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Land-use effects on the distribution of soil organic carbon within particle-size fractions of volcanic soils in the Transmexican Volcanic Belt (Mexico)

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Abstract

The aim of this study was to determine the effect of land-use and forest cover depletion on the distribution of soil organic carbon (SOC) within particle-size fractions in a volcanic soil. Emphasis was given to the thermal properties of soils. Six representative sites in Mexico were selected in an area dominated by Andosols: a grassland site, four forested sites with different levels of degradation and an agricultural site. Soils were fractionated using ultrasonic energy until complete dispersion was achieved. The particle-size fractions were coarse sand, fine sand, silt, clay and particulate organic matter from the coarse sand sized fraction (POM-CS) and fine sand (POM-FS). Soil organic carbon decreased by 70% after forest conversion to cropland and long-term cultivation; forest cover loss resulted in a decrease in SOC of up to 60%. The grassland soil contained 45% more SOC than the cropland one. Soil organic carbon was mainly associated with the silt-size fraction; the most sensitive fractions to land-use change and forest cover depletion were POM followed by SOC associated with the silt and clay-sized fractions. Particulate organic matter can be used as an early indicator of SOC loss. The C lost from the clay and silt-sized fractions was thermally labile; therefore, the SOC stored in the more degraded forest soils was more recalcitrant (thermally resistant). Only the transformation of forest to agricultural land produced a similar loss of thermally stable C associated with the silt-sized fraction.

Keywords: Andosols, soil physical fractionation, forest cover depletion, thermal analyses, agriculture, soil organic matter

Introduction

Soils formed from volcanic materials (Andosols) contain the largest amount of soil organic carbon (SOC) among the mineral soil orders (Eswaran *et al.*, 1993). However, forest cover loss decreases SOC which occurs in advance of complete deforestation when degraded forests are transformed into pasture, cropland and eroded areas (Cairns *et al.*, 1995).

Fractionation of soils is based on the assumption that soil organic matter (SOM) which is associated with different

particle sizes also differs in chemical composition or function depending on degree of humification (Christensen, 2001). Land-use practices including cultivation can affect the quality and quantity of SOM associated with particles (Christensen, 2001), and may affect the distribution between particulate organic matter (POM) and SOM associated with minerals (Cambardella & Elliott, 1993). Christensen (2001) proposes that the main effects of land use practices can be observed by changes in the distribution of SOC within particle-size classes. The size of POM which is strongly influenced by soil management has been used as an early indicator of trends in SOM in managed soils (Wander, 2004). Determination of particle-size fractions is useful in studying the effect of land-use change on soil carbon stocks, but few studies have been

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carried out to determine the effect of forest cover depletion on particle-size fractions, and even less so in volcanic soils.

Thermal stability of SOM is resistance to thermal oxidation during heating. Thermal properties have been used to assess SOM quality and decomposability (López *et al.*, 2005; Plante *et al.*, 2005). López *et al.* (2005) state that thermal analyses enable the distinction of labile and more recalcitrant components of physically separated SOM fractions. They found a correlation between fractions separated by thermal analyses and the results obtained from ^{13}C NMR analyses. Other authors have found consistent correlation between thermally separated fractions and results from pyrolysis (Leinweber *et al.*, 1992). Plante *et al.* (2005) conclude that the thermal properties of clay-associated organic matter can be related to biological decomposability and that thermal techniques can be used to detect changes in SOM fractions as a consequence of land-use change, but there are few similar studies. The objective of this study was to determine the effect of land-use and forest cover depletion on the distribution of C within particle-size fractions in a volcanic soil. The thermal properties of the SOM associated with the silt and clay-size fractions were also investigated.

Materials and methods

Site description

The field site was in the Atécuaro catchment located between 19°33' and 19°37' North and between 101°09' and 101°15' West within the Cuitzeo Lake basin (Michoacán, Mexico), covering an area of 44.2 km² with an altitude ranging from 2000 to 2700 m a.s.l. The climate is temperate subhumid, with a mean annual temperature of about 16.8 °C and mean annual precipitation of 844 mm/yr which is concentrated between June and October. The predominant soil parent materials are Quaternary lavas and pyroclasts. Dominant soils in the catchment are *Andosols* and *Cambisols* (silty-loam and clayey-loam soils with a pH ca. 5.0; Instituto Nacional de Estadística, Geografía e Informática (INEGI), 1982).

Pine-oak forests are located mainly in the south and south-eastern part of the catchment area between 2300 and 2500 m a.s.l. In 1975 pine and oak forests covered 17% of the Cuitzeo basin and this had increased to 20% by 2000 López *et al.* (2006). This suggests that the actual vegetation cover and soil use have not changed, at the least in the last 40 yr. Maize is cultivated on the foothills and small valleys close to human settlements.

