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## Abstract

In NW Spain, a European region with very high fire incidence and erosion risks, the effects on soils of a medium-to-high severity wildfire and two emergency stabilization techniques were studied. In burned plots (control, BS; seeded with cereal, BSS; straw mulched, BSM) and adjacent unburned plots (US), the topsoil (0-2 cm) pH and thirteen  $\text{NH}_4\text{Ac-DTPA}$  extractable elements were evaluated at  $t=0$ , 4, 8 and 12 months after the fire. Compared to US, fire increased by 0.3-0.5 units the soil pH which decrease slowly over time, but remaining significantly higher at  $t=12$  (BS, BSM, BSS>US). Ammonium nitrogen (N) levels were higher ( $p < 0.05$ ) in burned plots than in US, difference decreasing progressively from 48-fold ( $t=0$ ) to 25-fold ( $t=12$ ). Although no significant effect of fire was immediately observed, the extractable sodium (Na) and potassium (K) were higher ( $p < 0.05$ ) in burned plots than in US at  $t=4$  and  $t=8$ , probably due to cation leaching from the overlying ash. Fire did not modify the extractable magnesium (Mg), but at  $t=0$  the extractable calcium (Ca) and phosphorous (P) were transiently and significantly higher in burned plots than in US. Extractable aluminium (Al), iron (Fe), copper (Cu), cobalt (Co) and zinc (Zn) were lower and manganese (Mn) was higher in burned plots than in US. Neither seeding nor mulching significantly modified the topsoil concentrations of the elements considered. The PCA revealed that BS, BSM and BSS became more similar to US over the study period due to a rapid decrease in extractable Ca and Mg and a slow decrease in extractable Mn and  $\text{NH}_4^+\text{-N}$ . At  $t=12$ , the most notable differences between burned plots and US were in the concentrations of extractable Al and Zn. Data suggest that at least another 4-8 months will be required for full recovery of the burned plots to unburned conditions.

**Keywords:** Seeding, Mulching, Burned Area Emergency Response, Post-fire rehabilitation, PCA

## 1. Introduction

Although fire is a natural driving force in the evolution of the terrestrial flora and fauna, humans have largely modified the fire regimes (Pausas and Keeley, 2009) and the actual large-scale intense forest fires are considered a relatively recent artefact of human intervention in forest ecology, especially by the reduction of herbivores (Caldararo, 2002). Due to their increasing frequency and extent during the last half a century, anthropogenic wildfires are a global concern as a worldwide factor of forests destruction and soil degradation (Chandler et al., 1983; Certini, 2005). Climate change will very likely increase the length and severity of the fire season, as well as the extension of areas of risk, and recurrent droughts and reduced precipitation are likely to imperil ecosystem regeneration after fire (Biro, 2009). Moreover, the shift in land use as a consequence of rural exodus and

socio-economic factors will also contribute to increase the number of wildfires and the burned area (Pereira et al., 2011).

Despite its situation in a temperate-humid zone, the region of Galicia (NW Spain; surface 29574 km<sup>2</sup>) is one of the areas of Europe with the highest incidence of fire (Biro, 2009): more than 175000 wildfires burned a total area of 5100 km<sup>2</sup> between 1991 and 2010 (Ministerio de Agricultura y Medio Ambiente, 2012). The cause is a complex mixture of traditional use of fire as an agro-sylvo-pastoral tool, deep economic and demographic changes in rural areas and incendiarism as protest (Gómez-Rey et al., 2013).

The effects of fire on soil organic matter (SOM) and available macronutrients have been widely studied during the last 30 years. Although depending

on the fire severity SOM can increase, decrease or remain unchanged, most studies have reported short-term SOM losses (Carballas, 1997; Fisher and Binkley, 2000; Simard et al., 2001; Certini, 2005; Couto-Vázquez and González-Prieto, 2006; Certini et al., 2011), although a meta-analysis showed a significant increase 10 years after the fire (Johnson and Curtis, 2001). Usually, the concentration of available basic cations and inorganic phosphorous (P) increased transiently after the fire (Debano and Conrad, 1978; Trabaud, 1983; Carballas, 1997; Certini, 2005; Couto-Vázquez and González-Prieto, 2006; Gómez-Rey et al., 2013a), due to the accumulation of ashes rich in oxides and carbonates of basic ions (Chandler et al., 1983; Kutiel et al., 1990; Carballas, 1997; Pereira et al., 2011) and the heat-induced mineralization of the extractable organic P (Saá et al., 1993; Serrasolsas and Khanna, 1995). Until recently, the post-fire effects on soil trace elements were not well known; however, in the last decade more research has been devoted to this topic. Most studies indicate a post-fire increase in soil extractable manganese (Mn) and zinc (Zn) (García-Marco and González-Prieto, 2008; Close et al., 2011; Stankov-Jovanovic et al., 2011; Gómez-Rey et al., 2013a), although inconsistent results (Ponder et al., 2009) have also been reported for these nutrients, that can even decrease in the ash layer (Pereira et al., 2011). Conversely, a reduction of available iron (Fe) was usually found (García-Marco and González-Prieto, 2008; Ponder et al., 2009; Pivello et al., 2010; Pereira et al., 2011). Most results pointed to a post-fire increase of extractable copper (Cu) (Close et al., 2011; Stankov-Jovanovic et al., 2011; Gómez-Rey et al., 2013a), but García-Marco and González-Prieto (2008) did not find significant changes and Pivello et al. (2010) reported a diminution, probably due to differences in fire severity, soil type, vegetation cover, climate conditions and sampling strategy. The scarce published information shows an increment of extractable boron (B) (Ponder et al., 2009; Gómez-Rey et al., 2013a) and suggests the lack of a clear tendency for the extractable cobalt (Co) (García-Marco and González-Prieto, 2008; Aref et al., 2011).

Wildfire can lead to an increased runoff and erosion, especially when the soil is bare, intense rainfall events are frequent and topography is dominated by steep slopes (Díaz-Fierros et al., 1987; Robichaud and Brown, 1999; Cerdà and Lasanta, 2005; Vega et al., 2005). In these circumstances, the

burned area emergency response (BAER) must assess the need for, and to implement, emergency post-fire stabilization treatments “that provide essential and demonstrated protection at minimum cost while meeting emergency stabilization objectives” (Robichaud et al., 2010), i.e. that reduce the threat to life and property, loss of soil and onsite productivity, loss of control of water, and deterioration of water quality (Robichaud, 2009). Widely used BAER techniques include herbaceous seeding, to accelerate re-vegetation of the soil, and straw mulching, to provide immediate ground cover - as occurs naturally with needles or leaves from unburned canopy (Vega et al., 2005; Groen and Woods, 2008; Robichaud, 2009; Fernández et al., 2011). A literature search has shown that, although the effectiveness of BAER in reducing soil erosion has been evaluated, very few studies have demonstrated the effectiveness of the treatments involved. The highest effectivity have been reported for straw mulching, which can reduce soil erosion by 66-95% (Wagenbrenner et al., 2006; Groen and Woods, 2008; Fernández et al., 2011; Díaz-Raviña et al., 2012), while mean sediment yields in wood-chip mulch and erosion barrier treatments were similar to rates in the untreated plots (Fernández et al., 2011). Although in some cases grass seeding can reduce erosion losses by up to 34-42% (Díaz-Raviña et al., 2012), this treatment is often ineffective because of the limited increment in ground cover that it produces (Wagenbrenner et al., 2006; Groen and Woods, 2008). For the contour felling treatment, Wagenbrenner et al. (2006) found that it can be able to store much of the sediment generated in an average year, but will not reduce sediment yields from larger storms. The available information about the effects of BAERs treatments on the quality and fertility of burned soil is still very scarce. After an experimental fire of low severity, neither straw mulching nor grass seeding had effects on chemical properties of soils and sediments (Gómez-Rey et al., 2013a, 2013b, 2014), and on biomass, activity and diversity of soil microorganisms (Fontúrbel et al., 2012). After a wildfire, Díaz-Raviña et al. (2012) reported no short-term changes in soil physical, chemical and microbiological properties due to the application of mulching and seeding BAER treatments. However, as far as we know, there are not published information about the effects of BAERs treatments on nutrient availability in soils affected by medium or high severity wildfires, i.e., the scenarios in which BAERs treatments are more likely to be applied.

