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Discussions

Coupling sediment flow-paths with organic carbon dynamics across a Mediterranean catchment

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Abstract

Terrestrial sedimentation buries large amounts of organic carbon (OC) annually, contributing to the terrestrial carbon sink. The temporal significance of this sink will strongly depend on the attributes of the depositional environment, but also on the characteristics of the OC reaching these sites and its stability upon deposition. The goal of this study was to characterise the OC during transport and stored in the depositional settings of a medium sized catchment (111 km^2) in SE Spain, to better understand how soil erosion and sediment transport processes determine catchment scale OC redistribution. Total Organic Carbon (TOC), Mineral-Associated Organic Carbon (MOC), Particulate Organic Carbon (POC), Total Nitrogen (N) and particle size distributions were determined for soils (i), suspended sediments (ii) and sediments stored in a variety of sinks such as sediment wedges behind check-dams (iii), channel bars (iv), a small delta in the conjunction of the channel and a reservoir downstream (v) and the reservoir at the outlet of the catchment (vi). The data show that the OC content of sediments was approximately half of that in soils ($9.42 \pm 9.01\,g\,kg^{-1}$ vs. $20.45 \pm 7.71\,g\,kg^{-1}$, respectively) with important variation between sediment deposits. Selectivity of mineral and organic material during transport and deposition increased in a downstream direction. The OC mineralisation, burial or formation occurred in sediments depending on their transport process and on the post-sedimentary conditions. Upstream sediments showed low OC contents because they were partially mobilised by non-selective erosion processes affecting deeper soil layers. We hypothesise that the relatively short transport distances, the effective preservation of OC in micro-aggregates and the burial of sediments in the alluvial wedges give rise to low OC mineralisation, with C : N ratios similar to those in soils. Deposits in middle stream areas (fluvial bars) were enriched in sand, selected upon deposition and had low OC concentrations. Downstream, sediment transported over longer distances was more selected, dominated by silt and clay fractions and associated with OC. Overall, the study shows that OC redistribution in the studied catchment is highly complex, and that transport and deposition processes have a strong effect on

the concentration and quality of OC found at the different depositional settings, with important consequences for the temporal stability of the buried OC and in turn for the OC budget.

1 Introduction

Terrestrial ecosystems have captured up to 28 % ($2.6 \pm 0.8\,\mathrm{Pg\,yr^{-1}}$) of the CO_2 emitted annually over the last decade (Le Quéré et al., 2013). Among the processes involved in this terrestrial carbon (C) sink, terrestrial sedimentation of eroded soil has been regarded as an active component. The magnitude of its contribution to the sink has been estimated by some to be between 0.6 and 1.5 Pg of C annually (Stallard, 1998; Aufdenkampe et al., 2011) through the burial of large quantities of laterally transported organic carbon (OC). The significance of this contribution, however, will depend on the long-term preservation of the buried OC, an issue that remains under debate (Van Oost et al., 2012 and references therein). The fate of the redistributed OC will ultimately depend on the mechanisms of its physical and chemical protection against decomposition, its turnover rates and the conditions under which the OC is stored in sedimentary settings (Van Hemelryck et al., 2011; Berhe and Kleber, 2013).

The study of the temporal evolution of buried OC at depositional sites can be approached from different and complementary perspectives. It has been observed that organic matter exported from rivers into the sea is not necessarily identical to the organic matter of the plants and soils upstream in the river catchments (Raymond et al., 2001). This indicates that tracing sediment from source areas and the processes taking place during transport and deposition of eroded OC can also provide information on the quality and dynamics of the eroded OC (Nadeu et al., 2012 and refs therein). Actually, more than 90 % of the sediment generated annually in uplands is not exported from catchments (Trimble, 1983; Meade et al., 1990; Walling and Fang, 2003) but remains in transitory depositional sites such as lakes and reservoirs, colluvial deposits at the bases of hillslopes, alluvium in floodplains and channel bars (Meade et al., 1990). In fact, flood plains are expected to represent a key storage site for OC within the catchment C balance, and increasingly this function is fulfilled by reservoirs (Verstraeten et al., 2006; Hoffmann et al., 2013; Wisser et al., 2013; Ran et al., 2014). Most of these sinks are still unquantified pools. Although a large effort is being made to understand the flowpaths of OC at the catchment scale. Recently Ran et al. (2014) have estimated an OC budget for the Yellow River, concluding that over a period of 60 years, 49.5 % of the OC was buried in different sinks within the river system, 27 % was mineralized during the erosion and transport phases and 23.5 % was delivered into the ocean. However, there is still large uncertainty over the stability and residence times of OC in many of these sinks, which are affected greatly by geomorphological and hydrological dynamics (Hoffmann et al., 2013). Thus, characterising the OC at these transitory settings and acquiring knowledge on the processes and factors that influence OC stability at these sites contribute to the assessment of the significance of terrestrial deposition in the C cycle.

Understanding how OC moves along with sediments through the different phases and types of erosion and transport processes is crucial to understanding the large variation in C contents found in depositional sites.