Six representative sites were selected in the southern part of the catchment with a northern aspect in a *Silandic Andosol* dominated area along a slope where different forest conditions and land-uses were well represented:

1. A grassland site that was previously used for agriculture and then abandoned ca. 30 yr ago (GL),

2. Four forested sites under pine-oak vegetation with decreasing tree density downslope: pine-oak forest 1 (POF1), pine-oak forest 2 (POF2) and pine-oak forest 3 (POF3); note that a higher number indicates decreased forest cover; a fuelwood area (FW) suffered from a forest fire in 1998,
3. Recently abandoned agricultural land after long-term fallow (AL).

In April 2006, three composite soil samples (10 subsamples) were collected from the surface horizon (0–10 cm) at each site using a cylindrical probe. The sampling area was 1200 m² divided into three circular subplots of 400 m²; one composite sample was collected from each circular subplot. Soil samples were kept moist and stored at 4 °C prior to analysis because drying of volcanic-ash derived soils can affect soil physical properties (Nanzyo *et al.*, 1993).

Laboratory analyses

Soil analysis. The SOC concentration was determined by the dry combustion method using a LECO analyser. Total N was determined using the Kjeldahl digestion–distillation method (Bremner, 1965) and measured in a Bran Luebbe AA3 Autoanalyser.

Particle-size fractionation. The sonicator used was a Vibracell (Sonics & Materials Inc., USA) with a maximum power output of 600 W and with a probe of 13 mm diameter. The sonicator was calibrated by determining the real power output calorimetrically, as described by Roscoe *et al.* (2000) and Oorts *et al.* (2005).

For fractionation 20 g of equivalent oven-dried soil were passed through a 2-mm sieve and then transferred into a 150-mL glass beaker. Distilled water (100 mL) was added to give a ratio of soil to suspension of 1:5. The soil-water suspension was sonicated with the probe tip inserted 20 mm into the suspension. The minimum of energy required for complete dispersion was found by applying increasing amounts of ultrasonic energy before complete fractionation. From the results, it was decided to apply energy of 244 J/mL to fractionate soil samples which seemed an appropriate compromise to minimize further breakdown of particles.

Coarse sand (2000–200 µm) and fine sand (200–50 µm) were separated from the sonicated suspension by wet sieving. Then the sieve fractions were collected and further separated into mineral and organic material (POM) through flotation–decantation in water. The remaining suspension containing only silt (50–2 µm) and clay-sized particles (<2 µm) were separated by centrifugation. Fractions were transferred to bottles for oven-drying. After fractionation the following size fractions were obtained: (a) clay, (b) silt, (c) fine sand, (d) coarse sand, and (e) POM separated from fine sand (POM-FS) and (f) coarse sand (POM-CS).

1 *Thermal analyses.* Thermal analyses were performed on the
2 clay and silt-size fractions derived from the physical particle-
3 size fractionation as described above. Thermogravimetry
4 (TG) and differential thermal analysis (DTA) were performed
5 simultaneously using a TA SDT-Q600 thermal analyser. For
6 each sample, ca. 8 mg of the soil fractions were placed in a
7 platinum crucible and heated from room temperature to
8 800 °C at a heating rate of 10 °C/min in a synthetic air
9 atmosphere (100 mL/min). Three replicates per sample were
10 run. Analyses of the TG traces and DTA peaks (exotherms
11 represented as positive displacement) were performed using
12 the instrument software.

13 Thermograms from Differential Scanning Calorimetry
14 (DSC; data not shown) were simultaneously generated. The
15 exothermic peaks detected in the DTA and DSC were
16 comparable, indicating that the energy needed to degrade
17 SOM was constant for the whole range of temperature and,
18 therefore, it was justifiable to use both thermograms to detect
19 peak temperatures related to SOM degradation.

20 Total weight loss associated with thermal decomposition of
21 organic constituents between 200 °C and 600 °C was called
22 Exotot following the nomenclature proposed by Dell'Abate
23 **3** *et al.* (2002). Based on the first derivative of the TG (data not
24 shown), Exotot was divided into Exo1 (the weight loss
25 associated with the first exotherm as a proportion of Exotot),
26 and Exo2 (the weight loss associated with the second
27 exotherm as a proportion of Exotot). Each exotherm of the
28 DTA thermograms corresponded to a weight loss detected in
29 TG, which allowed quantification of the different fractions
30 involved in the reactions.

