Soil Organic Matter Vulnerability in Swiss Forest Mineral Soils

Assessment of SOM Vulnerability by Density Fractionation

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Abstract

Soils contain about three times as much carbon as either the atmosphere or the terrestrial vegetation. Hence, the understanding of the global carbon cycle and its steps is of high importance for a better evaluation of the storage of soil organic matter and its controlling factors.

The aim of this MSc thesis was to asess the SOM vulnerability in Swiss forest mineral soils in connection to factors with a high influence on ecosystem properties and on soil formation processes. It was hypothesized that the influence of climate (temperature and moisture) on SOM and its stability is stronger than the influence of soil properties (clay and pH) or terrain characteristics (aspect and slope). Furthermore, the aim was to enahnce the understanding of SOM fractions and turnover time in Swiss forest mineral soils.

From a WSL-database with more than 1000 already existing study sites, 54 Swiss forest sites were chosen based on a complex selection process. Two main climatic drivers were defined, namely the mean monthly temperature and a soil moisture proxy. With these two drivers, four climatic conditions (Warm-Dry, Warm-Moist, Cold-Dry, Cold-Moist) were created. In addition to these four climatic conditions co-variates of soil properties and terrain characteristics were defined, and together with the five Swiss productive regions, included in the selection process. Then, sites were selected with the aim to cover the whole heterogeneity inside each block. With the use of density fractionation 54 fresh samples and twelve corresponding archive samples (in average 19 years older than the fresh samples) were prepared and split into a fLF, oLF, cHF and fHF as well as WEOM.

With the use of multiple linear regression it was shown that especially soil properites and not the climatic conditons were driving the OC storage and the decomosition processes, which is mainly due to enhanced bindings of OC onto mineral surfaces in the fHF. But also the regionality had some effects on the C/N ratios most probably initiated by different litter inputs and by enhanced stabilization processes in the Southern Alps. Regarding the climate, the factor temperature infleunced the $\delta^{13}C$ values presumably through altitudinal-effects. Furthermore, higher relative ages were found in the fHF compared to the LFs. This difference was especially pronounced in the region Midland (fHF is 247 times older than the LF). Concerning the twelve archive sites and the corresponding twelve fresh sites, a stock change of +1.14 g OC/kg soil per year was calculated. To this positive stock change the light fractions contributed the main part. Further, almost no C was lost in the fHF and the cHF. This indicates that the HFs react less vulnerable through better stabilization processes against decomposition than the LFs. Therefore, the positive stock change in the LFs needs to be treated with more diligence since this stock is more labile bound.

1. Introduction

On a global scale, the carbon (C) stock in the pedosphere amounts to about 1500 to 2400 Pg C while the atmosphere and vegetation sequester only about 590 Pg C and 450 to 650 Pg C, respectively. Therefore, the soil contains about twice as much C as the atmosphere and the vegetation together (Intergovernmental Panel of Climate Change [IPCC], 2013). Thus, small changes of the soil organic carbon (SOC) stocks could already have a huge influence on the CO_2-concentration in the atmosphere (Cox et al., 2000; von Lützow et al., 2006). Regarding the global carbon cycle and its many processes, the formation, pool sizes and quality of soil organic matter (SOM) is to date one of the most poorly understood mechanisms (Quideau et al., 2001). SOM plays a key role for many soil functions (e.g. soil fertility, water supply, retention of contaminants) (Stevenson, 1972). Furthermore, an enhanced mineralization of SOM due to climatic warming may change soils into a CO_2 source (Davidson & Janssens, 2006; Hagedorn et al., 2010). Therefore, one of the most crucial topics in climate change research is to quantify SOM dynamic and its response to future climates (Kirschbaum, 1995).

1.1 SOM vulnerability

The vulnerability of SOM can be explained as a function of stabilization and destabilization mechanisms as well as disturbances. To predict how vulnerable soils react to environmental changes or to see which SOM is at most risk, the understanding of such stabilization and destabilization mechanisms is essential. Additionally, the type of disturbances that a soil undergoes (such as ploughing) is fundamental for assessing vulnerability and should be taken into account (Schmidt et al., 2011).

1.2 SOM stabilization processes

Degradation through microorganisms starts as soon as organic material gets into the soil (Kammer & Hagedorn, 2011). At this point, the composition of plant residues (C/N ratio) is decisive for the rate of degradation. The better the aggregation of organic material or the better the interaction of organic matter with mineral surfaces, the higher the protection against decomposition and the higher the protection against further degradation, then SOM is less likely to react vulnerable (Velde & Barré, 2010).

There are three main processes that stabilize SOM and therefore protect against decomposition. These are physical, chemical and biochemical stabilization processes (Schmidt et al., 2011; Six et al., 2002). Physically, SOM can be stabilized through microaggregation. Chemically stabilized SOM is protected through chemical and physico-chemical association with silt and clay particles and in particular with Fe- and Al-oxides. Biochemical stabilization processes refer to recalcitrant chemical composition of SOM such as lignin. However, there is also some SOM that is barely protected (Kaiser & Guggenberger, 2000; Six et al., 2002). These three processes (physical, chemical, biochemical processes) interact and respond to environmental changes (Heimann & Reichstein, 2008; Trumbore & Czimczik, 2008). In the following section an example of the combination of physical and chemical stabilization processes is presented.

Physico-chemical processes In general, physico-chemical processes influence the sorption of organic substances on mineral surfaces. However, the quantitative importance of such processes on the stabilization of SOM itself is still controversial (e.g. Schrumpf et al., 2013). The sorption is dependent on the strength of binding between the organic substances and the mineral surfaces as well as the structure of organic matter. Yet, it is not clear which mechanisms ensure the protection against microbial decomposition

(Kaiser & Guggenberger, 2000). Such physico-chemical sorption processes of organic compounds on mineral surfaces are further influenced by environmental factors (e.g. temperature, moisture). But to date only little is known about activation energies that are needed for such sorption processes (Davidson & Janssens, 2006). Further, it is also difficult to detect how sensitive the relative decomposition rate of recalcitrant SOM reacts on a change in temperature. Additionally, the change of the absolute decomposition rate is difficult to measure in experiments (Davidson & Janssens, 2006).

1.3 Time and space controlling SOM storage

On a longer term or larger space perspective, ecosystem properties in particular crucially influence the persistence of SOM and with this the stabilization of SOM, while other factors such as molecular structures appear to be less relevant (Schmidt et al., 2011). For example, weathering processes and thus the mineralogy of a soil is affected on a larger scale by time and space (Paustian et al., 1997). Firstly, over time, there is an ongoing development in a soil that influences for example the amount of SOM and its turnover rates (von Lützow et al., 2007). Therefore, with respect to residence time, some SOM components remain for thousands of years while other SOM compounds such as simple sugars and amino acids decompose much more rapidly (Schmidt et al., 2011). Secondly, with a change in space, not only the factor climate varies but also soil properties, the parent material of a soil or other factors such as vegetation are heterogeneous over space (Hudson, 1992; Jenny, 1941; Paul et al., 2002; Torn et al., 1997).
This means that SOC stocks as well as the three stabilization processes mentioned above are influenced by a large range of environmental factors that are important over a wide variety of spatial and temporal scales (Paustian et al., 1997). A clearer understanding of factors that determine the soil organic matter storage, and with this the stability and vulnerability of SOM, is therefore essential to obtain a proper insight into the system and its reactions.

In the debate about which space-driven environmental factor is the main driver in SOM dynamics and has the greatest influence in SOM persistence, some studies conclude that environmental properties such as land-use and its change may be the most important environmental factor determining the storage and stabilization of SOC (Poeplau et al., 2011). As already mentioned, a further uncertainty lies in the role of the vegetation when it comes to the accumulation of SOM, its formation and turnover (Quideau et al., 2001). Finally, the factor climate and its main drivers, temperature and moisture, have a major role in SOM dynamics especially over long-term development (Paul et al., 2002). Therefore, climate, land-use and vegetation are the main environmental factors that influence the dynamics of SOM and consequently the stabilization processes as well as the vulnerability of SOM. However, other factors, such as soil properties or parent material of a soil, can also play an important role (Jastrow, 1996) (see Figure 1). These four factors will now be discussed in the following sections.

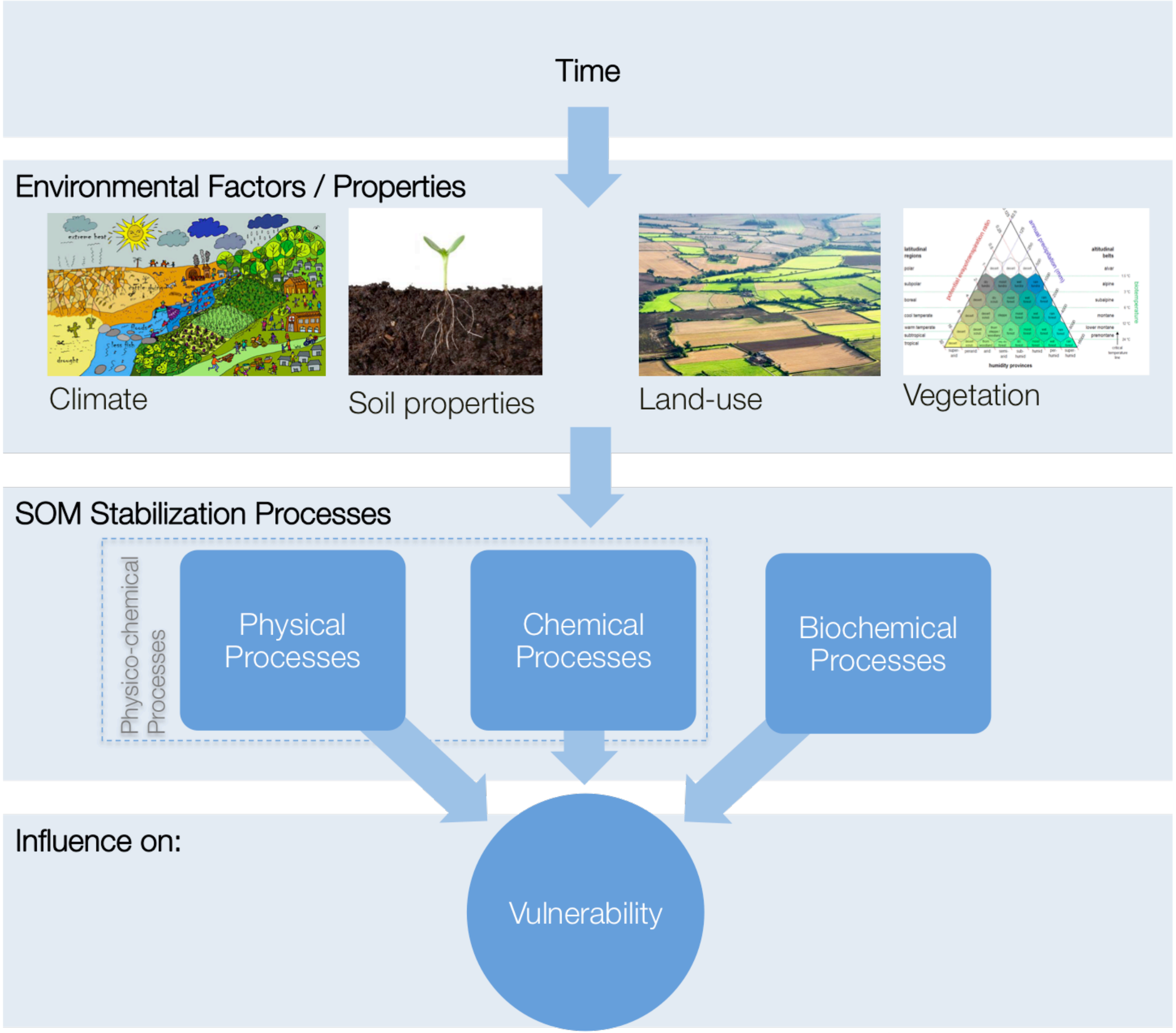


Figure 1: The influence of time and space on SOM vulnerability - adapted and extended from Jastrow (1996), Paul et al. (2002) and Six et al. (2002).

Climate The climate influences the input of C to the soil as well as the output of C from the soil. The warmer and the moister the climate, the more biomass is produced and with this, the more organic material is accumulated in the soil. (Davidson & Janssens, 2006; Figure 2).

However, temperature and precipitation not only influence the C inputs into soils but also the decomposition rate of SOM (Paul et al., 2002). In principle, microbial decomposition is higher in a warm and moist climate than, for example, in a warm and dry climate (Davidson & Janssens, 2006). Thus, microorganisms can influence the SOM cycle through decomposition on the one hand. On the other hand, microorganisms themselves are essential components of SOM (Kögel-Knabner, 2002; Schmidt et al., 2011). Hence, microbial activity has many linkages to ecosystem functions, but these connections are still uncertain (Morales & Holben, 2011; Raes & Bork, 2008; Schmidt et al., 2011). A change in environmental factors (e.g. climate) can have an impact on the SOM dynamics through alterations in the activity of microorganisms as well as in the structure of the microbial community (Schmidt et al., 2011; Streit et al., 2014).

Furthermore, specific climatic conditions also support the growth of roots or of the fungal mycelium. The fine network structure of fungi called hyphae leads to a proper aggregate formation, which physically protects the

SOM from disturbances and damage by developing barriers (Davidson & Janssens, 2006; Elliott & Coleman, 1988; Six et al., 2002).

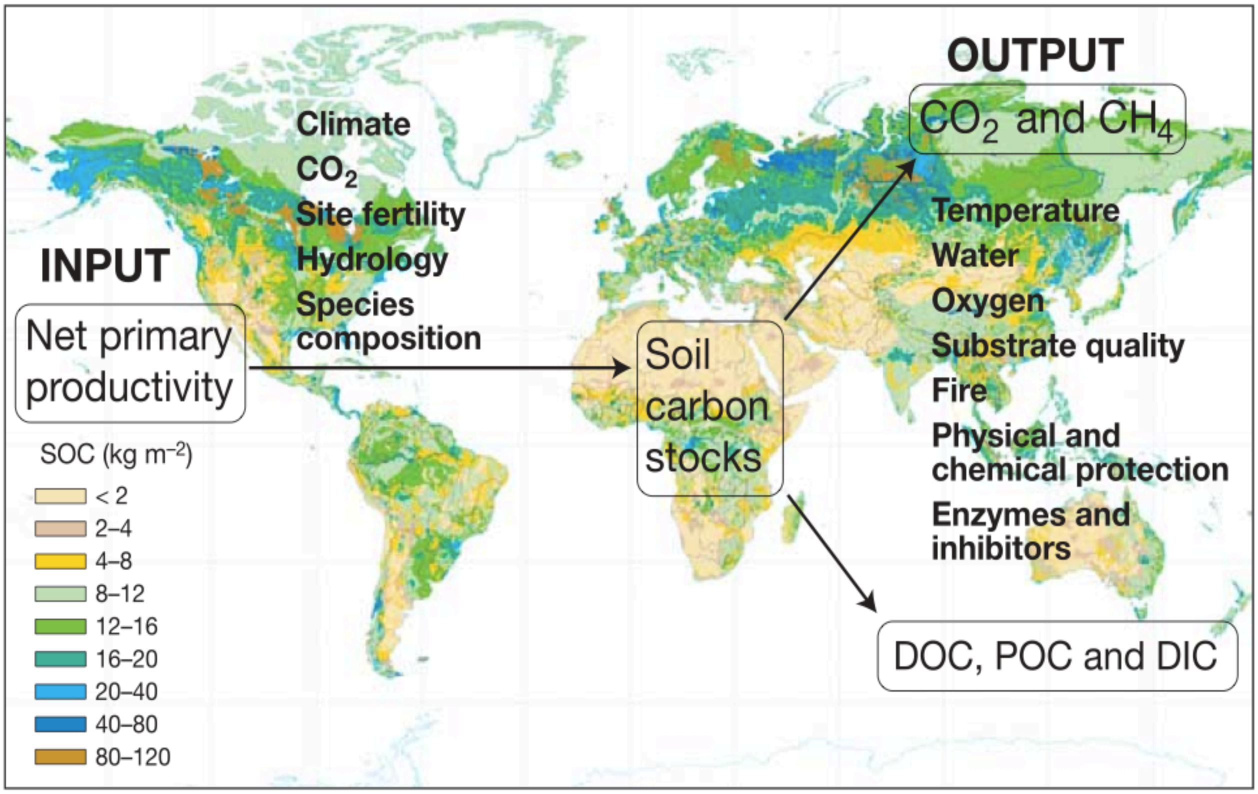


Figure 2: Diagram of factors controlling the main inputs and outputs of soil carbon, superimposed over a global map of soil organic carbon stocks (Davidson & Janssens, 2006).

Soil properties SOM dynamics are also influenced by soil texture (Paul et al., 2002). Especially fine silt and clay particles favour the sorption of organic substances on mineral surfaces through their large surface areas and Fe- and Al-oxides contained in the finer soil fractions (Grigal & Berguson, 1998; Schrumpf et al., 2013).

Due to the association of organic matter with mineral surfaces, SOM is strongly protected against decomposition in clayey soils, whereas in sandy soils plant residues and SOM decompose more quickly (Ladd et al., 1985; Sorensen 1981).

Land-use Land-use, for example, cropland, grassland or forest soils, was regarded as one of the most important factors determining the storage of SOM (Poeplau et al., 2011). Research is especially focused on the anthropogenic impact of different management practices. For example, cropland soils have a high potential to sequester carbon from the atmosphere under changed land-use regime or management technique (Wiesmeier et al, 2013). Poeplau et al. (2011) concluded that the intensity of management practices has a direct impact on the potential for storage of SOC. A reduced tillage of the soil, higher cropping rotation rates, development of yields, and the shift from annual crops to constant vegetation potentially enhance C sequestration (Bruce et al., 1999). Ogle et al. (2003) concluded that such management techniques lead to an increase of the SOC storage due to higher C inputs. On the other hand, other management practices may decrease the C output. Soil aggregates for example could be less broken because there is less tillage and less disruption. These aggregates protect SOC against the decomposition of microbes and therefore against the release of CO_2 (Davidson & Janssens, 2006; Six et al., 2000).

Another critical factor is a shift in land-use, for example when former cropland is converted to natural vegetation. This change often leads in longer-terms to an accumulation of SOM (Post & Kwon, 2000), while deforestation for agricultural land-use is generally associated with high SOM losses (Poeplau et al., 2011).

Vegetation High uncertainty lies in the role of the vegetation when it comes to the accumulation of SOM. An example for this is the unclear role of plant communities in regulating SOM formation and turnover (Quideau et al., 2001). Concerning the worldwide variety of vegetation, Quideau et al. (2001) concluded that the accumulation of SOM is directly influenced by the decomposability of plant tissues. The accumulation is also indirectly shaped by the occurrence of absorption of biomass-pathways into the soil (Quideau et al., 2001). Furthermore, vegetation influences microclimatic conditions with trees casting more shadow, which in turn leads to cooler temperatures on the soil surface than on bare fields (Post & Kwon, 2000).

Summarized, the dynamics and storage of SOM are strongly influenced by space-driven factors such as climate, soil properties, land-use and vegetation (Paul et al., 2002). And as already mentioned, time plays a crucial role in each of the above-mentioned factors (Hudson, 1992; Jenny, 1941; Paustian et al., 1997; Torn et al., 1997)

1.4 Studying SOM stabilization processes by density fractionation

A useful method to study the relevance of stabilization processes of SOM is the density fractionation, which separates SOM into four discrete fractions. In principle, these fractions characterize different degradation stages of SOM as well as different stages of associations with aggregates or minerals (Christensen, 1992; Griepentrog & Schmidt, 2013; Sollins et al., 1999). These are called free light fraction (fLF), occluded light fraction (oLF), coarse heavy fraction (cHF) and fine heavy fraction (fHF). The two light fractions (LF) comprise relatively young and only moderately decomposed SOM. Organic debris of the light fractions are attached inside and outside aggregates and not tightly associated with soil minerals (Griepentrog & Schmidt, 2013; Six et al., 2002). The two heavy fractions (HF) represent decomposed SOM, which is bound to the surface of soil minerals. Concerning the light fractions, the organic substances that are outside the aggregates can be found in the fLF and those that are inside aggregates can be found in the oLF (Griepentrog & Schmidt, 2013; Schrumpf et al., 2013; Six et al., 2002).

