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Labile carbon pools and biological activity in volcanic soils of the Canary Islands

Fracciones de carbono orgánico lábil y actividad biológica en suelos de origen volcánico de las Islas Canarias

Frações de carbono orgânico lábil e actividade biológica em solos de origem vulcânica das Ilhas Canárias

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ABSTRACT

It is important to assess the mineralisation of soil organic carbon (SOC) to predict the short-term response of biosphere carbon reservoirs to changing environmental conditions. We investigated the labile (easily-mineralisable) SOC in volcanic soils, where the bioavailability of SOC is typically affected by physico-chemical stabilisation mechanisms that are characteristic of these soils. Ten soils were selected that represent the most typical soil types (mainly Andosols) and natural habitats (xerophytic scrubland, laurel forest and pine forest) in the Canary Islands, a volcanic archipelago. Over two years we measured several physico-chemical SOC fractions with different degrees of bioavailability: water-soluble carbon in fresh soil samples (WSC) and in the saturated extract (WSC_{se}), hot water-extractable carbon (HWC), potassium sulphate-extractable carbon (PSC), microbial biomass carbon (MBC), particulate organic carbon (POC), humic substances carbon (HSC), and total organic carbon (TOC), and performed CO_2 emission incubation assays. We related these measurements to the potential C inputs of plant litter and roots and to the activity of certain hydrolytic enzymes (CM-cellulase, β-D-glucosidase, and dehydrogenase) that are involved in carbon turnover. In vitro carbon mineralisation measurements from short assays (ten days) were fitted with simple first-order kinetics to investigate SOC. This procedure was simple and allowed us to obtain estimates both for potentially mineralisable SOC and for the heterogeneity of the substrates that were consumed during incubation. The investigated volcanic soils had large labile SOC concentrations in which simple carbohydrates predominated and that were mainly derived from roots and aboveground non-woody residues. Among the analysed physico-chemical SOC fractions, HWC (3.1 g kg^{-1} on average at 0-30 cm depth in Andosols) was the most correlated with C_0 (1.2 g kg^{-1}) and therefore best represents potentially mineralisable SOC. PSC (0.77 g kg^{-1}), which represents an SOC pool of low bioavailability, was protected by its adsorption to allophane in silandic Andosols.

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RESUMEN

La medida de la susceptibilidad del carbono orgánico del suelo (SOC) a la mineralización es esencial para predecir la respuesta a corto plazo de los reservorios biosféricos de carbono a los cambios en las condiciones ambientales. En este trabajo abordamos el estudio del SOC lábil (fácilmente mineralizable) en suelos volcánicos, donde la biodisponibilidad del SOC se ve característicamente afectada por mecanismos de estabilización físico-química propios de estos suelos. Con este fin seleccionamos diez suelos representativos (sobre todo Andosoles) de los principales hábitats naturales (matorral xerofítico, laurisilva y pinar) en las Islas Canarias, un archipiélago de origen volcánico. Durante dos años medimos diversas fracciones de SOC a las que se atribuye un distinto grado de biodisponibilidad: carbono soluble en agua en muestras frescas de suelo (WSC) y en el extracto saturado (WSC_{se}), carbono extraíble en agua caliente (HWC), carbono extraíble con sulfato potásico (PSC), carbono ligado a la biomasa microbiana (MBC), carbono orgánico particulado (POC), carbono de sustancias húmicas (HSC), y carbono orgánico total (TOC), y realizamos ensayos de incubación de las emisiones de CO_2. Relacionamos estas medidas con los posibles aportes de carbono procedentes de la hojarasca y las raíces, y la actividad de enzimas hidrolíticas (CM-celulasa, β-D-glucosidasa, y deshidrogenasa) implicadas en el ciclado del carbono. La medida in vitro de la mineralización en ensayos cortos (10 días) se ajustó a un modelo cinético simple de primer orden, un procedimiento sencillo que nos permitió obtener no sólo una estimación del SOC más inmediatamente mineralizable, sino también de la heterogeneidad de los sustratos consumidos durante la incubación. Los suelos volcánicos investigados mostraron una gran riqueza de SOC lábil, en los que predominaron los carbohidratos simples procedentes principalmente de aportes orgánicos radiculares y de restos vegetales no-leñosos aéreos. Entre las fracciones físico-químicas de SOC analizadas, el HWC (3,1 g kg^{-1} de promedio a 0-30 cm de profundidad en Andosoles) fue el que mejor se correlacionó con el C_0 (1,2 g kg^{-1}) y por tanto el que mejor representó el SOC inmediatamente mineralizable. El PSC (0,77 g kg^{-1}), que representa un reservorio de baja biodisponibilidad, se encuentra protegido de la mineralización por su adsorción a la alófana en Andosoles silándicos.

KEY WORDS
Andosols, SOC fractionation, mineralisation kinetics, soil enzymatic activity, natural ecosystems

PALABRAS CLAVE
Andosoles, fraccionamiento de SOC, cinética de mineralización, actividad enzimática del suelo, ecosistemas naturales

PALAVRAS-CHAVE
Andossolos, fraccionamento do SOC, cinética de mineralização, actividade enzimática, ecossistemas naturais

RESUMO

A avaliação da susceptibilidade à mineralização do carbono orgânico do solo (SOC) é essencial para a previsão da resposta a curto prazo dos reservatórios de carbono da biosfera às alterações das condições ambientais. Neste trabalho investigou-se o estudo da fração lábil do SOC (fração facilmente mineralizável) em solos vulcânicos, onde a biodisponibilidade do SOC é afetada de forma típica por mecanismos de estabilidade físico-química caraterísticos destes solos. Com este objectivo selecionaram-se dez solos representativos (sobretudo Andossolos) de habitats naturais (vegetação xerofítica e floresta de loureiros e pinheiros) das Ilhas Canárias, um arquipélago vulcânico. Durante dois anos mediram-se diversas frações físico-químicas do SOC com diferentes graus de biodisponibilidade: carbono solúvel em água em amostras frescas de solo (WSC) e no extracto de saturação (WSC_{se}), carbono extraível com água quente (HWC), carbono extraível com sulfato de potássio (PSC), carbono da biomassa microbiana (MBC), carbono orgânico particulado (POC), carbono das substâncias húmicas (HSC), e carbono orgânico total (TOC) e fizeram-se medições das emissões de CO_2 com recurso a ensaios de incubação. Estas medições foram relacionadas com os "inputs" de carbono de resíduos vegetais e raízes bem como com a atividade de enzimas hidrolíticas (CM-celulase, β-D-glucosidase, e deshidrogenases) envolvidas das na ciclagem do carbono. A medição in vitro da mineralização do carbono através de ensaios de curta duração (dez días) foi ajustada a um modelo cinético simples de primeira ordem, que permitiu não só estimar a fração de carbono orgânico mais fácilmente mineralizável, como também a heterogeneidade dos substratos consumidos durante o período de incubação. Os solos vulcânicos estudados apresentaram uma grande riqueza de SOC lábil, em que predominavam hidratos de carbono simples com origem principalmente em resíduos orgânicos radiculares e residuos aéreos vegetais não lenhificados. Entre as frações físico-químicas de SOC analisadas, o HWC (3.1 g kg^{-1} em média, de a 0-30 cm de profundidade nos Andossolos) foi o que melhor se correlacionou com o C_0 (1.2 g kg^{-1}) e como tal o que melhor representa o SOC inmediatamente mineralizável. O PSC (0.77 g kg^{-1}), que representa um reservatório de baixa disponibilidade, encontra-se protegido da mineralização por adsorção à alofana nos Andossolos silândicos.

1. Introduction

Soil organic carbon (SOC) is an important component of soil quality because of its beneficial effects on soil physical structure, water-retention capacity, and plant nutrient availability (Gregorich et al. 1997; Haynes 2005). Recently, many studies have been conducted regarding the relationships between SOC and climate and land use changes, especially regarding SOC as a source or sink for greenhouse gases that influence the global climate (Post and Kwon 2000; Davidson and Janssens 2006).

