

**UNIVERSIDAD DE LA FRONTERA**  
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# **ORGANIC CARBON STORAGE CAPACITY OF CHILEAN ALLOPHANIC SOILS**

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## **“ORGANIC CARBON STORAGE CAPACITY OF CHILEAN ALLOPHANIC SOILS”**

Esta tesis fue realizada bajo la supervisión del director de Tesis Dr. FERNANDO BORIE BORIE, perteneciente al Departamento de Ciencias Químicas y Recursos Naturales de la Universidad de La Frontera y es presentada para su revisión por los miembros de la comisión examinadora.

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### **Dedicatoria / Dedication**

Dedicada a dos grandes mujeres, que a pesar de la adversidad lograron superar los obstáculos de la vida y consolidar una hermosa familia.

A mi Madre LIDIA, que con su ejemplo de superación, e incondicional amor me motiva cada día a luchar por mis sueños. Nunca olvidastes lo difícil que fue nuestra vida y aun así siempre tienes esa mano solidaria que ha sido de vital importancia en nuestro núcleo familiar. Eres un ejemplo de perseverancia y principalmente de generosidad que te hace grande entre los que te amamos.

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## Abstract

The conversion of natural ecosystems, such as native forest to arable farming systems reduce the contents of soil organic matter (SOM) causing a rapid increase of carbon (C) and nitrogen mineralization and erosion losses. Potential carbon sequestration in soil is the transfer of atmospheric CO<sub>2</sub> into more stable form of SOM. Mitigation of CO<sub>2</sub> emissions by soil carbon subsequent imply a fully knowledge and understanding of the process and mechanisms involved in SOM stabilization. On the other hand, volcanic soils are extremely important in terms of carbon storage, as they occupy only 0.8% of the global land area, but they can store more than five fold the amount of soil C than non-volcanic mineral soils. In Chile there are more than 5.1 millions hectares of volcanic soils, most belonging to Andisol, according to USDA classification. In this region most of the agriculture is developed on volcanic soils, generally developed under native forest of *Nothofagus* spp. before clearance and burning during the 19<sup>th</sup> century. Since that time, agriculture has been intensified, including burning practices and cropping intensity. Few studies exist however, in which the mechanism of SOM stabilization under different managements have been compared. To fill this gap, we studied the stabilization and the storage in forest and agricultural soils in southern Chile. First, in Chapter 1 we present the General Introduction. In Chapter 2 we present an overview of the factors and mechanisms involved in the volcanic soil carbon storage, particularly in allophanic soils. In Chapter 3 we study a temperate rain forest soils of *Nothofagus pumilio* (Poepp et Endl) occurring in the piedmont and dejections cones of important volcanoes in Chile. Soil carbon distribution in nine soil profiles as well as some relevant soil properties interacting with carbon preservation through combination of Al-SOM complexes and biological activity was examined. We also investigated the protective capacity of the chemically reactive fraction of Al in combination with SOM in these soils. We found that Al and Fe extracted by pyrophosphate explained much of the SOM variation. The stabilization of organic carbon, assessed by the stability ratio of the C extracted in pyrophosphate (C<sub>p</sub>) and the C in the whole soil was similar, either for the top and deep horizons. Furthermore, there was no relationship between C mineralization rates and the stability ratio, indicating that the stabilization of soil organic C (SOC) was at the same extent in all soils and depths. In Chapter 4 the forest soil studies were further

extended and compared with pasture of agricultural fields. The distribution of SOM fractions at various depths under managed pasture were compared with the forest soil. We used  $C_p$  as a measured of stabilized C in the top soil and a physical fractionation with sodium polytungstate to separate various density fractions (fPOM= free particulate organic matter; oPOM= occluded particulate organic matter and MF= mineral fraction). The results showed that the variation in stabilized C between ecosystems and soil depths was explained largely by differences in pyrophosphate extractable Aluminum ( $Al_p$ ) and iron ( $Fe_p$ ). The physical fractionation indicated that in both ecosystems a large amount of C was present in the MF (> 46 % of the total soil C), followed by oPOM and fPOM. Our results emphasize the importance of  $C_p$  linked to Al and Fe as a pool of organic carbon in volcanic soils and the POM formation as a mechanism of SOC stabilization in undisturbed ecosystems such as forest soils.

Volcanic soils offer an excellent opportunity to study SOM stabilization and its interaction with the mineral phase, because these soils contain large amounts of organic matter which is complexed with Al, Fe and allophane clays. In this study, the relationship between allophane content and SOC was not significant. This is contradicting the present hypothesis where it was proposed that both, the allophane like materials and Al-complexed with SOM are the key factors for SOM stabilization and storage. The general conclusions of this Thesis were: 1) the mechanisms of SOC stabilization on top and subsoils appear to be the same and provided an interesting strategy of this ecosystem to maintain nutrient cycling in deep soil. 2) the incubation results obtained when favorable conditions of moisture and temperature caused suggest that soil organic carbon from the deep soil provides sufficient energy to sustain active microbial populations as much as in the top soil and 3) two C pools were identified in the pastoral and forest ecosystems: *i*) A chemically stabilized pool constituted mainly by the Al and Fe linked to the SOC, and *ii*) The second pool corresponds to the occluded particulate organic matter fraction (oPOM), composed by C physically protected within soil aggregates.

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# CHAPTER 1

## *General Introduction*

## 1.1 General Introduction

Soils vary in their ability to accumulate organic matter, mainly due to by its physical, chemical and biological properties (Krull et al., 2003). However, the rates of C incorporation and its losses are directly affected by the land-use and soil management (Matus and Maire, 2000; Jones and Donnelly, 2004). The C in agricultural soils can increase or decrease depending on the C-input rate (Pulleman et al., 2005). For example, zero tillage promote the maintenance and accumulation of soil organic carbon (SOC) (Acevedo and Martinez, 2003; Wright and Hons, 2005, Wright et al., 2005), by the way of decreasing its decomposition rate and erosion and enhancing soil aggregation (Stewart et al., 2007). The results vary however, according to agro-ecological zone, soil type, cropping system and prevailing climate (Paustian et al. 1997; Wright and Hons, 2005).

Soil conversion from native to agricultural land produces the major effect on SOC. Typically the SOC concentration in the topsoil decays rapidly after several years of tillage and thereafter it stabilizes (Acevedo and Martinez, 2003; Paustian et al., 1997). Changes of agronomic managements such as crop species, fertilizer usage, crop rotations and tillage systems influence the rate of SOC accumulation and mineralization (Ringius, 2002).

It has been reported that tillage conservation can sequester different C amount depending of climate conditions, for example: 0.5-1 Mg C year<sup>-1</sup> in humid-temperate climates; 0.2-0.5 Mg C year<sup>-1</sup> in humid-tropical soils and 0.1-0.2 Mg C year<sup>-1</sup> in semi-arid areas (Lal, 2009). Six et al. (2002) found that under zero tillage the SOC stocks increased compared to conventional tillage in temperate and tropical agroecosystems. Therefore, the values of C sequestration were 0.43 Mg C ha<sup>-1</sup> year<sup>-1</sup> in tropical soils and 0.16 Mg C ha<sup>-1</sup> year<sup>-1</sup> in temperate soils (0-10 cm depth). Smith (2004) estimated in cultivated soils the potential for C storage in European soils was 0.38-0.62 Mg C year<sup>-1</sup> at the same depth.

The concept of effective stabilization capacity of soil organic matter (SOM) refers to the ability of a soil under certain land-use to accumulate and maintain a maximum level of SOM (Stewart et al., 2007). This can not be confounded with steady state or equilibrium level, the balance of C inputs and C outputs. Depending on land-use management, the SOC storing capacity is expressed in terms of its protection by the way of aggregation and chemical and physical stabilization properties (Baldock and Skjemstad, 2000). Then SOM accumulates as part of soil aggregates in the POM (particulate organic matter) and light fraction. In the literature there is a discrepancy.

On one side, metals such as Al and Fe complexed with SOM are the main agents for organic matter stabilization in volcanic soils and, on the other side, amorphous clays such as allophane and imogolite are the stabilizing agents.

Although crystalline clays with large surface area are often considered to play an important role in the stabilization of SOM protecting it from microbial attack (Six et al., 2001), several studies have suggested that in allophanic soils, Al hydroxides and organo-mineral complexes, instead of amorphous clays such as allophane, are the key agents for SOC stabilization. Matus et al. (2006) showed that the extraction of Al in ammonium acetate, rather than the clay content and climatic conditions, controls the SOC levels in Chilean allophanic soils. By the matter of facts it has been shown that the addition of allophanic materials by the way of mixing alluvial soil materials, reduced losses of CO<sub>2</sub> from glucose applied to this mixture (Zunino et al., 1982). Other studies have established the effect of chemical protection from the biodegradation using synthetic organo-mineral complexes (Al plus citric acid, Boudot, 1992). They concluded that the adsorption was dominated by the complex non-crystalline Al hydroxides that reduced mineralization and not by allophane and imogolite per se (Boudot, 1992).

On the other hand, the dissolved organic carbon (DOC) has been identified as key to the formation of stable complexes in acid forest soils (Scheel et al., 2007). These results therefore support the idea that both the Al and allophanic type materials are the determinants factors for the stabilization of SOM in volcanic soils. Recently it was found that approximately 35% of total soil C is complexed with Al, probably precipitated and the remaining is complexed by allophane materials and by soil aggregates (Matus et al., 2008). This indicates that both the physical and chemical SOC fractionation are the key methodological factors for understanding the mechanisms for C sequestration in volcanic soils.

## **1.2 Hypothesis**

In the literature there is a discrepancy. On one side, metals such as Al and Fe complexed with SOM are the main agents for organic matter stabilization in volcanic soils and, on the other side, amorphous clays such as allophane and imogolite are the stabilizing agents.

- In this thesis we propose that both, the allophane like materials and Al-complexed with SOM are the key factors for SOM stabilization and storage. The remaining fraction is thought to be physical protected by soil aggregates in C pools such as POM and light fractions.

## **1.3 General objective**

The objective of this study is to determine the stabilization capacity, storage and distribution of SOM of various fractions of allophanic soils under different land-use.

## **1.4 Specific objectives:**

The goals of this thesis were to:

- 1) To determine the SOM stabilization capacity and storage of allophanic soils under different land-uses managements (rain forest and managed pasture ecosystem).
- 2) To determine the physical distribution of SOM fractions in allophanic soils at various depths under different land-uses managements (rain forest and managed pasture ecosystem).

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## **CHAPTER 2**

### ***Allophanic soils: Storage capacity and stabilization mechanisms***

**This paper modified was accepted in European Journal of Soil Science**

## **Abstract**

The need to reduce CO<sub>2</sub> emissions into the atmosphere has encouraged several researchers to use the soil as a carbon sink. Approximately 81 % of the terrestrial carbon cycle is stored in the soil, whose mechanisms of stabilization are not well understood. Moreover, the conversion of natural ecosystems, such as native forest to arable farming systems, reduce the contents of soil organic matter (SOM), causing a rapid increase of decomposition at early stage of land cultivation. The long-term experiments indicate that conventional till and burning practices of stubbles harvesting crops may influence the quantity and composition of SOM. This is because of the potential losses of carbon by horizontal and vertical transportation. This may account for the lack of knowledge to understand the processes involved in SOM reduction. Therefore, measures must not only focus on mitigating CO<sub>2</sub> emissions, but also in understanding the changes in rapid decrease of SOM by the effect of land use and managements.

**Keywords:** Carbon sequestration, land use, managements, soil carbon accumulation.

## 2.1 Introduction

Carbon sequestration in soil is an important strategy to mitigate the increase of CO<sub>2</sub> concentrations, since it involves the transfer of atmospheric CO<sub>2</sub> in more stable soil organic carbon (SOC) fractions (Schimel et al., 1997). The permanence of SOC depends largely on the balance between contributions and the losses by decomposition, however there are factors that play a fundamental role in stabilizing of SOM such as mineralogy, climatic conditions and tillage. The process of stabilization and decomposition of SOM occurs simultaneously in the soil and depends on the interaction between the substrate and soil colloids. One of the most important stabilization mechanisms is the interaction of SOM with soil minerals (Rumpel et al., 2002; Six et al., 2002). But it should be bear in mind that there are other fractions of SOM such as particulate organic matter (POM) and protected organic matter in soil aggregates that may become important when attempting to prepare a carbon balance in soils.

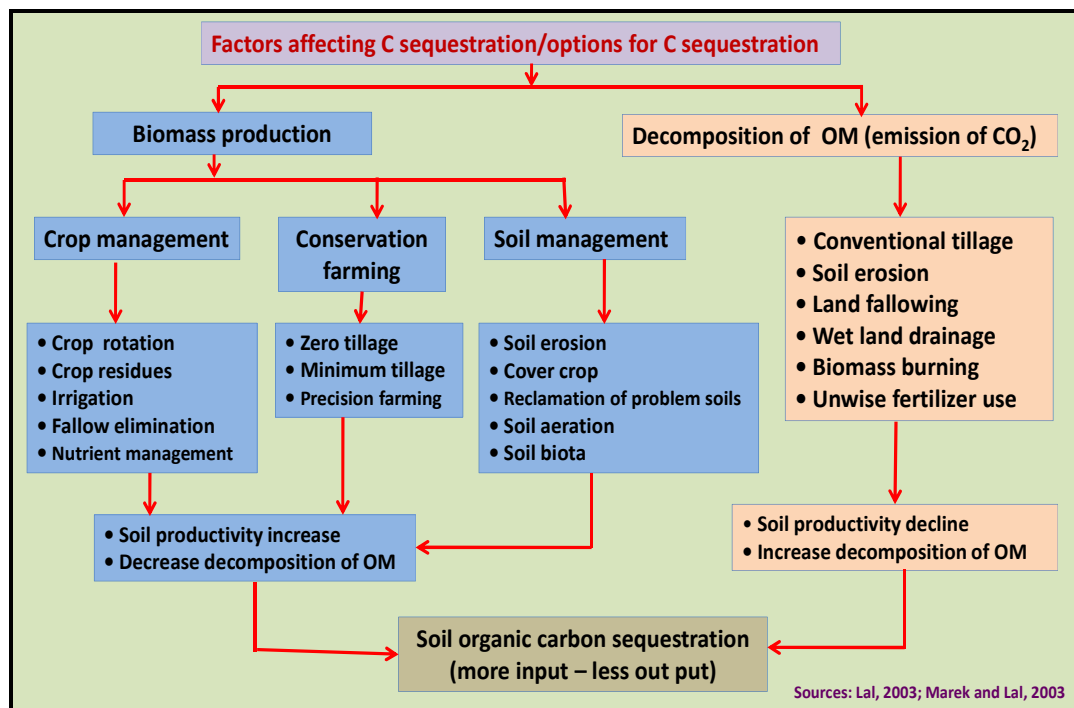
The stability of C in soil not only depends on physicochemical mechanisms, but also from practices such as conventional tillage. For example, zero tillage promotes the maintenance and accumulation of SOM, decreasing the rate of decomposition (Acevedo and Martinez, 2003). Therefore, the adoption of conservation management practices can increase the sustainability and consequently the soil fertility in the long-term. However, it is important to recognize that the results depend on soil type and climate conditions (Wright and Hons, 2005). Therefore, it is essential to understand the mechanisms of stabilization, considering that all soils do not have the same origin and thus, their behavior will be different under external factors (temperature and precipitation), as well as by their inherent characteristics, e.g. soil pH, clay type and topography.

## **2.2 Carbon sequestration**

The need to reduce CO<sub>2</sub> emissions into the atmosphere has stimulated the land-use as a reservoir of carbon. More than 2/3 of SOC actively involved in the terrestrial C cycle is stored in the soil (Wattel-Koekkoek et al., 2001). The study of this pool present comparative advantage in relation to other smaller pools (Mahieu et al., 1999). But the conversion of natural ecosystems to agricultural systems by soil cultivation, for instance by plowing, has decreased SOC content, promoting CO<sub>2</sub> release into the atmosphere (Lal, 2004). Therefore, the introduction of measurements and policies to reduce emissions should be directed to maintain practices that promote physical protection of soil losses and increase the levels of SOM.

## **2.3 Management and soil organic matter accumulation**

Soils have different capabilities to accumulate SOM. These are based on well-defined characteristics, including rates of incorporation, (Matus and Maire, 2000) which is directly affected by the use and management of soil. In Chile, approximately 5.1 million hectares of volcanic soils are devoted for agriculture (Mella and Khüne, 1985). At present, approximately 80 % of agricultural land area is destined to cereals and grasslands production (Matus et al., 2006b). The ability and potential to raise or lower the soil C storage depends on the balance between input and output. Therefore a change in soil management can alter the input and output balance, altering the C storage capacity of soil (Figure 2.1) (Bolan et al., 2010).



**Figure 2.1.** Factors affecting C sequestration (Lal, 2003; Marek and Lal, 2003 as supplemented by Chowdhury et al., 2011)

The adoption of appropriate land use and management practices such as zero tillage, promote the maintenance and accumulation of SOC (Acevedo and Martinez, 2003; Wright and Hons, 2005; Wright et al., 2005). This is supported by a lower rate of decomposition which is obtained with zero tillage compared to conventional tillage, as a result of non-inversion of soil. In this way we can maximize the accumulation of C and minimize losses by maintaining soil aggregates (Stewart et al., 2007). But the results vary according to the agro-ecosystem, soil type, cropping intensity, residue management and climate (Paustian et al., 1997; Robert, 2002; Wright and Hons, 2005). In this sense, more researchers focused on the activity of earthworms in soil ecosystems. Of special interest has been the key role played by earthworms in the formation and stability of soil aggregates and the cycling of nutrients (Edwards and Bohlen, 1996) by removing plant litter and other organic materials from the soil surface and their incorporation into soil aggregates (Martin, 1991). Early researchers (van de Westeringh, 1972) have stated that up to 50% of surface layer soil aggregates in temperate pastures are earthworm casts. Lee (1985) estimated that in an

average temperature pasture and grasslands, earthworms cast attained 40-50 Mg ha<sup>-1</sup> year<sup>-1</sup> on the surface and even more below the surface.

In addition, conservation practices included the incorporation of crop residues (Acevedo and Martinez, 2003) instead of burning them. Long-term burning residues have generated a pool of recalcitrant carbon, the so called black carbon, which may become significant in places where slash/burn is practiced together with burning stubbles residues (Baldock and Skjemstad, 2000).

## **2.4 Soil organic matter pools and mechanisms of stabilization**

The stabilization and accumulation of SOM depends on a variety of factors including the quality and rate of incorporation, soil texture, soil moisture and temperature, as well as the soil losses by erosion (Sparling et al., 2003; Lal, 2009). In this regard Baldock and Skjemstad (2000) point out that each parent materials has a unique ability to stabilize C, which not only depends on minerals to adsorb organic materials, but also the nature of mineral fraction of soil, presence of cations and architecture of the soil matrix.

The stabilization occurs through three main mechanisms (Sollins et al., 2006). Firstly, the chemical stabilization is the result of an associations between soil particles (mostly silt and clay) and SOM (Gonzalez and Laird, 2003) secondly, biochemical stabilization, a highly complex physico-chemical interaction between organic compounds such as lignin and polyphenols and soil particles, (Leinweber and Reuter, 1992; Six et al., 2002) and finally, physical stabilization in which aggregates act as a physical barrier between microorganisms and substrates (Elliott and Coleman, 1988; Six et al., 2002).

The scientific evidence shows that the stabilization of carbon is related to the fine fraction (clay and silt), which would be the decisive factor in stabilizing SOM (Hassink, 1997; Hassink and Whitmore, 1997). This interaction would occur through chemical protection between minerals and organic compounds by complexation and sorption (Feller et al., 2001; Krüll et al., 2003; Korschens et al., 1998). In this regard, Six et al. (2002) found positive relations between the carbon content and the fine fraction of the soil, together with the physical protection in stable soil



aggregates and biochemical protection given by the complexity of the substrate at molecular level. However it should be take into account that the land-use and soil management (West and Six, 2007), as well as the type of clay may influence those interaction to a greater extent. For instance, 1:1 clay stabilizes lesser amounts of carbon than 2:1 clay type. This support that 2:1 clay possess greater storage capacity due to their high specific surface area (Besoain, 1984). On a field scale the existence of a significant and positive correlation between soil organic carbon and clay content show that the nature and amount of clay are determinants factors for soil C accumulation in grasslands, forests and cropping soils (Homann et al., 1998; Matus and Maire, 2000).

