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Chapter 5

**EFFECT OF PARENT MATERIAL AND
PEDOGENIC PROCESSES ON THE DISTRIBUTION,
FORM AND DYNAMICS OF ORGANIC CARBON
IN FOREST ECOSYSTEMS IN NW SPAIN.
A BIOGEOCHEMICAL APPROACH**

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ABSTRACT

The main objective of the present study was to determine the effect of the type of pedogenesis generated by two different parent materials – amphibolite (AMP) and granite (GR) - and the effect of different forest stands - pine (P), eucalypt (E), and oak (O) – on the quality and quantity of organic C pools in udic, mesic and freely drained systems. Five C pools were studied: aboveground biomass, belowground biomass, dead wood, litter, and soil organic matter (SOM) in the Ah horizons. The three forest soils derived from AMP materials (AMP-P, AMP-E, AMP-O) were classified as Typic Fulvudands and Aluandic Andosols, and the three forest soils derived from GR rocks (GR-P, GR-E, GR-O) were classified as Humic Dystrudepts, and Leptic and Haplic Umbrisols. All soils are located in the surroundings of Santiago de Compostela (A Coruña, NW Spain), where the mean annual air temperature is 12.3 °C and the total annual precipitation is 1624 mm yr⁻¹. The results obtained indicate that highest total organic C stocks in the ecosystems studied (down to the lowest depth of the Ah horizons), i.e., the sum of the five reservoirs considered, always corresponded to the eucalypt stands, with stocks > 500 t ha⁻¹, whereas those of the oak and pine stands were always < 500 t ha⁻¹. The mean distribution of

organic C stocks in the five reservoirs considered was as follows: aboveground biomass, 18.4%; belowground biomass 4.6%; dead wood, 1.1%; litter 8.4%; and soil organic C, 67.2%; there were no significant differences ($P < 0.05$) between means of the AMP and GR ecosystems although the total C stocks were always higher in the AMP than in the GR ecosystems, and followed the order $E > P > O$ in both. There were significant differences ($P < 0.05$) in the quantity, quality and dynamics of organic C in the two types of ecosystems, when organic layers (L and F) and also Ah horizons (Ah1 and Ah2) were distinguished, as discussed below.

The results indicate that, in soils developed from GR, the lithology mainly determines the type of pedogenesis taking place in the surface horizons, with intense acidification (acid-complexolysis) associated with scarce or nil neoformation of secondary minerals in the most acidic compartments (L and F layers) and an abundance of aqueous and mobile organo-metal complexes. Under such conditions, decomposition of primary OM is very slow, leading to the accumulation of undecomposed debris in the organic layers. In soils developed from AMP, both lithology and plant species clearly affected pedogenesis in the surface horizons. Surface acidification occurred in the pine stand (although never as intense as that occurring on GR materials), but greater than that of AMP-E and AMP-O litters. In general, the more eutrophic conditions of the AMP soils, compared with the GR soils, appeared to allow rapid decomposition of primary OM. The geochemical conditions of the AMP Ah horizons also appeared to allow neoformation of metastable forms of gibbsite and different short-range order 1:1 aluminosilicates able to bind to secondary organic compounds. Under such conditions, decomposition of secondary OM was probably preserved, as reflected by the high organic C content of the Ah horizons. All of this may explain the existence of a moder-type OM in the GR soils, in comparison with the Al-mull type form of the AMP soils. Overall, the results obtained indicate that parent material affects the distribution within the soil profiles studied, as well as on its quality and dynamics within the soil profiles studied, whereas the organic C stocks present in the aboveground biomass were more affected by the type of forest species and management.

INTRODUCTION

Organic matter (OM) has multiple effects on soil properties as it is involved in chemical, physical, and biological processes. Loss of OM affects the capacity of soils to sustain crop growth, enhances the risk of soil erosion and decreases soil biodiversity; mineralization of OM contributes negatively to the global climate change by increasing levels of atmospheric CO_2 . Soil OM thus performs many functions vital to life, which explains the importance attached to it in international conventions on Desertification, Biodiversity, and Climate Change. Until the 1970s, increasing levels of atmospheric CO_2 were mainly attributed to agricultural practices, rather than to industrial and transportation activities (Lal, 2001). Currently agricultural practices still represent around 20% of global anthropogenic greenhouse gas emissions, with soils being an important source of the emissions (Lokupitiya & Paustian, 2006). This provides an idea of the magnitude of the organic C losses from agronomic soils (which in soils from Galicia, NW Spain, range between 30 and 50%), and manifests the urgent need to revert this trend and promote soils as a C sink. However, in order to enhance organic C accumulation in soils in a sustainable and efficient way, management

practices that result in the build up of organic C in soils and favour organic C stability must be encouraged. This demands (i) fundamental insights into the mechanisms of organic C stabilization in soils, which are still not well understood, and (ii) advanced knowledge of the ultimate potential of soils to accumulate organic C, which to date is still uncertain (Lützow et al., 2006). In a recent review of the mechanisms that are currently considered to contribute to OM stabilization in temperate soils, Lützow et al. (2006) defined stability as the integrated effect of (i) selective preservation (referred to as the relative accumulation of recalcitrant compounds), (ii) spatial inaccessibility, and (iii) interaction with surfaces and metal ions. The latter authors indicated that the major difficulties encountered in making advances in this area originate from the simultaneous occurrence of different stabilization processes.

The C accounting system to be used during the first commitment period (2008-2012) of the Kyoto Protocol, as described in the Good Practice Guidance for Land Use, Land-Use Change and Forestry (LULUCF) (IPCC, 2003), does not distinguish between OM characteristics, and only total organic C is considered. However, in the guidance, different types of soils are distinguished: (i) soils containing highly active clays, (ii) soils containing poorly active clays, (iii) sandy soils, (iv) spodic soils, (v) volcanic soils, and (vi) wetland soils. Thus, the existence of soils that differ in their ability to stabilize OM is implicitly recognized in the guidance, with the lithology being the most important factor in this type of soil grouping, although other soil forming factors, such as time, climate and drainage conditions, also exert effects. Parent material may directly affect OM stability by (i) surface chemistry and organo-mineral interactions (McKeague et al., 1986; Macías & Chesworth, 1992), which also change, along with mineral evolution, during pedogenesis (Chorover et al., 2004), and (ii) the effect that particle size has on particle aggregation.

Parent material also has an indirect effect on OM stability through the weathering rate and base cation release, which affect soil fertility and reactivity, and through effects on soil drainage and root architecture, all of which, in turn, affect aboveground and belowground biological activity. Thus, the lithology has many, probably concomitant, effects on the different OM stabilization mechanisms. In the present study biogeochemical analyses were carried out (i) to discern the extent to which the type of pedogenesis generated by amphibolite and granite materials in freely drained systems affect the organic C quality and quantity in different forest systems - pine, eucalypt, and oak – grown under the same climatic conditions, and (ii) to elucidate whether this affects the C cycle in these ecosystems.

MATERIALS AND METHODS

Site Description

The sampling sites were in Monte Pedroso and Boqueixon, both of which are close to Santiago de Compostela (A Coruña, Spain). The mean annual air temperature in Santiago de Compostela (altitude 260 m) is 12.3 °C, and total annual precipitation is 1624 mm yr⁻¹. The lithology of Monte Pedroso consists of a granitic massif, and that of Boqueixon of a metabasic amphibolitic massif. The dominant minerals in the former are quartz, microcline, acid plagioclases, muscovite and biotite, whereas in the latter minerals such as amphiboles (mainly hornblende) and plagioclases predominate (Macías et al., 1982). Three forest sites –

each consisting of different species (pine, eucalypt, and oak stands, respectively) - and a crop site, in which corn was cultivated, were studied on each type of parent material. The sampling and the field study were carried out in spring 2006. The three forest soils derived from amphibolite (AMP) rocks (AMP-P, AMP-E, AMP-O) were classified as Typic Fulvudands (Soil Survey Staff, 1999) and Aluandic Andosols (IUSS Working Group WRB, 2006), and the three forest soils derived from granite (GR) rocks (GR-P, GR-E, GR-O) were classified as Humic Dystrudepts (Soil Survey Staff, 1999) and Leptic and Haplic Umbrisols (IUSS Working Group WRB, 2006). The cultivated soils derived from AMP (AMP-C) and GR rocks (GR-C) were classified as Oxic Dystrudept and Humic Dystrudept (Soil Survey Staff, 1999), respectively, and Ferralic Cambisol and Cambic Umbrisol (IUSS Working Group WRB, 2006), respectively (Table 1).

Table 1. Site description

Site code	Site	Parent material	Vegetation	Approx. Trees Age	Soil Taxonomy (1999)	IUSS WRB (2006)	UTM coordinates
AMP-P	Boqueixon	Amphibolite	<i>Pinus pinaster</i> Ait.	35	Lithic Hapludand	Aluandic Andosol	29T 544231 4743446
AMP-E	Boqueixon	Amphibolite	<i>Eucalyptus globulus</i> Labill.	10	Lithic Hapludand	Aluandic Andosol	29T 543605 4745373
AMP-O	Boqueixon	Amphibolite	<i>Quercus robur</i> L.	40	Lithic Hapludand	Aluandic Andosol	29T 544259 4743920
GR-P	Pedroso	Granite	<i>Pinus pinaster</i> Ait.	25	Typic Dystrudept	Leptic Umbrisol	29T 535292 4748760
GR-E	Pedroso	Granite	<i>Eucalyptus globulus</i> Labill.	18	Typic Dystrudept	Leptic Umbrisol	29T 535333 4748224
GR-O	Pedroso	Granite	<i>Quercus robur</i> L.	30	Typic Dystrudept	Haplic Umbrisol	29T 534376 4751691
AMP-C	Boqueixon	Amphibolite	corn	-	Oxic Dystrudept	Ferralic Cambisol	29T 543747 4742070
GR-C	Pedroso	Granite	corn	-	Humic Dystrudept	Cambic Umbrisol	29T 534001 4751582

In the two pine stands (*Pinus pinaster* Ait.) (AMP-P and GR-P) studied, the understory basically consists of *Pteridium aquilinum* (L.), Kuhn and *Ulex* sp., and some ericaceous

species. In the granite site (GR-P), there are also some saplings of *Acacia melanoxylon* R. Br., whereas in the amphibolite site (AMP-P) there are some eucalypts (*Eucalyptus globulus* Labill.), probably because of the presence of eucalypt plantations in the surrounding area. Both eucalypt plantations (AMP-E and GR-E) show a high presence of *Ulex* sp. in their understory. There is a noteworthy presence of *Erica arborea* L. on amphibolites (AMP-E), whereas on granites (GR-E), ferns (*Pteridium aquilinum* L.), *Calluna* sp. and grasses were also present. There is a very dense coppice in the oak stand on amphibolites (AMP-O), and the forest floor is covered with *Hedera helix* L., with no understory. Together with the main species (*Quercus robur* L.) there are other species such as *Betula* sp., *Castanea sativa* Mill. and *Laurus nobilis* L. There are also some *Pinus pinaster* Ait. and eucalypt saplings in the oak stand on granite site (GR-O). The understory mainly consists of *Ulex* sp., heathers (*Calluna* sp; *Erica* sp.), and *Pteridium aquilinum* (L.) Kuhn; *Frangula alnus* Miller is also present.

For the quantification of total organic C present in each forest site, the IPPC Good Practice Guidance for LULUCF (2003) was followed (except for measuring the soil depth). The guidelines define five organic C pools: (i) litter, (ii) SOM, (iii) aboveground biomass, (iv) belowground biomass, and (v) dead wood, which – according to the Marrakech Accords (UNFCCC, 2001) - should all be accounted during the first commitment period (2008-2012) unless a country chooses “not to account for a given pool, if transparent and verifiable information is provided that the pool is not a source.” Thus, for sampling and biomass estimation, the former pools were considered, as described below.

LITTER AND SOIL ORGANIC MATTER

Sampling of Litter and Soil Organic Matter

According to the IPPC guidance, “litter includes all non-living biomass of a diameter less than a minimum diameter chosen by the country (for example 10 cm), in various states of decomposition above the mineral or organic soil.” This includes the layer containing fresh leaves (L), the decaying layer of fragmented leaves (F), and the humified layer (H). In the present study a diameter of 10 cm was chosen. The same guidance defines “soil organic C” as that present “in mineral and organic soils (including peat) to a specified depth chosen by the country and applied consistently through a time series”. The use of a standard depth of soil (e.g., 0-30 cm at Tier 1 level) for all soil types in different land cover uses is proposed. However, in this study soil samples were taken from the lower depth of the Ah horizons, which varied in the forest soils studied from 40 to 50 cm depth (Table 2). The depth of the Ap horizons in the cultivated soils was 25 cm. To estimate the organic C lost due to changes in land use (e.g., forestry to agriculture), comparisons were made on the basis of equal soil mass rather than on the basis of equal depth, as recommended by Ellert & Bettany (1995) and Post et al. (2001).

Table 2. Values of several physicochemical properties of the different litter samples

Hor.	Sample code	Depth (cm)	pH-H ₂ O	pH-ClK	pH-NaF	Al _p	Fe _p	C _p	Al _p /C _p	(Al _p +Fe _p)/C _p
						(g kg ⁻¹)			(mol mol ⁻¹)	
L	AMP-P	6-3	4.70	4.13	6.69					
	AMP-E	6-3	4.83	4.43	6.97					
	AMP-O	6-3	4.83	4.55	6.84					
	GR-P	4-3	3.41	2.77	6.29					
	GR-E	6-3	3.93	3.50	6.19					
	GR-O	6-3	4.41	3.96	6.36					
	AMP†		4.79a	4.37a	6.83a					
	GR†		3.92b	3.41b	6.28b					
F	AMP-P	3-0	4.15	3.42	7.98	18.20	10.54	134.3	0.06	0.08
	AMP-E	3-0	4.91	3.69	7.70	1.88	1.58	64.4	0.01	0.02
	AMP-O	3-0	4.93	4.20	8.41	8.98	6.34	84.9	0.05	0.06
	GR-P	3-0	3.78	2.68	6.30	1.49	1.29	49.0	0.01	0.02
	GR-E	3-0	3.83	2.76	6.39	5.37	3.03	96.5	0.03	0.03
	GR-O	3-0	3.59	2.60	6.44	4.99	4.59	75.3	0.03	0.04
	AMP†		4.66a	3.77a	8.03a	9.68a	6.16a	94.5a	0.04a	0.05a
	GR†		3.73b	2.68b	6.38b	3.95a	2.97a	73.6a	0.02a	0.03a

† Mean values of each variable studied within AMP and GR rows followed by the same letter are not significantly different at the 0.05 level of probability.

