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**Abstract**

The impacts of fire and fire-fighting chemicals (FFC) on soil properties and the soil-plant system were evaluated five years after treatment application. Unburnt soils (US) were compared with burnt soils treated with water alone (BS) or with foaming agent (BS+Fo), Firesorb polymer (BS+Fi), or ammonium polyphosphate (BS+Ap). Soils (0-2 cm depth) and foliar material *(Ulex micranthus, Pterospartum tridentatum, Erica umbellata* and *Pinus pinaster*) were analysed for total-C, total-N, $\delta^{15}N$, nutrients (soil-available; plant-total), pH and inorganic-N (soils) and vegetation cover and height. No long-term effects of FFC on soil properties were found except for pH (BS+Fo > BS+Ap), inorganic-N and P (BS+Ap > other treatments). BS+Ap plants usually showed higher values of $\delta^{15}N$, N, P and Na, but less K. Soil coverage by *Pterospartum* and *Ulex* was higher in BS+Ap than in other treatments, while the opposite was observed for *Erica*; shrubs were always taller in BS+Ap. After 3 years of growth, the size of pine seedlings followed the order BS+Ap > US > other treatments. Foliar N and P, scrub regeneration and growth of pines showed the long-term fertilizing effect of ammonium polyphosphate, although the second highest pine mortality was found in the BS+Ap treatment. The foaming agent did not affect vegetation cover, and Firesorb had no noticeable effect on shrubs but the highest pine mortality.

*Additional keywords:* flame retardants; $\delta^{15}N$; macro-nutrients; micro-nutrients; shrubs; trees.

## 1. Introduction

Wildfires produce important impacts on soils, whose physical, chemical and biochemical properties are more or less affected depending on fire intensity (Certini 2005). Due to these negative effects and the increasing frequency and extent of fires, the improvement of wildfire fighting techniques is a global concern. Since the beginning of 1930's, wildfire fighting tools include application of water together with fire-fighting chemicals (fire retardants and fire suppressant foam products) which in many countries are extensively used (Giménez *et al.* 2004).

As most fire-fighting chemicals are often applied in natural areas set aside for wildlife or environmentally sensitive areas, it is necessary to determine their potential effects on ecosystems (Basanta *et al.*

2002). Several authors have studied the effects of fire-fighting chemicals on plants and animals, both aquatic and terrestrial (Larson and Duncan 1982; Gaikowski *et al.* 1996; McDonald *et al.* 1997; Adams and Simmons 1999; Larson *et al.* 2000; Giménez *et al.* 2004; Hartskeerl *et al.* 2004; Bell *et al.* 2005). With regard to the effects of these products on plants, Luna *et al.* (2007) reported that the application of a common long-term fire-retardant significantly decreased both seed viability and germination in a group of 36 species. Larson *et al.* (2000) measured growth, re-sprouting, flowering and some community characteristics (species richness, evenness and diversity) on shrub steppe vegetation and found that only species richness declined, while the other characteristics were not affected by any chemical treatment. However, due to the high amounts of nitrogen and phosphorous in these chemical products, it has also been suggested that their application could cause effects similar to those produced by fertilisers. For example, Larson and Duncan (1982) reported that annual grassland in California doubled its biomass following application of di-ammonium phosphate retardant. The majority of these studies focus on the short-term, longer studies (at least 10 years) are needed to detect the true effects of fire-fighting chemicals on these organisms (Giménez *et al.* 2004).

Surprisingly, the effects of these compounds on soils, the base of terrestrial ecosystems, have scarcely been studied (see Giménez *et al.* 2004). Only a few papers, all in the recent years, have been published on this topic. Basanta *et al.* (2002) found no short-term effects of an acrylic-based synthetic terpolymer, used as fire retardant, on microbial biomass and enzymatic activities in both heated and unheated forest soils, but a significant reduction of net N mineralization. Díaz-Raviña *et al.* (2006) determined that, under laboratory conditions, the same fire retardant decreased the G(-)/G(+) bacteria ratio in the heated soils but tended to increase it in the unheated soils, the effect being dose dependent. Couto-Vázquez and González-Prieto (2006) reported that the transient increase of soil pH, exchangeable $NH_4^+$ and $\delta\ ^{15}N$ due to a prescribed fire was enhanced by the three fire fighting chemicals they studied, and the levels of some available cations were also increased. Moreover, these authors highlighted that the extremely high initial levels of $NH_4^+$-N and available P in the treatment with ammonium polyphosphate can delay the post-fire recovery of vegetation due to the toxicity of $NH_4^+$ to seeds and seedlings and the antagonistic effect of P on Fe and Zn uptake. Hopmans *et al.* (2007) found that a phosphate-based fire-fighting chemical increased the levels of labile N and P at both studied sites; while the former declined to background values after 12 months, the latter remained elevated and caused concern due to possible long-term impacts on growth and composition of heathland vegetation. García-Marco and González-Prieto (2008), working with the same plots as Couto-Vázquez and González-Prieto (2006), reported that the transient changes in micro-nutrient availability due to a prescribed fire (increase of Mn and Zn; decrease of Fe and Co) were enhanced by two out of three fire-fighting chemicals studied, although the only medium-term effect found was that of the ammonium polyphosphate on Mn availability and the Fe/Mn ratio. Results of García-Villaraco *et al.* (2009) showed that changes caused by the application of retardant to the soils did not lead to any major adverse effects on functional diversity and total activity of soil microorganisms in a Mediterranean pasture. Conversely, Barreiro *et al.* (2010) found long-lasting effects of fire-fighting chemicals at normal field application doses on the soil microbial communities on the basis of the PLFA pattern, although the induced changes were negligible compared to those provoked by the burning. In many cases, the fire-fighting chemicals are applied by aircraft and, therefore, it is virtually impossible that the chemical falls only in the fire line. Consequently, three scenarios are possible under realistic wildfire-fighting conditions: a) soils in the fire line that receive retardant, both the soil and the retardant being affected by the heating and oxidation caused by the fire; b) soils in the burnt area close to the fire line that, still hot or warm, receive the retardant; and c) soils in the unburnt area close to the fire line that receive the retardant but that are not affected by the fire. Usually studies focus on the last two scenarios, probably due to the difficulties in studying the narrow and very heterogeneous area of the first scenario, although Larson *et al.* (2000) used the approach of applying chemicals to extinguish prescribed fires in small plots (1 $m^2$) within a shrub steppe area. As Giménez *et al.* (2004) highlighted, there is a lack of studies investigating the effects of FFCs on living organisms in the long-term or on the plant-soil system. Therefore, the aim of this paper was to evaluate, 5 years after their application, the impact on the soil-plant system of fire and three fire-fighting chemicals applied immediately after a single prescribed fire in a medium-sized field experimental area (1000 $m^2$). The fire-fighting chemicals applied were foaming agent RFC-88 (Auxquimia SA), terpolymer Firesorb (Evonik Stockhausen Gmbh) and ammonium polyphosphate FR Cros 134 P (Budenheim). Compared with prescribed fires on small plots, this experimental design allows studying a burnt area affected by a higher severity fire and with much lower border effects. On the other hand, it does not allow the study of a scenario in which soil and retardants are affected by the heating and oxidation caused by the fire. For evaluating the impact of fire and fire-fighting chemicals, soils and foliar material of three shrubs and one tree species were analysed for total C, total N, $\delta^{15}N$ and macro- and micro-nutrient concentrations (soil-available and plant-total); moreover, soil pH and inorganic forms of N, as well as vegetation cover and height, were also studied.