Soils derived from volcanic ash with unique andic features (Andosols, according to USDA classification) are characterized by large content SOM, low pH and high phosphate retention capacity. Organic matter contains a number of high (humic acids) and low (fulvic acids) molecular weight compounds that carry functional groups such as carboxylic groups that are capable of complexing Al. This compound, the so called Al-humus strongly protects SOM from microbial attack, avoiding the transformation of SOC into CO<sub>2</sub> (Garcia-Rodeja et al., 2004).

The Chilean Andosols are characterized by high content of organic matter but also by a significant amount of active Al, mainly amorphous, poorly crystalline minerals, with low bulk density (Besoain, 1985). These soils cover a significant area of agricultural land, 50 % to 60 % of the arable soils (5.1 millions hectares), where most of cereals and livestock production is performed (Mella and Künhe, 1985).

#### **2.4.1 Soil organic matter stabilization in allophanic soils**

The factors in temperate zones that dominate the rate of SOM transformation are: climate, parent material and biota (fungi, bacteria, worms and roots). These characteristics allow the rate of decomposition of organic compounds to be lower in temperate soils leading a greater carbon residence time in soil (Six et al., 2002). In allophanic soils, the stability of C occurs mainly by the complexation of Al with humus (Boudot, 1992; Khale et al., 2003; Nanzzyo et al., 1993) and by adsorption of humic substances by allophane or imogolite type materials (Feller et al., 2001;

Matus et al., 2008). Sadzawka and Porte (1985) indicate that in soils derived from volcanic ash in Southern Chile, Al bound to humus is the major fraction of total C at the upper soil horizon, suggesting that SOC and Al bound together to form complexes of Al-humus, as described for other volcanic soils (Shoji and Fujiwara, 1984). However, climate factors and clay content and its mineralogy are unable to explain the dynamics of SOC accumulation and stabilization in allophanic soils (Percival et al., 2000; Matus et al., 2006a).

Nanzio et al. (1993) and Shoji et al. (1993) clearly elucidate that the Al extracted in sodium pyrophosphate ( $Al_p$ ) correlated positively with the SOC. Percival et al. (2000) found a strong relationship between  $Al_p$  and SOC on allophanic soil from New Zealand. This relationship improved when temperature and precipitation were incorporated. Recently, Matus et al. (2006) determined that extractable Al in acid ammonium acetate ( $Al_a$ ) explained the greatest variation of SOC in Chilean allophanic soils. It should be noticed that climatic conditions (mainly precipitation and temperature), as well as the content of clay+silt may have played a key role on SOC immobilization. The stabilizing effect in allophanic soils is due mainly to Al-humus interaction, while other important component such as allophane and imogolite type materials must also be considered (Parfitt, 2002).

The allophane mineral is a poorly crystalline aluminium-silicate with variable electrical charge and high surface area. The molar ratio of Al/Si ranges between 1 and 2, even when allophanic soils can be identified as Al-rich ( $Al/Si = 2:1$ ) and Si-rich ( $Al/Si = 1:1$ ) (Feller et al., 2001). Allophane minerals are strongly linked to organic component, generating a complex humus-allophane colloid of high stability (Zunino et al., 1982). These authors compared the mineralization of various organic compounds labelled with  $^{14}C$ . Their results showed a slow decomposition rates in volcanic soils, which is attributed to the direct adsorption of organic colloids, probably by the formation of complexes of Al-humus and allophane-humus interactions. These features allowed to Zunino et al. (1982) argue that the stabilizing factor on SOM is produced by the direct adsorption of organic compounds on the surface of allophane by forming a very stable organo-mineral complex.

To assess the role and chemistry of soil Al-humus complex, Al extracted by acid oxalate is considered to represent the sum of Al-humus complex and non-crystalline hydrous oxides in allophane and imogolite type minerals. Al extracted by NaOH is regarded to remove crystalline, amorphous and complexed Al with SOM, while Al extracted with Na-pyrophosphate is used to estimate the Al in organic complexes, because this has small effect on hydrous oxides and in allophane and imogolite (García-Rodeja et al., 2004). Various doubts, however, are linked with the use of pyrophosphate. It is efficient in extracting Al-humus complexes, but may also take out some interlayer Al and relatively labile forms of precipitated Al. It has been recognized that pyrophosphate also extract amorphous Al hydroxides and gibbsite (Kaiser and Zech, 1996). Extractions with unbuffered salts, such as  $\text{CuCl}_2$  (Juo and Kamprath, 1979) or  $\text{LaCl}_3$  (Bloom et al., 1979) have been proposed to remove Al from organic matter (Hargrove and Thomas, 1981; 1984; Oates and Kamprath, 1983; Walker et al., 1990). Extraction with KCl remove the Al from easy exchangeable sites and represents the less stable form of soil Al (García-Rodeja et al., 2004), while acid ammonium acetate may dissolve soluble forms from exchangeable sites plus some Al-humus complexes and some  $\text{Al}(\text{OH})_3$  in addition (McLean, 1965). Extraction with acid ammonium acetate is consequently not as effective as Na-pyrophosphate solution, but stronger than un-buffered KCl salt and it can be assumed to extract similar amount of  $\text{Al}_{\text{Cu}}$ . This makes  $\text{Al}_a$  an interesting agent but a rarely used dissolution method for studies of SOM where Al-SOM complexes and poorly crystalline Al-forms are common (Matus et al., 2006a).

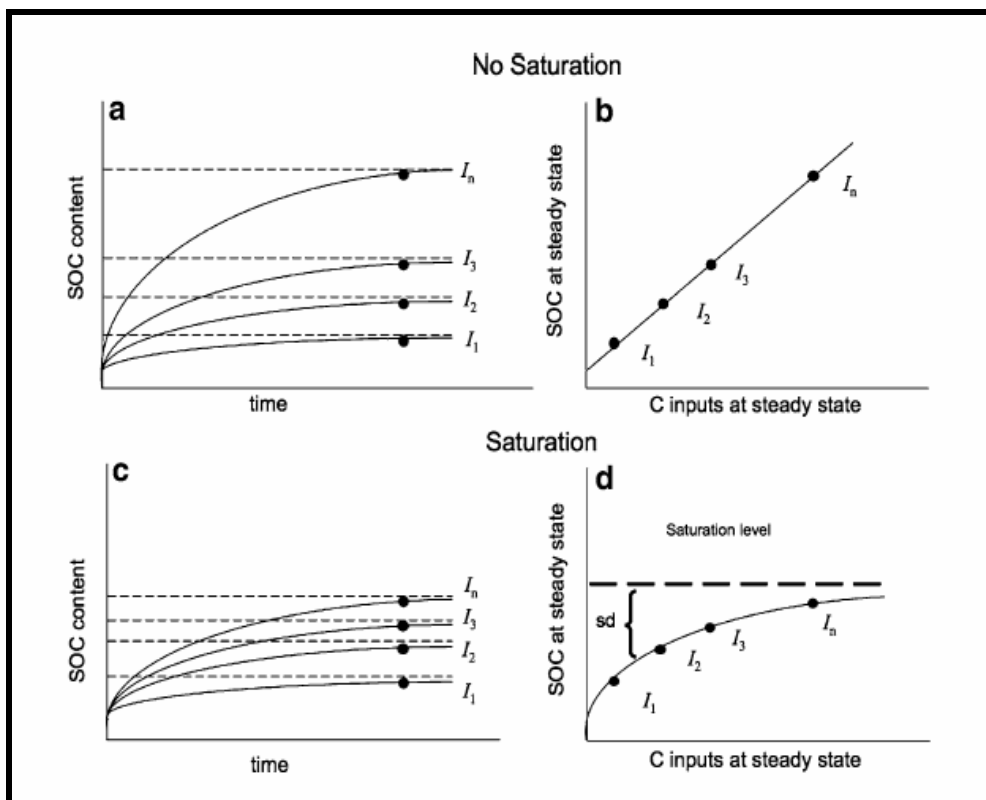
#### **2.4.2 New approach to assess Aluminium-humus complex in allophanic soils**

The SOM can be divided into different components according to the solubility, which are heavily dependent on the interaction with polyvalent cations and mineral surfaces (Sposito, 1984). This makes SOM an insoluble compound in many soils because of interaction with minerals (Sollins et al., 1996). We therefore, can assume that a relevant portion of SOM stability is related to its solubility. For instance, one may expect a large quantity of soluble organic C is linked to Al pyrophosphate. So far, few papers report this measurement, which can be an easy tool to assess the Al-humus carbon pool (Rodriguez et al., 2005; Donisa et al., 2003; Matus et al., 2008). The last authors found that approximately 35 % of the total organic carbon is extracted in Al pyrophosphate ( $\text{C}_p$ ). They recognize that pyrophosphates extract most Al-humus but some

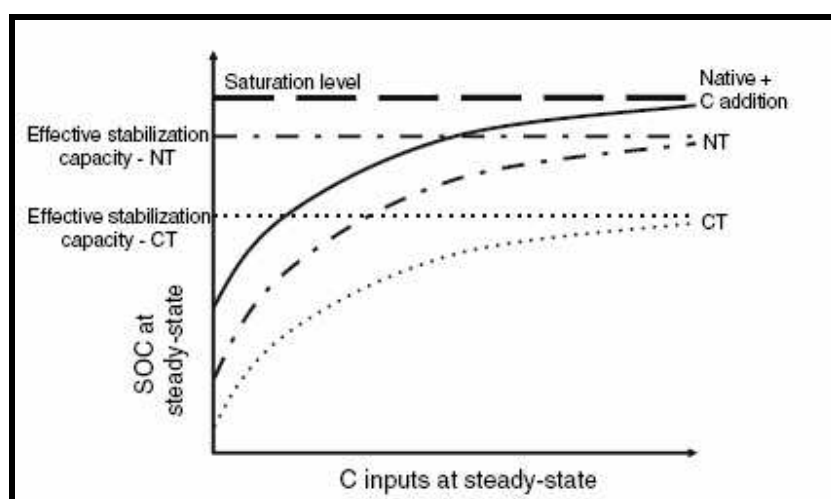
interlayer complexed Al in the silt+clay or relatively labile forms of surface-precipitated Al-OM can be dissolved (García-Rodeja et al., 2004). In spite of  $C_p$  was considered an independent C pool, other than SOC associated to allophane (Matus et al., 2008).

### **2.4.3 Stabilization capacity of soil organic matter**

The accumulation of SOM not only depends on the type and nature of clay and biochemical composition of plant materials that is incorporated into the soil, but also the frequency of carbon inputs. Hassink and Whitmore (1997) postulated that the texture largely influences the accumulation of C in soils, arguing that the ability for SOM protection is based on fine fraction content (silt + clay). They found that SOM in the silt and clay fraction of meadow and arable soils were the same, concluding that the soil reached a maximum, the so called protective capacity. Carbon input beyond the protective capacity are not fully stabilized and it is accumulated in the fraction  $> 20 \mu\text{m}$ , namely, macro-organic matter. It should be noticed that the protective capacity concepts is different from the equilibrium concepts. Equilibrium dictate that SOM can not be further accumulated in soil because the C input balances the C output (Figure 2.2a). The association between C input and SOM can be visualized as a linear relationship (Figure 2.2b) (Stewart et al., 2007). The effective stabilization capacity was defined by Stewart et al. (2007) and includes the soil protective capacity, but it takes into account that whole SOM can reach a maximum (Figure 2.2c) depending on land-use and soil management practices (Figure 2.3). Therefore the linear proportion now becomes asymptotic (Figure 2.2d). Different C input to the soil may have different balances, thus increasing the levels of C input; SOM can reach a new higher equilibrium. With new additions of organic matter, the effective stabilization capacity can be reached and SOM cannot be stored for longer period and therefore, it is mineralized quickly (Körschne et al., 1998; Stewart et al., 2008; Matus et al., 2008).



**Figure 2.2.** Relationship between theoretical levels of incorporation of C and the contents of things in balance, with and without saturation (Stewart et al., 2007).

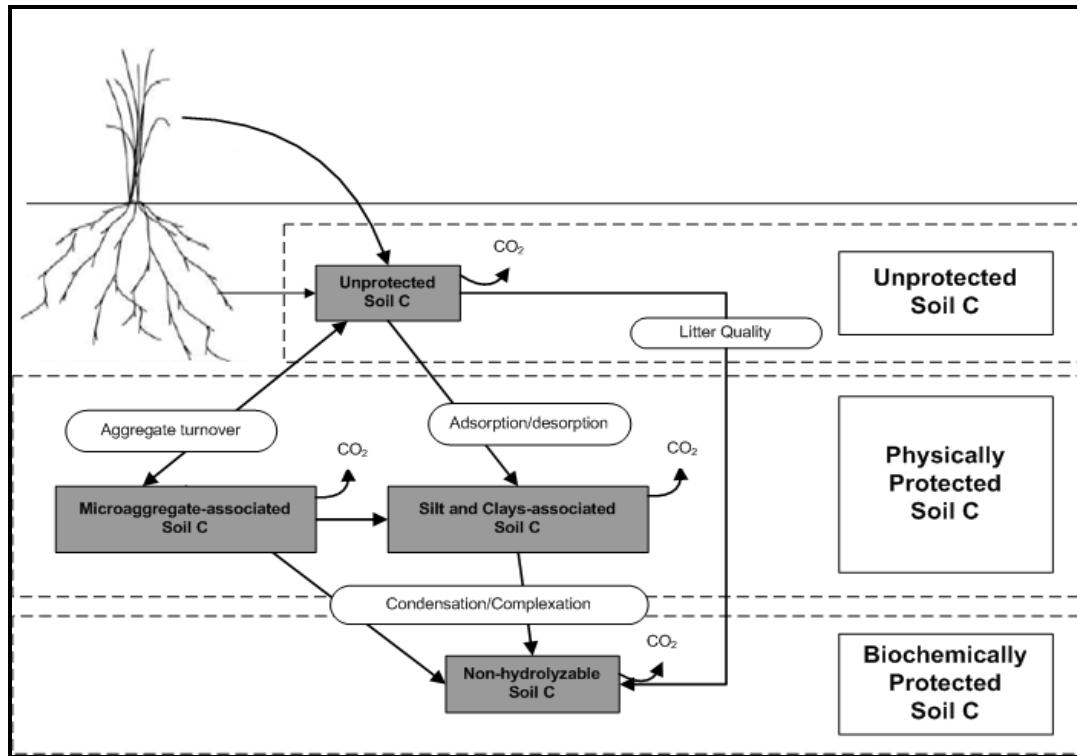


**Figure 2.3.** Effective stabilization capacity on two soil managements (Stewart et al., 2007).

These above mentioned concepts have been worked out well for non-volcanic soils. However, in volcanic soils this needs to be addressed regarding the effect of Al-complex as the key factor for SOM stabilization.

## **2.5 Physical fractionation of soil organic matter and modelling**

An approach to understanding the mechanisms of stabilization of carbon is the physical fractionation that allows separation of various fractions of organic matter, avoiding chemical changes when using reagents for SOM extraction. In this way we can increase the biological meaning that matches with ecological more sensitive change to management and land-use (Six et al., 2002). Basic mechanistic soil processes were incorporated in the model developed to study the soil C dynamics early. Six et al. (2002) proposed a conceptual pools (active, slow and passive) modified from C pools by Jenkinson and Rayner (1977) and Parton et al. (1987). The hypothesis presented was that the microaggregate-protected C plus silt- and clay protected C represents part of the slow pool whereas the unprotected pool represents the active fraction and part of the slow pool (Figure 2.4). The non-hydrolyzable fraction of the silt and clay-associated C represents the biochemically protected pool and was hypothesized to be comparable to the passive pool. The unprotected C pool is POM or LF not occluded within microaggregates whereas the microaggregate-protected C pool is the POM occluded within microaggregates (Six et al., 2002). The processes of microaggregate formation/degradation (i.e. microaggregate turnover), adsorption/ desorption, and condensation/complexation are the main mechanisms of protection and release of SOM. The direct transformation of unprotected soil C to the biochemically stabilized non-hydrolyzable soil C is mainly determined by litter quality. Incorporation of the processes of desorption and adsorption was used by Hassink and Whitmore (1997) to model silt- and clay-protection of SOM. Condensation and complexation dynamics have been studied and information is available in the literature (Six et al., 2002). Microaggregate formation and degradation are beginning to be understood, but more detailed information about microaggregate behavior must be obtained to accurately model these processes in allophanic soils.



**Figure 2.4** Pools of soil organic C with varying degrees of protection and mechanisms of stabilization (Six et al., 2002)

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## CHAPTER 3

### *Soil carbon storage in allophanic soils: Study of a temperate pristine rainforest Nothofagus pumilio in the altitudinal limit*

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# Soil carbon storage in allophanic soils: Study of a temperate pristine rainforest *Nothofagus pumilio* in the altitudinal limit

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## Abstract

We present an overview of the factors and mechanisms involved in carbon storage in Chilean allophanic soils with particular reference to porous steeped (30-70% slopes) volcanic materials occurring in the piedmont and dejections cones of the volcano range in Chile. These soils comprehend more than 50% of the volcanic soils area. We discuss the organic carbon stabilization in term of previous research in more well developed soils from agricultural sites in the southern regions of Chile. Rainforest ecosystems in the mountain range (most eastern part) standing on recent substratum, like porous volcanic soil, may become limiting in their carbon and nitrogen retention. Therefore, these ecosystems should present conservation strategies for soil carbon under conditions of high rainfall ( $> 5,000 \text{ mm y}^{-1}$ ) scenarios. In this context Antillanca soil is a black sand scoriaceous basaltic material occurring mainly on the upper slopes of Casablanca and Antillanca volcanoes ( $40^{\circ}47'S$ ,  $72^{\circ}12' W$ , 920-1,120 m a.s.l.), where the temperate pristine rainforest *Nothofagus pumilio* (Poepp et Endl) stand is close to the treeline. We studied the soil carbon distribution in nine soil profiles as well as some relevant soil properties interacting with carbon preservation through combination of chemical fractionation (Al-organic matter complex, including their recalcitrance) and biological measurements such as microbial biomass and soil carbon mineralization under incubation conditions. We also investigate the protective capacity of these soils, i.e. the upper limit of a soil to store organic carbon. All of these aspects and inferences are presented and discussed from an ecological point of view.

### 3.1 Introduction

Soil organic matter (SOM) turnover slows down by environmental factors such as low temperature. However, even under these conditions, the mechanisms favouring SOM preservation, including interaction of soil organic carbon (SOC) with clay minerals by physical adsorption via van der Waals forces, electrostatic attraction, cation and anion bridges, sorption of humic substances through polyvalent metal cations of  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Ca}^{2+}$ , provide the main stabilization processes and may occur very rapidly in milliseconds (Spark, 2003). These interactions often lead to a positive and significant relationship between the distinctive clay sized fraction and SOC. However, in Chilean allophanic soils, such relationship has not been found (Matus et al., 2003; Matus et al., 2008). Instead, Al and Fe are strongly correlated with SOC, probably via ligand exchange mechanism. Matus et al. (2008), pointed out that c.a. 40% of all soil C was like an independent C pool, other than the C associated to the mineral clay (and silt) fraction, indicating that the humic substances associated to Al and Fe complexes should be regarded as an easily measurable SOM pool.

In this paper we present an overview of the mechanisms involved on SOC stabilization in allophanic soils, particularly on those belonging to steeped volcanic soils from the southern temperate rainforest standing on the porous volcanic materials such the Antillanca soil in the National Park of Puyehue. We investigated the stability of the SOC in the top and deep soil layers by combining chemical fractionation (Al-organic matter complex, extracted by Na-pyrophosphate ( $\text{Al}_p$ ,  $\text{Fe}_p$ ) and C measured in the extract,  $\text{C}_p$ ) with the biological activity (microbial biomass and C mineralization). Finally, we studied the protective capacity of these soils (the upper limit of a soil to store SOC) by a theoretical and practical approach.

