Carbon distribution in top- and subsoil horizons of two contrasting Andisols under pasture or forest

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Summary

Volcanic ash soils display distinctive morphological, physical and chemical properties and they contain several times more organic matter than non-volcanic soils. So far, there are few studies of soil organic matter (SOM) distribution in different chemically and physically protected carbon pools of soil horizons of volcanic soils. The aim of this study was to determine the SOM distribution (and its \(\delta^{13}C\) and \(\delta^{15}N\) composition) in different chemical and physical fractions at various depth horizons of two Andisols under pasture or rain forest in southern Chile. We used the amount of humus-complexes (\(C_p\)) extracted with Na pyrophosphate as a measure of C stabilized by aluminum (\(Al_p\)) and iron (\(Fe_p\)) in combination with density fractionation to separate particulate organic matter as free (fPOM), occluded (oPOM) and organic matter associated with the mineral fraction (MF). The results showed that soil SOM stock (0–40 cm) in the pasture soil was 166 Mg C ha\(^{-1}\) (11.7 Mg N ha\(^{-1}\)) and in the forest soil 100 Mg C ha\(^{-1}\) (4.1 Mg N ha\(^{-1}\)). The SOM variation was explained largely by the differences in \(C_p\), \(Al_p\) and \(Fe_p\). About 34% of total soil C was found as \(C_p\) in both oPOM and MF in the topsoil, whereas 33–53% was found in the subsoil horizons. The oPOM fraction was more important in the forest soil and generally decreased in the subsoil where these fractions were enriched with \(\delta^{13}C\) and \(\delta^{15}N\). Our results emphasize the importance of the humus complex and oPOM formation as the SOM stabilization mechanism in the forest Andisol, whereas under pasture organo-mineral interaction, including the formation of humic-metal complexes, is the most important stabilization mechanism. A conceptual model is lacking to demonstrate the major areas of uncertainty within known mechanisms and factors that explain the distribution of SOM through soil profiles in Andisols.

Introduction

Allophanic soils derived from volcanic ash contain a disproportionate amount of soil organic matter (SOM); they occupy only 0.8% of the global land area, but contain 5% of the world’s soil carbon (C) (Dahlgren \textit{et al.}, 2004). Andisols display unique morphological, physical and chemical properties attributed to their mineral phase, which is lacking in long-range crystal atomic order, but is composed of short-range ordered (SRO) materials such as allophane, imogolite and ferrihydrite with a large degree of hydration, highly reactive surface areas and variable charge (Shoji \textit{et al.}, 1993).

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Received 23 August 2012; revised version accepted 23 August 2012

There are several mechanisms of SOM stabilization against decomposition, including recalcitrance of organic compounds, spatial SOM inaccessibility for decomposer organisms and metal ions that interact with the mineral phase (von Lützow \textit{et al.}, 2006). However, several studies have suggested that the amount of amorphous clay minerals, oxides or hydroxides of aluminium (Al) and iron (Fe) and organo-mineral complexes in volcanic soils control soil C stabilization against decomposition (e.g. Percival \textit{et al.}, 2000). Matus \textit{et al.} (2008a) found a positive relationship between soil C and the humic complexes pool (\(C_p\)) extracted with Na pyrophosphate. About 28–40% of whole soil C has been found as \(C_p\) in a range of allophanic soils (Garrido & Matus, 2012). Sodium-pyrophosphate extraction is commonly used as a proxy to remove the amount of Al and Fe complexed with SOM: this method has been criticized because pyrophosphate may dissolve...
Al hydroxide and removes interlayered Al and gibbsite (Page & De Kimpe, 1989) and increases soil peptization (Kaiser & Zeich, 1996). However, Bardy et al. (2007) recently demonstrated that pyrophosphate can remove Al bound to SOM as determined by $^{27}$Al-NMR spectra in tropical podzols.