Consequently, the objective of present work is to fill this gap of knowledge by studying, during the first year after a medium-to-high severity wildfire, the effects of two widely used BAERs stabilization techniques (cereal seeding and straw mulching) on the topsoil pH and extractable  $\text{NH}_4^+$ -N,  $\text{NO}_3^-$ -N, Na, K, Mg, Ca, P, Al, Fe, Mn, Zn, Cu and Co.

## 2. Material and methods

### 2.1. Site description

The experimental site is located close to the Montes do Invernadeiro Natural Park (UTM 29 T PG34168-71422, 1566 m a.s.l.) in Galicia (NW Spain). The climate of the area is temperate (mean annual temperature: 6-8 °C) and rainy (1600-1800 mm  $\text{y}^{-1}$ ). Due the high altitude of the site, the soil (especially the bare areas) is subjected to freezing and thawing cycles of variable length and intensity during the winter. For example, in the nearest meteorological station (Cabeza de Manzaneda, located 10 km NE at 1758 m a.s.l.; Meteogalicia, 2014) the mean soil temperature at a 10 cm depth during the winter season of the studied period varied as follows:  $0.5 \pm 0.1$  °C (December 16th to 31th, 2010),  $1.9 \pm 0.6$  °C (January 1st to 21th, 2011),  $-0.1 \pm 0.1$  °C (January 22th to February 15th, 2011) and  $0.2 \pm 0.1$  °C (February 16th to March 25th, 2011).

The entire study area was very homogeneous in terms of: a) orientation (245-250° WSW); b) slope (26-30%); c) soil type, a silty loam Entisol (IUSS Working Group, 2006) developed over metamorphic rocks (phyllites); and d) vegetation cover, dominated by a 7-year-old *Pinus sylvestris* L. plantation (1.0-1.6 m height) and by shrubs (0.9-1.3 m height) such as *Erica* spp., *Vaccinium myrtillus* L., *Pterospartum tridentatum* Willk. and *Cistus* spp., with 100% ground cover. Considering the results of Vega et al. (2006) for scrublands from the same region with similar height, cover and species composition, the estimated pre-fire fuel load was 24-45 Mg  $\text{ha}^{-1}$ .

In the first four days of September 2010, the area was affected by a moderate to highly severe wildfire (1700 ha), as identified by taking the following into account: a) complete consumption of the shrubs' stems and scorching of pine seedlings' trunks; b) almost complete consumption of the continuous litter layer (4-8 cm thick); c) high percentage of bare soil (42%); d) 0-1 cm layer of white and black ash and charred plant debris that covered 58% of soil; and e)

25% reduction in the organic matter content (C and N) in the 0-2 cm soil layer (for further details, see Gómez-Rey and Gonzalez-Prieto, 2013). We selected a hillside site for carrying out the study and took advantage of some unusual characteristics in relation to wildfires, i.e. the availability of a fully comparable unburned control in close proximity to a soil affected by a fire of medium-high severity. In the burned area an experimental zone of 3000  $\text{m}^2$  (100 m along the contour line, 30 m downslope) was delimited and nine experimental plots (three treatments x three replicates distributed alternately) of dimensions 4 x 20 m (each separated by 3 m) were established between planting rows with the longest dimension parallel to the maximum slope. The following plot types were thus established: untreated burned soil (BS), burned soil to which 250  $\text{g m}^{-2}$  of straw mulch was manually applied (BSM) and burned soil seeded with 10  $\text{g m}^{-2}$  of *Secale cereale* L. seeds (BSS). Similarly, close to the burned area (20 m to the East) and in the same slope position, an experimental zone of 600  $\text{m}^2$  (20 m along the contour line, 30 m downslope) was delimited in the unburned area and three untreated control plots were established for sampling unburned soil (US).

### 2.2. Soil sampling

The topsoil was sampled from the A horizon (0-2 cm depth) one week after the wildfire, and before any rain event ( $t=0$ ), and also 4, 8 and 12 months later. In each plot and at each sampling date, ten uniformly distributed square sampling quadrats (15 x 15 cm) were selected, the plant litter (unburned plots, US) or the ash layer (burned plots: BS, BSS and BSM) was removed and the topsoil was sampled. These ten subsamples were combined to yield one composite sample per plot and sampling date. The field-moist soil was sieved (< 2 mm) and homogenised; one sub-sample was stored at 4 °C for inorganic N quantification and another was air-dried for analysis of extractable nutrients.

### 2.3. Chemical analysis

The inorganic N content was analyzed by a modified diffusion method (Khan et al. 1997). Sequential release of  $\text{NH}_4^+$ -N and  $\text{NO}_2^- + \text{NO}_3^-$ -N (in the form of  $\text{NH}_3$ ) was achieved by placing 50 ml aliquots of soil extracts in a 500 ml wide-mouth glass jar and successively adding (for 24 h periods at 55 °C) MgO (0.1 g), to release and trap  $\text{NH}_3$  in  $\text{H}_2\text{SO}_4$ , followed by MgO (0.1 g) plus Devarda's alloy (0.4 g) to the same extract, to convert the  $\text{NO}_2^-$  and  $\text{NO}_3^-$ -N

into  $\text{NH}_3$ . Gaseous  $\text{NH}_3$  was then captured in 10 ml of 0.004 M  $\text{H}_2\text{SO}_4$  in a Teflon bottle attached to the glass jar and measured by back titration of the excess of  $\text{H}_2\text{SO}_4$  with 0.004 M NaOH.

For analysis of extractable Na, K, Mg, Ca, P, Al, Fe, Mn, Zn, Cu and Co, topsoil samples (10 g) were shaken for 2 h with a mixture of 1 M  $\text{NH}_4\text{Ac}$  and 0.005 M DTPA as extractants (soil:solution ratio, 1:5); the extracts thus obtained were then filtered through cellulose paper (Filter-Laboratory 1242, 90-mm diameter) before being analysed by simultaneous ICP-OES (Varian Vista Pro, Mulgrave, Australia).

All analyses were carried out in duplicate and the mean concentrations for each soil sample (i.e. plot) were used in the statistical procedure.

#### 2.4. Statistical analysis

The data on  $\text{pH}_{\text{H}_2\text{O}}$ ,  $\text{pH}_{\text{KCl}}$  and concentrations of extractable elements were examined by two-way ANOVA (with plot and sampling date as factors) after verifying the fulfilment of the assumption of normal distribution (Shapiro-Wilk's *W* test) and equality of variances among groups (Levene's test). Both assumptions were fulfilled in the cases of Ca, Mg, Mn and P, but departure from normality was found for  $\text{pH}_{\text{H}_2\text{O}}$  and Cu (only in sampling date groups) and heteroscedasticity was observed for  $\text{pH}_{\text{KCl}}$ ,  $\text{NH}_4^+\text{-N}$ ,  $\text{NO}_3^-\text{-N}$ , Al, Co, Cu, Fe, K, Na and Zn. Accordingly, the original data of the latter variables were subjected to Tukey's ladder of powers or Box-Cox transformations to yield normal distribution and equality of variances. The Bonferroni's test was used to detect significant differences between the group means, at  $p < 0.05$ .