### 3.2 Mechanisms of soil organic carbon stabilization

Soil C storage is controlled primarily by the input of net primary production (quantity and quality) and by its decomposition rate. Decomposition of organic matter in temperate soils is carried out mainly by soil heterotrophic microbes which constitute about 2-4% of SOC (Jenkinson and Ladd, 1981). Abiotic chemical oxidation is likely to account for less than 5% of

organic matter decomposition (Lavelle et al., 1993). There is a continuum from undecomposed to much decomposed organic material as a result of biotic oxidation in the early stage of decomposition. In this phase, namely the labile or active phase, the turnover time (the inverse of mean residence time of a molecule in a C reservoir<sup>1</sup>) is about 1 to 2 yr and 25-66% of the initial C is lost depending on the chemical nature of organic compounds (Jenkinson and Ladd, 1981). The intermediate stage of decomposition accounts for a total loss of about 90% of the initial C (turnover time ca. 10-100 year) and it is regarded as the transitional organic matter pool (Von Lutzöw et al., 2006). The complete decay process comprises a late stage of decomposition with a turnover time of ca. 100 to more than 1000 year, accounting for the long-term stabilization of C in soils (Von Lutzöw et al., 2006). The stabilization of soil C can be defined as the processes that contribute to reduce SOC losses and can be achieved by several mechanisms which have recently received a lot of attention due to its importance in the global terrestrial C cycling. Depending on the nature of soils (volcanic or non-volcanic) one or more of these mechanisms dominate.

The protection of SOC is often used as a generalized term in the specialized literature and involves all mechanisms of SOC stabilization (Von Lutzöw et al., 2006). One of this is the selective preservation of SOC due to recalcitrance, including plant litter, microbial by products, rhizodeposition of organic compounds, humic polymers, and charred organic matter. The spatial inaccessibility of organic matter for decomposers due to encapsulation, occlusion, intercalation, hydrophobicity and stabilization by interaction with mineral surfaces (Fe-, Al-, Mn-oxides, and phyllosilicates) and metal ions is a form of physical and chemical protection. However, these concepts are far from a complete understanding. For instance, molecular recalcitrance of organic compounds is a relative concept, because it is important during the early stage of decomposition while during the later stage, spatial inaccessibility and organo-mineral interactions acquire more relevance (Von Lutzöw et al., 2006). The main difficulty in predicting SOC dynamics is due to

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<sup>1</sup> Carbon reservoir: it is the available quantity of soil C for decomposition within one specific compartment (C pool). Any reservoir may evolve through exchanges with the other ones (biogeochemical or geochemical fluxes). Mean residence time is the average time of organic molecule remaining in a biogeochemical reservoir. Assuming that the pool of C at steady state (input SOM = output SOM =  $dQ/dt$ ) and contains an amount  $Q$  of organic matter, the mean residence time  $\tau = Q/(dQ/dt)$ .

the simultaneous occurrence of the various factors and mechanisms of SOC stabilization (Von Lutzöw et al., 2006).

The factors contributing to SOC stabilization are those residing in the soil environment for example, the amount and nature of clay, microbial activity, soil pH, and free Al and Fe. Other external conditions such as temperature and precipitation also play a key role in C stabilization.

### **3.2.1 Stabilization of organic carbon in Chilean allophanic soils**

Chilean volcanic soils are known to contain allophane (about 50% of clay weight) and they are rich in soil organic matter (up to 31%) (Matus et al., 2008). Furthermore, they contain also considerable amounts of reactive Al and amorphous Fe and poorly crystallized minerals and oxides, which cause their unique characteristics, e.g. low bulk density and high phosphate retention (Matus et al., 2006; Shoji et al., 1993). In general the input of organic matter and decomposition rates are controlled by factors such as climate, drainage and land use, which in turn control the SOM levels. There is also evidence that Al (extracted with Na-pyrophosphate) influences the SOM content in volcanic soils, since a positive and highly significant relationship has been found between these two variables (Matus et al., 2008; Percival et al., 2000). The stabilizing effect of Al is due to complexation with SOC in the soil solution and subsequent precipitation as insoluble Al–SOM complexes, suppressing microbial enzyme activity and substrate degradation (Sollins et al., 1996). Therefore, there may be a confounding effect between Al, clay content and mineralogy in volcanic soils. The clay fraction in many volcanic soils, rich in Al, Fe and oxides, together with allophanic and imogolite type materials may slow down SOM decomposition (Sollins et al., 1996; Zunino et al., 1982; Parfitt et al., 2002). Although phyllosilicate clays are considered to play an important role in stabilizing SOM decomposition, studies have pointed out that amorphous Al hydroxides and insoluble organically bond Al rather than allophane (or imogolite type materials) are the key parameters for SOM stabilization (Boudot, 1992). Matus et al. (2006) showed that extractable Al in acid ammonium acetate, rather than clay content and climatic factors, controlled the variation of SOC levels in Chilean allophanic soils on a regional scale from southern latitude 36 ° to 42 ° (Table 3.1; Figure 3.1). Basile-Doelsh et al. (2007), however, recently showed that the largest proportion (82.6%) of SOM in the top horizon was associated with minerals in organo-mineral complexes of imogolite

type materials. In contrast, Scheel et al. (2007) showed that between 13% and 84% of the dissolved organic C (DOC) was precipitated with Al, depending on pH, Al/C ratio and the type of DOC. These results therefore support the idea that both Al and allophanic materials are the major factors for immobilization of SOM in volcanic soils. Aluminium measured in the extract of Na-pyrophosphate at pH 10 is often used to estimate the Al complexed with organic matter. Matus et al. (2008) examined the effects of Al, silt plus clay content (particles size 0–53  $\mu\text{m}$ ) and clay mineralogy on the control of the SOC level in volcanic soils. They found that Al extracted with pyrophosphate ( $\text{Al}_p$ ) was highly correlated with the SOC ( $R^2 = 0.62$ ;  $P < 0.01$ ). They also found that the soluble C measured in the extract of pyrophosphate ( $C_p$ ) together with clay mineralogy, i.e. the quantity of allophane and its C associated in the silt plus clay fraction, rather than the silt and clay content of soil, controls the largest proportion of variation of SOM across volcanic soils in Chile. Thus,  $C_p$  accounted for about 40% of the whole SOC (Matus et al., 2008). Therefore, this C pool can be distinguished from the C associated with allophane by a C balance in which the sum of both accounted for most of the whole C in allophanic soils (Matus et al., 2011).

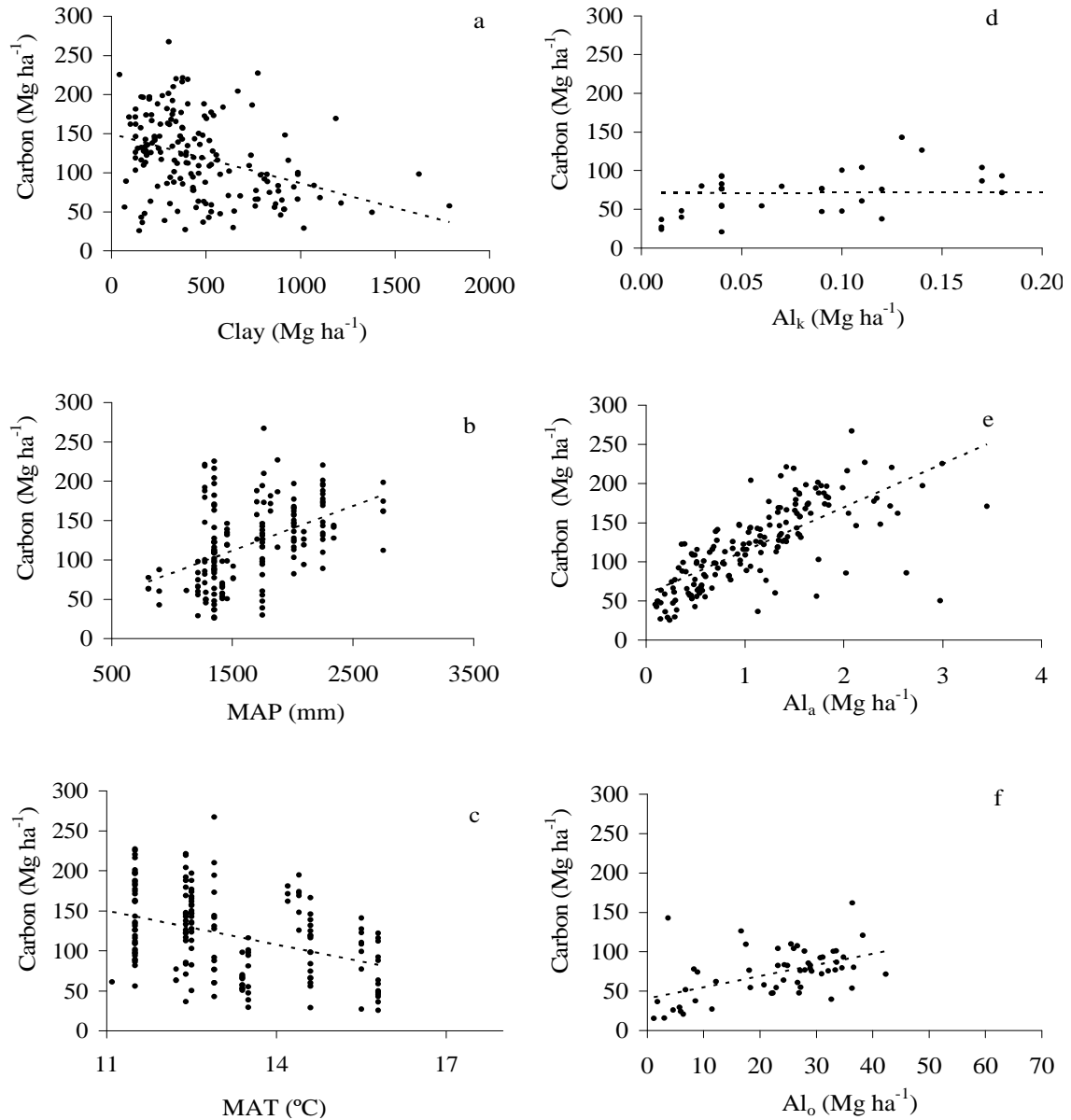
**Table 3.1.** Coefficient of determination ( $R^2$ ) of soil organic C ( $\text{Mg ha}^{-1}$ ) versus mean annual precipitation (MAP), mean annual temperature (MAT), and amounts  $\text{ha}^{-1}$  (0–20 cm) of silt, clay, and ammonium-acetate-extractable Al ( $\text{Al}_a$ ) for the investigated soil orders (After Matus et al. 2006) with permission from Elsevier).

Soil order	MAP (mm)	MAT ( $^{\circ}\text{C}$ )	Silt	Clay ( $\text{Mg ha}^{-1}$ )	$\text{Al}_a$	Multiple regression <sup>a</sup>
Alfisol (n = 14)	0.21 <sup>ns</sup>	0.21 <sup>ns</sup>	0.23 <sup>ns</sup>	0.16 <sup>ns</sup>	0.65***	0.84**
Andisol (n = 126)	0.09***	0.11***	0.03 <sup>ns</sup>	0.02 <sup>ns</sup>	0.40***	0.40***
Inceptisol (n = 14)	0.54**	0.53**	0.00 <sup>ns</sup>	0.00 <sup>ns</sup>	0.88***	0.88***
Ultisol (n = 15)	0.50**	0.54**	0.33*	0.09 <sup>ns</sup>	0.55**	0.55**
All (n = 169)	0.21***	0.15***	0.05**	0.14***	0.52***	0.55** <sup>b</sup>

ns= not significant; \*, \*\*, \*\*\* = significant at  $p < 0.05$ ,  $p < 0.01$ ,  $p < 0.001$ , respectively

<sup>a</sup>  $\text{Al}_a$  and MAT were the model parameter for Alfisols, and  $\text{Al}_a$  for other soil orders.

<sup>b</sup>  $C = 30.79 + 49.70 \times \text{Al}_a + 0.021 \times \text{MAP}$



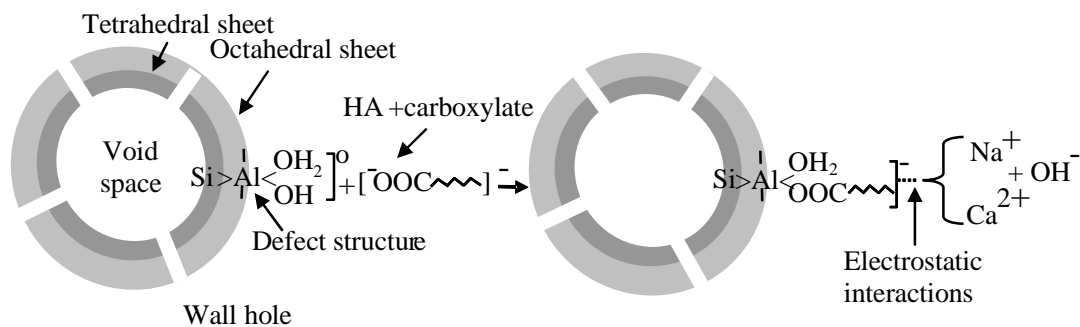
**Figure. 3.1** Relationships from simple regressions between soil organic C and (a) soil clay content, (b) mean annual precipitation (MAP), (c) mean annual air temperature (MAT), (d) KCl-extractable Al (Al<sub>k</sub>), (e) acid ammonium acetate-extractable Al (Al<sub>a</sub>) and (f) oxalate-extractable Al (Al<sub>o</sub>) for samples soils (0-20 cm), n = 169 from Table 3.1. Al<sub>k</sub> and Al<sub>o</sub> were not done for all soil samples (after Matus et al. (2006) with permission from Elsevier)



Many researchers have pointed out that ligand exchange (LE) is the major mechanism controlling the sorption of humic substances by variable-charge minerals (Spark, 2003; Percival et al., 2000; Yuan et al., 2000). We use Yuan et al. (2000) model to explain Al-SOM complex formation in our soils. An allophane particle is a hollow spherule with an external diameter of about 3.5-5.0 nm and a wall thickness of approximately 0.7 nm (Hall et al., 1985). There are structural defects (0.3 nm wide) within the outer wall where (OH)Al(H<sub>2</sub>O) groups occurs (Figure 3.2). These groups can attract or loose protons depending on the soil pH because the allophane is regarded as short-range ordered minerals with variable-charge (or pH-dependent). The Figure 3.2 represents the formation of a surface complex by LE mechanism between a hydroxyl group attached to Al in the allophane spherule and a carboxylate group from HA. The reaction produces a negative charge which is compensated by electrostatic interactions with Na<sup>+</sup> or Ca<sup>2+</sup> and perhaps Al<sup>3+</sup> ions. Thus HA sorption is promoted by the presence of electrolytes such as NaCl and CaCl<sub>2</sub>. Soil organic matter bound to spherule of allophane can interact again with Ca<sup>2+</sup> ions to form a new complex mediated by electrostatic attraction. On an analogous way, an identical mechanism should explain the large quantity of reported C<sub>p</sub> (Matus et al., 2008). In a recent study, C<sub>p</sub> in the silt and clay particles (n = 18 soil samples 0-10 cm) was just about 41% and 88% of the C measured in each fraction, respectively (Matus et al., 2011). This finding indicates that C<sub>p</sub> is unevenly distributed amongst the fractions and that the physical C in the silt fraction (C associated in the silt minus C<sub>p</sub> in the silt) was highly correlated with SOC. From the above-mentioned findings it may be anticipated that LE mechanism is the precursor for further electrostatic interactions to form a new nucleus of Al-SOM complexes that subsequently precipitate. In line with this, Huygens et al. (2005) studied the link between aggregate and SOC dynamics in a chronosequence (second growth *Nothofagus obliqua* (Mirb.) Oerst forest, grassland and *Pinus radiata* D. Don, plantation) in a Chilean Andisol (0-10 cm). Soil organic C in aggregate was studied using size and density fractionation,  $\delta^{13}\text{C}$  analysis and C mineralization experiments. The results showed that electrostatic interaction between amorphous Al and clay minerals was the main mechanism for stabilization of the soil aggregates and this result in the absence of an aggregate hierarchy in this type of soil. Indeed, in our volcanic soils, the allophane content was rather low (< 7% in 0-10 cm, Matus et al., 2008) and LE mechanism should be less important when the correlation between allophane and SOC is weak. Thus, electrostatic sorption and physical protection of SOC and soil aggregates can be the main processes of SOC

stabilization and its recalcitrance should not largely affect SOC stabilization (Huygens et al., 2005). However, when SOM is positive and significantly related with allophane (Matus et al., 2008) LE should be relevant.

The approach of soil organic matter recalcitrance in Chilean allophanic soils has been studied previously (Aguilera et al. 1992). However, the impact of agricultural practices such as burning crop residues and its effects on the amount of inert C (the so called black carbon, BC) produced by incomplete combustion, has recently been investigated (Matus et al., 2011). The distribution



**Figure. 3.2** Ligand exchange mechanism between external allophane spherule of 3.5-5 nm and humic acids (HA) with its carboxylate groups (COOH) which is bound to  $\text{Na}^+$  or  $\text{Ca}^{2+}$  electrolyte by electrostatic interactions (Yuan et al., 2000 (After B. K. G. Theng, personal communication). Draws are not proportional to the true size structure.

and isolation of the BC in agricultural allophanic soils was less than 10% of the SOC. Black C composition was studied by  $^{13}\text{C}$ -NMR spectroscopy. It was seen that there was no differences in aromatics compounds (most functional groups of BC) between burned and unburned treatments 15 years after continuous burning. These results were consistent with those of Rumpel (2008) in which no differences were found between a burned and unburned control after 30 years.

On the other hand, Borie et al. (2006) studied the impact of a glycoprotein termed glomalin. This compound is produced by arbuscular mycorrhizal fungi (AMF) which is recalcitrant to microbial

attack and mainly influences soil carbon storage and aggregation. Glomalin originally present in the AMF wall hyphae is secreted into the soil air-water interface and it is currently quantified from soil following an operational definition as glomalin-related soil protein (GRSP) (Rillig, 2004). The basic extraction method involves the use of a citrate buffer at neutral or slight alkaline pH at high temperature (Rillig, 2004). It has been postulated two glomalin fractions: an easily soluble extractable glomalin (EEG) after centrifugation and total glomalin (TG) which is the residue after centrifugation, extracted by citrate solution at pH 8 in the autoclave. The protein content of each fraction is quantified by Bradford assay. In a recent study the glomalin was determined at different soil depths (up to 40 cm) in agricultural soils and in an evergreen forest ecosystem. Surprisingly, the contribution of glomalin to the total amount of soil carbon in forest soils ranged between 19% and 26% and in the agricultural soils between 7% and 9%. Glomalin decreased as soil depth increased (Morales et al., 2005). Nowadays, glomalin extraction has been criticized, because the method is unspecific to quantify this glycoprotein (Rillig et al., 2001).

In conclusion, the most important mechanisms in Chilean allophanic soils appears to be a ligand exchange to form the primary complexes (Appelt et al., 1975) which in turn promote electrostatic attractions of cations such as  $\text{Ca}^{2+}$ ,  $\text{Na}^{+}$  and  $\text{Al}^{3+}$  to form stable soil aggregates. Ligand exchange should be less important when allophane is weakly or not related to the SOC as it is the case in our study of Antillanca soils (see below).

### **3.2.2 Protective capacity of soil organic matter in allophanic soils**

Hassink (1997) observed that the quantity of soil C in the silt and clay fraction (0-20  $\mu\text{m}$ ) of long-term Dutch temperate arable and grassland sandy soils (differing markedly in its SOM content) was similar, suggesting that soils have an upper limit of C saturation, determined by their capacity to protect organic matter by adsorption processes. When the protective capacity is fulfilled, further C addition is not longer stabilized by the silt and clay fraction and thus C accumulates in the sand-size fractions (20-2000  $\mu\text{m}$ ), enhancing C and N mineralization (Matus et al., 2008; Stewart et al., 2008). However, soils under different land-use managements may reach the effective carbon stabilization (ECS) which is a saturation level smaller than the protective capacity due to factor other than physico-chemical adsorption. The ECS may be

regarded as the threshold value for soils to act either as carbon sink or source, comparing soils within the same land-use managements (Matus et al., 2011). The protective capacity of a soil can be assessed by plotting the total soil C versus the C in the physical fractions (Matus et al., 2011). For the clay-sized particles in temperate soils an asymptotic response can be expected, indicating that further increases in the soil C are no longer reflected by an increase of SOM in this fraction. However, in volcanic soils the quantity of silt or clay (or both) is not related to SOC, but complexed with Al and Fe. Therefore, we pose the question if the volcanic soils can reach the protective capacity and how this limit can be envisaged.

