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Short- and medium- term effects of fire and fire-fighting chemicals

on soil micronutrient availability

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Abstract

The impact of fire and three fire-fighting chemicals (FFC) on soil micronutrient availability was evaluated 1, 90 and 365 days after a prescribed fire. Five treatments were considered: unburnt soil (US) and burnt soil with 21 m⁻² of water (BS) or water with foaming agent Auxquímica RFC-88 at 1% (BS+Fo), Firesorb at 1.5% (BS+Fi) and FR-Cross ammonium polyphosphate at 20% (BS+Ap). Prefire contents of available micronutrient were homogeneous among plots and high (Fe, Zn) or insufficient (Co, Cu, Mn) for plant nutrition. At t=1 day, Fe availability decreased greatly in burnt treatments, with significant differences in BS+Fi (-50%) and BS+Ap (-75%), contrasting with Fe richness of the ammonium polyphosphate. The fire induced a significant increase (9-16x) of available Mn in burnt treatments that lasted for at least three months; the FFC effect on soil available Mn was imperceptible, despite the noticeable amounts of Mn they supplied (especially Firesorb and ammonium polyphosphate). In burnt soils, the Fe/Mn ratio also decreased strongly (92-99%) and significantly till t=90 days. A high increase was also found, at t=1 day, for the available Zn in all burnt treatments and, although the ammonium polyphosphate provided more Zn than the Firesorb, the increment was only significant in BS+Fi plots (+100%). Neither fire nor FFC effects on soil Cu availability were found. The slight increase of Co availability in BS, BS+Fo and BS+Ap at t=1 day was followed by a transient decrease in all burnt treatments at t=90 days. Except the Mn and the Fe/Mn ratio in BS+Ap, which remained significantly higher and lower, respectively, the indices of available micronutrients at t=365 days in all burnt soils were similar to the pre-fire levels.

Key words: Available micronutrients; burnt soil; fire-fighting chemicals; prescribed fire; wildfire.

1. Introduction

Forest fires are a global problem, with increasing frequency and extent, that produce important impacts on soils, whose physical, chemical and biochemical properties are more or less affected depending on fire intensity. Fires lead to significant removal of soil organic matter, deterioration of soil structure and porosity, considerable losses of nutrients (through volatilisation,

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ash entrapment in smoke columns, leaching and erosion), and marked quantitative and qualitative alteration of the microbial and soil-dwelling invertebrate communities (Certini, 2005).

Fires induce changes in soil nutrient balances and biogeochemical cycles as a result of biomass combustion and the increase of runoff and soil erosion (Soto et al., 1997). Most studies on the effects of fire on soil chemical quality have been focussed on the determination of changes in organic matter (C, N) and available macronutrients (P, Ca, Mg, Na and K) (Carballas, 1997; Couto-Vázquez and González-Prieto, 2006; Khanna and Raison, 1986; Úbeda et al., 2005). The availability of macronutrients generally increases after burning, but it is dependent on the type of nutrient, vegetation and soil, and also on the pathway of leaching processes (Kutiel and Shaviv, 1992). In the case of micronutrients, González-Parra et al. (1996) found that both the total content and the easily reducible forms of Mn increased significantly after fire, thanks to Mn supplied by the ash, while the exchangeable Mn did not show any variation. Presumably, Fe, Cu and Zn could behave similarly to Mn. However, specific works analysing available micronutrients in soil, generally present in small quantities but essential for plant development, are still lacking (Certini, 2005), despite its interest in the recovery of burnt soils and vegetation.

Wildfire fighting tools include ground and aerial application of water added with firefighting chemicals (fire retardants and fire suppressant foam products) which in many countries are extensively used in fire control and fire prevention campaigns from the beginning of 1930's (Giménez et al., 2004). Since most fire-fighting chemicals are typically applied in environmentally sensitive areas, natural areas and areas set aside for wildlife, there is a need to determine their potential effects on terrestrial and aquatic ecosystems (Basanta et al., 2002). Despite the benefits they provide in terms of fire extinction, recent studies indicate negative impacts, especially in aquatic environments (Angeler et al., 2004). Several articles reported fish mortality (Dodge, 1970; Minshall and Brock, 1991), toxicity on algae and zooplankton species (McDonald et al., 1995), on amphipods (McDonald et al., 1997), and fish larvae (Buhl and Hamilton, 1998, 2000; Gaikowsky et al., 1996 a,b; Little and Calfee, 2002). However, in spite of its interest, their impacts on soil physical, chemical and biological properties have been scarcely studied until recently (see Giménez et al., 2004). Basanta et al. (2002) studied the short-term effects of a synthetic acrylamide polymer, used as fire retardant, on biochemical properties of both heated and unheated soil samples collected from two different forest ecosystems and Díaz-Raviña et al. (2006) determined the influence of the same fire retardant on the microbial community structure, under laboratory conditions, using two different textured soils under pine forest. Couto-Vázquez and González-Prieto (2006) reported the short- and mediumterm impact of three fire-fighting chemicals on several properties (pH, total C and N, inorganic forms of N, P and available macronutrient contents) of a burnt soil. Nevertheless, no information about the effect of these products on soil micronutrient availability has been found in the bibliographic search done.