Progressively, the geomorphic factors that control the redistribution of OC within watersheds are being defined (Berhe and Kleber, 2013; Evans et al., 2013; Hoffmann et al., 2013; Nadeu et al., 2011, 2012). The study of OC transport from erosion sites to depositional settings implies the consideration of a large number of factors and processes taking place along the whole way. Several studies have described the impact of the differing transport and deposition of different OC size-fractions and the role of OC mineralisation, as well as the breakdown of soil aggregates or re-aggregation at depositional settings (Wang et al., 2010; Van Hemelryck et al., 2011; Martínez-Mena et al., 2012) and the contribution of new OC formation from vegetation at depositional settings. Altogether, these factors are considered responsible for the transformations undergone by OC from source to sink. Yet, comprehensive studies of source to sink processes are, to the best of our knowledge, lacking.

The objective of this study is to characterise the OC in transit and at a range of depositional settings in a medium size catchment and to associate our observations with the catchment sediment dynamics. We aimed to: (i) characterise the OC concentrations in the main sedimentary deposits along the catchment's drainage system; (ii) assess the main processes involved in sediment redistribution; (iii) establish links between these processes and the OC concentration and quality.

2 Study area

The study area is located in the headwaters of the Segura catchment (Murcia, SE Spain), which drains to the Taibilla reservoir (Turrilla catchment) and is formed by three adjacent subcatchments (Rogativa, Arroyo Blanco and Arroyo Tercero) covering a total area of ∼ 111 km^2 (Fig. 1). The Taibilla reservoir, built in 1974, provides water to more than 2 million people. The dominant lithology of the catchment consists of marls, limestones, marly limestones and sandstones of the Cretaceous, Oligocene and Miocene. The mountains are mainly constituted by limestones, while the middle and bottom valley sections are dominated by marls (IGME, 1978).

The average annual rainfall for the period 1933–2004 was 583 mm and the average annual temperature 13.3 °C, at a station located in the centre of the basin at 1200 m a.s.l. Snow in the mountains, especially above 1700 m, is not abundant but is frequent in winter. The dominant soils in the area are Calcaric Regosols and Calcaric Cambisols.

The Rogativa catchment shows a dendritic channel pattern. The main channel has an average slope of 7.7° and a total longitude of 22 km. The stream is discontinuous upstream and continuous downstream.

The landscape is a mix of dryland farming (mainly barley), plantations of walnuts (*Junglans regia* L.), forests and shrublands. The forest is dominated by *Pinus nigra* Arn. subsp. *salzmanii*, although some individuals and masses of *Pinus pinaster* Ait. and *Pinus halepensis* Mill. are located in the lowest parts of the basin. Nowadays, masses of *Quercus rotundifolia* Lam. are isolated or associated with *P. nigra* subsp. *salzmanii*. The catchment has been affected by important land use changes since the second half of the twentieth century. These changes consisted mainly of a progressive abandonment of the dryland farming activities and an increase of the forest cover. In the 1970s, a network of check-dams was installed. A relevant proportion of the pine forest was planted in the reforestation works associated with dam construction in this period. Previous studies highlighted the important impact of land use changes and check dams on the catchment's sedimentary dynamics (Boix-Fayos et al., 2008; Quiñonero-Rubio et al., 2013), causing important morphological changes in the river bed and accelerated bank erosion processes (Boix-Fayos et al., 2007). Land use changes have been estimated to be responsible for about 50 % of the reduction in catchment sediment yield (Boix-Fayos et al., 2008) and have had an important impact on the soil carbon stocks of the catchment (Boix-Fayos et al., 2009). Geomorphological characterisations of channel reaches along the main and tributary streams of the Rogativa catchment indicated dominance of non-selective erosion processes such as gully, bank and river bed erosion (Nadeu et al., 2012), often activated as a consequence of the decrease in sediment input from the adjacent slopes caused by a generalised recovery of the vegetation, following agricultural land abandonment and reforestations (Boix-Fayos et al., 2007). Sediments reaching the streams originate from upper soil layers, through interrill erosion processes (Nadeu et al., 2012), and from deeper soil layers below the channel, due to massive erosion processes (bank collapses, deep gullies and channel erosion) (Boix-Fayos et al., 2007; Nadeu et al., 2011).

3 Methods

The field experimental design was based on the main pathways of sediment and soil OC during their transport through the catchment. Therefore, soils and different sedimentary deposits within the catchment were sampled as shown in Fig. 1.

3.1 Soil data

Topsoil (0–10 cm) samples were taken from 109 locations distributed from upstream to downstream in the catchment, representing all land uses and their spatial extent. Of these samples, 20 % were from high density forest soils, 30 % from low density forest soils, 20 % from shrubland soils, 13 % from pasture soils and 20 % from agricultural soils. Disturbed samples were taken for laboratory analyses and undisturbed samples (rings of 100 cm^3) for estimating soil bulk density.

3.2 Sediment data

3.2.1 Alluvial wedges (behind check-dams)

The sediment deposited behind the network of check-dams installed in the 1970s was used as representative of material mobilised by erosion processes and fluvial transport from the upper catchment areas (Fig. 1). Nineteen (sub) catchments, evenly distributed, were sampled. The sediment wedges deposited behind each check-dam were sampled at the front (close to the check-dam) to a maximum depth of 1.25 m. In addition, 14 of the sediment wedges were sampled also upstream, at the back of the sediment wedge, to a maximum depth of 96 cm. At all points, bulk samples of 100 cm^3 were taken at intervals of 7 cm depth until the maximum depth was reached. Moreover, for 14 wedges, replicate samples of the first layers were taken at 7 cm intervals, to 35 cm depth. A total of 537 undisturbed samples were collected.