SOC consists of a heterogeneous mixture of substances that have a wide range of decomposability (Post and Kwon 2000; Haynes 2005). Organic carbon enters the soil from litterfall, root turnover, and root exudation. The belowground inputs are generally more significant than the aboveground inputs (Rasse et al. 2005). Once in the soil, organic carbon is metabolised and mineralised by microorganisms. Only a small portion of the organic carbon (approximately 30 %) is stabilised by humification and association with mineral surfaces in the soil (Janzen et al. 1997; Haynes 2005). Thus, the two following major SOC pools can be distinguished: the labile fraction, which is more susceptible to mineralisation, and the recalcitrant and stable fraction. The labile SOC fraction consists of short-term cycling materials, mainly plant and microbial residues at different stages of decomposition (Janzen et al. 1997; Haynes 2005; Denef et al. 2009). The stable SOC fraction is mainly composed of humic substances that decompose very little due to their high molecular weight, their irregular and/or aromatic structures, and/or their associations with soil mineral components (Krull et al. 2003; von Lützow et al. 2006). Labile SOC is more active and shows a more rapid response to management (Janzen et al. 1997; Zagal et al. 2009) and climate change (Carrillo et al. 2011; Xu et al. 2012) than stable SOC. Precise knowledge regarding the composition of SOC and the factors that control the easily-mineralisable and labile SOC pool is required to model SOC dynamics and the response of SOC to changing environmental conditions (Cheng et al. 2007; Ahn et al. 2009).

Labile and stable SOC pools can be assessed by physical, chemical, and biological methods. Physical methods separate the SOC components based on attributes that are related to the physical soil particle arrangement, which controls the bioaccessibility of SOC (McLauchlan and Hobbie 2004; von Lützow et al. 2007; Denef et al. 2009). For example, the separation of different aggregate sizes by sieving separates the SOC that is encapsulated and protected from microbial activity within the aggregates. Particulate organic carbon (POC) can be obtained by dispersion followed by sieving. POC is mainly composed of scarcely transformed sand-sized organic fragments (e.g., plant fibres) that are free and easily decomposed. Similarly, SOC can be separated by density to isolate the heavy SOC fraction, which is complexed to soil minerals, and the light SOC fraction, which is free and easier to decompose.

Chemical methods can be used to assess SOC mineralisation by the extraction or removal of a specific SOC fraction using a chemical treatment that represents microbial attack. Some chemically extracted fractions are considered labile, including water-soluble carbon (WSC), hot-water extractable carbon (HWC), and $KMnO_4$-oxidisable carbon. By fumigating soil with chloroform, a K_2SO_4-extractable fraction is released, that is considered to be microbial biomass carbon and is generally included in the labile SOC pool. In contrast, the SOC fractions that are extracted with $Na_4P_2O_7$ or NaOH or are resistant to oxidation by HCl or NaOCl are considered recalcitrant or slowly-oxidisable (McLauchlan and Hobbie 2004; von Lützow et al. 2007; Denef et al. 2009).

Finally, biological assessment of labile SOC is mainly based on the experimental measurement of SOC mineralisation that results from microbial activity in soil sample incubation assays that are monitored for a few days or up to several months (McLauchlan and Hobbie 2004; Denef et al. 2009). Soil enzyme activities, which are considered valuable indicators of soil quality (Gregorich et al. 1997), are also potentially useful biological indicators of labile SOC. Although

enzyme activities do not directly measure labile SOC, the amount and potential activities of hydrolytic enzymes involved in different stages of carbon cycling (e.g., cellulase, glucosidase, and dehydrogenase) are controlled by the availability of their specific substrates. Thus, these enzyme activities provide information regarding the potential hydrolysis of distinct labile SOC components (Sinsabaugh et al. 2008).

Volcanic soils, particularly Andosols, are often characterised by high SOC concentrations. These high SOC concentrations result from organic matter stabilisation, which mainly results from the complexation of organic matter with short-range ordered minerals, such as allophane, and the encapsulation of organic matter inside highly stable soil aggregates (Fernández Caldas and Tejedor 1975; Macías et al. 1978; Driessen et al. 2001). Experimental assays show that microbial and plant residues decompose rapidly in Andosols (Zunino et al. 1982) and are rapidly incorporated into the humic fraction in these soils (González-Pérez et al. 2007). The turnover rate of SOC is slower (Parfitt 2009) and the labile SOC pool is relatively smaller in Andosols (Baisden et al. 2010) compared with other soil types. However, soil use changes can result in severe SOC losses from Andosols. These SOC losses occur from soil erosion and to the breakdown of soil aggregates by raindrops that exposes the carbon within the aggregates to microbial attack (Óskarsson et al. 2004; Mora et al. 2007).

Several authors have stressed the need to compare and correlate labile and stable SOC pools, which are obtained by physico-chemical fractionation techniques, with biological activities, which are obtained in vitro (Álvarez and Álvarez 2000; McLauchlan and Hobbie 2004; Ahn et al. 2009; Rovira et al. 2010). This issue is of special interest in volcanic soils, where the bioavailability of SOC is affected by stabilisation and early physico-chemical sequestration mechanisms in the humic fraction, which are typical of these soils.

We conducted this study with volcanic soils that were sampled from natural ecosystems with different environmental conditions and different degrees of conservation resulting from different historical land uses. Our goal was to approach the amount and origin of the labile SOC in volcanic soils and to determine which tools are most effective for assessing labile SOC and predicting the response of soil carbon to environmental changes. We determined the in vitro mineralisation of SOC by using incubation assays. In addition, we determined the activity of the soil enzymes relative to the different SOC metabolism stages and quantified the distinct physical and chemical SOC fractions of varying bioavailability. Interrelationships between the measurements were obtained, and the relations of these measurements with the soil's andic character, the type and amount of organic inputs supplied to the soil, and the type of land management were investigated.

2. Material and Methods

2.1. Study area

This study was performed on the Canary Islands, a volcanic archipelago located near the coast of Africa in the eastern sector of the North Atlantic Ocean (**Figure 1**). Three main natural ecosystems exist on the Canary Islands. These areas are distributed by altitude as follows: arid lowland, humid midland and xeric highland (**Figure 2**). The lowland areas are characterised by warm average temperatures between 18 and 21 ºC, a low average rainfall of less than 250 mm yr^{-1} and xerophytic succulent scrub vegetation. The midland areas on the northern side of the islands are under the influence of humid trade winds. Thus, these areas have moderate temperatures between 13 and 16 ºC and a high average rainfall of nearly 1,000 mm $year^{-1}$, which together facilitate the development of exuberant laurel forest vegetation. Canary pine (*Pinus canariensis*) forests typically occur in highland areas with temperatures between 10 and 15 ºC and approximately 400 mm $year^{-1}$ of precipitation

(Fernández-Palacios and de los Santos 1996). Generally, the midland and highland areas are dominated by Andosols. Andosols also occur in the lowland areas on recent volcanic ashes and certain andic characteristics are frequently found in other soil types, such as Cambisols, Luvisols, Phaeozems, and Leptosols (Rodríguez-Rodríguez and Mora 2000).

Study sites were carefully selected to cover the major habitats of the Canary Islands, including both mature and human-disturbed ecosystems. Based on these criteria, we selected the following ten study sites on the islands of Tenerife and La Gomera (**Table 1**): two sites in the lowland (L1 and L2), five in the midland (M1, M2, M3, M4, and M5), and three in the highland (H1, H2, and H3) areas (**Figure 1**). Sites L1, M1, M2, H1 and H2 include nearly mature and well-preserved ecosystems, whereas sites L2, M3, M4, M5 and H3 host secondary or anthropogenic vegetation. In all cases, these lands are unmanaged and are located in protected natural areas. All soils were formed on volcanic ash and scoriae that were emitted during the Quaternary period. Most of these soils have a relatively pronounced andic character, except for the lowland area soils (L1 and L2), in which short-range order minerals were not stabilised by organic matter and thus evolved into more crystalline forms. More detailed information regarding the soil and site characteristics can be found in Armas-Herrera et al. (2012).

