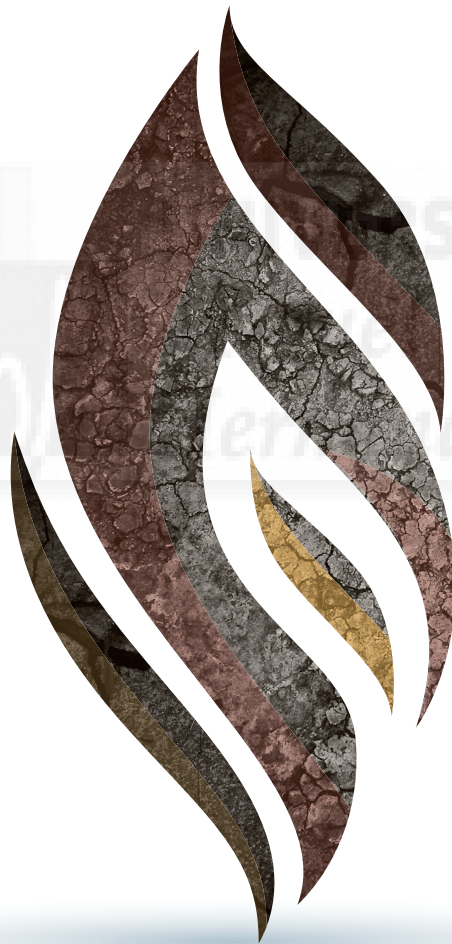


TESIS DOCTORAL

PATRICIA JIMÉNEZ PINILLA

Avances en el estudio de suelos mediterráneos afectados por incendios forestales

Advances in the study of Mediterranean soils affected by forest fires



Departamento de Agroquímica y Medio Ambiente. Universidad Miguel Hernández
Directores: Jorge Mataix Solera, Victoria Arcenegui Baldó y Lorena Martínez Zavala

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Departamento de Agroquímica y Medio Ambiente

GEA- Grupo de Edafología Ambiental



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CERTIFICA

Que la memoria adjunta, con título *“Avances en el estudio de suelos mediterráneos afectados por incendios forestales”*, presentada por Patricia Jiménez Pinilla, ha sido realizada en el Departamento de Agroquímica y Medio Ambiente de dicha Universidad.



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Director del Departamento

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Elche, septiembre de 2016

*La naturaleza no hace nada superfluo, nada inútil,
y sabe sacar múltiples efectos de una sola causa.*

Mikolaj Kopernik (1473 – 1543)



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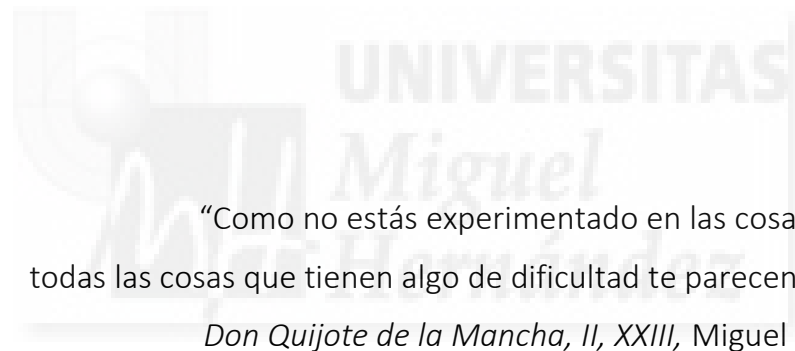
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"...Navega, velero mío,
sin temor,
que ni enemigo navío,
ni tormenta, ni bonanza
tu rumbo a torcer alcanza,
ni a sujetar tu valor..."

Canción del pirata, José de Espronceda



"Como no estás experimentado en las cosas del mundo,
todas las cosas que tienen algo de dificultad te parecen imposibles."

Don Quijote de la Mancha, II, XXIII, Miguel de Cervantes

*A Raquel: mi hermana,
mi amiga y compañera de aventuras;*



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RESUMEN/ABSTRACT

AVANCES EN EL ESTUDIO DE SUELOS MEDITERRÁNEOS AFECTADOS POR INCENDIOS FORESTALES

RESUMEN

El fuego es un factor ecológico natural presente en los ecosistemas terrestres, desde mucho antes de que apareciera el hombre. Éste se considera, por tanto, un factor esencial para el correcto funcionamiento de los ecosistemas. La modificación del régimen natural de los incendios forestales en el monte mediterráneo se ha hecho evidente en las últimas décadas, cuyos riesgos son cada vez mayores, debido, fundamentalmente, al continuo abandono del medio rural y los cambios de usos del suelo. Con el aumento de la cobertura vegetal, los incendios representan cada vez un riesgo más elevado, debido a que ocurren cada vez con mayor intensidad, y de manera más descontrolada. Este tipo de incendios descontrolados originan impactos ambientales negativos, y graves consecuencias socioeconómicas en las zonas afectadas.

El impacto del fuego modifica el suelo, el cual es clave para mantener los ciclos biogeoquímicos, hidrológicos y geológicos. Por tanto, el funcionamiento de los ecosistemas terrestres afectados por el fuego se ve alterado a corto, medio o largo plazo, pudiendo llegar a ser incluso permanente, lo que dependerá de múltiples factores. Todas estas modificaciones que se producen por el efecto del fuego en la vegetación, en las propiedades del suelo, la fauna, y los procesos hidrológicos y geomorfológicos, son derivadas del calentamiento directo producido por el propio incendio, así como, de los cambios indirectos generados sobre el paisaje y los recursos naturales, que surgen como consecuencia de la pérdida temporal de la cubierta vegetal y por el recubrimiento de las cenizas generadas debido a la combustión de la vegetación.

Resumen

El objetivo general de esta Tesis Doctoral “*Avances en el estudio de suelos mediterráneos afectados por incendios forestales*”, es contribuir en el estudio de los efectos provocados por los incendios forestales en algunas propiedades del suelo inmediatamente después, a corto y medio plazo, así como, de la influencia de diversos factores en la evolución temporal de estas propiedades. Se ha prestado especial atención a la repelencia al agua del suelo (*Soil Water Repellency, SWR*) y a la agregación del mismo, al ser dos de las propiedades físicas más relevantes en suelos recientemente quemados. Ambas juegan un papel fundamental en el control y la gestión del agua en el suelo, ya que influyen en la infiltración, y por tanto, en la potencial disponibilidad de agua en el suelo para la recuperación de la vegetación, la escorrentía superficial y, por consiguiente, en las tasas de erosión del mismo. La estabilidad de agregados (*Aggregate Stability, AS*), además, tiene un papel fundamental en la erosionabilidad del suelo, los stocks de materia orgánica, la microbiología edáfica, y en definitiva, la salud del suelo.

Esta tesis se desarrolla en tres capítulos con formato de artículos, los cuales han sido ya publicados en revistas científicas internacionales, de alto índice de impacto, como son *Science of the Total Environment* (Capítulo 1) y *Catena* (Capítulos 2 y 3). Asimismo, los resultados obtenidos a lo largo del desarrollo de la tesis, han sido presentados en congresos, tanto nacionales como internacionales, como son la asamblea general anual de la *EGU* (European Geosciences Union), y los congresos internacionales del *FESP* (Fire Effects on Soil Properties) y *FuegoRED* (Red temática nacional Efectos de los Incendios Forestales sobre los Suelos), en sus diferentes ediciones de 2012, 2014 y 2015.

En el Capítulo 1, se presentan los resultados del seguimiento temporal realizado durante dos años en campo de los efectos provocados por un incendio forestal, sobre el comportamiento de la repelencia al agua. Este seguimiento se ha realizado estableciéndose una comparación con una zona adyacente control

(no quemada), con características similares a las de la zona afectada. En este estudio se analiza, también, cómo influye el tipo de vegetación predominante (pino y matorral) sobre la evolución temporal de la repelencia al agua del suelo y la influencia de la presencia de cenizas. Para la determinación del efecto de las cenizas en la dinámica de la repelencia al agua del suelo, se establecen diferentes tratamientos: (1) la simulación de la erosión eólica de cenizas y (2) la incorporación de cenizas en los primeros centímetros del perfil del suelo, debido a una entrada inicial de agua tras el incendio. A lo largo de los dos años de monitorización en campo, también se establece una relación entre la evolución temporal de la repelencia al agua del suelo, y las fluctuaciones en el contenido de humedad del mismo. Los resultados obtenidos de la monitorización en campo de la repelencia al agua del suelo, se han comparado con resultados de medidas realizadas en muestras de suelo en condiciones de laboratorio. La repelencia al agua en el suelo sólo incrementa, inmediatamente después del efecto del incendio, bajo la influencia del pino. En general, a lo largo de todo el estudio, la evolución de la repelencia al agua es diferente en las parcelas afectadas por el fuego de las parcelas no afectadas, aunque, en ambas zonas, las fluctuaciones registradas de repelencia al agua, durante toda la monitorización, están altamente condicionadas por el contenido en humedad del suelo, de manera que, en los períodos en los que el suelo registra contenidos más elevados de humedad, la repelencia al agua disminuye, y al contrario. Por otro lado, se comprueba que las cenizas juegan un papel importante en la evolución de la repelencia al agua tras el paso del incendio, siendo el tratamiento en el que se eliminaron las cenizas, el que muestra los valores más bajos de este parámetro. Sólo las muestras analizadas en laboratorio bajo la influencia de pino mostraron repelencia al agua, aunque siempre con valores más bajos que los obtenidos en condiciones de campo.

Por otro lado se sabe, gracias a estudios previamente realizados, que la repelencia al agua del suelo es una propiedad altamente influenciada por las

Resumen

condiciones ambientales como son, la temperatura y la humedad relativa del aire, el contenido en agua del suelo y los ciclos de secado y humectación del mismo. La humedad relativa del aire y la morfología de la superficie del suelo, son dos de los factores que influyen en el comportamiento de la repelencia al agua del suelo. La influencia de la humedad atmosférica relativa y la morfología de la superficie del suelo, en la repelencia al agua del mismo, ya han sido previamente estudiados, pero siempre en suelos no afectados por el fuego. Por ello, el Capítulo 2 trata de aportar posibles respuestas sobre cómo afecta la influencia de la humedad atmosférica relativa y la morfología de la superficie de las partículas del suelo, en la repelencia al agua de un suelo quemado, estableciendo también, una comparación de la influencia del tipo de vegetación predominante (pino y matorral) de la zona. Los estudios de laboratorio bajo condiciones controladas ayudan a entender mejor lo que sucede en campo, aunque indiscutiblemente, los resultados obtenidos no son totalmente extrapolables. Para la realización de este estudio, se realizan calentamientos experimentales controlados en condiciones de laboratorio, a siete temperaturas diferentes (50, 100, 150, 200, 250, 300 y 350 °C), simulando diferentes severidades de un fuego, en un suelo calcáreo mediterráneo. Posteriormente, las muestras se someten a diferentes humedades ambientales relativas (30, 50, 70 y 95%) en una cámara sellada herméticamente, durante 48 horas. La persistencia de la repelencia al agua en las muestras se determina mediante el test del tiempo de penetración de la gota de agua (*Water Drop Penetration Time test*, WDPT), mientras que la severidad de la repelencia al agua se mide mediante los métodos del test de la molaridad del etanol (*Molarity of Ethanol Droplet test*, MED) y del ángulo de contacto (*advancing Contact Angle*, CA). Asimismo, también en este capítulo, se analizan dos materiales modelo con diferente morfología superficial (esférica y angular), previamente hidrofobizados y de dos tamaños diferentes, para comparar su comportamiento con el efecto causado en suelos calentados y demostrar, también, la influencia de la morfología superficial

de las partículas del suelo. Tanto la persistencia como la severidad de la repelencia al agua del suelo aumentan, con la humedad relativa, y, de manera más pronunciada, en las muestras calentadas a las temperaturas más elevadas. Dicho efecto fue observado, principalmente, en las muestras tomadas bajo la influencia de pino. Por otro lado también, ambos tipos de morfologías superficiales, de las partículas analizadas, muestran un patrón similar de repelencia al agua con la influencia de la humedad relativa.

Por último, en el Capítulo 3, se muestran los resultados de un estudio sobre agregación en suelos quemados. Las diferentes partículas que componen el suelo, se suelen unir de forma natural entre sí, formando unidades secundarias de mayor tamaño, con carácter persistente, y que se denominan agregados. La estabilidad de estos agregados (AS) viene determinada, principalmente, por la acción de los agentes cementantes (inorgánicos y orgánicos), que unen las partículas que los forman. La agregación del suelo es una propiedad de suma importancia para determinar la salud del suelo, y el efecto del fuego puede influir directamente sobre ella, debido a las alteraciones inducidas en los primeros centímetros del suelo, por el incremento brusco de la temperatura, las cuales van a depender, tanto de la severidad, como de la intensidad del fuego, como también del tipo de suelo y sus características. En estudios previos se ha observado que en algunos casos se produce un aumento de la misma, el cual puede deberse a diferentes factores, entre ellos incluso, debido a una destrucción de los agregados por la combustión de los agentes cementantes, tras el paso del fuego, produciéndose así una selección de los agregados más resistentes que persisten tras el incendio. Este aumento de la estabilidad, por tanto, no sería real, si no aparente. En éste último capítulo, se plantea dar respuestas a este supuesto, e intentar avanzar en el conocimiento del efecto que produce el fuego en la estabilidad de los agregados del suelo. En este caso, se analizan cinco tipos de suelos mediterráneos, de diferentes localidades del sur y este de España, todos ellos diferentes en textura, los cuales se queman a tres

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temperaturas diferentes (300, 500 y 700 °C), bajo condiciones controladas de laboratorio, para así conocer las posibles respuestas de la agregación ante el efecto de diferentes severidades de fuego. Estos resultados se comparan con muestras control (no quemadas) de los citados suelos. En ellas se analiza la distribución de tamaño de agregados tras los tratamientos, así como la estabilidad de los mismos, tras ser sometidos a una lluvia simulada de intensidad conocida. Para completar este trabajo, se seleccionan algunos de los agregados, tanto quemados como no quemados, y se analiza su superficie mediante microscopía electrónica de barrido (en inglés, *Scanning Electron Microscopy method*, SEM) y difracción de rayos X (en inglés, *X-ray diffraction method*, XRD). Ésta última parte del estudio se realiza para saber, si tras los calentamientos, se han producido cambios estructurales y mineralógicos en la superficie de los agregados, que nos ayuden a interpretar los resultados observados en la estabilidad de los mismos, y confirmar las hipótesis sobre si el aumento de la estabilidad de agregados es real o aparente. El efecto inmediato de las temperaturas de calentamiento produce una disminución en el contenido de la materia orgánica, por volatilización, y un aumento de la fracción fina de los agregados. A la vez, se observa un incremento en la estabilidad de los agregados remanentes en la fracción gruesa, debido al calentamiento. Debido al efecto del calor se observan cambios en la superficie de los agregados analizados, tanto estructurales como mineralógicos, que indican ser los responsables del aumento real, y no aparente, de la estabilidad de los agregados tras el efecto del calentamiento.

Esta Tesis Doctoral pretende contribuir, en primer lugar, al estudio de importantes cuestiones, aún poco estudiadas, sobre los efectos del fuego en las propiedades de los suelos y, en segundo lugar, propone nuevas líneas de investigación que arrojen luz sobre el complejo estudio de los incendios forestales.

ADVANCES IN THE STUDY OF MEDITERRANEAN SOILS AFFECTED BY FOREST FIRES

ABSTRACT

Fire is a natural ecological factor in terrestrial ecosystems, which has acted with different intensities, even before humans appeared. Therefore, it is considered as an essential factor in the proper functioning of ecosystems. The distortion of the natural regime of the forest fires in the Mediterranean forest has become evident in recent decades, where risks are increasing, due to the continuing abandonment of rural areas and changes in land use. With the recovery of forest vegetation, wildfires represent an increasingly higher risk, due to their occurring with increasing intensity, and more uncontrollability. These types of forest fires have adverse environmental impacts and serious socioeconomic consequences in the affected areas.

The impact of the fire modifies the soil system, which is key to maintaining the biogeochemical, hydrological and geological cycles. Therefore, the functioning of terrestrial ecosystems affected by fire is altered in either the short-, medium- or long-term, leaving a legacy for years, which may even be permanent, depending on many factors. All these changes are caused by the effect of fire on vegetation, soil properties, fauna, and hydrological and geomorphological processes, which are changed by the direct heating effect produced by the fire itself, as well as by the indirect changes generated in the landscape and natural resources, which arise as a result of the temporary loss of vegetation cover and the coating of ash generated due to the combustion of vegetation.

The general aim of this Doctoral Thesis "*Advances in the study of Mediterranean soils affected by forest fires,*" is to contribute to the study of the

effects of forest fires on some soil properties immediately following the fire, and also in the short- and medium-term, as well as, the influence of several factors on the evolution of these properties. It has paid particular attention to soil water repellency (SWR) and soil aggregate stability, being two of the most important physical properties in recently burned soils. Both play an essential role in the control of soil water management, as they influence the infiltration, and therefore, the potential water available in the soil for the vegetation recovery, surface runoff and consequently, in erosion rates. Aggregate stability (AS) also plays a crucial role in soil erodibility, stocks of organic matter, soil microbiology, and ultimately, the health of the soil.

This thesis has been structured in three chapters with journal format. All chapters have been already published as articles in international journals with a high impact factor such as *Science of the Total Environment* (Chapter 1) and *Catena* (Chapters 2 and 3). Likewise, the obtained results during the thesis development have been presented at conferences, both national and international, such as the annual general assembly of the EGU (*European Geosciences Union*), and international congresses FESP (*Fire Effects on Soil Properties*) and FuegoRED (National thematic network of the Forest Fire Effects on Soil), in their different editions, from 2011 to 2015.

As already mentioned, soil is a crucial component of the forest ecosystem, and the immediate effect of heating, after the impact of the fire, causes significant alterations, which may even remain in the long term. Therefore, it is of vital importance to study the evolution and the recovery of soil following the impact of the fire. In this regard, in Chapter 1 are presented the results of the temporary monitoring carried out for two years in the field of the effects caused by a forest fire, on water repellency behavior. Such monitoring has been performed comparing an adjacent control zone (unburned), with similar characteristics to the affected area. Also analyzed in this study is how the

predominant type of vegetation (pine and scrub) influences the evolution of soil water repellency, as well as, the influence of the ash presence. To determine the ash effect on the soil water repellency dynamics, different treatments were established: the simulation of the ash wind erosion and the ash incorporation in the first centimeters of the topsoil profile due to the initial input of water after the fire. During the two years of field monitoring, a relationship between the temporal evolution of the soil water repellency, and the moisture content fluctuations was also established. The obtained results of the field monitoring of soil water repellency were compared with the results obtained of measurements carried out on soil samples under laboratory conditions. Soil water repellency only increases, immediately after the fire effect, under the influence of pine. In general, throughout the complete study, the evolution of the water repellency is different in the plots affected by the fire from the non-affected plots, although, in both areas, the registered fluctuations of water repellency, during the whole monitoring, are highly conditioned by the soil moisture content, so that, during the periods in which the soil registers higher moisture contents, the soil water repellency decreases, and vice versa. On the other hand, it is found that ash plays an important role in the evolution of water repellency following the fire, the treatment where the ash was removed showing the lowest values of this parameter. Only samples analyzed under laboratory conditions beneath pine influence showed water repellency, although always with lower values than those obtained under field conditions.

Additionally, thanks to previous studies, it is known that soil water repellency is a property highly influenced by several environmental conditions such as temperature and relative air humidity, the soil water content and wetting and drying cycles. The relative air humidity and the soil surface morphology are two of the factors that influence soil water repellency behavior. Both factors, in soil water repellency, have been previously studied, but never in soils affected by fire. That is the reason for the starting point for the approach to the work

presented in Chapter 2: to provide possible answers as to how the influence of relative air humidity and surface morphology of soil particles affects soil water repellency after fire, also making a comparison of the influence of the predominant vegetation type (pine and shrub) of the area. Laboratory studies under controlled conditions contribute to a better understanding of what happens in the field, but indisputably, the results obtained cannot be extrapolated completely to the field behavior. For this study, controlled experimental heating was carried out over a Mediterranean calcareous soil, under laboratory conditions, with seven different heating temperatures (50, 100, 150, 200, 250, 300 and 350 ° C), in order to simulate different fire severities. Subsequently, the samples were exposed to different relative atmosphere humidities (30, 50, 70 and 95%) in a controlled climate chamber for 48 hours. The persistence of the water repellency in the soil samples was determined by the *Water Drop Penetration Time* (WDPT) test, while the severity of the water repellency was measured by both the *Molarity of Ethanol Droplet* (MED) test and the *advancing Contact Angle* (CA). Also, in this chapter, two model materials with two different surface morphologies (spherical and angular) and two different sizes, which were previously chemically hydrophobized, have been analyzed. The aim of this part of the study was to compare the behavior of both model materials with the effect on the soil samples heated, and also, to check the influence of the surface morphology of the soil particles. Both persistence and severity of soil water repellency increases, with the relative humidity, and more noticeably in the samples heated to the higher temperatures. This effect was mainly observed in soil samples taken under the influence of pine. In addition, both types of surface morphologies, of the analyzed particles, showed a similar pattern of soil water repellency with the influence of the relative humidity.

Finally, in Chapter 3, the results are shown of a study of soil aggregation in burned soils. The different particles that form the soil are naturally joined between them, forming larger secondary units, with persistent character, which

are named aggregates. The aggregate stability (AS) is mainly determined by the action of several cementing agents (inorganic and organic) that bind the particles, which form them. Soil aggregation is a property of superlative importance to determine the soil health. The effect of fire may directly influence it, due to the modifications induced in the first centimeters of the topsoil, by the sudden temperature increase, which will depend on both the severity and the intensity of the fire, as well as the type of soil and its characteristics. The response of soil aggregation to fire may be, therefore, very variable. In previous studies, in some cases, an increase in soil aggregation has been observed, which may be due to different factors, including destruction by the combustion of the cementing agents, after the fire occurs, producing a selection of the toughest aggregates, which persist after the fire. This stability increase, therefore, would not be real, but apparent. In this last chapter, it is proposed to respond to this statement, and try to advance understanding of the effect produced by the fire on the aggregate stability of the soil. For that, five Mediterranean soils types from different locations in Southern and Eastern Spain were analyzed, all of them different in texture, which were burned at three different heating temperatures (300, 500 and 700 ° C) under controlled laboratory conditions, in order to know the possible responses of the soil aggregation to the effect of different fire severities. These results were compared to control samples (unburned) of the named soils. In those samples the aggregate size distribution was analysed following the heating treatment, and also the aggregate stability, after being subjected to a simulated rainfall with a known energy. To complete this work some aggregates were selected, from both burned and unburned samples, to analyse their surfaces by *Scanning Electron Microscopy* (SEM) method and *X-ray Diffraction* (XRD) method. This latter part of the study was done to learn if after the heating treatments, structural and mineralogical changes had been produced on the aggregate surfaces, in order to help us to interpret the observed results in the aggregate stability, and also to confirm the hypotheses about whether the

increase of the aggregate stability is either real or apparent. The immediate effect of heating temperatures causes a decrease in the organic matter content, by volatilization, and also an increase of the fine fraction of the aggregates. At the same time, an increase in the stability of the remaining aggregates occurs on the larger fraction, due to the heating. Also, due to the heating effect, several changes are observed on the surface of the analysed aggregates, both structural and mineralogical, which appear to be responsible for a real increase, and not just an apparent increase, of aggregate stability after heating.

This Doctoral Thesis, firstly, expects to contribute to the study relevant issues about the effects of fire on soil properties, still little studied, and secondly, proposes new lines of research that sheds light on the complex study the forest fires.





INTRODUCCIÓN

EL FUEGO: FACTOR ECOLÓGICO VS PROBLEMA AMBIENTAL

El fuego, como fenómeno natural, ha estado presente en el medio ambiente mucho antes de que el hombre existiera, siendo ya desde hace 400 millones de años, y a lo largo de la historia, uno de los principales factores naturales modeladores del paisaje, junto con el clima y la vegetación (Mataix-Solera y Guerrero, 2007; Mataix-Solera y Cerdà, 2009). El oxígeno, el combustible y el calor producido por la ignición, son los tres componentes básicos para que el fuego se genere, y todos ellos se encuentran presentes en la superficie terrestre (Mataix-Solera y Cerdà, 2009). El fuego debe ser, por tanto, considerado como un factor ecológico natural de los ecosistemas terrestres (Naveh, 1975; Le Houerou, 1973), al cual incluso algunos autores, lo consideran también un factor formador del suelo, dada su influencia en el medio edáfico (Certini, 2005), tanto directa (modificaciones en propiedades del mismo) como indirecta, ya que el fuego elimina temporalmente la parte aérea de la vegetación, alterando la parte superficial del suelo y, por ende, condicionando los procesos erosivos e hidrológicos, lo que influye en el ciclo del agua y también, en la evolución de los ecosistemas. De este modo, el fuego debe ser entendido como uno de los factores ecológicos clave que ha condicionado la evolución y la dispersión de las plantas y el desarrollo de los biomas, la formación de suelos y el ciclo hidrológico y de erosión de los mismos (Mataix-Solera y Cerdà, 2009).

El régimen de incendios forestales depende de las características de cada ecosistema, y por tanto, las adaptaciones de las plantas estarán condicionadas por el tipo de incendio presente (Mataix-Solera y Cerdà, 2009), desarrollando mecanismos de regeneración como la capacidad de rebrotar o la protección de semillas para germinar tras el impacto del fuego (Pausas y Keeley, 2009).

Los incendios forestales forman parte de la dinámica de los ecosistemas de clima mediterráneo (Naveh, 1975), los cuales presentan una alta capacidad de

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resistencia al fuego (Keesstra et al., 2016), y en los que la presencia de una prolongada estación seca y de altas temperaturas a lo largo del año, favorece un aumento del combustible y se generan así, unas condiciones propicias para que el fuego sea un factor recurrente en el monte (Mataix-Solera, 1999). Este hecho, junto con los progresivos cambios en el uso del suelo, han modificado el régimen natural de incendios, estando éste controlado por la acumulación de combustible, e influenciado en gran medida por los episodios de sequías (Pausas y Fernández-Muñoz, 2011). Esto se debe, a que en un clima de tipo mediterráneo, se favorece la acumulación de combustibles ligeros en el monte, como son la hierba seca y la vegetación arbustiva, desarrollada gracias a la fuerte insolación tras las lluvias primaverales, lo que ayuda a la desecación de ese combustible ligero, llegando incluso a contenidos de humedad mínimos, y favoreciendo las condiciones óptimas para su combustión (Piñol et al., 1998; Pausas, 2004; Trigo et al., 2006; Founda y Giannakopoulos, 2009). Bajo estas condiciones, un incendio se puede iniciar desde cualquier pequeño foco de calor, estando éstos, en muchas ocasiones, avivados gracias a los fuertes vientos desecantes propios del verano (Mataix-Solera, 1999).

La intensa actividad humana desde el Neolítico y, especialmente tras la Edad del Bronce, cuando el hombre se convierte en agricultor y comienza a usar el fuego como herramienta para generar amplias zonas de cultivo, ha contribuido a cambios notables en el paisaje (De Celis et al., 2014, Pausas et al., 2008). Además, el fuego ha sido tradicionalmente utilizado para eliminar restos agrícolas, y también debido a la creencia tradicional de que el combustible residual que queda sobre la superficie, tras el impacto del fuego, ayuda a incrementar la fertilidad del suelo (Certini, 2014). Por lo tanto, el fuego debe considerarse también como un factor antrópico, usado como medio de gestión del ecosistema con el fin de acelerar los ciclos biogeoquímicos, ampliar las tierras de cultivo y de pastoreo, cazar, o aumentar la biodiversidad (Mataix-Solera y Cerdà, 2009; FAO, 2007). De manera conjunta, dicha incidencia antrópica, junto

con la ya mencionada incidencia natural de los incendios forestales, y sumado al aumento de las temperaturas durante el último periodo interglaciar, han determinado la evolución de los ecosistemas mediterráneos desde hace miles de años (De las Heras, 1994), formando y dinamizando los paisajes y ecosistemas mediterráneos tal como hoy los conocemos (Saura-Mas y Lloret 2010). Bien es cierto, que durante las últimas décadas, la superficie quemada en la región Mediterránea se ha visto incrementada debido a que éstos, los incendios forestales, ocurren con mayor frecuencia (Moreno y Oechel, 1994), siendo España un ejemplo representativo de este hecho (Enríquez y del Moral, 2012). La mayor parte y los incendios forestales más relevantes (en intensidad y extensión) que tienen lugar en el este de España, especialmente en la Comunidad Valenciana, se producen en época estival, mientras que las lluvias más intensas y de mayor volumen se suelen producir en otoño (Mataix-Solera, 1999). Esta coincidencia puede tener una significativa y devastadora consecuencia en el ecosistema cuando esta secuencia de eventos coincide espacial y temporalmente, ya que pueden dar lugar a la pérdida de una parte relevante de suelo (Calvo, 1987).

En la actualidad, el régimen de incendios se encuentra también condicionado por dos factores principales (Pausas, 2004): los cambios de usos del suelo y el aumento de la población. Procesos como la intensificación del espacio forestal para explotar los recursos del bosque o para crear zonas de recreo, han aumentado la degradación del suelo y la vegetación (Chuvienco et al. 2010), además de producir un aumento del abandono de los cultivos tradicionales, que permitía la compartimentación del paisaje, disminuyendo la aparición de incendios y facilitando su extinción cuando estos ocurrían (Bodí, 2012). Esta dinámica de los ecosistemas favorece algunos de los impactos adversos ya mencionados, como son la erosión y en algún caso extremo la desertificación (Rubio, 1989). Los cambios de uso de las zonas forestales, así como, las migraciones masivas de núcleos rurales a urbanos, son factores clave

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en el cambio de régimen de los incendios (Andreu et al., 2010; Margaris et al., 1996). La sociedad actual ha sido, por tanto, la que ha convertido al fuego en enemigo, donde el origen del impacto negativo del fuego sin control, ha sido debido al éxodo rural masivo de los años 50 y 60 (Mataix-Solera y Cerdà, 2009). Como consecuencia, estos terrenos han sido recolonizados por el bosque, favoreciendo así, la recurrencia de los incendios forestales, y convirtiéndolos en un elemento con importantes y devastadoras consecuencias ambientales, económicas y sociales, además del interés mediático despertado cuando afectan a zonas de interfaz urbano-forestal o zonas de especial protección, como algunos parques naturales. Esta problemática se ha visto acrecentada en las últimas décadas, por las políticas llevadas a cabo, por parte de las autoridades correspondientes, de lucha contra los incendios e intentos de supresión completa del fuego del medio (Naredo, 2004).

Los datos de los últimos años, demuestran que también la Comunidad Valenciana sigue sufriendo el impacto de algunos de estos incendios devastadores (Fig. 1), siendo sin duda el año 2012 el más castigado de la última década por este tipo de incendios, año en el que tan sólo dos incendios (en las localidades de Cortes de Pallás y Andilla) fueron responsables del 83% de la superficie quemada durante ese año (57.000 ha aproximadamente).

El suelo es un componente fundamental del ecosistema forestal (Mataix-Solera y Guerrero, 2007), necesario para su mantenimiento y sostenibilidad, a través de sus múltiples funciones. Estudiar y entender el funcionamiento del sistema suelo ayuda a conocer los posibles efectos ambientales causados por un incendio, ya que el fuego es un agente fundamental en los ciclos biogeoquímicos (Mataix-Solera y Cerdà, 2009; Lozano, 2015).

