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PhD Thesis - Tesis Doctoral

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PhD thesis written by

Dña. MARÍA LUISA FERNÁNDEZ ROMERO

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Córdoba, 17 de Noviembre de 2015

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INFORMAN

Que el trabajo, **"Efectos en el carbono orgánico del suelo en función del manejo, del uso y de las variables geográficas en climas Mediterráneo y Templado"**, realizado por la Licenciada en Ciencias Ambientales Dña. María Luisa Fernández Romero, bajo nuestra dirección se encuentra finalizado y puede ser presentado para su exposición y defensa como Tesis Doctoral en la Universidad de Córdoba.

Córdoba 17 de Noviembre de 2015

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TÍTULO DE LA TESIS

"Effects of management, land use and geographical variables on soil organic carbon in Mediterranean and Temperate climate" - "Efectos en el carbono orgánico del suelo en función del manejo, del uso y de las variables geográficas en climas Mediterráneo y Templado"

DOCTORANDO/A

María Luisa Fernández Romero

INFORME RAZONADO DEL/DE LOS DIRECTOR/ES DE LA TESIS

Esta tesis doctoral es una contribución, en términos generales, al conocimiento sobre el carbono orgánico del suelo-SOC en climas Mediterráneos y Templados y en términos particulares sobre la variación de SOC en función de los cambios de uso y manejo. El proyecto de tesis se realiza en Torredelcampo-Jaén (Comarca de la Campiña Sur de Jaén), Hinojosa del Duque, Pozoblanco y en Berkshire (Sureste de Reino Unido).

En la tesis se realiza en primer lugar el análisis de los stocks de SOC en función de la topografía (gradiente topográfico - catena de suelos) y su efecto en el cambio de uso de forestal a olivar. En segundo lugar, se analiza la distribución en profundidad del SOC en función del manejo en suelos de olivar. En tercer lugar, se analiza la calidad de los suelos a partir del índice de estratificación en los suelos de olivar estudiados anteriormente. Y en cuarto y último lugar, se aplican técnicas ópticas para la determinación y caracterización de la materia orgánica del suelo en los suelos estudiados con anterioridad, además de otros usos (cereal) en Jaén y en Berkshire.

De manera general, se ha intentado, analizar el papel del suelo como sumidero de carbono, comparando la evolución que han tenido los suelos, en función del cambio de uso y manejo (objeto de la presente memoria de tesis doctoral).

Los resultados que ofrece esta tesis pueden servir, en primer lugar, como estrategia en la reducción de gases efecto invernadero (CO_2) y en segundo lugar para reflexionar si el cambio de uso y manejo en el tiempo mejora o no las propiedades físicas y químicas del suelo.

La tesis doctoral, se articula en cuatro trabajos publicados o en fase de publicación, con los indicios de calidad que se mencionan a continuación:

- **Topography and land use change effects on the soil organic carbon stock of forest soils in Mediterranean natural area**s. Agriculture, Ecosystems and Environment 195 (2014) 1-9. DOI:10.1016/j.agee.2014.05.015. Base de indexación: ISI Web of Knowledge, Journal Citation Index. Lugar que ocupa en el área temática: Agriculture,

multidisciplinary: 1 de 56; Ecology: 36 de 145; Environmental sciences: 36 de 223. Impact factor 3.402. Número de citas hasta la fecha: Scopus (5), Google Scholar (6).

- **Effects of land management on different forms of soil carbon in olive groves in Mediterranean areas.** Land degradation & development (DOI: 10.1002/ldr.2327). Base de indexación: ISI Web of Knowledge, Journal Citation Index. Lugar que ocupa en el área temática: Environmental sciences: 50 of 223. Soil Science: 3 of 34. Impact factor 3.089. Número de citas hasta la fecha: Scopus (0), Google Scholar (3).

- **Evaluation of optical techniques for characterising soil organic matter quality in agricultural soils.** Soil & Tillage Research 155 (2016) 450-460 (DOI: 10.1016/j.still.2015.05.004). Base de indexación: ISI Web of Knowledge, Journal Citation Index. Lugar que ocupa en el área temática: Soil science: 9 of 34. Impact factor 2.622. Número de citas hasta la fecha: Scopus (0), Google Scholar (1).

- **Soil quality assessment based on carbon stratification index in different olive grove management practices in Mediterranean areas.** Catena 137 (2016) 449-458 (DOI: 10.1016/j.catena.2015.10.019). Base de indexación: ISI Web of Knowledge, Journal Citation Index. Lugar que ocupa en el área temática: Geosciences, multidisciplinary: 32 of 175. Soil science: 5 of 34. Water resources: 8 of 83. Impact factor 2.820. Número de citas hasta la fecha: Scopus (0), Google Scholar (0).

Por todo ello, se autoriza la presentación de la tesis doctoral.

Córdoba, 17 de Noviembre de 2015

Firma del/de los director/es

Fdo.: LUIS PARRAS ALCÁNTARA   Fdo.: BEATRIZ LOZANO GARCÍA

LA PIEDRA

El distraído tropezó con ella.

El violento la utilizó como proyectil.

El emprendedor construyó, con ella.

El campesino cansado la utilizó como asiento.

Para los niños fue un juguete.

David mató a Goliat y

Miguel Ángel le sacó la más bella escultura.

En todos los casos,

La diferencia no estuvo en la piedra,

sino en el hombre.

No existe piedra en tu camino que no puedas

aprovechar para tu propio crecimiento.

Anónimo

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ABREVIATURAS

BD: densidad aparente.

BIX: Índice biológico.

C: Carbono.

CEC: Capacidad de intercambio catiónico.

CMNUCC: Convención Marco de la Naciones Unidas sobre el Cambio climático.

CT: Labranza convencional.

CWC: Carbono extraído en agua fría.

DOC: Carbono orgánico disuelto.

DOM: Materia orgánica disuelta.

EEM: Matrices de excitación-emisión.

FI: Índice de fluorescencia.

GEIs: Gases efecto invernadero.

HIX: Índice de humificación.

HWC: Carbono extraído en agua caliente.

IPCC: Panel intergubernamental sobre el cambio climático.

LUC: Cambio de uso del suelo.

N: Nitrógeno.

NMR: Resonancia magnética nuclear.

NT: No labranza.

OM: Materia orgánica.

SC: Secciones de control.

SOC: Carbono orgánico del suelo.

SOCS: Carbono orgánico stock del suelo.

SR: Relación de estratificación.

T-SOCS: Total carbono orgánico stock del suelo.

VOC: Compuestos orgánicos volátiles.

ÍNDICE DE FIGURAS

RESUMEN

1. RESUMEN.

Los bosques mediterráneos tienen un importante papel para los ecosistemas ya que contribuyen a la protección del suelo (contra la erosión), participan en el ciclo del agua y regulan el clima tanto a nivel local (a través de la evapotranspiración), como mundial (gracias al almacenamiento de C); son el hábitat de numerosas especies y se consideran por ello protectores de la biodiversidad. En las últimas décadas los suelos forestales han sufrido un cambio de uso transformándose en suelos agrícolas como el olivar, que es uno de los principales apoyos económicos para los habitantes del área mediterránea debido a la importancia del aceite de oliva.

Se ha estudiado el efecto del cambio de uso (de bosque mediterráneo a olivar con labranza tradicional) en función de la topografía determinándose: las variaciones de concentración y stock de carbono y nitrógeno del suelo, además de la relación de estratificación en la campiña sur de Jaén (Torredelcampo). En términos generales, el carbono fue bajo en los dos usos estudiados (en comparación con los valores medios de carbono por tipo de suelo y uso en España), siendo mayor en forestal que en olivar. En forestal decreció en función de la topografía (Punto alto: 32,3 g kg^{-1}, punto medio: 38,3 g kg^{-1} y punto bajo: 33,4 g kg^{-1}, valores en S1). Sin embargo, en olivar la tendencia fue inversa (Punto alto: 11,0 g kg^{-1}, punto medio: 13,1 g kg^{-1} y punto bajo: 22,3 g kg^{-1}, valores en S1) debido a los procesos de erosión-sedimentación. El stock de carbono siguió un patrón similar al de la concentración de carbono en ambos usos. En general, la concentración de nitrógeno disminuyó con el cambio de uso. En olivar, el nitrógeno siguió el mismo patrón de comportamiento que la concentración y el stock de carbono, mientras que en forestal no se apreció una tendencia clara. La calidad del suelo también se vio reducida por el cambio de uso. Además se produjo un aumento de calidad de los suelos en las posiciones topográficas más bajas en olivar mientras que hubo una reducción en la calidad de los suelos en forestal en las mismas.

