Understanding the role of soil erosion on CO2-C loss using 13C isotopic signatures in abandoned Mediterranean agricultural land

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HIGHLIGHTS

• The soil C isotopic difference is a useful tracer for erosion processes studies.
• The main loss of Carbon was measured in soil sediment.
• The transport increased strongly the mineralization of organic carbon.

GRAPHICAL ABSTRACT

ABSTRACT

Understanding soil water erosion processes is essential to evaluate the redistribution of soil organic carbon (SOC) within a landscape and is fundamental to assess the role of soil erosion in the global carbon (C) budget. The main aim of this study was to estimate the C redistribution and losses using 13C natural abundance. Carbon losses in soil sediment, dissolved organic carbon (DOC) and CO2 emission were determined. Four bounded parallel plots were installed on a 10% slope. In the upper part of the plots, C3 soil was replaced with C4 soil. The SOC and δ13C were measured after 145.2 mm rainfall in the upper (2 m far from C4 strip), middle (4 m far from C4 strip) lower (6 m far from C4 strip) trams of the plot and in the sediments collected in the Gerlach collector at the lower part of the plot. A laboratory incubation experiment was performed to evaluate the CO2 emission rate of soils in each area. OC was mainly lost in the sediments as 2.08 g−2 of C was lost after 145.2 mm rainfall. DOC losses were only 5.61% of off-site OC loss. Three months after the beginning of the experiment, 15.90% of SOC in the upper tram of the plot had a C4 origin. The C3-SOC content decreased along the 6 m length of the plot, and in the sediments collected in the Gerlach collector. CO2 emission rate was high in the upper plot tram due to the high SOC content. The discrimination of CO2 in C3 and C4 portion permitted to increase our level of understanding on the stability of SOC and its resilience to decomposition. The transport of sediments along the plot increased

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1. Introduction

Water erosion is a natural process, which significantly affects the redistribution of soil organic carbon (SOC) within an ecosystem with a large impact on the net exchange of C between the soil and atmosphere (Berhe et al., 2012; Doetterl et al., 2012; Harden et al., 1999; Lal, 2005; Ritchie and Rasmussen, 2000; Starr et al., 2000).

As a result of erosion processes, the C distribution and transformation are altered due to three main mechanisms: (i) the detachment and replacement of OM at eroding sites; (2) deep burial of OM at sedimentation sites; and (3) enhanced decomposition of OM as a result of soil aggregate breakdown during either detachment or transport (Van Oost et al., 2007).

Studies on the impact of the first and second above mentioned mechanisms on terrestrial C balance are controversial. On the hand, Lal and colleagues (Jacinthe and Lal, 2001; Lal and Pimentel, 2008) showed that soil erosion has a negative impact on C sequestration, constituting a source for atmospheric CO₂. They argue that erosion increases CO₂ emissions due to a decrease of net primary production on eroded soil, and a relatively high decomposition of SOC in buried sediments. Van Oost and other authors (Berhe et al., 2007; Smith et al., 2005; Van Oost et al., 2008; Van Oost et al., 2007), on the contrary, consider erosion of agricultural soils as sink for atmospheric CO₂. The eroded sediments are mainly buried at deposition sites and are therefore protected from faster mineralization and erosion, which results in the exposure of the C depleted subsoil, reducing the organic matter turnover rates.

Regarding the third mechanism there seems to be more consensus among researchers. Wang et al. (2014) and Polyakov and Lal (2008) both consider the transport of SOC a potential C source as soil detachment increases CO₂ emission, resulting from aggregate breakdown due to raindrop impact and flow shear which leads to rapid mineralization by microbial biomass of encapsulated organic matter (Bremenfeld et al., 2013; Novara et al., 2012a). The contribution of transport mechanisms on the global C emission budget is difficult to assess due to the high discrepancy in literature results. Wang et al. (2014), for instance, found that cumulative C emission in the transport zone was 27% higher in comparison to non-eroded soils. On the contrary, other authors attributed only a minor relevance to SOC mineralization during transport as a C source (Quinton et al., 2010; Van Oost et al., 2005).