Tras el paso de un incendio forestal, el suelo puede sufrir múltiples modificaciones tanto directas como indirectas, producidas por el calentamiento y como consecuencia de la nueva situación después de la pérdida de la cubierta

vegetal, respectivamente (Mataix-Solera, 1999). Dichas alteraciones pueden retrasar, por tanto, el crecimiento de una nueva cubierta vegetal y exponer al suelo así, durante un periodo de tiempo más prolongado, a los agentes erosivos, causando alteraciones significativas en la estructura y funcionamiento de los ecosistemas áridos y semiáridos mediterráneos, tanto a escala regional como global (Cerdà y Robichaud, 2009; Guida et al., 2014). Las consecuencias de un incendio forestal serán, por tanto, más graves cuanto más intenso y severo sea éste (Keeley, 2009), y éstas dependerán también del área afectada y de la recurrencia del mismo (Tsitsoni, 1997; Pausas y Keeley, 2009; Broncano y Retana, 2004; Eugenio y Lloret, 2004).

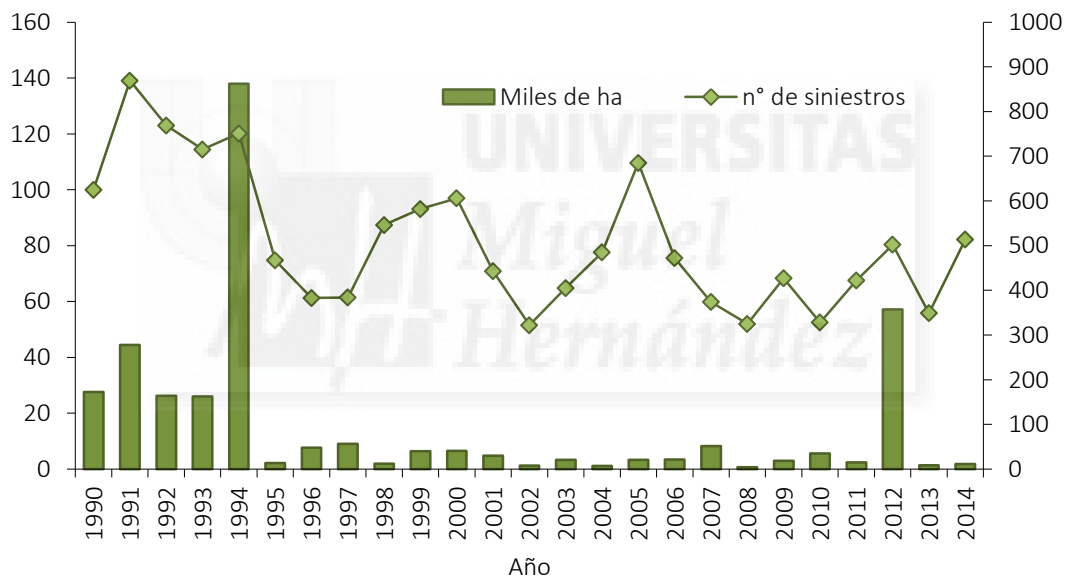


Figura 1. Superficie quemada (miles de ha) y número de siniestros por año en la Comunidad Valenciana. Fuente: elaboración propia a partir de datos de la Generalitat Valenciana.

EFFECTOS DEL FUEGO EN LAS PROPIEDADES DEL SUELO

Los efectos que el fuego puede producir en las propiedades de un suelo van a depender, entre otras cosas, de las temperaturas que se registren. Aunque el suelo es bastante buen aislante del calor, las temperaturas pueden llegar a ser elevadas en los primeros centímetros de suelo mineral (de entre 500-700 °C)

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según Dunn y DeBano (1977) y DeBano et al. (1977), y de hasta 900 °C según Úbeda et al. (2009). Asimismo, durante un fuego intenso, las temperaturas alcanzadas dentro de una masa forestal pueden llegar a alcanzar los 1200-1400 °C, mientras que a unos metros de la masa en combustión, el aire puede llegar a oscilar entre los 100-140 °C (Folch y Castelló, 1976). Por ello, el fuego puede modificar las propiedades edáficas a corto, medio y largo plazo, y en distinta medida, según la frecuencia, el tipo de fuego y situación edafológica y ecológica particular de la zona (Mataix-Solera, 1999). Las alteraciones producidas en el suelo por efecto del fuego, van a depender también de otros factores como la cantidad y del tipo de combustible que se queme (Bradstock et al., 1992; Bradstock y Auld, 1995; Baeza et al., 1997) y, por tanto, la velocidad y liberación de la energía (Alexander, 1982; Chandler et al., 1991), su contenido de humedad (Valette et al., 1994; Baeza et al., 1997), el contenido y tipo de materia orgánica edáfica (Nishita et al., 1970; Giovannini y Lucchesi, 1983; Lozano et al., 2013; 2014), el tiempo de residencia del calor en cada punto concreto (Aston y Gill, 1976; Dimitrakopoulos y Martin, 1990; Steward et al., 1990), y con ello, el tipo de combustión generada (Certini, 2014) (Fig. 2). Éste último factor es uno de los factores que más influye en la manera en que un incendio afecta indirectamente al ecosistema, y por ende, al suelo (Certini, 2005), ya que parte del “charcoal” o residuo generado debido a la combustión incompleta del material leñoso (Certini, 2014), el cual es difícilmente degradable, pasará a formar parte del suelo, favoreciendo algunas de las alteraciones indirectas en el mismo, debido a las nuevas propiedades inferidas.

El equilibrio de un suelo, el cual ha tardado años en conseguirse gracias a la interacción entre los diferentes ciclos biogeoquímicos, se rompe temporalmente al ser afectado por el fuego, y así los ecosistemas entran en una fase de cambio o tránsito (Cerdà y Mataix-Solera, 2009). Tras el paso del fuego, son muchas las propiedades edáficas (físicas, químicas y biológicas) que se pueden ver afectadas, como detallaremos más adelante.

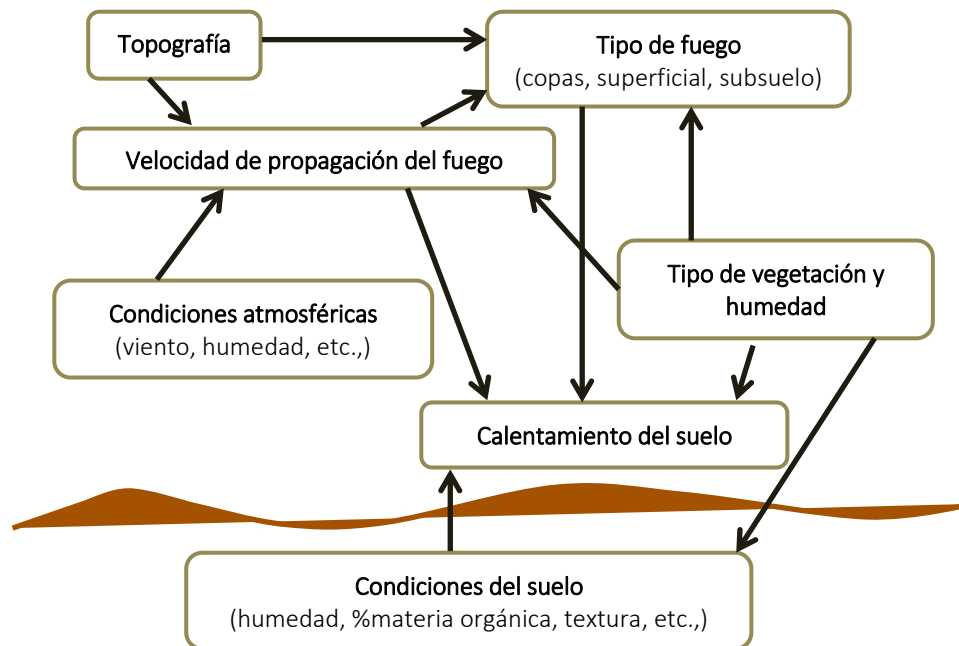


Figura 2. Principales factores implicados en el calentamiento del suelo durante un incendio forestal (Modificado de Mataix-Solera y Guerrero, 2007).

La recurrencia del fuego, como ya se ha dicho, tiene un gran impacto sobre los ecosistemas terrestres, que se verán alterados a corto plazo por el efecto del fuego, ya que modifica o elimina la cubierta vegetal (Mataix-Solera y Cerdà, 2009), mientras que las propiedades edáficas afectadas por el impacto del fuego se modificarán, en mayor o menor grado, a corto, medio, largo plazo, o incluso de manera permanente (DeBano et al., 1998), siendo los suelos, por tanto, los que transfieren el impacto del fuego a los ecosistemas (Mataix-Solera y Cerdà, 2009; Lozano, 2015), al modificar el ciclo de los nutrientes (Raison, 1979), sus propiedades físicas y químicas (Úbeda et al., 2009) y los procesos microbiológicos (Mataix-Solera y Cerdà, 2009; Bárcenas-Moreno et al., 2011a; Bárcenas-Moreno et al., 2011b). Los efectos del fuego, por tanto, pueden ser directos, por efecto del calor (Mataix-Solera, 1999), o indirectos, por la pérdida de la cobertura vegetal (Certini et al., 2011), la producción de charcoal (Certini, 2014), la presencia de cenizas (Bodí et al., 2014), las variaciones en el contenido de humedad (Doerr y Thomas, 2000; Doerr et al., 2002; Jiménez-Pinilla et al., 2016a) o el desarrollo de una capa repelente al agua (Doerr et al., 2000). Otro efecto

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derivado del calor producido suele ser la fracturación de rocas que están sobre la superficie del suelo, debido a las tensiones generadas por los súbitos cambios térmicos (termoclastia; Fig. 3). En general los incendios afectan de una manera muy compleja y heterogénea al sistema y con una elevada variabilidad espacial sobre el suelo (Certini, 2005; Neary et al., 2005).



Figura 3. Fracturación de las rocas por efecto del fuego (termoclastia) (Fotografías: J. Mataix-Solera).

Los cambios más significativos a causa del impacto del calentamiento, se producen principalmente en los primeros centímetros del suelo, ya que el aumento de la temperatura debido al efecto del fuego se produce en la capa más superficial de éste (Tabla 1). Según aumenta la profundidad en el suelo, las temperaturas alcanzadas por el impacto del fuego son cada vez menores. Aunque, bien es cierto, que las modificaciones sufridas en superficie debido al calentamiento, podrán tener también consecuencias en zonas más profundas del suelo.

Tabla 1. Alteraciones producidas en el suelo por el efecto del fuego, según la temperatura (°C) (Modificado de Neary et al., 1999).

Temperatura (°C)	Alteración
40-70	Degradación de proteínas y muerte de tejidos biológicos
48-54	Deshidratación de determinadas raíces o muerte
70-90	Muerte de determinadas semillas
50-121	Muerte de microorganismos edáficos
180-300	Destilación destructiva y combustión de alrededor del 85% del horizonte orgánico
200-250	Puede incrementarse la hidrofobicidad del suelo mineral
200-315	Comienza la destilación de la materia orgánica del suelo
270-300	Destrucción de la hidrofobicidad del suelo
200-400	Comienza la destilación de nutrientes (particularmente N)
>300	Los horizontes orgánicos superficiales del suelo son enteramente consumidos
420	Pérdidas de agua en los minerales de la fracción arcilla
≈450	Completo consumo de la materia orgánica
600	Máxima pérdida de fósforo y potasio, oxidación de enlaces metálicos
800	Oxidación de azufre
980	Cambios irreversibles en los minerales de la arcilla
1240	Volatilización del calcio

Tal y como hemos indicado, las modificaciones de las propiedades dependen, en mayor o menor grado, de las características del fuego, es decir, de la intensidad y severidad con la que éste actúe (Keeley, 2009) (Fig. 4). La intensidad de un fuego hace referencia a la velocidad a la que se libera la energía en el frente de la llama, expresada como kWm^{-1} . Éste es un parámetro que depende de factores tales como: cantidad y tipo de combustible, su continuidad, su humedad, la cual dependerá de las condiciones meteorológicas en el momento de la propagación y de los días previos, etc.

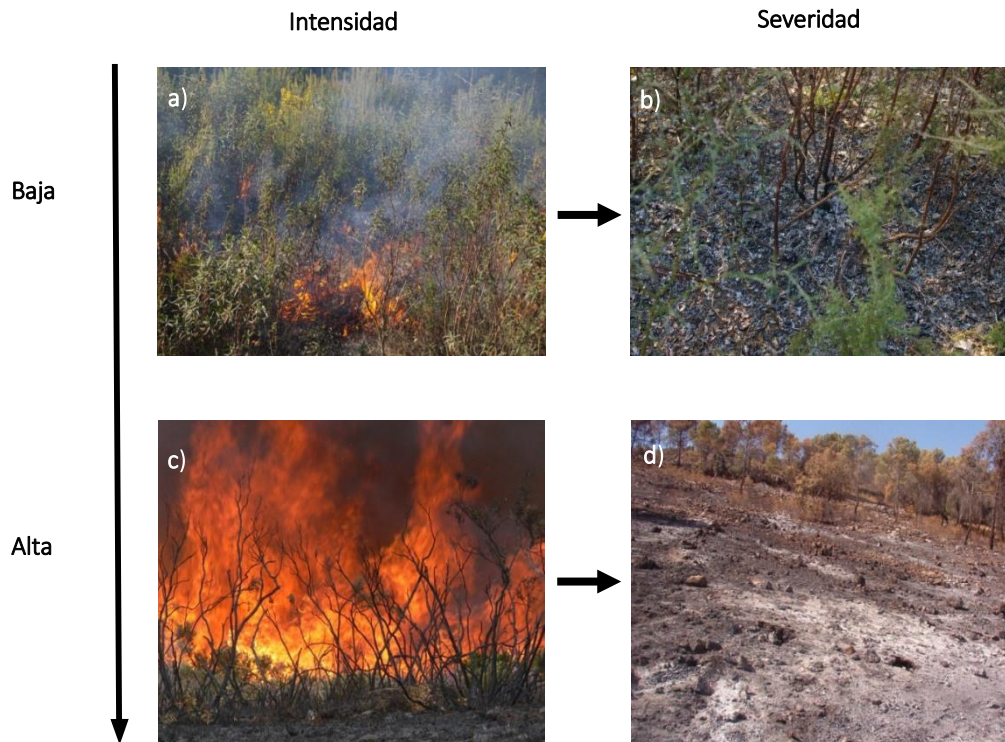


Figura 4. Fuego de baja intensidad, (a) poca altura de llamas y grado de afectación del suelo poco severo (b), se conservan las ramas y hojas y en las cenizas de color negruzco se distinguen las hojas quemadas. Fuego de alta intensidad (c) llamas de gran altura y grado de afectación altamente severo (d) cenizas de color blanquecino, no se distinguen hojas quemadas. Fotografías a, b y d: J. Mataix-Solera; c: V. Arcenegui (Extraída de Lozano y Jiménez-Pinilla, 2013).

La severidad de un fuego, es una medida indirecta de los cambios sobre el suelo, la vegetación o al ecosistema en general (Tabla 2). Éste es un parámetro, por tanto, que depende de la intensidad del fuego, pero también de otros factores tales como, el comportamiento del fuego, tipo de vegetación, o el tipo de suelo (Keeley, 2009). A través de la severidad de un fuego, se puede conocer cómo su intensidad afecta al ecosistema.

Tabla 2. Cambios en la vegetación y la materia orgánica del suelo según la severidad del fuego (Ryan y Noste, 1985). (Modificada de Keeley, 2009).

Severidad del fuego	Descripción
No quemado	Suelo y vegetación no alterada por los efectos del fuego
Chamuscado	Plantas no quemadas pero con muestra de pérdida de hojas por efecto del calor radiante
Suave	Copas de árboles con hojas verdes pero tallos chamuscados Hojarasca, musgos y hierbas carbonizadas o consumidas Horizontes orgánicos del suelo intactos o parcialmente afectados sólo en los primeros milímetros de profundidad. Fig. 4 (b)
Moderada o severa	Árboles con parte de las copas muerta, pero hojas no consumidas Sotobosque carbonizado o consumido Ramas finas muertas en superficie del suelo y troncos carbonizados Horizontes orgánicos del suelo casi completamente consumidos
Muy severa	Copas de árboles muertas y hojas consumidas Hojarasca de todos los tamaños y horizontes orgánicos de suelo completamente consumidos Deposición de cenizas blancas y materia orgánica carbonizada a varios centímetros de profundidad. Fig. 4 (d)

En cuanto a las propiedades del suelo, muchas se verán afectadas indirectamente si la fracción orgánica del suelo se ha visto alterada por el efecto del fuego, ya que ésta juega un papel esencial, e influye en multitud de propiedades edáficas, como son la microbiología del suelo, el reservorio de nutrientes, la porosidad, la infiltración, la capacidad de retención hídrica, la estabilidad de agregados, entre otras. Así, cualquier modificación en esta fracción del suelo, tendrá repercusión en muchas otras propiedades (González-Pérez et al., 2004).

Una de las propiedades del suelo que se ve afectada por el impacto del fuego de manera más evidente es el color. El color de un suelo permite deducir ciertas características del mismo, de modo que, a través de él, podemos conocer

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determinados procesos edáficos que han ocurrido, su contenido en materia orgánica, el contenido en carbonatos, incluso una aproximación de la composición mineralógica que posee (Porta et al., 2003). El cambio producido en el color de un suelo, tras un incendio forestal, se debe principalmente a varios motivos; uno es a la combustión de la cubierta vegetal y de la materia orgánica (Mataix-Solera y Cerdà, 2009), que produce la formación de una capa de cenizas inmediatamente después del fuego sobre la superficie del suelo, siendo éstas oscuras o blanquecinas, en función del menor o mayor grado de combustión de la materia orgánica, respectivamente, y/o de la severidad del fuego (Pereira y Bodí, 2013). Otro motivo que puede causar cambios en el color del suelo, es que éste puede sufrir modificaciones mineralógicas producidas por el efecto del calentamiento (Giovannini y Lucchesi, 1997; Notario del Pino, 2009), las cuales también pueden alterar el color del suelo, como por ejemplo, los óxidos de hierro, los cuales tienden a producir un enrojecimiento del mismo, debido a la transformación de estos óxidos en hematites, principalmente en el rango de temperaturas entre 300-500 °C (Pascual-Granged 2011; Terefe et al., 2008). El cambio de color del suelo tras un fuego, la eliminación de la cubierta vegetal, y la presencia de las cenizas, en ocasiones oscuras, suelen inducir a un aumento de la temperatura superficial del suelo, provocando mayores oscilaciones térmicas diarias (Mataix-Solera, 1999).

La textura, aun siendo una propiedad bastante estable, también puede verse afectada debido al efecto de la temperatura alcanzada por el fuego, siendo la fracción de la arcilla la más sensible al impacto del fuego (Pascual-Granged, 2011). Los incendios de alta intensidad favorecen la fusión térmica de esta fracción, aumentando el porcentaje de las fracciones limo y arena (Ulery et al., 1993; Nishita y Haug, 1972). Por tanto, tras el paso de fuegos de alta intensidad, y severos con el suelo, la textura podría tender a ser más gruesa (Mataix-Solera, et al., 2011; Mermut et al., 1997). Estas posibles variaciones porcentuales sólo se dan cuando la fracción arcilla es susceptible de variar con el calentamiento

(González et al., 1992). El impacto que un fuego puede tener sobre la fracción textural suele ser en el horizonte superficial, es decir, en los primeros centímetros del suelo, ya que el impacto del fuego va disminuyendo según se aumenta la profundidad. La organización de todos los componentes que forman la fracción textural, junto con la fracción orgánica, determina la estructura del suelo, y tanto la aireación del suelo como la posibilidad de presencia de vida en él, estarán determinadas, en su mayoría, gracias a esta propiedad edáfica (Porta et al., 2003). La manera en que se ordenan las partículas individuales de un suelo en partículas secundarias o agregados, con la formación de poros entre sí, determinará otras propiedades físicas del mismo, y éstas podrán ser muy diferentes de las de otro suelo, aunque ambos posean texturas similares (Pascual-Granged, 2011). Las uniones entre las diferentes partículas del suelo se deben, principalmente, a las interacciones físico-químicas entre dichas partículas, las arcillas, la materia orgánica y las sustancias cementantes presentes del suelo (Mataix-Solera et al., 2011). Esos agregados deben ser estables a los procesos de humectación y desecación, y juegan un papel fundamental en el funcionamiento del sistema suelo. Pero dicha estabilidad puede verse modificada por la severidad de un fuego (Mataix-Solera et al., 2011), y se han observado diferentes patrones de agregación dependiendo de una serie de factores que detallaremos más adelante, en el apartado específico sobre efectos del fuego en la agregación del suelo.

Tras el paso de un incendio forestal, el simple impacto de las gotas de lluvia, puede también modificar la estructura del suelo (Ellison, 1945; Moore y Singer, 1990), ya que la ruptura de agregados libera partículas finas que pueden obturar los poros y compactar el suelo (Bower, 1966; Moehring et al., 1966), creando un sellado o costra superficial (Giovannini y Lucchesi, 1997). Este hecho, puede hacer que la velocidad de infiltración del agua en el suelo disminuya favoreciendo la escorrentía superficial y, por tanto, aumente el arrastre de partículas y nutrientes (Chen et al., 1980; Ela et al., 1992). Debido a esto, la

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densidad aparente de ese suelo también puede verse aumentada, provocando un descenso en la tasa de oxigenación en los niveles inferiores del mismo, además de una falta de desarrollo en las raíces de la vegetación que haya sobrevivido tras el paso del fuego, y cambios en su estado químico y microbiológico (Mataix-Solera y Guerrero, 2007). La densidad aparente de un suelo puede oscilar entre 1 g/cm^3 para suelos bien estructurados, y $1,8 \text{ g/cm}^3$ para suelos compactados (Pascual-Granged, 2011). El descenso en la capacidad de retención hídrica, tanto en superficie como en profundidad, y el aumento de la densidad aparente en la capa más superficial, por el descenso de la porosidad, son procesos que pueden ocurrir bajo condiciones de un fuego de baja intensidad pero prolongado (Wahlenberg et al., 1939; Ralston y Hatchell, 1971; Boyer et al., 1994). La porosidad puede también disminuir, debido a la reducción de la materia orgánica tras el impacto del fuego (Pascual-Granged, 2011).

El fuego también puede producir una desecación inmediata en el suelo por la transferencia de calor, y además generar unas condiciones más secas a corto plazo, ya que la pérdida de la cubierta vegetal, la cual protege al suelo frente a la desecación en condiciones naturales, y el incremento de la temperatura debido a la presencia de cenizas más oscuras, puede provocar que el contenido de humedad de ese suelo disminuya (Campbell et al., 1977; Wells et al., 1979; Pietikainen y Fritze, 1995). El contenido en humedad de un suelo también se modificará, por efecto del fuego, debido a los cambios en la capacidad de retención hídrica, ya que aumenta la compactación, y el contenido de la materia orgánica disminuye en incendios severos (Mataix-Solera y Guerrero, 2007).

Los incendios forestales causan impacto también sobre propiedades edáficas químicas. Estas alteraciones químicas son producidas principalmente, aunque no exclusivamente, debido a la combustión de la materia orgánica del suelo y a su posterior aporte de cenizas, afectando al balance de nutrientes, el pH y la capacidad de adsorción e intercambio catiónico. También influye en la

propiedades químicas el efecto que el fuego tiene, al afectar a las poblaciones microbianas edáficas (Notario del Pino, 2013). El fuego transfiere calor al suelo mediante radiación, conducción o convección (Chandler et al.1991; Neary et al., 1999), lo que produce la volatilización de algunos componentes del suelo hacia la atmósfera (DeBano et al., 1998); la destilación y traslocación de sustancias orgánicas procedentes del combustible (Doerr et al., 2000); esterilización de la parte afectada del suelo (Acea y Carballas, 1996); y la transformación o eliminación de los componentes orgánicos (Notario del Pino, 2013). Todas estas alteraciones hacen que el impacto del fuego tenga importantes repercusiones sobre las propiedades del suelo, incluso llegando a ser irreversibles en algunos casos, lo que afectará a la recuperación post-incendio del mismo.

La materia orgánica es uno de los componentes presentes en el suelo que puede ser modificado drásticamente debido al efecto del fuego (Tabla 2), tanto en cantidad como en calidad (Mataix-Solera y Guerrero, 2007; Lozano et al., 2013; 2014). Un fuego de baja intensidad y severidad puede producir un incremento del carbono orgánico, debido a la incorporación de materia vegetal semipirolizada, es decir, no combustionada completamente, sobre la superficie (Fernández et al., 2007; Jonhson y Curtis, 2001; Mataix-Solera et al., 2002; Notario Del Pino et al., 2007). Mientras que, un fuego de alta intensidad y severidad, puede producir el efecto contrario, provocando una reducción en el contenido orgánico en las capas más superficiales del suelo (Bará y Vega, 1983; Fernández et al., 1997; Mataix-Solera et al., 2002). Cuando en el suelo se alcanza una temperatura en torno a 200-250°C, comienza la combustión de la materia orgánica, hasta su casi completa desaparición cuando ésta alcanza en torno a los 460 °C (DeBano, 1990; Giovannini et al., 1988). Por tanto, el efecto que la severidad del fuego tiene sobre el carbono orgánico puede ser desde una destilación parcial de algunos compuestos, hasta su completa eliminación (Simard et al., 2001). La calidad de la materia orgánica que queda tras el paso de un incendio forestal depende, en su mayor parte, del efecto que la intensidad del

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mismo ejerce sobre ella, es decir, de la severidad del fuego (Almendros, et al., 1984; Fernández et al., 2001 Salgado et al., 1995). Según aumenta la temperatura de calentamiento, el humus sufre alteraciones confiriendo propiedades más resistentes a la degradación microbiana, lo que se conoce como humus piromórfico (Almendros et al., 1984; González-Pérez et al., 2004; González-Vila et al., 2009). El grado de estabilidad y condensación de las fracciones húmicas aumenta según aumenta la temperatura incrementando, la relación C/N en el suelo (Mataix-Solera y Guerrero, 2007). El efecto del fuego también provoca que los componentes externos de las moléculas de los ácidos húmicos y los complejos arcillo-húmicos sean eliminados, reduciendo de manera rápida el contenido de nitrógeno y la capacidad de intercambio catiónico en las fracciones húmicas (Carballas, 1997; Oswald et al., 1999; González-Pérez et al., 2004).

Tras el paso del fuego, las alteraciones en el carbono orgánico hacia sustancias más recalcitrantes, inducirán modificaciones tanto en los recursos hídricos, como en los cationes disponibles en el suelo, convirtiendo al suelo, a largo plazo, en un medio algo menos fértil (Almendros et al., 1984). Por otro lado, se sabe que la alteración de la disponibilidad de cationes en un suelo, debido al impacto del fuego, puede producir modificaciones en el pH del mismo. Los valores de pH, generalmente, aumentan en un suelo quemado, debido principalmente, a que las cenizas aportan carbonatos, óxidos y cationes básicos (Ulery et al., 1993; Arocena y Opio, 2003), cuyo humedecimiento posterior produce la hidrólisis de los cationes básicos contenidos en ellas y, con ello, la elevación del pH (Kutiel et al., 1990; Ulery et al., 1995). También, contribuye a ello la destrucción de ácidos orgánicos por efecto del calentamiento en incendios de alta severidad, que provocan una gran combustión de la materia orgánica presente en el suelo, de manera que su pH puede llegar a aumentar hasta 4 ó 5 unidades (Ulery et al., 1995), debido principalmente, a la pérdida de grupos OH^- presentes en los minerales de la arcilla y a la formación de óxidos (Giovannini et

al., 1988; 1990a). Los aumentos en el pH pueden favorecer la actividad de los microorganismos y los procesos relacionados con ellos, aunque la variación de este parámetro también puede dar lugar a problemas de nutrición vegetal, al impedir la asimilación de algunos nutrientes (Mataix-Solera y Cerdà, 2007). Sin embargo, algunos autores han encontrado también descensos en el pH de suelos afectados por el fuego, debido a la desnaturalización de los ácidos orgánicos (Certini, 2005), y a la exposición de altas temperaturas por encima de 450-500 °C. La recuperación de los valores de pH del suelo va a depender de sus valores originales antes del fuego, del contenido de humedad y del tipo de vegetación presente antes del incendio, de la cual dependerá la composición química de las cenizas generadas al ser ésta combustionada (Gil et al., 2010). En ocasiones una recuperación relativamente rápida del pH original, suele deberse a la desaparición de las cenizas producidas por la combustión de la cubierta vegetal, que desaparecen por efecto de la erosión (Mataix-Solera y Cerdà, 2007), debido principalmente a la erosión eólica. La conductividad eléctrica y, por tanto, la salinidad del suelo afectado por el fuego, también aumentará debido a la incorporación y solubilización de las cenizas (DeBano, et al., 1977; Hernández et al., 1997; Badía y Martí, 2003). Del mismo modo que el pH, la recuperación de la conductividad eléctrica se producirá más rápidamente si las cenizas son movilizadas por erosión.

Tras el impacto de un incendio forestal, si éste actúa directamente sobre el suelo, aparte de producirse un descenso en el contenido de materia orgánica, de modo general se produce la disminución, en proporción más o menos directa, en la capacidad de intercambio catiónico (CIC) (Mangas et al., 1992; Carballas, 1997). Por ello, los cationes liberados no serán retenidos por el complejo de cambio, siendo así más fácilmente lixiviados a capas más profundas del suelo, o incluso arrastrados por las primeras lluvias tras el fuego (Mataix-Solera y Cerdà, 2007). La intensidad del fuego juega un papel importante en la liberación de nutrientes, y puede ser importante su repercusión a largo plazo en la

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productividad del suelo (Johnston y Elliott, 1998). Si el fuego ocasionado es de baja intensidad, y la materia orgánica no ha sido completamente destruida tras el incendio, estos cationes sí podrán ser retenidos por el complejo de cambio, al no haber sido destruido (Ibáñez et al., 1983). Así, Goh y Phillips, (1991) encontraron retenciones del 80-90% en el humus de potasio (K^+), calcio (Ca^{2+}) y magnesio (Mg^{2+}), procedentes de las cenizas producidas tras un fuego de baja intensidad. Sin embargo, si el incendio es de alta intensidad, se producirá un empobrecimiento nutricional del suelo, ya que aunque haya más nutrientes liberados disponibles, la capacidad de que éstos se mantengan en reserva, habrá disminuido (Mataix-Solera y Cerdà, 2007). En este sentido, DeBano y Conrad (1978) detectaron pérdidas notables de algunos nutrientes tras las primeras lluvias después del fuego. En el caso del fósforo (P), su contenido se aumenta tras el paso de un incendio en formas asimilables y en cantidades proporcionales a la cantidad de cenizas originadas por la combustión de la vegetación (Raison, 1979). El incremento del P inorgánico tras un fuego, depende de la temperatura alcanzada y de la mineralización del P orgánico (Saá et al., 1993), pero si se produce un incremento de la escorrentía y erosión después del incendio, se pueden producir pérdidas del mismo (Soto et al., 1991; Saá et al., 1998). Si las precipitaciones son escasas, las variaciones en la saturación del complejo de cambio del suelo serán por ello reducidas (Hatten et al., 2005).

Después de un incendio forestal, tal y como se ha mencionado anteriormente, se produce la aparición de una capa de cenizas que cubre la superficie del suelo (Badía y Martí, 2008; Jiménez-Pinilla et al., 2012; Pereira et al., 2014). Las cenizas están formadas por los residuos orgánicos e inorgánicos que provienen de la combustión, parcial o completa, de la cubierta vegetal y de la materia orgánica (Certini et al., 2011; Gordillo-Rivero, 2015), y que se depositan sobre el suelo (Moody et al., 2009). Las características de este residuo producido son un reflejo de las características de la especie vegetal afectada por el fuego (Pereira et al., 2010), y posee una importancia esencial en la protección

del suelo, pudiendo llegar a modificar sus propiedades físicas y químicas (Pereira y Bodí, 2013), e influyendo temporalmente a las poblaciones microbianas del suelo (Mataix-Solera et al., 2009). Las cenizas suponen una elevada fuente de nutrientes para el suelo (Raison, 1979; Ferreira et al., 2008). Algunos autores establecen también, que las cenizas pueden contener un elevado número de metales pesados, potencialmente tóxicos, como también, una elevada cantidad de metales alcalinos (Khanna et al., 1994; Saarsalmi et al., 2004; Karlton et al., 2008). Sin embargo, tanto la composición química y su aspecto físico, como sus propiedades, estarán determinados por el tipo de vegetación característica de la zona afectada por el fuego, la temperatura alcanzada por el mismo y su duración (Zhou, 2003; Pereira y Úbeda., 2010). El color de las cenizas generadas tras el paso del fuego nos puede dar información sobre la severidad del fuego, de manera que, cenizas de color oscuro, generalmente, son indicadoras de un fuego de baja intensidad y severidad, mientras que, unas cenizas de color gris o blancas, indicarán una severidad más elevada (Pereira et al., 2010). Sin embargo, en ocasiones un alto grado de combustión de la vegetación no tiene por qué corresponder con una elevada severidad del fuego en el suelo (Mataix-Solera y Guerrero, 2007).