Therefore, the aim of this paper is to study the short- and medium-term impact of fire and three fire-fighting chemicals (foaming agent RFC-88 from Auxquímica, Terpolymer Firesorb from Stockhausen and ammonium polyphosphate FR from Cross), applied immediately after a prescribed fire, on soil micronutrient availability and their possible effect on the post-fire recovery of soil and plants.

2. Material and methods

The soils used in this study come from the experimental field located at Alto da Pedrada (Tomiño, Galicia, NW Spain; UTM coordinates 29T ⁰⁵182 -⁴⁶509; altitude of 455 m a.s.l.) previously employed by Couto-Vázquez and González-Prieto (2006). The soil, developed over a parent material of paragneises and with a slope of 18-19%, has a vegetation cover dominated by *Ulex*, *Chamaespartium* and *Erica* 50-60 cm heigh. In the experimental assay described by these authors, five *in situ* treatments were considered: a) unburnt soil (US) as a control; b) burnt soil with 21 m⁻² of water (BS); c) burnt soil with 21 m⁻² of water plus foaming agent Auxquímica RFC-88 at 1 % (BS+Fo); d) burnt soil with 21 m⁻² of water plus Firesorb at 1.5 % (BS+Fi); and e) burnt soil with 2 m⁻² of water plus FR Cross ammonium polyphosphate at 20 % (BS+Ap). After a prescribed fire (i.e. with the fire extinguished but with the soil still warm), burnt soil treatments were arranged in a fully randomized design with four replications and 1 m separation around each plot (4 x 4 m), whereas the four unburnt soil replicates were established along the slope and adjacent to the burnt ones (see Couto-Vázquez and González-Prieto, 2006).

Soil samples were taken from 0 to 2 cm depth immediately before burning and 1, 90 and 365 days after the prescribed fire. Five 15 x 15 cm squares, uniformly distributed around each plot, were sampled and then sieved (< 4 mm), mixed and thoroughly homogenized at the laboratory.

Available Fe, Mn, Cu, Zn, Co and Mo were extracted from soils as described by Lindsay and Norvell (1978): a) the extracting solution consisted of 0.005 M DTPA (diethylenetriaminepentaacetic acid), 0.01 M CaCl_2 and 0.1 M TEA (triethanolamine) buffered at pH 7.30; b) the extraction ratio (w/v) was 1:2; and c) the shaking time was 2 hours, although, instead of a horizontal shaker, a rotatory shaker was used. Extracts were analysed for all the available micronutrients by inductively coupled plasma optical emission spectrometry (Varian Vista Pro simultaneous ICP-OES).

The total micronutrient content of the fire-fighting agents was measured after a microwave digestion for destroying the organic matter in samples and, hence, to allow the assessment of the elements by ICP-OES without interference. Diluted solutions (Fo: 5% (v/v), Fi: 0.1 % (m/v) and Ap: 1% (v/v)) of the commercial products were prepared. Aliquots of 10 ml of the diluted solutions were digested on duplicate for 50 min with 5 ml HNO₃ 65 % and 5 ml H₂O₂ 30 % in a high performance microwave digestion unit (Milestone 1200 mega, Sorisole, Italy). Once cooled, the solutions were filtered through quantitative filter paper (Filter-lab 1242, 90 mm diameter), transferred to 50 ml volumetric flasks and made to volume with water. The total micronutrient content in the fire-fighting products and the micronutrient amount added with their application to the 0-2 cm soil layer are shown in Table 1. Analytical grade chemicals were obtained from Merck Chemical Co. and Scharlau Chemie S.A. All aqueous solutions were prepared with type I water (electrical conductivity max: 0.056 μ S cm⁻¹ at 25 °C; electrical resistivity min: 18.0 M Ω cm at 25 °C; total organic C max: 100 μ g l⁻¹; Na max: 1 μ g l⁻¹; Cl⁻ max: 1 μ g l⁻¹; total Si max: 3 μ g l⁻¹) (ASTM, 1999).

Data of soil variables analysed at several dates after the fire were statistically analysed by ANOVA; equality of variances among treatment-sampling time groups was checked with the Levene's test. In the case of homocedasticity, significant differences among the mean groups were established at P < 0.05 using the Tukey test. In the case of unequal variances, the original data were subjected to Cox-Box transformations to obtain equality of variances, and significant differences among the mean groups were then established at P < 0.05 using the Tukey test. If variances remained heterogeneous after Cox-Box transformations, a Games-Howell test was used to find out significant differences (P < 0.05) among groups.

3. Results

Before the prescribed fire, there were no significant differences among the plots assigned to the different treatments for any of the available micronutrient concentration analysed. This fact shows spatial homogeneity of the experimental field.