3.2.2 Fluvial bars

Sedimentary fluvial bars located at two different reaches in the Rogativa main stream, 2 km apart in the middle section of the catchment, were sampled. One of the reaches is a permanent-flow reach where four different bars were sampled during three seasons (autumn 2009, winter and spring 2010), and the other is an intermittent reach where four bars were sampled in autumn 2009 and winter 2010 (the same dates as the bars of the permanent-flow reach). A disturbed sample of the first 5 cm of the bar was taken at each sampling period, as no different layers corresponding to different events could be distinguished in these bars.

Two more bars, also in an intermittent reach in the middle section of the catchment and in a confluence of a small subcatchment (11 ha, barranco Escalerica 2) and the Rogativa main stream, were sampled. The bars in the stream bed were incised during the last runoff event (winter 2010) that took place a few days before the sampling. The deposited layers corresponding to different runoff events could be identified (Fig. 1) and were sampled to a maximum depth of 30 cm (bar 1, seven layers, average depth of each layer 4.2 cm) or 20 cm (bar 2, six layers, average depth of each layer 3.3 cm). These bars represented a mixture of sediments coming from several erosion processes and were considered representative of the type of sediment being transported along the stream bed from further upstream (Nadeu et al., 2011). A total of 46 samples were collected.

3.2.3 Suspended sediment

Two devices for the sampling of suspended sediments were installed in the main stream of the Rogativa channel in October 2010: one was installed in the downstream area, draining a catchment area of 54.4 km^2, and the other was installed just below the confluence with the perennial stream of Arroyo Blanco, draining a total catchment area of 78.1 km^2.

The sampling devices consisted of a column of 6 bottles located at an averaged height difference of 7.5 cm from each other (Fig. 1). At both locations the upper bottle represented bank-full conditions of the incised stream. A total of 69 samples, corresponding to 13 events over a 2.5 year period, were collected.

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3.2.4 Delta sediments

Sediments in the confluence of the river channel and the reservoir were sampled. This delta area is characterised by a very gentle slope and point bars formed by the meandering contact between the river and the reservoir. A sampling scheme following the convex depositional areas of the meanders of the river towards the reservoir was implemented: a total of six positions with two replicates and two depths (0–5, 5–10 cm) were sampled, collecting a total of 24 samples.

3.2.5 Reservoir sediments

Sediments in the Taibilla reservoir were sampled in March 2010. Water height in the Taibilla reservoir is highly variable between years and during the year. Samples were taken at a distance of 500 m from the confluence of the main stream of Rogativa and the reservoir, in exposed sediments forming a terrace 20 cm above the water level at the moment of sampling. Sampling was done with a Cobra TT hydraulic hammer to a depth of 1 m. The 1 m-deep core was divided at 5 cm intervals to 20 cm depth and then at 10 cm intervals. A total of 23 samples were analysed.

3.3 Laboratory analysis

All soil and sediment samples (from erosion deposits and deposition bars) were air-dried or dried in an oven at a low temperature (< 60°) and then sieved at 2 mm. Primary particle size distribution was measured using a combination of wet sieving (particles > 63 µm) and laser diffractometry (particles < 63 µm) using a Coulter LS, for the sand fraction and the silt and clay fractions, respectively. The organic matter in these samples was oxidised with hydrogen peroxide and chemically dispersed with a mixture of sodium hexametaphosphate and sodium carbonate (anhydrous) for 18–24 h. The fractions obtained were classified as: coarse sand (2000–250 µm), fine sand (250–63 µm), coarse silt (63–20 µm), fine silt (20–2 µm) and clay (< 2 µm). The effective particle size distribution was measured by introducing air-dried samples into a Coulter LS, without previous physical or chemical dispersion. From these two measurements, micro-aggregation indices were derived.

The percentage of micro-aggregated particles of fine sand, coarse silt and fine silt sizes and two aggregation indices that give an indication of the total percentage of micro-aggregated particles were used: IA (Index of Aggregation), as the sum of the differences of the dispersed and non-dispersed material in each size group (Wang et al., 2010), and ASC (Aggregation Silt and Clay) as the difference between dispersed clay and silt and non-dispersed clay and silt (Igwe, 2000).

The OC was divided into physical fractions by wet sieving: particulate organic carbon (> 53 µm) (POC) was separated from mineral associated organic carbon (< 53 µm) (MOC) after shaking 10 g of air-dried soil sieved at 2 mm with 50 mL of sodium hexametaphosphate for 18 h (Cambardella and Elliot, 1992). Fractions were oven-dried at 60 °C for water evaporation and the dry material was weighed prior to OC determination. The OC and nitrogen contents were determined by dry combustion in an elemental analyser (FLASH EA 1112 Series Thermo). The total organic carbon (TOC) was assumed to be the sum of the POC and MOC. The MOC accounted for micro-aggregate and intra-aggregate OC associated to the silt and clay size fractions. Duplicate or triplicate soil samples were used for laboratory analysis.