## 2. Material and methods

The experimental field, located in NW Spain at an altitude of 455 m a.s.l, was that previously used by the authors' research team (Couto-Vázquez and González-Prieto 2006; García-Marco and González-Prieto 2008; Barreiro *et al.* 2010) after selecting an area of homogeneous slope, orientation, soil type and vegetation cover (*Ulex*, *Pterospartum* and *Erica* shrubs 50-60 cm height). Within a total surface of 40 x 25 m, five *in situ* treatments were established five years ago: plots in the unburnt area (US) as a control and plots in the burnt area that received 2 L $m^{-2}$ of water alone (BS) or water added with RFC-88 at 1% (BS+Fo), Firesorb at 1.5% (BS+Fi) or FR Cross 134 P at 20% (BS+Ap). For convenience, the soil from the burnt area and that from the unburnt area are hereafter referred to as burnt soil and unburnt soil, respectively. After a prescribed fire (i.e. the fire is extinguished but the soil is still warm), burnt soil treatments were arranged in a fully randomized design with four replications and a 1 m separation around each plot (4 x 4 m), whereas the four unburnt soil replicates were established along the slope (18-19%) and adjacent to the burnt ones (see Couto-Vázquez and González-Prieto 2006).

The fire-fighting chemicals were selected amongst the most widely used in countries of the Mediterranean basin: RFC-88 is a foaming agent produced by Auxquimia SA (Mieres, Spain); Firesorb is a light cross-linked terpolymer of acrylic acid, acrylamide and acrylamidopropansulfonic acid sodium salt, manufactured by Evonik Stockhausen Gmbh (Krefeld, Germany); and FR Cross 134 P is an ammonium polyphosphate produced by Chemische Fabrik Budenheim KG (Budenheim, Germany; Zaragoza, Spain). Data on density, total nutrient concentrations and $\delta\ ^{15}N$ in the three fire fighting chemicals are available in previous papers (Couto-Vázquez and González-Prieto 2006; García-Marco and González-Prieto 2008).

In late winter, seven months after the prescribed fire, 4 one-year-old pine seedlings (supplied by a forest nursery from a genetically similar stock) were planted in each plot to follow their development and to assess how the fire and flame retardants affect post-fire reforestation. During the first three years after plantation, height and basal diameter of pines were measured quarterly and then annually until the fifth year.

Five years after the prescribed fire, the soil-plant system was characterised. After removing the plant litter layer, soil samples were taken from the A horizon (0-2 cm depth,); five 15 x 15 cm squares, uniformly distributed around each plot, were sampled, mixed and thoroughly homogenized after sieving at 4 mm; soil sub-samples were air-dried, finely ground (< 100 μm) in a planetary ball mill (Retsch PM100, with cups and balls of zirconium oxide) and stored for analysis. Three slope-down transects with sampling points every 25 cm were established within each plot (discarding 50 cm at each side to avoid possible edge effects); at every sampling point, the presence or absence of the four dominant shrub species was recorded, as well as their maximum height. Leaf material from the upper half of *Pinus pinaster* (50 pairs of needles from the youngest branches), *Ulex micranthus*, *Erica umbellata* and *Pterospartum tridentatum* (about 10 g of spines, leaves and twigs, and whorls, respectively) was also collected; a fourth dominant shrub species, *Ulex europaeus*, was not collected because it was present only in two out five treatments. The plant material was washed successively with tap and deionized water, oven-dried at 60 °C for 48 h and finely ground in the same way as soils.

The dry matter content of soils and plant material was assessed by oven-drying aliquots at 110 °C to constant weight. Soil pH was measured with a pH-meter (Metröhm, Switzerland) in 0.1 M KCl employing a soil: solution ratio of 1:2.5. Total-C, total-N and $\delta\ ^{15}N$ of soils and plants were measured on ground samples with an elemental analyser coupled on-line with an isotopic ratio mass spectrometer (Finnigan Mat, delta C, Bremen, Germany). For soil $NH_4^+$-N and $NO_3^-$-N analysis an extraction-diffusion method described previously (Couto-Vázquez and González-Prieto 2006) was used, but with 24 h diffusion periods at 50 °C. Soil available Na, K, Ca, Mg and P were extracted with acetic acid 0.5 M (see Couto-Vázquez and González-Prieto 2006), while available Fe, Mn, Cu, Zn, Co and Mo were extracted from soils as described by Lindsay and Norvel (1978). Nutrients in soil extracts were analysed by simultaneous ICP-OES (Varian Vista Pro, Mulgrave, Australia). After a microwave digestion, the total nutrient content of plant material was measured by simultaneous ICP-OES. Aliquots of 500 mg were digested for 55 min with 8 mL $HNO_3$ 65% and 25 mL $H_2O_2$ 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 25 mL volumetric flasks and made to volume with water. Analytical grade chemicals were obtained from Merck Chemical Co., and all aqueous solutions were prepared with type I water (ASTM 2008). The macro-and micro-nutrient content of the fire-fighting agents, as well as their % N and $\delta\ ^{15}N$, was described in previous papers (Couto-Vázquez and González-Prieto 2006; García-Marco and González-Prieto 2008). All analyses were carried out in duplicate and the mean of both analyses was used in the statistical procedure.