1.5 Stable isotopes and relative stability

The element carbon has a stable isotope called ^{13}C and the stable isotope of nitrogen is called ^{15}N. Such isotopic concentrations are influenced by physiological processes and can vary for example in different kinds of vegetation (Marshall et al., 2007). A depletion of the lighter isotopes (^{12}C and ^{14}N) can be seen in processes during organic material decomposition, which leads to a relative enrichment of the heavy isotopes called ^{13}C and ^{15}N (Garten et al., 2007). The study of such stable isotopes and measurements of isotopic ratios allows an interpretation about processes of fractionation in a soil and about the decomposition state (Gunina & Kuzyakov, 2014).

To investigate the relative stability of the fractions (Figure 3) a comparison of the change in C/N ratio and the change in δ^{15}N value can be made (Conen et al., 2008). A large C/N ratio in the particulate organic matter (POM) together with a small δ^{15}N value is related to poor stability. With a decrease of the C/N ratio and an increase of the δ^{15}N value in the mineral-associated organic matter (mOM) the stability of OC increases (Conen et al., 2008; von Lützow et al., 2006). In this thesis the POM is represented by the light fractions (fLF and oLF) and the mOM is represented by the HF, in terms of the fHF (due to missing $\delta^{15}N$ measurements of the cHF).

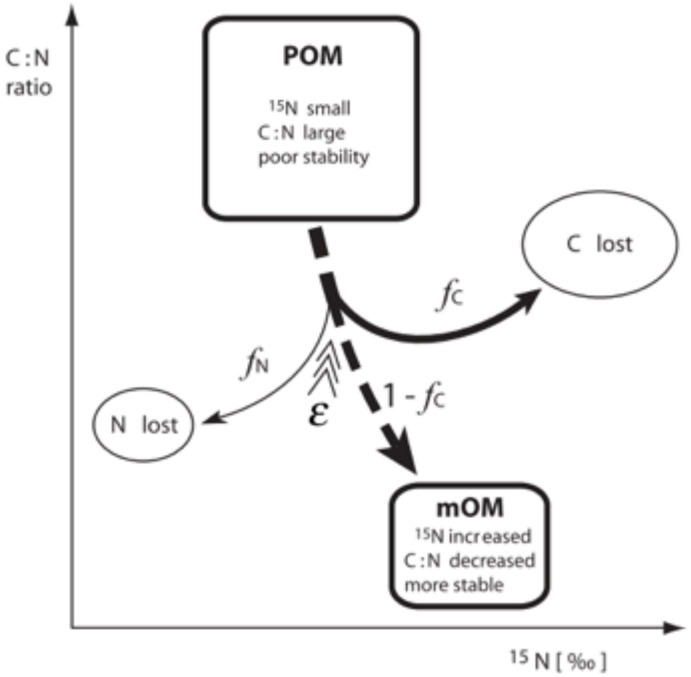


Figure 3: Relative stability of the fractions. In this thesis the particulate organic matter (POM) is represented by the light fractions and the mineral-associated organic matter (mOM) is represented by the fHF. ∈ = enrichment factor, f_N = proportion of N lost, f_C = proportion of C lost (Conen et al., 2008).

1.6 Context of this MSc thesis

As a part of the NRP 68 *soil as a resource* SwissSOM examines the vulnerability of soil organic matter in Swiss soils (WSL, 2013). This master thesis is a part of the NRP 68 which also contributes to the PhD project of Beatriz R. González Domínguez. In Beatriz R. González Domínguez' project it is studied whether soils are systematically influenced by their ecosystem properties. The vulnerability of SOM in Swiss soils is investigated in relation to the following two factors: soil ecosystem properties and factors with strong impact on soil formation processes (González Domínguez et al., 2014).

In this latter project, 72 research sites were selected trough a selection process that considers the factors climatic condition, soil properties, terrain characteristics and five Swiss productive regions while covering the heterogeneity within each factor. Out of these, 54 sites are Swiss forest sites, 14 sites are grasslands and 4 sites are croplands (González Domínguez et al., 2014). In this master project, 54 forest sites were examined (40 sites are general WSL sites and 14 are LWF sites).

2. Objectives

Schmidt et al. (2011) emphasized that the understanding of stabilization and destabilization mechanisms is essential to make predictions about the vulnerability of SOM to environmental changes.

The main drivers of C dynamics of a soil are climate properties such as temperature and moisture (Davidson & Janssens, 2006). Additionally, C dynamics are influenced by properties of the soil created through site-specific soil formation processes (González Domínguez et al., 2014).

But how important are factors such as climate or soil properties for SOM stability? Are some factors more determining than others when it comes to SOM vulnerability? Therefore, the aim of this MSc thesis was to asess the vulnerability of SOM in Swiss forest mineral soils in relation to factors with a high influence on ecosystem properties (climate) and on soil formation processes (e.g. pH and clay content). Furthermore, the aim was to reach a better understanding of SOM fractions and turnover time in Swiss forest mineral soil.

To answer the research questions, the influence of different space-driven factors on the stability of SOC, namely the climatic condition in Switzerland as a function of temperature and moisture, soil properties (clay content and pH) as well as terrain characteristics (aspect and slope) was analysed (González Domínguez et al., 2014; Figure 4, see space-axis). As a further space factor, the factor region comprising the levels Jura, Midland, Pre-Alps, Alpine and Southern Alps was included to make sure that the sites were selected from the whole area of Switzerland (González Domínguez et al., 2014). In a second step, the goal was to assess how SOC in Swiss forest mineral soils has changed over a time period of about 20 years and to estimate the SOC turnover time per year (Figure 4, see time-axis).

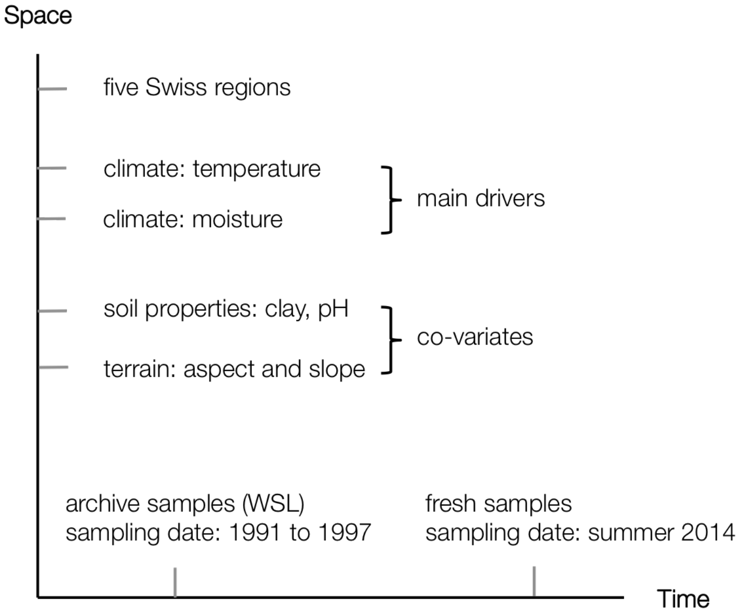


Figure 4: Space and time-driven factors to assess the SOM stability.

Based on this the following hypotheses were tested:

H1 The influence of climate (temperature and moisture) on SOM and its stability is more important than the influence of soil properties or terrain characteristics.

- H1.1 The distribution of C, ^{13}C, N and ^{15}N in the different soil fractions (fLF, oLF, cHF, fHF and water-extractable organic matter, WEOM) changes significantly between the climatic conditions (as a function of temperature and moisture).
- H1.2 Temperature and or moisture influences the amounts of C, ^{13}C, N and ^{15}N in the different soil fractions (fLF, oLF, cHF, fHF, WEOM) more than soil properties or terrain characteristics.

H2 The heavy fractions (cHF, fHF) are more stable and have higher relative ages than the light fractions (fLF, oLF).

H3 The SOC stock change per year in Swiss forest mineral soils has declined over the past 20 years.

3. Material and Methods

3.1 Sampling design and study sites

Switzerland comprises an area of 41’285 km^2. Of this area, approximately 12’582 km^2 are covered with forest. This means that slightly less than one third of the area of Switzerland is forest (Bundesamt für Statistik, 2014).

3.1.1 Site selection

From a WSL-database with more than 1000 already existing study sites, 54 Swiss forest sites were chosen with a complex selection process. Beatriz R. González Domínguez made this selection with the aim to have a number of sites that cover the variability of ecosystem properties in Switzerland on the one hand, and on the other hand also cover the whole area of Switzerland. Therefore, two main climatic drivers were defined, namely:

- the mean monthly temperature and
- a soil moisture proxy (González Domínguez et al., 2014).

Both drivers – the mean monthly temperature as well as the soil moisture proxy – refer to climatic data over the time span from 1981 to 2010. The soil moisture proxy was defined as follows: the soil moisture was defined by a number of dry months. This means that for example a dry month is a month where the precipitation is smaller than the potential evapotranspiration. The higher the accumulated number of dry months the lower the soil moisture is (González Domínguez et al., 2014). With the median of the mean monthly temperature and the soil moisture proxy the two climatic drivers are cut into four “climatic conditions” (Figure 5).

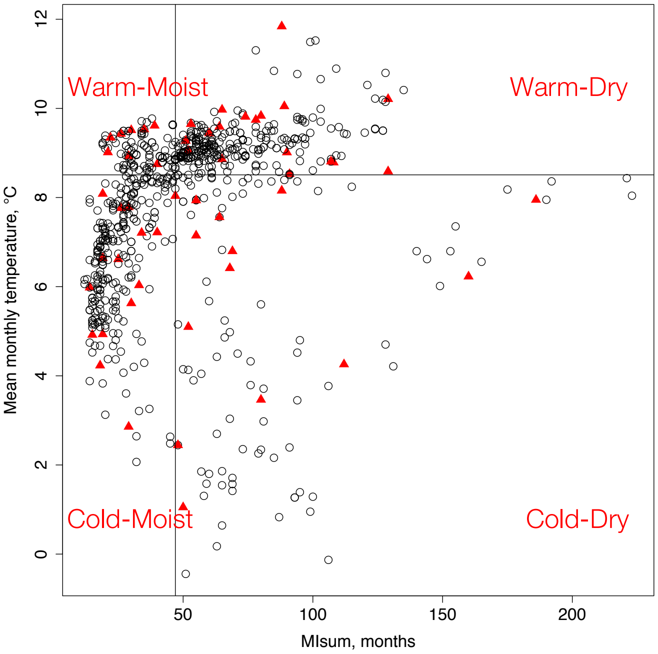


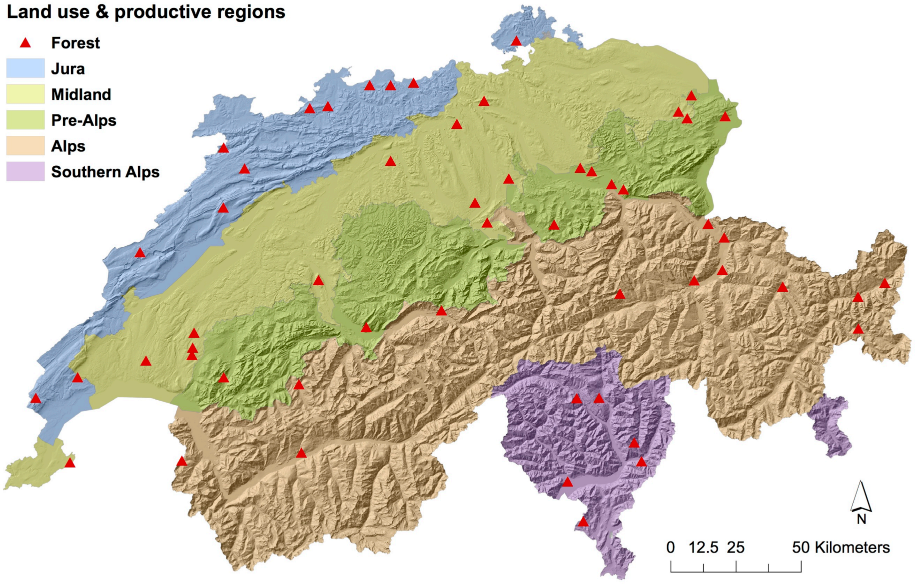
Figure 5: Climatic drivers and the four climatic conditions “Warm-Moist”, “Warm-Dry”, “Cold-Moist” and “Cold-Dry” (adapted from González Domínguez et al. (2014)).

The “Warm-Moist” climatic condition was defined as having a mean monthly temperature of over 8.5 °C and less than 47 dry months. The “Warm-Dry” climatic condition was defined as having a mean monthly temperature of over 8.51 °C but with more than 47 dry months. The “Cold-Moist” climatic condition was defined as having a mean monthly temperature of less than 8.51 °C and with less than 47 dry months. Finally, the “Cold-Dry” climatic condition was also defined as a mean monthly temperature of less than 8.51 °C but with more than 47 dry months (González Domínguez et al., 2014). In addition, co-variates were defined, namely:

- soil properties: clay content and pH value
- terrain characteristics: slope and aspect (González Domínguez et al., 2014).

To finalize the site selection, Beatriz R. González Domínguez also considered the 5 Swiss productive regions – Jura, Midland, Pre-Alps, Alps, and Southern Alps (Figure 6) (González Domínguez et al., 2014). These five productive regions or blocks are meant as a kind of replicates to consider the whole variability of the soil in a block.

Out of the four climatic conditions and the five Swiss regions twenty possible combinations were created. From these combinations the 54 Swiss forest sites were selected. The aim of this selection process was to spread the 54 Swiss forest sites into space-driven ecosystem properties and thereafter to assess the SOM vulnerability (González Domínguez et al., 2014).



Region	Number of sites
Jura	11
Midland	15
Pre-Alps	9
Alpine	13
Sothern Alps	6

Figure 6: Distribution of the 54 forest sites in the five Swiss regions (adapted from González Domínguez et al. (2014); source: swisstopo and Walthert et al. (2004)); including a table with the numbers of sites per each region.

3.1.2 Sampling of fresh samples

During the summer of 2014 Beatriz R. González Domínguez visited the 54 Swiss forest sites. To consider the spatial variability of each site three composites were created. The composites (40 x 40 m^2) were selected in a way that they do not overlap. Of each composite eight soil cores were collected. This means that per site 24 soil samples (3 composites x 8 soil cores) were taken. The soil cores were collected to a depth of 20 cm (average thickness of the A horizon in Swiss forest soils) of the mineral soil (González Domínguez et al., 2014).

3.1.3 Soil types

With the two main drivers, the four climatic conditions “Warm-Moist”, “Warm-Dry”, “Cold-Moist”, “Cold-Dry” were created (González Domínguez et al., 2014). These four climatic conditions as well as the type of soil (after WRB) are listed below (Table 1) along with the number of investigated soils:

Table 1: Climatic conditions and soil type of soil along with the number of investigated soils (González Domínguez et al. (2014); WSL database).

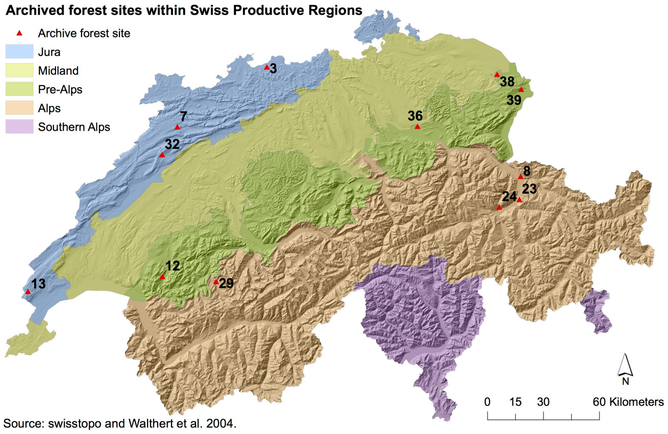
Climatic conditions	Sites	Calcisol	Cambisol	Gleysol	Kastanozem	Luvisol	Phaeozem	Planosol	Podzol	Regosol	Stagnosol	Umbrisol
Warm-Moist	8	0	1	1	1	3	0	2	0	0	0	0
Cold-Moist	14	0	6	2	1	1	1	1	1	0	1	0
Warm-Dry	18	4	4	1	1	2	1	0	0	1	1	3
Cold-Dry	14	5	4	0	0	0	1	0	3	0	1	0
Total	54	9	15	4	3	6	3	3	4	1	3	3

3.1.4 Archive samples

In addition to the fresh soil samples (hereinafter referred to as “fresh samples”) sampled by Beatriz R. González Domínguez, also archived soil samples from the Pedothek at the WSL were investigated (hereinafter referred to as “archive samples”).

A total of twelve archive sites were chosen that correspond to twelve “fresh” soil samples. Namely the following sites (Figure 7, Table 2):

Table 2: Archive soil samples with sampling years, regions and climatic conditions (González Domínguez et al. (2014); WSL database).



Nr	Year (MM.YY)	Region	Climatic Condition
3	08.93	Jura	Warm-Dry
7	10.93	Jura	Cold-Moist
8	04.96	Alpine	Warm-Dry
12	06.93	Pre-Alps	Cold-Dry
13	09.93	Jura	Cold-Moist
23	04.96	Alpine	Warm-Dry
24	06.97	Alpine	Warm-Dry
29	10.91	Alpine	Cold-Moist
32	09.92	Jura	Cold-Dry
36	08.97	Pre-Alps	Warm-Moist
38	09.97	Pre-Alps	Warm-Dry
39	09.97	Pre-Alps	Warm-Dry

Figure 7: Twelve archive sites (adapted from González Domínguez et al. (2014); source: swisstopo and Walthert et al. (2004)).

The twelve archive samples were all sampled in the 1990s and are in average 19 years older than the fresh samples. Those archive samples were included with the aim to assess a possible change of SOM stock and its vulnerability over time.

3.2 Sample preparation

For the fresh soil samples, a mixture of the three composites was made. Of each composite the same amount of soil was added to the mixture. The samples for the determination of water-extractable OC as well as the density fractionation were taken from these mixtures.

The archive samples were stored in the Pedothek horizon wise. Therefore, to prepare a mixture of soil samples up to a depth of 20 cm, equivalent subsamples of each horizon were mixed according to the horizons contribution to the total amount of fine earth.

3.3 Chemical analysis

3.3.1 Determination of water extractable organic matter (WEOM)

In a first step, of each site 10 g soil (dried and sieved <2mm) of 0–20 cm depth was used to determine the water-extractable organic matter (WEOM). In a centrifuge tube, 40 mL of deionised water was added to 10 g soil and shaken with an intensity of 100 rotations per minute for 10 minutes. Thereafter, the samples rested for 10 minutes. Finally, 10 mL of solute were extracted with a 20 mL syringe (Braun Inject 20 mL) and a glass-fibre prefilter (Chromafil GF/RC-45/25 glass-fibre prefilter and regenerated cellulose). Concentrations of non-purgeable organic carbon (NPOC) and total organic carbon (TOC), respectively, as well as total nitrogen (TN) were measured with a Shimadzu TOC-500 analyser at the WSL (Figure 8).

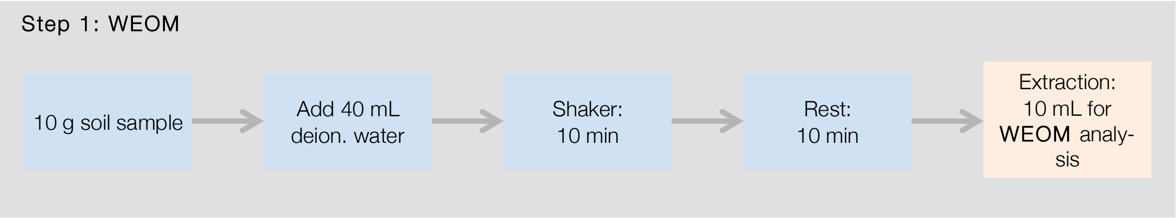


Figure 8: Scheme of water-extractable organic matter (WEOM) extraction.

3.3.2 Density fractionation

The density fractionation was conducted as described by Cerli et al. (2012) and Griepentrog et al. (2014). Griepentrog et al. (2014) demonstrated that the procedure yields four different fractions with specific turnover times and stabilities (Figure 9).