3.4 Statistical analysis

Significant differences between averages were tested using the non-parametric Kruskal–Wallis test at $p < 0.05$. Spearman correlations were performed to explore the relationships between the TOC and pools, as well as C : N ratios and the percentages of primary and micro-aggregated soil particles, together with different aggregation indexes, for all cases or each sediment reservoir type separately. All statistical analyses were performed with the software SPSS 19.0 (SPSS, Chicago, IL).

4 Results

4.1 Organic carbon and nitrogen in soils and sediments

The TOC concentrations of sediments were, on average, around half ($9.42 \pm 9.01\,\mathrm{g\,kg^{-1}}$) of the average TOC concentrations of surface soils (0–10 cm) ($20.45 \pm 7.71\,\mathrm{g\,kg^{-1}}$), being higher in alluvial wedges behind dams, in the suspended solids, in the delta and in the reservoir and lower in active alluvial bars in the main channel ($4.44 \pm 1.98\,\mathrm{g\,kg^{-1}}$) (Fig. 2). The C : N ratios were higher in soils and alluvial wedges and lower for the rest of the deposits (Fig. 2).

The concentrations of POC were highest in sediment samples taken from the alluvial wedges, while suspended solids and reservoir profiles contained the highest MOC concentrations. The lowest MOC concentration was found in the bars.

4.2 Primary particle size distribution of soils and sediments

The particle size distribution of soils differed from that of most of the sediments (Fig. 3). The alluvial bars showed, on average, higher sand contents and lower contents in the fine fractions than the soils (Fig. 3). This enrichment in coarse fractions in the alluvial bars was accompanied by the lowest values of TOC (Figs. 2 and 3). In contrast, the suspended solids and the delta and reservoir sediments had higher percentages of silt and clay than the soils. The high sand contents in the reservoir and delta sediments were similar to the sand content (around 20 %) of the wedges. The alluvial wedges showed particle size distributions more similar to those of the soils of the catchment than to those of the rest of the deposits.

4.3 Micro-aggregated particles in soils and sediments

Based on the micro-aggregation data, two groups can be distinguished. Soils and sediment wedges with similar IA and ASC values (Table 2) showed a significantly higher micro-aggregation level than suspended sediment and reservoir sediments. The sediments in alluvial wedges had 10 times more large aggregates (250–63 µm) than the suspended sediment and 6 times more than the reservoir sediments. This was the dominant class in soils and alluvial wedges, while no differences between size classes occurred in suspended and reservoir sediments. The percentages of medium-sized micro-aggregates (63–20 µm) in the alluvial wedges were around 3 and 7 times greater than in the suspended sediment and reservoir sediments, respectively. No significant differences were found between the percentages of micro-aggregated particles in the suspended sediment and reservoir sediments, regarding the total micro-aggregated material and size classes.

4.4 Correlations between primary and micro-aggregated particles, OC pools and C : N ratios

The Spearman correlation coefficients showed different patterns in the relationships between the percentages of primary and micro-aggregated particles and the OC pools and C : N ratios across the deposit types. The total amount of micro-aggregated particles (Index of Aggregation, IA) was positively correlated with the TOC (for all data), POC (for all data and alluvial wedges) and C : N ratio (in soils). Furthermore, the micro-aggregates in the 250–63 µm fraction were positively correlated with the POC (in the reservoir deposits) and C : N ratio (for all data, as well as in soils, wedges and suspended sediments separately). In contrast, the ASC index (micro-aggregated material of silt and clay size fractions), consistently, was negatively correlated with the OC pools and C : N ratio in soils and different deposits. In general, it seems that the TOC content and its fractions correlated positively with micro-aggregated material (IA), while this relationship became negative when smaller aggregate sizes were considered for the aggregation index (ASC).

There were no consistent correlation patterns in the relationships between the percentages of primary particles and the OC pools and C : N ratio across deposit types. The TOC was associated positively with the sand fraction and negatively with the clay fraction, for all the data considered together and the reservoir. By contrast, the clay

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fraction was associated positively with TOC in wedges and suspended sediment, and with MOC in alluvial wedges. The POC was correlated positively with the sand fraction in the reservoir sediments.

Overall, as may be expected, the OC content was positively correlated with the clay fraction in some deposits (e.g., alluvial wedges and suspended sediments), indicating selectivity during detachment and transport. However, OC was also positively correlated with the content of sand particles in the soils and reservoir, probably indicating the entrance of organic material from other processes (in situ formation of C in lakes (Tranvik et al., 2009)) in the reservoir and OC formation in the upper layers of sediment. Positive correlations of the sand and OC in soils are probably due to the presence of several samples of sandy soils covered by dense forest (25 % of dense forest soil samples had 45–70 % sand).

5 Discussion

Hoffman et al. (2013) pointed out that accounting for the non-steady state of C dynamics along flow-paths from hillslopes through river channels and into oceans is crucial to understand the overall C budget. The redistribution of OC through soil erosion and sediment transport is determined by processes that affect the mineral component of sediment (e.g. selectivity and non-selectivity of material during the detachment, transport and deposition phases) and by processes directly affecting the OC fraction within the sediments (mineralisation, fixation, protection, new OC formation). To better understand the role of soil erosion and sediment transport in the overall C budget, based on the data reported in this study, the following paragraphs discuss the importance of particle size selectivity as well as the OC dynamics of eroded sediments during detachment, transport and deposition phases.

