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EFFECTS OF FIRE TEMPERATURE ON THE PHYSICAL AND CHEMICAL CHARACTERISTICS OF THE ASH FROM TWO PLOTS OF CORK OAK (QUERCUS SUBER)

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ABSTRACT

Cork oak, (Quercus suber) is widely distributed in the Mediterranean region, an area subject to frequent fires. The ash produced by burning can have impacts on the soil status and water resources that can differ according to the temperature reached during fire and the characteristics of the litter, defined as the dead organic matter accumulated on the soil surface prior to the fire. The aim of this work is to determine the physical and chemical characteristics of ash produced in laboratory experiments to approximate conditions typical of fires in this region. The litter of Quercus suber collected from two different plots on the Iberian Peninsula, Mas Bassets (Catalonia) and Albufeira (Portugal), was combusted at different temperatures for 2 h. We measured Mass Loss (ML per cent), ash colour and CaCO₃ content, pH, Electrical Conductivity (EC) and the major cations (Ca²⁺, Mg^{2+} , K^+ and Na^+) released from ash slurries created by mixing ash with deionized water. The results showed that ML per cent is higher at all temperatures in Albufeira samples compared to Mas Bassets samples, except at 550°C, and the rate of loss increases faster with temperature than the Mas Bassets samples. At 150°C the ash colour is yellowish, becoming reddish at 200-250°C and black at 300°C. Above 400°C the ash is grey/white. This thermal degradation is mostly observed in Albufeira litter. The formation of CaCO₃ was identified at a lower temperature in Albufeira litter. At temperatures $< 300^{\circ}$ C, pH and EC values are lower, rising at higher temperatures, especially in Albufeira slurries. The concentration of cations at lower temperatures does not differ substantially from the unburned sample except for Mg^{2+} . The cation concentration increases at medium temperatures and decrease at higher temperatures, especially the concentration of divalent cations. The monovalent cations showed a larger concentration at moderate temperatures, mainly in Albufeira ash slurries. The analysis of the Ca:Mg ratio also showed that for the same temperature, a higher severity results for Albufeira litter. Potential negative effects on soil properties are observed at medium and higher temperatures. These negative effects include a higher percentage of mass loss, meaning more soil may be exposed to erosion, higher pH values and greater cation release from ash, especially monovalalent cations (K^+ , Na⁺) in higher proportions than the divalent ions (Ca^{2+} , Mg^{2+}), that can lead to impacts on soil physical properties like aggregate stability. Furthermore, the ions in ash may alter soil chemistry which may be detrimental to some plants thus altering the recovery of these ecosystems after fire. Low intensity prescribed fire can be a useful tool to land management in these sites, due to the reduced effects of fire temperatures on the physical and chemical properties of surface litter, and can reduce the risk of high temperature wildland fires by reducing fuel loadings. From the perspective of water resources, lower fire temperatures produce fewer impacts on the chemistry of overland flow and there is less probability that the soil surface will be eroded. Copyright © 2009 John Wiley & Sons. Ltd.

KEY WORDS: cork oak; Quercus suber; fire severity; mass loss; ash; physical and chemical parameters

INTRODUCTION

After fire, ash, consisting of the organic and inorganic residues of the combustion process, is left on the soil surface. The fire residues are, mainly in the form of oxides, hydroxides and carbonates and this ash is rich not only in elements

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such as Calcium (Ca), Magnesium (Mg), Potassium (K) and Sodium (Na) but also in Phosphorous (P) and Silica (Si). The mineralization of the original material depends on the quantity and composition of fuels and the temperature and length of exposure to heat (Khanna and Raison, 1986; DeBano, 1989; Etiegni and Campbell, 1991; Ulery *et al.*, 1993; Khanna *et al.*, 1994; Neary *et al.*, 1999; Gray and Dighton, 2006). Throughout a fire, the temperatures in the litter layer and soil surface can reach 900°C. However, due to the poor conductivity of dry soils, the temperature at 5 cm below the surface is not likely to exceed 150°C (DeBano, 1981). The nutrients in ash can be lost from the system by ash convection, volatilization, mineralization, erosion, runoff and leaching. Some nutrients are vaporized during the combustion process and this loss of nutrients to the atmosphere depends on the temperature. Ca volatilizes at temperatures > 1962°C, Mg at > 1107°C, K at > 774°C and Na at > 880°C (Weast, 1988; Neary *et al.*, 2005). The nutrients incorporated in ash are easily leached into overland flow and into the soil, leading to an increase in and transport of elements in the system that will affect water resources, mainly in the first months after the fire but also after several years (Hauer and Spencer, 1998; Thomas *et al.*, 2000; Malmer, 2004; Ferreira *et al.*, 2005).

Cork oak, (*Quercus suber*) belongs to the order of *Fagales* and the family of *Fagaceae*. It is an evergreen tree with sclerophyllous leaves and is a widely distributed species characteristic of the Mediterranean region both in Europe and North Africa between 33 and 45°N. The species grows in warm-humid areas with at least 450 mm of annual rainfall and in areas from sea-level to 2000 m a.s.l. The trees prefer siliceous- or carbonate-free soils and can colonize extremely acid soils. According to the Raunkiaer (1934) classification, the species is a mesofanerofit and has a period of floration between April and May (Boavida *et al.*, 1999). The *Quercus suber* forests are of the highest cultural, economic and ecological value and sustain a great variety of floral and faunal diversity (Loisel, 1976; Orgeas *et al.*, 2002).