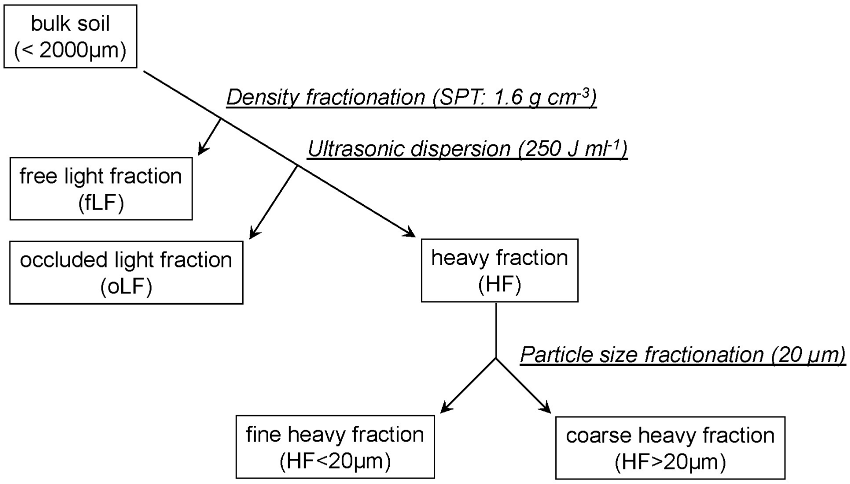


Figure 9: Fractionation scheme (Griepentrog et al., 2014).

Extraction of fLF (Figure 13, step 2) After the WEOM extraction (Figure 8, step 1) the fLF could be separated from the bulk soil (<2mm) with using a sodiumpolytungstate (SPT, TC Tungsten Compounds, Grub am Forst, Germany) solution (step 2). A density of 1.6 g/cm^3 was chosen because it is referred to be the most appropriate density for a separation of the maximal C content in the light fractions (Cerli et al., 2012; Griepentrog et al., 2014). To the remaining 10 g soil with 30 mL deionised water, 40 mL of SPT (2.05 g/cm^3) was added to obtain a 1.6 g/cm^3 density (with a mixing ratio of 1 : 7) in the centrifuge tube. After shallow stirring followed by 15 min of settling, the samples were centrifuged (Megafuge 1.0, Heraeus) with a speed of 4000 relative centrifugal force (rcf) for 10 min. Afterwards, the fLF was collected by carefully pouring the floating material through a vacuum filtration unit using glass-fibre filters (GF 6, Whatman, Dassel, Germany). Finally, fLF material was washed with deionised water until the electrical conductivity of the wash water stayed <50 µS/cm. Figure 10 shows two pictures of the extraction process of the fLF and the oLF.

Figure 10: Picture left: collection of oLF into round flask. Picture right: collected fLF in round flask.

Extraction of oLF (Figure 13, step 3) For the extraction of the oLF ultrasonic dispersion energy was used. Due to the fact that the amount of dispersion energies varies with aggregate stability, the amount of energies should generally be determined for every soil sample (Griepentrog et al., 2014). However, the determination of the optimum amount of energy for 54 soil samples would have exceeded the scope of this thesis. Therefore, based on literature research, a dispersion energy of 300 J/mL was chosen (Griepentrog et al., 2014; Pfenninger, 2014) and the probe was calibrated in accordance with Schmidt et al. (1999). This chosen approach could lead to a bias in the characteristics of the oLF (Cerli et al., 2012). By adding too much ultrasonic dispersion energy the oLF could be mixed with the HF or by adding too little amounts of ultrasonic dispersion energy not all of the oLF could be collected (Cerli et al., 2012).

For the extraction, the remaining material in the centrifuge tube was refilled with a total of 70 mL SPT and was allowed to settle again for 15 min. With the dispersion energy of 300 J/mL the samples were dispersed by ultrasound sonification (UW 3400, Bandelin, Berlin, Germany) wherein the samples were cooled in an ice bath to reduce the risk of thermal interferences. Finally, the samples were settled for another 15 min followed by the same routine of centrifugation, filtering and washing as for the extraction of the fLF.

Extraction of the HF (Figure 13, step 4) As a last step, the remaining material (HF) in the centrifuge tube was cleaned three times with deionised water (50 mL) to reduce the conductivity followed by centrifugation. After that, the HF is separable into the cHF (HF >20µm) and the fHF (HF <20µm) by a particle size fractionation of 20 µm (Griepentrog et al., 2013) by wet sieving (Retsch AS 200, Schieritz & Hauenstein AG). An amplitude of 2.00 mm/"g" was applied over 5 minutes. The material remaining in the sieve is the cHF and was collected. The fHF was collected after one week of sedimentation. Figure 11 shows two pictures during the process of HF extraction.

Figure 11: Picture left: collection of the cHF after wet sieving. Picture right: collected fHF after wet sieving – ready for one week of sedimentation.

All fractions were collected in 250 to 500 mL round flasks and freeze dried (Alpha 1-4 LD plus, Christ). The fLF and the cHF were milled with a horizontal mill (Retsch MM 301, Schieritz & Hauenstein AG) for 30 sec with a frequency of 25 and 30, respectively. The oLF and the fHF were already fine enough. Figure 12 shows fLF samples on the freeze dryer and some dried samples filled in glass vials.

Figure 12: Picture left: freeze-drying. Picture right: dried samples collected in small vials.

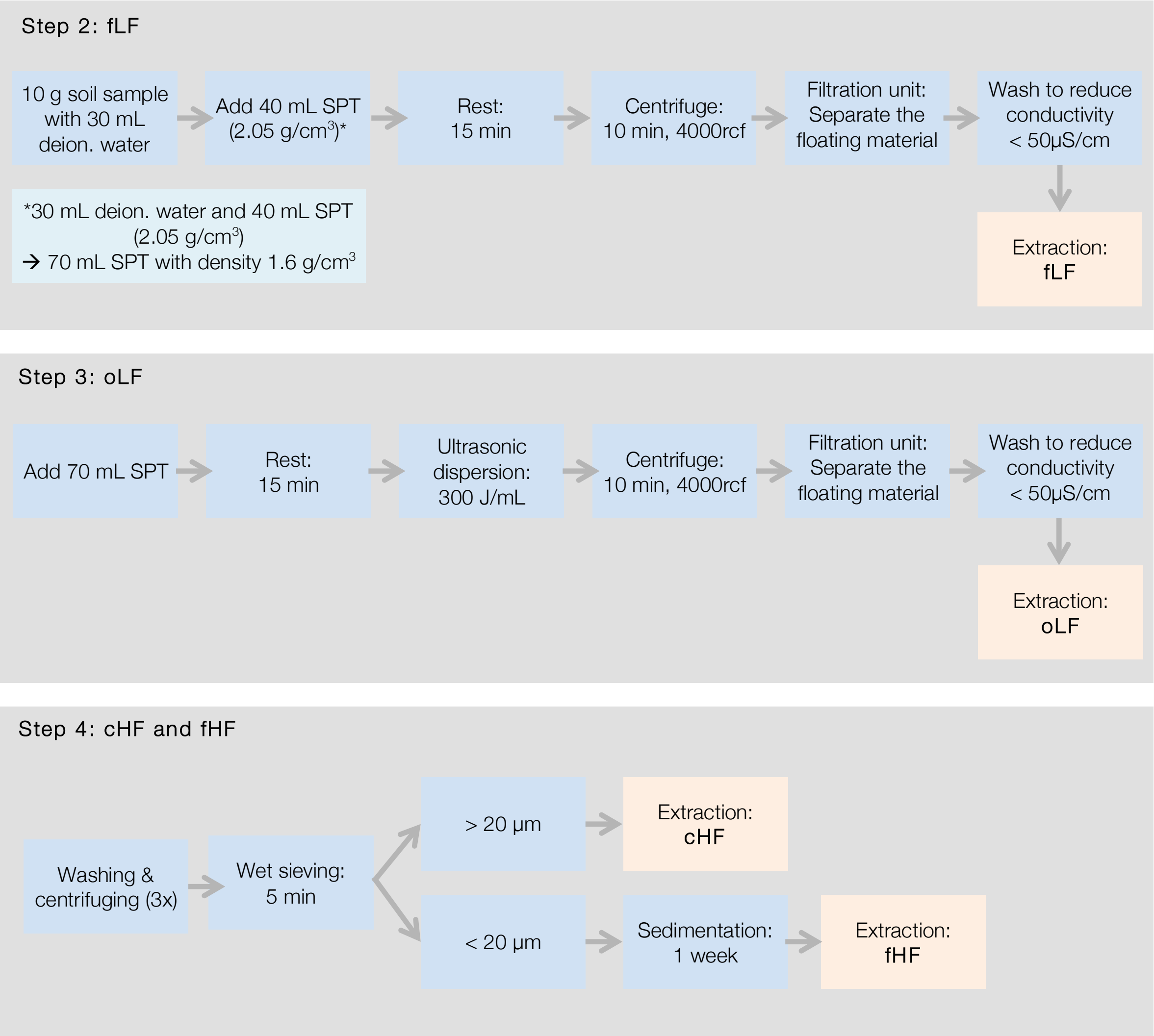


Figure 13: Fractionation scheme (adapted and extended from Griepentrog et al., 2014).

3.3.3 HCl fumigation

Prior to the C analysis, all samples with a pH-value >6 were fumigated with acid to remove carbonates from the soil (Walthert et al., 2010). Soil samples were filled into silver capsules and moistened. Thereafter, the samples were exposed to vapour from concentrated HCl in a desiccator for about 12 hours (Walthert et al, 2010).

3.3.4 Isotope analysis and relative ages

The measurement of C and N as well as δ^{13}C and δ^{15}N in the fLF, oLF and the fHF was done with an automated elemental analyser-continuous flow isotope ratio mass spectrometer (Euro-EA, Hekatech GmbH, Germany, interfaced with a Delta-V Advanced IRMS, Thermo GmbH, Germany). For the cHF samples, due to expected low C contents, only the TOC and δ^{13}C was analysed with a Picarro. All samples with a pH <6 were filled into tin capsules (5x8 for IRMS; 5x9 for Picarro) and weighed-in according to the expected C and N contents in the samples.

The expression of isotopic ratios is relative to the V-PDB standard and represented by δ notation. Including the WEOM samples a total of 330 samples were analysed (5x54 fresh samples and 5x12 archive samples).

Total organic carbon (TOC) and total N (TN) of the fractions Inorganic carbon forms are derived from geologic or soil parent material sources. If there is no inorganic carbon present, the TOC value corresponds to the organic carbon value (Schumacher, 2002). For the TOC analysis of calcareous soil samples, such inorganic carbon should be removed otherwise further analysis would be distorted (Walhert et al., 2010).

δ^{13}C- and δ^{15}N-signature Not only the C amounts are interesting when it comes to SOM accumulation and its vulnerability, but also the non-radioactive isotope ^{13}C is in the focus of research. The isotope ^{13}C is heavier than the ^{12}C isotope and is less common in the atmosphere (about 1.1% of ^{13}C and 98.8% ^{12}C) (O'Leary, 1988). Because of small physical and chemical differences between these isotopes, the ^{13}C isotope is discriminated during photosynthesis, which leads to a reduction of ^{13}C in plants (O'Leary, 1988). Furthermore, during microbial decomposition of SOM, the lighter isotope ^{12}C is preferably decomposed and released as CO_2, rather than the heavier isotope ^{13}C (Werth & Kuzyakov, 2010). This leads to a ^{13}C fractionation process during the stabilization of SOM and to different ^{13}C values in the fractions of SOM (Gunina & Kuzyakov, 2014).
For the fLF, the oLF and the fHF the δ^{13}C and δ^{15}N were measured with IRMS analysis. For the cHF samples, only the δ^{13}C was analysed with a Picarro. The isotope ratios of ^{13}C and ^{15}N were expressed relative to the V-PDB and air-standard.

$$\delta^{13}\mathrm{C} = \left(\frac{\mathrm{R}_{C\,\mathrm{sample}}}{\mathrm{R}_{C\,\mathrm{V-PDB}}} - 1\right) \times 1000\ \text{‰} \quad \mathrm{R_C} = \frac{^{13}C}{^{12}C} \tag{1}$$

$$\delta^{15}\mathrm{N} = \left(\frac{\mathrm{R}_{N\,\mathrm{sample}}}{\mathrm{R}_{N\,\mathrm{Air}}} - 1\right) \times 1000\ \text{‰} \quad \mathrm{R_N} = \frac{^{15}N}{^{14}N} \tag{2}$$

Relative age Furthermore, to assess the relative ages of the soil fractions, the calculation considering the approach by Conen et al. (2008) was made (the approach was used for grassland soil in the Swiss Alps). The following equations (3 to 5) were used, under the assumption that the soil remains under steady conditions.

$$f_N = 1 - e^{(\frac{\delta_h - \delta_l}{\in})} \tag{3}$$

$$f_C = f_N + (1 - f_N) \times (1 - \frac{r_h}{r_l}) \tag{4}$$

$$n = (\frac{C_h}{C_l \times (1 - f_C)}) \tag{5}$$

In the equation (3) the f_N is represented as the proportion of N loss during transformation and processes of re-synthesis (Högberg, 1997; Robinson, 2001). The factor ∈ ‰ represents the enrichment factor and stands for the fractionation. Conen et al. (2008) used an enrichment factor ∈ of 2.0 ‰ based on studies of Robinson (2001) and Vervaet et al. (2002). The same value of 2.0 ‰ was used in this MSc thesis. For the value δ_h the δ^{15}N value of the fHF was used and for the δ_l the LF value. With the equation (4), the portion of lost C (f_C) was calculated. The C/N ratio of the fHF is represented by r_h and the C/N ratio of the LF is represented by r_l. In equation (5) the factor n is calculated. This factor n represents the relative age or stability of the fHF relative to the LF (e.g. the fHF is n times older than the LF). C_h stands for the amount of C (in gC/kg soil) stored in the fHF and C_l for the amount of C in the LF.

3.4 Statistical analysis

The analysis was conducted with R (Version 3.1.2). All the data was tested for normal distribution (Q-Q plot). In chapter 4.1 the variables C, $\delta^{13}C$, N, $\delta^{15}N$ and C/N ratio were analysed and presented separately for each of the factors climatic condition, pH, clay and regions. Differences between and within fractions and factors were tested with an ANOVA. In chapter 4.2 a multiple linear regression (hierarchical ANOVA, SS type I) was applied to analyse and assess the influence in combination with all factors (ANOVA in order: region, temperature, moisture, soil properties, terrain characteristics) on the variables C, $\delta^{13}C$, N, $\delta^{15}N$ and C/N ratio. Results with a p value <0.05 were considered to be significant.

Due to the fact that the sites were selected after the described site selection process (so that sites include the whole heterogeneity of a block), the same structure was also used for the multiple linear regression with a hierarchical ANOVA. Hence, the discrete factors region (5 levels), temperature (cold, warm) and moisture (moist, dry) as well as the continuous factors soil properties (pco1, numeric combination of pH and clay) and terrain characteristics (pco2, numeric combination of aspect and slope) were used.

4. Results

4.1 General pattern of space-driven results – fresh samples

In the following sections, the results of the fresh samples are presented grouped by all space driven factors, starting with the two main drivers, temperature and moisture, then the co-variates clay and pH, as well as aspect and slope.

4.1.1 Density fractionation – mass distribution of fresh samples

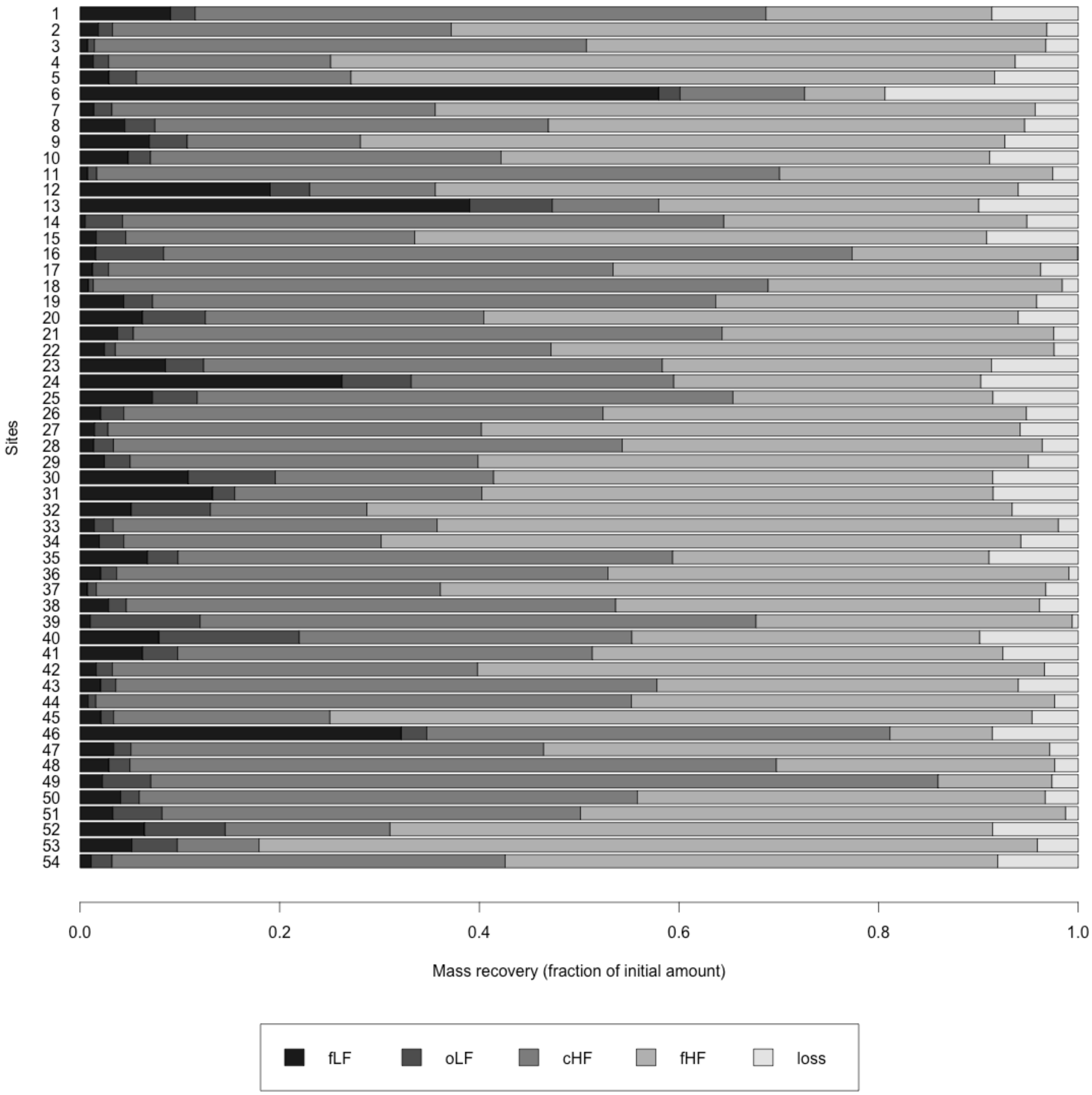


Figure 14: Mass distribution of density fractionation with fresh sites.

After the density fractionation, the average mass recovery of the 54 fresh soil samples was 94.4 ± 3.3% (Figure 14). In general, the fLF and the oLF had the lowest masses, averaging 6.4 ± 10.4% and 3.3 ± 2.7%, respectively. Except two sites (site number 6 and 13), all masses of the light fractions were below 35% and the majority was even below 20%. The fLF of site number 6 (in the climatic condition Warm-Dry, region Jura) and 13 (in the climatic condition Cold-Dry, region Jura) showed particularly high mass contributions (58% and 39%, respectively). The cHF as well as the fHF had a much higher relative mass than the LFs with values of 39.9 ± 16.9% and 44.6 ± 15.9% for the cHF and the fHF, respectively.

Among the four soil fractions, the highest concentration of organic C was measured in the oLF (38.0 ± 7.4%). In the fLF, only slightly lower values were measured (27.4 ± 3.7%). The C concentration in the cHF (1.7 ± 2.6%) as well as in the fHF (5.8 ± 3.1%) were significantly lower than in the LFs. The fLF of site number 6 and 13 showed OC concentrations of 36.4% and 29.7%, respectively. Together with the high relative mass, this results in a very high organic C amount of 210 gOC/kg soil and 116 gOC/kg soil, respectively. Therefore, those two sites were excluded from the following figures.