The effects of treatments on soil and plant variables 5 years after the prescribed fire were statistically analysed by one-way ANOVA. After checking the equality of variances among treatment groups with the Levene's test, significant differences among the mean groups were established at $P < 0.05$ using: a) the Tukey's test in the case of homocedasticity of the original data (or data after Cox-Box transformations); or b) Games-Howell's test if variances remained heterogeneous after Cox-Box transformations. The same was done to compare the significance of changes in soil variables from 1 to 5 years after the prescribed fire. All statistical analyses were done with SPSS 15.0. software.

## 3. Results

### *3.1. Effects of fire and fire-fighting chemicals (FFCs) on soil chemical properties*

Five years after the prescribed fire, no significant effect of fire or FFCs on soil $pH_{KCl}$ was found (Table 1), although BS+Ap treatment showed the lowest soil pH value, which was significantly different from that of BS+Fo.

Neither the fire nor the addition of FFCs affected the soil total N and C content, $\delta\ ^{15}N$ and bioavailable macro- and micro-nutrients (except P and N) in the long-term (Table 1). Burnt soils treated with ammonium polyphosphate showed higher contents of bioavailable P and N ($NH_4^+$ and $NO_3^-$) than the other treatments (except N content in US, Table 1). Available Cu levels were below analytical equipment detection limits (0.09 mg kg$^{-1}$) in more than 90 % of soil samples analysed and the same happened with Mo in most samples (detection limit, 0.03 mg kg$^{-1}$), so soil-available Cu and Mo are not shown.

### *3.2. Effects of fire and fire-fighting chemicals (FFCs) on plant nutrient concentrations*

Total N concentration was maximal in *U. micranthus* and *P. tridentatum* foliar material (Fig. 1A). Regarding treatment factor, a significant and negative effect of burning was only shown in *E. umbellata* and a positive effect of the application of ammonium polyphosphate in all species, which did not reach significant values in *P. tridentatum* and *P. pinaster;* significant differences were the following: a) *U. micranthus*, BS+Ap > US and BS+Fo; and b) *E. umbellata*, BS+Ap > BS, BS+Fo and BS+Fi. Plant $\delta\ ^{15}N$ values in the leguminous species were in a very narrow range, close to natural abundance and below soil $\delta\ ^{15}N$ (Fig. 1B). Meanwhile, non-legumes showed more variable values although always clearly negative, except BS+Ap pines. Two clear impacts of treatment on *E. umbellata* δ $^{15}$N were found: a) the approximately 0.5 ‰ more negative values in BS, BS+Fo and BS+Fi respect to US; and b) the 2-2.5 ‰ higher value in BS+Ap plots. Values of δ $^{15}$N in *Pinus* followed a similar trend to that observed for *E. umbellata* although, for each treatment, they were on average 1.5-2 ‰ more positive.

Table 1. Effect of fire and fire-fighting chemicals on soil chemical properties. 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, ...) indicate significant differences (P < 0.05) among treatments.

| | US | BS | BS+Fo | BS+Fi | BS+Ap |
|---|---|---|---|---|---|
| $pH_{KCl}$ | $3.14 \pm 0.08^{ab}$ | $3.21 \pm 0.07^{ab}$ | $3.29 \pm 0.10^{a}$ | $3.22 \pm 0.03^{ab}$ | $3.13 \pm 0.06^{b}$ |
| Total C (g $kg^{-1}$) | $138.7 \pm 30.2^{a}$ | $129.3 \pm 20.8^{a}$ | $112.2 \pm 14.7^{a}$ | $120.6 \pm 11.5^{a}$ | $121.7 \pm 13.2^{a}$ |
| $NH_4^+$-N (mg $kg^{-1}$) | $13.35 \pm 12.1^{a}$ | $0.61 \pm 0.17^{b}$ | $1.12 \pm 0.49^{b}$ | $0.93 \pm 0.20^{b}$ | $6.11 \pm 0.89^{a}$ |
| $NO_3^-$-N (mg $kg^{-1}$) | $2.57 \pm 1.89^{a}$ | $0.12 \pm 0.22^{b}$ | $0.35 \pm 0.23^{ab}$ | $0.06 \pm 0.07^{b}$ | $2.66 \pm 3.12^{a}$ |
| Total N (g $kg^{-1}$) | $8.43 \pm 1.72^{a}$ | $8.58 \pm 1.78^{a}$ | $7.54 \pm 1.60^{a}$ | $7.49 \pm 1.01^{a}$ | $8.14 \pm 1.54^{a}$ |
| δ $^{15}$N (‰) | $2.42 \pm 0.21^{a}$ | $2.80 \pm 0.69^{a}$ | $2.95 \pm 0.30^{a}$ | $2.92 \pm 0.34^{a}$ | $2.60 \pm 0.26^{a}$ |
| Al (mg $kg^{-1}$) | $375.9 \pm 29.3^{a}$ | $393.6 \pm 45.1^{a}$ | $424.3 \pm 57.0^{a}$ | $408.9 \pm 75.7^{a}$ | $407.6 \pm 69.4^{a}$ |
| P (mg $kg^{-1}$) | $0.50 \pm 0.27^{b}$ | $1.45 \pm 1.09^{b}$ | $0.56 \pm 0.62^{b}$ | $0.40 \pm 0.24^{b}$ | $17.50 \pm 3.72^{a}$ |
| Na (mg $kg^{-1}$) | $15.62 \pm 5.92^{a}$ | $17.11 \pm 6.32^{a}$ | $14.30 \pm 3.90^{a}$ | $18.21 \pm 0.53^{a}$ | $15.44 \pm 3.06^{a}$ |
| K (mg $kg^{-1}$) | $45.11 \pm 14.21^{a}$ | $38.61 \pm 11.51^{a}$ | $32.94 \pm 7.39^{a}$ | $46.00 \pm 17.73^{a}$ | $36.67 \pm 7.29^{a}$ |
| Ca (mg $kg^{-1}$) | $142.0 \pm 43.4^{a}$ | $146.4 \pm 68.4^{a}$ | $127.6 \pm 39.5^{a}$ | $136.3 \pm 16.7^{a}$ | $126.2 \pm 39.3^{a}$ |
| Mg (mg $kg^{-1}$) | $56.35 \pm 12.79^{a}$ | $47.25 \pm 20.06^{a}$ | $48.25 \pm 14.04^{a}$ | $48.92 \pm 9.42^{a}$ | $35.30 \pm 12.50^{a}$ |
| Fe (mg $kg^{-1}$) | $376.8 \pm 12.9^{a}$ | $347.6 \pm 29.6^{a}$ | $342.9 \pm 32.7^{a}$ | $340.0 \pm 15.1^{a}$ | $343.8 \pm 34.4^{a}$ |
| Mn (mg $kg^{-1}$) | $0.82 \pm 0.50^{a}$ | $0.81 \pm 0.41^{a}$ | $0.90 \pm 0.30^{a}$ | $0.76 \pm 0.23^{a}$ | $1.16 \pm 0.28^{a}$ |
| Fe/Mn ratio | $605.1 \pm 324.3^{a}$ | $508.9 \pm 243.7^{a}$ | $412.9 \pm 126.0^{a}$ | $485.7 \pm 179.3^{a}$ | $305.5 \pm 53.2^{a}$ |
| Zn (mg $kg^{-1}$) | $1.59 \pm 0.84^{a}$ | $1.27 \pm 0.42^{a}$ | $1.24 \pm 0.62^{a}$ | $1.37 \pm 0.29^{a}$ | $1.16 \pm 0.66^{a}$ |