31 *Statistical analyses*

32 The effects of land use and forest cover depletion on bulk soil
33 density, particle-size and thermogravimetric parameters were
34 analysed by one-way ANOVA using Statistica 6 software
35 **4** (StatSoft, 2000). A multiple comparison of means for each
36 class variable was performed using Tukey's HSD test
37 ($P < 0.05$).
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The effect of forest cover depletion on soils was assessed
 through comparing results from the conserved forest site
 (POF1), the forest with limited loss of tree cover (POF2), the
 more intensely harvested forest (POF3) and the area that was
 subject to a recent forest fire (FW). Land-use effects were
 investigated by comparing the most conserved forest site
 (POF1) with the grassland area (GL) and the agricultural
 land (AL).

44 Results

45 *Soil properties*

Results for the upper soil layer (0–10 cm) are summarized in
 Table 1. SOC ranged from 35 to 130 g C/kg. For forest sites,
 SOC decreased in the order POF1 > POF2 > FW = POF3
 (Table 2). Similarly, SOC concentrations decreased from the
 natural forest to agricultural land. Total N (Nt) varied
 between 2.6 and 8.3 g N/kg and was significantly greater in
 POF1 and 2 than in the other two forest sites (FW and
 POF3; Table 1). Nt was also affected by land use and
 decreased from POF1 to the agricultural land following a
 pattern similar to SOC. The C/N ratio ranged from 10 to 22
 and was significantly higher in the fuelwood area than in the
 other forest sites. Moreover, POF1 had a greater C/N ratio
 than soils in the fallow area (GL).

46 *Soil organic C in particle-size fractions*

Table 2 demonstrates the distribution of soil particle-size
 fractions as obtained using ultrasonic dispersion and also the
 C concentration associated with primary particles and POM.
 Total recovery of the initial amount of soil after fractionation
 ranged from 91 to 100%.

The amount of clay and silt-sized particles ranged from 27
 to 37% and from 44 to 49% respectively for all sites with no
 statistically different results according to forest soils or
 different land-uses. The amount of fine sand varied between 4
 and 11% with corresponding values between 4 and 8% for
 coarse sand; all forest soils had similar values. Non-forested

44 **Table 1** Soil characteristics of the upper horizons (0–10 cm) at the study sites

Site	SOC (g C/kg)	Nt (g N/kg)	C/N
Grassland (GL)	48.6 (5.7) B	4.5 (0.2) B	10.8 (1.4) B
Pine-oak forest 1 (POF1)	35.0 (4.2) C	2.8 (0.0) C	12.5 (1.5) AB
Pine-oak forest 2 (POF2)	130 (11.5) Aa	8.3 (1.1) Aa	15.9 (1.4) Ab
Fuelwood area (FW)	82.3 (10.2) b	6.1 (1.2) a	13.5 (1.5) b
Agricultural land (AL)	57.3 (6.8) c	2.6 (0.4) b	22.5 (3.3) a
Pine-oak forest 3 (POF3)	50.5 (8.1) c	3.1 (0.2) b	16.3 (2.0) b

45 Effect of land use: GL, AL and POF1 (differences in capital letters). Effect of forest cover depletion: POF1, POF2, POF3 and FA (differences in
46 small letters). Standard deviations are given in brackets. Different letters within the same column and effect indicate significant differences at
47 $P < 0.05$.
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Table 2 Particle-size fractions and organic carbon concentration within size-fractions from the 0 to 10-cm soil layer