5.1 OC redistribution from source to sink

All sediments studied within the Rogativa catchment showed, on average, OC concentrations ($9.42 \pm 9.01\,\mathrm{g\,kg^{-1}}$) less than half of those of soils ($20.45 \pm 7.71\,\mathrm{g\,kg^{-1}}$), indicating depletion of OC in sediment at this scale. This clearly contrasts with experimental data from erosion plots that usually show higher concentrations of OC in sediments than in the original source-soils (Owens et al., 2002; Girmay et al., 2009; Martinez-Mena et al., 2008). These relatively low OC concentrations found in sediments at the catchment scale raise the question: do the erosion and sediment transport processes lead to C losses to the atmosphere, or is there another explanation for this difference in C concentration between soils and sediments?

Previous studies have also found a depletion of OC in sediments measured at a catchment scale (Avnimelech and McHenry, 1984; Haregeweyn et al., 2008). For a small catchment (22 ha), Fiener et al. (2005) observed that sediment deposited in ponds was depleted in OC and clay relative to the source soils, while the sediment collected at the outlet of the pond was enriched in OC and clay compared to soils. This demonstrates the important changes in OC content that may occur during different transport and deposition phases due to preferential deposition. Similar results were reported by Wang et al. (2010) and Rhoton et al. (2006), who found OC impoverishment in deposited sediments within their study catchments, while the sediment transported in suspension and exported out of the catchment was enriched in OC (1.2–3 times) compared to the OC concentration in the source soils. Ran et al. (2014) attributes also lower values of OC than soils for different sedimentary settings, based on several methods, to estimate the OC carbon budget of the Yellow River. In our case, the suspended sediments as well as the reservoir sediments showed significantly higher concentrations of MOC compared to the other sediment deposits, while the MOC concentration in soils was similar to that in reservoir sediments and slightly higher than in suspended sediments.

Some authors have found sediments deposited in ponds with high trapping efficiencies and anoxic conditions to be enriched in OC, relative to the source soils (Amegashie et al., 2011). Except for the MOC concentration in reservoir sediments, in our case all sediments were depleted in different OC fractions and in TOC, while significant differences were also found between deposits. The fact that reservoir sediments showed higher TOC concentrations than sediments deposited in wedges behind check-dams, as also found by Amegashie et al. (2011), can probably be attributed partially to new, autochthonous formation of OC in the reservoir (Einsele et al., 2001).

5.2 Mechanisms of OC loss or gain in sediments

The following sub-paragraphs discuss three complementary explanations for the different OC concentrations observed in sediments, compared with the original soils: (i) size selectivity of material upon detachment, transport and deposition; (ii) variation in the sources of sediments and OC and (iii) processes that affect the organic components of the sediments during the erosion and fluvial transport pathway such as burial, mineralisation or new OC formation.

5.2.1 Size selectivity and sources of sediment

Wang et al. (2010) explained how selectivity of soil material determines the OC concentration during transport. They concluded that there was very little mineralisation of TOC during the erosion process, based partially on the C : N ratios being higher in sediments than in source soils and similar enrichment ratios of clay and C in deposited sediments. Our data show evidence to the contrary in the middle and lower catchment deposits (suspended sediments, delta and reservoir): higher clay contents than soils, low OC and low C : N ratios. These findings could indicate C losses by mineralisation during transport over longer distances.

However, low OC concentrations of sediments transported and deposited in the upper catchment areas seem to have different explanations. The sediments in the alluvial wedges showed textural classes and C : N ratios similar to those of the soils, but lower OC concentrations. The low OC concentration in the sediment wedges may be explained by the fact that the sediments originate from deeper soil layers, mobilised by non-selective erosion processes such as bank, gully and channel erosion, with lower OC concentrations than the surface soil. Geomorphological field assessments carried out in the area indicated these deeper operating erosion processes are important sources of sediments in the catchment that were activated by land use change and installation of check-dams (Boix-Fayos et al., 2007). Moreover, Nadeu et al. (2012) related the different dominant erosion processes to different OC pools transported (Nadeu et al., 2011a) and different ages of OC in mobilised sediments (Nadeu et al., 2012), in different subcatchments of the Rogativa catchment. Other studies related differences in the pools of OC exported by erosion to differences in rainfall intensity (Martínez-Mena et al., 2011; Zhang et al., 2013) or to the discharge. Smith et al. (2013) related high flows with transport of modern C, associated with erosion and the release of organic matter (Sanchez-Vidal et al., 2013), and C from vascular sources (Goñi et al., 2013). Low flows were associated with export of fossil OC (Smith et al., 2013), from biogenic sources dominated by non-vascular plants (Goñi et al., 2013) or from fresh water primary producers (Sanchez-Vidal et al., 2013).

A comparison of the particle sizes of the studied sediments and soils of the catchment points to a selection of transported material in a downstream direction. Finer micro-aggregated and single particles were present in the suspended load and in the reservoir. In the soils and in the alluvial wedges behind check-dams, the material was much more hierarchical, having similar particle size distribution and being micro-aggregated at a large size (sand fraction), indicating again its transport by non-selective erosion processes and over short distances.

In general, the micro-aggregation of particles (< 250 µm, e.g. IA index) and clay content were positively correlated with TOC, as found by other authors (Martinez-Mena et al., 2008, 2011; Jin et al., 2009), and with MOC in some deposits.

