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**Soil organic matter in the Peruvian Andes**

*Unravelling factors controlling soil organic carbon distribution and the underlying organic matter stabilization mechanisms*

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## Chapter 1

### General Introduction

Soil organic carbon (SOC) is a large terrestrial carbon (C) pool and plays an important role in global C dynamics. SOC stocks are large in alpine grasslands of the Peruvian Andes and contribute to ecosystem services such as agricultural production and water provision. The alpine grasslands of the Peruvian Andes are vulnerable against climate change, and the SOC stocks there act as a potential C sink or source for atmospheric CO<sub>2</sub>. Studies on SOC stocks and stabilization in the Andes have mostly been conducted on volcanic ash soils in Ecuador. In contrast, soils developed on other substrates in the Peruvian Andes have been less-studied. Furthermore, the heterogeneity in climate in the Peruvian Andean can potentially introduce spatial variability in SOC storage and stability. Also in this respect, relevant studies are rare.

SOC stocks are largely controlled by the stabilization of soil organic matter (SOM). Recently, we have seen a shift from traditional views of SOM stabilization based on the ‘humification’ model and molecular recalcitrance to a new paradigm based on the protection of SOM by the soil matrix against decomposers. In this emerging new view, SOM is stabilized by adsorption on mineral surfaces and occlusion in aggregates, whereas molecular composition is less important in long-term SOM stabilization (Lehmann and Kleber, 2015; Schmidt et al., 2011). Applying the new paradigm of SOM stabilization will help to gain insights into the underlying mechanisms for the storage and stability of SOC stocks in the Peruvian Andes.

The objectives of this thesis were to investigate SOC stocks and the underlying mechanisms controlling SOC persistence in the Peruvian Andes. The first step was to estimate SOC stocks of the study area and to identify key factors controlling the SOC spatial pattern. Afterward, soil samples were collected based on the key factor(s) previously identified plus two contrasting precipitation levels. SOM stabilization mechanisms based on the new paradigm were investigated using a combination of selective extraction methods, aggregate-size fractionation and an incubation experiment of intact versus crushed aggregates. Finally, we paid special attention to SOM molecular composition in relation to microbial

decomposition to gain insights into relationships between molecular composition and SOM stabilization.

## **1.1. Background**

### *1.1.1. Importance of soil organic carbon*

Soil is a large terrestrial C pool (2500 Gt), which is much larger than the sum of the atmospheric C pool and the vegetation C pool together (Lal, 2004). This soil C pool is comprised of SOC (1550 Gt) and soil inorganic carbon (950 Gt). Studies on global change indicate that the climate will be consistently warming in the 21<sup>st</sup> century (Field, 2014). On one hand, global warming can induce the loss of SOC storage and further stimulate the emission of greenhouse gases (e.g. CO<sub>2</sub> and CH<sub>4</sub>). On the other hand, global warming can be alleviated by SOC sequestration that stores greenhouse gases in the form of SOM (Lal, 2004). Based on the Paris Climate Agreement, increasing global SOC stocks by 0.4% per year (2.5 Gt C year<sup>-1</sup>) can potentially offset 30% of the global greenhouse gas emissions (Minasny et al., 2017). Given the importance of SOC for global warming, it is important to understand the impacts of global change on the SOC stock and its stability, as well as the underlying mechanisms of SOC stabilization.

### *1.1.2. Persistence of soil organic matter*

SOC stocks and persistence are largely controlled by SOM stabilization. Traditional theories assume that the persistence of SOM is dependent on the chemical recalcitrance of macromolecules formed by the “humification” process (Stevenson, 1994). However, recent studies show that compounds previously considered to be recalcitrant against decomposition (e.g. lignin) can be decomposed rapidly in soils. In contrast, compounds previously considered to be decomposed very fast (e.g. polysaccharides and proteins) can persist against microbial degradation for a long period in soils (Lehmann and Kleber, 2015; Schmidt et al., 2011). Furthermore, the macromolecules previously assumed to be important in the “humification” model have been shown to be self-assembled formations of small molecules (Myneni et al., 1999). Since the “humification” model and relevant concepts receive an increasing criticism, new emergent views argued that SOM degradation is a progressive decomposition and transformation