After 5 years, foliar levels of P were similar in plants growth on US and BS plots, showing a lack of long term effect of fire on this variable which, irrespectively of the species considered, had always significantly higher values in plants grown on BS+Ap soils (Fig. 2A), a result coinciding with that found for soils. Legumes (*Ulex* and *Pterospartum*) developed in US showed the highest K concentration and those developed in BS+Ap presented the lowest ones (Fig. 2B). However, the highest values for *Pinus* were found in BS+Ap and the lowest in BS and BS+Fo while burning did not cause significant differences in *Erica.* Calcium total concentration in foliar material did not differ among treatments, except for *E. umbellata* plants (BS+Ap > US; Fig. 2C). No clear trend for post-fire levels of total plant Mg was found in the present study (Fig. 2D): while *Pinus* needles showed the lowest values in plants from BS+Ap soils (significantly different with respect to BS and BS+Fi treatments), the highest Mg concentrations were in shrubs developed in BS+Ap soils, although differences among treatments were not always significant.

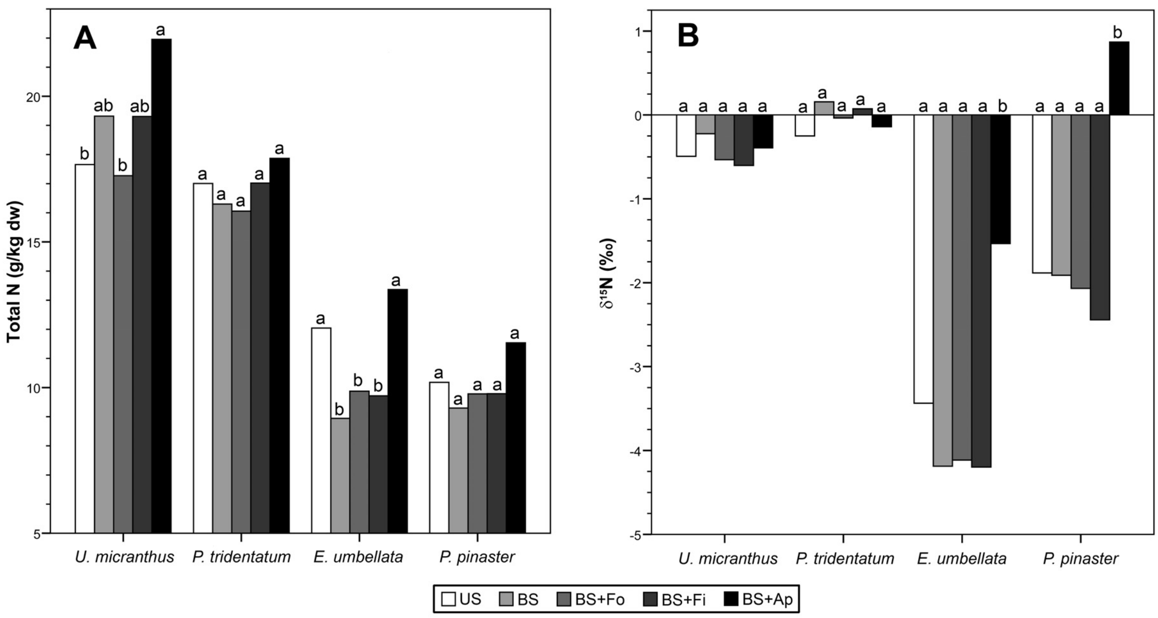


Fig. 1. Total nitrogen concentration (A) and δ $^{15}$N (B) in foliar materials 5 years after the prescribed fire. For each plant species and treatment, different letters (a, b, c,...) indicate significant differences (P < 0.05) among treatments. Key: US, unburnt soil; BS, burnt soil; BS+Fo, burnt soil + foam agent; BS+Fi, burnt soil + Firesorb; BS+Ap, burnt soil + ammonium polyphosphate.

All plant species showed small ranges in plant Fe concentration, without significant differences among treatments (Fig. 3A) except in the case of *Pterospartum (*plants from BS+Ap > plants from US). No clear effect of fire on plant Mn concentration was found in the long term (Fig. 3B). However, *Ulex, Pterospartum* and *Pinus* grown in BS+Ap soils presented the highest total Mn concentration, but only *Ulex* from US and *Pinus* developed in BS+Fo were significantly different. For *E. umbellata*, the highest Mn concentration was in plants grown in BS+Fo which were significantly different from US and BS+Ap plants. Only *Erica* and *Pinus* showed significant differences in the Fe/Mn ratio, the highest values being found in plants from US and BS+Fo (data not shown). Compared with the homogeneous *Pinus*-total Na concentration in all treatments, shrub species showed wider ranges with the highest values in plants from BS+Ap, which were always significantly different from those of US and, depending on the shrub species, with the other burnt soils (Fig. 3C). Regarding plant-total Al concentration, the mean values in *Pterospartum* and *Erica* were within a narrow range in all treatments while those in *Ulex* and *Pinus* were in a wider range, but without significant differences among treatments in any species (data not shown). Concerning plant-total Cu and Zn concentrations there were no significant differences among treatments (data not shown), while all plant-total Co and most of plant-total Mo values were below the detection limits of the analytical methodology used (0.005 and 0.008 mg kg$^{-1}$, respectively) and these data were not statistically analysed.