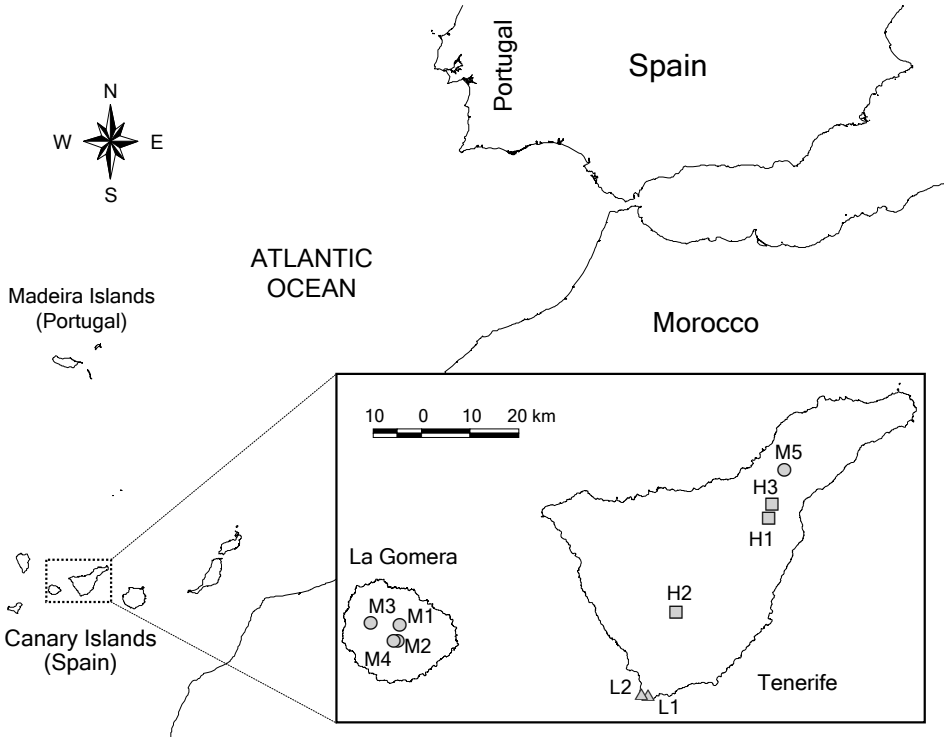

Figure 1. Location of the study sites.

Table 1. General characteristics of the experimental plots

Habitat type	Plot code	Site	Vegetation type	Dominant plant species	Soil classification (IUSS Working Group WRB 2006)
Lowland	L1	Tabaibal de Rasca	Primary xerophytic scrubland	*Euphorbia balsamifera, Euphorbia canariensis*	Hypersalic Solonchaks
	L2	Matorral de Rasca	Secondary xerophytic scrubland	*Schizogyne sericea, Launaea arborescens*	Haplic Solonetzs
Midland	M1	Los Aceviños	Primary laurel forest (riparian variant)	*Persea indica, Laurus novocanariensis*	Aluandic eutrosilic fulvic Andosols
	M2	Los Noruegos	Primary laurel forest (typical variant)	*Laurus novocanariensis, Ilex canariensis*	Silandic eutrosilic fulvic Andosols
	M3	Palos Pelados	Secondary heath forest	*Erica arborea, Myrica faya*	Aluandic eutrosilic fulvic Andosols
	M4	Pajaritos	Secondary heath scrubland	*Erica arborea, Adenocarpus foliolosus*	Leptic Luvisols
	M5	Ravelo	Pine plantation	*Pinus radiata, Ilex canariensis*	Silandic fulvic Andosols
Highland	H1	Los Frailes	Primary pine forest (humid variant)	*Pinus canariensis, Erica arborea*	Luvic Phaeozems
	H2	Pinalito	Primary pine forest (xeric variant)	*Pinus canariensis, Lotus campylocladus*	Leptic Cambisols
	H3	Siete Lomas	Secondary leguminous scrubland	*Chamaecytisus proliferus, Adenocarpus viscosus*	Silandic fulvic endoleptic Andosols


Figure 2a


Figure 2b


Figure 2c

Figure 2. Characteristic vegetation and soils of the study areas: (**a**) Lowland; (**b**) Midland; and (**c**) Highland.

2.2. Field work and sample preparation

A 25 x 25 m experimental plot was delineated at each study site. In these plots, we identified the existing plant species and determined their aboveground biomass by using pre-existing allometric equations (Fernández-Palacios and de los Santos 1996). Within each plot, several smaller sub-plots were randomly placed to collect litter, soil, and root samples as detailed below. Soil samples were collected seasonally (spring, summer, autumn, and winter) at two depths (0-15 cm and 15-30 cm) and over two annual periods that were separated by an interval of two years.

To quantify carbon inputs based on litterfall, four permanent litter traps (53 x 53 cm) were randomly placed in each plot. Each trap was emptied, and the plant residues were collected at the end of each season. In the lowland habitats, litter traps are not suitable due to the shrubby size of the vegetation, and instead, four 1 m^2 random subplots were delimited. Then, plant litter was removed from the soil surface, and litterfall residues were successively collected in each sampling period. In all cases, the woody residues (twigs and bark) were separated from the non-woody (leaves, flowers, and fruits) residues. Samples were washed with deionised water, oven dried at 60 ºC until a constant weight was achieved and then pulverised.

The amount of roots in each soil was estimated to determine the potential for organic root inputs. To accomplish this task, a permanent 4 x 4 m subplot was placed within each experimental plot. On each sampling date, two non-disturbed soil samples were taken from the top 30 cm of each subplot. These soils were passed through a 0.5 mm mesh sieve to collect the roots. The root samples were washed with deionised water, oven dried at 60 ºC until a constant weight was achieved, and pulverised.

For soil sampling, three 4 x 4 m subplots were placed at random within each experimental plot. Soil cores (10 cm diameter) were sampled at 0-15 and 15-30 cm depths from each subplot and were mixed to obtain average soil samples for each depth in each plot. Soil samples were sieved through a 2 mm mesh sieve before air-drying one portion and storing another portion at 4 ºC until analysis.

2.3. Analytical procedures

The carbon contents of the litter and root samples were determined with an elemental autoanalyser (LECO, St. Joseph, MI). The litter carbon supplies and the root carbon contents in the first 30 cm of the soils were calculated and expressed as g m^{-2}.

We studied several soil fractions that were obtained by different physico-chemical fractionation procedures and are known to have different turnover rates and susceptibility to mineralisation. The following fractions were analysed:

- Water-soluble C (WSC) was extracted from fresh soil samples by using a 1:10 (soil:water) ratio (Ghani et al. 2003).
- Water-soluble carbon in the saturated extract (WSC_{se}) was obtained from air-dried soil samples by using the saturated paste extraction method (Richards 1954).
- Hot water-extractable carbon (HWC) was obtained from fresh soil samples following the WSC 1:10 soil:water extraction procedure based on the methods of Ghani et al. (2003).
- Potassium sulphate-extractable carbon (PSC) (Vance et al. 1987) was obtained from fresh soil samples by using a 0.5 M potassium sulphate extraction (1:5 soil:extractant).
- Microbial biomass carbon (MBC) in fresh soil samples was determined with the chloroform-fumigation extraction procedure (Vance et al. 1987) using a calibration factor of K_c = 0.38 to correct for the efficiency of the extractive process.
- Particulate organic carbon (POC) in the sand soil fraction (Haynes 2005) was separated by dispersion with sodium hexametaphosphate and by sieving through a 50 µm sieve.
- Humic substances carbon (HSC) was extracted with 0.1 M sodium pyrophosphate (proportion 1:100 soil:extractant) (Stevenson 1994).
- Total organic carbon (TOC).

The carbon contents of the solid samples (POC, TOC) were determined with the Walkley and Black (1934) method, consisting of oxidisation with 1 N sodium dichromate in acid and back titration using 0.5 N ammonium-ferrous sulphate. The carbon contents of the soil extracts (WSC, WSC_{se}, HWC, PSC, MBC, and HSC) were determined in 10 ml aliquots by using 0.05 N potassium dichromate and 0.05 N ferrous-ammonium sulphate. Saline soil samples were treated with a silver sulphate solution to eliminate potential chloride interferences during analysis (Quinn and Salomon 1964). The soil carbon concentrations were expressed on a weight basis as g kg^{-1} or mg kg^{-1}.

SOC mineralisation was determined with short-duration incubation assays (ten days) of soil samples under optimal temperature (25 ºC) and moisture (pF 2 – field capacity) conditions. The emitted C-CO_2 was captured with soda traps (Guitián and Carballas 1976) and was determined on days 1, 2, 5, 8, and 10 following the beginning of the incubation. The cumulative C-CO_2 emitted after ten days of incubation (C_{10}) was expressed on a weight basis in units of C in the form of CO_2 (mg C-CO_2 kg^{-1} 10 d^{-1}).

We also determined the potential activities of several soil enzymes that are involved in different stages of the soil organic carbon cycle. Specifically, carboxymethyl cellulose (CM-cellulase), β-D-glucosidase, and dehydrogenase were determined by using the methods of Schinner and von Mersi (1990), Eivazi and Tabatabai (1988), and Camiña et al. (1997), respectively.

2.4. Data analyses

The amounts of C-CO_2 emitted during the incubation were fitted to simple first-order mineralisation models according to Mora et al. (2007). The first-order kinetics are described by the following equation:

$$C_t = C_0 (1 - e^{-kt})$$

where C_t is the amount of accumulated C-CO_2 (mg C kg $soil^{-1}$) emitted with time t, C_0 is the initial mineralisable carbon concentration (expressed as mg C kg $soil^{-1}$) and k is a constant that represents the daily flux rate ($days^{-1}$) (**Figure 3**). From this model, we obtained C_0, k, and R^2 values, which indicated how well the mineralisation data fit the first-order kinetics model. Moreover, we calculated the C_{10}/C_0 ratio, which is the proportion of mineralised carbon (C_{10}) to the total estimated mineralisable carbon (C_0), during the assay.

