

Fe and Al leaching in soils under laboratory-controlled burns

Lixiviación de Al y Fe en suelos sometidos a quemas controladas en laboratorio
Lixiviação de Al e Fe em solos submetidos a queimadas controladas em laboratório

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ABSTRACT

The influence of the severity of soil heating on aluminium and iron leaching was analysed, as well as its relationship with the solubility of organic matter. For this purpose, laboratory experiments were carried out under microcosm conditions where unaltered soil blocks were submitted to thermal shock and subsequently to rainfall simulation (300 mm), collecting the surface (0 cm) and subsurface runoff (12 cm). Soil heating was carried out using infrared lamps reaching temperatures of 222 and 401 °C at a depth of 1 cm, similar to those reached in moderate and high intensity fires respectively. The analysis of the drainage waters showed that the leaching of Al increased with the severity of the thermal shock, whereas for Fe perceptible effects were only seen at the highest temperature. Geochemical modelling with Visual MINTEQ indicated that Al and Fe were fundamentally mobilised and associated with dissolved organic matter. Weak interactions (electrostatic binding) predominated in the case of Al and strong interactions (bidentate complexes with dissolved organic matter) in the case of Fe. Only towards the end of the leaching experiment, when the concentration of dissolved organic carbon decreased, was there a perceptible mobility of Al and Fe in the inorganic form, in the subsurface leachate of the moderate temperature treatment.

RESUMEN

Se analizó la influencia de la severidad del calentamiento del suelo en la lixiviación de aluminio y hierro, y su relación con la solubilidad de la materia orgánica. Para tal fin, se realizaron experimentos de laboratorio, en condiciones de microcosmos, en los que bloques de suelo inalterados fueron sometidos a choques térmicos y posteriormente a la acción de lluvia simulada (300 mm), recogiendo las aguas de escorrentía superficial (0 cm) y subsuperficial (12 cm). El calentamiento del suelo se llevó a cabo por medio de lámparas infrarrojas, que permitieron alcanzar temperaturas de 222 y 401 °C, a 1 cm de profundidad, similares a las que se alcanzan, respectivamente, en incendios de severidad moderada y alta. El análisis de los lixiviados mostró que el lavado de Al aumentó con la severidad del choque térmico, mientras que para el Fe solo se observaron efectos apreciables para la temperatura más alta. La modelización geoquímica con el programa Visual Minteq indicó que Al y Fe se movilizaron fundamentalmente asociados a materia orgánica disuelta, predominando las uniones débiles (enlace electrostático) en el caso del Al y las uniones fuertes (complejos bidentados con la materia orgánica disuelta) en el caso del Fe. Únicamente hacia el final del experimento de lixiviación, cuando disminuyó la concentración de carbono orgánico disuelto, se observó una movilización apreciable de Al y Fe en forma inorgánica en el lavado subsuperficial del tratamiento de moderada temperatura.

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RESUMO

Analísou-se a influência da severidade do aquecimento do solo na lixiviação do alumínio e do ferro, bem como a sua relação com a solubilidade da matéria orgânica. Assim, realizaram-se ensaios laboratoriais desenvolvidos em microcosmos, com blocos de solo não alterados submetidos a choques térmicos e seguidamente a testes de chuva simulada (300 mm). Recolheram-se as águas de escoamento superficial (0 cm) e subsuperficial (12 cm). O aquecimento do solo foi feito com lâmpadas de infravermelho atingindo temperaturas de 222 e 401 °C a 1 cm de profundidade, à semelhança das alcançadas em incêndios florestais de média e alta intensidade. A análise dos lixiviados mostrou que a lixiviação do Al aumenta com a severidade do choque térmico, enquanto que no caso do ferro apenas foram perceptíveis efeitos para a temperatura mais elevada. A modelagem geoquímica com o programa Visual Minteq, indicou que o Al e o Fe sofrem mobilização em associação com a matéria orgânica dissolvida, com o predomínio de interações fracas (ligação eletrostática) no caso do Al e de interações fortes (complexos bidentados com matéria orgânica dissolvida) no caso do Fe. Apenas no fim do ensaio de lixiviação, quando as concentrações carbono orgânico dissolvido diminuem, ocorre mobilização apreciável de Al e Fe na forma inorgânica no lixiviado subsuperficial o tratamento da temperatura média.

1. Introduction

Forest fires cause drastic changes to the properties of the upper layers of soils affected by heat, altering their physical (Imeson et al. 1992; Everett et al. 1995; Robichaud 2000), chemical (Covington et al. 1991; Naidu and Srivasuki 1994; Knicker et al. 1996; Hernández et al. 1997; Cancelo-González et al. 2013) and biological characteristics (DeBano et al. 1998; Prieto-Fernández et al. 1998; Choromanska and DeLuca 2002; Carballas et al. 2009; Díaz-Raviña et al. 2010). The effects of fire have also been observed in the water quality of the affected areas (Tiedemann et al. 1979; Gluns and Toews 1989; Brass et al. 1996; Gerla and Galloway 1998; Neary et al. 2005). An extensive review of the works describing these effects on forest soils is found in Certini (2005), who states that severe fires, such as wildfires, generally have several negative effects on soil. They cause significant removal of organic matter, deterioration of both structure and porosity, considerable loss of nutrients through volatilisation, ash entrapment in smoke columns, leaching and erosion, and a marked alteration of both quantity and specific composition of microbial and soil-dwelling invertebrate communities.

Due to the effect of heating, soil organic matter (SOM) undergoes changes in its structure and properties (Almendros et al. 1988; Alcañiz et al. 1994; Fernández et al. 1997; Guinto et al. 1999). However, the most obvious effect of soil heating is the loss of SOM, which is substantial between 200 and 250 °C, and continues until its complete volatilization at about 460 °C (Giovannini et al. 1988). The pH values increase as a consequence of SOM combustion and also because of the resulting production of ash (Ulery and Graham 1993; Oswald et al. 1999), which is enriched in carbonates, oxides, hydroxides and basic cations of different solubility (Soto and Díaz-Fierros 1993; Ulery et al. 1993). Ash plays an important role in the recovery of these burnt areas as it acts as a reserve of available nutrients for plant growth (Úbeda et al. 2009; Pereira et al. 2011a, 2011b; Pereira et al. 2012).

