WATER EROSION OF ORGANIC CARBON FORMS AND NUTRIENTS IN FOREST ANDOSOLS

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Abstract

The overall objective of this work was to carry out a first assessment of nutrient loss and soil organic carbon (SOC) loss mechanisms due to water erosion in Canary Island Andosols after deforestation, and the forms of SOC most affected by these losses.

The study was performed in experimental erosion plots. Soil surface samples were collected in the soil plot in the first 5 cm at 10 randomly distributed sampling points. After each significant rainshower the amount of sediments and runoff generated was determined. For soil and sediments samples the following parameters were determined:

- pH, and available P, K, Ca, Mg
- Walkley-Black, pyrophosphate and potassium sulphate extractable SOC
- dissolved SOC
- oxalate extractable Fe, Al and Si, and pyrophosphate extractable Fe and Al.
- runoff water pH, EC and dissolved OC, K, Ca, Mg

The measured values of eroded OC in sediments oscillate around 116±30 g kg⁻¹, implying losses of OC bound to the solid phase of 114.4 g Cm⁻² yr⁻¹. The concentration of dissolved OC in runoff also varies in the different events, implying losses of dissolved OC oscillating between 0.8 and 18.0 mg m⁻². Nutrient losses oscillate between 0.9 g m⁻² yr⁻¹ in runoff waters and 2.1 g m⁻² yr⁻¹ associated with sediments.

Additional Keywords: adsorbed organic carbon, eroded organic carbon, Canary Islands, organomineral complex

Introduction

Although several studies have been conducted to assess the impact of soil erosion on organic carbon (OC) dynamics and on the global carbon balance in nature, there are still important gaps in the knowledge about their importance, the behavior of eroded OC as a sink or source of CO₂ and in general about the net effect of erosion on the evolution of atmospheric CO₂ (IPCC, 1996, Cihlar *et al.*, 2002).

An important factor in the dynamics of OC mobilized by erosion is the stability of the OC (Eswaran *et al.*, 1995), which is closely related with the degree of complexity of the humic molecules, with its position in the aggregates and with the way in which this is associated with secondary metals and minerals (Jastrow and Miller, 1998).

Organic matter in andosols is stabilized by short-range ordered minerals with high surface area (allophane, imogolite, ferrihidrite) or by the formation of Al-humus complexes (Dahlgren *et al*, 1993). These soils are highly resistant to water erosion and this low erodibility is closely related with their specific physical properties (Khamsouk *et al.*, 2003, Rodríguez Rodríguez *et al.*, 2002a).

Some studies in small plots have examined the flows of dissolved nutrients or associated with suspended sediments, showing a great variability in nutrient losses related to rainfall events (Schlesinger *et al.*, 2000, Ramos and Martínez-Casasnovas, 2004, Pardini *et al.*, 2003). Less known are nutrient losses in soils of volcanic origin, taking into account the special characteristics of charge and adsorption that these soils present (Mihara, 2001).

The aim of this work was, therefore, to determine losses of OC and nutrients that are produced by water erosion in andosols after deforestation and the forms of OC most affected by these losses. The possible influence of these on soil fertility and on the emission or sequestering of atmospheric CO_2 in the environmental conditions found in the Canary Islands was also contemplated.

Material and Methods

The study was carried out over a 10-year period in 200 m² (25 x 8 m) experimental plots installed on allophanic andosols (Ultic Fulvudands, Soil Survey Staff, 1999) or Sili-fulvic Andosols (WRB, 1998).

Soil samples were taken from the first 5 cm at 10 sampling points randomly distributed over the plot. These samples were fractionated into three aggregate size fractions (>2mm, 0.5-2.0 mm, <0.5 mm) by dry sieving. Both in the total soil sample sieved (2 mm mesh) and in the three aggregate fractions, the following parameters were determined:

- total organic carbon (TOC), by the method of Walkley-Black using 1.3 as a compensation factor.
- OC extractable with a 0.1 M solution of sodium pyrophosphate (Cp). The difference between TOC and Cp corresponds to slowly oxidizable OC and non complexed forms (OOC).
- OC extractable with a 0.5 M solution of potassium sulphate. The difference between Cp and OC extractable with SO₄K₂ corresponds to carbon complexed with active forms of Fe and Al (AOC).
- dissolved organic carbon (DOC) in the saturation extract (only in the total soil).
- pH (H₂O, 1:2.5))
- extractable P (Olsen and Sommers, 1982), K, Ca and Mg (NH₄Ac at pH 7 followed by AAS or FES)
- Fe_o, Al_o, Si_o: extractable with a 0.2 M solution of ammonium oxalate at pH 3.
- Fe_p, Al_p: extractable with a 0.1 M solution of sodium pyrophosphate.