At each forest site, soil cores were collected manually from soil pits, and the L and F layers, and the Ah1 and Ah2 horizons were distinguished. For laboratory analyses, a bulk sample was collected by removing approximately 1 kg of soil from each horizon sampled. For bulk density, soil cores of a known volume were collected from each horizon, and the dried soil (48 h at 105°C) was weighed. For microbial analyses, subsamples were stored at <4°C (for approximately 2 wk) until determinations were carried out. For chemical analysis of mineral soil samples, the samples were air-dried, sieved to 2 mm, and stored at room temperature. For chemical determinations of the L and F layers, the corresponding samples were oven-dried at 65° C for 24 h and then stored at room temperature.

General Chemical and Physical Characterization of Litter and Soil Organic Matter

The pH was measured in H₂O and in KCl using a 1:2.5 soil:solution ratio (except for the L and F layers for which a 1:5 soil:solution ratio was used). The pH in NaF at 2 min (Fieldes & Perrot, 1966) was also measured to identify either reactive Al or the presence of free organic acids. Organic C content and total N were analyzed by combustion with a LECO analyzer (Model TruSpec CHN, LECO Corp., St Joseph, MI). Sodium pyrophosphate (Bascomb, 1968) extractable Al, Fe, and C (Al_p, Fe_p, and C_p) were measured in each soil sample. Carbon in the sodium pyrophosphate extract was determined using a spectrophotometer for the UV-vis spectrum (Model UVIKON 930 Kontron Instruments),

whereas Al_p and Fe_p were determined by atomic absorption spectrophotometry (Perkin-Elmer 2380, Norwalk, CT). The major elemental composition of all samples was determined after acid digestion (6:2.5; $HNO_3:HCl$ ratio), except that of Si, which was determined after digestion with a mixture of HNO_3 , HF, and HCl concentrated acids (9:4:1 ratio) and later addition of boric acid to neutralize excess HF. Total Ca, Mg, Al, Si, and Fe were determined by atomic absorption spectrophotometry, Na and K by atomic emission spectrophotometry (Perkin-Elmer 2380, Norwalk, CT). The equilibrium solution was obtained in an aqueous suspension (1:10 soil:solution ratio) that was allowed to equilibrate for three days. Thereafter, pH and electrical conductivity (EC) were measured, and solutions were filtered through a 0.45 μm filter. Dissolved Al was determined by colorimetry with pyrocatechol violet (Dougan & Wilson, 1974). Total F was determined by use of an ion selective electrode with a Methrohm 692 meter (Methrohm Ltd, Herisau, Switzerland) and TISAB II-Orion decomplexing solution. Dissolved Ca, Mg, Al, Si, Fe, Na, NH_4 , and K were determined by ion chromatography (Model Dionex-4500i, Dionex Corp., Sunnyvale, CA), and dissolved organic C (DOC) using a FLOWSYS Third Generation Continuous Flow Analyzer (Systea, Anagni, Italy). Chloride, SO_4 , NO_3 , and PO_4 were determined with the same chromatograph. Species activities were calculated from the chemical data obtained from the equilibrium solution using the Solmineq88 program (Kharaka et al., 1989). A geochemical model of mineral stability was constructed (Chesworth, 2000) for the $SiO_2-Al_2O_3-H_2O$, by making use of the different chemical species used by Chesworth & Macías (2004). Finally, soil texture was determined by laser diffractometry (Model Mastersize 2000 with a high dispersion unit, Hydro MU, Malvern Instruments Ltd., UK).

Chemical and Biological Characterization of the Main Carbon Pools in Litter and Soil Organic Matter

Hot-water extractable C (HWC) was determined in moist field samples of the L layers following the method of Ghani et al. (2003). The extraction consists of a two-sequence step procedure involving the removal of readily soluble C from the litter followed by the extraction of labile components of soil C at 80°C for 16 h. Dissolved organic C in both extracts was determined with a FLOWSYS Third Generation Continuous Flow Analyzer (Systea, Anagni, Italy). Microbial biomass C (C_{mic}) was determined in field moist samples of the L and F layers following the procedure of Vance et al. (1987). Duplicate sub-samples (3 g dry weight) were fumigated with chloroform for 24 h and then extracted with 0.5 M K_2SO_4 for 2 h on an end-over-end shaker. The suspended samples were centrifuged and filtered through Whatman 42 filter paper. Similar sets of non-fumigated samples were extracted in the same way. The amount of total C in the extracts of the fumigated and non-fumigated samples was determined with a spectrophotometer at 445 nm for the UV-vis spectrum (Model UVIKON 930 Kontron Instruments). The C flush values were used as the indicator C_{mic} .

The oxidability of soil organic C by $KMnO_4$ (MnoxC) was determined with 33 mM $KMnO_4$ after 1 h incubation (Tirol-Padre & Ladha, 2004). Samples, each containing the equivalent of 15 mg of organic C (calculated from the known total C content of each layer studied), were added to centrifuge tubes. Twenty five mL of 33 mM $KMnO_4$ were dispensed into each centrifuge tube and the same volume of $KMnO_4$ was also dispensed into empty

centrifuge tubes to serve as blanks. The tubes were capped and covered with aluminium foil before shaking for 1 h on a reciprocal shaker. Samples were centrifuged at $1030 \times g$ for 5 min. Two mL aliquots of KMnO_4 from each sample and blank were transferred into 50-mL volumetric flasks and diluted to the final volume. The absorbance of the samples and blanks was then measured at 565 nm with a UVIKON 930 spectrophotometer (Kontron Instruments, Milan, Italy). The concentration of KMnO_4 in the samples and blanks was determined by use of a standard calibration curve. The amount of MnoxC in the sample was computed considering that C is oxidized from the neutral state (0) to C^{+4} , and that $\text{Mn}^{+7}\text{O}_4^-$ is reduced to Mn^{+4}O_2 (Tirol-Padre & Ladha, 2004; Clapp et al., 2005), and was expressed as the percentage of MnoxC in the total organic C of that fraction ($\text{MnoxC} \times 100/\text{SOC}$).

Basal respiration was measured with a Micro-Oxymax Respirometer (Columbus Instruments, Columbus, OH). The instrument includes gas sensors for continuous measurement of changes in the concentrations of O_2 and CO_2 in the head space of reaction vessels. Each vessel (250 mL volume) was filled with undisturbed field moist samples (20 g for the F layers and Ah horizons, and 10 g for the L layers), and connected to a closed circuit. Basal respiration was measured during 24 h. The metabolic quotient, $q\text{CO}_2$ ($\mu\text{CO}_2\text{-C mg biomass-C h}^{-1}$) was estimated by taking the hourly rate of basal respiration and dividing it by the estimated microbial biomass C. Finally, neutral (NDF) and acid (ADF) detergent fibres and acid detergent lignin (ADL) were determined following the fibre analysis of Van Soest and Robertson (1985). Neutral detergent fibre mainly contains cellulose, hemicellulose, and lignin, whereas ADF contains cellulose and lignin. The ADF fraction was further analyzed to determine the ADL, with 72% (v/v) H_2SO_4 .

Estimation of Aboveground Biomass, Belowground Biomass, and Dead Wood

According to the IPPC Guidance (2003), aboveground biomass is defined as “all living biomass above the soil including stem, stumps, branches, bark, seeds, and foliage”; belowground biomass is defined as “all living biomass of live roots. Fine roots of less than 2 mm diameter (suggested) are often excluded because these often cannot be distinguished empirically from soil organic matter or litter”; finally, dead wood is defined as “all non-living woody biomass not contained in the litter, either standing, lying on the ground, or in the soil”.

The standing biomass was estimated in the selected stands in a randomly located transect, 50 m long and 6 m wide. As the stands are small, this transect was usually large enough to cross the entire stand. A measuring tape was placed on the floor and the diameter at breast height (DBH; 1.3 m) of all standing trees, alive or dead, inside the transect area was measured. The height of at least the three trees with the largest DBH, three trees with the lowest DBH and three trees with average DBH was measured. The height of all trees of different species of the dominant tree and of all standing dead trees (snags) was also measured. Allometric equations developed for the studied species in Spain were used to estimate standing tree biomass (Montero et al., 2005). In the same transect and at both sides of the measuring tape, three randomly selected 2 x 2 m squares were destructively cut to the ground to estimate the understory biomass. The samples were transported to the laboratory, dried at 60°C until constant weight for at least one week and weighed. The biomass present in

the dead wood (> 0.4 cm) lying on the forest floor was estimated by the line intersect sampling protocol (Ringvall & Ståhl, 1999) and the wood volume ($\text{m}^3 \text{ha}^{-1}$) was estimated by equation [1] (Marshall et al 2003) applying the wood densities of the studied species found in the region (Miguel Ángel Balboa, pers. comm). All the dead wood was assumed to be fresh, and therefore of a similar density to that of the live trees.

$$V_i = \frac{\pi^2}{8 \times L} \sum_{j=1}^{m_i} d_{ij}^2 \quad (1)$$

In equation [1], V is the wood volume, d the diameter of the piece of dead wood intersecting the transect, and L the transect length. Finally, belowground biomass was calculated taking into account the default values given by the IPCC (2003), which vary depending on type of species and aboveground biomass.

RESULTS AND DISCUSSION

Litter

Chemical Characterization of Litter

The mean pH-H₂O values of the AMP L and F layers were significantly higher ($P < 0.05$) than the corresponding means of the GR L and F layers (L layers: 4.79 compared with 3.92, and F layers: 4.66 compared with 3.73, respectively) (Table 2); those of the AMP organic layers were in the pH range of acid-hydrolysis and were thus mainly controlled by dissolved CO₂, and those of organic GR layers were in the pH range of acid-complexolysis, whereby a combination of acid hydrolysis and complexolysis takes place (Pedro & Sieffermann, 1979), and is thus mainly controlled by free organic acids. The pH-NaF values should indicate, to a certain extent, the presence of free organic acids in the system. The aim of this test is mainly to identify reactive Al surface, in the presence of which the F anion should react and release OH⁻ to the solution (Mizota & Wada, 1980), causing an increase in the solution pH from its initial value of ~7.8. However, when organic acids are abundant, they may cause a decrease in the initial pH of the solution, even in the presence of reactive Al (Perrot et al., 1976), and thus this measure is a qualitative indicator of the presence of free organic acids when the pH of the soil suspension in NaF is lower than that of the NaF solution. Mean pH-NaF values of the L and F layers of the AMP soils were significantly higher ($P < 0.05$) than those of the L and F layers of the GR soils (L layers: 6.83 compared with 6.28; F layers: 8.03 compared with 6.38, respectively) (Table 2), thus confirming the greater presence of free organic acids in the GR systems. In a study of the same GR and AMP forest systems, Camps Arbostain et al. (2003) detected free organic acids, such as oxalic acid, in the GR Ah1 horizons, at pH-H₂O values < 4.4, although not in AMP Ah1 horizons, all of which had pH-H₂O values > 4.4.

Table 3. Values of pH and EC of the solutions after they were allowed to equilibrate for three days, and values of ionic strength, $\log(a\text{Al}^{3+}/a\text{H}^3)$, pSiO_4H_4 , and pSO_4 , estimated by the Solmineq88 program (Kharaka et al., 1989)

	Layer/ horiz.	pH	EC	Al	Ionic strength ($\times 10^{-4}$)	Log ($a\text{Al}^{3+}/a\text{H}^3$)	pSiO_4H_4	pSO_4	Termo-dynamic groups [†]
			$\mu\text{S cm}^{-1}$	mg L^{-1}					
AMP-P	L	4.5	234	0.17	1	7.5	3.7	3.5	II
	F	4.6	105	1.31	6	8.9	4.0	4.2	III
	Ah1	4.5	43	0.13	3	7.7	4.0	4.2	II
	Ah2	4.5	56	0.22	4	8.1	4.1	3.9	II
AMP-E	L	4.8	329	0.26	25	8.7	4.0	3.2	III
	F	5.3	98	0.98	4	10.5	4.7	4.4	IV
	Ah1	5.1	36	0.49	2	9.7	4.2	4.4	IV
	Ah2	5.6	38	0.28	2	10.3	4.3	4.3	IV
AMP-O	L	5.0	345	0.34	20	9.4	3.7	5.0	IV
	F	5.7	120	1.03	5	11.1	4.0	4.3	IV
	Ah1	4.6	28	0.32	2	8.6	4.3	4.4	III
	Ah2	5.4	26	0.11	2	9.6	4.3	4.3	IV
GR-P	L	4.2	154	0.17	4	6.5	4.1	4.1	I
	F	4.1	100	0.09	5	5.9	4.0	4.3	I
	Ah1	4.5	24	0.51	2	8.5	4.7	4.5	III
	Ah2	4.8	15	0.15	1	8.7	4.7	4.6	III
GR-E	L	4.3	233	0.17	20	6.9	4.0	4.3	II
	F	4.5	79	0.07	3	6.7	3.7	4.6	II
	Ah1	4.8	17	0.26	1	9.0	4.5	4.6	III
	Ah2	4.8	14	0.13	1	8.5	4.5	4.5	III
GR-O	L	4.5	543	0.18	20	7.7	3.5	3.9	II
	F	4.2	104	0.47	4	7.7	4.0	4.5	II
	Ah1	4.7	19	0.24	1	8.7	4.5	4.6	III
	Ah2	5.1	19	0.14	1	9.2	4.5	4.5	III

[†] Group I: None of the minerals is stable. Concentration of Al controlled by organo-Al complexes. Strong acid-complexolysis.

