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Characterization of water dissolved organic matter under woody vegetation patches in semi-arid Mediterranean soils

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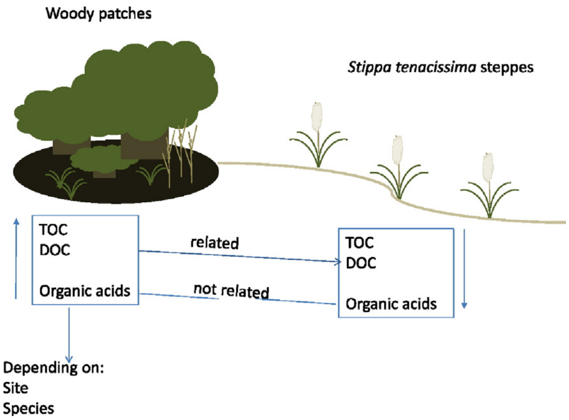
HIGHLIGHTS

- Vegetation patches have different ability to recruit new individuals.
- Dissolved organic matter plays an important role and is analyzed by UV–Vis and HPLC.
- Dissolved organic matter quality is influenced by soil, climatic and biotic factors.
- *E. fragilis* patches are the richest in organic matter.
- *R. lycioides* patches accumulate fumaric acid and are the most abundant in the area.

GRAPHICAL ABSTRACT



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ABSTRACT

Woody patches in semiarid environments favor the establishment of other plants. Facilitation may be favored by an increase in soil fertility. Dissolved organic matter (DOM), is the most active fraction of soil organic matter and may contain compounds affecting plant establishment, as allelochemicals, hormone-like substances and metal carriers. However, information on DOM contents and composition in these environments is scarce. In this paper, we study the impact of woody patches on DOM in *Stipa tenacissima* L. steppes and discuss its implications for community dynamics. DOM under patch- and inter-patch areas, was analyzed for elemental composition, UV–Vis indices and organic acid content. Element concentration and composition in DOM, and organic acid concentration were similar in patch- and inter-patch areas. Yet, soils under patches were richer in DOC, aromatic species and organic acids (particularly fumaric acid) than soils in inter-patch areas. Dominant species affected organic matter concentration and quality in complex ways. Thus, patches dominated by *Ephedra fragilis* showed higher concentrations of TOC and aromatics than those dominated by other species. *Rhamnus lycioides* patches showed the highest accumulation of fumaric acid, which may contribute to its successful recruitment rate and expansion in the area. Our results show substantial differences in the amount and composition of DOM and specific compounds affecting soil functionality and plant dynamics. Further studies on the effects of such changes on seedling performance are needed to increase our understanding of plant–plant interactions in semiarid environments.

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1. Introduction

In arid and semi-arid drylands, woody vegetation often forms discrete patches amid a matrix of herbaceous vegetation and bare soil (Aguiar and Sala, 1999; Ludwig and Tongway, 1995). Patch-forming species frequently act as keystone species, as they strongly affect community composition and ecosystem functioning (López and Moro, 1997; Maestre and Cortina, 2004; Maestre et al., 2009). Soils under patches are commonly richer in organic matter than soils in interpatch areas. Improved soil fertility under woody patches may reduce soil erosion and facilitate the recruitment of other plant species, increasing patch area and expanding its influence (Castro et al., 2004; Vasquez-Mendez et al., 2010; Amat et al., 2015). However, despite the key role of woody patches in drylands, and the accumulation of SOM underneath them, our knowledge on its composition and properties, and its role in plant–plant interactions is still scarce.

Soil organic matter (SOM) is a complex mixture of organic molecules with different structural and functional characteristics. Size, composition and structure of the organic components may vary greatly depending on soil origin and age (Chen et al., 2002). The most active and mobile fraction of SOM is dissolved organic matter (DOM; Corvasce et al., 2006) that consist of complex mixtures of organic compounds. (Zsolnay, 1996). DOM influences soil fertility, through mineral weathering, metal transport and biological activity (Chantigny, 2003), and may play an important role on patch dynamics in arid and semiarid drylands. For example, organic acids represent 1–3% of DOM mass, yet they are particularly active (van Hees et al., 1999). They affect soil pH and enzymatic activity, and play a key role in nutrient uptake, soil formation and ecological interactions (Vranova et al., 2013). Aliphatic and phenolic low molecular acids influence soil fertility and plant growth (Pizzeghello et al., 2006), particularly in calcareous soils, where Ca excess alters metabolic processes, and must be neutralized by precipitation (López-Bucio et al., 2000). Patch-forming species differ in their ability to facilitate seedling establishment. These differences may relate to their capacity to modify soil conditions, and particularly to differences in DOM production and composition.