Tras un incendio forestal es importante que las cenizas se mantengan en la superficie, ya que protegen al suelo de la erosión (Zavala et al., 2010; Bodí et al., 2012). Esta protección es especialmente importante en el período inmediato post-incendio (Chafer et al., 2016), cuando el suelo es más vulnerable a los agentes erosivos, como la lluvia y el viento (Fig. 5), y por ello, a la pérdida de nutrientes (Pereira et al., 2010). Sin embargo, el fuego puede tener un efecto fertilizante en la mayoría de casos, debido a una alta solubilidad de los nutrientes al entrar en contacto con el agua. Esta solubilidad depende del pH de las cenizas, el cual puede oscilar entre 5-6 en las cenizas generadas por efecto del fuego a bajas temperaturas, aunque puede alcanzar incluso pH de 12 si se crean bajo condiciones de temperaturas elevadas (Pereira et al., 2010). Como la distribución

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del tipo de cenizas es muy variable espacialmente según el tipo de vegetación y sus condiciones de humedad, la variabilidad espacial de la solubilidad de los nutrientes normalmente también aumenta (Pereira y Bodí, 2013).



Figura 5. Movilización de las cenizas producidas en un incendio forestal (Gorga, julio 2011), tras un periodo de lluvias abundantes en enero de 2012 (Fotografía: J. Mataix-Solera).

Muchos de los nutrientes aportados a través de las cenizas generadas tras un incendio, podrían no ser retenidos en el suelo (Carballas, 1997), ya que estas cenizas afectan a su vez también a los procesos de escorrentía y erosión post-incendio (Pereira y Bodí, 2013). La capacidad de retención hídrica de las cenizas es muy elevada, pudiendo llegar hasta un 80%, debido a su alta porosidad, y siempre que la intensidad de la lluvia sea menor que su conductividad hidráulica (Pereira et al., 2010). Así, las cenizas retardan el inicio de la escorrentía y la disminuyen también, protegiendo el suelo en la mayoría de casos (Zavala et al., 2010; Bodí et al., 2012). Este efecto es de relevada importancia cuando cubren

suelos repelentes al agua, en los que incluso pueden reducir la hidrofobicidad y mejorar, por tanto, su capacidad de infiltración (Bodí et al., 2013). Las cenizas pueden también producir un efecto desfavorable, en suelos repelentes al agua y con altos contenidos de carbonato cálcico, se puede formar una costra impermeable tras las primeras lluvias que tapone los poros del suelo, reduciendo así su capacidad de infiltración, y aumentando la escorrentía (Pereira y Bodí, 2013).

Aunque la influencia de las cenizas en el suelo producidas durante los incendios forestales ha sido estudiada en varias tesis doctorales recientes (Bodí, 2012; Pereira, 2010; Balfour, 2013), es necesario realizar más estudios para comprender mejor el funcionamiento del sistema suelo-planta y su influencia en los procesos hidrológico-erosivos post-incendio.

EFFECTOS DEL FUEGO SOBRE LA REPELENCIA AL AGUA DEL SUELO

La repelencia al agua o hidrofobicidad es una propiedad de los suelos que inhibe o reduce la afinidad del suelo por el agua (DeBano, 2000; Doerr et al., 2000). La afinidad o repelencia al agua entre las superficies de agua y sólidos, se origina por las fuerzas atractivas (adhesión) y la atracción entre las moléculas de agua (cohesión) (Jordán et al., 2010a). La molécula de agua posee una fuerte estructura dipolar, asociada a una gran tensión superficial, debido a la atracción entre sus polos (formada por un átomo de oxígeno con una carga parcial negativa y dos átomos de hidrógeno con una carga parcial positiva), y por lo que esta estructura presenta una gran resistencia a la reorganización (Hillel, 1998). El agua se adhiere a la mayoría de las superficies naturales, como lo es el suelo, ya que están formadas por iones que atraen a los polos opuestos de cada molécula de agua. Pero la característica dipolar del agua también produce fuerzas relativamente fuertes que pueden neutralizar la atracción entre cargas superficiales, resultando ser cero la suma de fuerzas de una molécula que actúa

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dentro de un líquido (Jordán et al., 2010a). La fuerza de atracción ejercida por el aire o fase gaseosa (altamente hidrofóbica) en contacto con el agua, es menor que la ejercida por las moléculas de agua entre sí, lo que crea una fuerza sobre la superficie líquida expuesta. Cuando un líquido moja una superficie sólida se extiende sobre ella, debilitándose las fuerzas de cohesión entre las moléculas del líquido, ya que parte de ellas, se han transformado en fuerzas de adhesión, siendo éstas superiores, en la fase líquido-sólido. Por el contrario, si las fuerzas de cohesión son dominantes, el líquido tenderá a asumir una forma esférica en forma de gota. Generalmente, los suelos minerales tienen una tensión superficial mucho más alta que la del agua, siendo hidrofílicos (Tschapek, 1984), por el contrario, algunas sustancias orgánicas, como las ceras o los polímeros orgánicos, tienen una tensión superficial con valores más bajos, siendo por tanto hidrofóbicos (Zisman, 1964).

La repelencia al agua en el suelo fue descrita por primera vez en 1910 por Schreiner y Shorey (1910). Esta propiedad ha sido observada prácticamente en suelos de todo el mundo, tanto forestales como agrícolas, bajo condiciones climáticas y ecológicas muy diversas (Doerr et al., 2000; Jordán et al., 2011), aunque hay una serie de factores, que como veremos más adelante, pueden hacer que su presencia sea más frecuente. Actualmente, se sabe que los compuestos capaces de inducir la hidrofobicidad en el suelo, son muy abundantes en los ecosistemas. Dichas sustancias son liberadas al suelo, normalmente de manera gradual, pudiendo proceder de diferentes fuentes como, por ejemplo, los exudados tanto de raíces (Dekker y Ritsema, 1996a; Doerr et al., 1998), como de la microbiota del suelo (Hallet y Young, 1999; Schaumann et al., 2007), o directamente procedentes de la descomposición de restos orgánicos (McGhie y Posner, 1981), principalmente vegetales y microbianos (Doerr et al., 2000), y también por efecto del calentamiento del suelo a determinadas temperaturas (DeBano, 2000). Las especies vegetales más asociadas al desarrollo de la repelencia al agua son los árboles perennes con una

elevada cantidad de resinas, ceras o aceites (Jordán et al., 2010a), como puede ocurrir en los suelos bajo la influencia de pino (Mataix-Solera y Doerr, 2004; Hubbert et al., 2006; Lewis et al., 2006; Jiménez-Pinilla et al., 2015; 2016b), alcornoques (Sevink et al., 1989; Jordán et al., 2008), y otras especies de *Quercus* (Cerdà et al., 1998; Mataix-Solera et al., 2007) y árboles de hoja caduca (Reeder y Jurgensen, 1979; Buczko et al., 2002). No obstante, esta propiedad también se ha encontrado bajo especies arbustivas en áreas templadas (Mallik y Rahman, 1985), matorral mediterráneo (Mallik y Rahman, 1985; Giovannini et al., 1987; Jordán et al., 2008; Jordán et al., 2010b; Jiménez-Pinilla et al., 2015), u otros tipos de bosques en condiciones de clima semi-desértico (DeBano, 1991). El mecanismo de incorporación de las sustancias hidrofóbicas en el suelo aún no se conoce completamente (Jordán et al., 2010a), pero sí se sabe que la hojarasca (Reeder y Jurgensen, 1979; McGhie y Posner, 1981) o la actividad de las raíces (Dekker y Ritsema, 1996b; Doerr, 1998), parecen ser algunas de las fuentes inductoras principales de la repelencia al agua en el suelo.

Además de los estudios sobre la influencia directa de la vegetación en la repelencia al agua del suelo, se han establecido relaciones generales entre la materia orgánica en los suelos y/o el contenido de carbono orgánico y el grado de repelencia (Doerr et al., 2000). Diferentes estudios han establecido correlaciones positivas entre el contenido de materia orgánica presente en el suelo y la persistencia de la repelencia al agua (Scholl, 1975; Rodríguez-Alleres et al., 2007; Martínez-Zavala y Jordán-López, 2009). Aunque también, otros autores, han determinado correlaciones pobres, negativas o no significativas entre ambos factores (DeBano, 1981; Jungerius y de Jong, 1989; Wallis et al., 1990; Ritsema y Dekker, 1994; Scott, 2000), e incluso resultados contradictorios (Martínez-Zavala y Jordán-López, 2009; Jordán et al., 2009). Muchos autores han concluido que la repelencia al agua del suelo puede estar controlada por el tipo y calidad de la materia orgánica, más que por su cantidad (DeBano et al., 1970; Wallis y Horne, 1992; Jaramillo, 2004). Lozano et al. (2013), observaron que el

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factor que mejor se correlacionaba con la persistencia de la repelencia al agua en el suelo era el contenido de lípidos extraíbles presentes en la materia orgánica del suelo, factor muy condicionado por el tipo de hojarasca, y por tanto, de la especie vegetal (Ito et al., 2002; Mallik y Rahman, 1985). Por otro lado, la relación de la repelencia al agua del suelo con ciertos tipos de vegetación podría ser no directa, ya que ésta también, está asociada al crecimiento de hongos y microorganismos del suelo (Molliard, 1910), los cuales están asociados con diferentes comunidades vegetales (Schantz y Piemeisel, 1917; Scheffer y Schachtsabel, 1989; DeBano, 2000). Un ejemplo es el fenómeno conocido como “anillos de hadas” observados por Shantz y Piemeisel (1917), formados por la actividad de micelios de basidiomicetos, que pueden producir repelencia en el suelo.

En condiciones naturales, el fenómeno de la repelencia al agua del suelo no se manifiesta de manera permanente, presentando su máxima intensidad en las épocas más secas y disminuyendo, o incluso llegando a desaparecer, en las épocas húmedas. Periodos largos de sequía generan alta severidad de repelencia al agua (Leighton-Boyce et al., 2003), siendo crítica incluso en regiones áridas, donde la mayor parte de las precipitaciones ocurren de manera torrencial (Mataix-Solera y Cerdà, 2009). En el caso de los suelos forestales calcáreos mediterráneos, la hidrofobicidad está asociada a las especies vegetales predominantes (Mataix-Solera, et al., 2007), especialmente bajo la influencia de pino. También, los suelos ácidos y de textura arenosa, son más propensos a desarrollar esta propiedad, debido a su baja superficie específica (Wallis y Horne, 1992). Así mismo, existe una heterogeneidad de la hidrofobicidad entre las distintas fracciones del suelo (Mataix-Solera et al, 2002), siendo ésta más intensa en las fracciones más finas del mismo (Mataix-Solera y Doerr, 2004; Mataix-Solera et al., 2005; Arcenegui et al., 2007). Este hecho implica que en condiciones de no saturación de agua en el suelo, las fracciones finas no se ponen en contacto con el agua, aunque se humedezca, y repercute en un bajo

intercambio catiónico necesario para la nutrición vegetal (Herrero-Gallur et al., 2002), adquiriendo, por lo tanto, consecuencias importantes sobre la fertilidad del mismo.

Aunque numerosas investigaciones han observado la repelencia al agua del suelo como un fenómeno natural (Jungerius y van der Meulen, 1988; Jungerius y de Jong, 1989; Witter et al., 1991; Ritsema et al., 1993; Dekker y Ritsema, 1994; Moral et al., 2002; Moral García et al., 2005;), asociado a diferentes tipos de suelos, en distintas zonas y climas del mundo (Doerr et al., 2000; Mataix-Solera et al., 2007; Jordán et al., 2010a), y debido a diversas causas, en general se ha observado que esta propiedad es más frecuente en suelos recientemente afectados por el fuego (Arcenegui et al., 2008). Este efecto fue descrito por primera vez a finales de los años 60 (DeBano et al., 1970). Se sugiere así, que el fuego puede ser un factor inductor de la misma (Jordán et al., 2010a) (Fig. 6), en suelos que antes del impacto del fuego no la manifestaban (DeBano y Krammes, 1966; DeBano et al., 1970; Savage, 1974), aunque también puede verse reducida o incrementada en suelos que sí la presentaban (DeBano et al., 1970; Savage, 1974). También, otros estudios han determinado que, aunque el efecto del fuego hubiera destruido la repelencia al agua en el suelo en superficie, éste habría desarrollado una capa hidrófoba en los primeros centímetros de profundidad (McNabb et al., 1989; Brock y DeBano, 1990; Scott y van Wyk, 1990), dependiendo de las temperaturas registradas en el perfil, ya que ésta suele mostrar un incremento, cuando el rango de temperaturas alcanzados en el suelo está entre 175-200 °C (DeBano, 1981).



Figura 6. Repelencia al agua en el suelo, en Gorga (Alicante), tras un incendio forestal en julio 2011 (Fotografía: J. Mataix-Solera).

El efecto del fuego sobre la repelencia al agua del suelo depende de varios factores, como son la temperatura alcanzadas durante la combustión, el tiempo de residencia del calor, la cantidad y tipo de combustible, el tipo de suelo y el contenido en humedad existente en el suelo previamente al paso del fuego (Doerr et al., 2000; Robichaud y Hungerford, 2000). Las temperaturas alcanzadas en el suelo durante el fuego varían mucho en función de todos los factores implicados, y debido a que el suelo es un mal conductor del calor, las temperaturas alcanzadas en las capas profundas del suelo suelen ser bajas (DeBano et al., 1998), aunque en superficie el fuego puede llegar a alcanzar entre los 500 y 800 °C, llegando incluso a ser de hasta 900 °C según Úbeda et al. (2009), y de 1400 °C en las llamas. Si la temperatura durante el fuego alcanza los 200-250 °C, la repelencia al agua se puede inducir o aumentar (DeBano y Krammes, 1966; DeBano, 2000; Doerr et al., 2005), debido a la volatilización de los compuestos orgánicos durante la combustión y su posterior condensación alrededor de las partículas del suelo, siguiendo el gradiente térmico hasta

condensarse de nuevo, a pocos centímetros bajo la superficie. La acumulación de las cenizas generadas por la combustión de ese material orgánico, puede transferir al suelo los compuestos hidrofóbicos presentes en ellas (Osborn et al., 1964), lo que también puede inducir un aumento de la repelencia al agua del suelo (Moody et al., 2009). Por otro lado, a partir de diferentes trabajos de laboratorio, se ha determinado que temperaturas entre 300 y 350 °C son suficientes para eliminar la repelencia al agua del suelo (DeBano et al., 1979; Robichaud y Hungerford, 2000; García-Corona et al., 2004; Mataix-Solera y Guerrero, 2007).

La repelencia al agua en el suelo, puede causar una disminución del contenido de humedad del mismo (Úbeda et al., 2002; Keesstra et al., 2016), lo que tiene importantes consecuencias para la recuperación de la cubierta vegetal, y, por tanto, también hidrológicas y geomorfológicas (Jordán et al., 2010a). La persistencia de la repelencia al agua en el suelo suele ser muy variable, y los valores del tiempo hasta que el agua penetra en el suelo, pueden oscilar desde unos pocos segundos, hasta horas, días o incluso semanas (Doerr y Shakesby, 2009; Jordán et al., 2013; Jiménez-Pinilla et al., 2015). Se ha comprobado en multitud de estudios, que la variabilidad espacial de esta propiedad suele ser muy elevada (Mataix-Solera y Doerr, 2004; Arcenegui et al., 2008). Según un estudio presentado recientemente por Keesstra et al. (2016), la dinámica y las fluctuaciones en la repelencia al agua del suelo difieren en magnitud, y en base a al contenido en humedad del suelo, según la influencia de las diferentes especies vegetales predominantes, ya que, la cubierta vegetal, representa uno de los factores clave en la distribución espacial natural de la repelencia al agua en el suelo, en los ecosistemas mediterráneos y, especialmente, durante los períodos post-incendios. Keesstra et al. (2016) determinaron que en dichos periodos post-incendios, la repelencia al agua en el suelo aumentaba inmediatamente tras el efecto del fuego, como efecto directo del calentamiento y por el depósito de la capa de cenizas sobre el suelo; sin embargo, posteriormente la repelencia

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disminuía, alcanzando valores menores que los registrados en condiciones naturales, o incluso desapareciendo, 2-3 meses después del paso del fuego, volviendo a aparecer años después, debido a la nueva incorporación de materia orgánica al recuperarse la cubierta vegetal.

Mataix-Solera et al. (2014) comprobaron que pequeñas variaciones de algunas propiedades del suelo, como la textura o el contenido de materia orgánica, pueden condicionar los valores de la repelencia al agua en suelos quemados, o incluso evitar que aparezca cuando los suelos contienen más presencia del mineral de la caolinita en la fracción arcilla (Mataix-Solera et al., 2008; 2013). Por otro lado, la repelencia al agua del suelo es un componente clave en los modelos hidrológicos (Doerr et al., 2003; Doerr y Shakesby, 2009), de manera que, el aumento de las sustancias hidrofóbicas en el suelo, puede favorecer la obturación de los poros, potenciando la disminución de la capacidad de infiltración del agua de los suelos, y el aumento de la escorrentía (Sanroque et al., 1985; Úbeda et al., 1990; Jordán et al., 2010b). También, la cantidad de precipitaciones suficientes, pueden llegar a desarrollar vías de flujo preferencial (Dekker y Ritsema, 2000), tanto superficiales como en profundidad. La relación de la repelencia al agua del suelo con otras propiedades tales como la acidez, la textura, la mineralogía o el contenido en materia orgánica, y las variaciones espaciales de cada una de ellas, favorecen una distribución espacial muy heterogénea de la misma y, por tanto, de la respuesta erosiva del suelo (Jordán et al., 2008). Ésta debe ser, también, una propiedad muy a tener en cuenta en los estudios sobre los factores condicionantes de la agregación del suelo y su estabilización, de acuerdo a las conclusiones obtenidas por Chrenková et al. (2014). Aunque la tasa de erosión en un suelo hidrofóbico forestal puede ser baja, debido a la presencia de cobertura vegetal (Cerdà y Doerr, 2007), tras el impacto del fuego, ésta puede aumentar drásticamente debido a la pérdida de dicha cobertura (Scott, 1993; Úbeda y Sala, 1998; Cerdà y Doerr, 2007), viéndose

incrementada, con las primeras lluvias en climas con un marcado factor estacional como el mediterráneo, (Cerdà et al., 1998; Doerr et al., 2003).

Actualmente, hay pocos estudios que hayan analizado la evolución temporal de la repelencia al agua en suelos calcáreos mediterráneos tras incendios forestales (Granged et al., 2011; Jordán et al., 2014; Keesstra et al., 2016). Para profundizar en esta cuestión, en uno de los trabajos presentados en esta Tesis Doctoral, se estudia el comportamiento de la evolución de la repelencia al agua en el suelo, a corto y medio plazo, tras ser afectado por un incendio forestal.

EFFECTOS DEL FUEGO SOBRE LA AGREGACIÓN DEL SUELO

La agregación de un suelo es el proceso mediante el cual las partículas individuales, minerales y orgánicas, y agregados de diferentes tamaños se unen o se asocian (Fig. 7), mediante agentes estabilizadores o cementantes (Mataix-Solera et al., 2011). Estos agentes cementantes pueden ser inorgánicos y orgánicos. Las partículas inorgánicas forman las unidades de fábrica de menor tamaño (cluster y dominios), a través de las fuerzas de atracción y cohesión entre ellas (Singer, 1994), como son las arcillas, los metales polivalentes, los carbonatos, los óxidos e hidróxidos de hierro y aluminio. Mientras que las orgánicas, favorecen la estabilización de los agregados uniando las partículas por mecanismos de adsorción, segregando productos mucilaginosos (Amézketa, 1999) y envolviendo partículas (cementos húmicos), como son los polisacáridos procedentes de los microorganismos, y de los restos vegetales, las raíces, las hifas de hongos y el material húmico (Bronick y Lal, 2005; Nimmo y Perkins, 2002). De ahí el importante papel estabilizador de la materia orgánica en la agregación (Oades, 1993), y su importancia en suelos quemados, ya que, si debido al efecto del fuego, los compuestos orgánicos cementantes se volatilizan, la estructura del suelo puede, también, verse alterada (Badía y Martí, 2003). Las

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interacciones físico-químicas entre todos estos agentes cementantes, influyen en las uniones entre las diferentes partículas del suelo, favoreciendo, por tanto, la formación de los agregados (Harris et al., 1964; Insam y Domsch, 1988).



Figura 7. Muestra de suelo bien agregado. Parque Natural del Montgó, Javea (Alicante) (Fotografía: J. Mataix-Solera).

Los agregados se forman de manera más o menos estable, gracias a los fenómenos de floculación de coloides, creando inicialmente microagregados (<0,25 mm), que si siguen evolucionando formarán agregados de mayor tamaño, o macroagregados (>0,25 mm). Este proceso de agregación estará favorecido además, por la acción floculante de determinados cationes di- o trivalentes como el calcio, el hierro y el aluminio (Porta et al., 2003). Por ejemplo, en suelos calcáreos el carbonato cálcico actúa también como un agente cementante; mientras que en suelos donde hay presencia de óxidos de hierro, éstos ejercen

un papel adherente entre las superficies de las arcillas. Por otro lado, el complejo arcillo-húmico, pieza clave en los procesos de agregación, será más estable cuanto más polimerizados estén los ácidos húmicos (Mataix-Solera et al., 2010).

La estabilidad de agregados hace referencia a la resistencia que tienen éstos para mantener su propia estructura cuando se encuentran sometidos a fuerzas externas (Hillel, 1998). La rotura de los agregados puede deberse a diferentes causas, como pueden ser el impacto de las gotas de lluvia, la compactación de la superficie del suelo (Epstein y Grant, 1973; Poesen y Savat, 1981; Hoogmoed y Stroosnijder, 1984), o incluso por el efecto del fuego (Mataix-Solera et al., 2011). Su destrucción puede favorecer el desarrollo de costras o el sellado superficial del suelo, limitando así la infiltración del agua, e incrementando la erosión potencial del mismo (Mataix-Solera et al., 2010). Por tanto, la estabilidad de agregados aporta información sobre la estructura y salud del suelo, que al ser dependiente de la química y de la biología del mismo, se convierte en un parámetro integrador del complejo sistema suelo (Mataix-Solera et al., 2011). Por ello, la agregación es una propiedad clave en el control y la gestión del agua en el suelo, la cual influye en la infiltración, la escorrentía superficial y la erosionabilidad del mismo (Imeson, 1984), siendo una de las propiedades que más influye en todos los procesos hidrológicos, biológicos y atmosféricos de los suelos.

Como ya se ha mencionado anteriormente, los incendios forestales pueden provocar cambios en la superficie del suelo, debido al aumento brusco de la temperatura (Certini, 2005; Úbeda et al., 2009), lo que puede influir directamente en la estructura del suelo (Mataix-Solera y Guerrero, 2007). Los principales factores que influyen en la agregación en un suelo afectado por un incendio forestal son la intensidad y severidad del fuego, las características del suelo previas al paso del mismo, como su contenido en materia orgánica y de humedad, y otras propiedades edáficas como son la repelencia al agua y la

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mineralogía del suelo, ya que se pueden producir también cambios que afectan a los minerales, como consecuencia de las temperaturas alcanzadas (Fig. 8).

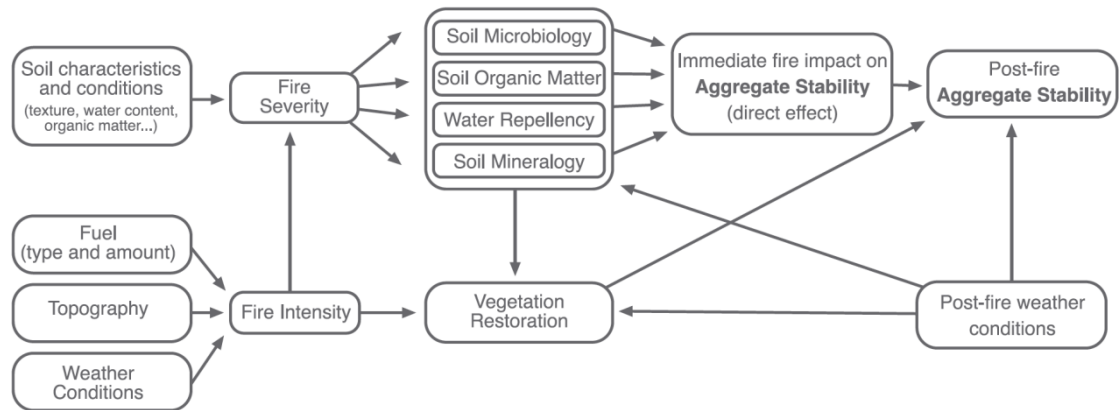


Figura 8. Factores que pueden inducir cambios en la estabilidad de agregados inmediatamente después y a corto plazo tras el impacto de un incendio (Fuente: Mataix-Solera et al., 2011).

Todos estos factores pueden afectar directamente a algunas de las propiedades del suelo relacionadas con la agregación, a corto y medio plazo, e incluso pueden llegar a ser permanentes, debido al efecto del calor liberado durante el paso del fuego (Fig. 9) y, por tanto, consideramos que es una propiedad de especial importancia para el estudio de los efectos del fuego en los suelos (Mataix-Solera et al., 2010). Sin embargo, los estudios previos nos han demostrado que la respuesta de los agregados al efecto del fuego es muy compleja de evaluar, ya que ésta depende, como hemos indicado, de muchos factores a tener en cuenta (Mataix-Solera et al., 2011). Por un lado, los microorganismos son muy sensibles al efecto del fuego (Bárcenas-Moreno, et al., 2011a), de manera que su efecto directo inmediato es una reducción de las poblaciones microbianas del suelo, especialmente los hongos, directamente relacionados con la agregación (Mataix-Solera et al., 2009).

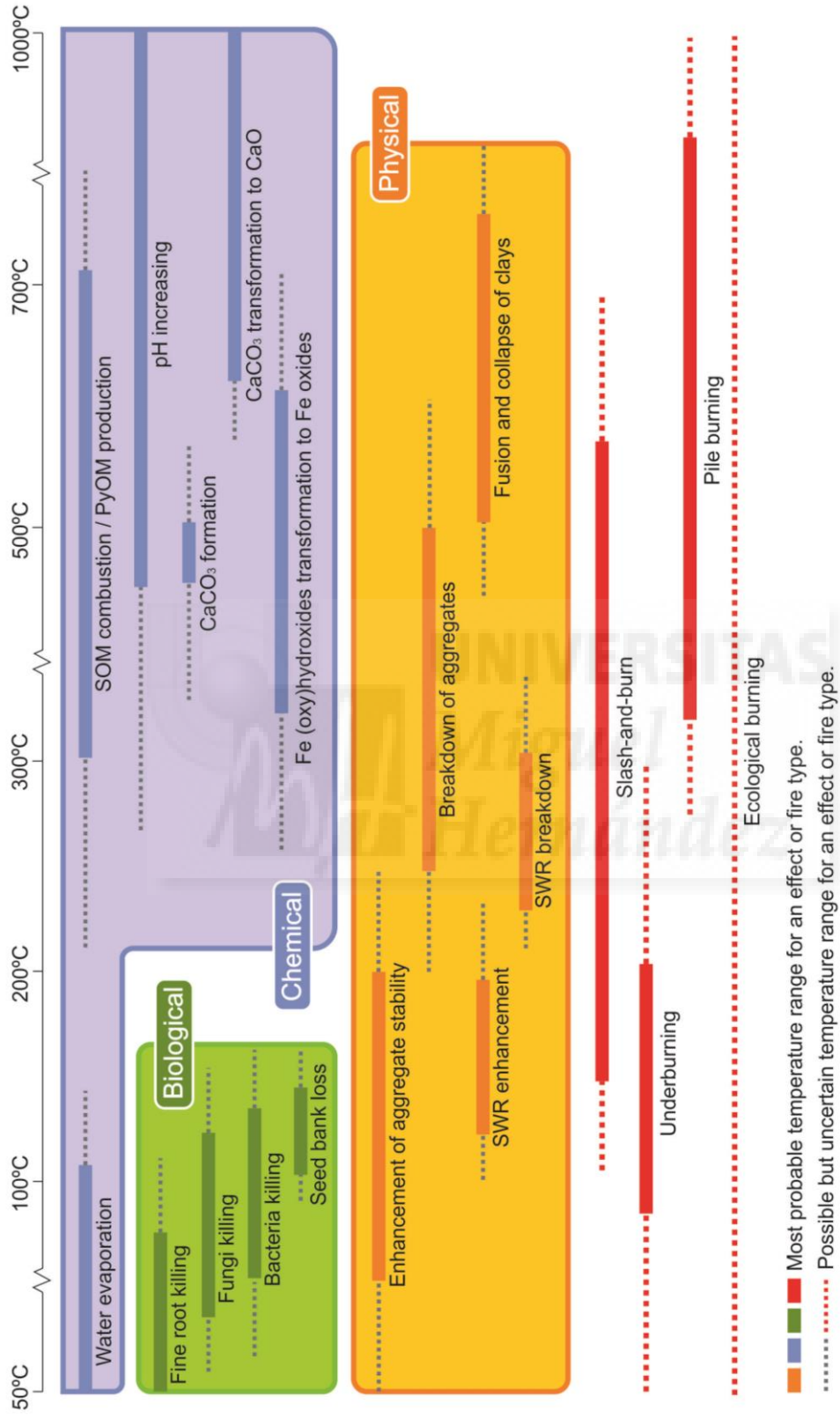


Figura 9. Cambios en las propiedades biológicas, químicas y físicas del suelo por efecto del calor. SOM: materia orgánica del suelo; PyOM: materia orgánica pirogénica; SWR: repelencia al agua del suelo (Cortés de Santín y Doerr, 2016).

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Por otro lado, y como hemos mencionado en apartados anteriores, el fuego produce efectos en la materia orgánica, tanto cuantitativos como cualitativos, si éste es de severidad moderada o alta (González-Pérez, et al., 2004). De producirse estos cambios, habrá una repercusión directa sobre los agregados, ya que se producirá una destrucción de parte de los mismos, o una pérdida de estabilidad, al verse afectada una fracción del suelo que actuaba como agente cementante. Otro factor que puede influir en la agregación del suelo, por ser importante en la estabilidad estructural, son las transformaciones mineralógicas del suelo, derivadas del impacto del calentamiento (Mataix-Solera et al., 2010). Éstas se producen cuando en el suelo se alcanzan temperaturas moderadas o elevadas, aunque bien es cierto que algunas transformaciones minerales no necesitan de temperaturas muy altas para producirse. Estos cambios, sin embargo, estarán también muy controlados por el tipo de suelo y dependerán, en gran medida, de su composición mineralógica original (Mataix-Solera et al., 2010; 2011).

La respuesta de la agregación del suelo, debido al efecto del fuego, puede ser por tanto, muy variable. De la combinación de todos los factores mencionados, se pueden esperar, principalmente, tres patrones de comportamiento diferentes de la estabilidad de agregados (Fig. 10), en función de la severidad del fuego, y el tipo de suelo (Mataix-Solera et al., (2011). Estos tres patrones son:

- a) Un aumento de la estabilidad de agregados progresivo con la severidad del fuego (Arcenegui et al., 2013; Jiménez-Pinilla et al., 2014; 2016b), y que se ha observado, principalmente, en suelos con mayor contenido de arcilla, y con otros agentes cementantes, como el carbonato cálcico, y óxidos de Fe y Al (Guerrero et al., 2001; Arcenegui et al., 2008), a pesar de irse destruyendo la materia orgánica.

