

## HEAVY METALS RELEASED FROM LEAF LITTER EXPOSED TO DIFFERENT FIRE TEMPERATURES. A LABORATORY EXPERIMENT

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**Abstract.** *The leaf litter of three Mediterranean species, Quercus suber (Q.S.), Quercus robur (Q.R.) and Pinus pinea (P.P.), was exposed to different fire temperatures, 150°, 200°, 250°, 300°, 350°, 400°, 450°, 500°, and 550°C in a muffle furnace for 2 hours. We measured the Calcite (CaCO<sub>3</sub>) content of the ash and the pH and release of heavy metals Aluminium (Al), Manganese (Mn), Iron (Fe) and Zinc (Zn) in a slurry of ash and deionised water. CaCO<sub>3</sub> in the ash appears at 400°C and increases with temperature. The pH values are low at low fire temperatures, rise at medium temperatures, followed by a stabilization at higher temperatures. Heavy metals concentration in solution are higher in the low pH slurries where CaCO<sub>3</sub> is absent in the ash. In general, at low and medium fire temperatures, Al and Mn in ash slurries are more soluble than in an unheated control sample and this concentration in test solution decreases at higher temperatures. Fe and Zn in solution decrease with exposure to higher temperatures, even at low pH. At higher temperatures, the effect of pH and CaCO<sub>3</sub> inhibits the presence of heavy metals in solution.*

**Keywords:** *Fire, Quercus suber, Quercus robur, Pinus pinea, fire temperatures,, Calcite, pH, Aluminium, Manganese, Iron and Zinc*

### INTRODUCTION

Fire is an excellent mineralizing agent of vegetation, leading to the availability on the soil surface of a great quantity of nutrients, mainly in the form of oxides, hydroxides and carbonates that can be leached by water. This mineralization depends on the temperature and length of exposure to heat (Gray and Dighton 2006). The ash produced by fire is primarily composed of Calcium (Ca),

Potassium (K), Magnesium (Mg) and Phosphorous (P), and is characterized by a high alkalinity (Etegni and Campbell 1991; Ulery *et al.* 1993). In addition to the fire temperature and duration, the chemistry of the ash is a function of the type, quantity and part of vegetation burned (leaves, bark, twigs, litter), soil, climatic conditions during combustion, and the collection and storage of samples (Khanna *et al.* 1994; Someshwar, 1996; Demeyer *et al.* 2001). Wood ashes also are com-

posed by a higher content of heavy metals (Someshwar 1996). They could be defined as metals ions of the second or third row transitions, normally associated with contamination and potential toxicity or ecotoxicity (Shaw 1999). Heavy metals are natural elements in the environment and differ from place to place due their concentrations in bedrock, play a an essential role in ecosystems and some are necessary to in small amounts for a great part of the organisms to have a normal and healthy grow. They can not be excluded from the environment. The problem is when the human activities produced wastes where heavy metals are transported by air, water or other deposits, increasing their concentrations. The presence of heavy metals in soils and aquatic systems is of major concern, because of their potential reactivity, toxicity and mobility. They can be involved in a serie of a complex chemical and biological interactions and reactions as surface-solution phase complexation, precipitation dissolution, volatilization and oxidation-reduction (Selim and Amacher 1996; Greger 2003; van der Perk 2006).

Aluminium (Al), Manganese (Mn), Iron (Fe) and Zinc (Zn) are some of the heavy metals more common in wood ashes as described by several studies. Etegni and Campbell (1991), showed that these components had the highest concentrations of the trace elements in Lodgepole pine (*Pinus contorta*) ash, generated at 538°, 646° and 760°C. With increasing temperatures, the authors observed an increase in Mn and Fe and a decrease in the Zn concentration. The Al concentration remains constant. Similar results were found by Liidakis *et al.* (2007), analyzing the ash composition of some

Mediterranean species, *Pinus halepensis*, *Pinus brutia*, *Olea europaea*, *Pistacia lentiscus* and *Quercus coccifera* generated at 600°, 800° and 1000°C: an increase in Mn and Fe with increasing temperatures, and a decrease of Zn. Misra *et al.* (1993), identified an enhancement of Al and Fe, and a reduction of Mn and Zn in relation to Ca with increasing temperatures in the ash of *Populus tremuloides* Micx., produced at temperatures between 600°-1400°C. Ferreira *et al.* 2005, also identified higher concentrations of Zn (201 mg/kg), Fe (1466 mg/kg) and Mn (2570 mg/kg) in relation to other elements in ash collected in a *Pinus pinaster* stand after a forest fire. Someshwar (1996) reported the presence of 3485 mg/kg of Mn and 329 mg/kg of Zn in wood boiler ash. These elements were the ones present in large quantities in wood-fired boiler ash from different sources, as described by Vance (1996) (2430 mg/kg for Mn and 316 mg/kg for Zn, respectively).