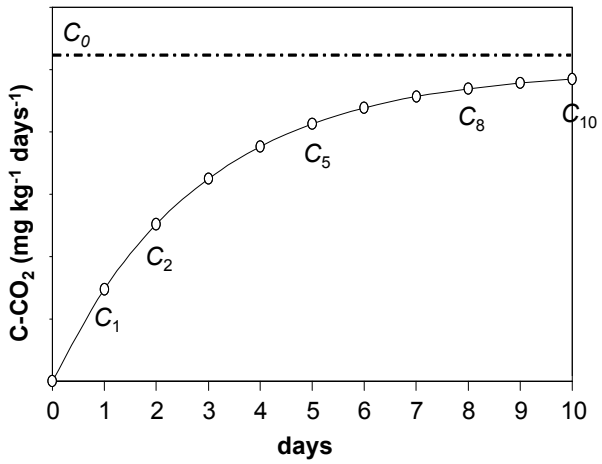

Figure 3. Schematic diagram of the mineralisation assays and fitting to simple first-order kinetics.

We used a multifactorial analysis of variance (ANOVA) and a Tukey test to analyse the main effects and first-order interactions of depth and sampling time (season, year) on the C_0, k, R^2, and C_{10}/C_0 values in each of the investigated soils. We analysed the correlations between C_0, the physico-chemical SOC fractions, the possible labile SOC (litter, roots) sources, and the soil enzyme activities with a Pearson test. In addition, we used Principal Component Analysis (PCA) to visualise the interrelationships between the different SOC fractions and biological measurements and their variation gradients in the investigated soils.

The mineralisation kinetics analysis was performed with the XLSTAT (version 2006, Addinsoft SRL, Paris) add-in for Microsoft Excel. The ANOVA and correlation analyses were conducted with SPSS in Windows (version 17, SPSS Inc., Chicago IL). In addition, the PCA was performed with the Canoco for Windows software (version 4.5, Biometris - Plant Research International, Wageningen).

3. Results

3.1. Potential carbon sources

The carbon supplied to the soils by litterfall was closely related to the aboveground vegetation biomass at the study sites ($r = 0.817$, $p < 0.001$). The lowest levels of litterfall organic carbon occurred in the lowland scrubland areas, and the highest levels occurred in the forested midland and highland areas (**Table 2**). The non-woody residue inputs were generally larger and more regular than the woody residue inputs, except in the lowland degraded site (L2), where the woody inputs were more continuous and dominant over the non-woody inputs. The root carbon contents (**Table 2**) did not correlate with aboveground biomass and often had similar or higher values under shrubby vegetation than under forest vegetation because of the exuberant root growth of certain shrubs in the topsoil layer. The temporal variation (intra and inter-annual) of root carbon and the carbon fluxes into the soils are not reported here, but they have been described in detail by Armas-Herrera et al. (2012).

Table 2. Carbon inputs via litterfall and root carbon content depending on the sampling plot. Mean values ± SEM (between sampling periods)

	LIG	UNL	ROO
L1	6.1 ± 3.3	7.3 ± 10.4	297 ± 264
L2	18.0 ± 4.9	0.1 ± 0.2	25 ± 21
M1	131.5 ± 147.3	211.1 ± 101.2	800 ± 271
M2	40.7 ± 27.8	299.2 ± 75.5	1165 ± 593
M3	29.2 ± 30.8	163.3 ± 97.4	1561 ± 464
M4	9.2 ± 9.2	165.7 ± 80.1	1766 ± 642
M5	87.9 ± 163.3	221.9 ± 191.6	383 ± 157
H1	58.3 ± 82.1	196.7 ± 121.1	538 ± 175
H2	168.5 ± 221.6	236.6 ± 118.4	402 ± 153
H3	26.5 ± 57.8	184.5 ± 189.1	498 ± 252

L1 = Hypersalic Solonchaks under xerophytic scrubland; L2 = Haplic Solonetzs under xerophytic scrubland; M1 = Aluandic eutrosilic fulvic Andosols under riparian laurel forest, M2 = Silandic eutrosilic fulvic Andosols under laurel forest; M3 = Aluandic eutrosilic fulvic Andosols under heath forest, M4 = Leptic Luvisols under heath scrubland; M5 = Silandic fulvic Andosols under pine plantation; H1 = Luvic Phaeozems under humid pine forest, H2 = Leptic Cambisols under xeric pine forest; H3 = Silandic fulvic endoleptic Andosols under leguminous scrubland; LIG = lignified litterfall carbon inputs (g C m^{-2} $year^{-1}$); UNL = unlignified carbon inputs (g C m^{-2} $year^{-1}$); ROO = root carbon content at 0-30 cm depth (g C m^{-2})

3.2. SOC fractionation

In most cases, the carbon concentrations were higher at the 0-15 cm depth than at the 15-30 cm depth (**Table 3**). However, the water-soluble forms (WSC, WSC_{se}) in the lowland area soils (L1, L2) had similar concentrations in both layers. The lowest carbon contents occurred in the L2 soil (Solonetz under secondary xerophytic scrubland in the lowland area), and the highest contents occurred in the M3 soil (Andosol under secondary heath forest in the midland area). Temporal variation (intra and interannual) in the SOC fractions was observed and is discussed in Armas-Herrera et al. (2012).

The contributions of each SOC fraction to the total SOC reservoir are shown in **Table 4**. POC and HSC were the most abundant SOC fractions in all but the lowland soils (L1, L2), in which the HSC content was negligible. In the other soils, HSC was relatively more abundant (ANOVA, $P < 0.01$) at the 15-30 cm depth than at the 0-15 cm depth. In turn, the lowland soils (L1, L2) had rel-

Table 3. Contents of SOC fractions (g C kg) depending on sampling depth and plot. Mean values ± SEM (between sampling periods)

Plot	Depth	WSC	WSC_{se}	HWC	PSC	MBC	POC	HSC	TOC
L1	0-15 cm	0.06 ± 0.04	0.02 ± 0.01	0.38 ± 0.13	0.19 ± 0.14	0.18 ± 0.14	0.64 ± 0.07	n.d.	4.1 ± 1.1
	15-30 cm	0.07 ± 0.05	0.01 ± 0.00	0.26 ± 0.05	0.20 ± 0.15	0.14 ± 0.12	0.43 ± 0.16	n.d.	2.4 ± 0.6
L2	0-15 cm	0.05 ± 0.03	0.01 ± 0.01	0.23 ± 0.09	0.10 ± 0.06	0.15 ± 0.09	0.48 ± 0.26	n.d.	2.3 ± 0.8
	15-30 cm	0.07 ± 0.05	0.01 ± 0.00	0.20 ± 0.08	0.10 ± 0.07	0.11 ± 0.09	0.16 ± 0.12	n.d.	1.7 ± 0.4
M1	0-15 cm	0.15 ± 0.07	0.52 ± 0.20	4.10 ± 1.02	0.56 ± 0.23	2.80 ± 1.39	32.4 ± 6.5	51.2 ± 6.3	179.1 ± 38.5
	15-30 cm	0.11 ± 0.06	0.22 ± 0.10	1.77 ± 0.36	0.40 ± 0.19	1.48 ± 0.79	7.6 ± 1.6	43.8 ± 7.9	96.8 ± 19.4
M2	0-15 cm	0.16 ± 0.08	0.38 ± 0.17	4.16 ± 1.56	0.74 ± 0.20	1.74 ± 0.49	70.0 ± 9.7	58.6 ± 5.1	163.8 ± 37.7
	15-30 cm	0.11 ± 0.04	0.25 ± 0.11	2.16 ± 0.56	0.61 ± 0.23	1.27 ± 0.34	18.9 ± 5.6	50.5 ± 7.1	99.2 ± 13.7
M3	0-15 cm	0.23 ± 0.06	0.67 ± 0.38	5.26 ± 0.66	0.74 ± 0.24	2.85 ± 0.82	82.3 ± 2.5	75.5 ± 4.8	196.7 ± 17.2
	15-30 cm	0.18 ± 0.03	0.55 ± 0.14	3.19 ± 0.16	0.66 ± 0.15	1.77 ± 0.68	34.8 ± 3.3	67.2 ± 5.8	141.3 ± 10.5
M4	0-15 cm	0.27 ± 0.15	0.79 ± 0.29	4.66 ± 1.11	0.95 ± 0.38	2.30 ± 0.57	56.3 ± 12.0	55.0 ± 6.2	166.2 ± 27.7
	15-30 cm	0.14 ± 0.05	0.42 ± 0.32	2.21 ± 0.88	0.49 ± 0.19	1.47 ± 0.56	20.4 ± 3.7	45.7 ± 7.7	98.8 ± 13.1
M5	0-15 cm	0.11 ± 0.05	0.21 ± 0.13	2.31 ± 0.40	0.60 ± 0.17	1.66 ± 0.75	47.3 ± 2.8	64.4 ± 3.0	157.0 ± 21.1
	15-30 cm	0.08 ± 0.04	0.14 ± 0.06	1.05 ± 0.32	0.67 ± 0.16	1.38 ± 0.66	15.4 ± 2.4	51.2 ± 3.6	110.2 ± 11.7
H1	0-15 cm	0.13 ± 0.07	0.12 ± 0.07	1.68 ± 0.57	0.42 ± 0.19	0.98 ± 0.24	14.2 ± 5.2	24.4 ± 5.2	62.3 ± 15.2
	15-30 cm	0.10 ± 0.05	0.05 ± 0.03	0.67 ± 0.19	0.26 ± 0.08	0.65 ± 0.20	4.1 ± 1.1	12.5 ± 2.8	29.6 ± 6.5
H2	0-15 cm	0.20 ± 0.21	0.14 ± 0.19	1.90 ± 1.45	0.50 ± 0.39	1.10 ± 0.56	15.1 ± 3.6	18.1 ± 12.6	47.1 ± 29.8
	15-30 cm	0.08 ± 0.03	0.03 ± 0.02	0.54 ± 0.23	0.26 ± 0.08	0.39 ± 0.09	4.7 ± 1.4	8.0 ± 2.1	17.1 ± 6.5
H3	0-15 cm	0.13 ± 0.12	0.18 ± 0.05	1.91 ± 0.51	1.07 ± 0.39	1.03 ± 0.37	77.1 ± 11.4	47.6 ± 9.5	110.7 ± 28.5
	15-30 cm	0.05 ± 0.05	0.05 ± 0.02	0.65 ± 0.15	1.52 ± 0.35	0.57 ± 0.16	20.5 ± 2.2	30.8 ± 4.3	60.6 ± 12.0