Site	Clay-size	Silt-size	Fine sand-size	Coarse sand-size	Fine-sand particulate organic matter	Coarse-sand particulate organic matter
Fraction size (%)						
Grassland	34.8 (3.8) A	48.6 (2.1) A	9.5 (3.0) A	4.7 (0.8) B	1.9 (1.2) A	0.5 (0.3) B
Agricultural land	28.9 (1.3) A	44.9 (1.9) A	11.0 (0.7) A	7.8 (0.6) A	1.2 (0.4) A	0.7 (0.3) B
Pine-oak forest 1	26.5 (5.8) Aa	47.8 (1.8) Aa	3.5 (1.0) Ba	5.3 (1.5) ABa	3.7 (1.2) Aa	4.1 (2.5) Aa
Pine-oak forest 2	32.0 (6.6) a	49.0 (0.9) a	6.4 (2.9) a	6.3 (3.0) a	3.0 (2.0) a	2.0 (1.0) b
Fuelwood area	38.1 (1.3) a	45.0 (2.1) a	4.3 (0.4) a	3.3 (0.2) a	1.6 (0.5) a	1.9 (1.7) b
Pine-oak forest 3	33.6 (3.9) a	47.6 (3.7) a	7.3 (1.0) a	5.3 (0.6) a	1.2 (0.5) a	1.0 (0.2) b
C concentration (g C/kg soil fraction)						
Grassland	76.1 (10) B	64.5 (0.7) B	13.1 (2.6) A	17.3 (4.1) B	172 (19) B	324 (60) B
Agricultural land	63.9 (2.2) B	56.2 (1.9) C	6.4 (1.1) A	9.5 (2.3) C	141 (19) B	295 (0.0) B
Pine-oak forest 1	155 (3.5) Aa	136 (9.8) Aa	12.5 (2.2) Aa	14.9 (0.1) Ab	380 (12) Aa	422 (8.2) Aa
Pine-oak forest 2	124 (7.1) a	101 (6.9) b	10.4 (1.1) a	13.7 (4.5) b	356 (31) a	394 (6.8) a
Fuelwood area	56.4 (0.8) b	82.6 (5.5) c	13.8 (1.6) a	30.2 (5.1) a	313 (43) a	449 (11.8) a
Pine-oak forest 3	60.7 (7.6) b	71.5 (6.6) c	10.8 (1.3) a	14.9 (2.5) b	343 (37) a	390 (55) a
C distribution (g C/kg soil)						
Grassland	27.6 (3.6) B	32.7 (0.4) B	0.7 (0.1) A	1.2 (0.5) B	1.7 (0.5) B	3.2 (0.6) B
Agricultural land	18.6 (1.9) B	23.4 (1.7) C	0.9 (0.4) A	0.8 (0.2) B	2.7 (1.3) B	2.0 (1.0) B
Pine-oak forest 1	42.6 (7.7) Aa	69.1(4.3) Aa	0.6 (0.1) Aa	5.1 (1.7) Aa	17.1 (1.6) Aa	22.2 (7.8) Aa
Pine-oak forest 2	36.7 (2.3) a	50.1(3.3) b	0.7 (0.3) a	0.8 (0.2) b	13.5 (3.3) a	9.9 (2.2) b
Fuelwood area	22.8 (0.2) b	38.3(0.9) c	0.6 (0.1) a	1.0 (0.2) b	5.5 (1.3) b	5.1 (2.2) b
Pine-oak forest 3	21.1(1.0) b	35.4 (2.9) c	0.8 (0.1) a	0.8 (0.1) b	4.3(1.3) b	4.1(0.9) b

Effect of land use: grassland, agricultural land and pine-oak forest 1 (differences in capital letters). Effect of forest cover depletion: pine-oak forest 1–3 and fuelwood area (differences in small letters). Standard deviations are given in brackets. Different letters within the same column and effect indicate significant differences at $P < 0.05$.

areas had statistically greater amounts of fine sand particles and the AL had the highest amount of coarse sand particles. The amount of FS-POM was greater in the conserved forest than in the GL and AL. The amount of CS-POM was higher in the most conserved forest soil (POF1) than in the other forest sites.

In general, the C concentration of the particle-size fractions decreased in the order POM > clay = silt > sand. The C concentration of the POM fractions was similar for forest soils and was higher in the forest than in the other land-uses. The clay-associated C concentration ranged from 56 to 155 g C/kg fraction. The best conserved forest soils (POF1 and POF2) had higher concentrations than the two degraded forest soils (FW and POF3). Similarly, the forest soil had a higher C concentration than soil under the other two land uses. The concentration of C associated with the silt-size fraction (ranging from 56 to 136 g C/kg fraction) in soils decreased from natural to degraded forests, and among land uses decreased from the natural forest to the long-term fallow. The fine sand-associated C ranged from 6 to 14 g C/kg and no significant differences were found between sites. However, the coarse sand-associated C had the highest concentration in the FW, higher than the other forest soils. Among the land-uses, the forest had the highest C

concentration for this particle-size fraction, followed by GL and AL.

The silt-associated C was the largest C pool for all the soils (49% of total soil C, on average), followed by the C associated with the clay-sized fraction (34% of total soil C, on average). The C associated with the POM fractions accounted for 20–25% of the total soil C in the conserved forest soils (POF1 and 2; Figure 1), but was < 10% in the other land uses (GL and AL).

Soils in conserved forests (Pine oak forest 1 and 2) had in general a greater amount of C associated with the different particle-sizes; only the fine sand-sized fraction had similar values for all forest sites. Soils under different land-uses also had differences in the distribution of C associated with particle-size fractions. The proportions of C linked to the clay-size, coarse sand-size and POM fractions were significantly different under forest than in the GL and AL. Silt-associated C decreased in the order: forest > GL > AL.