Group II: Kaolinite stable, gibbsite unstable. Concentration of Al controlled by organo-Al complexes and kaolinite. Moderate acid-complexolysis.

Group III: Kaolinite stable, gibbsite saturation. Concentration of Al by gibbsite of different degrees of crystallinities. Acidolysis.

Group IV: Kaolinite stable, gibbsite and allophane saturation. Concentration of Al controlled by microcrystalline gibbsite. Andic character. Moderate acidolysis.

The solution equilibrium data (Figure 1) indicates that the L and F layers of the soils studied corresponded to three out of the four situations encountered. The L and F layers of the GR soils under pine were included in group I, which corresponds to a highly acidic system, in which there is no stable mineral, except quartz. The pH of both equilibrium systems was ≤ 4.2 (Table 3), concentrations of organic acids were high (as estimated from the pH-NaF values) (Table 2), and the Al saturation was very low ($\log(\text{Al}^{3+} + 3\text{pH}) \leq 6.5$) (Figure 1; Table 4), i.e.

considerably lower than that needed for the stability of either kaolinite or gibbsite. Under these conditions neither pedogenic Al hydroxides nor Al silicates are thermodynamically stable (Skylberg, 2001) and Al solubility is likely to be controlled by complexation with OM (Gustafsson et al., 2001).

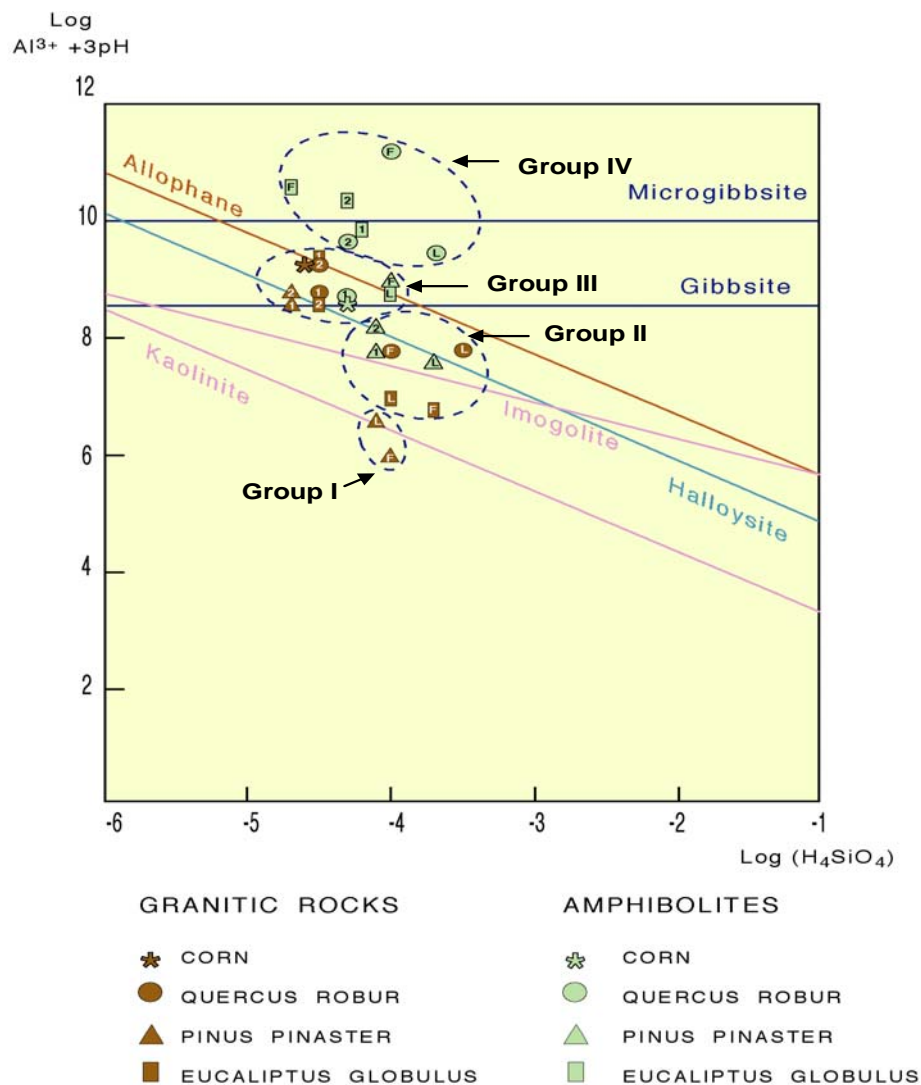


Figure 1. Soil solution equilibrium data for the SiO_2 - Al_2O_3 - H_2O system. Group I: None of the minerals is stable. Concentration of Al controlled by organo-Al complexes. Strong acid-complexolysis. Group II: Kaolinite stable, gibbsite unstable. Concentration of Al controlled by organo-Al complexes and kaolinite. Moderate acid-complexolysis. Group III: Kaolinite stable, gibbsite saturation. Concentration of Al by gibbsite of different degrees of crystallinities. Acidolysis. Group IV: Kaolinite stable, gibbsite and allophane saturation. Concentration of Al controlled by microcrystalline gibbsite. Andic character. Moderate acidolysis.

The L and F layers of the other two GR soils (under eucalypt and under oak stands), together with the L layer of the AMP-P soil, were all included in the second group of samples – group II - (Figure 1), which also corresponds to a very acidic system with an important presence of free organic acids (as estimated from the pH-NaF values; Table 2), but with some mineral saturation and with kaolinite as the most thermodynamically stable mineral, occurring along with metastable forms of short-range ordered 1:1 aluminosilicates, such as imogolite and halloysite, in some samples. The saturation index of Al ranged between 6.5 and 7.7 (Figure 1; Table 3), and was thus below the saturation index of gibbsite. Taking into account that kaolinite crystallizes very slowly, mineral neoformation should be practically negligible under the present conditions and, therefore, Al mainly forms bonds with organic acids.

Finally, the L and F layers of the other AMP soils (under eucalypt and under oak) were included in the third and fourth groups of soils. In group III, the Al saturation index ranges between 8.2 and 9.0, indicating that the system is evolving towards the formation of kaolinite, although metastable forms, such as gibbsite, halloysite, and imogolite (Figure 1), and boehmite and alunite (not shown) may also exist. In group IV, the saturation index is so high (> 9.0) that the solutions are even oversaturated with allophanic compounds (Figure 1).

Independently of the groups identified, none of the Al_p/C_p nor $(Al_p + Fe_p)/C_p$ ratios in any of the organic layers studied were >0.1 (Table 2). On the basis of the amount of functional groups of humic substances, the maximum capacity of the OM to complex metals is indicated by a metal/C molar ratio (in the pyrophosphate extract) of between 0.1 and 0.2 (Higashi et al., 1981; Higashi, 1983; Dahlgren et al., 1993), although the critical ratio is dependent on pH (Buurman, 1985). The results therefore indicate that, independently of whether there was a stable mineral phase or not, in all cases, the OM of the litter samples was undersaturated with metals.

The higher acidity of the GR systems, in relation to the AMP systems, is mainly attributed to (i) the elemental composition of the parent materials (the former is poorer in bases and, thus, more acidic), (ii) the weatherability of the materials, as the GR rock is less weatherable than the AMP material, and (iii) the fact that soils developed from GR rock studied here are excessively well drained, implying that the percolating water has little time to interact with the mineral phase and therefore to allow the formation of secondary aluminosilicates (Macías & Chesworth, 1992). The effect the elemental composition of the parent material on that of litter and Ah horizons is clearly shown in the concentrations of CaO of these reservoirs (Figure 2). Concentrations of CaO in the litter were significantly lower ($P < 0.05$) in the GR soils than in the AMP soils (L layers: 5.6 compared with 14.5 g kg⁻¹, and F layers: 0.8 compared with 7.6 g kg⁻¹, respectively) (Figure 2A-B). Moreover, CaO contents were always greater in the L than in the F layers and Ah horizons (Figure 2). This was attributed to the effect of the biotic pump produced by forest stands; the concentration effect of base cations in the L layers can also be observed in the Chesworth diagram (Figure 3) (Chesworth, 1973), with percentages of CaO and MgO in the L layer being even greater than those of the fresh (AMP-FR, GR-FR) and weathering materials (AMP-WR, GR-WR) (Figure 3). This was not only due to an increase in the absolute concentration of bases (Figure 2), but also to the low mobility of Fe, Si, and Al in relation to that of Ca, Mg and K. In contrast, the concentration effect of base cations in the F layers was almost negligible (Figure 2 and 3), with values falling close to those of the Ah horizons (Figure 3), and all very close to the area typical of the “residual system” described by Chesworth (1973). This effect was independent of lithology, although the effect of concentration of Ca in the litter relative to that

in the Ah horizons was more evident in the L layers of the GR soils than in the AMP soils (Figure 2), despite the higher concentrations of Ca in the latter (Figure 2; Figure 3).

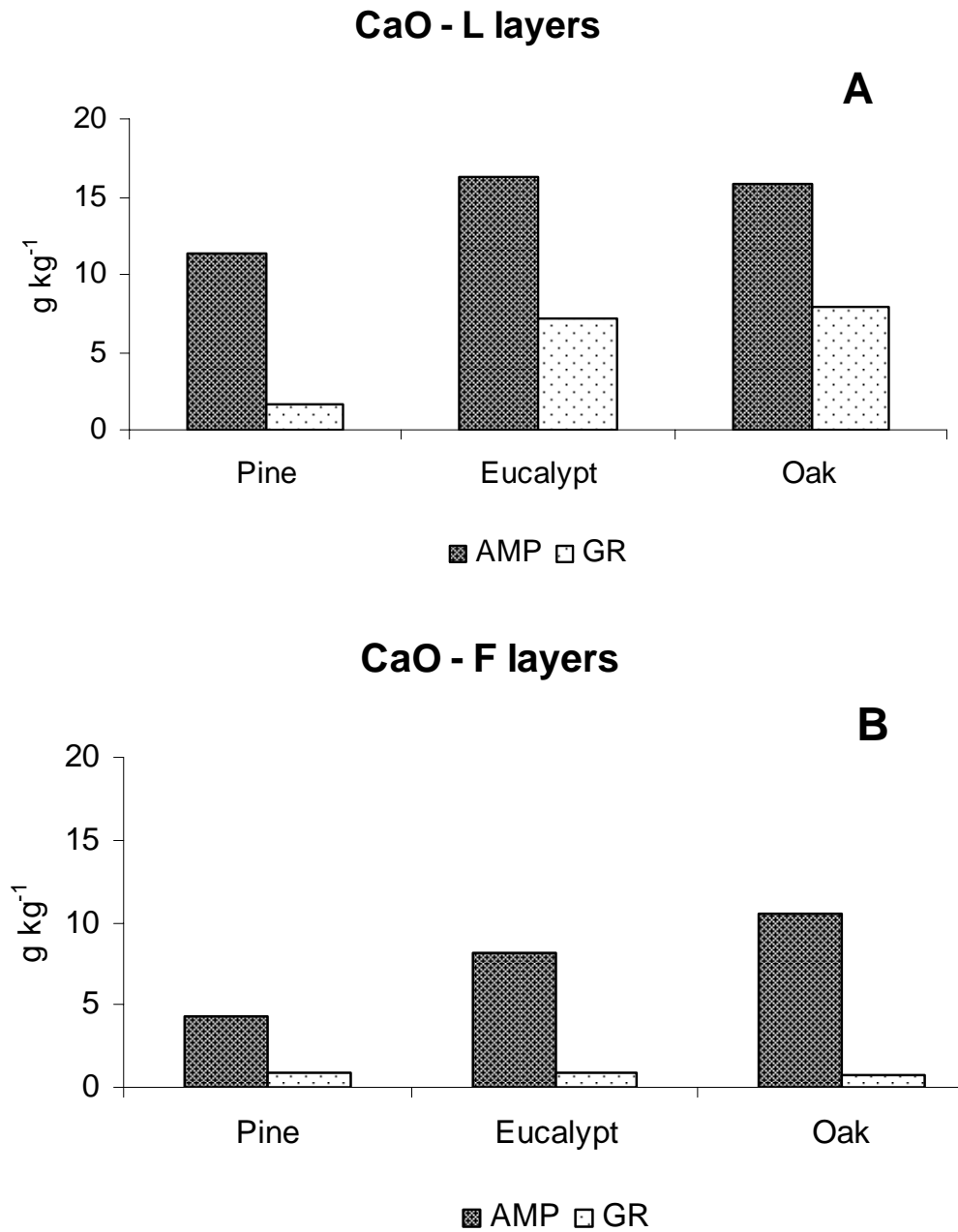


Figure 2. (Continued)

