Runoff losses of dissolved carbon and nitrogen in mountain Mediterranean agro- and forest ecosystems

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Abstract
The objective of this research was to estimate the dissolved carbon and nitrogen loads lost by runoff from soils under agricultural and forest land uses, in a Mediterranean mountain basin in Catalonia. Twelve Gerlach boxes and sixteen 0-tension lysimeters were installed under forest, agricultural and pasture land uses, and 172 water samples were analysed for total dissolved carbon and mineral nitrogen ($N\text{-}NO_3^-$), from October 2007 to December 2008. Total C losses were between 10 and 200 kg/ha/year. Most of them through subsurface runoff, since surface runoff coefficients are very low in these soils (less than 0.5 %). Nitrogen losses were lower, between one to two orders of magnitude. No differences were observed depending on land use cover, but when considering single rainfall events, *Pinus nigra* forest have more C losses than the rest. Pastures and crops are the land uses that export more N by surface and subsurface runoff respectively in some single events. The results suggest that OM with a low degree of polymerisation is responsible for OM mobility. According to these results, the control of runoff volume by appropriate management practices is one of the key factors determining the C and N loads from these environments.

Key Words
Dissolved carbon, $N\text{-}NO_3^-$, surface runoff, subsurface runoff, Mediterranean soils, mountain soils.

Introduction
Runoff is one of the sources of non-point diffuse pollution in agricultural soils. Losses of nutrients and carbon not only affect the fertility of soils, but also the quality of water resources. They increase the risk of eutrophication of downstream waters and nitrate pollution of aquifers, among other effects (Govers 1991; Martin *et al.* 1998). These processes have to be studied through a multiscale approach, from field to watershed, in order to see the pathways of the elements and their relation with the biotic components, as well as with the different compartments of water storage in the watershed.

Strong land use changes are affecting large agricultural areas in Europe in the last century, due to set-aside policies and to socio-economical changes that have brought about the abandonment of agricultural land. The transformation to pastures or forest has changed the water balance components, mainly by changes in soil characteristics. The Catalan Pre-Pyrenees are one of these regions where the soil water regime is determined by the land use (Loaiza-Usuga and Poch 2009) and where the effects of the land use on the hydrochemistry of the watersheds has been shown (Orozco *et al.* 2006). The objective of this study is to assess the contribution of dissolved nitrogen and carbon lost through runoff waters from soils under different land uses (crops, forest, pastures), both surface and subsurface, at field scale.

Methods
The physical environment
The Ribera Salada drainage basin is located in the Catalan Pre-Pyrenees (NE of Iberian Peninsula). It drains an area of 222.5 km^2, and has an altitude between 2385 m and 420 m. Mean annual precipitation is around 800 mm, with a seasonal minimum in winter (160 mm). Average annual potential evapotranspiration (estimated using the Thornthwaite equation) is around 700 mm. The soil temperature and the water regimes (Soil Survey Staff 2006) are mesic and ustic respectively, changing to udic in the highest areas. The substrate consists of folded limestones Triasic to Eocene age, marls and some evaporites (gypsum and salts) at the headwaters, and an extense Eocene-Oligocene molassic sequence in the central and lower parts of the basin. Calcareous sediments of both structures are partly karstified. The soils are shallow, calcareous and stony and are characterized by a low water-holding capacity and moderate to high infiltration rates (Orozco *et al.* 2006). Decarbonated soils occur in the highest parts of the basin. Land use is mainly pine and oak forest (60%), followed by agricultural areas (24.5%).