of plant- and microbe-derived OM. For the decomposition and transformation, the accessibility of SOM to microbial decomposition and the surrounding environment is now thought to play an important role (Lehmann and Kleber, 2015). In general, SOM is protected against decomposition by interacting with the soil matrix. The underlying mechanisms are: (1) interactions of SOM with mineral surfaces and metal ions, (2) physical occlusion of SOM by soil aggregates, and (3) chemical recalcitrance of SOM (Lützow et al., 2006).

The formation of organo-mineral associations promotes long-term SOM stabilization as it strongly reduces the biological availability of mineral-associated OM. Literature reports lower mineralization rates for SOM associated with mineral as compared to other SOM fractions (Chenu et al., 2002; Schrumpf et al., 2013). Generally, SOM stabilized by mineral surfaces is characterized by lower C/N ratios, higher microbial-origin and longer resident time compared to bulk SOM and other SOM fractions (Kleber et al., 2015; Kögel-Knabner et al., 2008). Mineral-controlled SOM stabilization is dependent on soil pH values. In acid soils, SOM interacts with Fe, Al and Mn oxides via ligand exchange, whereas in alkaline and neutral soils, polyvalent cation bridges (e.g.  $\text{Ca}^{2+}$ ) are considered crucial to the interactions between SOM and mineral surfaces (Lützow et al., 2006; Rowley et al., 2018). Kleber et al. (2007) created a conceptual model in which the formation of OM-mineral association is explained as a self-organized process. In this model, amphiphilic compounds and proteins are adsorbed on mineral surfaces via strong interactions forming the stable inner layer, whereas other compounds are retained loosely outside the inner layer forming the kinetic zone via weak interactions (Kleber et al., 2007). The OM-mineral fraction is usually separated from the bulk SOM using density fractionation because the OM-mineral associations have higher densities than other OM fractions (Cerli et al., 2012; Moni et al., 2012). In general, the mineral-associated OM is the major fraction of bulk SOM. In addition to the OM-mineral associations, SOM can also be stabilized by complexed with metal ions (e.g.  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$ ) in acidic soils, especially soils of volcanic origin (Lützow et al., 2006).

SOM can be stabilized by occlusion in aggregates due to their physical inaccessibility to decomposers (Lützow et al., 2006). Compared to unprotected OM and mineral-associated OM, aggregate-occluded OM is characterized by an intermediate residential time, C/N ratios and the presence of microbial-derived OM (Schrumpf et al., 2013; Wagai et al., 2009). Microaggregates (<0.25mm) in

macroaggregates (>0.25mm) play an important role in stabilizing SOM (Six et al., 2000). Macroaggregates act as the habitat for microorganisms, in which plant-derived SOM is decomposed. The SOM decomposition in macroaggregates controls the formation of microaggregates and further determines the turnover and stabilization of microaggregate-protected SOM (Six et al., 2000; Six and Paustian, 2014). Similarly, Wagai et al. (2009) suggested dividing aggregate-occluded SOM into two fractions, which are similar to the two SOM fractions protected by macroaggregates and by microaggregates. SOM occluded in aggregates can be separated using a combination of density fractionation and ultrasonic. First, a density fractionation without an ultrasonic treatment is conducted to isolate free light (unprotected) OM from other OM fractions. Afterward, the ultrasonic treatment is applied to release occluded OM, followed by another density fractionation to separate occluded OM from mineral-associated OM (Cerli et al., 2012; Kaiser and Berhe, 2014).