It has been postulated that interaction of SOM with metals in the humus-complexes of volcanic soils can be either fully occupied (saturated) or partially saturated with Fe and Al (Higashi et al., 1981). Matus et al. (2009) calculated the atomic metal:C$_p$ ratio as an indicator of humic complex formation and saturation with metals in the top- (0.13) and subsoil (0.07) of Andisols. When an atomic metal:C$_p$ ratio exceeds 0.12, Al will no longer be complexed with SOM (saturated), favouring Al synthesis for SRO inorganic components (such as allophane and imogolite-type materials). Thus SOM that is not complexed will react with the amorphous clay minerals mainly in the subsoil or will be accumulated as free organic C or as particulate organic matter (POM) (Matus et al., 2008b). Physical fractionation techniques, such as density fractionation, have been emphasized for studying the role of soil minerals in SOM stabilization. Different POM fractions obtained by density fractionation have been proposed (Golchin et al., 1997). The occluded particulate organic matter (oPOM) is derived from macro-aggregates whereas the free SOM, regarded as free particulate organic matter (fPOM), is neither associated with the mineral phase nor included in soil aggregates.

The role of SOM associated with Al and Fe oxides as a measure of chemical protection and density fractions to assess the physical protection as key factors controlling SOM stabilization in Andisols of different ecosystems need to be elucidated. Up to now, there have been few studies of SOM distribution in physical fractions throughout the soil profile (Mueller & Kögel-Knabner, 2009; Moni et al., 2010; Rumpel et al., 2004) and even fewer of them have addressed Andisols (Huygens et al., 2005; Rumpel et al., 2012). In the present paper we hypothesize that the interaction of amorphous minerals with SOM in the top- and subsoil of contrasting Andisols controls the C stabilization and their distribution in different physical and chemical soil fractions. Two differently textured Andisols developed under either pristine temperate rain forest or pastures were studied. All soil horizons were fractionated by physical and chemical methods. The aim was to study the SOM distribution and the C isotopic composition in various physical and chemical fractions through the soil profile of both soils.

Materials and methods

Site characteristics and soil sampling

In Chile, most Andisols (Soil Survey Staff, 1999) are allophanic, derived from basaltic coloured parent materials from Holocene and or late-Pleistocene tephas (Besoain & Sepulveda, 1985). About 50% of the 5.1 million hectares of volcanic soils in Chile belong to the pristine temperate rain forest and the remainder are distributed in agricultural areas (Matus et al., 2006). The pasture soil (about 3 ha) is located in the Valdivia area (39°48′S and 73°14′W), which is dominated by mixed species, perennial ryegrass (Lotium perenne L.) and white clover (Trifolium repens L.). It has been managed as pasture and arable rotation with a cereal crop once every 5 years for the last 30 years. Inorganic fertilizers (60–80 kg urea-N, 35–44 kg P and 33 kg K ha$^{-1}$) have been incorporated only during the years when sowing occurred years (Huygens et al., 2011). The site has been mown once a year for silage, and then grazed by dairy cows. At sampling, the site had been under pasture for four years. The annual net primary productivity at this site has been calculated as 6 Mg ha$^{-1}$ dry matter (Huygens et al., 2011). The soils are well-drained and the topography is undulating with slopes between 2 and 5%, and the climate is temperate with a mean annual temperature of 12.1°C and mean annual precipitation ranging between 2200 and 2700 mm per year, concentrated mainly in winter (1000–1200 mm). The soil belongs to the Valdivia family, which is medial, mesic, Duric Hapludands (Soil Survey Staff, 1999). The soil has been developed from pyroclastic parent material and is characterized by a large SOM content, small bulk density and a clay fraction dominated by SRO minerals. The soil is located in the depression of San José at 9–20 m above sea level and corresponds to a deposit on a compacted marine tuff locally called Cancagua. Soil texture is silty loam in surface horizons and sandy loam at depth. In the managed pasture, three soil pits were excavated 100 m apart and up to 40 cm depth, and about 2 kg of soil at Ap (0–7 cm), B1 (7–32 cm) and B2 (32–40 cm) horizons were collected. The sampling scheme used followed the most widespread type of experimental design involving a single replicate per treatment when a large-scale experimental unit (as our pasture and forest) is the only option and the knowledge is restricted to a particular treatment (Webster, 2007).

