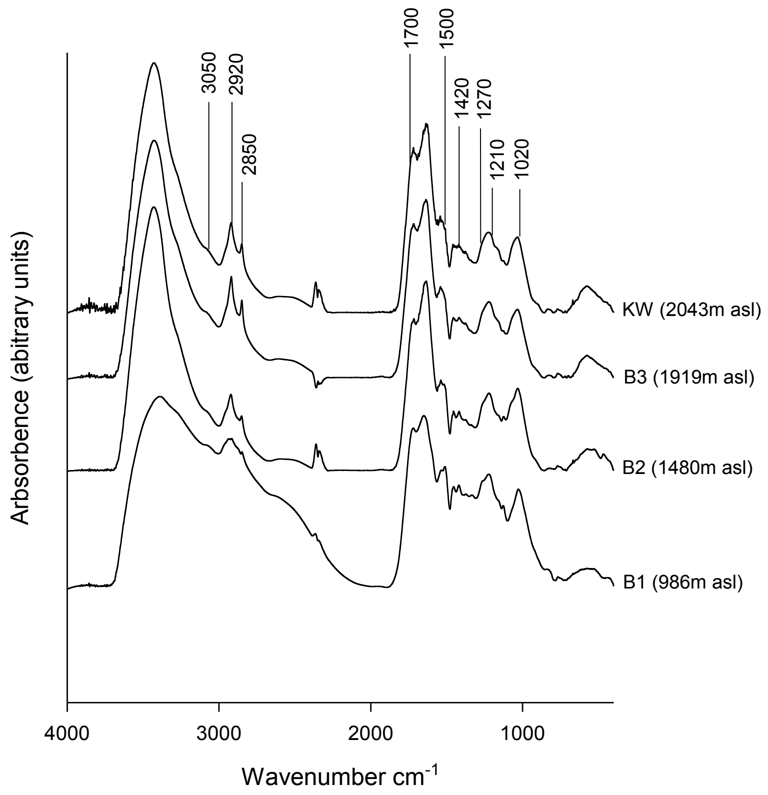


Figure 8: Fourier-Transform Infrared Spectroscopy (FT-IR) from a selected soil layer (5-10 cm) along the elevation gradient. Some of the 18 evaluated bands (Table 2) are labelled to give an orientation.

The aliphatic stretch at 2850 cm^{-1} increased along the elevation gradient (Figure 9). In our study the band at 2850 cm^{-1} correlated negatively with pH values ($r = -0.420$, $p < 0.01$, $n = 60$), indicating inhibited decomposition conditions and hence higher amount of aliphatic bands at the sites with lower pH values. Increased intensity of aliphatic bands has also been found at sites with limited decomposition along a climosequence under native vegetation in the Limestone Alps (DJUKIC ET AL., 2010).

Observed differences between the two high-elevation sites B3 and KW could be mainly attributed to the different management (pasture vs. meadow) and consequently changed vegetation composition at the sites. The meadow (KW; *Festuco-Agrostietum*) showed a lower amount of aliphatic bands compared to the pasture (B3; *Siversio-Nardetum strictae*). The exposition (B3 SSW; KW SSO) and the moisture regime at the sites (data not available) could have influenced the HA composition.

Furthermore a positive correlation was found between the band at 2850 cm^{-1} and the OC contents of the bulk soil ($r = 0.531$, $p < 0.01$, $n = 60$), as well as with EXOtot ($r = 0.567$, $p <$

0.01, n = 60) from the STA analysis. This shows that sites with higher OC and SOM contain more aliphatic functional groups.