KEY WORDS

Fires, rainfall simulation, mobility, iron, aluminium, complexation

PALABRAS

CLAVE

Incendios, simulación de lluvia, movilidad, hierro, aluminio, complejación

PALAVRAS-

CHAVE

Incêndios, simulação de chuva, mobilidade, ferro, alumínio, complexação

Nevertheless, not all the elements present in ash are in easily available forms for mobilisation through soil and plant absorption. Monovalent cations are much more soluble than divalent cations (Soto and Díaz-Fierros 1993; Khanna et al. 1994; Úbeda et al. 2009) and, therefore, more of the former should be lost through leaching. Khanna et al. (1994) separates the nutrients that accumulate in the ash into three classes based on solubility: (i) K, S, and B, easily soluble but with a residual component (30%) which is not solubilised by further dilution; (ii) Ca, Mg, Si, and Fe, relatively insoluble but at a degree related to dilution; and (iii) P, highly insoluble.

The availability of macronutrients generally increases after burning, but it is dependent on the type of nutrient, vegetation and soil, and also on the pathway of the leaching processes (Kutiel and Shaviv 1992). In the case of micronutrients, which have been much less studied, González-Parra et al. (1996) found that both the total content and the easily reducible forms of Mn increased significantly after fire due to Mn supplied by the ash, while the exchangeable Mn did not show any variation. García-Marco and González-Prieto (2008) studied the short- and medium- term effects of fire and fire-fighting chemicals on soil micronutrient availability, and found that the prescribed fire caused short-term changes in the soil micronutrient availability, increasing that of Mn and Zn, and decreasing that of Fe and Co; conversely, no effect was found on Cu availability.

The effects of heating on the solubility of Fe and Al have not been extensively studied. Smith (1970) observed increases in acid-extractable Fe and Al, 192% and 156% respectively, in the ash produced in soil subjected to high temperatures (1000 °C on the surface) in comparison with the soil before the fire. However, this effect was not observed in the mineral horizons, where five weeks after the fire the concentrations of extractable Fe and Al were below those of the soil not affected by the fire; the author attributed this to the fixation of these metals to the soil and, in particular, their reaction with the phosphorus. The temperature reached during the fire can have some influence on the behaviour of these

elements. Therefore, in laboratory simulations in which the soil was heated to a moderate temperature, the water-extractable Al⁺³ was higher in the ash than in the unburnt *Q. suber* litter extracts (Pereira et al. 2011b), whereas in a field study that analysed soil affected by medium to high temperatures, the concentrations of water-extractable Al and Fe were lower in the ash than in the unburnt *P. pinaster* litter (Pereira et al. 2014).

The solubility of Fe and Al is highly dependent on the pH. The degree of the increase in pH in burnt soils depends greatly on the temperature reached and the type of plant species burnt (Pereira et al. 2011b). Within the pH range usually found in natural systems, the solubility of Fe and Al is very low at neutral pH values and increases at acidic pH values. Consequently, the solubility of Fe and Al is not favoured by the pH increase observed in the surface of the burnt soils. It has also been observed that when the pH decreases after successive washes, the (previously inhibited) solubility of the transition elements increases (Soto and Diaz-Fierros 1993; Steenari and Lindqvist 1997).

The solubility of Fe and Al in the soil profile can also be affected by changes in the mineral forms of these elements caused by heating. Ketterings et al. (2000) ascertained that temperatures exceeding 600 °C noticeably reduced gibbsite concentration and converted goethite into ultra-fine maghemite, and Torrent et al. (2010) also noted that heating caused the dehydration of the Fe minerals and the appearance of magnetic minerals, particularly maghemite.

On the other hand, heating can affect the Fe and Al complexed with organic matter, which are fundamental in the genesis of the soil structure and properties derived from this. At high temperatures, organic cements are disrupted affecting soil structure (Badía and Martí 2003). However, the surviving aggregates can show a higher stability than the original ones due to the formation of cementing oxides (Giovannini and Lucchesi 1997; Ketterings et al. 2000). In deep horizons, not affected by heating, organic matter can remain unchanged and maintain

2. Material and Methods

its reactivity, contributing to cementation. Giovannini et al. (1987) showed that three years after an experimental burn on a soil, the subsurface layers appeared more strongly cemented because the translocated hydrophobic organic matter complexed polyvalent metals and increased the organometallic cements.

Despite the important role that Fe and Al play in soil properties and forming processes, there is still an important lack of knowledge about their physico-chemical behaviour in soils affected by fires. This work aims to provide information about the effect of soil heating at different intensities on the solubility and mobility of Fe and Al; heating can be important not only due to its influence on the modification of soil properties, particularly those related to the reactivity and aggregation capacity of the soil, but also because of its effect on the quality of basin water affected by fires. To do so, laboratory experiments were carried out on a microcosm scale by subjecting unaltered soil samples to thermal shock and subsequently to leaching using simulated rainfall, analysing the concentration and chemical forms of these elements on the leachates, and assessing their relationship with the pH and dissolved organic matter.

2.1. Description and analysis of the soil samples

The soil samples were taken from a sparse *Pinus pinaster* Ait. stand, with a herbaceous understory consisting of graminaceous plants, located in Carnota (A Coruña, NW Spain) ($42^{\circ} 51' N$, $9^{\circ} 06' W$) at 12 m above sea level. The soil is a Leptic Umbrisol (IUSS Working Group 2007), over granitic bedrock, with a sandy-loam texture, pH in water of 5.64, 13.4% organic matter, 1.3% total Fe, 7.7% total Al and a total cation exchange capacity of $28.6 \text{ cmol}_{(+) } \text{ kg}^{-1}$. Three undisturbed soil blocks were collected within an area of 4 m^2 without trees by inserting a steel box of $20 \times 40 \text{ cm}$ (sides) and 15 cm deep into the ground (**Figure 1**) with the minimum disturbance that allowed thermal shock treatments and rainfall simulation effects to be explored while keeping the soil structure unaltered (**Figure 1**).