Fire is considered the most serious problem affecting the sustainability of *Quercus suber* forests. However, this species is perfectly adapted to the impacts of fire due the capacity of the bark to protect against high temperatures (Barberis *et al.*, 2003; Úbeda *et al.*, 2006). The bark provides an efficient protection to dormant buds which exist in the trunk and there is a good positive relationship between bark thickness and recovery after fire. After a fire, a tree can resprout from the stem and it is the only European tree with above-ground sprouting capability, similar to the genus *Eucalyptus* from Australia. Even at higher fire intensities, a great proportion of burnt trees sprout from the stump. For these reasons this species is probably one of the best adapted to fire impacts (Pausas, 1997, 1998; Silva and Catry, 2006). However, when bark is stripped for the cork industry, the resistance of trees to fire effects is reduced. According to Barberis *et al.* (2003) who monitored 200 scorched trees of different ages, mortality was less than 10 per cent for trees not harvested in the last 30 years, and 40 per cent for old trees which have been stripped several times. Fire recurrence also has implications for *Quercus suber* distribution. Trabaud and Galitie (1996) observed that in areas burnt three times, the surface occupied by *Quercus suber* was reduced in favour of scrubland and in areas with less fire recurrence the distribution of *Quercus suber* was higher as was the diversity of species in the ecosystem.

The flammability of different species has been shown to vary and depends, among other factors, on the chemical composition of the plants, their physical structure and architecture, and moisture content, which differs seasonally. In general, the majority of species showed a major flammability in summertime due to lower levels of humidity (Nuñez-Reguira *et al.*, 1996; Weise *et al.*, 2005). Conifers are more flammable than hardwood species due the great quantity of resins and essential oils produced (Nunez-Regueira *et al.*, 2000). Litter from needle-leaved tree species has lesser concentrations of water soluble phenolics than litter from broad-leaved trees (Kuiters and Sarink, 1986). Species that have a variety of secondary metabolic compounds and constituents as well as diverse surface area-to volume ratios and fuel particle densities will respond differently to different fire temperatures (Kuiters and Sarink, 1986; Dimitrakopoulos and Panov, 2001).

Flammability and the consequent fire severity (defined below) are also observed as an interaction between plant communities and environment over the time (Mutch, 1970) and in this sense, important differences can be found between ecosystems in response to fire temperatures. However, there is a lack of studies about the effects of fire temperatures on *Quercus suber*, one of the most common species in the Mediterranean environment, and little assessment of the different vulnerability of these ecosystems to fire severity. The *Quercus suber* flammability is low

in relation to other *Quercus* species and this species is only flammable during the summer season (Vélez, 1991; Vallette, 1997; Pausas, 1997). Moreover, from the perspective of water resources and the long-term response of the cork oak ecosystems, it is of crucial importance to understand the effects of fire temperatures on the physical and chemical characteristics of ash from this species and solute mobility and whether differences exist in these characteristics between *Quercus suber* populations located in different environments.

The duration and temperature of fire affect the physical and chemical properties of ash. However little knowledge exists about the relation between temperature and the range of effects on ash properties. Collecting ash generated at exact temperatures is impossible under field conditions and in this sense, laboratory experiments subjecting leaf litter to several temperatures is a good methodology to identify the relation between fire temperatures, fire severity and solute release. Fire severity is evaluated by the magnitude of the effect that fires have on the environment and especially in the loss of or change in organic matter aboveground and belowground (Keeley, 2009). This work assesses the impacts of temperature on physical and chemical changes of *Quercus suber* litter. Fire severity can be also evaluated through the properties of the fuels (size, flammability and moisture or mineral content) (DeBano *et al.*, 1998; Suguihara *et al.*, 2006) and some experiments have been conducted using Mediterranean species at a specific temperature (Nunez-Regueira *et al.*, 1996, 2000; Liodakis *et al.*, 1997, 2005; Dimitrakopoulos and Panov, 2001; Dimitrakopoulos and Papaioannou, 2001; Guijarro *et al.*, 2002). However, no one has evaluated changes in ash properties according to temperature gradients and no studies have focussed on *Quercus suber*. In addition, only a few studies have measured major cation solute release from ash produced at specific temperatures (Soto and Diaz-Fierros, 1993; Blank *et al.*, 1996; Gray and Dighton, 2006; Quintana *et al.*, 2007; Marcos *et al.*, 2007).

The purpose of this study is to analyse the effects of fire temperatures (150, 200, 250, 300, 350, 400, 450, 500 and 550° C) on Loss of Mass (ML per cent), ash colour and CaCO₃ content, pH, electrical conductivity (EC) and the major cations (Ca²⁺, Mg²⁺, K⁺ and Na⁺) released from ash slurries in a laboratory experiment using the litter from two *Quercus suber* plots located in different areas of the Iberian Peninsula. These temperatures were chosen to complement ongoing studies that are measuring the hyperspectral signature of combusted litter and the range covers those temperatures expected during many prescribed fires and wildland fires. At these temperatures is unlikely that nutrients are vaporization and thus the great majority of elements still remain in the ash after combustion. Because the ash is produced under controlled laboratory experiments, differences in the ash properties will lead to a better understanding of the pattern of temperatures effects on *Quercus suber* populations located in two different ecosystems.

METHODS AND MATERIALS

Study Sites

The *Quercus suber* leaf litter of Mas Bassets was collected in the Gavarres Mountains (Catalonia), located at 41° 87′ N and 02° 87′ W and the Albufeira samples were collected near the Albufeira Lagoon situated on the Portuguese western coast, at 38° 31′ N and 9° 08′ W (Figure 1) during the spring and summer of 2007. The sites had similar litter depths and distribution on the soil surface. The geologic substrate of Mas Bassets is mainly composed of granite rocks of fragile structure (Úbeda *et al.*, 1998) and the Albufeira site is underlain by Plio-Pleiostocene dunes with low cementation (Freitas, 1995). The soils of Mas Bassets are classified as *Luviarenosols* and in Albufeira as *Podzols* (Soil Survey Staff, 2006) both with a higher content of sand and low in organic matter, pH, Electrical Conductivity (EC), and Cation exchange capacity (CEC) (Table I). The temperature in Mas Bassets has an annual mean of 13.9°C and in Albufeira of 14.8°C. The annual precipitation is an average of 768.31 mm in Mas Bassets and of 639.2 mm in Albufeira. In Mas Bassets, the vegetation is primarily composed of *Quercus suber* with a smaller proportion of *Quercus ilex, Quercus robur, Pinus pinea* and *Pinus pinaster*. The Albufeira site has *Quercus suber*, *Pinus pinea* and *Pinus pinaster*. Both sites in this study are representative of the *Quercus suber* distribution in the Iberia Peninsula. In Catalonia, the major occurrence of the species is in the Gavarres Mountains area and in Portugal in the Mesocenozoic Tagus and Sado Basins. Soil properties (Table I), climate characteristics and historic and present land use are similar for both sites. In Mas Bassets the sample collection site is well-developed forest



