Effects of prescribed burning for pasture reclamation on soil chemical properties in subalpine shrublands of the Central Pyrenees (NE-Spain)

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Graphical Abstract

	Buisán		Tella	
	B0	B12	B0	B12
Soil organic C	-	-	-	-
Total N	-	-	-	-
pH	+	+	=	+
Electrical Conductivity	=	-	=	-
Σ Exchangeable Cations	-	=	=	-
Cation Exchange Capacity	=	-	=	=
Σ Water-extractable cations	=	-	=	-
$N\text{-}NH_4^+$	=	+	=	+
$N\text{-}NO_3^-$	=	=	=	-
Available P	=	-	=	=

Changes in the studied soil properties immediately (B0) and one year (B12) after burning as compared to unburned soils.

Highlights

- Prescribed burning is used to remove shrubs and recover subalpine pastures
- We studied its effect on soil chemical properties immediately and one year after
- Fire had few direct effects on nutrient content but it decreased one year later
- New SOM inputs induced changes in cation exchange capacity and exchangeable cations
- Research further in time is needed to assess the sustainability of this practice

Abstract

The abandonment of the traditional pastoral activities in the subalpine grasslands of the Central Pyrenees (NE-Spain) has resulted in shrub encroachment processes that are dominated by species such as the *Echinospartum horridum*. Therefore, prescribed burning has been recently readopted in this region as a management tool to stop the spread of shrubs and recover grasslands. We aimed to assess the effect that this practice may have on soil chemical properties such as SOC, N, pH, EC, water-extractable and exchangeable cations (Ca^{2+}, Mg^{2+} and K^{+}), cation exchange capacity, inorganic N forms ($N\text{-}NH_4^+$ and $N\text{-}NO_3^-$) and available P. We studied two prescribed burnings conducted at the subalpine level of the Central Pyrenees in the municipalities of Tella-Sin (April, 2015) and Buisán (November, 2015). At each site, the topsoil was sampled in triplicate at soil depths of 0-1, 1-2 and 2-3 cm immediately before (U), immediately after (B0) and one year after (B12) burning, and litter and/or ashes were removed prior to sampling. The results indicate that in the B0 samples, burning significantly reduced the SOC and N contents as well as the exchangeable Ca^{2+} and Mg^{2+} at 0-1 cm, whereas the rest of the studied properties remained virtually unchanged. However, in the B12 samples we detected a decrease of nutrient content that was probably related to leaching and/or erosion processes.

Keywords: soil nutrients, cation exchange capacity, prescribed fire, shrub encroachment, pasturelands

1. Introduction

Pasturelands in the Central Pyrenees (NE-Spain) have traditionally been maintained by livestock grazing and occasional burnings (Nadal-Romero et al., 2018). However, due to rural exodus and the reduction in livestock densities, this activity has suffered from remarkable reductions over the past decades (Komac et al., 2013). The mesophytic pastures that can be found in the Pyrenees below the timberline require shrub management (i.e., grazing, burning or clearcutting) for survival (Halada et al., 2011); therefore, the reduction in grazing activity led to shrub encroachment processes that were dominated by species such as *Echinospartum horridum* (Vahl) Rothm (Komac et al., 2013; Nuche et al., 2018). The development of this species poses a threat to biodiversity and an increase in flammability risks (Caballero et al., 2010) because it forms large and dense monospecific covers (Komac et al., 2011).

A suitable procedure to reduce shrub encroachment in grazing lands can be the use of prescribed burnings (Goldammer & Montiel, 2010), which are defined as the planned use of fire to achieve precise and clearly defined objectives (Fernandes et al., 2013). Nevertheless, fire can affect most soil properties directly by burning and indirectly as a consequence of the new post-fire conditions (Santín & Doerr, 2016). The extents of the effects of fire on soils are highly influenced by environmental conditions; so, prescribed burnings are conducted when the soil and fuel moisture, temperature and topography conditions are favorable, to limit the impact of the burnings on soils and prevent fire from escaping (Vega et al., 2005; Molina, 2009). However, prescribed burnings show contrasting effects on soil properties, as has been recently reviewed in Alcañiz et al. (2018).

Previous works dealing with prescribed burnings of *Echinospartum horridum* in the Central Pyrenees have shown that this practice may severely affect soil organic matter (SOM) content (Armas-Herrera et al., 2016, 2018; Girona-García et al., 2018a, 2018b) in the first few centimeters of the topsoil. The combustion of SOM and vegetation may produce an increase in the available nutrients by either the mineralization of organic compounds or the production of ashes (González-Pérez et al., 2004; Knicker, 2007). Then, the incorporation of ashes into the soil can lead to increases in pH and electrical conductivity (EC) (Certini, 2005). The literature shows that the available concentrations of Ca^{2+}, Mg^{2+}, K^{+} and Na^{+} are commonly increased after prescribed burning (Arocena & Opio, 2003; Lavoie et al., 2010; Alcañiz et al., 2016). Inorganic N forms can also increase after burning from either the contribution of ashes or the mineralisation of soil organic N. For this reason, it is common to detect ammonium gains immediately after burning that will result in nitrates increases via nitrification over time (Gundale et al., 2015; San Emeterio et al., 2016). Fire may also boost the contents of available P in the soil via both the contributions of ashes as well as the mineralization of its organic forms that can occur even at relatively low temperatures (Úbeda et al., 2005; Badía-Villas et al., 2014; Larroulet et al., 2016; García-Oliva et al., 2018). This enrichment in nutrients produced by fire may promote the rapid establishment of herbaceous species. However, another consequence of SOM destruction is the loss of adsorption sites in the soil, thereby reducing the cation exchange capacity (CEC) (Badía & Martí, 2003). In this way, depending on the severity and recurrence of burning, these practices could also lead to nutrient losses (Wanthongchai et al., 2008). Nevertheless, the CEC usually remains unchanged after prescribed burning (Larroulet et al., 2016; Fonseca et al., 2017).

The main objective of our study was to detect the effects of prescribed burning of *Echinospartum horridum* for pasture reclamation on soil chemical properties, focusing on soil nutrient content and availability, at the subalpine level of the Central Pyrenees (NE-Spain). We analyzed the immediate effects of burning on total soil organic C (SOC), total N, pH, EC, water-extractable and exchangeable cations, CEC, inorganic N forms (N-NH_4^+ and NO_3^-) and available P, as well as their changes one year after the fire at soil depths of 0-1, 1-2 and 2-3 cm.