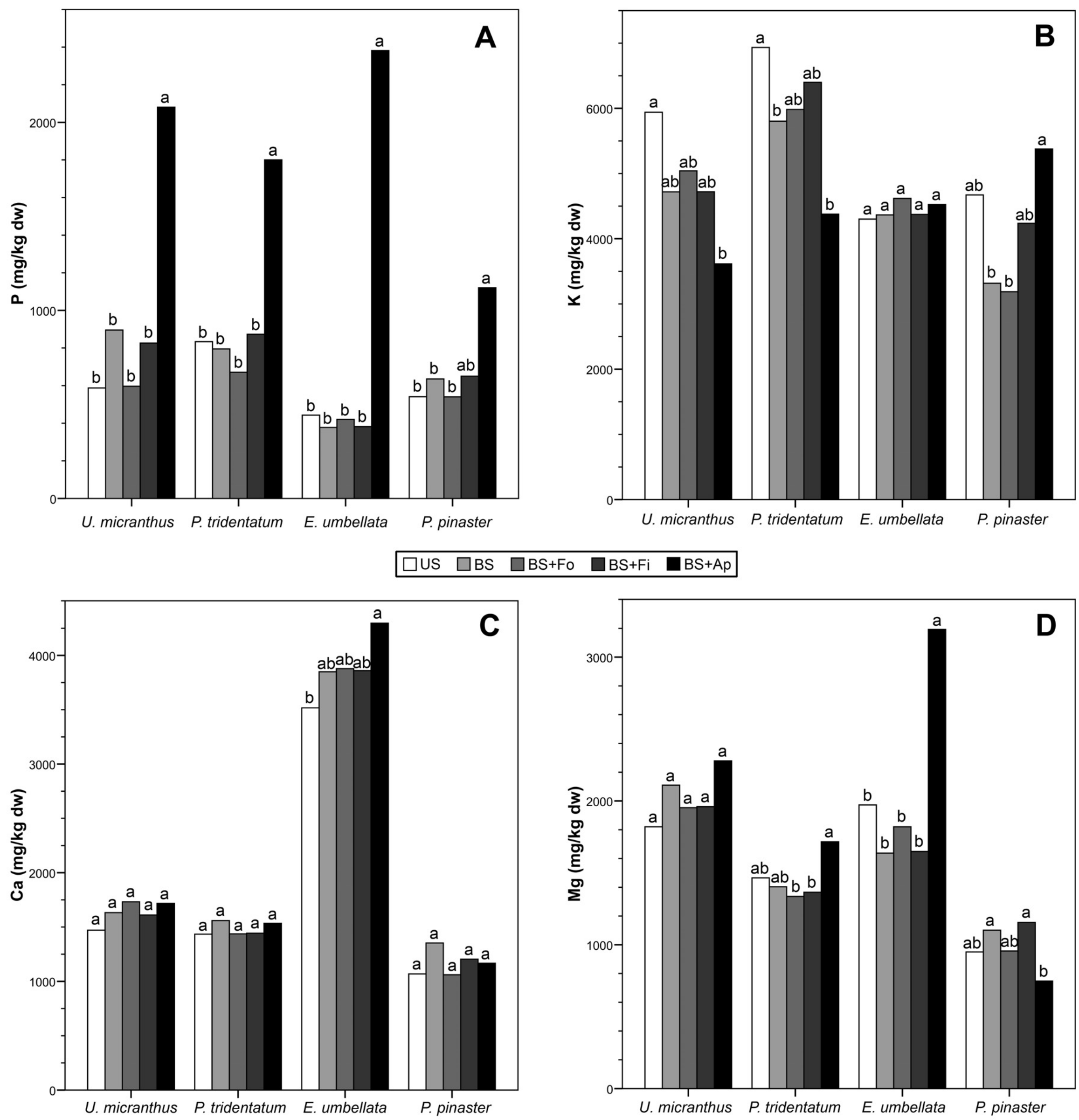


Fig. 2. Concentration of total macro-nutrients in foliar materials 5 years after the prescribed fire: phosphorous (A), potassium (B), calcium (C) and magnesium (D). For each plant species and treatment, different letters (a, b, c,...) indicate significant differences (P < 0.05) among treatments. See key in Fig. 1.

### *3.3. Effects of fire and fire-fighting chemicals (FFCs) on vegetation cover*

During the first 6 months after reforestation, pine seedlings planted in US were slightly taller than the rest but at t = 9 months its average height was matched by that of BS+Ap pines, while trees of the other burnt soil treatments were significantly shorter (Fig. 4A). At the third year after reforestation three groups could be identified (BS+Ap > US > BS, BS+Fo and BS+ Fi), and differences between them were wider at the fourth and fifth year. The evolution of seedlings basal diameter (Fig. 4B) revealed similar trends to height, although significant differences were only detected from the second year: BS+Ap > other treatments. These same two groups were maintained, with a widening gap, until the fifth year when BS+Ap > US ≈ BS, BS+Fo and BS+Fi. Although differences among treatments were not significant due to inter-plot variability, pine mortality 5 years after planting increased in the order US (6.3 ± 6.3%; mean ± s.d.), BS+Fo (12.5 ± 7.2%), BS (18.8 ± 12.0%), BS+Ap (25.0 ± 17.7%) and BS+Fi (43.8 ± 21.3%).

As far as natural regeneration of vegetation cover is concerned, 5 years after the prescribed fire both burnt and unburnt plots presented 3 common dominant shrub species: *Ulex micranthus*, *Pterospartum tridentatum* and *Erica umbellata*; a fourth dominant species, *Ulex europaeus*, was also present in the BS and BS+Ap treatments. For *Pterospartum* and *Ulex* spp., the percentage of soil covered by each species was significantly higher in BS+Ap plots than in the other treatments, but the reverse was true for *E. umbellata* (Fig. 5A). This exception for coverage in the case of *E. umbellata* did not exist for shrub height, which was significantly higher in BS+Ap plots irrespectively of the species considered (Fig. 5B).