- b) Un ligero incremento de la estabilidad de agregados con la severidad del fuego (Giovannini y Lucchesi, 1983; García-Corona et al., 2004; Mataix-Solera y Doerr, 2004), debido al desarrollo o aumento de la repelencia al agua a determinadas temperaturas, seguido de un descenso de la misma, cuando dichas temperaturas alcanzadas son suficientemente altas para destruir la materia orgánica (Soto et al., 1991; García-Corona et al., 2004; Marcos et al., 2007). Este comportamiento se produce en suelos cuyo principal agente cementante es, también, la materia orgánica y, que previamente al impacto del fuego, no mostraban repelencia al agua o mostraban una repelencia muy baja.
- c) Descenso progresivo de la estabilidad de los agregados con la severidad del fuego. Este comportamiento se ha observado, principalmente, en suelos arenosos, que originalmente muestran algo de repelencia al agua y valores altos de estabilidad de agregados, y suelos donde la materia orgánica es el principal agente cementante (Giovannini et al., 1987; Sanroque et al., 1985; Badía y Martí, 2003; Zavala et al., 2010).

Según el patrón de comportamiento (a), el efecto del calentamiento puede producir una mayor estabilidad de los agregados remanentes tras el paso del fuego (Guerrero et al., 2001; Mataix-Solera y Doerr, 2004; Arcenegui et al., 2008; Arcenegui et al., 2013; Jiménez-Pinilla et al., 2014; 2016b), siendo éstos más resistentes a la dispersión o rotura (Giovannini et al., 1990b; Ulery et al., 1993).

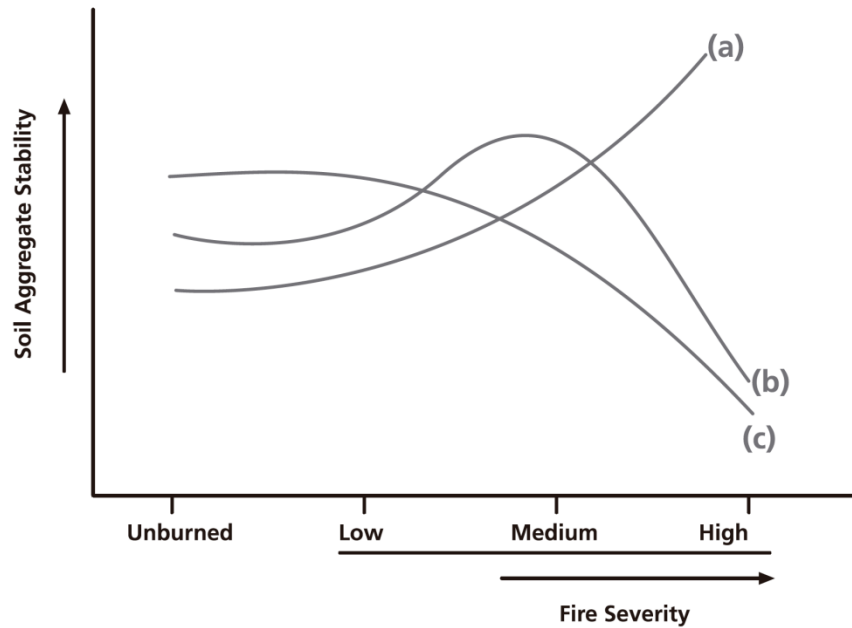


Figura 10. Esquema de los tres tipos de patrones diferentes de comportamiento observados en la agregación en función de la severidad del fuego: a) suelos con un alto contenidos de arcilla, carbonato de calcio, óxidos de Fe y Al como principales agentes cementantes; b) suelos con materia orgánica como principal agente de estabilización de agregados e inicialmente hidrofílico o con baja repelencia al agua; c) suelos arenosos altamente repelentes al agua y en los que la materia orgánica actúa como el principal agente cementante (Fuente: Mataix-Solera et al., 2011).

El aumento en la estabilidad de agregados como consecuencia del fuego, pueden deberse a diversos factores, como son:

- 1) El tipo de incendio: en el caso de los incendio de copas, donde el fuego no afecta directamente al suelo, se puede producir un aumento del contenido en materia orgánica edáfica debido a la incorporación del material semipirolizado procedente de la vegetación, lo que podría explicar un aumento a medio o largo plazo tras el incendio (Mataix-Solera et al., 2010).
- 2) El recubrimiento de los agregados por condensación de los compuestos hidrofóbicos desarrollados tras el impacto del fuego, impidiendo su humedecimiento (Chenu et al., 2000; Hallett et al., 2001; Mataix-Solera y Doerr, 2004; Varela, 2007; Arcenegui et al., 2008).

- 3) Altas temperaturas alcanzadas, suficientes como para generar fusiones térmicas de partículas y recristalizaciones de minerales de la fracción arcilla o transformaciones de óxidos de hierro o aluminosilicatos formando agregados más resistentes físicamente (Giovannini y Lucchesi, 1997; Guerrero et al., 2001).
- 4) El aumento aparente observado en la estabilidad de los agregados (Mataix-Solera y Doerr, 2004; Arcenegui et al., 2013), es decir, que el fuego haya destruido una proporción de los agregados por la combustión, debido a la alteración de cualquiera de los agentes cementantes presentes, y provocando ya una selección de los agregados más resistentes, puesto que son los que permanecen tras el incendio (Jiménez-Pinilla et al., 2014; 2016b).

El estudio de uno de los capítulos de esta Tesis Doctoral se ha basado en este último supuesto, tratando de dar respuesta a las dudas que a día de hoy todavía no están resueltas, y avanzar más en el conocimiento sobre cómo influye el efecto del calentamiento en la estabilidad estructural del suelo.



JUSTIFICACIÓN Y OBJETIVOS

El suelo, como sabemos, es un recurso esencial para la vida. Éste en ocasiones, tras verse afectado por un incendio forestal, puede sufrir modificaciones en sus propiedades, tanto de manera directa por el efecto del calor, como indirecta por la desaparición temporal de la cubierta vegetal y/o la aparición de una capa de cenizas tras la combustión de la vegetación. Estos cambios físicos, químicos o biológicos, pueden alterar el equilibrio y funcionamiento del ecosistema terrestre.

Aunque el fuego ha sido desde siempre un factor ecológico que ha jugado un papel fundamental como agente modelador de los ecosistemas mediterráneos, en las últimas décadas se han producido cambios en el régimen de los incendios forestales, alterando su frecuencia e intensidad, lo que ha propiciado, en muchos casos, impactos negativos. En la cuenca mediterránea, tanto las características climáticas propias de la estación estival, esencialmente seca y cálida, como las precipitaciones torrenciales en otoño, hacen que los riesgos derivados de los grandes incendios forestales sean un grave problema.

En esta Tesis Doctoral hemos abordado algunos aspectos todavía poco conocidos sobre los efectos del fuego en algunas propiedades del suelo, su evolución temporal, la influencia de la presencia de las cenizas, y otros factores como el tipo de vegetación y las condiciones ambientales. Hemos prestado una atención particular a la repelencia al agua del suelo y a la estabilidad de agregados, junto al estudio de otras propiedades íntimamente relacionadas con éstas.

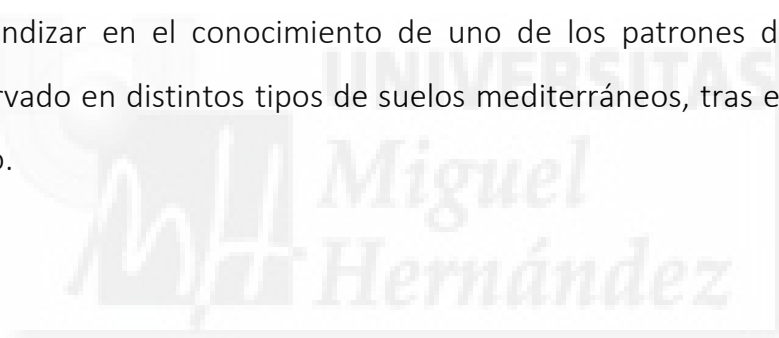
La repelencia al agua puede ser una propiedad común en los suelos calcáreos de los bosques mediterráneos, la cual puede aparecer de manera natural, favorecida por la influencia de la vegetación de la zona, entre otros factores (Mataix-Solera et al., 2007; Lozano et al., 2013). Esta propiedad puede

tener efectos importantes sobre la distribución del agua en el suelo, su disponibilidad para las plantas y en el comportamiento hidrológico del suelo, afectando así, a las tasas de escorrentía y, por tanto, a la erosión (Cerdà y Doerr, 2007). Hemos comprobado que la persistencia de la repelencia al agua en el suelo, se ve muchas veces inducida o incrementada tras el impacto del fuego (DeBano y Krammes, 1966; Doerr y Thomas, 2000; Arcenegui et al., 2007 y 2008), siendo las características del suelo (Mataix-Solera et al., 2008 y 2014), así como las temperaturas registradas por el incendio, las principales responsables de dicho comportamiento (Arcenegui et al., 2007). De igual manera, se sabe que el contenido en humedad del suelo, la humedad relativa del aire y la estructura de la superficie del suelo, son algunas de las características determinantes en la presencia de la repelencia en el suelo, y que además son propiedades sensibles al impacto del fuego. Pensamos que aún son necesarios más estudios sobre su evolución temporal, tras el paso del fuego, y los factores que condicionan su comportamiento.

Por otro lado, la agregación del suelo es otra propiedad clave en suelos quemados, y se ha comprobado que dependiendo de una serie de factores como el tipo de suelo y la severidad del fuego, los patrones de comportamiento pueden ser muy diversos y complejos (Mataix-Solera et al., 2011). En la literatura se comprueba que hay estudios que han encontrado descensos en la estabilidad de agregados, y otros que han observado aumentos, sin estar del todo claro, si este último es un aumento real o aparente al dejar el fuego una selección de los agregados más resistentes.

Siendo conscientes de que tanto los efectos del fuego, como la evolución de las propiedades afectadas por éste, dependen, en gran medida, de las condiciones climáticas, edáficas, biogeográficas y estacionales de cada zona concreta, los trabajos experimentales realizados para esta Tesis Doctoral, se plantean bajo los siguientes objetivos generales:

1. Contribuir al conocimiento de la evolución temporal de las propiedades del suelo, a medio plazo tras un incendio forestal, con especial énfasis en la repelencia al agua del suelo.
2. Estudiar la influencia de las distintas coberturas vegetales (pino vs matorral) en la evolución temporal de las propiedades edáficas.
3. Analizar la influencia de la ausencia o presencia de cenizas en la evolución temporal de las propiedades del suelo.
4. Estudiar el efecto de la humedad ambiental relativa sobre los cambios de la repelencia al agua de un suelo mediterráneo calcáreo afectado por el fuego.
5. Profundizar en el conocimiento de uno de los patrones de agregación observado en distintos tipos de suelos mediterráneos, tras el impacto del fuego.





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CAPÍTULO 1

TEMPORAL CHANGES IN SOIL WATER REPELLENCY AFTER A FOREST FIRE IN A MEDITERRANEAN CALCAREOUS SOIL: INFLUENCE OF ASH AND DIFFERENT VEGETATION TYPE

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ABSTRACT

Forest fires usually modify soil water repellency (SWR), and its persistence and intensity show a high variability both in space and time. This research studies the evolution of SWR in a Mediterranean calcareous soil affected by a forest fire, which occurred in Gorga (SE Spain) in July 2011, comparing the effect of the main vegetation cover between pine (*Pinus halepensis*) and shrubs species (*Quercus coccifera*, *Rosmarinus officinalis*, *Cistus albidus*, *Erica arborea* and *Brachypodium retusum*) and the relationship with soil moisture content (SMC). Also the study analyzed the effect of ash on SWR dynamics under field conditions. Six plots were established on the fire-affected area and the unburned -control- adjacent area to monitoring SWR with the water drop penetration time (WDPT) test, SMC through moist sensors (5 cm depth) and three different ash treatments: ash presence, ash absence and incorporation of ash into the soil. An immediate increase of SWR was observed in the fire-affected area, mainly in pine plots. SWR changes in control (unburned) plots were quite similar between different types of vegetation influence, despite higher SWR values being observed on pine plots during the study period. A noticeable decrease of SWR was observed during the first months after fire in affected areas, especially after the first rainy period, both in pine and shrubs plots. SWR increase was registered in all plots, and the highest levels were in March 2012 in burned pine plots. SWR decrease was higher in plots where ash was removed. Fire-affected soils became wettable one year and a half after the fire.

Key words: hydrophobicity, soil water repellency, ash, soil moisture content, wildfire.

INTRODUCTION

Soil water repellency (SWR) reduces the affinity of water for soil and, as a

consequence, water-repellent soils may offer high resistance to water infiltration (Doerr et al., 2000; Jordán et al., 2013), modifying the soil hydrological balance (Doerr et al., 2000; Bodí et al., 2011). SWR is naturally occurring in many ecosystems (Doerr et al., 2000), and is caused by hydrophobic organic compounds coating soil mineral surfaces or included in the soil matrix as interstitial particles (Doerr et al., 2009). These substances are slowly released into the soil after the transformation of organic residues by chemical processes and microbial activity (Doerr et al., 2005; Hallet and Young, 1999; Wallis and Horne, 1992). Persistence and intensity of SWR show a high variability in space and time (Woods et al., 2007). SWR has been observed under different climatic conditions (Doerr et al., 2000) and may be controlled by many factors (Mataix-Solera et al., 2014) such as soil organic matter (OM) content and chemical properties (Doerr and Thomas, 2000), soil mineralogy (Lichner et al., 2006; Mataix-Solera et al., 2008; Zavala et al., 2009a), soil texture (Bachmann et al., 2006; Jordán et al., 2013; Woche et al., 2005), vegetation type (Dekker and Ritsema, 1994; Doerr et al., 2000; Zavala et al., 2009a, 2009b), soil moisture content (SMC) (Doerr and Thomas, 2000; Ritsema and Dekker, 1994) or fire (Doerr et al., 1996; Granged et al., 2011b). Also, Lozano et al. (2013, 2014) suggested a strong association between SWR and the composition of soil microbial communities. Often, all these factors combine, and favour the increase of SWR below critical SMC. Soils exceeding a certain threshold of moisture content may shift from water-repellent to a wettable state (DeBano, 1981; Huffman et al., 2001). The reorientation of amphiphilic compounds, meaning particles with both hydrophilic and hydrophobic fractions, over mineral surfaces in contact with water may also contribute to this process (Jordán et al., 2010b). Although SWR may vary irregularly during drying (Bayer and Schaumann, 2007; González-Peñaloza et al., 2013), it usually decreases or disappears when SMC is above critical thresholds (Dekker et al., 2001; Doerr and Thomas, 2000; Poulénard et al., 2004; Regalado and Ritter, 2005).

Hydrological and geomorphological effects of SWR cannot be fully assessed without considering these SWR fluctuations over time (Doerr and Thomas, 2000). Although the relation between SWR and SMC may vary if soil is wetting or drying (Doerr et al., 2002; Urbanek et al., 2015), positive relations between SWR and SMC may have important repercussions in terms of runoff generation and soil erosion risk (Ahn et al., 2013; Cerdà and Doerr, 2008; Shakesby et al., 1993) and the development of preferential flow paths (Cerdà and Doerr, 2005; Granged et al., 2011a; Ritsema et al., 1998), having major consequences for plant growth (Doerr et al., 2000). For those reasons, SWR is especially relevant in arid and semiarid areas, such as Mediterranean ecosystems, where water resources may be especially limited and distribution of rainfall is strongly seasonal. SWR in Mediterranean soils has been closely related to some plant species (Gimeno-García et al., 2011), such as certain evergreen tree types (Doerr et al., 2000; Zavala et al., 2009a, 2009b), pines (Granged et al., 2011b; Mataix-Solera et al., 2007), deciduous trees, shrubs and herbaceous species (Doerr et al., 2000; Martínez-Zavala and Jordán-López, 2009; Zavala et al., 2009b). Recent research has attributed these relationships to the chemical properties of soil OM, particularly to its lipid fraction (Jiménez-Morillo et al., 2014; Lozano et al., 2013).

An important ecological agent affecting Mediterranean ecosystems is fire. Forest fires can produce dramatic changes in soil chemical, physical and microbiological properties (Certini, 2005; DeBano et al., 1998; Neary et al., 1999). Depending on soil temperature peaks and water content, fire usually induces or increases SWR, in previously wettable or water-repellent soils (Doerr et al., 2000; Mataix-Solera and Doerr, 2004; Zavala et al., 2010) due to the rapid volatilization of hydrophobic compounds from the litter layer, that are released during combustion and condensed in cooler/deeper parts of soil profile, and the transformation of organic fractions (DeBano et al., 1970). But fire can also reduce or destroy SWR in previous water repellent soils. In fact, contrasted statements have been established in previous works owing to the immediate effects

following a fire. Granged et al. (2011b) found that water repellency (both under field and laboratory conditions) from soils beneath shrubs decreased or was destroyed in the first millimeters of depth in burned soils, due to high temperatures (peaks above 400 °C) reached on the soil surface. On the other hand, Gimeno-García et al. (2011) observed different SWR frequency patterns following fire amongst two shrubs species studied: a significant increase of SWR was observed in soil beneath *Rosmarinus officinalis* but SWR was completely destroyed beneath *Quercus coccifera* species affected by fire. They established that differences in SWR persistence immediately following the forest fire seems to be mainly related to differences between vegetation species burned and how they are spatially distributed, and also SMC at the moment of fire. Fire causes changes in OM content (partly or completely destroying it) and its quality (Almendros et al., 1988; Jiménez-Morillo et al., 2014; Knicker et al., 2005), affecting SWR (Arcenegui et al., 2008; Jordán et al., 2010a; Robichaud, 2000). The severity of these impacts depends mostly on the duration of heating and temperatures reached during burning (DeBano, et al., 1976; Doerr et al., 2004; Gordillo-Rivero et al., 2014). Based on the same study parameters Tessler et al. (2008), Malkinson and Wittenberg (2011) suggested that post-fire hydrophobic peaks are conditioned by pre-fire vegetation properties, and the rapid decrease of SWR and the ecosystem recovery are associated with biotic activity.

SWR is also influenced by the presence of ash (Bodí et al., 2012; 2014), and depends on the plant species burned and the degree of combustion (Bodí et al., 2011; Neary et al., 2005). After a fire, an ash layer covers the ground playing an important role in soil ability to absorb water (DeBano, 2000), applying complex influences to SWR, as soil sealing by ash particles (Bodí et al., 2014), and also including but not limited to its effect on water absorption and infiltration rates (Balfour and Woods, 2013; Bodí et al., 2014; Woods and Balfour, 2010). Woods and Balfour (2008) found that ash may significantly reduce the runoff and erosion from burned areas in the period shortly after fire, and consequently, the

largest post-fire hydrogeomorphic hazard will occur after the ash layer has been removed by wind and water erosion.

To date, few studies have been carried out in Mediterranean areas that monitor the evolution of post-fire SWR. Tessler et al. (2008) studied monthly SWR measurements in burned and unburned areas during a 7-month period in at Mount Carmel, Israel. Their results showed fire induced water repellency in previously wettable soils, which presented as high levels of SWR persistence at the soil surface during the first six weeks after fire, but decreased with time. Tessler et al. (2012) suggested that lower values of SWR following recurrent fires may be observed than in control sites, and although there are differences between the soil types that may cause different natural SWR, the similar general trends of SWR was the same for a long period after fires. Keizer et al. (2008) monitored temporal and spatial variations of SWR (at 2-3 cm and 7-8 cm depth) over a 10-month period after a wildfire in North-Central Portugal. The SWR pattern that they found agreed reasonably well with the Mediterranean seasonal cycle of low SWR frequency during wet winter conditions and greatest SWR frequency in dry summer characteristic in our study area, despite the below average rainfall received during their study period. Their results revealed that major changes in SWR levels can occur within a period of a few weeks. In pine forest soils from NW Spain, Rodríguez-Alleres et al. (2012) found that fire severity influences the persistence of SWR. They observed that fifteen months after the fire, both burned and unburned zones showed SWR throughout the sampled profile (0-40 cm depth).

The wildfire in our study occurred in a calcareous soil, which is predominant in the Eastern of Spain. Currently there are only some studies focusing on the temporal evolution of SWR in calcareous soils (Granged et al., 2011b; Jordán et al., 2014). Therefore, this work aims to shed light on this issue. The main objectives of this research are: i) to carry out an extensive monitoring of fire-

induced SWR in a burned Mediterranean calcareous soil, comparing it with an unburned area; ii) to determine the effect of ash on SWR dynamics establishing different treatments simulating aeolian ash erosion and an initial rainfall. This last treatment was done on the basis of the hypothesis that if low-intensity rainfall at the beginning of the wet season favours a good water input into the soil profile, this must be relevant in the evolution of soil properties, including post-fire SWR and also could favour the vegetation recovery; iii) to analyze differences between the temporal evolution of SWR beneath the main plant species present, comparing the influence of trees (*Pinus halepensis*) and shrubs (*Quercus coccifera*, *Rosmarinus officinalis*, *Cistus albidus*, *Erica arborea* and *Brachypodium retusum*) in burned and unburned areas, establishing a relation with SMC fluctuations. This study expects to amplify the limited bibliography regarding such matters, and to provide valuable reference data for future research.

MATERIAL AND METHODS

Study site, experimental design, field measurements and samplings

On July 2011, an area of 50 ha was affected by a forest fire in Gorga (N 38° 43'44'', W 0° 22'58''), province of Alicante (SE Spain), and according to historical data of the "Generalitat Valencia" (Government of the Valencian Community), the study site was not affected by previous fires for at least last 50-60 years. According to fire severity classifications (Keeley, 2009; Parsons et al., 2010), fire severity of our study area can be classified as moderate (tree canopy cover killed, but some needles not consumed, all shrubs charred or consumed, fine dead twigs on soil surface consumed, pre-fire litter largely or completely consumed). The study area has a Mediterranean climate type. According to the Alcoy weather station (10 km distance: 38° 41' 48.66" N; 0° 28' 20.75" W), mean monthly rainfall ranges between 11.5 (July) and 71.7 mm (October), with mean annual rainfall of 494.6 mm. Mean monthly temperature varies between 8 °C

(January) and 23.4 °C (July), with mean annual temperature of 15.1 °C. Vegetation type is mainly composed of *Pinus halepensis* forest and an understory stratum formed by Mediterranean shrubs, including *Quercus coccifera*, *Rosmarinus officinalis*, *Cistus albidus*, *Erica arborea* and *Brachypodium retusum*. Soil type is classified as a Lithic Xerorthent (Soil Survey Staff, 2014), developed from limestone with a silt loam texture (49.7% of sand, 40.7% of silt and 9.6% of clay).

Immediately after fire, 12 plots (1 m × 2 m) were installed: 6 plots in the burned area (B) and 6 control plots (C) in unburned adjacent areas, 100 meters distance from fire-affected area, with similar conditions regarding lithology, type of soil, relief, aspect (south-eastern facing slopes) and vegetation cover. In both, burned and unburned areas, 3 of the plots were installed below the canopy of pines (P) and 3 plots below shrub species (S).

In order to monitor the effects of ash during the post-fire, three different treatments were also applied in the burned area below the canopy of pines. Those three treatments were only carried out over pine plots due to the immediate fire effect on SWR beneath pine was much more noticeable than on shrubs. The three treatments established (Table 1) were: i) keeping the ash layer intact (BP); ii) removing the ash layer to simulate the loss of ash by wind or rainfall-induced erosion (BPwa), and iii) keeping the ash layer and inducing infiltration carefully manually with water spilled (10 L m⁻²) to imitate the effects of an infiltration after a precipitation immediately after burning (BPr) with an expected ash incorporation onto first centimeters of soil profile. At each plot, sensors (SM300, Delta-T Devices) were installed for monitoring SMC (5 cm depth), which was recorded every 60 minutes by a data logger. A portable weather station (NOMAD by Casella CEL) was installed in the study area in order to record rainfall and air moisture data every single hour, processed by Online PRO 1.2 and DeltaLINK 2.5.1 software, respectively.

Table 1. Treatments applied in the burned area below the canopy of pines, in order to monitor the effects of ash during the post-fire evolution beneath pine influence.

Code	Treatment
BP	The ash layer was kept intact
BPwa	The ash layer was removed to simulate the loss of ash by wind or rainfall-induced erosion
BPp	With an expected ash incorporation onto first centimeters of soil profile, an induced infiltration was carefully and manually with water spilled (10 L m^{-2}) to imitate the effects of an infiltration after a precipitation immediately after burning

Each plot was divided into an area remaining intact for monthly assessment of SWR under field conditions and monitoring vegetation recovery between July 2011 and July 2013, and a destructive area for periodic soil sampling (0–2.5 cm depth; Fig. 1). In the tested area of each plot, 3 equidistant sampling points were established. Five soil samplings were carried out during a two-year period immediately after burning (July 2011, December 2011, March 2012, July 2012 and July 2013). In each case, soil samples were kept in plastic bags, sealed and quickly transported, within 2 or 3 hours after sampling, to the laboratory for analysis. In all soil samples SMC was gravimetrically measured by weight differences as described Reynolds (1970) and SWR by the WDPT test (method described below).

Ash samples (1 cm depth) were also collected, after carefully removing coarse plant residues and remaining vegetation by hand, 7 days immediately after forest fire from burned sites beneath pine (BP) and shrub (BS) canopy, previous to any storm, in order to measure ash water repellency under laboratory conditions, as explained as follow in next section.

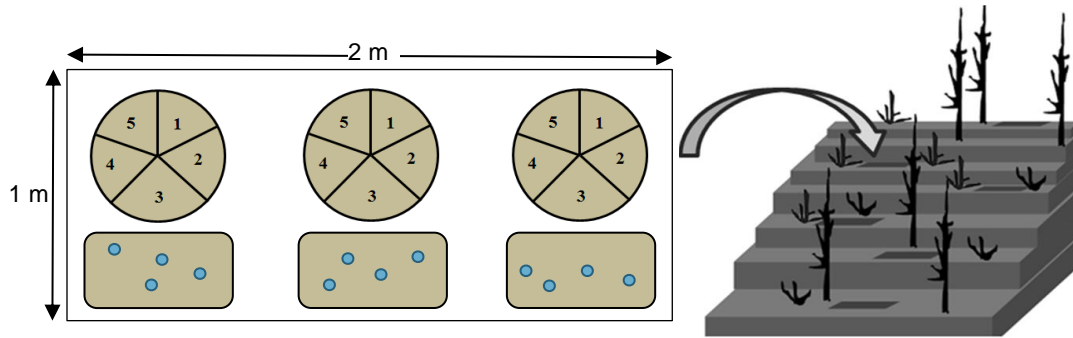


Figure 1. Plot organization diagram only for soil sampling and SWR field measuring in burned and control plots with pine and shrub influence (BP, BS, CP and CS). Each plot has been divided into a 3 equidistance-sampling wedges with similar area approximately between them. On the top, circles represent the soil sampling points (where numbers correspond to each one of the total five soil sampling carried out, respectively over the time). On the bottom, rectangular wedges, with similar area between them, remained intact for field water repellency measurements.

Soil and ash water repellency measurements

Persistence of SWR was assessed by the Water Drop Penetration Time (WDPT) test (Wessel, 1988). The test involved placing three drops of distilled water (~ 0.05 mL) onto the soil surface, after carefully removing ash and litter by hand, in B and C soil plots. In each case, the time (s) required for infiltration was recorded and classified according to Bisdom et al. (1993) (Table 2).

The same method was used to determine SWR in soil and ash samples under laboratory conditions. Soil and ash samples were dried at room temperature (~ 25 °C) during a week and carefully sieved (< 2 mm) and coarse material was discarded. Approximately 10 g of sample material was placed into separate plastic dishes (diameter 50 mm), and exposed to a controlled laboratory atmosphere (20 °C, 50% relative humidity) for 24 hours to eliminate potential effects of any variations in preceding atmospheric humidity on SWR (Doerr et al, 2002).

Table 2. WDPT ranges and classes used in this study (after Bisdom et al., 1993).

Water repellency	WDPT (s)	WDPT class
Wettable	≤ 5	≤ 5
Slight water repellency	6 - 10	10
	11 - 30	30
	31 - 60	60
Strong water repellency	61 - 180	180
	181 - 300	300
	301 - 600	600
Severe water repellency	601 - 900	900
	901 - 3600	3600
Extreme water repellency	> 3600	> 3600

Data analysis

The normal distribution of SWR and SMC data was checked using the Kolmogorov-Smirnov test. As normality of SWR data was rejected, data were transformed to Neperian logarithm (ln), to reduce the range of variation of WDPT data. Relative value of each plot was obtained by dividing the monthly average ln WDPT by the average ln WDPT value immediately after fire. These calculations were carried out to find the relative changes of WDPT, with the aim of examining how SWR varied throughout two years after fire occurred. Relative changes of ln WDPT determined under field conditions were represented in Principal Components Analysis (PCA) score, to analyse how they were grouped based on the effects of fire and vegetation. Mann-Whitney U test was used to check the statistical differences between plots and also between sampling periods for data obtained ($p < 0.05$). Spearman's rank correlations were analyzed to investigate the relation between SMC measured in field conditions with soil moisture sensors (m^3/m^3) and SMC measured in laboratory samples (%) ($p < 0.05$); and between SWR (seconds) and SMC (%) both measured under

laboratory conditions ($p < 0.05$). Statistical analyses were carried out with the IBM® SPSS (© SPSS Inc, 1989) version 22 for Windows software package.

RESULTS

Immediate effects of fire on soil water content and water repellency under field conditions

Comparing burned and control (unburned) plots below the pine canopy, it was observed that fire contributed to increasing the frequency of occurrence of SWR (Fig. 2). Results revealed that 100% of burned samples were water repellent (with WDPT ranging from 30 to 3600 seconds), 44% of them severely water repellent (WDPT between 900 and 3600 seconds in most cases). In contrast, 66% of control samples below the pine canopy were classified as water-repellent, with only 22% of them classified as severely water-repellent (Fig. 2). Regarding the areas below the shrub canopy, the increased observed was less evident, with a proportion of water-repellent cases from 55% (control) to 77% (burned) (Fig.2) but without significant differences comparing mean WDPT values (Table 3).

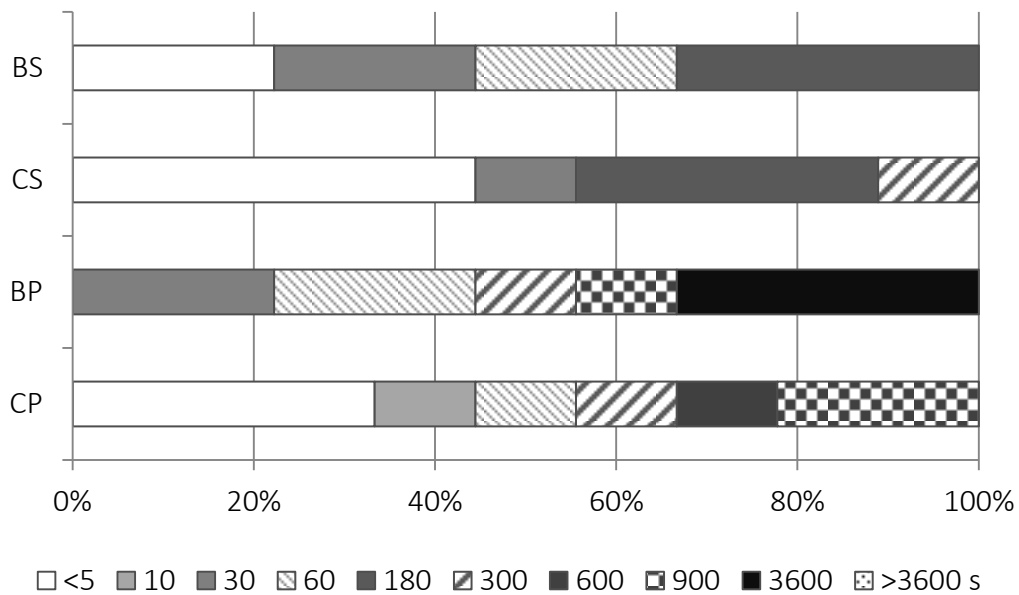


Figure 2. Relative frequency of SWR classes (seconds) measured under field conditions immediately after fire (July 2011); where BP: burned plots beneath *Pinus* influence; BS: burned plots beneath shrubs influence; CP: control plots beneath *Pinus* influence; and CS: control plots beneath shrubs influence.