2. Material and methods

2.1. Study sites

The study sites are located in two subalpine areas of the Central Pyrenees (NE-Spain) in the municipalities of Buisán and Tella-Sin (Fig. 1). The Buisán plot is located in an area with a mean slope of 10 % at 1760 m.a.s.l., while the Tella plot was located on a steeper slope of 25 % at 1875 m.a.s.l., and both sites face south. The mean annual temperature in Buisán is 6 ºC and 5 ºC in Tella. The mean annual precipitations are 1500 mm (Buisán) and 1700 mm (Tella). The topsoil Ah horizons (0-5 cm) of both sites are characterized by high SOM contents, high CEC and fine textures; the pH in Buisán is neutral whereas it is moderately acidic in Tella. Soils in Buisán are classified as Eutric Cambisol and those in Tella as Eutric Epileptic Cambisol (IUSS Working Group WRB, 2014), and the complete soil characterization of the study sites can be found in Armas-Herrera et al. (2016) and Girona-García et al. (2018a), respectively. In Buisán and Tella, the bedrock is composed of fine detritic sediments over clayey limestones alternated with Eocene marls. As a consequence of the decreased grazing activity and the prohibition of fire after 1980, these areas have been invaded by *Echinospartum horridum,* which covered more than 75 % of the surface area before the prescribed burning was conducted. Pastures in the study sites that surround the *Echinospartum horridum* shrubs are composed of herbaceous species such as *Bromus erectus* Huds., *Festuca nigrescens* Lam., *Agrostis capillaris* L., *Briza media* L., *Onobrychis pyrenaica* (Sennen) Sirj., *Trifolium pratense* L. and *Trifolium repens* L.

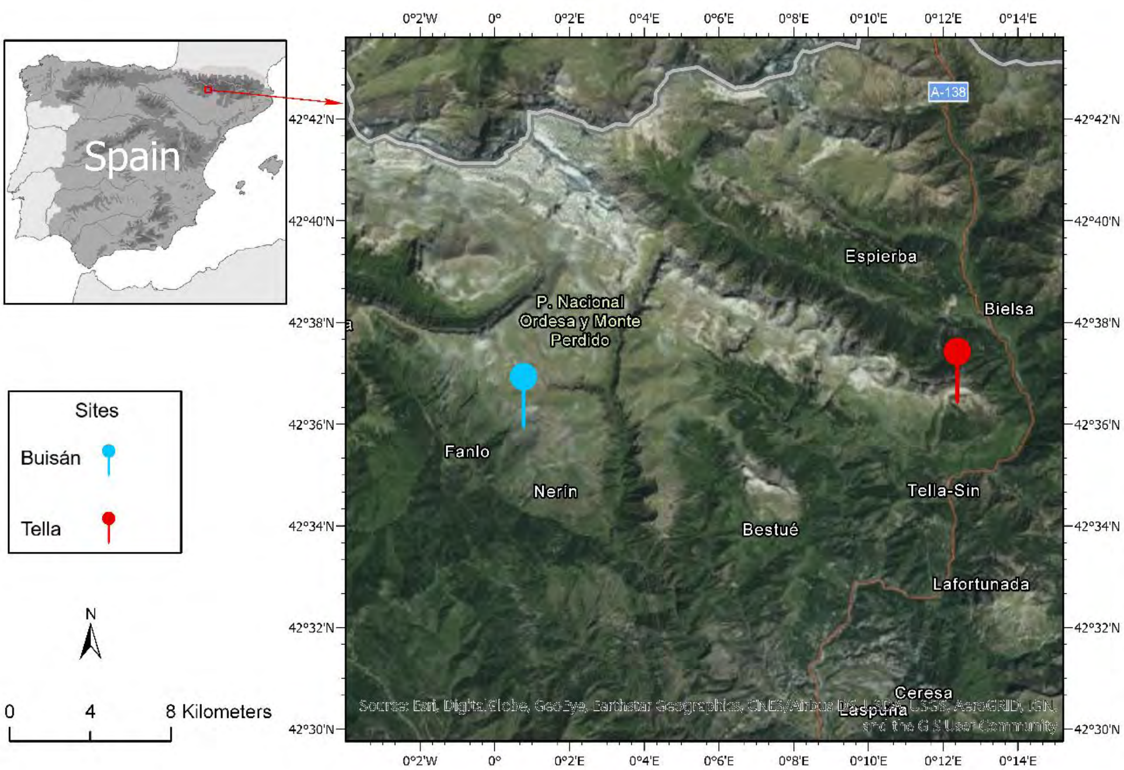

Fig. 1. Location of the Buisán and Tella areas of study

2.2. Prescribed burning characteristics

The prescribed burnings were conducted in April, 2015 (Tella) and November, 2015 (Buisán) by qualified firefighters of the EPRIF (Wildfire Prevention Team) of Huesca and BRIF (Reinforcement Brigades against Wildfires) of Daroca units. The environmental conditions met the established parameters for *Echinospartum horridum* burning: no heavy rainfall took place prior to the burning date, the temperature was between 5 and 15 ºC, the relative humidity of the air was 35-70 %, and the wind speed ranged from 5 to 10 km h^{-1}. An approximation of the temperatures reached during burning at each site was obtained via type-K thermocouples placed in one sampling point at each of the different soil depths (Table 1). The Buisán burning was performed by applying the point source fire technique and creating a grid of spot ignitions that burned from the east to the west flanks that followed a slow progression (0.63 ha h^{-1}). In Tella, a backing fire was ignited to spread against the wind and downslope, and it was faster (2.82 ha h^{-1}) than that in Buisán. At both sites, the aerial biomass of *Echinospartum horridum* was mostly eliminated by burning, resulting in burned trunks, partially charred litter and patches of black and gray ashes.

2.3. Soil sampling

At each burning site, we chose three representative sampling spots that were covered by *Echinospartum horridum* prior to burning. At each of these points, after removing the shrubs and organic layers from an approximate surface area of 0.25 m^2, the topsoil Ah horizon was carefully sampled at depths of 0-1, 1-2 and 2-3 cm (Fig. 2). These samplings were carried out early in the morning immediately before the prescribed burnings were conducted, and unburned (U) samples were collected and considered the control. To detect the immediate effects of fire (B0), we sampled points adjacent to U shortly after burning (<2 h), after removing ashes and charred remains. Additionally, in both study sites, points contiguous to U and B0 were sampled one year later (B12) to assess the short-term evolution of soil properties after burning.