The relationships among  $\text{pH}_{\text{H}_2\text{O}}$ ,  $\text{pH}_{\text{KCl}}$  and the 13 macronutrients and trace elements analysed in the 48 soil samples (4 plots  $\times$  3 replicates  $\times$  4 sampling dates) were examined by factor analysis (Principal Component Analysis based on the correlation matrix, to extract the factors, plus Varimax rotation with Kaiser normalization). This method was used with the aim of identifying the following: a) the relationships among the studied variables; b) the main factors differentiating the plots; and c) the factors characterizing the plots treated by different post-fire stabilization techniques during the first year after the fire. The anti-image correlation matrix (comprising the negative values of the partial correlation coefficients) was analysed to detect any soil variables that were not suitable for inclusion in

the factor analysis ( $\text{pH}_{\text{H}_2\text{O}}$  and  $\text{NO}_3^-\text{-N}$  in this case). After this procedure, the Kaiser-Meyer-Olkin measure of sampling adequacy increased from 0.64 (low) to 0.72 (acceptable), and the Barlett's test of sphericity was highly significant ( $p < 0.0005$ ). All statistical analyses were done with the SPSS 15.0 statistical package.

### 3. Results

The two-way ANOVA showed that treatment and sampling date explained, respectively, 85-89% and 79-82% of the pH variance, while the interaction between both factors was not significant (Table 1). Compared with the unburned soil, soil pH increased by 0.3 ( $\text{pH}_{\text{H}_2\text{O}}$ ) to 0.5 units ( $\text{pH}_{\text{KCl}}$ ) just after the fire and, despite a slow decrease with time, remained significantly higher in all burned plots (without differences among them) during the whole study period (Fig. 1). Although the  $\text{pH}_{\text{H}_2\text{O}}$  and  $\text{pH}_{\text{KCl}}$  were strongly correlated (Pearson's correlation coefficient,  $r = 0.774$ ;  $p < 0.0005$ ;  $n = 48$ ), the relationships of the latter with the extractable macronutrients and trace elements were stronger, except for Al ( $r = -0.588$  with  $\text{pH}_{\text{H}_2\text{O}}$ ;  $r = -0.414$  with  $\text{pH}_{\text{KCl}}$ ;  $p < 0.005$ ) and Zn ( $r = -0.483$  with  $\text{pH}_{\text{H}_2\text{O}}$ ,  $p < 0.001$ ; uncorrelated with  $\text{pH}_{\text{KCl}}$ ). The  $\text{pH}_{\text{KCl}}$  has strong positive correlations with the extractable Ca and Mn ( $r = 0.603$  and  $r = 0.710$ , respectively,  $p < 0.0005$ ) and weak with Mg and P ( $r = 0.321$  and  $r = 0.397$ , respectively;  $p < 0.05$ ), whereas it has weak negative correlations with the extractable Fe and Al ( $r = -0.337$  to  $r = -0.414$ ;  $p < 0.05$ ) and moderate with Na and Cu ( $r = -0.467$  to  $-0.516$ ;  $p < 0.001$ ).

#### 3.1. Macronutrients

The fire led to a huge increase in the concentrations of soil  $\text{NH}_4^+\text{-N}$ , which were 48 times higher in the burned than in the unburned plots (BS, BSM, BSS  $>$  US;  $p < 0.05$ ), the treatment explaining almost all (96%) of the variance associated with  $\text{NH}_4^+\text{-N}$ . The treatment  $\times$  sampling date interaction (60% of variance explained) reflected that  $\text{NH}_4^+\text{-N}$  levels decreased over time in the burned plots but did not vary significantly in US plots; consequently, differences between burned and unburned soils were halved at the end of the study period, but still remained significant (BS, BSM, BSS  $>$  US;  $p < 0.05$ ; Table 1; Fig. 2). Although to a lesser extent, the fire also caused an increase in the  $\text{NO}_3^-\text{-N}$  levels (BS, BSM, BSS  $>$  US, until  $t = 8$  months;  $p < 0.05$ ), but the treatment had less effect on  $\text{NO}_3^-\text{-N}$  variance (70% of

the variance explained) than the sampling date (85% of variance explained) (Table 1). The treatment x date interaction was also important (57% of  $\text{NO}_3^-$ -N variance explained), with the highest values (although always  $< 11 \text{ mg kg}^{-1}$ ) occurring in winter,

and to the resume of differences between treatments one year after the fire. Neither the  $\text{NH}_4^+$ -N nor the  $\text{NO}_3^-$ -N content was significantly affected by the stabilization treatments applied to the burned plots.

**Table 1.** Results of the two-way ANOVA for soil  $\text{NH}_4^+$ -N,  $\text{NO}_3^-$ -N, macro-nutrients and trace element concentrations with treatment (T) and date (D) as factors.

	Treatment (T)		Date (D)		T x D interaction	
	partial $\eta^2$	p	partial $\eta^2$	p	partial $\eta^2$	p
$\text{NH}_4^+$ -N ( $\text{mg kg}^{-1}$ )	0.957	***	0.288	*	0.598	***
$\text{NO}_3^-$ -N ( $\text{mg kg}^{-1}$ )	0.701	***	0.845	***	0.571	***
Extractable Na ( $\text{mg kg}^{-1}$ )	0.702	***	0.794	***	0.527	**
Extractable K ( $\text{mg kg}^{-1}$ )	0.531	***	0.661	***	0.582	***
Extractable Mg ( $\text{mg kg}^{-1}$ )	0.066	n.s.	0.623	***	0.274	n.s.
Extractable Ca ( $\text{mg kg}^{-1}$ )	0.245	*	0.570	***	0.334	n.s.
Extractable P ( $\text{mg kg}^{-1}$ )	0.576	***	0.953	***	0.808	***
Extractable Al ( $\text{mg kg}^{-1}$ )	0.612	***	0.285	**	0.338	n.s.
Extractable Fe ( $\text{mg kg}^{-1}$ )	0.269	*	0.366	**	0.455	*
Extractable Mn ( $\text{mg kg}^{-1}$ )	0.778	***	0.538	***	0.539	**
Extractable Cu ( $\text{mg kg}^{-1}$ )	0.773	***	0.569	***	0.456	*
Extractable Zn ( $\text{mg kg}^{-1}$ )	0.303	***	0.297	***	0.205	n.s.
Extractable Co ( $\text{mg kg}^{-1}$ )	0.596	***	0.448	***	0.302	n.s.

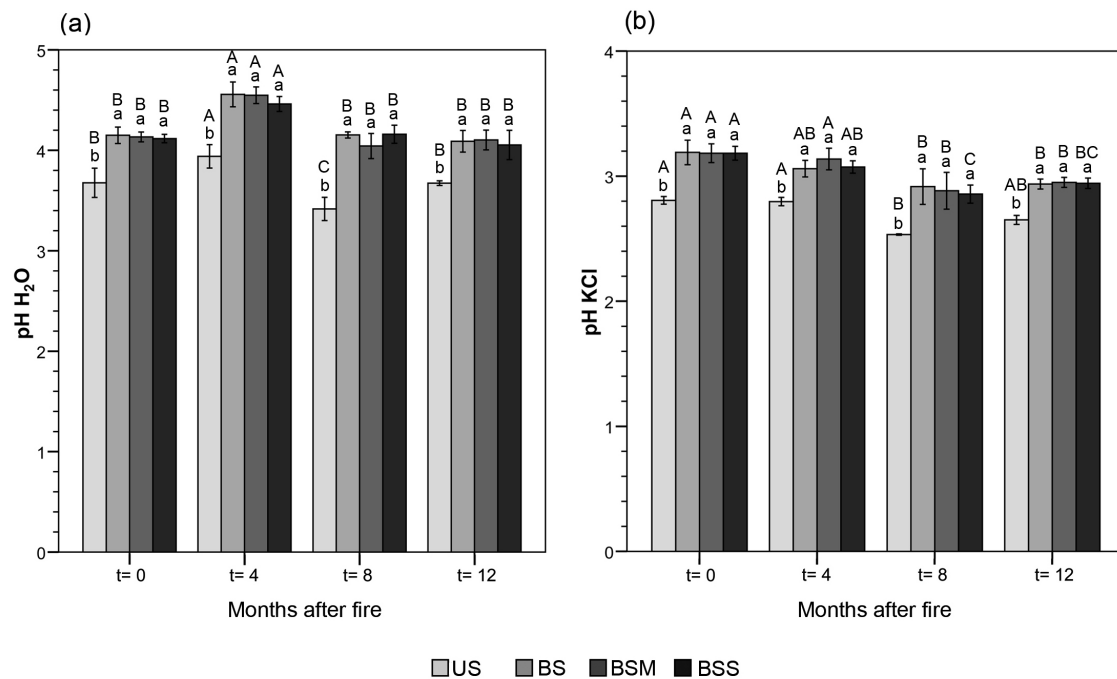
Note: \*  $p < 0.05$ ; \*\*  $p < 0.01$ ; \*\*\*  $p < 0.001$ .