The comparison of findings on the quantification of a single process in the global C balance proves to be difficult due to different research approaches used (field measurement or incubation experiment) and the combined effect of erosion mechanisms in the whole C cycle would be (Kirkels et al., 2014). The contribution of transport to the global C budget in an eroded site, was studied by many researchers through measurements of soil CO₂ emission at detachment, transport and deposition sites. In such cases, differentiating the erosion induced C losses by aggregate transport from the C losses due to detachment or exposure of subsoil OC could be difficult, resulting in an uncertain evaluation of the relevance of each mechanism as sink/source of atmospheric CO₂.

Improvement of knowledge on the magnitude of the sink/source function of erosion processes (detachment, transport and deposition) is fundamental to understand the fate of SOC in agricultural abandoned landscapes, evaluate the potential of C sequestration of soil and as consequence the economical and societal benefit analysis. In order to expand the knowledge on losses of SOC during transport and mineralization at eroding sites, the main aim of the present study was to evaluate the redistribution and transformation of SOC using natural abundance of 13C as SOC marker. The following processes were analyzed: (i) quantification of SOC erosion at different positions in and outside the plots, (ii) determination of DOC in the soil solution and in the runoff and (iii) evaluation of SOC mineralization during soil transport by measuring CO₂ emission at different plot positions.

2. Materials and methods

2.1. Study area and experimental plots

The study area is located in Trapani Province, Sicily Region, Italy (37°58′N; 12°35′E) (Fig. 1a). The climate in the area is typical Mediterranean with dry, hot summers and moist cool winters. The precipitation data were collected at the weather station at Fontanasalsa station located 3 km from the experimental site. Mean annual rainfall (28 years average) is 630 mm with mean monthly maximum temperatures (32.5 °C) in August and minimum (15.3 °C) in February (Fig. 1b). Soil is classified as a Vertisol according to the World Reference Base (WRB, 2007) with 58.3% sand, 11% silt, and 30.7% clay and 41% CaCO₃.

Four bounded plots of 1 m width and 6.5 m in length, were designed on a slope of 10%. All the plots were parallel oriented (Fig. 2). The land had been abandoned from agriculture since 2000. The previous land use was a cereal/leguminous cropping system. The measurements were carried out from November 2014 till February 2015. The C isotopic composition (δ13C value) and SOC of the soils before the plots were installed were −27.03 ± 0.2 ‰ and 0.46 g kg⁻¹, respectively.

A strip of soil (1 m wide, 0.5 m long, triangle shaped) was removed, carefully weighted and replaced with the same amount of C₄ soil then compacted until the original slope profile and original bulk density was reached (Fig. 2). The C₄ soil was collected under Cynodon dactilon grass (C₄ species) in the experimental farm of the University of Palermo. The C₄ soil has under isotopic steady state a δ13C value of 18.0 ± 0.2 ‰.

2.2. Erosion measurement and soil sampling

Runoff and sediment were intercepted using a 1 m wide Gerlach trap (Gerlach, 1967) installed with a 40 L collector plastic tank. Total runoff and soil loss were measured after each erosive event (i.e. an event producing measurable runoff) or, occasionally, after a series of events if they were separated by a short time interval. The tanks were weighted, the content of each tank was carefully mixed and 1 l sampled, dried at 50 °C and stored for chemical analysis. The erosion was calculated using the concentration of the sediment per liter and related to the total weight of the tank. The weight of the empty tank was subtracted from the total weight.

Soil samples were collected at the beginning of the experiment (November) and after three months (February) in each plot. Three soil sub-samples of each plot were taken at 0–15 cm and 15–30 cm depth along the plot with an interval of 2 m from C₄-SOC strip. The positions with respect to the plot are referred to as: upper (2 m), middle (4 m) and lower (6 m) trams (Fig. 2). Furthermore, three soil subsamples for each plot were taken in the C₄-SOC strip (Fig. 2). All the soil samples were air-dried and sieved with a 2 mm sieve for laboratory analysis.