From Matus et al. (2008) and Dahlgren et al. (1993) it can be calculated that one mol of  $Al_p$  can complex 8.3 moles  $C_p$ , i.e. 0.12 ( $= 1/8.3$ ) moles of Al can complex one mole of  $C_p$ . Dahlgren and Ugolini (1991) established a strong linear relationship between pyrophosphate-extractable C and organically complexed Al and Fe ( $Al+Fe)_p$  ( $R^2 = 0.97$ ;  $P < 0.001$ ). Assuming that most  $Al_p$  and  $Fe_p$  was extracted from humus complexes, these data indicated that Al and Fe form metal-humus complexes with a metal:carbon atomic ratio of 0.18 (the slope of the regression). According to Higashi et al. (1981), a theoretical calculation from previous literature can be made and a ratio of 0.12 should be regarded as the saturation of humic substances with metals. When this ratio is exceeded, the metals will not be longer complexed by humic substances and it will then be available for synthesis of inorganic components like allophane and imogolite type materials (Dahlgren and Ugolini, 1991). Therefore, we addressed these and other related matters in a study case of Antillanca's soils in the next section.

### 3.3 Study case of Antillanca

#### 3.3.1 Introducción

More than 2.5 million ha (50 % of the total volcanic soils in Chile) occur on steep slopes within the limits of the Andean ranges between latitude 36° and 47°. The landforms associated with these soils range from moderately steeped to precipitous; however, slopes between 30-70% predominate. The prevalence of steep landforms is due to the late tertiary history of uplift and tilting of land surfaces, associated with the Andean orogeny (Wright, 1965). On this land basement, volcanoes through their successive eruptions had deposited several deep mantles of volcanic ash which in part have been reduced by anthropogenic and natural erosion. Many of the Chilean volcanoes in this area are currently active, associated with the regional climate and plant covering. Stepped soils, most are derived from basaltic materials date from recent eruptions which formed dejection cones from sloppy piedmonts in the volcanoes leaving a large area of scoriaceous porous soils. Vegetation in these ecosystems is evergreen formation composed with species such as: *Laureliopsis philippiana* Loseer, *Aextoxicum punctatum* R. et Pay, *Drimys winteri* J. R. et G. Forster and *Nothofagus* sp (Godoy et al., 1999). In the upper altitudinal limit *Nothofagus pumilio* (Poepp et Endl Krasser) can be found close to the treeline (1,000-1,120 m a.s.l.). An example of this ecosystem is Antillanca's soils in the Puyehue National Park resulting from activities of the Casablanca and Antillanca volcanoes. The mean annual precipitations in this ecosystem is > 5,000 mm yr<sup>-1</sup> with snow covering during June to November, with the mean annual temperature of 4.5°C ranging between -8.7°C to 24.8 °C inside the forest. In this area three experimental sites were established, differentiated by tree density and height (Godoy et al., 2001; Oyarzún et al., 2004), where the distribution of SOM in the uppermost and subsoil has not been studied.

The aims of this study were to examine: i) the distribution of soil C in the Antillanca soil and the stability of SOC in its profile; ii) the biological activity and its relationship with the stabilizing agent such as Al- and Fe-SOM complex and iii) the protective capacity of the soil, i.e. the upper limit of a soil to store SOM.

### 3.2.2 Methodology

#### 3.2.2.1 Experimental site description

The present study was carried out in an experimental microcatchment dominated by *Nothofagus pumilio* forest types in southern Chile (40°47'S, 72°12' W, 1,120 m a.s.l.) with a mean annual precipitation (>5,000 mm) whose chemistry still reflects the pre-industrial conditions (Godoy et al., 1999). Thus, the productivity of the ecosystem depends on the internal cycling of soil organic C. Three sites were selected where *N. pumilio* forest has a mean height of 9, 13 and 23 m, and a stand density of 5,900, 3,600 and 1,734 trees ha<sup>-1</sup> effectively, namely Site 1, Site 2 and Site 3, respectively. The average tree age was about 120 yr. The understory is dominated by *Drimys andina* (Reiche). Rodr. et Quez. and *Maytenus disticha* (Hook. F.) Urban (Godoy et al., 1999). *N. pumilio* is an important and representative deciduous tree in Chile and has a wide latitudinal distribution over approximately 2,000 km, reaching from latitude 35° to 55° (Hildebrandt-Vogel et al., 1990). This species grows mainly at high altitude, close to the treeline at both sides of the mountain range 'cordillera de los Andes' and 'cordillera de la Costa'. Soil samples were taken by core cylinder from horizons A, AC and C at Site 1, Site 2 and Site 3 from three soil pedons excavated up to 100 cm depth, spaced each other for about 10 m. A total of 27 soil samples for analysis and 27 soils cores for bulk density were collected by pushing a steel cylinder with a known volume (5 x 8.2 cm) into the undisturbed soil. Soil characteristics are presented in Table 3.2.

#### 3.2.2.2. Chemical analysis

All soils were analysed for pH in water using a 1:2.5 soil:solution ratio. For the Al, Fe and Si extraction, air dried samples were used in duplicate. For a detailed description of this extraction methods see García-Rodeja et al. (2004). The following analyses were conducted: (a) oxalate extraction (Al<sub>o</sub>, Si<sub>o</sub> and Fe<sub>o</sub>), (b) pyrophosphate extraction (Al<sub>p</sub> and Fe<sub>p</sub>), (c) allophane content and (d) particle size analysis as described by (Matus et al., 2002). Carbon determination in the whole soil and in the pyrophosphate extract (C<sub>p</sub>) was determined in two replicates using potassium dichromate (Donisa et al., 2003).

**Table 3.2.** Soil characteristics (average of three pedons per site  $\pm$  standard error of the mean) in *Nothofagus pumilio* forest of southern Chile.

Site	Soil horizons	Bulk density	SOC <sup>1</sup> stock	Soil pH <sub>water</sub>	Sand <sup>2</sup>	Silt <sup>2</sup>	Clay <sup>2</sup>	Allophane <sup>3</sup>
	cm	Mg m <sup>-3</sup>	Mg m <sup>-2</sup>		----- (g kg <sup>-1</sup> soil) -----			
1	A (0-11)	0.71 $\pm$ 0.04	6.1 $\pm$ 3.8	5.9 $\pm$ 0.10	760	160	80	23 $\pm$ 0.6
	AC (11-51)	0.90 $\pm$ 0.04	15.0 $\pm$ 7.8	6.2 $\pm$ 0.10	860	80	60	37 $\pm$ 6.4
	C (51-100)	0.92 $\pm$ 0.03	12.3 $\pm$ 3.2	6.2 $\pm$ 0.10	820	120	60	30 $\pm$ 1.6
	Total stock		34.3 $\pm$ 4.9					
2	A (0-16)	0.56 $\pm$ 0.04	9.4 $\pm$ 1.9	6.1 $\pm$ 0.30	740	180	80	21 $\pm$ 1.8
	AC (16-36)	0.79 $\pm$ 0.09	9.4 $\pm$ 2.6	6.0 $\pm$ 0.03	700	220	80	42 $\pm$ 2.3
	C (36-100)	0.99 $\pm$ 0.03	10.7 $\pm$ 3.0	6.1 $\pm$ 0.10	840	80	80	27 $\pm$ 5.8
	Total stock		29.5 $\pm$ 2.5					
3	A (0-19)	0.54 $\pm$ 0.06	11.0 $\pm$ 2.44	5.6 $\pm$ 0.10	740	180	80	21 $\pm$ 1.5
	AC (19-41)	0.74 $\pm$ 0.04	8.1 $\pm$ 8.1	5.9 $\pm$ 0.01	760	180	60	43 $\pm$ 6.1
	C (41-100)	0.92 $\pm$ 0.05	19.6 $\pm$ 8.2	6.1 $\pm$ 0.03	860	80	60	41 $\pm$ 9.3
	Total stock		38.7 $\pm$ 6.2					

<sup>1</sup>Soil organic carbon

<sup>2</sup>One replicate only

<sup>3</sup>Calculated as Parfitt and Wilson, 1985.



**Figure. 3.3** Site 1 of Antillanca showing (A) the *Nothofagus pumilio* forest of Southern Chile and (B) the soil profile in *Nothofagus pumilio* forest of Southern Chile.

### 3.2.2.3. Carbon stabilization and protective capacity

Soil C stability was examined by plotting the carbon stability ratio,  $C_p$ :SOC versus SOC. The two variables,  $C_p$  and SOC are strongly correlated (see Figure 3.6c) and therefore we minimize the risk of plotting spurious correlation which take place when the denominator of a ratio (in this case SOC) is used in both axis x and y in a regression line. On the other hand, the protective capacity of soils has been defined as the upper limit of soil C associated with the physical fraction of silt and clay particles in non-volcanic temperate soils (Hassink, 1997). We use this approach by plotting  $C_p$ , expressed as  $\text{g kg}^{-1}$  soil against the corresponding whole SOC content on a normalized scale. This enabled us to compare all soil pedons developed under similar climate conditions. An asymptotic relationship is expected where no longer SOC can be complexed (stabilized) by Al and Fe to form  $C_p$ . The level of soil C at which this saturation takes place was called critical SOC level, determined by a graphical statistical tool (see data analysis).



#### 3.2.2.4. Microbial biomass and carbon respiration

Microbial biomass C and C mineralization rates were estimated in all pedons from Site 1 and Site 3. Microbial biomass was estimated by the fumigation-extraction method using a  $K_c = 0.38$  (Vance et al., 1997) in all soil depth and results were expressed on an oven-dry soil basis. For fumigation, liquid ethanol free  $\text{CHCl}_3$  was used. Soil organic carbon in  $\text{K}_2\text{S}_2\text{O}_8$  extracts from fumigated and unfumigated samples was analyzed using a dichromate oxidation (Walkley and Black, 1934). Carbon mineralization rates were carried out by mixing 50 g of soil (dry weight basis), sieved through 0.005 m mesh size and moistened to a water potential of -33 kPa. The soil was placed in a 2 liters airtight glass jar containing a vial with 10 mL of 0.5 M NaOH and incubated at 22 °C ( $\pm 2$  °C) in the dark during 1, 3, 7 and 15 days. At each sampling time, trapped  $\text{CO}_2$  was precipitated as carbonate with excess 0.75 M  $\text{BaCl}_2$  and excess NaOH was back titrated automatically with 0.5 M HCl to reach pH 8.3 (Dalal, 1979). At each sampling time, a new vial containing NaOH was placed into the glass jar. The rate of carbon mineralization was calculated as:

$$\frac{dy}{dt} = k(h - y) \quad (1)$$

Where  $\frac{dy}{dt}$  is the C mineralization rate ( $\text{mg CO}_2 \text{ } 100 \text{ g}^{-1} \text{ soil d}^{-1}$ ) and  $y$  is an asymptotic exponential model:

$$y = h(1 - e^{-kt}) \quad (2)$$

Where  $y$  is the cumulative soil respiration,  $h$  the maximum C respired,  $k$  the constant rate ( $\text{day}^{-1}$ ) and  $t$  the incubation time (days). To obtain the C mineralization rates we first estimate the  $h$  and  $k$  by non-linear regression by successive iteration using the chi-square for each parameter ( $h$  and  $k$ ) as a function of the iteration number. These values give information to optimize the parameters (optimization means reducing the chi-square value as much as possible). The fitting for each incubated soil was done using Curve Expert release 1.37.

### 3.2.2.5. Data analysis

Comparison of multiple means for SOC distribution, microbial biomass and soil C respiration rates for all horizons at each site to test differences amongst the means (average of three pedons) was carried out by the least significant difference (LSD) using Tukey-Kramer HSD (honestly significant difference test). All statistical analyses were computed using the JMP statistical software (SAS Institute, Cary, NC, U.S.A.). The critical SOC level to look at the C saturation of the soils was essayed by the 'Cate-Nelson split' technique (Cate and Nelson, 1971) by plotting the  $C_p$  in ordinate and SOC in abscissa. Differences in  $C_p$  values (if any) were found by clustering the data points in two groups with maximum statistical homogeneity within the groups to maximize the chi-square test. Graphically  $C_p$  values are separated by placing a vertical line intersecting a horizontal line that maximize the numbers of data points in the first (left bottom) and third (right top) quadrants I and III, respectively (see Figure 3.6c). The vertical line intersecting the abscissa is regarded as the critical SOC level in which additional organic matter cannot form more  $C_p$ . The critical SOM best separates the high from low  $C_p$  groups. Statistically the vertical line represents the highest  $R^2$  that accounts for the observations into two population groups at the postulated critical level of SOC.

### **3.3.3 Results and general discussion**

First, we present a general morphological description of the studied soils (Mella and Kühne, 1985; Wright, 1965) together with our own observations. Secondly, we discuss the SOC distribution and its stabilization, including the C saturation concept. Thirdly, we linked all above-mentioned findings with measured biological activities.

#### **3.3.3.1 General soil description**

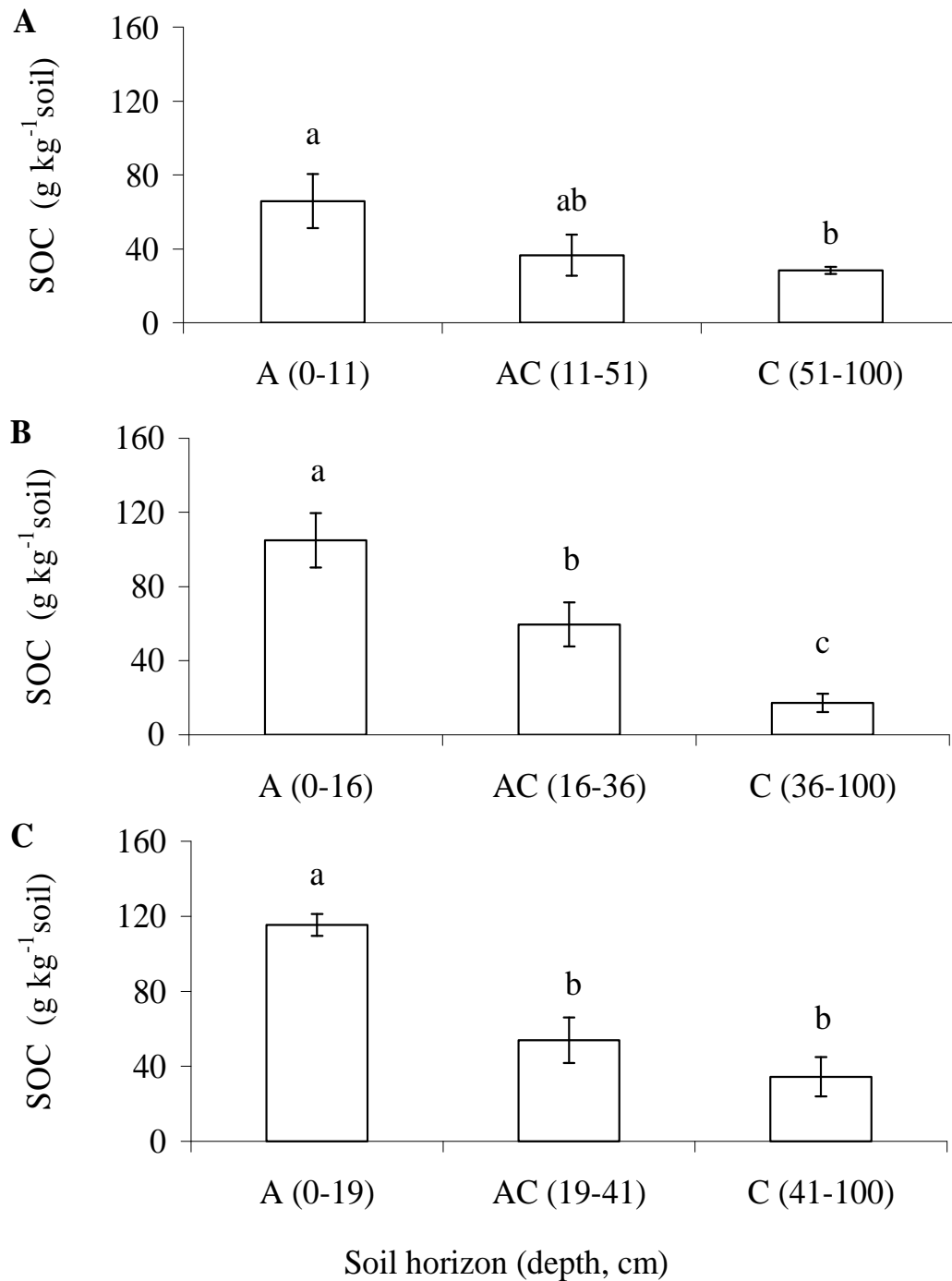
At all sites a partially decomposed litter layer (4-5 cm) was observed. The top mineral A horizon (for the thickness of each horizon of the three sites see Fig. 3.3b) is dark brown (10YR 3/3, moist) with loamy sand texture, non-sticky and non-plastic, friable with granular structure and abundant fine roots. The middle horizons (AC) is gray (10 YR 5/1, moist), loamy sand with fine scoriaceous gravel, friable with non recognizable structure, non-sticky and non-plastic. Finally, the C horizon is very dark gray (2.5 YR 3/0, moist) loamy sand to coarse sand, partially cemented, with an appreciable amount of pomes (Figure 3.3a). At all sites and profiles we found visually identifiable zones in the form of light brown 'hot spots' in the AC horizons (Figure 3.3b). These zones have been described as small, spatially separated soil areas in the profile with distinct physicochemical properties; young SOM depleted in  $^{15}\text{N}$  and high microbial biomass (Bundta et al., 2001; Chabbi et al., 2009). Our hot spots seem to be hydrophobic, because they were drier than the soil samples from the adjacent soil matrix, having abundant albic fungal hyphae. This spots are being studied for chemical characteristics as well.

#### **3.3.3.2 Soil organic matter, microbial biomass and carbon mineralization**

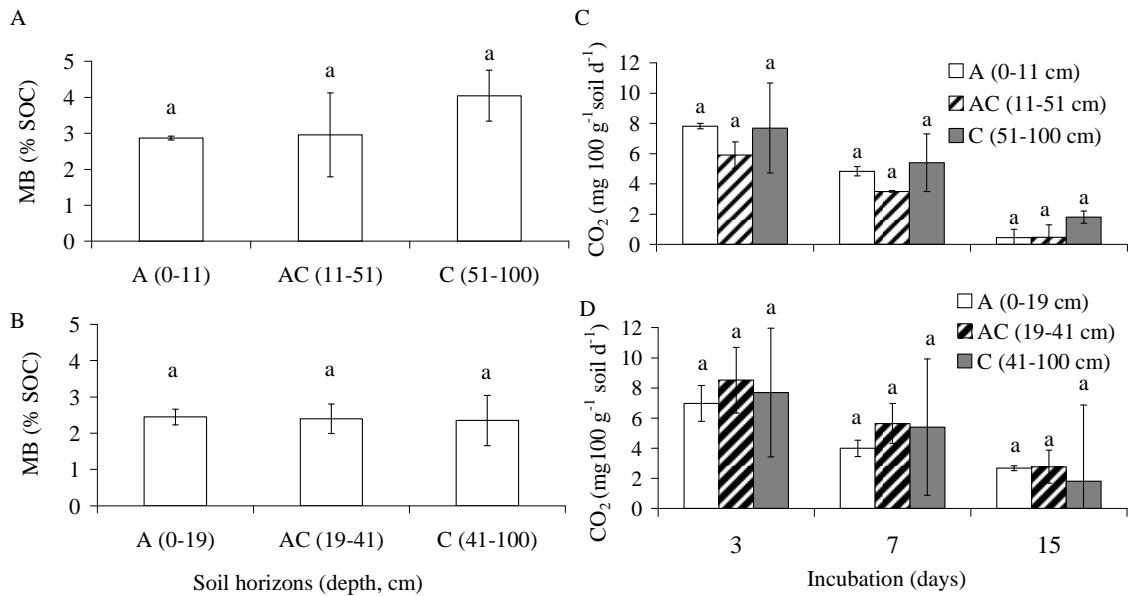
Soil organic carbon is the result of long-term accumulation of recalcitrant humified C, interacting with the soil mineral phase, microbial community and soil depth. Our questions were addressed to gain information about SOM storage in these porous materials and what are the mechanisms and factors operating on its accumulation.