5.2.2 Processes affecting organic carbon dynamics during transport and deposition

The OC contents, variation in C : N ratios and different associations of OC with textural classes in the studied deposits indicate different processes of loss or gain of OC during the transport along the studied catchment.

The C : N ratios showed clearly two groups (Fig. 3): lower values in suspended sediments and delta and reservoir sediments, and higher values in soils and alluvial wedges. This suggests a relatively low mineralisation of OC in the sediments of alluvial wedges possibly due to efficient burial or a short transport time because of the proximity to sediment sources in the upper catchment areas, as reported also by Smith et al. (2013) and as suggested by Ran et al. (2014). Further downstream in the suspended sediment, delta and reservoir sediments, the lower C : N ratios could indicate mineralisation of OC in sediment transported over longer distances (Fig. 3) (Bouchez et al., 2010; Hovius et al., 2011; Raymond and Bauer, 2001). Ran et al. (2014) recently reported a mineralization of 27 % during erosion and transport of sediment and associated OC through the Yellow River catchment.

Apart from the indications of OC mineralisation, the MOC values of suspended sediments were low and very variable (2.08–0.29 %) which can be attributed to the diverse characteristics of the events that mobilise material from different sources (Smith et al., 2013; Goñi et al., 2013; Sanchez-Vidal et al., 2013) or to sediments mobilised by different erosion processes (Nadeu et al., 2011, 2012).

Furthermore, the relatively high OC content of the reservoir sediments could indicate in situ organic matter formation from ecological lake processes (Einsele, 2001) or OC input from the establishment of vegetation and soil formation in the frequently exposed upper sediment layers (as observed in the field). Moreover, while other deposits (wedges and suspended sediment) showed the well-known relationship between clay and OC (Rodriguez-Rodriguez, 2004; Rhoton et al., 2006), the reservoir showed a correlation between the sand fraction and OC pools, indirectly indicating in situ C formation.

The combined interpretation of OC pools, textural analysis and C : N ratios in the soils and different sediment deposits indicates that at catchment scale C redistribution by lateral fluxes is controlled by both the organic and the mineral nature of sediments:

i. Sediments in upstream depositional areas (alluvial wedges) showed significantly lower OC concentrations than soils, but sediment texture and OC characteristics were more similar to those in soils than to those in sediments transported further downstream, showing little indication of mineralisation (similar C : N than in soils) and low selectivity of particles (similar primary and aggregated particle size distribution to soils). This is probably related to the non-selective character of dominant erosion processes and to the proximity of sediment sources, giving less opportunities for aggregate breakdown or C mineralisation.

ii. In middle stream areas, preferential deposition of coarse particles can be seen in the channel bars, enriched in the sand fraction and showing the lowest concentrations of all OC fractions, among all deposits.

iii. Downstream, the suspended sediment in transit and the sedimentary deposits (delta and reservoir) showed higher contents of fine particles (clay and silt) – accompanied by lower C : N ratios and a slightly higher OC concentration, though still lower than in soils. The sand contents of the delta and reservoir deposits indicate also bedload contribution to the deposits downstream. Moreover, the differences in the C : N ratio indicate different degrees of mineralisation of OC along the flow-path, the OC being protected more when associated with large micro-aggregated particles in soils and in the deposits of the upper catchment areas.

5.3 Implications for the fate of eroded OC

The results from this study suggest that sediment reaching depositional settings is composed of a heterogeneous mixture of OC particles and different states of decomposition. The role of the source area and sediment transport processes was revealed as crucial to understanding the characteristics of the OC and differences among the analysed deposits and distinct phases of the erosion process. Although mineralisation fluxes were not addressed directly, the decrease in the level of particle aggregation downstream suggests a potential increase in OC decomposition by microorganisms, leading to higher mineralisation rates. Distance from source areas, selective transport and deposition were identified as important factors controlling the characteristics of the OC in sediments and, potentially, its fate.

6 Conclusions

A non-homogeneous redistribution of OC by water flow takes place within catchments, which can be associated with the geomorphological processes and dynamics of sediment transport and deposition. The redistribution of OC in sediments at the catchment scale is controlled by factors affecting their organic component (mineralisation, protection of OC within micro-aggregates and new OC formation in some deposits) and by factors affecting their mineral component (selectivity of sediment sizes during the detachment, transport and deposition phases of erosion, and the type of erosion processes: selective vs. non-selective).

These processes determining OC distribution by the sediments in catchments seem also to be associated with the erosion phase (i) during detachment: size selectivity, type of erosion process and source of material; (ii) during transport: size selectivity, protection of OC in micro-aggregates and transport distances, and (iii) during deposition and in the post-deposition phase: size selectivity, protection of OC from mineralisation by stabilisation of micro-aggregates and burial and new OC formation are important.

The OC mobilised in catchments is associated very closely with the sediment dynamics and can have long residence times, linked to the fate of the sediments. In addition, it can be increased by ecological processes and by replacement in eroded areas, converting catchments into relevant sinks for C budgets.

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Table 1. Main location and characteristics of the sampling areas within the catchment.

