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Aggregate and soil organic carbon dynamics in South Chilean Andisols

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Abstract. Extreme sensitivity of soil organic carbon (SOC) to climate and land use change warrants further research in different terrestrial ecosystems. The aim of this study was to investigate the link between aggregate and SOC dynamics in a chronosequence of three different land uses of a south Chilean Andisol: a second growth *Nothofagus obliqua* forest (SGFOR), a grassland (GRASS) and a *Pinus radiata* plantation (PINUS). Total carbon content of the 0–10 cm soil layer was higher for GRASS ($6.7\,kg\,C\,m^{-2}$) than for PINUS ($4.3\,kg\,C\,m^{-2}$), while TC content of SG-FOR ($5.8\,kg\,C\,m^{-2}$) was not significantly different from either one. High extractable oxalate and pyrophosphate Al concentrations (varying from 20.3–$24.4\,g\,kg^{-1}$, and 3.9–$11.1\,g\,kg^{-1}$, respectively) were found in all sites. In this study, SOC and aggregate dynamics were studied using size and density fractionation experiments of the SOC, $\delta^{13}C$ and total carbon analysis of the different SOC fractions, and C mineralization experiments. The results showed that electrostatic sorption between and among amorphous Al components and clay minerals is mainly responsible for the formation of metal-humus-clay complexes and the stabilization of soil aggregates. The process of ligand exchange between SOC and Al would be of minor importance resulting in the absence of aggregate hierarchy in this soil type. Whole soil C mineralization rate constants were highest for SGFOR and PINUS, followed by GRASS (respectively 0.495, 0.266 and $0.196\,g\,CO_2$-$C\,m^{-2}\,d^{-1}$ for the top soil layer). In contrast, incubation experiments of isolated macro organic matter fractions gave opposite results, showing that the recalcitrance of the SOC decreased in another order: PINUS>SGFOR>GRASS. We deduced that electrostatic sorption processes and physical protection of SOC in soil aggregates were the main processes determining SOC stabilization. As a result, high aggregate carbon concentrations, varying from 148 till $48\,g\,kg^{-1}$, were encountered for all land use sites. Al availability and electrostatic charges are dependent on pH, resulting in an important influence of soil pH on aggregate stability. Recalcitrance of the SOC did not appear to largely affect SOC stabilization. Statistical correlations between extractable amorphous Al contents, aggregate stability and C mineralization rate constants were encountered, supporting this hypothesis. Land use changes affected SOC dynamics and aggregate stability by modifying soil pH (and thus electrostatic charges and available Al content), root SOC input and management practices (such as ploughing and accompanying drying of the soil).

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1 Introduction

Andisols develop from volcanic ash and are characterized by a high soil organic matter (SOM) content, good physical properties, and a high potential anion- or cation exchange capacity (AEC and CEC) (Galindo and Bingham, 1977). Their clay fraction consists mainly of poorly crystalline allophane, imogolite, and oxides and oxyhydroxides of Fe and Al (Besoain, 1958). Allophane is a group of clay minerals made up of silica, aluminum, and water in a chemical combination (Parfitt, 1990). In southern Chile (35°–49° S), Andisols cover a large part of the surface area of the Central Valley and Andes mountain ranges (FAO-UNESCO, 1971).

Temperate native forests covered most of southern Chile for the last 3,000 years, remaining almost intact until the arrival of the Europeans, 450 years ago (Lara et al., 1999). Significant land use changes have taken place in this region (Lara et al., 1999). Today, only 56% (or 10.3 million ha) of this original forest cover remains. Most affected are the *Sclerophyllus* and the *Nothofagus* forest types, with 3 and 30% of the original forest cover remaining, respectively (Lara et al., 1999). On the other hand, grasslands and shrublands have doubled in area, from 2.5 to 5.5 million ha (Lara

et al., 1999). New land use types, such as urban areas (55 000 ha), arable lands (2.8 million ha) and forestry plantations (2.1 million ha), now occupy a significant area as well.

General overviews of changes in soil organic carbon (SOC) stocks after land use conversions are given by Guo and Gifford (2002) and Paul et al. (2002). Guo and Gifford (2002) revised changes in SOC stocks as a result of land use conversion, using data from 74 publications. They indicated that SOC stocks increase after land use change from native forest to pasture (+8%, based on 170 observations), but declined after pasture conversion to plantation (−10%, based on 83 observations). However, rainfall has a strong influence on changes in SOC stocks. It was concluded that in areas receiving 1500–2000 mm of rainfall per year a conversion from forest to pasture did not result in changes in SOC stock. A land use change from grassland to plantation resulted in a significant decrease in SOC stock with −23%. Paul et al. (2002) concluded that afforestation decreased soil stocks by 3.5% per year during the first five years of afforestation. Later on, a decreasing rate of decline or eventually a recovery of SOC would occur. De Koning et al. (2003) concluded more specific that in Al-rich soils, changes in SOC stocks follow a pattern according to land use history and accompanying changes in soil characteristics.

Soil organic matter has a very complex and heterogeneous composition and is generally mixed or associated with the mineral soil constituents to form soil aggregates (Del Galdo et al., 2003). SOC dynamics are mainly influenced by its recalcitrance and accessibility, and interactions between SOC and soil components (Sollins et al., 1996). Recalcitrance is the inherent molecular level resistance of a molecule to microbial and enzymatic breakdown. Accessibility is the extent to which the location of substrates controls access by microbes, fungi or enzymes. Interactions of organic substrates with organic or inorganic molecules may alter the degradation rate of the substrates (Swanston et al., 2002). Several studies have shown that in Al rich soils, such as Andisols, chemical stabilization is the determining process for carbon accrual (Zunino et al., 1982; Percival et al., 2000). However, the exact role of SOC and Al in the process of chemical stabilization, and which kind of interactions occurs between the different soil components is not yet fully understood.

The objective of this study was to evaluate the role of Al on SOC dynamics in Chilean Andisols and to investigate SOC stabilization by electrostatic Al-C binding, and occlusion within soil aggregates. Via a case study, we tried to assess the effect of changes in certain physical and chemical soil characteristics – which resulted from the land use conversions – on SOC, physical protection of SOC in aggregates, quality of SOC, and organo-mineral associations. A chronosequence of three different land uses was studied: a second growth *Nothofagus obliqua* forest (SGFOR), a grassland (GRASS), and a plantation of *Pinus radiata* (PINUS).

2 Materials and methods

2.1 Site description and soil sampling

Soil samples were taken in August 2002 near Paillaco, in the Central Valley of southern Chile (40°07 S, 72°51 W). The mean annual precipitation varies from 1600–1800 mm, while mean annual temperature is 10.8°C. All soils were classified as trumao's or Andisols, Typic Dysandrepts (Tosso, 1985). They have typical variable electrical charge characteristics (i.e. pH dependent) as a result of their particular clay mineral and humus content (Radcliffe and Gillman, 1985; Nanzyo et al., 1993). A mixture of 1:1 and 2:1 clay minerals (e.g. halloysite, vermiculite, etc.) has been documented in Chilean Andisols as well as the generally observed poorly crystalline minerals (Besoain, 1958, 1969; Galindo and Bingham, 1977; Besoain et al., 2000).

The three sites are all located in close proximity (100 m apart) and were originally all under the same forest vegetation dominated by *Nothofagus obliqua*. Nowadays, only the SGFOR site is still under this original vegetation. The land use of the GRASS and PINUS sites changed 50–100 years ago from second growth *N. obliqua* forest to grassland for agricultural livestock activity. Finally, 16 years ago, a *Pinus radiata* plantation was established on part of the GRASS site.

The second growth *N. obliqua* forest (SGFOR) has a mean tree height of 35 m, a stand density of 757 ha^{-1} and a canopy cover of 70% during the growing season. The average tree age is 120 years, while mean diameter at breast height equals 42.5 cm. In this forest, the overstorey is dominated by *N. obliqua* (32 m) with a cover of 40%. The understorey (25 m) consists of *Aextoxicon punctatum*, *Persea linque*, *Nothofagus obliqua*, *Eucriphia cordifolia*, *Laurelia sempervirens*, *Nothofagus dombeyi* and *Gevuina avellana* with a cover of 70%. The lower understorey (10 m) is dominated by *Aextoxicon punctatum*. In the shrub stratum (<4 m) *Chusquea quila* and *Raphithamnus spinosus* are dominant.