2.2. Thermal shock

In the laboratory, each sample was heated with 8 infrared lamps (300 W Philips IR375CH) situated 10 cm above the soil surface (Cancelo-González et al. 2012). The temperature was monitored by three thermocouples placed at 1, 3 and 6 cm depths. Two samples, named TA and TB, with



Figure 1. Equipment used for unaltered sample collection on site.

an initial moisture content of about 10%, were respectively heated to 200 °C and 400 °C at 1cm depth, equivalent to moderate and severe fire conditions (Chandler et al. 1983), and then the soil was allowed to cool down to room temperature. The third sample was not subject to heating treatments and was used as a control (TC).

2.3. Degree-hour calculation

Accumulated heat degree-hour data (DH) allow us to characterise thermal shock in terms of severity (maximum temperature reached and heating duration). The calculation of the accumulated heat during the thermal shock was carried out using the modified degree-hour method (Cancelo-González et al. 2012), based on the following equation, using room temperature (21 °C) as the reference temperature:

$$DH_{21} = \sum \frac{(T_{5(x\text{ cm})} - 21)}{12}$$

where $T_{5(x\text{ cm})}$ is the temperature (°C) registered every 5 minutes at x cm depth (1, 3 and 6 cm).

2.4. Rainfall simulation and water sampling

After heating, burnt and unburnt soil samples were positioned under the rainfall simulator at a slope of 20% and subject to rainfall simulations using a water jet system (Benito and Díaz-Fierros 1989) (Figure 2) that generated simulated rainfall with a mean intensity of 75 mm h⁻¹ based on historical observations in the study area, and intensified to promote full soil washing. Two consecutive rainfall simulation experiments were carried out totalling 300 mm rain, each one of 2 h duration, and separated by an interval of 15 days. Surface runoff (0 cm) and subsurface leachate water (12 cm) were collected in 300 mL aliquots (8-15 water samples) during the rainfall simulations.

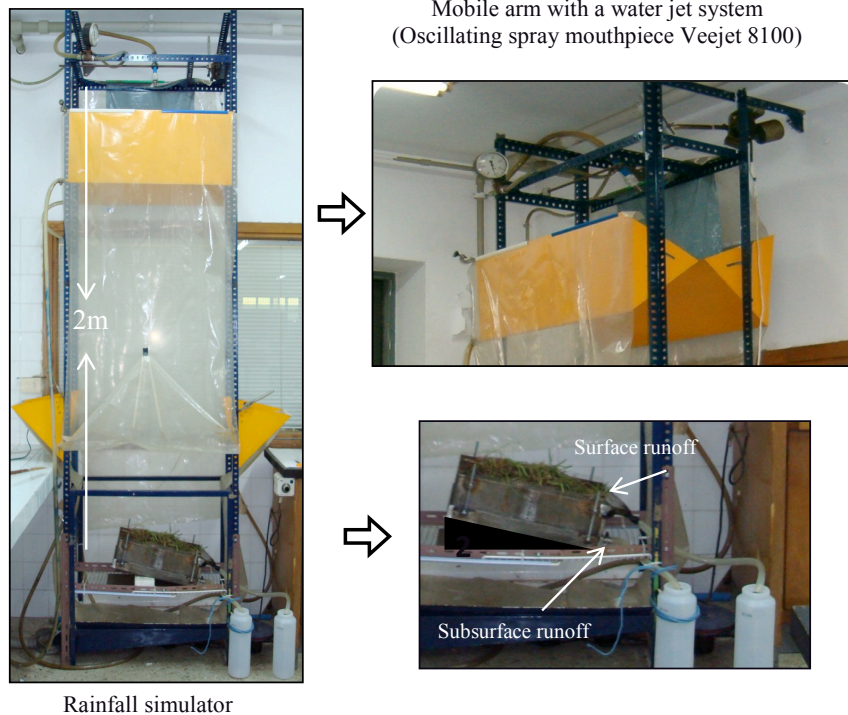


Figure 2. Rainfall simulation and collection of surface and subsurface water samples.

2.5. Chemical analysis of water samples

In the surface and subsurface water samples collected during the simulated rainfall events, the pH was immediately recorded using a portable electrode (HANNA HI 9025C). In filtered samples (0.45 mm), Fe and Al concentrations were analyzed by atomic absorption spectrometry (SPECTRAA220 FS from VARIAN), dissolved organic carbon (DOC) was estimated by catalytic oxidation at 950 °C, and the determination of carbonic anhydride by IR analyzer (TOC-5000 from SHIMADZU).

2.6. Chemical speciation of the leachates

In order to estimate the composition of the leachates, the chemical equilibrium model for the calculation of metal speciation Visual MINTEQ version 3.0 (Gustafsson 2013) was applied to every second water sample along the leaching experiment. Dissolved Fe and Al concentrations, pH and DOC concentration were introduced as inputs in the model. To determine the proportion between DOC and dissolved organic matter (DOM), the default factor used was 1.65, which is an average of the results obtained for lakes and streams in the Swedish environmental monitoring area (Sjöstedt et al. 2010).

Visual MINTEQ allows us to model the equilibrium and speciation of inorganic and organic solutes, as well as to determine the saturation states with respect to the different mineral phases in the system by calculating the saturation index (SI); this is the relationship that exists between the activity in solution of the ions which form a certain mineral, and the equilibrium constant of the dissolution reaction of a mineral. In general, positive SI values indicate that the mineral species can precipitate and negative values indicate that the water in contact with these mineral phases could dissolve them. Values around 0 (-0.5, 0.5) would indicate that those solid phases may be present and in contact with the water, which would be saturated with respect to these mineral phases.

