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Erosion, deposition and replacement of soil organic carbon in Mediterranean catchments: a geomorphological, isotopic and land use change approach

E. Nadeu¹, A. A. Berhe², J. de Vente^{3,4}, and C. Boix-Fayos¹

¹Centro de Edafología y Biología Aplicada del Segura (CEBAS-CSIC),
Campus Universitario de Espinardo, 30100 Murcia, Spain

²School of Natural Sciences, University of California-Merced, 4225 N. Hospital Rd,
Castle # 47, Atwater, CA 65301, USA

³Estación Experimental de Zonas Áridas (EEZA-CSIC), General Segura 1,
04001 Almería, Spain

⁴Department of Geography and Environment, School of Geosciences,
University of Aberdeen, St. Mary's Aberdeen AB243UF, UK

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Correspondence to: E. Nadeu (enadeu@cebas.csic.es)

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BGD

8, 8351–8382, 2011

**Erosion, deposition
and replacement of
soil organic carbon**

E. Nadeu et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abstract

The assessment of the net effect of soil erosion on the global carbon budget is still incomplete because of lack of enough focused studies and field data. Two of the major gaps on our understanding of the erosion induced terrestrial carbon sink issue include rate of eroded soil organic carbon (OC) replacement by production of new photosynthate and stability of eroded OC post deposition. Here we examine the effect of erosion processes and land use change on the stock, type and stability of OC in two medium-sized subcatchments (18 and 50 ha in size) in SE Spain. We analysed soil samples from drainage areas and depositional settings for stock and isotopic composition of OC (^{14}C and ^{13}C) and particle size distribution. In addition, we conducted land use change analysis for the period 1956–2008 and a geomorphological survey of the current erosion processes taking place in the slope-streambed connections. Our findings demonstrate how land use change influenced the dominating erosion processes and, thus, the source of eroding sediments. Carbon isotopes used as tracers revealed that in one of the subcatchments the deposited sediments derived from deep soil (average $\Delta^{14}\text{C}$ of -271.5‰) through non-selective erosion processes. In the other subcatchment, topsoil material was predominantly eroded and the average $\Delta^{14}\text{C}$ in sediments was -64.2‰ . Replacement of eroded soil OC was positive (4 and 11 times-fold losses by erosion) for the analyzed soil profiles in the slopes suggesting that erosion processes do not necessarily provoke a decrease in soil OC stock.

1 Introduction

Soil erosion is a ubiquitous process that redistributes topsoil and associated soil organic carbon (C) within and out of watersheds. Over the last 15 yr, it has become clear that improved understanding of how soil OC is detached, transported and deposited over the landscape, and the factors that can cause this to change, is essential to close the global carbon budget (Berhe et al., 2007; Stallard, 1998). Moreover, there is a

BGD

8, 8351–8382, 2011

Erosion, deposition and replacement of soil organic carbon

E. Nadeu et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



critical need to get better understanding of the stability and stabilization mechanisms of eroded OC in depositional sites and to what extent OC lost from eroded slopes can be replaced by new OC input from vegetation (Berhe et al., 2008; Van Oost et al., 2007).

5 Proper identification and accounting of the source and fate of eroded soil OC arriving at different types of depositional environments remain among the most significant gaps in our ability to accurately quantify the contribution of soil erosion to terrestrial carbon dioxide (CO₂) sequestration (Berhe et al., 2007; Harden et al., 1999; Van Hemelryk et al., 2011). Identification of sediment sources (from different parts of a catchment or different catchments) and factors that control source variability are critical since the
10 concentration and composition of OC in the mobilized sediment, the rate of OC enrichment in sediments (Collins et al., 1997) and the fate of the mobilized OC depend on the characteristics of the source material – which can include soil, plant debris, litter, and bedrock. Lithology and geomorphic variables, such as slope gradient and length, exert a primary control on the type of erosional processes and the rate of sediment
15 redistribution (Romero-Diaz et al., 2007). Land use changes and changes in precipitation regimes also strongly influence the nature and rate of erosion through their effect on hydrological and sedimentary dynamics at the catchment scale (Boix-Fayos et al., 2007) and, consequently, the concentration and composition of OC in the exported
20 sediments can vary depending on the nature of the prevailing erosional processes (Nadeu et al., 2011). Additionally, shifts in water flowpaths over time can also lead to changes in amount and composition of eroded OC (Gómez et al., 2010; Hilton et al., 2008; Raymond and Bauer, 2001; Schiff et al., 1997) with implications for greenhouse gas emissions in source soils and depositional settings.

25 The fate (post-detachment decomposition kinetics) of the eroded OC during transport and deposition and its replacement in the soils of eroded landform positions constitutes a second key step towards a better understanding of the role of erosion in OC sequestration. The criterion for soil erosion to constitute a net carbon sink states that dynamic replacement of eroded OC in eroding sites, and reduced decomposition rates

**Erosion, deposition
and replacement of
soil organic carbon**

E. Nadeu et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



at depositional sites must together more than compensate for erosional losses of soil OC from the catchment (Berhe et al., 2007). Thus, only if at least some of the eroded OC is preserved in depositional sites, and/or replaced by new photosynthate at eroding slopes can soil erosion constitute a net carbon sink (Berhe et al., 2008; Stallard, 1998).

5 Therefore, in order to assess the effect of different factors on OC sequestration and replacement, catchment scale studies are needed to complement and verify laboratory based results, which, in some cases, mismatch field observations (Van Hemelryck et al., 2011).

10 In this study we aim to shed light on these two issues, source and fate of OC after erosion, and their implications on OC sequestration. We evaluate the role that land use change and dominant erosion processes have played in controlling the sources and fate of OC in two contrasting Mediterranean subcatchments. Questions to be addressed include: how do land use changes influence the dominant erosion processes and the sediment sources? How do the dominant erosion processes affect OC sequestration at depositional sites? Is the OC lost from eroding slopes annually replaced by new photosynthate? To answer these questions, we used a combined approach based on a carbon isotope study (^{13}C and ^{14}C), geomorphological surveys and land use change analysis.