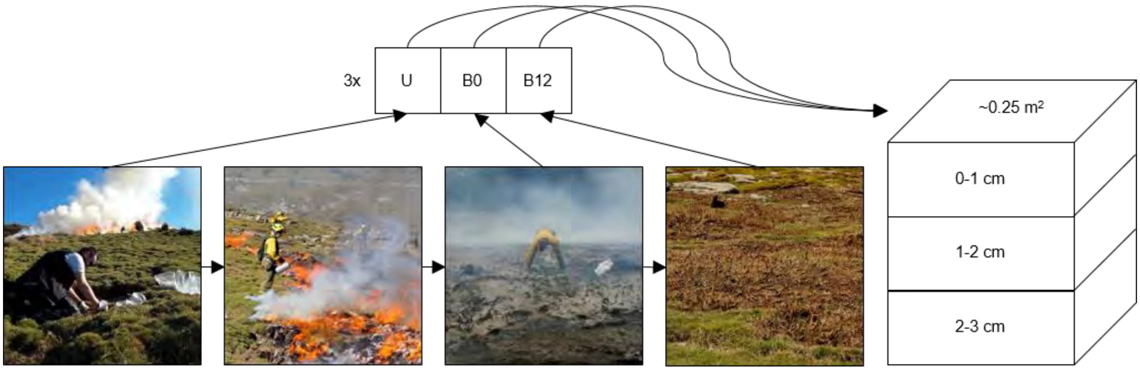

Fig. 2. Sampling design followed in each study site. Unburned (U), immediately after (B0) and one year after burning (B12) samples

2.4. Sample preparation and analysis

The collected soil samples were air-dried at room temperature until constant weight and sieved through a 2 mm mesh sieve. A small portion of each sieved sample was then ground to fine powder, from which total soil organic C (SOC) and total nitrogen (N) were determined using an elemental analyzer (Vario Max CN Macro Elemental Analyser, Germany).

Soil pH was determined from potentiometric measurements of a 1:5 (w v^{-1}) suspension of soil and distilled water and the electrical conductivity (EC) was determined using an electrical conductivity meter in a 1:10 (w v^{-1}) suspension of soil and distilled water (McLean, 1982). Water-extractable (WE) cations (Ca^{2+}, Mg^{2+} and K^{+}) in the soil samples were determined by atomic absorption (Mg^{2+}) and emission (Ca^{2+} and K^{+}) spectrometry (AAS/AAE Spectrometer Varian SpectrAA 110) in 1:10 (w/v) filtered extracts of soil and distilled water after 2 hours of shaking. (Sharpley & Kampath, 1988). Ammoniacal (N-NH_4^+) and nitric (N-NO_3^-) forms of nitrogen were determined according to the methods in

Bremner & Keeney (1965) in 1:5 (w v^{-1}) filtered extracts of soil and 1M KCl after 30 minutes of shaking. The ammonia was separated by steam distillation from an aliquote of the extract and collected in a boric acid solution; then, it was determined by titration using 0.005N H_2SO_4. Then, in the same extract, Devarda alloy was added to reduce the remaining nitrate to ammonium and the same procedure was followed for its distillation and titration. Available P was determined following the method of Olsen & Sommers (1982). P was extracted using 0.5M $NaHCO_3$ buffered at pH 8.5 (1:20 w $v^{-1}$of soil and extractant). Then, an aliquot of each sample was taken and its P content was determined colorimetrically by measuring the concentration of the complex formed by the reaction of phosphate with acid ammonium molybdate, using a UV/visible spectrophotometer (Cole-Parmer, Jenway 6300 Spectrophotometer, United Kingdom). To determine the exchangeable Ca^{2+}, Mg^{2+} and K^+ as well as the cation exchange capacity (CEC), a sequential extraction procedure was followed. Exchangeable cations were determined by atomic spectroscopyin the leachate obtained after three consecutive extractions (total shaking time of 15 minutes) with 1M CH_3COONa buffered at pH 8.2 (ratio 1:20, w v^{-1}). After that, samples were washed three times with ethanol (ratio 1:20, w/v) to remove the excess of the displacing solution without disturbing the adsorbed Na^+. Then, the adsorbed Na^+ was displaced after three consecutive extractions (total shaking time of 15 minutes) with 1M CH_3COONH_4 buffered at pH 7 (ratio 1:20, w v^{-1}), and it was determined by atomic emission spectrometry, considering its value equal to that of the CEC (Bower et al., 1952; Rhoades, 1982).

2.5. Statistical analysis

To identify the differences in the studied soil properties related to the treatments (burning and time), as well as their variations within soil depths, one-way ANOVA tests were used because the interaction between time and depth was significant in most cases. Sampling time (U, B0, B12) was considered a fixed factor, and the data were split by soil depth (0-1, 1-2 and 2-3 cm) to detect the effects of fire and time at each of the studied soil depths.

Furthermore, changes in soil properties among soil depths were tested using soil depth (0-1, 1-2 and 2-3) as a fixed factor, for which the data were split by sampling time (U, B0, B12). These tests were performed using StatView for Windows version 5.0.1 (SAS Institute Inc. Cary, North Carolina, USA). We also conducted a principal component analysis (PCA) to identify further relationships between soil properties, using a Pearson correlation, with XLSTAT software (XLSTAT 2017: Data Analysis and Statistical Solution for Microsoft Excel. Addinsoft, Paris, France).

3. Results and discussion

3.1. Prescribed burning intensity and severity

The fire severity of both prescribed burnings was estimated as low-moderate based on the indicators defined by Parsons et al. (2010). After burning, part of the litter was charred, and a thin layer of black to gray ash could be found with recognizable litter beneath it. The soil structure remained unchanged (Girona-García et al., 2018b), and aggregates were not weakened by the consumption of soil organic matter. The *Echinospartum horridum* shrubs were mostly consumed, and only their main trunks remained. The partial consumption of litter allowed for the transfer of heat into the soil, especially at the Tella site, as can be observed in the temperature analysis shown in Table 1. It is noteworthy that these measurements can only be considered observations, and the fire intensity was approximated because the temperatures were measured only at one point in each site. In the Buisán site, a maximum temperature of 438 ºC was recorded on the soil surface and the temperature remained over 400 ºC for 4.8 minutes. However, little heat transfer into the soil was detected as the temperatures at a depth of 1 cm depth raised to only 31.1 ºC and very slight increases were observed in deeper soil layers. On the other hand, at the Tella burning, temperatures at a depth of 1 cm reached a maximum of 397 ºC and stayed in a range of 300-400 ºC for 3 minutes, whereas at 2 cm, temperatures increased to 121 ºC and stayed at 100-200 ºC for 8.5 minutes. Apart from the fire intensity and soil thermal inertia, the contrasted heat transfer into the soil that was observed during burning could be related to the water content of the soil (Table 1). The high pre-fire soil water content in Buisán (137 ± 3 %) and Tella (100 ± 32 %) could have limited the heating of the soil as heating is normally slowed until after complete water vaporization (Campbell et al., 1995; Badía et al., 2017). According to that, the soil water content in Tella tended to decrease after burning at the three studied soil depths, while in Buisán the water content decreased at only the 0-2 cm depth. From all the gathered data, we can conclude that the Tella burning was characterized by a fast (2.82 ha h^{-1}) and intense fire, whereas the Buisán burning was less intense but the fire residence time was longer (0.63 ha h^{-1}).