Heavy metals present in wood ash can be dissolved easily, mainly in low pH environments, causing negative consequences on soil solutions, surface and underground waters (Demeyer *et al.* 2001; Ludwig *et al.* 2005). Rumpf *et al.* (2001) identified a rise in Zn concentrations in soil solutions after ash addition in a pine stand in Germany. No changes were observed in Al.

During prescribed fires and wildland fires, it is impossible collect ashes generated at a specific temperature. Regarding this, laboratory fire experiments at several temperatures is a very useful methodology to understand the dynamic of heavy metals concentration in ash slurries and estimate possible effects of fire temperature on the release of metals

in the environmental system from a de-terminated specie.

Studies about the effects of fire in mi-cronutrients are lacking (Certini 2005). In this sense little attention has been paid to the release of heavy metals from the ash generated at different temperatures. The majority of the studies are directed to the behaviour of base cations and ani-ons because of their higher concentra-tion, for example the studies of Soto and Diaz-Fierros (1993), Blank *et al.* (1996) and Gray and Dighton (2006).

This paper examines the behaviour of Al, Mn, Fe and Zn released as solutes from leaf litter of three Mediterranean species, *Quercus suber* (Q.S.), *Quercus robur* (Q.R.) and *Pinus pinea* (P.P.), when exposed to different fire temperatures (150°, 200°, 250°, 300°, 350°, 400°, 450°, 500° and 550°C) in a muffle furnace. In order to understand the concentra-tion of metals in the test solution we also analyzed other parameters, including the CaCO<sub>3</sub> content of the ash and pH.

Volatilization also affects the quan-tity of nutrients in wood ash and their content depends of the temperature reached during the fire. Each element has a specific threshold and present differ-ent vulnerabilities to temperature effects (Neary *et al.* 1999; Neary *et al.* 2005). In the heavy metals analyzed in our study, the temperatures of volatilization are higher than the selected. Al volatilizes at temperatures near 2467°C, Mn at tem-perature around of 1962°C, Fe almost at 3000°C and Zn at 907°C (Raison *et al.* 1985a,b, Merien 1991). In this case is very likely that in the temperatures applied in this laboratory experiment the great ma-jority of this metals stay available in the ashes, beside they could take a place by

ash convection (Gillon *et al.* 1995)

Regarding the impossibility to iden-tify the impacts of concentration of met-als in solution at a specific temperature in the field, the lack of investigations about heavy metals solute released from wood ashes and the great quantity avail-able to dissolution in the ash due metal high volatilization temperatures, it is of major importance and inters study their concentration in solution with labora-tory experiments, in order to observe the potential increase of soil acidity, toxicity, impacts on plants and contamination of surface and groundwater reserves in the forests dominated by the species in study affected by the temperatures.

## 1. STUDY AREA AND METHODOLOGY

The leaf litter was collected in the spring/summer of 2007, in the Gavarres mountains located in the northeast of Catalonia (Iberian Peninsula) at 41° 87' N and 2° 92' E. The geologic substrate is dominated by granite rocks with a frag-ile structure (Úbeda *et al.* 1998) and the climate is classified as Mediterranean sub-humid with an annual average tem-perature of 13.98°C and an annual pre-cipitation of 768.31 mm, with a high in-terannual variability during the autumn and winter. Soils are classified as *Luvi-arenosols*, with a high content of sand and a low pH. The vegetation is primarily composed of *Quercus suber*, mixed with *Quercus ilex*, *Quercus robur*, *Pinus pinea* and *Pinus pinaster*.

The leaf litter collected in the study area, corresponds to the tree dominants from the site. After this task, samples were taken to the laboratory and separated

from leaves from other species and twigs and the remaining material cleaned with deionised water to remove all impurities. Subsequently, samples were air-dried for 24 hours, before exposing them to different temperatures in a muffle furnace for a 2 hour period also applied in other studies (Stark 1977; Gray and Dighton 2006; Pereira *et al.* 2008).

After the leaf litter was exposed to heat, in the samples subjected to fire temperatures, CaCO<sub>3</sub> of the ash was measured with a Bernard's calcimeter calibrated with 0.2 g of pure CaCO<sub>3</sub> using a 1:2 hydrochloric acid solution (50% concentrated HCl and 50% deionised water). Subsamples of ash weighing 0.2 g were mixed with the 1:2 solution. The CaCO<sub>3</sub> was estimated by calculating the difference between the volume of CO<sub>2</sub> before and after introducing all samples from the species subjected to fire temperatures with a mix of the ash and the acid solution.

An ash slurry was created by mixing 6 g of the ash generated at different temperatures with 36 ml of deionised water, which was mixed for 2 hours on a Thermo Scientific Variomag Poly inductive-drive stirrer. This solution was filtered through a Whatman QMA, 4.7 cm filter using a Millipore 220/240 Volts, 50 Hz pump. After this task, the pH was measured with a Crisol GLP 22 pH meter. Heavy metals (Al, Mn, Fe and Zn) were determined by producing an ash slurry, 1:40 (1g of ash and 40 ml of deionised water), that was mixed for 24 hours and then filtered through a Whatman 0.45 µm pore size filter QMA quartz fibre. After this task, the solution was analyzed 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 sample was treated in the same manner as the heated samples.