In this study, we characterize DOM in open areas, and under woody vegetation patches in a semi-arid steppe. Woody patches are dominated by species that differ in their recruitment and expansion ability. We explore DOM properties affecting soil fertility and ecological interactions. Semi-arid steppes are particularly suitable to develop this type of studies because (i) vegetation cover is discontinuous, promoting a strong interaction between vascular plants and the soil underneath them, (ii) woody patches are key components of these steppes, affecting ecosystem and landscape dynamics, and (iii) semi-arid steppes cover large areas and are particularly prone to desertification.

2. Materials and methods

The soil underneath forty-two woody patches was sampled together with the corresponding 42 inter-patch areas in four *Stipa tenacissima* L. steppes of Alicante (Aigües, Campello, Orihuela and Tibi), in southeast Spain (from 678,032 E, 4,242,106 N to 731,450 E, 4,267,575 N) (Fig. 1). Patches are mono and pluri-specific assemblages of resprouting shrubs as *Pistacia lentiscus* L., *Quercus coccifera* L., *Ephedra fragilis* Desf., *Juniperus oxycedrus* L. and *Rhamnus lycioides* L. (Amat, 2015; Maestre and Cortina, 2005).

Interpatch soil samples were taken at a minimum distance of 2 m from the edge of any patch to avoid patch influence as much as possible. Four subsamples of 5 × 5 × 5 cm were collected, from each patch or interpatch area and mixed in a plastic bag for subsequent analysis. Soils are classified as Calciorthids and Torriorthents (Soil Taxonomy, 1994). Bedrock is calcite in Aigües, Campello and Tibi, and dolomite mixed with calcite in Orihuela. Site was also characterized by climatic

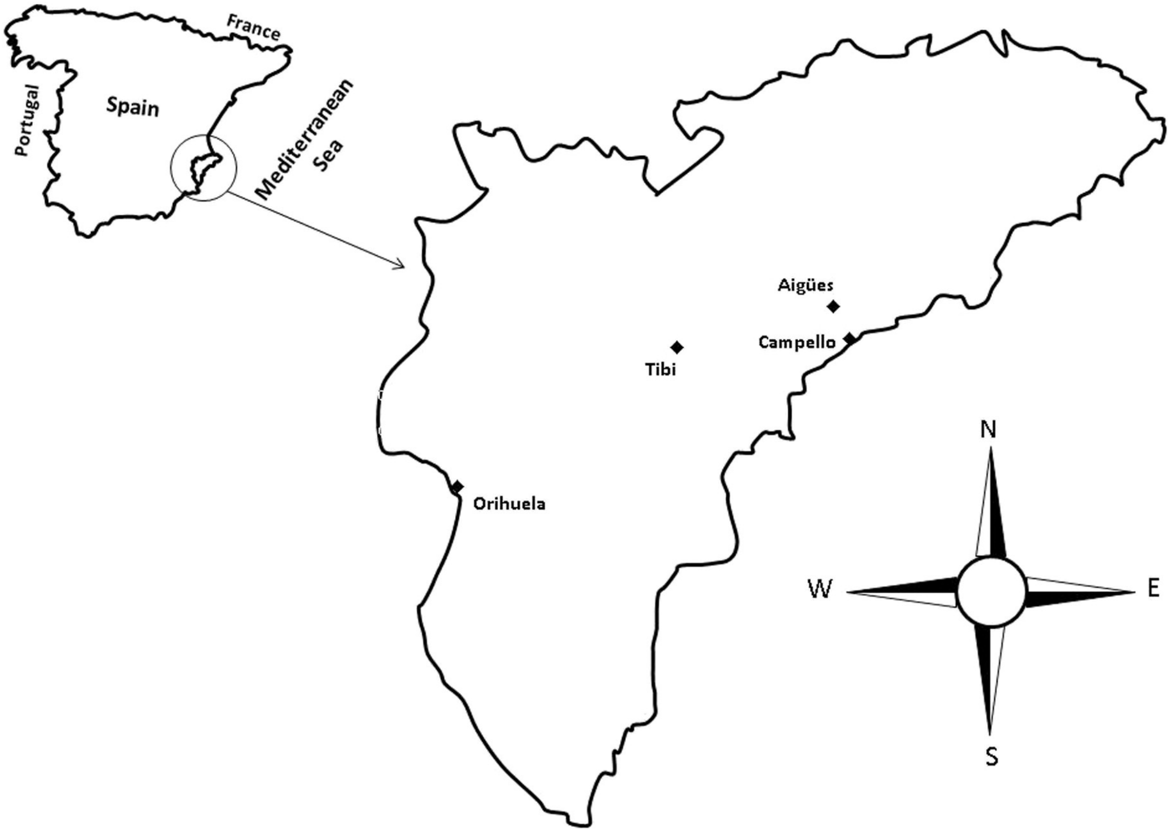

Fig. 1. Location of the sampling areas.