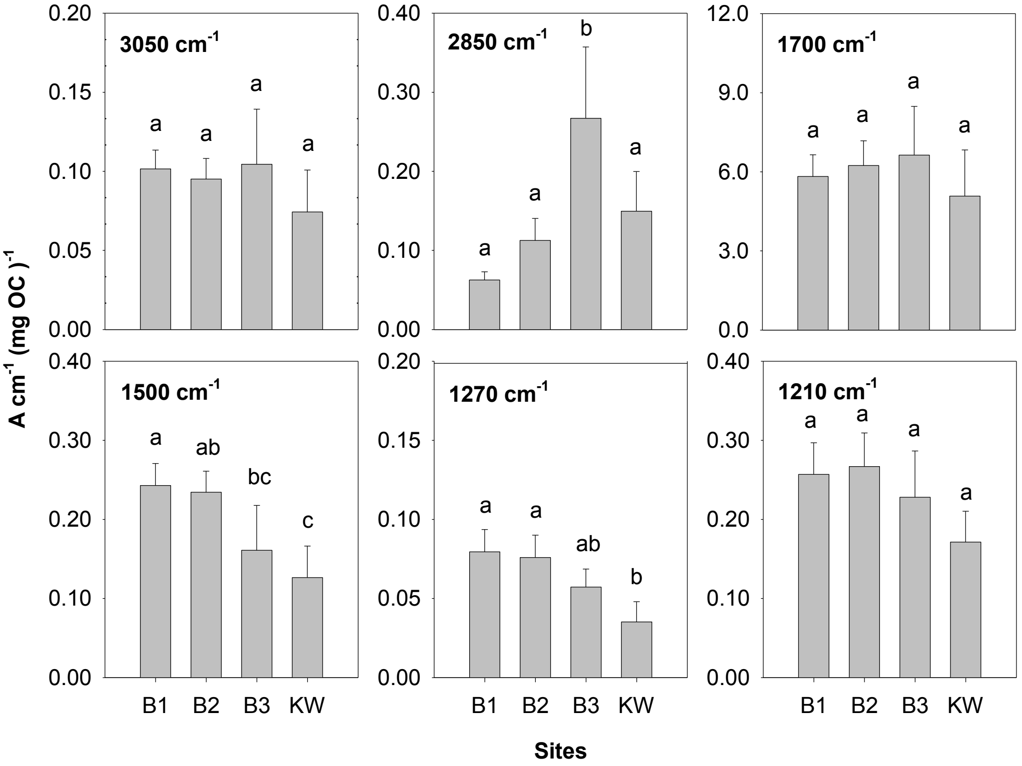


Figure 9: Areas of selected FTIR bands (means and standard deviation) along the studied elevation gradient (5 - 10 cm soil depth). Different letters indicate significant differences ($p < 0.05$; n = 3 field replicates: ANOVA, Duncan's test). A= absorbance, OC = organic carbon. B1 = 986m asl, B2 = 1480m asl, B3 =1919m asl and KW = 2043m asl. Assignments for evaluated bands are shown in Table 2. Note different scaling in the figures.

FTIR bands at 1500 and 1270 cm^{-1} related to N compounds were significantly more present at the lower elevation sites. The amount of these N-related bands correlated positively with pH-value (1500 cm^{-1}; r= 0.654, $p < 0.01$, n = 60 and 1270 cm^{-1}; r= 0.525, $p < 0.01$, n = 60) and negatively with the C:N ratio (1500 cm^{-1}; r= -0.638, $p < 0.01$, n = 60 and 1270 cm^{-1}; r= -0.591, $p < 0.01$, n = 60) of the bulk soil, implying that at the lower elevation sites (B1, B2) with good decomposition conditions (i.e. higher pH value, more narrow C:N ratio), the compounds giving rise to these FTIR bands is increased. This is in accordance with observations reporting an increase of N during the decomposition process (e.g. BERG & MCCLAUGHERTY, 2003, p14ff).

Since we observed an altitudinal trend for the aliphatic and N-related FTIR groups among sites, differences along the elevation gradient for the more stable aromatic and carboxylic groups (3050 and 1700 cm^{-1}, respectively) which accumulate during later stages of decomposition would also be expected. However, no significant trend was observed for these bands (Figure 9).

The FT-IR band at 1210 cm^{-1} showed no trend (n.s.) along the elevation gradient.

4.3.2 Alteration of Functional Groups in the Soil Profile

The FT-IR spectra from the different depths of the soil profile showed similar numbers of absorption bands. In Figure 10 the FT-IR spectra from the various soil layers at KW are presented as an example. Any changes in selected bands are shown more in detail in Figure 11.

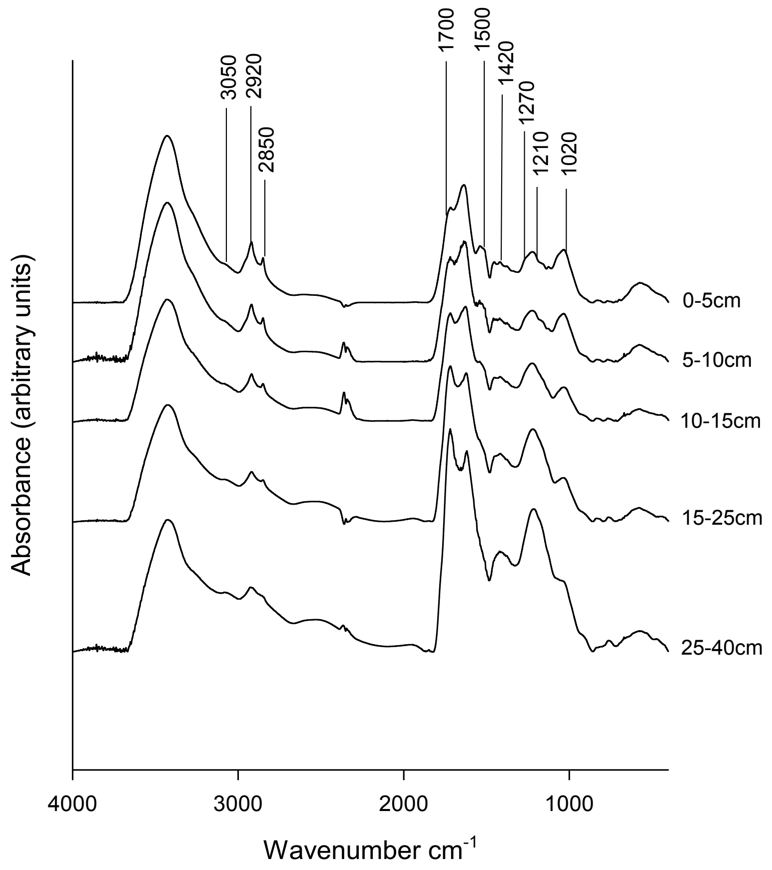


Figure 10: Fourier-Transform Infrared spectroscopy (FT-IT) in soil profile at the KW site. Some of the 18 evaluated bands (Table 2) are labelled to give an orientation.