On average, for all horizons, the SOC ranged from 30 to about 120 g kg<sup>-1</sup> soil and there were significant differences amongst sites. Soil organic matter contents amongst pedons were highly variable and, therefore scarce differences in depth horizons were observed, although more distinctive quantity of C was measured in the top soil (Figure 3.4). These differences were expected because large root volume was observed in the top soil. Fontaine et al. (2007) recently focused a study on the recalcitrance of SOM. In the surface layer (A horizon) the supply of fresh C by plants (litters and exudates) enables microbial biomass to decompose the recalcitrant C compounds, otherwise stored over long-time period (>1000 yr). When fresh-C is available at deep soils by illuviation, leaching, incorporation by earthworms and termites (pedoturbation), recalcitrant humus can be available for soil microbes promoting extra C mineralization called priming effect (Fontaine et al., 2007).

In the present study, microbial biomass as the percentage of SOC ranged between 2.5% and 4% of the whole SOC, the normal range found in the literature (Jenkinson and Ladd, 1981) (Figure 3.5a and 3.5b). Soil C mineralization rates were also calculated and they decreased as the time of incubation increased (Figure 3.5c and 3.5d). However, both, microbial biomass and mineralization rates were not significantly different in the top and deep soils. Assuming that the microbial community and the efficiency of soil C use by microbial biomass does not change (because the clay content was similar across soil site and depth (Table 3.1) (Hassink and Whitmore, 1997), our results suggest that the active (or labile) organic matter pool, either for the surface and deep soil were comparable. With high stability of SOM in deep soils less labile C and less microbial biomass should be expected. It is also possible that the priming effect may compensate the stability of SOC in deep soils, because vertical transfer of fresh C can be important.



**Figure 3.4.** Soil organic C (SOC) distribution (average of three pedons) along the profile of Antillanca soil for (A) Site 1, (B) Site 2 and (C) Site 3 of *Nothofagus pumilio* forest of Southern Chile. Bars followed by the same letter indicates not significant differences at *P* level 0.05. Vertical line on top of each bars indicate the standard error of the mean.

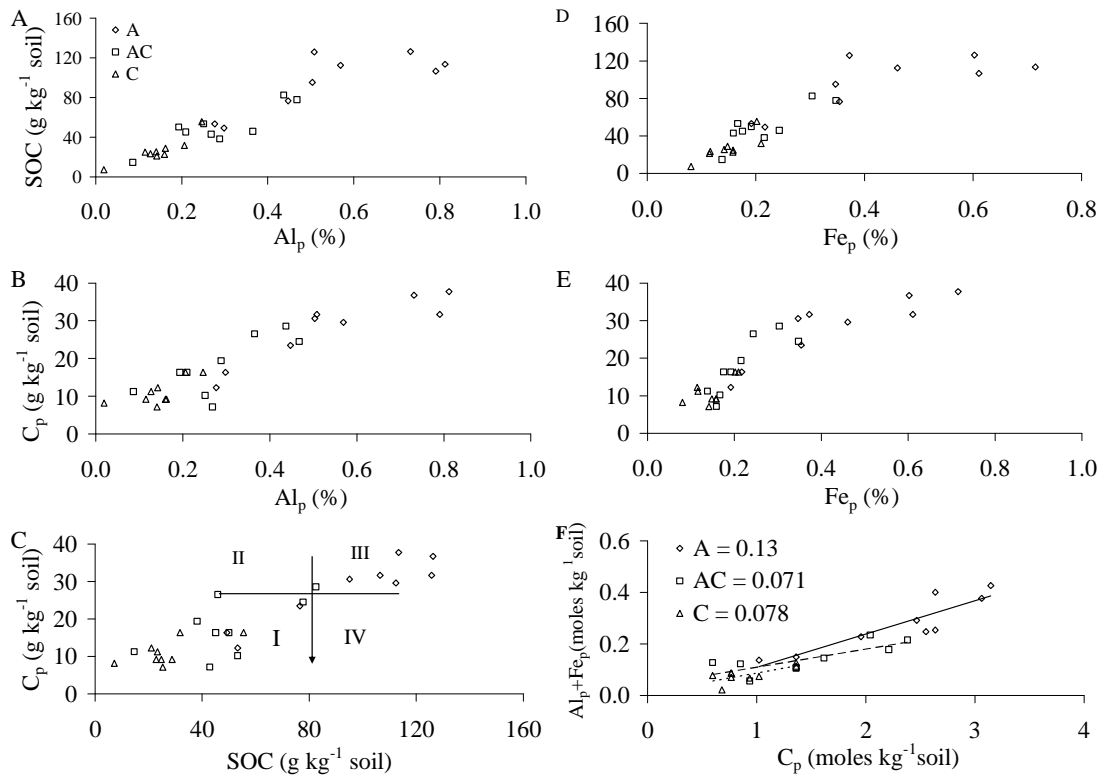


**Figure 3.5.** Microbial biomass (MB) fumigation-extraction (average of three pedons) as percentage of soil organic carbon (SOC) for (A) Site 1 and (B) Site 3. Soil carbon mineralization rate for (C) Site 1 and (D) Site 3 of *Nothofagus pumilio* forest of southern Chile. Bars followed by the same letter for MB and for C mineralization at the same time of incubation, indicate not significant differences at *P* level 0.05.

### 3.3.3.3 Stability ratio and protective capacity

There was a weak correlation between the weight of the physical silt- and clay-fractions and SOC content of the soils. Similar results were observed between allophane and SOC. Therefore, the stability of organic matter was assessed by extraction of Al and Fe with Na pyrophosphate, which reflects the metals complexed with SOM as indicator of SOM recalcitrance. The pyrophosphate extraction of  $Al_p$  and  $Fe_p$  and its relationship with SOC and  $C_p$  is shown in Figure 3.6. Firstly,  $Al_p$  ( $y = -7.2 + 250.3x - 113.4x^2$ ,  $R^2 = 0.88$ ,  $P < 0.01$ ) and  $Fe_p$  ( $y = -35.1 + 494.6x - 399x^2$ ,  $R^2 = 0.88$ ,  $P < 0.01$ ) were well related with SOC, indicating that Al and Fe complex with humic substances explained most of the variation of the SOC level. Note that the best fit for both  $Al_p$  and  $Fe_p$  was a quadratic regression, suggesting that no more SOC can be complexed with metals beyond 0.5% and 0.35% (eye guessing) Al and Fe, respectively (Figure 3.6a and 3.6d). The metal in excess is

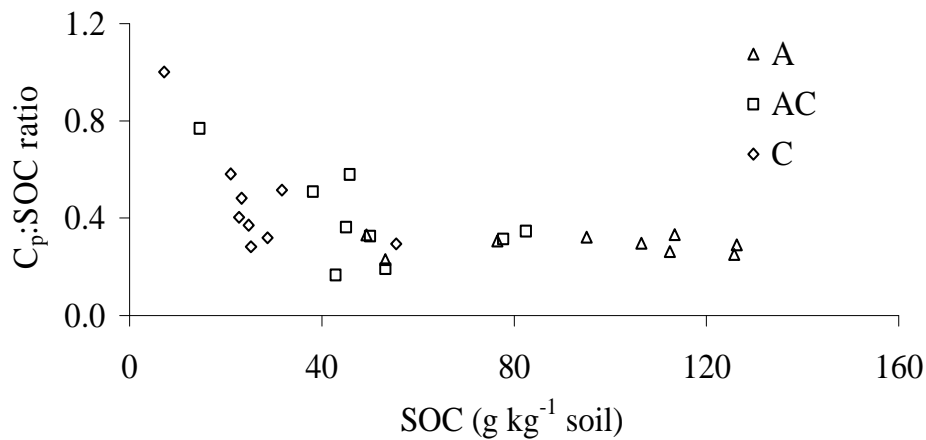
the Al and Fe extracted from other sources (such as minerals structure free of SOM, gibbsite and interlayer Al) (Higashi et al., 1991; Kaiser and Zech, 1996). Similar results were obtained between  $Al_p$  ( $y = 3.4 + 54.7x - 15.9x^2$ ,  $R^2 = 0.86$ ,  $P < 0.01$ ) and  $Fe_p$  ( $y = -4.54 + 121.5x - 91x^2$ ,  $R^2 = 0.89$ ,  $P < 0.01$ ) versus  $C_p$  (Figure 3b and 3e). The critical level of SOC is shown in Figure 3.6c, at which no more Al- and Fe-SOM complex can be formed. According to the graphical split technique the  $C_p$  values are best separated at  $80 \text{ g kg}^{-1}$  of SOC. On the other hand, Dahlgren and Ugolini (1991) related  $C_p$  values with  $(Al+Fe)_p$  and they found a positive and significant relationship with a slope of 0.18 representing the atomic ratio  $(Al+Fe)_p/C_p$ . According to Higashi et al. (1981) theoretically, it seems impossible that organic matter can bind metallic ions at ratios higher than 0.12. In our case the regression between  $C_p$  and  $(Al+Fe)_p$  for all soil samples was  $y = 0.12x - 0.0027$ ,  $R^2 = 0.85$ ,  $P < 0.01$ . However, the slopes for the individual horizons A, AC and C were: 0.13, 0.071 and 0.078 (Figure 3f). This indicates that humus in the top soils is fully saturated with metals, but subsoils are still far (40%) from this limit. This means that pyrophosphate extract a  $C_p$  partially saturated and any metals produced by weathering will be either complexed with SOM or it will go to form allophane (Higashi et al., 1981). Our results were also supported by the literature (Dahlgren and Ugolini, 1991; Higashi et al., 1981). Differences such as origin and type of SOM and pH may be combined to vary the complexing ability of humic substances between different soils and vegetation types, making the ratio somehow, variable. However, for any given soil and horizon, a ratio may exist which corresponds to the saturation of the humic complex with metals (Dahlgren and Ugolini, 1991).



**Figure 3.6.** Relationship between (A) Al<sub>p</sub> and (D) Fe<sub>p</sub> (both metals extracted in pyrophosphate) and soil organic C (SOC) and (B) Al<sub>p</sub> and (E) Fe<sub>p</sub> with the carbon extracted by pyrophosphate (C<sub>p</sub>). Relationship between (C) SOC and C<sub>p</sub>. The arrow on abscissa indicates the critical level of SOM at which no more C<sub>p</sub> is formed. Relationship between atomic ratios (F) C<sub>p</sub> and (Al+Fe)<sub>p</sub> for all soil samples of Antillanca from *Nothofagus pumilio* forest of southern Chile. The slope of the regression is shown for each horizon.

Secondly, we related the amount of SOC with the stability ratio (C<sub>p</sub>:SOC) (Figure 3.7), provided that both variable are correlated (Figure 3.6c). The ratio ranged between 0.17 and 1, showing more stability of SOC in deep horizons. Although, the fitted quadratic model ( $y = 0.65 - 0.0087 + 5E-05x^2$ ,  $R^2 = 0.37$ ,  $P < 0.01$ ) was significant (data point = 1 was not considered) there was a weak relationship, because the differences disappear when the ANOVA test was run per horizons (data not shown). This was consistent with lack of significance for microbial biomass and C mineralization rates. Indeed, there was no relationship at all between the stability ratio and the C mineralization rates of the soils.





**Figure 3.7.** Relationship between SOC and the stability ratio  $C_p$ :SOC for all samples of Antillanca's soils from *Nothofagus pumilio* forest of Southern Chile.

### 3.3.4 Summary and Conclusions

We conducted a study in an Antillanca soil, being a scoriaceous and porous allophanic soil, weakly developed from dejection cones of Antillanca and Casa Blanca volcanoes. In this area *Nothofagus pumilio* is the dominant forest specie. We studied the soil organic C stability by combining chemical (Al, Fe and C extracted in pyrophosphate) and biological methods (microbial biomass and C mineralization rates) in nine soil samples profiles distributed in three sites of different tree density and height (the same altitudinal level 1120 m.a.s.l). We found that Al and Fe extracted by pyrophosphate explained much of the SOC variation. However, SOC stabilization, assessed by the stability ratio of the C extracted in pyrophosphate and the C in the whole soil was similar, either for the top and deep horizons. These findings were consistent with the fact that, despite of the soils horizons: i) microbial biomass as percentage of the whole soil C and ii) C mineralization rates were similar. Furthermore, there was no relationship between C mineralization rates and the stability ratio, indicating that the stabilization of soil organic C was at the same extent in all soils and depth. It seems that humus bound to metals (Al and Fe) represented by the C extracted in pyrophosphate is limited at a critical level of SOC of 80 g kg<sup>-1</sup> soil, beyond which no more complex can be formed. This was consistent with the fact that the atomic ratio of (Al+Fe):C (all extracted in pyrophosphate) was close to 0.12 (the theoretical limit

for C saturation with metals (Higashi et al. 1981). However the humus in the subsoil seems to be less saturated with Al and Fe.

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## CHAPTER 4

### *Carbon storage distribution in soil organic matter fractions of different ecosystems*

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# Carbon storage distribution in soil organic matter fractions of different ecosystems

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## Summary

Soils vary in their capacity to accumulate organic matter. This variation is attributed to their intrinsic properties such as soil texture and soil moisture, as well as amount and quality of carbon (C) input. The ability of soils to store C depends on the balance between input stabilization and destabilization mechanisms. A change in soil management practices can alter this balance. The aim of this study was to determine the distribution of soil organic matter (SOM) fractions and to examine the C stabilization capacity in volcanic soils at various depths under managed pasture and rain forest ecosystems in southern Chile. We used Na-pyrophosphate extractable C ( $C_p$ ) as a measure of C stabilized by interaction with soil minerals in the soil profile in combination with density fractionation to separate particulate organic matter (fPOM,  $< 1.6 \text{ g cm}^{-3}$ ), occluded particulate organic matter (oPOM,  $1.6\text{-}2.0 \text{ g cm}^{-3}$ ) and mineral associated organic matter (MF,  $> 2.0 \text{ g cm}^{-3}$ ). The results showed that the variation in mineral associated C between ecosystems and soil depths was explained largely by differences in pyrophosphate extractable Aluminum ( $Al_p$ ) and iron ( $Fe_p$ ). On average 24 and 20  $\text{g C kg}^{-1}$  extracted by pyrophosphate ( $C_p$ ), equivalent to 33 % and 29 % of total soil C was found in the top soil of pasture and forest, while 7.8 and 3.9  $\text{g C kg}^{-1}$ , equivalent to 28 % and 55 % were found in the deep soils, respectively. The physical fractionation indicated that in both ecosystems a large amount of C was present in the mineral fraction ( $> 46$  % of the total soil C), followed by oPOM and fPOM. Our results emphasize the importance of SOM linked to Al and Fe as a pool of soil organic carbon (SOC) in volcanic soils and the POM formation as a mechanism of SOC stabilization in undisturbed ecosystems. The natural abundance of  $^{13}\text{C}$  and  $^{15}\text{N}$  was enriched in deeper horizons in the two ecosystems. This was more marked along to a decrease in the C to N ratio through the soil profile.

*Keywords:* organic carbon, volcanic soils, physical and chemical soil C protection.

## 4.1 Introduction

Carbon sequestration in soil is an important strategy to mitigate the increase of atmospheric CO<sub>2</sub> concentrations, since it involves the transfer of atmospheric CO<sub>2</sub> in more stable SOC fractions (Lal, 2001). The conversion of natural ecosystems, such as native forest into arable farming systems, reduces the contents of SOM, causing a rapid increase of decomposition at early stage of land cultivation (Lal, 2001). On the other hand, agronomic practices such as zero tillage promote the maintenance and accumulation of SOM, decreasing the rate of decomposition (Six et al., 1999). The permanence of SOC depends largely on the balance between biomass contributions and the losses by decomposition. Controlling factors of carbon sequestration in soil are its properties such as mineralogy as well as climatic conditions and land management practices (Lal, 2009).

The process of stabilization and decomposition of SOM occurs simultaneously in the soil. One of the most important C stabilization mechanisms is the interaction of SOM with soil minerals (Rumpel et al., 2002; Six et al., 2002). Although crystalline clays with large surface area are often considered to play an important role in the C stabilization in soils, protecting SOM against decomposition by microorganisms, several studies have suggested that in amorphous volcanic soils, the non-crystalline Al hydroxides and organo-mineral complexes rather than their crystalline counterparts are the key agents for the stabilization of SOM (Percival et al., 2000). Sadzawka and Porte (1984) indicated that in soils derived from recent volcanic ash in southern Chile, Al-complexed humus constitutes the largest fraction of SOM in the surface horizons when the supply of organic matter was abundant. Shoji et al. (1993) revealed that Al extracted in sodium pyrophosphate strongly correlated with SOC, exerting a strong influence on the content of organic matter. Similarly, Percival et al. (2000) found that although the texture was not correlated with the accumulation of SOC in volcanic soils, the active Al extracted by sodium pyrophosphate presented a high correlation ( $R^2 = 0.60$ ,  $P < 0.05$ ). Huygens et al. (2005) determined that electrostatic sorption processes and physical protection of SOC are the principal mechanisms of C stabilization in Chilean Andisols (USA classification, Soil Survey Staff, 1996). Matus et al. (2006; 2009) showed that Al extractable in acid ammonium acetate, rather than clay content and climatic conditions, controls the level of SOC in allophanic soils of Chile at a

regional scale. Moreover, it has recently been shown, that allophanic nanoclays store significant amounts of recalcitrant C (Calabi-Floody et al., 2011).

Physical SOM fractionation has been used to obtain the particulate organic matter (POM) which may become important C pool when attempting to quantify C balance in soils. Recently it has been shown, that physical protection of POM through aggregation is a significant, but poorly considered C sequestration mechanism in subsoil horizons (Moni et al., 2010). Up to now, few studies have been published presenting C distribution in physical fractions throughout the soil profile (e.g. Mueller and Kögel-Knabner, 2009) and even fewer of them addressed in Andisols. Considering that Andisols are the soil type which most efficiently sequesters organic carbon, it is evident that the capacity to stabilize organic matter in volcanic soils needs to be investigated. The proportion of organic carbon fractions stabilized by Al (and Fe) through complexation and the distribution of various physical fractions such as POM then acquires relevance. Understanding their mechanisms of stabilization we will know the practical implications on biogeochemical cycling of SOC in these types of soils. We hypothesized, that the combination of sodium pyrophosphate extractable Al as a measure of chemically stabilized C in bulk soil and density fractionation as a measure of physico-chemical stabilized C may help to understand the mechanisms of C stabilization considering pedogenetic differences driven by external factors (temperature and precipitation).

This study was carried out in two different ecosystems (rain forest and pasture). The soils were sampled through their entire depth and SOM fractionated according to a physical as well as chemical fractionation scheme. The aims of this study were: (i) to determine the distribution of various chemical and physical fractions of SOM at different depths of soil profiles sampled from Andisols under different land-use (forest and pasture) and (ii) to examine the contribution of physical and chemical fractions to the C stabilization in the same soil ecosystems.

## 4.2 Materials and Methods

### 4.2.1 Site characteristics and soil sampling

The managed pasture study area is located 1.5 km north of the city of Valdivia (39°48' S, 73°14' W). The pasture is dominated by perennial ryegrass (*Lolium perenne* L.) and white clover (*Trifolium repens* L.). The site is comprised of flat topography with deep (> 120 cm) and well drained soils. The climate of the study area is very similar to maritime with an average of annual temperature 12.1 °C and rainfall range between 2200 and 2700 mm per year, concentrated mainly in winter (1000-1200 mm). The soil belongs to Valdivia family member, medial, mesic, Typic Dystrandept, developed from recent volcanic ash which occupies a position of remaining terraces in depression land, at an altitude of 9 to 20 meters above the sea level. The soil texture is silty loam in surface horizons and sandy loam in depth soils. The soil substrate corresponds to a tuff deposit of volcanic materials mixed with strong compaction and altered clasts, locally known as 'cancagua' (CIREN, 2003).