Forest soil samples were collected from three permanent soil plots (0.1 ha), located at a variable distance of 50–150 m from each other, previously established to study the chemistry of rainfall in a pristine environment (Godoy et al., 2001). The pristine temperate rain forest study area of Antillanca is dominated by Nothofagus pumilio (Poeppe & Endl.) Krasser, with an age of about 120 years, Drymis andina (Reiche) R.A. Rodr. et Quez and Maytenus disticha (Hook. f.) Urban in the understory. It is located in the Puyehue National Park (40°47′S and 72°12′W). Although seasonal litter falls at these sites have not been measured, estimation from Nothofagus pumilio in southern Chile has been calculated to be 2.0 Mg ha$^{-1}$ of dry matter (Caldentey et al., 2001). The Andisol belongs to the Antillanca family, which is ashly frigid Typic Ududirand (Soil Survey Staff, 1999) resulting from activities of the Casablanca and Antillanca volcanoes ejecta of basaltic composition resting on granitoids and related bedrock. The mean annual precipitation in this ecosystem is >5000 mm per year, with the mean annual temperature of 4.5°C, ranging between −8.7 and 24.8°C inside the forest (Godoy et al., 2001). All plots possessed similar aspect (southern), altitude (1000–1120 m above sea level) and soil depth (120 cm). One soil sample was taken as described before at A (0–19 cm), AC (19–41 cm) and C (41–100 cm) horizons from each plot, and defined as a replicate (n = 3) (Matus et al., 2009).
A total of 18 samples were collected from two sites, three pits per site and three horizons per pit. A partially decomposed litter layer was observed at all sites, which was removed before sampling. Each soil sample was homogenized, and coarse organic matter (leaves, wood and roots) was removed by hand. For bulk density (BD) measurement, soil samples were obtained by pushing a core steel cylinder (5 x 8.2 cm) into the undisturbed horizon from each pit at each site (Table 1).

**Chemical analysis**

Soil pH was measured in demineralized water in 1:2.5 soil:solution. For the Al, Fe and Si extraction, air-dried samples were analysed in duplicate as follows. First, extraction with 0.2 M ammonium oxalate/oxalic acid at pH 3 (Al₉, Si₉ and Fe₉) (soil:solution ratio 1:50) and shaking for four hours in the dark (García-Rodeja et al., 2004). The suspension was centrifuged for 15 minutes at 1270 g, with three drops of flocculant (Superfloc, Kerima de Mexico S.A., Xoxtla, Tlaxcala, Mexico), and the supernatant was transferred to a plastic container and stored in the dark for Fe and Al analyses. Second, extraction with 0.1 M Na-pyrophosphate (pH 10) (Alₕ and Feₕ) (soil:solution ratio 1:100) and shaking for 16 hours. The suspension was centrifuged (15 minutes at 1270 g, with three drops of superfloc) and the supernatant was filtered. The suspension and undissolved materials were removed through acid-washed paper (7–11 μm pore size) filtration and the solution passed again through 0.45-μm millipore acid-washed filter paper. The concentration of Al, Fe and Si in each extract was measured in duplicate using atomic absorption spectroscopy (AAS, Perkin Elmer 3110, Waltham, Massachusetts, USA).