Figure 1. Study Sites.

mainly comprised of *Quercus suber* trees, exploited during the last centuries for the cork industry. However, since the last quarter of the 20th century, this activity was abandoned as people migrated from rural lands to urban areas. In Portugal, the forest where we collected the samples was also exploited for industrial proposes (cork oak and *Pinus* exploitation), and, as in Catalonia, the exodus from rural areas, resulted in a decrease in the importance of the cork oak area since the last 20–30 years of the last century. Hence, the lack of forest management has resulted in a higher accumulation of biomass, increasing the risk of wildfire occurrence in these areas with vulnerable climatic conditions for a fire event. These socio-economic and land use changes have been observed in other locations of the Iberian Peninsula and, with the recent climatic warming since the last quarter of the 20th century, are the major causes of the modification of fire regimes and the increase in area affected by wildland fires (Lavorel *et al.*, 1998; Millan *et al.*, 1998; Pausas, 2006; Viegas *et al.*, 2006).

Sample Preparation, Loss of Mass Per cent and Ash Colour

The leaf litter was collected under the dominant trees from each site. About 3 kg samples were collected from the surface of the forest soil, from an area of approximately 15 m^2 . The litter was taken to the laboratory, the *Quercus suber* litter separated from leaves and twigs of other species, and the remaining material cleaned with deionized water to remove all impurities. After this task, the samples were air-dried for 24 h before exposing them to the specified temperatures (Pereira *et al.*, 2008). Subsequently, samples were subjected to the specified temperatures in porcelain crucibles for 2 h in a muffle furnace (Dinko Mod.D – 61-D), a period of heating also applied in other studies (Gray and Dighton, 2006). The ML per cent of the samples was measured as the weight difference before and after the litter was heated. After this task, 1 g of the ash produced was pulverized in the Frich Pulverizate 23 for about 2 min in order to homogenize the sample to analyse the ash colour. To classify colour, we utilized the Munsell colour chart (Munsell, 1975), and observed the ash colour of samples exposed to each temperature.

Chemical Analysis

The calcium carbonate $(CaCO_3)$ of the samples subjected to each temperature was measured with a Bernard's calcimeter calibrated with 0.2 g of pure CaCO₃ using a 1:2 hydrochloric acid solution (50 per cent concentrated HCl

Table I. Some characteristics of the upper 5 cm soil (<2 mm fraction) collected in both areas of study. EC in μ /cm³, base cations and CEC in mg/l (N=1 per sample per element)

Specie	OM per cent	Sand per cent	Silt per cent	Clay per cent	pН	EC	Ca ²⁺	Mg ²⁺	Na ⁺	K^+	CEC
Mas Bassets	8·85	86	4	10	5·35	0.118	5·15	1.66	11.98	5.33	24·12
Albufeira	4·82	85	2	13	5·97	0.100	1·66	0.48	16.20	2.93	21·27

and 50 per cent deionized water). Subsamples of ash weighing 0.2 g were mixed with the 1:2 solution. The CaCO₃ was estimated by calculating the difference between the volume of CO₂ before and after introducing each sample. An ash slurry was created for each sample by mixing 6 g of the ash generated at the different temperatures with 36 ml of deionized water, which was mixed for 2 h on a Thermo Scientific Variomag Poly inductive-drive stirrer. This solution was filtered through a 4.7 cm diameter Whatman QMA 0.45 µm pore size quartz fibre filter, using a Millipore 220/240 Volt, 50 Hz pump. After this task, the pH was measured with a Crisol GLP 22 pH meter and EC with a Hanna instruments HI 8820. Major cations were determined by producing an ash slurry, 1:40 (1 g of ash and 40 ml of deionized water), that was mixed for 24 h and then filtered though a Whatman QMA 0.45 µm pore size quartz fibre filter. The solution was analysed by inductively coupled plasma mass spectrometry (ICP-MS) with a PerkinElmer, model Elan-6000 Spectrometer, and by optical emission spectrometry (OES) with the PerkinElmer Optima 3200 RL Spectrometer. An unheated control subsample was treated in the same manner as the heated subsamples.

Statistical Analysis

To observe the significance of ML per cent with temperature gradient an F-test was performed. Analysis of variance, Tukey's HSD test, was applied in order to identify differences between the exposure temperatures within each site. Data normality was analysed with the Shapiro-Wilk test (Shapiro and Wilk, 1965) for all temperatures in this study. Since all distributions were considered normal at p > 0.05, and in order to identify significant statistical differences among species at each temperature, we compared the average ML per cent with a student t-test. The differences found in all analyses were considered significant at a p < 0.05. In order to understand the relationship between ash colour and temperature we compared the temperatures and the chroma value of the Munsell colour chart (Munsell, 1975). In this analysis we did not consider the 150°C treatment because at this temperature the oak leaves only lose their water content and no air oxidation process is likely to occur (Grier, 1975; Pospisil and Klemchuk, 1990; Misra et al., 1993). In the examination of CaCO₃ and major cations we only used one sample per species per temperature. Thus, CaCO₃ data are presented as per cent of ash sample subjected to the temperatures and major cations data were presented as a per cent of the values in comparison to unheated control samples in order to observe the impacts of the temperatures on cation release in the test solution. All treatments were compared by cluster analysis (CA) according to the complete linkage amalgamation rule and the distance measure of 1-Pearson r. The comparison between the release of divalent and monovalent cations released by the ash slurries of Mas Bassets and Albufeira at the temperatures under analysis is presented in Log mg/l. All analyses were performed with STATISTICA[®] 6.0 for Windows (Statsoft, Tulsa OK, USA).