2 Study site and methods

2.1 Study site

20 The study was carried out in two subcatchments of the La Rogativa catchment ($\sim 50\text{ km}^2$) located in Murcia (SE Spain) (Fig. 1). The region is characterized by a Mediterranean climate with a mean annual temperature and precipitation of 13.3°C and 583 mm, respectively. The area has undergone considerable land use changes in the last thirty years, through decreasing proportion of land area used for rainfed agriculture and increasing proportion of area covered by secondary forests as a result of

BGD

8, 8351–8382, 2011

Erosion, deposition and replacement of soil organic carbon

E. Nadeu et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



both natural succession and reforestation. Vegetation is currently dominated by forest cover (*P. nigra-salzmannii*, *P. halepensis*, *P. pinaster*) (Boix-Fayos et al., 2007). Two contrasting subcatchments with the same pluviometric conditions, at a distance of 6 km from each other, were selected for this study: subcatchment C51 (50 ha), ravine of “La Suerte Estrecha” (38°8′11″ N, 2°13′42″ W) and subcatchment C24 (18 ha), ravine of ‘Loma Parrilla’ (38°6′3″ N, 2°14′15″ W). In general terms, C51 has a larger drainage area, while average slope of the drainage area and the stream are similar for both subcatchments (Table 1). Lithology at both sites is characterized by a mixture of marls, limestones and sandstones from the Cretaceous (IGME, 1978) in addition to an outcrop of quaternary glacia in C24. The two subcatchments differ with regards to the nature of erosion processes. Water flows through the streams very seldom throughout the year with a strong dependence on the occurrence of precipitation events. The subcatchments are delimited by a check-dam at their outlet that was built following hydrological correction works that were promoted by the regional government during the 1970’s. These check-dams, built in 1977, have a trapping efficiency of 71 % and 87 %, for C51 and C24, respectively (Boix-Fayos et al., 2008). C51 and C24 were chosen for this study because they represent contrasting history of land use changes and, therefore, allow examination of the effect of different land use histories on OC dynamics. C24 represented a relatively stable land use situation of semi-continuous forest cover during the whole period of observation, from 1956 to 2008. In contrast, C51 experienced reduction in agricultural land over the last 40 yr (Boix-Fayos et al., 2008). Mean annual erosion rates in both subcatchments were derived from the estimation of the volume of sediments deposited behind the check-dams (Table 1) (Boix-Fayos et al., 2008).

2.2 Sampling of soils and sediments

To observe the erosion process and determine mean residence time of OC, two landform positions were selected: eroding slopes and depositional sites. The sediment wedge retained behind the check-dam was defined as the depositional site at the

BGD

8, 8351–8382, 2011

Erosion, deposition and replacement of soil organic carbon

E. Nadeu et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



subcatchment scale. In each subcatchment, four soil profiles on the neighbouring slopes and two sediment profiles were sampled. Soil samples were taken at 5 cm increments for the topsoil (0–5, 5–10), then every 10 cm (10–20, 20–30) and finally every 15 cm down to 90 cm or until the saprolite boundary was reached. In total 32 in-depth soil samples were collected in each subcatchment in spring 2010 (8 for each profile). Bulk density cores (100 cm³) were taken for each sampled depth. Sediment samples were taken in Summer 2009 in 5 cm increments until bedrock was reached in two locations (Fig. 2): behind the check-dam (A profile) (down to 70 and 80 cm depth for C51 and C24, respectively) and at the end of the sediment wedge (B profile) (reaching 50 cm depth in C51 and 20 cm depth in C24). A replicate was taken for both locations (A and B in each subcatchment) in 15 cm increments.

2.3 Geomorphological mapping and land use change

A geomorphological survey based on the methodology proposed by Hooke (2003) was conducted in each subcatchment to identify dominant erosion processes and current sediment source areas along the slope-streambed connections. The whole stream was characterized in C24 (430 m aprox.), while only two thirds of it were mapped in C51 (500 m aprox.). Processes were classified as: interrill erosion, rill erosion, gullies, creeping and bank erosion. Further, the stream bed was surveyed to detect aggradation and degradation features in the channel.

Land use data was derived from manual digitalization of three ortophotos from 1956 (American flight, spatial resolution 1 m), 1981 (General Directorate of Landscape Planning, Region of Murcia, spatial resolution 1 m) and 2008 (Natmur-08 Project of the General Directorate of Natural Heritage and Biodiversity, Region of Murcia, spatial resolution 0.45 m). Land use units were digitalized and coded using GRASS software and classified into one of these five categories: high density forest (HDF), low density forest (LDF), reforested areas (REF), shrubland (SH) and dry-land agriculture (DLA) (Boix-Fayos et al., 2007). Geology and lithology were derived from the digital geological maps of the IGME (1978) at 1:50 000 and field observations.

BGD

8, 8351–8382, 2011

Erosion, deposition and replacement of soil organic carbon

E. Nadeu et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



2.4 Particle size distribution and OC

All soil and sediment samples were oven-dried at 60 °C, gently crushed and passed through a 2 mm sieve. Particle size distribution was determined on chemically dispersed samples using a combination of wet sieving (>63 µm particles), for the sand fraction, and laser diffractometry techniques (<63 µm) for the silt and clay fractions. Samples for analysis of total carbon and N were passed through a 2 mm sieve and ground using a 8000M SPEX mill before they were analysed by the dry combustion technique using a Costech ECS 4010 at UC Merced (Berhe et al., 2008). Particulate organic carbon (POC; >53 µm) was separated from mineral-associated organic carbon (MOC; <53 µm) by wet sieving after dispersion with sodium hexametaphosphate and organic carbon was determined through the wet oxidation method (Yeomans and Bremner, 1988). Enrichment ratios in sediment samples for a given parameter were calculated as the ratio between the value measured in sediments to the average parameter value computed from soils sampled in the drainage area (top 0–30 cm) (Nadeu et al., 2011).

2.5 ¹³C and ¹⁴C analysis

The use of carbon isotopes (¹³C and ¹⁴C) is of special interest for catchment scale assessments of OC erosion, deposition and replacement because they can be used as tracers of sediment sources (Gómez et al., 2010; Hilton et al., 2008; Masiello and Druffel, 2001; Schiff et al., 1997) and to study soil OC dynamics (Trumbore, 2009).

One soil and one sediment profile in both subcatchments were selected for ¹⁴C analysis on bulk soil OC. Visible roots were removed from the samples to ensure sample homogeneity prior to grinding them to fine powder using a 8000M SPEX mill. Ground samples were washed with 1N HCl to remove carbonates. The carbonate free samples were processed following the methods of Xu et al. (2007) to determine the ¹⁴C/¹²C and ¹³C/¹²C ratios. The Δ¹⁴C and δ¹³C values reported are the ‰ deviation of a standard corrected to a δ¹³C of –25‰ and they represent a mean of the OC pools present

BGD

8, 8351–8382, 2011

Erosion, deposition and replacement of soil organic carbon

E. Nadeu et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



in each bulk soil and sediment sample. $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ values are reported with an analytical error of 0.15‰ and 1.5–2‰, respectively.

2.6 OC replacement and storage estimates

OC replacement rates in the eroding slopes of C51 and C24 were obtained by combining previous estimated erosion rates for each subcatchment (Boix-Fayos et al., 2008) and the input of OC into the soil matrix (I), as described in Berhe et al. (2008). To obtain “ I ” – the fraction of net primary productivity that, after rapid initial decomposition, remains as actual input of carbon to the soil OC pool – rate of OC accumulation in the soil profiles was reconstructed according to a first order model of OC accumulation (Trumbore and Harden, 1997). This model assumes that OC in soil accumulates preferentially from top to bottom where the inventory of OC is calculated as:

$$\text{OC}_{\text{inv}} = \sum \Delta Z_i \cdot \rho_i \cdot (1 - R_i) \cdot (\% \text{OC}_i / 100) \quad (1)$$

Where OC_{inv} is the OC inventory for the whole profile (g m^{-2}), ΔZ_i the depth of layer “ i ” (m), ρ_i bulk density of the “ i ” layer (g m^{-3}), R_i the rock fraction in the “ i ” layer and % OC the OC content in the “ i ” layer. The OC_{inv} on a certain moment in time (t) is expressed as:

$$\text{OC}_{\text{inv}}(t) = \frac{I}{k} \left[1 - e^{-kt} \right] \quad (2)$$

Where $\text{OC}_{\text{inv}}(t)$ is the OC inventory at “ t ” moment (g m^{-2}), I is the input rate of OC into the soil matrix ($\text{g m}^{-2} \text{yr}^{-1}$) and k is the coefficient of first-order carbon loss (yr^{-1}). The OC_{inv} was plotted in a graph against the ^{14}C age in each soil layer, calibrated to calendar years using OxCal (OxCal-IntCal09 from Oxford University, Bronk Ramsey, 2009). The plotted data were fitted in Eq. (2) and solved using a least squares approach with the solver function in Excel (MS Office 2003) to obtain the I and k parameters.