**Soil organic matter density fractionation**

The protocol used for SOM density fractionation was similar to that described by John et al. (2005). Briefly, the physical fractions were obtained with sodium polytungstate (SPT, 3Na₂WO₄·9WO₃·H₂O, Sometu-Europa, Berlin, Germany) at two densities: 1.6 and 2.0 g cm⁻³. About 20 g of each soil sample (oven-dry basis) from the three horizons of the two field sites was suspended in 50 ml of SPT solution (1.6 g cm⁻³) in a 250-ml centrifuge tube. The tube was gently turned upside down five times by hand. After sedimentation for 30 minutes, the solution was centrifuged at 5100 g for 30 minutes. The supernatant with floating particles was filtered (Whatman 47 μm GF/C, GE Healthcare Biosciences, Piscataway, NJ, USA) using a vacuum and washed with demineralized water. The material remaining on the top filter was named as free particulate organic matter (fPOM >2), was rinsed with demineralized water three times to remove the salt, centrifuged (5100 g) and the supernatant discarded. All fractions were freeze-dried, ground within a mortar and stored for further analyses. The C and nitrogen (N) content of each physical fraction was obtained by multiplying the dry mass of the physical fraction by its corresponding C and N concentrations.

**Analysis of C, N and stable isotopes ¹³C and ¹⁵N**

Total C and total N for the characterization of whole soil and the physical fractions (POM and MF) were determined using
an elemental analyser (CHN NA1500; Carlo Erba Elemental Analyzer, Stanford, CA, USA). Inorganic C was negligible (<0.44 g kg⁻¹ soil). The natural abundance of stable isotopes ¹⁵N and ¹³C in the physical fractions was measured using the same elemental CHN analyser coupled to a mass spectrometer for stable isotopes (Micromass-GVI Optima, V-G Isogas Ltd., Middlewich, UK). The natural abundance of δ¹³C and δ¹⁵N was expressed in parts per thousand (‰) using Vienna Pee Dee Belemnita international standards (V-PDB) and atmospheric N₂, respectively.

Soil organic carbon complex determination

The Cp obtained in the supernatant of pyrophosphate extraction was regarded as C linked to Alₚ and Feₚ in a complex with SOM. The Cp was determined with a total organic C analyser (TOC-V CPH, Shimadzu, Kyoto, Japan). As the metal humus-complexes (Higashi et al., 1981) of metal-humus complexes (Higashi et al., 1981), ¹³C in the physical fractions was measured using the same fractionation procedure. Therefore, the amounts of Cp associated with MF₁,₂ and oPOM₁,₆,₂ were measured and considered in the C balance. We also assume that IPOM₁,₆ was Cp free. The atomic (Alₚ+Feₚ)∶Cp ratio of 0.12 was regarded as the maximum metal value complexed with SOM. This limit indicates that a metal∶Cp > 0.12 will be favoured to form allophane and SOM association. In contrast, a metal∶Cp < 0.12 indicates the formation of metal-humus complexes (Higashi et al., 1981).

Data analysis

Gaussian distribution of all variables was tested using a skewness test value of 0.5 (Webster & Oliver, 2001). If the skewness value was ≥0.5 (i.e. non Gaussian), we log-transformed the variables. At each study site, a two-way analysis of variance was performed to test the effects of soil depths (horizons) and physical fractionation on the expected values of C and N and their isotopic distribution. We computed the correlation coefficients amongst all pairs of soil properties and soil depths, by site. It is important to point out that no between-site comparisons were carried out, but only comparisons within a site. All analyses were computed using the software SPSS 12.0 Inc (SPSS, Chicago, IL USA) at (P ≤ 0.01).