For the modelling of these interactions between metallic ions and humic substances, the NICA-

Donnan model was used, a combination of the non-ideal competitive adsorption (NICA) isotherm description of binding to a heterogeneous material, coupled with a Donnan electrostatic sub-model describing the electrostatic interactions between ions and the humic material. In the NICA-Donnan model, the specific bond between the cations and the negatively-charged functional groups is described using the NICA isotherm, whereas the non-specific electrostatic bond with any negative charge is described using the Donnan model (Kinniburgh et al. 1996). The model assumes that the humic substances present two binding sites, mainly attributed to the carboxylic and phenolic functional groups (Milne et al. 2001). The model additionally considers that the humic substances are formed by a mixture of 90% fulvic acid (FA) and 10% humic acid (HA), which are representative values of humic substances in natural water (Tipping 2002). The model is able to describe the binding of metal ions to fulvic acids (FA) or humic acids (HA) over a wide range of conditions (Milne et al. 2003).

3. Results and Discussion

3.1. Heating and degree-hour curves

The time-temperature curves (TTC) for the 1, 3 and 6 cm depths are shown in **Figure 3**. TTCs enable the effect of heat temperature and heat duration on soil to be determined. The curves obtained in this experiment are very similar to those observed in soils affected by forest fires (DeBano et al. 1998). The curve of the heating phase follows an overall sigmoidal pattern, with a characteristic inflection point in the rate of heating between 60 °C and 100 °C, which may be attributed to the energy consumption required to evaporate the water contained in the soil (Campbell 1995). At 1 cm depth, a maximum temperature of 222 °C and 401 °C was reached in treatments TA and TB, respectively. At 3 cm,

a maximum temperature of 85 °C was reached in TA and 167 °C in TB. At 6 cm depth, a very gradual increase was observed, reaching similar temperatures in both treatments and not exceeding 100 °C in any of the cases. In

comparison with the 1 cm heating curves, those obtained at 3 and 6 cm showed a time delay to reach the maximum temperatures, and also a more gradual cooling with depth.

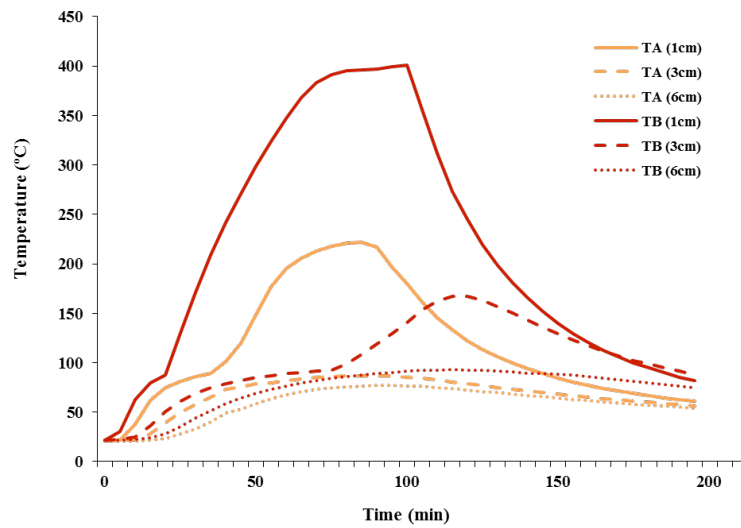


Figure 3. Heating curves obtained from the thermocouples placed at 1, 3 and 6 cm depths, for the two heating treatments.

In order to calculate the accumulated heat degree-hours (DH) at 1, 3 and 6 cm in both thermal treatments (Table 1), only the rising phase of the heating curve was taken into account until reaching the maximum registered temperature (Tmax). It is considered that during this phase the main changes in the organic matter and the soil pH occur (DeBano et al. 1979; Giovannini et al. 1988; Giovannini 1994), which

are also the parameters that can most influence the possible loss of Fe and Al. The differences in the degree-hours between treatments TA and TB are more pronounced than those between the temperatures, showing that this parameter, including the duration of heating, can be a more sensitive indicator of the severity of the fire, as Certini (2005) suggests.

Table 1. Degree-hours (DH) and maximum temperatures (Tmax) reached in the thermal treatments at 1, 3 and 6 cm depths

Treatment	DH			Tmax (°C)		
	1 cm	3 cm	6 cm	1 cm	3 cm	6 cm
TA	160	68	50	222	85	77
TB	414	148	100	401	163	92

3.2. pH behaviour and DOC, Fe and Al concentration in the leachates

In order to understand the changes in leachates of the soil samples subjected to heat treatment compared to the control sample, it is important to know the chemical changes in the soil properties. A decrease in OM of about 10% was observed in TA and 82% in TB compared to TC. CEC decreased by 70% at 220 °C (TA) and by approximately 75% at 401 °C (Cancelo-González 2012). This behaviour may be considered normal in soils in which the CEC depends mostly on the organic matter content. S increased in the samples subjected to thermal treatment (TA and TB) respect to TC, showing values of 5.8 (TC), 7.4 (TA) and 12.5 (TB) $\text{cmol}_{(+)}$ kg^{-1} .

Figure 4 shows the evolution of the pH over time, as well as the quantity of accumulated DOC, Fe and Al in the leachates of the control soil and those subjected to heating. The pH of the leachates of the control treatment remains close to 7, with the exception of the first aliquot of the subsurface washing, which is close to 4, probably due to the movement of soluble Al present in the soil. In the burnt soils, the pH increases with the severity of the thermal shock, with initial values of 8.6 and 8.8 in the surface runoff from treatments TA and TB respectively. These then decrease slightly with washing until reaching values of 7.1 and 7.7 respectively, at the end of the simulated rainfall experiment.