The two-way ANOVA for soil extractable Na revealed that 70%, 79% and 53% of the variation was explained respectively by the treatment, sampling date and the interaction between these factors (Table 1), but that the seeding and mulching treatments had no effect on Na concentrations. Considering all samples together, the extractable Na was around 40% lower in the burned than in the unburned plots (BS, BSM, BSS  $<$  US;  $p < 0.05$ ), and the differences were always significant, except on the first sampling date. In winter and spring ( $t = 4$  and 8 months), soil Na concentration tended to be higher than in late summer ( $t = 0$  and 12 months), especially in the unburned plots (Fig. 3).

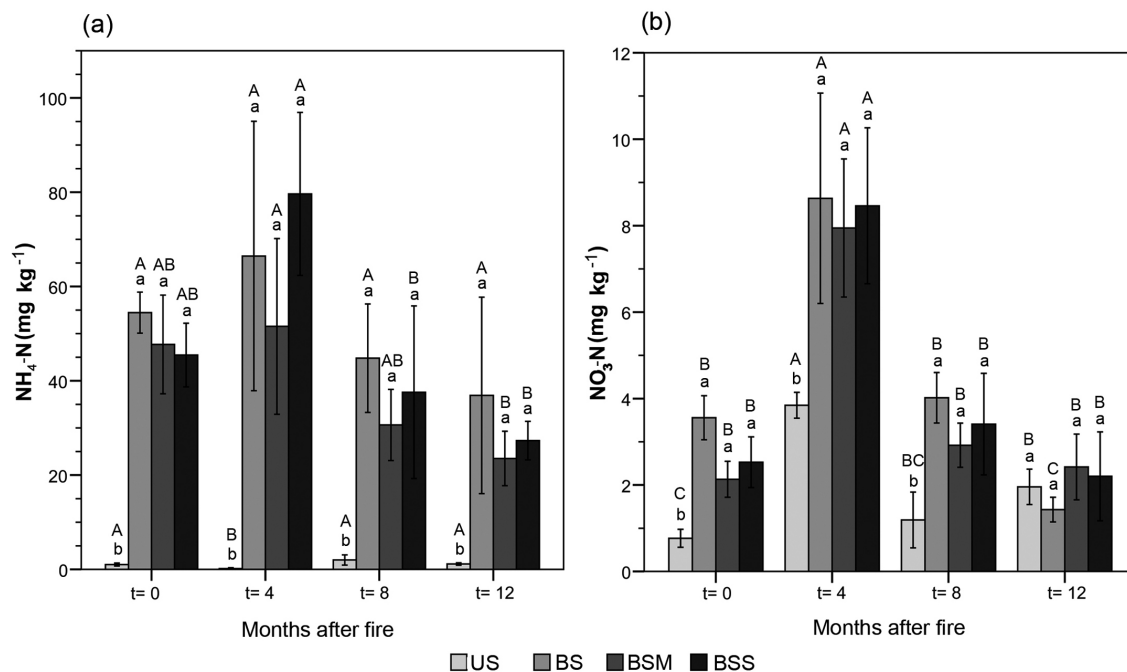
The soil extractable K was also significantly affected by both factors under study (treatment and sampling date) and their interaction, which each explained respectively 53%, 66% and 58% of the

variation in K (Table 1). The soil stabilization treatments did not have any effect on the concentrations of K. The highest values were recorded in late winter in the burned soil and in late winter and spring in the unburned plots (Fig. 3). Considering the four sampling dates together, the extractable K was around 19% higher in the unburned than in the burned plots, that not differ among them (US  $>$  BS, BSM, BSS;  $p < 0.05$ ).

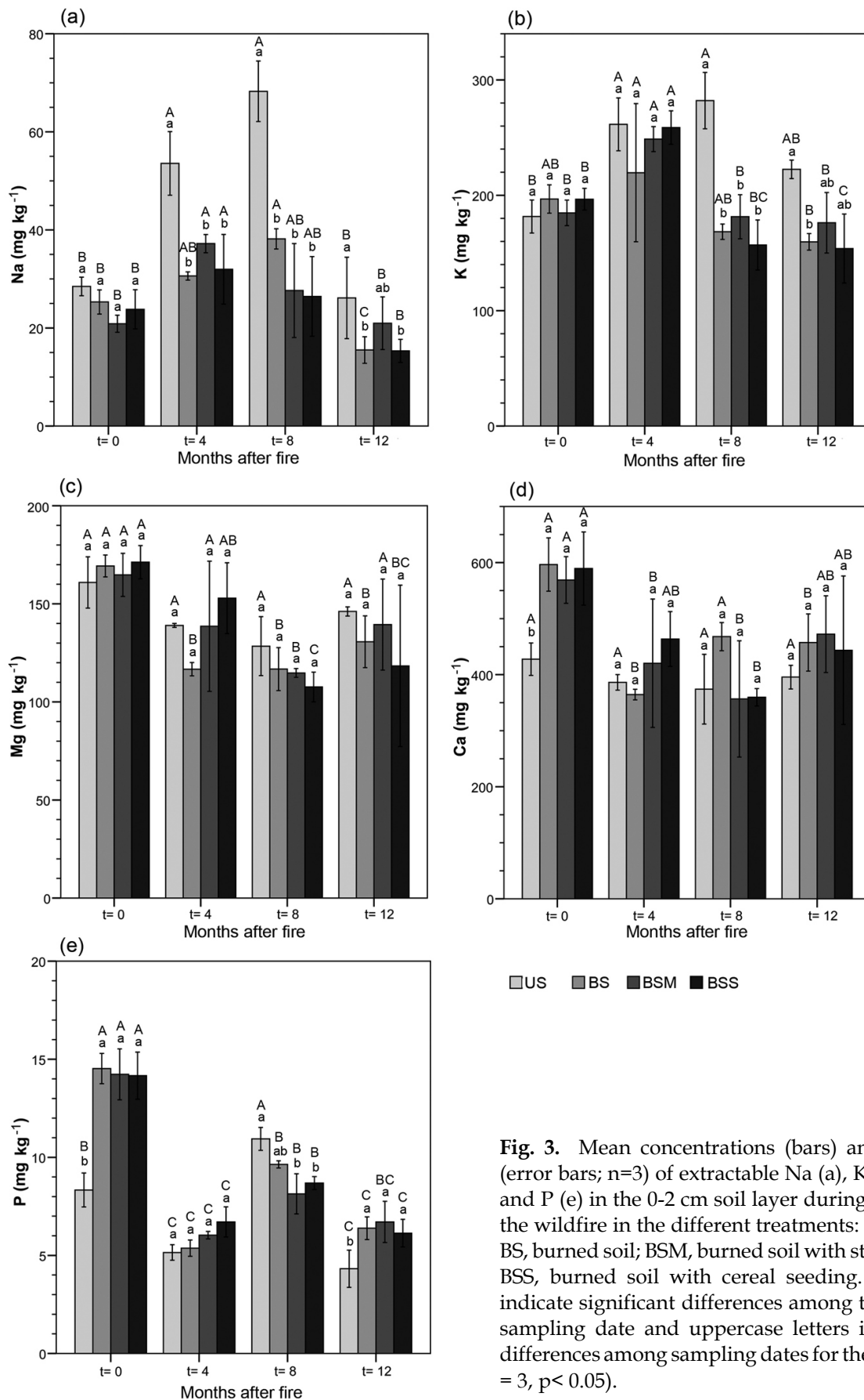
The two-way ANOVA revealed that the only factor that had significant effect on the extractable Mg was the sampling date, which explained 62% of the variance in Mg concentrations (Table 1). Jointly considering all samplings, no significant differences between treatments were found. Regardless of treatment, the lowest concentrations of extractable Mg were observed in summer samples (Fig. 3).