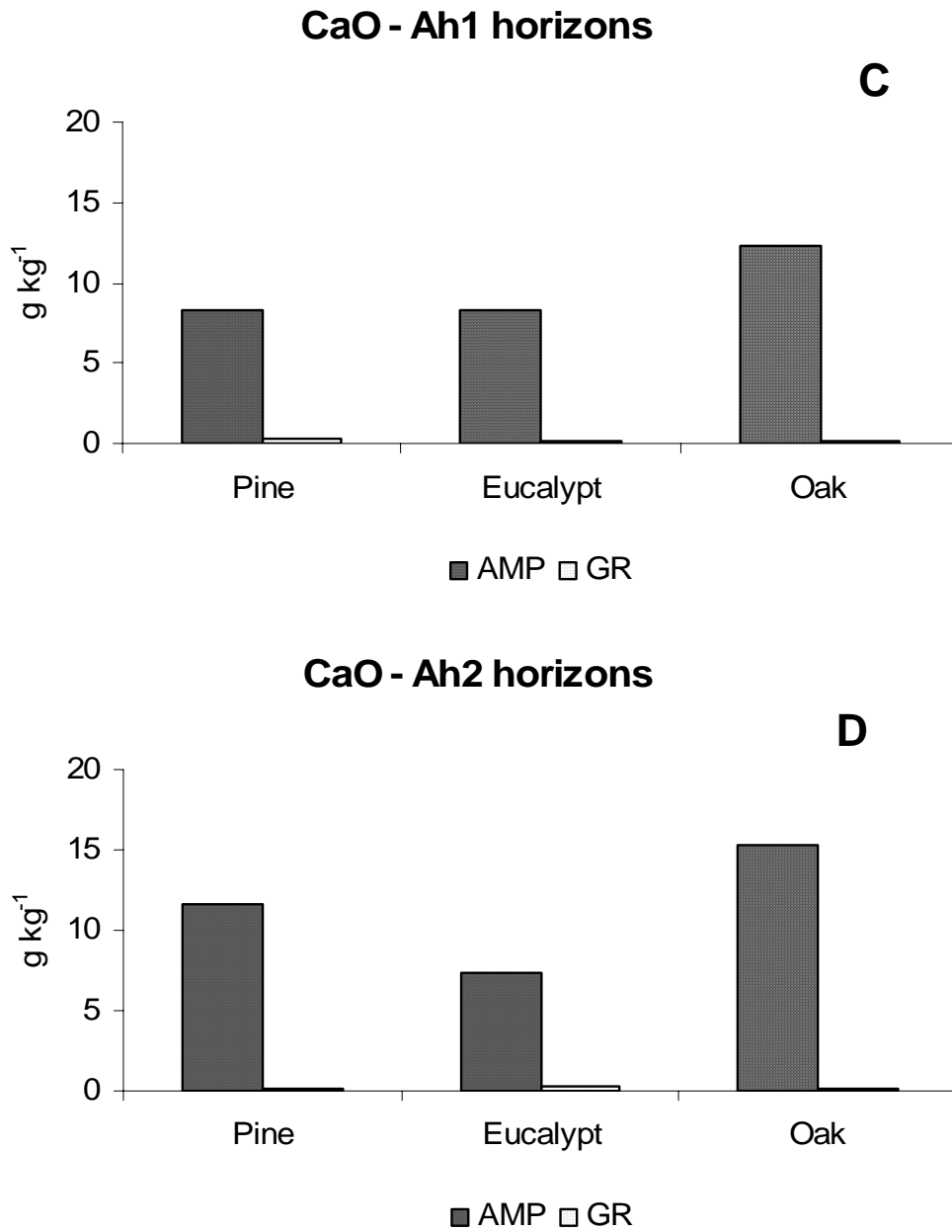


Figure 2. Mean concentrations of CaO in the L (a) and F (b) layers and Ah1 (c) and Ah2 (d) horizons, grouped by the different forest stands studied.

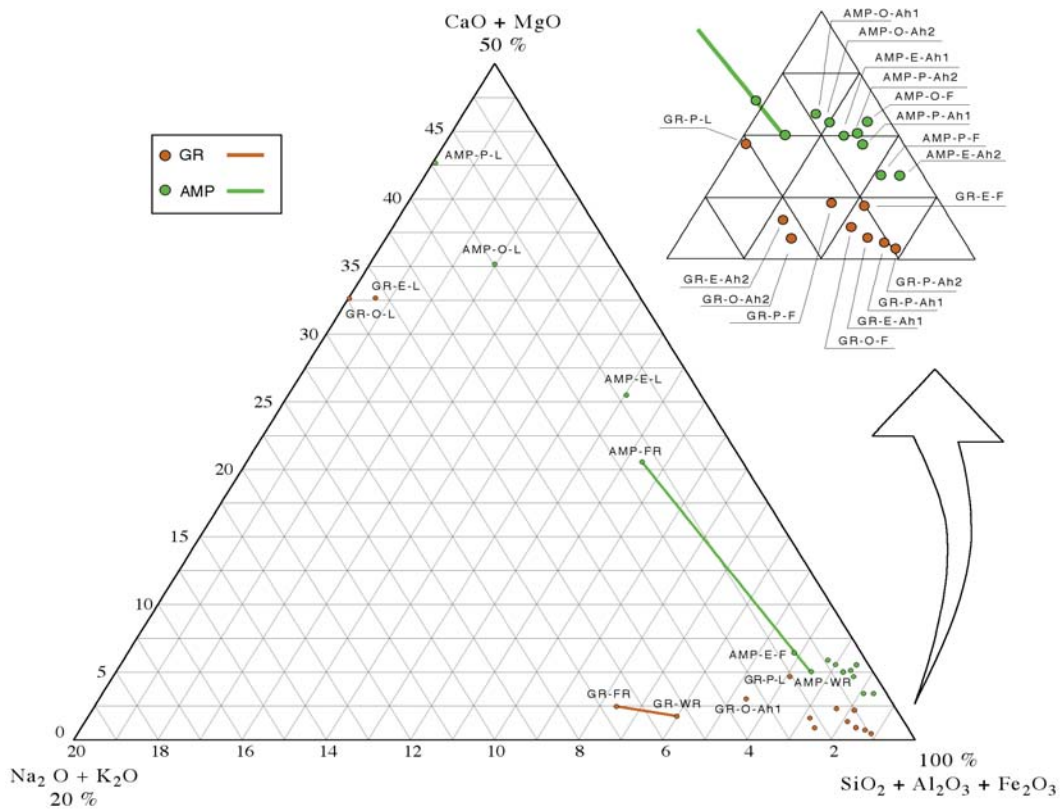


Figure 3. Chesworth diagram of the samples studied.

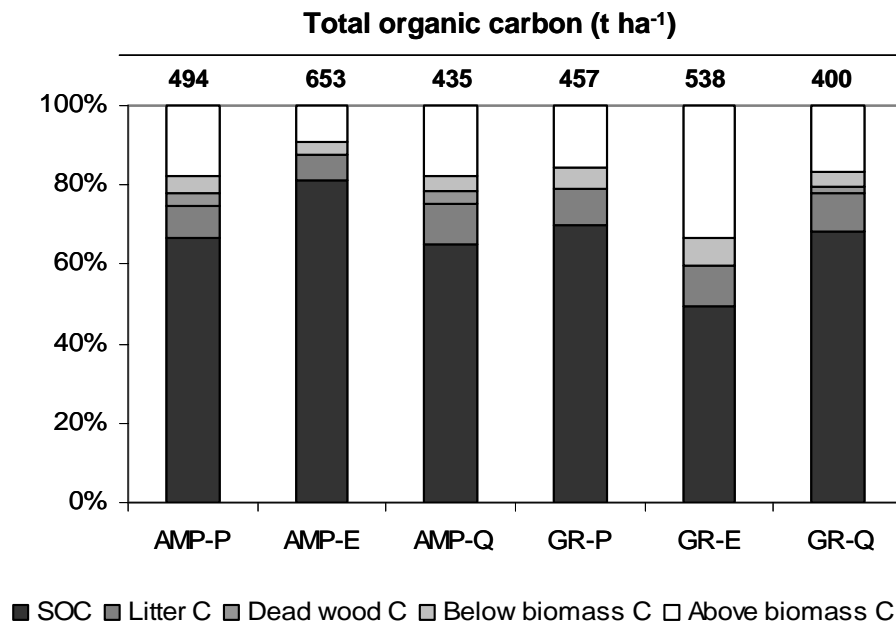


Figure 4. Percentage distribution of total organic C in the different pools identified within each forest ecosystem.

In summary, conditions in the GR litter systems, especially under pine and eucalypt, are dystrophic, whereas in the AMP litter systems they are more eutrophic. Acid-complexolysis dominates in the former systems, with the presence of strongly complexing organic acids (Camps Arbestain et al., 2003), which lead to the destruction of all minerals, except quartz. Under these conditions, organic acidity and complexing ability dominate in the systems, in contrast with the AMP litter systems, especially in the F layers under eucalypt and oak, which are governed by CO₂-acidity. All this may affect the characteristics of OM and the microbial activity in these soils, as will be discussed in the following section.

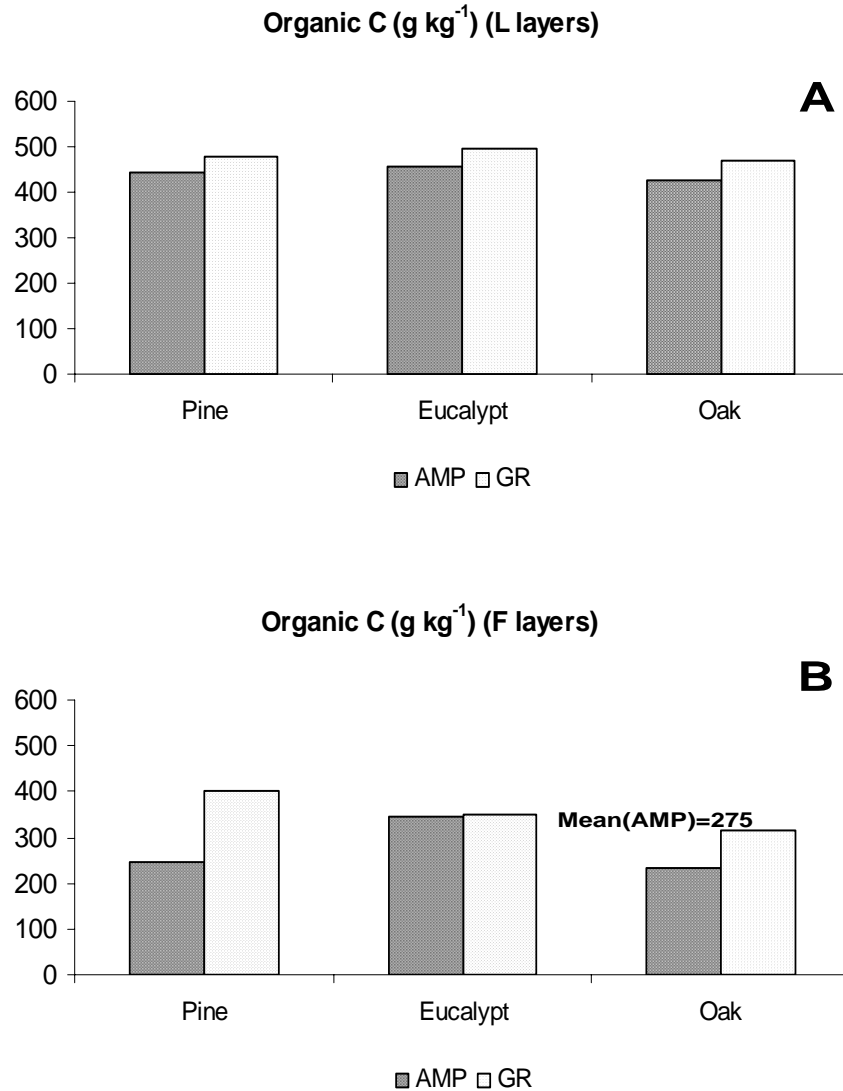


Figure 5. Continued on next page.

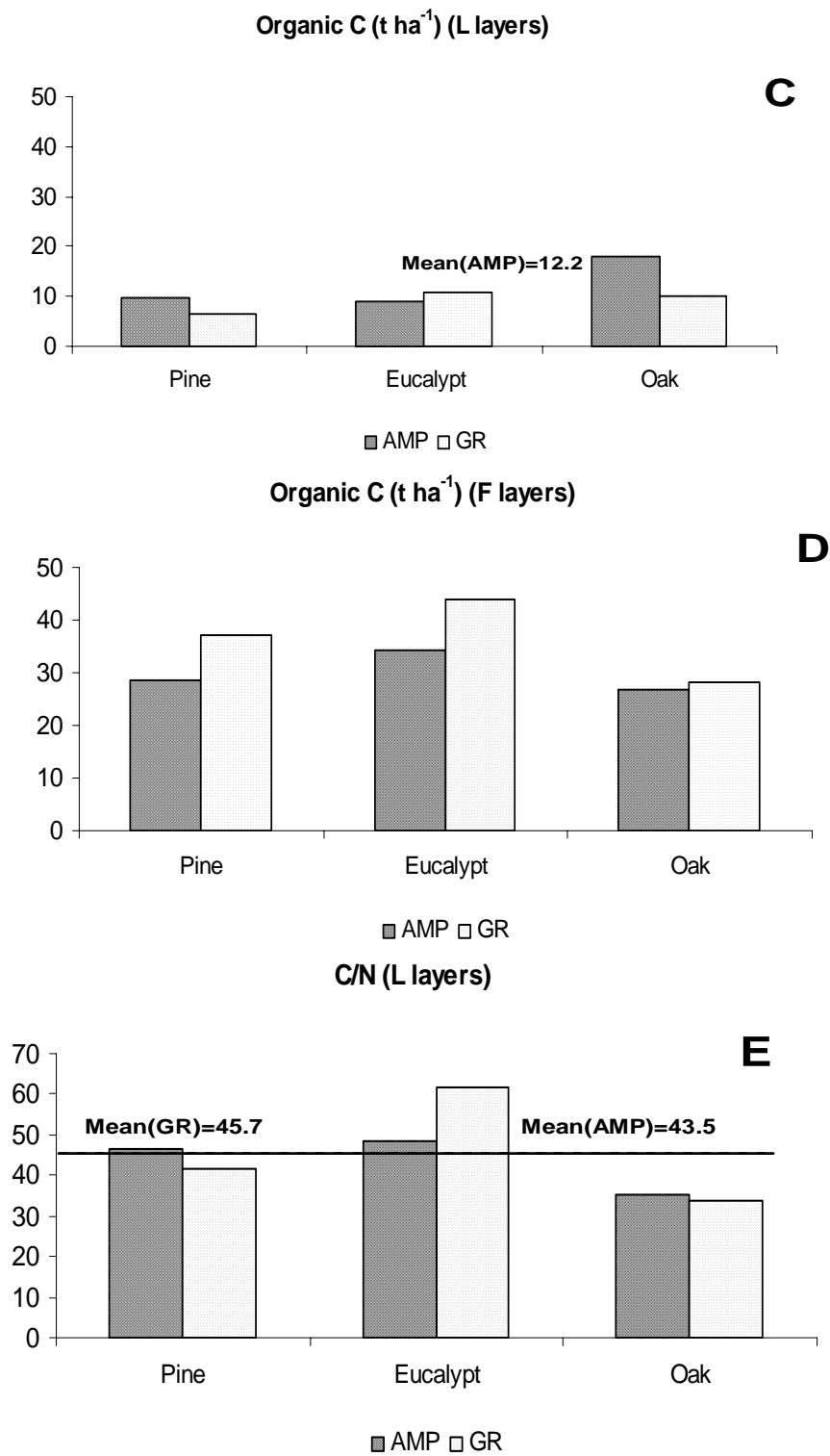


Figure 5. (Continued)