2.3. Incubation experiment

A short-term aerobic incubation procedure was used to determine the potential of the soil samples to mineralize organic C. Soils sampled at the end of the trial (February) from the upper, middle, lower trams of the plot C₄-SOC strip and the Control site (soil neighbor to the plot)
were used for the incubation experiment. Soil samples (10 g) at 50% of their water holding capacity were pre-incubated for five days at room temperature; then, after readjustment of the moisture, they were incubated at 25 °C in 125 cm³ air-tight glass bottles. CO₂ measurements were done after 1, 3 and 7 days from the start. Twenty-four hours before the CO₂ sampling, all flasks were ventilated for 30 min with fresh room air and then immediately sealed with rubber stoppers. Thus, evolved CO₂ from soil was allowed to accumulate for 24 h and then sampled. To correct the dilution by atmospheric CO₂ in the incubation glass bottles, for each sampling date, the CO₂ concentration and isotopic composition of the air inside three glass bottles without soil was also measured.

2.4. Chemical analysis

Organic C in soil and sediment was measured using an elemental analyzer (NA1500 Carlo Erba, Milan, Italy). For δ¹³C analysis of soil, sediment and CO₂, an EA-IRMS (elemental analyzer isotope ratio mass spectrometry) was used. The reference material used for analysis was IA-R001 (Iso-Analytical Limited wheat flour standard, δ¹³CV-PDB = −26.43 ‰). IA-R001 is traceable to IAEAeCHe6 (cane sugar, δ¹³CV-PDB = −10.43 ‰). IA-R001, IA-R005 (Iso-Analytical Limited beet sugar standard, δ¹³CV-PDB = −26.03 ‰), and IA-R006 (Iso-Analytical Limited cane sugar standard, δ¹³CV-PDB = −11.64 ‰) were used as quality control samples for the analysis. The International Atomic Energy Agency (IAEA), Vienna, distributes IAEA-CH-6 as a reference standard material. The results of the isotope analysis are expressed as a δ value (‰) relative to the international Pee Dee Belemnite standard as follows:

$$\delta(\text{‰}) = \frac{R_s - R_{st}}{R_{st}} \times 1000$$

where $\delta = \delta^{13}C$, $R = ^{13}C/^{12}C$, $s = \text{sample}$, and $st = \text{standard}$.

Inorganic carbon was removed prior to stable isotope analysis by acid fumigation following the method of Harris et al. (2001).

Dissolved organic carbon (DOC) in runoff was collected after each rainfall event and measured with TOC Analyzer Shimadzu.

2.5. Data calculation

Natural abundance of δ¹³C was used to determine the proportion of C in SOC that was derived from the new C₄-SOC input. These proportions were calculated by the mixing equation separately for each sampling point of the slope and sediments:

$$\text{New Carbon Derived (NCD)} = \frac{\delta^{13}C_{\text{Sample}} - \delta^{13}C_{\text{new input}}}{\delta^{13}C_{\text{old soil}} - \delta^{13}C_{\text{new input}}}$$

Fig. 1. a) Study area; b) Mean rainfall and temperature in the area study and during the trials.

Fig. 2. Experimental trial and sampling point.
where NCD is the fraction of new C derived, \( \delta^{13}C \) sample is the isotope ratio of the soil sample, \( \delta^{13}C \) old soil is the isotope ratio of the soil before the plot installation, and \( \delta^{13}C \) new input is the isotopic ratio of soil in the strip (Cynodon dactilon soil, \( \delta^{13}C = 18.0 \pm 0.2 \)).