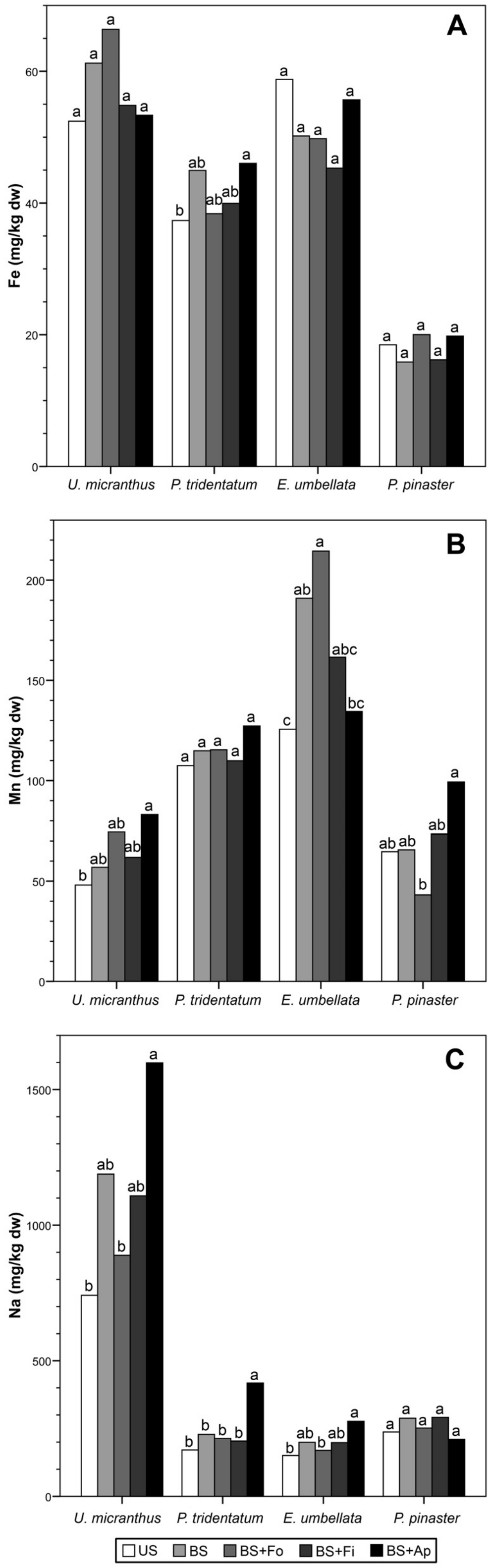


Fig. 3. Concentration of total micro-nutrients in foliar materials 5 years after the prescribed fire: iron (A), manganese (B) and sodium (C). For each plant species and treatment, different letters (a, b, c,...) indicate significant differences (P < 0.05) among treatments. See key in Fig. 1.

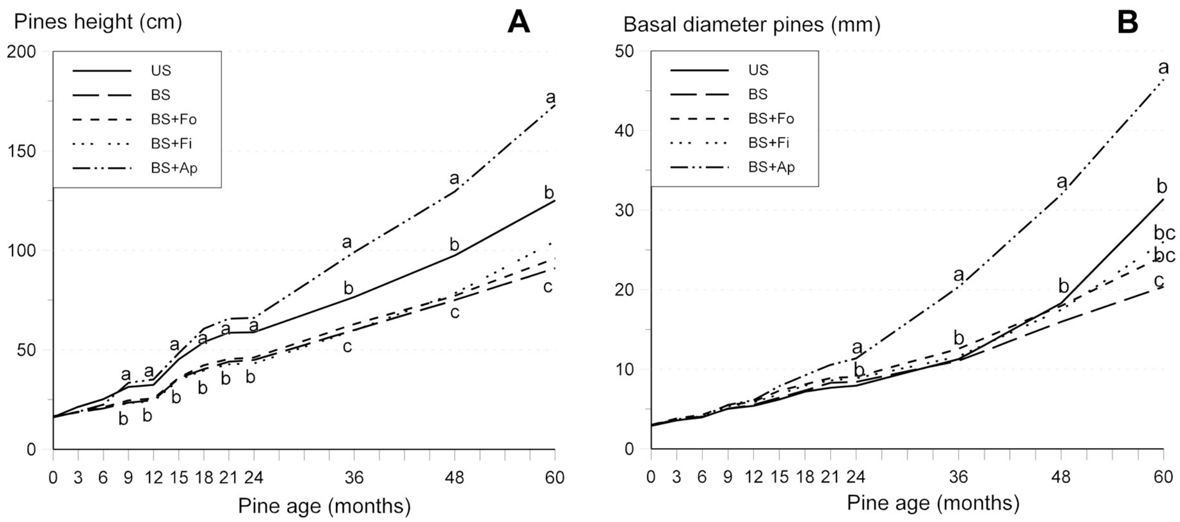


Fig. 4. Evolution of *Pinus pinaster* height (A) and basal diameter (B) during the first 5 years after the prescribed fire. For each date, different letters (a, b, c,...) indicate significant differences (P < 0.05) among treatments. See key in Fig. 1.

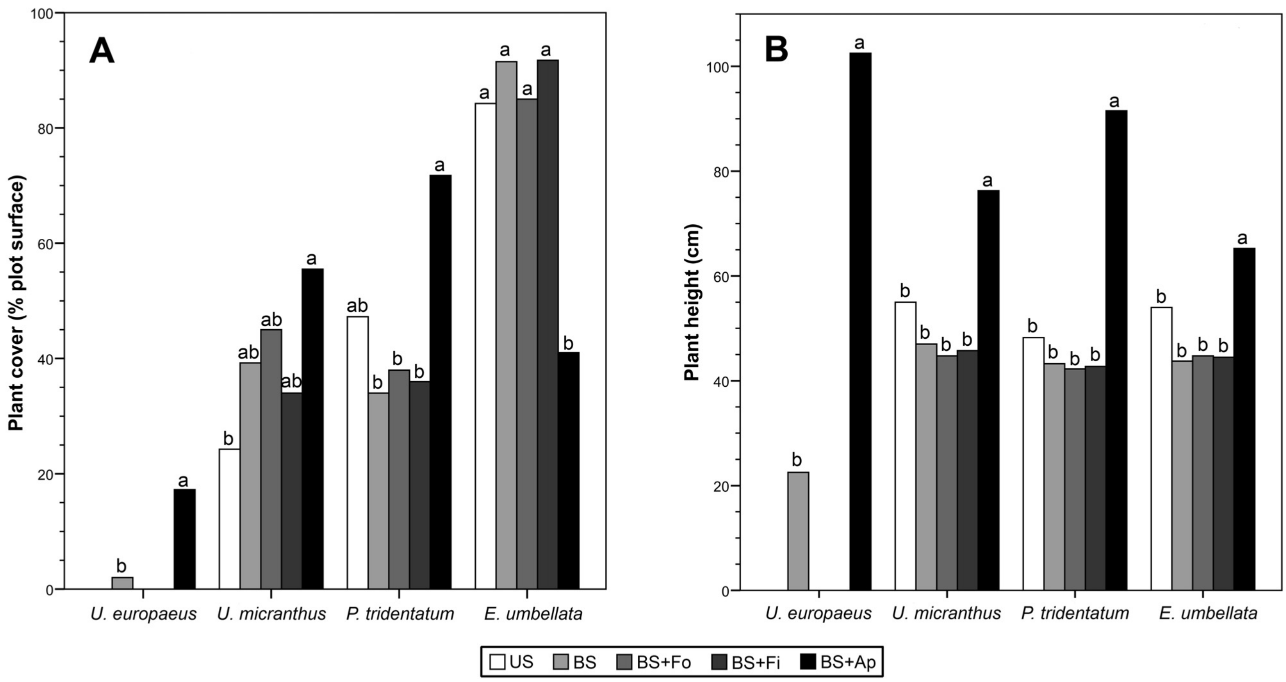


Fig. 5. Shrub cover (A) and height (B) 5 years after the prescribed fire. For each species, different letters (a, b, c,...) indicate significant differences (P < 0.05) among treatments. See key in Fig. 1.