**Fig. 1.** Mean values (bars) and standard errors (error bars; n=3) of pH<sub>H<sub>2</sub>O</sub> (a) and pH<sub>KCl</sub> (b) in the 0-2 cm soil layer during the first year after the wildfire in the different treatments: US, unburned soil; BS, burned soil; BSM, burned soil with straw mulching; and BSS, burned soil with cereal seeding. Lowercase letters indicate significant differences among treatments for each sampling date and uppercase letters indicate significant differences among sampling dates for the same treatment (n = 3, p < 0.05).



**Fig. 2.** Mean concentrations (bars) and standard errors (error bars; n=3) of NH<sub>4</sub><sup>+</sup>-N (a) and NO<sub>3</sub><sup>-</sup>-N (b) in the 0-2 cm soil layer during the first year after the wildfire in the different treatments: US, unburned soil; BS, burned soil; BSM, burned soil with straw mulching; and BSS, burned soil with cereal seeding. Lowercase letters indicate significant differences among treatments for each sampling date and uppercase letters indicate significant differences among sampling dates for the same treatment (n = 3, p < 0.05).



**Fig. 3.** Mean concentrations (bars) and standard errors (error bars; n=3) of extractable Na (a), K (b), Mg (c), Ca (d) and P (e) in the 0-2 cm soil layer during the first year after the wildfire in the different treatments: US, unburned soil; BS, burned soil; BSM, burned soil with straw mulching; and BSS, burned soil with cereal seeding. Lowercase letters indicate significant differences among treatments for each sampling date and uppercase letters indicate significant differences among sampling dates for the same treatment (n = 3, p < 0.05).

Although the sampling date explained 57% of the extractable Ca variance, the treatment only accounted for a quarter of the variation in Ca, and the interaction factor did not have any notable effect (Table 1). Considering the whole dataset, no significant effect of treatment in soil extractable Ca was found; however, samples from all burned soils considered together contained 17% more extractable Ca than the unburned soil. The concentrations of Ca were higher in the burned than in the unburned plots just after the fire (BS, BSM, BSS > US;  $p < 0.05$ ), but not at the subsequent samplings. The concentrations of Ca remained relatively stable in the unburned plots throughout the study period, but decreased during the winter season in the burned plots and then varied randomly (Fig. 3).

The sampling date explained almost all the variance associated with the extractable P (95%), while treatment accounted for 58% the variance, with significantly lower values in the unburned plots (BS, BSM, BSS > US;  $p < 0.05$ ) when all samplings were jointly considered, while seeding and mulching did not have any effects. However, the strong interaction term (81% of variance explained) revealed a complex pattern of variation in the extractable P throughout the study period (Table 1). Phosphorus concentrations were significantly higher in the burned than in unburned plots in late summer, especially immediately after the fire, while the reverse was observed in samples collected in spring, and no treatment effect was observed in samples collected in winter (Fig. 3).

### 3.2. Trace elements

The treatment and sampling date explained respectively 61% and 28% of the variation in soil extractable Al (Table 1). Compared with the unburned plots, the Al concentrations in the whole dataset were around 15% lower in the burned plots ( $p < 0.05$ ), among which no effects of BAER treatments were observed. The extractable Al was minimal in samples collected in late winter from the unburned plots, but not from the burned ones and differences between treatments were not always significant (Fig. 4).

Iron availability was only slightly affected by the

factors under study, which explained 27% (treatment), 37% (sampling date) and 46% of the variation (treatment x date interaction) (Table 1). Although the value was minimal in seeded soil eight months after the fire, the soil stabilization treatments did not have any consistent effects on extractable Fe. There was no clear temporal trend in the extractable Fe, which was around 10% lower in the burned than in the unburned plots considering all sampling dates together, although the differences rarely reach significant levels (Fig. 4).