Results

Soil characteristics

Soil pH in forest ranged from 5.6 to 6.1 and in pasture from 5.3 to 5.7 and it increased with depth at both sites (Table 1). Soil C contents ranged from 7.1 g kg⁻¹ soil to 73.5 g kg⁻¹ soil and decreased (P ≤ 0.0001) with depth in both sites. A similar trend was observed for soil N values, which ranged between 0.4 and 5.6 g kg⁻¹ soil. Bulk density generally showed similar values at both sites and ranged from 0.54 to 0.92 kg dm⁻³ (Table 1). They decreased throughout the pasture profile; the opposite was true in the forest soil. The latter soil at 0–41 cm depth (A and AC horizons) stored 100 Mg ha⁻¹ of C, whereas larger C stocks were recorded for pasture soil horizons (Ap, B₁ and B₂). The C:N ratio in the forest ranged between 18 and 24 and in the pasture between 13 and 16. Soil texture in the pasture soils was similar across the soil profile, with dominance of silt and sand size particles (>29%). In contrast, in the forest soils the sand size fraction was >74% (Table 1). Pyrophosphate extractable metals (Alₚ and Feₚ) were obtained in similar proportions from both soils, although Feₚ was always largest in the forest soil samples (Table 2). The Alₚ ranged between 1.8 and 7.8 g kg⁻¹ soil in both soils and was larger than Feₚ extracted with pyrophosphate and decreased with depth (Table 2). Along with Alₚ and Feₚ in the forest and in the pasture soils, similar Cp (C bound to Al and Fe) values were determined for the topsoil (20–24 g kg⁻¹), whereas they decreased in the subsoil (3.9–18.0 g kg⁻¹). The amounts

Table 2 Chemical soil properties (g kg⁻¹ soil) in pasture and pristine rain forest

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Pasture Horizons / cm</th>
<th>Rain forest Horizons / cm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ap/0–7</td>
<td>B₁/7–32</td>
</tr>
<tr>
<td>Alₚ</td>
<td>6.9 ± 0.19</td>
<td>4.8 ± 0.19</td>
</tr>
<tr>
<td>Feₚ</td>
<td>3.0 ± 0.07</td>
<td>1.7 ± 0.01</td>
</tr>
<tr>
<td>Cp</td>
<td>24 ± 0.01</td>
<td>18 ± 0.01</td>
</tr>
<tr>
<td>Alₒ</td>
<td>30.3 ± 0.50</td>
<td>33.2 ± 1.30</td>
</tr>
<tr>
<td>Feₒ</td>
<td>13.0 ± 0.40</td>
<td>14.7 ± 0.25</td>
</tr>
<tr>
<td>Siₒ</td>
<td>9.3 ± 0.28</td>
<td>11.7 ± 0.28</td>
</tr>
<tr>
<td>Allop⁵</td>
<td>89.0 ± 1.16</td>
<td>107.0 ± 0.71</td>
</tr>
<tr>
<td>Allop % clay</td>
<td>36</td>
<td>42</td>
</tr>
<tr>
<td>(Alₚ + Feₚ)∶Cp</td>
<td>0.15</td>
<td>0.14</td>
</tr>
<tr>
<td>Alₚ∶Alₒ ratio</td>
<td>0.23</td>
<td>0.15</td>
</tr>
</tbody>
</table>


*Standard deviation (n = 3).

of amorphous Si0 and Al0, the oxide-extractable fraction, were generally large in the pasture soil, which contained more allophane (Table 2). Over all depths, allophane contributed about 40 and 55% to the total clay content in pasture and forest soil, respectively (Table 2). The atomic metal:Cp ratio that represents the saturation of organic C with metal with values ≤0.12 was less in the pasture profile (0.14–0.16), but more saturated values (0.23–0.27) were recorded in the forest soils.

A correlation matrix for the main chemical and physical soil properties was established. The signs and coefficients of correlation between the two sites were similar; therefore, only the data from forest soils are presented (Table 3). In general, the correlations with absolute values ≤0.3 were not significant whereas values ≥0.52 were significant at P ≤ 0.05. There was a strong relationship between Cp with Alp and Fe p, (P ≤ 0.01). The coefficients of correlation for Cp were 0.95 and 0.96, respectively (Table 3). The Al0 and Fe0 were strongly correlated with soil C (P ≤ 0.01) at both sites, indicating that most variation in soil C was explained by the complex formation between metals and humic substances. Table 3 also shows that there was an inverse, but highly significant relationship between Cp and allophane content (r = −0.62, P ≤ 0.01) and between Cp and pH (r = −0.91, P ≤ 0.01).