Corrections for dilution by atmospheric CO2 in the incubation jars were made with the following equation:

\[
\delta^{13}C_{\text{measured}} = f \cdot \delta^{13}C_{\text{atm}} + (1 - f) \cdot \delta^{13}C_{\text{sample}},
\]

such that:

\[
\delta^{13}C_{\text{sample}} = \delta^{13}C_{\text{measured}} - f \cdot \delta^{13}C_{\text{atm}},
\]

where f is the fraction of the sample value contributed by atmospheric CO2 which is calculated using a back-ground concentration of spheric (laboratory air) CO2.

\[
\delta^{13}CO_2 \text{sample} = \delta^{13}CO_2 \text{measured} - \delta^{13}CO_2 \text{atm}.
\]

The following mixing model was used to determine the portions of CO2 deriving from C3-SOC and C4-SOC:

\[
[CO_2]_{\text{C3-SOC}} = \frac{[CO_2]_{\text{C3-SOC}}}{[CO_2]_{\text{C4-SOC}}} \times \frac{1}{1 + \frac{[CO_2]_{\text{C4-SOC}}}{[CO_2]_{\text{C3-SOC}}}}
\]

The portion of C4-SOC of the SOC was around 16% in the upper tram of the plot and in the collected sediment (Table 2). The SOC content in the 15–30 cm depths did not significantly change along the plot. The SOC was significantly changed 71 days along the plot, ranging from \( 25.15 \pm 0.05 \) in the upper plot tram (0–2 m away from C4 soil strip) to \( 15.90 \pm 0.05 \) in the lower tram of the plot (4–6 m away from C4 soil strip) (Fig. 3). As consequence of sediment transport and organic matter within, the portion of C4-SOC in the upper tram of the plot was 15.90% of the whole SOC and decreased in the soil along the slope and in sediment (Fig. 3). The portion of C4-SOC of the SOC was 3.4% instead, because the source of C4 was only in the C4-SOC strip, and was not uniformly distributed in the plot.

### 3.2. Soil erosion effect on \( \delta^{13}C \)

The \( \delta^{13}C \) values of C3-SOC (fallow soil) significantly changed 71 days after, since the addition of C4 soil (C. dactilon soil). The \( \delta^{13}C \) decreased along the plot, ranging from \( -25.15 \pm 0.05 \) in the upper plot tram (0–2 m away from C4 soil strip) to \( -25.55 \pm 0.03 \) in the lower tram of the plot (4–6 m away from C4 soil strip) (Fig. 3). As consequence of sediment transport and organic matter within, the portion of C4-SOC in the upper tram of the plot was 15.90% of the whole SOC and decreased in the soil along the slope and in sediment (Fig. 3).

### 3.3. Soil CO2 emission along the plot

The cumulative CO2 emission 7 days after the start of incubation was high in the upper (26.49 \( \pm \) 3.26 \( \mu \)g CO2-C g\(^{-1}\)) and lower tram of sediment (23.16 \( \pm \) 1.72 \( \mu \)g CO2-C g\(^{-1}\)) of the plot. The CO2 emission rate ranged between 2.74 \( \mu \)g CO2-C g\(^{-1}\) d\(^{-1}\) and 4.9 \( \mu \)g CO2-C g\(^{-1}\) d\(^{-1}\), with the lowest rate during the...
3rd day since the start of incubation (Fig. 4a). The $\delta^{13}$C of CO$_2$ ranged from $-20.2$‰ to $-22.2$‰. The CO$_2$ was considerably enriched in comparison to C$_3$ soil emission (the soil collected in the area neighboring the experimental plot) due to the new C$_4$-SOC input. According to Eq. (5), the contribution of recent C$_4$ soil to CO$_2$ flux during the 7 days of incubation was significantly higher than that of the C$_3$ soil. The fresh organic matter of C$_4$ eroded soil was easier consumed by microbial biomass. The C$_4$ contribution to CO$_2$ flux decreased during incubation period due to the preferential microbial utilization of fresh versus old C (Fig. 4b); and decreased along the plot from the upper to the lower tram (Fig. 4b). On the other hand, the ratio between the CO$_2$ emissions and SOC was highest in the lower tram of the plot in comparison to the upper tram for the C$_4$ portion of the plot and was higher for C$_4$ than for the C$_3$ portion (Fig. 5). Therefore, the soil in the lower tram of the plot emitted more enriched CO$_2$ in comparison to the upper and middle trams of the plot; this finding indicated the C$_4$-SOC at the lower tram of the plot was more easily decomposed by soil microbial biomass and therefore the mechanism of sediment transport affected significantly the CO$_2$ emission.