The CaCO<sub>3</sub> data is presented in % ash dry sample Heavy metals data are presented as a % of the values in comparison with the unheated control in order to observe the effects of the temperature in metals release in the test solution.

## 2. RESULTS AND DISCUSSIONS

### 2.1 CaCO<sub>3</sub>

CaCO<sub>3</sub> is one of the main components of the ash. It is formed at different temperatures depending on the type of vegetation combusted, temperature and length of exposure (Pitman 2006). Quintana *et al.*, 2007 pointed out that the formation of this mineral is due the thermal degradation of calcium oxalate. Ulery and Graham (1993) and Goforth *et al.* (2005) observed that the principal component of the ash from a high intensity fire was CaCO<sub>3</sub>, In this study, the formation of CaCO<sub>3</sub> was identified, after the litter was exposed to 400°C (figure 1), but in different quantities according to the plant species. However, this concentration of CaCO<sub>3</sub> increased with increasing temperature, especially in Q.R., but also in P.P. At all temperatures the Q.S. contained the smallest amount of CaCO<sub>3</sub>. The impacts of temperature on the formation of CaCO<sub>3</sub>, are higher in P.P and Q.R and lower in Q.S.. The formation of CaCO<sub>3</sub> at these temperatures was identified by other studies. Iglesias *et al.* (1997) observed the creation of CaCO<sub>3</sub> in dead leaves of *Juniperus oxycedros* and branch-

es of *Quercus pyrenaica* when ashed at 500°C. Quintana *et al.* (2007) also identified CaCO<sub>3</sub> formation at 400°C using XRD analysis after exposing *Juniperus thurifera* L. to several fire temperatures. Also with XRD, Misra *et al.* (1993) identified a predominance of CaCO<sub>3</sub> in ash of *Pinus ponderosa* Dougl. ex Laws, *Populus tremuloides* Micx., *Liodendron tupilifera* L. and *Quercus afba* (sic; *alba*) heated to 600°C. After ashing several Mediterranean species (*Pinus halepensis*, *Pinus brutia*, *Olea europea* and *Quercus coccifera*), Liodakis *et al.* (2007), founded CaCO<sub>3</sub> at 600°C.

## 2.2 pH

The mineralization of organic matter induced by fire leads to an increase in pH of the solution due to the release of cations in solution and is very influenced by CaCO<sub>3</sub> values of the ash (Ulery *et al.* 1993; Neary *et al.* 2005). Our results showed a rise in pH with an increase in fire temperatures. This increase has been

documented by Quintana *et al.* (2007) and Henig-Sever *et al.* (2001) in laboratory environments after exposure of soils (O-horizon) and pine leaves to fire temperatures. In this study at low fire temperatures pH may not exhibit an increase, as can be observed in figure 2. Up to 300°C, the pH values were between 4 and 5 for Q.S. and Q.R., and 5 and 6 for P.P.. At 300°C, there was a slight dip of pH values for all species, also identified by Úbeda (2001) for values of soil pH at temperatures between 200-300°C in *Quercus suber* and *Pinus pinaster* forests. Giovannini (1994) observed also a decrease in soil pH, with exposures of soil to 220°C and attributed this to an oxidation of certain metallic elements such as Al or Fe. The last element starts to oxidize around 200°C, as mentioned in some studies (Nelson 1938; Driscoll 1981; Abdel Halim *et al.* 2007). After 300°C, a rise of pH values was observed up to 450°C, followed by a stabilization up to 550°C, but at higher pH values, mainly in P.P.

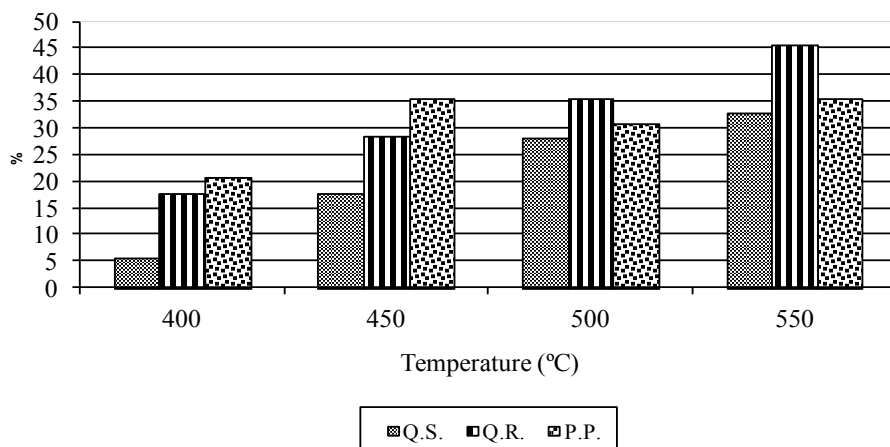


Fig 1. Presence of CaCO<sub>3</sub> as a percentage in *Quercus suber* (Q.S.), *Quercus robur* (Q.R.) and *Pinus pinea* (P.P.) ashes.