Although recent studies indicate that molecular composition is less important in controlling SOM persistence than previously thought (Lehmann and Kleber, 2015; Schmidt et al., 2011), a consensus is still absent for the importance of SOM molecular composition on SOM persistence. An important reason for this is that the effects of SOM molecular composition on interactions between SOM and the soil matrix are not well understood. In general, microbial-derived SOM is considered to be preferentially stabilized by mineral surfaces (Moni et al., 2012). However, plant-derived SOM can also be protected by mineral surfaces. With regard to aggregate-controlled SOM stabilization, some studies reported that fire-induced aromatic compounds are preferentially stabilized by occlusion in aggregates. Furthermore, Angst et al. (2018a) reported that soil lipids with different origins are selectively stabilized by different-sized aggregates. In contrast, Wagai et al. (2009) summarized that aggregate-occluded SOM has a large range of molecular characteristics. Thus, further research is needed for a better understanding of the molecular composition of SOM and how this affects its stabilization.

### *1.1.3. Factors controlling soil organic matter persistence*

The persistence and turnover of SOM are largely controlled by soil formation and environmental (SFE) factors. Climate factors, especially precipitation and temperature, act as primary drivers for the persistence and turnover of SOM. In

general, soils with cool and humid climate accumulate more OM compared to soils under warm and dry climate (Wiesmeier et al., 2019). Precipitation regulates not only primary productivity and SOM input but also SOM decomposition through affecting soil water availability. Temperature can potentially constrain SOC storage because the microbial decomposition of SOM is stimulated under warm conditions (Chaplot et al., 2010; Wiesmeier et al., 2019). In addition, climate factors can also change soil mineralogy by controlling weathering processes and further govern SOM stabilization via mineral surfaces (Doetterl et al., 2018, 2015b). Vegetation plays an important role in controlling the input and decomposition of SOM, especially at the regional scale. However, the effects of vegetation decrease with soil depth and are largely controlled by climate factors (Wiesmeier et al., 2019). Lithology (or parent material) is also an important predictor for SOM persistence as reported by different studies (Angst et al., 2018a; Hobbey et al., 2015; Wagai et al., 2008). This can be explained by the close relationships between lithology and soil mineralogy that controls SOM stabilization. However, the relative importance of lithology is also dependent on the scale and the interactions with other factors (Wiesmeier et al., 2019). Furthermore, topographical factors (e.g. slope angle and aspect) can also impact SOM accumulation through the controls of soil wetness, soil erosion, redox status and soil formation process (Wang et al., 2014; Wiesmeier et al., 2019).

Human activities also have crucial impacts on SOC storage and decomposition. Land use (change) has important effects on the stability and storage of SOM. In general, SOC stocks are higher in grassland and forest soils compared to cultivated soils (Guo and Gifford, 2002). Land use change that shifts from grassland or forest to cultivation causes depletion of SOC, whereas cropland abandonment and afforestation stimulate SOC storage (Poeplau et al., 2011). Furthermore, land use change also induces changes in SOM fractions and in SOM stabilization (Hamkalo and Bedernichek, 2014; Rolando et al., 2017a). Grazing in grasslands is reported having positive, negative and no obvious effects on SOC stocks and stability. This might be attributed to the interactions between grazing and other factors (McSherry and Ritchie, 2013). Nevertheless, overgrazing has significantly negative effects on SOC sequestration in the Andes (Podwojewski et al., 2002). The loss of SOC stocks related to land use change and overgrazing can be attributed to declined C input, soil erosion and SOM destabilization caused by aggregate destruction (Wiesmeier et al., 2019).

## 1.2. Soil organic carbon in alpine grasslands of the Andes

### 1.2.1. General information

Tropical alpine grasslands occur between the upper forest line and the snow line, with altitudes ranging from 3400m to 5000m. The Andes have the largest area of the tropical alpine grasslands, known as páramo, jalca and puna, depending on vegetation and precipitation (Buytaert et al., 2011). Although these grasslands cover limited areas, they provide important ecosystem services including biodiversity conservation, carbon sequestration, water provision and food production (Buytaert et al., 2011; Rolando et al., 2017b). Also, these grasslands are disturbed by human activities including cultivation, grazing, tree plantation and mining activities (Rolando et al., 2017b).