RESULTS AND DISCUSSION

Loss of Mass

The results of the ML per cent are plotted in Figure 2. The ML per cent increased with temperature up to 400° C in the Albufeira samples and to 450° C in the Mas Bassets samples. After about 90 per cent ML, differences in ML per cent are not statistically significant. The results obtained from our study showed that leaf litter of the same species located in different environments had diverse responses to same fire temperatures. At the temperatures of 200 and 500° C, no significant differences between species were observed. With the exception of 550° C, for all the remaining temperatures the ML per cent of the Albufeira samples were always higher than the Mas Bassets samples (Table II). According to Oregas *et al.* (2002) the nutrient content of soil is likely to be the most spatially variable factor influencing leaf nutrition of *Quercus suber*. Although, leaf litter chemical characteristics influence fuel flammability (Nuñez-Regueira *et al.*, 2000; Wise *et al.*, 2005), since the soil composition of both environments is similar, as is litter moisture content, other variables must determine the higher flammability of Albuferia litter. Leaves collected from the Albufeira plot are larger than Mas Bassets leaves and they burn more easily. This higher flammability of the Albufeira sample may be due to the spaces between leaves and the better ventilation, which enhanced the circulation of oxygen. If the oxygen supply is reduced, the speed of organic matter pyrolysis decreases



Figure 2. Mean mass loss (ML per cent) with the temperature gradient from *Quercus suber* litter of Mas Bassets and Albufeira. All values are present in mean per cent \pm SE. (N = 9 per samples per temperature). F-test was applied with df = 9·39 and Tukey's HSD test with df = 40·00 was applied between the temperatures. The mean separation: A > B > C > D > E > F (A = higher mean, F = lower mean). All differences are significant at a p < 0.05.

(Drysdale, 1999). According to Scarff and Westboy, (2006) large leaves created an open litter-bed structure that burns faster and releases more heat due the better ventilation.

Ash Colour and $CaCO_3$

Changes in ash colour with the temperature gradient are represented in Figure 3a. Our study shows that the colour of litter heated to 150° C is yellowish due to the loss of the water content from the leaves. According to Misra *et al.* (1993) and Grier (1975) the loss of mass at temperatures lower than 200°C is a consequence of the vaporization of the water absorbed in the leaves. Marcos *et al.* (2007) found from differential thermal analysis (DTA) that the removal of hygroscopic water was complete at 177° C.

Table II. Mass loss (ML per cent) differences between *Quercus suber* litter from Mas Bassets and Albufeira. The statistical significance was tested under the *student t-test* means comparison. * < 0.05 and ** < 0.001. Higher mean(A) and lower mean(B). *NS* (No significant) (N = 9 per samples per temperature)

Temperature (°C)	р	Mas Bassets	Albufeira	
550	**	А	В	
500	NS			
450	**	В	А	
400	**	В	А	
350	*	В	А	
300	*	В	А	
250	*	В	А	
200	NS			
150	**	В	А	



Figure 3. (a) Evolution of ashes colours of *Quercus suber* litter from Mas Bassets and Albufeira with temperature gradient, (b) Relationship between temperature gradient and ash Munsell colour chroma value of produced of *Quercus suber* litter of Mas Bassets and Albufeira. (N = 1 per sample per temperature) and (c) CaCO₃ content of the ashes of *Quercus suber* litter of Mas Bassets and Albufeira according the temperature gradient. (N = 1 per sample per temperature).

Between 200–250°C in Mas Bassets and at 200°C in Albufeira ashes, the colours are reddish due the oxidation of iron minerals which occur at temperatures lower than 300°C (Driscoll, 1981; Stucki *et al.*, 2002; Markl *et al.*, 2006). At temperatures near 300°C for Mas Bassets and 250°C for Albufeira litter, the ash becomes black, a product of the incomplete combustion of the litter and the higher proportion of organic carbon as observed by Khanna *et al.*, (1994). At these temperatures, total carbon was higher in the ash produced from the litter of both sites (Úbeda *et al.*, 2009) and may correspond to the formation of black carbon (Vaughan and Nichols, 1995; Certini, 2005; Brodowski *et al.*, 2005; Knicker *et al.*, 2007). At 400°C, the ash became grey and white, indicating that fire severity is higher at these temperatures and at 450°C, complete combustion is observed and there is a higher reduction in Total Carbon in the ash (Úbeda *et al.* 2009). Similar results were found elsewhere, as pointed out by Ulery *et al.*, (1993), that severe burning produced white ash that remained after complete combustion of the fuel at 500°C.

The ash colour is variable depending on the temperature gradient the severity is more pronounced in Albuferia litter than in Mas Bassets litter. Black carbon appears at lower temperatures in Albufeira samples (250°C), as does greyish (400°C) and white ashes (450°C) compared to Mas Bassets samples, which indicates that the same fire temperatures had a greater impact on Albufeira litter, mainly at higher exposure temperatures. The correlation between temperature and the chroma of Munsell colour chart is r = 0.92 (p < 0.001) for both litters (Figure 3b), thus the higher the temperature, the greater the chroma value.

White ash from wood combustion is largely composed of CaCO₃ (Ulery and Graham, 1993; Steenari *et al.*, 1999; Goforth *et al.*, 2005). Similar to the trend for the creation of grey/white ash, our results confirmed that $CaCO_3$ is formed at different temperatures for each litter source (Figure 3c). The formation of this mineral at these temperatures is, according to Quintana et al. (2007), due the thermal degradation of calcium oxalate. In Albufeira samples, we observed the creation of small amounts of this mineral at 350° C, increasing with higher exposure temperatures and reaching values greater than 35 per cent of the total ash sample. CaCO₃ is only identified in Mas Bassets ash starting at 400°C and had the same behaviour of Albufeira samples with increasing temperatures without attaining the high CaCO₃ values of the Albufeira samples. These data demonstrate that the impacts of the temperature gradient are more significant in Albufeira litter and the thermal degradation takes a place at lower temperatures. Similar results were documented in other studies. Quintana et al. (2007) identified the formation of CaCO₃ at 400°C after heating leaves of Juniperus thurifera L. at several temperatures. Iglesias et al. (1997) observed the creation of this mineral at 500°C after ashing leaves and branches of Juniperus oxycedros and Quercus pyrenaica and Misra et al. (1993) and Liodakis et al. (2007) found a predominance of CaCO₃ in ash after subjecting Pinus ponderosa Dougl. ex Laws, Populus tremuloides Micx., Liodendron tupilifera L. and Quercus afba (sic; alba) and some Mediterranean species (Pinus halepensis, Pinus brutia, Olea europea and Quercus coccifera) to 600°C, respectively.