Thermal analyses

The DTA traces of soil fractions showed an endothermic region between ambient temperatures and 150 °C because of water release and an exothermic region between 200 and

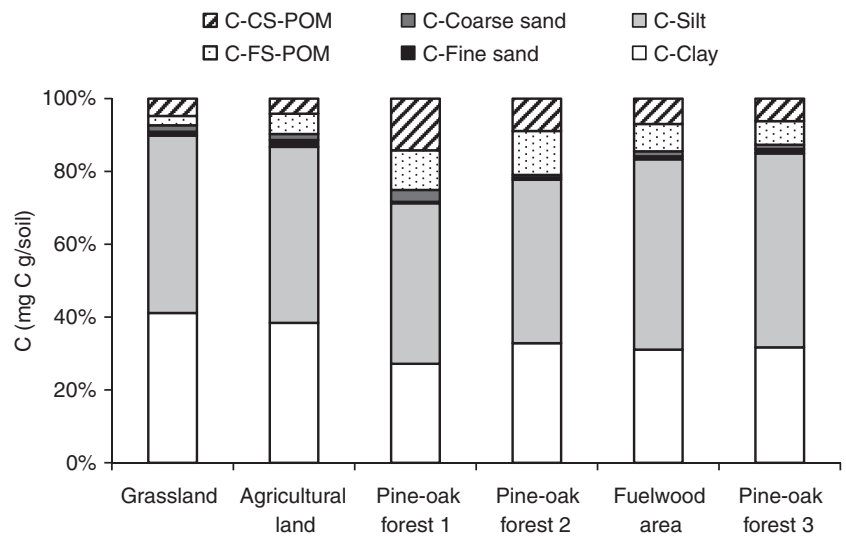


Figure 1 The C distribution within particle-size fractions of volcanic soils under different land-uses in Central Mexico. (note: The C content of each fraction was calculated by taking total soil C as the sum of the C associated with all separate particle-size fractions, including POM fractions).

600 °C (Figure 2). This region comprises two exothermic peaks because of the combustion and degradation of different SOM compounds. A smaller SOC concentration was associated with the smaller peak of the two detected exothermic ones and this was evident especially in the clay-sized fraction. The thermogravimetric results are presented in Table 3.

Clay-sized fraction. The DTA traces for the clay-sized fraction had in all cases an exothermic peak at 320–327 °C. Only in the GL did a second peak appear at 443 °C, but for the other soils it was more a shoulder than a real peak. The Exotot varied from 21 to 35% and in general the Exo1 (10–27%) was larger than the Exo2 (7–11%). For the forest soils, the POF1 had the highest Exotot and Exo1 followed by the POF2 and the other two forest soils (FW and POF3). The Exo2 was similar for all forest sites. Land-use affected the values of Exotot, Exo1 and Exo2. POF1 had the highest value for the three thermal variables. The fallow and agricultural land had a similar Exotot, but the GL had a higher Exo1 and Exo2 was higher in the AL than in the GL.

Silt-sized fraction. The DTA traces for the silt-size fraction had exothermic peaks at 333–342 °C and at 418–446 °C. Forest sites had similar peak temperatures for the first exothermic peak (341 ± 1 °C) and for the second the range of temperature differed by 8 °C between sites. For the different land uses the forest soil had significantly higher temperatures for the first exothermic peak and the GL for the second.

Results for Exotot (16.5–28.5%) and Exo1 (6.7–13.4%) have a similar pattern, decreasing in the following order among forest soils: POF1 > POF2 > FW = POF3. Exotot and Exo1 were largest for the forest soils followed by GL and finally AL. Exo2 (7–15%) was in general larger than the

Exo1 and decreased in the order: POF1 > POF2 = FW > POF3. The forest soil had the largest Exo2 among the land-uses with AL having a larger value than for GL.

Discussion

Effect of land-use on soil C pools

In the Atécuaro sequence, SOC in the upper soil layer (0–10 cm) varied by 70% between the most conserved forest soil (POF1) and AL. This accords with results of Cambardella & Elliott (1992), Balesdent *et al.* (1998) and Chenu & Plante (2006) who also found that the conversion from natural vegetation to agriculture leads to a depletion in SOC in different types of soils. Guo & Gifford (2002) and Murty *et al.* (2002) report that the magnitude of the SOC loss may vary from 25 to 75%, depending on the antecedent C pool, land use, management and climate. SOC losses are caused by a number of factors, including lower organic matter input to soil, increases in mineralization, soil erosion and leaching (Guo & Gifford, 2002).

The soil under cropland contained 45% less C than the grassland soil. Grassland in the area includes shrub and herbaceous vegetation which resulted in a higher litter input compared with agricultural land where crop residues and harvested crops are removed. In grassland soils, much of the litter input is from root biomass (Tate *et al.*, 2000). Overall, grassland sequesters more C than cropland (Guo & Gifford, 2002).