Immediately after the fire, available Fe content decreased in burnt soils (either treated or not with fire-fighting chemicals) compared with the unburnt soils, although significant differences were only found in burnt soils treated with Firesorb and ammonium polyphosphate (Fig. 1). The lowest Fe content was measured in BS+Ap (82 mg kg⁻¹), five times lower than the value recorded for US (426 mg kg⁻¹). Ninety days after the fire, the Fe concentration found in burnt soils, either treated or not with fire-fighting agents, was still lower than that found in unburnt soils, although the difference was only significant for BS+Ap. However, one year after the fire, the Fe content increased in all burnt soils until levels comparable to those obtained for unburnt soils.

Initially, the available Mn content in all soils was around 1 mg kg⁻¹, but immediately after the prescribed fire it increased significantly in all burnt soil treatments, that did not differ among them (Fig. 2). The highest increase was found in BS+Ap (16 times higher than US) and the lowest in BS (11 times higher than US). At t = 90 days, in all burnt soil treatments the levels of available Mn continued to increase in comparison with the corresponding ones at t=1 d, except BS+Ap, and remained significantly higher than in US but, again, significant differences were not found among fire-fighting chemicals. In contrast, one year after the fire, the Mn content decreased significantly in all burnt soils, reaching values near to those of the unburnt soils during the whole studied period, although the level of available Mn in BS+Ap was still significantly higher than in the other treatments (except BS).

The Fe/Mn ratio follows the same temporal trend than the Fe content (Fig. 3). Irrespectively of the burnt soil treatment, the Fe/Mn ratio decreased significantly after the prescribed fire, this decrease lasting for at least three months. However, one year after the fire the Fe/Mn ratio has increased significantly in all burnt treatments, compared with the two preceding sampling dates, reaching values similar to that of the unburnt soil (except in BS+Ap). Besides the fire effect on the Fe/Mn ratio, there was also a long-lasting effect due to the addition of ammonium polyphosphate, the Fe/Mn ratio in BS+Ap being the lowest among all treatments at any post-fire sampling date.

Fig. 4 shows the evolution with time of the available Cu content in soils. No significant differences were found among treatments at any sampling date for Cu levels that were within tight ranges at each date: 0.14-0.21, 0.17-0.25, 0.09-0.14 and 0.09-0.17 mg kg⁻¹ at time 0, 1, 90 and 365 d, respectively. Moreover, for any given treatment the changes in soil available Cu were hardly ever significant during the studied period.

Compared with the natural levels of available Zn in all plots before the prescribed fire (very homogeneous around 1.30 mg kg⁻¹; Fig. 5), a noticeable increase was found in all burnt treatments at t=1 (+40 % in BS, +75 % in BS+Fo and BS+Ap), although the increase was only significant in BS+Fi (+100 %). The differences among treatments were less pronounced at t=90 d and disappeared one year after the fire due to the decrease of the available Zn content in all burnt treatments, which was statistically significant except for BS+Ap.

Before the prescribed fire, the available Co content ranged from 0.06 to 0.11 mg kg⁻¹, without significant differences among plots (Fig. 6). One day after burning, the Co content increased in two burnt soil treatments (BS and BS+Fo) and decreased in the others (BS+Fi and BS+Ap), but statistically significant differences were not found among them or with the pre-fire values. Three

months later, the Co content decreased in all treatments, being significantly lower in BS, BS+Fo and BS+Ap than the corresponding contents found immediately after burning. At *t*=365 days, the Co content was slightly higher than 9 months before, but only significantly for BS+Ap.

Irrespectively of soil treatment and sampling date, in more than 90 % of the soil samples analysed the levels of available Mo (data not shown) were close or below the detection limits of the analytical equipment used (0.03 mg kg^{-1}). For this reason, the Mo data obtained were not statistically analysed.

4. Discussion

Before the prescribed fire, the content of bioavailable Fe found in the plots ranged from 348 to 426 mg kg⁻¹, surpassing the threshold of 250 mg kg⁻¹ that, according to Jones (2003), indicates a very high availability of this micronutrient. Immediately after the fire, there was a generalized decrease in the available Fe: -25 to -30 % in BS and BS+Fo, - 50 % in BS+Fi and -75 % in BS+Ap, the reduction being significant in the two latter treatments. The fire induced depletion of Fe levels could be associated with losses (by convection in smoke columns, transport by wind, erosion and leaching) and/or conversion to insoluble oxidized forms in soils, that have been reported for several nutrients (Raison et al., 1985a,b; Khanna and Raison, 1986; Brye et al., 2002). An additional decrease in the available Fe levels was observed in the BS+Fi and BS+Ap plots. In the latter treatment this decrease was strong and contrasts with the substantial amount of total Fe supplied by this firefighting chemical (around 350 mg kg⁻¹; see Table 1); this result could be related with the higher pH and/or the very high content of available NH₄⁺ and P reported for this treatment by Couto-Vázquez and González-Prieto (2006). The differences of available Fe among treatments decreased with time, being less important at t=90 d and not significant at t=365 d. The recovery of the available Fe content in the burnt soils at the medium term took place simultaneously with a decrease of pH in all burnt plots and also with a strong reduction of the NH⁺₄ and P content in the BS+Ap treatment (see Couto-Vázquez and González-Prieto, 2006). The transient post-fire decrease of the available Fe could be specially important for plants considering that: a) fires strongly reduce soil microbial populations (Díaz-Raviña et al., 1996, 2006); and b) a decrease in microbial siderophores seems implicated in some cases of post-fire iron deficiency (Perry et al., 1984; Ballard, 2000).