pH and Electrical Conductivity

Several studies have documented a rise of pH levels in soil solutions and water resources after fire (Stark, 1977; Belillas and Rodà, 1993; Khanna et al., 1994; Úbeda, 2001; Úbeda and Sala, 2001; Rhoades et al., 2004; Úbeda et al., 2005; Afif Khouri and Oliveira Prendes, 2006, among others) due to the higher content in ash of carbonates, oxides, and hydroxides of basic cations, available to leaching (Ulery et al., 1993). The results of pH values with temperature gradient are plotted in Figure 4a, and show an increase in the slurry pH with increasing temperature, especially in the Albufeira ash slurries. The coefficients of correlation are 0.96 (p < 0.001) for Mas Bassets and 0.92 (p < 0.001) for Albufeira samples, respectively. These findings were also identified by Soto and Diaz-Fierros (1993); Iglesias et al. (1997); Henig-Sever et al. (2001); and Quintana et al. (2007). In our study, up to 300°C the pH values in the test solutions are low and are similar for both litter samples At 300°C we recognized a slight decline in pH, and thereafter we observed a large increase, mainly in the Albufeira samples, reaching the highest pH values after 450°C due to the presence of CaCO₃, as reported elsewhere (Etiegni and Campbell, 1991; Ulery et al., 1993; Henig-Sever, 2001). As observed for ash colour and CaCO₃ per cent in ash, the temperatures had a greater effect on pH rise in Albufeira samples than in Mas Bassets samples. Similar results were observed by Marcos et al. (2007) who did not find important differences in pH after subjecting soils to temperatures of 100 and 200°C for different exposure times, and Giovannini (1994), Ubeda, (2001) and Badía and Martí (2003) who documented a reduction of pH levels at 220, 300 and 250°C in soil solutions, respectively. Also, higher pH values were identified by Iglesias et al. (1997) and Quintana et al. (2007) after ashing soils at 400 and 500°C.

Water salinity rises after fire due to the release of ions from ash as reported by some investigations (Kutiel and Naveh, 1987; Iglesias *et al.*, 1997; Badía and Martí, 2003; Lasanta and Cerdà, 2005; Notario del Pino *et al.*, 2008). In our study we observed a rise of EC with increasing temperature, 0.96 (p < 0.001) for Mas Bassets ash and 0.90 (p < 0.001) for Albufeira ash (Figure 4b). Up to 300°C we identified for both litters a low EC value in ash slurries and above this temperature, we observed an increase in ionic concentration in the test solutions, mostly in Albufeira samples, reaching high levels at 450°C and decreasing afterwards, due to the high pH levels and CaCO₃ content. The CaCO₃ sorption capacity for all metals rises with increasing pH, and at value pH > 8 the CaCO₃ surfaces are



Figure 4. (a) pH evolution with temperature gradient in *Quercus suber* litter from Mas Bassets and Albufeira (N=1 per samples per temperature) and (b) EC evolution with temperature gradient in *Quercus suber* litter from Mas Bassets and Albufeira (N=1 per samples per temperature).

negatively charged (Zachara *et al.*, 1991; Brady *et al.*, 1999; Ettler *et al.*, 2006) thus decreasing the EC of ash slurries (Wen *et al.*, 2003). This decrease was also documented by Mellbo *et al.* (2008). This can explain the decrease of EC in Albufeira ash slurries created at higher temperatures. Similar results were also documented by Iglesias *et al.* (1997) and Badía and Martí (2003). Quintana *et al.* (2007) identified a reduction in ion concentration in solution after heating soils at 400 and 500°C.

MAJOR CATIONS

Calcium and Magnesium

The results of Ca^{2+} released from the ash slurries are plotted in Figure 5a and showed also a non-significant relationship with temperature gradient, Mas Bassets r = 0.08 and Albufeira r = 0.64, both at *p* value > 0.05. At low temperatures 150–300°C, the Ca²⁺ released in test solution is different between the two litters. In Mas Bassets ash, the Ca²⁺ release is higher than in the unburned sample and in Albufeira ash, the release is lower. Above 300°C, the concentration of Ca²⁺ in solution rises, mainly in Mas Bassets ash slurries up to 400°C, decreasing significantly thereafter and in Albufeira litter, this rise continues to 450°C followed by a reduction. Similar results were found elsewhere. Stark (1977) observed that higher losses of Ca²⁺ were identified when soil surface temperatures exceeded 300°C and Úbeda and Sala (2001) reported a reduction in the concentration of this metal in the overland flow from high intensity burned areas in relation to medium intensity burned areas. In laboratory experiments, soluble Ca increased with temperature in soil samples heated to 25, 150 and 250°C, but then decreased in samples heated to 500°C for 15 min. The authors attribute the reduction of Ca²⁺ in solution to the creation of insoluble forms of CaCO₃ as we observed in this study. In comparison to the unburned sample, the Ca²⁺ content in solution is always higher in Mas Bassets samples than in Albufeira samples.

Up to 300°C, the low concentration of Ca^{2+} is a function of pH, and at higher temperatures, the low rate of CaCO₃ dissolution at elevated pH values can be inhibited by the presence of Ca²⁺ in solution as documented by several studies (Steenari *et al.*, 1999; Arvidson *et al.*, 2003; Quintana *et al.*, 2007). According to Mellbo *et al.* (2008) the solubility of CaCO₃ is lower between values of pH 10–12 in water. However, Ca²⁺ ions can precipitate onto or be sorbed by CaCO₃ surfaces in the form of Ca-phosphates (Badía and Martí, 2003). Calcium has a tendency to form complexes with HCO₃⁻ and dissolved organic compounds and the processes of precipitation are linked with CaCO₃ (Christensen *et al.*, 2001). Even in solution Ca²⁺ adsorption by CaCO₃ surfaces can occur, as has been reported by Brady *et al.* (1999).