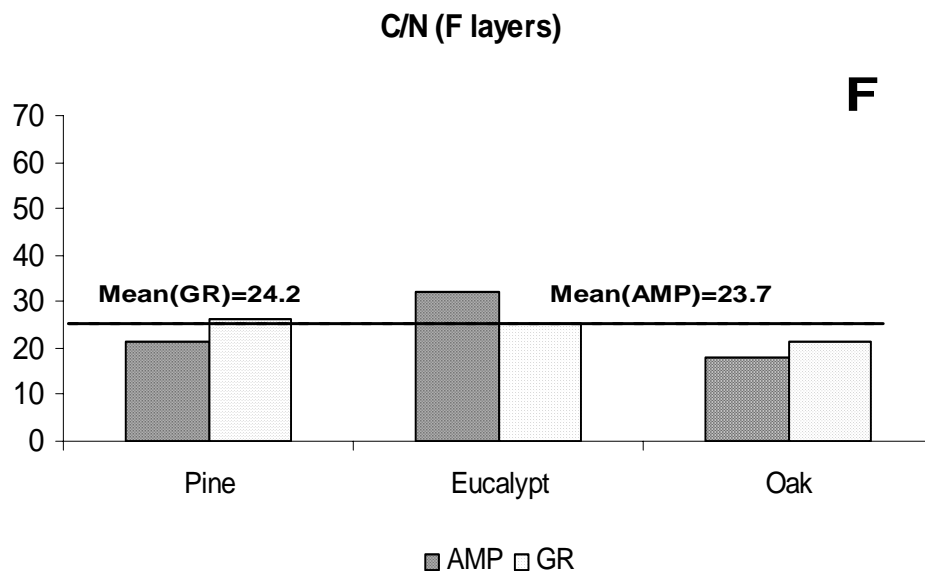


Figure 5. Organic C concentrations (a and b) and contents (c and d), and C/N ratios (e and f) of the L and F layers, grouped by the different forest stands studied.

Characterization of the Organic C Pools in Litter

In the present study, the presence of organic C in the litter (L and F layers) accounted for 7-10% of total organic C of the ecosystem, down to the lowest limit of the Ah horizons (Figure 4), as calculated from estimations of organic C stocks for each of the reservoirs per unit of surface (t ha^{-1}). The concentration of total organic C in the L and F layers was always higher (significantly different at $P < 0.01$ and 0.10 , respectively) in the GR than in the AMP soils (Figure 5A-B), with mean values of 481 and 354 g C kg^{-1} for the L and F layers of the GR soils, respectively, and 441 and 275 for the L and F layers of the AMP soils, respectively. When the total amounts of organic C of these horizons were considered rather than concentrations, the same trend was observed in the F layers (Figure 5D) (means: 36.5 and 29.9 t C ha^{-1} , for the GR and AMP soils, respectively), but not in the L layers (Figure 5C) (means: 9.1 and 12.2 t C ha^{-1} , for the GR and AMP soils, respectively), mainly because the amount of organic debris present at the surface differed widely among soil profiles (Table 2; L layers depths).

As far as litter composition is concerned, there were no significant differences (at $P < 0.10$) between the ADF values (assumed to estimate cellulose + lignin) of the two groups of soils, with means of 64 and 61% , for the GR and AMP soils, respectively (Table 4). In contrast, the NDF values, which were assumed to estimate cellulose + hemicellulose + lignin, and the ADL values, which were assumed to estimate lignin, were consistently higher in the GR soils than in the AMP soils (means NDF: 69 and 61% ; means ADL: 40 and 37% for the GR and AMP soils, respectively), especially in the oak and pine stands. Moreover, the NDF-ADF values, which were assumed to estimate hemicellulose, were significantly higher ($P < 0.05$) in the GR than in the AMP soils (means: 4.5 and 0.4% , respectively). The results obtained thus suggest that decomposition of litter is probably faster in the AMP soils than in the GR soils, because of the existence of less dystrophic and less acidic conditions of the

former, thereby leading to a lower concentration organic C and lower presence of fresh plant tissue components in the decomposing organic debris. Acceleration of litter decomposition was observed when the Ca concentration and pH of acidic forest soils was increased by the addition of lime, thereby decreasing Al toxicity (Bauhus et al., 2004). The latter authors noted that, with this practice, a moder humus of an acid forest soil turned into a mull-moder type humus.

The mean percentages of MnoxC/SOC in the L and F layers were significantly higher ($P < 0.10$) in the GR soils than in the AMP soils (L layers: 14.1 compared with 12.4%; F layers: 16.5 compared with 14.7%, respectively) (Figure 6A-B), which may indicate the presence of a less decomposed OM - and therefore more oxidizable OM - in the litter of the GR soils than in that of the AMP soils, in agreement with the results discussed above. This method has been shown to be particularly sensitive to the presence of lignin and lignin-like compounds (Loginow et al., 1987; Tirol-Padre & Ladha, 2004; Skjemstad et al., 2006), which are also more abundant in the GR litter. Moreover, the mean percentages of MnoxC/SOC in the L layers (Figure 6A) were significantly lower ($P < 0.05$) than in the F layers (Figure 6B) (means: 13.2 compared with 15.6%, respectively). These results were somewhat unexpected, as litter is assumed to be less decomposed in the L layers than in the F layers, and thus, the former should be more susceptible to being oxidized. However, the results obtained may be explained by the fact that part of the oxidizable C present in the L layers may be still protected by the plant architecture (e.g., cellulose within lignin). In any case, it should be remembered that the rate and extent of OM oxidation with KMnO_4 is governed by characteristics such as functional groups, stereochemistry and solubility, with anionic forms generally being more readily oxidized than neutral and cationic forms (Clapp et al., 2005). More research is needed in this area to discern the reasons behind the patterns observed in these samples.

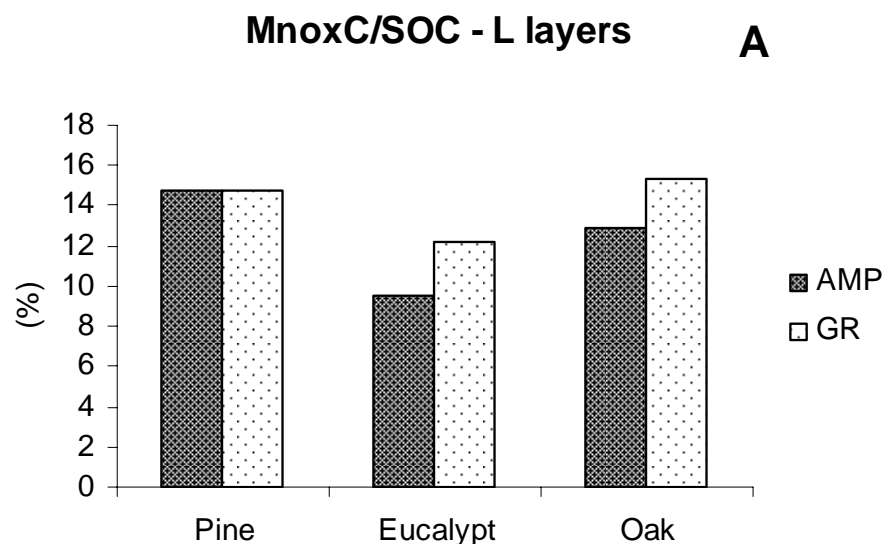


Figure 6. (Continued)

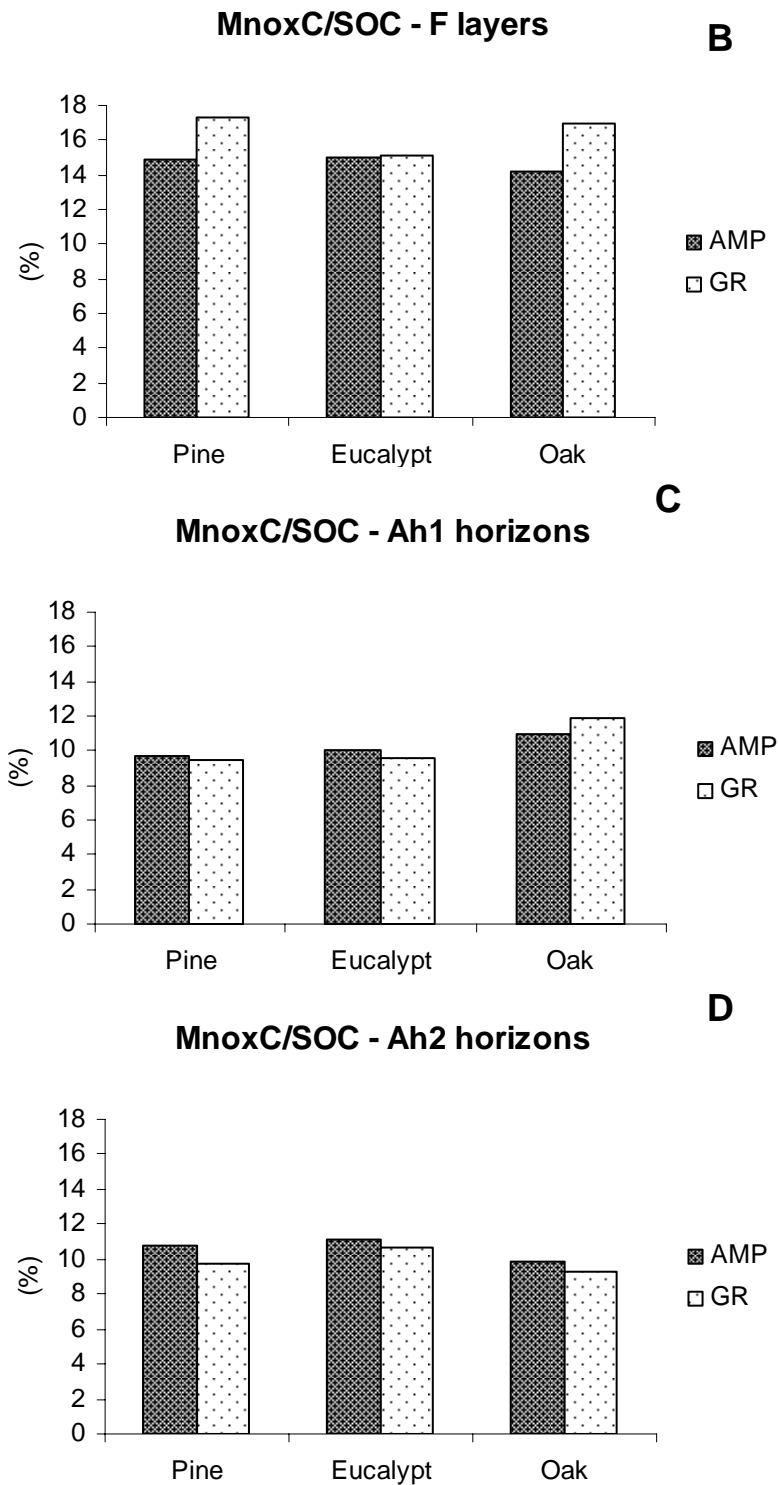


Figure 6. Percentages of MnoxC/SOC in the L (a) and F (b) layers and Ah1 (c) and Ah2 (d) horizons, grouped by the different forest stands under study.

The hot-water extractable C (HWC) of the L layers was also determined. Ghani et al. (2003) proposed this extraction as a means of estimating the fraction of the labile soil OM that is closely related to C_{mic} , as well as to soluble soil carbohydrates and mineralizable N. However, in the present study, C_{mic} was not significantly correlated with HWC at $P < 0.05$ (Table 4), although a positive correlation was observed ($r = 0.69$); the sample with the highest C_{mic} , AMP-O ($10.1 \text{ g } C_{mic} \text{ kg}^{-1}$) was also that with the highest HWC ($26.0 \text{ g HWC kg}^{-1}$). Litter under pine stand had the lowest HWC in both sites (GR and AMP), thus indicating a forest species effect, whereas no clear relationship was found between HWC and type of parent material (Table 4), as expected. Values of C_{mic} ranged between 3.4 and $10.1 \text{ mg } C_{mic} \text{ g}^{-1}$ soil in the L layers, and between 1.8 and $5.2 \text{ mg } C_{mic} \text{ g}^{-1}$ soil in the F layers (Table 3), which represents between 0.7 and 2.4% of the organic C in the L layers, and between 0.5 and 1.7% in the F layers (i.e., C_{mic} -to- C_{org} percentages). No clear effects of parent material were observed in either C_{mic} or C_{mic} -to- C_{org} (%) (Table 4).