## 4. Discussion

*4.1. Effects of fire and fire-fighting chemicals (FFCs) on soil chemical properties*

No significant effect of fire or FFCs on soil $pH_{KCl}$ was found in the long-term, but a significant soil acidification (up to 0.25 pH units, $P<0.05$) was observed in all soils irrelevant of the treatment applied, compared with the corresponding values at t=1 year (US: 3.39±0.04; BS: 3.41±0.03; BS+Fo: 3.50±0.08; BS+Fi: 3.39±0.02; BS+Ap: 3.36±0.05 mean values reported by Couto-Vázquez and González-Prieto 2006). Although pH may remain elevated for years after the fire (Antos *et al.* 2003), due to an increased availability of cations and consumption of organic acids by litter and soil organic matter oxidation (Fisher and Binkley 2000), it should slowly return to pre-disturbance levels as conifers regain dominance of the study area. However, as soil acidification led to lower pH than initial values in burnt and unburnt plots, factors other than post-fire pH evolution must play an important role in our case; this factor could be the grazing exclusion in our study area as other authors have reported (Basher and Lynn 1996; Dormaar and Willms 1998).

Fire induces changes in soil nutrient balances. Most studies on the effect of fire on chemical quality have been focussed above all on the determination of C, N and P; fewer studies have been undertaken on available macro-nutrients (Ca, K, Mg) and studies analysing available micro-nutrients (Cu, Fe, Mn, Na and Zn) are lacking (Certini 2005). Moreover, little information about FFCs effects on soil macro- and micro-nutrient availability has been found. In the present study, neither the fire nor the addition of FFCs affected the soil total N and C contents, and bioavailable macro- and micro-nutrients (except P and N) in the long-term; the same was true for soil $\delta\ ^{15}N$, which reflects the net effect of biotic and abiotic environment on N-cycling processes (see Dawson et al. 2002). Burnt soils treated with ammonium polyphosphate showed higher contents of bioavailable P and N ($NH_4^+$ and $NO_3^-$) than the other treatments, mainly due to the great amount of P and $NH_4^+$ supplied with this FFC; similar results in the medium-term (1 year) were previously reported for ammonium-phosphate FFCs (Couto-Vázquez and González-Prieto 2006; Hopmans *et al.* 2007). The significantly higher content of mineral $NO_3^-$-N in US and BS+Ap than in the other plots suggested a higher net nitrification in these soils.

In agreement with tendencies observed during the first year after the fire (see Couto-Vázquez and González-Prieto 2006), soil total C, total N, $NH_4^+$-N and $NO_3^-$-N at t=5 years were slightly, but not significantly, lower than at t=1 year, while $\delta\ ^{15}N$ increased significantly ($P<0.05$) in US and BS+Fi plots (1.75 ‰ and 2.57 ‰, respectively; data from Couto-Vázquez and González-Prieto 2006).

In unburnt and burnt soils, and irrelevant of the FFC applied, at t=5 years the concentrations of soil available nutrients decreased significantly ($P<0.05$) compared with the corresponding treatment four years before in the case of Mg (US: 137±25; BS: 103±30; BS+Fo:91±21; BS+Fi: 104±16; BS+Ap: 102±29) and P (US: 5.9±0.9; BS: 9.3±2.4; BS+Fo: 8.1±2.5; BS+Fi: 9.6±1.8; BS+Ap: 118±24) (all data are the mean values in $mg \cdot kg^{-1}$ dry soil reported by Couto-Vázquez and González-Prieto 2006). For Ca the differences were only significant in the unburnt soil (US: 326±62, reported by Couto-Vázquez and González-Prieto 2006) and no significant differences were found for the other nutrients. Post-fire vegetation recovery could have depleted some available-soil nutrients and the $Mg^{2+}$ decrease (a basic cation) could have led to the significant soil acidification observed in soils during the last four years. Úbeda *et al.* (2006) also found a reduction in $Ca^{2+}$ and $K^{+}$ one year after a prescribed fire, and the authors proposed that uptake by vegetation during the first year can cause the nutrient losses.

*4.2. Effects of fire and fire-fighting chemicals (FFCs) on plant nutrient concentrations*

Although the important effects of FFCs on streams and aquatic organisms are a cause of major concern, few research has evaluated their impact on terrestrial vegetation (Giménez *et al.* 2004). The effects on yield, growth and coverage level of different species were assessed by several authors (Larson *et al.* 2000; Hartskeerl *et al.* 2004; Bell *et al.* 2005; Cruz *et al.* 2005), but plant nutrition status has not been studied.

Differences among species in total N concentration were mainly explained by the symbiosis of legumes with atmospheric $N_2$-fixing microorganisms, while differences among treatments showed a negative effect of burning only in *E. umbellata* and a positive effect of the application of ammonium polyphosphate in all species. Legumes $\delta\ ^{15}N$ values suggested a common major N source, close to natural abundance and below soil $\delta\ ^{15}N$, that might be atmospheric $N_2$ (see Shearer and Kohl 1993). In both *E. umbellata* and *P. pinaster*, ammonium polyphosphate addition led to higher $\delta\ ^{15}N$ values. The very negative values of *E. umbellata* plants growing in US appeared that, like in other ericaceous species, mycorrhizal associations provided much of its N requirements (Hobbie and Hobbie 2008); the strong isotopic fractionation that takes place in the N transfer from the symbiont to the host would be responsible for ensuring that plant $\delta\ ^{15}N$ was 4-5 ‰ lower than that of the soil. Two clear impacts of treatment on *E. umbellata* $\delta\ ^{15}N$ were found: a) the approximately 0.5 ‰ more negative values in BS, BS+Fo and BS+Fi respect to US suggested that this species is more dependent on N supplied by mycorrhiza because of lower soil N availability (as also indicated by plant N concentration); and b) the 2-2.5 ‰ higher values in BS+Ap suggested lesser dependence on mycorrhizal N supply, either by increased N availability because of the previously discussed fertilizer effect or by a possible toxic effect of this FFC on mycorrhiza. In *Pinus*, probably due to their ectomycorrhizal associations, $\delta\ ^{15}N$ values followed a similar trend to that observed for *E. umbellata* although, for each treatment, values were on average 1.5-2 ‰ more positive.