Since the establishment of the pasture, agricultural activities (cattle breeding) have taken place on the GRASS and PINUS sites with an animal density of 1.5–2 cows ha^{-1}. The grassland has a species composition consisting of *Lolium perenne* and *Trifolium repens,* and is ploughed and resown every two years. A mixture of various forms of acidifying fertilizers has been applied yearly on the GRASS site at high levels, though no data were available on the exact fertilizer type or application rate.

On the PINUS site, fertilization was stopped with the establishment of the plantation, 16 years ago. This *P. radiata* monoculture has a mean tree height of 15–18 m, while stand density is around 1500 ha^{-1}.

Sampling was done after selection of representative plots in the three ecosystem sites (land use treatments). In each land use treatment, three sampling plots were selected based on pedological, forestry and ecological experience, and were located approximately 20 m apart from each other. Samples
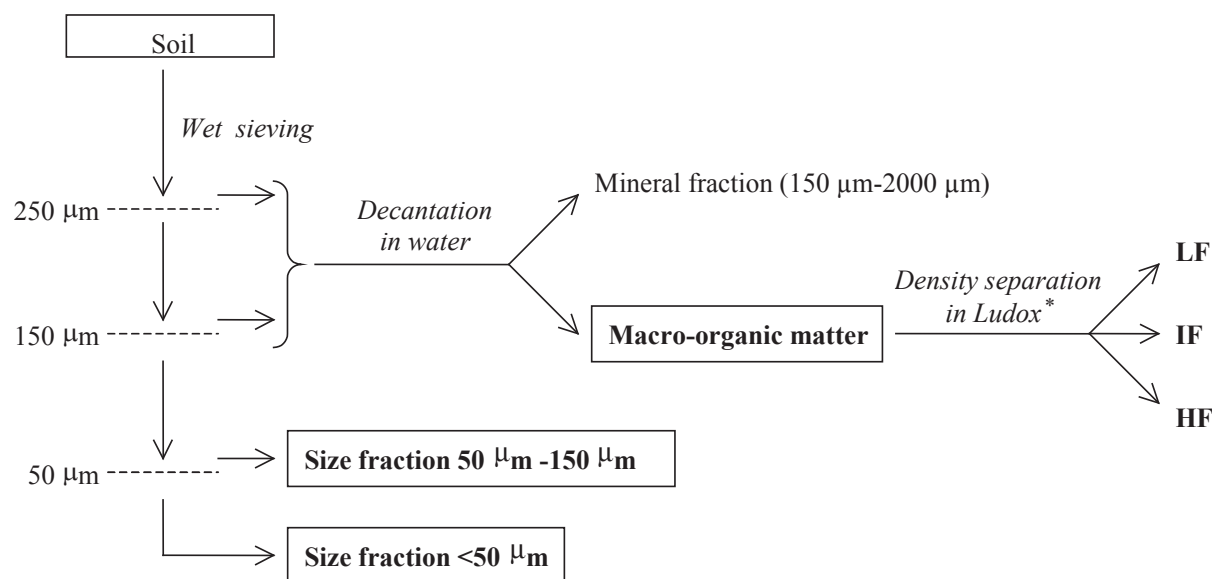
*Ludox : silica suspensions with different density

Fig. 1. Scheme of the density fractionation of SOC; LF=light density fraction (density$<1.13\,\mathrm{Mg\,m^{-3}}$), IF=intermediate density fraction ($1.13\,\mathrm{Mg\,m^{-3}}<$density$<1.37\,\mathrm{Mg\,m^{-3}}$), HF=heavy density fraction (density$>1.37\,\mathrm{Mg\,m^{-3}}$) (adapted from Accoe et al., 2002).

originating from a different sampling plot in the same land use treatment were considered as replicates, and were kept separate for later analysis. In each sampling plot, one soil sample has been taken at 0–10, 10–20 and 20–30 cm depth from a soil pit. Thus, in total 27 soil samples were taken. After transport to the laboratory, the recognizable plant material was removed. All soil samples were dried, homogenized and sieved (2 mm) for later analyses. Soil samples were dried in open air to a gravimetric water content of approximately 20%. Volcanic-ash soils can granulate irreversibly when completely dried (Kubota, 1972), and this can affect the subsequent fractionation of SOC. We will refer to these partly dried samples using the term "air dried samples".

Bulk densities were determined by pushing steel cylinders with a known volume into the undisturbed soil (Klute, 1986). After transport to the laboratory, the cylinders were dried at 105°C during 24 h, after which its weight was determined. Three replicates per land use treatment were performed. Soil texture was determined in the field according to a method described by Milford (1997).

2.2 Size and density fractionation of SOC

The size fractionation procedure was performed by separately wet sieving a soil sample of 100 g over three sieves (250 μm, 150 μm and 50 μm) with tap water. The suspension passing the bottom size was collected and left about 48 h at room temperature to settle. After settling, the clear solution was removed and the size fraction $<50\,\mu$m was

collected. Four size fractions (2000–250 μm, 250–150 μm, 150–50 μm and $<50\,\mu$m) were obtained, dried at 40°C for 48 h and homogenized using a planetary ball mill (PM400, Retsch, Germany) for subsequent analysis.

To evaluate the soil aggregate stability or susceptibility of the aggregates against disruption processes, we used a modification of the procedure described by De Leenheer and De Boodt (1959). The size fractionation was performed at two different times, using the same procedure: (1) starting from "air dried" soil (slaking) and (2) after an 80 day laboratory incubation experiment (wet sieving of field moist soil) (see below). In the incubation experiment, the soil was exposed to several supplementary disruption processes such as rewetting and mixing of the soils. The distribution of the soil weight among the different size fractions was expressed using the weighted average diameter (WAD) and could thus be quantified as one single parameter for further statistical analyses. The difference in WAD between the two fractionation experiments can be related to the stability of the soil aggregates (De Leenheer and De Boodt, 1959). A smaller difference in WAD indicates a higher stability of the soil aggregates.

Density fractionation of the SOC was performed using the method of Meijboom et al. (1995) (Fig. 1). Air dried soil samples (400 g) were wet sieved over two sieves with tap water (top sieve mesh size 250 μm, bottom sieve mesh size 150 μm), until the passing water became clear in order to destroy aggregates $>150\mu$m. Only a water jet was applied as dispersive energy in order to destroy soil aggregates. Next,

the two size fractions retained on the sieves were washed into a bucket and swirled with a jet of water to separate the organic matter (OM) from the mineral fraction by decantation. Swirling and decanting were repeated until no more floating organic matter appeared. The obtained macro organic matter (MOM) from both size fractions (250–2000 and 150–250 μm) was recombined to be further separated into a light (LF, density <1.13 Mg m^{-3}), intermediate (IF, 1.13 Mg m^{-3} < density <1.37 Mg m^{-3}) and heavy (HF, density >1.37 Mg m^{-3}) fraction by subsequent submersion in two colloidal silica suspensions (Ludox, Dupont, USA) with a respective density of 1.13 Mg m^{-3} and 1.37 Mg m^{-3}. The obtained density fractions were washed with distilled water and dried at 40°C for 48 h.

The C concentrations increase with decreasing density of the fractions (LF>IF>HF). The IF and HF show a higher association of the SOC of these heavier fractions with soil minerals (Hassink, 1995). The LF consists mainly of recognizable plant material in an early stage of decomposition and serves as readily decomposable substrate for the microbial biomass (Six et al., 1999; Solomon et al., 2000).

2.3 C mineralization experiments

The C mineralization experiments consisted out of two different experiments. In a first experiment, whole soil C mineralization was measured. In a second experiment, isolated macro organic matter fractions (LF and HF) were incubated to determine the specific C mineralization of these fractions.