Table 1
Mean values of C concentration in soil OM fractions of patch and interpatch areas. Different letters indicate statistically significant differences between soil types ($p < 0.001$).

	Patch	Interpatch
TOC (C g soil kg^{-1})	56a	28b
DOC (C g soil kg^{-1})	0.18a	0.11b
DOC/TOC (C g C kg^{-1})	0.40a	0.52a

data (annual and monthly average rainfall, and annual and monthly average, maximum and minimum temperature), altitude and location (UTMx and UTMy coordinates). Patches were characterized in terms of their surface area, maximum height, aspect and the composition of patch-forming large resprouting shrubs (Amat et al., 2015).

Total organic carbon (TOC) was measured as oxidable C, and total N content by semi-micro-Kjeldahl distillation (Tecator Kjeltec Auto 1030 analyzer, Hogana, Sweden). Dissolved organic carbon (DOC) was obtained by shaking 10 g of soil with deionized water (100 mL), centrifugation at 4000 rpm for 10 min, and filtration through 0.45 μm cellulose nitrate filters (Gigliotti et al., 2002). Fifty milliliters of the solution containing DOC were freeze-dried for elemental analysis. The remaining was used for UV–Vis analysis. Elemental analysis was conducted on a CHNS elemental microanalyzer with Micro detection system TruSpec LECO. UV–Vis analysis was registered between 200 and 800 nm in a 1 cm path-length quartz cell (Jasco UV–Vis spectrophotometer). Several absorbance relationships were calculated: E2/E3 (ratio between the absorption at 250 nm and absorption at 365 nm), E4/E6 (ratio between the absorption at 465 nm and absorption at 665 nm), the slope of the spectrum in the 275–295 nm and 350–400 nm regions (SR index), $SUVA_{254}$, $SUVA_{280}$ (the absorbance at 254 nm or 280 nm divided by the concentration of C in the sample in mg L^{-1}). The quotients E280/E472, E280/E664, E472/E664 (i.e. the quotients between the absorption at 280, 472, 664) represent molecular relationships between low (E280); medium (E472) and high (E664) degree of humification, (Purmalis and Klavins, 2013). Finally, Δlogk defined as the difference between the logarithms of the absorbances at 400 and 600 nm. Organic acids were determined in 1:4 (w/v) soil/water extracts. Soil water suspensions were stirred for 4 h at 20 °C and centrifuged at 15,000 *g* for 5 min according to Mimmo et al. (2008). The supernatant was collected and frozen at −20 °C until further analysis. Low molecular weight organic acids were separated by reversed-phase high performance liquid chromatography (HPLC) using a C18 column at 30 °C, in isocratic elution with NaH_2PO_4 (20 mM) as carrier solution at a flow rate of 0.5 mL min^{-1} (Ding et al., 2006). Organic acids were detected at 210 nm using a photodiode array UV—Vis detector model SPD-M6A. Standard acids were prepared as individual stock solutions, using Sigma™ free acids, and then combined to give diluted reference standards. Organic acids were identified by comparing retention times of unknowns to pure organic acids, UV–Vis spectra and by standard addition. Although soil pH was always above 7, and organic acids were in their deprotonated form, we will refer to them as "organic acids" for simplicity.

We used one-way analysis of variance for a fixed factor with 4 levels to study the effect of site on organic matter characteristics (TOC, DOC and organic acids content) for interpatch soils. Finally, we used correlation analysis to relate OM properties between them and with climatic variables. Statistical analyses were performed using the SPSS™ and Unscramble™ software (SPSS for Windows, Version 21.0SPSS Inc, Chicago, IL; UNSCRAMBLE (Camo Software).

3. Results

3.1. Organic carbon concentration

TOC values ranged between 8 C g soil kg^{-1} and 130 C g soil kg^{-1}, most soils being below 60 C g soil kg^{-1}. TOC content under woody patches almost doubled TOC content in interpatch areas (Table 1). The amount of DOC ranged between 0.04 and 0.4 (C g soil kg^{-1}), corresponding to 0.08–1.8 (DOC g TOC kg^{-1}). DOC values were also higher for patch soils than for interpatch soils (Table 1). In contrast, the ratio DOC/TOC did not differ between soils in patches and in inter-patch areas (Table 1).

We found a positive relationship between DOC measured in patch vs. interpatch areas (Fig. 2). Interestingly, the slope of this relationship was well below 1, suggesting that differences between patches and interpatches increased as overall DOC concentration increased.

The relation is valid in soils with a wide range of concentration of C. Soils from Campello contained less TOC and the patches were poorer in species, than soils from other sites ($p < 0.01$). DOC was lower in Aigües and higher in Tibi ($p < 0.01$). Campello soils had the highest relative amount of DOC (DOC/TOC; $p < 0.01$).