SMC registered in the period immediately after the fire, on July 2011, was considerably low in both burned ($0.044 \text{ m}^3/\text{m}^3$ and $0.067 \text{ m}^3/\text{m}^3$, for pine and shrub, respectively) and unburned ($0.072 \text{ m}^3/\text{m}^3$ and $0.061 \text{ m}^3/\text{m}^3$, for pine and shrub, respectively) plots with the two vegetation covers (Fig. 3). The lowest SMC registered immediately after the fire was in pine plots affected by fire ($0.044 \text{ m}^3/\text{m}^3$, Fig. 3), where also was registered the highest SWR values in that first soil sampling ($670 \pm 627 \text{ s}$, Table 3).

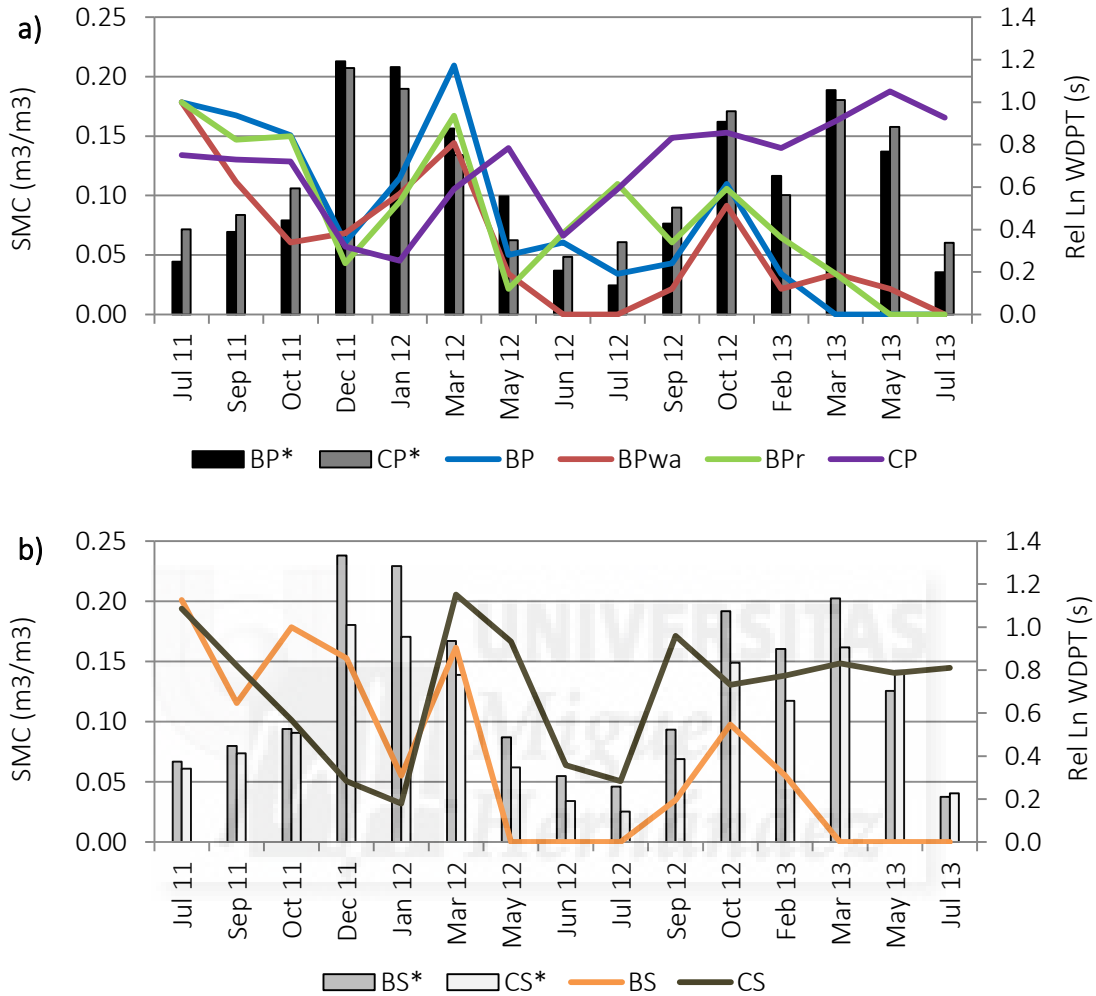


Figure 3. Temporal evolution under field conditions of relative changes of SWR and SMC. Lines represent Rel Ln WDPT, which were obtained dividing every Ln WDPT mean of each month by its Ln WDPT mean value immediately after fire, in seconds. Columns (*) represent SMC (m³/m³). Where: a) BP: burned plots beneath *Pinus* influence where ash were kept; CP: control plots beneath *Pinus* influence; BPwa: burned plots beneath *Pinus* influence with ash removed; BPr: burned plots beneath *Pinus* influence with initial water infiltration; and b) BS: burned plots beneath shrubs influence; and CS: control plots beneath shrubs influence.

Table 3. Monthly WDPT mean values and standard deviations (s) in plots beneath different treatments. BP: burned plots beneath Pinus influence where ash were kept; BPwa: burned plots beneath Pinus influence with ash removed; BPr: burned plots beneath Pinus influence with initial water infiltration; BS: burned plots beneath shrubs; CP: control plots beneath pines; and CS: control plots beneath shrubs.

	Jul 11	Sep 11	Oct 11	Dec 11	Jan 12	Mar 12	May 12	Jun 12	Jul 12	Sep 12	Oct 12	Feb 13	Mar 13	May 13	Jul 13
BP	670±627	217±85	127±129	7±2	40±59	839±745	5±3	7±10	3±2	4±2	34±26	3±1	1±0	1±1	1±0
BPwa	670±627	36±48	7±7	9±5	26±29	103±151	3±3	1±0	1±0	2±1	19±6	2±1	3±2	2±1	1±0
BPr	670±627	113±108	124±83	4±1	21±34	215±167	2±0	9±10	34±45	7±4	30±9	8±10	3±2	1±0	1±0
BS	55±56	10±10	35±35	21±22	3±2	25±26	1±0	1±0	1±0	2±1	7±1	3±3	1±0	1±0	1±0
CP	228±196	108±112	94±126	4±1	3±1	13±5	30±41	5±3	13±11	37±44	41±46	30±32	52±33	359±574	56±46

Temporal changes of soil water repellency in pine and shrub plots under field conditions

In a first analysis of results, pooling all relative SWR data from all plots and soil samplings PCA shows the distribution of scores on the first two axes (Fig. 4). PC1, which explained 47% of variability, clearly separated all samples in two different groups (burned and control). The temporal evolution of SWR is different in burned plots regarding to control ones, regardless of vegetation influence, highlighting temporal changes of SWR due to fire effects.

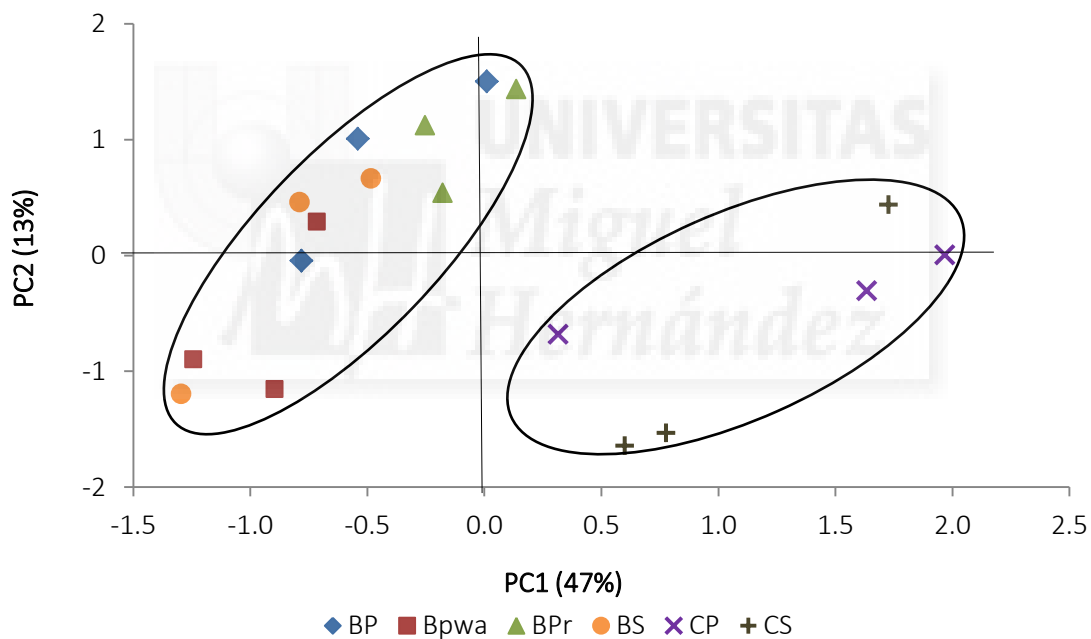


Figure 4. Scores of the two principal components (PCs) analyses of relative changes of \ln WDPT (Rel \ln WDPT, which were obtained dividing every \ln WDPT mean of each month by its \ln WDPT mean value immediately after fire); where: BP: burned plots beneath Pinus influence where ash were kept; BPwa: burned plots beneath Pinus influence with ash removed; BPr: burned plots beneath Pinus influence with initial water infiltration; BS: burned plots beneath shrubs influence; CP: control plots beneath Pinus influence; and CS: control plots beneath shrubs influence.

During a two-year monitoring we found a large spatial and temporal SWR variability on studied field-plots, as standard deviation of data showed, in both burned and control plots (Table 3). Results revealed that the temporal evolution of SWR in control plots was similar between different types of vegetation, with variations in mean values but there were not statistically significant differences between the sampling periods ($p > 0.05$). However, higher SWR mean values were found below pines than below shrubs along the overall study period (Table 3; Fig. 3). SMC seasonal fluctuations observed during the study period in control areas follow a similar pattern for both vegetation types studied, although SWR observed in CP plots was generally higher than in CS plots (Table 3). However, SWR changes could not always be associated with SMC variations. SMC varied between 0.049 and 0.207 m^3/m^3 below CP and between 0.025 and 0.18 m^3/m^3 below CS (Fig. 3a and b, respectively).

In burned plots, after the first SWR increase immediately following the fire, we identified a fast SWR decrease pattern in all field-plots monitored, especially under pine and especially after the first rainy period (Fig. 3 and Table 3), being this decrease with significant differences regarding first soil sampling in samplings of October 2011, December 2011 and January 2012 ($p < 0.05$) for pine plots and only statistically significant different in sampling of January 2012 for shrub plots. After that first wet post-fire period, SWR mean values increased in all plots studied, the highest values registered were in March 2012, where severe SWR was observed in BP plots (Table 3) and registering similar SWR values (not statistically different, $p > 0.05$) to those immediately after fire. During the rest of the experiment, SWR in BP plots remained relatively low, with WDPT values progressively going from slightly water repellent (May – October 2012) to wettable (October 2012 – July 2013).

Regarding SMC, it was observed that it was higher in CP than in BP plots immediately after burning ($p < 0.05$). This trend was also observed in dry periods

below pine canopy and the opposite occurred during wet periods (Fig. 3a). In contrast, SMC in shrubs plots was slightly lower in CS than in BS during the whole study, such differences increasing in wet periods (Fig. 3b).

One year and a half after the fire, all soil samples from burned areas were rendered wettable under field conditions.

The effect of presence, absence or initial incorporation of ash on soil water repellency and its changes over time under field conditions

After fire, SWR decreased progressively in burned plots below the canopy of pines with different treatments (BP, BPwa and BPr) (Table 3), being this SWR decline more important in plots where ash was removed (BPwa) with significant lower WDPT values in second soil sampling (October 2011) than in the other two treatments (Fig. 3a). This decreasing trend of SWR was similar between October 2012 and the end of the experiment in BP, BPwa and BPr plots, in contrast to the more irregular behavior in control plots below pines and shrubs (CP and CS) (Fig. 3a).

Water repellency measured under laboratory conditions in ash and soil samples

Laboratory results showed that 50% of ash samples below pines and 66% of ash samples below shrubs, were slightly water repellent (WDPT classes 10 and 30 s) (Fig. 5).

Only soil samples collected from BP plots showed SWR under laboratory conditions, where the SWR data were: 143 ± 79 s, 3 ± 2 s, 44 ± 70 s, 184 ± 312 s and 9 ± 8 s, for soil sampling carried out on July 2011, December 2011, March 2012, July 2012 and July 2013, respectively. These data always showed lower values of persistence than those measured in the field. Soil samples from the rest of plots

remained wettable under laboratory conditions. In BP plots, significant correlations were found between SMC values measured under laboratory and field conditions ($r = 0.732$, $p < 0.01$; Fig. 6a), and between SMC and SWR (ln WDPT) measured under laboratory conditions ($r = -0.573$, $p < 0.05$; Fig. 6b).

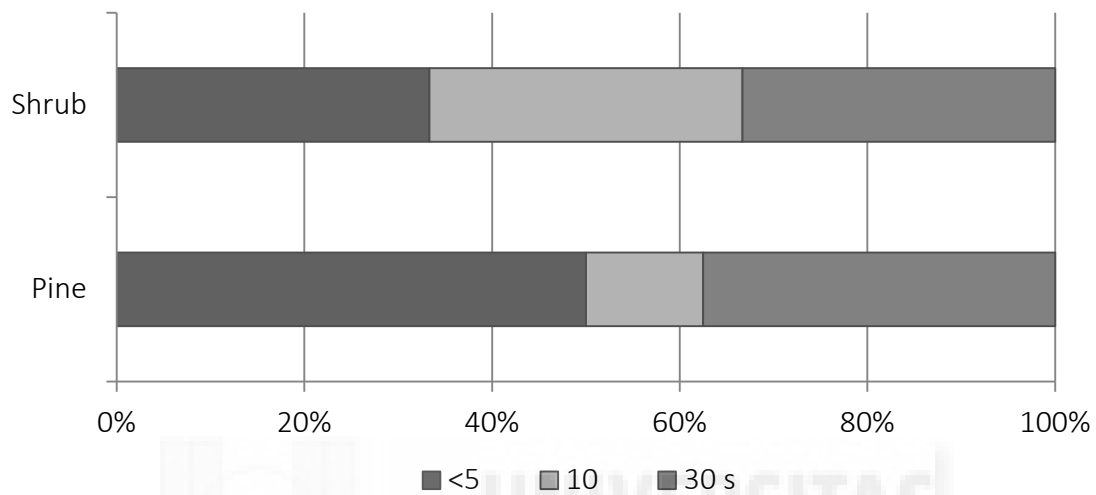


Figure 5. Relative frequency of ash water repellency in WDPT classes (seconds) measured under laboratory conditions; where water repellency mean values and standard deviations (seconds) were $(7 \pm 5$ s) for those collected beneath *Pinus* influence and $(9 \pm 4$ s) for those collected beneath shrub influence.

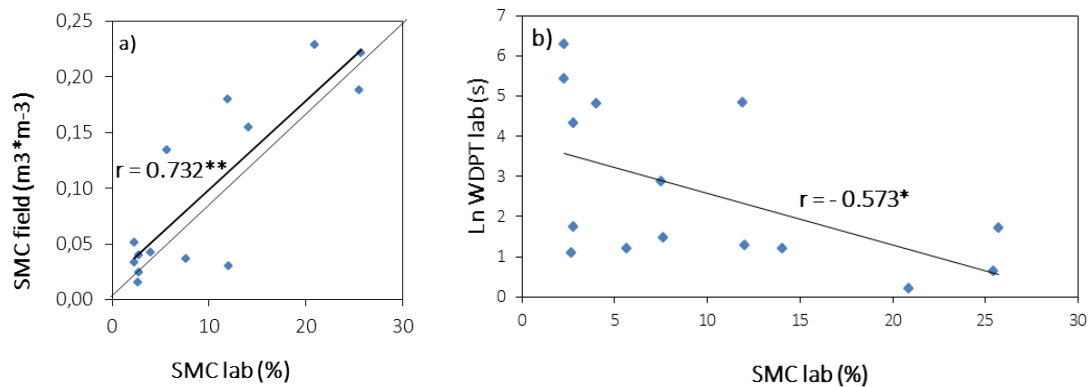


Figure 6. Relations between a) SMC measured under field with soil moisture sensors ($m^3 \cdot m^{-3}$) and SMC in laboratory samples (%), and b) SWR (seconds) and SMC (%) both measured under laboratory conditions. All data for burned plots with *Pinus* influence (BP). (r = Spearman's coefficient, where **, * mean significant at $P \leq 0.01$ and 0.05 respectively).

DISCUSSION

Immediate effects of fire on soil water repellency

The majority of studies have established that forest fire modifies soil wettability (DeBano and Krammes, 1966; Dlapa et al., 2008; Doerr et al., 2004). An increase of SWR as an immediate effect of a forest fire has been previously reported by some earlier studies (Doerr et al., 2004; Larsen et al., 2009; Tessler et al., 2008), and our results, obtained from plots below the canopy of pines (both under field – at the soil surface – and laboratory conditions – 0-2.5 cm depth) are in agreement with all of them. In contrast, fire did not affect SWR in soil plots beneath shrubs. This is also in agreement with other studies in Mediterranean soils where soils below pines showed higher SWR values than below shrubs. Arcenegui et al. (2008) observed that SWR persistence and frequency generally increased in calcareous Mediterranean soils as a consequence of forest fires, and especially in pine plots sites. In a previous study, Arcenegui et al. (2007) noticed in a laboratory experiment that type and quantity of burned vegetation were decisive factors conditioning fire-induced SWR. *Pinus* species contain compounds capable of inducing severe SWR (Doerr et al., 1998), as shrubs do, although its persistence is usually shorter (Zavala, 2014). Such differences are probably due to the resins, waxes and aromatic oils of these species. In a review, Doerr et al. (2000) reported the occurrence of SWR related to particular plant species, *Pinus halepensis* being one of the species inducing more severe SWR.

But in literature, some contrasted results are also found regarding the immediate effect of fire; while some studies have observed a decrease of SWR (Granged et al., 2011b) or even its destruction (Gimeno-García et al., 2011), others have observed an increase (Arcenegui et al., 2008).

Temporal changes of SWR along the 2 monitoring years beneath pine and shrub plots

In accordance to Tessler et al. (2008), we also observed in our results an immediate SWR increase due to the fire, followed by a clear SWR decrease with time (6-14 weeks). Others studies observed a SWR decreasing effect, but differing in time after the fire: very rapidly (Larsen et al., 2009), within a few weeks (Hubbert and Oriol, 2005), few months, or even a couple of years (Doerr et al., 2009). As we could observe (Table 3), decreasing SWR pattern was more noticeable on burned plots with pine (BP) than shrubs plots (BS). Along the whole monitoring period, SWR beneath pine plots supported higher persistence values than beneath shrubs plots, in accordance with Cerdà and Doerr (2005) and Varela et al. (2005). According to Larsen et al. (2009), shortly following the fire, SWR was significantly stronger in burned (BP and BS) than unburned (CP and CS) plots (see September 2011 in Fig. 3a, b). The important spatial and temporal SWR variability discovered in our SWR data may be caused by different factors, such as soil texture spatial variations, mineralogy, organic matter content, type of vegetation and related litter cover, etc. Those factors may be responsible for the patchy patterns of SWR persistence and occurrence for measurements carried out under field conditions (Lozano et al. 2013; Martínez-Zavala and Jordán-López, 2009; Mataix-Solera et al., 2008). Having patchy soil water repellent distribution in a fire-affected area could contribute to an heterogeneous water redistribution on the soil superficial layer, and affect to the vegetation recovery. Regarding temporal changes in SWR, one of the factors affecting directly and indirectly is SMC (Bodí et al., 2013), that varies seasonally. The pattern that we have observed during the study period and related to the seasonal fluctuations was an increasing of SWR with the decreasing of soil moisture seasonal fluctuations and vice versa in some periods but not always (see Table 3 and Fig. 3), thus no correlation between these two parameters were found for field data.

Bodí et al. (2013) reported a recognizable pattern between SWR and SMC variable with the period of the year. In our case this could be observed only in some periods of our study, and for the samples of BP measured under laboratory conditions ($r = -0.573$; $p < 0.05$, Fig. 6b).

Several months following the fire, we observed that SWR progressively decreased in the area affected by the forest fire. But also, SWR fluctuations were detected mainly conditioned by seasonal moisture variations and the persistent hydrophobic compounds of charred vegetation that remained over soil surface. In March 2012 the most significant SWR recovery occurred in burned plots. This fact coincided with a SMC diminution due to the reduction of seasonal rainfalls (Fig. 3), the highest rise being in pine plots (Table 3). With regard to our results, we observed that vegetation type has an effect on SWR frequency of occurrence and its persistence (Cerdà and Doerr, 2007; Zavala et al., 2009b) but this has not an effect on SWR evolution.

Our laboratory results also revealed that SWR reappeared even more strongly just one year after fire, in July 2012, but only in burned samples beneath *Pinus halepensis* plots. There could be several explanations for that, one could be that the ash hydrophobic compounds, coming from charred vegetation, might remain mixed with mineral particles into the first centimeters of the soil profile (0 to 2.5 cm depth) following fire combined with drier conditions in pine burned plots (Doerr et al., 2000).

During the two-year monitoring, from July 2011 to July 2013, data revealed a seasonal fluctuation on control (unburned) areas, where pine plots induced usually higher SWR values than shrubs species. Lozano et al. (2013), Mataix-Solera et al. (2007) or Moral et al. (2002), demonstrated a relation between plant species (*Pinus halepensis*, *Quercus rotundifolia*, *Cistus albidus*, *Rosmarinus officinalis* and *Juniperus oxycedrus*) and their influence on naturally occurring SWR.

Following our field and laboratory results we have established that two years after forest fire occurred, areas affected by fire became wettable (Table 3). It is possibly due to the absence of vegetation in burned area, thus not intercepting rainwater and allowing the erosion of water-repellent particles and washing hydrophobic compounds, and not contributing to new inputs of hydrophobic substances. Some other causes, which may contribute to a decrease of SWR with time might be the vegetation recovery and associated microbiological and invertebrate activity (Pereira et al., 2014). The biological activity associated with vegetation recovery has implications on the SWR decrease (Doerr et al., 2009).

Laboratory measurements showed SWR only in samples taken in BP plots. The differences in SWR that we have observed between field and laboratory results could be mainly explained, by different reasons, as Mataix-Solera et al. (2013) described in a previous study. The authors observed that it was due to the fact that field measurements of SWR were made over the soil surface (undisturbed) and laboratory measurements were done in disturbed samples, with mixed soil from depths sampled, in our case from 0 to 2.5 cm. Graber et al. (2006) also found differences between disturbed and undisturbed soil samples, proposing surface roughness, pore size distribution, pore connectivity and soil bulk density as the main factors involved in the differences of SWR. Likewise, it is commonly accepted that SWR varies with depth, and also sample disturbance and sieving may contribute to create SWR differences, that would be reflected in laboratory observations.

Ash effect on SWR evolution

Our data revealed that ash collected 7 days after forest fire, was slightly water repellent, in agreement with some other previous studies. Bodí et al. (2011) concluded that wildfire and laboratory ash may exhibit water repellency being influenced by the degree of combustion, vegetation type and subsequent rainfall events. Gabet and Sternberg (2008) also observed strong water-repellent ash from burned vegetation, and observed that ash can reduce water infiltration capacity, having implications for runoff behavior after ash incorporation into the soil (Bodí et al., 2011). This is probably due to the ash creating a thin hydrophobic layer orientated parallel to the soil surface (Woods and Balfour, 2007). In contrast, some other studies have considered ash as highly wettable (Kinner and Moody, 2008) and that ash layer can store rainfall during the pre-ponding stage (Cerdà and Doerr, 2008; Woods and Balfour, 2008). Other authors have also reported that soil water retention capacity increased with addition of ash (Chang et al., 1977; Stoof et al., 2010; Wood and Balfour, 2008). Concerning our field study, we have observed that plots where ash was removed (BPwa) showed shorter SWR persistence, promoting infiltration, than BP and BPr treatments during the whole study period. On the contrary, Woods and Balfour (2008) suggested that the infiltration in plots with ash increased threefold compared to plots without ash. According to the authors, the most likely explanation for this was that the surface sealing (caused by compaction and reduction of the pore size due to the drop beating action during rainfall) reduced the soil infiltration in the no-ash plots by 90% relative to unsealed soils. Different trends of SWR between each treatment were much more noticeable in our study during the first year monitored since the fire (Table 3). BP and BPr plots, with higher hydrophobic conditions in time than BPwa, had different behavior between them during the first year monitored than in the second year. Ash presence facilitated

hydrophobic compounds being incorporated into the soil immediately (BPr) or even more progressively (BP) after the fire occurred.

The most important sources of uncertainty in this field-work were mainly influenced by the high spatial variability of the soil properties and also by the seasonal fluctuations of the study area. Small differences in some soil properties as for example mineralogical composition and also texture, within the same fire-affected area can be the key factor for SWR behaviour (Mataix-Solera et al., 2014) and also soil recovery following the fire. Besides, the influence of small weather seasonal fluctuations plays an important role highly influencing on soil properties behaviour under field conditions, as it has been proved in this study (see Fig. 3). SWR increases detected due to the incorporation of hydrophobic ash compounds onto the first centimeters of soil following a wildfire, may contribute, in a short-term period, to higher runoff and erosion risks over the time (Woods and Balfour, 2008). Other important consequences might be the loss of nutrients due to the washing of soluble substances by preferential flow pathways (Cerdà and Doerr, 2007), thereby affecting the spatial soil distribution of water content and therefore the vegetation recovery (Wallis and Horne, 1992; Hendrickx et al., 1993; Ritsema and Dekker, 1995) and influencing the soil erosion risk (Dekker and Ritsema, 1994).

CONCLUSIONS

With regard to our observations we concluded that immediately after the fire a notable increase in SWR was only observed in *Pinus halepensis* plots. We also observed that the evolution of SWR throughout the complete study was significantly different in plots affected by fire than in control plots. We could also determine that ash presence, absence and its incorporation into the soil played an important role in SWR evolution following the forest fire. Roughly one year and a half after the fire, SWR disappeared in plots affected by fire.

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CAPÍTULO 2

EFFECTS OF RELATIVE HUMIDITY ON THE WATER REPELLENCY OF FIRE-AFFECTED SOILS

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ABSTRACT

Soil water repellency (SWR) is a common feature in unburned and particularly in fire-affected soils, and can enhance several environmental risks. It can be affected by many factors such as vegetation cover, moisture content and, in fire-affected areas, the degree of heating during burning. In addition, experiments using unburned soils have shown that atmospheric relative humidity can affect their water repellency. The purpose of this laboratory study was to examine how ambient relative humidity (RH) affects SWR of burned soils, and to explore its implications for fire-affected regions. Soil samples were taken from under fire-prone, but long unburned *Pinus halepensis* and a shrub site in Gorga, Alicante (SE Spain). In order to simulate different fire severities, samples were heated for 20 minutes at different temperatures (50, 100, 150, 200, 250, 300 and 350 °C). Samples were then equilibrated at different RHs (30, 50, 70 and 95%) in a sealed climate chamber at a constant temperature of 20°C. The water drop penetration time (WDPT) test, molarity of ethanol droplet (MED) test, and advancing contact angle (CA) measurements were performed inside the sealed climate chamber to assess SWR for each sample and treatment. Overall, increasing heat treatments enhanced SWR, which in turn was enhanced further following exposure to high RHs. The WDPT test showed that soils under pine were water repellent at the lowest heating temperature and became strongly water repellent at the higher heating temperatures and near saturation (95% RH). Shrubland soils were mostly wettable at the onset and remained so at every RH level studied except being slightly SWR at 95% RH. A similar trend was found after MED and CA measurements. The results demonstrate that high RH contributes to enhanced SWR also in burned soils, where high temperatures had already led to a substantial enhancement of SWR. These findings suggest that SWR levels determined for fire affected areas ambient under field or laboratory conditions may underestimate the apparent SWR levels present at the high RH

levels that often precede major storm events. This in turn has implications for predicting post-fire runoff and erosion events.

Key words: Hydrophobicity; relative humidity; contact angle; pre-heated temperatures; forest soils; mediterranean calcareous soils;

INTRODUCTION

Soil water repellency (SWR) may be defined as the condition of a soil which does not wet spontaneously when water comes in contact with the soil surface (Leelamanie et al., 2008a). This behaviour modifies infiltration and evaporation rates, erodibility and other hydrological processes of soils (Feng et al., 2001; Jordán et al., 2009; Wallis et al., 1991; Wallis and Horne, 1992). SWR is a common property of soils under many vegetation types and is often induced in previously wettable soils or enhanced by fire (DeBano, 2000; Doerr et al., 2000; Granged et al., 2011a; Jordán et al., 2013; Jordán et al., 2014). It has been shown that environmental conditions such as ambient temperature (King, 1981; Goebel et al., 2011), drying temperature (Franco et al., 1995; Dekker et al., 1998), water content (Berglund and Persson, 1996; Bodí et al., 2013; DeJonge et al., 1999; Dekker and Ritsema, 2000) and the wetting and drying history of samples (Doerr and Thomas, 2000) can strongly affect SWR. Atmospheric relative humidity (RH) is another important factor conditioning SWR. Jex et al. (1985) and Doerr et al. (2002) reported that SWR increased when soil was exposed to > 90% RH (near saturation) over a short period (< 1 day), but gradually decreased when exposed to an ambient laboratory atmosphere of ~40% RH. Leelamanie et al. (2008b) reported a positive correlation between RH and SWR at RHs between 33 and 94%. Another main factor that recently has been considered responsible of the severity of SWR is the soil surface structure (Ahn, 2014). SWR appears on low-energy surfaces where the attraction between the molecules of the solid and liquid interface is weak (Heslot et al., 1990; Roy and McHill, 2002). Under natural

conditions, high-energy soil mineral surfaces are often covered by films of low-energy organic compounds (Doerr et al., 2000; Goebel et al., 2004) forming water repellent surfaces (Jiménez-Morillo et al., 2014; Leelamanie et al., 2008a) and this can be amplified by surface structure (Wenzel, 1936; Cassie and Baxter, 1944). It has been reported that the overall susceptibility to developing soil water repellency is higher in sandy and coarser textures (González-Peñaloza et al., 2013; McGuie and Posner, 1980; Roberts and Carbon, 1971) and lower in those containing clay (Crockford et al., 1991; Zavala et al., 2014). A soil surface may minimize the contact area with a water drop by its porous structure. In soils prone to develop water repellency, the upper soil layers tend to exhibit the greatest severity. This effect is usually enhanced as soil dries and water is lost from the pores, enlarging the air-solid interface, which critically increases the net contact angle (Ahn, 2014). The contact angle (CA) between the solid and water can be measured at the three-phase interface (gas-liquid-solid). According to Goebel et al. (2011) SWR occurs if $CA > 0^\circ$; soils show reduced wettability with CA varying between 0 and 90° (i.e. infiltration of water into the soil matrix decreases); and values of $CA > 90^\circ$ indicate extreme SWR. A zero CA occurs when the surface tension of solid and liquid are equal to each other (Bachmann and van der Ploeg, 2002). Although, numerous studies have used CA to determine SWR (Carrillo et al., 1999; Bachmann et al., 2000a, b; Leelamanie et al., 2008b; Doerr et al., 2009), and some studies exist in which the effect of RH on SWR has been examined (Jex et al., 1985; Doerr et al., 2002; Leelamanie et al., 2008b). All previous studies have been carried out on unburned soils.