Alpine grassland ecosystems are highly vulnerable to climate change, which potentially threatens the ecosystem services they deliver (Field, 2014; Rolando et al., 2017b). Changes in precipitation and temperature can potentially cause shifts in species range, distribution of vegetation zones and fragmentation of the habitat (Buytaert et al., 2011). If the alpine grasslands receive less precipitation, water provision for the lowland with dry climate will decline. When the climate becomes warmer, the Andean grassland ecosystems tend to shift to higher elevation due to an upper shift of the cloud forest and degradation of the glacier. In addition, agriculture activities like cultivation and grazing will also move to higher altitudes. Furthermore, glacier melting due to warming can cause severe water scarcity for the adjacent populated areas (Chevallier et al., 2011; Rolando et al., 2017b).

### 1.2.2. SOC stocks and stability

Alpine grasslands of the Andes are characterized by their high SOC storage compared to other ecosystems (Buytaert et al., 2011; Tonneijck et al., 2010; Yang et al., 2018). These large SOC stocks act as a potential source of C loss to the atmosphere as CO<sub>2</sub> under global change and are crucial to the ecosystem services including water provision and food production (Buytaert et al., 2011; Rolando et al., 2017b). Precipitation is an important driver for the spatial distribution of SOC stocks in alpine grasslands of the Andes. SOC stocks decrease from up to 530±40 Mg ha<sup>-1</sup> in the Ecuadorian humid páramo grassland (Farley et al., 2004; Tonneijck et al., 2010) to a level between 118±15 and 136±4 Mg ha<sup>-1</sup> in the Peruvian dry



puna grassland (Muñoz-García and Faz-Cano, 2012; Rolando et al., 2017a; Zimmermann et al., 2009). Surprisingly, spatial distributions of SOC stocks are not clearly controlled by vegetation in Andean grasslands (Nierop et al., 2007; Tonneijck et al., 2010; Zimmermann et al., 2009). In addition, land use except for overgrazing also has limited impact on SOC stocks in this region (Podwojewski et al., 2002; Rolando et al., 2017a; Yang et al., 2018).

SOM stabilization mechanisms are little studied in the Andean grasslands. Buytaert et al. (2006b) and Tonneijck et al. (2010) reported that SOM is stabilized by interacting with mineral surfaces and/or complexed with Fe and Al in volcanic ash soils in the Ecuadorian Andes. Rolando et al. (2017b) reported that SOM is stabilized by adsorption on mineral surfaces and occluded in aggregates in the wet puna of Central Peru. In addition, alleviated SOM degradation due to the cold and humid environment and Al toxicity due to the low pH of volcanic-ash soils can also be potential factors promoting SOM accumulation in the Andes (Hribljan et al., 2016). For the Southern Andes in Chile, Doetterl et al. (2015) conducted a study on SOC stabilization in grassland through a 4000-km-long transect with a wide range of climate and geological conditions. Their results showed that soils with mild and wet climate had the largest SOC stocks and the SOM stabilization was largely controlled by interactions between climate and soil mineralogy (Doetterl et al., 2015).

### *1.2.3. What is unknown*

It is important to understand the underlying mechanisms for the large SOC stocks in the alpine grasslands of the Andes. Studies on SOC storage and stabilization in the Andes were mostly conducted in Ecuadorian Páramo, where soils are generally developed on volcanic ash. However, soils in the jalca or wet puna in Northern Peru are rich in SOC but developed from substrate other than volcanic ash. These soils have been less studied, especially with regard to the SOM stabilization related to OM-mineral interaction, soil aggregation and OM molecular composition. Furthermore, alpine grasslands of the Peruvian Andes are characterized by heterogeneity in climate conditions (Merkel, 2017). As climate factors are primary drivers controlling SOC distribution by regulating OM input and weathering processes, it is important to know the effects of climate factors (e.g. precipitation) in the Peruvian Andes. However, relevant studies were rare in the Peruvian Andes based on the knowledge of the author.