The relationship between species richness in a patch and TOC concentration was stronger when considering adjacent interpatch areas than patch areas ($r^2 = 0.1284$, $p < 0.01$); $r^2 = 0.0814$, $p < 0.05$, respectively).

DOC decreased as mean annual rainfall increased (Fig. 3).

TOC concentration underneath patches dominated by different patch species was similar, except for *E. fragilis*. This species showed higher TOC concentration than other patch-forming species (Table 2).

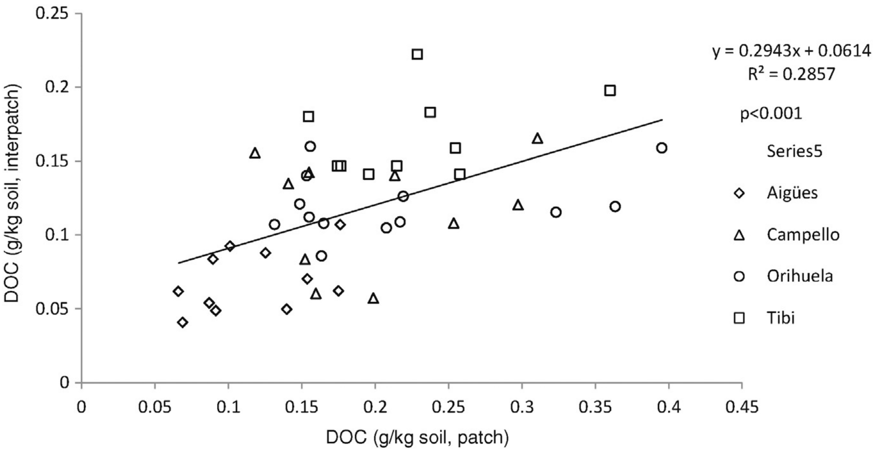

Fig. 2. Relationship between DOC concentrationt in the soil surface under woody patches and interpatch areas. Points correspond to patches/interpatches in each of the four studied semiarid steppes.

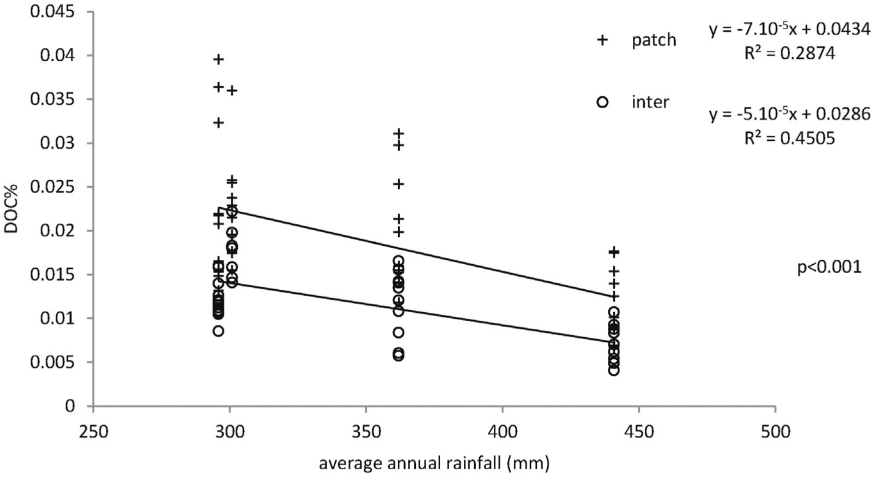

Fig. 3. Changes in soil DOC content with average annual rainfall in patch and interpatch soils in semi-arid steppes. Linear regression models are shown for both soil types.

DOC concentration and the ratio of dissolved vs. total carbon were remarkably similar in all species.

3.2. Organic matter characteristics

3.2.1. Sulfur, carbon and nitrogen concentration of DOM

Elemental analysis showed no traces of S in DOM. The average values of the H/C ratio in patch and interpatch soils were similar: 1.5 and 1.4, respectively. The C/N ratio of SOM and DOM differed widely (17.5 vs. 26.5, respectively), but, no differences were observed in the C/N ratio of SOM and DOM between patch and interpatch soils, despite substantial differences in TOC and DOM content.

3.2.2. UV–Vis indices

UV–Vis spectra of the DOC solutions were similar in all patches (data not shown). They showed the exponential decay with increasing wavelength commonly shown by soil organic matter (He et al., 2014). No significant differences in UV–Vis indices were found between patch and interpatch soils, except for SR, $SUVA_{280}$ and $SUVA_{254}$ (Table 3).

SR values observed correspond to small organic compounds. $SUVA_{254}$ and $SUVA_{280}$ were higher under patches than in interpatch areas (Table 3).