Fire is an important ecological agent, which has increasingly affected Mediterranean ecosystems in the last decades, leading to changes in chemical, physical and microbiological soil properties (Neary et al., 1999; Certini, 2005). Fire may induce or increase SWR in previously wettable or water-repellent soils (Doerr et al., 2000; Mataix-Solera and Doerr, 2004; Zavala et al., 2009a), but can also destroy it after intense combustion of organic matter (Arcenegui et al.,

2008; Granged et al., 2011b; Jordán et al., 2010; Robichaud and Hungerford, 2000). The specific effect depends mostly on the duration of heating and temperatures reached (DeBano, et al., 1976; Doerr et al., 2004; Gordillo-Rivero et al., 2014), but also oxygen availability (Bryant et al., 2005) and soil water content (Robichaud and Hungerford, 2000; Zavala et al., 2010).

The influence of increasing temperatures and RH on SWR is of substantial importance in affecting ecosystem processes, which regulate the soil system during post-fire recovery. Given the fact that fire-affected soils often exhibit particularly high levels of SWR, the removal of the protective vegetation cover during fire can make such soils particularly susceptible to accelerated hydrological and geomorphological responses (Doerr et al., 2009). An important research gap thus exists in elucidating the effects of RH on SWR of soils that have been exposed to heating during vegetation fires.

The main aim of this study was therefore to explore the effect of different ambient RHs on SWR variations that might prevail under very dry surface conditions following a wildfire. We focused here on a Mediterranean calcareous soil under *Pinus halepensis* and mixed shrub vegetation, which is a common soil-vegetation combination subjected to fire in Eastern Spain (Mataix-Solera et al., 2002; Arcenegui et al., 2008; Mataix-Solera et al., 2013; Jiménez-Pinilla et al., 2015).

MATERIAL AND METHODS

Sampling site, soil sampling and experimental design

The sampling site is located in a formerly cultivated area in Gorga (N 38° 43'44'', W 0° 22'58''; 545 masl), province of Alicante (SE Spain), with a Mediterranean climate type and approximate annual average rainfall of 500 mm. Vegetation type is mainly composed of *P. halepensis* forest and an understory

stratum formed by Mediterranean shrubs, including *Quercus coccifera*, *Rosmarinus officinalis*, *Cistus albidus* and *Erica arborea*. The soil is classified as a Lithic Xerorthent (Soil Survey Staff, 2014), developed over limestone with a silt loam texture (49.7% sand, 40.7% silt and 9.6% clay). Surface soil samples (0 - 2.5 cm depth) were collected beneath either well-demarcated pine or shrub areas after carefully removing any superficial litter by hand. Samples were stored in plastic bags, transported to the laboratory, air dried at room temperature (~25 °C) for one week and then carefully sieved through a < 2-mm mesh.

Soil samples were homogenized before the heating procedure. Then triplicate soil samples (~30 g) were heated at selected temperatures under controlled laboratory conditions (50, 100, 150, 200, 250, 300 and 350 °C), during 20 minutes in ceramic crucibles using a muffle furnace (Nabertherm, P320, Bremen, Germany). This range of temperatures was selected in order to simulate different potential heating scenarios of wildfires and also in agreement with previous studies which have shown notable heat-induced increases in SWR (Neary et al., 1999; Bachmann et al., 2003; Doerr et al., 2005a; Mataix-Solera et al., 2011). For each case, the furnace was pre-heated to the desired temperature and each sample was heated separately. The experiment includes also unheated control samples.

Exposure to selected relative humidities and associated water repellency measurements using WDPT and MED tests

For each experiment, each heated soil sample was divided into 3 subsamples (10 g, approximately), which were then put in petri dishes (5-mm diameter and 7-mm depth), and placed inside a climate chamber (SANYO Gallenkamp, model PLC CF4; range: 30-90% RH and -40 to 180 °C temperature) and subsequently exposed for equilibrium under a different prescribed atmospheric conditions of 30, 50, 70 and 95% RH at 20 °C. Each sample type, in

triplicate, was kept for 48 hours inside the chamber prior to the water repellency assessments, to ensure the entire sample was fully adjusted to the selected humidity. Soil samples remained within the sealed climate chamber throughout the experiments, with manipulations and measurements conducted by using gloves attached to sealed portholes in the chamber window. This ensured that samples remained under constant environmental conditions and without any other environmental variables affecting them.

Persistence of SWR was assessed using the water drop penetration time (WDPT) test, which measures how long SWR persists on a porous surface. Given that SWR usually decays with prolonged water contact, it relates to the hydrological implications of reduced wettability as the amount of surface runoff is affected by the time required for the infiltration of raindrops (Wessel, 1988; Doerr, 1998). It involved placing three drops of distilled water ($\sim 0.02 \pm 0.05$ mL) onto the soil sample surface. In each case, the time (in seconds) required for a complete droplet infiltration was recorded and a SWR persistence class assigned according to Bisdom et al. (1993) (Table 1).

Table 1. WDPT test classes and class increments used in this study. (After Bisdom et al., 1993).

Water repellency	WDPT (s)	ln WDPT
Wettable	≤ 5	≤ 1.6
	6-10	1.8-2.3
Slight	11-30	2.4-3.4
	31-60	3.4-4.1
Strong	61-180	4.1-5.2
	181-300	5.2-5.7
	201-600	5.7-6.4
Severe	601-900	6.4-6.8
	901-3600	6.8-8.2
Extreme	> 3600	> 8.2

Severity of SWR was also assessed inside the chamber using the molarity of an ethanol droplet (MED) test (expressed as % ethanol; Doerr et al., 1998) (Table 2). This test is an indirect measure of the surface tension of the soil surface and indicates how strongly a water drop is repelled by a soil at the time of application (King, 1981; Doerr, 1998). It involved placing 3 droplets ($\sim 0.02 \pm 0.05$ mL) using an applicator of water-ethanol solution (0, 1, 3, 5, 8.5, 13, 18, 24, 36 % ethanol) (Table 2) onto the soil samples surfaces. The number of droplets that penetrate the soil within 5 seconds (Crockford et al., 1991) was recorded for each ethanol solution and the solution that allowed more than one drop to penetrate was then taken to assign a SWR severity class (Doerr, 1998) (Table 2).

Table 2. MED test classes and class increments used in this study. (Modified from Doerr, 1998).

Ethanol concentration (%)	Water repellency class	Description
0	1	Very wettable
1	2	Very wettable
3	3	Wettable
5	4	Slightly water repellent
8.5	5	Moderately water repellent
13	6	Strongly water repellent
18	7	Severely water repellent
24	8	Very severely water repellent
36	9	Extremely water repellent

Additional water repellency assessments using advancing contact angle measurements

The advancing contact angle (CA) of a water droplet on a soil can also be used to determine the severity of SWR (Letey, 2000; Leelamanie, 2008a). In surface science, a CA of 90° is usually taken as demarcating water repellent and wettable conditions on flat media (Letey, 2000). For porous granular media such

as soils, it has been suggested that reduced wettability is present for $0^\circ < CA < 90^\circ$; and values of $CA > 90^\circ$ indicate extreme SWR (Goebel et al., 2011; Fig. 1). More specifically, Shirtcliffe et al. (2006) found that the critical contact angle for penetration was $52\text{-}61^\circ$ using soil models and test liquids (pentane and hexane), but years before Bán et al. (1987) had determined CA even lower ($49.5\text{-}57.7^\circ$) using ethanol and sulphur pellets, polyamide and polytetrafluoroethylene. CA measurements were included in this study as third measure of SWR (i) to provide wider comparability of the SWR data obtained here and (ii) as CA measurements have not been included in any previous study in which the effect of RH on SWR had been examined.

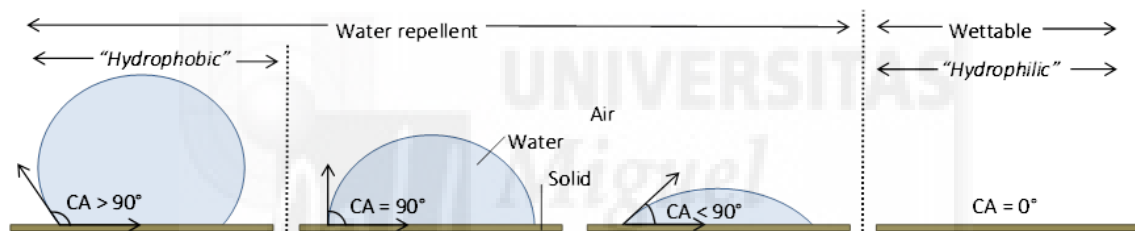


Figure 1. Schematic diagrams showing the solid-water contact angle (CA) as a measure of soil water repellency (SWR). The CA is determined by interactions of the three-phases: solid, liquid, air. A value of $CA = 0^\circ$ indicates complete wettability; and values of $CA > 90^\circ$ indicates increasing values of soil water repellency. (Modified from Goebel et al., 2011).

To measure the CA of a sample, a monolayer of soil particles was immobilized on a microscope glass slide ($1.5\text{ cm} \times 3\text{ cm}$) using double-sided adhesive tape to accomplish a plain homogeneous surface (Bachmann et al., 2000b). Samples were then placed on a tray inside the sealed climate chamber and exposed to the selected RH's as in the previous experiments, except that samples were only exposed for 24 hours given that only a monolayer of soil was used.

We also included two different hydrophobic control 'model soil' materials in this experiment: spherical glass beads to represent smooth-spherical particles (obtained from Whitehouse Scientific, UK); and natural quartz sand (collected from fluvial deposits, South Wales, UK) to represent textured-angular particles typical of soils. Both materials were used in two different size ranges: 710-850 μm and 1120-1180 μm and were chemically hydrophobized using chlorotrimethylsilane as described in Ahn et al. (2013), resulting in static (temporally stable) water repellency. They were then packed as closely as possible and immobilized on the glass slides as described above.

It is now well established that hydrophobicity can be enhanced by the micro-topography of a surface when compared to flat surfaces (McHale et al., 2005). For particle arrays as presented by a soil surface, the texture of the particle surface itself seems to have a significantly greater influence in the amplification of the CA (i.e. and hence SWR) than the coarser-scale particle-based structure or particle shape (Bachmann et al., 2006; Ahn, 2014). Hence these 'model soil' materials, varying in surface texture (glass beads: spheres with no particle surface texture and sand: textured-angular particles), were included to explore the fundamental physical impact of RH and surface texture on SWR behaviour for a static (i.e. chemically more stable) hydrophobic coating that is expected not to be altered by microbial activities.

For CA assessment, drops of distilled water were placed onto the surfaces of soils and chemically treated materials using a 1-mL syringe with a blunt tip needle (19 gauge Luer-Lock blunt ended needles, Sylmaste, UK). The advancing contact angles of sessile drops were recorded by a video camera (30 fps) while the water drop was being gradually enlarged ($\sim 10\text{-}100 \mu\text{L}$). The left and right hand side contact angles of each advancing moment were determined using the software *ImageJ* (Version 1.48, National Institutes of Health, USA) and averaged, and then 3-5 advancing CAs were averaged from each sample in triplicate. All

samples remained in the sealed climate chamber throughout the experiments, as described above.

Statistical analysis

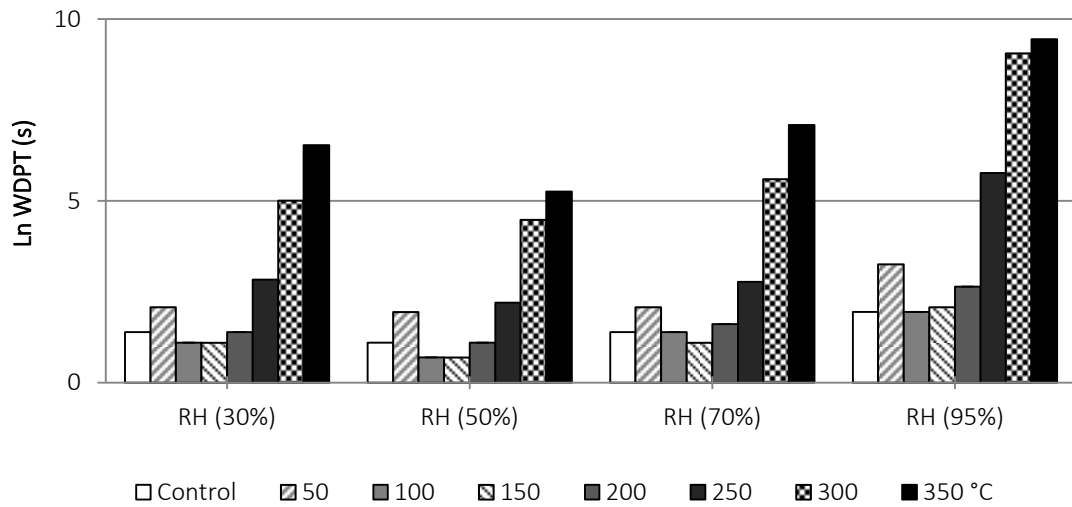
The normal distribution of SWR data was checked using the Kolmogorov-Smirnov test. As normality of SWR data was rejected ($p < 0.05$), WDPT data were transformed (Ln) to allow a better data display given their large variability. Mann-Whitney U test was used to check the statistical differences between SWR data at each temperature treatment regarding to unheated (control) samples for every RH studied ($p < 0.05$). Statistical analyses were performed by IBM® SPSS (© SPSS Inc., 1989) version 22 for Windows software package.

RESULTS

Heating effects on soil water repellency at a standard humidity (50% RH)

Heating has a similar effect for both persistence (WDPT test) and severity (MED and CA tests) of water repellency for samples at a standard laboratory RH of 50%. For the WDPT test, an apparent slight increase in SWR for pine soils was observed at 50 °C compared to the control samples (unheated), and also an apparent decrease between 100 and 200 °C, although in both cases, no significant differences were observed ($p > 0.05$) (Fig. 2a). For the highest heating temperatures (300-350 °C), a substantial increase in SWR was observed, with significant differences ($p < 0.05$), with the peak occurring at 350 °C (Fig. 2a). SWR was not found at 50% RH in shrub soils for any heating treatment (Fig. 2b).

a) Pine



b) Shrubs

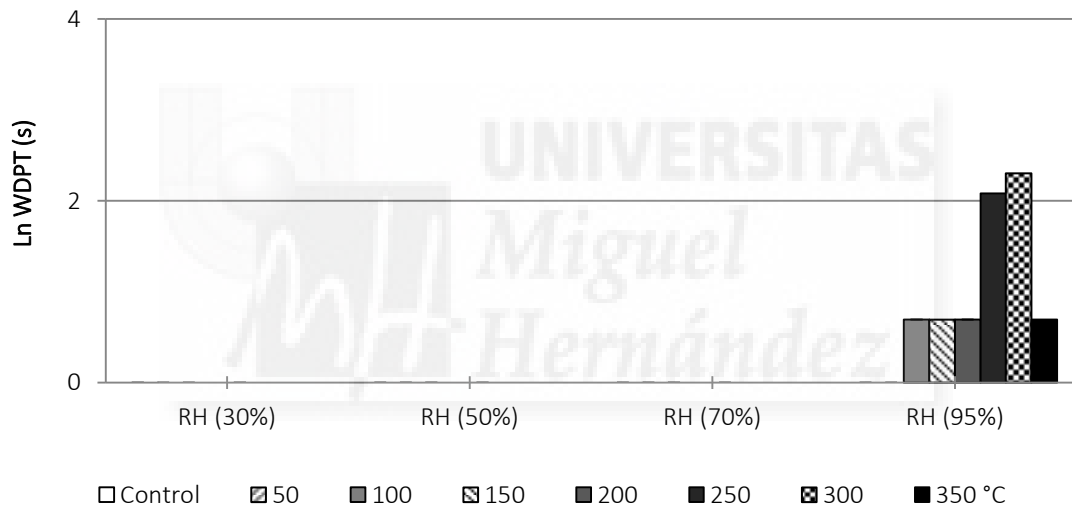
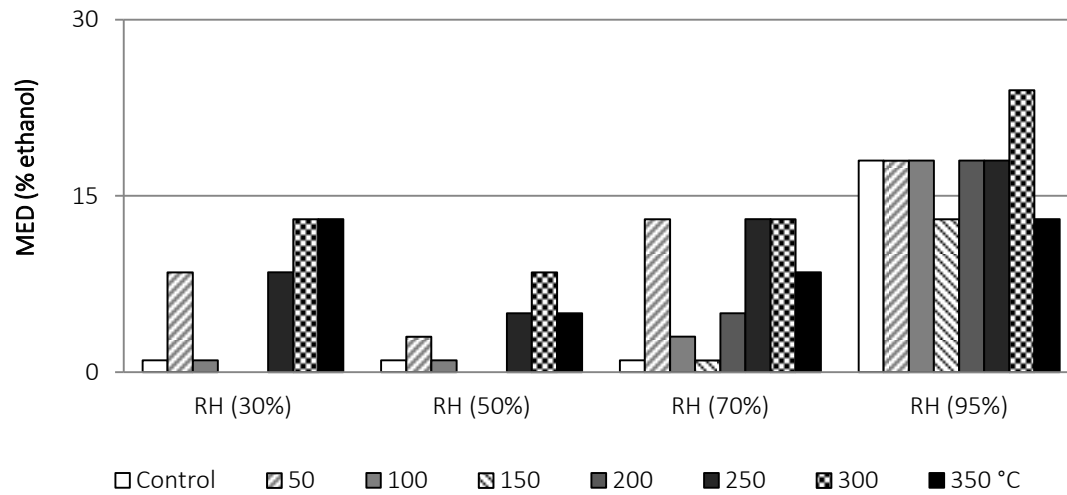


Figure 2. Soil water repellency in seconds (median values), determined using the WDPT test for samples heated to different temperatures and exposed to different RH (30, 50, 70 and 95%) for (a) pine and (b) shrub soil samples. Note that y-axis scales (LnWDPT) differs between (a) and (b). Control refers to unheated samples (median values).

The MED tests showed a similar pattern with WDPT tests for both pine and shrub soils (Fig. 3a and 3b, respectively). Nevertheless, significant differences ($p < 0.05$) were found on SWR pine samples from 250 °C to 350 °C compared to the unheated samples. SWR was not detected by MED tests in pine soils heated at 150 °C and 200 °C (Fig. 3a).

a) Pine



a) Shrub

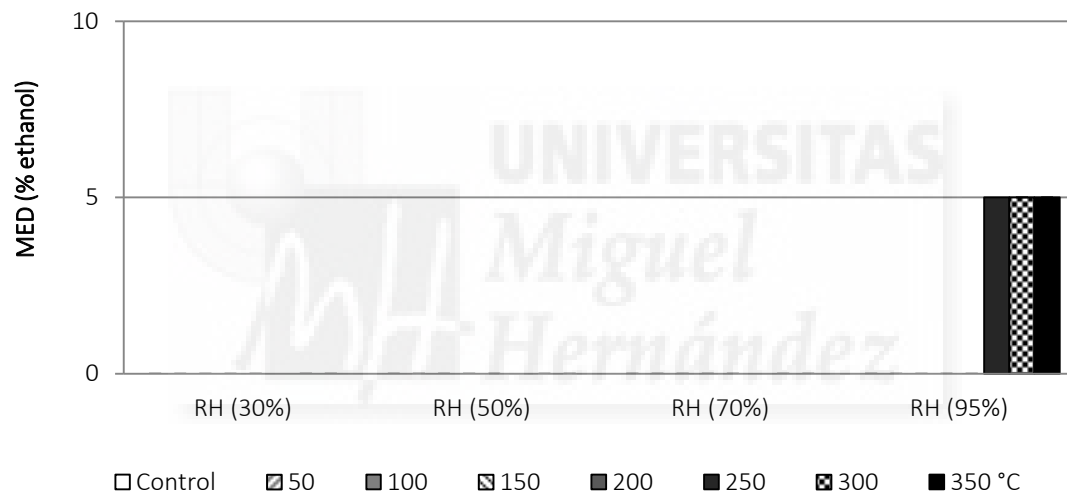


Figure 3. Soil water repellency of MED test classes (expressed as ethanol %; Doerr et al., 1998), (median values), measured for samples heated to different temperatures and exposed to different RH (30, 50, 70 and 95%) for (a) pine and (b) shrub soil samples. Note that y-axis scales (% ethanol) differs between (a) and (b). Control refers to unheated samples (median values).

The results of CA measurements showed a similar pattern with the WDPT results. CA measurements at 50% RH showed a general trend of increasing SWR with heating temperatures showing the largest CA at the highest heating range, where significant differences were found from 200 °C to 350 °C with regarding to unheated (control) samples ($p < 0.05$) (Fig. 4).

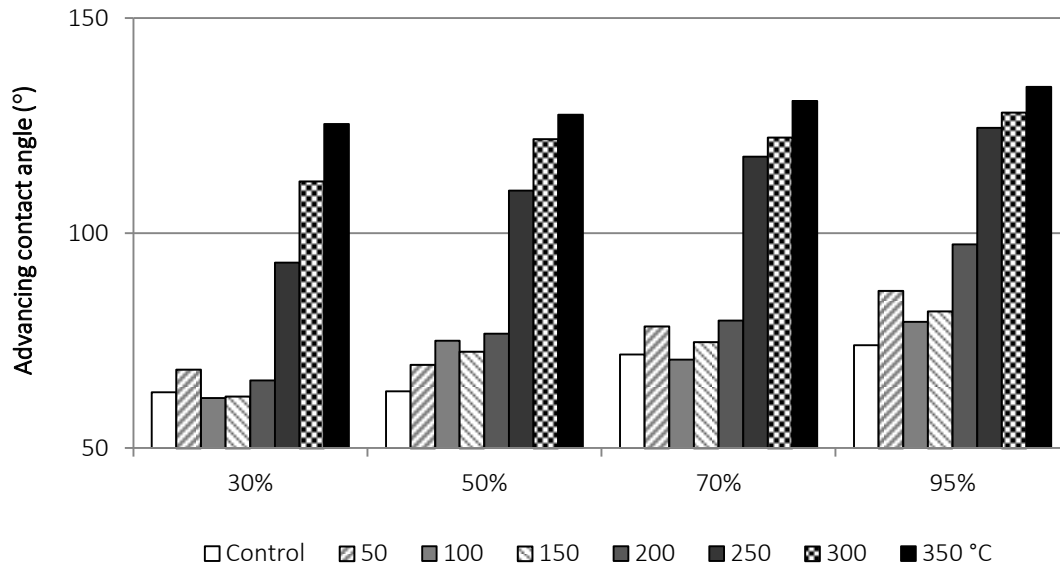


Figure 4. Advancing contact angle (median values) of *Pinus halepensis* soil samples heated at different temperatures.

Relative humidity effects on soil water repellency persistence (WDPT test)

Persistence of SWR in pine soils increased with RH for all heating temperatures. The WDPTs were longest at the highest RH (95%) for the most of heating treatments (Fig. 2). Particularly, for the heating treatments at 300 °C, the ln WDPT increased from 5.1 s at 50% RH to 8.6 s at 95% RH, and for the treatment at 350 °C, the ln WDPT increased from 5.1 s at 50% RH to 8.4 s at 95% RH (Fig. 2a), being in both cases significantly different ($p < 0.05$). For these samples for the 300 °C and 350 °C treatments were 'severely water repellent' (ln WDPT 6.4-6.8 s in Table 1) at 30% RH (Fig. 2a), whereas 'extremely water repellent' (ln WDPT > 8.2 s in Table 1) at 95% RH (Fig. 2a).

Shrub soils were wettable at the onset (ln WDPT < 1.6 s) and remained stable at each considered RH except at 95% RH, where the samples heated at 250 °C and 300 °C were 'slightly water repellent' (ln WDPT 1.8-3.4 s in Table 1; Fig. 2b), and there were statistically significant differences ($p < 0.05$).

Relative humidity effects on soil water repellency severity (MED and CA tests)

For the MED test, an influence of RH on SWR was observed mainly for the pine soils, showing a consistently increasing severity of water repellency with increasing RH (Fig. 3). At 30 and 70% RH, severity of SWR ranged between very wettable and strongly water repellent (classes 1 to 6; Table 2), with the highest values occurring for the highest temperature treatments (Fig. 3a), and where also statistically significant differences were detected for both RHs at 250 °C and 300 °C ($p < 0.05$). At 95% RH (Fig. 3a), SWR ranged between moderately and extremely water repellency (classes 5 to 9; Table 2), and the increase of SWR detected at 300 °C was statistically significant different ($p < 0.05$).

In contrast, the influence of RH on SWR was not shown from the shrub soils at low RH levels, as the shrub soils were wettable at the onset (ethanol $< 0\%$), and remained so at every RH level monitored except at 95% RH. Even at 95% RH, only the samples heated at 250, 300 and 350 °C (Fig. 3b) were 'slightly water repellent' (class 4; Table 2), and with no significant differences ($p > 0.05$).

The CA measurements were only conducted on samples taken from the pine site as only these showed a resistance to wetting sufficient for conducting CA measurement ($LN_{WDPT} > 1.6$ s). Shrub soils had rapid infiltration of water droplet, and thus, CAs were not technically measurable.

The CA measurements for the pine soils also showed an effect of RH at all heating temperatures at 30 and 70% RH (Fig. 4). The most noticeable increase in CA was found in the samples heated between 250 and 350 °C, particularly for 30 and 70% RH (Fig. 4), where significant differences were also detected ($p < 0.05$). The highest CA was observed at 95% RH after all heating treatments (Fig.4), finding significant differences ($p < 0.05$) from 200 °C forward.

Relative humidity effects on 'model soils': glass beads and sand

Both glass beads and sand showed a similar pattern where CA increased with RH (Fig. 5). CAs observed on glass beads of different sizes ranged from 77.91° (66.5°, 85.6°) to 100.9° (88.5°, 107.9°) (Fig. 5a), and on sands from 117.7° (100.0°, 126.0°) to 125.9° (118.3°, 128.9°) (Fig. 5b). The CAs of glass beads at different relative humidities all indicated water repellency (according to the classification of Goebel et al., 2011). The CA of the glass beads of size 1120-1180 μm at 95% RH was 100.9° (88.5°, 107.9°), indicating a fully water repellent behaviour ($\text{CA} > 90^\circ$) (Fig. 5a). The sand of both size groups also had consistent water repellent behavior ($\text{CA} > 90^\circ$). The CA was 123.2° (111.3°, 127.1°) for size 710-850 μm and 125.9° (118.3°, 128.9°) for size 1120-1180 μm (Fig. 5b). Regarding the differences between two sizes of sands, we observed that CAs were slightly larger for the smaller particles (710-850 μm) compared to the larger ones (1120-1180 μm) at 30, 50 and 70% RH, and the opposite at 95% RH (Fig. 5b).

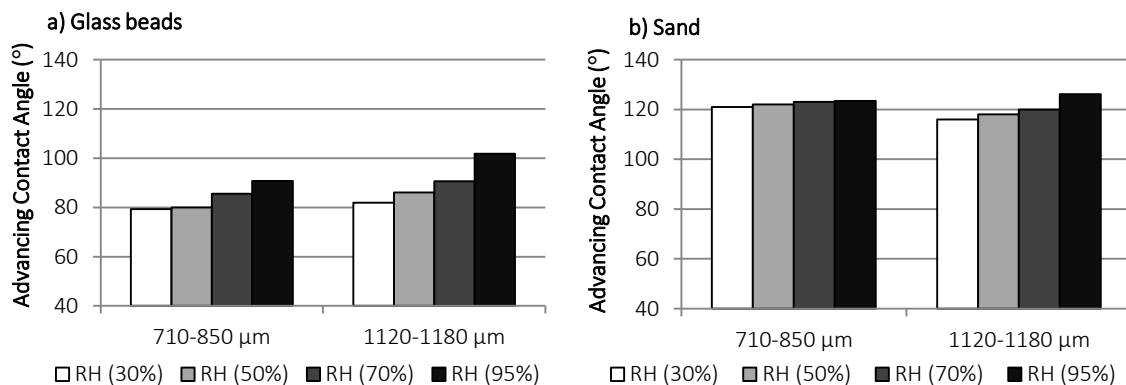


Figure 5. Advancing contact angle (median values) of chemically hydrophobized 'model soil'. (a) glass beads, (b) sand with different size range (710-850 μm and 1120-1180 μm). (* mean statistically significant differences at $p \leq 0.05$).

DISCUSSION

Heating effects on soil water repellency at different pre-established laboratory relative humidities

An overall increasing trend of both persistence (determined using the WDPT test) and severity (MED and CA tests) of SWR with increasing heating temperature was detected from pine soils at a standard RH of 50%. More specifically, SWR increased somewhat at the lowest heating temperature (50 °C) compared to unheated samples (Fig. 2a, 3a, 4). The SWR increasing can be caused by increased alignment of hydrophobic molecule chains (Doerr et al., 2005b). This was followed by a slight reduction for 100 and 150 °C treatments. The reason for this is unclear. Following heating at 200-300 °C a strong increase in SWR was observed (Fig. 2a, 3a, 4) which is in agreement with established knowledge based on previous laboratory studies, which have shown intensification of SWR when soil temperatures reach 175-270 °C (Doerr and Shakesby, 2009). Amongst the suggested causes for strong increases in SWR by heating are migration of hydrophobic material from interstitial organic matter onto soil particles (Franco et al., 1994) and chemical changes such as the relative increase in long chain (<C20) fatty acids aromatic compounds (Atanassova and Doerr, 2011). Krammes and DeBano (1965) found that SWR is destroyed at temperatures between 280 and 400 °C, with the specific destruction temperature being closer to 280 °C for shorter heating durations (Doerr et al., 2004). In the current study, however, heat treatments at 350 °C seem to be remained below the threshold for SWR destruction.

Shrub soils remained wettable after all heating treatments, highlighting the importance of vegetation type on the development of water repellency. It has been previously reported in burned (Arcenegui et al., 2007; Mataix-Solera et al.,

2008) or unburned soils (Jordán et al., 2008; Martínez-Zavala and Jordán-López, 2009; Zavala et al., 2014).

Relative humidity effects on the persistence and severity of soil water repellency

Persistence and severity of SWR were substantially enhanced at the highest RH applied in our experiments. At 95% RH, SWR in pine soils exhibited the highest values for each heating temperature (Fig. 2a, 3a, 4), and the shrub soils that were wettable at all other RHs turned into slightly water repellent at 95% (Fig. 2b, 3b).

A notable increase in SWR also occurred for pine soils at 70% RH compared to the standard atmosphere of 50% RH, particularly when considering SWR severity measured by MED test. This was evident in all samples irrespective of heating temperatures (Fig. 3a). These results demonstrate a considerable enhancing influence of high RHs (near atmosphere saturation: 95% RH) on SWR persistence and severity of already water-repellent soil. This fact suggests that air humidity is a key control of SWR. It supports findings from previous work on a variety of unburned soils (Jex et al., 1985; Doerr et al., 2002; Leelamanie and Karube, 2007; Leelamanie et al., 2008b), and demonstrates that this also applies to heat-affected soils. Given the relatively rapid change observed also in previous laboratory tests, Doerr et al. (2002) proposed that physicochemical rather than microbiological processes may be responsible for this soil behaviour. They suggested that the prior interactions between soil components and water vapour at high RH may be of significant influence, as a considerable quantity of energy is released, which might be disrupting the mineral and organic hydrophobic bonds within the soil. They speculated that, similar to heating effects, the condensation and adsorption of water vapor onto soil associated with an increase in RH might

lead to reorientation of the hydrophobic organic molecule chains, expanding more strongly into pore spaces, thereby enhancing SWR.

In this study, the heated samples, in which SWR had already been increased through the effect of temperature, showed further enhanced SWR by high RHs. Considering that high temperature treatments up to 300 °C would have led to a substantial reduction in any viable soil microbial population (Guerrero et al., 2005; Mataix-Solera et al., 2009), thereby limiting the growth of both bacteria (Díaz-Raviña et al., 1996) and also fungi (Widden and Parkinson, 1975), the intensified SWR by RH does not seem to be driven by increased microbial activity within a relatively short-duration of exposure to high humidities (Doerr et al., 2002).