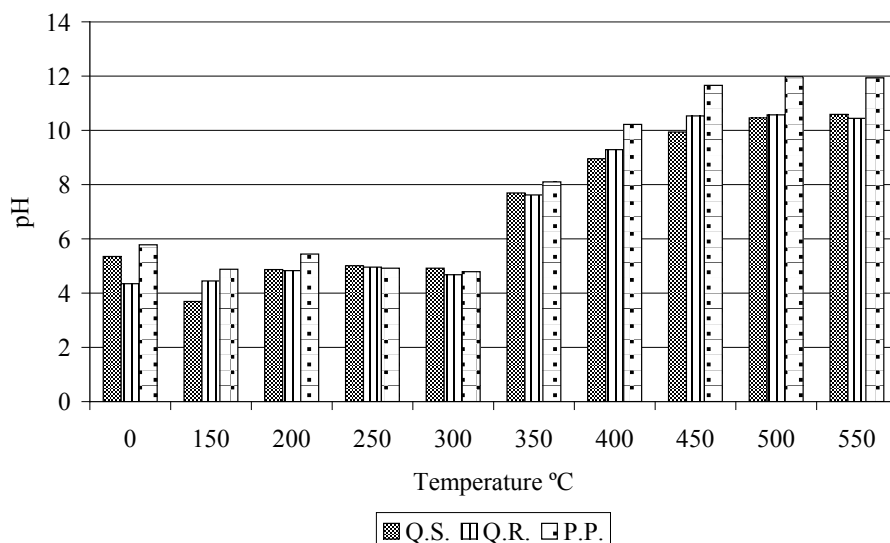


Fig 2. Evolution of *Quercus suber*, *Quercus robur* and *Pinus pinea* ashes pH with increasing temperature.

### 2.3 Heavy metals

Before discussing each parameter in study, should be highlighted that concentration of metals in water depends on pH or Eh values, temperature and sorption onto charged sites of fine-grained solids (Siegel 2002). Carbonate minerals, mainly calcite and aragonite, have a great ability to sorb metals from solution in varying degrees (Zavarin and Doner, 1999; Astilleros *et al.* 2006), by adsorption (metals bind to mineral surfaces), absorption (incorporation of metals into  $\text{CaCO}_3$ ), precipitation (generation of secondary mineral phases) or co-precipitation (uptake of metals onto mineral surfaces during crystal growth), or during crystal growth on  $\text{CaCO}_3$  surfaces, that can affect the morphology (Lorens 1981; Fernández-Díaz *et al.* 2006; Elzinga *et al.* 2006). Several studies show that the initial reaction is a rapid capture of metals by physical adsorption (chemisorption), followed by a decline, probably because of a decrease

in the availability of surface sites or a rise in the  $\text{CaCO}_3$  surface charges. After the adsorption, a slow process of uptake of metals begins by precipitation or co-precipitation (Lorens 1981; Comans and Middelburg 1987; Zachara *et al.* 1988). These processes increase with rising pH,  $\text{CO}_2$  gas pressure, a decrease of Ca levels in solution (controlled by pH and  $\text{CO}_2$  pressure), and metal content in solution (Zachara *et al.* 1990, 1991; Brady *et al.* 1999). According to Chirenje *et al.* (2006), the increase of metal sorption under high pH, may be a consequence of less competition of protons for sites on  $\text{CaCO}_3$  or ash particles. Gomez del Rio *et al.* (2004), pointed out that the adsorption of metallic cations could be reduced at pH values under 8.2 (the pH of zero point charge) where  $\text{CaCO}_3$  surfaces have a positive charge. At a pH value higher than 8, the surfaces are negatively charged, and metals in solution are easily adsorbed (Ettler *et al.* 2006). However, the sorption

of metals is a function of the size of each ionic radii. Many studies show that metals with ionic radii greater than Ca are poorly sorbed by calcite surfaces. In contrast, ions with ionic radii smaller than or similar in size to Ca, are easily sorbed (Comans and Middelburg 1987; Mucci 1988; Zachara *et al.* 1991; Temmam *et al.* 2000; Ettler *et al.* 2006; Menadakis *et al.* 2007). This selectivity and competition for sorption sites should have implications for the quantity of metals in solution when in contact with  $\text{CaCO}_3$ , and it is important to understand the concentration of metal in the test solution and sorption behaviour of cations in ash slurries, mainly in ash generated at higher temperatures.