DOC properties measured by UV–Vis, are characteristic of organic molecules of low molecular weight.). E2/E3 values were relatively high in all sites (11-4.6). All soils showed high values of E4/E6, (150-11) which is characteristic of organic material which may contain proteins and carbohydrates. Aigües soils showed the highest values of E4/E6 (50 in patch areas, and 150 in interpatch areas) ($p < 0.01$).

Variability in SOM properties was related to climatic variables such as average temperature and average rainfall (Table 4). The concentration of low molecular weight molecules was directly related to average temperature and inversely related to precipitation.

The effect of the plant species on UV–Vis indices of DOM is shown in Table 5. *E. fragilis* showed higher values of E2/E3 ratio and $SUVA_{254}$ and $SUVA_{280}$ than the other species.

3.2.3. Organic acids

Retention times and UV–Vis spectra of the organic acids used as standards are shown in Appendix I. Four different spectra were obtained for aliphatic acids without conjugated double bounds, aliphatic acids with conjugated double bonds, aromatic acids, and phenols (Appendix I). In all cases, HPLC chromatograms of soils in patches and interpatch areas, showed similar patterns, with three main peaks that are not completely resolved (Fig. 4).

The corresponding UV–Vis spectra (Appendix II) were similar, They may represent a mixture of various organic acids, or molecules with aromatic rings and aliphatic chains.

The peak at 5.9 min was more defined, and was compatible with fumaric acid. Total area, and the area of the three individual peaks were higher in patch soils than in interpatch soils. However, there was no significant relationship between these areas and TOC or DOC. Unlike DOC, we found no significant relationship between organic acid concentration in patches and interpatches, or between organic acid concentration and rainfall, i.e. these substances are mainly concentrated in the patches.

We found substantial differences in fumaric acid concentration between patches dominated by *R. lycioides* and those dominated by other shrub species (Fig. 5).

4. Discussion

4.1. Soil organic matter content

Higher levels of soil organic matter under woody patches than in interpatch areas have been frequently reported in drylands (Cortina and Maestre, 2005; Vasquez-Mendez et al., 2010). The positive

Table 2
Soil organic matter as affected by dominant shrub species in woody patches of *Stipa tenacissima* steppes. Different letters indicate statistically significant differences between species ($p < 0.01$).

	Ephedra fragilis	*Juniperus oxycedrus*	*Pistacia lentiscus*	*Quercus coccifera*	*Rhamnus lycioides*
TOC (C g soil kg^{-1})	95a	60b	46b	52b	52b
DOC (C g soil kg^{-1})	0.21a	0.14a	0.18a	0.16a	0.15a
DOC/TOC (C g C kg^{-1})	3.9a	3.0a	4.9a	3.9a	3.7a

Table 3
UV–Vis indices for DOC in patch and soils in interpatch areas. Different letters indicate significant differences between both soil types ($p < 0.001$).

	Patch	Interpatch
SR	0.9a	1.0b
$SUVA_{280}$ ($L\ mg^{-1}\ m^{-1}$)	2.5a	1.2b
$SUVA_{254}$ ($L\ mg^{-1}\ m^{-1}$)	4.0a	1.4b

relationships found between patch and interpatch TOC and patch and interpatch DOC may reflect similarities in C dynamics at the microsite scale that persist despite the influence of woody patches. In addition, despite that the litter layer is commonly confined to the limits of the projected canopy area (Amat, 2015), and patch effect on the establishment of other plants is spatially limited (Amat et al., 2015), roots of patch-forming shrubs may extend beyond their canopy, contributing to OM accumulation in inter-patch areas. Small organic molecules can be also dispersed into the surrounding soil by climatic events and faunal activity. DOC may be leached in soils with higher organic matter content (Tipping et al., 1999).

In spite of the benefits of organic matter on soil fertility, the abundance of DOC and TOC does not completely explain the recruitment potential of woody patches. Thus, *E. fragilis* differed from other species in terms of TOC content, although these patches were not particularly larger or richer in species than the other patches.

The cause–effect relationships are difficult to establish in this case, and other soil factor affecting TOC accumulation in soils may be involved.

4.2. DOM characteristics

The value of 1.5 for the H/C ratio obtained in our study suggests the balanced presence of aromatic and aliphatic groups in DOM. Humic substances with high aromaticity commonly show H/C ratios close to 1 (Kang et al., 2002), whereas when aliphatic groups predominate, the ratio is close to 2 (He et al., 2014). Aranda and Comino (2014) found similar values of the H/C ratio in reforested soils in southern Spain. Their study included oak and pine forests, and scrublands with *S. tenacissima*.