The great post-fire decrease of available Fe could be an important fertility problem in soils with low levels of plant available Fe, generally alkaline and calcareous soils.

Contrarily to Fe, the pre-fire levels of plant available Mn (0.14-0.22 mg kg⁻¹) were lower than the adequate range for normal plant growth indicated by Jones (2003). Compared with the unburnt control, the prescribed fire induced an important (9-16x) and significant increase of the available Mn levels in all burnt soils that lasted for at least three months. At the medium-term (one year later), the available Mn in burnt soils decreased until levels comparable to those of US except in BS+Ap, with Mn contents still 2-3 times higher. In spite of the noticeable contribution of the Firesorb (0.3 mg kg⁻¹ soil) and the ammonium polyphosphate (0.7 mg kg⁻¹ soil) to the Mn pool of the soil studied (around 1-2 mg kg⁻¹), no perceptible effects of the fire-fighting agents in the available Mn content were found. The initial increase of available Mn could be due to: a) the incorporation of vegetationderived ashes that could be enriched in this element (Mn usually accumulates in leaves of forest species, reaching amounts of > 1000 µg g⁻¹; see references in González-Parra, 1996); and b) the fire induced changes in the main soil constituents (organic matter, clay, oxides, minerals, etc).

As the amount and the chemical composition of ashes vary depending on the fire intensity

and the vegetation characteristics (Carreira and Niell, 1995), contrasting results have been reported on post-fire Mn availability. González-Parra et al. (1996) observed a significant increase in total and easily reducible oxide forms of Mn, partly attributed to Mn supplied by the ashes of *P. pinaster*, while the content of exchangeable Mn (extracted with 1 M ammonium acetate solution at pH 7) did not vary; similar results were found by Solla-Gullón et al. (2001) in soils added with ashes from *Pinus* bark. However, Brye (2006) observed a significant decrease in available Mn (extracted with Mehlich 3) as the result of 12 years of annual burning on a tall-grass prairie.

The great post-fire accumulation of Mn found in this study may be harmful for seed germination and/or plant growth, because of the possible antagonistic effects on the absorption of other nutrients essential for plant development, as usually reported for Mg, Fe and other micronutrients (YeunKyu, 2004; Lidon, 2002).

The Fe/Mn ratio before burning was very high (> 400), but after the prescribed fire it decreased strongly (by 92-99 %) and significantly in the burnt soils until three months. One year later, the ratio increased significantly in all burnt soils, reaching values similar to those found in US. The BS+Ap treatment showed the lowest Fe/Mn ratio at any sampling time after burning, although the differences were not always statistically significant. The strong decrease of the Fe/Mn ratio due to the fire and its persistence for at least 3 months could exacerbate post-fire deficiencies of available Fe in soils poor in this micronutrient (which is not the case of the studied soils) as a consequence of the antagonistic effect of Mn on Fe uptake, reducing or delaying the recovery of the vegetation cover.

Initially, all plots showed a high content of plant available Zn (1.24-1.34 mg kg⁻¹) according to Jones (2003). The prescribed fire produced an important (25-100 %) increase in the availability of this micronutrient during at least three months, although only BS+Fi at t=1 d showed values significantly different. This short-term increase could be due to the Zn provided by the vegetal-derived ashes, which contain significant quantities of this element (Khanna et al. 1994), although some fire-induced changes in the soil constituents (mineralization of organic matter, etc) could also contribute to this increase as well as the Zn provided by the fire-fighting chemical in the BS+Fi treatment (see Table 1). One year after the fire, in all burnt plots the available Zn contents decreased to the pre-fire levels, with the relative exception of the BS+Ap treatment.

The availability of Cu in all plots before the prescribed fire was very low (< 0.2 mg kg⁻¹; see Jones, 2003). After the burning, neither fire nor fire-fighting chemicals effects on soil available Cu were found, although Brye (2006) reported that annually prescribed burning for 12 years increased significantly the Mehlich 3-extractable Cu in soils under tall-grass prairies.