Además del deterioro de la calidad del suelo debido al cambio de uso, los suelos de olivar están sujetos a una intensa degradación y su grado de deterioro depende fundamentalmente del clima, textura y manejo. Debido a que la gestión del suelo puede afectar a sus propiedades físico-químicas (particularmente el carbono orgánico del suelo) se han desarrollado una serie de alternativas en los últimos años con el fin de paliar esos efectos negativos. Hay varias razones para la introducción de diferentes manejos. Por un lado, el interés en paliar los efectos adversos de la labranza tradicional (degradación de los suelos debido a las elevadas tasas de erosión y empobrecimiento de los mismos por la pérdida de nutrientes que conlleva), y por otro lado, la necesidad de reducción de la concentración de CO_2 atmosférico que deriva en el intento de utilizar el suelo como sumidero de C, apostando por aquellos manejos que consigan almacenar más carbono orgánico en suelo. Además, cuando el suelo contiene más carbono orgánico, no sólo funciona como sumidero de C reduciendo la cantidad de CO_2 atmosférico sino que también mejoran las propiedades físico-químicas del mismo convirtiéndose en un mejor soporte para la agricultura. Algunas de estas alternativas

pasan por la agricultura de conservación (mínimo laboreo y siembra directa) y otras por el uso de ciertos subproductos a modo de cubiertas vegetales. Para ello, la labranza convencional, que es la que normalmente se emplea, se usó como control. A esta labranza tradicional se le añadió alperujo, y hoja de olivo procedente del proceso de limpieza de la aceituna en la almazara antes de su molturación y se estudiaron además suelos no labrados con la adición de restos de poda, y con restos de poda y cubierta vegetal. En éste caso se determinó tanto carbono orgánico como carbono orgánico disuelto del C extraído en agua caliente. El carbono orgánico total del suelo fue muy similar al control y para los manejos con alperujo y no labranza con restos de poda, mientras que en el caso de la no labranza con restos de poda y cubierta vegetal y el de labranza tradicional con hoja tuvieron valores más elevados (49,5 y 158,1 g kg^{-1} respectivamente). En todos los casos el carbono orgánico disminuyó en profundidad salvo en el segundo horizonte del manejo de labranza tradicional con hoja, que incrementó en comparación con el horizonte superficial. El manejo de no labranza con restos de poda no tuvo diferencias significativas con el control. Sin embargo, el otro manejo de no labranza sí supuso un incremento en el contenido de carbono orgánico del suelo debido a que incluía la cubierta vegetal. El stock de carbono orgánico fue muy similar para el control y los manejos de labranza tradicional con alperujo y no labranza con restos de poda. Las principales diferencias en el contenido de stock de carbono orgánico se encontraron en los primeros 100 cm de todos los tratamientos (siendo el mayor valor en el manejo con labranza tradicional y adición de hoja). El carbono disuelto extraído en agua caliente disminuyó con la profundidad en todos los manejos excepto en el de labranza tradicional y adición de hoja. Los valores de carbono disuelto extraído en agua caliente fueron muy similares en el control y los manejos de labranza tradicional con alperujo y no labranza con restos de poda, pero no así en el de no labranza con restos de poda y cubierta vegetal, donde fue mayor en su horizonte superficial. En el caso del manejo con labranza tradicional y la adición de hoja, los valores son mucho más altos que en el resto de tratamientos.

En los suelos con labranza (control, alperujo y con hoja) la materia orgánica se distribuyó a lo largo del perfil, almacenándose (stock de carbono orgánico) en las capas más profundas. Sin embargo, en la no labranza con restos de poda no ocurrió lo mismo, ya que la materia orgánica se mantuvo en la capa superficial del suelo. En el manejo sin labranza y con restos de poda y cubierta vegetal las raíces de la cubierta vegetal facilitaron su distribución. El stock de nitrógeno siguió el mismo patrón que el stock de carbono orgánico.

También se determinó la calidad de los suelos bajo estos cinco manejos mediante la relación de estratificación. Ésta siempre fue mayor bajo no labranza que bajo labranza tradicional. La relación de estratificación del carbono orgánico del suelo aumentó desde la capa superficial a las más profundas en todos los casos. En este sentido, el 65 % del total de los valores de relación de estratificación presentaron valores mayores a 2. La adición de alperujo y hoja a los suelos bajo labranza tradicional mejoraron el carbono orgánico del suelo en los horizontes superficiales en comparación con horizontes más

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profundos. Por otra parte, el manejo de labranza tradicional con hoja mostró un contenido de carbono orgánico mucho mayor en el primer y segundo horizonte que en horizontes más profundos. La relación de estratificación de nitrógeno disminuyó con la profundidad para todos los manejos. Aproximadamente la mitad de éstas fueron mayores a 2. La relación de estratificación del cociente C:N se caracterizó por valores muy bajos para todos los manejos. A pesar de ello los valores más elevados fueron para suelos bajo no labranza.

Aparte de la determinación de la relación de estratificación, el contenido y caracterización de la propia materia orgánica nos da una idea del estado de las propiedades del suelo, así como de sus condiciones. Es relevante el estudio de las sustancias húmicas en suelos agrícolas ya que aumentan la productividad de los cultivos. Además, su determinación y caracterización da una información clave de la maduración y estrés de los suelos, así como su salud. La resonancia magnética nuclear de protón es una de las técnicas más ampliamente aceptada para este fin debido a su eficacia, pero su gran coste económico, equipamiento, material, sofisticación y tiempo requerido hace que no esté al alcance de todos los usuarios. Se estudió una selección de algunas de las técnicas ópticas (absorbancia, fluorescencia y medición de carbono orgánico disuelto de la extracción caliente) más eficientes económicamente para estimar su potencial para sustituir a técnicas que requieren más recursos como la resonancia magnética nuclear de protón. Para mejorar la precisión de los resultados y validarlos, se han usado muestras de suelos de diferentes zonas climáticas (Mediterránea (Andalucía, Sur de España) y Templada (Berkshire, sureste de Inglaterra)). Se encontraron fuertes correlaciones ($p < 0,001$) entre la fracción aromática medida con resonancia magnética nuclear y SUVA-254[1] (Rs = 0,95), carbono orgánico disuelto de la extracción caliente (Rs = 0,90) e índice de fluorescencia (Rs = -0,976). Por lo tanto, se concluyó que las técnicas ópticas tienen el potencial para caracterizar la materia orgánica (predecir la fracción aromática) y de esta forma sustituir a la resonancia magnética nuclear de protón para algunas aplicaciones, lo cual ha sido verificado en suelos bajo dos condiciones climáticas distintas.

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[1] Cociente entre la absorbancia a 254 nm y la concentración de carbono orgánico disuelto expresado en L mg^{-1}m^{-1}

ABSTRACT

2. ABSTRACT.

Mediterranean forests are fundamental to ecosystem function. They contribute to soil protection (against erosion), participate in the water cycle and assist in regulating climate at local (evapotranspiration) and global (C storage) level. They also include habitats of many species and are therefore considered biodiversity protectors. In the last decades, forest soils have suffered from land use change to become agricultural soils supporting activities such as olive oil production, a mainstay of the Mediterranean economy.