4.1.2 SOC contents in soil fractions in the five Swiss regions

Table 3 shows the mean with standard deviation of the OC content in g/kg soil for the five Swiss regions in each soil fractions.

Table 3: Organic C contents in the soil fractions and the WEOM for each of the five Swiss productive regions. The bulk soil values represent the sum of the 5 soil fractions. *The site number 6 and 13 were excluded from the fLF due to very high organic C values.

Swiss regions	Sites	WEOM	fLF	oLF	cHF	fHF	Bulk soil
		g OC/kg soil ± SD					gOC/kg soil
Jura	11	0.08 ± 0.03	10.7 ± 10.7*	10.4 ± 8.1	3.7 ± 3.0	30.2 ± 17.8	55.1*
Midland	15	0.06 ± 0.02	6.7 ± 6.5	9.9 ± 11.3	3.4 ± 2.9	20.4 ± 4.0	40.5
Pre-Alps	9	0.06 ± 0.03	13.3 ± 19.0	17.2 ± 14.4	8.8 ± 9.4	21.6 ± 9.2	61.0
Alpine	13	0.08 ± 0.04	14.7 ± 9.5	14.1 ± 9.6	7.4 ± 7.0	21.3 ± 9.1	57.6
Southern Alps	6	0.04 ± 0.02	21.7 ± 30.0	11.1 ± 4.0	7.0 ± 3.8	28.5 ± 9.9	68.3

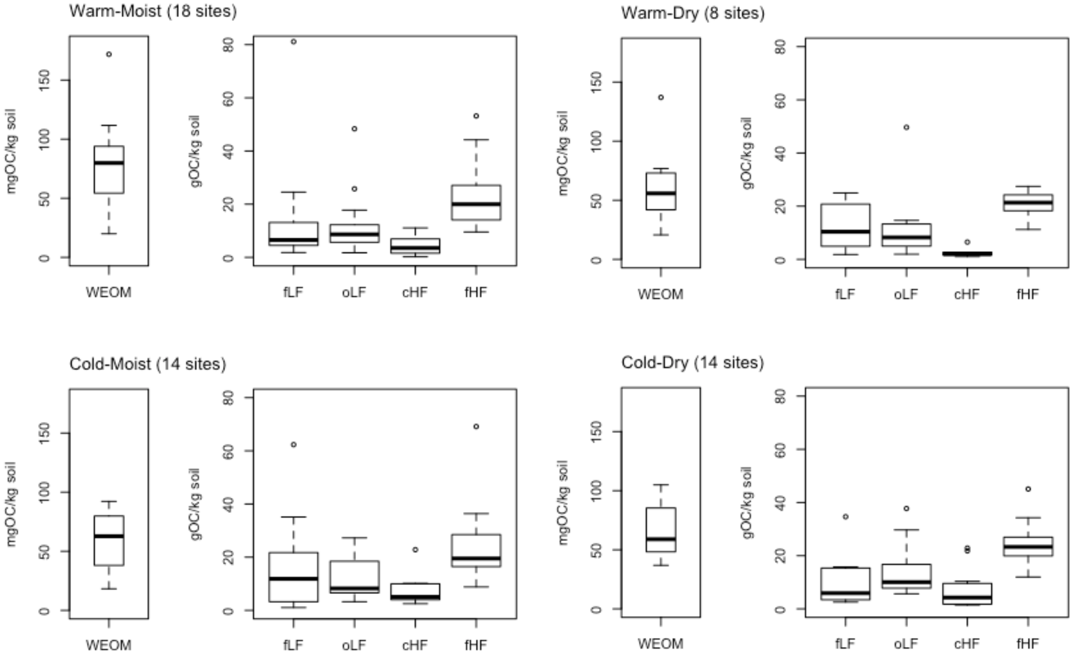
Over all fractions including WEOM, significant differences between the fractions were found ($p<0.001$). Furthermore, the fHF OC stocks were significantly higher than in the LFs in all regions ($p<0.001$).

The WEOM contained the smallest stocks of all fractions (Table 1). Among the five regions, the Southern Alps had the highest SOC stocks with 68.3 gOC/kg soil in the bulk soil from which 31% were in the fLF. The region Midland had the smallest SOC stocks with 40.5 gOC/kg soil. Here, only 17% were stored in the fLF.

4.1.3 Results of the two main drivers: temperature and moisture

Concerning all the results grouped into the four climatic conditions, for all variables (OC, N, $\delta^{13}C$ and $\delta^{15}N$) significant differences between the fractions were found ($p<0.001$ for OC, N and $\delta^{15}N$; $p<0.01$ for $\delta^{13}C$). And, within all climatic conditions significantly higher values were stored in the fHF ($p<0.001$).

Climate – SOC



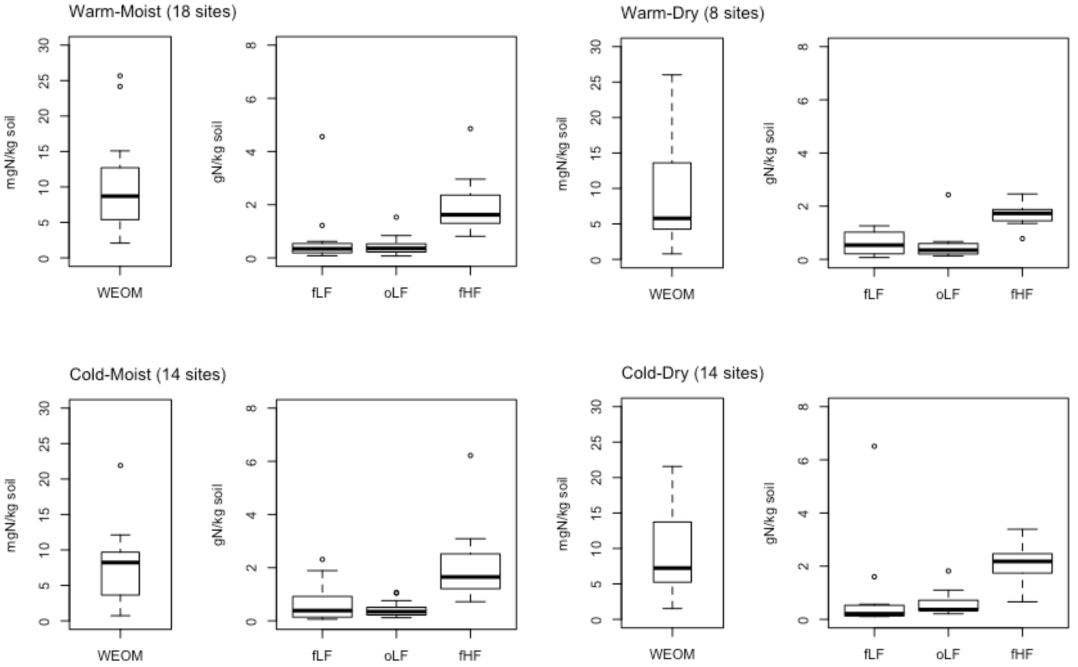
	Between all fractions	Between LF and fHF	Between WEOM	Between climatic conditions of all 4 soil fractions	Between 4 soil fractions of climatic conditions
Climate					
Significance	p<0.001	p<0.001	NS	NS	NS
Direction		fHF: higher OC stocks	-	-	-

Figure 15: OC values in mgOC/kg soil for the WEOM and in gOC/kg soil for the fLF, oLF, cHF and fHF classified after the four climatic conditions Warm-Moist, Warm-Dry, Cold-Moist and Cold Dry. Including a table with indication of the significances and directions of the significant differences. The values of the sites 6 and 13 in the fLF were excluded due to very high OC values (over 100 gOC/kg soil).

Regarding all fractions, primarily the fHF contributed to the C storage, while especially the importance of the cHF for the C storage is very little. The LFs played about the same role concerning the amount of total OC contribution within all climatic conditions (Figure 15). For the WEOM, the highest contents were found in the climate Warm-Moist (WM) followed by the climate Cold-Moist (CM), Cold-Dry (CD) and Cold-Moist (CM). No significant differences in the WOEM values were found.

Lowest stocks of OC were stored in the cHF (medians: WD with 1.9 gOC/kg soil, WM with 3.5 gOC/kg soil, CD with 4.3 gOC/kg soil and CM with 5.1 gOC/kg soil) across all climatic conditions. The medians of the LFs were very similar with an exception in the Cold-Dry climatic condition where the oLF was slightly higher than the fLF: CD 5.9 gOC/kg soil, CD 10.1 gOC/kg soil).

Climate – Nitrogen

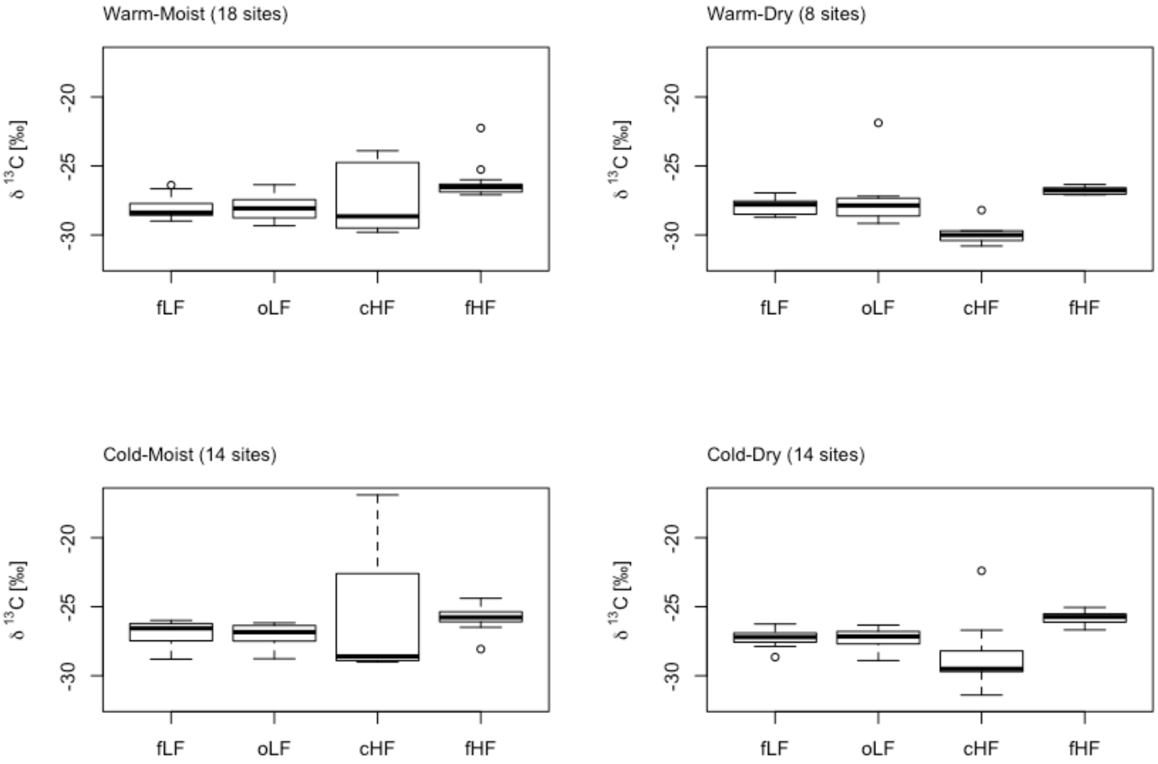


	Between all fractions	Between LF and fHF	Between WEOM	Between climatic conditions of all 3 soil fractions	Between 3 soil fractions of climatic conditions
Climate					
Significance	p<0.001	p<0.001	NS	NS	NS
Direction		fHF: higher N stocks	-	-	-

Figure 16: N values in mgN/kg soil for the WEOM and in gN/kg soil for the fLF, oLF and fHF classified after the four climatic conditions Warm-Moist, Warm-Dry, Cold-Moist and Cold Dry. Including a table with indication of the significances and directions of the significant differences.

Nitrogen was measured in the soil fractions fLF, oLF and fHF and in the WEOM (Figure 16). Between the four climatic conditions no significant differences were found for the N stocks of the soil fractions. The N stocks in the LFs played about the same role in all climatic conditions. In the WEOM values with slightly higher differences within the climatic conditions were found, but no significant ones.
The lowest median of the fHF of 1.62 gN/kg soil was observed in the climatic condition Warm-Moist. The highest median was reached in the climatic condition Cold-Dry with a value of 2.2 gN/kg soil. The medians for the fLF in the climatic groups were between 0.2 and 0.5 gN/kg soil (WD>CM>WM>CD). The medians of the oLF had smaller ranges than the fLF and were between 0.34 and 0.37 gN/kg soil (CD>WM>CM>WD). The medians of the N amounts in the WEOM were between 5.8 mg to 8.7 mgN/kg soil (WM>CD>CM>WD).

Climate – δ^{13}C



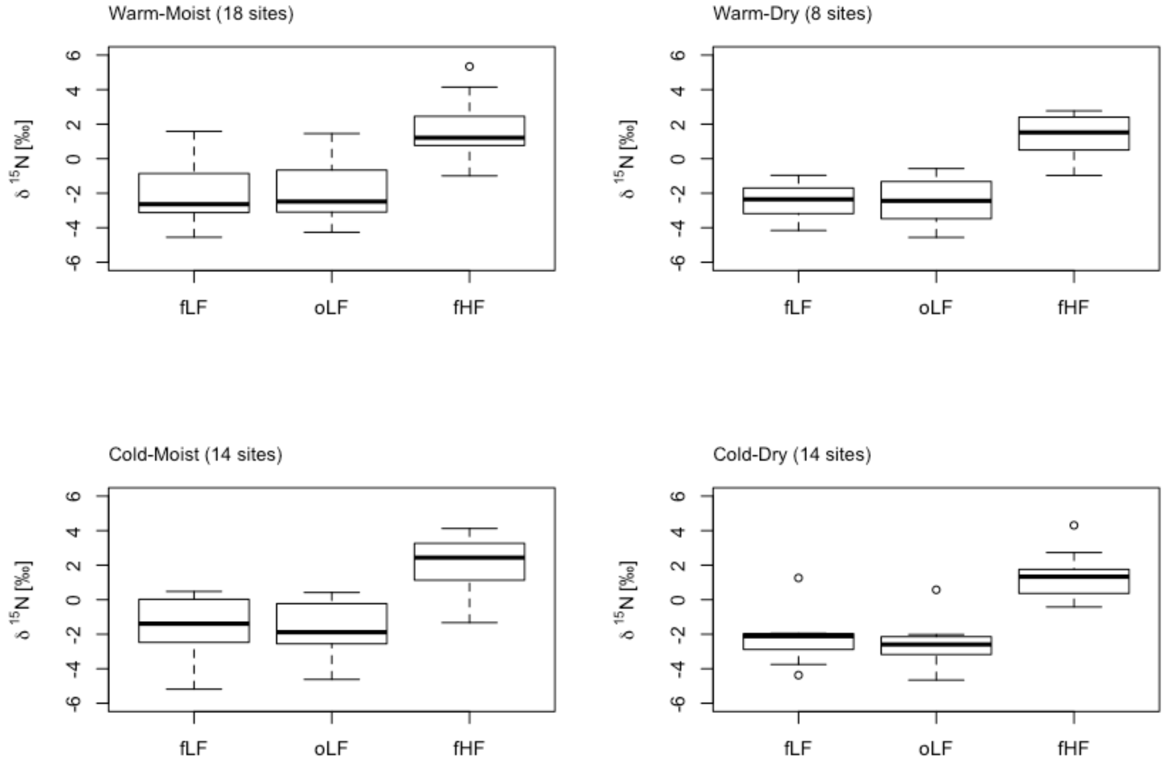
	Between all fractions	Between LF and fHF	Between climatic conditions of all 4 soil fractions	Between 4 soil fractions of climatic conditions
Climate				
Significance	p<0.01	p<0.001	p<0.05 p<0.001 (without cHF)	p<0.01 NS (without cHF)
Direction		fHF: higher δ13C values	the colder the higher (less negative) the δ13C values	

Figure 17: δ^{13}C values in ‰ for the fLF, oLF, cHF and fHF classified after the four climatic conditions Warm-Moist, Warm-Dry, Cold-Moist and Cold Dry. Including a table with indication of the significances and directions of the significant differences.

Figure 17 presents the results of the δ^{13}C measurements for each climatic condition. Significantly higher δ^{13}C values were found in the fHF compared to the LFs. Including the cHF results of δ^{13}C values, significant differences were found between the climatic conditions ($p<0.05$). This was especially pronounced between warm and cold climatic conditions, indicating that colder climatic conditions led to higher (less negative) δ^{13}C values. Including the cHF, also the interaction (difference between fractions of climatic conditions) was significant ($p<0.01$). This effect was mainly due to the high differences in the ranges of the cHF. With the cHF excluded there was still a significant difference between the climatic conditions ($p<0.001$) for the δ^{13}C values but none for the interaction.

The light fractions showed over all climatic conditions very similar results with a median between -28.3 to -26.7‰ for the fLF (CM>CD>WD>WM) and -28.1 to -26.8‰ for the oLF (CM>CD>WD>WM). The medians of the fHF were between -26.7 to -25.7‰ (CM>CD>WM>WD). The cHF samples showed the lowest δ^{13}C values (medians between -30.0 to -28.6‰) and a very high range from over -30 to below -20‰.

Climate – $\delta^{15}N$



	Between all fractions	Between LF and fHF	Between climatic conditions of all 3 soil fractions	Between 3 soil fractions of climatic conditions
Climate				
Significance	p<0.001	p<0.001	NS	NS
Direction		fHF: higher δ15N values	-	-

Figure 18: $\delta^{15}N$ values in ‰ for the fLF, oLF and fHF classified after the four climatic conditions Warm-Moist, Warm-Dry, Cold-Moist and Cold Dry. Including a table with indication of the significances and directions of the significant differences.

The climatic conditions did not affect the $\delta^{15}N$ values significantly in any of the fractions (Figure 18). The $\delta^{15}N$ values of the fLF and the oLF were very similar across all climatic conditions and varied between -2.6 to -1.4‰. The results of the fHF were significantly higher than the ones of the LF and varied between +1.2 and +2.4‰.