The methodology for the extraction of the available Co and Mo is not as standardized as that for the main micronutrients previously discussed. Among the extractants proposed for the analysis of available Mo are ammonium oxalate at pH 3.3, hot water, anion exchange resin and ammonium bicarbonate-DTPA (Sims, 1996). In the case of the available Co, acetic acid and EDTA or DTPA extractants have been employed with limited success, because Co extraction is greatly affected by temperature and extraction time (Sims, 1996; Kumar et al., 2004). Taking into account this situation and the fact that various of the extractants proposed included a chelating agent, like EDTA and DTPA, we use the soil DTPA extracts to measure also the available Co and Mo contents due to its interest for plant growth, specially in burnt soils. Both are constituents of certain enzymes involved in redox processes such as nitrate reductase, xanthine dehydrogenase, aldehyde oxidase, sulfite oxidase (probably) and nitrogenase that plays a key role in atmospheric N₂ fixation by legumes (Zimmer and Mendel 1999). The pre-fire levels of available Co in all plots (0.06-0.11 mg kg⁻¹) were below the critical threshold of 0.24 mg kg⁻¹ in soil DTPA extracts reported by Kumar et al. (2004). Immediately after the fire, the availability of Co increased in the BS, BS+Fo and BS+Ap treatments, but not significantly. Hereinafter, there was a transient decrease of the available Co in all burnt treatments at *t*=90 d and a subsequent recovery of the Co levels one year later.

In the case of available Mo, the levels were below the detection limit of the analytical instrument used and, therefore, the data obtained were not statistically analysed. This result could be due either to a low soil Mo content or to the inadequacy of DTPA for the extraction of available Mo. This question will need further research because, although the concentration of soil assimilable Mo is usually sufficient for plants, it can be limiting in acid soils where it is joined to Fe and Al oxides. Moreover, low availability of Mo and toxicity of Mn can prevent the acquisition of N_2 by legumes (Rosolem and Caires, 1998) that play an important role in the recovery of N cycling in burnt ecosystems, by counteracting the losses of N in the soil-plant system as a result of fire (Towne and Knapp 1996; Hendricks and Boring 1999).

Conclusions

The prescribed fire caused short-term changes in the soil micronutrient availability, increasing that of Mn and Zn and decreasing that of Fe and Co; conversely, no effect was found on Cu availability. Mn and Zn increase could result in part from the accumulation of vegetal-derived ashes and some fire-induced changes in the soil constituents, although the amounts provided by the Firesorb and ammonium polyphosphate also contribute. Depletion of Fe and Co contents could be associated with losses and conversion to insoluble forms due to changes in the soil pH and other nutrient contents; this decrease was intensified in the treatments with ammonium polyphosphate (Fe, Co) and Firesorb (Fe). The only medium-term effect found was that of the ammonium polyphosphate on Mn availability and Fe/Mn ratio.

These results provide new insight concerning the influence of fire on micronutrient availability that are useful to understand its effect on the post-fire recovery of soils and plants. The great post-fire accumulation of Mn combined with the depletion of Fe, and their persistence for at least 3 months, suggest a possible fertility problem that could delay the recovery of the vegetation cover, which is irreplaceable to protect the burnt soil against erosion.

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REFERENCES

- Angeler DG, Rodriguez M, Martin S, Moreno JM. Assessment of application-rate dependent effects of a long-term fire retardant chemical (Fire Trol 934 (R)) on *Typha domingensis* germination. Environ Int 2004; 30: 375-81.
- ASTM. Standard Specification for Reagent Water. In: Annual Book of ASTM Standards; American Society for Testing Materials: West Conshohocken, PA, 1999; p 11.01.

- Ballard, TM. Impacts of forest management on northern forest soils. Forest Ecol Manag 2000; 133: 37-42.
- Basanta MR, Diaz-Raviña M, González-Prieto SJ, Carballas T. Biochemical properties of forest soils as affected by a fire retardant. Biol Fertil Soils 2002; 36: 377-83.
- Brye, KR. Soil physiochemical changes following 12 years of annual burning in a humid-subtropical tallgrass prairie: a hypothesis. Acta Oecol 2006; 30: 407-13.
- Brye KR, Norman JM, Gower ST. The fate of nutrients following three and six-year burn intervals in restored tallgrass prairie in Wisconsin. Am Midl Nat 2002; 148: 28-42.
- Buhl KJ, Hamilton SJ. Acute toxicity of fire-retardant and foam suppressant chemicals to early life stages of chinook salmon (*Oncorhynchus tshawytscha*). Environ Toxicol Chem 1998; 17: 1589–99.
- Buhl KJ, Hamilton HJ. Acute toxicity of fire-control chemicals, nitrogenous chemicals and surfactants to rainbow trout. Trans Am Fish Soc 2000; 129: 408–18.
- Carballas T. Effects of fires on soil quality. Biochemical aspects. In: Balabanis P, Eftichidis G, Fantech, R editors. Forest fire risk and management. European Commission, Brussels, Belgium, 1997, pp. 249-61.
- Carreira JA, Niell FX. Mobilization of nutrients by fire in a semiarid gorse-shrubland ecosistem of Southern Spain. Arid Soil Res Rehabil 1995; 9: 73-89.
- Certini G. Effects of fire on properties of forest soils: a review. Oecologia 2005; 143: 1-10.
- Couto-Vázquez A, González-Prieto SJ. Short- and medium-term effects of three fire fighting chemicals on the properties of a burnt soil. Sci Total Environ 2006; 371: 353-61.
- Díaz-Raviña M, Bååth E, Martín A, Carballas T. Microbial community structure in forest soils treated with a fire retardant. Biol Fertil Soils 2006; 42: 465-71.
- Díaz-Raviña M, Prieto A, Acea MJ, Bååth E. Bacterial activity in a forest soil afer soil heating and organic amendments measured by the thymidine and leucine incorporaron techniques. Soil Biol Biochem 1996; 28: 419-26.
- Dodge M. Nitrate poisoning, fire retardants and fertilizers any connection? J Range Manag 1970; 23: 244–7.
- Gaikowsky MP, Hamilton SJ, Buhl KJ, McDonald SF, Summers CH. Acute toxicity of three fireretardant and two fire-suppressant foam formulations to the early life stages of rainbow trout (*Onkorhynchus mykiss*). Environ Toxicol Chem 1996a; 15: 1365–74.
- Gaikowsky MP, Hamilton SJ, Buhl KJ, McDonald SF, Summers CH. Acute toxicity of firefighting chemical formulations to four life stages of fathead minnow. Ecotoxicol Environ Saf 1996b; 34: 252–63.
- Giménez A, Pastor E, Zárate L, Planas E, Arnaldos J. Long-term forest fire retardants: a review of quality, effectiveness, application and environmental considerations. Int J Wildland Fire 2004; 13: 1-15.
- González Parra J, Cala Rivero V, Iglesias López T. Forms of Mn in soils affected by a forest fire. Sci Total Environ 1996; 181: 231-6.
- Hendricks JJ, Boring LR. N-2-fixation by native herbaceous legumes in burned pine ecosystems of