Before starting the whole soil C mineralization experiment, the air dried soil was rewetted and pre-incubated during six days at a temperature of 15°C. Air dried bulk samples were brought to a gravimetric water content of 46% for SGFOR and PINUS, respectively, and 32% for GRASS, corresponding to a water-filled pore space of 25% at the bulk density in the field (using a bulk density for all the layers of 0.45 Mg m^{-3} for SGFOR and PINUS, and 0.60 Mg m^{-3} for GRASS (see Table 1) and a soil particle density of 2.65 Mg m^{-3}). As such, a realistic microbial soil activity could be restored. An exact quantity of soil was put in PVC tubes (4.6 cm diameter, 13 cm high) and compressed manually to the corresponding bulk density. The tubes were covered with parafilm, which permits sufficient gas exchange and aeration, but reduced moisture loss. During the entire experiment, the moisture content and temperature were kept constant. Carbon dioxide emission was measured on eight different time points (day 1, 3, 7, 11, 17, 35, 43 and 62). This was done by putting the PVC-tubes into glass jars, which were closed airtight. The headspace of the glass jars was sampled after 0, 27, 54 and 81 minutes through a rubber septum. Before sampling, the CO$_2$ concentration in the headspace was homogenized by repeatedly sucking and reinjecting the headspace. A gas sample of 1 mL was injected into a gas chromatograph (GC-14B, Shimadzu, Japan) (Porapack Q, mesh size 80/100 column specification, electron cap-

ture detector (ECD)). The CO$_2$ concentration was calculated via a linear calibration using a certified CO$_2$ concentration (1% CO$_2$ in dry air, Air Liquide, France). Linear regression between the measuring points at 0, 27, 54 and 81 min gave the CO$_2$ mineralization flux.

The incubation of the isolated HF and LF was only performed for SOC originating from the 0–10 cm soil layer of each land use treatment, following the method described by Swanston et al. (2002). For LF, 2.00 g substrate was mixed with 18.00 g inert quartz sand (acid washed, 580–650 μm diameter) in a glass flask. For HF, 5.00 g substrate was mixed with 15.00 g inert quartz sand. A microbial inoculum was added at the beginning of the incubation. A water extract from the mineral soil originating from the same soil layer was used as inoculum source. The inoculum was made by adding distilled water to a wet soil in a 1/1.5 ratio, followed by placing the mixture on a rotary shaker for 30 min. After settling down, 4 mL of the supernatant was added to each flask and the substrate was pre-incubated for two days. During the entire experiment, the inoculated flasks were stored in an incubation room at a constant temperature of 15°C. The CO$_2$ concentration was measured through a septum in the cap of the flasks after 0, 27, 54 and 81 min and on six different time points (day 1, 3, 7, 11, 17 and 35) with a gas chromatograph (GC-14B, Shimadzu, Japan), using the same method as described above.

2.4 Physico-chemical analyses

Measurement of ^{13}C and total C (TC) content in the different soils and SOC fractions was performed using an elemental analyser (ANCA-SL, PDZ-Europa, UK) coupled to an Isotope Ratio Mass Spectrometer (20-20, PDZ Europa, UK). The measured ^{13}C/^{12}C ratios are expressed as δ^{13}C values (‰) vs. the international Vienna Pee Dee Belemnite (VPDB) standard:

$$\delta^{13}C = \frac{R_{sample} - R_{standard}}{R_{standard}} \times 1000 \quad (‰) \tag{1}$$

R_{sample} and $R_{standard}$ refer to the ^{13}C/^{12}C ratio of the measured sample and the standard, respectively. The working standard was flour with a δ^{13}C value of -27.01 ± 0.04‰ vs. VPDB and TC of 39.95 ± 0.40‰ (certified by Iso-Analytical, UK).

A modified procedure of the method described by Schwertmann (1964), using a mixture of ammonium oxalate (0.2 M) and oxalic acid as extractant, was applied for the determination of the extractable aluminum oxalate (Al$_{ox}$), and silicon oxalate (Si$_{ox}$) content. In the absence of light, a soil:solution (1:10) mixture was placed on a rotary shaker for 2 hours. A pyrophosphate reagent (0.1 M) was used in soil:solution ratio of 1:10 (shaking time 16 h) for the determination of the pyrophosphate extractable Al content (Al$_{py}$). All supernatants were centrifuged at 3000 rpm for 10 min, filtrated (folded filters, Schleicher & Schüell, Germany) and

Table 1. Chemical and physical properties of the second growth forest (SGFOR), grassland (GRASS) and plantation (PINUS) for the 0–10, 10–20 and 20–30 cm soil layer (Standard deviations between brackets, significant differences ($p<0.05$) between land use treatments within one soil depth layer are indicated by different letters).

Soil layer	Land use class	Texture	pH_{H_2O}	ρ_b	Al_{ox}	Al_{py}	Si_{ox}	Allophane	TC		TN		C/N
cm				$Mg\,m^{-3}$	—	$g\,kg^{-1}$	—	%	$kg\,C\,m^{-2}$	$g\,kg^{-1}$	$kg\,N\,m^{-2}$	$g\,kg^{-1}$	
	SGFOR	sandy loam	6.1^a	0.42	20.3^b	6.4^b	9.6	6.00^a	$5.8^{a,b}$	139^a	0.31^b	7.4^b	18.9
			(0.1)	(0.06)	(0.5)	(0.9)	(0.4)	(0.33)	(0.5)	(7)	(0.05)	(0.2)	(1.2)
	GRASS	sandy loam	5.7^b	0.60	23.6^a	11.1^a	8.1	5.22^b	6.7^a	111^b	0.53^a	8.9^a	12.5
0–10			(0.1)	(0.09)	(0.5)	(0.9)	(0.6)	(0.28)	(1.1)	(1)	(0.08)	(0.1)	(4.5)
	PINUS	sandy loam	6.2^a	0.45	22.9^a	6.3^b	9.1	6.46^a	4.3^b	94^c	0.31^b	6.8^b	13.8
			(0.0)	(0.07)	(0.4)	(0.8)	(0.2)	(0.21)	(0.9)	(6)	(0.06)	(0.6)	(5.0)
	SGFOR	sandy loam	6.3^a	0.44	21.2^b	5.4^b	11.4	6.99^a	4.0^b	93^b	0.23^b	5.5^b	16.9
			(0.0)	(0.12)	(0.6)	(0.7)	(0.6)	(0.12)	(0.9)	(6)	(0.02)	(1.2)	(0.6)
	GRASS	sandy loam	5.4^b	0.46	24.1^a	10.5^a	8.5	5.57^b	4.8^b	105^a	0.37^a	8.1^a	13.0
10–20			(0.1)	(0.10)	(0.2)	(1.0)	(0.3)	(0.27)	(1.0)	(5)	(0.08)	(0.1)	(0.8)
	PINUS	sandy loam	6.4^a	0.46	23.4^a	6.1^b	9.1	6.63^a	3.3^a	71^c	0.26^b	5.6^b	12.7
			(0.1)	(0.04)	(0.6)	(0.6)	(0.6)	(0.47)	(0.3)	(3)	(0.03)	(0.2)	(1.5)
	SGFOR	sandy loam	6.3^a	0.52	22.3^b	4.3^b	11.8	7.59^a	3.4^b	64^b	0.21^b	4.0^b	16.1
			(0.1)	(0.05)	(0.5)	(0.7)	(0.8)	(0.28)	(0.3)	(9)	(0.05)	(1.0)	(2.2)
	GRASS	sandy loam	5.8^b	0.60	24.4^a	10.7^a	9.0	5.75^b	5.8^a	98^a	0.44^a	7.3^a	13.4
20–30			(0.3)	(0.08)	(0.3)	(0.6)	(0.1)	(0.05)	(1.0)	(5)	(0.10)	(0.8)	(1.1)
	PINUS	sandy loam	6.7^a	0.47	22.2^b	3.9^b	10.2	7.19^a	2.4^b	51^b	0.18^b	3.9^b	13.1
			(0.1)	(0.05)	(0.4)	(1.0)	(0.3)	(0.38)	(0.4)	(7)	(0.03)	(0.6)	(1.0)

ρ_b=Bulk density
Al_{ox}=Ammonium oxalate extractable Al content
Al_{py}=Pyrophosphate extractable Al content
Si_{ox}=Ammonium oxalate extractable Si content
Allophane=Estimated allophane content
TC=Total carbon content
TN=Total nitrogen content

the Al and Si content of the solutions were determined with respectively ICP-OES (Inductive Coupled Plasma – Optical Emission Spectrometry) (VISTA-MPX CCD Simultaneous ICP-OES, Varian, USA), and AAS (SpectrAA 600, Varian, USA). Allophane contents were calculated using the formula proposed by Parfitt and Wilson (1985), and later simplified by Mizota and van Reeuwijk (1989):

$$\text{Allophane} = 100\,Si_{ox} \times \left[23.4 - 5.1 \left(\frac{Al_{ox} - Al_{py}}{Si_{ox}} \right) \right] (\%) \quad (2)$$

2.5 Statistical analyses

Statistical analyses were performed using SYSTAT version 10.0 (SPSS, USA). Statistical differences of means (95% significance level) were distinguished using ANOVA (3 replicates) followed by a Duncan's multiple range post-hoc test. Paired samples T-tests were used to determine differences in C mineralization rates between LF and HF fractions.