Experimental design
Six locations were monitored (Table 1), in order to collect surface and subsurface runoff. Subsurface flows were measured by tension zero lysimeters per site (rectangular metal plate 20 x 30 cm inserted horizontally into the soil) at depths ranging from 20 to 50 cm, depending on the soil type. The collection area for the subsurface runoff was 0.059 m^2. Surface runoff was measured by means of modified Gerlach boxes with widths of 50 and 100 cm, collecting runoff from areas ranging between 9.4 and 48 m^2 and delimited by galvanized plates when possible. Slopes of these areas ranged between 22 and 45%. Hourly rainfall was obtained from the *Xarxa Agrometeorològica de Catalunya* meteorological station of Lladurs for La Torra, Altés, Canalda and Cogulers locations; and Baró meteorological station (*Centre Tecnològic Forestal de Catalunya*) for Ramonet locations. The period of monitoring was from October 2007 to December 2008.

Table 1. Location and characteristics of the experimental plots

Location	Land use	Soil (SSS 2006)	Gerlach boxes	Lysimeters
La Torra	Oak forest (*Quercus ilex*)	Typic Calciustept	2	2
Ramonet	Pasture (*Onobrychis viciifolia*)	Typic Calciudoll	2	2
	Crop (potatoes, *Solanum tuberosum*)	Typic Calciudoll	2	2
	Pine forest (*Pinus sylvestris*, *Pinus uncinata*)	Typic Calciudoll	2	2
Prat	Pasture (poliphytic)	Typic Haplustept	2	2
Altés	Pine forest (*Pinus nigra*)	Typic Udorthent	2	-
Cogulers	Pine forest (*Pinus sylvestris*, shaddy)	Typic Ustorthent	-	2
	Pine forest (*Pinus sylvestris,* sunny)	Typic Calciustept	-	2
Canalda	Brook forest (*Pinus sylvestris, Buxus sempervirens ,Quercus ilex*)	Typic Ustifluvent	-	2

Sampling and analyses
Runoff and subsurface water volume was measured in the field and water samples were collected fortnightly or after every rainfall event. They were kept frozen until the moment of the analysis. Mineral nitrogen was determined using the Merckoquant® test strips and a Nitracheck® reflectometer. Total dissolved carbon was measured with a LECO total analyser. Ninenty two samples of surface runoff and eighty samples of subsurface runoff, from ten rainfall periods from October 2007 to December 2008, were analysed. The total rainfall in this period was around 1000 mm. In order to obtain the nitrogen and carbon exported the results were referred to the collection area. Runoff coefficients and infiltration water percentages were calculated for each event.

Statistical analyses consisted in studying differences of the variables depending on land use: *Pinus nigra*, *P. sylvestris, Quercus ilex*, pastures and crops, through ANOVA. The analyses considered both the whole monitoring period and also individual rainfall events.

Results and discussion
The results corresponding to the whole period of analysis are reported in Tables 2 and 3. No significant differences are found between treatments, except for higher total dissolved carbon in surface runoff under *Q. ilex* (P<0.01) and higher nitrogen as nitrate in subsurface runoff under crops (P<0.001). Fertiliser leaching is probably the reason for the latter. The total carbon losses are between 10 and 200 kg C/ha/year, similar to those found by Jacinthe and Lal (2001), who estimate losses due to erosion in agricultural watersheds ranging from 5 to 100 kg C/ha/year. Measurements in the Venezuelan Andes by Bellanger *et al.* (2004) show C losses in eroded soil between 2.1 and 270 kg C/ha/year under different crops. Estimates of the range of dissolved organic carbon (DOC) loss from non-cultivated temperate ecosystems range from 1 to 146 kg C/ha/year (Hope *et al.* 1994).

The main C and N losses are due to subsurface runoff, since runoff is very low (runoff coefficients < 0.5%). Average total carbon concentrations are higher in surface (0.161 g/L) than in subsurface runoff (0.089 g/L), but the higher volume of subsurface flow substantially increases the carbon loss by percolation. In the case of mineral nitrogen, there are no significant differences in concentration, but losses are two orders of magnitude higher in subsurface flow, due to the higher runoff volume. Considering that the origin of dissolved carbon is mainly organic (the baseline of inorganic carbon is constant for all sites due to the same substrate), higher losses of C would correspond to OM with a low degree of polimerisation, rich in fulvic acids. It is surprising the large difference in the composition of water in the oak forest (*Quercus ilex*), where the subsurface flow contains much more nitrogen than surface runoff. This fact points to the difficulty of