The similar foliar P level in plants from US and BS plots contrasted with the results of Brockway *et al.* (2002) and showed in our case a lack of any long term effect of fire on this variable. On the contrary, the significantly higher foliar P concentration in all plants grown on BS+Ap plots coincided with the similar result in soils and both were a long-lasting consequence of P supplied by the ammonium polyphosphate FFC.

In contrast to the significantly higher foliar levels of K, Ca, Mg and Mn reported by Brockway *et al.* (2002), no clear and common tendency was found for the different species in the present study. Although the differences with other treatments were not significant in all cases, the highest concentration of Na and Mn were usually found in plants from Bs+Ap plots. Concerning plant-total Fe, Cu and Zn concentrations there were no significant differences among treatments.

*4.3. Effects of fire and fire-fighting chemicals (FFCs) on vegetation cover*

The evolution of the planted *P. pinaster* seedlings showed three distinct patterns: a) trees in US plots with the lowest mortality and higher height, but not basal diameters, than trees from BS, BS+Fi and BS+Fo plots along the whole studied period; b) trees from BS+Ap plots, that had an early growth (0-6 months) slower than those from US, but that became the biggest after 2-3 years, although with the second highest mortality; and c) trees from BS, BS+Fi and BS+Fo plots with the lowest growth rates, and intermediate mortalities (except those from BS+Fi with the highest one).

As far as natural regeneration of vegetation cover is concerned, 5 years after the prescribed fire the percentage of soil covered by legumes was significantly higher in BS+Ap plots than in the other treatments; the reverse was true for *E. umbellata,* which is the only one of these species that regenerates exclusively from seeds (Reyes *et al.* 2009). This result was likely due to the well documented negative effect of ammonium polyphosphate on seed germination and viability (Luna *et al.* 2007).

The good long-term vegetation development in BS+Ap plots from the second year after the fire showed that the short-term strong negative effects of ammonium polyphosphate on seed viability, germination and seedling establishment (Cruz *et al.* 2005; Couto-Vázquez and González-Prieto 2006; Luna *et al.* 2007) may have disappeared in nature once the retardant was eliminated, as reported for normal application rates (Angeler *et al.* 2004). Both the natural regeneration of scrubs and the growth of planted trees showed that ammonium polyphosphate had a long-term fertilizing effect that enhanced vegetation growth, resulting in an increased soil coverage and overall size for most species. This result agreed with those of Larson and Duncan (1982) who reported that a grassland burned area that received a di-ammonium phosphate FFC yielded twice as much as the unburned control area during at least two years. Our results also agreed partially with those of Bell *et al.* (2005) who found that the fertilizing effect of a P-bearing FFC generally increased shoot growth of the key species considered, but did not significantly increase the overall height of these species. However, it must be highlighted that three causes of concern arose on the use of ammonium polyphosphate FFCs: a) it was the FFC with the second highest effect on the soil microbial communities at the long-term (Barreiro *et al.* (2010); b) the very low *E. umbellata* cover in BS+AP plots (only 40-50% of that on the other treatments) showed that even in mesotrophic ecosystems some species can be displaced by others favoured by the fertilizing effect of these FFCs, a process that can be worse in the case of sensitive oligotrophic species or ecosystems; and c) BS+Ap was the second treatment with highest percentage of dead *P. pinaster* trees. This latter result may be related to changes in micro-nutrient availability: one year after the prescribed fire, BS+Ap soils had the highest available Mn concentration and the lowest available Fe/Mn ratio (García-Marco and González-Prieto 2008); four years later, needles of pines from BS+Ap exhibited the highest Mn concentration, although the value was well within the range for normal pine growth (Kavvadias and Miller 1999)(see Bergmann, 1993 and Fürst, 1997, in Tausz *et al.* 2004).

Gorse (*Ulex* spp.), characteristically regrowing from stumps, seemed not to suffer the short-term deleterious effect of ammonium polyphosphate on seeds and their seedlings, and was greatly favoured by the fertilizing effect in the medium- to long-term which resulted in the largest vegetation size and coverage. As gorse is a $N_2$-fixing legume, the ammonium polyphosphate fertilizer effect was likely due to the great contribution of P because, as reported for *Ulex* (Augusto *et al.* 2005), both mean annual biomass increment and $N_2$ fixation increased with P fertilization dose. The lesser coverage of *E. umbellata* in burnt plots agreed with its regeneration exclusively from seed that, during the secondary succession after fire, led to slower recovery than strongly re-sprouting species like *Ulex* spp. (Reyes *et al.* 2009). Although *P. tridentatum* is a strong resprouter (Reyes *et al.* 2009), the results suggested that, at least in the studied case, burning have had a negative impact on its germination or regrowth.

The lack of significant effects of the tested foaming agent on the vegetation cover agreed with no detectable impacts of fire-fighting foams on a range of vegetative growth characteristics (Hartskeerl *et al.* 2004).

No published information was found about the effects of acrylamide polymers on vegetation, but Barreiro *et al.* (2010), working in our experimental plots, recently reported that, at normal field application doses, Firesorb had the higher long-lasting effects on the soil microbial communities on the basis of the PLFA pattern. In the present study we did not find noticeable effects on shrubs, but a very high pine mortality in the BS+Fi plots; these contrasting results suggest that more research is needed regarding the effects on vegetation of FFC containing acrylamide polymers.

*Conclusions*

From the results of present study and those previously reported from the same experimental plots (Couto-Vazquez and Gonzalez-Prieto 2006; Garcia-Marco and Gonzalez-Prieto 2008; Barreiro *et al.* 2010) it can be concluded that: a) the foaming agent had the lowest influence on the soil-plant system; b) the acrylamide polymer had low effects on soil properties and shrubs, but the highest effects on soil microbial communities and pine mortality; and c) the ammonium-polyphosphate had the strongest and long-lasting effects on soil properties and vegetation cover, as well as the second highest effect on soil microbial communities and pine mortality.

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