L1 = Hypersalic Solonchaks under xerophytic scrubland; L2 = Haplic Solonetzs under xerophytic scrubland; M1 = Aluandic eutrosilic fulvic Andosols under riparian laurel forest, M2 = Silandic eutrosilic fulvic Andosols under laurel forest; M3 = Aluandic eutrosilic fulvic Andosols under heath forest, M4 = Leptic Luvisols under heath scrubland; M5 = Silandic fulvic Andosols under pine plantation; H1 = Luvic Phaeozems under humid pine forest, H2 = Leptic Cambisols under xeric pine forest; H3 = Silandic fulvic endoleptic Andosols under leguminous scrubland; WSC = Water-soluble carbon; WSC_{se} = water-soluble carbon in saturated extract; HWC = hot water-extractable carbon; PSC = potassium sulphate-extractable carbon; MBC = microbial biomass carbon; POC = particulate organic carbon; HSC = humic substances carbon; TOC = total organic carbon; n.d. not detected.

Table 4. Relative contribution (%, mean) of the investigated SOC fraction to the total amount of SOC

Plot	Depth	WSC	WSC_{se}	HWC	PSC	MBC	POC	HSC
L1	0-15 cm	1.46	0.49	9.3	4.6	4.4	15.6	n.d.
	15-30 cm	2.92	0.42	10.8	8.3	5.8	17.9	n.d.
L2	0-15 cm	2.17	0.43	10.0	4.3	6.5	20.9	n.d.
	15-30 cm	4.12	0.59	11.8	5.9	6.5	9.4	n.d.
M1	0-15 cm	0.08	0.29	2.3	0.3	1.6	18.1	28.6
	15-30 cm	0.11	0.23	1.8	0.4	1.5	7.9	45.2
M2	0-15 cm	0.10	0.23	2.5	0.5	1.1	42.7	35.8
	15-30 cm	0.11	0.25	2.2	0.6	1.3	19.1	50.9
M3	0-15 cm	0.12	0.34	2.7	0.4	1.4	41.8	38.4
	15-30 cm	0.13	0.39	2.3	0.5	1.3	24.6	47.6
M4	0-15 cm	0.16	0.48	2.8	0.6	1.4	33.9	33.1
	15-30 cm	0.14	0.43	2.2	0.5	1.5	20.6	46.3
M5	0-15 cm	0.07	0.13	1.5	0.4	1.1	30.1	41.0
	15-30 cm	0.07	0.13	1.0	0.6	1.3	14.0	46.5
H1	0-15 cm	0.21	0.19	2.7	0.7	1.6	22.8	39.2
	15-30 cm	0.34	0.17	2.3	0.9	2.2	13.9	42.2
H2	0-15 cm	0.42	0.30	4.0	1.1	2.3	32.1	38.4
	15-30 cm	0.47	0.18	3.2	1.5	2.3	27.5	46.8
H3	0-15 cm	0.12	0.16	1.7	1.0	0.9	69.6	43.0
	15-30 cm	0.08	0.09	1.1	2.5	0.9	33.8	50.8

L1 = Hypersalic Solonchaks under xerophytic scrubland; L2 = Haplic Solonetzs under xerophytic scrubland; M1 = Aluandic eutrosilic fulvic Andosols under riparian laurel forest, M2 = Silandic eutrosilic fulvic Andosols under laurel forest; M3 = Aluandic eutrosilic fulvic Andosols under heath forest, M4 = Leptic Luvisols under heath scrubland; M5 = Silandic fulvic Andosols under pine plantation; H1 = Luvic Phaeozems under humid pine forest, H2 = Leptic Cambisols under xeric pine forest; H3 = Silandic fulvic endoleptic Andosols under leguminous scrubland; WSC = Water-soluble carbon of fresh samples; WSC_{se} = water-soluble carbon in saturated extract; HWC = hot water-extractable carbon; PSC = potassium sulphate-extractable carbon; MBC = microbial biomass carbon; POC = particulate organic carbon; HSC = humic substances carbon; n.d. not detected.

atively higher labile SOC concentrations (WSC, WSC_{se}, HWC, PSC, MBC) compared with the midland and highland soils. The water-soluble carbon concentration was higher in the air-dried soil samples (WSC_{se}) than in the fresh samples (WSC) for the M1, M2, M3, M4, M5, and H3 soils. All of these soils had andic characteristics. In the other soils, especially in L1 and L2, the drying procedure corresponded with decreasing water-soluble carbon concentrations.

3.3. Biological activity

Soil biological activity (**Table 5**) measurements were generally higher at the 0-15 cm depth than at the 15-30 cm depth. The highest enzyme activities were recorded in the midland area with degraded vegetation (sites M4 and M3). Soil M4 had the highest recorded mineralisation during the incubation assays. The lowest enzyme activities were found in the lowland areas, particularly in areas with degraded vegetation (L2). The

Table 5. Soil carbon mineralisation and soil enzyme activities depending on the sampling depth and plot. Mean values ± SEM (between sampling periods)

Plot	Depth	C_{10}	CEL	GLU	DEH
L1	0-15 cm	68 ± 32	n.d.	0.21 ± 0.10	0.11 ± 0.06
	15-30 cm	73 ± 42	n.d.	0.07 ± 0.04	0.06 ± 0.05
L2	0-15 cm	96 ± 63	n.d.	0.10 ± 0.07	0.08 ± 0.05
	15-30 cm	73 ± 43	n.d.	0.02 ± 0.02	0.07 ± 0.06
M1	0-15 cm	919 ± 279	0.14 ± 0.09	4.89 ± 0.79	0.63 ± 0.11
	15-30 cm	271 ± 126	0.06 ± 0.07	1.49 ± 0.69	0.28 ± 0.02
M2	0-15 cm	849 ± 320	0.35 ± 0.09	4.70 ± 2.20	0.49 ± 0.27
	15-30 cm	356 ± 155	0.30 ± 0.08	1.52 ± 0.52	0.33 ± 0.14
M3	0-15 cm	834 ± 272	0.56 ± 0.08	7.95 ± 2.30	0.65 ± 0.33
	15-30 cm	312 ± 92	0.46 ± 0.13	2.51 ± 1.02	0.36 ± 0.19
M4	0-15 cm	1679 ± 315	0.60 ± 0.18	8.11 ± 2.82	0.86 ± 0.52
	15-30 cm	421 ± 160	0.41 ± 0.13	3.52 ± 1.35	0.41 ± 0.24
M5	0-15 cm	736 ± 216	0.31 ± 0.19	3.89 ± 1.49	0.55 ± 0.14
	15-30 cm	376 ± 174	0.32 ± 0.09	2.89 ± 1.08	0.43 ± 0.15
H1	0-15 cm	487 ± 116	0.20 ± 0.08	2.54 ± 0.85	0.43 ± 0.16
	15-30 cm	177 ± 60	0.08 ± 0.04	0.96 ± 0.23	0.21 ± 0.12
H2	0-15 cm	734 ± 290	0.36 ± 0.17	4.17 ± 2.27	0.39 ± 0.19
	15-30 cm	189 ± 73	0.11 ± 0.06	0.80 ± 0.25	0.19 ± 0.11
H3	0-15 cm	505 ± 151	0.37 ± 0.13	4.72 ± 1.57	0.23 ± 0.07
	15-30 cm	125 ± 64	0.17 ± 0.07	1.18 ± 0.46	0.14 ± 0.07