Within the soil profile both aliphatic (2850 cm^{-1}) and N-related bands (1500 and 1270 cm^{-1}) decreased with soil depth, whereas the more stable aromatic (3050 cm^{-1}) and carboxylic (1700 cm^{-1}) groups and the FT-IR band at 1210 cm^{-1} showed a slightly increasing trend (n.s.) from 5 to 40 cm soil depth. The observed decrease of easily degradable compounds suggests a progressing decomposition and an increasing humification from the top to the bottom of the soil profiles. Similar observation was repeated by HABERHAUER ET AL. 1999, TATZBER ET AL., 2007, DJUKIC ET AL., 2010.

For all evaluated bands, the number of the different functional groups was much greater in the upper 0 – 5 cm than in the soil depths below. We explain this mainly by the repeated addition of manure which contains considerable amount of functional groups (HE & OHNO, 2012) influencing the composition SOM (TATZBER ET AL., 2009, DEMYAN ET AL., 2012)

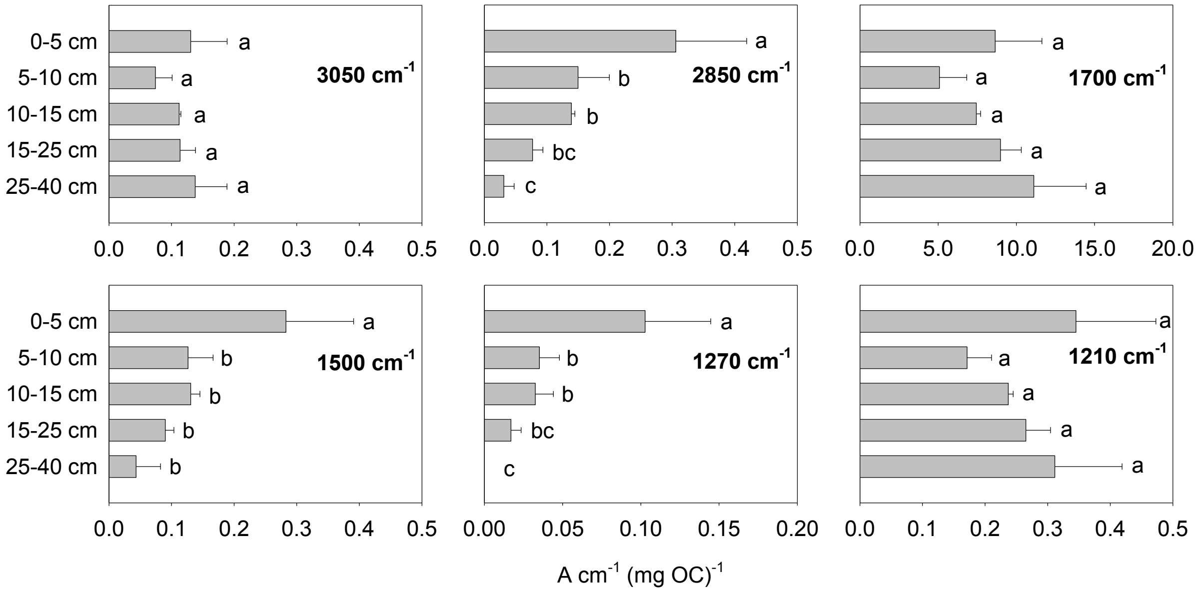


Figure 11: Areas of selected FT-IR bands (means and standard deviation) in soil profiles at KW. Different letters indicate significant differences ($p < 0.05$; n = 3 field replicates: ANOVA, Duncan's test). A= absorbance, OC= organic carbon. Assignments for evaluated bands are shown in Table 2. Note different scaling in the figures.

The amount of labile (aliphatic) compounds has been linked to the EXO1 of the STA measurement and the fractions decomposing at higher temperatures (EXO2 and EXO3) to the more stabile, aromatic bounds (DELL'ABATE ET AL., 2002, DE LA ROSA ET AL., 2008, DJUKIC ET AL., 2010). In our sites the aliphatic band at 2850 cm^{-1} correlated positively with EXO1 ($r = 0.528$, $p < 0.01$, $n = 60$). On the other hand, the aromatic (3050 cm^{-1}) and carboxylic (1700 cm^{-1}) showed similar trends as EXO2 and EXO3, although no significant correlation could be found.

The STA analysis gives an overview of the biochemical pools in SOM, whereas FT-IR on humic acids allows to semi-quantitatively differentiate between various stages of humification in the studied soils. The correlation between aliphatic bands and the EXO1 pool from the STA analysis indicate that NaOH extracted SOM is presenting mainly the labile SOM (brown HAs) in the soils (compare TATZBER ET AL. 2009, TATZBER ET AL., 2011) and only a smaller proportion of the aromatic compounds in the bulk soil (see also previous study mentioned under Material and Methods at page 17).