### **1.3. Aim and objectives**

Given the importance of the alpine grasslands of the Peruvian Andes for ecosystem services and the vulnerability of the ecosystem to global change, it is important to having insights into the factors that drive SOC stocks and the underlying mechanisms of SOM stabilization in these areas. The objectives of the research were to quantify SOC stocks and the underlying mechanisms controlling SOC persistence in the alpine grassland of the Peruvian Andes.

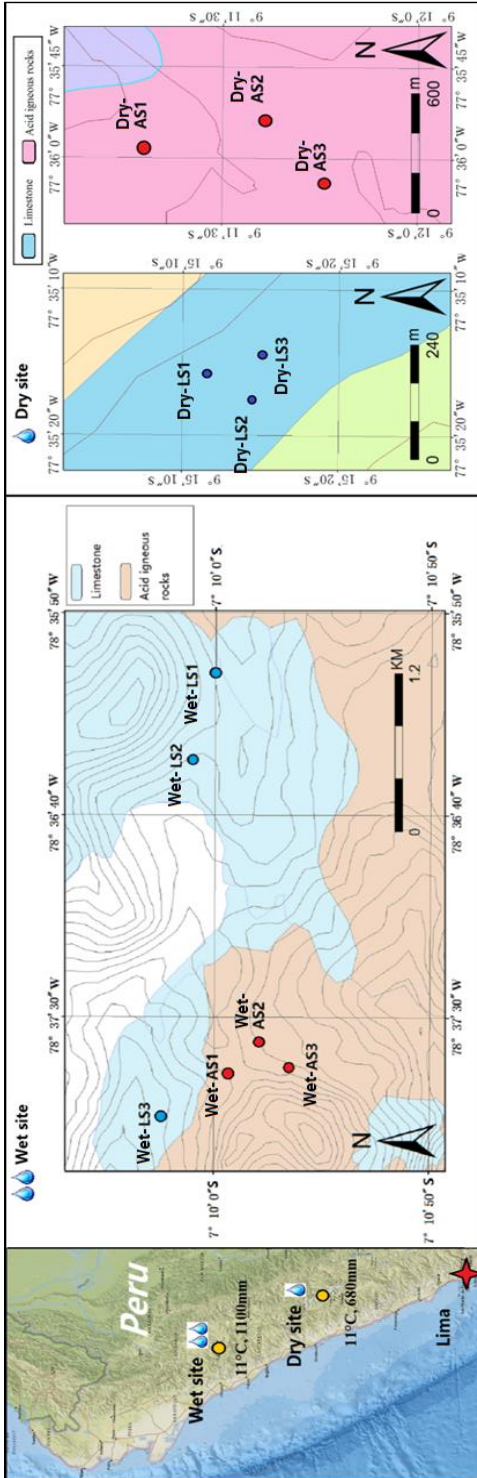
The following specific objectives were formulated:

- To estimate SOC stocks of the study area and to identify key factors controlling the spatial pattern of SOC distribution (Chapter 2).
- To determine SOM stabilization controlled by adsorption on mineral surfaces in soils developed on contrasting bedrocks (Chapter 3).
- To investigate the effects of precipitation and lithology on SOC stocks and stability, as well as to what extent soil aggregation contribute to stabilizing SOM (Chapter 4).
- To gain insights into relationships between SOM molecular composition and SOM stabilization controlled by the soil matrix (Chapter 5).

### **1.4. Description of the study area**

#### *1.4.1. Site description*

The study area is located in the Peruvian Andes and belongs to the Neotropical alpine grasslands, namely wet puna or jalca, which are considered as a transition between the páramo and the dry puna (Sánchez Vega et al., 2005). This region is also subject to disturbance including cultivation and grazing as a result of human activities. In addition, plantation of pine trees and eucalypt trees is also common in the study area (Rolando et al., 2017b). Precipitation decreases from the north to the south, whereas temperature has almost no changes through the latitude gradient. However, the climate has large temporal and spatial heterogeneity in this region (Merkel, 2017; Rolando et al., 2017b).