The amount of clay- and silt-sized C fractions in the grassland and especially the cropland is lower than in the conserved forest site. The mean residence time (MRT) of C associated with clay- and silt-sized fractions is greater than that of the C associated with coarser sized particles (García-Oliva *et al.*, 1994) as finer-sized separates are usually better aggregated to thus offer better protection from microbial

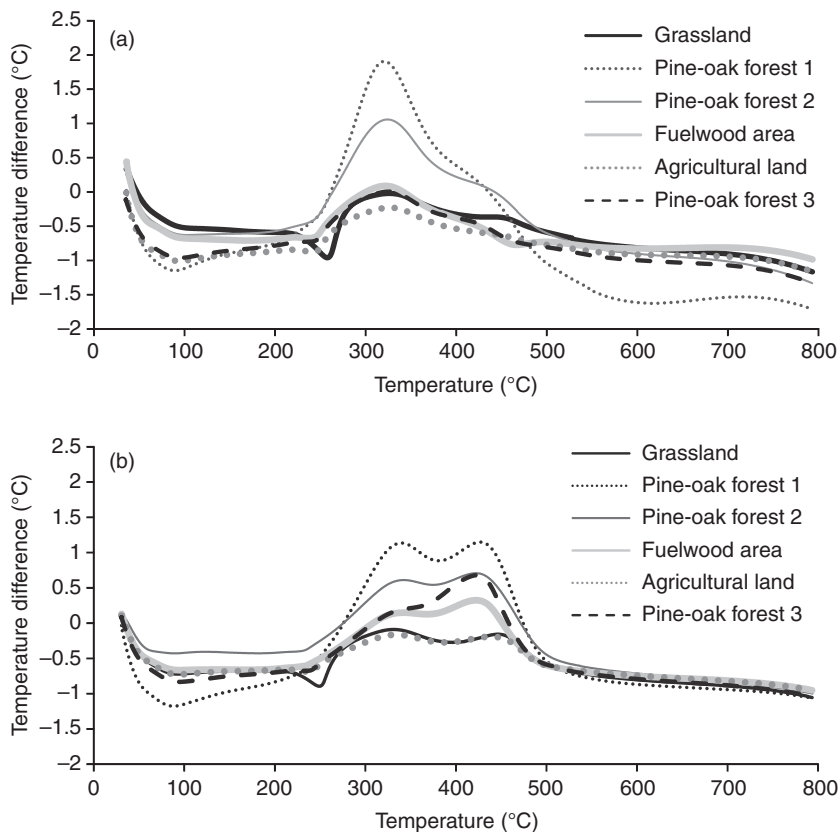


Figure 2 Differential thermal analysis of the: (a) clay-sized fraction and (b) silt-sized fraction of volcanic soils under different land-uses in Central Mexico.

Table 3 Mean values of the thermogravimetric analyses of the clay- and silt-sized fractions

Site	1nd exothermPeak (°C)	2nd exothermPeak (°C)	Exo1 (% of initial sample mass)	Exo2	Exotot	Exo2/Exo1
Clay-sized fraction						
Grassland	327 (1.8) A	443 (0.02)	17 (1.0) B	7 (0.2) C	23 (1.1) B	0.40 (0.02)
Agricultural land	325 (1.0) A	N.P.	12 (0.5) C	9 (0.5) B	21 (0.3) B	0.70 (0.06)
Pine-oak forest 1	323 (2.2) Aab	N.P.	27 (1.1) Aa	10 (0.2) Aa	34 (2.3) Aa	0.36 (0.02)
Pine-oak forest 2	324 (0.2) ab	N.P.	20 (0.6) b	10 (0.6) a	30 (2.4) b	0.51 (0.02)
Fuelwood area	320 (2.2) b	N.P.	10 (1.2) c	11 (0.4) a	21 (0.9) c	1.11 (0.16)
Pine-oak forest 3	327 (2.7) a	N.P.	11 (1.2) c	9 (0.3) a	21 (1.0) c	0.84 (0.84)
Silt-sized fraction						
Grassland	333 (1.3) B	446 (0.7) A	12.1 (0.5) B	7.4 (0.2) C	19.9 (1.2) B	0.61 (0.03)
Agricultural land	334 (1.3) B	432 (7.4) B	6.7 (0.2) C	9.6 (0.3) B	16.5 (0.7) C	1.42 (0.04)
Pine-oak forest 1	342 (1.9) Aa	426 (3.7) Ba	13.4 (0.5) Aa	15.0 (1.0) Aa	28.5 (1.2) Aa	1.12 (0.07)
Pine-oak forest 2	339 (4.0) a	424 (2.7) ab	9.7 (0.6) b	13.2 (0.5) b	23.0 (0.3) b	1.37 (0.13)
Fuelwood area	N.P.	418 (4.0) b	6.9 (0.7) c	13.7 (0.5) b	20.8 (0.6) c	2.00 (0.24)
Pine-oak forest 3	342 (2.5) a	425 (1.0) ab	7.5 (0.4) c	11.1 (0.5) c	19.0 (0.7) c	1.48 (0.15)