5 Summary and Outlook

This study described the quantity and composition of SOM under intensively used grassland along an alpine elevation gradient. The content of SOC increased by 0.48 kg m^{-2} per 100 m altitude (in 0 – 15 cm) and was concentrated in the uppermost layers due to the depth of the main rooting zone in grasslands and the annual application of farmyard manure. Thermal analysis of bulk soil indicated that in all soils along the elevation gradient SOM was dominated by biochemical labile organic material (EXO1) which accumulated to a greater extent with increasing altitude than the more stable organic compounds (EXO2, EXO3). Yields of HAs and their spectroscopic analysis confirmed that the decomposition/ humification process at all sites is slowed down, possibly by the high annual input of easy degradable animal manure and the unfavourable environmental conditions for decomposition (e.g. MAT; MAW; pH-value). Contrary to our expectation, the results could not confirm any significant increase of more stable aromatic functional groups with increasing soil depth, indicating that the decomposition processes in all soil layers are hampered – so that the degree of humification in all soils is remains at a “labile stage”.

In order to compare our findings with the following translocation study, where soil monoliths have been translated from KW to B2 and from B2 to B1, simulating a rapid change of MAT and management intensity, we calculated which consequences the forecasted increase of MAT by 3°C would have for the upper 0 – 15 cm soil depth. With consistent precipitation (+ irrigation) and management the studied sites at 1500 and 2000 m asl will experience a loss of 2.4 kg m^{-2} SOC (0 – 15 cm). Our data shows that there are considerable amounts of SOC in also below 15 cm. Due to an already limited decomposition process (by physical protection of organic compounds by the mineral phase and the low activity of microorganisms), the SOM stocks in the deeper soil layers have been found to be less sensitive to changing environment (i.e. MAT and management practices) (RASSE ET AL., 2004, KLEBER ET AL., 2010). Even though the turnover is slowed down this SOC does take part in the C-cycle and has to be considered by any ecosystem modelling.

The increasing MAT might favour new soil formation in higher elevations, which could sequester the released carbon in the long term (>100 years). However; due to a lack of large areas with new soil formation and the long-term scales for carbon sequestration in mineral soils, grassland soils may act as a source for atmospheric CO_2 in the future by the predicted climatic scenario. As a result, in order to fully understand the consequences of a changing climate on SOM in the studied area, it will be necessary to combine obtained data on SOM quantity and quality with other ecosystem properties, i.e. soil moisture, measurements of microbial community and activity, nutrient availability, particle size distribution, aboveground NPP as well as the rates of SOM decomposition influenced by temperature and moisture.

We found the STA to be a rapid and simple method to determine the thermal stability and composition of SOM. The results from the chemical extraction of HAs and FT-IR measurements correlated to the data from bulk soil STA analysis and gave a more specific insight in the decomposition processes.

6 References

ANTISARI, L. V., DELL'ABATE, M. T., BUSCAROLI, A., MASSIMO, G., LUIGI, N. & VIANELLO, G. (2010): Role of soil organic matter characteristics in a pedological survey: "Bosco Frattona" natural reserve. Geoderma, 156, 302 – 315.

BALDOCK, J.A. & SKJEMSTAD, J. O. (2000): Role of soil matrix and minerals in protecting natural organic materials against biological attack. Organic Geochemistry, 31, 697 – 710.

BENISTON, M., DIAZ, H. F. & BRADLEY, R. S. (1997): Climatic Change at High Elevation Sites: An Overview. *Climatic Change*, 36, 233 – 251.

BERG, B & MCCLAUGHERTY C. (2003): Plant Litter, Decomposition, Humus Formation and Carbon Sequestration. Springer Verlag, Berlin-Heidelberg.

BOT, A. & BENITES, J. (2005): The importance of soil organic matter, Key to drought-resistant and sustained food production. *FAO Soils Bulletin* 80. Food and Agriculture Organization of the United Nations, Rome.

BOSATTA, E. & ÅGREN, G. I. (1999): Soil organic matter quality interpreted thermodynamically, *Soil Biology and Biochemistry,* 31, 1889 – 1891.

BRADY, N. C. and WEIL, R. R. (2008): The Nature and Properties of Soil, revised fourteenth edition, Pearson Education Inc., New Jersey.

BUCHGRABER, K. & GINDL, G. (2009): Zeitgemäße Grünlandbewirtschaftung, 2. Völlig neu bearnb. Auflage. Stocker Verlag, Graz.

BUDGE, K., LEIFELD, J., HILTBRUNNER, E. & FUHRER, J. (2011): Alpine grassland soils contain large proportion of labile carbon but indicate long turnover times. *Biogeosciences* 8, 1911 – 1923.

BÜHL, A. (2008): SPSS 16, Einführung in die moderne Datenanalyse, 11., überarb. und erw. Auflage. Pearson Studium, München.

CHAPIN III, F. S., MATSON, P. A. & MOONEY, H. A. (2002): Principles of Terrestrial Ecosystem Ecology. Springer Verlag, New York.