Table 2. **Amount of surface runoff and C and N loads depending on land use. Estimations for a measurement period of 381 days. Values followed by the same letter are not different with a significance level of *P*<0.01.**

Land use	$N\text{-}NO_3^-$ (g/ha)	Total Dissolved Carbon (kg/ha)	$N\text{-}NO_3^-$ (mg/L)	Total Dissolved Carbon (g/L)	Runoff (mm)	Runoff coefficient (%)
Pinus nigra	37.6	3.02	10.33	0.150b	1.08	0.10
Pinus sylvestris	18.7	0.98	15.72	0.085b	1.49	0.16
Quercus ilex	25.6	12.90	25.91	0.385a	3.37	0.33
Pastures	53.5	2.68	9.29	0.170b	1.95	0.19
Crops	48.6	3.75	17.03	0.084b	2.41	0.26

Table 3. Amount of subsurface runoff and C and N loads depending on land use. Estimations for a measurement period of 349 days. Values followed by the same letter are not different with a significance level of *P*<0.001.

Land use	$N\text{-}NO_3^-$ (g/ha)	Total Dissolved Carbon (kg/ha)	$N\text{-}NO_3^-$ (mg/L)	Total Dissolved Carbon (g/L)	Percolation (mm)	Percolation coefficient (%)
Pinus sylvestris	3583	156.27	12.85b	0.104	41.33	4.45
Quercus ilex	2100	17.28	23.11b	0.063	25.63	2.81
Pastures	817	70.79	7.35b	0.057	33.14	3.78
Crops	7510	196.33	142.17a	0.111	38.23	4.26

humification of organic matter from oak leaf residues, indicated by the higher total carbon values in surface waters under this treatment, which circulate through the O horizons. This environment has a more degraded soil and has a more xerophytic character than the coniferous forests, and thus, the incomplete humification of plant residues.

When considering individual events, significant differences ($P<0.05$) were found between land uses for the variables shown in Figure 1. Nitrogen losses through subsurface flow are higher for crops in two rainfall events, which indicate the effect of the external source of mineral N (fertilisation), at a given moment of the crop management. In surface runoff, the losses are higher in pastures only in one event, probably linked to the availability of animal manure on the soil surface. Regarding carbon losses, they are higher in *Pinus nigra* in most of the events. No significant differences were found in runoff volumes, therefore these losses are due to a higher concentration of dissolved organic carbon when water flows on their surface. These are shallow and humid entisols on limestones, with a well developed O horizon that may favour, more than under other types of cover, the formation of humic compounds that can be incorporated as dissolved fractions in runoff water.