Table 1 General characteristics of the prescribed burnings of Buisán and Tella. Temperature analysis comprises the elapsed time since a temperature increase was detected until it stabilised during the cooling stage

Study Site	Buisán				Tella			
Burning Date	November, 2015				April, 2015			
E. horridum cover (%)	75				80			
Estimated Fuel Loads (kg m^{-2}):								
Aerial biomass	9.24				9.86			
Litter (OL + OF)	1.62				1.73			
Burned surface (ha)	3.8				12.5			
Wind speed (km h^{-1})	<8				10-15			
Firing technique	Point Source Fire				Backing Fire			
Mean flame height (m)	1				0.4			
Mean flame length (m)	1.5				1.7			
Burning rate (ha h^{-1})	0.63				2.82			
Temperature analysis	Surface	1 cm	2 cm	3 cm	Surface	1 cm	2 cm	3 cm
Maximum temperature (°C)	438	31.1	18.5	18.5	n.d.	397	121	n.d
Initial temperature (°C)	13.1	9.77	9.60	8.93	n.d.	16.0	16.2	n.d
Final temperature (°C)	27.5	22.2	17.6	18.2	n.d.	25.5	25.7	n.d
Duration (min)								
< 100 °C	17.5	30.0	30.0	30.0	n.d.	33.0	42.0	n.d.
100 - 200 °C	6.00	0.00	0.00	0.00	n.d.	5.00	8.50	n.d.
200 - 300 °C	4.00	0.00	0.00	0.00	n.d.	9.50	0.00	n.d.
300 - 400 °C	2.00	0.00	0.00	0.00	n.d.	3.00	0.00	n.d.
> 400 °C	0.50	0.00	0.00	0.00	n.d.	0.00	0.00	n.d.

Pre-fire soil water content (%, w w^{-1})	n.d.	137	72.8	58.8	n.d.	100	108	84.2
Post-fire soil water content (%, w w^{-1})	n.d.	60.7	55.7	53.9	n.d.	74.5	78.6	59.0

n.d.: not determined

3.2. Effects of fire on soil organic matter

The soil organic C (SOC) and total N (N) contents were very high in the unburned (U) soils of both the Tella and Buisán sites (Fig. 3). At the Buisán site, the SOC concentration was 243 ± 10 g kg^{-1} at 0-1 cm and decreased to 78.8 ± 14.1 g kg^{-1} at 2-3 cm soil depth; and the N content was of 14.6 ± 0.7 g kg^{-1} at 0-1 cm and decreased to 6.15 ± 0.91 g kg^{-1} at 2-3 cm. On the other hand, a higher SOC content was detected at the Tella site, which was 338 ± 59 g kg^{-1} at 0-1 cm and decreased to 216 ± 77 g kg^{-1} at 2-3 cm. The N content at this site was also higher than that in Buisán, which was 20.9 ± 2.9 g kg^{-1} at 0-1 cm and decreased to 15.2 ± 4.6 g kg^{-1} at 2-3 cm.

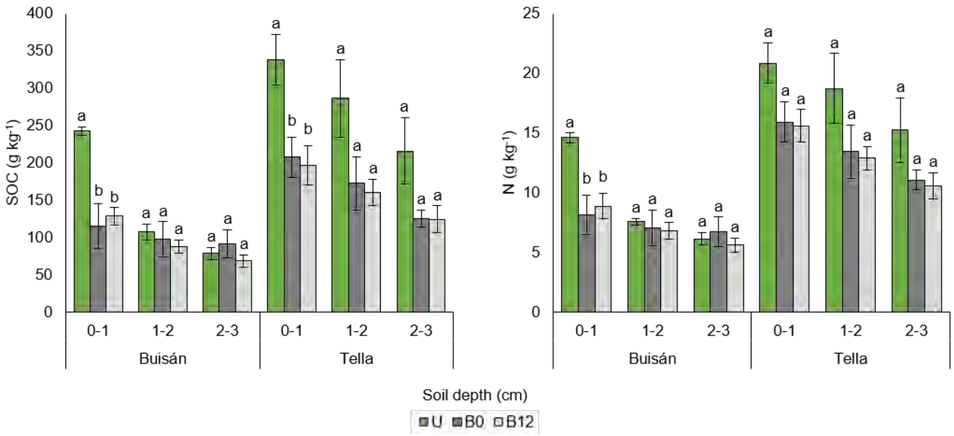

Fig. 3. Soil organic C (SOC) and total N (N) in unburned (U), immediate post-fire samples (B0) and one year after burning samples (B12) for each soil depth and site (mean value ± SE of three field replicates). For same sampling depth, lowercase letters indicate significant differences among sampling times ($p < 0.05$).

At the Tella site, prescribed burning (B0) significantly reduced the SOC at 0-1 cm (-38 %) compared to U and a decreasing trend, that was close to statistical significance was also detected at soil depths of 1-2 cm ($p = 0.0770$) and 2-3 cm ($p = 0.0633$) cm soil depth. The N content also showed a decreasing trend (-24 %) at 0-1 cm that was close to significance ($p = 0.0716$). At the Buisán site, only the first cm of soil was significantly affected, where burning decreased the SOC and N contents in B0 by -52 % and -44 %, respectively. This severe disturbance could be explained by the temperatures reached during prescribed burning, as explained in the previous section, since the combustion of SOM begins when temperatures in the range of 200-250 ºC are reached (Certini, 2005; Santín & Doerr, 2016). Furthermore, the slow spread of fire at the Buisán site indicates a higher fire residence time compared to that of the Tella site, which could explain the greater SOC and N reductions. Fire effects were still detectable at both sites one year after burning (B12) and recovery signs in SOC and N contents were not observed when compared to the contents of the U samples. The lack of short-term changes in SOC and N at the Tella site could be related to the removal of ash and charred material by wind and/or rain after burning. On the other hand, at the Buisán site, ashes mixed with partially charred litter were still observed at B12, suggesting limited incorporation of ash into the soil. Extensive discussions of the effects of prescribed burning on SOC and N at the Buisán and Tella sites can be found in Armas-Herrera et al. (2016, 2018) and Girona-García et al. (2018a).

3.3. Fire effects on soil pH, electrical conductivity and nutrients

Unburned (U) soils at the Buisán site showed pH values between 7.19 ± 0.10 and 7.55 ± 0.12 at 0-1 cm and 2-3 cm, respectively (Fig. 4). In B0, an increase in pH was observed at 0-1 cm (7.59 ± 0.10), and this effect was still present at B12 (7.68 ± 0.07). On the other hand, at the Tella site, soils presented more acidic pH values (average of 4.5 at all studied depths) in U soils than those at the Buisán site, and these values remained unchanged in the B0 samplings indicating that this property was not affected by the fire.

However, at the Tella site, the pH of the B12 samples dramatically increased at all studied soil depths to values between 6.26 and 6.70. These pH increases in acidic topsoils could be related to a series of factors such as the: 1) accumulation of K and Na hydroxides, 2) formation of Mg and Ca carbonates and/or 3) elimination of organic matter acidic groups (Knicker, 2007 and references therein).