Frequent increases in the pH have been described in soils after a fire (Kutiel and Shaviv 1989; Dimitrakopoulos 1994; Giovannini 1994, 1997; Hernández et al. 1997). These increases can be attributed to the destruction of the organic matter, contribution of carbonates and oxides from the ash (Ulery and Graham 1993; Giovannini 1994), and the increase of the exchangeable cations of the soil (Viro 1974; Raison 1979) that occurs simultaneously with the increase in temperature (Cancelo-González et al. 2013). Temperatures over 200 °C are necessary in order to see noticeable changes in the organic matter of the soil (Schnitzer and Hoffman 1964; Nishita and Haug 1972; Sertsu and Sánchez 1978). This threshold was reached

in the first centimetre of the samples subjected to heating (222 °C and 159.7 DH in TA, and 401 °C and 413.8 DH in TB) and would justify the pH increase that takes place simultaneously with the decrease in SOM concentrations from 13.4% in TC to 12.1% in TA, and 2.3% in TB (reaching a temperature above 400 °C where an almost complete thermal decomposition and combustion of SOM is expected). It should be noted that few differences were observed between the surface and subsurface leachates of TA, whereas in TB, subjected to a higher heating, the pH of the surface runoff is 0.5-2.3 units above that of the subsurface runoff. In TA this suggests liberation of soluble bases and their redistribution at depth as a consequence of the heating, whereas in TB where a much more complete destruction of the SOM occurred, the surface pH increase is attributed to the formation of basic oxides as part of the ashes.

With regard to the leaching of the organic matter, it is worth noting that the sum of DOC exported by two pathways increases with the intensity of the heating (194, 235 and 1512 mg DOC in TC, TA and TB, respectively) despite the decrease in the SOM as a consequence of the burning. Diverse DOC behaviour in burnt soils can be found in the literature. Shibata et al. (2003) found that fires significantly reduced DOC concentration in the burnt surface moss layer compared to that in the unburnt site one month after the burning, due in part to soluble organic carbon loss after ignition. A short-lived peak DOC concentration in soil water after burning was observed by Clay et al. (2009), while elevated DOC contents in burnt soils compared to the unburnt soils were observed by Zhao et al. (2012), but only for the first year after burning.

In this experiment, important differences are seen in the priority pathway of the DOC leaching depending on the severity of the treatment. Hence, in the control treatment, the mobilization of DOC, which is maintained throughout all the rainfall simulation experiment, is greater in subsurface pathways. In the most severe treatment, TB, the main pathway of DOC leaching is also subsurface but it practically runs out after 150 mm of simulated rainfall. In the TA sample, subjected to moderate

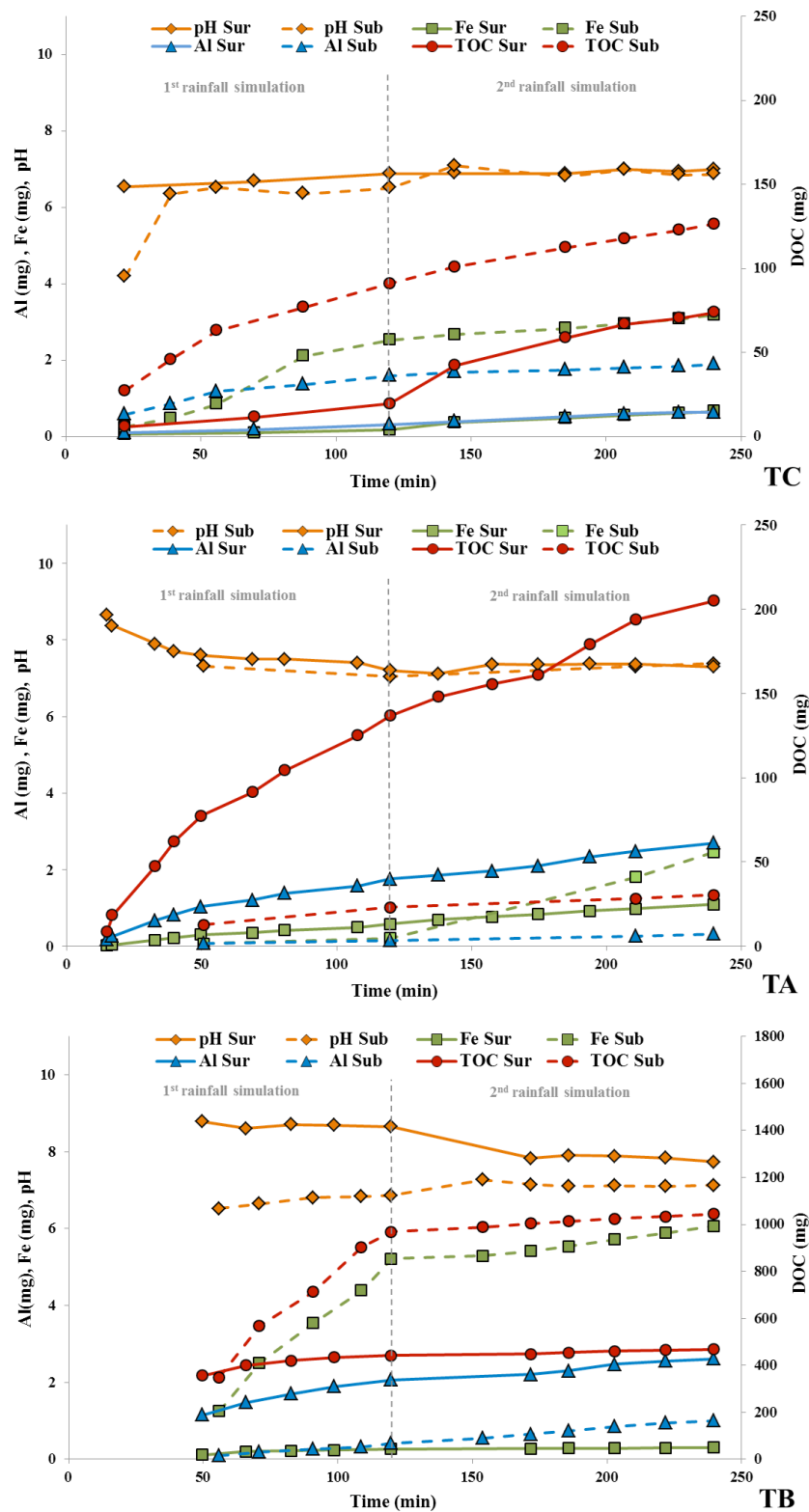


Figure 4. pH values and accumulated quantities (mg) of total organic carbon (DOC), Fe and Al leached through surface (Sur) and subsurface (Sub) pathways during the rainfall simulations for both treatments (TA (222 °C) and TB (401 °C) and the control soil (TC)). Each aliquot analysed represents 300 mL of leachate.