The rain forest study area is dominated by *Nothofagus pumilio* (Poepp & Endl.) Krasser. with an average tree age of about 120 years and understorey mainly represented by *Drymis andina* (Reiche) R.A. Rodr. et Quez. and *Maytenus disticha* (Hook. f.) Urban. in the National park of Puyehue (40°47' S, 72°12' W). The soil site belongs to Antillanca family, mesic, Umbric Vitrandept resulting from activities of the Casablanca and Antillanca volcanoes. The mean annual precipitations in this ecosystem is > 5,000 mm per year with the mean annual temperature of 4.5 °C ranging between -8.7 °C and 24.8 °C inside the forest (Godoy et al., 2001). These tree species grow mainly at high altitude (1,000-1,120 meter above sea level), close to the treeline at both sides of the mountain range of Chile. Forest soil samples were collected from three permanent plots (30 x 30 m) previously established by Godoy et al. (2001) to study the chemistry of rainfall in pristine environment. At the centre of each plot a soil pit was excavated and used as replicate (Matus et al., 2009). About 2 kg of soil sample were taken by a shovel from horizons A (0-19 cm), AC (19-41 cm) and C (41-100 cm). Soil samples were mixed and homogenized, and coarse organic matter (leaves, wood, and roots) was removed by hand. For bulk density (BD) measure soil samples were also collected by pushing a core steel cylinder (5 x 8.2 cm) into the undisturbed soil horizon. In the managed pasture, the same procedure was followed by taking

soil samples at Ap (0-7 cm), B1 (7-32 cm) and B2 (32-40 cm) horizons. In all sites a partially decomposed litter layer was observed which was removed before sampling.

Three field replicates were taken from each horizon at both sites. A total of 18 composite soil samples and 18 soil core cylinders were collected. Some soil characteristics are presented in Table 4.1.

**Table 4.1.** Soil characteristics of three soil pedons in managed pasture and pristine rain forest. In bracket standard error of the mean (n=3, round figures).

Parameters	Rain forest			Pasture		
	Horizon/cm			Horizon/cm		
	A /0-19	AC /19-41	C /41-100	Ap /0-7	B1 /7-32	B2 /32-40
pH /wáter	5.6 ± 0.1	5.9 ± 0.01	6.1 ± 0.01	5.3 ± 0.01	5.4 ± 0.01	5.7 ± 0.01
SOC /g kg <sup>-1</sup> soil	69.4 ± 0.2	17.8 ± 0.1	7.1 ± 0.1	73.5 ± 0.2	64.4 ± 0.4	27.9 ± 0.2
N /g kg <sup>-1</sup> soil	2.7 ± 0.1	0.8 ± 0.01	0.4 ± 0.01	5.6 ± 0.3	4.5 ± 0.2	1.7 ± 0.1
BD <sup>1</sup> /Mg m <sup>-3</sup>	0.54 ± 0.01	0.74 ± 0.01	0.92 ± 0.01	0.75 ± 0.01	0.70 ± 0.04	0.65 ± 0.01
Stock C /Mg ha <sup>-1</sup>	71.0 ± 2.4	29.0 ± 8.1	38.5 ± 8.2	38.6 ± 0.3	113.0 ± 1.3	14.5 ± 0.01
C:N ratio	24	24	18	13	15	16
Soil texture <sup>2</sup> /%						
Sand	74	76	86	38.7	39.2	42.7
Silt	18	18	8	36.4	35.5	29.4
Clay	8	6	6	24.9	25.2	27.8

<sup>1</sup>Bulk density

<sup>2</sup>Estimated by Matus et al. (2009)



#### 4.2.2 Chemical analysis

All soils were analysed for pH in water using a 1:2.5 soil:solution ratio. For the Al, Fe and Si extraction, air dried samples were used in duplicate as follow: a) extraction with 0.2 M ammonium oxalate oxalic acid at pH 3 ( $Al_o$ ,  $Si_o$  and  $Fe_o$ ) with a soil: solution ratio 1:50 and shaken for 4 hours in dark (García-Rodeja et al., 2004). The suspension was centrifuged for 15 minutes at 1,270 g, with three drops of flocculant (superfloc) and the supernatant was transferred to a plastic container and stored in dark for Fe and Al analyses; b) extraction with 0.1 M Na-pyrophosphate (pH 10) ( $Al_p$  and  $Fe_p$ ) with a soil:solution ratio 1:100 and shaken for 16 hours. The suspension was centrifuged (15 minutes at 1,270 g, with three drops of superfloc) and the supernatant was filtered. The suspension and undissolved materials were removed through filtration with acid-washed paper (7–11  $\mu$ m pore size) and the solution passed again through 0.45  $\mu$ m millipore acid-washed filter paper. The concentrations of Al, Fe and Si in each extracts were measured in duplicates using atomic absorption spectrometry. Soluble C in the supernatant of pyrophosphate extraction was regarded as the C linked to  $Al_p$  and  $Fe_p$  complex with SOM and was analyzed with a total organic carbon analyzer (TOC-V CPH, Shimadzu). The allophane content was calculated by Parfitt and Wilson (1985):

$$\text{Allophane (g kg}^{-1}\text{)} = Si_o \text{ (g kg}^{-1}\text{)} \times \frac{100}{y}, \quad (1)$$

$$y = \frac{23.4 - 5.1 \times (Al_o - Al_p)}{Si_o}, \quad (2)$$

Where  $Al_o$ ,  $Al_p$  and  $Si_o$  are expressed in  $\text{g kg}^{-1}$ .

#### 4.2.3 Density fractionation of soil organic matter

The protocol used for density fractionation of SOM is a modification of the methodology described by John et al. (2005). Briefly, the physical fractions were obtained from one soil pit from the forest and pasture using sodium polytungstate (SPT:  $3Na_2WO_4 \cdot 9WO_3 \cdot H_2O$ ) at two densities: 1.6 and 2.0  $\text{g cm}^{-3}$ . About 20 g soil sample (oven dry basis) in triplicate was suspended

in 50 mL of SPT solution ( $1.6 \text{ g cm}^{-3}$ ) in a centrifuge tube of 250 mL. The suspension was hand shaken and centrifuged at 5100 g for 30 minutes. The supernatant in the tube then was filtered ( $47 \text{ }\mu\text{m}$  GF/C, Whatman) and the material remaining on the top filter was designated as free particulate organic matter (fPOM). The pellet in the bottom of the centrifuge tube was re-suspended in 50 mL of SPT solution ( $2.0 \text{ g cm}^{-3}$ ), shaken for 16 hours, centrifuged and filtered. The fraction on the filter is referred to as occluded particulate organic matter (oPOM). The pellet remaining in the bottom of the centrifuge tube, the mineral fraction (MF) was washed ten times with demineralised water and stored. The C and N content of each physical fraction was obtained by multiplying the dry weight of the physical fraction by their corresponding C and N concentration.

#### **4.2.4 Analysis of C, N and stable isotopes $^{13}\text{C}$ and $^{15}\text{N}$**

The C and total N for the characterization of whole soil and the physical fractions were determined using an elemental analyzer CHN NA 1500 (Carlo Erba). The soil C in the pyrophosphate extractant ( $C_p$ ) was determined using a total organic carbon analyzer (TOC-V CPH, Shimadzu). The natural abundance of stable isotopes  $^{15}\text{N}$  and  $^{13}\text{C}$  in the fractions was measured using the same elemental CHN analyzer coupled to a mass spectrometer for stable isotopes (VG Sira 10). The natural abundance of  $\delta^{13}\text{C}$  y  $\delta^{15}\text{N}$  were expressed in parts per thousand (‰) on the international standards Viena Pee Dee Belemnita (V-PDB) and atmospheric  $\text{N}_2$ .

#### **4.2.5 Data representation and statistical analysis**

Statistical analysis was carried out using the software SPSS 12.0 Inc. Correlations were performed amongst all soil properties for all soil depths. One way ANOVA was used to test for differences between ecosystems. Significance differences between means were tested using the Tukey at  $P \leq 0.05$ . A principal component analysis (PCA) was conducted to identify the factors ( $\text{BD}$ ,  $\text{Fe}_p$ ,  $\text{Al}_p$ ,  $\text{Fe}_o$ ,  $\text{Al}_o$  and soil pH) that explain the data variation within each ecosystem.

## 4.3 Results

### 4.3.1 Soil characteristics

The soil pH was slightly higher in forest than pasture ecosystem and it increased with depth in both ecosystems. Carbon contents ranged between  $7.1\pm 0.1$  and  $73.5\pm 0.2$  g kg<sup>-1</sup> soil and they were lower for forest compared to pasture soil (Table 4.1). Similar trend was observed for soil nitrogen which ranged between  $0.4\pm 0.01$  and  $5.6\pm 0.3$  g kg<sup>-1</sup>. The bulk density generally showed the same behavior in both ecosystem, but the values decreased throughout the pasture profile from  $0.75\pm 0.01$  to  $0.65\pm 0.01$  Mg m<sup>-3</sup>, whereas an increase from  $0.54\pm 0.01$  to  $0.92\pm 0.01$  Mg m<sup>-3</sup> was recorded in the forest profile. The C stocks in each horizon were higher for rain forest soil ( $29\pm 8.1$  -  $71\pm 2.4$  Mg ha<sup>-1</sup>), compared with pasture ( $14.5\pm 0.01$  -  $113\pm 1.3$  Mg ha<sup>-1</sup>) soil with the exception of AC horizon of forest soil. The SOC stock in forest soil (0-41 cm) stored 100 Mg ha<sup>-1</sup>, while in the pasture soil (0-40 cm) accumulated 166 Mg ha<sup>-1</sup>. The C to N ratio was generally higher in the forest soil samples (18-24) than that in the pasture (13-16). Soil texture in the pasture, the proportion of sand, silt and clay was fairly constant, while in the forest, the sand size fraction was more than 74 %.

The pyrophosphate extractable metals (Al<sub>p</sub> and Fe<sub>p</sub>) were removed in similar proportions from both soils ecosystems, although Fe<sub>p</sub> was always highest in the forest soil samples (Table 4.2). For example, Al<sub>p</sub> ranged between  $1.8\pm 0.01$  and  $7.8\pm 0.02$  g kg<sup>-1</sup> in both soil ecosystems. It was higher than pyrophosphate extractable Fe<sub>p</sub> and decreased with depth (Table 4.2). Along with Al<sub>p</sub> and Fe<sub>p</sub>, similar amounts of C<sub>p</sub> which represents the C bound to Al and Fe were extracted in the top soil. These values ranged between  $20\pm 0.9$  and  $24\pm 0.8$  g kg<sup>-1</sup> and for the last horizons were higher in the pasture ( $7.8\pm 0.4$  -  $18.0\pm 0.9$  g kg<sup>-1</sup>) than in the forest ( $3.9\pm 0.5$  -  $8.3\pm 0.9$  g kg<sup>-1</sup>). In general C<sub>p</sub> paralleled the pattern of Al and Fe in the whole soil profile (Table 4.2). The percentage of C<sub>p</sub> as total SOC ranged from 29 % to 33 % in the two ecosystems in the top soil. These figures were 28 % and 55 % in the deep horizons. Amorphous Al contributed generally in higher amounts to the oxalate extractable fraction than Fe and Si. Higher amounts of amorphous Al were determined in the soil under pasture compared to soil under forest, which also showed lower allophane contents (Table 4.2). Overall allophane content contributed about 39 % and 55 % of the total clay content in pasture and forest, respectively (Tables 4.1 and 4.2). The atomic metal:carbon ratio, which indicates the saturation of organic C with metal were different in the

pasture profile samples (0.14-0.16) compared with forest soil (0.23-0.27). The  $Al_p$  to  $Al_o$  ratio, which is the proportion of Al-humus relative to the total amorphous Al ranged between 0.07 and 0.71 and was higher for the soil under forest compared with pasture soils. Principal component analysis (PC) indicated that  $Al_p$  and  $Fe_p$  explained the greatest variability in SOC content in the two ecosystems (Figure 4.1). It also shows that there was a strong correlation between SOC and  $Al_p$ ,  $Fe_p$  or  $C_p$ . The  $Al_p$  (PC 1) and  $Fe_p$  (PC 2) explained 98.98 % (81.61+17.37) of the total data variance in pasture (Figure 4.1A) and 97.96 % (61.17+36.79) in rain forest (Figure 4.1B). Allophane did not play a significant role in explaining the variance and its contribution was < 1 % in all cases studied.

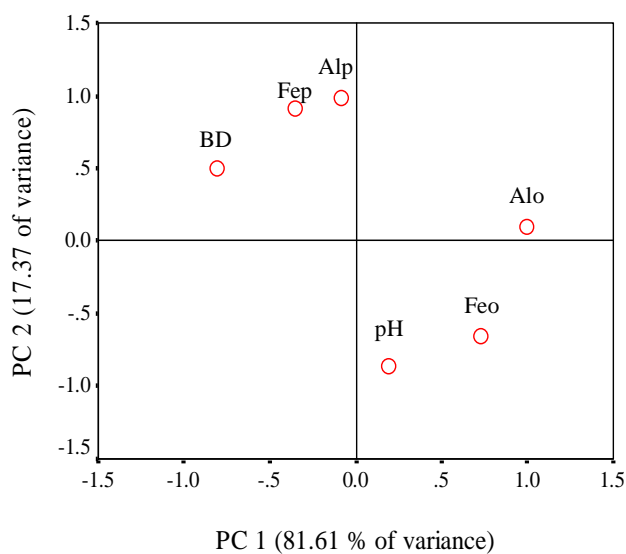
**Table 4.2** Chemicals soil characteristics in managed pasture and pristine rain forest. In bracket standard error of the mean (n=3, round figures).

Parameter	Rain forest			Pasture		
	Horizon /cm			Horizon /cm		
	A /0-19	AC /19-41	C /41-100	Ap /0-7	B1 /7-32	B2 /32-40
Chemical <sup>1</sup> /g kg <sup>-1</sup> soil						
$Al_p$	7.8 ± 0.2	3.7 ± 0.2	1.8 ± 0.01	6.9 ± 0.1	4.8 ± 0.1	2.4 ± 0.01
$Fe_p$	6.4 ± 0.1	2.7 ± 0.01	1.7 ± 0.01	3.0 ± 0.01	1.7 ± 0.01	0.5 ± 0.01
$C_p$	20.0 ± 0.9	8.3 ± 0.9	3.9 ± 0.5	24.0 ± 0.8	18.0 ± 0.9	7.8 ± 0.4
$Al_o$	11.1 ± 0.2	14.0 ± 0.3	12.2 ± 0.6	30.3 ± 0.4	33.2 ± 0.9	33.4 ± 0.7
$Fe_o$	12.7 ± 0.3	10.3 ± 0.2	7.7 ± 0.3	13.0 ± 0.3	14.7 ± 0.2	17.4 ± 0.4
$Si_o$	3.9 ± 0.03	6.5 ± 0.2	6.7 ± 0.3	9.3 ± 0.2	11.7 ± 0.2	12.6 ± 0.4
Allop <sup>2</sup>	21 ± 1.5	43 ± 6.1	41 ± 9.3	89 ± 0.6	107 ± 1.5	116 ± 2.2
$(Al_p+Fe_p)/C_p$	0.27	0.23	0.26	0.15	0.14	0.16
$Al_p/Al_o$	0.71	0.27	0.18	0.23	0.15	0.07

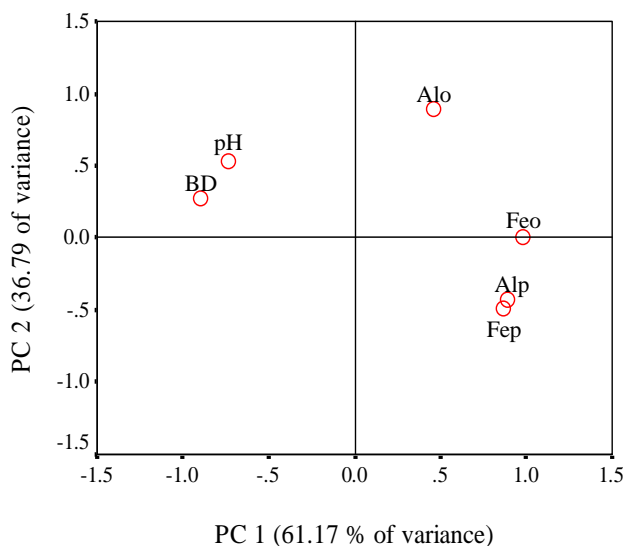
<sup>1</sup>Al<sub>p</sub>: pyrophosphate extractable Al; Fe<sub>p</sub>: pyrophosphate extractable Fe; C<sub>p</sub>: C in the supernatant of pyrophosphate extraction; Al<sub>o</sub>: acid oxalate extractable Al; Fe<sub>o</sub>: acid oxalate extractable Fe; Si<sub>o</sub>: acid oxalate Si.

<sup>2</sup>Allophane from Parfitt and Wilson (1985).

**A**



**B**



**Figure 4.1.** Principal component analysis of the data from (A) managed pasture and (B) rain forest.

For the two ecosystems similar correlations for the main chemical and physical soil properties were established. Therefore a correlation matrix for forest soils is presented only (Table 4.3). There was a strong relationship between  $C_p$  with  $Al_p$  and  $Fe_p$ . The coefficient of correlation for  $Al_p$  and  $Fe_p$  were 0.95 and 0.96, respectively in forest (Table 4.3). In agreement with the results of PC, Table 4.3 showed that  $Al_p$  and  $Fe_p$  were highly correlated with SOC, independent of management, indicating that most variations in the levels of soil carbon between soil depths and ecosystems were explained by the complexation between metals and humic substances. Table 4.3 also shows that there was an inverse, but a highly significant relationship between  $C_p$  and allophane content ( $r = -0.62$ ) and between  $C_p$  and pH ( $r = -0.91$ ).

**Table 4.3.** Correlation matrix for main soil chemical and physical constituents in pristine rain forest (n=18). \*, \*\* correspond to  $P < 0.05$ ,  $P < 0.01$ , respectively, NS means not significant.

	<b>SOC<sup>1</sup></b>	<b>Al<sub>p</sub></b>	<b>Fe<sub>p</sub></b>	<b>C<sub>p</sub></b>	<b>Allop</b>	<b>Al<sub>o</sub></b>	<b>Fe<sub>o</sub></b>	<b>Al<sub>p</sub>/Al<sub>o</sub></b>	<b>pH</b>	<b>BD</b>
<b>SOC<sup>1</sup></b>	1									
<b>Al<sub>p</sub></b>	0.87**	1								
<b>Fe<sub>p</sub></b>	0.82**	0.99**	1							
<b>C<sub>p</sub></b>	0.90**	0.95**	0.96**	1						
<b>Allop</b>	-0.43 <sup>NS</sup>	-0.55*	-0.56*	-0.62**	1					
<b>Al<sub>o</sub></b>	0.07 <sup>NS</sup>	0.07 <sup>NS</sup>	0.03 <sup>NS</sup>	-0.03 <sup>NS</sup>	0.75**	1				
<b>Fe<sub>o</sub></b>	0.88**	0.83**	0.84**	0.81**	-0.17 <sup>NS</sup>	0.30 <sup>NS</sup>	1			
<b>Al<sub>p</sub>/Al<sub>o</sub></b>	0.74**	0.89**	0.90**	0.91**	-0.81**	-0.29 <sup>NS</sup>	0.60**	1		
<b>pH</b>	-0.77**	-0.87**	-0.87**	-0.91**	0.77**	0.25 <sup>NS</sup>	-0.61**	-0.92**	1	
<b>BD</b>	-0.92**	-0.95**	-0.96**	-0.97**	0.57*	-0.10 <sup>NS</sup>	-0.84**	-0.86**	0.90**	1

<sup>1</sup>For symbols and units definition see Table 4.1 and 4.2.

### 4.3.2 Physical fractionation

The mass distribution of various physical fractions of organic matter is shown in Figure 4.2. Overall the total dry mass recovery of the total soil sample was close to 100%. The mineral fraction represented > 95 % of the total weight of whole soil in pasture (Figure 4.2A). The fPOM comprised between 0.8 % and 1.5 % and oPOM between 0.7 % and 3.4 %. In general the soil C recovery in the various fractions was about 97 % of SOC. More than 84 % of the carbon was found in the MF of soil under pasture in all depths, whereas oPOM contributed with the highest carbon in Ap horizon (13.3 % of total carbon) follow by B1 and B2 horizons (~7 %) (Figure 4.2B, Table 4.4). The fPOM contribution ranged from 2.5 % - 3.1 %. Similar trends were found for N (Table 4.4), although the total recovery (102 %) of N from each fraction was higher especially in pastures soils. The MF in the rain forest was > 81 % of total soil weight (Figure 4.2C), but in this case the contribution of fPOM and oPOM were higher than that of pastures, especially in the A and AC horizons. The rain forest showed a more uniform C distribution in various physical fractions in A and AC horizons (Figure 4.2D). However, the C in the mineral fractions was always lower in the forest than that in the pasture soil and increased in soil depth (Table 4.4). The opposite trends were true for the fPOM. Forest soil showed the highest fPOM compared to the pasture. The fPOM contributed 24.8 % in AC horizon and oPOM 34.8 % in A horizon of the total C (Figure 4.2D, Table 4.4). Again similar trends were found for N (Table 4.4).