Log transformation was used to improve normality and homoscedastisticy in the data when necessary. In case no homogeneity of variance was reached after log transformation, Tamhane's T2 test was used as post-hoc test. Correlations were determined by the Pearson's correlation factor.

3 Results

3.1 Physico- chemical soil properties

The chemical and physical properties of the soils are listed in Table 1. Averaged over the three soil layers, land use changes significantly affected SOC stocks with +31 and −42% for the conversion from SGFOR to GRASS and GRASS to PINUS, respectively. The N content was highest in GRASS, followed by SGFOR and PINUS. Nitrogen stocks varied from 0.53 to 0.18 kg m⁻². Fertilizer additions on the GRASS site are responsible for the higher N contents in this site. The bulk
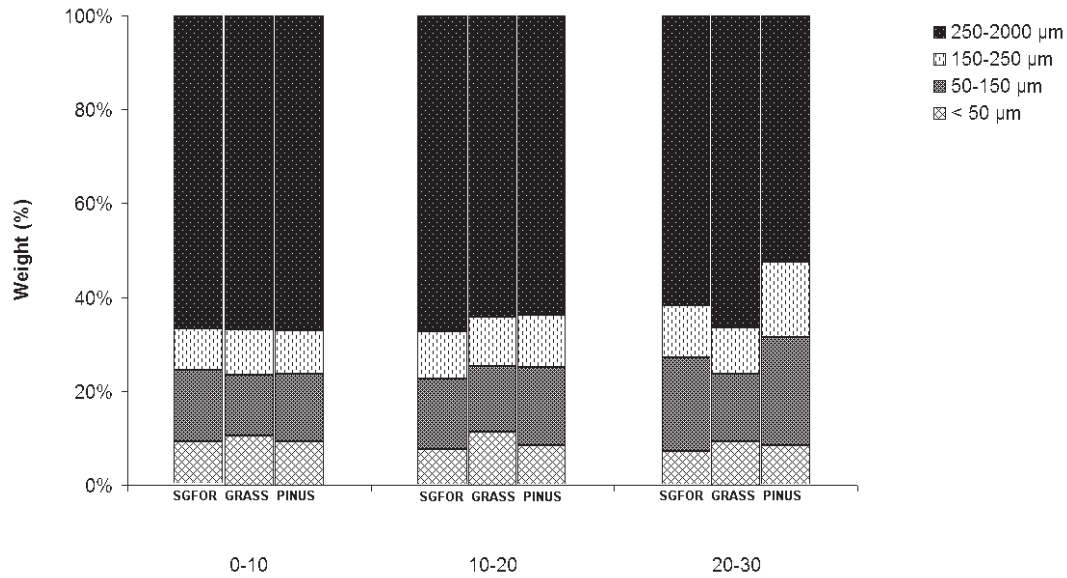
Fig. 2. Distribution of the soil weight over the different size classes (2000–250 μm, 250–150 μm, 150–50 μm, and <50μm) after the first fractionation procedure (starting from "air-dried" soil) for the second growth forest (SGFOR), grassland (GRASS) and plantation (PINUS) and for the three soil layers (0–10 cm, 10–20 cm, and 20–30 cm).

Fig. 3. Distribution of the soil weight over the different size classes (2000–250 μm, 250–150 μm, 150–50 μm, and <50 μm) after the second fractionation procedure (starting from field moist soil) for the second growth forest (SGFOR), grassland (GRASS) and plantation (PINUS) and for the three soil layers (0—10 cm, 10–20 cm, and 20–30 cm).
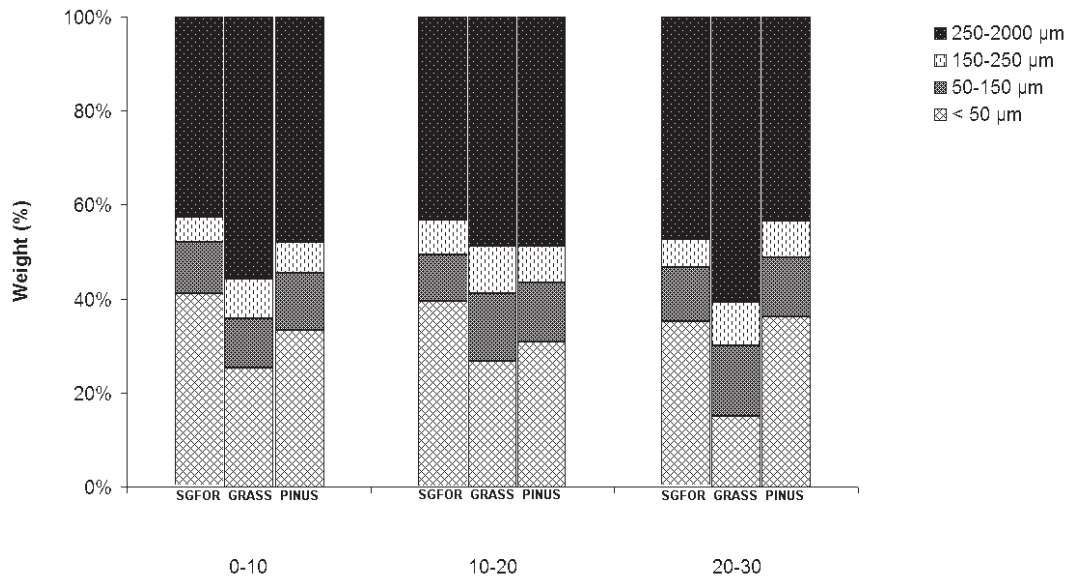
density was higher in GRASS than in SGFOR and PINUS and is as well a result of agricultural livestock activities. Soil texture was categorized as sandy loam (USDA texture class) for all land use treatments. The soils in SGFOR and PINUS showed an average pH_{H_2O} between 6.1 and 6.7. In contrast, GRASS showed a lower pH_{H_2O} (around 5.5). The extractable Al_{ox} and Al_{py} concentrations in the GRASS site were higher than for SGFOR and PINUS, though differences between GRASS and PINUS were not always significant for Al_{ox}. Soil pH was negatively correlated with Al_{ox} ($r=-0.45$; $p=0.02$), and Al_{py} ($r=-0.83$; $p=0.00$). Allophane contents were, for all three soil layers, significantly lower for GRASS compared to SGFOR and PINUS.

Table 2. Distribution of the soil weight according to the size fraction in Fig. 2 and Fig. 3, expressed as weighted average diameter (WAD), of the first and second fractionation procedure, and difference in WAD between the two fractionation procedures for the three soil layers of the second growth forest (SGFOR), grassland (GRASS), and plantation (PINUS) (Standard deviations between brackets, significant differences ($p<0.05$) between land use treatments are indicated by different letters).

	0–10 cm			10–20 cm			20–30 cm		
	SGFOR	GRASS	PINUS	SGFOR	GRASS	PINUS	SGFOR	GRASS	PINUS
WAD first fractionation procedure (μm)	786^A	788^A	790^A	794^A	760^A	758^A	739^A	785^A	647^B
	(40)	(26)	(13)	(15)	(27)	(50)	(19)	(14)	(34)
WAD second fractionation procedure (μm)	511^A	662^A	572^A	522^A	590^A	585^A	565^B	720^A	526^B
	(118)	(59)	(124)	(84)	(73)	(54)	(33)	(53)	(5)
Difference in WAD (μm)	275^A	126^A	218^A	273^A	170^A	173^A	174^A	65^B	$120^{A,B}$
	(84)	(84)	(125)	(90)	(97)	(103)	(25)	(43)	(34)

3.2 Size and density fractionation of SOC

The highest weight percentage after the first size fractionation was found in the size fraction 250–2000 μm (Fig. 2). The other size fractions contain smaller amounts of soil weight, varying from 23.1 to 7.0% for all land use treatments. The WAD was not significantly different between the different land use treatments, except for PINUS 20–30 cm where a significant lower value was found (Table 2). TC concentration (%) was not significantly different among the different size fractions in all the sites, with exception of the 0–10 cm layer of SGFOR (Table 3).