heating, a continuous DOC mobilization occurs, with the surface pathway predominating in this case. This behaviour can be explained by the higher surface hydrophobicity present in TA in comparison with TC and TB (Cancero-González 2012), which would make water infiltration difficult and, therefore, also leaching through subsurface pathways. Different studies (DeBano et al. 1976; DeBano 1981; Varela et al. 2005) have established threshold temperatures for soil heating in relation to water repellence. Between 175-200 °C, as in the case of TA where the temperature reached at 1 cm was 222 °C, hydrophobicity increases, whereas above 275-300 °C, as in TB where the temperature reached at 1 cm was 401 °C, water repellence disappears. The higher hydrophobicity of the sample subjected to moderate heating (TA) would make infiltration difficult and explain the scarce volume of subsurface runoff collected in TA (1.2 L), four times lower than those of TB and TC. In this sense, the volume of surface runoff in treatment TA (11.5 L) is about twice as high as those of treatment TC and TB (5.5 L and 4 L, respectively).

With regard to the metals in this study, it should be pointed out that the total amount of Al mobilised through washing increased with heating intensity (2.52 mg, 3.01 and 3.62 mg in TC, TA and TB, respectively). Nevertheless, the percentage of leached Al with respect to the concentration of total Al was very low, with values of $2.77 \cdot 10^{-4}$, $3.20 \cdot 10^{-4}$

and $4.04 \cdot 10^{-4}$ for treatments TC, TA and TB, respectively. In the control treatment, Al leaching was predominantly via subsurface pathways (75%), whereas in the samples subjected to thermal shock, the surface pathway predominated (90% and 72% in TA and TB, respectively).

The total quantity of leached Fe was 3.84, 3.55 and 6.37 mg for treatments TC, TA and TB, respectively, showing that only intense heating affected the mobility of this element. The percentage of leached Fe with respect to total Fe was low ($2.49 \cdot 10^{-3}$, $2.22 \cdot 10^{-3}$ and $4.19 \cdot 10^{-3}$ for TC, TA and TB, respectively), although approximately one order of magnitude higher than that of the leached Al. In all cases, Fe mobilization was predominantly via subsurface pathways. In TB, Fe loss mainly occurred during the first simulated rainfall event and took place simultaneously with an important movement of organic matter, which was 43 times higher than that of the control soil. As the pH conditions of the leachates of the burnt soils are usually neutral or slightly alkaline, the theoretical solubility of Fe would be low (about $1 \cdot 10^{-9} \text{ mol L}^{-1}$), whereas concentrations of about $1 \cdot 10^{-4} \text{ mol L}^{-1}$ are reached in the first washing event (data not shown). Therefore, it is obvious that DOC plays a fundamental role in the leaching of these metals, which confirms the high correlations between the analysed metals and DOC when the two washing pathways are examined separately for each treatment (Figures 5 and 6).

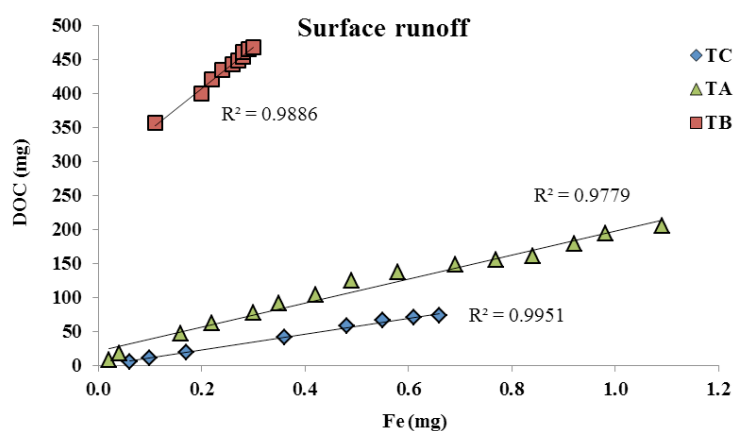


Figure 5. Correlations between Fe and DOC in the leachates derived from the surface runoff for all the treatments.

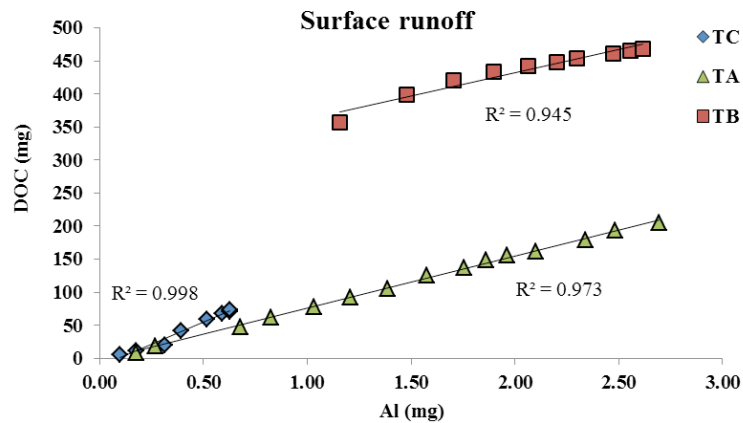


Figure 6. Correlations between Al and DOC in the leachates derived from the surface runoff for all the treatments.

3.3. Chemical speciation of the leachates

The chemical speciation model Visual MINTEQ version 3.0 confirms the aforementioned by predicting that the predominant forms of Fe and Al in the leachates are associated with the organic matter, either by means of weak interactions (electrostatic binding) or as strongly complexed species (Figures 7 and 8). In all the analysed samples, negative SI values were obtained, indicating that the conditions were not favourable for the formation of Fe and Al mineral precipitates in the leachates.

In accordance with the model, Al is found mainly associated with the humic substances by means of weak electrostatic binding (88-97% of the Al in solution), predominantly binding to AF (between about 84-94% of the Al in solution). Among the complexed forms of Al, bound to the humic substances by means of stronger interactions, binding to AF also predominates, mainly by means of interactions with the phenolic groups.