Wet site		Dry site			
Site	Parent material	Altitude m	Soil depth cm	Ave. depth in LM fractions %	Gravels in LM fractions %
LS1	Limestone	3716	57	6.86	8.70
LS2	Limestone	3717	66	3.13	5.42
LS3	Limestone	3517	60	0.16	13.01
AS1	Granite/ignimbrite	3583	68	10.86	50.28
AS2	Granite/ignimbrite	3585	45	14.12	39.57
AS3	Granite/ignimbrite	3586	35	28.60	61.05

**Fig. 1.1 Sampling site description.** LS: limestone soil, AS: acid igneous rock soil, LM: large macroaggregates (>2 mm). The ArcGIS Online World Topographic Map basemap (Estri., 2013) was used for the map of Peru on the left, whereas the data for the contour lines in the maps of the wet site and the dry site was derived from Geo GPS Perú, (2014).

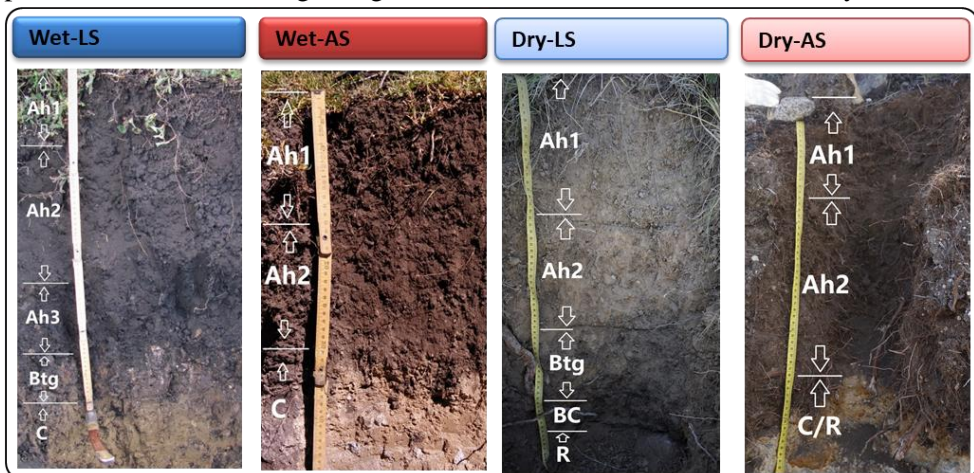
### 1.4.2. Sampling plots

Soil samples were collected from two separate sites with similar altitudes and temperatures but with different precipitation levels, the wet site and the dry site, respectively. Fig. 1.1 gives the locations of the wet site and the dry site, whereas Table A1.1 presents detailed information in sampling sites and soil profiles.

The wet site is located on the continental divide between the Pacific and the Atlantic Ocean, which is to the west of the city of Cajamarca (7° 11' S, 78° 35' W) in the Peruvian Andes. The sampling area has altitudes between 3400 m asl and 3900 m asl. The annual average temperature is estimated as 11 °C, with large daily variation and minor seasonal change. The area receives 1100 mm precipitation per year, which mainly occurs between October and April (Merkel, 2017; Sánchez Vega et al., 2005). The geology is comprised of a basement of folded Cretaceous sedimentary formations and a layer of igneous materials that are partially-overlying the basement. The basement, which belongs to the Formations of Cajamarca, Chulec-Calizas, Pariatambo, Farrat and Yumagual, consists of bedrocks such as limestones, marls, shales and quartzites. The igneous materials belong to the San Pablo Formation, and consist of ignimbrite and granite (Geo GPS Perú, 2014; Reyes-Rivera, 1980). Soil types of this region are dependent on topography and lithology. For topography, shallow and less-developed soils (e.g. Leptosols and Regosols) are distributed at the mountain top, whereas soils rich in SOC in relation to humid soil conditions (e.g. Histosols and Gleysols) are common in the valley bottom. For lithology, soils developed on calcareous bedrocks are generally classified as Phaeozems due to their large SOC stocks and high base saturation, whereas soils formed on acid igneous rocks usually belong to Umbrisols or Andosols because of their low base saturation and volcanic bedrock types (WRB, 2014). The land use in the wet site is characterized by a rotation of cultivation, land abandonment and grazing that was applied in a period of 3-5 years, which is considered to sustain the fertility and the productivity of the soils.