4. Discussion

The results of the present study confirmed that SOC loss by water erosion is a natural processes with a significant impact on persistence of fertility in soils and in terrestrial ecosystems as a whole (Berhe et al., 2012; Chaplot and Cooper, 2015). In the experimental plot, 2.08 g OC loss was recorded per square meter after a rainfall event of 145.2 mm. This result, apparently not significant, corresponds to 0.8% of the 0.5 cm soil C stock. It was much lower than the 18.9% reported in South Africa (648 mm rainfall) by Chaplot and Cooper (2015), but significantly higher than the 0.01% reported in Spain (730 mm) by Rodriguez et al. (2004). The enrichment ratio (OC in sediment/SOC) was double than the value measured by Rodriguez (0.9), although the soil in the experimental plot was poor in organic matter. The high enrichment ratio measured can be due to the combined effect of (i) the high presence of smaller aggregate in the eroded sediments and (ii), the C accumulation in the finest aggregate fraction (Novara et al., 2013; Novara et al., 2012b), characteristic of the soils with low OC content. The OC was mainly lost attached to the transported sediment as the losses in DOC were only 5.61% of off-site OC loss (Fig. 6).

In the present study the use of natural abundance of $^{13}$C was helpful in order to trace the movement of SOC during redistribution of the soil particles, and allowed to analyze the variation of SOC after transport. After the rainfall event of 145.2 mm, a significant movement of SOC from the C$_4$ strip to the lower tram of the plot was recorded (Fig. 6). In the upper tram of the plot 15.90% of the whole SOC was composed of C$_4$-SOC. These high values were also the consequence of the higher OC content of the C$_4$ soil strip added in the plot in comparison to original C$_3$ soil.

This study provides new data on CO$_2$ emission in a natural landscape during sediment transport due to erosion processes. Although, it is not possible to scale up these results of CO$_2$ emissions to the landscape level, it is important to know the variation of CO$_2$ fluxes and the difference in SOC decomposition within a plot as this can shed light into the connectivity process, from the particle, to the pedon, and then to the slope tram, slope and watershed scale. Further studies are needed to understand these processes in more detail. The CO$_2$ emission during incubation experiment was higher in the upper tram of the plot, in comparison to the low part of the plot. This can be attributed to the high SOC content, especially C$_4$-SOC, in the upper part due to proximity of the C$_4$ soil strip. The CO$_2$ mainly had a C$_4$ origin, because of the preferential utilization by microbial biomass of the recent C$_4$-C input (Novara et al., 2014). The main C$_4$ origin of CO$_2$ should also be the result of the low utilization by microbes of C$_3$-SOC due to low content of SOC.

**Table 2**

A) SOC, C$_4$-SOC and C$_3$-SOC trams of the plot. B) OC, C$_3$-OC and C$_4$-OC portion in the sediments. Values followed by the same letter are not significantly different at P ≤ 0.05 (LSD test).