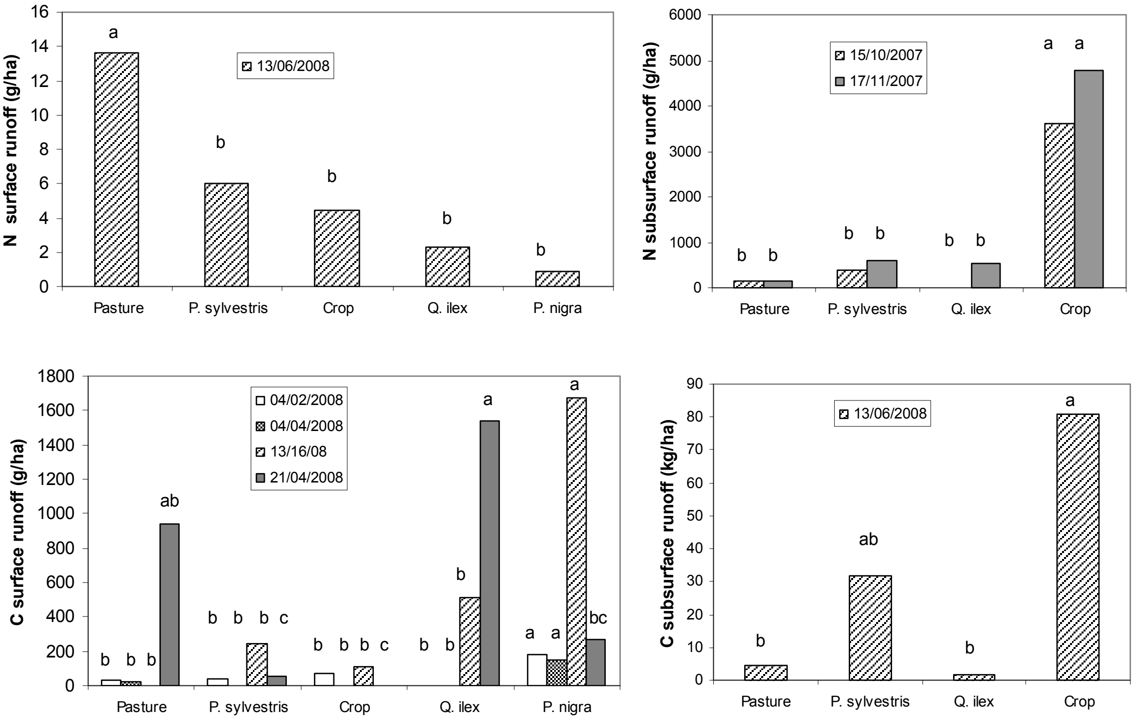

Figure 1. Variables and dates with significant differences depending on land use, in subsurface and surface runoff. Bars with the same letters indicate no differences (α=0.05) between land uses for the same date according to Duncan Multiple Range Test.

Conclusions

Carbon losses through runoff are normal values for a natural system, and much higher than those of nitrogen. This is probably due to OM with a low degree of humification, which is more mobile, although no analyses of OM composition are provided. The losses are much higher (one to two orders of magnitude) in subsurface flow than in surface flow, maily due to high infiltration rates.

According to the results, the most effective management techniques to minimize these losses should try to minimize runoff volumes and also to favour a better humification of the organic matter, that could be attained by a rational fertilisation and forest management techniques that maintain soil quality. This is suggested by the fact that C losses by surface runoff are higher under a *P. nigra* forest in some single events, and not under crops.

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References

Bellanger B, Huon S, Velasquez F, Vallès V, Girardin C, Mariotti A (2004) Monitoring soil organic carbon erosion with $\delta^{13}C$ and $\delta^{15}N$ on experimental field plots in the Venezuelan Andes. *Catena* **58,** 125-150.

Govers G (1991) Time-dependency of runoff velocity and erosion: the effect of the initial soil moisture profile. *Earth Surface Processes and Landforms* **16**, 713-729.

Hope D, Billet MF, Cresser MS (1994) A review of the export of carbon in river water: fluxes and processes. *Environmental Pollution* **84**, 301-324.

Jacinthe ,PA Lal R 2001 A mass balance approach to assess carbon dioxide evolution during erosional events. *Land Degradation and Development* **12**, 329-339.

Loaiza–Usuga JC, Poch RM (2009) Evaluation of soil water balance components under different land uses in a mediterranean mountain catchment (Catalan Pre-Pyrenees, NE Spain). *Zeitschrift für Geomorphologie* **53,** 519-537.

Martín F, López P, Calera A (1998) 'Agua y Agronomía'. (Universidad Castilla-La Mancha: Spain).

Orozco M, Poch RM, Batalla RJ, Balasch JC (2006) Hydrochemical balance of a Mediterranean mountain basin in relation to land uses (The Ribera Salada, Catalan Pre-Pyrenees, NE Spain) *Zeitschrift für Geomorphologie* **50,** 77-94.

Soil Survey Staff (2006) 'Keys to Soil Taxonomy. 10th Ed'. (Soil Conservation Service-USDA: Madison).