High C/N ratios in SOM and DOM, are typical from fresh organic residues (Vallejo, 1993; Aerts, 1997). Drought affects biological activity and therefore organic matter humification and mineralization (Krasilnikov et al., 2013). Haney et al. (2012) found that the C/N ratio of DOM better represents microbial activity than the C/N ratio of total organic matter; thus, in soils where C/N values are above 20, most N may be immobilized by microorganisms and no net N mineralization may be expected. Soils show a strong capacity to homogenize SOM properties (decay filter or chemical convergence hypothesis, Melillo et al., 1989; Wickings et al., 2012), which may explain the absence of differences in the element composition of the organic matter in soils in patches and in interpatch areas, and in patches dominated by different species.

These data are in agreement with those obtained by UV–Vis analysis. DOM properties related to molecular size, were characteristic of low altered organic matter. E2/E3 values were relatively high in all sites. High E2/E3 ratios indicate low molecular weights, and characterize organic molecules that can be easily transported (Guo and Chorover, 2003). All soils showed high values of E4/E6, which is characteristic of organic material which may contain proteins and carbohydrates. Likewise, E280/E472 indicates the relationship between low humified and partially humified organic molecules (Purmalis and Klavins, 2013). Aigües soils had the highest values of these indexes. These results are consistent with the values of logΔk that, in all cases, corresponded to scarcely transformed substances (Cunha et al., 2009).

However, results of UV–Vis spectrophotometry, and particularly indicators of aromaticity and humification ($SUVA_{254}$ or $SUVA_{280}$, and SR, respectively), highlighted differences in DOC properties in soils in patches and interpatch areas. Humification index (*SR*) was high both in patch and interpatch areas. Organic molecules with high grade of condensation commonly show SR values under 0.7 (He et al., 2014). However, SR values in patches were significantly lower than in interpatch areas, i.e. higher condensation as a consequence of the higher biological activity in soils in patches. High $SUVA_{254}$ has been associated with high aromaticity (Peuravuori and Pihlaja, 1997). Moreover, He et al. (2014), associated the absorption in the range 268–287 nm to lignin, and specifically, $SUVA_{280}$ to lignin degradation products, such as phenols. Biotic and abiotic processes may be involved in these reactions. Sørensen (1962), found that abiotic decomposition of lignin resulted in brown, water soluble substances, especially when the substrate was dry. Lignin is abundant in wood, incorporated to soil in patches, and these molecules may be present in DOM. The high values of $SUVA_{254}$ and $SUVA_{280}$ in DOM of *E. fragilis* patches with respect to the other species may be explained by the higher incorporation of C and then of lignin to these soils. Phenolics play important roles in soils. They affect SOM evolution (Toberman et al., 2010) and nutrient cycling (Kraus et al., 2004). Yet, these results must be taken with care, because only four patches were dominated by *E. fragilis* in this study, and they were all located in a single site (Aigües). However they suggest a

Table 4
Correlation coefficients between soil organic matter properties and climatic conditions. Significant coefficients in bold ($p < 0.05$). Precipitation and T°C correspond to mean annual precipitation and temperature, respectively. utmx and utmy stand for geographical UTM coordinates. Rock corresponds to rock outcrop cover.

	E2/E3	*E4/E6*	*SR*	*E280/E472*	*E280/E664*	*E472/E664*	*E270/E400*	*Δlogk*	*DOC/TOC*
Interpatch soil									
Altitude	0.058	−0.145	0.246	**−0.435**	0.047	0.030	**−0.504**	−0.168	**−0.597**
Precipitation (mean)	**0.852**	**0.505**	0.051	**0.472**	**0.586**	**0.593**	**0.323**	**0.658**	−0.056
T°C (mean)	**−0.864**	**−0.401**	−0.122	−0.232	**−0.589**	**−0.585**	−0.044	**−0.541**	**0.375**
Utmx	**0.525**	**0.384**	−0.246	**0.570**	**0.352**	**0.362**	**0.481**	**0.505**	**0.302**
Utmy	**0.562**	**0.356**	−0.256	**0.502**	**0.374**	**0.380**	**0.385**	**0.480**	0.180
Rock	**−0.533**	−0.163	−0.012	−0.014	**−0.353**	**−0.343**	0.139	−0.246	**0.407**
Patch soil									
Altitude	0.242	**−0.317**	**0.440**	0.062	−0.180	−0.299	**0.396**	**−0.352**	**−0.332**
Precipitation (mean)	**0.722**	**0.791**	−0.117	0.298	**0.804**	**0.798**	0.070	**0.631**	−0.248
T°C	**−0.889**	**−0.534**	−0.207	−0.319	**−0.648**	**−0.554**	**−0.379**	**−0.309**	**0.503**
utmx	0.274	**0.561**	−0.264	0.091	**0.503**	**0.555**	−0.115	**0.416**	0.003
utmy	**0.346**	**0.477**	−0.148	0.093	**0.456**	**0.475**	0.006	0.285	−0.100
Rock	**−0.544**	−0.080	**−0.318**	−0.142	−0.202	−0.097	−0.412	0.126	**0.430**

Table 5
Mean values for UV–Vis indices of DOM, related to the dominant species in woody patches of *Stipa tenacissima* steppes. Different letters indicate statistically significant differences between soil types ($p < 0.01$).