The effect of land use change (from a Mediterranean forest to olive grove under conventional tillage) dependant on the topography has been studied. The following has been determined: soil organic carbon and nitrogen concentration and stock variations, as well as the stratification ratio in the southern countryside (*campiña*) of Jaen (municipality of Torredelcampo). In general terms, soil organic carbon concentration was low in both of the studied land uses (compared to mean values per soil and land use type in Spain), with higher values in forest soils than in olive grove soils. Soil organic carbon decreased according to topography (Summit: 32.3 g kg^{-1}, backslope: 38.3 g kg^{-1} and toeslope: 33.4 g kg^{-1}; in S1). However, the trend was the opposite in olive grove soils (Summit: 11.0 g kg^{-1}, backslope: 13.1 g kg^{-1} and toeslope: 22.3 g kg^{-1}; in S1) due to erosion-sedimentation processes. Soil organic carbon stock followed a similar pattern to that of the soil organic carbon concentration for both land uses. Generally, nitrogen concentration decreased as a result of land use change. In olive grove soils, nitrogen followed a similar pattern to that of the soil organic carbon concentration and stock, whereas no clear pattern was observed in the forest soils. Soil quality was reduced as a result of land use change. Also, there was an increase of the quality of olive grove soils in the lower topographical positions, whereas there was a decrease in the quality of forest soils in these topographical positions.

Apart from the deterioration of soil quality due to land use change, olive grove soils suffer significant degradation, with a severity which depends on climate and on soil texture and management. Management techniques may affect physical-chemical properties of soils (particularly soil organic carbon) and several alternatives have been developed in recent years in order to mitigate negative effects. There are various reasons that led to the introduction of the various soil management techniques that exist. On the one hand, they aim to alleviate the adverse effects of conventional tillage (soil degradation due to high erosion rates and soil impoverishment caused by the loss of nutrients). Also, they seek to achieve significant levels of soil organic carbon capture as part of providing a C sink to mitigate increases in atmospheric CO_2. Higher soil organic carbon levels in soils also improve physical-chemical properties related to agriculture. Techniques include those with low levels of disturbance, such as minimal tillage and direct sowing (conservative management), and others which use by-products from agricultural processing as vegetative cover. In order to assess the efficacy of different techniques, conventional tillage, which is most commonly used, was chosen as a

control. It was compared with the following alternatives: conventional tillage with *alperujo*[2]; conventional tillage with olive tree leaves from the olive cleaning process at oil mills; No-tillage soils with the addition of olive prunings; and no-tillage soils with olive prunings and vegetative cover. All techniques were assessed for soil organic carbon and dissolved organic carbon of the hot-water extraction. Total soil organic carbon levels were very similar for the control and under conventional tillage with alperujo and no-tillage with olive prunings; whereas the cases of no-tillage with olive prunings and vegetative cover and conventional tillage with leaves showed higher values (49.5 g kg^{-1} and 158.1 g kg^{-1}, respectively). Soil organic carbon decreased with depth in all cases except for the second horizon in the case of soil under conventional tillage with leaves, where it was higher than in the first horizon. The management technique consisting of no-tillage with olive prunings did not show a significant difference in soil organic carbon from the control. However, SOC increased in the other technique with no-tillage due to the vegetative cover. Soil organic carbon stock was very similar for the control and for the management techniques with conventional tillage and alperujo, and no-tillage with olive prunings. For all techniques, the main differences in measured soil organic carbon stock values were found in the upper 100 cm of the soil layer with the highest value under conventional tillage with the addition of olive leaves. Dissolved organic carbon of the hot-water extraction decreased with depth for all techniques except under conventional tillage with the addition of olive leaves. The values of dissolved organic carbon of the hot-water extraction obtained were very similar for the control and under conventional tillage with alperujo and no-tillage with olive prunings. However, this was not the case under no-tillage with olive prunings and vegetative cover, which showed a surface horizon with higher values while the technique with conventional tillage and olive leaves had much higher values.

Organic matter was distributed throughout the entire profile for soils under conventional tillage (control, alperujo and olive leaves) with organic matter stored (Soil organic carbon stock) in the deepest soil layers. However, under no-tillage with olive prunings, organic matter remained in the surface while under no-tillage with olive prunings and vegetative cover, organic matter was evenly distributed despite not being tilled, due to the vegetative cover. Under all techniques, nitrogen stock followed the same pattern as the soil organic carbon stock.

The quality of the soils managed using the five techniques was also determined with the stratification ratio. Measured values were always higher in soils with no-tillage than with conventional tillage. The stratification ratio of soil organic carbon increased from the surface to deeper layers in all cases. Overall, 65 % of all the stratification ratio values were higher than 2. The addition of *alperujo* and olive tree leaves to soils under conventional tillage increased soil organic carbon in the surface horizons compared to deeper horizons. On the other hand, soils under conventional tillage with olive tree leaves showed a much higher soil organic carbon content in the first and second horizon

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[2] Alperujo is the solid sludge waste generated by the new two-phase method of olive oil extraction

than in deeper horizons. The stratification ratio of nitrogen decreased with depth for all treatments.

Approximately half of the stratification ratios of N were higher than 2. The stratification ratio of C:N ratio was characterised by very low values for all techniques. Nevertheless, the highest values among these were found in soils under no-tillage.

Alongside the stratification ratio, organic matter content and characterisation give an idea of the soil's condition and properties. The study of humic substances is relevant, since their presence increases crop yield. Moreover, by determining and characterising humic substances, it is possible to obtain essential information about maturity, stress and health of soils. Proton nuclear magnetic resonance is one of the most widely accepted methods for organic matter determination and characterisation due to its effectiveness. However, its high costs and associated requirements for equipment, material, sophistication and time makes it unsuitable for some applications. A selection of some of the most efficient optical techniques (absorbance, fluorescence and measurement of the dissolved organic carbon of the hot-water extraction) were assessed in this study to estimate their potential for the replacement of other techniques that require more resources such as proton nuclear magnetic resonance. In order to improve accuracy and validate results, samples from soils located in two different climatic zones (Mediterranean (Andalusia, south of Spain) and temperate (Berkshire, southeast England)) were used. High correlations ($p < 0.001$) were found between the specific aromatic fraction measured with proton nuclear magnetic resonance and SUVA-254[3] (Rs = 0.95), dissolved organic carbon of the hot-water extraction (Rs = 0.90), and fluorescence index (-0.976). Therefore, it was concluded that optical measures have the potential to characterise organic matter effectively through prediction of the aromatic fraction and replace proton nuclear magnetic resonance for some applications, which has been verified in soils with various climatic conditions.

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[3] Ratio of absorbance measured at 254 nm and the concentration of dissolved organic carbon expressed as L mg^{-1}m^{-1}

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INTRODUCCIÓN

3. INTRODUCCIÓN.

3.1. CAMBIO CLIMATICO Y ACTIVIDAD HUMANA.

3.1.1. Visión global del cambio climático y sus implicaciones ambientales.

Hay una aceptación generalizada de que el clima está cambiando debido a las emisiones antropogénicas de los gases de efecto invernadero (GEIs). Estos cambios afectarán a todos los sectores de la sociedad y el medio ambiente, a todas las escalas (desde el territorio continental hasta los niveles nacional y local). Los ciudadanos interesados y personas encargadas de tomar decisiones deben de poder acceder a información fiable y con base científica que les ayude a reaccionar frente a los riesgos de los impactos del cambio climático y evaluar sus oportunidades de adaptación (Kovats *et al.*, 2014).

La intensidad y la certeza de las señales del cambio climático producidas por una gama de modelos climáticos globales y regionales han permitido determinar los efectos de los impactos del cambio climático en el futuro y sugieren que el Mediterráneo podría ser una región especialmente vulnerable (Kovats *et al.*, 2014).