**Table 4.4.** Carbon (C) and nitrogen (N) in SOM fractions in rain forest and managed pasture.

SOM fraction <sup>1</sup>	Rain forest			Pasture		
	Horizon/cm			Horizon /cm		
	A /0-19	AC /19-41	C /41-100	Ap /0-7	B1 /7-32	B2 /32-40
<i>Carbon /g kg<sup>-1</sup> soil</i>						
fPOM <sup>1</sup>	7.98	4.99	0.84	1.76	1.81	0.73
oPOM	20.24	5.93	1.49	9.55	4.53	1.63
MF	29.94	9.19	4.93	60.58	54.79	21.21
<i>Nitrogen /g kg<sup>-1</sup> soil</i>						
fPOM	0.28	0.19	0.04	0.10	0.10	0.03
oPOM	1.06	0.28	0.07	0.44	0.19	0.05
MF	1.38	0.45	0.29	5.06	5.81	1.68
<i>C to N ratio</i>						
fPOM	28.77	26.05	21.83	18.45	17.35	21.62
oPOM	19.07	21.13	20.21	21.61	23.76	33.92
MF	21.65	20.20	17.00	11.96	9.43	12.65

<sup>1</sup>fPOM: free particulate organic matter; oPOM: occluded particulate organic matter; MF: mineral fraction.



### 4.3.3 Natural abundance of $^{13}\text{C}$ and $^{15}\text{N}$

In general  $\delta^{13}\text{C}$  values for the two ecosystems remained constant throughout the soil profile. In pasture soil,  $\delta^{13}\text{C}$  values ranged from -27.85 to -27.15 ‰ in fPOM and from -28.06 to -28.20 ‰ in oPOM. In MF the values ranged from -28.12 ‰ to -26.75 ‰ (Figure 4.3A). In the rain forest the average  $\delta^{13}\text{C}$  values ranged from -27.89 to -25.74 ‰ and -27.89 to -25.30 ‰ in fPOM and oPOM, respectively. Finally, the values in MF ranged from -28.69 to -26.33 ‰ (Figure 4.3C).

The  $^{15}\text{N}$  showed higher values in the pasture than in the rain forest. In the pasture, the values ranged from 3.83 to 5.52 ‰ in fPOM, while the oPOM ranged from 3.2 to 3.47 ‰. The MF presented the highest values with averages of 4.82 to 7.92 ‰ (Figure 4.3B). On the other hand, the rain forest showed figures between -4.01 and -2.61 ‰ in the MF. The fPOM and oPOM were higher, averaging between -0.97 to -4.01 ‰ and -1.89 to -3.57 ‰, respectively (Figure 4.3D).

The positive and significant relationship between the  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  concentration for both forest and pasture, shows a  $\delta^{15}\text{N}$  depleted values in forest soils (Figure 4.4). The  $\delta^{13}\text{C}$  ranged between -28 to -24 ‰ for both ecosystems, while the  $\delta^{15}\text{N}$  in the forest varied between -4.19 and 0.91‰ and for pasture between 2.94 to 7.91 ‰.

## 4.4 Discussion

### 4.4.1 Soil organic matter storage and mechanisms of stabilization

The two Andisols studied have high contents of SOC, slightly acid pH and low bulk density. The bulk density in the soil profile increased in the forest soil as a consequence of an increase of coarse soil texture (Klein et al, 2008) (Table 4.1). In contrast the bulk density in pasture varied less with depth, because soil texture was more uniform through the soil profile. These characteristics are unique to soils derived from recent volcanic ash in southern Chile (Mella and Kühne, 1985). In this region the climatic conditions enhance carbon accumulation due to a lower decomposition of organic compounds compared to non-volcanic soils (Mella and Kühne, 1985).

The total carbon stocks in the soil profile were between 14.5-113 Mg ha<sup>-1</sup> in both ecosystems (Table 4.1) and they are higher than those recorded for volcanic soils (0-30 cm depth) in Island Canarias (Rodríguez-Rodríguez et al., 2005). In our case, we found that soil C stock at the first 40 cm depth were higher in pasture (166 Mg ha<sup>-1</sup>) than in forest (100 Mg ha<sup>-1</sup>). Total nitrogen showed the same trend, 10.5 and 4.0 Mg ha<sup>-1</sup>, respectively. Similar to our results, Huygens et al. (2005) who compared *Nothofagus sp.* and pasture in central Andisols of Chile reported that pasture presented higher C (17.3 kg m<sup>-2</sup>) and N (1.34 kg m<sup>-2</sup>) than forest, 13.2 and 0.75 kg N m<sup>-2</sup> respectively in the first 30 cm depth.

García-Rodeja et al. (2004) pointed out that Al extracted with Na-pyrophosphate at pH 10 (Al<sub>p</sub>) is used for Al in organic complexes, as this extractant has little action on hydrous oxides, allophane or imogolite, although the opposite has been indicted (Kaiser and Zech, 1996). Pyrophosphate-extractable Al (and Fe) has been questioned because may dissolve Al hydroxide and increase peptization (Kaiser and Zech, 1996). This technique can also remove interlayered Al and gibbsite (Page and De Kimpe, 1989). However, Bardy et al. (2007) demonstrated that pyrophosphate is capable to remove the Al bound to SOM as determined by <sup>27</sup>Al-NMR spectra in tropical Podzols. Thus, Al linked to organic matter can be distinguished from mineral secondary Al phase. Considering that active Al and Fe is the determining factor controlling organic matter levels in volcanic soils (Tonneijck et al., 2010; Jensen et al., 2011), it is expected that a large amount of C is associated with Al<sub>p</sub> and Fe<sub>p</sub> (Matus et al., 2006; Matus et al., 2008). This is mainly due to soil pH and soil C saturation with metals (Garrido and Matus, 2011). These

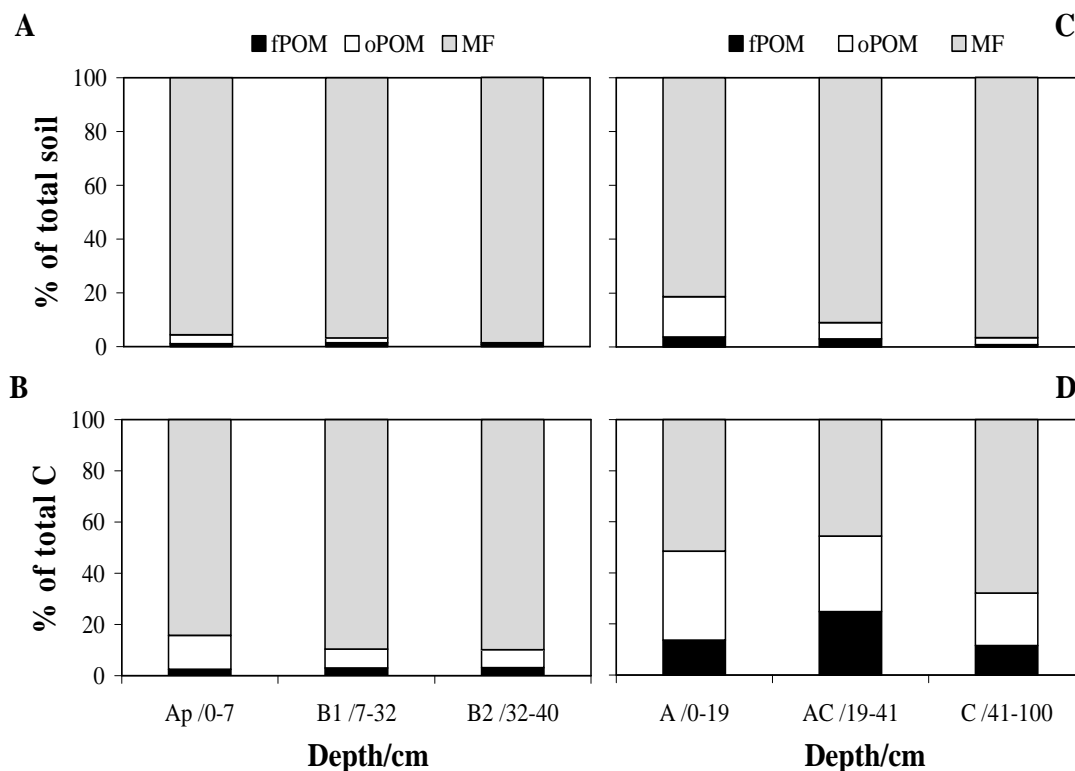
authors found an inverse relationship between soil pH and Al- (and Fe-) complexed with SOM and a positive relationship between pH and allophane content of Andisols. In chemically saturated volcanic soils (metal:C ratio > 0.12 with pH ~5.5) the weathered Al and Fe will react with silica to form allophane, while in non-saturated soils Al and Fe will react with SOC to form humus complex. The present results supported the above, because on average we found an inverse relationship between soil pH and  $C_p$  and a highly positive relationship between soil pH and allophane content in both ecosystems. The facts that the soils used in this study present high SOC due to Al- and Fe-complex were also revealed by strong relationship between SOC with  $Al_p$  and  $Fe_p$ , indicating that a large part of C is stabilized by forming Al-humus complexes (Imaya et al., 2010). However, Huygens et al. (2005) compared a *Nothofagus* forest Andisol in Southern Chile with a forest converted to grassland in adjacent areas. They concluded that the stabilization of SOC was due to electrostatic sorption between amorphous Al components and clay minerals. Unlike the work of Huygens et al. (2005), in the present research we show that SOC is not associated with amorphous clays (Table 4.3). However, the same relationship was negative and highly significant for  $C_p$  in both ecosystems, indicating the competition of Al for allophane or Al- (and Fe) complex formation. About 28-33 % and 29-55 % of SOC of pasture and forest soils, respectively corresponded to  $C_p$  in the soil profile. These percentages were higher (rain forest) than those reported by Matus et al. (2008) who found average values between 29-38 % in allophanic soils (0-40 cm depth). On other hand more allophane content was found in the subsoil in both ecosystems. This is typical of volcanic soils in which Si migration contributes to allophane formation (Shoji et al., 1993). In fact  $Si_o$  in the present study increased from 4 g kg<sup>-1</sup> in the top to 13 g kg<sup>-1</sup> in the subsoil. The differences were especially more marked in the forest coarse sandy soils. Coarse-textured soils allow good aeration and infiltration conditions that facilitate the movement and redistribution of products of the mineralization and humification (Klein et al., 2008). These characteristics are present in the rain forest, an ecosystem in which there is a flux of DOC to deeper soil horizon that microbial activity increases at lower depths (Matus et al., 2009). Rumpel et al. (2002), although working with Podzol suggests that in temperate climates large amounts of organic carbon are probably stored in B and C horizons in forest soils indicating that the storage potential in subsoil horizons is often underestimated. Their research found 45 % of the C is stored in the mineral fraction (horizon B), particularly bound

with Fe oxides. In our case for the first 40 cm depth the second horizon in forest stored 47 % of the total C while in pasture this value was 56 %.

#### **4.4.2 Physical SOM fractions**

The carbon distribution of the physical fractions followed a similar pattern to those described in the literature. It means a large amount of soil C in the MF was found followed by POM (John et al., 2005). This is more obvious in pasture than in forest soil samples, where the MF constitutes over 84 % of the SOC. Basile-Doelsch et al. (2007) noticed that 82.6 % of the total of organic matter was found in MF (Bw horizon) in a volcanic soil, similar to the results found in the pasture soil samples of this study. The situation changed in forest soil, mainly because the fPOM and oPOM had the highest proportion of SOC (12-35 %). This was expected, because the summer green forests of Antillanca have conditions of low temperature and high rainfall resulting in low mineralization rates of SOM (Godoy et al., 2001). Pasture soil samples concentrated a significant amount of C in the oPOM (5-12 % of SOC). These results are consistent with those found for the A horizons of pastoral ecosystems studied by Elliot and Cambardella (1991) who found approximately 15 % of SOC was in the oPOM fraction of the soil. It is necessary to emphasize that the major contribution of oPOM to SOC in pasture occurs because there is no alteration in soil structure, thereby contributing to the formation of aggregates, which physically protects organic matter (Six et al., 1999). Huygens et al. (2005) working with a pasture in a Chilean Andisol found that the light density fraction ( $< 1.13 \text{ Mg m}^{-3}$ , equivalent to our fPOM) concentrate more than 50 % of C in all depths, while in our study this range was 2.5-3.1%. These differences were attributed due to Huygens et al. (2005) studied a pasture which was plowed every two years, resulting in a breaking of the aggregates and therefore all new organic matter to the soil were less decomposed, ultimately placed in a more labile fraction. Zimmermann et al. (2007) note that low intensity soil management cultivation practices are likely to cause a strong aggregation of soil particles. Therefore, it is expected that forest ecosystems without intervention, display strong aggregation between its components and oPOM represents an important pool of C. This is in line with Poirier et al. (2005) who established that the slow transformation of POM fraction in soil is also attributed to chemical recalcitrance, humification and physical stabilization by occlusion in soil aggregates. In subsoil

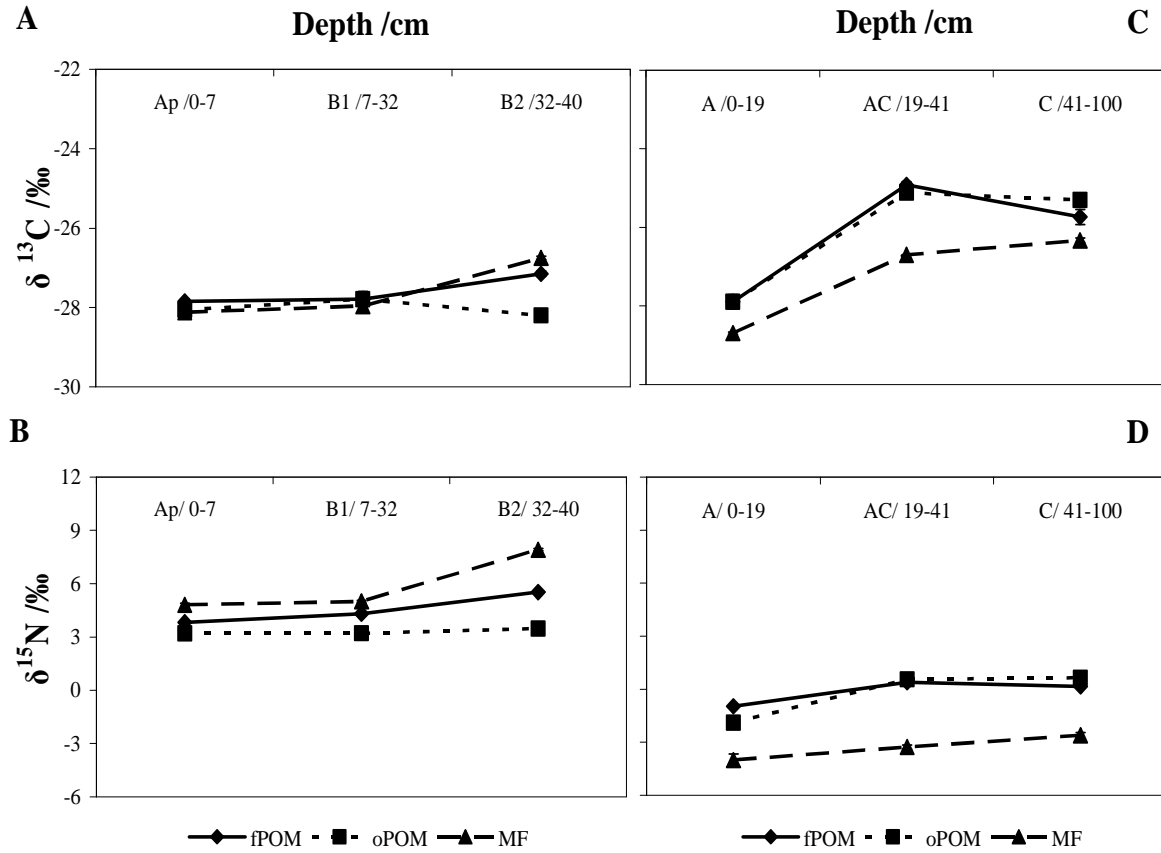
horizons, physical protection of oPOM within micro-aggregates is identified as a stabilization mechanism together with the chemical stabilization (Rumpel and Kögel-Knabner, 2011). In the present study differences between ecosystems were established in the carbon stored in fPOM and oPOM. Forest stores twice as much C in these fractions compared to pasture soils especially in the A and AC horizons. These differences in C storage are accentuated primarily by the rainfall in each ecosystem. While in the pasture the annual rainfall ranges between 2200- and 2700 mm per year, in the forest this value is over 5,000 mm per year. Low temperatures, high rate of incorporation of litter and high rainfall have a strong influence on the stock of C in the forest soils (Huygens et al., 2005; Godoy et al., 2001). The POM fraction in the forest soils also showed a higher C to N ratio than that in the pasture supporting the idea of less decomposed plant material in the POM fraction. Broquen et al. (2005) noted that the input of organic matter in *Nothofagus* forest is mostly litterfall with C to N ratio ranging from 25 to 28, values which were slightly lower than that reported in this study (13-24).



**Figure 4.2.** Distribution of soil weights in various physical fractions from (A) managed pasture and (C) rain forest. Distribution of carbon in various physical fractions from (B) managed pasture and (D) rain forest.

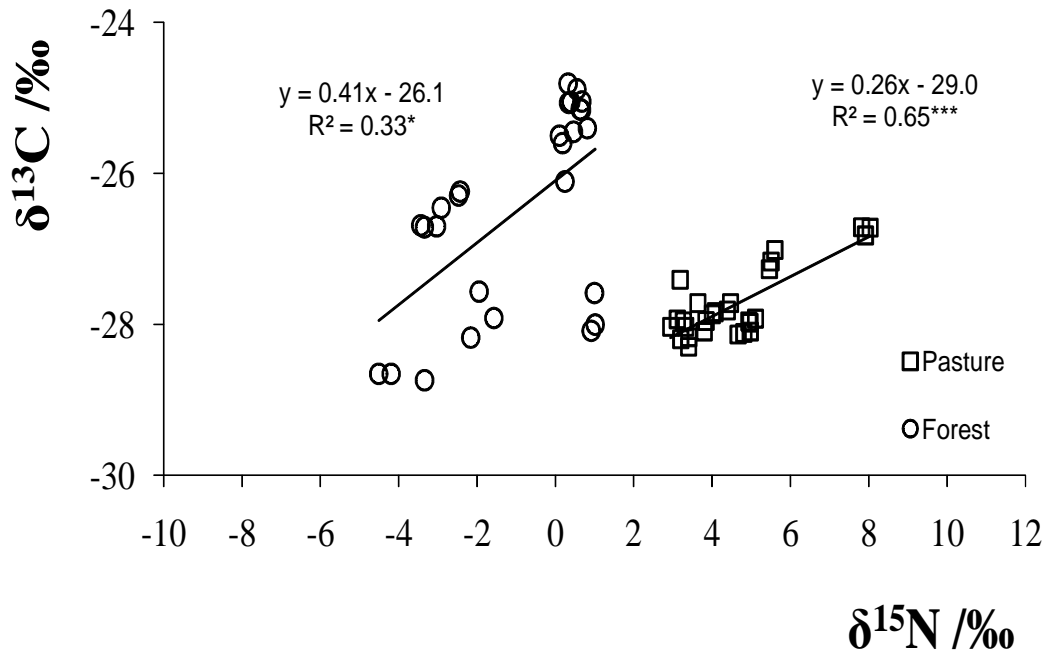
#### 4.4.3 Stable isotopes

The  $\delta^{13}\text{C}$  values found in this study are characteristic for soil under C3 vegetation (Glaser, 2005). The concentration of stable isotopes  $^{13}\text{C}$  and  $^{15}\text{N}$  increased with soil depth. This behavior is explained by the increase in the degree of decomposition of SOM with depth, especially in soils with no change in vegetation over time (He et al., 2008). Krull and Skjemstad (2003) found in temperate ecosystems,  $^{13}\text{C}$  enrichment ranged between 1 ‰ and 3 ‰. These values are consistent with our results, 2 ‰ enrichment in the forest, however we found no differences in the profile of the pasture soils. Arai et al. (2010) concluded that in natural forests, enrichment of  $^{13}\text{C}$  in subsoil resulted from intense decomposition of SOC. Krull et al. (2006) points out that the enrichment of C and N in depth was produced by decomposition of the upper layers, resulting in the accumulation of oldest carbon. The  $\delta^{13}\text{C}$  enrichment is related to the decrease in particle size and is attributed to preferential loss of  $^{12}\text{C}$  during microbial degradation, which favours the enrichment of organic compounds that are less available for microorganisms (Gerzabek et al., 2001). Muñoz et al. (2008) noted that the increase  $\delta^{13}\text{C}$  values with depth may suggest a large residence time in the MF, providing greater stability of this fraction respect to oPOM and fPOM fractions.