BGD

8, 8351–8382, 2011

Erosion, deposition and replacement of soil organic carbon

E. Nadeu et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



In addition, the storage effectiveness of the eroding vs. depositional positions for OC in the soil and sediment profiles, respectively, was determined according to methods of Massiello et al. (2004) and Berhe et al. (2008):

$$FM_w = \frac{1}{OC_{inv,tt}} \cdot \sum FM_i \cdot OC_{inv,i} \quad (3)$$

Where FM is the fraction modern of OC, FM_w is the mean value of the FM weighted with the OC content; $OC_{inv,tt}$ the total OC inventory, FM_i the fraction modern of OC in the “ i ” depth and $OC_{inv,i}$ the OC inventory in the “ i ” depth. The FM_w value is comprised between 0 and 1, where 0 represents the maximum OC storage effectiveness (storage of old OC) and 1 represents the opposite, least OC storage effectiveness.

3 Results

3.1 Land use changes, erosion processes and sediment sources

The two study subcatchments had different land use history, but both experienced a greening-up and densification of vegetation cover since 1956 (Table 1). About 14 ha (~28% of the total area) of dry-land agriculture of C51 present in 1956 were reforested in 1981. By 2008, the vegetation in the reforestation terraces had grown and was classified as a low density forest. In contrast, C24 remained mostly under a continuous cover of forest and shrubland, and the small patches of agricultural land present in 1956 were converted to high density forest cover by 2008 (Table 1). These changes observed in both subcatchments are in agreement with the general pattern of afforestation and agriculture abandonment described in the region (Boix-Fayos et al., 2008).

Gully erosion and bank and river erosion were the main erosion processes supplying sediments to the stream channel in C51. The channel presented signs of degradation (an average incision of 60 cm and an armour layer) in several reaches. Interrill erosion

BGD

8, 8351–8382, 2011

Erosion, deposition and replacement of soil organic carbon

E. Nadeu et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



was identified on south facing slopes of the channel but those slopes appeared disconnected to the channel due to a continuous shrub cover at the bottom of the slopes which acted as sediment trap (Fig. 3). C24 was characterized by the dominant presence of non-point sources of sediment. The lateral slopes of the channel were well connected to the streambed through interrill erosion processes and the entrance of debris from the colluvial/glacis slopes. The channel showed aggradation in many reaches (Fig. 3).

3.2 OC concentration, OC fractions and particle size distribution

No significant differences in the OC concentration and particle size distribution in soil profiles were found between C51 and C24 (Table 2). However, we observed high spatial variability between soil profiles at similar depths in each subcatchment. All soils and sediments had silt to loam particle size distribution, with no significant differences between them. Carbon concentration was negatively correlated to clay content at both sites (for C51 $r = -0.99$, $p < 0.001$ and for C24 $r = -0.89$, $p < 0.005$) and decreased with depth in both C51 and C24 (from 2.8 % and 3.8 % in the topsoil to 0.9 % and 1.6 % in the deepest soil layer in C51 and C24, respectively). POC represented between 24 % and 64 % of total OC measured in the soils of both subcatchments and decreased with depth as well. No significant differences ($p < 0.001$) among the measured parameters were found in C51, except for silt content, when soil and sediment samples were compared. In C24, significant differences ($p < 0.001$) were found between soil and sediment samples for OC concentration, silt, POC and MOC concentration in each subcatchment.

We observed important differences in particle size distribution in the profiles at both the eroding and depositional landform positions. Silt was the dominant particle size fraction in the sediment samples collected behind the check-dams (A profiles) being sand content very low (<20%), especially in C51 sediments. The sediment wedge was not homogeneous in particle size distribution in C51 as significant differences in sand, silt and clay content were found between the A and B profiles ($p < 0.001$). In

BGD

8, 8351–8382, 2011

Erosion, deposition and replacement of soil organic carbon

E. Nadeu et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



the opposite, no significant differences were observed between A and B profiles in C24 for particle size distribution. POC contributed to 34% of total OC in C51 sediments and its contribution was significantly higher (50%) in C24 (Table 3). In the sediment profiles of C51 (A and B) OC concentration was positively correlated to silt and clay content ($\rho = 0.510$ and $\rho = 0.547$, $p < 0.05$) while in C24 only MOC was correlated to silt content ($\rho = 0.714$, $p < 0.01$).

Carbon concentration was highly reduced in the sediment profiles in comparison with the soil profiles as evidenced by the low enrichment ratios (< 0.6) (Table 4). The reduction in OC concentration was greater in C24 than in C51, especially for the A sediment profile. Reduction in MOC concentration was lower than POC concentration. Also the POC concentration was correlated ($\rho = 0.661$, $p < 0.001$) to the sand fraction in the A profiles as well. In both, C51 and in C24, sediments were enriched ($ER > 1$) in silt and had clay content similar than that of the soils sampled in the drainage area. In C51, the sediments just behind the dam (profile A) had an $ER < 1$ for sand content and an $ER > 1$ for silt and clay content, while those remaining in the back part of the sediment wedge had an $ER > 1$ for sand content. In C24, no significant ($p < 0.05$) differences could be found in the particle size ER between A and B sediment profiles.

3.3 Isotopic composition of soils and sediments and C:N ratio

The radiocarbon composition of the soil profiles in C51 and C24 indicated that near surface OC was modern (post 1963, photosynthate produced after the atmospheric thermonuclear bomb tests, positive or near zero $\Delta^{14}\text{C}$ values) and $\Delta^{14}\text{C}$ got progressively more negative, possessing longer mean residence times (MRT) with depth (Fig. 4). The $\Delta^{14}\text{C}$ analyses conducted on bulk soil samples reflect an average radiocarbon concentration in all OC pools and do not enable determination of loss or enrichment of OC from specific fractions. More negative $\Delta^{14}\text{C}$ values were found in the deeper layers of the C51 soil profile than in the soil profile at C24. Sediment profiles sampled just behind the check-dams (A profiles) showed very different $\Delta^{14}\text{C}$ values between both subcatchments. The A profile in C51 contained OC associated to a very negative $\Delta^{14}\text{C}$

Erosion, deposition and replacement of soil organic carbon

E. Nadeu et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



on the surface that gradually became less negative (from -400 to -170 ‰) with depth. In C24 the $\Delta^{14}\text{C}$ values of the A profile varied with depth and ranged between -150 ‰ and 0 ‰ showing no specific trend.