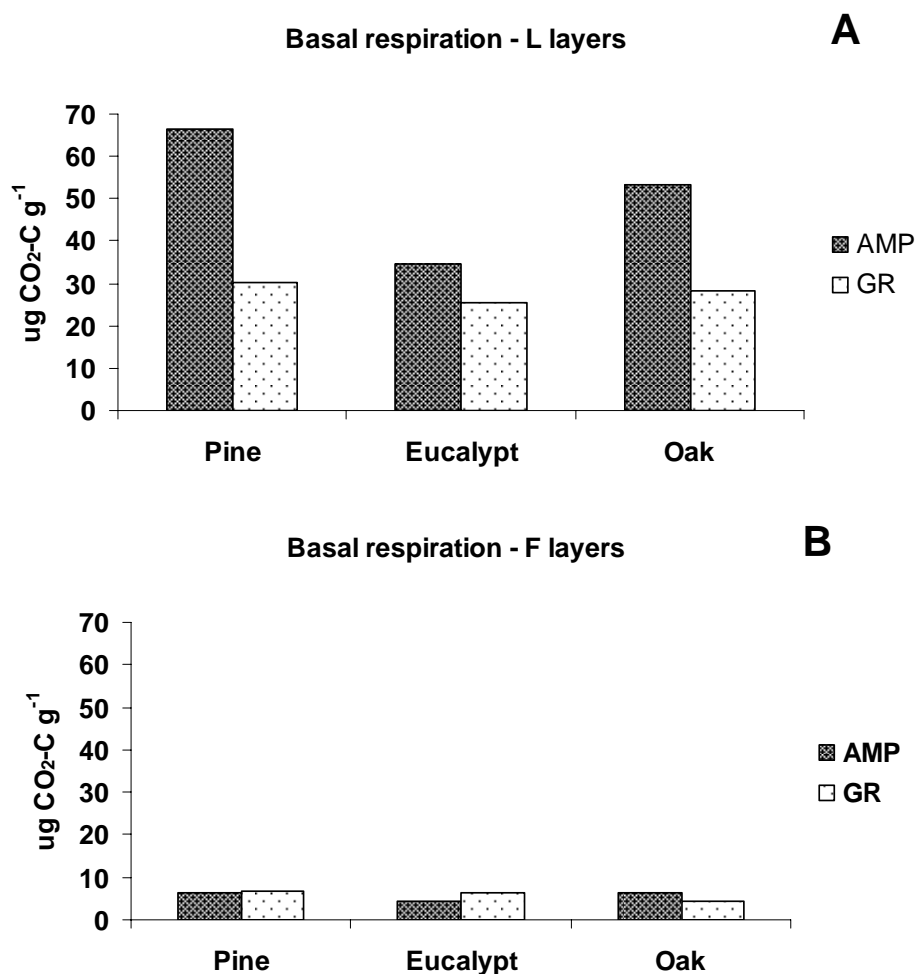


Figure 7. (Continued)

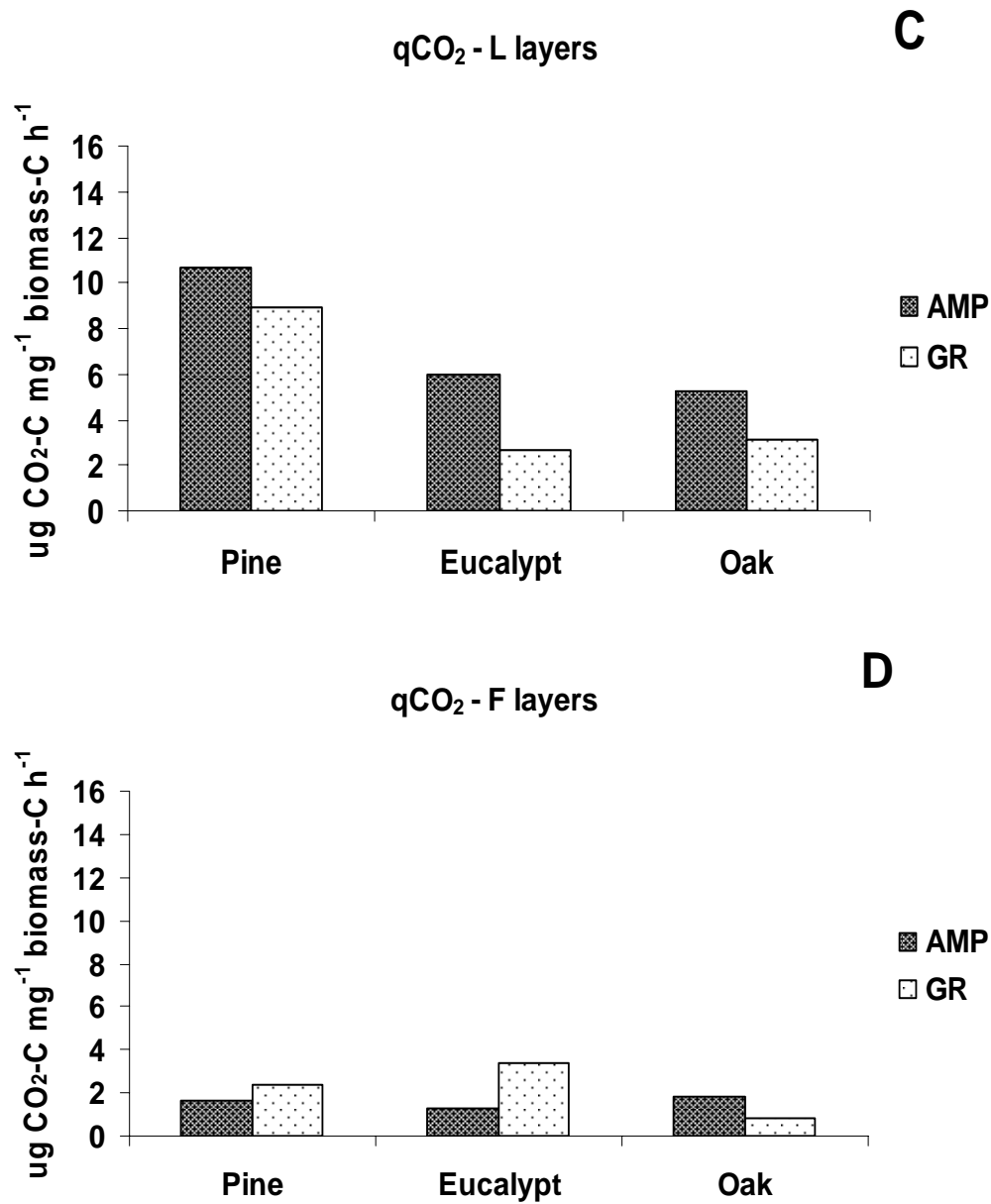


Figure 7. Basal respiration (a and b) and metabolic quotient (c and d) of the L and F layers, grouped by the different forest stands under study.

Basal respiration in the AMP L layers was significantly higher ($P < 0.05$) than in the GR L layers (means: 51.5 compared with 28.0 $\mu\text{g CO}_2\text{-C g}^{-1} \text{h}^{-1}$, respectively) (Figure 7A), whereas no clear pattern was observed in the F layers (Figure 7B) (means: 5.6 and 5.8 $\mu\text{g CO}_2\text{-C g}^{-1} \text{h}^{-1}$, respectively). Moreover, plant species did not have a clear effect on basal respiration, which is consistent with the findings of Raich & Tufekcioglu (2000), i.e., that vegetation type had relatively little effect on soil respiration rates. When basal respiration was reported per unit of

biomass, i.e. the specific respiration of the biomass, qCO_2 ($\mu g CO_2-C mg^{-1} biomass-C h^{-1}$) (Figure 7C-D), mean values of the AMP L layers were again significantly higher ($P < 0.05$) than those of the GR L layers (means: 7.3 compared with 4.9 $\mu g CO_2-C mg^{-1} biomass-C h^{-1}$, respectively) (Figure 7C), and no clear pattern was observed in the F layers (means: 1.6 compared with 2.2 $\mu g CO_2-C mg^{-1} biomass-C h^{-1}$, respectively) (Figure 7D). Blagodotskaya & Anderson (1998) observed a higher qCO_2 in soils of low pH than in neutral soil, in contrast to the present results. However, the pH range in the present study was probably not wide enough to allow detection of the same patterns as observed by these authors. In the present study, species had an effect on qCO_2 in both organic horizons as, in the L layers, the mean qCO_2 of pine soils (9.8 $\mu g CO_2-C mg^{-1} biomass-C h^{-1}$) was more than twice that in eucalypts and oak soils (4.3 and 4.2 $\mu g CO_2-C mg^{-1} biomass-C h^{-1}$, respectively) (Figure 7C). Moreover, in the F layers, this pattern was also observed for the GR samples (Figure 7D). Therefore, oak, which was the native forest stand in the area, generally had the lowest qCO_2 values (Figure 7C-D) and the lowest C/N ratio of the litter samples studied (Figure 5E-F). Blagodotskaya & Anderson (1998) compared acid soils under conifer stands (spruce) and deciduous stands (beech) and observed a higher qCO_2 in the former, as in the present results. Moreover, Wardle (1993) and Wardle et al. (1995) indicated that despite the general trend of decreasing qCO_2 throughout litter decomposition, a significant increase could eventually occur in types litter resistant to decomposition, which could be the case with pine. Wardle & Ghani (1995) suggested that factors able to increase values of qCO_2 during ecosystem development are (i) stress (e.g., pH), and (ii) disturbance, either of which could explain the higher qCO_2 in pine and eucalypt plantations than in oak forest.

Thus, in summary, the effect of parent material on the characteristics of the organic matter of the litter samples was mainly observed in the concentration of total organic C, oxidability, basal respiration, and the metabolic quotient (qCO_2). Overall, it appears that the higher acidity and dystrophication observed in the GR litter than in the AMP litter slowed down the microbial decomposition of the organic debris, explaining the higher concentration of total organic C and oxidability by $KMnO_4$ of the litter present in the GR materials than in the AMP soils, as well as the lower basal respiration and metabolic quotient of the former. On the other hand, the effect of the forest species on the characteristics of the OM of the litter samples was mainly observed in the C/N ratio and in the qCO_2 , and the behaviour of the oak litter generally differed from that of the other two species. The more aggressive forest management of the pine and eucalypt stands (greater disturbance), together with the greater recalcitrance and acidity of the pine litter (greater stress), may explain the differences observed in the qCO_2 among the three forest species studied, although more research is needed to confirm this.

Table 4. Estimated composition of litter using different extractants. AMP = amphibolite and GR =granite

Litter layers	Forest species	Acid detergent fibre		Neutral detergent fibre		Acid detergent lignin		DOC [†]		Water-soluble C		Hot water-soluble C		Microbial biomass C		C _{mic} -to-C _{org}	
		AMP	GR	AMP	GR	AMP	GR	AMP	GR	AMP	GR	AMP	GR	AMP	GR	AMP	GR
		%DM		%DM		%DM		µg C g ⁻¹ litter		µg C g ⁻¹ litter		µg C g ⁻¹ litter		µg biomass C g ⁻¹ litter		%	
L	Pine	62	70	62	76	36	43	1752	1912	6409	14965	10990	16119	6252	3397	1.41	0.71
	Eucalyptus	63	62	63	64	38	38	1158	2680	11306	25251	17300	23007	5830	9622	1.28	1.94
	Oak	58	61	59	66	37	39	1822	1670	32543	17127	26010	17337	10109	9014	2.38	1.92
	Mean‡	61a	64a	61a	69a	37a	40a	1577a	2087a	16752a	19113a	19100a	18821a	7397a	7344a	1.69a	1.52a
F	Pine	-	-	-	-	-	-	934	693	-	-	-	-	3844	2842	1.57	0.71
	Eucalyptus	-	-	-	-	-	-	700	568	-	-	-	-	3236	1847	0.94	0.53
	Oak	-	-	-	-	-	-	706	888	-	-	-	-	3496	5227	1.50	1.67
Mean‡								780a	716a					3305a	3525a	1.33a	0.97a

[†] Dissolved organic C determined in a 1:10 litter:water mixture equilibrated for three days .

[‡] Mean values of each variable studied within AMP and GR rows followed by the same letter are not significantly different at the 0.05 level of probability.

Table 5. Values of several physicochemical properties of the different Ah samples

Hor.	Sample code	Depth	pH-H ₂ O	pH-ClK	pH-NaF	Al _p	Fe _p	C _p	Al _p /C _p	(Al _p +Fe _p)/C _p	Coarse sand	Fine sand	Silt	Clay	Texture †	Moisture content‡	Bulk density
		(cm)				(g kg ⁻¹)			(mol mol ⁻¹)		(%)					(%)	g cm ⁻³
Ah1	AMP-P	0-25	4.92	4.12	11.50	27.66	11.90	83.3	0.15	0.18	4.3	19.2	66.7	9.8	si-l	37.8	0.75
	AMP-E	0-25	4.94	4.13	11.42	29.34	10.74	102.1	0.13	0.15	5.3	21.4	46.7	26.6	l	45.0	0.71
	AMP-O	0-25	4.95	4.28	11.26	21.07	10.78	66.9	0.14	0.18	6.7	22.6	58.3	12.4	si-l	30.7	0.82
	GR-P	0-25	4.69	3.89	10.90	10.03	11.88	48.5	0.09	0.14	22.3	36.3	30.5	10.9	sa-l	26.5	0.97
	GR-E	0-25	4.32	3.66	9.30	10.07	5.98	27.8	0.16	0.21	17.1	44.9	32.4	5.6	sa-l	17.2	1.00
	GR-O	0-25	4.21	4.00	10.81	19.34	15.38	59.7	0.14	0.20	11.5	37.2	41.2	10.1	sa	13.2	0.98
		AMP¶		4.94a	4.18a	11.39a	26.02a	11.14a	84.1a	0.14a	0.17a	5.5a	21.1a	57.2a	16.3a		37.8a
	GR¶		4.41b	3.85b	10.34b	13.14a	11.08a	45.3a	0.13a	0.18a	17.0b	39.5b	34.7b	8.5a		19.0a	0.98b
Ah2	AMP-P	25-40	4.76	4.24	11.53	22.83	10.63	58.1	0.18	0.21	3.7	17.1	68.7	10.4	si-l	38.6	0.83
	AMP-E	25-50	5.07	4.13	11.45	28.18	10.19	82.9	0.15	0.18	2.2	14.8	53.7	29.4	si-c-l	45.2	0.75
	AMP-O	25-40	5.33	4.33	11.29	21.60	13.25	44.5	0.22	0.28	11.2	23.9	52.3	12.6	si-l	31.3	0.73
	GR-P	25-40	4.79	4.14	11.35	16.29	14.81	48.4	0.15	0.22	34.9	29.2	29.1	6.9	sa-l	32.5	1.01
	GR-E	25-50	4.75	4.10	11.18	15.61	8.74	38.5	0.18	0.23	11.7	42.9	37.8	7.7	sa-l	24.8	1.04
	GR-O	25-50	4.68	4.01	10.55	20.99	15.55	35.5	0.28	0.38	12.9	38.4	39.4	9.5	l	21.2	0.98
		AMP¶		5.05a	4.23a	11.42a	24.20a	11.36a	61.8a	0.18a	0.22a	5.7a	18.6a	58.3a	17.4a		38.4a
	GR¶		4.74a	4.08a	11.03a	17.63a	13.03a	40.2a	0.20a	0.27a	19.8a	36.8b	35.4b	8.0a		26.1a	1.01b
Ap	AMP-C	0-25	5.18	4.30	10.70	5.4	10.59	35.7	0.17	0.24	2.8	16.1	34.5	46.6	c	7.4	1.10
	GR-C	0-25	4.81	4.39	10.92	5.0	7.79	18.5	0.28	0.37	11.9	46.3	34.4	7.5	sa-l	18.5	0.97

† Si-l = silty-loam; l = loam; sa-l = sandy-loam; sa = sandy; si-c-l = silty-clay-loam; clayey = c.