Physical fractionation

The mass distribution of various physical fractions of organic C is shown in Figure 1. Over all soils and horizons, the total dry mass recovery of the total soil sample was near 100%. The MF1.3–2 represented >95% of the total mass of whole soil under pasture (Figure 1a). The fPOM1.6–2 comprised between 0.8 and 1.5% dry mass and oPOM1.3–2 ranged between 0.6 and 3.4%. In forest soil, the MF2.2 recovered was 81% of the total mass and fPOM1.6–2 ranged between 0.8 and 3.7% and oPOM1.3–2 between 2.5 and 15% (Figure 1b).

The soil C recovery in the various fractions was about 95% in pasture and forest soil, and slightly >100% for N. Soil deep horizons and physical fractionation had a marked impact on SOM concentration (and its isotopic composition), as indicated by analysis of variance (an example for soil C in the forest is given in Table 4). More than 84% of the soil C was found in the MF1.3–2 of the pasture soil and increased with depth, whereas oPOM1.6–2 contributed 13.3% of soil C in the Ap horizon followed by B1 and B2 horizons (about 7% each) (Figure 2a). The fPOM1.6–2 contribution ranged from 2.5 to 3.1% of the soil C and similar trends were recorded for N (Figure 3a). The C contribution in the

Table 3 Correlation coefficients for main soil chemical and physical properties in a rain forest (n = 27)

<table>
<thead>
<tr>
<th>Soil C</th>
<th>Soil N</th>
<th>Alp</th>
<th>Fe</th>
<th>Cp</th>
<th>Allop</th>
<th>Alop</th>
<th>Feo</th>
<th>Alp/Alo</th>
<th>pH</th>
<th>Bulk density</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.98</td>
<td>0.87</td>
<td>0.82</td>
<td>0.90</td>
<td>−0.43</td>
<td>0.07</td>
<td>0.88</td>
<td>0.74</td>
<td>−0.77</td>
<td>−0.92</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.92</td>
<td>0.91</td>
<td>0.92</td>
<td>−0.72</td>
<td>0.03</td>
<td>0.52</td>
<td>0.98</td>
<td>−0.88</td>
<td>−0.85</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>−0.55</td>
<td>0.07</td>
<td>0.83</td>
<td>0.89</td>
<td>−0.87</td>
<td>−0.95</td>
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<td></td>
<td></td>
<td>−0.56</td>
<td>−0.03</td>
<td>0.84</td>
<td>0.90</td>
<td>−0.87</td>
<td>−0.96</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>−0.62</td>
<td>−0.91</td>
<td>0.84</td>
<td>0.91</td>
<td>−0.91</td>
<td>−0.97</td>
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<tr>
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<td></td>
<td></td>
<td>1</td>
<td>0.75</td>
<td>0.81</td>
<td>−0.17</td>
<td>0.77</td>
<td>−0.10</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>0.75</td>
<td>0.81</td>
<td>0.57</td>
<td>−0.10</td>
<td>−0.84</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>0.90</td>
<td>0.90</td>
<td></td>
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</tbody>
</table>

Table 4 Summary of analysis of variance test for significant effects of horizons and physical density fractions on log-transformed soil C content in a pristine rain forest

<table>
<thead>
<tr>
<th>Source</th>
<th>Degrees of freedom</th>
<th>Sum of squares</th>
<th>F ratio</th>
<th>P &gt; F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Horizons</td>
<td>2</td>
<td>4.118</td>
<td>1220.5</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>Density fraction</td>
<td>2</td>
<td>1.314</td>
<td>389.49</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>Horizons × density fraction</td>
<td>4</td>
<td>0.307</td>
<td>45.56</td>
<td>&lt;0.0001</td>
</tr>
</tbody>
</table>

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MF$_{>2}$ of forest soils was 52–68%, in IPOM$_{<1.6}$ 12–25% and in oPOM$_{1.6-2}$ 21–35% (Figure 2c), and again, a similar pattern was found for N (Figure 3b). There was a positive and strong relationship ($P \leq 0.001$) between soil C and MF$_{>2}$ and between soil N and these fractions (data not shown).