Exo1, Weight loss associated with the first exotherm; Exo2, Weight loss associated with the second exotherm; Exotot, Weight loss between 200 and 600 °C. Effect of land use: grassland, agricultural land and pine-oak forest 1 (differences in capital letters). Effect of forest cover depletion: pine-oak forest 1–3 and fuelwood area (differences in small letters). Standard deviations are given in brackets. Different letters within the same column and effect indicate significant differences at $P < 0.05$. N.P., no peak. N.d., not determined.

attack (van Veen & Kuikman, 1990). Long-term agriculture and grassland had the effect of reducing the stable SOM pool of the soil where the C is very humified and contributes to long-term C sequestration.

The amount of C associated with sand fractions is very low and is a consequence of the C being in the form of finer particle-sizes which coat sand surfaces. C associated with POM fractions was on average 87% lower in the soils under

the non-forested land-uses than under the conserved forest soil. The POM fractions had the highest decrease among the different size separates, which accords with the results of Balesdent *et al.* (1998) and Cambardella & Elliott (1992). Chenu & Plante (2006) report that free organic matter (FOM) was more depleted by cultivation than by clay-bound organic matter. This suggests a reduction in SOM renewal to thus constrain microbial activity and nutrient availability.

Effect of forest cover depletion on soil C pools

Soil organic carbon was from 37 to 61% lower in degraded forest sites compared with the best conserved area (POF1) which had the highest SOC content. Forest cover depletion had a significant impact on C associated with the clay- and silt-sized fractions, being 60% and 50% lower in the degraded forest (POF3) compared with the conserved forest (POF1).

The C concentration in the clay-sized fraction was higher for the silt-sized fraction of the conserved forest soils (POF1 and POF2) and lower or similar for the degraded forest soils (FW and POF3). These results suggest that C is lost preferentially from the clay-sized fraction with increasing forest cover loss. García-Oliva *et al.* (1994) report that the C silt-associated fraction was subject to a lower loss rate than the clay-associated C fraction in a tropical deciduous forest after conversion to pasture. This is because the clay-fraction was more enriched in new SOM because of microbial activity which decomposed faster than the silt-sized aggregate fraction (Gregorich *et al.*, 1991).

The amount of POM recovered after particle-size fractionation in the degraded POF3 was 80% lower than in the conserved POF1. Therefore, POM seems to be the most sensitive fraction to detect degradation processes. Soil organic matter depletion in forest areas results from the decrease in vegetation density and biomass, and therefore there is a decreasing organic input to the soil which causes increases in soil temperature and thus mineralization.

Thermal properties of the organic matter associated with the clay- and silt-sized fractions

The exothermic parts of the DTA thermograms from the SOM fractions indicate a coincidence of two main exothermic processes, suggesting that SOC associated with different size-fractions have different thermal stabilities as reported by Leinweber *et al.* (1992), Dell'Abate *et al.* (2002) and Plante *et al.* (2005). These reactions determine soil weight loss at different temperature steps as recorded on the TG curves (Dell'Abate *et al.*, 2002).

Endothermic peaks above 150 °C are attributed to the dehydroxylation of clay minerals (Mackenzie & Mitchell, 1972). Hutchinson (1974) proposes that the first endothermic

peak (240–250 °C) can correspond to cristobalite or allophone (only in andic soils) and the second (464 °C) to kaolinite.

On the basis of all the samples, the first exotherm gives a maximum in the range 320–342 °C because of the decomposition of the more labile aliphatic compounds and decarboxylation of carboxylic groups (Leinweber *et al.*, 1992). These results are consistent with the temperatures reported by Dell'Abate *et al.* (2002) for humic substances. The second exotherm indicates a maximum at ca. 418–446 °C because of the breakdown of aromatic structures (Leinweber *et al.*, 1992) and to the decomposition of aliphatic biopolymers which are protected by clays or sesquioxides. This temperature range is in accordance with results of Dell'Abate *et al.* (2002) and López *et al.* (2005).