Algunos de los cambios que evidencian la presencia del cambio climático (Jiang *et al.*, 2015; Moniruzzaman, 2015; Purton *et al.*, 2015; Simonneaux *et al.*, 2015) son:

(1) Cambios en el clima (temperatura, precipitación y viento): Desde 1950, cada vez han sido más frecuentes las altas temperaturas extremas (días calurosos, noches tropicales, y olas de calor), mientras que las bajas temperaturas extremas (olas de frío, días de heladas), se han vuelto menos frecuentes (EEA, 2012). Desde esta misma fecha, la precipitación anual se ha incrementado en el norte de Europa más de 70 mm por década, mientras que en algunas partes del sur han disminuido (Kjellström *et al.*, 2011; EEA, 2012). En cuanto al viento, su velocidad media en Europa ha disminuido en las últimas décadas (Vautard *et al.*, 2010). Por el contrario, el nivel medio del mar se ha caracterizado por un aumento con variaciones regionales, excepto en el norte del Mar Báltico debido al movimiento vertical de la corteza (Haigh *et al.*, 2010; Menéndez y WoodWorth, 2010; Albrecht *et al.*, 2011; EEA, 2012). En un futuro se prevé una disminución de la precipitación en los meses de verano hasta el sur de Suecia y un aumento en invierno, con más lluvia que nieve en las regiones montañosas (Steger *et al.*, 2013; Kovats, *et al.*, 2014).

(2) Cambios en las masas de agua: Los caudales han disminuido en el sur y este de Europa, mientras que en el norte se ha producido un aumento (Stahl *et al.*, 2010; Wilson *et al.*, 2010). Las diferencias entre el norte y el sur de Europa en relación a los recursos hídricos serán cada vez mayores. En el sur, las condiciones de saturación y drenaje estarán cada vez más restringidas a los períodos de invierno y primavera. Mientras que el norte y Europa continental presentarán un mayor riesgo de inundación, aumentando

los daños en cultivos, así como la complejidad para manejar el suelo y la variabilidad en la producción (Falloon y Betts, 2010; García-Ruiz *et al.*, 2011; Olesen *et al.*, 2011).

También aumentará la demanda de agua de regadío (Savé *et al.*, 2012). En el área mediterránea, donde se reducirán tanto la escorrentía como las aguas subterráneas, la irrigación no puede ser una opción viable (Olesen *et al.*, 2011). Por ello, para asegurar el suministro de agua en un futuro y evitar de esta forma tensiones entre los usuarios, es conveniente llevar a cabo una gestión adecuada.

(3) *Aparición de sequías, plagas e incendios forestales*: Según Sousa *et al.* (2011), las sequías aumentarán en el sur de Europa, siendo éstas más intensas y largas, aunque todavía los indicios detectados son inconsistentes. El cambio climático ha afectado a la salud animal en Europa, ya que ha sido el causante de la propagación de virus (Arzt *et al.*, 2010; Randolph y Rogers, 2010; Van Dijk *et al.*, 2010; Guis *et al.*, 2012; Petney *et al.*, 2012). Sin embargo, los países nórdicos han estado protegidos de los daños causados por los patógenos de plantas y plagas de insectos debido a los fríos inviernos y al aislamiento geográfico que poseen. Esto puede cambiar para el año 2050 a causa del cambio climático (Hakala *et al.*, 2011; Roos *et al.*, 2011). Algunas plagas podrían ampliar su nicho climático y expandirse hacia otras áreas. Además, la producción ganadera se verá afectada negativamente por las altas temperaturas (Kovats, *et al.*, 2014).

En relación con los incendios forestales, hay que señalar que desde la década de 1970 se ha ido incrementando la frecuencia y la extensión de los mismos en el sur de Europa (Lindner *et al.*, 2010; Carvalho *et al.*, 2011; Dury *et al.*, 2011; Vilén y Fernandes, 2011). Esto ha sido fomentado por el cambio climático, la acumulación de combustibles y los fenómenos meteorológicos extremos (Carvalho *et al.*, 2011; Koutsias *et al.*, 2012; Pausas y Fernández-Muñoz, 2012). La cuenca mediterránea ha sido especialmente castigada por este fenómeno en los últimos años (Fernandes *et al.*, 2010; Marques *et al.*, 2011; Koutsias *et al.*, 2012; Pausas y Fernández-Muñoz, 2012).

(4) *Agricultura:* La distribución regional de los impactos del cambio climático en la producción agrícola puede variar ampliamente (Donatelli *et al.*, 2012; Iglesias *et al.*, 2012). Alcamo *et al.* (2007) afirmaron que la idoneidad de los cultivos es probable que cambie en toda Europa. Durante los calurosos veranos de 2003 y 2010 las pérdidas de grano/cosechas fueron del 20 y 25-30 % en las regiones afectadas de Europa y Rusia, respectivamente (Barriopedro *et al.*, 2011; Kovats *et al.*, 2014). En la década de 2080, se prevé un aumento de semillas oleaginosas templadas (por ejemplo, girasol), cultivos de almidón (por ejemplo, patatas), cereales (por ejemplo, cebada) en el norte de Europa como resultado del incremento de las temperaturas, mientras que en el sur de Europa se espera una disminución debido al aumento de las sequías (Kovats *et al.*, 2014). El sur de Europa experimentaría las mayores pérdidas de producción (25 % en 2080, con un calentamiento de 5,4 ºC) (Ciscar *et al.*, 2011). Estos aumentos no siempre han producido efectos negativos históricamente. En Europa del norte podría darse un incremento en la productividad de los cultivos, esto sucedería en combinación con la

expansión climática (entre 2,5 °C y 5,4 °C de calentamiento regional) (Bindi y Olesen, 2011).

Los bosques reaccionarán al cambio climático con una serie de cambios en la tasa de crecimiento, fenología, composición de las comunidades animales y vegetales. El deterioro de los bosques y la mortalidad de los árboles se ha observado en el sur de Europa debido a las sequías, incluyendo Italia, Chipre, Grecia, Bélgica, Suiza y Francia (Affolter *et al.*, 2010; Allen *et al.*, 2010; Charru *et al.*, 2010; Giuggiola *et al.*, 2010; Bertini *et al.*, 2011; Kint *et al.*, 2012; Rigling *et al.*, 2013). En los bosques húmedos (no considerados en riesgo de sequía) también se ha observado una disminución de su masa vegetal (Choat *et al.*, 2012).

Otro componente que se espera que incremente en los bosques es el dióxido de carbono (CO_2) atmosférico, que junto con las elevadas temperaturas hará que aumente el crecimiento de los mismos y por lo tanto favorezca la producción de madera en el norte de Europa y el Atlántico, al menos a corto y medio plazo (Lindner *et al.*, 2010). Mientras que en el sur y este europeo se darán condiciones adversas debido al aumento de las sequías, por lo tanto, la productividad disminuirá (Lindner *et al.*, 2010; Hlásny *et al.*, 2011; Keenan *et al.*, 2011; Silva *et al.*, 2012). Un aumento en las concentraciones de CO_2, supondría un beneficio inicial para las cosechas de secano, pero esto contrastaría a finales de siglo con reducciones en la productividad agrícola para la mayoría de las subregiones de Europa (Supit *et al.*, 2010). Según las condiciones climáticas previstas, se calcula que para la década de 2070 haya una reducción en la producción de pastizales bajo elevados niveles de CO_2 según unas proyecciones realizadas en Francia (Cantarel *et al.*, 2013).

El cambio climático podría alterar el almacenamiento de carbono (C) terrestre e incluso acelerar el cambio de uso del suelo (LUC, en sus siglas en inglés) debido a los cambios de temperatura, precipitación y concentraciones de CO_2, ya que podrían afectar a la producción primaria, a las entradas de C en el suelo y a sus tasas de descomposición (Srinivasarao *et al.*, 2015). Por lo tanto, con este calentamiento global, la agricultura se enfrenta tanto a las reducciones de las emisiones como a la adaptación en un entorno cambiante (Smith y Olesen, 2010). Esto es de gran relevancia, teniendo en cuenta que esta actividad aporta alrededor de un 10 % del total de las emisiones de GEIs en la Unión Europea (UE) (EEA, 2010).