The subsurface leachates from the first rainfall simulation in TB and the second in TA, are an exception to this general behaviour. The Al fraction weakly bound to AF by means of electrostatic binding -a majority in the other leachates- decreased 43% and 53%, respectively. In the case of TB, the remaining Al fraction is found complexed to AF through the phenolic groups, while in TA, 41% is found in an inorganic form (mainly as the anion $\text{Al}(\text{OH})_4^-$). The behaviour observed in the second rainfall simulation for TA

is related to the low DOC concentration and the high Fe and Al concentrations in these leachates. Both elements compete for binding sites with the dissolved organic matter, the first one being more favourable according to the model.

In the case of Fe, the major forms in solution are the complexes with humic substances, mainly bidentate complexes with AF. In this fraction, interactions with the phenolic groups predominate in the majority of the analysed cases and represent more than 90% of the Fe in solution. However, in the subsurface leachates in the second washing event for TA, weak electrostatic interactions with AF (20-22%) are relevant as well as the inorganic form $\text{Fe}(\text{OH})_2^+$ (23-28%); this may be related to the higher Fe and lower DOC concentrations in these leachates.

Together, the results obtained indicate that heating favours the leaching of Fe and Al in burnt soils, preferentially bound to and moving with dissolved organic matter, which also increases with the severity of the heating. Only in the leachates with high metal concentrations and low DOC concentrations, can an important mobilisation of these elements in their inorganic form be observed. Although the proportion of the mobilised element in relation to its total is low, and if we assume it affects the most active Fe and Al fractions (exchange cations, low crystallinity compounds, organometallic complexes), it may have important repercussions on the soil properties, particularly those related to aggregation and adsorption capacity.

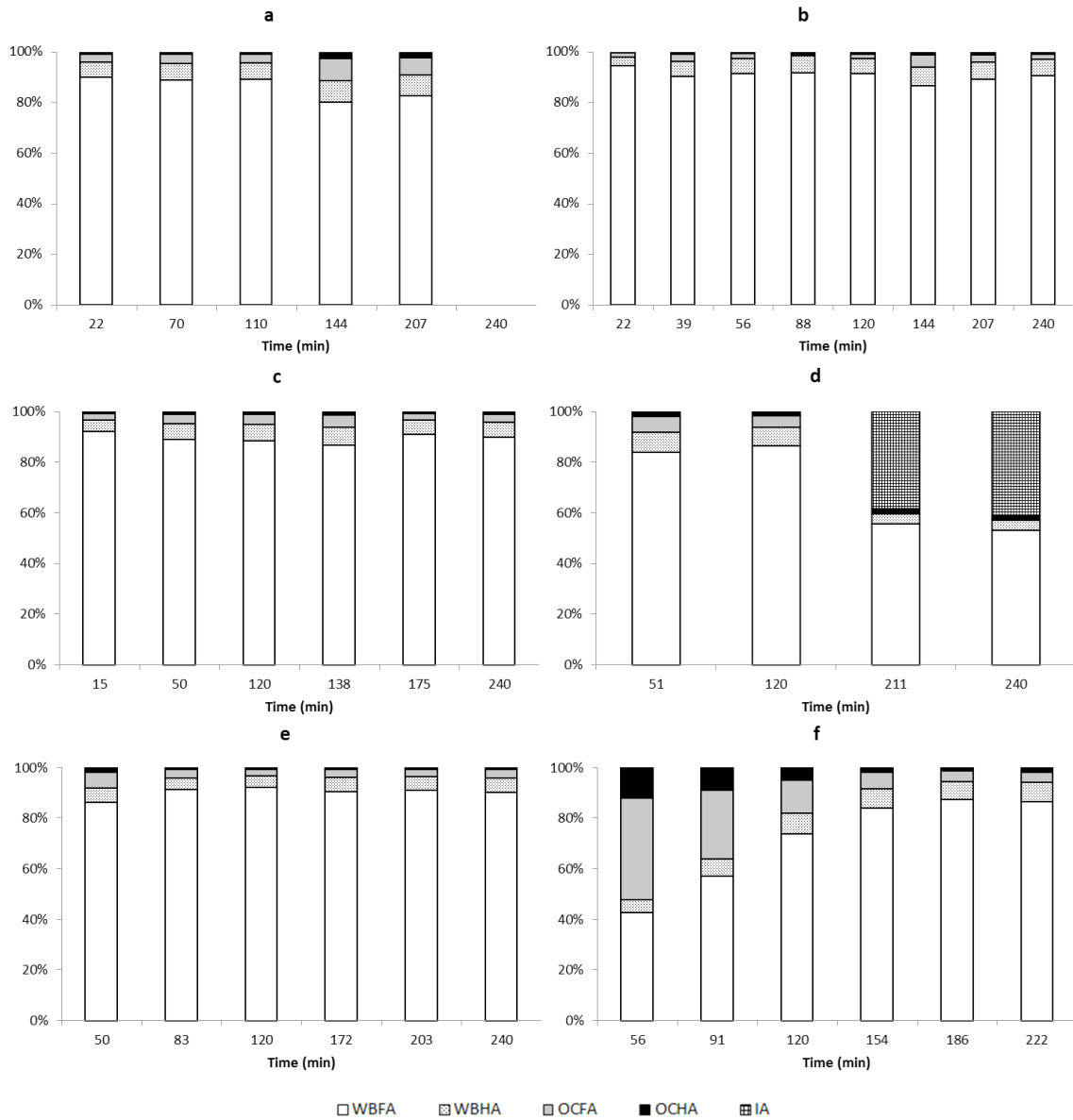


Figure 7. Distribution of aluminium forms in the leachates obtained by means of modelling using Visual MINTEQ. Figures **7a** and **7b** correspond, respectively, to surface and subsurface washing for TC. Figures **7c** and **7d** correspond, respectively, to surface and subsurface washing for TA. Figures **7e** and **7f** correspond, respectively, to surface and subsurface washing for TB. Legend: WBFA: Weakly (electrostatically) bound to dissolved fulvic acid; WBHA: Weakly (electrostatically) bound to dissolved humic acid; OCFA: Organically complexed to dissolved fulvic acid; OCHA: Organically complexed to dissolved humic acid; IA: Inorganic Al. For treatment A in the subsurface washing, $Al(OH)_4^-$ appears as the main inorganic form (34.5 and 37.9% at 211 and 240 min, respectively).