the southeastern United States. Forest Ecol Manag 1999; 113: 167-77.

- Jones JB. Agronomic Handbook: management of crops, soils and their fertility. CRC Press, Boca Raton, 2003, 450 pp.
- Khanna PK, Raison RJ. Effect of fire intensity on solution chemistry of surface soil under a *Eucalyptus pauciflora* forest. Aust J Soil Res 1986; 24: 423-34.
- Khanna PK, Raison RJ, Falkiner RA. Chemical properties of ash derived from *Eucalyptus* litter and its effects on forest soils. Forest Ecol Manag 1994; 66: 107-25.
- Kumar B, Prasard NK, Roy HK. Cobalt nutrition of stylo (*Stylosanthes guianensis* L.) in acid soil. J Research, Birsa Agricultural University 2004; 16: 23-29.
- Kutiel P, Shaviv A. Effects of soil type, plant composition and leaching on soil nutrients following a simulated forest-fire. Forest Ecol Manag 1992; 53: 329-43.
- Lidon FC. Micronutrient uptake and translocation in Mn-treated rice. J Plant Nutr 2002; 25: 757-68.
- Lindsay WL, Norvell WA. Development of a DTPA soil test for zinc, iron, manganese, and copper. Soil Sci Soc Am J 1978; 42: 421-8.
- Little EE, Calfee RD. Effects of fire retardant chemical products on fathead minnows in experimental streams. Report to US Forest service; 2002. http://www.cerc.usgs.gov/pubs/center/pdfDocs/ECO-04.pdf.
- McDonald SF, Hamilton SJ, Buhl KJ, Heisinger JF. Acute toxicity of fire control chemicals to *Daphnia magna* (Straus) and *Elenastrum capricornutum* (Printz). Ecotoxicol Environ Saf 1995; 33: 62–73.
- McDonald SF, Hamilton SJ, Buhl KJ, Heisinger JF. Acute toxicity of fireretardant and foamsuppressant chemicals to *Hyalella azteca* (Saussure). Environ Toxicol Chem 1997; 6: 1370–6.
- Minshall GW, Brock JT. Observed and anticipated effects of forest fire on Yellowstone stream ecosystems. In: Keiter RB, Boyce MS, editors. Greater Yellowstone ecosystem. Redefining America's wilderness heritage. New Haven, CT, USA: Yale University Press; 1991. pp. 123–35.
- Perry DA, Rose SL, Pilz D, Schoenberger MM. Reduction of natural ferric iron chelators in disturbed forest soils. Soil Sci Soc Am J 1984; 48: 379-82.
- Raison RJ, Khanna PK, Woods PV. Transfer of elements to the atmosphere during low-intensity prescribed fires in 3 Australian subalpine eucalypt forests. Can J For Res 1985a; 15: 657-64.
- Raison RJ, Khanna PK, Woods PV. Mechanisms of element transfer to the atmosphere during vegetation fires. Can J For Res 1985b; 15: 132-40.
- Rosolem CA, Caires EF. Yield and nitrogen uptake of peanuts as affected by lime, cobalt, and molybdenum. J Plant Nutr 1998; 21: 827-35.
- Sims JL. Molybdenum and Cobalt. In: Sparks, DL, editor. Methods of Soil Analysis: Chemical Methods. Part 3. SSSA Book Series No. 5, Madison, Wisconsin, USA, 1996, pp. 723-37.
- Solla-Gullón F, Rodríguez-Soalleiro R, Merino A. Evaluación del aporte de cenizas de madera como fertilizante de un suelo ácido mediante un ensayo en laboratorio. Invest Agr: Prod Prot Veg 2001; 16: 379-93.