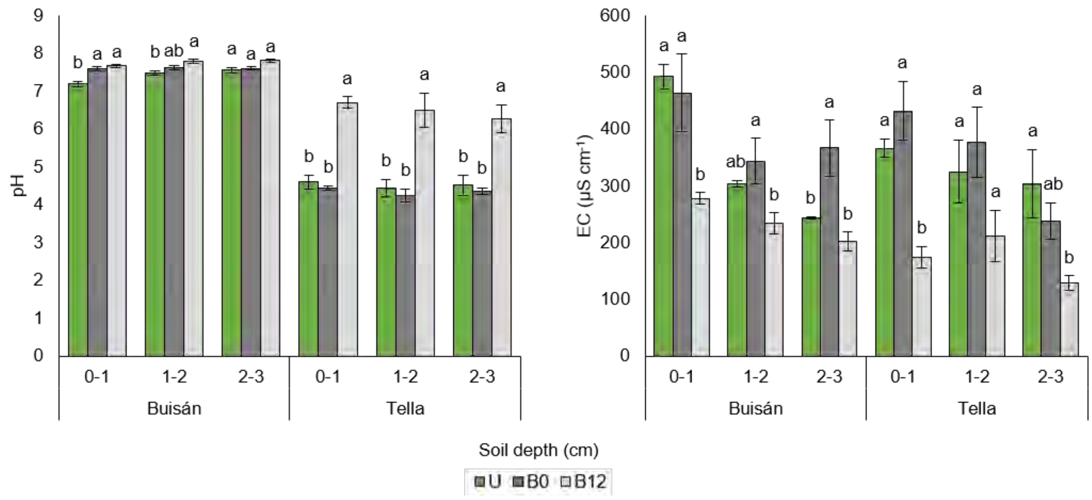

Fig. 4. pH and electrical conductivity (EC) in unburned (U), immediate post-fire samples (B0) and one year after burning samples (B12) for each soil depth and site (mean value ± SE of three field replicates). For same sampling depth, lowercase letters indicate significant differences among sampling times ($p < 0.05$).

A decreasing gradient in electrical conductivity (EC) with depth was detected in the Buisán U samples while in the Tella U samples, no differences were observed among soil depths (Fig. 4). The fire induced no direct changes in EC at either the Buisán or Tella sites although, in B12, the EC significantly decreased in all the studied soil depths in both sites.

In the U soils of Buisán, the content of water-extractable cations (WE-Ca^{2+}, WE-Mg^{2+} and WE-K^{+}) was higher at 0-1 cm than that in the underlying layers (Fig. 5). After burning (B0), no changes were detected in WE-Ca^{2+} and WE-K^{+}, although WE-Mg^{2+} was significantly decreased at 0-1 cm. In B12, significant reductions were detected in WE-Ca^{2+} (0 to 3 cm) and WE-Mg^{2+} (0-1 cm) compared to U and B0 and WE-K^{+} remained unchanged. However, at the Tella site, the WE-cations showed no differences in B0, but their contents also decreased at all studied soil depths in B12, indicating losses by soil erosion and/or leaching (Francos et al., 2018). Our results contrast those traditionally reported in the literature after fire as it is common to find increases in pH, EC and WE-cations related to the release of cations by the combustion of SOM, as well as the incorporation of ashes into the soil (Badía & Martí, 2003; Pereira et al., 2011; Badía et al., 2014; Bodí et al., 2014). Nevertheless, in our study, these effects could not be observed because soils were sampled immediately after burning, and ashes were meticulously removed prior to sampling; however, these effects could have probably occurred within the first year after burning. Furthermore, the results obtained in B12 indicate that ashes were either redistributed at the soil surface or leached downwards into the soil, as previously observed by Bodí et al. (2014), since WE cations, and thus EC, decreased at all studied soil depths. On the other hand, the differences observed in our study compared to those conducted in Mediterranean environments could be related to the high mean annual precipitation of our study sites.