Las emisiones de CO_2, óxidos de nitrógeno (NO_x), y metano (CH_4) procedentes de la ganadería estaban compensadas por el sumidero de CO_2 proporcionado por los bosques y pastizales entre los años 2000 y 2005 (Schulze *et al.*, 2010). Los residuos de los cultivos y el estiércol aplicados al suelo para mejorar la capacidad de retención de agua pueden contribuir también a la mitigación y adaptación (Smith y Olesen, 2010), al igual que la labranza reducida (o la no labranza (NT, en sus siglas en inglés)) que tienden a reducir la erosión del suelo y la escorrentía (Soane *et al.*, 2012).

(5) *Calidad del aire:* El cambio climático también tendrá efectos complejos y locales sobre la química de la contaminación. La contaminación aérea tiene efectos adversos sobre la salud humana, la biodiversidad y la productividad agrícola (Kovats *et al.*, 2014). Las temperaturas más altas afectan a las emisiones de los compuestos orgánicos volátiles (VOC, en sus siglas en inglés) naturales, que son precursores del ozono (O_3) (Hartikainen *et al.*, 2012).

3.1.2. El contexto socio-político y económico del cambio climático.

En las últimas décadas, ha habido un progreso considerable tanto en la planificación y desarrollo de medidas de adaptación al cambio climático, incluyendo análisis económicos, como en el desarrollo de los servicios climáticos (WMO, 2011; Medri *et al.*, 2012).

La adaptación es la habilidad que tienen las sociedades para ajustarse al cambio climático, buscando su protección frente a la naturaleza, moderando los daños potenciales, aprovechando las oportunidades o haciendo frente a las consecuencias. Las respuestas de adaptación pueden ir desde actividades puramente tecnológicas (como por ejemplo, sistemas de alerta temprana), pasando por cambios de comportamiento (como la variación en la elección de alimentos y actividades recreativas), hasta cambios en la gestión (alteración de prácticas agrícolas) y la política (nuevas regulaciones) (IPCC, 2007a; Aquino, 2011).

A nivel internacional, la UE ha comenzado a planificar la adaptación, a través del intercambio de información (Clima-ADAPT plataforma) y legislación (EC, 2013a). Existe el Libro Blanco de la UE sobre la adaptación al cambio climático (EC, 2009), en el cuál se anima a los Estados Miembros a integrar esta adaptación. Mientras tanto, a nivel nacional y local los gobiernos también están comenzando a supervisar los progresos en materia de adaptación, incluyendo el desarrollo de una serie de indicadores (UK-ASC, 2011).

3.1.3. Regulación y marco de actuación. Protocolo de Kioto.

Tres años después de ser aprobada la Convención marco de la Naciones Unidas sobre el cambio climático (CMNUCC), el Panel intergubernamental sobre el cambio climático (IPCC) publicó su segundo informe en el que concluía que el clima se veía afectado a causa de las emisiones de los GEIs. En 1997, los gobiernos acordaron incorporar el Protocolo de Kioto en respuesta a este informe. Éste contaría con una serie de compromisos jurídicos de los principales países desarrollados y los países en proceso de transición a una economía de mercado.

El Protocolo de Kioto se define como un acuerdo internacional de la CMNUCC que busca "la estabilización de la concentración de GEIs en la atmósfera a un nivel que impida interferencias antropogénicas peligrosas en el sistema climático" y establece una estructura general para los esfuerzos intergubernamentales encaminados a resolver el desafío del cambio climático (FAO, 2002). Fue adoptado en Kioto (Japón) el 11 de diciembre de 1997 y entró en vigor el 16 de febrero de 2005.

Su objetivo era la reducción de las emisiones de los países industrializados en torno a un 5 % con respecto a los niveles de referencia de 1990. Éste debía alcanzarse en el período de 2008 a 2012, fecha en la que se establecerían más períodos de compromisos. Esto es lo que se conoce como el primer período del compromiso del Protocolo de Kioto.

En dicho Protocolo se reconocen todas aquellas actividades que emiten GEIs y que pueden dañar al sistema climático, dado que éste es un recurso compartido y vulnerable. Las fuentes de las que proceden estas actividades son; (1) energía (*quema de combustible*; la industria energética, industria manufacturera y construcción, transporte y otros sectores. *Emisiones fugitivas de combustible*; combustibles sólidos, petróleo y gas natural y otros), (2) procesos industriales (minería, industria química, metalurgia, producción y consumo de halocarbonos y hexafluoruro de azufre y otros procesos), (3) utilización de disolventes y otros productos, y por último, (4) la agricultura (fermentación entérica, aprovechamiento del estiércol, cultivo del arroz, suelos agrícolas, quema en el campo de residuos agrícolas y otros) (FAO, 2002).

La Conferencia sobre el Cambio Climático de Doha celebrada en diciembre de 2012 sirvió para establecer un segundo período de compromiso del Protocolo de Kioto, del 1 de enero de 2013 al 31 de diciembre de 2020. Este compromiso se conoce como la enmienda de Doha. El Consejo acordó proponer una reducción de emisiones del 20 % para la UE, ratificado por sus Estados Miembros.

Asimismo, la UE se ha ofrecido a avanzar hacia una reducción del 30 % antes de 2020 en comparación con los niveles de 1990, como parte de un acuerdo global y completo para el período posterior a 2012, siempre que otros países desarrollados se comprometan a reducciones comparables de emisiones y que los países en desarrollo contribuyan adecuadamente, con arreglo a sus responsabilidades y capacidades. Esta oferta también queda reflejada en la enmienda de Doha.

3.1.4. Cambio climático en España.

La temperatura media en los últimos 100 años se ha elevado ligeramente más en España que en el resto de la UE, siendo especialmente alta en primavera y verano. Este aumento de temperatura media fue de 1,2-1,5 ℃ en España, mientras que fue de 0,74 ℃ globalmente y de 1 ℃ en Europa. Desde 1850 las temperaturas máximas y mínimas en

España han aumentado en un promedio de 0,12 ºC y 0,10 ºC / década respectivamente. Desde 1960, hay una clara tendencia a un menor número de días frescos, siendo estos más cálidos. El aumento de la variabilidad que año tras año se produce en los climas estivales, con una mayor incidencia en las olas de calor y sequías, afecta en mayor medida al sur que al resto de la Península Ibérica.

En las próximas décadas, se pronostican los siguientes cambios: las temperaturas en España irán aumentando de manera constante, aproximadamente unos 0,4 ºC / década en invierno, y 0,6-0,7 ºC en verano. En 2100 la temperatura en el interior de la Península será 5-7 ºC mayor en verano y 3-4 ºC mayor en invierno. Las proyecciones del cambio climático para finales de este siglo (2071-2100) muestran un aumento en la duración media de los períodos de sequía.

La cubierta de nieve en las montañas será menor probablemente, ya que en las regiones más templadas la temperatura de la nieve está cerca del punto de fusión y, por tanto, será muy sensible a los cambios de temperatura. Los Pirineos son propensos a experimentar veranos más calurosos y secos con una disminución de las precipitaciones de hasta el 20 % en 2050. Sin embargo, para la Península Ibérica no hay consenso sobre los cambios en la frecuencia de lluvias torrenciales desde 2070 hasta 2100.

Y por último se prevé que España experimente un alargamiento y una suavización de la temporada turística en 2030. Las tasas de ocupación asociadas a una temporada turística en el Mediterráneo más larga se distribuirán uniformemente, y por lo tanto se aliviará la presión en el suministro de agua en verano y la demanda de energía (WWF, 2007).