Climate – C/N to $\delta^{15}N$

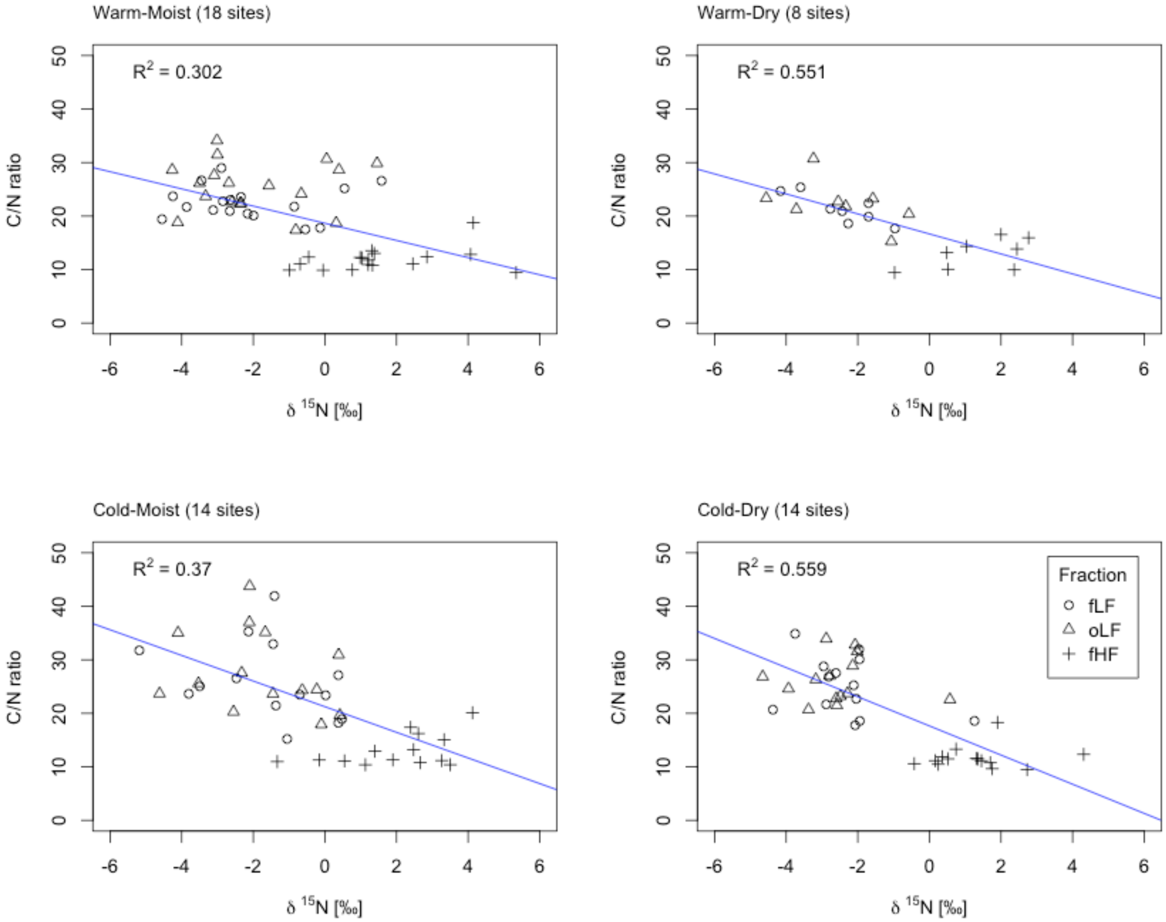


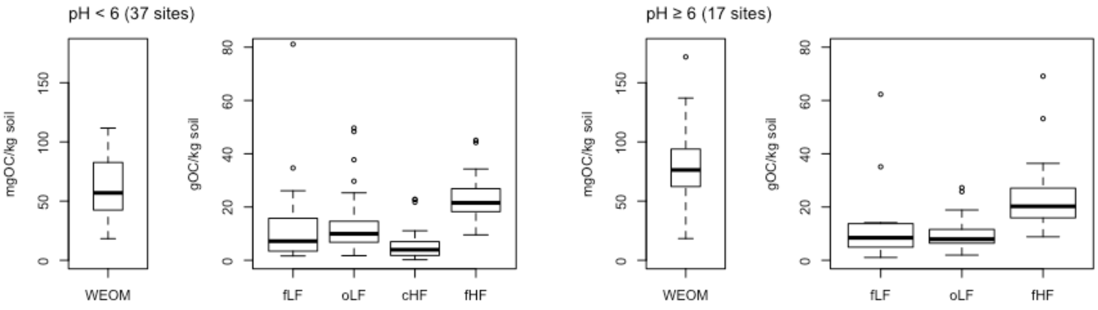
Figure 19: C/N ratio over $\delta^{15}N$ values in ‰ of the fractions fLF, oLF and fHF classified after the four climatic conditions Warm-Moist, Warm-Dry, Cold-Moist and Cold Dry.

In general, the C/N ratios of the light fractions were larger than the C/N ratios of the fHF (Figure 19). The $\delta^{15}N$ values increased from the LFs to the fHF. This indicated a stabilization process towards the fHF in all groups. Furthermore, the samples of the LF and the fHF were spread more in the Cold-Moist climate as for example in the Cold-Dry climatic condition. A shift from the LFs to fHF seemed to be pronounced stronger in dry climates. The R^2 value varied strongly between the climatic conditions – R^2 of 0.3 in the climatic condition Warm-Moist and R^2 of 0.6 in Cold-Dry. The highest R^2 value of the regression was found in the climatic conditions Warm-Dry and Cold-Dry with an R^2 of 0.551 and 0.559, respectively.

4.1.4 Results of the co-variates: clay and pH

All soils were grouped in five clay classes according to their clay content (0 to 10%, 10.1 to 15%, 15.1 to 20%, 20.1 to 30% and >30%) and for the pH in two pH classes (pH higher or lower than 6).
When grouped by pH and clay classes, for all variables (OC, N, $\delta^{13}C$ and $\delta^{15}N$) significant differences between the fractions were found ($p<0.001$; $p<0.01$ for $\delta^{13}C$ in the clay classes). Within all pH and clay classes significantly higher values were stored in the fHF ($p<0.001$).

pH – SOC

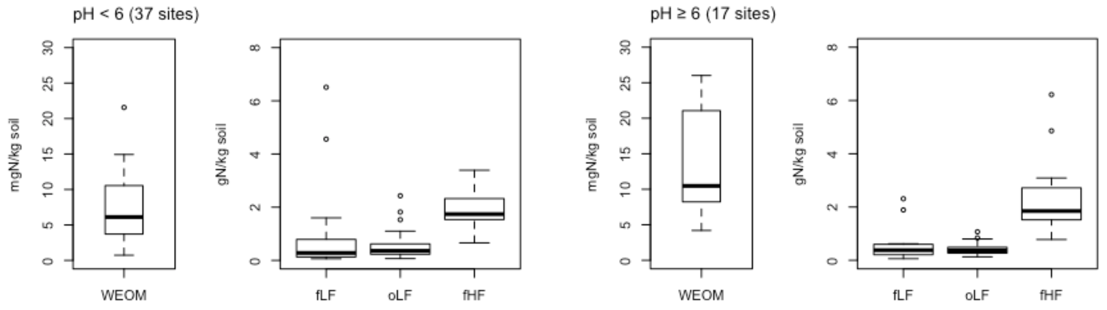


	Between all fractions	Between LF and fHF	Between WEOM	Between classes of all soil fractions	Between soil fractions of classes
pH					
Significance	p<0.001	p<0.001	p<0.05	NS	NS
Direction		fHF: higher OC stocks	higher pH higher WEOC	-	-
Clay					
Significance	p<0.001	p<0.001	NS	Trend	NS
Direction		fHF: higher OC stocks	-	unclear	-

Figure 20: OC values in mgOC/kg soil for the WEOM and in gOC/kg soil for the fLF, oLF, cHF (only for pH values below 6) and fHF classified after two pH classes (pH <6 and pH ≥6). Including a table with indication of the significances and directions of the significant differences for the pH classes and for the clay classes. The values of the sites number 6 and 13 in the fLF were excluded due to very high OC values (over 100 gOC/kg soil).

OC was measured in the fractions fLF, oLF, cHF (only for pH smaller 6) and fHF. Concerning the WEOM values, there were higher values in the group with a pH over 6 (56.9 and 76.2 mgOC/kg soil, respectively; $p<0.05$) Between the two pH groups including the four soil fractions no significant differences were found for the OC stocks of the soil fractions. The median in the fHF was 21.6 gOC/kg in the soils with a pH lower 6, which was similar than in the soils with a pH higher 6 (20.3 gOC/kg, Figure 20). Also, in the light fractions, the soil with pH <6 had similar C contents than in the high pH soils. The results of the cHF were only for illustration but were excluded from the calculation due to the fact that the results of the cHF with a pH ≥6 were missing (destroyed fumigated samples during Picarro measurement). Concerning the clay classes, a trend was found for the OC values between the clay classes. This trend could not be found for the pH classes (see chapter Annex; Figure 31).

pH – Nitrogen



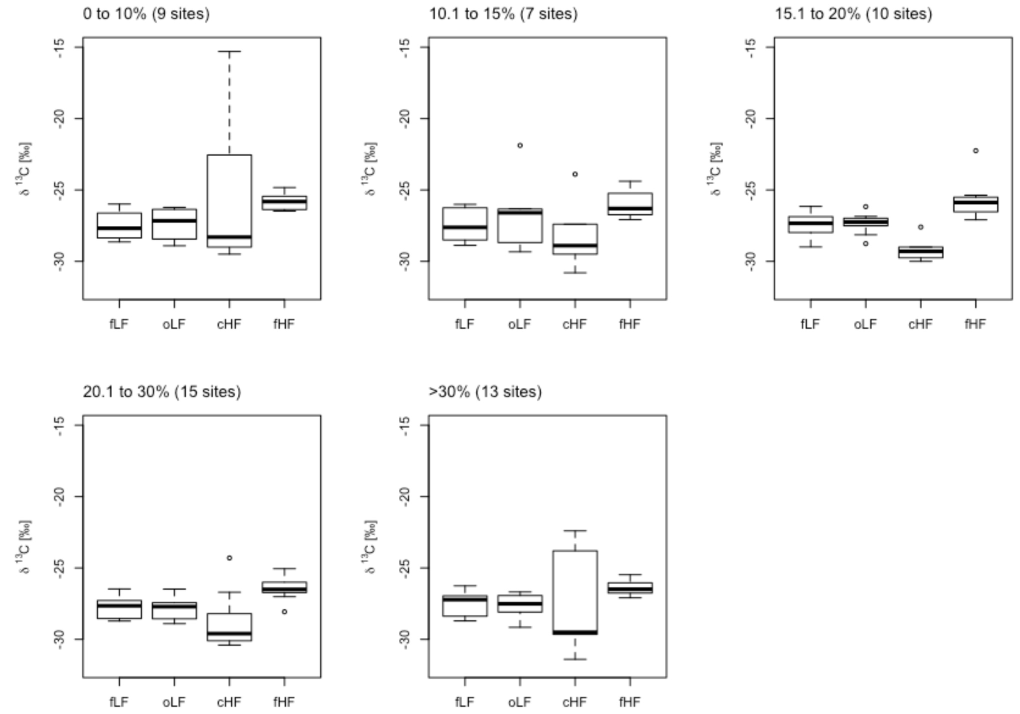
	Between all fractions	Between LF and fHF	Between WEOM	Between classes of all 3 soil fractions	Between 3 soil fractions of classes
pH					
Significance	p<0.001	p<0.001	p<0.001	NS	NS
Direction		fHF: higher N stocks	higher pH higher WEON	-	-
Clay					
Significance	p<0.001	p<0.001	p<0.01	p<0.01	NS
Direction		fHF: higher N stocks	more clay higher WEON	unclear	-

Figure 21: N values in mgN/kg soil for the WEOM and in gN/kg soil for the fLF, oLF and fHF classified after two pH classes (pH <6 and pH ≥6). Including a table with indication of the significances and directions of the significant differences for the pH classes and for the clay classes.

Nitrogen was measured in the fractions fLF, oLF and fHF (Figure 21). A significant difference between the pH classes was found for the WEOM values (p<0.001) with higher WEON contents at higher pH values. Between the two pH groups no significant differences were observed for the four soil fractions. Concerning the N stocks in the clay classes, a significant difference between the clay classes themselves (p<0.01) was found but the direction remained unclear (see chapter Annex; Figure 32).

The N values in the LFs were very similar in both groups and in both pH classes (median between 0.28 and 0.37gN/kg soil)

Clay – δ^{13}C



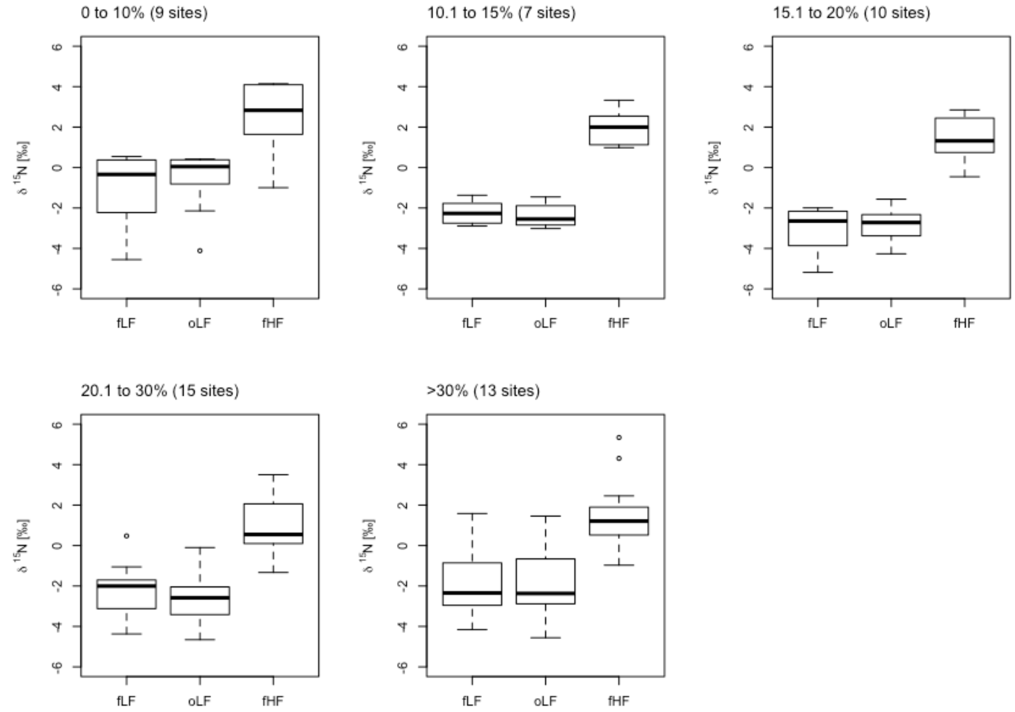
	Between all fractions	Between LF and fHF	Between classes of all 4 soil fractions	Between 4 soil fractions of classes
Clay				
Significance	p<0.01	p<0.001	NS	NS
Direction		fHF: higher δ13C values	-	-
pH				
Significance	p<0.05; p<0.001 without cHF	p<0.01	NS	NS
Direction		fHF: higher δ13C values	-	-

Figure 22: δ^{13}C values in ‰ for the fLF, oLF, cHF and fHF classified after five clay classes (0-10%, 10.1-15%, 15.1%-20%, 20.1-30%, >30%). Including a table with indication of the significances and directions of the significant differences for the pH classes and for the clay classes.

The δ^{13}C values were determined in the fractions fLF, oLF, cHF (with the Picarro) and fHF. No significant differences were found between the clay groups (and the pH groups) for the δ^{13}C values of the soil fractions (Figure 22). The cHF samples showed the lowest δ^{13}C values (medians between -29.6 to -28.3‰). Especially in the clay group 0 to 10% and >30% the range of the cHF results was very high.

Concerning the pH groups, no further differences were found (see Annex, Figure 33).

Clay – $\delta^{15}N$



	Between all fractions	Between LF and fHF	Between classes of all 3 soil fractions	Between 3 soil fractions of classes
Clay				
Significance	p<0.001	p<0.001	p<0.001	NS
Direction		fHF: higher δ15N values	clay amount under 10% led to higher δ15N values	-
pH				
Significance	p<0.001	p<0.001	p<0.01	NS
Direction		fHF: higher δ15N values	higher pH lower δ15N values	-

Figure 23: $\delta^{15}N$ values in ‰ for the fLF, oLF and fHF classified after five clay classes (0-10%, 10.1-15%, 15.1%-20%, 20.1-30%, >30%). Including a table with indication of the significances and directions of the significant differences for the pH classes and for the clay classes.

For the $\delta^{15}N$ values, significant differences were found between the clay groups ($p<0.001$; Figure 23). This difference is especially pronounced in the clay class 0 to 10%. A clay amount under 10% led to higher $\delta^{15}N$ values. No significant differences were found between the interaction of the fractions and the groups. Considering the pH, significant differences between the two pH groups were found ($p<0.01$; see Annex; Figure 34).

Correlation clay content – relative mass fHF

To determine the influence of the clay content on the fHF a correlation between clay content (%) and the relative mass of the fHF (%) was done (Figure 24).

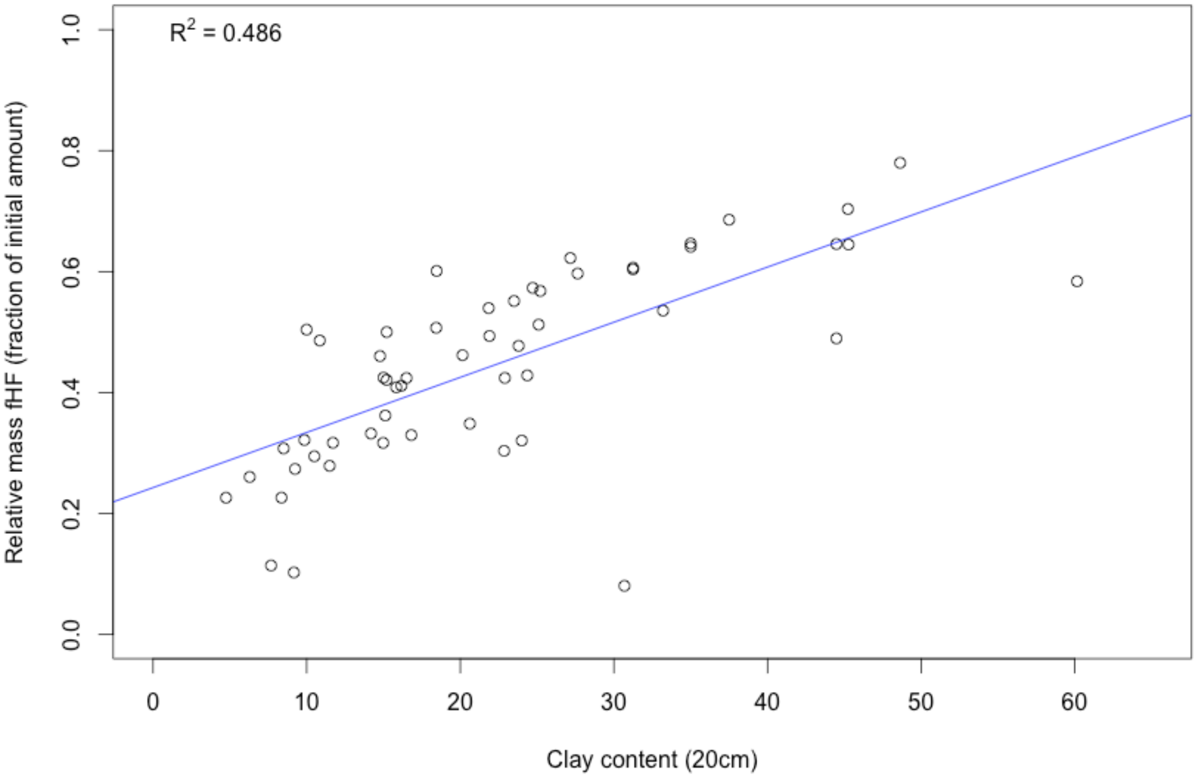


Figure 24: Correlation of clay in % and relative mass of fHF in fraction of the initial amount.

In general, soil texture showed a strong influence on the relative mass of the fHF. The more clay content inside the fHF was the higher the mass of the fHF got. The correlation was very strong with an R^2 = 0.486.

4.1.5 Results of the co-variates: aspect and slope

The second co-variate included covers terrain characteristics. It contains the parameters aspect and slope. Due to lack of statistical significance and relevance of the terrain characteristics in this analysis, it will not be discussed further in this MSc thesis.

The most important results regarding the fresh sites classified after the main drivers and the co-variates are summarized as follows:

- Relative mass of the HF was much higher and showed much higher variation than the relative mass of the LF.
- Region:
  - Midland: In all fractions except WEOM the lowest OC values
  - Midland: Lowest OC stocks in bulk soil
  - Southern Alps: Highest OC stocks in bulk soil and in LFs
- Across all factors highest organic C, N, $\delta^{13}C$ and $\delta^{15}N$ values were stored in the fHF ($p<0.001$), followed by the LF and the cHF.
- Climate: Colder climatic conditions led to higher (less negative) $\delta^{13}C$ values ($p<0.01$).
- Soil properties:
  - Higher pH values led to higher WEOC values ($p<0.05$) and WEON values ($p<0.001$).
  - Clay amounts under 10% led to higher $\delta^{15}N$ values ($p<0.001$)
  - Higher pH values led to lower $\delta^{15}N$ values ($p<0.01$)
- A shift from a large C/N ratio associated with the LF to a small C/N ratio associated with the fHF is there, but the phenomenon is not equally pronounced.
  - The shift from LF to fHF was best pronounced in dry climates
- Positive correlation ($R^2 = 0.486$) between mass distribution of the fHF an the clay content

4.2 Effects on SOM: multiple linear regression analysis

To analyse and assess the influence of all considered factors (temperature, moisture, soil properties, terrain characteristics and regions) on SOM vulnerability a multiple linear regression model was used. The results of the multiple linear regression are presented in the following sections.