The $\delta^{13}\text{C}$ signature of the soil samples became less negative with depth in both C51 and C24, ranging from -26.1 to -23.7 ‰ (Table 2). The enrichment of $\delta^{13}\text{C}$ with depth has been related to: (1) the fractionation during decomposition of organic matter and, thus, stabilization of OC fractions that are on average harder to decompose than bulk OC, and (2) to the ^{13}C reduction in the atmosphere and plants due to fossil fuel emissions (Torn et al., 2002), the Suess effect. $\delta^{13}\text{C}$ values in sediments showed very little variation with depth and overall, the mean (\pm std. deviation) $\delta^{13}\text{C}$ value in soils (-24.8 ± 0.2 ‰) was not significantly different than that in sediments (-24.7 ± 0.1 ‰). Sediment $\Delta^{14}\text{C}$, $\delta^{13}\text{C}$ and OC concentrations were within a range of soil values below 30 cm in C51 (Figs. 4, 5) but in C24, $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values of sediment samples corresponded, in all cases, to values found in the top 30 cm of C24 soil samples (Fig. 4). Also in C24 sediment samples with an OC concentration similar to that of other soil samples had more negative $\delta^{13}\text{C}$ and less negative $\Delta^{14}\text{C}$ values (Fig. 5).

The C:N ratio decreased in depth in the soil profiles of C51 and C24 ranging between 21.4 (topsoil) and 9.8 (deep soil) in C51, while in C24 the ratio ranged between 24.4 (topsoil) and 17.1 (deep soil). The sediments at the depositional site in C51 showed a mean C:N ratio that was significantly higher ($p < 0.05$) than that of soils, whereas in C24 no differences were found between both.

Table 5 shows correlation coefficients for the analysed profiles between carbon isotopes and OC, POC, C:N and clay content. We observed a significant negative correlation ($p < 0.05$) of $\delta^{13}\text{C}$ with $\Delta^{14}\text{C}$, OC and POC and a positive correlation with clay content though only significant ($p < 0.05$) in soil samples.

3.4 Replacement of eroded OC and burial efficiency

The OC input (I) obtained by our calculations combined with OC erosion rates showed that OC was being replaced by new photosynthate 11 times over annually

Erosion, deposition and replacement of soil organic carbon

E. Nadeu et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



in the sampled slope of C51 (where the $I = 22 \text{ g m}^{-2} \text{ yr}^{-1}$ and the erosion rate = $1.9 \text{ g m}^{-2} \text{ yr}^{-1}$), and replaced 4 times over in the slope of C24 ($I = 24 \text{ g m}^{-2} \text{ yr}^{-1}$ and the rate of erosion = $5.6 \text{ g m}^{-2} \text{ yr}^{-1}$). Further, the OC inventory was higher in soils than in sediments in C51 and C24 (Fig. 6) due to the higher OC content in soil profiles. However, burial efficiency, that depends also on $\Delta^{14}\text{C}$ values, was greater in sediments in C51 (lower FM_w value) while in C24 it was greater for the soil than the sediment profile.

4 Discussion

4.1 OC sources and land use changes

The geomorphological survey, OC concentrations, OC distribution among fractions (POC versus MOC) and the isotope signatures all suggested that the dominating erosion processes in the drainage area or slope-streambed connections determined the sources of sediment reaching depositional sites within the catchments. We found that sediments reaching the check-dam in C51 were mainly derived from erosion processes that lead to transport of deep soil, such as mass wasting, gullies and bed erosion. Moreover, these sediments presented OC characteristics ($\Delta^{14}\text{C}$, $\delta^{13}\text{C}$) that matched those of deeper soil layers (i.e. $>30 \text{ cm}$) of the drainage area in the subcatchment. This observation is in agreement with other studies that reported transport of old OC in rivers when the dominant erosion processes deliver material from deeper soil layers and bedrock in the source areas into river channels (Gómez et al., 2010; Longworth et al., 2007; Masiello and Druffel, 2001).

The occurrence of erosion processes that transport deep soil in C51 was related to land use change and lithology, both of which can greatly influence the characteristics of the mobilized OC in catchments (Longworth et al., 2007). In C51 the land use change analysis indicated a conversion of dry-land agriculture to forest through reforestation from 1956 to 1981, and an increase in forest cover density from 1981 to 2008. Those

BGD

8, 8351–8382, 2011

Erosion, deposition and replacement of soil organic carbon

E. Nadeu et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



changes suggest that rill and interrill erosion of topsoil are likely to have decreased due to the disappearance of dry-land agricultural areas and the recovery of vegetation in former agricultural land. These shifts may have led to a decreased input of sediments from the slopes to the river channel causing a sediment deficit in fluvial transport and activated other erosion processes such as river bed erosion and bank erosion, as was previously described for other areas of La Rogativa (Boix-Fayos et al., 2007). This change in sediment sources, and sediment availability, is consistent with the $\Delta^{14}\text{C}$ signature in the A sediment profile. In this profile, less negative $\Delta^{14}\text{C}$ values were found at the bottom of the profile and gradually shifted towards more negative $\Delta^{14}\text{C}$ values close to the surface. In addition, lithology, a key component in sediment delivery (de Vente et al., 2011; Haregeweyn et al., 2006) was highly erodible and sensitive to the formation of gullies and mass movements in the slope-streambed connection of C51.

C24 was characterised by few changes in shrubland and forest over the previous 50 yr and by a very small presence of agricultural land, and, given the absence of any climatic trends, it is unlikely to have experienced a shift in the dominant erosion processes during this time period. The very small changes in $\Delta^{14}\text{C}$, $\delta^{13}\text{C}$ and OC values with depth in the A sediment profile also point towards the input of sediments with uniform characteristics. This input was also influenced by the outcrop of quaternary glacia that resulted in a high input of coarse particles and rocks (debris) that were incorporated into the channel by rill erosion and gravity and led to channel aggradation. Evidence for the mobilization of topsoil material in the sediment wedge also came from the matching of the sediment $\Delta^{14}\text{C}$, $\delta^{13}\text{C}$ and OC values with those in the top 20 cm of the sampled soil profiles in the eroding subcatchment and the fact that in this subcatchment POC fraction represented 50 % of total OC (while in C51 it was only 34 %), and POC fraction is higher in the upper soil horizons (Table 2).