L1 = Hypersalic Solonchaks under xerophytic scrubland; L2 = Haplic Solonetzs under xerophytic scrubland; M1 = Aluandic eutrosilic fulvic Andosols under riparian laurel forest, M2 = Silandic eutrosilic fulvic Andosols under laurel forest; M3 = Aluandic eutrosilic fulvic Andosols under heath forest, M4 = Leptic Luvisols under heath scrubland; M5 = Silandic fulvic Andosols under pine plantation; H1 = Luvic Phaeozems under humid pine forest, H2 = Leptic Cambisols under xeric pine forest; H3 = Silandic fulvic endoleptic Andosols under leguminous scrubland; C_{10} = carbon mineralisation during the incubation (mg C-CO_2 10 d^{-1}); CEL = CM-cellulase activity (µmol glucose g^{-1} h^{-1}); GLU = β-D-glucosidase (µmol PNP g^{-1} h^{-1}); DEH = dehydrogenase activity (µmol INTF g^{-1} h^{-1}); n.d. not detected.

CM-cellulase activity was negligible in the arid lowland soils. However, the lowest CM-cellulase activity in the midland and highland areas were found in the most humid sites (M1 and H1, respectively).

The mineralisation kinetics (**Figure 4**, **Table 6**) analysis resulted in the highest, intermediate, and lowest readily-mineralisable SOC (C_0) estimates in the midland, highland, and lowland area soils, respectively. The midland and highland area soils showed consistent patterns that contrasted with those observed in the lowland soils. Thus, the midland (M1-M5) and highland (H1-H3) soils had higher C_0 concentrations and generally lower k rates in the surficial layer (0-15 cm) than in the deep layer (15-30 cm) (**Figures 4a**, **4b**; **Table 6**). Significant seasonal differences were not observed for C_0 but were often observed for k, which had the lowest values in the winter (although the variations often differed between the two sampling years, as shown by the significant interaction of season and year). In general, the first-order kinetic model fits were

very good with values near 1, especially for the midland soils at a depth of 0-15 cm (**Figure 4c**). The relative mineralisation during the incubation assay (**Figure 4d**) was generally greater at a depth of 15-30 cm than at 0-15 cm, with average values of approximately 50 and 70 %, respectively.

In contrast, the lowland ecosystem soils (L1, L2) were similar between the two depths (**Table 6**). The C_0 fraction in the L1 soil was the only case in which significant differences occurred between 0-15 cm and 15-30 cm depths. However, important seasonal differences accrued (**Table 6**). For example, the highest C_0 (**Figure 4a**) values and

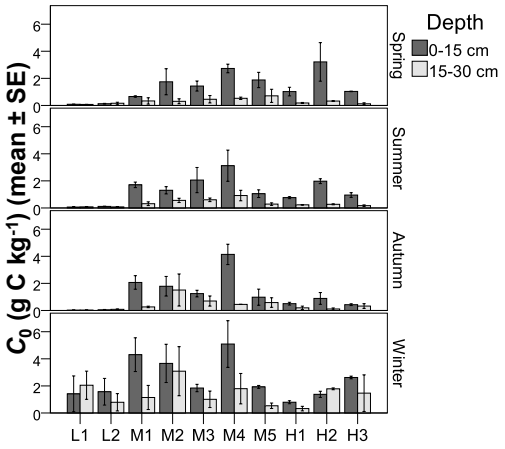

Figure 4a

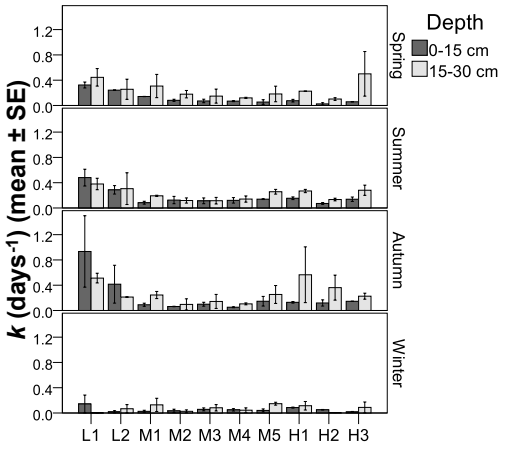

Figure 4b

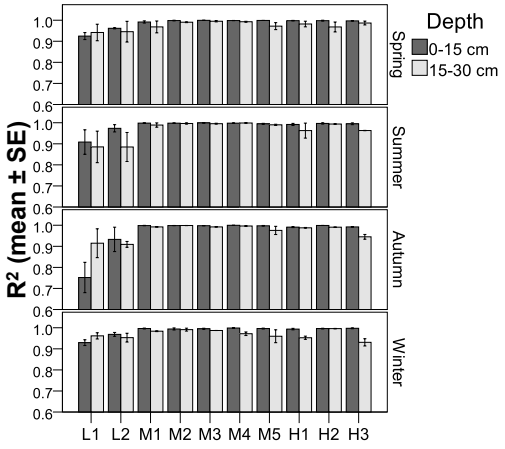

Figure 4c

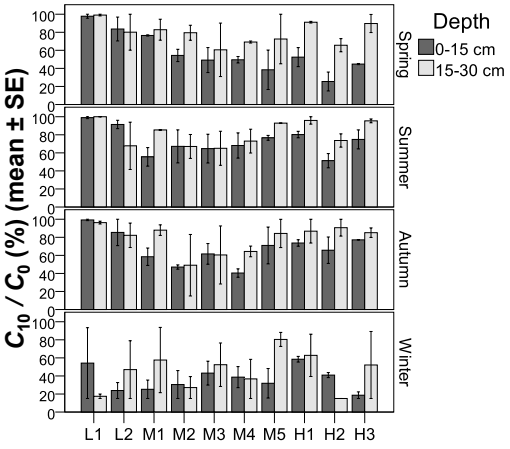

Figure 4d

Figure 4. Soil carbon mineralisation parameters in relation to the sampling season, depth and plot. Mean values ± SEM (between years).

L1 = Hypersalic Solonchaks under xerophytic scrubland; L2 = Haplic Solonetzs under xerophytic scrubland; M1 = Aluandic eutrosilic fulvic Andosols under riparian laurel forest, M2 = Silandic eutrosilic fulvic Andosols under laurel forest; M3 = Aluandic eutrosilic fulvic Andosols under heath forest, M4 = Leptic Luvisols under heath scrubland; M5 = Silandic fulvic Andosols under pine plantation; H1 = Luvic Phaeozems under humid pine forest, H2 = Leptic Cambisols under xeric pine forest; H3 = Silandic fulvic endoleptic Andosols under leguminous scrubland; C_0 = potentially mineralisable carbon; k = mineralisation rate; C_{10}/C_0 = ratio of carbon mineralised during the incubation; R^2 = fit to first order kinetics.