### 2.3.1 Aluminium

The effect of ash on Al dissolution in soil solution is a decrease in its concentration due to an increase in pH, as shown by studies by Kahl *et al.* 1996, Vance 1996, Saarsalmi *et al.* 2001, and Demeyer *et al.* 2001. Nevertheless, our investigation showed that the concentration of Al in the solution depends on the temperature at which the ash is generated and subsequently of the pH of the ash slurry. At low and medium fire temperatures (150°-350°C), Al was founded in solution at even higher levels than founded in unburned samples (figure 3) and is variable,

and depends on the plant species. Compared with the control, Al in solution was almost 3 fold higher at 200°C for Q.R. and 2 fold at 250°C for Q.S. and P.P. However the greater impact of Al released in concentration in the test solution at 150-300°C is observed in Q.S, followed by P.P and for Q.R.

In this study concentration of Al is high at pH <5 and at pH >8 no Al is found in solution, which is coincident with the formation of  $\text{CaCO}_3$  in the ash at 400°C (figure 3). This toxic element is highly mobile at pH < 5, but shows a low solubility in a range between 5 and 8 (Kabata-Pendias and Pendias 2000; Sposito 2000; Lee *et al.* 2002) which is in concordance with our results. The affinity of Al for calcite surfaces, is related to its smaller ionic radius relative to Ca (Al=0.535 Å, Ca=0.99 Å), the valence of this metal and the formation of negative surfaces at a pH >8, mainly by adsorption. This propensity of Al ions to bind to  $\text{CaCO}_3$  surfaces is discussed by Zachara *et al.* (1990). The reduction of Al in concentration in test solution is a result of precipitation of Al forms. For example, Komnistas *et al.* (2004) founded that Al precipitates rapidly when limestone is dissolved and pH rises, as amorphous  $\text{Al(OH)}_3$  and insoluble basic aluminium sulphate ( $\text{AlOHSO}_4$ ).

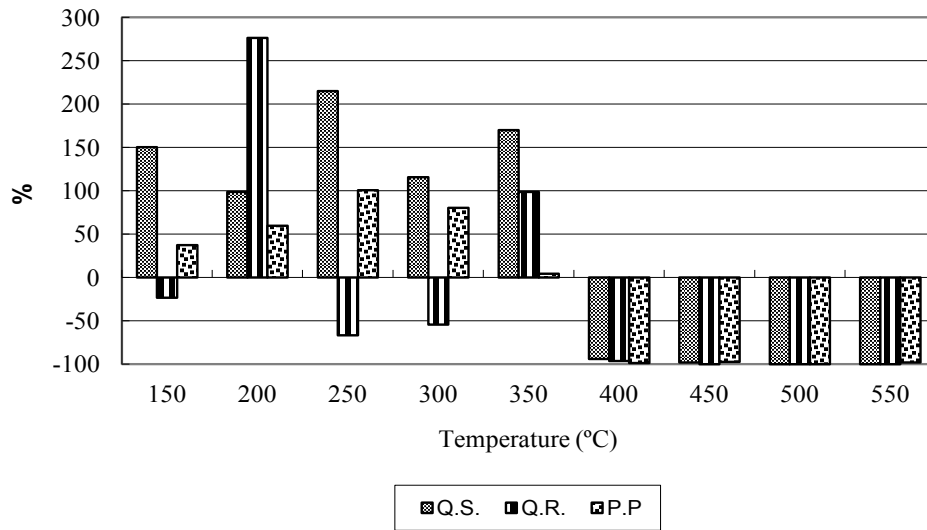


Fig 3. Variation of Al concentration in solution as a percentage of the unheated control at different temperatures

### 2.3.2 Manganese

The results showed that Mn has a high concentration in the test solution at low and medium fire temperatures, 150°-350°C (figure 4), mainly due to the influence of pH and CaCO<sub>3</sub> absence. Compared to the control, impacts of temperature were mainly evident in P.P. where Mn concentrations increased up to 19 fold more at 350°C. For Q.S. at low-medium temperatures (150°-350°C), the impacts were always higher than 200%. The Mn in solution in Q.R. ash slurry was only higher than the control at 150°C and 200°C. As we founded in our study, higher levels of Mn in soil solution were founded also by Parra *et al.* (1996) after a forest fire in a *Pinus pinaster* stand. The authors attributed this increase of Mn in soil surface to ash effect. The magnitude of the change of Mn in solution with increasing temperatures followed the decreasing sequence is mainly evident in P.P. and lesser in Q.R.

The concentration of Mn in the test solution decreased drastically at a pH >8 and with the generation of CaCO<sub>3</sub>, even though Mn from P.P. exposed to at 400°C existed a higher levels in the ash slurry than the control. Our results are in agreement with Lee *et al.* (2002), who identified a precipitate of Mn at a pH ~ 8. Zachara *et al.* (1991) identified that at a pH of 8.4, the precipitation of Mn<sup>2+</sup> was higher at elevated concentrations of Mn<sup>2+</sup> in solution. The relation between Mn<sup>2+</sup> and CaCO<sub>3</sub> surfaces is complex (Franklin and Morse 1983). However, our findings showed a rapid decrease of Mn in concentration of test solution when CaCO<sub>3</sub> is formed and are supported by Lorens (1981), who documented a rapid reduction of Mn in solution when in contact with CaCO<sub>3</sub> surfaces. Comans and Middelburg (1987), Zavarin and Donner (1999) and Ettler *et al.* (2006) show that Mn<sup>2+</sup> was easily sorbed on calcite surfaces as consequence of its smaller and similar