In our study, Mg^{2+} showed a behaviour similar to Ca^{2+} in solution and we also report non-significant relations with increasing temperatures, r = 0.23 for Mas Bassets and r = 0.29 for Albufeira both with a p > 0.05 (Figure 5b). Up to 300°C, we identified Mg^{2+} values for the Mas Bassets samples that were almost 4-fold higher than those for the unburned sample, with reduced variability compared to Albufeira samples. At 350°C our results demonstrated a rise to maximum values of this metal concentration in the test solution for the Albufeira ash slurry and at 400°C for the Mas Bassets ash slurry, decreasing thereafter at higher temperatures. As for Ca^{2+} , Stark (1977) observed that after 300°C the Mg^{2+} in solution rises significantly and Úbeda and Sala (2001) observed a reduction in the Mg^{2+} content in overland flow from high intensity burned areas. Other laboratory studies are consistent with our findings. Soto and Diaz-Fierros (1993) and Badía and Martí (2003) found a decrease of Mg^{2+} in solution at the temperature > 460 and 500°C respectively after heating soil samples. Though, Blank *et al.* (1996) observed an increase of this metal in solution at 350°C and a decrease at 450°C after 15 min of exposure. Gray and Dighton (2006) identified a reduction in this metal in ash slurries at the temperatures of 400 and 500°C due to insoluble forms of magnesium minerals.

Our results showed that with the exception of the temperatures of 350, 500 and 550°C the impact of temperature in Mg^{2+} in test solutions is always higher in Mas Bassets samples. As for Ca^{2+} , the lower concentration of this metal at lower temperatures is due to the lower pH values and at higher temperatures as a consequence of the high pH. According to Wetzel (1991) magnesium carbonates have a low solubility at pH of 10 or higher. Also, at elevated exposure temperatures, the presence of CaCO₃ inhibited the presence of Mg^{2+} in ash slurries. Metals with ionic radii smaller than Ca are easily sorbed onto CaCO₃ surfaces, mainly at elevated pH values (Zachara *et al.*, 1991). Since the ionic radii of Mg (0.72 Å) is smaller than Ca (0.99 Å), the reduction of Mg^{2+} in solution can be explained by this mechanism. Astilleros *et al.* (2006) attributed the incorporation of Mg^{2+} ion into CaCO₃ surfaces due to their small radii. Also Brady *et al.* (1999) reported that CaCO₃ has the capacity to sorb this ion onto its surface.



Figure 5. (a) Ca^{2+} concentration in the test solution with temperature gradient in *Quercus suber* litter from Mas Bassets and Albufeira in relation with unburned sample. (N = 1 per samples per temperature), (b) Mg^{2+} concentration in the test solution with temperature gradient in *Quercus suber* litter from Mas Bassets and Albufeira in per cent relation with unburned sample. (N = 1 per samples per temperature) and (c) Ca^{2+} : Mg^{2+} ratio concentration in the test solution with temperature gradient in *Quercus suber* litter from Mas Bassets and Albufeira. (N = 1 per samples per temperature) and (c) Ca^{2+} : Mg^{2+} ratio concentration in the test solution with temperature gradient in *Quercus suber* litter from Mas Bassets and Albufeira. (N = 1 per samples per temperature).

In order to analyse the effects of fire temperature on severity we analysed the ratio between $Ca^{2+}:Mg^{2+}$ of all samples. According to Marion *et al.* (1991) Ca:Mg ratios < 1 are an evidence of extremely severe burning. The ash chemical composition plays an essential role in this behaviour (Notario del Pino *et al.*, 2008) and thus we are able to study this dynamic. Our results showed that this ratio had a negative correlation with the temperature gradient, however this correlation is weak and non-significant in Mas Bassets samples, r = -0.21, p > 0.05 and stronger in



Figure 5. (Continued).

the litter of Albufeira, r = -0.79, p < 0.05. This means that with increasing temperature this ratio displays a tendency to be < 1, especially in Albuferia ash slurries. With exception of the temperature of 450°C, the values of Ca:Mg ratio is always > 1 in Mas Bassets ash slurries (Figure 5c) In Albufeira samples only at temperatures of 150°C and 200°C were the values < 1. These findings further support the observation that the same temperature produced a higher severity in the samples collected from the Albufeira plot.

Sodium and Potassium

The results obtained in our study of the concentration of Na⁺ in the test solution with temperature gradient are represented in Figure 6a. These results showed a significant increase with temperature, $r = 0.79 \ p < 0.05$ in litter combusted from Mas Bassets and a non-significant relationship in the Albufeira ash slurry, $r = 0.26 \ p > 0.05$. The enhancement of Na⁺ in solution after a fire has been pointed out by several studies (Lewis Jr, 1974; Grier, 1975; Stark, 1977; DeBano and Conrad, 1978; Blank and Zamudio, 1998; Gimeno-Garcia *et al.*, 2000; Úbeda and Sala, 2001; Lasanta and Cerdà, 2005; Ferreira *et al.*, 2005, among others). Up to 300°C, the values of Na⁺ are less than the unburned sample in the test solution for both *Quercus* plots, reaching a maximum at 350°C in Albufeira samples, decreasing thereafter and in Mas Bassets ash slurry this rise in solution continues until a maximum at 500°C. Similar results were found elsewhere. Marcos *et al.* (2007) observed a low concentration of Na⁺ in solution at 100 and 200°C and a significant rise at 500°C. However, Badía and Martí (2003) observed an increase in Na⁺ in solution with increasing temperature.