<table>
<thead>
<tr>
<th>A</th>
<th>C$_4$-SOC (%)</th>
<th>C$_3$-SOC (%)</th>
<th>SOC (g kg$^{-1}$)</th>
<th>C$_4$-SOC (g m$^{-2}$)</th>
<th>C$_3$-SOC (g m$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper</td>
<td>15.90</td>
<td>84.10</td>
<td>0.48a</td>
<td>38.09a</td>
<td>201.475a</td>
</tr>
<tr>
<td>Middle</td>
<td>16.06</td>
<td>83.94</td>
<td>0.48a</td>
<td>38.75a</td>
<td>202.574a</td>
</tr>
<tr>
<td>Lower</td>
<td>11.19</td>
<td>88.81</td>
<td>0.41b</td>
<td>23.15b</td>
<td>183.695b</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>B</th>
<th>C$_4$-OC (%)</th>
<th>C$_3$-OC (%)</th>
<th>OC (g m$^{-2}$)</th>
<th>C$_4$-OC (g)</th>
<th>C$_3$-OC (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sediment</td>
<td>10.67</td>
<td>89.33</td>
<td>0.86</td>
<td>1.33</td>
<td>11.12</td>
</tr>
</tbody>
</table>

* C$_4$-OC and C$_3$-OC are related to the whole period.

**Fig. 4.** a) CO$_2$ emission rate and b) relative contribution (%) of recent C$_4$ soil to CO$_2$ rate during incubation of soil from upper (black), middle (gray) and lower (green) trams of the plot. Histograms with different letters are significantly different among samples (P ≤ 0.05). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Fig. 5.** Ratio CO$_2$/SOC calculated for C$_4$ (gray) and C$_3$ (black) portion after 1 day from the start of incubation. Histograms with different letters are significantly different among sampling points for C$_4$ (capital letters) and C$_3$ (lower case letters) (P ≤ 0.05).
and was poorly available for microbial biomass. On the contrary, the sure of the protected organic matter, the SOC was physically protected that, despite of the raindrop impact, breakdown of aggregates and expo-
crease of SOC decomposition during sediment transport. Improvement

5. Conclusions
The present study showed the relevance of transport processes on CO$_2$ losses as a result of water erosion. Although the deep burial of sedi-
entary processes are considered by many authors as a C sink of CO$_2$, the loss of C during the transport phase should be taking into ac-
count when considering the global C budget because of the relevant in-
crease of SOC decomposition during sediment transport. Improvement of our knowledge about the carbon sink/source in the process of soil erosion and subsequent sediment transport and deposition requires comprehensive research of all relevant processes at broad spatio-temporal scales. We need to consider processes from hillslope to catch-
ment, to landscape to global scales and covering the present up to the late Holocene. For this an eco-geomorphologic approach can be key, encompassing biological, pedogenic and geomorphologic processes in-
tegrated over three landscape domains: eroding sites, the transport
pathway along hillslopes and depositional sites, to link sediment, lateral and vertical carbon fluxes.

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Doo et al., 2010. Erosion impact to agricultural soil. Geoderma 143, 216.

C$_3$ and physical protection in the finest aggregates. It is confirmed by the results of the ratio CO$_2$/SOC, which was higher for C$_3$ than C$_P$.

The ratio C$_3$-CO$_2$/C$_3$-SOC was stable along the plot and indicated that, despite of the raindrop impact, breakdown of aggregates and exposure of the protected organic matter, the SOC was physically protected and was poorly available for microbial biomass. On the contrary, the ratio C$_P$-CO$_2$/C$_P$-SOC was significantly different along the plot; it was 43% higher in the lower tram of the plot in comparison to the upper plot tram (Fig. 6). This result highlighted the variation of SOC decomposition during sediment transport, indicating that the organic matter becomes more easily mineralizable due to transport processes. Results of previous studies have no consensus regarding the C fraction mineralized during transport and consequently the magnitude of this source in the global C budget. Lal (2003) and Schlesinger (1995) assumed transport as a major source, considering 20% of the eroded SOC to be emitted. On the contrary, Van Oost et al. (2005) and Quinton et al. (2010) gave minor relevance as C source to SOC mineralization associated to transport. The main limitation of this unsolved issue is the difficulty to compare different studies due to the different spatial and temporal scales and different environments these studies were executed. The quality of soil organic matter, soil structure, the microbial activity and the rainfall intensity are, in fact, important parameters that should be evaluated and correlated to assess the fate of C during transport.

Fig. 6. Schema on erosion impact on C losses.