3.1.5. El efecto invernadero.

Los científicos han conocido el fenómeno del efecto invernadero natural desde hace más de un siglo (Arrhenius, 1896). Éste consiste en el mantenimiento de la temperatura de equilibrio de la Tierra y se da por el balance entre la energía solar entrante que absorbe la Tierra (radiación de longitud de onda corta) y la energía infrarroja que ésta emite (radiación de longitud de onda larga). Algunas de éstas, se escapan al espacio (UNEP, 2006) (Figura 1).

Los GEIs (vapor de agua, CO_2, CH_4, NO_x, O_3 y clorofluorocarbonos (CFC)) permiten que la radiación solar pase a través de la atmósfera casi sin obstáculos, pero absorben la radiación infrarroja de la superficie terrestre y la emiten de nuevo a la Tierra (UNEP, 2006).

Figura 1. Esquema del efecto invernadero. Disponible en: http://cuadrosinoptico.info/cuadros-sinopticos-sobre-el-efecto-invernadero/. Consultado el día 2/10/2015.

Los GEIs se han ido incrementando considerablemente dando lugar a lo que se conoce como el calentamiento global (UNEP, 2006). Entre 1990 y 2013 sufrieron un incremento de un 34 % (Huang *et al.*, 2015a), suponiendo una amenaza no sólo para el futuro de la sociedad sino también para el medio ambiente (Breyer *et al.*, 2015). Estas emisiones de GEIs se distribuyen desigualmente entre regiones y países. Los países industrializados son los responsables de la mayoría de éstas actualmente y a lo largo de la historia (UNEP, 2006).

El IPCC (2001) concluyó que la mayor parte del calentamiento observado durante los últimos 50 años es debido a actividades humanas. En el pasado, la principal causa de las concentraciones de CO_2 en la atmósfera era la agricultura pero posteriormente y hasta la actualidad, estas cantidades fueron superadas por los combustibles fósiles (mayoritariamente originados por la industria y el transporte) (FAO, 2002). Las emisiones antropogénicas globales por combustibles fósiles y por la producción de cemento están estimadas en aproximadamente 10 Pg C año^{-1} (Le Quere *et al.*, 2014). Una quinta parte del total de las emisiones de CO_2 en la UE son causadas por el transporte por carretera. Entre los años 1990 y 2010, las emisiones derivadas de este sector aumentaron alrededor de un 23 %. Según datos de la Comisión Europea, éste es el único sector donde las emisiones de GEIs siguen aumentando en la UE (EC, 2013b). La población mundial va aumentando (alcanzó los 7000 millones de personas en 2013) y se espera alcanzar 9000 millones de personas en 2050 según las Naciones Unidas (United Nations, 2013). Como consecuencia de este crecimiento y de las mejoras en la calidad de vida, seguirá habiendo una movilidad a lo largo del tiempo y con ello,

aumentarán las emisiones a no ser que haya un cambio en las emisiones por vehículo. Por ello, la movilidad sostenible se ha erigido como una de las opciones para reducir las emisiones de GEIs del transporte por carretera (Viguria *et al.*, 2015).

La agricultura es la responsable del 30 % del total de las emisiones de CO_2, N_2O y CH_4 (Denman *et al.*, 2007; Popp *et al.*, 2010; Srinivasarao *et al.*, 2015), así que puede afirmarse que el uso del suelo juega un papel importante en las emisiones. El CO_2 se libera por medio de las raíces y organismos presentes en el suelo (Nair *et al.*, 2011). La liberación de N_2O se produce por la aplicación de fertilizantes nitrogenados, tales como el nitrato de amonio. Por otro lado, las pérdidas de CH_4 se generan durante la descomposición anaeróbica de la materia orgánica (OM, en sus siglas en inglés), especialmente cuando el estiércol se almacena en forma líquida.

Por tanto, los suelos son una de las principales fuentes de emisión de GEIs. La mayor o menor emisión depende de factores tales como la temperatura, la humedad y las características del suelo (textura, pH, y el contenido de OM y N). Además los LUC y/o una mala gestión de los mismos provocan una mayor emisión de C atmosférico. En el estudio de los GEIs, es importante determinar el impacto generado por el manejo del suelo (Panday y Nkongolo, 2015), ya que los cambios en el carbono orgánico del suelo (SOC, en sus siglas en inglés) pueden tener un importante impacto en las emisiones de GEIs. Normalmente no se tienen en cuenta capas del suelo mayores a los 30 cm y sin embargo éstas pueden tener un gran impacto positivo o negativo en las emisiones globales de GEIs (Wilhelm *et al.*, 2010; Schmer *et al.*, 2015). Además, el suelo puede actuar como sumidero de CO_2 atmosférico y de esta forma aumentar el secuestro de C en los suelos agrícolas con el fin de mitigar el efecto de los GEIs (Pritchard *et al.*, 2014; Yan *et al.*, 2015).

Es necesario tomar una serie de medidas para reducir las emisiones de GEIs en todos los ámbitos, ya sea industrial, comercial o doméstico (Masuda *et al.*, 2015). Por ejemplo, las concentraciones de CO_2 atmosférico están estrechamente relacionadas con el ciclo del C terrestre y el clima. Es necesario reducir el contenido de CO_2 atmosférico para compensar las pérdidas de C en el ecosistema terrestre. Para conseguir esto hay que reducir el consumo de combustibles fósiles y la deforestación como un primer paso (Cox *et al.*, 2000).

3.1.6. Características generales de los sistemas: olivar, cereal y forestal. Repercusión en el cambio climático.

Como se ha comentado con anterioridad, el crecimiento de la población mundial va en aumento, lo que provoca la necesidad de aumentar la producción agrícola (United Nations, 2013).

La producción agrícola mundial ha crecido a una media de entre 2 y 4 % al año durante los últimos 50 años, mientras que el área cultivada se ha incrementado sólo un 1 % anualmente. Más del 40 % del aumento de la producción ha venido de cultivos de regadío, que han duplicado su extensión desde la década de 1960 (FAO, 2013a).

La degradación del suelo supone una amenaza para la seguridad alimentaria. Las principales causas son la erosión, la pérdida de nutrientes y la pérdida de C. Los suelos agrícolas son más susceptibles a la degradación debido a la eliminación de vegetación antes de plantar los siguientes cultivos. Se ha estimado que el 30 % de la superficie arable mundial está severamente degradada y cada año 10 Mha de cultivo se pierden por la erosión acelerada del suelo (Pimentel y Burges, 2013; Srinivasarao *et al.*, 2015).

En general, la intensidad de uso y la explotación descontrolada han ido aumentando drásticamente desde el siglo pasado provocando erosión, salinización del suelo y pérdida de nutrientes, induciendo todos ellos a la reducción de la calidad del suelo. Todo esto se ha visto acentuado en las regiones áridas (Caravaca *et al.*, 2002; Abbasi y Zafar, 2007; Majaliwa *et al.*, 2010). En esas zonas juegan un papel importante las propiedades del suelo, ya que el contenido de nutrientes y la humedad, entre otros componentes, son clave en los ecosistemas y por tanto determinan el desarrollo agrícola sostenible de estos lugares (Majaliwa *et al.*, 2010; Yang *et al.*, 2012).

El cambio de estrategia hacia una agricultura sostenible no solamente mantiene e incluso mejora la calidad del suelo sino que también contribuye a la reducción de los GEIs y la optimización de la productividad agrícola (Panettieri *et al.*, 2014). Para lograr estos objetivos, se han sugerido diferentes alternativas: por una parte, varios investigadores han sugerido el uso de la labranza de conservación (Franzluebbers, 2004; Lal *et al.*, 2007; Panettieri *et al.*, 2014). Este tipo de labranza conserva la OM del suelo ante la degradación (Álvaro-Fuentes *et al.*, 2009; Panettieri *et al.*, 2013). Para que esta práctica funcione óptimamente, el suelo debe estar cubierto de residuos orgánicos como aquellos que se obtengan de la cosecha anterior en un 30 % (Gajri *et al.*, 2002). Por otra parte, existe una serie de investigaciones que apoyan el uso de diferentes residuos como cubierta del suelo, algunos ejemplos son: restos de poda de los cultivos (Lozano-García y Parras-Alcántara, 2013a; Velázquez-Martí *et al.*, 2011; Repullo *et al.*, 2012), residuos de industrias alimentarias (Calleja-Cervantes *et al.*, 2015; Qaryouti *et al.*, 2015) e incluso compost (Pérez-Lomas *et al.*, 2010; Papafilippaki *et al.*, 2015; Madejón *et al.*, 2016).