SOC

The factor soil properties was the factor with the highest influence on the OC stocks. Soil properties mainly influenced the OC stocks in the fLF, the fHF and the WEOM ($p<0.05$ for all). This means that soil properties with a high clay content and high pH led to higher OC stocks in the fHF and the WEOM (fHF: correlation of R^2 0.09, $p<0.05$; WEOM correlation of R^2 0.13, $p<0.01$). This correlation could not be found for the fLF, indicating that the OC values in the fLF did not change in a linear direction. The influence of the soil properties on OC stocks in the fLF and the fHF were not found before, when the soil properties were analysed separately (clay and pH separate). It is very likely, that this influence of the soil properties that was found in the multiple linear regression model is because of the combination of clay and the pH to one factor called soil properties (pco1). This combination seemed to strengthen the influence of the soil properties on the OC stocks. The factor terrain characteristics showed no influence on the OC stocks.

The factor region tended to influence the WEOM values (Table 4). The factor temperature showed a trend in the fraction cHF, indicating that colder climatic conditions led to higher OC contents (trend). The factor moisture tended to indicate that dry climatic conditions led to low OC stocks (trend) and moist climatic conditions led to higher OC stocks (trend).

To summarize: soil properties determined the stocks of OC.

Table 4: Multiple linear regression results for organic C for the fractions fLF, oLF, cHF, fHF and WEOM. The sites 6, 13 and 46 were excluded from the fLF calculations. Trend: p<0.1.

Factors	fLF	oLF	cHF	fHF	WEOM
Region	NS	NS	NS	NS	Trend
Temperature	NS	NS	Trend	NS	NS
Moisture	Trend	NS	NS	NS	NS
Soil properties	$p<0.05$	NS	NS	$p<0.05$	$p<0.05$
Terrain	NS	NS	NS	NS	NS

$\delta^{13}C$

The factors moisture and terrain characteristics showed no influence on the $\delta^{13}C$ values (Table 5) (only a trend for moisture). The soil properties were influencing the values of $\delta^{13}C$ in the fHF ($p<0.05$). There, it seemed that higher clay and pH values led to lower (more negative) $\delta^{13}C$ values in the fHF. However, the correlation of fHF and soil properties was not significant.

The factors region and temperature were both determining the values of $\delta^{13}C$ in the fLF and the fHF. Concerning the fHF significant higher $\delta^{13}C$ values in the region Alpine as in Midland ($p<0.01$) and as in the Pre-Alps ($p<0.01$) were found. For the fLF significant higher $\delta^{13}C$ values were found in the region Alpine than in Jura ($p<0.05$) and in Midland ($p<0.01$). Therefore, $\delta^{13}C$ values in the fLF and the fHF were highest in the region Alpine.

Concerning the factor temperature colder climatic conditions led to higher (less negative) $\delta^{13}C$ values in the fLF ($p<0.01$) and in the fHF ($p<0.05$).

In the section before, a significant influence of the climatic conditions on the $\delta^{13}C$ value was found. With this multiple linear regression model, it could be seen that the main influence comes from the factor temperature and controls the fLF and the fHF.

The influence of the soil properties on $\delta^{13}C$ values in the fHF was also not found before when the soil properties were analysed separately (clay and pH separate). Also here, the combination of clay and pH seemed to strengthen the influence of the soil properties on the $\delta^{13}C$ values.

Table 5: Multiple linear regression results for $\delta^{13}C$ values for the fractions fLF, oLF, cHF and fHF. The sites 6, 13 and 46 were excluded from the fLF calculations. Trend: p<0.1.

Factors	fLF	oLF	cHF	fHF
Region	p<0.05	Trend	NS	p<0.01
Temperature	p<0.01	NS	NS	p<0.05
Moisture	NS	NS	Trend	NS
Soil properties	NS	NS	NS	p<0.05
Terrain	NS	NS	NS	NS

Nitrogen

The factors region, temperature, moisture and terrain characteristics showed no influence on the N stocks in all fractions (Table 6). Same as for the OC, the main influence on the stocks of N in the fractions fHF ($p<0.001$) and WEOM ($p<0.001$) was determined by the factor soil properties. A higher clay content and a higher pH value led to higher N stocks in the fHF and to higher WEOM stocks (fHF: correlation with R^2 0.22, $p<0.001$; WEOM correlation with R^2 0.19, $p<0.001$).

In the sections before, only a significant influence of the clay classes on the N stocks could be found ($p<0.01$). In the combination with the pH values, the influence of the soil properties on nitrogen stocks was even stronger.

To summarize: soil properties determined the stocks of N.

Table 6: Multiple linear regression results for nitrogen for the fractions fLF, oLF, fHF and WEOM. The sites 6, 13 and 46 were excluded from the fLF calculations. Trend: p<0.1.

Factors	fLF	oLF	fHF	WEOM
Region	NS	NS	NS	NS
Temperature	NS	NS	NS	NS
Moisture	NS	NS	NS	NS
Soil properties	NS	NS	p<0.001	p<0.001
Terrain	NS	NS	NS	NS

$\delta^{15}N$

For the $\delta^{15}N$ values only the factor region determined the stocks in the oLF (Table 7).

Table 7: Multiple linear regression results for $\delta^{15}N$ values for the fractions fLF, oLF and fHF. The sites 6, 13 and 46 were excluded from the fLF calculations. Trend: p<0.1.

Factors	fLF	oLF	fHF
Region	Trend	p<0.05	NS
Temperature	NS	NS	NS
Moisture	NS	NS	NS
Soil properties	NS	NS	NS
Terrain	NS	NS	NS

C/N ratio

In the analysis of the C/N ratio the terrain characteristics showed no influence (Table 8). The temperature turned out to be a trend for the fLF. The factor moisture had a significant influence on the C/N ratio of the oLF. The moister a climate, the lower was the observed C/N ratio.

The factor region defined the C/N ratio for the oLF and the fHF ($p<0.05$ for both). A significant difference between the region Southern Alps and Jura ($p<0.05$) and Southern Alps and Midland ($p<0.01$) was found for the fHF (with significantly higher values in the Southern Alps for both). For the oLF a significant difference between the region Southern Alps and Alpine ($p<0.05$) was observed with lower values in the Southern Alps.

The factor soil properties also defined the C/N distribution in the fHF ($p<0.001$) and the WEOM ($p<0.001$) with the direction: the higher the clay content and the pH value the lower the C/N ratio. (fHF: correlation with R^2 = 0.24, $p<0.001$; WEOM correlation with R^2 = 0.14, $p<0.01$)

Table 8: Multiple linear regression results for the C/N ratio for the fractions fLF, oLF, fHF and WEOM. The sites 6, 13 and 46 were excluded from the fLF calculations. Trend: $p<0.1$.

Factors	fLF	oLF	fHF	WEOM
Region	NS	p<0.05	p<0.05	p<0.05
Temperature	Trend	NS	NS	NS
Moisture	NS	p<0.05	NS	NS
Soil properties	NS	NS	p<0.001	p<0.001
Terrain	NS	NS	NS	NS

The most important results regarding the multiple linear regression are summarized as follows:

- Over all the soil properties showed the highest influence on OC, N and C/N ratio.
- SOC
  - Soil properties determined the stocks of OC in the fLF, fHF and WEOM ($p<0.05$). → Soil properties with a high clay content and a high pH value led to higher OC stocks in the fHF and the WEOM (fHF: correlation with $R^2 = 0.09$, $p<0.05$; WEOM correlation with $R^2 = 0.13$, $p<0.01$)
- $\delta^{13}C$
  - Soil properties influenced the values of $\delta^{13}C$ in the fHF ($p<0.05$). → Higher clay and pH values led to lower (more negative) $\delta^{13}C$ values (no significant correlation)
  - Colder climatic conditions led to higher (less negative) $\delta^{13}C$ values in the fLF ($p<0.01$) and in the fHF ($p<0.05$).
  - The factor region determined the values of $\delta^{13}C$ in the fLF and the fHF. $\delta^{13}C$ values in the fLF and the fHF were highest in the region Alpine.
- Nitrogen
  - Soil properties determined the N stocks in the fHF ($p<0.001$) and the WEOM ($p<0.001$). → Higher clay and pH values led to higher N stocks in the fHF and WEOM (fHF: correlation with $R^2 = 0.22$, $p<0.001$; WEOM correlation with $R^2 = 0.19$, $p<0.001$).
- $\delta^{15}N$
  - The factor region determined the $\delta^{15}N$ values in the oLF ($p<0.05$).
- C/N ratio
  - Soil properties determined the C/N ratio in the fHF and WEOM ($p<0.001$). → Higher clay contents and higher pH values led to lower C/N ratios in the fHF and the WEOM (fHF: correlation of R^2 0.24, $p<0.001$; WEOM correlation of R^2 0.14, $p<0.01$)
  - A moister climate led to a lower C/N ratio of the oLF.
  - Regions: effect on oLF, fHF and WEOM (both $p<0.05$).

4.3 Relative stability

The relative stability was calculated for all fresh sites (see calculation details in section 3.3.4). Table 9 shows the relative stabilities grouped after the five Swiss productive regions.

Table 9: Relative stability LF:fHF for each region.

Region	Content (gOC/kg soil)		δ15N (‰)		C/N ratio		Average relative age
	LF	fHF	LF	fHF	LF	fHF	LF:fHF
Jura	10.4	30.2	-4.7	0.9	25.0	11.6	161
Midland	10.0	20.4	-4.9	1.5	24.6	11.2	247
Pre-Alps	17.2	21.4	5.4	1.3	27.1	12.7	157
Alpine	14.1	21.3	-3.9	1.8	29.0	12.8	136
Southern Alps	11.2	28.6	-0.7	3.0	21.8	14.9	35

A large relative age difference between the productive regions varying between relative ages of 35 to 247 was found. The C stored in the fHF of the Southern Alps was in general 35 times older than in the LF. The highest difference was found in the region Midland where the C stored in the fHF is about 247 times older than in the LF. The relative ages of the region Jura, Pre-Alps and Alpine are in-between, with relative ages of 161, 157 and 136.

This high difference between the relative ages in the regions is supported by the results of the multiple linear regression of the C/N ratio, were a significant difference in the regions for the oLF and the fHF was found.

Different than in the table above, the relative ages classified by climatic conditions did not vary that much (Table 10). The relative ages were lowest in the climatic condition Cold-Dry (fHF is 145 times older than the LF) and highest in the climatic condition Warm-Dry (fHF is 193 times older than the LF). A trend might be seen towards higher ages with increasing temperature and moisture.

Table 10: Relative stability LF:fHF for the climatic conditions.

Climatic Condition	Content (gOC/kg soil)		δ15N (‰)		C/N ratio		Relative age
	LF	fHF	LF	fHF	LF	fHF	LF:fHF
Cold-Dry	14.1	24.7	-4.8	1.3	26.2	11.7	145
Cold-Moist	11.6	24.8	-3.3	2	27.8	13	152
Warm-Dry	13.1	20.8	-4.9	1.3	22.4	13.1	168
Warm-Moist	11.4	23.02	-4.2	1.5	25.5	11.9	193

The correlation of the soil properties clay and pH with the relative age is depicted in Figure 25. With an increase in clay and pH value (increase in soil properties) the relative ages decreased (but this effect is not significant).

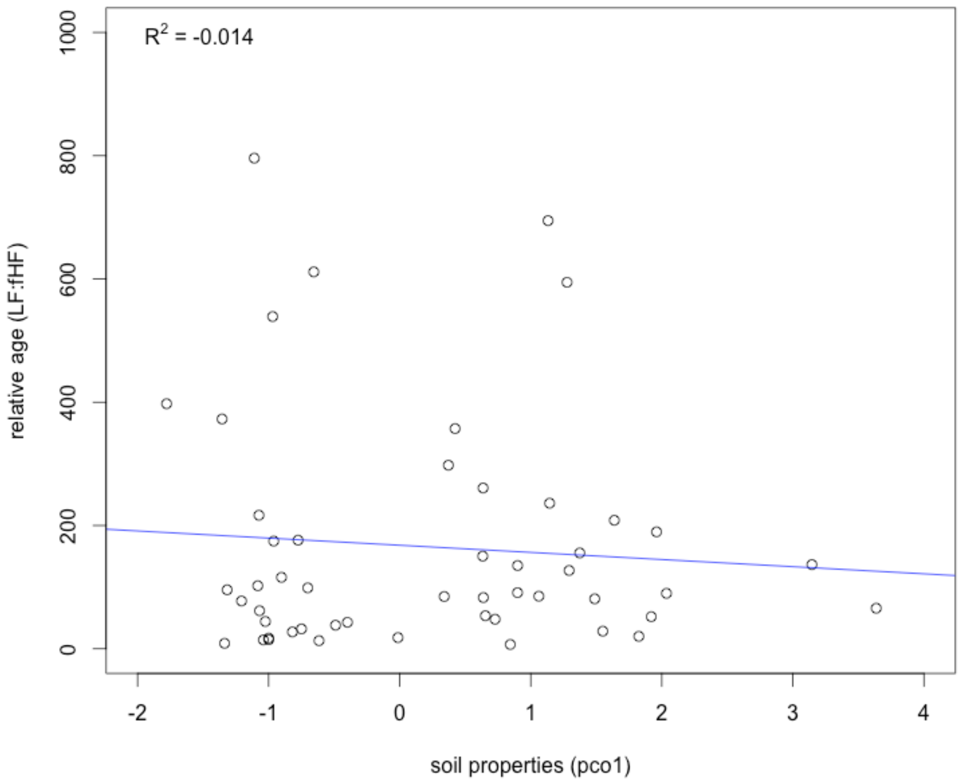


Figure 25: Correlation between soil properties (pco1) and relative age (LF:fHF).

The most important results regarding the relative stability are summarized as follows:

- In general, the fHF seemed to be older than the LF
- The region Midland was characterized by higher relative age differences between the LF and the fHF (fHF is 247 times older than the LF) as the other regions
- Differences in relative age between climatic conditions were less pronounced. A trend from cold and dry to warm and moist with increasing relative ages can be interpreted
- With increasing clay and pH values (soil properties, pco1) the relative ages decreased (but not significantly)

4.4 Time-driven results – archive samples

In the following section, the results of the archive sites are presented. To proper estimates the differences between the archive and the fresh samples, also the corresponding twelve fresh sites are presented.

4.4.1 Density fractionation – mass distribution of archive samples

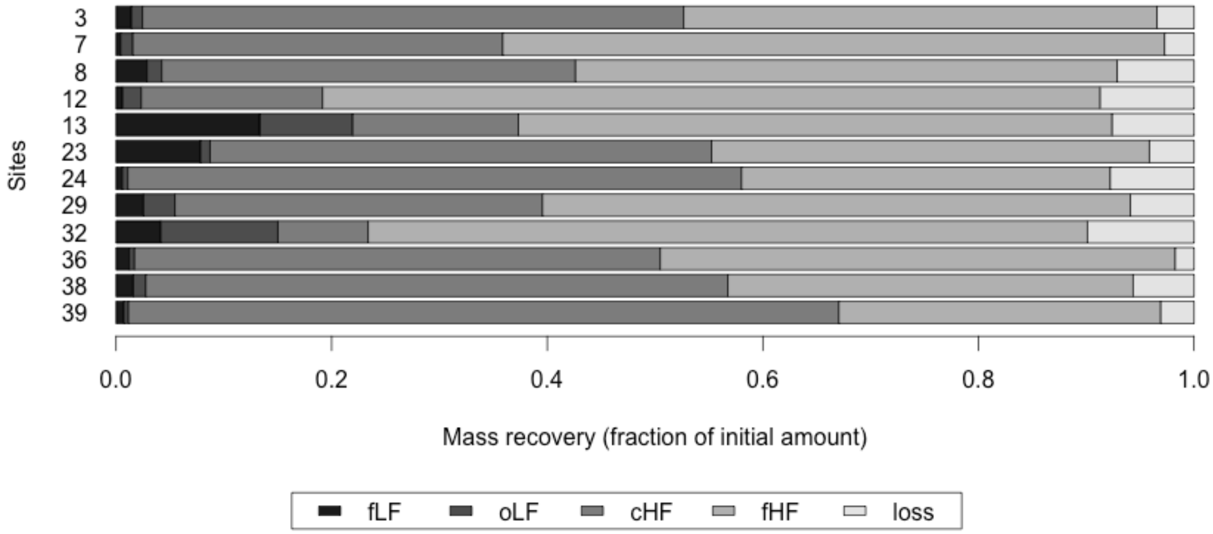
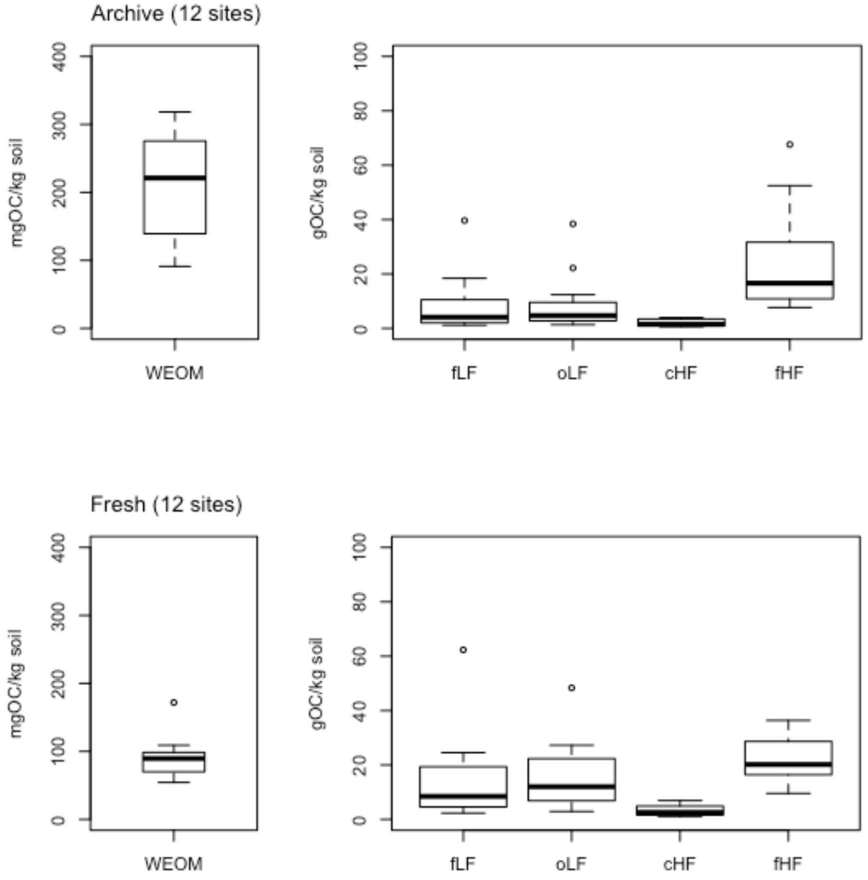


Figure 26: Mass distribution of density fractionation with twelve archive sites.

The mass recovery after density fractionation of the twelve archive samples was in average 94.3 ± 2.6%. After density fractionation the mass of all fractions was set into relation to the initial amount of weighing. Figure 26 shows the relative mass of all twelve archive sites.

In general, it is characteristic for the fLF and the oLF that they have a very low mass. In average, the values of the fLF and oLF are 3.1 ± 3.8% and 2.6 ± 3.4%, respectively. The cHF as well as the fHF had a much higher relative mass than the light fractions. The values of the heavy fractions were on average 39.1 ± 18.0% for the cHF and 49.5 ± 13.0% for the fHF.

4.4.2 Results of the archive samples



	Between all fractions	Between WEOM	Between archive and fresh of all 4 soil fractions	Between 4 soil fractions of groups
Origin				
Significance	p<0.001	p<0.001	NS	NS
Direction		younger soil samples lower WEOC	-	-

Figure 27: OC values in mgOC/kg soil for the WEOM and in gOC/kg soil for the fLF, oLF, cHF and fHF classified after fresh and archive sites. Including two tables with indication of the significances and directions of the significant differences.

Figure 27 shows the organic carbon stocks for the twelve archive sites as well as for the corresponding twelve fresh sites. There was a significant reduction (p<0.001) of the WEOM values from the old archive samples (with median of 221 mgOC/kg soil) to the younger fresh samples (with a median of 90 mgOC/kg soil). Differences in the median of the OC value of the four soil fractions were not that obvious. Still, some changes in the range of the OC values were recognisable.