After each significant rain event, sediments and run off were collected and measured. Analytical determinations of the sediments were carried out following the same procedures as those used for the soil. The following parameters were measured in runoff and rainwater: pH and electrical conductivity (EC), K, Ca and Mg by AAS and DOC according to the Walkley-Black procedure. All samples were analyzed in triplicate and average results are reported.

Results and Discussion

The TOC in the first surface 5 cm is around 120 g C kg⁻¹ (2.4 kg C m⁻²), of which 70.8% (85 g C kg⁻¹) appear in a form complexed (adsorbed) with the mineral fraction (AOC), 26.6% (32 g C kg⁻¹) in a slowly oxidizable and noncomplexed form (OOC), 2.5% (3 gC kg⁻¹) in labile forms (LOC) and only 0.1% (188 mg C L⁻¹) appears dissolved in the soil solution (DOC) (Table 1). Therefore, most of the OC in these soils is found in relatively stable complexes formed with the mineral fraction, as several authors have already reported (Dahlgren et al., 1993, Parfitt et al., 1997, Powers and Schlesinger, 2002).

Table 1. Nutrients and eroded organic forms or in the soil surface

| | Soil surface (0-5 cm) | Rainwaters (n=14) Media±SD | Sediments (n=14) Media±SD | Runoff (n=14) Media±SD | Enrichment ratio (sediments) |
|------------------|----------------------------|-----------------------------------|---------------------------------|---|------------------------------|
| Total (TOC) | $120(g kg^{-1})$ | | $116\pm30(g \text{ kg}^{-1})$ | | 0.97 |
| Oxidizable (OOC) | $32(g kg^{-1})$ | | $63\pm11(g kg^{-1})$ | | 1.97 |
| Adsorbed (AOC) | $85(g kg^{-1})$ | | $52\pm12(g kg^{-1})$ | | 0.61 |
| Labile (LOC)) | $3(g kg^{-1})$ | | $1.0\pm0.7(g \text{ kg}^{-1})$ | | 0.33 |
| Disolved (DOC) | $188(g kg^{-1})$ | | | $12\pm10 \text{ (mg L}^{-1}\text{)}$ | 0.06 |
| pН | 6.0 | 6.87 ± 0.02 | 5.9 ± 0.2 | 6.71 ± 0.08 | |
| EC | $0.63 (dS m^{-1})$ | $0.76\pm0.08 \text{ (dS m}^{-1})$ | $0.71\pm0.09(dS m^{-1})$ | $0.96 \pm 0.10 (dS m^{-1})$ | |
| P | $5.4 (\text{mg kg}^{-1})$ | | 13.9 (mg kg ⁻¹) | | 2.57 |
| K | $0.8 (g kg^{-1})$ | $1.2\pm0.4~(\text{mg L}^{-1})$ | $0.9\pm0.2 \text{ (g kg}^{-1})$ | $2.7\pm0.8~(\text{mg L}^{-1})$ | 1.12 |
| Ca | $2.5 (g kg^{-1})$ | $3.4\pm0.8~(\text{mg L}^{-1})$ | $1.0\pm0.7 \text{ (g kg}^{-1})$ | $4.4\pm 1.2 \text{ (mg L}^{-1}\text{)}$ | 0.40 |
| Mg | $1.0 (g kg^{-1})$ | $1.3 \pm 0.4 (\text{mg L}^{-1})$ | $0.3\pm0.1~(g~kg^{-1})$ | $3.4 \pm 0.5 \; (\text{mg L}^{-1})$ | 0.30 |