3.1.6.1. Olivar.

En regiones de clima mediterráneo, el olivo (*Olea europaea L.*) es uno de los árboles frutales más extendidos y probablemente uno de los cultivos más antiguos del Mediterráneo (Sánchez-Moreno *et al.*, 2014; Proietti *et al.*, 2015). Estos paisajes típicos de las zonas mediterráneas se han ido convirtiendo en el principal apoyo económico

para sus habitantes (IOC, 2012). El olivar puede estar presente en una gran variedad de ecosistemas, en hábitats mediterráneos con veranos muy calurosos e inviernos fríos, o bien hábitats mediterráneos continentales con veranos templados e inviernos secos (Ordano *et al.*, 2015). Según la FAO (2012), en 2010 alcanzó 9,5 Mha en todo el mundo. España, es el país que mayor área oleícola posee en el mundo con 2,5 Mha. La mayoría ($1,9 \times 10^6$ ha) se localiza en Andalucía (MAGRAMA, 2013). Esto supone que el 20 % de la superficie ocupada por este cultivo en España se encuentra en esta región (EUROSTAT, 2012). El interés por este tipo de cultivo ha ido en aumento en la UE (Tous *et al.*, 2010; Alonso *et al.*, 2011). Este aumento se ha llevado a cabo con el fin de obtener una mayor producción. Tanto los subsidios como el incremento en el precio del aceite de oliva lo han hecho posible (Lozano-García y Parras-Alcántara, 2013b). Sin embargo, autores como Gómez-Limón y Arriaza (2011) consideran el cultivo de olivar andaluz eco-ineficiente, debido a la fuerte perturbación que se origina en el suelo por el sistema de gestión usado, siendo éste el causante de la erosión del suelo y del lixiviado de agroquímicos. Siempre teniendo en cuenta que el agricultor busca maximizar la producción de aceite, sería conveniente contemplar otros aspectos tales como la obtención de un producto de mayor calidad o la posibilidad de que los productores intervengan en la cadena de valor (fases de envasado y de comercialización minorista) (MARM, 2010).

Además podrían contemplarse otras alternativas en cuanto a la gestión del suelo con el fin de minimizar los efectos negativos generados por la mala gestión del cultivo. Éstas podrían ser la sustitución del laboreo convencional por el de conservación. Además debería mantenerse la cubierta vegetal entre los árboles, añadir al suelo hojas del propio cultivo y mantener los restos de poda en la capa superficial. De esta forma aumentaría el contenido de C en el suelo trayendo consigo una serie de beneficios (ver apartado 3.2) y se minimizarían los GEIs (Repullo *et al.*, 2012; Fernández-Romero *et al.*, 2014a).

3.1.6.2. Cereal.

Los cereales son plantas herbáceas que incluyen especies como trigo, cebada, avena, centeno, maíz, sorgo, alforfón, mijo y alpiste originarios de zonas templada y subtropicales, pertenecientes a la familia de las gramíneas. Se caracterizan por su estructura morfológica formada por un tronco con forma de caña, que proporciona unos granos (semillas) que sirven de alimento humano y animal. Se han extendido por países en desarrollo y desarrollados debido a su fácil adaptabilidad a diferentes suelos y condiciones climáticas (MAGRAMA, 2015).

El trigo es un cultivo de secano que supone el 30 % de la producción mundial de cereal (FAO, 2013b; Balkovič *et al.*, 2014). Se encuentra ampliamente distribuido y sus condiciones óptimas de crecimiento están en ambientes templados (Gooding, 2009; Röder *et al.*, 2014). Su rendimiento puede ser mayor de 10 t/ha (Röder *et al.*, 2014). En Europa, el rendimiento de los cereales ha mostrado una tendencia de crecimiento

constante durante la segunda mitad del siglo XX (Brisson *et al.*, 2010). El trigo es el cultivo más extendido, con un 32 % de la producción europea (Montesino-San Martín *et al.*, 2014).

En Reino Unido, constituye el 65-70 % de la producción total de cereal (es una de las más altas en todo el mundo) (DEFRA, 2009; FAO, 2013b). Éste se va alternando con el maíz y la cebada. Se producen cerca de 15 Gt/año en una superficie de aproximadamente 1,9 Mha (DEFRA, 2009), por lo que es el tercer mayor productor de trigo europeo. Reino Unido es uno de los países que se beneficiarán del cambio climático ya que experimentaran mejoras en el rendimiento de este cultivo (siendo éste hasta del 25 % en 2050) (IPCC, 2007b). Así que deben asumir la responsabilidad de mantener y aumentar la producción de trigo con el fin de mantener la seguridad alimentaria mundial (Röder *et al.*, 2014).

En España la producción de trigo ha ido aumentando ligeramente desde el año 2009. En este año la producción de trigo fue de 4805 t en una superficie de 1773 ha, mientras que en el año 2011 ocupaba una superficie de 1993 ha y su producción fue de 6900 t (su rendimiento de 3,5 t/ha) (MAGRAMA, 2015).

En los suelos agrícolas es importante llevar a cabo una adecuada gestión del suelo con el fin de aumentar su contenido en C y productividad. Pan *et al.* (2009) encontraron una correlación significativa entre el C y la productividad de los cereales, de tal manera que el aumento de retención de C mejora la productividad de los cultivos, contribuyendo además a la mitigación de los GEIs (Martín *et al.*, 2010).

3.1.6.3. Bosque.

Con el paso del tiempo, la superficie forestal se fue reduciendo sustituyendo su vegetación natural por otros cultivos de mayor rendimiento económico asegurando de esta forma el desarrollo humano. Esta tendencia trajo consigo graves problemas para los suelos, provocando su degradación y acelerando la erosión (Nieto *et al.*, 2013). Sin embargo, durante las últimas décadas esta tendencia se ha invertido en Europa donde se ganaron unos 11 Mha entre 1990 y 2010 como consecuencia de su expansión natural y de las labores de reforestación. Actualmente, los bosques se extienden a lo largo de 159 Mha (un 4 % de la superficie forestal mundial). Su distribución depende principalmente de los factores clima, suelo, altitud y topografía. Solamente un 4 % de ellos no se han visto afectados por la acción antrópica; el 8 % son plantaciones y el resto son bosques semi-naturales, es decir, modelados por el hombre. Además, los bosques europeos son, en su mayoría, de propiedad privada (alrededor de un 60 % de la superficie) (MAGRAMA, 2015).

España ha seguido la misma tendencia europea y actualmente cuenta con una superficie forestal de 27,7 Mha. Es el segundo país de la UE (solo precedido por Suecia) con una

mayor extensión de bosque, mientras que Reino Unido solo dedica un 11 % de su superficie a este uso (MAGRAMA, 2015).

Los bosques contribuyen a la protección del suelo (contra la erosión), participan en el ciclo del agua y regulan el clima tanto a nivel local (a través de la evapotranspiración), como mundial (gracias al almacenamiento de C, que supone aproximadamente un tercio de las emisiones antropogénicas de CO_2 en la atmósfera). La repoblación, reducción de la deforestación, degradación y LUC de los bosques contribuyen a la captura de C en el suelo (Hunt y Elgar, 2010). Los bosques son el hábitat de numerosas especies y se consideran por ello protectores de la biodiversidad (MAGRAMA, 2015).

3.2. CARACTERISTICAS DEL CARBONO. CICLO DEL CARBONO.

3.2.1. Flujo de C. Ciclo biogeoquímico del carbono.

El C es un elemento fundamental de la tierra. Éste participa en los continuos intercambios complejos existentes entre la tierra, la atmósfera y el océano (Brevik, 2012; Debasish-Saha y Bawa, 2014).