The amount of C in MF$_{>2}$ and oPOM$_{1.6-2}$ of pasture and forest soils was substantially reduced when Cp was subtracted from these fractions. The soil C was reduced in MF$_{>2}$ and oPOM$_{1.6-2}$ of the pasture soil was reduced by 19 and 34%, respectively (Figure 2b), whereas in the forest the respective values were 34 and 60% (Figure 2d). The total amounts of Cp ranged from 30% of the total soil C in the topsoil to 54% in the subsoil horizons (Figure 2b and d).

The SOM variation was explained primarily by Cp, Alp and Fep because 34–53% of total soil C was found as Cp in both oPOM and MF along the soil profile described in the pasture soils (Figure 4a). However, the differences amongst the fractions were more marked ($P \leq 0.0001$).

Discussion

Soil organic matter storage and mechanisms of stabilization

Andisols developed under pasture (silty loam) or forest (coarse sand) had different soil C storage and distribution in different physical and chemical soil fractions. Indeed, the SOM stock in the first 40 cm under pasture was 166 Mg C ha$^{-1}$ and 11.7 Mg N ha$^{-1}$, whereas under forest it was 100 Mg C ha$^{-1}$ and 4.1 Mg N ha$^{-1}$. Similar results have been reported for pasture and forest Andisols in Chile (Huygens et al., 2005).

The SOM variation was explained primarily by Cp, Alp and Fep because 34–53% of total soil C was found as Cp in both oPOM and MF along the soil profile of both soils. This was also supported by positive and significant correlations between soil C and these

Natural abundance of $^{13}$C and $^{15}$N

The $^{13}$C values for the two soils ranged between $-24.9$ and $-28.7\%$ and $^{15}$N ranged between $-4.0$ and $7.9\%$ (Figure 4). Soil depth and physical fractionation had an impact on the enrichments of SOM. In the pasture, all fractions in the topsoil were generally depleted in $^{13}$C ($P \leq 0.001$) compared with more enriched fractions in the subsoil, except for oPOM$_{1.6-2}$ (Figure 4a). Similar patterns were observed for $^{15}$N too (Figure 4c). However, $^{15}$N of MF$_{>2}$ was more enriched with respect to oPOM$_{<1.6}$ and oPOM$_{1.6-2}$. These latter fractions were all depleted along the soil profile. The $^{13}$C and $^{15}$N in the rain forest paralleled the pattern described in the pasture soils (Figure 4b and d). However, the differences amongst the fractions were more marked ($P \leq 0.0001$).

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soil properties. Results showed that $C_p$ occurs in different physical fractions and it was probably redistributed during the fractionation procedure too. Therefore, comparison of POM and MF without $C_p$ determination in allophanic Andisols should be treated with caution. The present research also demonstrated that metal-humus complex or allophane formation is related to soil pH (Garrido & Matus, 2012), as revealed by an inverse correlation between pH and $C_p$ and a positive one between pH and allophane content (Table 3). As active Al and Fe content rather than the climate conditions is the determining factor controlling organic matter level in volcanic soils (Matus et al., 2006; Tonneijck et al., 2010; Jansen et al., 2011), a large amount of SOM stabilized with $Al_p$ and $Fe_p$ in the topsoil (Imaya et al., 2010) and a small quantity in subsoil horizons was expected. The opposite is true for the allophane content in deep soil (Rumpel et al., 2012).