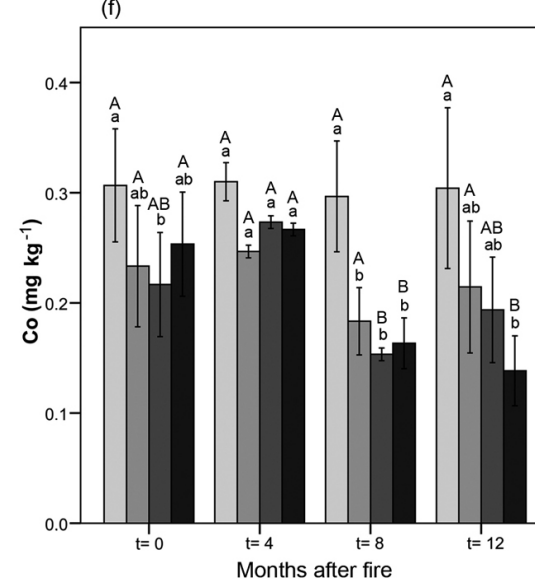
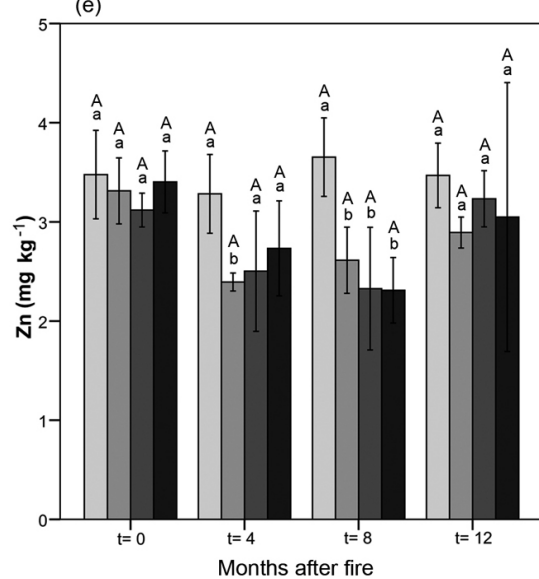
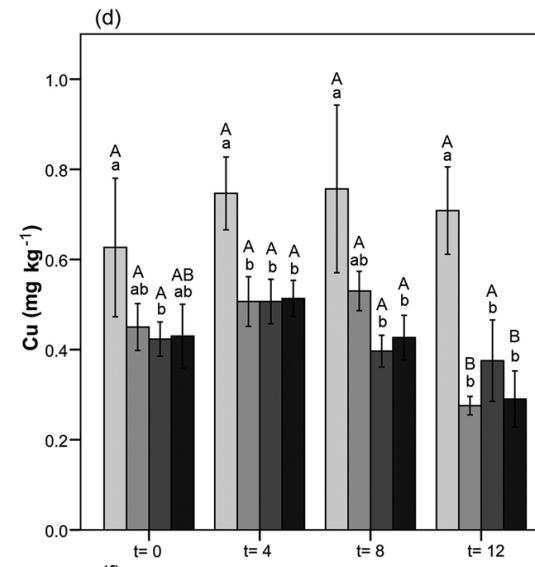
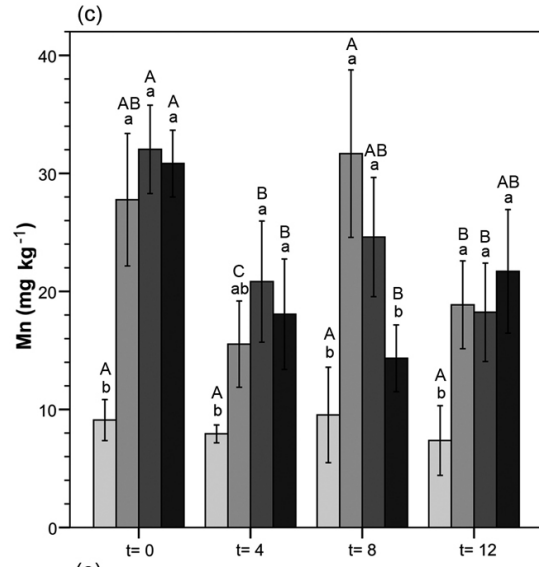
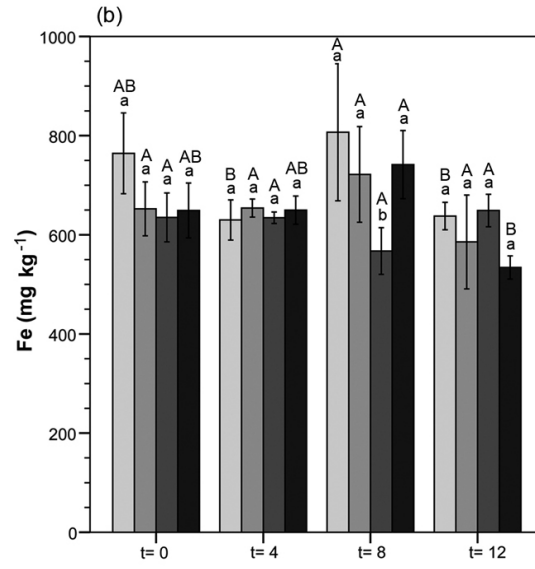
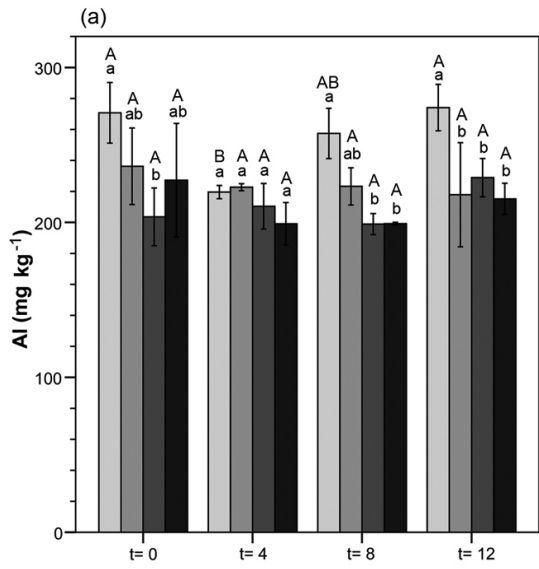
Both factors under study and their interaction explained a significant fraction of the variance in extractable Mn (treatment, 78%; sampling date, 54%; interaction, 54%), (Table 1). Except in a couple of pairwise comparison, at every sampling date the extractable Mn levels were similar in the burned plots (with or without BAER treatment) and higher ( $p < 0.05$ ) than in the unburned plots (Fig. 4), differences being greater immediately after the fire. Contrasting with the much more stable values over time observed in the unburned plots, the extractable Mn in the burned plots varied considerably during the study period, but without a clear temporal trend. Considering all samples together, the extractable Mn was three times higher ( $p < 0.05$ ) in the burned than in the unburned plots.

Most of the variation in Cu was explained by the treatment factor, although the sampling date factor and their interaction also had a notable effect (77%, 57% and 46% of variance explained, respectively, Table 1). The extractable Cu remained relatively constant in the unburned soil, whereas it was 31% lower ( $p < 0.05$ ) in all burned soils immediately after the fire and by an additional 25% one year later. BAERs treatments did not have measurable influence on this trace element which, globally considering all data, was decreased by 37% due to fire (Fig. 4).

Zinc (together with Fe) was the extractable trace element least influenced by the factors under study, and both the treatment and sampling date explaining only 30% of the variance in Zn (Table 1). Burning decreased the extractable Zn by around 30%, but differences between burned (BS, BSM and BSS) and unburned plots were rarely significant (Fig. 4).

**Fig. 4. (Next page).** Mean concentrations (bars) and standard errors (error bars;  $n=3$ ) of extractable Al (a), Fe (b), Mn (c), Cu (d), Zn (e) and Co in the 0-2 cm soil layer during the first year after the wildfire in the different treatments: US, unburned soil; BS, burned soil; BSM, burned soil with straw mulching; and BSS, burned soil with cereal seeding. Lowercase letters indicate significant differences among treatments for each sampling date and uppercase letters indicate significant differences among sampling dates for the same treatment ( $n = 3, p < 0.05$ ).