	Ephedra fragilis	*Juniperus oxycedrus*	*Pistacia lentiscus*	*Quercus coccifera*	*Rhamnus lycioides*
E2/E3	18.8a	5.2b	5.5b	5.6b	5.7b
$SUVA_{254}$($L\ mg^{-1}\ m^{-1}$)	13.1a	3.3b	2.5b	3.2b	2.9b
$SUVA_{280}$ ($L\ mg^{-1}\ m^{-1}$)	3.8a	2.4b	2.2b	2.6b	2.5b

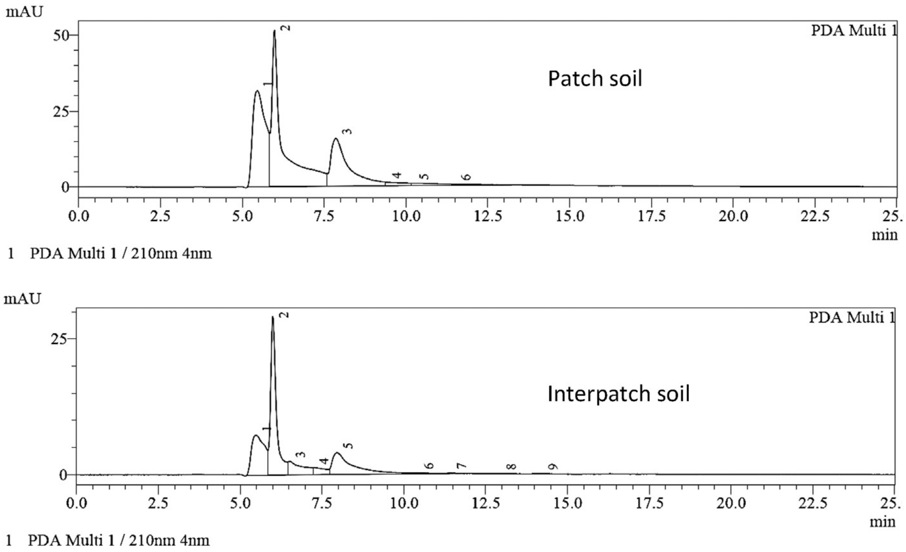

Fig. 4. HPLC chromatogram for soils under woody patches and interpatch areas in *S. tenacissima* steppes.

particular role of this species on C storage in soils that may be worth exploring.

Higher concentrations of fumaric acid found under *R. lycioides* were particularly puzzling. Nambu et al. (2008) reported high concentrations of fumaric acid in soils derived from alkaline parent materials. Fumaric acid is an important plant metabolite and a sub-product of lignin degradation by fungi (Roy and Archibald, 1993). Thus, higher fumaric acid concentration may result from higher production by this species, or the consequence of higher lignin inputs or particular lignin decay conditions. It is worth noting that *R. lycioides* dominates woody patches in most *S. tenacissima* steppes, and it shows relatively high recruitment rates (Amat, 2015). In addition, its litter favors the germination of some key species (Amat, 2015). Fumaric, malonic, and L-malic acids show GA-like activity, which improves forest growth (Pizzeghello et al., 2006).

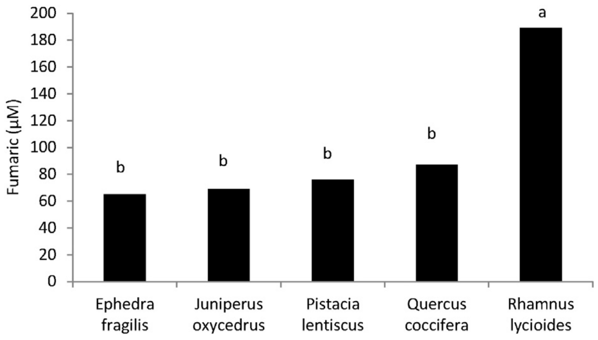

Fig. 5. Fumaric acid concentration in patches with different dominant species. Different letters indicate statistically significant differences between species ($p < 0.05$).

5. Conclusions

TOC and DOM concentrations were substantially higher under woody patches than in adjacent interpatch areas. However, OM properties were similar in both microsites. We found remarkable differences in SOM accumulation and properties under patches dominated by different shrub. These included the higher levels of SOM and lignin-derived compounds under *E. fragilis*, and higher concentration of fumaric acid under *R. lycioides*. The relationship between TOC and DOM concentration and composition and plant dynamics is complex. Yet, our results show that patch-forming species affect SOM in an idiosyncratic way, and changes in SOM accumulation and properties may affect plant–plant interactions and patch potential for facilitation.