At the depositional sites, selective deposition of soil particles, pebbles and rocks was observed. Based on Stocke's law, coarser particles settle before finer ones (Gee and Boudier, 1986) and because finer particles are associated with higher OC contents, it can be expected sediment exported beyond depositional sites will often be C-enriched,

Erosion, deposition and replacement of soil organic carbon

E. Nadeu et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



while sediment remaining at these sites can become C-depleted (Wang et al., 2010). In our case, higher proportion of fine particles was found in sediments, compared to the soils in the drainage area, but they were not associated with an increase in OC concentration. Selective deposition of coarse particles before finer ones was best observed when comparing the two sediment profiles (A and B) in each wedge. In C51, an enrichment in finer particles was observed for the A profile (in the wedge front) whereas, in profile B (in the wedge back), we could see an enrichment in coarser particles that indicated that a gradual deposition within the sediment wedge. The higher MOC content in A as compared to B was also associated to the enrichment of fine particles and selective deposition within the sediment wedge in C51. However, preferential deposition of coarser particles at the back of the sediment wedge was not observed in C24, where the differences between the A and B sediment profiles pointed only to higher OC, POC and MOC concentration in A. This suggested that most of the sediment was of fine texture, transported in suspension, and was deposited in a uniform manner in the sediment wedge behind the check-dam. Moreover, coarser fractions were deposited within the channel as was observed in the aggrading channel bed. Overall, suspended sediment may have been an important source of material in the depositional site of C24 while bedload, carrying coarser particles, was relatively more important in C51.

4.2 Importance of the OC replacement rate in eroded slopes

Replacement of eroded OC in soil profiles, one component of the criterion for erosion to constitute a carbon sink (Berhe et al., 2007 and 2008; Stallard, 1998), was met in the soil profiles of C51 and C24. Enough recent plant derived-OC input (e.g. leaf-litter and fine root detritus) was produced to replace eroded soil OC eleven and four times over annually, respectively. These values are similar to those obtained by Almagro et al. (2010) at a nearby analogous site. If we compare their measured OC input to soil through litterfall with their reported slope erosion rates, we obtain 22-times over replacement. Further, in a naturally eroding catchment in Northern California, Berhe et al. (2008) reported effective replacement of OC transported from upland eroding

BGD

8, 8351–8382, 2011

Erosion, deposition and replacement of soil organic carbon

E. Nadeu et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



landform positions (5 to 15-times over). The rates of eroded OC replacement reported in this study and that of Berhe et al. (2008) indicate that the first part of the criterion for erosion to constitute a sink can be met in a variety of ecosystems. However, unanswered questions remain as to whether the rate of replacement of eroded OC is equally distributed in different OC pools, or if, as Van Oost et al. (2007) suggest, it can only be effective for certain carbon pools (those more active) reducing the capacity of the sink.

4.3 Mineralization, selective deposition, and preservation of buried OC

The OC enrichment ratios observed in the sediment profiles in our subcatchments were low compared to those observed in sediments of other drainage areas of similar size (Avnimelech and McHenry, 1984; Chaplot et al., 2005; Fiener et al., 2005; Jacinthe et al., 2004). Low OC enrichment ratios at transitory depositional sites can indicate that selective deposition of coarse mineral particles with low OC content is taking place while fine mineral particles rich in OC are exported with runoff (Fiener et al., 2005; Starr et al., 2000; Wang et al., 2010) or that OC is being mineralized before or after deposition (Gregorich et al., 1998).

OC mineralization is always considered an important factor affecting sediment OC content although it has very seldom been assessed at a field scale due to the influence exerted by several factors (soil moisture, porosity, temperature) that interact in a complex way (Van Hemelryck et al., 2011). By using an indirect approach (as in Wang et al., 2011) we discuss the importance of mineralization at our study sites based on C:N ratios, OC and clay enrichment ratios and $\delta^{13}\text{C}$ values. At our depositional sites, low OC enrichment ratios and high fine particle (clay) enrichment ratios, or close to unity, point towards mineralization as a mechanism that could have removed OC from sediments. However, considering that the C:N ratio tend to decrease when mineralization takes place (Conen et al., 2008), the lower or equal C:N values found in soil samples compared to sediment samples in both subcatchments, indicated non important mineralization processes in sediments. Similarly, $\delta^{13}\text{C}$ values tend to become less negative as OC decomposes, but we observed no differences between soil and sediment values

Erosion, deposition and replacement of soil organic carbon

E. Nadeu et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



in both subcatchments. Therefore, we found no evidences of significant mineralization by using these indicators.

Further studies on the effect of erosion on OC dynamics could benefit from consideration of stability and stabilization mechanisms of eroded OC after it is deposited downslope or downstream that constrain OC decomposition. In our study, reduced accessibility to OC through burial appears to have served as an effective mechanism of OC stabilization in the sediment profiles. The reduced accessibility, in the case of C51, was enhanced by the effect of dominant non-selective erosion processes (e.g. – channel erosion) leading to a higher FMw than that found in C24. Non-selective erosion processes often imply fast particle deposition and have a smaller effect on aggregate breakdown than more gradual and superficial erosion processes (sheet and rill erosion), enhancing OC protection (Beuselinck et al., 2000; Van Hemelryck et al., 2011). These non-selective erosion processes at our C51 study site also mobilized older OC that, being less reactive, could have reduced OC mineralization rates as well (Lal, 2003; Stallard, 1998).

5 Conclusions

Our findings in this study lead us to conclude that the mobilization and deposition of OC by water erosion in the La Rogativa catchment are strongly controlled by the prevailing erosion processes and land use changes in the drainage area. Two different scenarios are likely to have taken place: (i) a dominance of selective erosion processes (interrill and rill erosion) in a subcatchment with a relatively dense and stable vegetation cover, that delivered material to the streambed and transported it in suspension before being deposited behind a check-dam, and (ii) processes of concentrated erosion (mass waste, gullies, channel erosion) in a subcatchment where important land abandonment and greening up took place over the past 50 yr, increasingly leading to erosion of deeper soil layers, and a higher preservation of eroded OC on the depositional site through burial. These differences in the type of erosion processes were confirmed by

Erosion, deposition and replacement of soil organic carbon

E. Nadeu et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Erosion, deposition and replacement of soil organic carbon

E. Nadeu et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



a geomorphological survey of the slope-streambed connections. The use of carbon isotopes (^{14}C and ^{13}C) as tracers exemplified how differences in the dominant erosion processes may lead to very different sediment OC characteristics in depositional sites, with important implications for OC preservation. The estimated positive replacement rates of eroded OC by input of recent plant-derived-OC on the eroding slopes showed that OC was entering the soil carbon pool at higher pace than was being eroded in the two analyzed soil profiles. These findings suggest that soil erosion can lead to a net sequestration of OC if replacement of eroded OC in the slopes takes place, and it can further increase if the rate of OC decomposition is reduced in the depositional landforms. Assessments of the overall carbon budget at the catchment scale should consider which erosion processes are responsible for the main part of sediments and how these may vary over time due to land use changes.

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Erosion, deposition and replacement of soil organic carbon

E. Nadeu et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- Berhe, A. A., Harden, J. W., Torn, M. S., and Harte, J.: Linking soil organic matter dynamics and erosion-induced terrestrial carbon sequestration at different landform positions, *J. Geophys. Res.*, 113, G04039, doi:10.1029/2008JG000751, 2008.
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BGD

8, 8351–8382, 2011

Erosion, deposition and replacement of soil organic carbon

E. Nadeu et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Erosion, deposition and replacement of soil organic carbon

E. Nadeu et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Erosion, deposition and replacement of soil organic carbon

E. Nadeu et al.

Table 1. Morphological and land use change characteristics of study subcatchments C51 and C24 (positive land use change values indicate increase in 2008 and viceversa).