Table 6. ANOVA results of the soil carbon mineralisation parameters in relation to the sampling depth, season and year in each plot. Significance levels are: ** for P < 0.01; * for P < 0.05. Non-significant results are omitted

		L1	L2	M1	M2	M3	M4	M5	H1	H2	H3
C_0	Depth	*		*	*	*	***	*	**	*	*
	Season	**	*								
	Year	*									
k	Depth			*	**		*	**	*	*	*
	Season	*	*	*	*			*			*
	Depth x Season				*			*			*
	Depth x Year				*			*			*
	Year x Season			*	**	*	*	**			
C_{10}/C_0	Depth			*			***		*	*	**
	Season	*	*								
R^2	Depth			*		**	*	*	*	*	**
	Season					*					

L1 = Hypersalic Solonchaks under xerophytic scrubland; L2 = Haplic Solonetzs under xerophytic scrubland; M1 = Aluandic eutrosilic fulvic Andosols under riparian laurel forest, M2 = Silandic eutrosilic fulvic Andosols under laurel forest; M3 = Aluandic eutrosilic fulvic Andosols under heath forest, M4 = Leptic Luvisols under heath scrubland; M5 = Silandic fulvic Andosols under pine plantation; H1 = Luvic Phaeozems under humid pine forest, H2 = Leptic Cambisols under xeric pine forest; H3 = Silandic fulvic endoleptic Andosols under leguminous scrubland; C_0 = potentially mineralisable carbon; k = mineralisation rate; C_{10}/C_0 = ratio of carbon mineralised during the incubation; R^2 = fit to first order kinetics.

the lowest k values (Figure 4b) and C_{10}/C_0 ratios (Figure 4d) were observed in the winter. Mineralisation during the incubation period approached 100 % of the potentially mineralisable pool in most samples, particularly in the L1 soil, except in the winter samples. The first-order kinetics (Figure 4c) fit was poor and often below 0.9. In this case, no significant seasonal patterns were observed (Table 6).

3.4. Relationships between variables

When considering all ten study sites, all the forms of SOC and the enzyme activities were significantly related to the C_0 concentrations (Table 7). At each study site, the closest and most consistent correlation with readily-mineralisable SOC for the different sampling times and depths was with the HWC fraction (followed by the POC fraction). The other labile fractions (WSC, WSC_{se}, MBC, and PSC) were less correlated with C_0, than TOC or HSC. The PSC was negatively correlated with C_0 in the L1, L2, M5, and H3 soils. The temporal PSC variations that were observed in soils L1 and L2 potentially occurred at the expense of MBC, which was negatively correlated with PSC ($r = -0.618$, $P < 0.05$ in L1; $r = -0.509$, $P < 0.05$ in L2). Among the soil enzyme activities, the glucosidase activity had the highest correlation with C_0 variations within each study site.

Using PCA (Figure 5), we obtained a synthetic view of these interrelationships for all ten study sites. In general, the potentially mineralisable SOC content, the various SOC fractions, and the enzyme activities were strongly positively correlated with each other and with the kinetic model fit and were negatively correlated with the flux rate and with the ratio of carbon mineralised during incubation. According to the diagram, the highest positive correlations for C_0 were with

Table 7. Correlation of the potentially mineralisable carbon (C_0) with the various SOC fractions and the enzyme activities investigated in each sampling plot and in total. Significance levels are: *** for P < 0.001; ** for P < 0.01; * for P < 0.05. Non-significant results are omitted

	L1	L2	M1	M2	M3	M4	M5	H1	H2	H3	Total
WSC				*		*	*		*	*	***
WSC_{se}			*		*	**		*	*	**	***
HWC			**	***	*	***	***	**	**	**	***
PSC	*ng	*ng				**	*ng		*	*ng	***
MBC	*	*				**		**	**		***
POC			*	*	*	*		**	**	*	***
HSC				*	*	*	*	**	**	**	***
TOC			**	***	*	**	***	***	**	**	***
CEL	.	.	*					*	*	*	***
GLU			**	***	*	**	*	**	***	*	***
DEH		*	***	*		*			*		***

[ng] = Negative correlation; L1 = Hypersalic Solonchaks under xerophytic scrubland; L2 = Haplic Solonetzs under xerophytic scrubland; M1 = Aluandic eutrosilic fulvic Andosols under riparian laurel forest, M2 = Silandic eutrosilic fulvic Andosols under laurel forest; M3 = Aluandic eutrosilic fulvic Andosols under heath forest, M4 = Leptic Luvisols under heath scrubland; M5 = Silandic fulvic Andosols under pine plantation; H1 = Luvic Phaeozems under humid pine forest, H2 = Leptic Cambisols under xeric pine forest; H3 = Silandic fulvic endoleptic Andosols under leguminous scrubland; WSC = Water-soluble carbon of fresh samples; WSC_{se} = water-soluble carbon in saturated extract; HWC = hot water-extractable carbon; PSC = potassium sulphate-extractable carbon; MBC = microbial biomass carbon; POC = particulate organic carbon; HSC = humic substances carbon; TOC = total organic carbon; CEL = CM-cellulase activity; GLU = β-D-glucosidase activity; DEH = dehydrogenase activity.

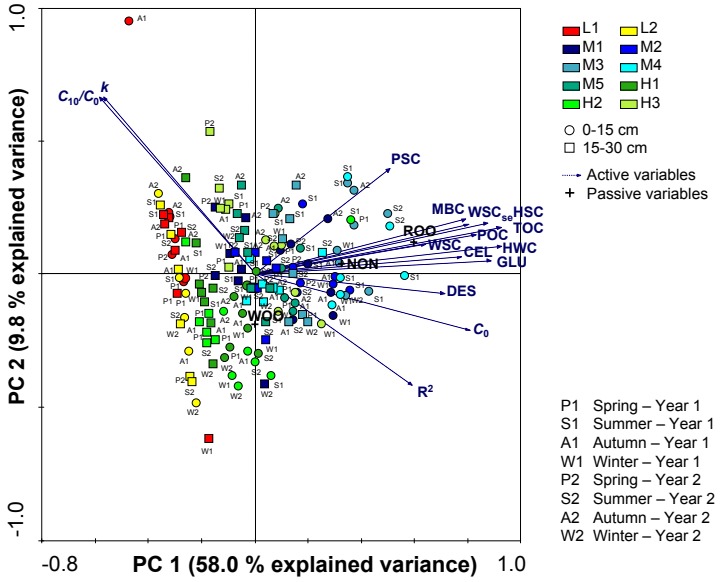

Figure 5. Principal component analysis of the potentially mineralisable carbon (C_0), the various SOC fractions and the soil enzyme activities investigated.

L1 = Hypersalic Solonchaks under xerophytic scrubland; L2 = Haplic Solonetzs under xerophytic scrubland; M1 = Aluandic eutrosilic fulvic Andosols under riparian laurel forest, M2 = Silandic eutrosilic fulvic Andosols under laurel forest; M3 = Aluandic eutrosilic fulvic Andosols under heath forest, M4 = Leptic Luvisols under heath scrubland; M5 = Silandic fulvic Andosols under pine plantation; H1 = Luvic Phaeozems under humid pine forest, H2 = Leptic Cambisols under xeric pine forest; H3 = Silandic fulvic endoleptic Andosols under leguminous scrubland; C_0 = potentially mineralisable carbon; k = mineralisation rate; C_{10}/C_0 = ratio of carbon mineralised during the incubation; R^2 = fit to first order kinetics. WSC = Water-soluble carbon; WSC_{se} = water-soluble carbon in saturated extract; HWC = hot water-extractable carbon; PSC = potassium sulphate-extractable carbon; MBC = microbial biomass carbon; POC = particulate organic carbon; HSC = humic substances carbon; TOC = total organic carbon; CEL = CM-cellulase activity; GLU = β-D-glucosidase; DEH = dehydrogenase activity; WOO = woody litterfall carbon inputs; NON = non-woody carbon inputs; ROO = root carbon content at 0-30 cm depth.

HWC, the soil enzyme activities (especially with the dehydrogenase activity), and the degree of fit with the kinetic model. In contrast, the lowest positive correlation was with PSC, and negative correlations were observed with *k* and the C_{10}/C_0 ratio.

Principal component 1, which represents 58 % of the total variance in the data, condenses most of the collinear variation in the analysed variables. Principal component 1 is positively correlated with the supplies of non-woody residues via litterfall and by root biomass (which are included in the diagram as passive variables). However, this component is not correlated with woody residue supplies. The investigated soil samples are ordered in the following sequence (in order of increasing scores) with principal component 1: lowland soils < highland soils < midland soils and 15-30 cm depth < 0-15 cm depth.

Component 2, which has a much lower explained variance (approximately 10 %), mainly reflects variations that occurred within each study site. This type of variation is related to the season. For example, winter samples had much lower scores (-0.157 ± 0.149, mean ± SEM) than those for spring (0.033 ± 0.169), summer (0.060 ± 0.171) or autumn (0.060 ± 0.192) (data presented as the mean ± SEM). Along this axis, a negative relationship was observed between C_0 and PSC in some soils as one decreased and the other increased.