According to the results and to the "binary composition" sustained by Mizota and van Reeuwijk, 1989, the $Al_p/Al_o=0.45$ ratio suggests that 45% of total active Al is found as "active Al" in the Al-humus complexes while the rest is found as allophane. This is in accordance with the allophane contents of these surface horizons (14%) estimated from the $(Al_o-Al_p)/Si_o$ atomic ratio (Parfitt and Wilson, 1985, Mizota and van Reeuwijk, 1989). Therefore, we can assume that the active colloidal fraction of these soils is dominated by compounds with short range ordination such as allophane and, to a lesser extent, by Al-humus complexes, highly resistant to microbial attack, formed by interaction of the metal with carboxylic functional groups of the organic matter (Schnitzer, 1978).

After monitoring the erosion dynamics in erosion plots, it was found that the runoff generation in these soils is relatively low, with mean values of 13% (86 L m⁻² year⁻¹), in no case exceeding 45%, revealing the high infiltration capacity of the andosols, at least in surface horizons. This gives rise to a loss of soil by sheet erosion, with an

interannual mean value of 9.6 t ha⁻¹ y⁻¹, although losses of up to 317 t ha⁻¹ can occur during some rain events. Figure 1 shows the interannual distribution over the 9 years of the study of rainfall, erosion and runoff.

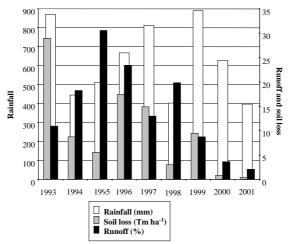


Figure 1. Soil loss, runoff (%) and rainfall. 1993–2001.

Table 2 shows that clay particles are the most eroded ones, although not in a disperse state, but rather in the form of highly stable granular and crumb aggregates in which more than 36% of the sediments are comprised by aggregates smaller than 0.5 mm. Hence, values of the enrichment ratio higher than 1 are only observed for the clayey fraction (ER = 2.02) and for aggregate fractions smaller than 2 mm and especially < 0.5 mm (ER = 2.34). We can, therefore, observe a clear tendency for the smaller aggregates to be eroded more easily.

Table 2. Physical properties of soil surface and sediments

| | Soil surface (0-5 cm) (g kg ⁻¹) | Sediments (n=14) Mean±SD (g kg ⁻¹) | Enrichment ratio |
|-------------------------------|---|--|------------------|
| Particle-size | | | |
| Clay | 190 | 383±39 | 2.02 |
| Silt | 714 | 572 <u>±</u> 47 | 0.80 |
| Sand | 63 | 47±12 | 0.75 |
| Aggregate size (mm) | | | |
| >2.0 | 502 | 268±14 | 0.53 |
| 0.5-2.0 | 350 | 357±21 | 1.02 |
| < 0.5 | 156 | 365±37 | 2.34 |
| Dispersed clay, silt and sand | | 30±8 | |

The TOC contents of sediments oscillates between 86 and 145 g kg⁻¹ (116 ± 30 g kg⁻¹)(Table 1), corresponding to losses of OC by erosion bound to the solid phase ranging between 0.1 and 3.1 g m⁻², depending on the amount of sediments generated in each event, since there does not seem to be any association between the amount of OC lost in sediments and the concentration of TOC they contain. This seems to depend more on the fractions most eroded in each event. If we consider that the erosion rates measured reflect a mean sediment production of 0.91 kg m⁻² year⁻¹, annual losses of OC resulting from erosion and bound to the solid phase are 114.4 g C m⁻² y⁻¹.

The value of the OC enrichment ratio in the sediments is close to 1 reflecting a low selectivity of the erosion process in relation to OC. The concentration of DOC in the runoff is also variable in the different rain events (2-45 mg L⁻¹), corresponding to DOC losses ranging from 0.8 to 18.0 mg m⁻², depending on the runoff generated at each event and its concentration. The mean generation of runoff is 85.8 L m⁻²year¹, corresponding to losses of organic carbon in solution of 1.03 gC m⁻²year⁻¹. When we compare the forms of organic carbon present in the soil surface and in the eroded sediments, these are mainly enriched in the forms of OC that are the least oxidizable (OOC) (ER = 1.97), while the proportion of AOC, LOC and DOC are much smaller (Figure 2).