As with divalent cations, at low temperatures the reduced concentration of this metal in solution is a function of pH. Nevertheless, for Na⁺, elevated pH values have a minor effect on sorption and precipitation processes (Christensen *et al.*, 2001). However at higher temperatures both ash slurries showed a different pattern of Na⁺ concentration in the test solution. As mentioned above, ionic radii influence the sorption process onto CaCO₃ surfaces. Since the Na⁺ ion has a larger radius (1.02 Å) than Ca this dynamic is difficult. In addition, this monovalent ion does not substitute for Ca²⁺, has a low valence and does not bind easily onto the CaCO₃ surfaces. Furthermore, Na⁺ has a great solubility and a lower complex precipitation (Busenberg and Plummer, 1985). This is a logical explanation why we found greater concentrations of Na⁺ in test solutions of Mas Bassets ash slurries. On



Figure 6. (a) Na⁺ concentration in the test solution with temperature gradient in *Quercus suber* litter from Mas Bassets and Albufeira in per cent relation with unburned sample. (N=1 per samples per temperature) and (b) K⁺ concentration in the test solution with temperature gradient in *Quercus suber* litter from Mas Bassets and Albufeira in per cent relation with unburned sample. (N=1 per samples per temperature).

the other hand under certain conditions, Na^+ ions can be incorporated onto CaCO₃ surfaces. In the presence of a large surface and crystal defects this ion can be sorbed. As pointed out by Ishikawa and Ichikuni (1984) and Busenberg and Plummer (1985), Na^+ ion sorption increase is directly proportional to the log rate of crystal growth and the quantity of Na^+ captured by CaCO₃ surfaces is greatly dependent on the existence of crystal defects. Moreover, the rates of crystal growth increases with increasing pH and thus the number of defects and the capture of Na^+ ions in solution will increase (White, 1977, 1978). Due the high content of CaCO₃ in the ash and the high pH in

the test solutions, this process explains rationally the smaller number of Na^+ ions found in ash slurries from Albufeira litter burned at high temperatures.

Our results documented a similar behaviour between K^+ and Na^+ ions in solution (Figure 6b). As with Na^+ , we observed a significant correlation with temperature gradient in Mas Bassets ash slurry, r = 0.74 (p < 0.05) and a non-significant relation in the Albufeira test solution, r = 0.31 (p > 0.05). The rise of K^+ in solution after a fire has been reported elsewhere (Lewis Jr, 1974; Tomkins *et al.*, 1991; Belillas and Rodà, 1993; Rhoades *et al.*, 2004; Úbeda *et al.*, 2005, among others). Up to 300°C there is almost no variation of K^+ released to solution in relation to the unburned sample, rising substantially at 350°C in the Albufeira test solution, and decreasing thereafter. In the Mas Bassets samples, this increase is observed at 450°C followed by a reduction. As documented by Badía and Martí (2003), other laboratory experiments support our findings that the concentration of K^+ in test solution rises with exposure temperature. In addition, as we observed in our study, Marcos *et al.* (2007) identified a reduction of K^+ in a test solution after exposing soil samples to 500°C for several minutes.

The mechanism of the precipitation process for K^+ is similar to Na⁺ (Ishikawa and Ichikuni, 1984). We observed a maximum in K^+ concentration in ash slurries of Mas Bassets at 450°C and for Albufeira slurries at 350°C, respectively, decreasing thereafter. This reduction in solution is related to the higher CaCO₃ content in ash as explained before. The lower valence of this ion, the higher solubility and the larger ionic radii (1.38 Å) in relation to Ca can explain the higher concentration of K^+ in solution at higher temperatures, yet under certain circumstances K^+ is sorbed onto CaCO₃ surfaces. Also as with Na⁺, the incorporation of K^+ ion onto CaCO₃ surfaces increases with crystal defect formation and solution pH (White, 1977; Ishikawa and Ichikuni, 1984).

RELATION BETWEEN VARIABLES

Figure 7 shows the relation between all variables in this study. To identify the main groups we applied a cut line at the distance of 0.6 because the great majority of the variables are clustered under this linkage distance, as we identified in the screen plot produced. We observed the formation of four main groups and the behaviour of their elements are linked with the temperature gradient. The first group is composed by the variables whose value rises with the temperature and it can be observed that ML per cent and pH of both study areas have a good correlation. Ash chroma value also has a substantial relationship with CaCO₃ content for each type of sample, which means that ash colour is a good predictor to estimate the presence of CaCO₃. The second group is composed of cations whose behaviour in the test solution is conditioned by the CaCO₃ content of the ash. All major elements analysed, with the exception of Na⁺ and K⁺ of the Mas Bassets samples, showed a decrease in solution in the ash slurries with an increase in the proportion of this mineral in the ash. Groups 3 and 4 consist of the Ca²⁺:Mg²⁺ ratio for Mas Bassets and Albufeira samples, respectively, which showed an inverse relationship of this ratio with increasing temperature.

STUDY IMPLICATIONS

The temperatures that occur during a fire induce important changes in soil physical, chemical and biological properties and the magnitude of these impacts will influence the capacity of ecosystems to recuperate. These effects include the breakdown in soil structure, decrease in soil moisture retention and capacity, formation of a hydrophobic layer, changes in nutrient pools and cycling rates, vaporization of elements to atmosphere, erosion losses, combustion of forest litter, decrease or loss of organic matter, changes and loss of microbial and invertebrates species and activity, and decomposition of plant roots (Mataix-Solera, 1999; Neary *et al.*, 2005).

We observed in this study that ML per cent increases with increasing temperatures, leading to a loss of litter and a decreased ash cover, leaving the soil surface unprotected and more vulnerable to erosion agents. This effect was more pronounced in the samples collected from the Albufeira plot where increasing fire temperatures produced a greater effect. This increase in ML per cent in the Albufeira litter is coincident with a higher fire severity compared to the Mas Bassets plot, especially at middle and higher temperatures, where major differences were identified between two plots, observed by the analysis of ash colour, per cent of CaCO₃, chroma value and the values of pH, EC and Ca:Mg ratio in solution.



Figure 7. Dendogram of the relationship between the variables in study of Mas Bassets (MB) and Albufeira (Alb) with temperature gradient. Cut line in bold. The numbers indicate the groups identified. (N = 9 per variable).