4.4.3 C-loss over time

To calculate the loss of SOC over time, the difference between the SOC value of the fresh sample and the archive samples was calculated and divided by the number of years between the sampling date of the fresh and the archive samples. The archive samples are on average 19.4 years older than the fresh samples. Despite the different storage methods (dry storage of archive samples vs. fresh samples) an average stock change for the WEOM of -6.92 mgOC/kg soil per year (Figure 28) was calculated. For the four soil fractions the stock changes per year are also presented in the table below (Table 11).

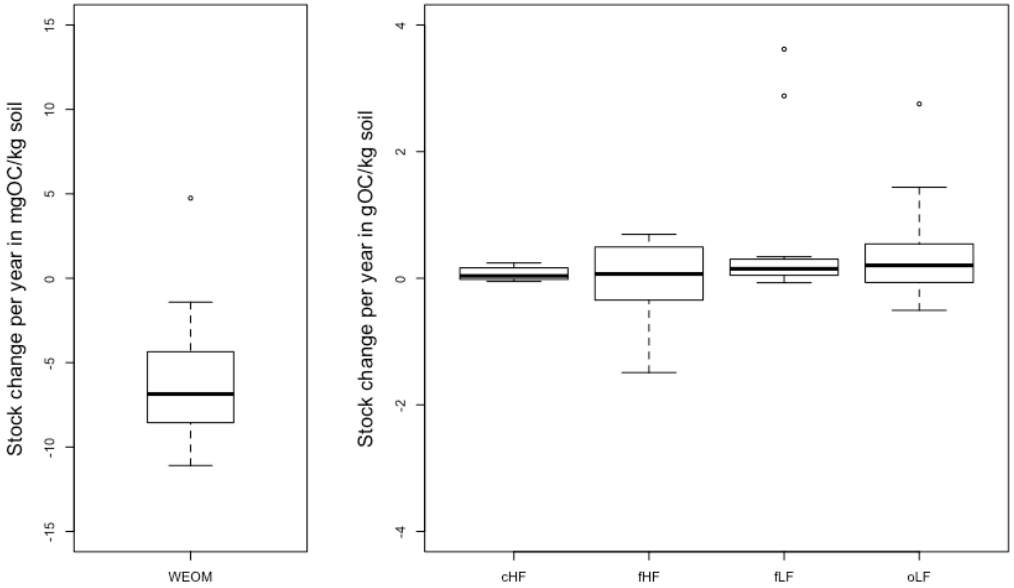


Figure 28: Stock change (fresh minus archive values divided by amount of years) of OC in the fractions WEOM (in mgOC/kg soil per year) and fLF, oLF, cHF and fHF (in gOC/kg soil per year). Site number 13 in the WEOM data with a value of -22.46 mgOC/kg soil per year is not represented in the figure.

Table 11: Stock change of OC in g/kg soil per fraction per year.

Soil Fraction	Fraction	SOC stock change g/kg soil per year
fLF	11	+0.69
oLF	12	+0.44
cHF	6	+0.07
fHF	12	-0.05
Total		+1.14

Considering those twelve archive sites with the corresponding fresh sites, on average, 1.14 g OC/kg soil per year were gained, which corresponds to a 0.1% increase per year. This gain is mainly caused by the gain in the fLF, the oLF and a small gain in the cHF. The highest stock change was reached in the fLF with a value of 0.69 g OC/kg soil per year. A reduction in the stock change was only found in the fHF with a loss of 0.05 gOC/kg soil per year.

The strongest pronounced reduction could be found in the average stock change of the WEOC with a reduction of -6.92 mgOC/kg soil per year. For further statistical analysis (e.g. multiple linear regression) the number of sites is too small.

The most important results regarding archive and fresh sites are summarized as follows:

- WEOM: Lower OC stocks in the younger (fresh) samples ($p<0.001$)
- fLF, oLF and cHF: OC stocks slightly increased to the younger (fresh) samples (zero to positive stock change per fraction per year)
- fHF: OC stocks slightly decreased to younger (fresh) samples (zero to negative stock change per fraction per year)
- Strongest pronounced stock change: Average stock change of WEOC: -6.92 mg OC/kg soil per year
- Average stock change of +1.14 g OC/kg soil per year over all twelve sites

5. Discussion

5.1 Discussion of space-driven results

5.1.1 Soil properties are driving SOC storage

General pattern The results showed that the fractions of SOM are sensitive to site characteristics like soil texture, which corresponds to other studies (e.g. Schrumpf et al., 2013). In general, the C contents of the LFs were higher compared to the HFs and varied between 9 to 50% (HFs between 0.1 to 14%), which is in line with the 10 to 31% for the LFs and 0.5 to 4% for the HFs observed in a lysimeter study of Gunina & Kuzyakov (2014). The only deviation is that the C contents of the LFs and the HFs reached higher maximum values in this MSc thesis. This could be explained through differences in study type. In this thesis, only forest sites were included combined with a high variation in study sites. Gunina & Kuzyakov (2014) conducted an experimental study with open lysimeters (installed in 1965) and plant communities of coniferous and deciduous forest plots as well as arable and grassland plots located in Moscow. This difference could have resulted in a higher variation in C contents in this MSc thesis.

Effect on vulnerability Soil properties were found to be the main drivers of the storage of OC in Swiss forest mineral soils, while temperature, moisture, terrain characteristics and the Swiss regions were less important. Especially temperature and moisture showed no effect on the OC stocks in the soil fractions studied. These findings are not completely in agreement with the review conducted by Schmidt et al. (2011). Environmental and biological factors do control the SOM stability, but the results indicated that not the climate is the most crucial factor for the storage of OC in the soil fractions but the soil properties.

In this MSc thesis, within the first 20cm, the soil properties (clay and pH) influenced the fLF, fHF and WEOM significantly and led to higher OC stocks in the fHF and WEOM with increasing clay and pH values (significant correlations). This is in line with the meta-analysis by Paul et al. (2002) including 204 sites from different countries (e.g. Australia, Germany, India, Sweden, United States etc.) of 43 studies. The authors observed that the soil texture had a strong influence on the dynamics of SOM. They found that with increasing clay content in the first 10cm, the C stocks decreased, but including depths of more than 10cm or up to 30cm, the C stocks increased with increasing clay contents. Further, the correlated accumulation of SOC with increasing clay amounts found in this thesis is in agreement with the findings in the review by Lugo et al. (1986). The authors reported that an accumulation of SOC correlated inversely with the amount of sand in the soil. Furthermore, they concluded that especially the relation between SOC accumulation and soil texture is strongest in soils with high SOC contents (Lugo et al., 1986). Such positive relationship of SOC in soil fractions with clay contents can be attributed to the high surface area of such soil particles, which enhances bindings between mineral surfaces and organic compounds (Grigal & Berguson, 1998; Paul et al., 2002). Due to such associations SOM is strongly protected against decomposition in clay-rich soils (Ladd et al., 1985; Sorensen 1981), and is therefore less vulnerable.

In this regard, Kaiser and Guggenberger (2000) found that the concentration of binding between soil organic matter and mineral surfaces as well as the sorption process of DOM are connected to so-called reactive mineral phases. This applies for example for Al or for Fe oxyhydroxides, which was also found by Schrumpf et al. (2013). Furthermore, also in the study of Kögel-Knabner et al. (2008) it was indicated that in all soils investigated, especially the Fe oxides, were most important for the long-term preservation of OC.

Concerning the fLF, the results of this MSc thesis showed that the soil properties had a significant effect on the OC stocks in the fLF but no correlation was found between the fLF and clay content as well as between the fLF and the soil properties (including pH value). However in the investigation of twelve study sites, an effect of higher clay contents leading to higher OC stocks in the HFs was found in the study of Schrumpf et al.

(2013). The authors further concluded that higher clay contents led to lower OC stocks in the LFs. Therefore, with the inclusion of more data in this thesis, this effect on the LFs was no longer visible.

Furthermore, the results of this MSc thesis indicated that the combination of clay and pH contents seemed to strengthen the influence on the OC stocks rather than the clay content or pH content alone. Therefore, the factor soil properties (consistency of clay and pH) predominantly determines the vulnerability of SOC rather than clay or pH alone.

5.1.2 Soil properties have a primary effect on decomposition (C/N ratio and isotopes)

General pattern (C/N ratio) Almost the same effect as for the OC was found for the N stocks in the soil fractions. The soil properties determined the N stocks in the fractions fHF and WEOM, while an influence of temperature, moisture, terrain characteristics and the five Swiss regions was not observed. In general, C/N ratios are often the parameters used to assess the state of decomposition and therefore the stability (e.g. Gunina & Kuzyakov, 2014; Schrumpf et al., 2013; von Lützow et al., 2006).

In this MSc thesis, the C/N ratio of soil fractions decreased from the LFs to the fHF (Figure 29) indicating a progressive degradation of OC. These findings are in line with previous studies of Gunina & Kuzyakov (2014) and Schrumpf et al. (2013). Schrumpf et al. (2013) also found a significant reduction of the C/N ratio from fLF to HF in depths to 5cm, which is also in line with Poirier et al. (2005) who explained that OC in HFs is more decomposed than the OC in the LFs. Additionally, the contribution of microbial derived OC is higher in the HFs than in the LFs (Poirier et al., 2005).

While the fLF and the oLF had an average C/N ratio of 23.9 and 25.8, respectively, the fHF had an average C/N ratio of 12.3 (Figure 29). This is in line with the study by Tan et al. (2007) concerning the distribution of light and heavy fractions of SOC. They described an average C/N ratio in forest soil of 22.1 and 8.8 for the LF and the HF, respectively. Very similar results were found in the study of Schrumpf et al. (2013) with an average C/N ratio in the fLF and the oLF of 28 and 24, respectively. The C/N ratio of the HF was indicated with an average value of 14. This validates the found results, indicating that more decomposed fractions have lower C/N ratios

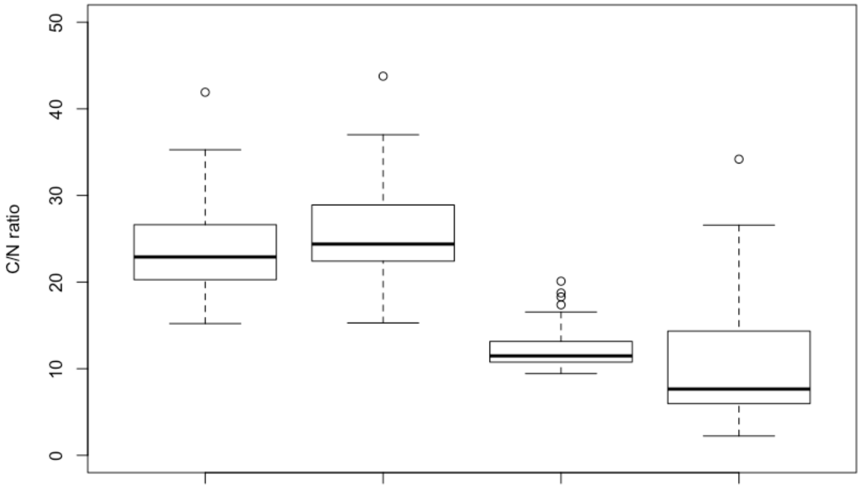


Figure 29: C/N ratio in all soil fractions and WEOM.

General effects on vulnerability (C/N ratio) Surprisingly, the C/N ratios of the oLFs were slightly higher than those of the fLFs. Further, it is very likely that the LF samples (which represents material from the mineral soil) already experienced decomposition processes in the O horizon. For instance, freshly fallen leaves usually have C/N ratios above 30 (Brady & Weil, 2007). The C/N ratio (in this case in the LFs) generally represents the quality of the litter coming from trees (Côté et al., 2000). But due to the fact that degradation through microorganisms starts as soon as organic material comes into contact with the soil (Kammer & Hagedorn, 2011) the C/N ratio in the litter and or O horizon is in general higher than in the more processed and already decomposed SOM in deeper horizons (Manzoni et al., 2010). With the use of an extended stoichiometric model of the mineralization of nitrogen Manzoni et al. (2010) further indicated that nitrogen tended to be immobilized at the beginning of decomposition.

The observed lower C/N ratio in the fHF can be connected to more processed material due to microbial decomposition and therefore considered more stable (Conen et al., 2008). The lowest C/N ratios were reached in the WEOM, where the median was even lower than in the fHF. Kalbitz and Kaiser (2008) concluded that dissolved organic matter (DOC) is very important for the transportation of C into the mineral soil. Thus, the DOC is either adsorbed onto the surface of minerals or immobilized through microbes. Therefore, the low values of the WEOM could be explained with microbial derived compounds. Similar results were found in a study of the characteristics of WEOM during composting by Said-Pullicino et al. (2006) where more mature compost showed lower WEOC/ON ratios (values below 10 after 25 days of composting) than fresh compost with a value of 26.8. But it might also be possible that the WEOM contained inorganic N (e.g. NH_4, NO_3). Therefore, the low C/N ratios could have been favoured through such inorganic compounds (Curtin et al., 2006).

Effects of soil properties on vulnerability (C/N ratio) The C/N ratio was mainly driven by the factors soil properties, region and moisture. The finding that the C/N ratio in the fHF decreased with higher clay contents and pH values indicated that clay promotes the binding of OC on mineral surfaces, particularly of strongly transformed SOM. This is in line with Velde and Barré (2010) who concluded that the better the aggregation of organic material or the interaction of organic matter with mineral surfaces, the higher is the protection against further degradation, therefore the less vulnerable SOM reacts. Therefore, a higher clay content promotes the binding of OC on mineral surfaces and with this, the SOM in these fractions reacts less vulnerably.

Effects of regionality on vulnerability (C/N ratio) The factor region had also an effect on the C/N ratio in the oLF, the fHF and the WEOM. The C/N ratio, especially in the LFs, is influenced through the material from trees that is available, e.g. coniferous trees generally have a higher C/N ratio than deciduous trees (Gunina & Kuzyakov, 2014). Furthermore, the quality of litter affects the microbial community and therefore determines the C/N ratio of SOM in forest soils (Côté et al., 2000). To understand the influence of the region, it is necessary to take a closer look at the five Swiss regions. Schwaab et al. (2015) described the five Swiss productive regions and its biogeographical features as follows:

- Jura: oceanic low mountain range, average elevation: 800 m a.s.l.
- Swiss plateau (Midland): oceanic low-lands, average elevation: 550 m a.s.l.
- Northern Pre-Alps (Pre-Alps): subalpine mountain range, oceanic, average elevation: 1400 m a.s.l.
- Central Alps (Alpine): continental alpine mountain range, average elevation: 2150 m a.s.l.
- Southern Pre-Alps (Southern Alps): Mediterranean/Insubric line subalpine mountain range, average elevation: 1500 m a.s.l.

In this MSc thesis, the fHF in the Southern Alps in particular had significantly higher values than in the region Midland ($p<0.01$) and in the region Jura ($p<0.05$) (Figure 30). A possible explanation for these differences could be found in the influence of the vegetation. Different vegetation types can lead to different C/N ratios in the soil (Schwaab et al., 2015). In each of the five Swiss regions, mixed deciduous forests and deciduous forests are dominant at low elevations with generally Fagus sylvatica occurring (Schwaab et al., 2015). At higher elevations, mainly the Picea abies species occurs – and with this coniferous forests are dominant (Schwaab et al., 2015). Côté et al. (2000) also support this approach and concluded that the SOM quality in forest soil for the mineralization of C and N is not only influenced by soil type but also by stand type and stand age (Côté et al., 2000).

The results are further in agreement with the study by Eckmeier et al. (2010) concerning the accumulation of organic matter in the Southern Alps. The authors concluded that the Southern Alps provide very good conditions for the stabilization processes of SOM through organo-mineral associations especially through Fe- and Al-oxides (Eckmeier et al., 2010).

In the oLF the Southern Alps had significantly lower C/N values than in the region Alpine ($p<0.05$).

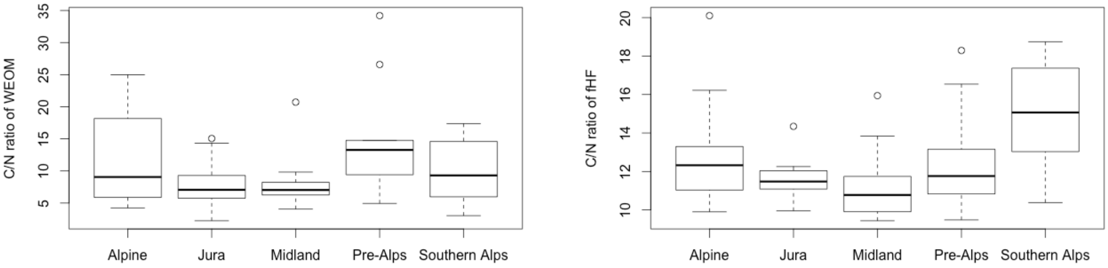


Figure 30: C/N ratio of WEOM for all five Swiss regions (left) and C/N ratio of fHF for all five Swiss regions (right).

Effects of moisture on vulnerability (C/N ratio) The factor moisture influences the dynamics of the C/N ratio in the oLF. The moister the climate, the lower became the C/N ratio in the oLF.

General pattern (δ^{13}C and δ^{15}N) The results of this MSc thesis showed that again the soil properties influence the values of δ^{13}C in the fHF. These results are in line with Schrumpf et al. (2013). In this MSc thesis, the lowest δ^{13}C values were observed in the cHF with an average of about -27.3‰ over all fresh sites, while for example in the fHF an average of -26.1‰ was found. These lower values could probably be attributed to products in needles of coniferous such as lipids or lignin (Gleixner et al., 1993). Such products can be depleted in ^{13}C by 1 or 2‰ (Gleixner et al., 1993).

Effects on vulnerability (δ^{13}C and δ^{15}N) The observation that δ^{13}C values increased from the LFs to the fHF and that the soil properties were mainly influencing the values in the fHF are in line with the study of Gunina & Kuzyakov (2014). They related the increase in δ^{13}C values from the fLF towards the heavier fractions to the bindings of more processed OC, reflecting the flow of C from the LF to the HF (Gunina & Kuzyakov, 2014). This pattern is also supported by Schrumpf et al. (2013), where the LFs were also characterized by lower δ^{13}C values and the opposite for the HFs.

Colder climatic conditions led to higher (more positive) δ^{13}C values in the fLF and in the fHF. This effect is probably connected to differences in the altitude. Körner (2003) found that the δ^{13}C value in plants becomes more positive with increasing altitude.

The factor region determines the values of δ^{13}C in the fLF and the fHF. δ^{13}C values in the fLF and the fHF were highest in the region Alpine. However, the factor region can also be connected to the altitude effect for δ^{13}C values (Körner, 2003). Highest δ^{13}C values were found in the region Alpine (for the fLF and the fHF), indicating that on average in the highest regions the δ^{13}C values are also highest.

With respect to the $\delta^{15}N$ values, only the factor region determined the values in the oLF ($p<0.05$). This again shows, that some regional effects influence the decomposition and mineralization process for example through differences in the five Swiss productive regions (Schwaab et al., 2015) and with this also through different litter quality, stand type and stand age (Côté et al., 2000).

5.1.3 What about the oLF?

The multiple linear regression indicated that there was almost no effect on the oLF. The results of the C/N ratio in the oLF were slightly higher than the ones in the fLF. For example in the study of Gunina & Kuzyakov (2014), the fLF showed higher C/N values than the oLF due to progressive degradation.

Already Schrumpf et al. (2013) concluded that the characterization of the oLF (especially the OC in the oLF) is more difficult than of the fLF, where the OC is completely unprotected, and the HF, where the OC is associated to mineral surfaces. In multiple linear regression differences in C/N ratio as well as in other values measured such as $\delta^{13}C$ and $\delta^{15}N$ were not clearly pronounced or not recognizable for the oLF. Therefore, statements about vulnerability are difficult to make. Schrumpf et al. (2013) also had a similar problem in their study. Due to that lack of such consistent differences, the idea of a more degraded oLF than the fLF could not be supported (Schrumpf et al., 2013).

Possible factors that influence the values of the oLF in this MSc thesis can be found in the sample preparation, in particular in the amount of ultrasonic dispersion energy (Cerli et al., 2012). For all soil samples the same amount of ultrasonic dispersion energy was used. Therefore, for some soils, the applied dispersion energy might have been too high and for some soils dispersion energy was too low to collect the optimum amount of oLF. Thus, the oLF can be mixed with the HF (by adding too much energy) or not all of the oLF can be collected (by adding too little energy) (Cerli et al., 2012). Therefore, the method changes the outcome of the oLF. Nevertheless, with the use of the same ultrasonic dispersion energy for all soils the results became comparable and the procedure was much less time consuming.