The results of the weight distribution of the second size fractionation experiment (after an 80 day incubation period, starting from field moist soil) are shown in Fig. 3. A considerable shift in soil weight towards the finer size fractions could be noticed, resulting in a smaller WAD compared to the first fractionation procedure (Table 2). Between land use treatments, GRASS showed the coarsest aggregate distribution but due to relative large standard deviations (on average 50 μm), differences in WAD were only significant for the 20–30 cm layer. As in the first fractionation procedure, the TC concentration did not differ significantly among the different size classes for all land uses, though a few exceptions were observed here (data not shown).

Averaged over the three soil layers, the aggregate stability decreased in the following order: GRASS>PINUS>SGFOR. However, only significant differences were observed for the 20–30 cm layer between SGFOR and GRASS (Table 2). The difference in WAD was negatively correlated with the extractable Al_{ox} content of the soil ($r=-0.50$; $p=0.01$), but not with the TC content ($r=-0.18$; $p=0.38$), extractable Al_{py} content ($r=-0.23$; $p=0.25$) or allophane content ($r=0.11$; $p=0.60$) of the soil. The relation between extractable Al_{ox} content and difference in WAD for the different land use treatments and soil depths is given in Fig. 4.
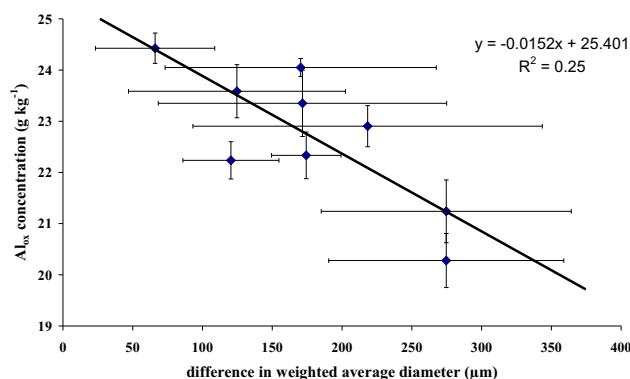

Fig. 4. The Al_{ox} concentration in function of the difference in weighted average diameter for the different land use treatments and soil depths (error bars indicate plus/minus one standard deviation).

The amounts of MOM are expressed relative to the TC content (i.e. as % of total C) (Table 4). The differences between land use treatments diminished with depth and were only significant between SGFOR, GRASS and PINUS for the 0–10 cm and 10–20 cm layer.

Table 5 shows the complete mass and SOC balance for the 0–10 cm. It was found that the C content of the MOM is only a small fraction of the TC content (2.4%–8.3%) in the soil. Though the concept of the fractionation procedure assumes that aggregates larger than 150 μm are broken and the enclosed organic matter is released, still 56–74% of the total SOC content of the soil was found in the remaining mineral fraction (i.e. the fraction 150–2000 μm, from which the MOM is isolated).

3.3 δ^{13}C signature in size and density fractions

The δ^{13}C values of the whole SOC and the different size fractions in the three land use treatments and soil layers are presented in Table 6. Within the different size fractions of a

Table 3. Carbon concentrations (g kg^{-1}) for the soil layers of the second growth forest (SGFOR), grassland (GRASS), and plantation (PINUS) (Standard deviations between brackets, significant differences ($p<0.05$) between aggregate size classes for a certain land use treatment and soil depth are indicated by different letters).

	Carbon concentration (g kg^{-1})								
	0–10 cm			10–20 cm			20–30 cm		
	SGFOR	GRASS	PINUS	SGFOR	GRASS	PINUS	SGFOR	GRASS	PINUS
250 μm–2000 μm	141$_{a,b}$	111$_a$	93$_a$	90$_a$	105$_a$	71$_a$	66$_a$	98$_a$	52$_a$
	(16)	(13)	(13)	(6)	(5)	(15)	(6)	(9)	(8)
150 μm–250 μm	146$_a$	111$_a$	98$_a$	88$_a$	106$_a$	69$_a$	63$_a$	99$_a$	50$_a$
	(7)	(17)	(12)	(6)	(1)	(13)	(11)	(7)	(7)
50 μm–150 μm	148$_a$	107$_a$	99$_a$	93$_a$	105$_a$	72$_a$	67$_a$	97$_a$	52$_a$
	(19)	(19)	(14)	(3)	(4)	(10)	(10)	(6)	(7)
<50 μm	122$_b$	110$_a$	84$_a$	81$_a$	106$_a$	68$_a$	61$_a$	96$_a$	48$_a$
	(5)	(15)	(12)	(2)	(2)	(6)	(8)	(4)	(6)

Table 4. Percentage of total C of the macro organic matter fractions (MOM) for the second growth forest (SGFOR), grassland (GRASS) and plantation (PINUS) (Standard deviations between brackets, significant differences between land use treatments in the same soil layer are indicated by different letters).

Soil layer (cm)		% of total C					
		SGFOR		GRASS		PINUS	
0–10	Macro organic matter	8.3^A	(1.9)	2.4^B	(0.5)	5.0^C	(0.8)
	HF	0.8^A	(0.1)	0.4^B	(0.0)	1.1^A	(0.3)
	IF	1.0^A	(0.1)	0.3^B	(0.0)	0.8^C	(0.1)
	LF	6.5^A	(1.9)	1.7^B	(0.5)	3.1^B	(0.7)
10–20	Macro organic matter	2.8^A	(0.6)	1.6^B	(0.1)	3.6^C	(0.2)
	HF	0.3^A	(0.1)	0.3^A	(0.0)	0.8^B	(0.1)
	IF	0.4^A	(0.2)	0.2^A	(0.1)	0.7^B	(0.2)
	LF	2.1^A	(0.3)	1.1^B	(0.1)	2.1^A	(0.3)
20–30	Macro organic matter	3.8^A	(1.4)	1.1^B	(0.1)	3.4^A	(0.5)
	HF	0.4^A	(0.2)	0.3^A	(0.0)	1.0^B	(0.2)
	IF	0.7^A	(0.3)	0.1^B	(0.1)	0.8^A	(0.2)
	LF	2.7^A	(0.9)	0.6^B	(0.1)	1.6^{A,B}	(0.4)

HF=Heavy density fraction (density>1.37 Mg m^{-3})
IF=Intermediate density fraction (1.13 Mg m^{-3}<density<1.37 Mg m^{-3})
LF=Light density fraction (density<1.13 Mg m^{-3})

certain land use, no significant differences in δ^{13}C value were found. However, a significant difference of 1–2‰ was found between the δ^{13}C value of the size classes and MOM density classes for the different land use treatments, with exception for PINUS 0–10 cm.

3.4 C mineralization experiments

3.4.1 Whole soil C mineralization

The cumulative C mineralization curves were calculated for all land use treatments as shown in Fig. 5 for SGFOR. The

linear part of each curve (from day 17 to 62) was used to estimate the potential C mineralization rate via linear regression (Table 7). The differences in potential C mineralization rates between the different land use treatments were significant in the 0–10 cm soil layer: SGFOR>PINUS>GRASS. However, differences between the three land use treatments disappeared gradually with depth. In the 10–20 cm and 20–30 cm layer SGFOR still showed the highest potential mineralization rate, but differences were no longer significant. For all land use treatments, potential C mineralization rates decreased with soil depth. The C mineralization rate constant,

Table 5. Weight, C concentration, and % of total C of the different soil organic carbon fractions for the second growth forest (SGFOR), grassland (GRASS) and plantation (PINUS) for the 0–10 cm soil layer (Standard deviations between brackets, significant differences ($p<0.05$) between land use treatments are indicated by different letters).