- Soto B, Basanta R, Diaz-Fierros F. Effects of burning on nutrient balance in an area of gorse (*Ulex europaeus* L.) scrub. Sci Total Environ 1997; 204: 271-81.
- Towne EG, Knapp AK. Biomass and density responses in tallgrass prairie legumes to annual fire and topographic position. Am J Bot 1996; 83: 175-9.
- Úbeda X, Bernia S, Simelton E. The long-term effects on soil properties from a forest fire of varying intensity in a Mediterranean environment. In: García C, Batalla RJ editors. Catchment Dynamics and River Processes: Mediterranean and other climate regions. On Developments in earth surface processes, 7. Elsevier, Amsterdam, 2005, pp. 87-102.
- YeunKyu J. Effects of systematic variation application of Fe, Mn, Cu, and Zn on the growth, root/nodule, and flowering of orchardgrass and white clover. J Korean Soc Grassland Sci 2004; 24: 105-14.

Zimmer W, Mendel R. Molybdenum metabolism in plants. Plant Biol 1999; 1: 160-8.

	Foaming agent Auxquímica RFC-88		Firesorb		Ammonium polyphosphate FR Cross	
	Total nutrient content (mg l ⁻¹)	Amount of nutrient added with (mg kg ⁻¹ soil)	Total nutrient content (mg l ⁻¹)	Amount of nutrient added with (mg kg ⁻¹ soil)	Total nutrient content (mg l ⁻¹)	Amount of nutrient added with (mg kg ⁻¹ soil)
Fe	16.7 ± 2.9	2	622 ± 13	93	17755 ± 25	355
Mn	4.3 ± 0.1	1	210 ± 8	32	36.4 ± 0.2	73
Cu	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Zn	5.7 ± 0.4	1	233 ± 15	35	41.6 ± 1.5	83
Со	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Мо	5.4 ± 0.1	1	244 ± 19	37	66.0 ± 0.5	132

Table 1.Total micronutrient content (mean \pm s.d.; n=2) in the three fire-fighting chemicals
used (n.d.= not detectable) and amount of each micronutrient they supplied to the
0-2 cm soil layer at the dose usually used in the field.

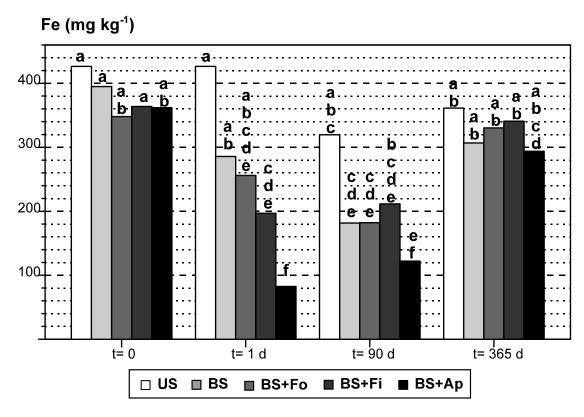


Fig. 1. Evolution of the available Fe content in the 0-2 cm soil layer along a year after the prescribed fire. Key: US, unburnt soil; BS, burnt soil; BS+Fo, burnt soil + foam agent; BS+Fi, burnt soil + Firesorb; BS+Ap, burnt soil + ammonium polyphosphate. Different letters (a, b, c,...) indicate statistically significant differences (P < 0.05) among treatment-sampling time groups.

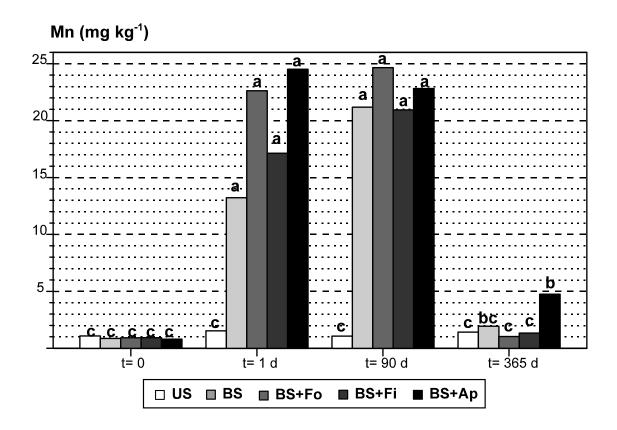


Fig. 2. Evolution of the available Mn content in the 0-2 cm soil layer along a year after the prescribed fire. Key: US, unburnt soil; BS, burnt soil; BS+Fo, burnt soil + foam agent; BS+Fi, burnt soil + Firesorb; BS+Ap, burnt soil + ammonium polyphosphate. Different letters (a, b, c,...) indicate statistically significant differences (P < 0.05) among treatment-sampling time groups.