Id	Morphological variables					Land use change 1956–2008			
	Area (ha)	Slope (°)	Elevation (m)	SLN (°)	SY (tn y ⁻¹)	HDF (%)	LDF (%)	SH (%)	DLA (%)
C51	50	16.4	1213.2	11.5	45.7	1.4	25.6	-1.4	-25.6
C24	18	17.8	1274.7	10.4	34.4	2.2	-2.8	8.4	-7.8

SLN: average slope of the drainage network, SY: sediment yield, HDF: high density forest, LDF: low density forest, SH: shrubland, DLA: dry-land agriculture

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Erosion, deposition
and replacement of
soil organic carbon

E. Nadeu et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Table 2. Bulk density (BD), clay content, OC concentration, C:N ratio, POC % (fraction) and $\delta^{13}\text{C}$ in soil samples (standard error between brackets).

	Depth (cm)	BD (g cm^{-3})	Clay (%)	OC (%)	C:N ratio	POC % (%) ^a	$\delta^{13}\text{C}^{\text{b}}$ (‰)
C51	0–5	1.5 (0.2)	11 (1)	2.8 (0.9)	17 (2)	48 (6)	–26.1
	5–10	1.0 (0.2)	12 (2)	1.9 (0.6)	15 (2)	40 (8)	–25.2
	10–20	1.3 (0.1)	12 (2)	1.7 (0.4)	16 (2)	35 (7)	–25.4
	20–30	1.5 (0.2)	13 (2)	1.4 (0.4)	15 (2)	33 (6)	–25.0
	30–45	1.9 (0.1)	13 (2)	1.4 (0.4)	15 (2)	29 (8)	–24.8
	45–60	1.8 (0.2)	12 (2)	0.9 (0.2)	14 (2)	29 (9)	–24.2
	60–75	2.0 (0.2)	10 (3)	0.8 (0.4)	12 (2)	25 (6)	–23.8
	75–90	1.5 (0.1)	14 (6)	0.9 (0.2)	12 (3)	24 (4)	–23.9
	mean	1.5 (0.5)	12 (8)	1.5 (1.4)	15 (6)	33 (20)	–24.8 (0.8)
C24	0–5	1.3 (0.2)	11 (1)	3.8 (0.7)	21 (2)	54 (4)	–25.4
	5–10	1.6 (0.1)	10 (1)	3.2 (0.4)	21 (2)	47 (4)	–25.3
	10–20	1.6 (0.1)	12 (1)	2.5 (0.4)	20 (2)	49 (2)	–24.9
	20–30	1.5 (0.1)	12 (1)	2.0 (0.2)	20 (1)	40 (6)	–24.2
	30–45	1.7 (0.1)	11 (1)	2.0 (0.2)	20 (2)	44 (9)	–24.2
	45–60	1.6 (0.1)	11 (1)	1.5 (0.1)	20 (2)	38 (7)	–24.1
	60–75	1.7 (0.1)	12 (1)	1.3 (0.0)	18 (1)	37 (1)	–23.9
	75–90	1.7 (0.1)	12 (1)	1.6 (0.2)	20 (5)	36 (2)	–23.7
	mean	1.5 (0.3)	11 (3)	2.2 (1.0)	20 (7)	43 (14)	–25.1 (0.6)

^a Average from 2 soil profiles.

^b Data from 1 soil profile, standard deviation reported.

Erosion, deposition and replacement of soil organic carbon

E. Nadeu et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Table 3. Bulk density (BD), clay content, OC concentration, C:N ratio, POC % (fraction) and $\delta^{13}\text{C}$ in the A profile of the sediment samples (standard error for the whole profile reported).

	Depth (cm)	BD (g cm ⁻³)	Sand (%)	Silt (%)	Clay (%)	OC (%)	POC % (%)	$\delta^{13}\text{C}$ (‰)	C:N ratio
C51	0–5	1.3	1	86	13	1.1	15	–24.0	18.6
	5–10	1.3	0	84	16	0.8	19	–24.2	15.7
	10–15	1.0	4	83	13	1.3	27	–24.2	19.3
	15–20	1.5	6	81	13	1.2	39	–24.5	19.5
	20–25	1.5	4	82	14	1.1	33	–24.4	19.2
	25–30	1.8	5	81	14	1.1	36	–24.6	17.9
	30–40	1.7	12	75	13	1.4	53	–24.9	22.1
	40–50	1.8	6	81	13	1.1	38	–24.2	21.6
	50–55	1.7	7	81	12	1.0	37	–24.2	20.3
	55–60	1.6	7	80	13	1.2	46	–24.5	21.3
60–70	1.3	4	82	14	1.0	33	–24.5	19.2	
	mean	1.5(0.1)	5(1)	81(1)	13(0)	1.1(0)	34(3)	–24.4(0.2)	19.5(1.8)
C24	0–5	1.6	16	72	12	1.4	60	–25.1	17.1
	5–10	1.7	16	73	11	1.6	63	–25.0	19.6
	15–20	1.7	7	80	13	1.5	48	–25.3	16.1
	20–25	1.6	8	80	12	1.4	49	–25.0	15.4
	25–30	1.4	9	79	12	2.1	63	–25.3	20.8
	35–38	0.8	10	78	12	1.5	56	–25.1	17.9
	38–43	1.6	17	73	10	1.7	58	–25.2	18.8
	43–48	1.5	14	75	11	1.6	55	–25.2	19.3
	48–53	1.6	9	79	12	1.3	41	–25.1	16.3
	58–63	1.7	10	81	9	1.2	37	–24.8	14.7
68–73	1.7	7	81	12	1.0	29	–24.9	12.9	
75–80	2.2	–	–	–	0.7	42	–24.9	18.2	
	mean	1.6(0.1)	11(1)	77(1)	12(0)	1.4(0.1)	50(3)	–25.1 (0.2)	17.3 (2.3)

Erosion, deposition and replacement of soil organic carbon

E. Nadeu et al.

Table 4. Mean Enrichment Ratio (ER) and standard error (SE) of deposited sediments for A and B profiles (taking 0–30 cm reference soil values).

		A						B					
		Sand	Silt	Clay	OC	POC	MOC	Sand	Silt	Clay	OC	POC	MOC
C51	ER	0.18b*	1.39*	1.11*	0.57a*	0.52	0.93a*	1.56a*	0.79b*	0.66b*	0.42*	0.37a	0.43*
	SE	0.03	0.01	0.02	0.02	0.04	0.08	0.05	0.04	0.05	0.02	0.03	0.03
C24	ER	0.36a	1.35	1.02	0.52b*	0.43*	0.53b*	0.51b	1.28a	0.94a	0.34*	0.24b*	0.37*
	SE	0.04	0.02	0.03	0.04	0.02	0.02	0.02	0.00	0.02	0.03	0.03	0.03

ab: significant differences within A sediment profiles in C51 and C24 (per columns) ($p < 0.05$).