Location of soil and sediments	Group name	Drainage area (ha)	Deposition areas	Profiles/ Subcatchments/ Events	Maximum depth (cm)	Samples (*n*)
Soils						
Slopes	Soils	11 000		109	10	109
Sediments						
Subcatchments in the third and fourth order channels	Wedges	8–146	Sediment wedges behind check-dams	19	125	537
Main channel and a tributary stream	Bars	5000	Channel bars	10	3–30	46
Main channel	Suspended sediment	5000–7800	Suspended load	13	7–42	69
Main channel	Delta	11 000	Delta in the conjunction of the main channel and reservoir	6	10	24
Reservoir	Reservoir	32 000	Reservoir sediments at the outlet of the catchment	2	100	23

Table 2. Percentages of micro-aggregated particles in different size classes and micro-aggregation indices (IA, Wang et al., 2010; ASC, Igwe et al., 2000).

Group name	250–63 µm	63–20 µm	20–2 µm	IA	ASC
Soils (*N* = 16)	24.99 ± 16.27 aA*	3.91 ± 6.99 aB	7.34 ± 16.06 aB	73.91 ± 21.03 a	12.51 ± 34.91 a
Wedges (*N* = 25)	36.49 ± 17.88 aA	9.59 ± 8.87 bB	0	92.18 ± 23.50 a	36.48 ± 17.92 a
Suspended sediment (*N* = 41)	3.60 ± 9.21 bA	3.19 ± 3.22 aA	2.52 ± 6.40 aA	18.22 ± 12.29 b	0.98 ± 2.26 b
Reservoir (*N* = 12)	6.65 ± 7.87 bA	1.46 ± 2.70 aA	2.44 ± 3.46 aA	24.94 ± 14.30 b	−0.41 ± 9.71 b

* Different lower case letters mean significant differences among sediments and soil groups. Different capital letters mean significant differences within sediments and soil groups, with regard to micro-aggregated class sizes. (Kruskal–Wallis test, $p < 0.05$).

Table 3. Spearman correlation coefficients between primary and micro-aggregated particle indicators and organic carbon (%) pools and C : N ratios.

		Micro-aggregated particles					Primary particles	
Groups	250–63 µm	63–20 µm	20–2 µm	IA	ASC	Sand	Silt	Clay
TOC					–			
All data	**−0.356***	–	–	**0.477**	–	**0.701**	**−0.264**	**−0.642**
Soils	–	–	–	–	−0.512	0.574	–	–
Wedges	–	**−0.504**	–	–	–	−0.494	–	**0.497**
Suspended sed	–	−0.351	–	–	–	–	**−0.480**	**0.474**
Reservoir	–	–	−0.694	–	–	0.636	–	**−0.713**
POC								
All data	–	–	–	**0.488**	–	–	–	−0.273
Soils	–	–	–	–	−0.618	–	–	–
Wedges	–	–	–	**0.529**	–	**−0.720**	0.450	–
Suspended sed	–	–	–	–	–	–	–	–
Reservoir	0.582	–	−0.664	–	−0.674	**0.825**	–	**−0.874**
MOC								
All data	–	**−0.379**	–	–	−0.281	–	–	–
Soils	–	–	–	–	–	0.588	–	–
Wedges	–	**−0.577**	–	–	–	–	–	**0.724**
Suspended sed	–	–	–	–	–	–	–	–
Reservoir	–	–	–	–	−0.655	0.629	–	**−0.727**
C : N								
All data	**0.438**	**−0.549**	**−0.403**	–	**−0.552**	**0.414**	**−0.269**	−0.229
Soils	**0.747**	**−0.980**	**−0.902**	0.597	**−0.742**	–	–	–
Wedges	**0.505**	**−0.791**	–	–	**−0.533**	–	–	–
Suspended sed	0.345	–	**−0.519**	–	−0.374	–	−0.259	–
Reservoir	–	–	–	–	–	–	–	–

* Only significant correlations are shown.
Bold correlation indices are for $p < 0.005$, the rest have $p < 0.05$.