The soil C distribution followed a similar trend of a small proportion stored as POM and the majority being present in the MF as shown by Basile-Doelsch et al. (2007). These authors found that 82.6% of the SOM was in MF (Bw horizon) in a volcanic soil, similar to the results found in the pasture soil samples of our study. Under pristine forest, POM represents the largest proportion of SOM found that may be explained by low temperature and large rainfall conditions, resulting in small SOM mineralization rates (Godoy et al., 2001). The POM fraction in the forest topsoils also had a large C:N ratio, indicating less decomposable plant material in this fraction caused by the vegetation type and climate conditions (Broquen et al., 2005). Unlike the work of Huygens et al. (2005), who found that the light density fraction ($<1.13 \text{g cm}^{-3}$) of pasture soil concentrated more than 50% of soil C at all depths, we show that POM1,6 contents of pasture were only 2.5–3.1%. The differences may be attributed to cultivation effects: Huygens et al. (2005) studied a pasture that was ploughed every 2 years, resulting in disaggregation and an increase in a more labile fraction. Our pasture soil samples concentrated a considerable amount of C and N in oPOM1,6–2 compared with POM1,6. The results indicated that POM formation is a key mechanism of SOM stabilization in the forest, and mineral-associated organic matter the key one in pasture Andisols.

**Stable isotopes**

The $\delta^{13}C$ values found in this study are typical for soil under C3 vegetation (Glaser, 2005). Concentrations of stable isotopes $^{13}C$ and $^{15}N$ generally increased with soil depth. The classical assumption that $\delta^{13}C$ generally increases with depth in temperate ecosystems (Krull & Skjemstad, 2003) agrees with our results of 2‰ in the forest and 1‰ in pasture soils. The $\delta^{13}C$ enrichment related to the decrease in particle size, attributed to preferential loss of $^{12}C$ during microbial degradation (Gerzabek et al., 2001), was not supported here because the MF of forest soils was depleted in $\delta^{13}C$ where the finest fractions were more concentrated (Figure 4). It has been hypothesized that the mixing of new and older SOM components during decomposition results in $\delta^{13}C$ enrichments in deep soils (Arai et al., 2010). This is because (i) the microbial and fungal carbon residues account for an enrichment of $\delta^{13}C$ relative to their substrate and (ii) the $\delta^{13}C$ ratios of atmospheric CO2 have been decreasing because of the combustion of $^{13}C$-depleted fossil fuels (Ehleringer et al., 2000). The $\delta^{15}N$ enrichment was greatest in the pasture soil and in the mineral fraction; the opposite was found in the forest soil. The $\delta^{15}N$ enrichment in the pasture indicated that the SOM was more processed, more enriched and less available for microorganisms and concurs with the large C:N ratio in the forest soils.

**Conclusions**

In the present study, the SOM distribution of Andisols under temperate rain forest (coarse sand) or pasture (silty loam), as assessed in various chemical and density fractions (fPOM1,6–2, oPOM1,6–2 and MF1,6–2), was strongly influenced by texture through the soil horizons. The stocks of C and N up to 40-cm depth were largest in the pasture soil. The C contribution to MF1,6–2 dominated both soils and all depths followed by the C in oPOM, which was more important in the forest soils. Besides soil texture, these differences are also attributed to external factors such as climate conditions and vegetation type. The presence of the humus complex needs to be evaluated in the POM fractions when assessing the mechanism of C stabilization and their distribution by physical density fractionation. An enrichment of $\delta^{13}C$ and $\delta^{15}N$ was observed in both soils studied; it was more evident in the deeper horizons, which was attributed to a mixing of new and old SOM components throughout the soil profile. The present results highlight the importance of the humus complex and oPOM formation as important mechanisms of SOM stabilization in forest and mineral interactions as the stabilization mechanism in pasture Andisols. We need a conceptual model that includes the external factors and the stabilization mechanisms that can explain the distribution of SOM in Andisols in the top- and subsoil horizons.

**Acknowledgements**

The authors gratefully acknowledge the FONDECYT project No 1080065 for their financial support. We also acknowledge the ECOSSUD-CONICYT C08U01 project for their financial support of French and Chilean research groups; the first author thanks INRA-Grignon Laboratories. We also thank the CONICYT-MEC Program 80100008 for financial support in Chile of one of the authors (NB). We greatly thank Dr Christian Salas for statistical advice and Noelia Sepulveda for dedicated laboratory support (both from La Frontera University). We acknowledge Dr Mauricio Escudey from Universidad de Santiago for technical assistance and the two anonymous reviewers for their time and effort in commenting on the manuscript.

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