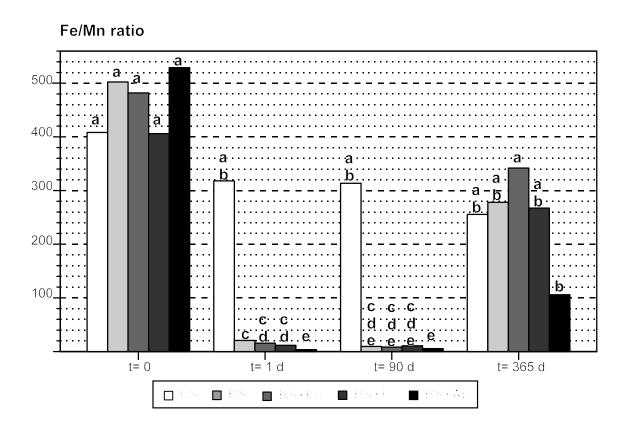


Fig. 3. Evolution of the Fe/Mn ratio in the 0-2 cm soil layer along a year after the prescribed fire. Key: US, unburnt soil; BS, burnt soil; BS+Fo, burnt soil + foam agent; BS+Fi, burnt soil + Firesorb; BS+Ap, burnt soil + ammonium polyphosphate. Different letters (a, b, c,...) indicate statistically significant differences (P < 0.05) among treatment-sampling time groups.</p>

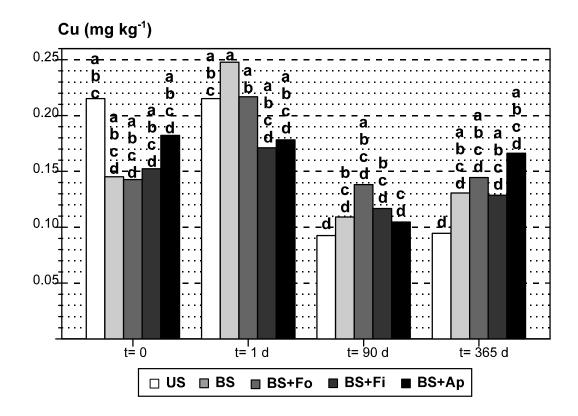


Fig. 4. Evolution of the available Cu content in the 0-2 cm soil layer along a year after the prescribed fire. Key: US, unburnt soil; BS, burnt soil; BS+Fo, burnt soil + foam agent; BS+Fi, burnt soil + Firesorb; BS+Ap, burnt soil + ammonium polyphosphate. Different letters (a, b, c,...) indicate statistically significant differences (P < 0.05) among treatment-sampling time groups.

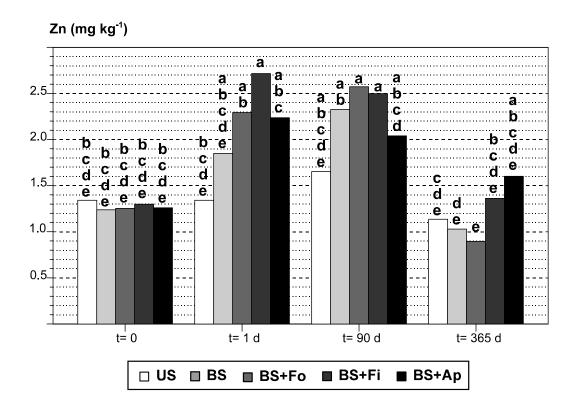


Fig. 5. Evolution of the available Zn content in the 0-2 cm soil layer along a year after the prescribed fire. Key: US, unburnt soil; BS, burnt soil; BS+Fo, burnt soil + foam agent; BS+Fi, burnt soil + Firesorb; BS+Ap, burnt soil + ammonium polyphosphate. Different letters (a, b, c,...) indicate statistically significant differences (P < 0.05) among treatment-sampling time groups.

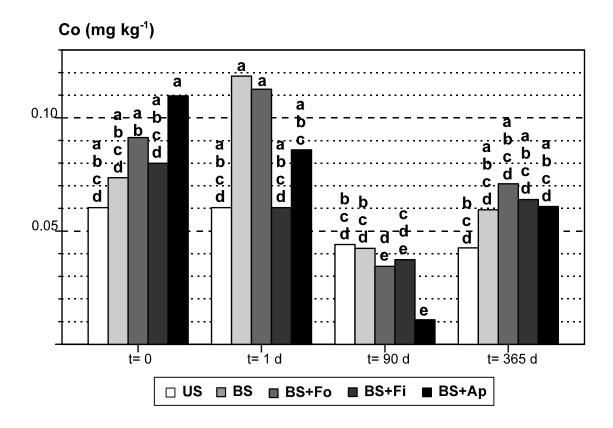


Fig. 6. Evolution of the available Co content in the 0-2 cm soil layer along a year after the prescribed fire. Key: US, unburnt soil; BS, burnt soil; BS+Fo, burnt soil + foam agent; BS+Fi, burnt soil + Firesorb; BS+Ap, burnt soil + ammonium polyphosphate. Different letters (a, b, c,...) indicate statistically significant differences (P < 0.05) among treatment-sampling time groups.