DAVIDSON, E. A. & JANSSENS, I. A. (2006): Temperature sensitivity of soil carbon decomposition and feedbacks to climate change. *Nature*, 440, 165 – 173.

DE LA ROSA, J. M., KNICKER, H., LÓPEZ-CAPEL, E., MANNING, D. A. C., GONZÁLES-PEREZ, J. A. & GONZALES-VILA, F. J. (2008): Direct Detection of Black Carbon in Soils by Py-GC/MS, Carbon-13 NMR Spectroscopy and Thermogravimetric Techniques. *Soil Science Society of American Journal,* 72, 1, 258 – 267.

DELL'ABATE, M. T., BENEDETTI, A., TRINCHERA, A. & DAZZI, C. (2002): Humic substances along the profile of two Typic Haploxerert. *Geoderma,* 107, 281 – 296.

DEMEZ, A. (2011): Auswirkungen des Klimawandels auf den landwirtschaftlichen Ertrag von Mähwiesen in einem inneralpinen Trockental, Diplomarbeit. Institut für Ökologie, Universität Innsbruck.

DEMYAN, M. S., RASCHE, F., BREULMANN, M., MÜLLER, T. & CADISCH, G. (2012): Use of specific peaks obtained by diffuse reflectance Fourier transform mid-infrared spectroscopy to study the composition of organic matter in a Haplic Chernozem. *European Journal of Soil Science*, 63, 189 – 199.

DJUKIC, I. ZEHETNER, F., TATZBER, M. & GERZABEK, M. H. (2010): Soil organic-matter stocks and characteristics along an Alpine elevation gradient. *Journal of Plant Nutrition and Soil Science,* 173**,** 30 -38.

DÜMIG, A., SMITTENBERG, R. & KÖGEL-KNABER, I. (2011): Current evolution of organic and mineral components during initial soil development after retrait of the Damma glacier, Schwitzerland. *Geoderma*, 163, 83 – 94.

ERICH, M. S., PLANTE, A. F., FERNÁNDEZ, J. M., MALLORY, E. B. & OHNO, T. (2012): Effects of Profile Depth and Management on the Composition of Labile and Total Soil Organic Matter. *Soil Science Society of American Journal,* 76, 408 – 419.

FANG, C., SMITH, P., MONCRIEFF, J. B. & SMITH, J. U. (2006): Similar response of labile and resistant soil organic matter pools to changes in temperatures. *Nature,* 433, 57 – 59.

Gavazov, K. S. (2010): Dynamics of alpine plant litter decomposition on a changing climate. *Plant and Soil*, 337, 19 - 32

Gerzabek, M., Antil, R. S., Koegler-Knabner, I., Kirchmann, H. & Habenhauer, G. (2006): How are soil use and management reflected by soil organic matter characteristics: a spectroscopic approach. *European Journal of Soil Science*, 57, 485 – 494.

Gracia-Pausas, J., Casals, P., Camarero, L., Hugnet, C., Sebastíà, M.-T., Thompson, R. & Romanyà, J. (2007): Soil organic carbon storage in mountain grasslands of the Pyrenees: effects of climate and topography. *Biogeochemistry,* 82, 279 – 289.

Gregorich, E.G. & Janzen, H., H. (1996): Storage of Soil Carbon in the Light fraction and Macroorganic Matter. IN: Carter, M., R. & Stewart, B.A.: Structure and Organic Matter Storage in Agricultural Soils, CRC, Boca Ratin

Grisi, B., Grace, C., Brookes, P.C., Benedetti, A. & Dell'abate, M. T. (1998): Temperature effects on organic matter and microbial biomass dynamics in temperate and tropical soils. *Soil Biology and Biochemistry*, 30, 1309 – 1315.

Haberhauer, G. & Gerzabek, M. H. (1999): Drift and transmission FT-IR spectroscopy of forest soils: an approach to determine decomposition processes of forest litter. *Vibrational Spectroscopy* 19, 413 – 417.

Haddix, M. L., Plante, A. F., Conant, R. T., Six, J., Steinweg, J. M., Magrini-Bair, R., Morris, S. J. & Paul, E. A. (2010) : The Role of Soil Characteristics on Temperature Sensitivity of Soil Organic Matter. *Soil Science Society of American Journal,* 75, 56 – 68

He, Z. & Ohno, T. (2012): Fourier Transform Infrared and Fluorescence Spectral Features of Organic Matter in Conventional and Organic Dairy Manure. *Journal of Environmental Quality,* 41, 911 – 919.

Hell, V. (2010): Bodentextur. IN: Demez, A. (2011): Auswirkungen des Klimawandels auf den landwirtschaftlichen Ertrag von Mähwiesen in einem inneralpinen Trockental, Diplomarbeit. Institut für Ökologie, Universität Innsbruck.