* Significant differences between profiles A and B in each wedge ($p < 0.05$).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Table 5. Correlation coefficients between $\delta^{13}\text{C}$, $\Delta^{14}\text{C}$ and selected variables (Spearman's rho reported).

	$\delta^{13}\text{C}$ (‰)	OC (%)	POC (%)	MOC (%)	C:N ratio	Clay (%)
Soil 51						
$\Delta^{14}\text{C}$	-0.932 ²	0.964 ²	0.872 ²	0.969 ²	0.524	-0.971 ²
$\delta^{13}\text{C}$		-0.973 ²	-0.925 ²	-0.954 ²	-0.371	0.977 ²
Sediment 51						
$\Delta^{14}\text{C}$	-0.789 ²	0.471	0.824 ²	-0.736 ¹	0.631	-0.356
$\delta^{13}\text{C}$		-0.499	-0.748 ²	0.563	-0.381	0.129
Soil 24						
$\Delta^{14}\text{C}$	-0.878 ²	0.784 ²	0.801 ¹	0.750 ¹	-0.219	-0.687
$\delta^{13}\text{C}$		-0.860 ²	-0.895 ²	-0.818 ¹	0.467	0.780 ¹
Sediment 24						
$\Delta^{14}\text{C}$	-0.797 ²	0.837 ²	0.758 ²	0.253	0.702 ¹	0.178
$\delta^{13}\text{C}$		-0.784 ²	-0.733 ¹	-0.218	-0.557	-0.530

¹ $p < 0.05$, ² $p < 0.01$

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



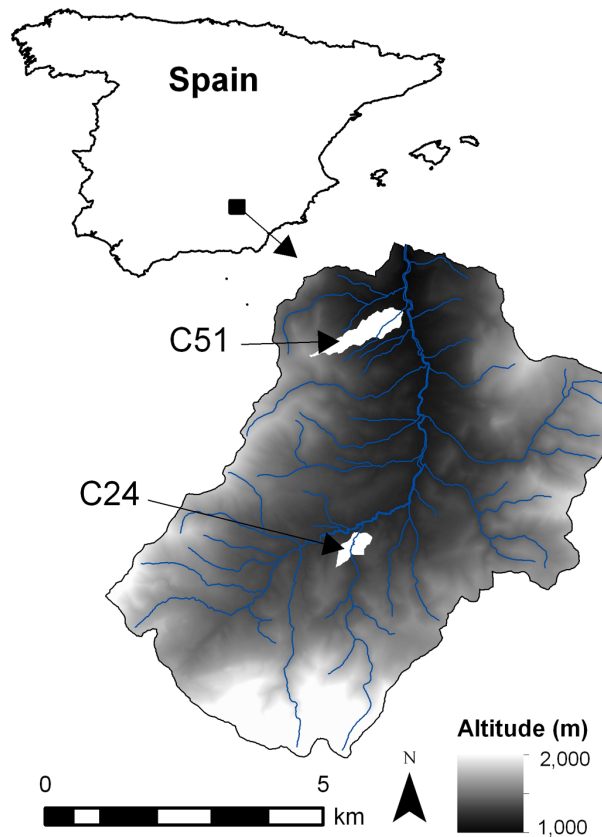


Fig. 1. Location of the two subcatchments (C51 and C24) within La Rogativa catchment and Spain.

Erosion, deposition and replacement of soil organic carbon

E. Nadeu et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Erosion, deposition and replacement of soil organic carbon

E. Nadeu et al.

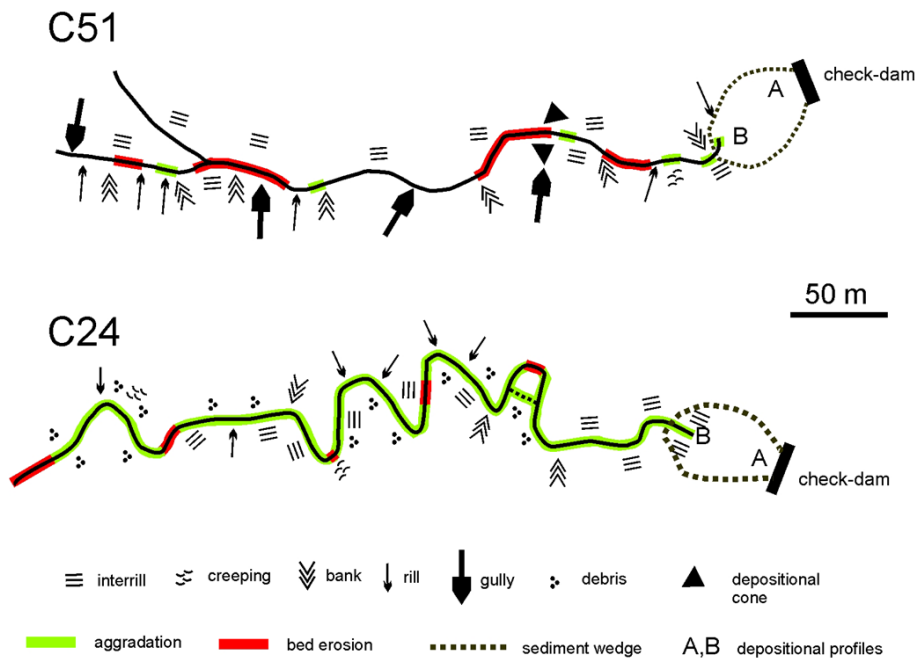


Fig. 2. Schematic geomorphological representation of the two streams indicating the main sediment sources and erosion processes.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Erosion, deposition and replacement of soil organic carbon

E. Nadeu et al.

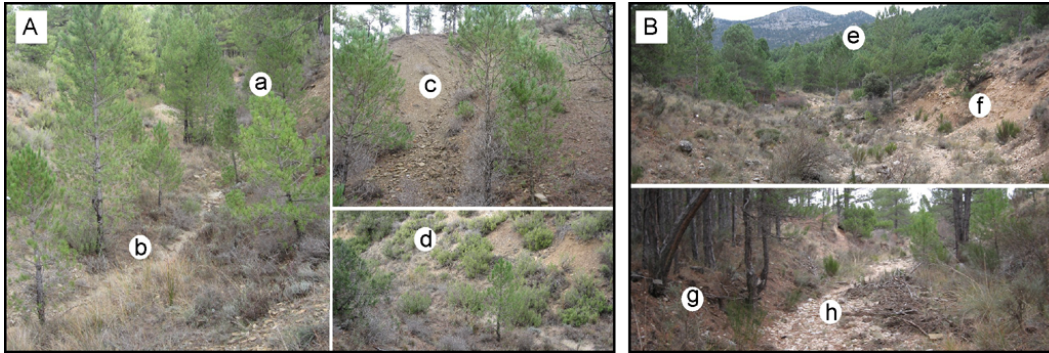


Fig. 3. **A** (C51): (a) low density forest; (b) vegetation encroachment and channel incision; (c) talus slope with input of sediments by mass waste processes and (d) vegetated margin slopes retaining eroded material. **B** (C24): (e) high density forest; (f) talus slopes with a concave base; (g) well-connected lateral slopes with interrill erosion and litter input to the channel and (h) channel aggradation.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Erosion, deposition
and replacement of
soil organic carbon