	Weight (g kg^{-1} soil)			C-concentration (g C kg^{-1} fraction)			% of total C (%)		
	NO	GR	PR	NO	GR	PR	NO	GR	PR
Whole soil	1000	1000	1000	139^A	111^B	94^C			
				(7)	(1)	(6)			
SOC fractions									
MOM	31.5^A	8.6^B	14.4^B	366^A	309^B	325^B	8.3^A	2.4^B	5.0^C
	(5.8)	(1.8)	(2.8)	(5)	(12)	(32)	(1.9)	(0.5)	(0.8)
HF	4.6^A	1.7^B	4.5^A	239^A	251^A	230^A	0.8^A	0.4^B	1.1^A
	(0.4)	(0.1)	(1.6)	(28)	(8)	(34)	(0.1)	(0.0)	(0.3)
IF	4.5^A	1.1^C	2.4^B	328^A	284^A	305^A	1.0^A	0.3^C	0.8^B
	(0.1)	(0.2)	(0.6)	(20)	(18)	(47)	(0.1)	(0.0)	(0.1)
LF	22.5^A	5.8^C	7.6^B	399^A	332^B	385^A	6.5^A	1.7^B	3.1^B
	(5.5)	(1.7)	(1.5)	(5)	(16)	(14)	(1.9)	(0.5)	(0.7)
Mineral fraction	738^A	756^A	749^A	108^A	109^A	90^B	56.4^A	74.4^B	71.5^B
150 μm–2000 μm	(28)	(16)	(8)	(11)	(9)	(3)	(3.8)	(3.2)	(4.3)
50–150 μm	152^A	130^A	143^A	149^A	107^B	99^B	16.7^A	12.5^A	15.0^A
	(40)	(23)	(9)	(19)	(4)	(10)	(6.3)	(1.8)	(0.9)
<50 μm	91^A	104^A	93^A	122^A	110^A	84^B	7.9^A	10.3^B	8.3^{A,B}
	(15)	(6)	(14)	(5)	(2)	(8)	(0.7)	(0.7)	(1.7)
Sum of the fractions							89.5^A	99.6^A	99.7^A
							(8.2)	(3.6)	(5.5)

SOC=Soil organic carbon
MOM=Macro organic matter ($>150\,\mu$m)
HF=Heavy density fraction (density$>1.37\,$Mg m^{-3})
IF=Intermediate density fraction ($1.13\,$Mg m$^{-3}<$density$<1.37\,$Mg m^{-3})
LF=Light density fraction (density$<1.13\,$Mg m^{-3})

which can be used as an indicator of the degradability of the SOC, was calculated by dividing the observed potential C mineralization rate (expressed per gram soil) by the corresponding TC content in each soil layer (Table 7). For the 0–10 cm soil layer, these values varied from 0.029 for SGFOR to 0.023 for PINUS and 0.011 yr^{-1} for GRASS. In all soil layers, the decomposability of the SOC was significantly lower for GRASS than for PINUS and SGFOR. The SOC from GRASS showed the highest stability against microbial breakdown. Statistical correlation tests showed that the C mineralization rate constants were significantly correlated with the difference in WAD ($r=0.39$; $p=0.04$) and the extractable Al$_{ox}$ content ($r=-0.68$; $p=0.00$).

3.4.2 Incubation of the isolated MOM density fractions HF and LF

In this procedure, the MOM was isolated by the density separation procedure, through which the physical protection of SOC in soil aggregates could be removed (Fig. 1).
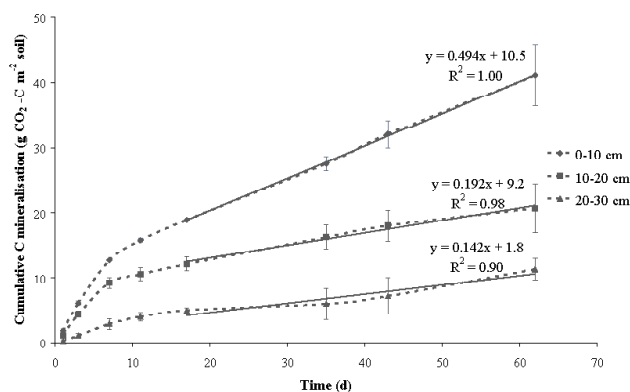

Fig. 5. Evolution of the cumulative C mineralization for the second growth forest (SGFOR) for the 0–10 cm, 10–20 cm and 20–30 cm soil layer (day 1 to day 62) (error bars indicate plus/minus one standard deviation), and linear regression of the curves (from day 17 to day 62).

Table 6. $\delta^{13}C$ values (‰) of the soil organic carbon fractions for the second growth forest (SGFOR), grassland (GRASS) and plantation (PINUS) (Standard deviations between brackets, significant differences ($p<0.05$) between soil organic carbon fractions are indicated by different letters).

Fraction	$\delta^{13}C$ (‰)								
	0–10 cm			10–20 cm			20–30 cm		
	SGFOR	GRASS	PINUS	SGFOR	GRASS	PINUS	SGFOR	GRASS	PINUS
Whole soil	−27.2	−26.7	−27.8	−26.4	−26.8	−26.7	−26.2	−26.7	−26.4
	(0.1)	(0.3)	(0.2)	(0.4)	(0.1)	(0.2)	(0.2)	(0.3)	(0.1)
Macro organic matter	$−28.3_b$	$−28.7_b$	$−29.2_b$	$−27.7_b$	$−27.8_b$	$−28.2_b$	$−27.7_b$	$−27.5_b$	$−28.2_b$
	(0.4)	(0.6)	(0.6)	(0.1)	(0.1)	(0.3)	(0.1)	(0.3)	(0.2)
Size fractions									
250 µm–2000 µm	$−27.2_a$	$−26.7_a$	$−27.9_a$	$−26.4_a$	$−26.8_a$	$−26.7_a$	$−26.3_a$	$−26.7_a$	$−26.4_a$
	(0.1)	(0.6)	(0.6)	(0.4)	(0.1)	(0.2)	(0.2)	(0.4)	(0.1)
150 µm–250 µm	$−27.2_a$	$−26.7_a$	$−27.9_a$	$−26.4_a$	$−26.8_a$	$−26.7_a$	$−26.2_a$	$−26.7_a$	$−26.3_a$
	(0.2)	(0.5)	(0.6)	(0.4)	(0.1)	(0.1)	(0.3)	(0.3)	(0.2)
50 µm–150 µm	$−27.1_a$	$−26.6_a$	$−27.7_a$	$−26.4_a$	$−26.8_a$	$−26.7_a$	$−26.2_a$	$−26.7_a$	$−26.3_a$
	(0.2)	(0.7)	(0.7)	(0.4)	(0.1)	(0.1)	(0.2)	(0.3)	(0.2)
<50 µm	$−27.2_a$	$−26.7_a$	$−27.7_a$	$−26.4_a$	$−26.8_a$	$−26.7_a$	$−26.1_a$	$−26.6_a$	$−26.2_a$
	(0.2)	(0.6)	(0.7)	(0.3)	(0.1)	(0.1)	(0.3)	(0.1)	(0.1)

Table 7. Potential C mineralization rates and decomposition rate constants for the second growth forest (SGFOR), grassland (GRASS) and plantation (PINUS) for 0–10 cm, 10–20 cm and 20–30 cm soil layer (Standard deviation between brackets, significant differences between land use treatments ($p<0.05$) are indicated by different letters).

Land use class	Potential mineralization rate			Mineralization rate constant		
	0–10 cm	10–20 cm	20–30 cm	0–10 cm	10–20 cm	20–30 cm
	$g\,CO_2\text{-C}\,m^{-2}\,d^{-1}$			—	yr^{-1}	—
SGFOR	0.495^a	0.192^a	0.142^a	0.029^a	0.017^a	0.018^a
	(0.108)	(0.061)	(0.041)	(0.005)	(0.005)	(0.003)
GRASS	0.196^c	0.092^a	0.087^a	0.011^b	0.005^b	0.005^b
	(0.021)	(0.021)	(0.034)	(0.001)	(0.001)	(0.002)
PINUS	0.266^b	0.135^a	0.087^a	0.023^a	0.015^a	0.014^a
	(0.041)	(0.034)	(0.044)	(0.001)	(0.008)	(0.006)

Especially, the accessibility of the HF has been increased, as this fraction is more associated with soil minerals and components compared to the LF. The LF is mainly present in the soil as free MOM. Only a small fraction is bounded in soil aggregates (Hassink, 1995; Swanston et al., 2002). Potential C mineralization rates and C mineralization rate constants of the isolated density fractions were calculated using the same method as the whole soil C mineralization experiment (Table 8). In this experiment, the mineralization rate constants are an indicator of the recalcitrance of the MOM fractions. Statistical analyses showed that the potential C mineralization rates of the LF and HF were significantly different for all land use treatments. The C mineralization rate constants of the LF and HF are significantly different for GRASS, but not for SGFOR and PINUS.