Hell, V. (2012): Bulk density etc.; personal communication; Skype; 11.04.2012

Hesse, M., Meier, H. & Zeeh, B. (2005): Spektroskopische Methoden in der organischen Chemie, 7. überarb. Auflage. Thieme, Stuttgart

Hitz, C., Egli, M. & Fitze, P. (2001): Below-ground and above-ground production of vegetational organic matter along a climosequence in alpine grasslands. *Journal of Plant Nutrition and Soil Science,* 164, 389 – 397.

IPCC (2007): The Physical Science Basis. Fourth Assessment Report: Climate Change 2007, Europe, Intergovernmental Panel on Climate Change http://www.ipcc.ch/publications_and_data/ar4/wg2/ en/spmsspm-c-10-europe.html on 29.10.2011.

Janzen, H. H. (2004): Carbon cycling in earth systems – a soil science perspective. *Agriculture, Ecosystems and Environment*, 104, 399 – 417.

Jobbàgy, E. & Jackson, R. B. (2000): The vertical distribution of soil organic carbon and its relation to climate and vegetation. *Ecological Applications* 10, 423 – 436.

Karrer, G. (2011): Autoökologie und Populationsbiologie agrarisch relevante Pflanzen, Vorlesung, BOKU, Wien.

Kirschbaum, M. U. F. (2000): Will changes in soil organic carbon act as a positive or negative feedback on global warming? *Biogeochemistry*, 48, 21 – 51.

Kirschbaum, M. U. F. (2006): The temperature dependence of organic-matter decomposition – still a topic of debate. *Soil Biology & Biochemistry*, 38, 2510 – 2518.

Kleber, M. (2010): What is recalcitrant soil organic matter? *Environmental Chemistry*, 7, 320 – 332.

Knorr, W., Prentice, I. C., House, J. I. & Holland, E. A. (2005): Long term sensitivity of soil carbon turnover to warming. *Nature*, 433, 298 – 301.

Körner C. (2003): Alpine Plant Life, Functional Plant Ecology of High Mountain Ecosystem, Second Edition,Springer Verlag, Berlin-Heidelberg.

Leifeld, J., Franko, L. & Schulz, E. (2006): Thermal stanility responses of soil organic matter to long-term fertilization practices. *Biogeosciences*, 3, 371 – 374-

LEIFELD, J., ZIMMERMANN, M., FUHRER, J. & CONEN, F. (2009): Storage and turnover of carbon in grassland soils along an elevation gradient in the Swiss Alps. *Global Change Biology* 15, 668 – 679.

LOPEZ-CAPEL, E., SOHL, S. P., GAUNT, J. L. & MANNING, D. A. C. (2005): Use of Thremogravimetry-Differential-Scanning Calorimetry to Characterize Modelable Soil Organic Matter Fractions. *Soil Science Society of American Journal* 69, 136 – 140.

LÜTZOW, M. V., KÖGEL-KNABNER, I., EKSCHMITT, E., GUGGENBERGER, G., MARSCHNER, B. & FLESSA, H. (2006) Stabilization of organic matter in temperate soils: mechanisms and their relevance under different soil conditions – a review. *European Journal of Soil Science,* 57, 426 – 445.

LÜTZOW, M. V. & KÖGEL-KNABER, I. (2009): Temperature sensitivity of soil organic matter decomposition – what do we know? *Biology and Fertility of Soils,* 46, 1 – 15.

NIEDRIST G, TASSER, E., LÜTH, C., VIA DALLA, J. & TAPPEINER, U. (2009): Plant diversity decline with recent land use changes in European Alps. *Plant Ecology*, 202, 195 – 210.

NIEDRIST, G. (2011): Interview IN: LARCHER, M.: Im Klimastress. *ff – Das Südtiroler Wochenmagazin*, 1.9.2011

PLANTE, A. F., FERNÁNDEZ, J. M. & LEIFELD, J. (2009): Application of thermal analysis techniques in soil science. *Geoderma*, 153, 1 – 10.

PLANTE, A. F., FERNÁNDEZ, J. M., HADDIX, M. L. STEINWEG, J. M. & CONANT, R. T. (2011): Biological, chemical and thermal indices of soil organic matter stability in four grassland soils. *Soil Biology & Biogeochemistry,* 43, 1051 – 1058.

RASMUSSEN, C. & WHITE, D.A.II (2010): Vegetation Effects on Soil Organic Carbon Quality in an Arid Hyperthermic Ecosystem. *Soil Science,* 175, 438 – 446.

RASSE, D. P., RUMPEL, C. & DIGNAC, M.-F. (2005): Is soil carbon mostly root carbon? Mechanisms for a specific stabilisation. *Plant and Soil,* 269, 341 – 356.

REY, M., GUNTINAS, E., GIL-SOTRES, F., LEIRÓS, M. C. & TRASAR-CEPEDA, C. (2007): Translocation to stimulate climatic change: CO2 emissions and modifications to soil organic matter. *European Journal of Soil Science*, 58, 1233 – 1243.

ROUNSEVELL, M. D. A., EVANS, S. P. & BULLOCK, P. (1999): Climate Change and Agricultural Soil: Impacts and Adaption. *Climatic Change* 43, 683 – 700.

RUSTAD, L. E. (2006): From transient to steady-state response of ecosystem to atmospheric CO2-enrichment and global change: conceptual challenges and need for an integrated approach. *Plant Ecology*, 181, 43 – 62.