The relative proportions of Exo1 and Exo2 differed between the particle-size fractions. The DTA curves indicate that the clay-size fraction had a larger 'labile peak' than a 'recalcitrant one' whereas the silt-sized fraction had a larger 'recalcitrant peak', also found by García-Oliva *et al.* (1994). The silt-sized fraction may therefore contain more humified or recalcitrant SOM. The silt-sized fraction was more difficult to disrupt into finer particles (clay-size fraction) through sonication requiring an energy input of > 350 J/mL which can be explained by the presence of 'pseudo-silt' (formed by very stable organo-mineral complexes), a common feature in volcanic ash derived soils. These results confirm that C sequestration takes place mainly within the silt-sized fraction.

To study the effect of land-use on organic matter quality, Plante *et al.* (2005) used results obtained from a conserved forest area as a reference and calculated ratios of other soil land uses to forest for TG masses, peak heights and areas. Based on this example, the POF1 soil was used in the present study as a reference (Table 4). The Exo1 ratios of the clay-sized fraction had the lowest values for degraded forest soils and long-term agricultural use to indicate that the C lost in this fraction was thermally labile, scarcely protected by inorganic colloids and poorly sorbed. In all cases > 50% of the clay associated C was related to Exo1 suggesting that half of the clay-associated C was vulnerable to loss. By contrast, the Exo2 ratios had values near to 1.0, indicating that the thermally stable C remained in the soil as a very stable, recalcitrant pool even after land-use change and long-term agricultural use.

The Exo2 ratios of the silt-size fraction decreased significantly with increasing forest cover depletion. Based on the Exo2 components (Exo1 and Exo2) up to 50% of the C lost was thermally labile (Exo 1), while the thermally stable C (Exo 2) was lost more slowly. In the long-term fallow, the Exo1 ratio was similar to those from the most degraded forests, but in this case C was also lost from Exo2, indicating that long-term agricultural use may also deplete the thermally stable C. By contrast, the soil under long-term grassland (GL) was the only one that had a higher ratio for Exo1 than

Table 4 Ratios of the thermogravimetric weight losses (Exotot, Exo1 and Exo2) of the grassland area, agricultural land, pine-oak forest 2, fuelwood area and pine-oak forest 3 compared with the selected reference site (pine-oak forest 1)

Site	Clay-sized fraction			Silt-sized fraction		
	R-Exotot	R-Exo1	R-Exo2	R-Exotot	R-Exo1	R-Exo2
Grassland (GL)	0.68	0.63	0.70	0.70	0.90	0.49
Pine-oak forest 1 (POF1)	0.61	0.46	0.90	0.58	0.50	0.64
Pine-oak forest 2 (POF2)	0.86	0.76	1.08	0.81	0.72	0.88
Fuelwood area (FW)	0.60	0.37	1.13	0.73	0.52	0.92
Agricultural land (AL)	0.60	0.42	0.98	0.67	0.56	0.74

R-Exotot: ratio of the weight loss between 200 and 600 °C from the studied plots to the reference plot (POF1). R-Exo1: ratio of the weight loss associated with the first exotherm from the studied plots to the reference plot (POF1). Exo2: ratio of the weight loss associated with the second exotherm from the studied plots to the reference plot (POF1).

for Exo2, indicating the presence of a small pool of thermally stable C.

The grassland soil had the lowest values of C associated with Exo2, both in the clay and silt-sized fractions. This depletion in the C associated with Exo2 may be a consequence of loss of tree cover making the site more susceptible to erosion (Kimble *et al.*, 2000).

Conclusions

The change of forested land to other uses caused the depletion of labile SOM, thus lowering SOC in the upper soil layers. The SOC in the conserved forest soil was 70% greater than the agricultural soil and 60% greater than the soil under the most degraded forest. POM was the most sensitive fraction to land-use change and declined by almost 90%, followed by the silt- and clay-sized fractions which had 53–66% and 35–56% less C after the conversion of forest to cropland and grassland, respectively. Forest cover loss could be the reason for the decrease in POM (<80%), and clay (<60%) and silt (<50%) sized fractions.

The C lost from the clay-sized fraction as a result of changes in land-use and forest cover depletion totalled ca. 50% and can be attributed to the thermally labile fraction (aliphatic C or weakly sorbed). At the forest sites the C associated with the silt-sized fraction was also lost (the thermal labile fraction). Therefore, the SOM stored in the more degraded forest soils was more recalcitrant (aromatic C or protected by inorganic colloids) as only this C remained in the soil. The transformation of forest to agricultural land also produced a loss of C from the more thermally stable silt-fraction.

The results demonstrate that thermogravimetry and differential thermal analysis of the clay and silt-sized fractions are useful techniques for detecting changes in SOM as a consequence of changes in land-use management, and thus allows determination of the extent to which soil has been degraded.

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