‡ Moisture content of soils at the time of sampling, determined after drying at 105°C.

¶ Mean values of each variable studied within AMP and GR rows followed by the same letter are not significantly different at the 0.05 level of probability.

Soil Organic Matter

Chemical Characterization of Soil Organic Matter Present in the Ah Horizons

The pH values of the umbric Ah1 horizons in the GR soils were significantly lower (at $P < 0.05$) than those of the fulvic A1 horizons in the AMP soils (means: 4.4 compared with 4.9, respectively), whereas no significant differences were observed in the Ah2 horizons, although the same trends were detected (means: 4.7 compared with 5.1, respectively) (Table 5). As indicated above, at pH values < 4.2 - 4.4 , as in the organic horizons of the GR soils, the acidity of the system is determined by free organic acids. However, the pH increases with depth, while the activity of organic acids decreases because they become buffered by the mineral alkalinity of the soil, and the acid-base equilibrium is determined by CO_2 and hydroxyaluminum ions (Macías & Calvo de Anta, 1992). The observed increase in pH was paralleled by a decrease in the EC of the equilibrium solutions, in which the concentration of all major anions and cations decreased sharply with depth, with the lowest decreases in Al (Table 3). The Al_p/C_p and $(\text{Al}_p + \text{Fe}_p)/\text{C}_p$ molar ratios of the Ah1 horizons ranged between 0.09 to 0.21 (Table 5), with mean values of 0.14 and 0.18, respectively, indicating saturation of SOM with Al and Fe. Thus, the acidity of the SOM decreased, as the interaction of the soil solution with the mineral phase became more intense, and metal-saturation of SOM increased. The Al_p/C_p and $(\text{Al}_p + \text{Fe}_p)/\text{C}_p$ molar ratios in the Ah2 horizons ranged between 0.15 and 0.38 (mean values 0.19 and 0.25, respectively; Table 5). Values of the ratio of > 0.2 may indicate the presence of polymeric metal-OH forms, which can react with negatively charged organic compounds, and are susceptible to being dissolved by sodium pyrophosphate (Kaiser & Zech, 1996). There were no significant differences between the two types of parent materials ($P < 0.05$), but a species effect was observed in the Ah2 horizons, with the values of ratios for the oak species always being the highest (Table 5).

In the mineral surface horizons, the reactivity to the NaF test was high in both groups of soils, with mean values of 10.3 and 11.0 for the Ah1 and Ah2 horizons of the GR soils, respectively, and of 11.4 and 11.4, for the same horizons from the AMP soils, respectively (Table 5). The high NaF-pH values indicate the presence of reactive Al in these horizons, which are more abundant in the AMP soils (Camps Arbestain et al., 2003). However, differences in mean NaF-pH values in these two groups of soils were not significantly different ($P < 0.05$). As this measurement is a qualitative indicator of the presence of reactive Al it therefore cannot be used to distinguish differences in their total amounts, in contrast to other measurements, such as Al_p or Al extractable with ammonium oxalate. The Al_p data (Table 5) reflects the significantly greater ($P < 0.10$) presence of Al-humus complexes in the AMP than in the GR soils (26.0 vs 13.1 g kg^{-1}), and these compounds, together with short-range order compounds are susceptible to reacting with NaF. Reactive Al compounds, mostly short-range order compounds -as well as stable organo-Al complexes- have frequently been found in large quantities in incipient soils from Galicia derived from basic and metabasic materials (Macías et al., 1978; García-Rodeja et al, 1987).

Examination of the solution equilibria systems displayed in Figure 1, reveals that the Ah horizons developed from GR rock are included in group III, in which the Al saturation index ranges between 8.2 and 9.0, and which indicates that the system evolves towards the formation of kaolinite, although metastable forms, such as gibbsite, halloysite, and imogolite (Figure 1), and boehmite and alunite (not shown) may also occur. The Ah horizons of the

eucalypt and oak stands developed from AMP materials are mostly included in group IV, in which the AI saturation (> 9.0) is so high that the solutions are even oversaturated with allophanic compounds (Figure 1), which contrast with those of pine stands developed from the same materials, which are included in group I. In the group IV systems, non crystalline metastable forms can interact with secondary organic components leading to the formation of abundant and probably stable, organo-mineral bondings, and giving rise to the typical aluandic character of these soils. Buurman (2006) suggested that the high water retention of allophanic Andosols (containing primary aggregates of around $10 \mu\text{m}$) under perudic conditions, may cause the slow decomposition of secondary OM and, therefore, the well-known accumulation of SOM in these soils. To our knowledge, there are no studies of aluandic Andosols in NW Spain that attribute the high water retention of these soils, as an additional mechanism involved in the accumulation of SOM. In the present study, soil texture of the aluandic Andosols ranged from loam, to silty loam, and to silty clay loam, whereas it was sandy loam for all Umbrisols (Table 2). The coarser texture of the GR soils was mainly related to the higher presence of quartz in the granite rock compared with the AMP materials, and resulted in a lower water holding capacity of the former, but differences may have been further accentuated by the presence of amorphous compounds in the AMP soils. Differences in the water holding capacity between the two groups of soils were confirmed by the soil moisture contents at the time of sampling - which was carried out on the same dates for both types of soils - with those of the AMP samples generally being higher than those of the GR samples (Table 5), thus indicating faster drainage and higher susceptibility of the GR soils to drying under identical climatic conditions to those to which the AMP soils are subject. Nonetheless, more research is needed in the study region to determine the extent to which the different water moisture regimes of the AMP and GR soils affect the quantity, quality, and dynamics of SOM in these ecosystems, as proposed by Buurman (2006) for allophanic Andosols under perudic conditions.

Characterization of the Organic C Pools in the Soil Organic Matter Present in the Ah Horizons

The amount of organic C present in the surface mineral horizons (Ah1 and Ah2 horizons) accounted for 50-82% of total organic C of the ecosystem (down to the lowest depth of the Ah horizons) (Figure 4), with mean values of 71 and 63% for the AMP and GR soils, respectively (not significantly different at $P < 0.05$). The values provide a clear idea of the importance of the SOM stocks in forest ecosystems relative to those accumulated in the aboveground biomass, which ranged between 9 and 34%. The mean values of the organic C stocks accumulated in the Ah horizons were 381 and 286 t ha^{-1} for the AMP and GR soils, respectively (i.e. 8.3 and $6.5 \text{ t ha}^{-1} \text{ cm}^{-1}$, respectively), which are well above the default values (*Tier 1* level) outlined in the IPCC Good Practice Guidance (IPCC, 2003) for surface horizons of soils under humid temperate conditions (e.g., 80 t ha^{-1} for the first 30 cm of Andosols; i.e., $2.7 \text{ t ha}^{-1} \text{ cm}^{-1}$). This emphasizes the need for different countries to define C stocks for the different pedoclimatic regions and land-use systems, as required at the *Tier 2* level in the same guidance.

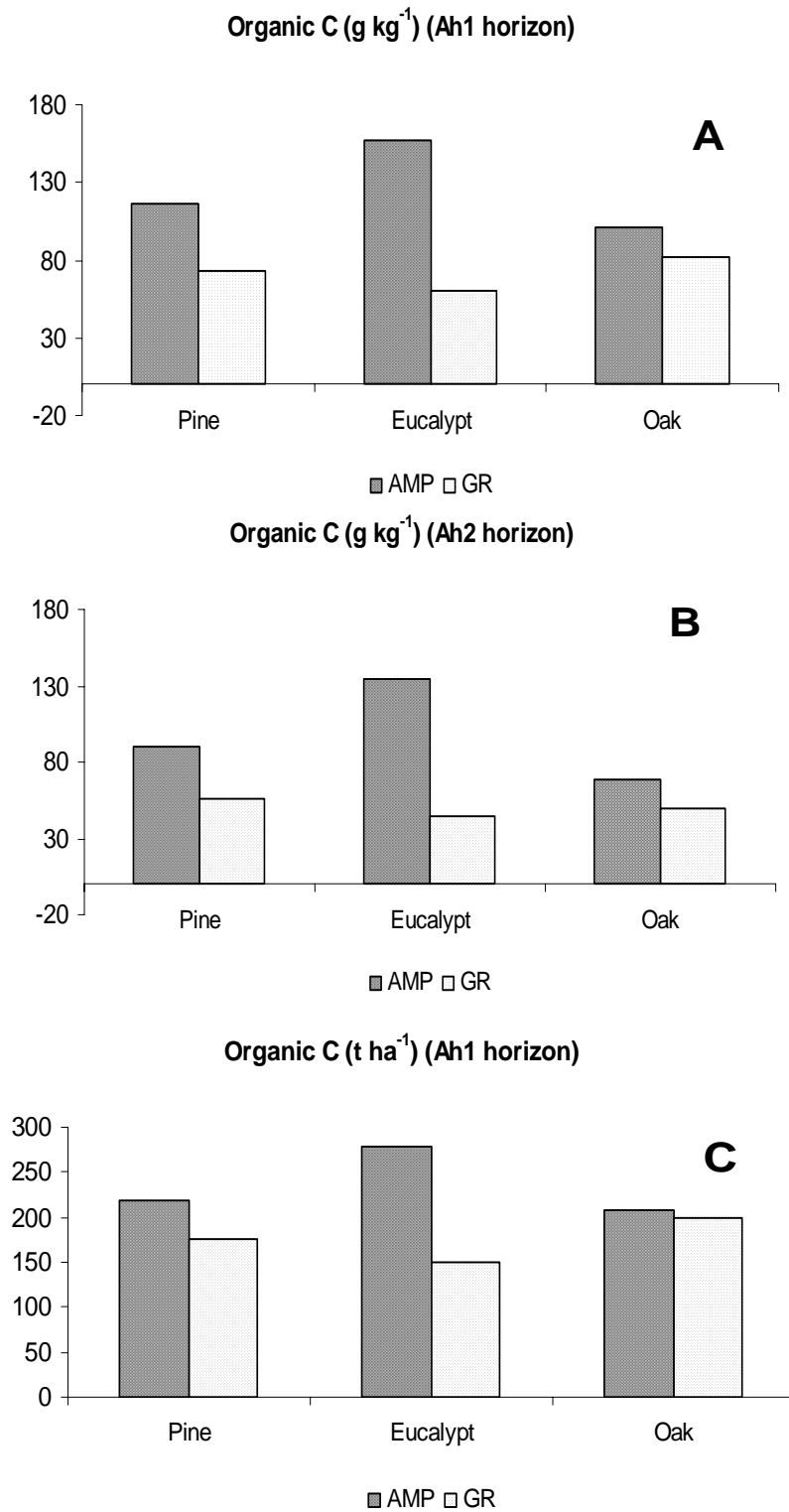


Figure 8. Continued on next page.

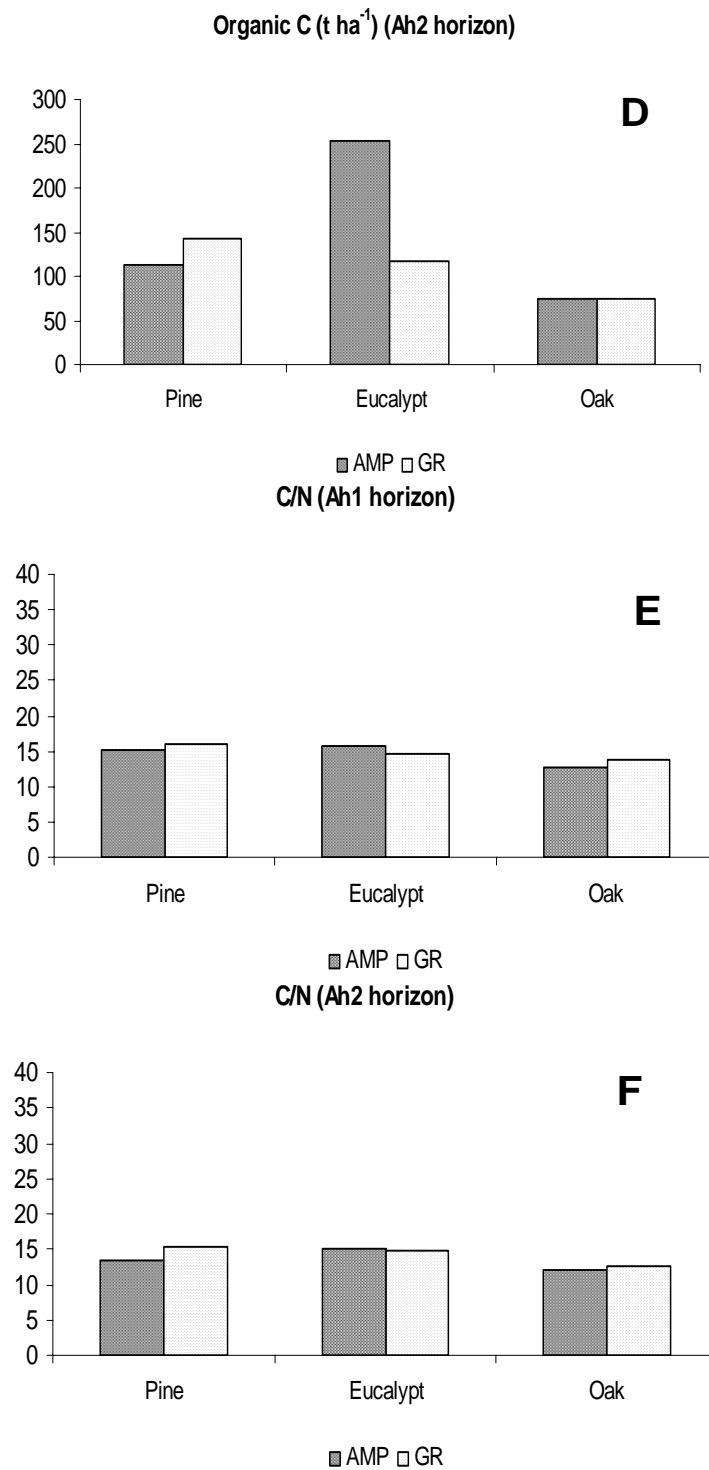


Figure 8. Concentrations (a and b) and contents (c and d) of organic C, and C/N ratios (e and f) of the Ah1 and Ah2 horizons, grouped by the different forest stands studied.