SCHEFFER/SCHACHTSCHABEL (2002): Lehrbuch der Bodenkunde, 15. Auflage. Springer-Verlag, Berlin Heidelberg 2008.

SINGH, S. K., PANDEY, C. B., SIDHU, G. S., SARKAR, D. & SAGAR, R. (2011): Concentration and stock of carbon in the soils affected by land uses and climates in western Himalaya, India. *Catena*, 87, 78 – 89.

SJÖGERSTEN, S., ALEWELL, C., CÉCILLON, L., HAGEDORN, F, JANDEL, R.,JANDL, R., LEIFELD, J., MARTINSEN, V., SCHINDLBACHER, A. SEBASTIÀ, M.-T. & VAN MIEGROET, H. (2011): Mountain soils in a changing climate – vulnerability of carbon stocks and ecosystem feedback. IN: JANDEL, R., RODEGHIERO, M. & OLSSON, M. (2011): Soil Carbon in Sensitive European Ecosystems, From Science to Land Management, Jon Wiley & Sons, Ltd.

SCHMIDT, M. I. S., TORN, M. S., ABIVEN, S., DITTMAR, T., GUGGENBERGER, G., JANSSENS, I. A., KLEBER, M., KÖGEL-KNABER, I., LEHMANN, J., MANNING, D. A. C., NANNIPIERI, P., RASSE, D. P., WEINER, S. & TRUMBORE, S. E. (2011): Persistence of soil organic matter as an ecosystem property. *Nature,* 478, 49 – 56.

THANEI, G. (s.a.): Geschichtliches über Matsch. http://www.thaneihof.com/matsch/die-geschichte-von-matsch/ _ 29.09.2012

TATZBER, M. (2012): personal communication, 27.07.2012

TATZBER, M., MUTSCH, F., MENTLER, A., LEITGEB, E., ENGLISCH, M. & GERZABEK, M. (2011b): Capillary electrophoresis characterization of humic acids: applications to diverse forest samples. *Environmental Chemistry*, 8, 589 – 601.

TATZBER, M., STEMMER, M., SPIEGEL, H., KATZBERGER, C., HABERHAUER, G., MENTLER, A. & GERZABEK, M.H. (2007): FTIR-spectroscopic characterization of humic acids and humin fractions obtained by advanced NaOH, Na4P2O7 and Na2CO3 extraction procedures. *Journal of Plant Nutrition and Soil Science,* 170, 522 – 529.

TATZBER, M., STEMMER, M., SPIEGEL, H., KATZLBERGER, C., ZEHETNER, F., HABENHAUER, G., GRACIA-GRACIA, E., & GERZABEK, M. (2009): Spectroscopic behavior of 14C-labeled humic acids in a long term field experiment with three cropping systems. *Australian Journal of Soil Research*, 47, 459 – 469.

TRUMBORE, S. E. & CZIMCZIK, C. I. (2008): An uncertain Future for Soil Carbon. *Science,* 321, 1455 – 1456.

TRUMBORE, S. E., CHADWICK, O.A. & AMUNDSON, R. (1996): Rapid Exchange Between Soil Carbon and Atmospheric Carbon Dioxide Driven by Temperature Change. *Science*, 272, 393 – 396.

ZEBISCH, M. (s.a.): Kapitel 1 Klimawandel, 10 – 22, IN: EURAC reasearch (s.a.): Klimareport, Südtirol, EURAC, Bozen

ZEHETNER, F., LAIR, G. J. & GERZABEK, M. H. (2009): Rapid carbon accretion and organic matter pool stabilisation in riverine floodplain soils. *Global Biochemical Cycles*, 23, doi:10.1029/2009GB003481

ZIMMERMANN, M. (2012): personal communication, 19.06.2012

7 Appendix

Table 5: Decline of EXOtot in the different soil depths (0 – 40cm) along the elevation gradient (986 to 1919 m asl), –K = soil organic matter, d = °C.

Depth	-K	D	R2
0-5cm	-2.36	29.78	0.966
5-10cm	-1.39	17.93	1.000
10-15cm	-1.14	15.04	0.993
15-25cm	-0.78	12.46	0.753
25-40cm	-0.33	7.27	0.920

Table 6: Results of STA analysis of bulk soil samples along the elevation gradient (5 – 10 cm), pretreated with 1 M NaOH.

Site	**Depht**	**EXOtot %**	**%EXO1 of EXOtot**	**%EXO2 of EXOtot**	**%EXO3 of EXOtot**	**DSC peak °C**
m asl	cm			samples pretreated by 1M NaOH		
986	5 – 10	4.1	53.6	20.4	26.1	291.0
1480	5 – 10	4.8	55.4	22.8	21.8	283.5
1919	5 – 10	5.6	58.8	21.5	19.8	288.5
2043	5 – 10	4.7	57.2	21.6	21.2	261.0

Table 7: Yield of humic acids (HA) in mg and in % of OC in bulk soil, + ash content from the humic acid extraction.