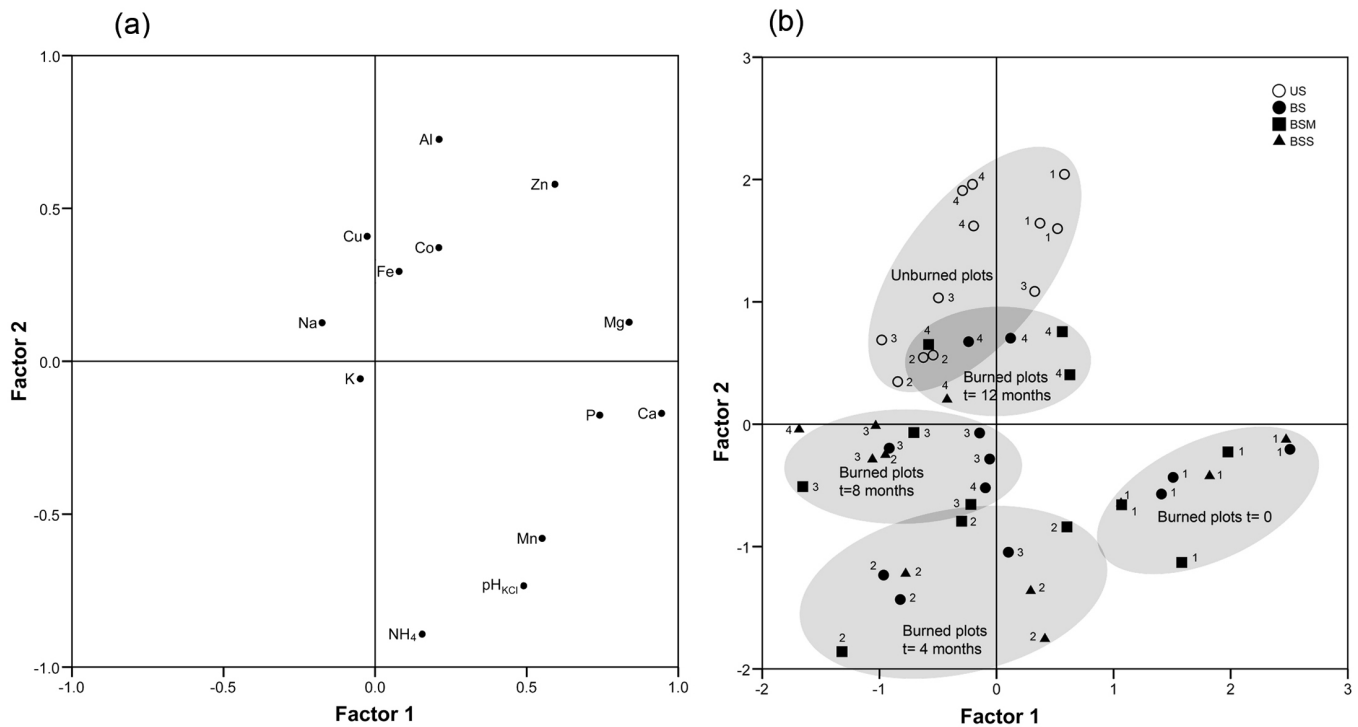
US BS BSM BSS

Treatment had a greater effect than sampling date on extractable Co (60% and 45% of variance explained, respectively), but the interaction between both factors did not have a significant effect (Table 1). The Co concentrations remained relatively constant throughout the study period in the unburned plots, but they were lower ( $p < 0.05$ ) in the burned plots immediately after the fire and also on the two last sampling dates (Fig. 4). In the whole dataset, Co levels were around 30% lower in the burned plots than in the unburned plots ( $p < 0.05$ ) and were not affected by the seeding or mulching treatments.

The first three factors obtained by principal component analysis jointly explained three quarters of the total variance (39.3%, 24.9% and 10.9%, respectively). The richness in divalent basic cations (Ca,  $r = 0.945$ ; Mg,  $r = 0.838$ ) and extractable P ( $r = 0.741$ ) were strongly associated with the positive side of factor 1 (Fig. 5a), to which the extractable Zn ( $r = 0.593$ ) and Mn ( $r = 0.551$ ) were also moderately associated, while no variables showed relevant correlation with the negative side. In factor 2 (Fig. 5a),

a strong polarization was found between the variables that defined the positive and negative side: its positive extreme was defined by the extractable contents of Al ( $r = 0.726$ ) and Zn ( $r = 0.579$ ), whereas the  $\text{NH}_4^+\text{-N}$  ( $r = -0.892$ ) and  $\text{pH}_{\text{KCl}}$  ( $r = -0.734$ ) were strongly associated with its negative arm, to which the extractable Mn was also moderately correlated ( $r = -0.579$ ). The concentrations of extractable K, Co and Cu, with strong correlations ( $r = 0.898$ ,  $0.834$  and  $0.677$ , respectively), and the extractable Na with moderate correlation ( $r = 0.515$ ), defined the positive side of the third factor, while Mn was the only variable on its negative side, with moderate correlation coefficient ( $r = -0.457$ ).

The distribution of topsoil samples on the plane defined by the first two factors (Fig. 5b) revealed that the unburned and the burned soil immediately after the fire appeared clearly opposed, with the burned soils sampled at  $t = 4$ ,  $t = 8$  and  $t = 12$  months forming a gradient that gradually approached that of the unburned soils, but which was still different even one year after the fire.



**Fig. 5.** Distribution of the studied variables (a) and soil samples (b) on the plane defined by factors 2 and 3, as obtained by Principal Component Analysis.

#### 4. Discussion

As a consequence of organic acids denaturation and the accumulation of ashes rich in oxides, hydroxydes and carbonates of basic cations (Chandler et al., 1983; Kutiel et al., 1990; Carballas, 1997; Certini, 2005; Pereira et al., 2011), soil pH, either in H<sub>2</sub>O or in KCl, increased due to the fire and remained significantly higher in the burned than in the unburned plots during the whole study period.

Wildfires of moderate to high severity convert a substantial fraction of soil organic N into inorganic forms (Certini, 2005) and a post-fire increase in soil NH<sub>4</sub><sup>+</sup>-N (a direct product of combustion) is often observed in burned soils. However, the effect observed in the present study was stronger (48 times vs. 2-13 times higher) than the reported by other authors (Weston and Attiwill, 1990; Prieto-Fernández et al., 1993; Couto-Vázquez and González-Prieto, 2006; Gómez-Rey et al., 2013a). Moreover, the effects we found lasted longer (more than 12 months vs. 1-6 months) than those after low- (Couto-Vázquez and González-Prieto, 2006; Gómez-Rey et al., 2013a) to medium-severity fires (Weston and Attiwill, 1990), and were similar to those of slash fire following timber harvesting reported by the latter authors. This difference can probably be attributed to the higher soil organic matter content, the more severe fire and the harsher post-fire weather in the present study because: a) moderate to high intensity fires convert most soil organic N to inorganic forms (Certini, 2005) and a higher soil organic-N content provides more substrate to be mineralized; and b) the harsher winter weather with freeze-thaw cycles often results in flushes in C and N mineralization (Neilson et al., 2001; Herrmann and Witter, 2002) and retards the recovery of vegetation cover, reducing, consequently, plant uptake of inorganic N.

We observed a much lower increase in NO<sub>3</sub><sup>-</sup>-N levels than in NH<sub>4</sub><sup>+</sup>-N levels immediately after the fire, as also found other authors (Chandler et al., 1983; Prieto-Fernández et al., 1993, and references therein), and a peak in the NO<sub>3</sub><sup>-</sup>-N concentration some weeks or months later, due to nitrification of the NH<sub>4</sub><sup>+</sup>-N produced by burning, which is consistent with previous findings (Covington and Sackett, 1992; Certini, 2005; Couto-Vázquez and González-Prieto, 2006). Also consistent with the findings of the latter authors, the NO<sub>3</sub><sup>-</sup>-N returned to pre-fire levels one year after the fire. Neither the mulching nor seeding treatment had significant effects on NH<sub>4</sub><sup>+</sup>-N and

NO<sub>3</sub><sup>-</sup>-N concentrations in the topsoil layer; therefore, these emergency stabilization treatments did not affect the net budget of N in the burned soil-plant system, as also found in a previous study (Gómez-Rey et al., 2013a). This was an expected result in the case of seeding which did not increase significantly the plant cover and, thus, the uptake of soil N by plants. In the case of mulching, a short-term immobilization of N could be expected taking into account the high C/N ratio of the applied straw, but the lack of differences with the control soil suggested that this expected immobilization was counterbalanced by other factors, probably including the effects of mulching on soil microclimate (moderating soil moisture and temperature oscillations) as well as on dissolved C and N availability and N fluxes (see Huang et al., 2012, and references therein).

We did not observe an immediate effect of fire on the concentrations of Na and K in the topsoil, unlike reported in other studies (Couto-Vázquez and González-Prieto, 2006; Gómez-Rey et al., 2013a); this result was undoubtedly due to differences in the sampling methodology. In the present study, we removed ash (rich in oxides and carbonates of basic ions; Certini, 2005) from the topsoil before collecting the soil samples, unlike in the above-cited studies. The increase in extractable Na and K in the topsoil 4 and 8 months after the fire can be explained by leaching of these cations from the layer of ashes and charred plant material in the burned soils (see Bodí et al., 2014, and references therein). Nonetheless, the increase in these cations in the unburned soil on those sampling dates was striking (especially the twofold increase in extractable Na). As the study site is 120 km inland, it is unlikely that important amounts of Na and K would be supplied (via rainwater) from marine sources because the falling off of marine salts was over 85% in the first 500 m inland and there are not published results for distances to the sea higher than 3 km (Meira et al., 2006, and references therein); moreover, any such input would be similar in burned and unburned soils, which was not the case. The higher levels of these cations in the autumn-winter period may be explained by: a) a decrease in nutrient uptake by plants during the dormant season, although no such effect was observed for other nutrients; and b) the deposition of ash from the burned area on the vegetation growing in the unburned area, and the subsequent leaching of the cations from the vegetation to the soil during rainy

periods. The latter hypothesis is supported by the following: a) nutrients can be removed off-site in particulate form by convection in smoke columns during fire or by surface wind transport (Certini, 2005; Alves et al., 2010; Bodí et al., 2014, and references therein), the major water-soluble ionic species in the removed particulates being  $\text{Na}^+$  (Alves et al., 2010) and  $\text{K}^+$  (Falkovich et al., 2005); and b) the prevailing wind during the wildfire and the following week was easterly, i.e. it blew from the direction of the main burned area to the unburned plots, which were sited at the eastern border of the area affected by the wildfire.