ionic radii (0.80 Å) relative to Ca. Manganese carbonate ( $\text{MnCO}_3$ ) has a structure similar to  $\text{CaCO}_3$  and Mn can substitute directly for Ca on  $\text{CaCO}_3$  surfaces. However, the precipitation of Mn as  $\text{MnCO}_3$  decreases with increasing precipitation rate (Lorens 1981; Mucci 1988). Sibrell *et al.* (2007) pointed out that Mn is a metal strongly attracted to calcite surfaces,

where co-precipitation could happen if the solids were oversaturated. At lower concentrations, Mn is quickly incorporated into the  $\text{CaCO}_3$  structure and at higher values forms a precipitated surface (Zavarin and Donner, 1999). Only small amounts of  $\text{Mn}^{2+}$  are required to increase dramatically the growth of calcite (Fernández-Díaz *et al.* 2006).

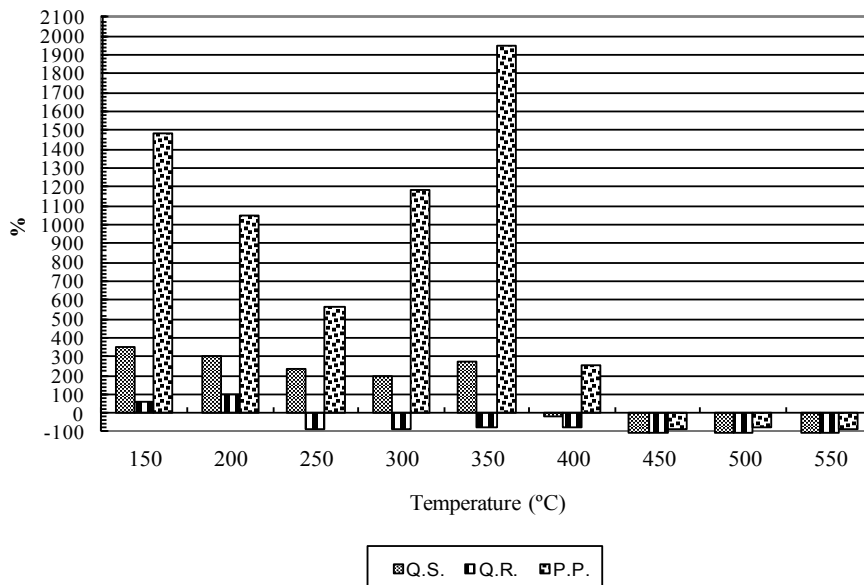


Fig 4. Variation of Mn concentration in solution as a percentage of the unheated control at different temperatures.

### 2.3.3 Iron

Our results demonstrated that the effect of increasing combustion temperature was a decrease of Fe in solution, also founded by Stark (1977) despite the fact that at 200°C the ash of Q.R. showed high values of Fe compared to the control. At 300°C, the presence of Fe in the ash slurries is less than the unburned control for all species (figure 5). The magnitude of the change of Fe in solution does not show a clear pattern between species.

The lower concentrations in the test solution at low temperatures is caused by the existence of insoluble forms of Fe or pH (Kabata-Pendias and Pendias 2000; Siegel 2002). The pH levels of the ash slurries are never <4, except in Q.S. at 150°C, and this can explain also why there is a lower concentration of Fe in solution. Lee *et al.* (2002), identified a residual concentration of Fe in solution at a pH>4, and Morgan and Lahav (2007) showed in their experiments that  $\text{Fe}^{2+}$  dominates at

a pH<4 because the oxidation is very low. These reduced levels of Fe are also related with the presence of higher quantities of other metals in the test solution, as Mn (Kabata-Pendias and Pendias, 2000).

At temperatures higher than 400°C, the presence of Fe in solution for all species was below 80% compared with the control and in some cases it is nonexistent. Even if the concentration in test solution of this metal is reduced at higher pH and temperatures, the presence of CaCO<sub>3</sub> had an influence on the concentration of this metal in solution. There are only a few studies about CaCO<sub>3</sub> effects on Fe sorption. However, El-Korashy (2003) showed that the uptake of Fe<sup>2+</sup> by CaCO<sub>3</sub> is by a direct exchange with surface Ca<sup>2+</sup>, which could be facilitated by the smaller ionic radius of Fe (0.64 Å) in relation to Ca (Ettler *et al.* 2006). Komnistas *et al.* (2004) investigated the effect of limestone in Fe removal from water and had concluded that this ion precipitated, mainly as ferrihydrite (Fe(OH)<sub>3</sub>) and goethite (FeOOH), on limestone surfaces. The precipitation or co-precipitation on CaCO<sub>3</sub> will induce a crystal growth. According to Wada *et al.* (1995), the presence of Fe<sup>2+</sup> favoured the formation of aragonite and caused co-precipitation of calcite solid solution.