Site m asl	Depht cm	HA Yield mg-1	HA % von OC bulksoil	HA Ash %
B1	0 – 5	0.42	20	4.1
986	5 – 10	0.31	19	3.4
	10 – 15	0.21	19	3.5
	15 – 25	0.16	15	3.8
	25 – 40	0.10	12	5.5
B2	0 – 5	0.98	21	3.8
1480	5 – 10	0.45	16	4.4
	10 – 15	0.32	14	5.5
	15 – 25	0.32	14	5.3
	25 – 40	0.14	8	5.0
B3	0 – 5	1.13	20	5.2
1919	5 – 10	0.47	14	3.7
	10 – 15	0.46	16	4.8
	15 – 25	0.30	15	2.7
	25 – 40	0.15	12	3.7
KW	0 – 5	0.48	8	3.9
2043	5 – 10	0.39	13	4.4
	10 – 15	0.21	14	3.9
	15 – 25	0.10	11	1.6
	25 – 40	0.08	10	4.5

Conference contribution 1: Abstract for the annual conference of Österreichische Bodenkundliche Gesellschaft in Innsbruck, Austria 27 – 28th of June 2012

ÄNDERUNGEN IN DER ORGANISCHEN BODENSUBSTANZ ENTLANG EINES HÖHENGRADIENTEN IN DEN ÖTZTALER ALPEN

Cecilie B. FOLDAL[a], Ika DJUKIC[a], Georg J. LAIR[a,b], Verena HELL[c], Georg NIEDRIST[b,c] und Ulrike TAPPEINER[b,c]

[a]Institut für Bodenforschung, Universität für Bodenkultur, Peter-Jordan-Straße 82, 1190 Wien

[b]Institut für Ökologie, Universität Innsbruck, Technikerstrasse 25, 6020 Innsbruck

[c]Europäische Akademie Bozen, Drususallee , 39100 Bolzano/Bozen, Italien

Gebirgsökosysteme beherbergen große Kohlenstoffvorräte, die vorwiegend in organischer Bodensubstanz gespeichert sind und sensibel auf Klimaveränderung und Nutzungsänderungen reagieren. In dieser Studie untersuchten wir die Einflüsse von Klima und Grünlandbewirtschaftung auf die Quantität und Qualität der organischen Bodensubstanz entlang eines Höhengradienten (i.e. 1000, 1500 und 2000 m ü.A.) im Matschertal, Südtirol. Die untersuchten Bergwiesenstandorte weisen mit zunehmender Seehöhe verändernde klimatische Bedingungen (kühler und feuchter) sowie eine unterschiedliche Vegetationszusammensetzung und eine geringere Mahd-Häufigkeit auf.

Die Böden der Untersuchungsflächen wurden als tief- bis mittelgründige Braunerden auf Biotitglimmerschiefer klassifiziert. Bodenanalysen zeigten ausreichende Nährstoffgehalte für intensive Grünlandbewirtschaftung sowie eine tendenzielle Verschlechterung der Abbaubedingungen für organische Substanz durch einen starken pH-Abfall mit zunehmender Höhe. Der organische Kohlenstoffgehalt im Oberboden (0-15 cm) korrelierte stark mit der mittleren Jahrestemperatur und der Niederschlagsmenge (R^2 = 0,98 bzw. R^2 = 0,87) und nahm mit rund 0,48 kg/m^2 pro 100 Höhenmeter zu. Thermogravimetrische Untersuchungen am Gesamtboden und Transmissions-Infrarotspektroskopie-Messungen (FTIR) an Huminsäuren zeigten eine signifikante Abnahme von labilen Kohlenstoffverbindungen mit der Bodentiefe an den untersuchten Standorten, während Gehalte an hochmolekularen Kohlenstoffverbindungen nur sehr geringe Änderungen in den Bodenprofilen aufwiesen.

Die FTIR Charakterisierung der Huminsäuren zeigte klare Unterschiede entlang des Höhengradienten. Die aliphatischen FTIR Banden nahmen mit der Seehöhe zu, während die Banden 1500 cm^{-1} (Amide) und 1270 cm^{-1} (Nitrate) abnahmen. Stabilere Kohlenstoffverbindungs-Banden wie die 3050 (Aromaten) und 1700 cm^{-1} (Carboxylgruppen) zeigten jedoch keine signifikanten Trends in den untersuchten Böden.

Unsere Ergebnisse zeigen, dass sowohl die vorherrschenden klimatischen Bedingungen als auch die Intensität der Grünlandbewirtschaftung (Nährstoffzufuhr) und der pH-Wert des Bodens einen starken Einfluss auf die Quantität von labilen Kohlenstoffverbindungen ausüben. Stabilere Kohlenstoffverbindungen in Böden werden hauptsächlich vom Ligninabbau kontrolliert, für welchen vor allem die Pilze unter den Mikroorganismen verantwortlich sind. Das Fehlen von Pilzen unterhalb von 15 cm Bodentiefe entlang des untersuchten Höhengradients könnte eine der Ursachen für die minimale Änderung der stabileren Kohlenstoffverbindungen sowohl im Bodenprofil als auch über die Seehöhe sein.