To summarize, it was found in this MSc thesis that associates with minerals seemed to be the most important controlling factor when it comes to stabilization processes of SOC. This was indicated by the soil properties (clay content and pH) that influence the contents of C and N most dominantly in the fHF and also in the WEOM and fLF. This is mainly due to a sheltered protection of the SOM against its decomposition (Schrumpf et al., 2013).

Concerning the C/N ratio, the soil properties again drive the C/N distribution in the soil fractions (fHF and WEOM) but not exclusively. The factor region (e.g. by different kinds of vegetation or by regional advantages in the Southern Alps) also significantly influences the distribution of the C/N ratio in the soil fractions.

5.1.4 Relative ages

In general, the results of this MSc thesis showed that the fHF seems to be older than the LF. This is in agreement with the findings by Schrumpf et al. (2013). The authors concluded that the LFs are not only characterized by higher C/N ratios and lower $\delta^{13}C$ values but also by lower ages with the opposite for the HFs. Also Buyanovsky et al. (1994) described shorter turnover times in more labile fractions from 1 to 3 years and longer turnover times in more stable fractions of about 7 years.

First, the region Midland was characterized by higher relative age differences between the LF and the fHF (fHF is 247 times older than the LF) than the other regions. This again indicates that some regional effects influence the decomposition and mineralization process through differences in the five Swiss productive regions (Schwaab et al., 2015) and also with this, the time that is needed for such processes. Secondly, differences in relative ages between climatic conditions were less pronounced. A tendency from cold and dry to warm and moist with increasing relative ages can be interpreted. Thirdly, with increasing clay and pH values (soil properties, pco1) the relative ages decreased. But this correlation was not significant and therefore, is of less importance.

5.2 Discussion of time-driven results

General pattern The results of this MSc thesis indicated that after about 20 years the WEOM stocks decreased to lower OC stocks in the younger (fresh) samples than in the old samples. The stock change in the WEOM was the strongest pronounced stock change with an average stock change of -6.92 mgOC/kg soil per year. However, this effect could be influenced by the storage methods of the samples (dry storage: archive samples vs. fresh samples).

Concerning the fLF, the oLF and the cHF the OC stock slightly increased over time to the younger (fresh) samples (zero to positive stock change per fraction per year). In the fHF the OC stock slightly decreased to younger (fresh) samples (zero to negative stock change per fraction per year). These findings are in line with Schrumpf et al. (2013). They confirmed that higher ages of the HF than of the fLF (measured with ^{14}C) are characterized by longer turnover times of the OC in the HF. This indicates that the HF is more stable against degradation than the fLF (Schrumpf et al., 2013) and therefore less vulnerable and stays longer in the soil.

The table below shows the calculated relative ages of the archive and the fresh samples (Table 12).

Table 12: Relative stability LF:fHF for the archive and the fresh samples.

Origin	Content (gOC/kg soil)		δ15N (‰)		C/N ratio		Average relative age
	LF	fHF	LF	fHF	LF	fHF	LF:fHF
Archive	8.8	23.9	-2.0	1.66	28	11	72
Fresh	16.3	22.1	-5.2	1.04	29	12	112

The results showed that the average relative ages increased towards the younger samples (Table 12). Therefore, it can be interpreted that the age or stability of the fHF increased relative to the LFs over time.

Effects on vulnerability Over 20 years, almost no C was lost in the fHF. This result indicates that, physico-chemical stabilization processes such as binding between mineral surfaces and SOM is an important factor when it comes to the residence time of C in the soil (Baisden & Parfitt, 2007). Therefore, this strongly indicates that OC associations to minerals are more stable over time. In the cHF, which also represents a more stable fraction, almost no change was detectable from a zero to a slightly positive change. Mainly, the light fractions contribute to the stock change over time. In particular, due to these fractions an average stock change of +1.14 gOC/kg soil per year over all twelve sites was calculated. But this positive stock change is not stably bound and therefore needs to be treated with more diligence. However, this could also be influenced by the different storage methods of the samples. Furthermore, sieving processes and the separation of the O horizon could also lead to differences in the results. Generally, it is remarkable that over 20 years, the OC stocks in the light soil fractions in particular, did not change more.

6. Limitations

Sample loss Although the average recovery after density fractionation was over 94%, still some material of the soil samples got lost during lab work. There are possible sources of sample loss during the procedure such as the extraction of the WEOM or the wet sieving of the HF.

First, during the extraction of the WEOM, it might happen that soil material gets into or stick onto the syringe tip that extracts the WEOM. But those are usually very little amounts. Second, during wet sieving sample material can be lost for example by too short sedimentation time. In this thesis, the sedimentation time for the fHF was usually one week. Therefore, it might be that not all the material had time to sediment. This could also result in a sample loss. Cerli et al. (2012) further mentioned that the losses could be connected to cleaning and filtering processes or to dissolved particles in the SPT solution.

Ultrasonic dispersion energy for the oLF As already mentioned in the section *5.1.3 What about the oLF?*, the amount of ultrasonic dispersion energy for the collection of the oLF is crucial (Cerli et al., 2012). The applied dispersion energy might have been too high or too low for some soils to collect the optimum amount of oLF. Thus, not all of the oLF can be collected or the oLF can be mixed with the HF (Cerli et al., 2012). However, the results became comparable with the use of the same ultrasonic dispersion energy for all soils.

Different analysis for cHF Especially in the results of the $\delta^{13}C$ values of the cHF a rather wide range in the values was measured. This could be due to a technical problem during measurement with the Picarro. Therefore, the comparability with the other fractions might be limited. This is why some of the statistical tests were also done without the cHF.

Lack of measurement replicates Within this MSc thesis of each of the 330 samples one measurement was done. To reach a more founded result, further measurements per sites could be done with the remaining material of each fraction.

Material >2mm The material >2mm was not included in this MSc thesis. It might be interesting also to analyse and investigate the OC contents in that material especially concerning the LFs.

7. Conclusion

The aim of this MSc thesis was to asess the vulnerability of SOM in Swiss forest mineral soils in relation to factors with a high influence on ecosystem properties (climate) and on soil formation processes (pH and clay content). Furthermore, the aim was to reach a better understanding of SOM fractions and turnover time in forest mineral soils.

The influence of the climate (temperature and moisture) on SOM was not found to be more important than the influence of the co-variates. Especially the soil properites and not the climatic conditons were driving the OC storage and the decomosition processes (H1 not supported). This is mainly due to enhanced bindings of OC onto mineral surfaces in the fHF. But also the regionality had some effects on the C/N ratios most probably initiated by (i) very good conditions for the stabilization processes of SOM through organo-mineral associations especially through Fe- and Al-oxides in the Southern Alps and (ii) the differences in the productive regions and therefore by different litter inputs. Concerning the climatic condition, the factor temperature had infleunce on the $\delta^{13}C$ values most probably through altitudinal effects.

The hypothesis (H2) that the HFs are more stable and have higher relative ages than the LFs was supported. Higher relative ages and thus higher stabilities were found in the fHF than in the LF, especially in the region Midland (fHF is 247 times older than the LF).

No support for the hypothesis (H3) that the SOC stock change per year in Swiss forest mineral soils declined over the past 20 years was found. Over a time span of on average 19 years a stock change of +1.14 gOC/kg soil per year over all twelve sites was calculated. The light fractions contributed the main part to the positive stock change over time and almost no C was lost in the fHF and the cHF. This indicates that the OC in the HFs is more stabilized against degradation than in the LFs and therefore reacts less vulnerable and stays longer in the soil. The positive stock change in the LFs is less stable bound and therefore needs to be treated with more diligence.

8. Outlook

The large amount of data that was collected in this MSc thesis provides an interesting basis for further analysis. Together with the existing database from the WSL more analyses about the influence of for example the altitude on OC storage, or about the influence of tree species on the C/N ratio, could be done to refine the understanding of environmental factors and its influence on SOM vulnerability. Elevational gradients, for example, provide a 'natural' experimental design where climatic conditions change with altitude (Zimmermann et al., 2010). In this context, Hagedorn et al. (2010) studied the influence of a climatic gradient in Swiss forest soils on change in soil C storage. They found that SOC stocks decreased with decreasing altitude of the sampling location. This means that SOC stocks are rather lower under favourable growing conditions. In particular, the stock in the organic layer increases significantly with increasing altitude (a doubling in the SOC stock with a change of about 1000 vertical meters). In the mineral soil, this change is less pronounced in relative terms than in the organic layer (about 20 % more SOC stock with a change of about 1000 vertical meters). Nevertheless, the absolute increase is of a comparable order of magnitude (Hagedorn et al., 2010). This approach for studying the influence of the altitude could also be used for further analyses of data collected in this thesis. Furthermore, data about the corresponding subsoils could provide informative data to supplement the image of stabilization processes in Swiss forest mineral soils. And last but not least, it would be interesting to investigate the vulnerability of SOM with the approach of this MSc thesis but on a larger scale and to incorporate a higher variability of the climatic condition.

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Annex

I. Additional figures

Soil Organic Carbon – clay

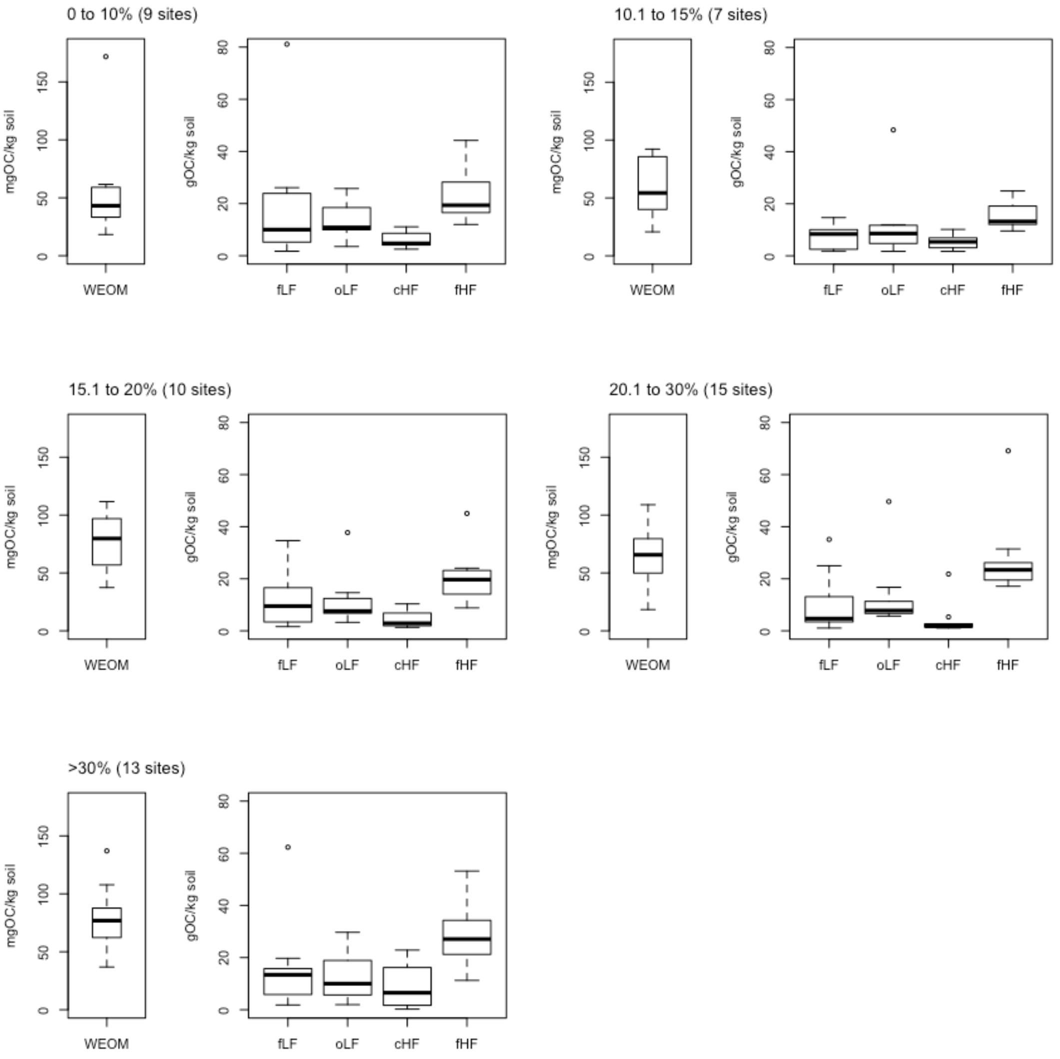

Figure 31: OC values in mgOC/kg soil for the WEOM and in gOC/kg soil for the fLF, oLF, cHF and fHF classified into five clay classes. The values of the sites number 6 and 13 in the fLF were excluded due to very high OC values (over 100 gOC/kg soil).

Nitrogen – clay

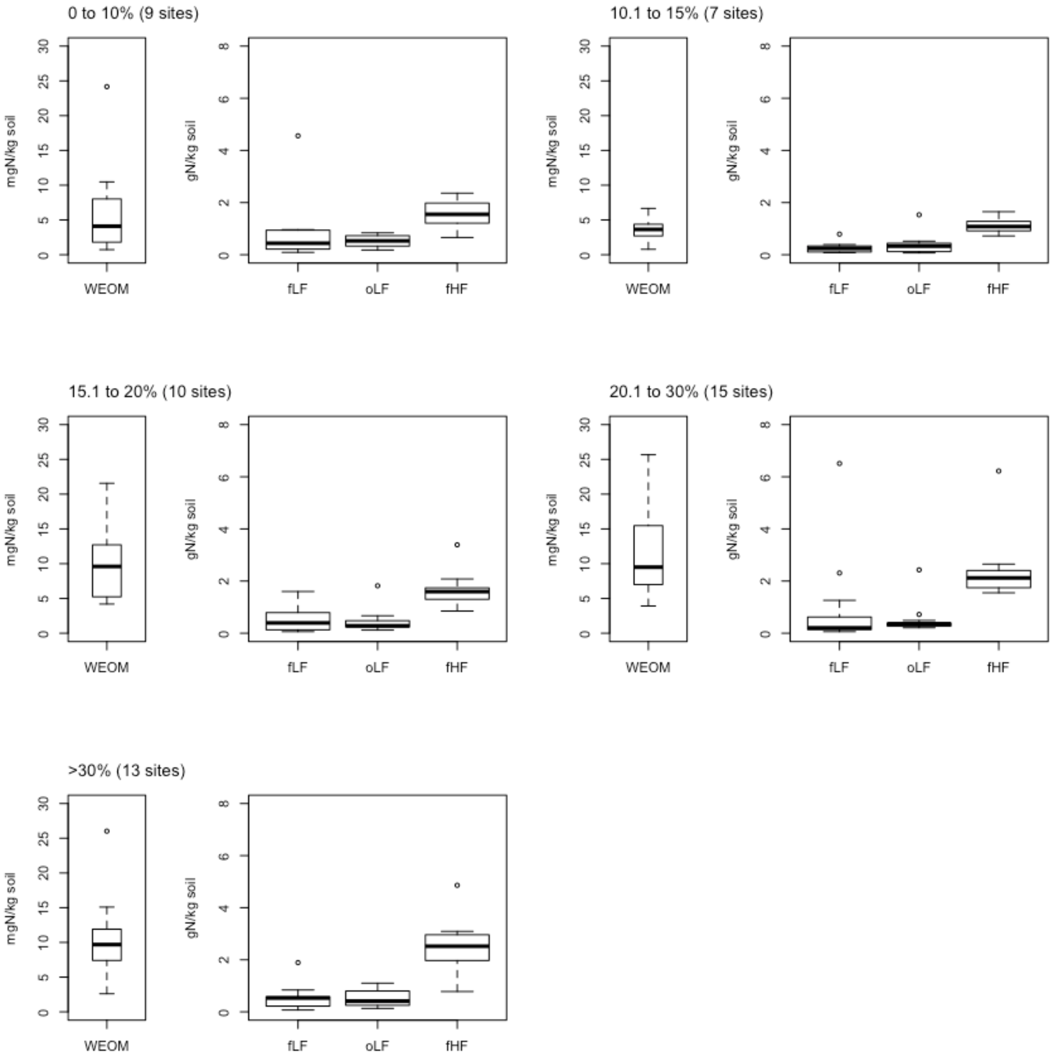

Figure 32: N values in mgN/kg soil for the WEOM and in gN/kg soil for the fLF, oLF and fHF classified into five clay classes.

δ^{13}C – pH

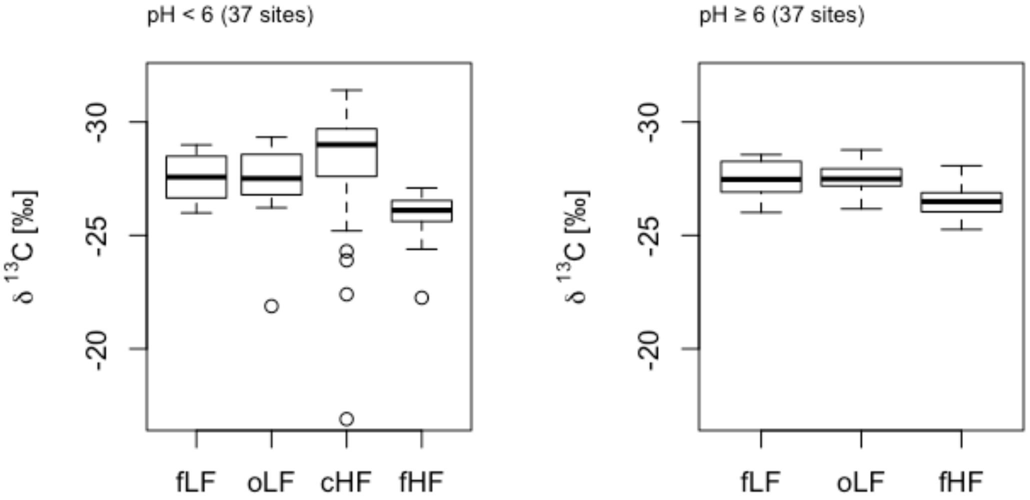

Figure 33: δ^{13}C values in ‰ for the fLF, oLF, cHF (only for a pH below 6) and fHF classified after two pH classes.

δ^{15}N – pH

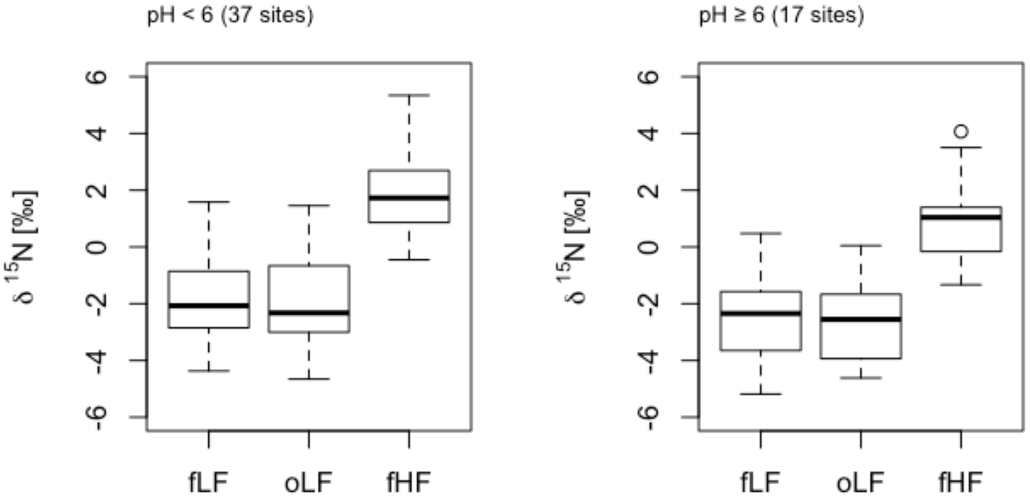

Figure 34: δ^{15}N values in ‰ for the fLF, oLF and fHF classified into two pH classes.

II. Personal declaration

I hereby declare that the submitted thesis is the result of my own, independent work. All external sources are explicitly acknowledged in the thesis.