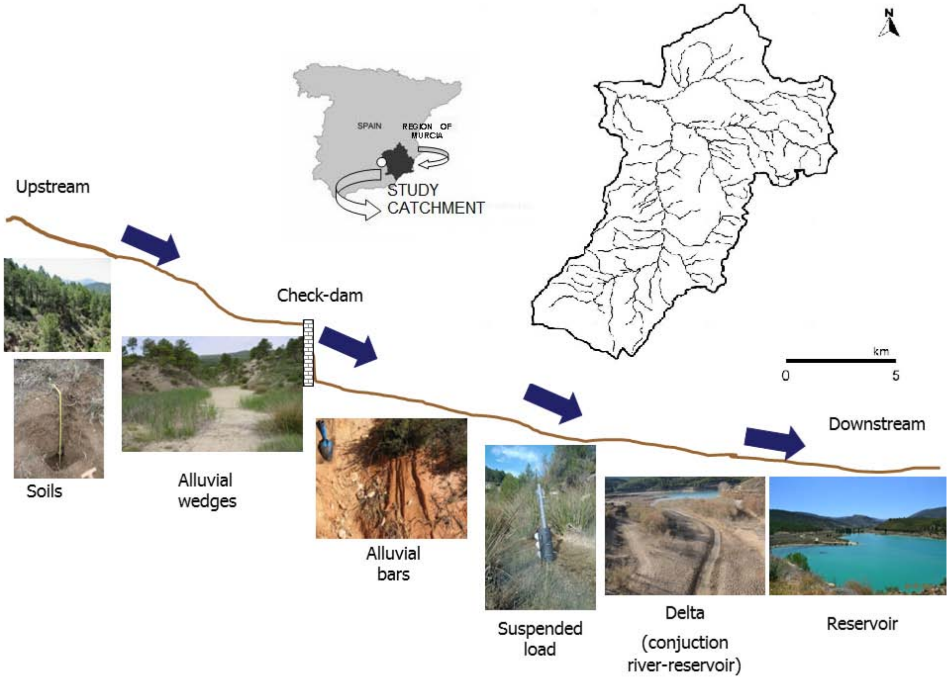

Fig. 1. Location of the study area and sketch representing the morphological positions selected for sampling of the soil and sediments. Soils were sampled all around the catchment in all the different land use classes: alluvial wedges behind check-dams predominantly in the upper and middle parts of the catchment, while alluvial bars and suspended solids were sampled in the middle and downstream areas. Delta and reservoir represent sampling areas downstream, at the entrance and in more central parts of the reservoir.

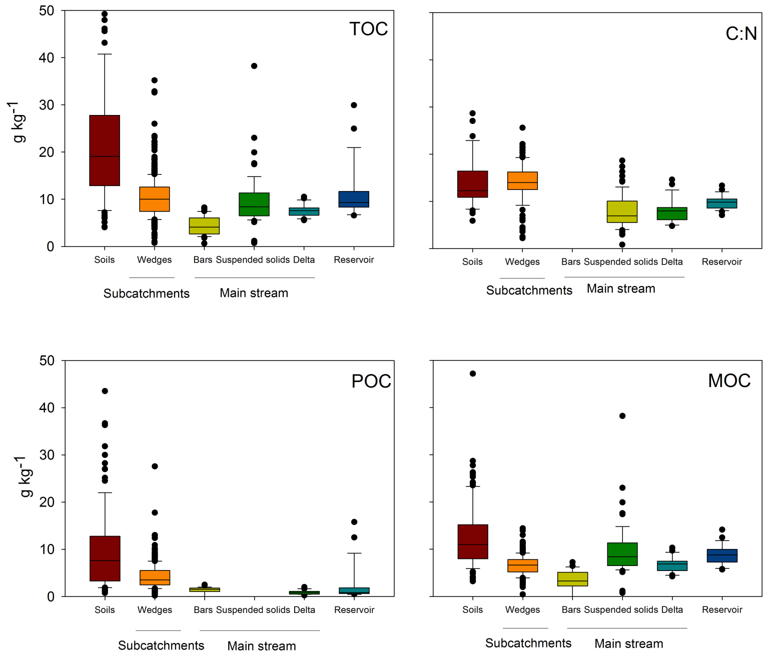

Fig. 2. Median, percentiles (10th, 25th, 75th and 90th) and error of the total organic carbon concentration (TOC), particulate organic carbon (POC), mineral associated organic carbon (MOC) and C : N ratios in soils and different types of sedimentary deposits within the Rogativa catchment. Different letters (a–e) indicate significant differences according to the Kruskal–Wallis test ($p < 0.05$). ND = No data available, * = suspended solids measured contained only the MOC fraction.

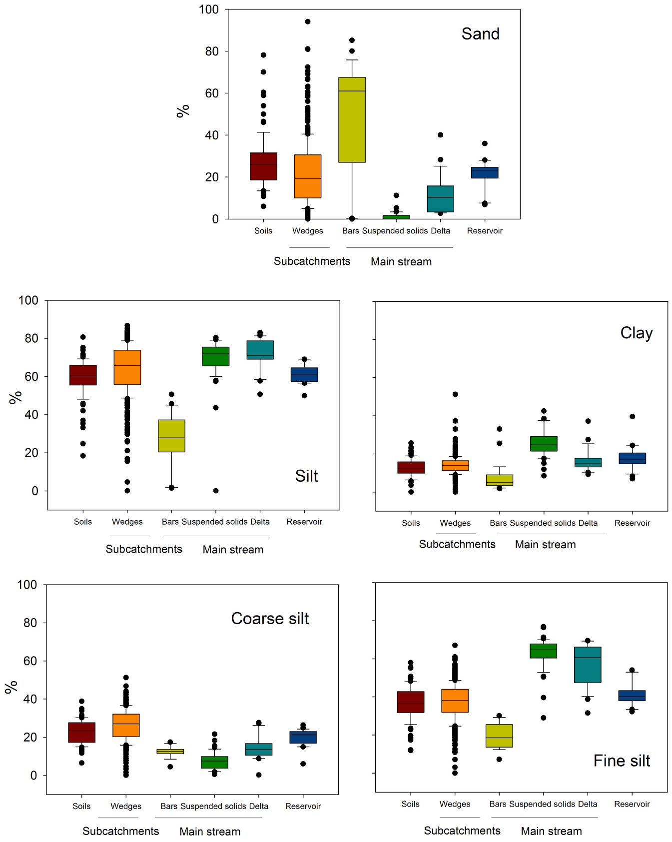

Fig. 3. Median, percentiles (10th, 25th, 75th and 90th) and error of the main textural classes of the different types of sedimentary deposits within the Rogativa catchment. Different letters mean significant differences according to the Kruskal–Wallis test ($p < 0.05$).