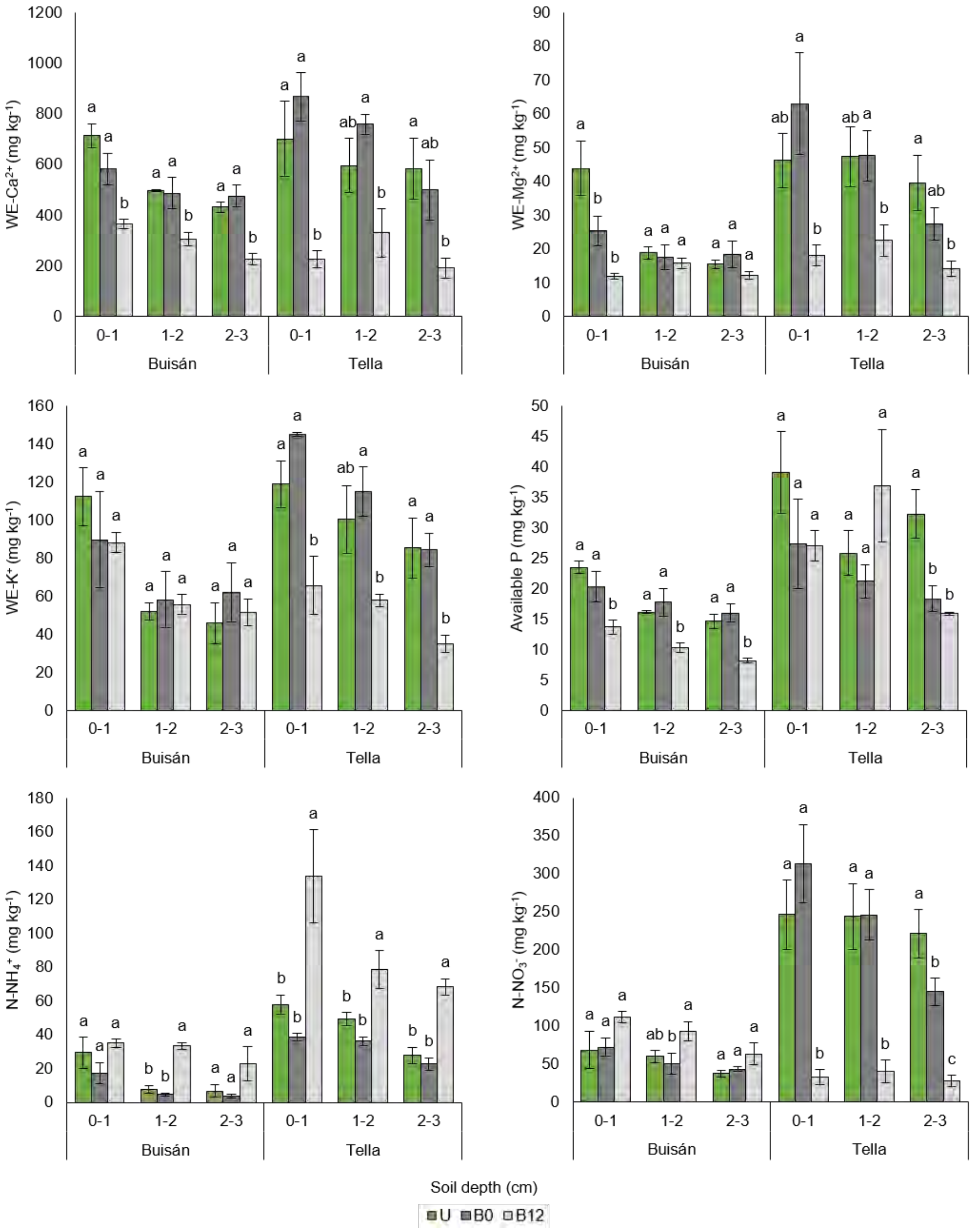

Fig. 5. Water-extractable cations (WE-Ca^{2+}, WE-Mg^{2+} and WE-K^{+}), available P and inorganic N forms (N-NH_4^+ and N-NO_3^-) in unburned (U), immediate post-fire samples (B0) and one year after burning samples (B12) for each soil depth and site (mean value ± SE of three field replicates). For same sampling depth, lowercase letters indicate significant differences among sampling times ($p <0.05$).

Inorganic N species (N-NH_4^+ and N-NO_3^-) at both the Buisán and Tella sites showed no differences between U and B0 at the studied soil depths (Fig. 5). At both sampling times and sites, the nitrate content was higher than the ammonium content, indicating the occurrence of active nitrification processes. Despite the reduction in N in B0 at 0-1 cm, no changes were observed in ammonium or nitrate contents, which is unexpected because they are by-products of organic N combustion (Certini, 2005). Furthermore, apart from organic N mineralization, increases in inorganic N forms are usually found after prescribed burning due to the incorporation of ashes (Alcañiz et al., 2018 and references therein). Thus, the removal of ashes prior to sampling explains the neutral effects of prescribed burning on soil inorganic N forms that were observed in our study immediately after the fire. In B12, no changes were detected in ammonium or nitrate contents at the Buisán site. Nevertheless, at the Tella site, an increase in the ammonium content and a decrease in the nitrate content were detected at all studied soil depths in B12. This finding contrasts the inorganic N dynamics after fires that are commonly reported in the literature, in which an immediate pulse in ammonium content is followed by increases in nitrate content related to nitrification processes up to one year later (Gundale et al., 2005; Badía et al., 2014; San Emeterio et al., 2016). This could be a consequence of the reduction in soil biological activity after burning that is evidenced by a drastic reduction in microbial biomass (Armas-Herrera et al., 2016, 2018) and thus, nitrification rates because ammonium could be adsorbed in the soil and nitrates could be leached when they are not rapidly taken up by soil biota or plants (Mroz et al., 1980). These N losses could have a negative impact on vegetation succession if there is no prompt plant regrowth (Knicker, 2007).

The available P contents at both the Buisán and Tella sites remained virtually unaffected by fire (Fig. 5), which is in accordance with the results of previous studies conducted after prescribed and experimental burnings (Niemeyer et al., 2005; Marcos et al., 2009). Many studies have also indicated that available P increases after burning (Úbeda et al., 2005; Badía-Villas et al., 2014; Larroulet et al., 2016), and these increases are mainly related to the incorporation of ashes into the soil. In our case, ashes were removed prior to sampling, so this effect could not be detected in B0. On the other hand, the lack of changes in available P is unexpected given the temperatures that were reached in the topsoil, as organic P mineralization occurs at temperatures over ~200 ºC (García-Oliva et al., 2018), which would have led to increases in available P (Fontúrbel et al., 2016). However, the absence of differences might also be related to the fact that P losses by volatilization do not occur until temperatures of ~775 ºC are reached (Bodí et al., 2014). Santín et al. (2018) also observed that available P did not significantly change after a moderate/high-severity prescribed eucalypt forest burning, and this result was related to the oligotrophic characteristics of that forest system. One year after burning, the available P values at the Tella site were heterogeneous, and no significant differences were found when these values were compared to those of U and B0. Nevertheless, the available P significantly decreased at the Buisán site at all studied soil depths. The losses of available P after burning may be due to leaching (Pereira et al., 2012), and similar results were also observed by Alcañiz et al. (2016) one year after prescribed understory burning in a Mediterranean forest.

3.4. Fire effects on soil cation exchange complex

The cation exchange capacity (CEC) in the U samples of both study sites showed high values, that ranged from 31.7 to 41.6 $cmol_{(+)}$ kg^{-1}. Burning had no significant effects on CEC, as seen in its B0 values (Fig. 6), although a decreasing trend was detected at the Buisán site. Similar results were found by Larroulet et al. (2016) and Fonseca et al. (2017), who also detected no significant changes in CEC after prescribed shrub burning in semi-arid regions. The CEC in soils is tightly related to SOM, so the greater impacts on SOC and N that were observed at Buisán site could explain the decreasing trend exhibited by this property. This suggests that although SOM was reduced by burning, this reduction had not reached a threshold in which CEC was significantly affected because SOM content was still high after the fire. Additionally, experimental studies that addressed the effects of heat on CEC indicated that this property could be affected when temperatures exceed 250 ºC (Badía & Martí, 2003), 300 ºC (Inbar et al., 2014) or 350 ºC (Thomaz, 2017) for a certain period of time. In the B12 samples, the CEC values at the Tella site showed no differences when compared to the U and B0 samples; nevertheless, in Buisán, the CEC values decreased significantly at depths of 0 to 3 cm. As SOM undergoes mineralization and/or stabilization processes, CEC increases concomitantly (Stevenson, 1982). Then, the detected decrease in Buisán in the B12 samples could be related to the incorporation of new SOM that is less transformed and therefore has lower CEC values.