Among the major cations, Ca was the only one that increased (transiently and significantly) just after the fire. This result may not be due to Ca supplied by ashes or charred vegetation, because these materials were removed just before soil sampling. Therefore, the immediate post-fire increment of soil extractable Ca must be due to direct effects of fire on the topsoil layer and perhaps related to the partial combustion of SOM, that, by reducing the total mass, could lead to a relative enrichment in nutrients. However, similar changes in the other divalent cation (Mg) were not observed, as the availability of Mg did not follow a clear trend, thus complicating the interpretation of these results. Post-fire changes in soil Ca and Mg availability varied widely in magnitude, increments ranging from two- (Couto-Vázquez and González-Prieto, 2006) to 5-7 fold (Kutiel and Inbar, 1993; Gómez-Rey et al., 2013a), and also in persistence, the effects being from short-lived (1-3 months, Adams and Boyle 1980; Couto-Vázquez and González-Prieto, 2006) to long-lasting (1-3 years, Khanna and Raison, 1986; Simard et al., 2001; Gómez-Rey et al., 2013a). Considering all samples together, Ca was also the only cation that tended to be present at slightly higher concentrations in the burned plots than in the unburned plots and that is positively and significantly correlated with pH. The emergency stabilization treatments did not have any effects on basic cations, which is consistent with the findings of a previous study (Gómez-Rey et al., 2013a).

The increase in extractable P immediately after the fire was probably related to the oxidation of organic P and a consequent increase in inorganic P (Saá et al., 1993); moreover, within the pH range of the studied plots, P solubility increases with pH and, thus, in the burned plots. The lack of any effects of seeding and mulching on the extractable P, as also found (Gómez-Rey et al., 2013a), suggested that these

treatments did not affect phosphatase activity or the P fractions distribution in the burned topsoil.

The lower concentrations of soil extractable Al in burned than in unburned plots were correlated with the higher pH of the former and are consistent with the reduction in exchangeable Al in surface soils after repeated prescribed fires (Pivello et al., 2010). Opposite trends have been usually reported for extractable Fe and Mn (decrease and increase due to the fire, respectively) in recently burned soils (González-Parra et al., 1996; Certini, 2005; García-Marco and González-Prieto, 2008; Close et al., 2011; Gómez-Rey et al., 2013a) as was also observed in the present study, although Pereira et al. (2011) found a decrease in water soluble Fe and Mn in ashes compared with the original oak litter. However, in comparison with the effects observed after experimental fires (García-Marco and González-Prieto, 2008; Gómez-Rey et al., 2013a), the effects observed in the present study, after a wildfire, were more ephemeral for Fe and much longer lasting for Mn. Within the pH range of the studied plots, the solubility of both Fe and Mn decreases with pH. Therefore, the negative correlation of pH with the extractable Fe was logical, but the positive one with Mn suggested that factors other than pH are involved in the post-fire increment of extractable Mn, maybe the mineralization of organic Mn contained in the litter because it usually accumulates in dead leaves of various forest species, even when the soil has only minor concentrations of this element (González-Parra, et al., 1996).

Although an initial increase (Close et al., 2011; Stankov-Jovanovic et al., 2011; Gómez-Rey et al., 2013a) or no short-term fire effects (García-Marco and González-Prieto, 2008) on available Cu have been reported, we observed a decrease in the concentration of this element in the study plots. This difference may be related to site specific characteristics. As the increment we observed in pH must contribute to increase Cu availability, other(s) fire-derived effect(s) on soil physical or chemical properties must counterbalance the effect of pH, leading to a net reduction of extractable Cu. These fire-derived effects could be related with the organic matter content, the amounts and forms of oxides and carbonates, charge characteristics or mineral composition that influence the availability Cu and other trace elements (Fageria et al., 2002). Differences in the concentrations of extractable Cu between the burned and unburned plots increased by the end of the first post-fire year,

probably due to solute or particulate Cu losses, as reported in several studies (Chirenje et al., 2002; Smith et al., 2011; Gómez-Rey et al., 2013c). Although the scarce information available did not indicate any significant post-fire changes in extractable Co (Aref et al., 2011; García-Marco and González-Prieto, 2008; Gómez-Rey et al., 2013a), the present findings indicate a slight reduction in soil Co immediately after the fire and a further decrease in the second half of the study period. These contrasting results may be due to differences in soil type, climate, vegetation and fire severity with the study of Aref et al. (2011) and in sampling strategy and fire type compared with the studies of García-Marco and González-Prieto (2008) and (Gómez-Rey et al., 2013a). The latter authors jointly sampled the topsoil with the ash layer (usually enriched in nutrients compared with the soil; Khanna et al., 1994; Pereira et al., 2011) after experimental fires, while in the present study we collected the soil-only samples after a medium-to-high severity wildfire. The (rarely significant) decrease of soil extractable Zn we observed was in agreement with the reduction of water-soluble Zn in ashes from the litter layer of an oak forest after a low severity prescribed fire (Pereira et al., 2011), but contrasts with the slight and transient increase after prescribed fires reported by several authors (García-Marco and González-Prieto, 2008 and Gómez-Rey et al. 2013a, in soil+ashes samples; Close et al., 2011). As Zn solubility is inversely related with pH, a decrease in burned soils, as we found, is expected unless other fire-derived effect(s) on soil physical or chemical properties counterbalance the effects of the usual post-fire increment in pH. Regarding the soil stabilization treatments, we did not observe any consistent effects on extractable trace elements.

Summarizing the preceding discussion, the plane of factors 1 and 2 extracted by Principal Component Analysis revealed changes in the burned plots so that they increasingly resembled the unburned plots, due to a relatively fast decrease in extractable Ca and Mg accompanied by a slower decrease in the concentrations of Mn and, in particular,  $\text{NH}_4^+\text{-N}$ . Soil extractable Al and Zn were the studied variables that best differentiated the burned and unburned soil plots by the end of the study period. One year after the fire (late summer), all BSM plots and two thirds of BSS and BS plots were loosely grouped with the unburned plots sampled in the preceding winter and late spring, indicating that at least 4-8 additional months will be necessary for full recovery of the

studied chemical properties in burned plots.

## 5. Conclusions

The important post-fire changes in soil pH (increase) and soil extractable macronutrients and trace elements (increase of  $\text{NH}_4^+\text{-N}$ , Ca, P, Mn, Na and K; decrease of Al, Fe, Cu, Co and Zn) tended to disappear during the first year after the fire. The burned plots gradually became similar to the unburned plots thanks to a relatively rapid decrease in some extractable nutrients (Ca, Mg > Mn >  $\text{NH}_4^+\text{-N}$ ) and a slow increase in others (Al and Zn), although at least 4-8 additional months will be necessary before full recovery of the burned plots. The emergency stabilization treatments studied (cereal seeding and straw mulching) did not significantly modify the soil concentrations of any of the individual macronutrients or trace elements considered. However, the similarity with the unburned plots was higher for the mulch-treated than for the seeded plots, when all the studied variables were jointly considered. As mulching does not have any negative effects on soil extractable nutrients and, according with other studies, greatly reduces soil losses by erosion, it appears to be a useful emergency stabilization treatment for burned soils in temperate-humid regions.

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