It is also noteworthy that a slight increase in SWR was observed for pine soils at 30% RH, compared to the standard atmosphere of 50% RH. This was less consistent across the heat-treated soils and was evident predominantly from WDPT and MED tests (Fig. 2a, 3a), and also from CA test for control treatment (Fig. 4). This behaviour might be related to a conclusion of Moody and Ebel (2012), in where the time scale for rewetting of fire-affected soils under “hyper-dry” conditions is much slower (days to weeks) than the time scale of rainstorms (minute to hours). RHs of 30% can be considered a threshold for hot dry summer weather conditions in the Mediterranean climate (Harpaz et al., 2014), and this behaviour may therefore be relevant to the study region.

Assessments of relative humidity effects on ‘model soils’: glass beads and sand

The observed increase in SWR severity of hydrophobic ‘model soil’ samples after a short exposure (24 h) to relatively high RHs (> 50%) (Fig. 5a, b) suggests that the enhanced water repellency with RH observed here is a generic effect by a physical mechanism. The ‘model soils’ were hydrophobized with a

chemically relatively stable compound, and thus there is lowest possibility for microbial activities to get involved for these materials.

It supports the conclusion already stated above that physical rather than microbial processes are responsible for enhanced SWR at high RH.

Implications of enhanced soil water repellency for pre-heated soils with relative humidity

SWR is a widespread phenomenon with the capacity to condition hydrological and geomorphological processes (Whelan et al., 2015). It can reduce infiltration rates (Wallach and Graber, 2007) and water retention capacity (Naasz et al., 2005). Important environmental consequences of the reduced infiltration rate include increased soil erosion, enhanced overland flow and non uniform wetting fronts with fingered flow (Burch et al., 1989; Imeson et al., 1992; Ritsema et al., 1993; Jordán et al., 2008; Zavala et al., 2009b). These environmental impacts can affect important ecosystem processes such as soil organic matter decomposition, plant regeneration, succession of vegetation and microbial activities. The intensity of these effects depends upon the severity and spatial variability of SWR (Jungerius and de Jong, 1989; Ritsema and Dekker, 1994) and its severity and persistence (Zavala et al., 2009b). The enhanced SWR by high RH found in this study, therefore, can result in more intensive environmental change than the generic SWR under dry conditions. In nature, high RH conditions often precede precipitation events or wetting front advances in the soil, which in turn could increase SWR (Doerr et al., 2002; Zavala et al., 2009b).

The results of the current study suggest that this will also be the case for soils in which water repellency was enhanced by soil heating during fire. Considering that the removal of the protective vegetation cover by fire increases the susceptibility of burned hillslopes to accelerated hydrological and erosional responses (Shakesby and Doerr, 2006), the enhancement of SWR at high RH may

be even more influential in recently burned compared to unburned environments.

CONCLUSIONS

To the authors' knowledge, this is the first study in which RH effects on SWR have been examined for heat-affected (burned) soils. It was found that heat-affected soils also show the enhanced SWR that has been previously reported for soils not affected by heating. This effect was observed at 70% RH and was most pronounced at 95% RH. The effect of RH was shown in all heat-treated samples, and most pronouncedly in the samples heated at high temperatures (250-300 °C) that already had a substantial increase in SWR. The fact that the latter soils, as well as model soil particles treated with a hydrophobic coating, behaved in this manner suggests that physicochemical rather than microbial effects are responsible for the rapid increases in SWR induced by RH. The finding that soils in which SWR has already been enhanced by heating exhibit further increases with RH emphasizes the importance of considering RH when investigating the environmental impact of SWR in burned areas. Furthermore, a fire burns off protective vegetation and litter, and makes burned areas even more vulnerable to hydrological and erosional responses. Enhanced SWR at high RH could, therefore, be of greater significance than in unburned vegetated terrain.

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CAPÍTULO 3

ADVANCES IN THE KNOWLEDGE OF HOW HEATING CAN AFFECT AGGREGATE STABILITY IN MEDITERRANEAN SOILS: A XDR AND SEM-EDX APPROACH

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ABSTRACT

Aggregate stability (AS) is a key property in the soil system and it has been previously observed that its response to the fire can be very different with patterns that can show opposite trends depending on the principal cementing agents that control the aggregation between particles. In the case of some Mediterranean soils, previous studies observed an increase of AS. However it is not clear if this increase is real or apparent since fire could destroy a part of the aggregates and, therefore, what we are measuring is the AS that remains after fire. Soils from five different areas were heated in a muffle furnace at different temperatures (300, 500 and 700 °C) for 20 min. The weight of aggregate size fractions of 0.25 - 4 mm and <0.25 mm before and after heating treatments was quantified. The loss of weight by the combustion, the organic matter content and AS were also measured in all samples studied. A selection of aggregates of the three studied soils (control and heated at 700 °C) were also analysed by X-ray diffraction (XRD) and the surface soils were observed by scanning electron microscopy (SEM-EDX), in order to identify mineralogical and structural changes in the surface of aggregates due to heating. Results showed an initial decrease in the proportion of the macro-aggregates at 300 °C with regard to control (unheated) samples for all the soils analysed ($p < 0.05$). We presumed it is mainly due to the loss of SOM by combustion and subsequent disruption of some aggregates in lower sizes. However, this effect was not enhanced by heating the soils at 500 and 700 °C compared to 300 °C for any soil studied. Moreover, the heating treatments caused an increase in AS with heating temperature, despite no significant decrease for 0.25 – 4 mm aggregate fraction and the the decrease of SOM produced by the combustion. Therefore, these results are not apparent as a consequence of the selection of the most resistant aggregates because of the destruction of other soil aggregates. X-Ray diffraction patterns and SEM-EDX analyses results in selected aggregates assisted us to explain the above-

mentioned results of the increase of AS with heating temperature. The relative mineral abundances of the heated aggregates at 700 °C were slightly modified with regard to control. We observed some changes in the iron (hydr)oxides minerals, where the intensities had decreased and dehydroxylated to form maghemite. The presented results also show the disappearance of kaolinite for one of the soils. An increase of relative content of dolomite and calcite was also observed in the other two soils. In general, changes in compactness of soil micro-fabric units that have been produced as the consequence of the recrystallizations and micro-structural modifications observed by SEM-EDX in the surface of the soil aggregates after heating. These changes in cementing minerals may lead to a stabilization of the aggregate structure and hence an increase in the AS.

Key words: soil aggregate stability; forest fires, mineralogical changes; scanning electron microscopy; soil microfabric

INTRODUCTION

Fire may cause important variations in the first centimetres of soil profile inducing chemical, physical and biological changes in soil properties (Certini, 2005). These changes, despite usually only affecting the topsoil centimetres, e.g.: 1-3 cm depth under field and under laboratory conditions with different semiarid soils (Aznar et al., 2016; Badía et al., 2014; Badía-Villas et al., 2014); can have important implications for the soil functioning of the system and therefore on the ecosystem (Mataix-Solera and Cerdà, 2009). Soil structure is one of the most affected properties since it is controlled by many factors that fire can also affect (organic matter, water repellency, microbial populations, mineral changes, etc.; Mataix-Solera et al., 2010). Soil aggregate stability (AS) provides key information about the capacity of soil functions to define the soil quality (Chrenková et al., 2014; Brevik et al., 2015). It also has an important role in avoiding erosion and degradation and in the ability to transfer liquids and gases, which are important

features for the ecosystem health (Tisdall and Oades, 1982). AS is largely controlled by organic and inorganic soil components, such as, the quantity and quality of organic matter (Oades, 1993), and the clay content and its mineralogy (Singer, 1994).

There is a discrepancy in the previous literature regarding the effect of heat on AS. On one hand, soils in which organic matter is the main stabilizing agent are very prone to the degradation produced by high heating temperatures (Campo et al., 2014), producing the destabilization of aggregates (Giovannini, 1994; García-Corona, et al., 2004; Cerdà et al., 2009). On the other hand, soils in which inorganic compounds like iron and aluminium oxides and also carbonates (Andreu et al., 2001; Cerdà et al., 2009; Ketterings et al., 2000) are the main soil stabilizing agents, heating can also cause increases in soil aggregation (Campo et al., 2014). Other minerals like Kaolinite have been shown to decompose at temperatures between 500 and 700 °C (Richardson, 1972). Badía and Martí, (2003a) and Zavala et al. (2010) found a decrease of AS due to the destruction of soil organic matter (SOM) during burning under laboratory and field conditions, respectively. However, an AS increase could occur despite the decrease in SOM. Guerrero et al. (2001) and Arcenegui et al. (2008) explained that in some cases, increased AS after burning could be induced by other factors, such as changes in soil mineralogy (recrystallization of Fe and Al oxyhydroxides), after the soil has been exposed to moderate to high temperatures. Gibbsite may be completely destroyed by heating at 200 °C (Rooksby, 1972), and goethite is altered to hematite at ≈ 300 °C (Cornell and Schwertmann, 1996) for example. It is presumably known that all soils will not have an equal response to the heat impact and the mineralogical changes. Mataix-Solera et al. (2011) stated in a revision of state-of-the-art about this topic that AS may either increase or decrease depending on soil properties and temperature peaks reached during burning, and also on the heating residence time (Cerdà and Mataix-Solera, 2009), but from their review manuscript they conclude that in some cases with regard

to the observed AS increase it is not sure whether this is real or apparent since fire and destruction of some aggregates can lead to a selection of the most resistant, which are those subjected to the AS analyses.

Important amounts of SOM are lost when temperatures in soils reach around 300 °C (Ulery and Graham, 1993; Iglesias et al., 1997; Ketterings et al., 2000), producing the consequent destabilization of the aggregates (Giovannini, 1994; García-Corona et al., 2004; Cerdà et al., 2009). Also, regarding the heating effects on soil properties, the most important changes occur at different temperatures thresholds (Giovannini, 1997; Doerr et al., 2000; Certini, 2005; Mataix-Solera et al., 2011). These changes were summarized by Campo et al. (2014) as: 25-100 °C: soil dehydration; 170-220 °C: hydrophobicity increasing and dehydration of the gel forms; 220-460 °C: combustion of SOM, re-aggregation of particles into sand-sized particles and hydrophobicity disappearance; 550-700 °C: loss of OH⁻ groups of clays; 700-900 °C: carbonate decomposition. The consideration that the internal reorganization and recrystallization of these inorganic compounds contribute to increase the resistance of the soil aggregates, particularly in concomitance with the combustion of the SOM, suggests that during the heating process, the soil undergoes “a kind of laterization” (Giovannini, 1997) with its consequent evolution. Despite the interest in how heating can affect soil structure, very few studies (e.g., Arocena and Opio, 2003) were addressed by SEM-EDX and related specific techniques.

The AS values in Mediterranean calcareous soils are usually high for long-term undisturbed or even natural forest soils (Mataix-Solera et al., 2002; Zornoza et al., 2007, 2008; Arcenegui et al., 2008). Mediterranean calcareous soils mostly belong (>90%) to the orders of Soil Taxonomy Entisol, Inceptisol, Vertisol and Alfisol (Torrent, 1995). Entisols and Inceptisols represent about 80% of Spanish surface (Gómez-Miguel and Badía-Villas, 2016). In our region for forest soils main orders are Entisol and Alfisol. Although there are a few previous studies which

have included the soil type as a factor in experiments of fire effects on soils (Badía and Martí, 2003a; 2003b), it is not very common and therefore a novel additional part of this research.

The main objective of this study is to make advances on how different heating temperatures influence AS behaviour under laboratory conditions in some different soils of Mediterranean areas (southeast Spain). For this, a laboratory heating experiment was designed to study aggregation before and after heating treatments at different temperatures and in addition, to complete this study, some selected aggregates from three of the study sites considered as representatives have been analysed by X-ray diffraction (XRD) and the scanning electron microscopy (SEM-EDX) methods. The key aim of using these X-ray and electronic methods in this work was to establish the first contact with these techniques to identify potential mineralogical, micromorphological, and microanalytical changes, mainly related to mineral species and their relative abundance, fabric types (particle organization and voids), cements and other soil constituents, sensitivity to heat, produced by the impact of high temperatures and also, to study the relation of such effects with the apparent increasing stability of the remaining aggregates trying to confirm our hypothesis that the increase of AS due to heating is real and not apparent.

MATERIAL AND METHODS

Soil samples used for laboratory experiments

Samples of five different sites were used for this study (Fig. 1). Three from Alicante, SE Spain, (S-1, Llíber; S-3, Gorga; and S-4, Sierra de la Grana), one from Valencia, E Spain, (S-2, Navalón) and one from Cádiz, S Spain, (S-5, Sierra del Aljibe in Parque Natural de Los Alcornocales). Soils S-1 and S-5 were Alfisols (Soil Survey Staff, 2014) and S-2, S-3 and S-4 Entisols. Parent materials were (Table 1):

Cretaceous limestone (S-1), Cretaceous calcarenite (S-2); Miocene marly limestone (S-3), Tertiary limestone (S-4) and Miocene sandstone (S-5). Soil samples were taken from 0-2.5 cm depth of topsoil mineral horizon and beneath vegetation influence mainly composed of: *Pinus halepensis* in the case of S-1, S-2, S-3 and S-4, and *Pinus pinaster* in the case of S-5. The mean annual rainfall for each soil sampling area is: 556 mm for Llíber; 405 mm for Sierra de la Grana; 495 mm for Gorga; 479 mm for Navalón; and 1440 mm for Sierra del Aljibe.



Figure 1. Study area and location of sampling sites.

Table 1. Soil materials used: soil type, and selected properties analysed in fine earth (<2 mm) from 0-2.5 cm of mineral horizon.

Sample	Soil type ^a	Munsell color (moist)	Soil structure ^b	Texture	Sand (%)	Silt (%)	Clay (%)	SOM (%)	pH	EC (µS/cm)	CaCO ₃ equiv. (%)
S-1	<i>Rhodoxeralf</i>	2.5YR3/6	abk, c, 3	Clay loam	18	44	38	9	7.3	248	1
S-2	<i>Xerorthent</i>	7.5YR3/2	gr, m, 3	Sandy silt loam	42	44	14	13	8.3	309	42
S-3	<i>Xerorthent</i>	10YR3/3	sbk, m, 2	Silt loam	50	41	9	7	8.2	214	57
S-4	<i>Xerorthent</i>	10YR3/2	gr, m, 2	Sandy loam	58	34	8	10	8.1	402	68
S-5	<i>Haploxeralf</i>	10YR4/2	gr, m, 2	Sandy loam	62	18	20	10	6.3	54	3

^a Soil Survey Staff (2014)

^b Structure: Type: pl= platy; pr= prismatic; abk= angular blocky; sbk= subangular blocky; gr= granular. Size: f= fine; m= medium; c= coarse; vc= very coarse. Grade: 0= structureless; 1= weak; 2= moderate; 3= strong.

Abbreviations: SOM= soil organic matter; EC= electrical conductivity; CaCO₃ equiv.= Calcium carbonate equivalent.

Laboratory experiments

All soil samples were dried at room temperature (~ 25 °C) during a week. Triplicate soil samples were carefully dry-sieved to obtain 0.25 - 4 mm and < 0.25 mm sieve fractions, recording the weights of both fractions, and discarding coarser material (>4 mm). Sieve fractions were mixed again and placed on porcelain containers to be heated in a pre-heated muffle furnace at 300, 500 and 700 °C during 20 minutes, simulating different heating scenarios (samples were stirred after 10 minutes heating to mix and homogenize the heating conditions). After each heating treatment, samples were sieved again through a 0.25-mm mesh and both fractions were separately weighted for control and for each heating temperature for the two fractions studied. Triplicate unheated samples were used as control. With this data we determined the percentage of mass lost by volatilization after heating (VL: volatilization loss), and the percentage of mass weight (MW) in each fraction to know if heating treatments produced a direct destruction of aggregates of fraction 0.25 - 4 mm and transferred to the < 0.25 mm fraction.

Soil aggregate stability (AS) was measured in the 0.25 - 4 mm sieved fraction in control (unheated) and in 300, 500 and 700 °C heated samples ($n = 60$), and determined with the rainfall simulator method according to Roldán et al. (1994) and based on the method of Benito and Díaz-Fierros, (1989). This method examines the proportion of macroaggregates that remained intact after a soil sample was subjected to artificial rainfall of a specific energy. Four grams of soil material (4-0.25 mm) were placed into a 0.25-mm sieve and exposed to an energy of 270 J m^{-2} applied by an artificial rainfall. After treatment, the material remaining within the sieve was dried and weighed. The material on the sieve, consisting of remaining aggregates, mineral particles and organic debris was then washed until only mineral particles and organic debris remained. The dry weight of the remaining mineral particles and organic debris material allowed for the

difference in aggregate weight (%) within a sample before and after artificial rainfall to be calculated (AS). Results are based on the mean value of three replicate experiments per soil sample. SOM content was determined using the Walkley and Black (1934) method.

Persistence of soil water repellency (WR) was assessed by the Water Drop Penetration Time (WDPT) test (Wessel, 1988). Soil samples were dried at room temperature (~25 °C) during a week and carefully sieved (<2 mm) and coarse material was discarded. Approximately 10 g of sample material was placed into separate plastic dishes (diameter 50 mm), and exposed to a controlled laboratory atmosphere (20 °C, 50% relative humidity) for 24 h to eliminate potential effects of any variations in preceding atmospheric humidity on WR (Doerr et al., 2002). The average time for triplicate drops has been taken as the WDPT value of a sample, and were classified according to Bisdorf et al. (1993) and Doerr et al. (1998), as follow: wettable (WDPT <5 s), slightly water repellent (WDPT: 5–60 s), strongly water repellent (WDPT: 60–600 s), severely water repellent (WDPT: 600–3600 s), and extremely water repellent (WDPT >3600 s).

Laboratory analyses described next were only determined for control (unheated) samples in <2 mm fraction to complete their characterization. For granulometry test, soil samples were treated with H₂O₂ (6%) to remove organic matter and then textural analysis was determined by the Bouyoucos method (Gee and Bauder, 1986). Percentage of CaCO₃ equivalent content was determined by the Bernard calcimeter method (Hulseman, 1966).

X-ray diffraction and scanning electron microscopy methods

For an initial approximation of the knowledge of the probable mineralogical variations due to the heating impact on the remaining aggregates following a heating treatment, selected separated soil aggregates (~2 mm size) from S-1, S-2 and S-3 soil samples were analysed. The mineralogical analysis were done with

the X-ray diffraction (XRD) methods in crystalline dust of soil and in orientated aggregate of sample finely ground (<50 µm) suspended in water (using sodium hexametaphosphate as dispersing agent). The identification of mineral species and semiquantitative analysis was done as described in Delgado et al. (2003). The equipment used was a Bruker D8 Advance diffractometer (Cu K α radiation $\lambda = 0.15406$ nm, range 3° – 70° 2 θ , 40 kV, 40 mA, 0.01 °2 θ step size, 192 s counting time per step). The study of the aggregates micromorphology and microanalysis was carried out over fresh surfaces of the selected aggregates in unheated (control) samples and in samples of the heating treatment of 700 °C, with the scanning electron microscopy (SEM) method, using the SEM Hitachi S-510 and microanalysis EDX Rontec. Methodology used is described in Calero et al. (2009). The surface was coated with C or Au to improve the observation.

Statistical analysis

Normality was tested using the Kolmogorov-Smirnov test. Homogeneity of variances for all data was carried out with the ANOVA-one way test. Tukey HSD test was used to check the significant differences between temperature treatments for each soil ($p \leq 0.05$). Pearson's correlation coefficient (r) was calculated to quantify the linear relationship between parameters. Statistical analyses were performed by IBM® SPSS (© SPSS Inc., 1989) version 22 for Windows software package.

RESULTS

Analytical characteristics

The sand content (Table 1) shows that the range for the different soils varied between 18% (S-1) to 62% (S-5); while the range of the clay content varied between 8% (S-4) to 38% (S-1). All studied soils show medium values of SOM

content for forest soils, which ranged between 7% (S-3) to 13% (S-2). Soils with higher presence of carbonates (S-4, S-3 and S2, with 68%, 57% and 42% CO_3Ca equivalent, respectively) were essentially the most basic soils, with a pH ranging between 8.1 and 8.3. In the most evolved soils, Alfisols, the lower pH ranges were detected (7.3 for S-1 and 6.3 for S-5), showing a lower content of carbonates, which varied between 1% (S-1) and 3% (S-5). The range of the EC for the soils studied varied between 54 and 402 $\mu\text{S}/\text{cm}$ (S-5 and S-3, respectively). All soil samples were initially wettable (WDPT test < 5 s).

For the three soil used for XDR and SEM-EDX analyses, the mineralogical data obtained with XRD (Table 2) allow us to affirm that S-1 has a high content of phyllosilicates, while its content of carbonates and iron (hydr)oxides was low. Meanwhile, S-2 was mainly a dolomitic one (rich in dolomite: $\text{CaMg}(\text{CO}_3)_2$), also with a relatively high phyllosilicates content. And finally, S-3 was mainly composed of calcite (CaCO_3). Quartz was a ubiquitous component in the three soils. Fig. 2 graphically summarizes the previous affirmation that the Alfisol, S-1 was almost free of carbonates (a small peak of calcite can be observed) and is dominated by phylosilicates with the presence of iron forms. On the other hand, S-2 and S-3, both Entisols, have a high content of carbonates with dominant presence of peaks of calcite sand. These mineralogical compositions are common in the Mediterranean region (Torrent, 1995).

Table 2. Mineralogical analysis (XRD) of soil aggregates of soils S-1, S-2 and S-3 (Llíber, Navalón and Gorga, respectively).

Soil	Temperature (°C)	Quartz	Feldspars	Calcite	Dolomite	Fe Oxide	Phyllosilicates
S-1	Control	xxx	tr	x		xx ^a	xxxxx ^c
	700	xxx	x	x		x ^b	xxxxx
S-2	Control	xxx	x	x	xxx	tr	xxxxx ^d
	700	xxx	x	xx	xxxx	tr	xxxx
S-3	Control	xxx		xxxxx	x	tr	xxx ^e
	700	xxx		xxxxx	x	tr	xxx

Relative abundance *versus* percentage: tr: traces (< 1%); x: very few (≤ 5%); xx: few (5 - 10%); xxx: common (10 - 25%); xxxx: many (25 - 50%); xxxxx: very many (> 50%).

^a Mainly goethite (and hematite).

^b Mainly maghemite (and hematite).

^c Smectite (x), interstratified phyllosilicates (xx), illite (xxx), paragonite (x), kaolinite (xxxx), chlorite (x).

^d Smectite (x), interstratified phyllosilicates (xx), illite (xxxx), paragonite (x), kaolinite (xxx), chlorite (x).

^e Illite (xxx), kaolinite (x), chlorite (x).

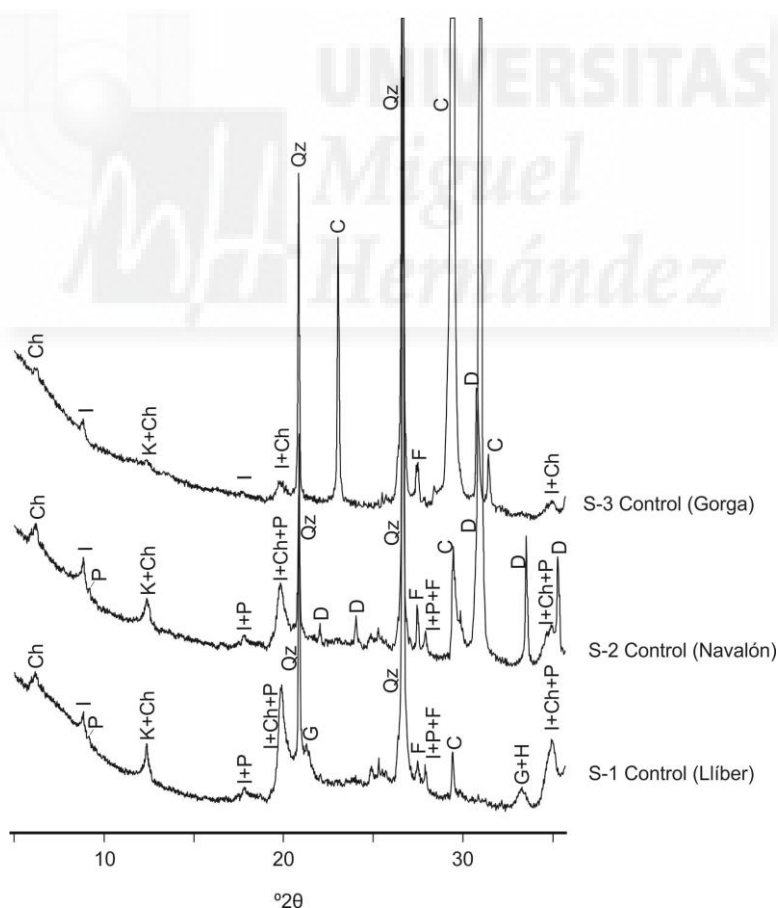


Figure 2. XRD profiles for samples S-1, S-2 and S-3 Control (non-oriented dust) in the sector 5 – 35 °2θ. Abbreviations: C = calcite; Ch = chlorite; D = dolomite; F = felspar; G = goethite; H = hematite; I = illite; K = kaolinite; P = paragonite; Qz = quartz.

Changes in soil organic matter content, water repellency and aggregation due to the effects of heating

Heating produced a loss of weight by volatilization (VL) progressively with heating temperature as observed in Fig. 3. These changes are significant among temperatures for all studied soils ($p < 0.05$; $n = 45$). Also, a significant decrease in the SOM content is observed with heating treatments in all samples (Fig. 4). A decrease in the proportion of aggregates (MW) from the 0.25 – 4 mm sieve fraction was observed at 300 °C with regard to control (unheated) samples (Fig. 5) for all soils analysed ($p < 0.05$). These decreases ranged from 14% in S-3 to 3% in sample in S-1. Thus, the finest fraction (<0.25 mm) increased in all soils, especially in S-2, S-3, S-4 and S-5, in part, probably due to the loss of SOM by combustion and subsequent disruption of some aggregates in lower sizes. However, this effect was not enhanced at 500 and 700 °C compared to 300 °C for any soil studied (Fig. 5). It was also observed that heating treatments caused changes in AS of the aggregates (0.25 – 4 mm), observing an increase in AS with heating temperature, despite the decrease of SOM (Fig. 4). Significant and negative correlations were found between AS and SOM pooling the data of all soils together ($r = -0.677$; $n = 60$), and separately with the best correlations for soils S-1, S-4 and S-5 ($r = -0.951$, $r = -0.930$, and $r = -0.984$, respectively; $n = 12$). In the case of WR, we only detected for S-4 at 300 °C, extreme (WDPT >3600 s). The other soil samples showed wetttable conditions (WDPT < 5 s) in unheated and at any temperature of heating.

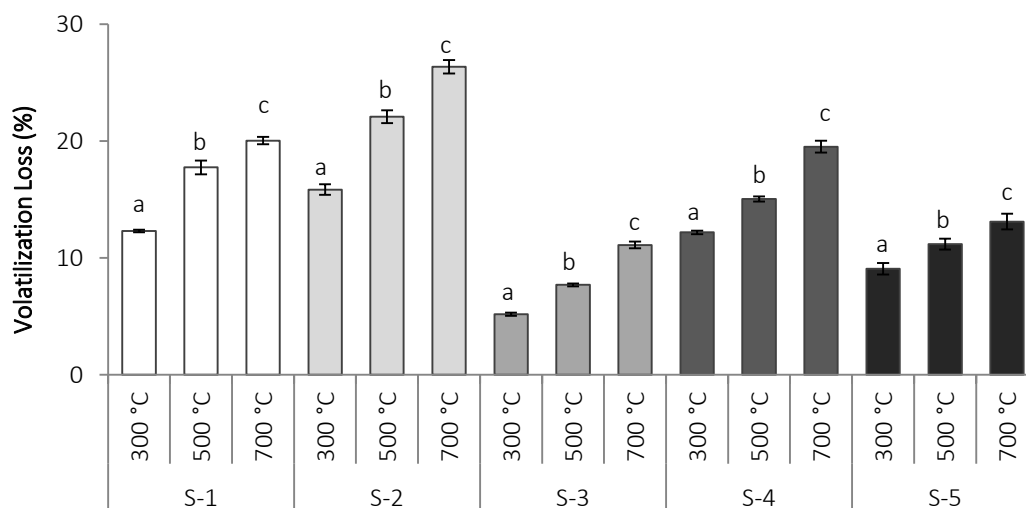


Figure 3. Percentage of volatilization loss (VL) for each heating temperature treatment (300, 500 and 700 °C); where: S-1) Llíber, S-2) Navalón, S-3) Gorga, S-4) Sierra de la Grana and S-5) Sierra del Aljibe. Mean values and standard deviation. Different letters show the statistically significant differences between the different heating treatments for each soil with the Tukey test ($p \leq 0.05$).

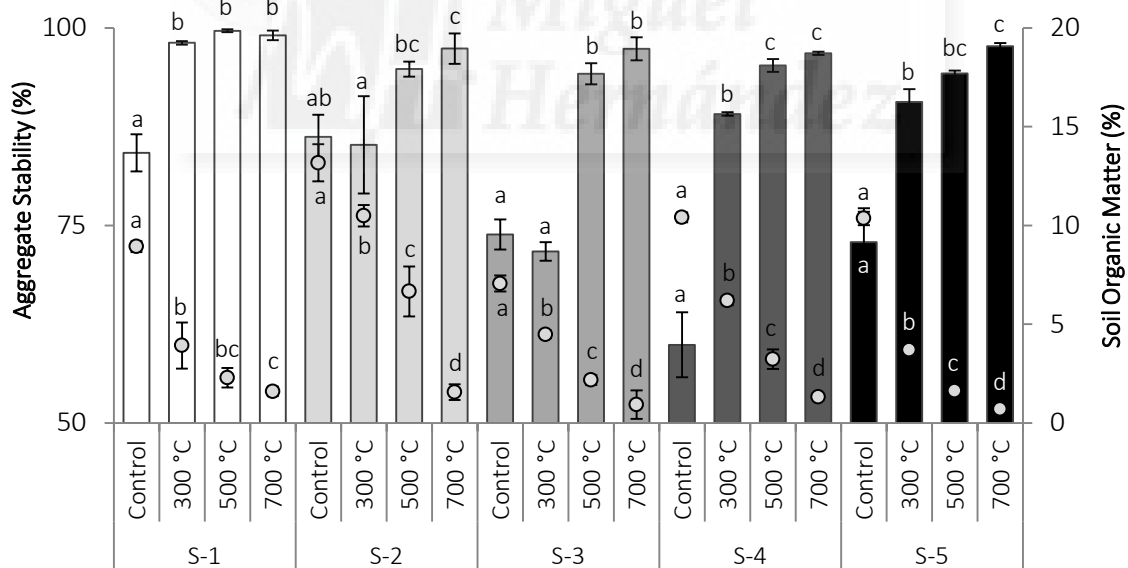


Figure 4. Percentage of aggregate stability (columns) and percentage of soil organic matter (dots) for control (unheated) and for each heating temperature treatment (300, 500 and 700 °C) in fraction 0.25 - 4 mm; where: S-1) Llíber, S-2) Navalón, S-3) Gorga, S-4) Sierra de la Grana and S-5) Sierra del Aljibe. Mean values and standard deviation. Different letters show the significant differences between the different heating treatments for each soil with the Tukey test at $p \leq 0.05$.