The C mineralization rate constants showed that the MOM from GRASS decomposes fastest. The recalcitrance of the LF decreased in the following order: PINUS>SGFOR>GRASS. For the HF, PINUS showed a higher recalcitrance than GRASS, whereas the value of SGFOR was not significantly different from PINUS and GRASS (Table 8).

4 Discussion

In a first section of the discussion, we will focus on the interaction of Al, SOC and soil minerals. The potential role of Al-humus complexes and electrostatic-C binding on aggregate structure will be assessed in this Andisol. In a second

Table 8. Potential mineralization rates and mineralization rate constants of the light (LF) and heavy (HF) density fraction for the second growth forest (SGFOR), grassland (GRASS) and plantation (PINUS) (Standard deviations between brackets, significant differences ($p<0.05$) are indicated by different letters (upper case letters between LF and HF, lower case letters between land use treatments)).

Land use class	Potential mineralization rate		Mineralization rate constant	
	LF	HF	LF	HF
	mg CO_2-C kg^{-1} fraction d^{-1}		yr^{-1}	
SGFOR	131.2^A_a	$59.7^B_{a,b}$	0.120^A_a	$0.090^A_{a,b}$
	(11.4)	(14.6)	(0.010)	(0.022)
GRASS	137.4^A_a	73.0^B_a	0.151^A_b	0.106^B_a
	(6.2)	(7.6)	(0.007)	(0.011)
PINUS	74.7^A_b	37.6^B_b	0.071^A_c	0.060^A_b
	(14.2)	(8.4)	(0.013)	(0.013)

part, we will evaluate the results of C mineralization experiments. In a third section, a link between aggregate structure, C mineralization and SOC stabilization will be made. In a last section, the potential role of pH on aggregate structure and SOC stabilization will be discussed.

4.1 Aggregate structure in south Chilean Andisols

In literature, two main sorption mechanisms are documented in Al rich soils. As sorption tends to promote aggregation (Sollins et al., 1996), these mechanisms lead to aggregate build up and might be responsible for the occurrence of high amounts of water-stable aggregates in this soil type (e.g. Hoyos and Comerford, 2005; see Sect. 3.2). Firstly, metal-humus complexes would act as binding agents between aggregates or soil particles. In metal-humus complexes, SOC can be sorbed by allophane through ligand exchange between functional groups of SOC and Al (Parfitt et al., 1977; Skjemstad, 1992; Parfitt et al., 1999). In this mechanism, an organic ligand replaces a hydroxyl group, which is coordinated to the metal ion on the surface of the oxide to form a surface complex. Since surface hydroxyls are characteristic for variable charge surfaces, sorption of negatively charged organics by ligand exchange should be most important in oxide-rich and allophanic soils, such as Andisols (Sollins et al., 1996). Other bounding types involved in sorption between SOC and metals include cation bridging (Varadachari et al., 1995), water bridging, hydrogen bounding, and van der Waals forces (Burchill et al., 1981). However, distinction between potential types is impossible bearing in mind the methodology of this study. In this first case, the mechanism of aggregate hierarchy (Tisdall and Oades, 1982) would be adequate to describe C dynamics as SOC (bonded to Al) acts as principal binding agent between soil components.

Secondly, electrostatic attractions could occur between and among amorphous Al components and clay minerals due to the simultaneous existence of positive and negative charges at field pH (Schofield and Samson, 1954; El-Swaify,

1980; Six et al., 2000b; Six et al., 2000c; Denef et al., 2002). Thus, here aggregate formation is partly induced by electrostatic interactions between soil minerals and Al components and aggregate hierarchy should be less pronounced (Oades and Waters, 1991).

We conceptually tested the occurrence of aggregate hierarchy for the different land use treatments. Three consequences of this theory are: (1) a gradual breakdown of macroaggregates into microaggregates before they dissolve into primary particles, as increasing dispersive energy is applied to the soil (Oades and Waters, 1991), (2) an increase in percentage C concentration with increasing aggregate-size class because large aggregate-size classes are composed of small aggregate-size classes plus organic binding agents (Elliott, 1986), and (3) younger and more labile organic matter is contained in macroaggregates rather than in microaggregates (Elliott, 1986; Puget et al., 1995; Jastrow et al., 1996). Firstly, the fractionation of the soils at two different periods allowed us to test the aggregate stability. A gradual breakdown of macroaggregates into microaggregates could be observed (Figs. 2, 3). It was shown that this breakdown could not be explained by the TC content, allophane content or extractable Al$_{py}$ content of the soil, but by the extractable Al$_{ox}$ content of the soil (Fig. 4). In the latter Al-extraction procedure, only amorphous and poorly crystalline Al-oxides and Al bound to organic complexes could be isolated (Bertsch and Bloom, 1996). Secondly, the TC concentration did not differ among the different size classes for a certain land use treatment (Table 3). Absence of differences in C concentration between aggregate-size classes in Andisols was also documented by Hoyos and Comerford (2005). Thirdly, there were no significant differences in δ^{13}C values among the different size classes for a certain soil (Table 6). In contrast to e.g. Accoe et al. (2002), no gradual shift in δ^{13}C value towards finer aggregate classes could be observed as a result of increasing decomposition (O'Brien and Stout, 1978). In this study, we could only distinguish two different SOC pools: the MOM and the mineral soil pool. It was indicated that the

SOC in the different size fractions is at the same degree of decomposition.

The results of these experiments indicated that metal-humus complexes are probably not the main binding agents between soil aggregates in these Andisols. Aggregate build-up would be mainly a result of electrostatic attractions between and among Al and Al-oxides and clay minerals, as documented as well by Schofield and Samson (1954), Violante and Huang (1992) and Denef et al. (2002). SOC would only play a minor role in these strong bindings between larger aggregates. Absence of aggregate hierarchy in this soil type has earlier been documented by Hoyos and Comerford (2005).

On the other hand, ploughing (Beare et al., 1994; Six et al., 1999) and drying of the soil might influence the aggregate structure. Every two year, the GRASS site is disturbed by ploughing. Drying of Andisols might cause dramatic changes of the physical properties of aggregates, and lead to a coarser aggregate size distribution (Shoji et al., 1993). Even air-drying can affect the particle size and micro-aggregate distribution. Tillage on the GRASS site might have exposed the soil unprotected to the sun and resulted in drying of the topsoil layer, leading to an increase in stable aggregates. Continued ploughing would lead to a mixture of the aggregates in the upper 30 cm of the soil.

4.2 C mineralization experiments

Land use changes affect SOC dynamics by differences in SOC input, and by direct effects of accompanying soil disturbances (Guo and Gifford, 2002). Pastures maintain a continuous vegetation cover on the soil and have high turnover rates and productivity, particularly belowground. As a result more intense humus formation would take place (Brown and Lugo, 1990; Yakimenko, 1998). Jobbagy and Jackson (2000) indicated that the annual turnover of SOC from dying tree roots is smaller than from grass roots. In forested ecosystems, the SOC inputs originate partly from aboveground and accumulate more in and on the surface soil due to non-mixing of the litter (Paul et al., 2002). SOC tends to decompose partly before it is incorporated into the forest soil, involving a smaller formation of SOC. Thus, under grassland a thicker A horizon is formed compared with forests (e.g. Birkland, 1984). According to Guo and Gifford (2002), the lower SOC content in plantations may partly be attributed to soil disturbances and consequent loss in physical protection of the SOC involved in the establishment of plantations. The transformation from a multi-storey forest to a single storey plantation lacking understorey vegetation results in less SOC input (Guo and Gifford, 2002). Also, during the first years after the establishment of a plantation, reduced SOC sequestration takes place as a result of low SOC input (due to a small forest biomass and low litter fall rate) (Wilde, 1964) and a continued decomposition of the SOC present in the soil profile. Carbon

storage as well is affected by forest type (species, deciduous, evergreen) (Lal et al., 1995).

In our study, the whole soil C mineralization rate constant decreased in the following order: SGFOR≈PINUS>GRASS. Our values are in accordance to those found in Columbian Andisols by Boudot et al. (1986), who measured a mineralization rate constant of approximately $0.01\,\mathrm{yr}^{-1}$ in the 5–20 cm layer. Based on the C mineralization rate constants of the incubated MOM fractions, we were able to distinguish differences in the recalcitrance of the SOC of the different land use treatments (see below).