The dry site is located on the west side of the Cordillera Blanca of the Andes, to the northeast of the city of Carhuaz (9°22' S, 77°59' W). Altitudes of the sampling sites are between 3490 m asl and 3700 m asl. Similar to the wet site, the annual average temperature is 11 °C. However, the annual precipitation is estimated as 680 mm in the dry site at an altitude of 3600 m (Merkel, 2017),

which is only 60% of that in the wet site. The batholith of the high mountain chain (>5000 m asl) of the Cordillera Blanca are comprised of Neogene intrusive igneous rocks, which have a major contribution of granodiorite. The western foot slopes of the high mountain chain are partially covered by fluvio-glacial sediments, which contain a large proportion of granodiorite fragments. For the foot slope region not covered by the fluvio-glacial materials, extrusive igneous rocks such as ignimbrite are found in the Yungay Formation, whereas folded limestones, cherts and shales are distributed in the Carhuaz Formation and the Santa Formation (Coldwell et al., 2011; Geo GPS Perú, 2014). Similar to the wet site, soil classification of the dry site is also dependent on topography and lithology. For example, soils developed on limestone or shale are predominantly classified as Phaeozems or Umbrisols, whereas soils developed on granodiorite and ignimbrite generally belong to Umbrisols or Andosols. In addition, Histosols and Gleysols are often found on sub-glacial or alluvial materials located in the valley bottom (WRB, 2014). The typical land use type is grassland with shrub patches. Cultivation and grazing are common human activities in the dry site.



**Fig 1.2** Typical soil profiles from the sampling sites with the combination of each precipitation level and bedrock type. Wet: the wet site, dry: they dry site, LS: limestone soil, AS: acid igneous rock soil.

## 1.5. Research outline and structure

In **Chapter 1**, a general introduction to the topic and a description of the study area are provided. A literature review on SOC stock and stabilization including

current knowledge gaps is conducted in this chapter. Base on the knowledge gaps, the objectives and the outline of this thesis are presented.

In **Chapter 2**, we quantified SOC stocks of the study area and identified the key factors controlling the distribution of SOC stocks. For this, soil samples were collected from 69 sampling plots in the wet site and SOC stocks were assessed to C or R horizons. Significant predictors for SOC stock patterns were selected from environmental factors and soil properties, namely lithology, land use, grazing intensity, slope position, slope angle, altitude, soil moisture and soil depth, using linear models.

In **Chapter 3**, soils developed on limestone and acid igneous rocks in the wet site were collected to investigate potential differences in SOC stocks and underlying stabilization mechanisms. We applied a selective extraction method to separate active Fe, Al and Ca fractions that explain OM stabilization governed by interacting with mineral surfaces.

In **Chapter 4**, the objectives were to investigate the potential controls of lithology and precipitation in soil aggregation and OM stabilization by occluded in aggregates. Soil samples were collected from both limestone and acids igneous rocks in two sampling sites with two different precipitation levels. A dry-sieving method was applied to determine soil aggregate-size distribution, and a 76-day incubation was used to estimate SOC stability against microbial decomposition. Furthermore, intact aggregates and crushed aggregates were incubated to estimate SOC protected by occlusion in soil aggregates.

In **Chapter 5**, we aimed to investigate potential controls of SOM molecular composition on their persistence to microbial degradation. For this, a combination of an incubation experiment of intact versus crushed aggregates and pyrolysis-GC/MS analyses were applied. Specifically, the objectives included: (1) to assess whether inherent properties of OM control OM stability against decomposition, and (2) to assess whether the potential controls of OM stability can be explained by OM stabilization by soil matrix.

In **Chapter 6**, the major findings of this thesis are synthesized and integrated. In addition, discussions are made for the implications of the findings for the management of the Andean grasslands and for SOM stabilization in general.