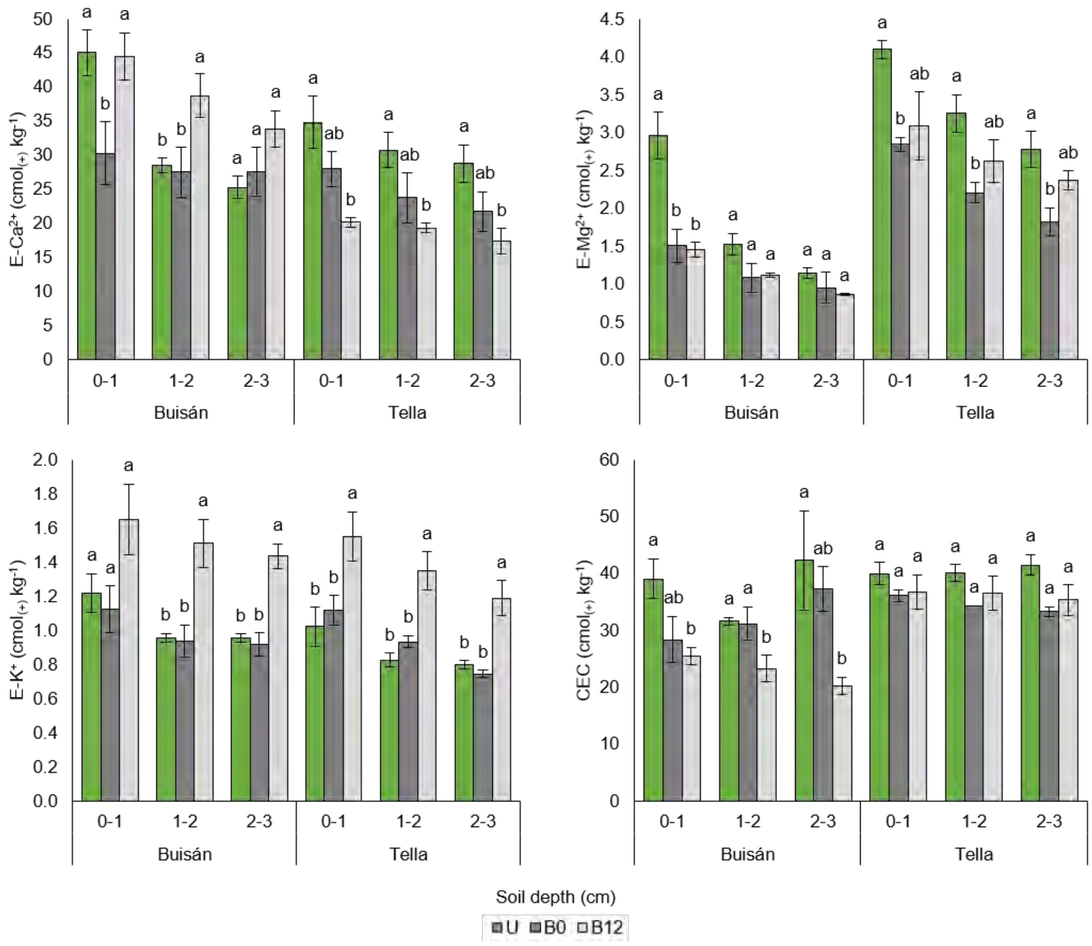

Fig. 6. Exchangeable cations (E-Ca^{2+}, E-Mg^{2+} and E-K^{+}) and cation exchange capacity (CEC) in unburned (U), immediate post-fire samples (B0) and one year after burning samples (B12) for each soil depth and site (mean value ± SE of three

field replicates). For same sampling depth, lowercase letters indicate significant differences among sampling times ($p < 0.05$).

The exchangeable cation contents (E-Ca^{2+}, E-Mg^{2+} and E-K^{+}) were similar in the U soils of both study sites, with Ca^{2+} being the predominant cation (Fig. 6). At the Buisán site, burning decreased E-Ca^{2+} at 0 to 2 cm and Mg^{2+} at 0 to 1 cm, whereas E-K^{+} remained unchanged. On the other hand, at the Tella site, a significant reduction in E-Mg^{2+} and a decreasing trend in E-Ca^{2+} were observed at all studied soil depths in the B0 samples. In the same way as at the Buisán site, K^{+} showed no changes after burning in the Tella site. In this way, the results show the loss of divalent exchangeable cations after burning at both sites, which is probably a consequence of the destruction of organic functional groups (González-Pérez et al., 2004). Consequently, the exchange sites would have been occupied by K^{+}, therefore showing no differences in its content in the B0 samples.

Our findings contrast the results found in the literature that show that increases (Arocena & Opio, 2003; Lavoie et al., 2010) or neutral effects (Wang et al., 2013; Fontúrbel et al., 2016; Larroulet et al., 2016; Fonseca et al., 2017) on exchangeable cations occur after prescribed burning. Apart from the differences in burning intensity and vegetation type, the contrasting effects detected in our study compared to the literature could be related to the removal of ash prior to sampling and the detailed sampling scale since the studies mentioned above sampled greater soil thicknesses, which could dilute the effects of burning (Badía-Villas et al., 2014). One year after burning at the Buisán site, E-Ca^{2+} recovered to U values and E-K^{+} showed an increasing trend, although E-Mg^{2+} still showed values similar to B0 at the Buisán site. An opposite trend was detected at the Tella site, where E-Ca^{2+} significantly decreased, K^{+} significantly increased, and E-Mg^{2+} showed a recovering trend in all the studied soil depths. The different evolutions of these properties observed at both sites could be attributed to surface processes and topographical characteristics. The Buisán site is characterized by low slopes, and no signs of erosion were observed during the study period. Furthermore, one year after burning, charred remains and ashes were still present in the plots. This could have been caused by the snowfall that followed the burning, which stabilized the ash and remaining litter, allowing a slower release of cations over time (Hamman et al., 2008). On the other hand, the burning at the Tella site was performed in April on a steep slope, and was followed by spring rains and summer drought, which could have resulted in leaching and erosion processes. In this way the probable short-term increase in cations after the fire was reversed by erosion and/or leaching, explaining the loss of exchangeable cations (Francos et al., 2016).

3.5. General discussion

SOM is of vital importance for nutrient cycling and cation exchange because nutrients can be volatilized or transformed into available forms via the combustion of SOM (Knoepp et al., 2005). Moreover, SOM, as well as the clay type and content determine the CEC (Ulery et al., 2017). Prescribed burnings are characterized by low intensities; therefore, the temperatures that are reached could be sufficient to produce the combustion of a part of the SOM but lower than the temperatures necessary to induce mineral alterations (Bodí et al., 2014). Despite the effects of fire on SOM, the CEC did not decrease accordingly, suggesting that the SOM content threshold that would have reduced the CEC had not been reached. However, the elimination of organic functional groups can lead to the loss of divalent cations, resulting in a decrease in the CEC immediately after burning. The displacement of exchangeable cations after burning could have led to an increase in water-extractable cations. However, this effect was not observed and could be related to a reduction in cation extractability in water that is probably related to cation precipitation (Badía & Martí, 2003). Divalent cations are released after combustion of organic materials as water-soluble oxides that can be rapidly transformed to less soluble carbonates and chlorides (Thiffault et al., 2008). For this reason, no changes were observed in EC at either the Tella or Buisán sites and only a minor increase in pH was detected at the Buisán site, although transient changes could have also been produced between the sampling times. In a similar way, burning had no effects on inorganic N forms and available P. The increases in pH, EC and nutrients usually reported in the literature after prescribed burning (Alcañiz et al., 2018) are related to the incorporation of ashes into the sampled soil, which we tried to avoid by all means. Although fire exerted few direct changes on the studied soil nutrients, some differences compared to the unburned soil could be observed one year after burning. Apart from the different seasons when each prescribed burning was performed, the slope also played an important role in the post-fire evolution. As explained in the previous section, the Buisán burning was conducted in a plain area and was followed by snowfall that allowed the ashes and partially charred litter layers to stabilize so leaching of soluble ions only occurred in the B12 samples. On the other hand, nutrient losses in the soil after the Tella burning could be explained by: 1) the soil losses as the prescribed fire was conducted in April on a south-facing steep slope, making it more prone to erosion, 2) leaching during the spring rainy season that is favored by the acidic soils. These effects are favored by the slow vegetation recovery at both study sites as reported in Armas-Herrera et al. (2018) and Girona-García et al. (2018a). At the Buisán site, one year after burning, vegetation represented only a small surface of the burned plots, which were mainly covered by partially charred litter and ashes. In the B12 samples from the Tella site, herbaceous plant coverage was of only 14 %, whereas bare soil represented 42 % of the ground surface.