E. Nadeu et al.

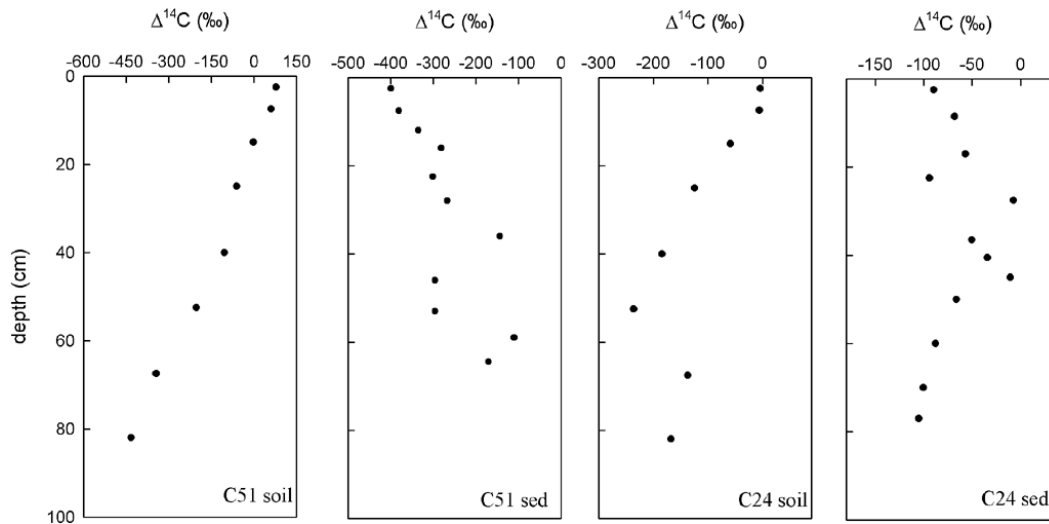


Fig. 4. $\Delta^{14}\text{C}$ (‰) values at the different depths in the soil (soil) and sediment depositional profiles (sed).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Erosion, deposition
and replacement of
soil organic carbon

E. Nadeu et al.

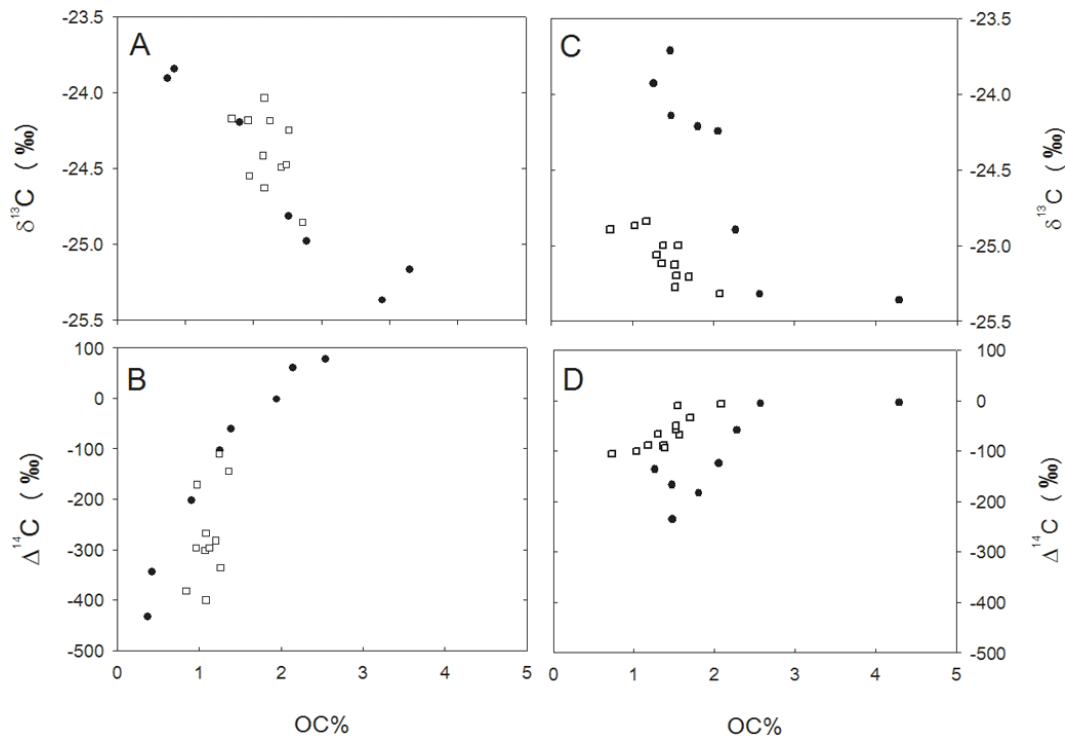


Fig. 5. $\Delta^{14}\text{C}$, $\delta^{13}\text{C}$, and OC% in C51 (A and B) and C24 (C and D). Black dots represent soil samples and white squares sediment samples.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



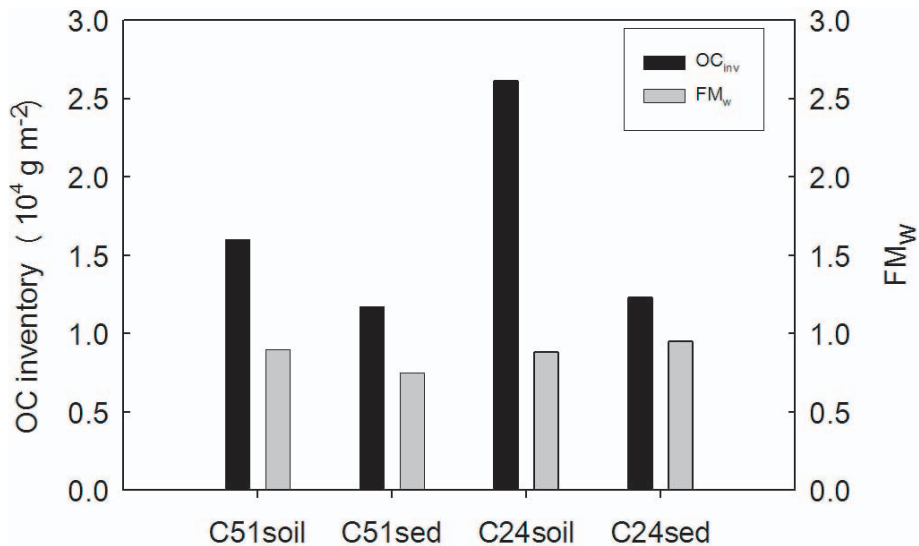


Fig. 6. Organic carbon inventory and FM_w at the eroding (soil) and depositional sites (sed).

Erosion, deposition and replacement of soil organic carbon

E. Nadeu et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