### 2.3.4 Zinc

Our results showed that the impact of temperatures on Zn in solution was a decrease in its concentration relative to the control (figure 6), except for P.P. at temperatures of 150° and 350°C. These results are supported by Stark (1977) that also founded a reduction in Zn soil leaching after medium and hot burns. The Zn in solution did not show a clear pattern between species. This lower concentration

in the test solution even at low temperatures are a consequence of pH values, the precipitation with other metals, mainly as oxides and (oxi)hydroxides of Al, Fe or Mn, that could co-precipitate with Zn and the high capacity to be adsorbed by mineral and organic compounds. In this study the concentration of Zn in the ash slurry decreased to values less than 2 ppm at a pH range 4.92-5.01. Our results are consistent with findings reported elsewhere. In solution, Zn is more sensitive to pH changes compared to other metals (Chirenje *et al.* 2006). Scokart *et al.* (1983) found that the mobility of Zn in soil solutions only increases at pH <5. Speir *et al.* (2003) identified a substantial reduction of Zn in a soil solution at pH between 5-6 and Agbenin and Olojo (2004) showed a maximum adsorption of Zn at a pH of 6.8 in an Alfisol. Gibert *et al.* (2005) demonstrated that the presence of Fe and Al in water reduces the presence of Zn in solution by approximately 60% by co-precipitation. Lee *et al.* (2002) founded that from natural waters contaminated with acid mine drainage, that at a pH 6 – 7.5, 50% of Zn was removed from the water.

At higher temperatures, the results obtained in this study demonstrated that at 400°–450°C, there was a decrease of Zn<sup>2+</sup>, relative to the control greater than 80%, rising to 90 % at 500–550°C for all species. Despite the effects of pH, the capacity of CaCO<sub>3</sub> to sorb Zn is well known, as shown in the studies by Tsusue and Holland (1966), Zachara *et al.* (1989, 1991) and Shahwan *et al.* (2005). The ionic radius of Zn (0.74 Å) is smaller compared to Ca and this mechanism influence their sorbtion by CaCO<sub>3</sub> as discussed by Comans and Middelburg (1987) and Ettler *et al.* (2006). Wang *et al.*

(2001) identified a reduction of 96 % of extractable Zn in contaminated soils after the application of CaCO<sub>3</sub>. The quantity of sorbed Zn<sup>2+</sup> depends on the concentration and surface area of CaCO<sub>3</sub>, and it is rapidly adsorbed by exchange of Zn<sup>2+</sup> and ZnOH<sup>+</sup> with surface-bound Ca<sup>2+</sup> (Zachara *et al.* 1988; Cheng *et al.* 1998). As with the other metals, Zn also precipi-

tates on CaCO<sub>3</sub> surfaces, mainly in the form of hydrozincite, Zn<sub>5</sub>(OH)<sub>6</sub>(CO<sub>3</sub>)<sub>2</sub>, as highlighted by several studies (Zachara *et al.* 1989; Garcia-Sanchez and Alvarez-Ayuso 2002; Freij *et al.* 2005; Shahwan *et al.* 2005), but also via crystallization of ZnCO<sub>3</sub>, when in reaction with CaCO<sub>3</sub> (El-Korashy, 2003).

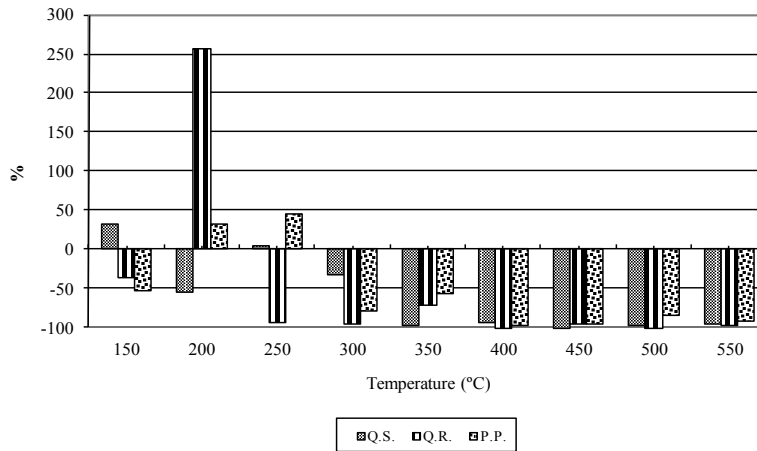


Fig 5. Variation of Fe concentration in solution as a percentage of the unheated control at different temperatures.