4. Discussion

4.1. SOC fractionation

The sequestration of organic carbon in stable forms in forest Andosols has been extensively studied. However, few studies have reported the concentrations of the different labile SOC forms in these soils. Here, the investigated Andosols with tree and shrub vegetation had WSC, PSC, MBC, and HWC concentrations that were much higher than those reported by other authors for Andosols in grasslands or herbaceous croplands (Murata et al. 1998, Nishiyama et al. 2001, Ghani et al. 2003, Uchida et al. 2012). These differences are a result of the greater amounts of organic inputs from forest vegetation. The labile SOC concentrations determined in this study were closely related to the abundance of roots and the supply of aboveground easily decomposable residues, such as leaves, flowers, and fruits. However, no correlation was observed with the aboveground woody residue inputs. Thus, we concluded that these residues, which are mainly composed of cellulose and lignin, contribute little to the labile SOC pool.

4.2. Soil enzyme activities

The β-D-glucosidase and dehydrogenase activities fell within the ranges of variations that are typical for forest soils (García et al. 2003). However, the CM-cellulase activity was generally low and was negligible in the lowland soils. The latter result is not unusual in arid areas, where cellulase activity is often only detectable at certain times of the year and coincides with favourable meteorological and/or phenological conditions (Doyle et al. 2006). Because of low cellulase activity, organic residues may accumulate with little transformation, as observed in the L1 soil by González-Pérez et al. (2007). In the midland and highland areas we found the lowest cellulase activity levels in the M1 and H1 soils, which is consistent with the POC concentrations in these soils, which were the lowest in the midland and highland ecosystems, respectively.

4.3. Kinetic model

First-order kinetic models describe reactions in which the rate only depends on the concentration of one substrate. If the soil contains a large amount of very labile SOC (which is typical in the surficial layers of the midlands and highland area soils) or if the respiratory rate is very low (as observed in the winter samples), the mineralisation during incubation will only affect the most readily-mineralisable SOC. Thus, in this scenario, the labile SOC is not depleted during

the incubation period, which is reflected by the low C_{10}/C_0 ratio values. In this case, the R^2 value will be near 1 because the process fits a simple first-order model well.

In contrast, if the most labile SOC fraction is depleted during incubation, sequential mobilisation will occur of SOC fractions that are more resistant to mineralisation. Therefore, the R^2 values will be lower because the process will not fit a first-order model well. Instead, this process will fit a more complex first-order model, as shown below:

$$C_t = \sum_{i=1}^{n} C_i (1 - e^{-k_i t})$$

where C_t is the amount of accumulated mineralised SOC, C_i is the initial content of the n kinetic pool in the SOC and k_i is the flux rate of each kinetic pool. Long-term incubation assays usually allow for the separation of between 2 and 5 SOC reservoirs. Each of these reservoirs is characterised by certain sensitivity to mineralisation (Cheng et al. 2007).

Thus, the degree of fit between the first-order kinetics and the C_{10}/C_0 ratios was obtained from our assays and was used to determine the chemical diversity of the compounds that were mineralised during incubation. In the dominantly andic soils in the midland and highland areas, the fit approached 100 %, which reflected the mineralisation of highly-bioavailable SOC forms that were easily metabolised. These SOC forms were abundant in these soils and were only partially consumed during the incubation. In turn, the lowland soils had the lowest degree of fit with the simple kinetic model. This result is consistent with the low labile SOC concentrations found in the lowland soils. Our interpretation is that, as a consequence of the low availability of readily decomposable compounds in the lowland soils, several substrates that have different sensitivities to mineralisation took part in this process during the incubation of these soils.

4.4. Relationships between the soil biological activity and the SOC fractions

Among the physico-chemical SOC fractions, the HWC fraction was most closely related to C_0. Thus, the HWC fraction could be considered to be the best predictor for potentially mineralisable carbon. The HWC fraction is mainly composed of carbohydrates and nitrogen-rich organic compounds, such as amido- and amino-N, which are mainly derived from the desiccation of microbial cells (Haynes, 2005). Many of these compounds are dissolved in the soil solution or are weakly adsorbed to mineral surfaces or humic macromolecules (Leinweber et al., 1995). Armas et al. (2007) reported that HWC plays a central role in SOC cycling in these investigated soils and can be used to determine the degree of carbon storage and biogeochemical equilibrium in these soils along with the respiratory fluxes and the hydrolytic soil enzyme activities.

POC is considered an important labile SOC fraction and is transient between plant materials and humified organic matter (Haynes 2005). In our results, C_0 was more correlated with HWC than with POC. Moreover, the strongest correlation between C_0 and enzyme activity occurred for the dehydrogenase enzyme within sites and for the β-D-glucosidase enzyme for all sites. However, the relationship between cellulase and C_0 was less significant. The reservoir of labile SOC in the analysed soils depended more on di- and oligosaccharides, which are substrates of glucosidase, than on cellulose-type polymers, which are substrates of cellulose and are a major component of POC. The seasonal changes in the labile SOC concentration may be related to changes in contents of simple sugars, which are the substrate of dehydrogenase. Murata et al. (1999) observed seasonal fluctuations in simple sugars in soils similar to ours.

Because of its water solubility, WSC is often considered to be highly accessible for microorganisms, as discussed in detail elsewhere (von Lützow et al. 2007). However, in this study, WSC did not play an important role in the labile SOC pool, potentially due to its low contribution to total labile SOC (rather than due to its

low bioavailability). WSC concentrations were higher than WSC_{se} concentrations in the less andic soils, probably due to mineralisation resulting from soil drying. However, WSC_{se} concentrations were higher than WSC concentrations in the more andic soils. The reason for this behaviour in Andosols is uncertain, but it may be caused by the release of soluble compounds from initially protected SOC reservoirs during drying, as suggested by Verde et al. (2010).

In the arid lowland soils (L1, L2), the potentially mineralisable carbon depended on the microbial biomass and was highest in the winter, which coincided with the highest soil water availability. During the rest of the year, the C_0 and MBC concentrations decreased and the PSC concentrations increased. Potassium sulphate (0.5 M) has a higher extracting capacity than pure water due to its highest ionic strength. Thus, potassium sulphate can be used to extract forms of SOC that are adsorbed on clay surfaces and soil organic matter (Chen et al. 2005). Our results indicated a seasonal transfer of organic matter between the MBC pool, which is considered labile, and the PSC pool, which is less bioavailable due to its association with soil colloids.

The PSC concentrations were negatively correlated with C_0, but not with MBC, in the M5 and H3 soils. These soils are silandic Andosols that are characterised by a colloidal fraction in which allophanic minerals are dominant (soil M2 also qualifies as a silandic Andosol, but its topsoil layers have aluandic characteristics). Nishiyama et al. (2001) found that PSC was more abundant in Andosols than in non-andic soils. These authors attributed this result to the association of organic compounds with short-range ordered mineral surfaces (allophane, imogolite, and ferrihydrite), through the formation of strong bonds with active aluminium via specific anion adsorption (i.e., inner-sphere complexation). These adsorbed organic compounds are not highly bioavailable, but can be extracted with ligand-exchange reactions by using a 0.5 M potassium sulphate solution. Our results highlight the association of SOC with short-range ordered minerals in the M5 and H3 soils. This association limits the bioavailability of the SOC and the resulting mineralisation. However, these associations do not occur in aluandic Andosols, in which the colloidal fraction is dominated by aluminium-humus complexes. Additional research is needed to determine the nature, amount, and stabilisation mechanisms of PSC. In addition, the antagonistic behaviour of PSC against potentially mineralisable carbon in allophanic and non-allophanic Andosols should be investigated.

5. Conclusions

Measuring the CO_2 emitted during short (ten days) incubation assays is a useful method for assessing labile SOC in soils of volcanic origin. By fitting the mineralisation results with simple first-order kinetics, we estimated the readily mineralisable SOC reservoir and obtained information regarding the metabolised substrate diversity during incubation. Specifically, this information was obtained from the mineralised to potentially mineralisable carbon (C_{10}/C_0) ratios and the R^2 values, which were used to determine the model fit.

The investigated volcanic soils had large labile SOC concentrations in which simple carbohydrates predominate and that are mainly derived from roots and aboveground non-woody residues. Among the analysed physico-chemical SOC fractions, HWC was the most correlated with C_0. Therefore, HWC is the most useful surrogate for potentially mineralisable carbon. In the arid lowland soils, the potentially mineralisable carbon fluctuated distinctly with season and depended on the proliferation of soil microorganisms under different soil moisture conditions. The PSC fraction had low bioavailability probably due to its absorption to short-range ordered minerals in silandic Andosols.

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