Low fire temperatures ($< 300^{\circ}$ C) will not have important consequences on values of pH and EC in solution, though these effects increase at medium and higher temperatures of litter combustion ($> 350/400^{\circ}$ C). At lower temperatures the cations released into the test solution were not substantial in comparison with the unburned sample, except for Mg²⁺, rising abruptly at moderate temperatures mainly in Albufeira ash for Mg²⁺, Na⁺ and K⁺ and in Mas Bassets for Ca²⁺. At higher temperatures the formation of CaCO₃ reduced the concentration of ions the test solution, mainly for the divalent cations because of their major susceptibility to sorption onto CaCO₃ surfaces, and the higher solubility of monovalent cations as discussed by Zachara *et al.* (1991) and Sinan Bilgili *et al.* (2007). This means that under the described temperatures in a real fire, the release of ions into soil solution will be lower at lower temperatures. However, different patterns were observed in both ash slurries that can be related to the formation of CaCO₃ at moderate to high temperatures and subsequent ion capture on CaCO₃ surfaces.

Temperature is a key point in determining the chemical composition of ash and its subsequent solubility (Etiegni and Campbell, 1991; Pereira *et al.*, 2008). In this sense, fire temperatures have a relationship with type and amount of ions released that potentially cause adverse effects on soil. After a fire the nutrients dissolved from ash will induce high soil fertility in the majority of the cases. On the other hand, the ash can generate some problems such as an excess of salts, which are detrimental to some plants and inhibit the absorption of some elements (Porta *et al.*, 1994; Mataix-Solera *et al.*, 2007).

Also, the chemical composition of water mixed with ash has several implications for soil aggregate stability (Rahimi Barzegar *et al.*, 1994) and after the fire the elements released by ash will have effects on the soil physical status resulting in increased soil erodibility. The higher presence of some major cations will produce the dispersion of clay minerals. According to Porta *et al.* (1994), the flocculation of clay minerals is higher when Ca^{2+} and Mg^{2+} are the dominant ions and minor when Na^+ and K^+ are the principal ions in soil solution. For example, the disaggregation of clay minerals such as kaolinite increases with increasing pH (Durgin and Vogelsand, 1984). Our results showed that at low temperatures, up to 300°C, the presence of the divalent cations is always higher than monovalent cations, and the potential effect of the water extracts released by the ash generated at these temperatures on clay dispersion is negligible (Figure 8). Nevertheless, at medium and higher temperatures—greater than 350°C in Albufeira ash slurries and at 450°C for Mas Bassets ash slurries—the proportion of Ca^{2+} and Mg^{2+} decreases significantly in relation to Na⁺ and K⁺ and is accompanied by an increase in pH. The chemistry of ash slurries can lead to an enrichment of the monovalent cations in soil solutions and increase the susceptibility of soils to erosion.



Figure 8. $Ca^{2+}+Mg^{2+}$ and Na^++K^++ concentration in the test solution with temperature gradient in *Quercus suber* litter from Mas Bassets and Albufeira (N=1 per element per variable).

This means that the potential effect of water released by ash on soil clay dispersion increases at medium and higher temperatures.

Overall, temperature had more significant effects on *Quercus suber* litter of the Albufeira plot, than that of the Mas Bassets plot. The higher flammability and consequent ML per cent of Albufeira samples point to a higher thermal degradation of the Albufeira leaf litter than the Mas Bassets samples, evident also by the formation of grey/ white ash at lower temperatures. This response has the potential to expose the soil surface to erosion. At lower temperatures the pH values and the cation release are not substantial. However, this release of cations, particularly monovalent cations, increases at moderate and higher temperatures, especially in Albufeira ash slurries. This means that at higher temperatures the reduction of ML per cent, the combustion of the organic matter, the impact of temperatures on soil physical status and the water soluble elements released by the ashes will cause a higher desegregation of soil mineral particles, leaving them more vulnerable to erosion transport.

Fire can is a useful tool used by humans for land management, but also can develop lead to the degradation of the land and its resources. The impacts of fire are a function of the intensity of a fire, including the duration of the heat impulse, and the resulting fire severity on the biophysical conditions of the ecosystem affected (Neary *et al.*, 2005; Siva Kumar and Ndiang'ui, 2007). Mediterranean ecosystems are well adapted to fire effects.. In particular, *Quercus suber* can resprout after fire. However, during high intensity fire, the bark that insulates trees from high temperatures can be combusted, thereby reducing the capacity of these system to recover after wildfire.

The results obtained in this study are a useful contribution that will help inform land management decisions in the study areas. Using this information, we know that low fire temperatures do not lead to the substantial release of the elements we studied to soil solutions or overland flow. Forest management with low intensity prescribed fires can be a constructive tool. Medium and higher temperatures produce ash that is susceptible leaching, which may release ions that have effects on aggregate stability and long-term soil fertility. These potential effects are more pronounced for the Albufeira site. For these reasons, it is of major interest protect these sites from wildfire occurrence, due the potential negative effects of ash on soil properties and water resources. Management objectives can be accomplished with the application of prescribed fires, which still release nutrients to the soil but reduce the amount of biomass in the forests, decreasing the risk of wildfire occurrence in these environments vulnerable to fire events.

CONCLUSION

The results obtained from this study showed that combustion temperatures had diverse effects on *Quercus suber* populations located in different environments and that litter characteristics influence the vulnerability of the species to fire temperatures. The potential effects of the elements concentrated in test solutions on soil physical and chemical status and water resources were reduced at low temperatures and elevated at medium and higher temperatures, mainly in the samples collected in Albufeira litter, where we found a higher presence of monovalent cations in relation to divalent cations. The results obtained from this study are of major importance, because the leaf litter characteristics and the environment play an important role in the fire severity response of each ecosystem where *Quercus suber* is located. The application of low intensity prescribed fires does not have damaging impacts in the ecosystem and their use could be a useful instrument to land management to reduce the risk of wildfires and their negative effects on these sites.

In order to validate our laboratory simulations, the next step is to collect ash samples from prescribed and wildland fires from the environments where we collected the litter to expand this study to observe if these differences are also evident in field conditions.

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