These results were well summarized in the PCA analysis (Fig. 7), in which samples were clearly separated by site and treatment. Axis 2 (25.17 %) distributed samples by study site, showing that the Buisán site is characterized by higher pH values and therefore higher cation contents. On the other hand, the Tella site showed higher SOC, N, P and inorganic N contents. Axis 1 (47.28 %), however, separated the samples by treatment according to the previous discussion. The U samples at 0-1 cm from the Buisán site showed higher positive loadings compared to the equivalent B0 samples. The U and B0 samples from the deeper layers at the Buisán site formed a large cluster that indicated the limited depth in which burning exerted direct changes. Additionally, the B12 samples showed higher negative loads, which is in accordance with the decreases detected at this sampling time for the studied properties. At the Tella site, burning did not have the same effects on the studied properties as those at the Buisán site; therefore, U and B0 are not clearly separated by axis 1. However, in the same way as at the Buisán site, the B12 samples from the Tella site also showed higher negative loadings.

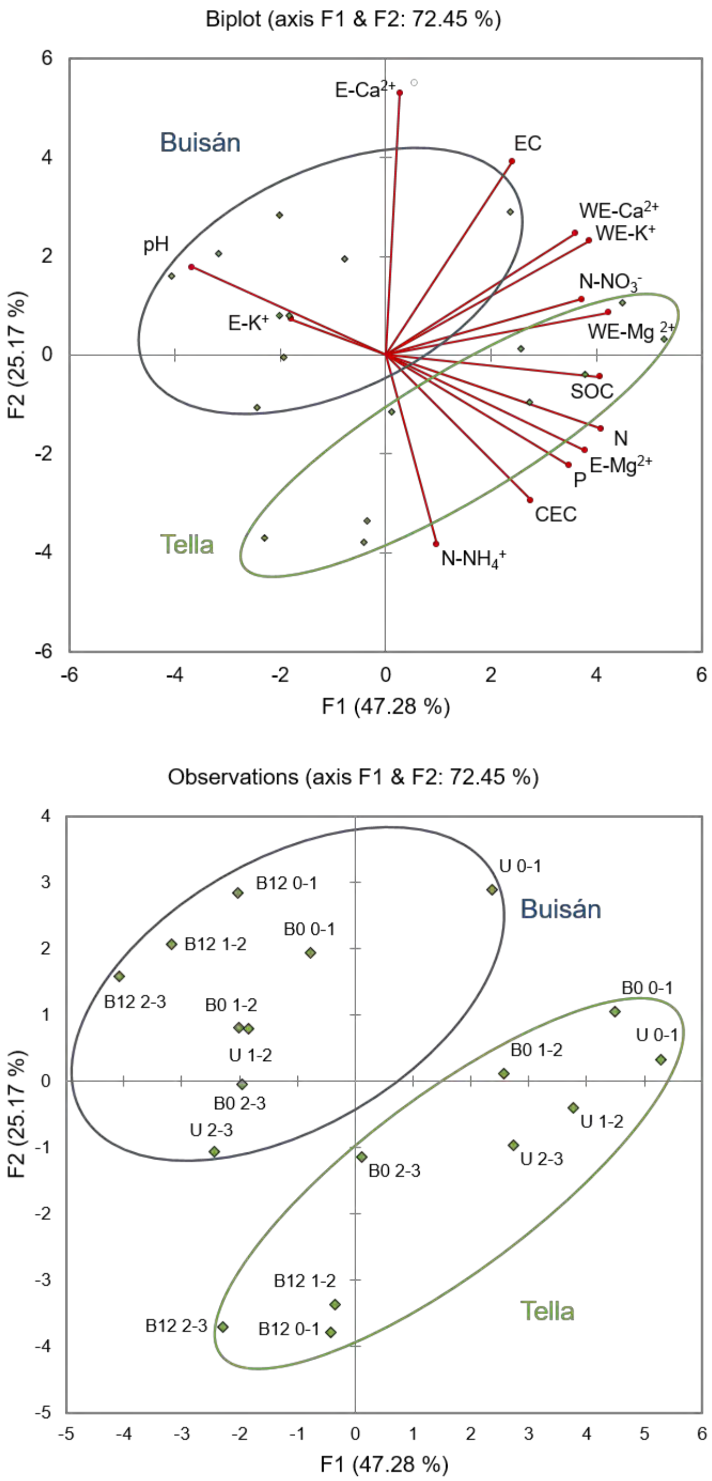

Fig. 7. Results of the Principal Component Analysis (PCA). Variables: Soil organic C (SOC), total N (N), pH, electrical conductivity (EC), water-extractable cations (WE-Ca^{2+}, WE-Mg^{2+} and WE-K^{+}), inorganic N forms (N-NH_4^+ and N-NO_3^-), available P (P), exchangeable cations (E-Ca^{2+}, E-Mg^{2+} and E-K^{+}) and cation exchange capacity (CEC). Observations: unburned (U), immediate post-fire samples (B0) and one year after burning samples (B12) for each soil depth and site.

4. Conclusions

Despite the spatial and temporal variations expected from sampling such a thin topsoil layer (0-1, 1-2, and 2-3 cm depth), we showed the importance of how samplings are performed (i.e., sampled soil depth, time since burning and ash removal) to isolate the direct effects of fire on soils. Our results indicate that the SOM content was severely affected in the first centimetre of the topsoil, although it had few repercussions on soil nutrient content and availability. However, as a consequence of site characteristics (i.e., burning season, slope and precipitation), high nutrient losses were detected one year after burning that were probably related to leaching and/or erosion. Therefore, the long-term impact of prescribed fire on soils may differ depending on the burning season and topography, and these changes could negatively impact the recovery of vegetation over time. The results highlight the need to further monitor the evolution of the studied properties to assess the sustainability of this practice from the perspective of soil and plant recovery.

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