**Figure 4.3.** Natural abundance of  $^{13}\text{C}$  in various physical fractions from (A) managed pasture and (C) rain forest. Natural abundance of  $^{15}\text{N}$  in various physical fractions from (B) managed pasture and (D) rain forest.

The  $\delta^{15}\text{N}$  concentration was higher in the pasture and highest in the mineral fraction compared with forest soil. In contrast  $\delta^{15}\text{N}$  in the forest was lowest in the mineral fraction. The  $\delta^{15}\text{N}$  enrichment in the pasture, as for C is attributed to preferential loss of  $^{15}\text{N}$  during microbial degradation, which indicated a more processed organic materials, a more enriched organic compounds that are less available for microorganisms (Gerzabek et al., 2001). In fact the relationship between  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  for forest soils were more depleted for N than for C when both, forest and pasture are compared (Figure 4.4).



**Figure 4.4.** Relationship between  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  for managed for managed pasture and rain forest.

This supported the idea that the N in forest soils fractions is a fresh material than that in the pasture soils. This was in line with the high C to N ratio than any other fraction in the forest soils. Although we did not measure the dissolved organic C, this C pool could be mixed in the mineral fraction and be transported to deep soils as consequence of high precipitation and coarse texture of forest soils. This can explain the depleted  $\delta^{15}\text{N}$  enrichment found in the mineral fraction of forest soils.



## 4.5 Conclusions

The soil C stock in the soil profile of pasture was 166 Mg ha<sup>-1</sup> (0-40 cm) and in the forest 139 Mg ha<sup>-1</sup> (0-100 cm). Pasture accumulates more carbon than the rain forest at 0-40 cm depth. Also two pools of carbon were identified in the pastoral and forest ecosystem. The main pool was mineral associated C such as Al<sub>p</sub> and Fe<sub>p</sub> linked to SOM and SOM in the heavy fractions. The second pool corresponds to the oPOM which corresponds to C physically protected within aggregates. This reservoir was more important in the forest than in the pasture, mainly in the subsoil where it represented a significant proportion of C. A <sup>13</sup>C and <sup>15</sup>N enrichment was observed in both ecosystems assessed, being more evident in the deeper horizons. In line with this the C to N ratio decreased through the soil profile. This was supported by more depleted <sup>15</sup>N in all fractions of forest soils.

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## **CHAPTER 5**

### ***General Discussion, Conclusions and Projections***

## 5.1 General Discussion and Conclusions

- In the present study we found that Al and Fe extracted by pyrophosphate explained much of the SOC variation in both, managed pasture and pristine rain forest. The relationship between allophane content and SOC was not significant. This is contradicting the present hypothesis where it was proposed that both, the allophane like materials and Al-complexed with SOM are the key factors for SOM stabilization and storage. This study established the relationship among different soil properties such Al-, Fe-complexes and allophane content on soil C levels in Chilean volcanic soils as well as the effect of soil pH on metal-OM complexes. We found an inverse relationship between soil pH and  $Al_p$  (and  $Fe_p$ ), Chapter 4 indicating that the soil pH was significantly correlated with  $Al_p$  (-0.91) and  $Fe_p$  (-0.87) while the allophane content was positively related (0.77) with soil pH. Soils studied here are young allophanic pedons weathered from basaltic coloured volcanic rock. These soils are known to have high natural soil pH >5, even if weathering occurs under strongly leaching conditions, because of the abundant release of bases from the basic parent ashes. Under such conditions, high soil pH and silica gel promote allophane formation. However, the amount of allophane in all soils was low between 21 and 116 g kg<sup>-1</sup> soil, indicating that this cannot explain the C level is did  $C_p$  which varied between 20 to 80 % of SOC.

The results of our study have several implications:

- First, the mechanisms of SOC stabilization on top and subsoils in forest appear to be the same and provided an interesting strategy of this ecosystem to maintain nutrient cycling in deep soil.
- Second, the incubation results under favorable conditions of moisture and temperature show that SOC from the topsoil provides sufficient energy to sustain an active microbial population as much as in the deepsoil of the forest.
- Third, two C pools were identified in the pastoral and forest ecosystems. A chemically stabilized pool constituted mainly by the Al and Fe linked to the SOC which represented



30% of the SOC in pasture and 44% in forest. The second pool corresponds to the occluded POM fraction (oPOM) and associated to C physically protected within aggregates. This pool was more important in the forest than in the pasture, mainly due to the organic matter incorporated into soils is less decomposed than the pasture. Also there was an enrichment of  $^{13}\text{C}$  and  $^{15}\text{N}$  in depth soils for both ecosystems, indicating that the C in topsoil is more stable than the deepsoil.

- Finally, although the forest sites studied correspond to a coarse textured Andisols, pastures presented more C stock than forest in the top 40 cm. On the other hand, the Al and Fe extracted with sodium pyrophosphate largely explain the variation in SOC in pastoral ecosystem. This was ratified by the strong correlations found between the  $C_p$  ( $\text{Al}_p + \text{Fe}_p$ ) and the SOC. The SOC of the top soil of the forest soils were more saturated with metals cations (Al and Fe) than the subsoils. On the other hand, the pasture has not reached the maximum limit of accumulation of carbon as  $C_p$  in the surface horizons.

## 5.2 Projections

The SOC corresponds to 615 Gt C in the top 0.2 m and 2,344 Gt C at depths of up to 3 m (Jobbágy and Jackson, 2000). This is particularly important in Chilean allophanic soils, where organic matter can be reached up to 31%.

The response to climate change, especially in pristine unpolluted forest, remains uncertain. For instance, about 50 % of the allophanic soils area in Chile is found on steep slopes in the limits of the Andean ranges between latitude  $36^\circ$  and  $47^\circ$  (mostly covered by evergreen forest formation). At southern latitude the mean precipitation may reach more than 5,000 mm per year in sandy soils (Antillanca soils) where percolation, bioturbation and leaching push down soil organic matter to deep soil horizons. In this area, there are also other well developed soils (Matus et al., 2008) but, water retention capacity can be easily exceeded and anoxic conditions can be generated.

The mean residence time of soil organic carbon strongly increases with soil depth, reaching a range of 2,000–10,000 year in deep soils (Fontaine et al., 2007). However, little is known about the factors and mechanisms controlling the stability of carbon in deep soils (Chabbi et al., 2009).

The vast majority of studies have focused on understanding the factors and mechanisms that control levels of SOM in the ecosystems. However, a large proportion of these researches and the concept associated to the SOM dynamics have been developed for crystalline clay in tropical regions. Often clay content is well correlated with the SOC and clay plus silt content of soil. However, in allophanic soils no relationships have been found at a regional scale. One of the difficulties in the study of soil carbon dynamic in non-volcanic soil is the low carbon content and climatic conditions, which prevents a proper characterization of the carbon. To this end, Andisols provide an excellent opportunity to study the organic matter stabilization by the mineral phase, since they contain large amounts organic matter stabilized by Al, Fe and allophane interactions. The existence of a finite capacity to store SOM (protective capacity) is relevant, because the soils can act as source or sink, depending on the degree of carbon saturation. It appears imperious to study whether the C associated to the physical fraction of clay (allophane) is saturated with SOM or not. Therefore, improved knowledge of the factors and mechanisms of SOC stabilization is essential to determine whether the nutrient will react to global change impact and how we are globally going to face this problem in these types of soils.

Although the mechanisms for SOM protection differ because of differences in the existing pedogenic processes, allophane and imogolite and location of SOM in stable micropores can also play a key role in SOM stability by entrapment within the aggregates. Differences in weatherable minerals parent materials on fresh organic matter by environmental factor that promote SOM stabilization need further attention too.

There is a lack of knowledge on processes and mechanisms of stabilisation and storage of organic matter in volcanic soils. More attention is needed to experimentally manipulate soils at broad, regional scale, preferably across a range of different soil ecosystem such as forest and managed allophanic soils. Biophysical variables such as elevation, soil vegetation, composition of clay colloidal fraction and in situ active  $\text{Al}^{3+}$  competition for allophane or metal-SOM complex formation are determinants for the relationship between allophane and SOM or between amorphous Al-oxides and SOM in allophanic soils. It seems that metal:soil C ratio between 0.12 and 0.18 represent the upper boundary for SOM complexation. Any metal above this limit will not be complexed with SOM, but it will be available for allophane and imogolite formation.

Finally the impact of land-use and climate change on SOM stabilization is poorly understood. One reason is that most studies on Andisols have been carried out in forests; comparison with other land-uses is limited.

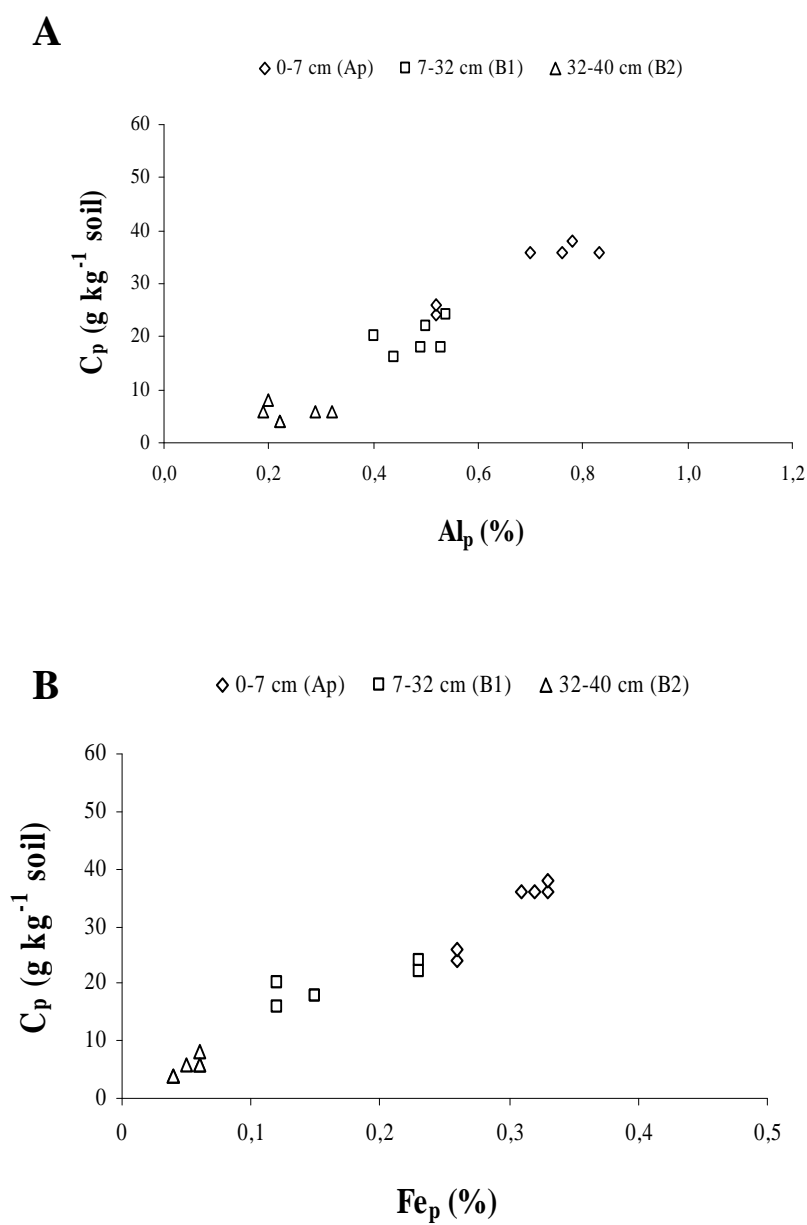
### 5.3 References

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# Annexes

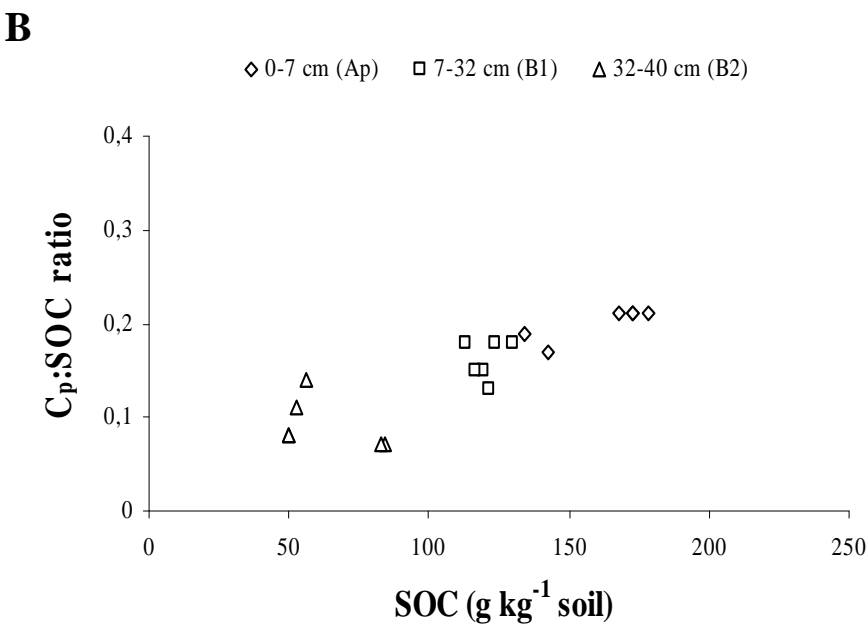
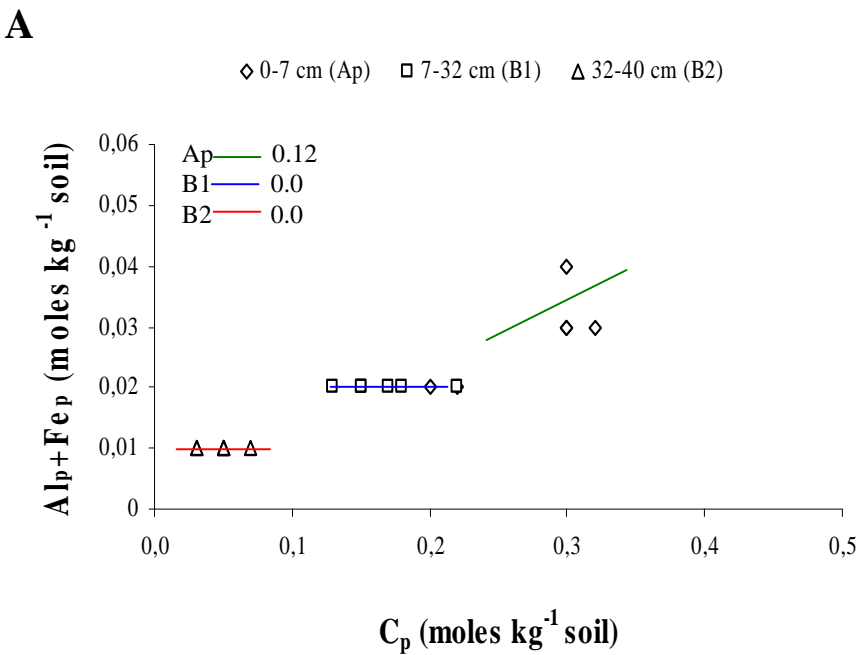
## Anexx 1

Relationship between (A)  $C_p$  and  $Al_p$  and (B)  $C_p$  and  $Fe_p$  in managed pasture.



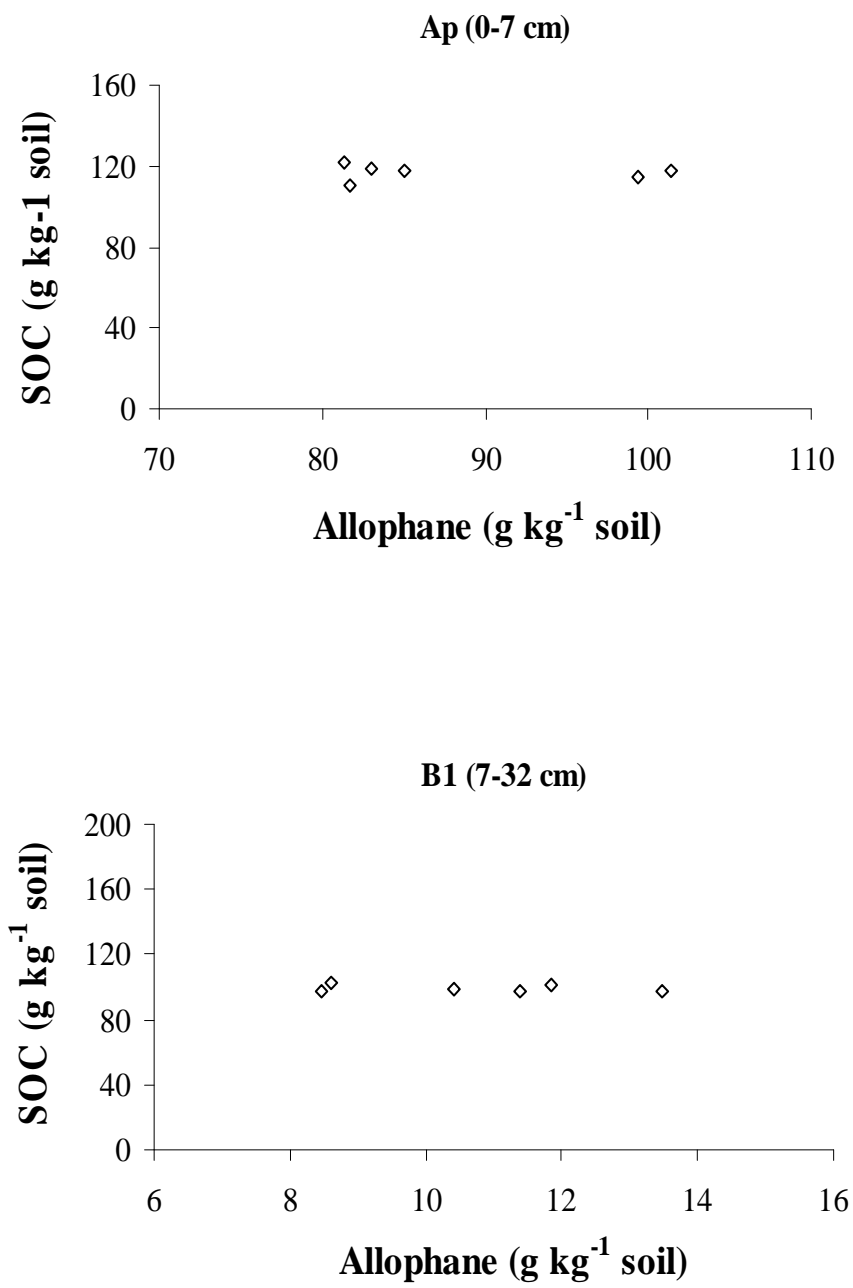
Anexx 2

Relationship between atomic ratios  $Al_p+Fe_p$  and  $C_p$  for managed pasture. The slope of the regression is shown for each horizon.



**Anexx 3**

Relationship between SOC and allophane from (A) Ap horizon and (B) B1 horizon in managed pasture.



**Anexx 4**

Relationship between C<sub>p</sub> and SOC in managed pasture.