The concentration of total organic C in the Ah1 and Ah2 horizons was always higher (and significantly different at $P < 0.10$) in the AMP than in the GR soils (Figure 8A-B), with mean values of 125 and 98 g C kg⁻¹ for the Ah1 and Ah2 horizons of the AMP soils, respectively, and 71 and 51 g C kg⁻¹ for the Ah1 and Ah2 horizons of the GR soils, respectively. Thus, the opposite pattern was observed in the mineral horizons (Figure 8A-B; AMP soils > GR soils) than in the organic horizons (Figure 3A-B; AMP soils < GR soils). When the total amounts of organic C of the Ah1 horizons were considered rather than concentrations, differences between the two groups of soils were reduced (Figure 8C) - because of the greater soil bulk densities of the GR soils than of the AMP soils (Table 5) (mean values 220 and 186 t ha⁻¹, respectively). Stocks of organic C in the Ah2 horizons did not follow a common trend (Figure 8D) as depths of these horizons varied among soil profiles (Table 5). Moreover, the concentration of total organic C in the surface horizons of two cultivated soils close to the AMP and GR forests were well below the values for the forest sites (43 and 48 g C kg⁻¹ soil, respectively). The results suggest that the rapidly metabolized primary OM of the AMP soils becomes stabilized by reactive Al compounds, which are abundant in these soils, and which slow down the decomposition of secondary OM. In contrast, in the GR soils, the acidic and dystrophic conditions appear to lead to the slow decomposition of primary OM in the litter layers, but not in the more eutrophic Ah horizons. In fact, basal respiration per unit of organic C of litter layers were greater in the AMP soils than in the GR soils, whereas the inverse pattern was observed in the Ah layers (data not shown). All this may explain the existence of a moder type OM, in contrast to the Al-mull OM of the AMP soils.

The mean percentages of Mn_{ox}C/SOC in the Ah1 horizons did not differ significantly ($P < 0.05$) in AMP and GR soils (means: 10.2 and 10.3%, respectively) (Figure 6C), but those of Ah2 did differ significantly between the two types of soils at $P < 0.05$, with the mean of the AMP soils being greater than that of the GR soils (means: 10.6 and 9.9%, respectively) (Figure 6D). Thus, again, the pattern observed at depth was the opposite of that observed in the organic horizons (Figure 6A-B; AMP soils < GR soils). When comparing organic and mineral horizons, the results indicate that the content of permanganate-oxidizable C was always greater in the litter layers than in the Ah horizons (14.4 compared with 10.3%, respectively; Figure 6), as expected from the presence of less decomposed materials in the former. The mean percentages of Mn_{ox}C/SOC in the Ap horizons of the cultivated soils were 7.9 and 8.9%, for the AMP and GR soils, respectively, i.e. lower than in the Ah1 horizons of the forest soils, indicating that, in addition to a decrease in total organic C, cultivation probably accelerates decomposition of the most oxidable soil OC, leaving behind the least oxidable soil OC, in agreement with the previous results (Blair et al., 1995; Bell et al., 1998). The results of calculations made using the values corresponding to oak stands as reference values for natural soils and carried out on the basis of equal depth (down to 25 cm depth) indicate that the losses of organic C from the cultivated Ap horizons were 89 and 84 t ha⁻¹ for the AMP and GR soils (43 and 42% lost, respectively), and 134 and 122 t ha⁻¹, respectively, when the litter layers were included (53 and 51% lost, respectively) in addition to soil organic C. When the same calculations were made on the basis of equal soil mass (35 cm depth for the AMP-O soil; 25 cm depth for the GR-O, AMP-C, and GR-C soils), the losses of organic C from the cultivated Ap horizons (down to 25 cm depth) were 138 and 84 t ha⁻¹ for the AMP and GR soils, respectively (53 and 42%, respectively), and 182 and 122 t ha⁻¹, respectively, when the litter layers were included (60 and 51% lost, respectively). On the other hand, losses

of $M_{nox}C$ in the cultivated Ap horizons on the basis of equal depth (down to 25 cm depth) were 13 t ha^{-1} for both type of soils, and 20 t ha^{-1} when the litter layers were included in addition to soil organic C. When the same calculations were made on the basis of equal soil mass, the losses of organic C from the cultivated Ap horizons were 18 and 13 t ha^{-1} for the AMP and GR soils, respectively, and 24 and 20 t ha^{-1} , respectively, when the litter layers were included.

The similar ease of oxidation by $KMnO_4$ of the Ah1 horizons of both types of soils suggest that, despite the well-known ability of soils with andic properties to accumulate OM under natural conditions, the extent to which this becomes depleted after changes in land use, such as the conversion of forest soils to agricultural soils, may be similar in both types of soils. This is further corroborated by the observed decrease in the $M_{nox}C/SOC$ ratio of the cultivated AMP and GR soils, and the estimated losses of total organic C with the change in land use, as estimated above. Verde et al. (2005) studied the effect of cultivation of soils with andic properties and observed high lability of the least stable organo-Al complexes, which were estimated by $CuCl_2$ extraction, with values in the agricultural soils being less than 40% of the corresponding values in the forest soils.

Overall, the results indicate that, in the GR soils, the type of pedogenesis taking place in the surface horizons is mainly determined by the lithology, with intense acidification (acid-complexolysis) associated with scarce or nil neoformation of secondary minerals in those compartments of greatest acidity (L and F) and abundance of aqueous and mobile organo-metal complexes. Under such conditions, OM decomposition is very slow, leading to the accumulation of undecomposed debris in the organic layers, although decomposition might be enhanced in the Ah horizons, once the conditions become more eutrophic. On the other hand, in the AMP soils, both lithology and plant species have a clear effect on the type of pedogenesis occurring in the surface horizons. The results show that the pine stand is able to produce greater surface acidification (although never as intense as that on GR materials) than in the eucalypt and the oak litter. In general, the eutrophic conditions of these soils allow rapid decomposition of primary OM. The geochemical conditions of the surface mineral horizons appear to allow neoformation of metastable forms of gibbsite and different short-range order 1:1 aluminosilicates, which may bind to secondary organic compounds. Under such conditions, decomposition of secondary OM is slowed down.

Aboveground Biomass, Belowground Biomass and Dead Wood

As indicated above, the estimates of the organic C stocks for each of the reservoirs per unit of surface (t ha^{-1}) down to the lowest depth of the Ah horizons (Figure 5) indicate that organic C in SOM was always higher than the amount of organic C in living biomass, with the highest (82%) and lowest (50%) relative values of SOM corresponding to the eucalypt stands (Figure 4). The relative amounts of soil organic C for the pine and oak stands were very similar (ranging from 65 to 70%), independently of the parent material. The fact that eucalypts are managed more intensively than the other species (they are managed in rotation periods of 10-15 years, with heavy machinery used for harvesting and site preparation) may have a variable impact on the SOM stock and this may explain the large differences observed in the eucalypt stands. The accumulation of SOM is a slow process, which can be interrupted by practices such as clear cutting (Constantini et al., 1991), and the use of heavy machinery.

The latter practice has similar effects on SOM as cultivation, as it leads to disruption of soil aggregates, which favours mineralization of the occluded labile SOM (Plante et al., 2006). Both practices may also lead to greater fluctuations in temperature and moisture (no canopy is present) with subsequent increased SOM mineralization, and furthermore to increased erosion, with the concomitant loss of SOM. In any case, it should be noted that the highest total organic C stocks, i.e., the sum of the five reservoirs considered, always corresponded to the eucalypt stands (Figure 4), with stocks above 500 t ha^{-1} , whereas the oak and pine stands had stocks below 500 t ha^{-1} , and when comparing each forest species between the two types of ecosystems, the total organic C stocks were systematically greater in the AMP than in the GR ecosystems.

Apart from the inherent species characteristics (fast growth - eucalypts; medium-speed growth - pines, and slow growth - oaks), the different management regimes applied to the different species may also have an important impact on the biomass C pools present in the studied stands. Oaks are managed as a coppice, and the density of trees is very high (AMP-O: 2340; GR-O 3150 trees ha^{-1}), with many trees of small diameter (average diameter; AMP-O: 12.4; GR-O: 5.3 cm). However, clear differences were observed between the two eucalypt stands studied. The fast-growing eucalypts showed a high proportion of organic C in the aboveground biomass pool in the GR stand (34%), whereas there was very little organic C in the biomass from the AMP site (9%), which is probably attributable to the age difference (8 compared with 13 years) and to several severe attacks by *Gonipterus scutellatus* Gyllenhal in AMP-E in recent years. Attacks by the insect generally cause severe reduction in production. The relative amounts of organic C in the aboveground biomass of oak and pine stands were very similar (ranging from 15 to 18%). The dead wood (standing and on the floor) present in both oak stands showed high relative values ($>1\%$) (Figure 4). Despite the small diameters, this may also be very important for biodiversity. The AMP-P plot is an old and abandoned pine plantation and the tree density is therefore low (< 350 live trees ha^{-1} , including new regeneration) and there is a considerable amount of dead wood for a commercial plantation (18 Mg C ha^{-1} ; $>3\%$ of the total C stock). Finally, GR-P is a younger well-managed pine plantation with no dead wood.

CONCLUSION

The results obtained indicate that highest total organic C stocks in the ecosystems studied down to the lowest depth of the Ah horizons, i.e., the sum of the five reservoirs considered, always corresponded to the eucalypt stands, with stocks $> 500 \text{ t ha}^{-1}$, whereas those of the oak and pine stands were always $< 500 \text{ t ha}^{-1}$. The mean distribution of organic C stocks in the five reservoirs considered was as follows: aboveground biomass, 18.4%; belowground biomass 4.6%; dead wood, 1.1%; litter 8.4%; and soil organic C, 67.2%, with no significant differences ($P < 0.05\%$) between means for the AMP and GR ecosystems, although for each type of forest species, total C stocks were consistently higher in the AMP than in the GR ecosystems. There were significant differences ($P < 0.05$) in the quantity, quality and dynamics of organic C of these two types of ecosystems, when the different organic layers (L and F) and also the different Ah horizons (Ah1 and Ah2) were considered separately.

To understand the possible mechanisms of OM stabilization taking place in the organic layers and Ah horizons of the soils under study, the processes involved in pedogenesis must be understood. For this, we could consider the incipient formation of an acid soil in a humid and percolating environment as a titration of the primary parent material against an excess of organic acids ultimately derived from the biomass (Camps Arbestain et al., 2007; Macías et al., 2007). The net release of acid breaking products from organic debris is mainly affected by environmental conditions (favoured when microbial activity is impaired) and type of vegetation, whereas the acid buffering capacity of the parent material is mainly affected by lithology and/or climate (Camps Arbestain et al., 2007; Macías et al., 2007). The shifting point of this titration, which depends on both the total organic acid loading and the base supplied, determines whether downward movement of organic acids takes place, and if this occurs, at what depth the movement stops, with the formation of new phases.

During incipient weathering of amphibolites under humid temperate conditions in a percolating environment, rapid dissolution of Si, Al, Fe, and non-hydrolyzing cations (e.g., Ca, Mg) from primary minerals takes place. Large quantities of the latter are removed via leaching, whereas Al, Fe, and to a lesser extent Si, are retained preferentially, producing rapid buffering of the organic acid loading, and there being almost no downward movement of complexing organic acids. In these soils, solubilization of primary minerals takes place at a faster rate than crystallization of secondary minerals, leading to formation of meta-stable short-range order compounds, such as allophane and imogolite, together with stable organo-metal complexes, which increases both the sorption properties of these soils and water retention. Moreover, the base supply from major primary minerals favours the existence of eutrophic conditions, and the pH of the system is maintained in the range of acid-hydrolysis, and is mainly controlled by dissolved CO₂. All of this favours OM decomposition and the bonding of the metabolized organic compounds with reactive Al surfaces. Under such conditions, decomposition of secondary OM is slowed down, and this process is could be further retarded by the high water content capacity of these soils, as proposed by Buurman (2006) for allophanic Andosols under perudic conditions, although more research is required to confirm this. All this explains the accumulation of soil OM in natural soils with andic properties.

On the other hand, incipient weathering of granite rocks under humid temperate conditions in a percolating environment drastically eliminates the scarce bases present in the GR parent material, leading to a more acidic system. At the surface there is practically no mineral stability, and the pH of the system is mainly determined by biogeochemical processes. Under such conditions, the acidity produced through the release of organic acids cannot be totally buffered by mineral alkalinity, and the solubility of Al and Fe becomes determined by complexation reactions, with the formation of aqueous organo-mineral complexes, which can be transported to deeper layers (e.g., from organic horizons to mineral surface horizons, such as the Ah horizons) until they become saturated and precipitate. This situation corresponds to strong acid-complexolysis under highly dystrophic conditions in the litter layers where decomposition of organic debris is slow and primary OM tends to accumulate, although decomposition which be enhanced in the Ah horizons, once the conditions become more eutrophic. This may explain the existence of a moder-type OM in the former in comparison with the Al-mull type of OM in the latter. However, in spite of these differences, estimated losses of organic C in the Ah1 horizons of forest soils converted to agricultural use were similar in both type of soils (despite the well-known ability of soils

with andic properties to accumulate OM under natural conditions), and indicates the vulnerability of both types of OM to being depleted when they are subject to conventional agricultural practices.

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