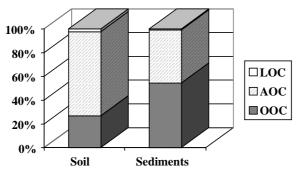


Figure 2. Organic carbon forms in soil surface and in sediments

These results appear to be somewhat contradictory since, if the most eroded fraction is that containing aggregates smaller than 0.5 mm and the AOC forms predominate in this fraction, it would be logical to assume that sediments are rich in AOC. However, they are actually enriched in OOC instead, thus suggesting that aggregates <0.5 mm predominant in sediments with an enrichment ratio of 2.34 do not exactly correspond to aggregates of the same size present in the soil, but rather to fragments of larger aggregates, therefore, with a high OOC contents $(69 \pm 10 \text{ g kg}^{-1})$. This confirms that erosion in these soils seems to start by the breakdown of larger aggregates at the surface due to the impact of raindrops and by smaller fragments (0.1-0.2 mm) being dragged along by the laminar flow (Rodríguez Rodríguez, 2002 a, b).

The total concentration of nutrients (K, Ca, Mg) in runoff is relatively low (10.5 mg L⁻¹) (Table 1) and there is little variation between erosive events. Therefore, nutrient loss in solution is more closely related with the amount of runoff generated in each event. If we consider an annual production of 85.8 L m⁻² of runoff the annual losses of nutrients in solution would reach 0.9 g m⁻² y⁻¹. This affects Ca to the greatest extent (0.38 g m⁻² y⁻¹) followed by Mg (0.29 g m⁻² y⁻¹) or K (0.23 g m⁻² y⁻¹). The pH and EC of the run off water are only slightly higher than those recorded in the surface soils of the plots.

The total concentrations of K, Ca and Mg in the sediments is 2.2 g kg^{-1} and the total loss of elements bound to the solid phase is more closely associated with the production of sediments in each erosive episode than with its concentration. If we consider that the annual production of sediments in the plots is $9.6 \text{ t ha}^{-1}\text{y}^{-1}$ the losses of these elements reach $2.1 \text{ g m}^{-2} \text{ y}^{-1}$. Although the selective erosion of plant nutrients in runoff is a well known phenomena (Sharpley, 1985, Gafur et al., 2003), in sediments we found that they only enrich in P and K in comparison to the soil surface (ER > 1), probably bound to the finest fractions and the smallest aggregates, which are the most erosive.

The concentration of nutrients was lower in the rainwater (Table 1) than in runoff (5.9 mg L⁻¹) although if we consider an interannual rainfall of 625 L m⁻², this corresponds to an input of 3.7 g m⁻² y⁻¹ mainly of Ca (2.1 g m⁻² y⁻¹) and to a lesser extent of Mg and K, which is sufficient to compensate for losses of these nutrients produced by erosion.

Conclusions

The results obtained reflect important losses in OC by erosion (114.4 g C m⁻² y⁻¹) mainly bound to the solid phase, since losses of DOC in runoff waters are very small (1.03 g C m⁻² y⁻¹). Although complexed forms of OC in the form of allophone-Al-humus and Al-humus complexes (AOC) predominate in the soil (71% of the TOC), in the sediments slowly oxidizable and non complexed OC predominate (OOC) (54%). These results demonstrate that a substantial proportion of the sediments are made up of small aggregates (<0.5 mm) that come from fragments that have broken off from the larger aggregates because of the impact of raindrops. These aggregates, which are larger than 2 mm predominate in the soil surface and contain in their interior a high content of occluded OOC. The physical encapsulation of AOC in the larger aggregates and the chemical stabilization of AOC by allophone-Alhumus and Al-humus complexes in the smaller aggregates seem to be the main mechanisms for OC accumulation in these types of andosols. The fact that the more labile and, theoretically, the more mineralizable forms (OOC) comprise only a small proportion of eroded OC, lead us to consider that the mineralization of OC mobilized by sheet erosion is an important source of atmospheric CO₂.

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