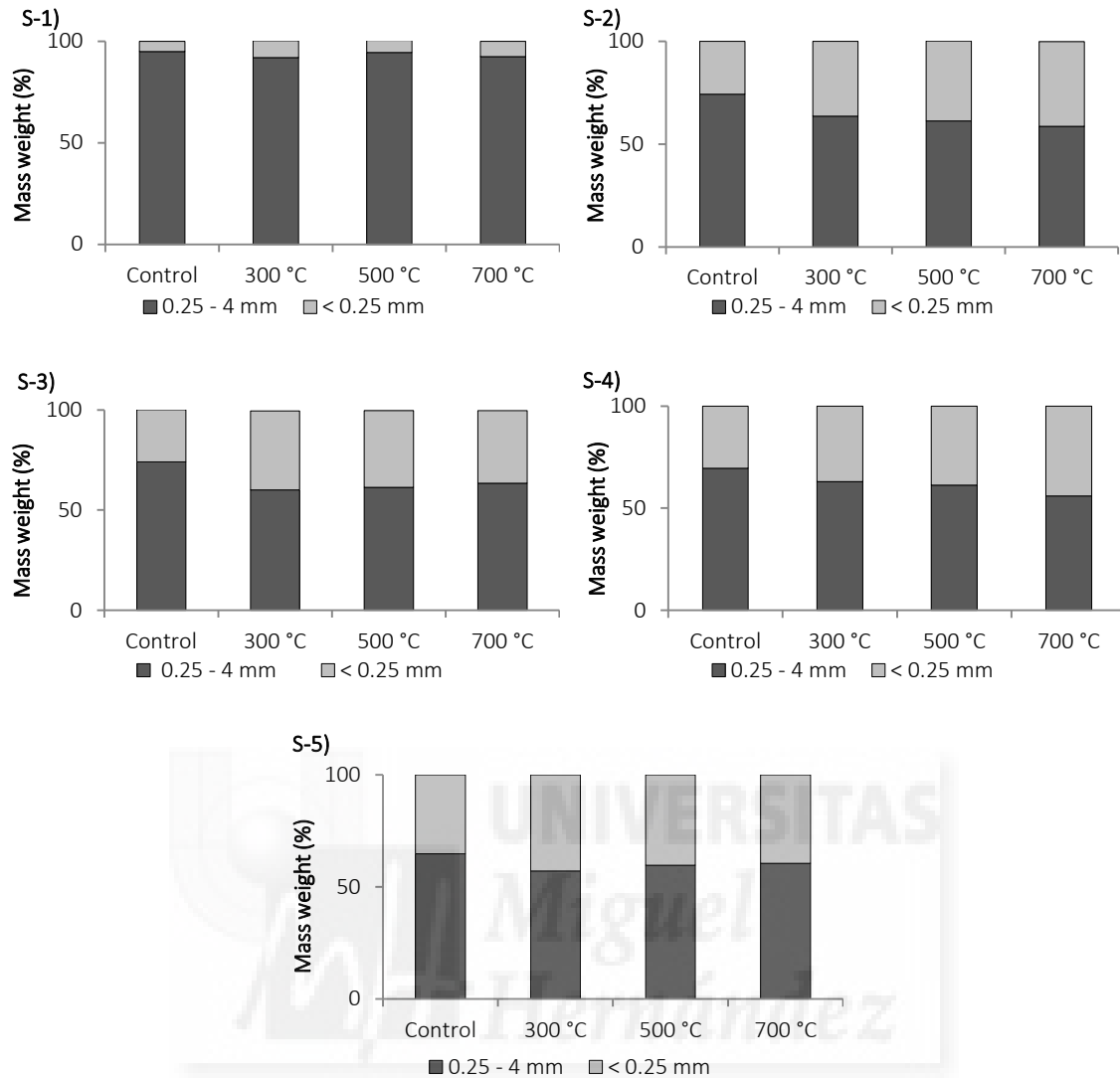


Figure 5. Percentage of mass weight (MW) for the two aggregate fractions studied (0.25 - 4 mm and <0.25 mm) for control (unheated) and for each heating temperature treatment (300, 500 and 700 °C); where: S-1) Llíber, S-2) Navalón, S-3) Gorga, S-4) Sierra de la Grana and S-5) Sierra del Aljibe. Data represented correspond with the mean values (n = 3).

Mineralogical variations due to the heating impact, analysed by X-ray diffraction

Mineralogical composition, estimated in relative abundance, of the aggregates analysed (~2 mm), including phyllosilicates (<2 μm), by XRD for control (unheated) and heated (700 °C) samples is shown in Table 2 and in Figs. 5 and 6. The minerals detected for the unheated selected aggregates tested were

mainly: phyllosilicates (mostly composed of illite, kaolinite, smectite, interstratified phases, chlorite and paragonite), quartz, carbonates (calcite and dolomite), and also, in lower abundance, iron (hydr)oxides (mainly composed of goethite with minor contents of hematite) and feldspar.

The relative mineral abundances of the heated aggregates at 700 °C were very slightly modified with regard to control (Table 2). For S-1: the iron (hydr)oxides content was reduced and modified in nature to maghemite, also with the presence of hematite; another difference was the disappearance of kaolinite as will be discussed later. For S-2: the content of dolomite and calcite was relatively increased. S-3 did not show differences in the abundance of the different minerals.

Micromorphological variations due to the heating impact

Several micro-structural modifications were observed (Fig. 6), by the SEM-EDX method, on the aggregates analysed due to the heating treatment applied at 700 °C with regard to control aggregates samples. The control aggregates sample for S-1 (Fig. 6a) showed a laminar cemented and relatively compacted fabric, highly anisotropic, and with limited porosity. The presence of phyllosilicates and iron (hydr)oxides (cement agents), indicated before in the results of XRD, can now also be evidenced by the laminar-fused appearance of the fabric and the EDX spectra where the peaks of Si, Al, K and Fe are dominant. Laminar cemented fabric was maintained after the heating impact (Fig. 6b). However, the porosity between grains increased, also thermal contraction crevices and vesicles appeared that can reach a diameter of >20 µm in which small crystals appear on the edges with concentrated calcium. For S-2, the control aggregates (Fig. 6c) showed a cemented skeletal fabric, slightly anisotropic, mainly composed of calcium carbonate matrix (very exalted peak of Ca in EDX spectra), and silty

grains (10 to >20 μm) mostly composed of dolomite, small sheets (<10 μm) of phyllosilicates and iron forms. Immersed into the matrix can also be recognized

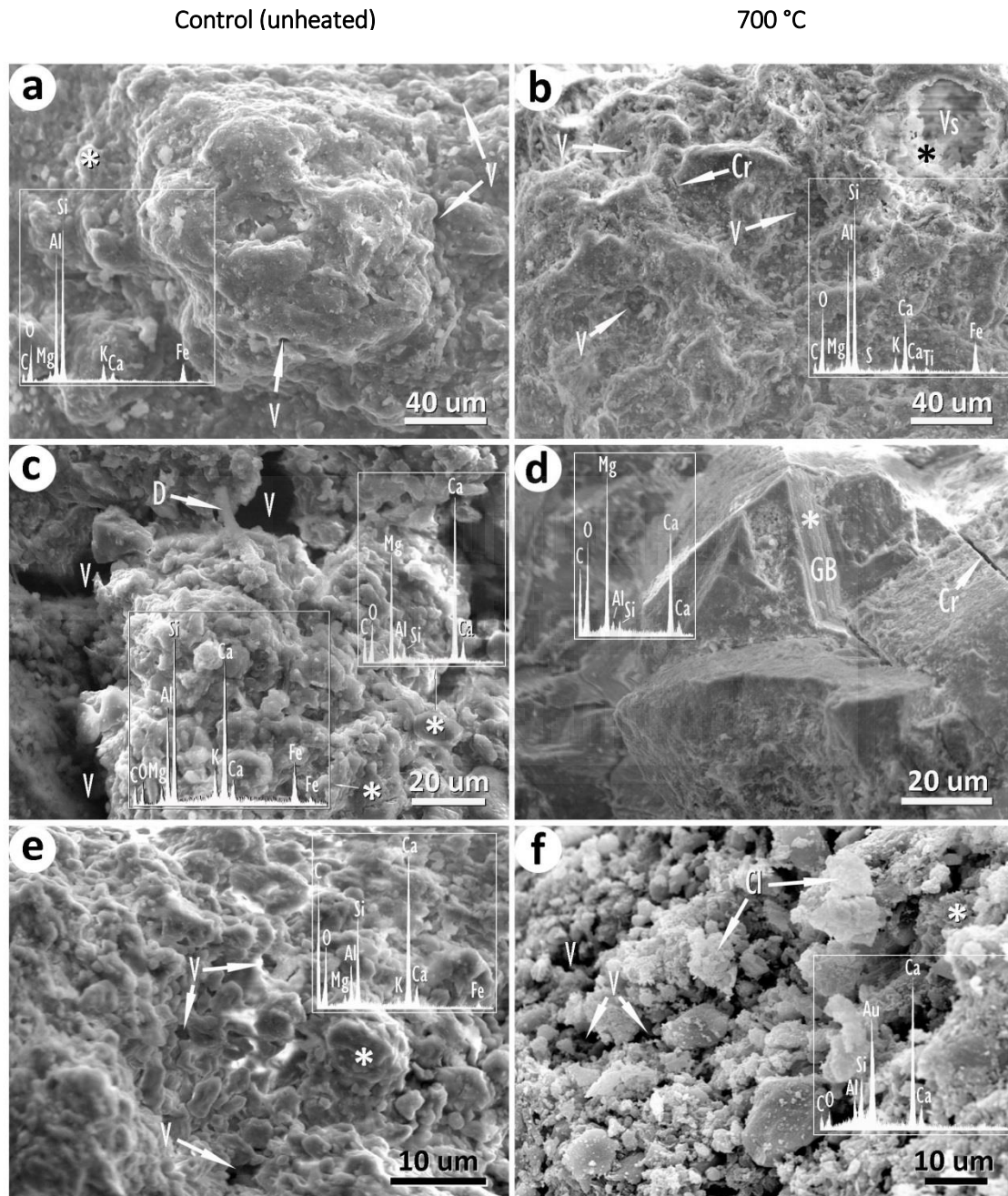


Figure 6. SEM images and EDX spectra of soil aggregate surfaces, where: a) Laminar cemented microfabric (S-1). b) Laminar cemented microfabric (S-1). c) Skeletal cemented microfabric. EDX left spectra corresponds to a dolomite grain; an EDX right spectra corresponds to the cemented matrix of CaCO_3 with phyllosilicates and iron forms (S-2). d) Aggregated surface of dolomite crystals (S-2). e) Skeletal cemented microfabric (S-3). f) Microfabric close to skeletal (S-3). '*' indicates position of EDX microanalyses; a part of C peaks (images a, b, c, d, e) and the total of Au (image f) is due to the simple preparation for the SEM observation. Abbreviations: Cl = cluster of particles; Cr = crevices; D = vegetal debris; GB = grow bands; V = void; Vs = vesicle.

forms that seem to be calcified vegetal debris contributing to soil structure. Pores of diverse sizes can be also detected. The heated aggregates at 700 °C, revealed that the cemented matrix is transformed into a set of small crystals (<2 µm) in many zones with a tendency to individualize each other, increasing the porosity generated in the contact between them. Calcified vegetal debris is not easily recognized now, and the fabric can be qualified as skeletal microcrystalline, with certain porosity. In drusiform aggregates of dolomite grains (often in this sample, >50%, Table 2) (Fig. 6d) crystal faces (possibly rhombohedral $hk(-i)l$) can be recognized, and over them growth bands and some thermal crevices. For S-3, the control aggregates (Fig. 6e) also showed a cemented skeletal fabric slightly anisotropic, with silty grains embedded into the carbonated matrix. High content in calcium carbonate (calcite), and presence of quartz and phyllosilicates (Table 2) was detected by EDX with the peaks of Ca, Si, Al. This seems to be a labile structure, where porosity is evident. The heat impact (Fig. 6f) provoked a destruction of continuity of the cemented matrix generating individual clusters of particles (>10 µm) with cemented appearance (inside them) and small grains (2 – 5 µm); the mean size of structural units therefore decrease and the microfabric can be qualified as near to skeletal. Porosity increases showing big pores that can reach 10 µm of diameter. The EDX spectra revealed a high content of calcium carbonates, indicated by the prominent peak of Ca.

DISCUSSION

The SOM contents of the control samples are typical for pine forest Mediterranean areas of southern Spain in accordance with Mataix-Solera and Doerr (2004), who said that it could explain the relatively high AS of these soils, also when we compared these AS values with the same soils but after long-term agricultural land use which provoked a decrease of SOM content (Chrenková et al., 2014). The values of AS in control samples used in this work (60-86%; Fig. 4) were also within the normal range for forest soils of the region as reported in

previous researches, which used the same rainfall method for determination (60-90%, Mataix-Solera et al., 2002; >80%, Mataix-Solera and Doerr, 2004; 45-82%, Chrenková et al., 2014). Our results showed that heating treatments produced a decrease in SOM content in soils and consequently a loss of weight by volatilization with increasing temperature of heating due to the combustion (Soto et al., 1991; García-Oliva et al., 1999; Jordán et al., 2011). This must be the reason for the observed initial destruction of a part of the macro-aggregates fraction (0.25 – 4 mm) in the heating treatment of 300 °C (Fig. 5). Such significant differences ($p \leq 0.01$) demonstrate that there was an initial loss of structural stability with the loss of SOM, which act as a cementing agent of mineral particles (Giovannini et al., 1987; Sanroque et al., 1985; Mataix-Solera et al., 2011). In accordance with these results, some other previous works have found destruction and a decrease of AS associated with the combustion of SOM content (DeBano et al., 1979; Soto et al., 1991; Badía and Martí, 2003a). However, a relative increase of AS values was observed in our results with the increasing heating temperature (Fig. 4).

Mataix-Solera et al. (2011) pointed out in their revision of fire effects on soil aggregation, that for burned soils, more complex patterns of AS can be observed, in many cases, despite SOM being reduced by the fire, AS of remaining aggregates increased. However, such pattern depends on the type of soil and temperatures reached on the surface of soil during heating (Guerrero et al., 2001). In some soils the impact of heating during burning can produce a new aggregation due to mineralogical changes (Giovannini et al., 1990), which will act as new cementing agents, and therefore, the resistance of aggregates to breakdown will increase. Depending on fire severity and temperatures reached, the impact of heating on SOM consists of slight distillation, charring or complete oxidation (Certini, 2005), and substantial consumption of organic matter begins in the 200-250 °C range to complete at around 460 °C (Giovannini et al., 1988), or even at 500 °C (Badía and Martí, 2003a). After that, we can observe that the

remaining aggregates increased their stability at 500 and 700 °C with regard to 300 °C, despite the fact that SOM continued decreasing with the increase of heating temperatures (Fig. 4) due to its volatilization (Fig. 5) and, despite there being no more destruction of the macro-aggregates (0.25 – 4 mm) fraction (Fig. 3). Therefore, our results might demonstrate that real increases in AS have been produced with heating, and these results are not apparent as a consequence of the selection of the most resistant aggregates because of destruction of other ones, as one of the possible explanations previously pointed by Mataix-Solera et al. (2011). Such behaviour might be attributed to the possible mineralogical modifications due to the effect of heating temperatures, which create new cementing agents (Giovannini et al., 1990), and some micromorphological changes in surface of soil aggregates as were observed by XRD and SEM and will be discussed later. At low temperatures of heating, an increase of AS can also be attributed to an increase of WR, when this occurs (Mataix-Solera and Doerr, 2004). WR induced by fire is caused by partial combustion of organic matter that produces volatile organic substances which condense at cooler sites and coat the mineral soil particles (DeBano et al., 1970). DeBano (1981) found that heating soil between 175 °C and 200 °C resulted in increased WR and above 270-300 °C WR was destroyed, but these ranges depend on times of heating and also on heating atmosphere used, being higher under oxygen-deprived conditions (Bryant et al., 2005). In our study, taking into account the results, this could be only for S-4 at 300 °C when we detected extreme WR in that soil at that temperature of heating. In previous studies it has been observed that small variations in soil properties can control the development of WR by heating, and one of the most important is the soil texture (Mataix-Solera et al., 2014). Sandy soils are more prone to develop WR because of the lower specific surface area to be cover by hydrophobic substances (Doerr et al., 2000; González-Peñaloza et al., 2013). Therefore it is not strange that we only detected WR at 300 °C in this sample, which corresponds with the one with coarser texture. This can also

contribute to explain that the increase of AS was higher in S-4 after heating at this temperature in comparison to the other ones (Fig. 4).

Regarding changes in mineral fraction, some authors pointed that these are dependent on temperature reached. Mataix-Solera et al. (2011) showed in their revision different temperature ranges for some mineralogical compounds that act as cementing agents, where: Fe and Al (hydr)oxides suffer variation from 400 to 600 °C; between 600 to 700 °C thermal fusion of clay minerals may occur; and from 700 to up of 900 °C the collapse-destruction of clay may arise. In general, relatively high temperatures must be reached for these transformations, which are uncommon in soil depth or inside aggregates due to their low thermal conductivity, but it is hypothesized that they can be reached on soil surfaces and then these mineral changes and morphology structure could be in part responsible for the observed increased AS. When soil is heated to temperatures higher than 400 °C, this can produce thermal transformations (recrystallization) of Fe and Al oxides. For example Gibbsite may be completely destroyed by heating at 200 °C (Rooksby, 1972), and goethite is altered to hematite at ~ 300 °C (Cornell and Schwertmann, 1996). Other minerals like Kaolinite have been shown to decompose at temperatures between 500 and 700 °C (Richardson, 1972). Other authors also reported soil textural modifications as a consequence of via aggregate binding mechanisms during burning (Betremieux et al., 1960). Badía and Martí (2003a) found that heating at 500 °C a calcareous soil a third of the clays became sand. Ketterings et al. (2000) reported that exposure of the soil to temperatures >600 °C resulted in an increase in the amount of sand and a decrease in silt, and especially, clay. Giovannini and Lucchesi (1997) observed that alteration of iron and aluminosilicates led to a fusion of the aggregates into robust particles with higher AS compared to the unburnt controls.

Carbonates, the main constituent of calcareous soils, resist up to 1000 °C of heating (Rabenhorst, 1988), and thus rarely undergo fire-induced changes, but as

mentioned above it may occur at some specific point on the soil surface, where the accumulation of fuel was very high or even where the period time of the flame was more durable (Keeley, 2009), which means at aggregate surface level of topsoil mineral horizon. In our study, the unheated S-2, S-3 and S-4 revealed the highest values of carbonates, and S-1 and S-5 showed the lowest (Table 1). It could be observed that the carbonates might be also act as an important cementing agent, causing the significant AS increase observed with the heating effect, once SOM is substantially decreased at 500 and 700 °C for those soils with especially higher carbonates content S-2, S-3 and S-4 (Fig. 4). The results of XRD and the observations by SEM-EDX in this study for selected soil samples corroborate the hypothesis that mineralogical and micromorphological changes over aggregate surfaces produced by heating at high temperatures help to explain the observed increase in AS. A detailed discussion of our specific results of this part of the study is necessary to understand and confirm our hypothesis.

The main mineralogical composition described of the S-1, S-2 and S-3 soils was practically maintained, during the heating treatment (Table 2). However, we found some transformations within some of the mineral groups. In the case of S-1 for the iron oxides and the phyllosilicates. Goethite present in low quantity (5 – 10%) in control sample, when it is submitted to heat treatment is transformed in maghemite in lower proportions ($\leq 5\%$); detected in XRD diagrams (Fig. 7) as a loss in heated sample in the peaks of 0.418 and 0.269 nm of goethite and in the band between 30 y 31 °2 θ (approx.), corresponding with the existence of the reflexion of 0.295 nm of maghemite. This process: 2FeOOH (goethite) $\rightarrow \text{Fe}_2\text{O}_3$ (maghemite) + H_2O has been described by different authors and the presence of maghemite in soil has often been attributed to the dehydroxylation of goethite or lepidocrocite by burning in the presence of organic matter (Taylor and Schwertmann, 1974; Annand and Gilkes, 1987; Stanjek, 1987). Taking as reference the goethite, the weight loss to be transformed into maghemite would be of 10.1 g per 100 g of goethite. This loss of weight is accompanied by a

volume loss, since maghemite is denser (4.9 g/cm^3 for maghemite versus 4.3 g/cm^3 for goethite; Cornell and Schwertmann, 1996). Considering both (weight and volume) loss together, results that 1 cm^3 of goethite produce with the heating treatment 0.78 cm^3 of maghemite (22% volume loss). On the other hand, S-1 (as S-2) contains the phyllosilicate kaolinite in a relatively abundant phase (Table 2), which is sensitive to heating and at around $700 \text{ }^\circ\text{C}$ would be destroyed (Richardson, 1972). This fact is also observable in Fig. 7 with the disappearance of the 0.358 nm peak of kaolinite in the heated sample. The thermic reaction produced is: $\text{Si}_2\text{O}_5(\text{OH})_4\text{Al}_2$ (kaolinite) \rightarrow $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (metakaolinite) + H_2O . The loss of weight in this case is a (13.9 %) accompanied by a similar loss of volume taking into account that both minerals have a similar density (approx. 2.60 g/cm^3 ; Varga, 2007). These mineralogical modifications in iron oxides and phyllosilicates that imply changes in weight and volumes must be taken into account in the discussion of the microfabric transformations evidenced as a consequence of the heating treatment.

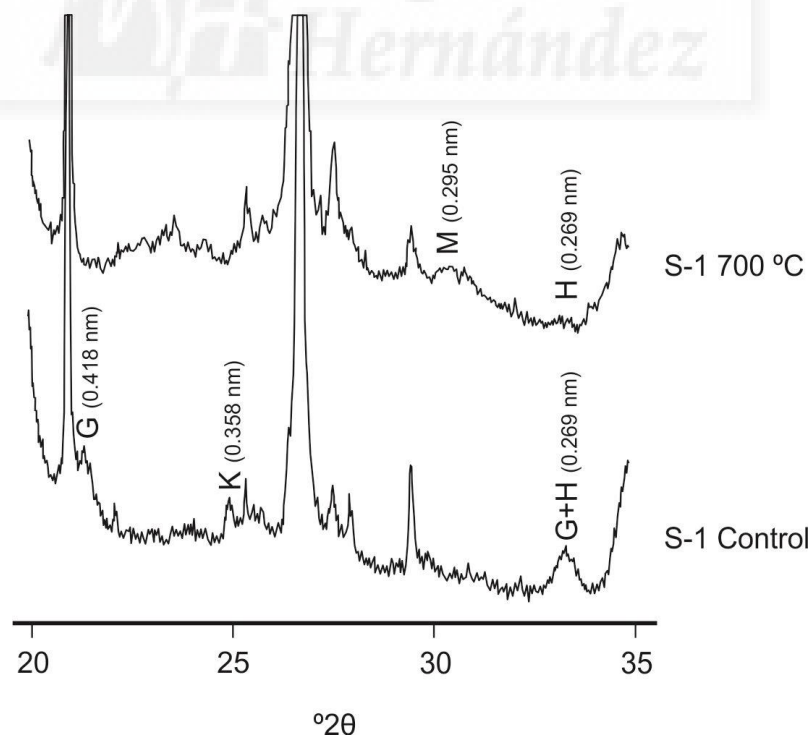


Figure 7. XRD profiles for S-1 samples (non-oriented dust) in the sector $20 - 35 \text{ }^\circ 2\theta$. Abbreviations: G = goethite; H = hematite; K = kaolinite; M = maghemite.

The observed changes in the micro-structure (SEM-EDX) of the analysed aggregates, and the images and data obtained, help to corroborate our hypothesis about the direct relationship between the heating impact and the increase of AS. The most immediately observable heating impact on the surfaces of the aggregates appears to be the increase of the soil porosity (Fig. 6b, 6f). However, this fact was accompanied by processes causing an increase in the compactness of the structure units if we compare them with the control (unheated) aggregates (Figs. 6a, 6c, 6e).

We can also see differences in the microfabric response to heating between the Alfisol and the Entisols. S-1 (Alfisol) retained the cemented laminar fabric observed in the unheated sample (Fig. 6a) when heated (Fig. 6b), but the mineralogical variations which occurred, mainly in phyllosilicates (kaolinite) and iron (hydr)oxides (goethite) –the two main cementing agents responsible for this laminar cemented micro-structure– caused some changes. Due to the above mentioned loss of weight and volume as a consequence of the transformations of goethite and kaolinite to maghemite and metakaolinite, respectively, together with weight loss because of SOM combustion (9%, Table 1), a compaction and retraction of the mass is produced in S1 generating thermal contraction crevices clearly visible in SEM (Fig. 6b). In addition, these soil components modified by the heating impact produced new gas and liquid compound that have to be liberated by escaping out of the sample. This is done by opening new pores between particles and relatively big vesicles (>20 μm) in a way as “smokestacks” (Fig. 6b). The nature of these fleeting phases at 700 °C will be mainly H₂O, as discussed with the mineral transformations and because the SOM combustion will be generated also H₂O together with CO₂ and other gases, including sulfur as can be demonstrated by the S peak found in the EDX-spectra of vesicle edge (Fig. 6b). With SEM-EDX analysis we have also recognized small crystals rich in Ca with a neoformation appearance in the edge vesicles formed by outgassing. They are probably carbonates, formed from the CO₂ of SOM and Ca (included in SOM or in

soil solution in the soil pores). Presumably this mineral phase is calcite (CaCO_3), stable calcium carbonate in the supergene conditions of these soils.

The Entisols S-2 and S-3, showed a different reaction to heating than the Alfisol, S-1, as their microfabric and cementing agents are different: essentially calcium carbonate and SOM. The microfabric of S-2 and S-3 control samples (Figs. 6c, 6e) is skeletal-cemented by a CaCO_3 matrix, with SOM presence (manifested by vegetal debris). At 700 °C (Fig. 6f) the fabric evolves closer to skeletal, with an increase in porosity. We can then refer to a CaCO_3 recrystallization, as more labile cement with heat than iron forms or phyllosilicates as kaolinite, and fitting moreover with combustion of SOM, generating CO_2 , basic component of CaCO_3 . The weight and volume loss involved induces an increase in porosity, justified by the 13% and 7% of SOM in S-2 and S-3, respectively. The recrystallization process of the carbonated matrix at 700 °C is evident with SEM images in both soils, S-2 and S-3. For S-2 this process is also corroborated by the increase in the relative abundance of the two carbonates present, calcite and dolomite (Table 2), and also supported by the observations of growth bands in the faces of dolomite crystals after the heating treatment of 700 °C (Fig. 6d).

Despite the two Entisols of the study showing common characters in their micro-structure and later evolution when heated to 700 °C, they also showed differences. In S-2 the carbonate is mainly dolomite, although with small quantities of calcite detected (Table 2), these are enough to cement aggregates, as can be checked in the EDX spectra of the matrix with an important peak of Ca (Fig. 6c). When S-2 is heated, perhaps due to a higher contents of phyllosilicates (and iron, as can be recognized in the EDX spectra), regarding S3, the microfabric does not develop a system of big pores, and does not show (as in S-3) a beginning of destruction of structure (Fig. 6f).

The AS increase observed with the heating treatment in S-1, S-2 and S-3 (Fig. 4) can be explained with the results of SEM-EDX, since the structural units (particles, clusters, or microaggregates) are more compact as a consequence of the processes described above regarding mineral changes, recrystallizations and the combustion of labile cements as SOM.

In view of the mineralogical and microstructural-microanalytical evidences found with XRD y SEM-EDX, we are, in general, in agreement with Giovannini et al. (1990). They established that in some soils, the heat during a fire, produces a new aggregation of particles by mineral recrystallization. Giovannini (1997) affirmed that the recrystallization of iron forms could be considered as a kind of “laterization” because of the increase of resistance of aggregates to breakdown. However, we disagree with the use of this term for this process. Despite the fact that we have observed the transformation from goethite to maghemite in S-1 and an increase in AS, other features necessary in the identity of laterization process (extreme leaching of basic cations and silice by weathering process; typical of tropical soils) are not involved here.

CONCLUSIONS

High heating temperatures produced an increase in the AS despite the decrease of the SOM content and the initial aggregate destruction with the heating temperature treatments. The real AS increase observed was mainly caused by the mineralogical modifications due to the heating impact, supporting our initial hypothesis. The three studied soils by SEM-EDX, at the unheated conditions, were different in types of fabric. Such differences were mostly dependent on their mineralogical composition, particle size and various properties in which is highlighted the cementation: model and components. The heating impact caused structural modifications on the selected aggregates studied, with mineral modifications that were accompanied by a loss of weight

and volume and an increase of compactness of soil micro-fabric units. These changes in cementing minerals lead to a stabilization of the aggregate structure and hence an increase in the AS, but these processes are accompanied by a loss in SOM and an initial destruction of macro-aggregates. Therefore, despite this increase in AS, soils affected to this temperatures of heating suffer degradation. More detailed studies of mineralogical and microfabric changes in these Mediterranean soils as a result of the heating impact would be interesting to conduct in the near future with the aim of achieving much more definitive conclusions.

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CONCLUSIONES/CONCLUSIONS

CONCLUSIONES

La investigación realizada en esta Tesis Doctoral supone una contribución con avances en el conocimiento del efecto del fuego en varias propiedades edáficas, como son la agregación y la repelencia al agua de suelos mediterráneos, tratando de dar respuesta a algunas preguntas que hasta la fecha no estaban resueltas. Los resultados obtenidos de los experimentos realizados, tanto en campo como en laboratorio, han permitido obtener las siguientes conclusiones generales que se detallan a continuación:

- i. El fuego produjo un aumento de la repelencia al agua del suelo, sólo bajo la presencia de pino y no bajo matorral. El comportamiento de esta propiedad tras el impacto del fuego, y a lo largo del proceso de evolución post-incendio, fue significativamente diferente respecto a la zona control (no afectada por el fuego). Durante los primeros años tras el paso del incendio, la repelencia al agua tendió a disminuir, aunque con algún aumento ocasional tras los períodos de sequía estival. El tipo de vegetación dominante en la zona afectada y la presencia, ausencia o incorporación de las cenizas generadas por la combustión, en los primeros centímetros del suelo, juegan un papel decisivo en el comportamiento de esta propiedad tras el paso del fuego.
- ii. La repelencia al agua en suelos quemados es sensible a la humedad relativa del aire. Este efecto es ligeramente mayor cuanto mayor es la humedad relativa del aire. Dicho comportamiento se observa a las temperaturas de calentamiento de 250, 300 y 350 °C y en las muestras tomadas bajo pino.
- iii. En los suelos mediterráneos estudiados, la estabilidad de los agregados del suelo se ve incrementada con temperaturas altas de calentamiento. Según los resultados obtenidos, este aumento es principalmente debido a las

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alteraciones mineralógicas producidas, sobre la superficie de los agregados, por el efecto del calentamiento. Dichos cambios mineralógicos, junto con la también observada destrucción de materia orgánica, producen una pérdida de peso y volumen en los agregados, al igual que un aumento de la compactación de la micro-fábrica de las partículas que los forman, generando cambios morfológicos y estructurales, que ayudan a explicar el aumento de la resistencia de los mismos a la ruptura.



CONCLUSIONS

Research carried out in this Doctoral Thesis is a contribution to advances in the understanding of the effect of fire on several soil properties, such as aggregation and water repellency in Mediterranean soils, trying to respond to some questions that have not been resolved so far. The results of the experiments conducted in both field and laboratory conditions, have yielded the following general conclusions that are detailed below:

- i. The fire caused an increase in soil water repellency, only under the influence of pine and not under shrubs. The behavior of this property following the impact of the fire, and throughout the whole post-fire evolution process, was significantly different from the control area (not affected by the fire). During the first years after the passage of the fire, water repellency tended to decrease, however, with some occasional increases after summer drought events. The dominant vegetation type in the affected area and also the presence, the absence or even the incorporation of the ash generated by the combustion, in the first few centimeters of topsoil, all play a decisive role in behavior after the impact of the fire.
- ii. The water repellency detected in burned soil is sensitive to air relative humidity. This effect is slightly increased with greater relative air humidity. Such behavior is observed in samples heated at 250, 300 and 350 °C and taken under pine influence.
- iii. The soil aggregate stability is increased with the high heating temperatures in the studied Mediterranean soils. According to the obtained results, this increase is primarily due to the mineralogical changes produced on the aggregate surfaces by the effect of heating. Such mineralogical changes along with the observed destruction of organic matter, involve a weight and volume loss of the aggregates, and also a micro-fabric compaction increase

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of their particles, generating morphological and structural changes which help to explain the increased resistance of the aggregates to be broken.