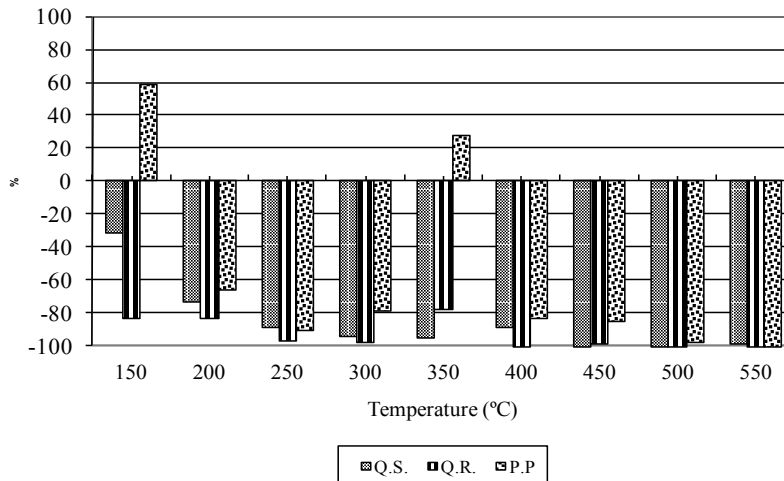


Fig 5. Variation of Fe concentration in solution as a percentage of the unheated control at different temperatures.

## CONCLUSIONS, STUDY IMPLICATIONS AND FUTURE RESEARCH

The results obtained from this laboratory experiment demonstrated that the fire temperatures in the range in analysis has important effects on the concentration of heavy metals in the test solution, are variable according to the specie and the temperature and depend of the pH values and ash CaCO<sub>3</sub> content. CaCO<sub>3</sub> appeared at 400°C and increased with the temperature of exposure mainly in P.P and Q.R. ashes. At lower fire temperatures (150°-300°C) pH is reduced (4-6), rising abruptly at average fire temperatures (350°-400°C) – mainly in P.P. – showing values between 5 and 9, stabilizing at higher fire temperatures (>450°C) but at levels above 9-10. Compared to the control, the impact of fire temperatures depends on the metal analysed and the temperature of exposure, leading to a complex solubility dynamic. Al and Mn show a higher concentration in the test solution in the ash slurries generated at low-medium fire temperatures (150-350°C), mainly Mn, decreasing substantially thereafter due the formation of CaCO<sub>3</sub>, that capture metals into their surfaces from the solution and higher pH values. Fe and Zn show a reduction in concentration in test solution at all fire temperatures, mainly due precipitation with other metals, higher pH levels and presence of CaCO<sub>3</sub> surfaces at temperatures >400°C.

The temperatures analyzed in this study are suitable to occur in prescribed fires as documented by Gimeno-Garcia *et al.* 2000, 2004, Úbeda *et al.* 2005 or wildland fires in summer season .Accord-

ing DeBano *et al.* 1981 during the wildland fire the temperatures could reach at 900°C in soil surface and litter layer, and due to the poor conductivity of dry soils, at 5 cm the temperature below the surface the temperature is not likely to exceed 150°C. In this sense is very likely the occurrence of the temperatures range selected in this study. Low-medium fire temperatures (150°-350°C) experienced during prescribed fires or wildland fires in portions of the forests dominated by the species in study will have a decrease of Fe and Zn and an increase of Al and Mn in soil solution, leading to a higher toxicity and effects on soil productivity and consequently a acidification of water resources mainly in Q.S. and P.P forests. These effects will be more coercive because the soils where the samples were collected have acid properties. Porta *et al.* 1994 pointed out that the negative effects in plants are mainly due the higher toxicity of Al and Mn ions. Al is not an element essential to plant growth, contrary to Mn (Helyar, 1981). Elevated levels of Al and Mn on soils will cause an inhibition of Ca, Mg and Fe absorption by plants and toxic effects on vegetation (Kabata-Pendias and Pendias, 2000, Varrenes, 2003). Also, higher levels of Al affect mycorrhiza, fine root systems and growth of terrestrial plants (Rosseland *et al.* 1990). The most characteristic symptom of Al toxicity in soil solution is the development of thickened, stubby and distorted root systems. In soil solution, higher levels of Mn lead to cell Mn high concentrations in plants, and the control of the Mn activated enzymes is lost (Helyar, 1981).

Fires with temperatures between 400-550°C in the forests dominated by the species in analysis are considered of

high severity due the formation of  $\text{CaCO}_3$ , mainly in P.P forests. In the portions of the watershed affected by these temperatures, a high reduction of the concentration in solution of all metals studied will occur, because of the metal capture effect of  $\text{CaCO}_3$  surfaces and higher pH.

During a fire, spatial temperature distribution can be very heterogeneous, leading to a mosaic of areas burned at different severities and as consequence to a complex pattern of type and amount of nutrients release (Neary et al. 2005). In our laboratory experiment, the results suggest that concerns should be taken about the effects of low-medium fires temperatures in Al and Mn release in order to evaluate their effects in the environment.

The next steps in this work will be to determine the total concentration of metals in the wood ash produced in the laboratory in order to understand the quantity of metals dissolved into solution, and to assess the potential risks of the metals in the wood ash produced by each plant species. The second step is to collect ash from prescribed and wildland fires where these plants species are dominant with the aim of comparing and validating the research done in the laboratory environment with field conditions.

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