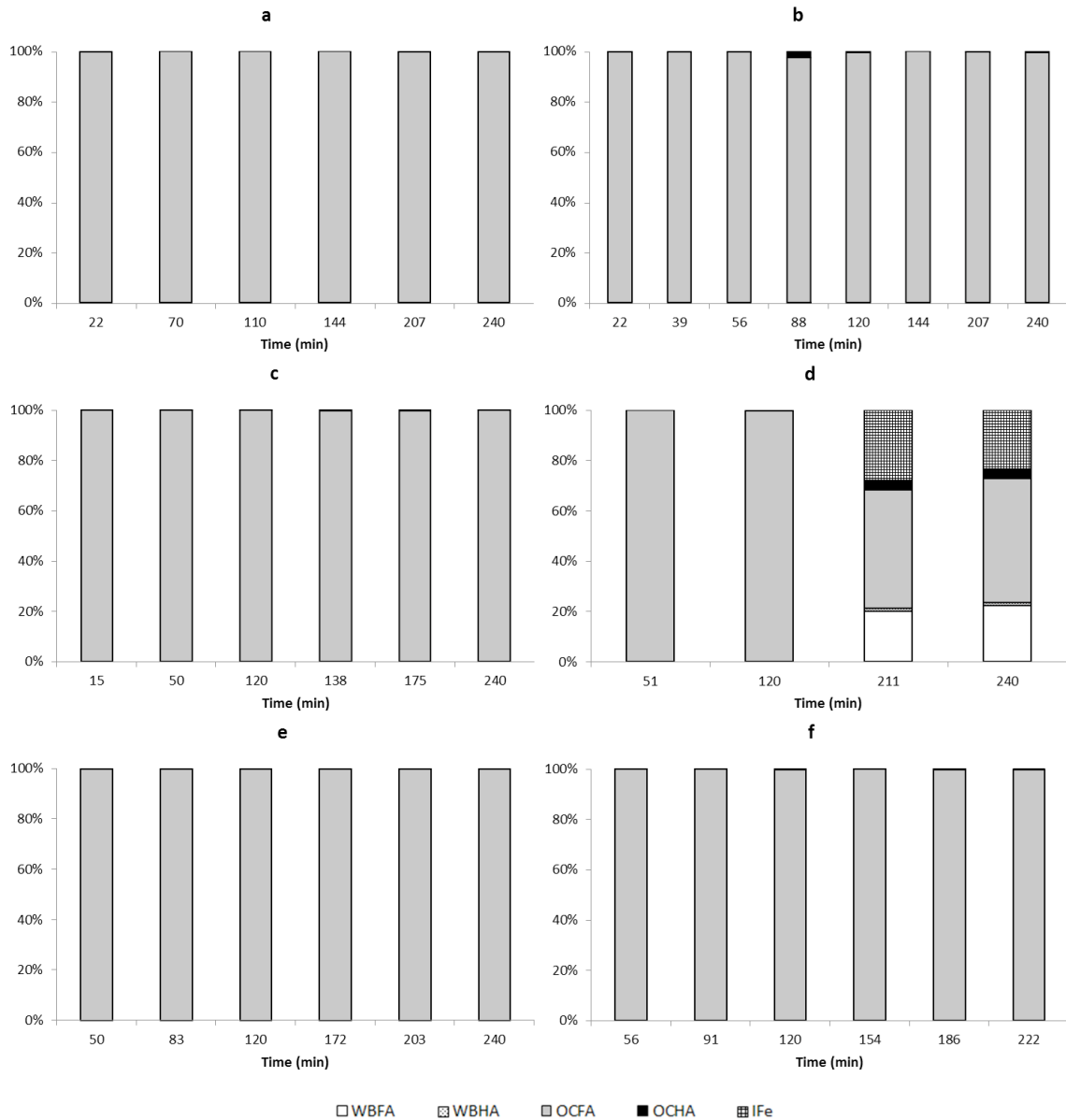


Figure 8. Distribution of iron forms in the leachates obtained by means of modelling using Visual MINTEQ. Figures **8a** and **8b** correspond, respectively, to surface and subsurface washing for TC. Figures **8c** and **8d** correspond, respectively, to surface and subsurface washing for TA. Figures **8e** and **8f** correspond, respectively, to surface and subsurface washing for TB. Legend: WBFA: Weakly (electrostatically) bound to dissolved fulvic acid; WBHA: Weakly (electrostatically) bound to dissolved humic acid; OCFA: Organically complexed to dissolved fulvic acid; OCHA: Organically complexed to dissolved humic acid; IFe: Inorganic Fe. For treatment A in the subsurface washing, $\text{Fe}(\text{OH})^{+2}$ appears as the main inorganic form (27.7 and 22.9% at 211 and 240 min, respectively).

4. Conclusions

Heating of a soil subjected to different severities of thermal shock (222 °C and 159.7 DH; 401 °C and 413.8 DH at 1 cm depth) under controlled conditions affects Al and Fe leaching when the heated soil is subjected to simulated rainfall. Al leaching is greater in the samples subjected to heating, increasing with the intensity of the treatment, with surface runoff being the main leaching pathway. The increase in Fe leaching is only clear in the soil subjected to the more severe thermal shock, in which case the Fe mobilisation is up to 10 times greater than that of Al. Fe leaching mainly occurs via subsurface pathways. The association with dissolved organic matter increases the solubility of both metals, reaching much higher dissolved concentrations than those expected in the pH conditions of the leachates. The predominant forms of Al and Fe in the leachates are associated with the dissolved organic matter, either by means of weak interactions (electrostatic binding) in the case of Al or by forming bidentate complexes in the case of Fe. Only when the Fe and Al concentrations are high, and the concentrations of dissolved organic carbon decrease, do these metals move significantly in their inorganic ion forms.

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