4.3 Evaluation of SOC stabilization mechanisms

As stated by Sollins et al. (1996), SOC can be stabilized by different mechanisms. We will consider each factor or process that controls the rate of stabilization, and discuss its potential effects on SOC stabilization in our soils. Sollins (1996) brought forward following sets of characteristics affecting the stability of SOC: recalcitrance, interactions and accessibility. Though we mainly focus on the aspect of accessibility, one has to bear in mind that several mechanisms and processes interact to determine the stability or biodegradability of SOC in soils (Marschner and Kalbitz, 2003). Keeping in mind the used methodology of this study, we cannot deduce conclusions on all aspects. In order to assess the importance of certain mechanisms, we will refer to the state-of-the-art in literature.

Recalcitrance

We tried to assess the importance of this parameter for the studied land use treatments by performing mineralization experiments of the isolated MOM fractions. We encountered that the degree of the whole soil C mineralization rate constants was opposite to the degree of the C mineralization rate constants of the isolated MOM fractions. Therefore, recalcitrance of the SOC did not appear to control SOC stabilization. Thus, other stabilization mechanisms should overrule the influence of litter quality on whole soil C mineralization rates.

Interactions between soil components

We showed that in our soils, Al is associated to clay minerals by electrostatic sorption. These clay minerals are associated to SOC, leading to the formation of metal-humus-clay complexes. Direct adsorption of SOC to Al by ligand exchange is considered of minor importance in our soils. Many studies (e.g. Percival et al., 2000) assume ligand exchange to be very important in Andisols, based on data of pyrophosphate extractable Al. In the literature (Bertsch and Bloom, 1996), the extractable Al_{py} content is often related to the directly organically bound Al, while the

quantity of poorly ordered amorphous or noncrystalline Al phases plus the organically bound Al would be proportional to Al_{ox}. However, we believe that in a very close association between SOC, Al and soil minerals, as occurring in our soils, extractants cannot be completely selective for one certain phase. This as well was brought forward by Bertsch and Bloom (1996). Kaiser and Zech (1996) indicated that pyrophosphate also removed Al hydroxides and stated that it should not be used to estimate Al in humus complexes.

The formation of metal-humus-clay complexes by sorption onto clay minerals is usually assumed to stabilize SOC. It is known that such metal-humus-clay complexes are resistant to microbial decomposition (Juste et al., 1975; Martin et al., 1982) in Andisols. These adsorption reactions would provide a mechanism of stabilizing SOC against biological attack (Baldock and Skjemstad, 2000). However, the relevance of SOC stabilization remains poorly understood (Sollins et al., 1996). Sollins et al. (1996) indicated the difficulty to separate physico-chemical processes and physical protection (see below) as factors influencing SOC stabilization. Physico-chemical associations namely tend to promote aggregation. Boudot et al. (1989) observed that the binding of metals (such as Al and Fe) per se in metal-humus-clay complexes could not be regarded as responsible for any significant protective effect against biodegradation. The formation of an insoluble metallic hydroxide trapping and wrapping SOC molecules, and therefore either preserving it from access by soluble soil enzymes or preventing their movement to immobile enzymatic constituents associated with microbial cells (=inaccessibility or physical protection), would better account for the observed protective effect than the chemical binding per se.

Physical protection

Physical protection and aggregation can influence accessibility of substrate to microbes and fauna. Theoretical calculations suggest that aggregation should limit access to SOC (e.g. Van Veen and Kuikman, 1990). Six et al. (2000a) underscored the importance of soil aggregation and more specifically the interactions of SOC and aggregate dynamics in controlling SOC sequestration in soils. Gijsman and Sanz (1998) investigated the physical protection of macroaggregates in Andisols. After crushing of macroaggregates, these authors observed a significant increase in CO_2 mineralization compared to intact soil samples. Plante and McGill (2002) indicated that macroaggregate turnover results in the exposure of labile organic matter. Jastrow (1996) found evidence for a relationship between macroaggregate formation and SOC accrual. Aggregate stability affects the C mineralization process in Andisols by a physically protecting SOC from microbial breakdown. In our soils, the latter was confirmed by the significant correlation between the whole soil C mineralization rate constants and the difference in WAD ($r=0.39$, $p=0.04$).

We believe that this phenomenon is the most important SOC stabilization parameter occurring in our soils. However, it is probably an indirect effect of sorption mechanisms due to the presence of amorphous Al minerals as described above. Further statistical evidence for this conclusion was found in a significant correlation between the C mineralization rate constant and Al_{ox} content ($r=-0.68$, $p=0.00$), and the difference in WAD (Fig. 4). High Al_{ox} contents lead to the formation of stable soil aggregates which offer physical protection to the SOC. The importance of amorphous clay materials for SOC stabilization and aggregation in allophanic Andisols has often been documented (e.g. Boudot et al., 1989; Nanzyo et al.,1993; Torn et al., 1997), and is assumed to be the main stabilization mechanism in this soil type.

4.4 Effect of soil pH on SOC stabilization

Under lower pH conditions, Al is more soluble and available for complexation with soil components (Wesselink et al., 1996). The pH differences between GRASS and both SG-FOR and PINUS were significant for all soil layers, and most probably a result of the acidifying fertilizer applications. As a result of a lower pH, the extractable Al_{ox} and Al_{py} concentrations in the GRASS site were higher than for SGFOR and PINUS. We found that allophane contents were significantly lower for GRASS than for SGFOR and PINUS. It was indicated that as a result of a lower pH, Al was released from allophanic compounds and consequently resulted in a higher Al content associated with the Al-humus complexes. Statistical evidence for this conclusion was found by the strong significant correlation between soil pH and allophane ($r=0.74$, $p=0.00$). Increased Al release from allophane at decreasing pH was also found by Farmer and Lumsdon (2002). Takahashi et al. (2005) found that as a result of liming treatments, the amounts of organically complexed Al decreased significantly. Dahlgren and Saigusa (1994) found in Andisols evidence for the precipitation of released Al from allophanic components on soil surfaces, while Walker et al. (1988) found more specifically that soluble Al was adsorbed extremely rapid on common soil minerals such as vermiculite. Violante and Huang (1992) found in OM rich soils that sorption and aggregation between soil particles was promoted by increasing Al precipitation. Tama and El-Swaify (1978) stated that soil pH affects the ability of soil particles to aggregate differently in variable charge soils. The electrostatic contribution of oxides to aggregate stability is pH dependent and affects the extent of aggregate breakdown at different pH values. In lowering soil pH, the amount of positive charges of the Al-oxides and allophane increases (Espinoza et al., 1975). As such, more electrostatic forces are involved in aggregating soil particles. However, in our statistical analyses of the aggregate stability test no significant correlation was found between soil pH and difference in WAD between the two fractionation procedures. Possibly,

the sigmoid retention curves, relating the effect of soil pH and positive charges, documented in south Chilean Andisols (Espinoza et al., 1975) might be responsible for the absence of a linear correlation.

5 Conclusions

It can be concluded that by electrostatic sorption between and among amorphous Al compounds and clay minerals, physico-chemical stabilization of the SOC occurs. As clay minerals are closely associated with organic matter compounds, stable metal-humus-clay complexes can be formed. The principle of aggregate hierarchy was not valid in this soil type as metal-humus complexes formed as a result of ligand exchange did not appear to be important binding agents between soil aggregates. Soil pH is an important parameter in the studied Andisol as it influences aggregate stability. It was shown that SOC stabilization occurred via the formation of metal-humus-clay complexes and physical protection of SOC in soil aggregates. The recalcitrance of the SOC did not appear to influence SOC stabilization.

The whole soil C mineralization constants of the different land use treatments decreased in the following order: SGFOR≈PINUS>GRASS. In this study, land use conversion from a second growth forest (SGFOR) to a grassland (GRASS) showed, indirectly, a positive effect on C stabilization in the soil. As a result of management practices soil pH decreased in GRASS and more metal-humus-clay complexes and stable soil aggregates could be formed. A higher physical protection of the SOC was reached on this site, resulting in lower C mineralization rates. Other influences due to management practices (ploughing and direct exposure to sunlight due to the absence of a vegetation cover), and differences in root C input might influence as well SOC stabilization in the different sites.

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