Acknowledgments

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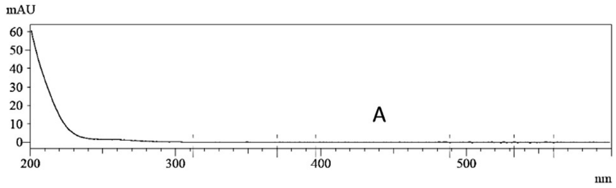
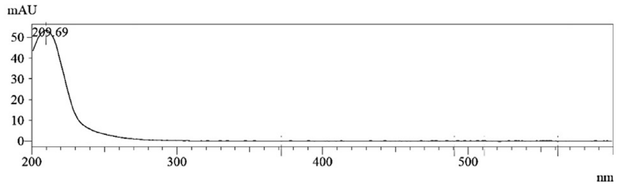
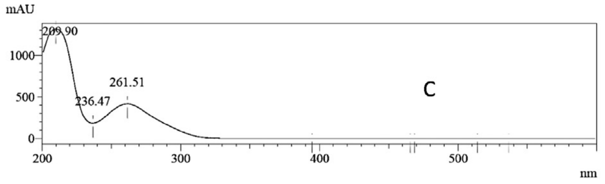
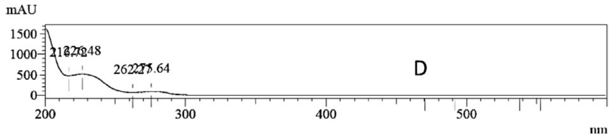
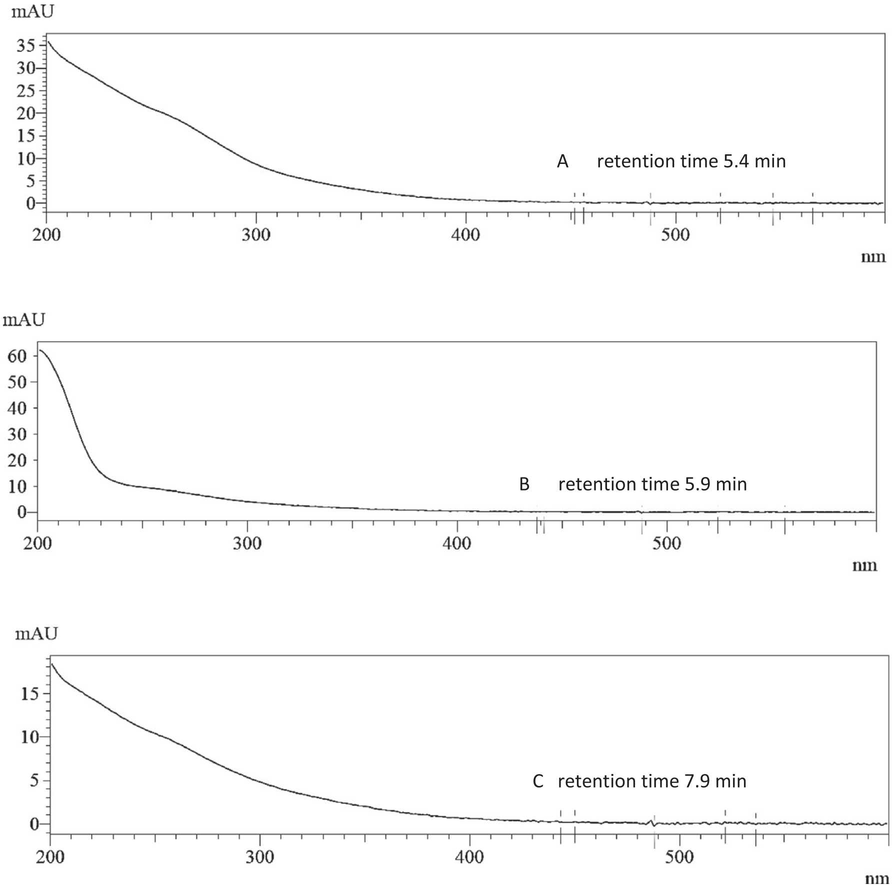
Appendix I. UV–Vis spectra models for several organic acids usually present in soils (standard solutions)

Organic acid	Retention time (min)	UV-Vis spectra
oxalic	5.4	
malic	5.8	
citric	5.9	
malonic	6.5	
fumaric	5.8	
t-aconitic	6.1	
pyruvic	6.9	
α-ketoglutaric	7.1	
maleic	12.8	
gallic	16.6	
phenol	42.7	

Appendix II. UV–Vis spectra for the main peaks in Fig. 4



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