Los diversos procesos entrelazados de síntesis y descomposición por el cual el C circula a través del suelo, las plantas, los animales y el aire, comprenden el ciclo del C (Figura 2) (Sparks, 2011). Se considera un ciclo perfecto compuesto tanto de entradas (secuestro) como de salidas (emisiones) de C en diferentes formas hacia el medio ambiente, en el que el C se devuelve al medio tan rápido como se retira (Mukherjee *et al.*, 2007; Sparks, 2011).

El ciclo biológico del C realiza dos grandes transferencias: el flujo de CO_2 de la atmósfera a las plantas como resultado de la fotosíntesis y el regreso del mismo a la atmósfera por la respiración de las plantas, así como por la descomposición de la OM. En ellos el C es absorbido, liberado y descompuesto en los ecosistemas. Los animales y las plantas utilizan los carbohidratos en el proceso de respiración, usan la energía contenida en los carbohidratos y emiten CO_2 a la atmósfera. Así mismo, a través de la descomposición orgánica (respiración de bacterias y hongos) se devuelve el C biológico fijado en los reservorios terrestres (los tejidos de biota, el permafrost del suelo y la turba) a la atmósfera. Se ha contabilizado que por la fotosíntesis se absorben 110 Gt de C/año, por la respiración se emiten 55 Gt de C/año y por la descomposición entre 54-55 Gt de C/año (Bolin et al., 1986).

Según Eswaran *et al.* (1993) en ausencia de la influencia antropogénica este ciclo presenta tres grandes depósitos, reservas, stocks o pools: el terrestre (1500 Gt de C en suelos y 550 Gt de C en plantas), el atmosférico (750 Gt de C) y el oceánico (38100 Gt de C). Schimel *et al.* (2011) señala que los flujos de C en el planeta sin interferencias antropogénicas, son aproximadamente equivalentes con una lenta variación a escala geológica.
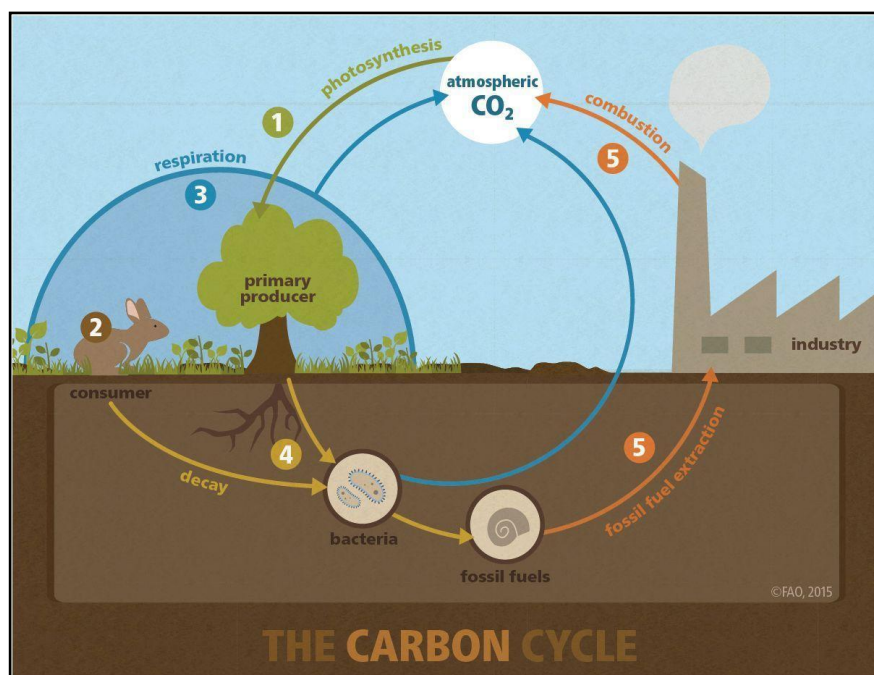
Figura 2. Ciclo del C según FAO, 2015.

Durante los últimos 200 años, la liberación de CO_2 a la atmosfera procedente de los combustibles fósiles, la respiración de los organismos, la deforestación y los incendios, ha superado al secuestro de C en los organismos vivos y muertos de la tierra y en el agua (Sparks, 2011). De esta manera, el C del suelo no afecta sólo al balance global del C sino también al cambio mundial de temperatura (Tan *et al*., 2014), debido a que la OM del suelo se ha considerado como la principal fuente y sumidero de C (Simón *et al.*, 2010).

3.2.2. Carbono en el suelo.

El 75 % del C que hay en la Tierra se almacena en el suelo (Sparks, 2011). Por ello, cualquier cambio en la reserva de C terrestre puede verse reflejado en importantes cambios en las concentraciones de CO_2 atmosférico (Schuman *et al.*, 2002; Glendell y Brazier, 2014) y posiblemente en el clima mundial (Simón *et al.*, 2010).

Los aportes de C al suelo pueden efectuarse en superficie o en profundidad. La hojarasca y los residuos de la poda normalmente se quedan en la capa superficial del suelo mientras que la OM procedente de la mortalidad de las raíces o del exudado de las mismas se puede incorporar a capas mucho más profundas que las anteriores. Además, las raíces ayudan a la descomposición de la OM. El C del suelo se protege de la descomposición microbiana mediante la formación de agregados (especialmente microagregados), que se dan por la unión de residuos orgánicos con partículas minerales del suelo (Six y Paustian, 2014). Aunque, la mitad del SOC total se encuentra en los

primeros 30 cm del suelo (Batjes, 1996), el C derivado de las raíces se estabiliza en el suelo antes que el C aportado superficialmente debido a la protección física de los pelos radicales dentro de los agregados del suelo, o por la recalcitrancia química de la raíz; o bien también por la adsorción de los exudados de las raíces o productos de descomposición en partículas de arcilla (Cardinael *et al.*, 2015). Los aportes de OM derivados de las raíces son diversos químicamente, su complejidad puede ser desde sustratos que no se degradan fácilmente a otros que sí (casi exclusivamente por bacterias), tales como azúcares solubles, aminoácidos y ácidos orgánicos. Los hongos juegan papeles importantes en la degradación de materiales orgánicos recalcitrantes tales como la lignina, la celulosa y la hemi-celulosa (Stockmann *et al.*, 2013).

El SOC es el componente más vulnerable a cambios en las condiciones del suelo y contribuye a varias funciones biológicas, físicas y químicas importantes (Brevik *et al.*, 2015). Es un componente esencial del suelo, usado como indicador de su calidad y productividad y cuando se tienen unos niveles adecuados, mejoran las propiedades tales como la estructura del suelo, la capacidad de intercambio catiónico, la retención de agua y el suministro de nutrientes a las plantas (a través de la mineralización), incrementando así el crecimiento de las mismas y la actividad biológica. Por todo ello, su agotamiento es un importante motor de la degradación del suelo, ya que tiene consecuencias negativas para su fertilidad, la capacidad de retención del agua y el suministro de otros servicios de los ecosistemas importantes como la regulación del clima (Christensen *et al.*, 2011; Batjes, 2014a). De manera que es bueno aumentar las concentraciones de SOC en suelos degradados (Fialho y Zinn, 2014, Mi *et al.*, 2014; Srinivasarao *et al.*, 2014; Bruun *et al.*, 2015). El SOC es la mejor medida de rehabilitación del suelo cuando su valor es igual o superior a 2 % (Clay, 2011).

Tabla 1. El SOC de los suelos a nivel mundial. Adaptado de Martínez et al. (2008). 1- Soil Survey Staff (1996), 2- 2 SOC, 3- 1 Pg: 1015 g.

Orden[1]	Área (10^3 km^2)	SOC (Pg)[2]	SOC/Área (Pg 10^{-3} km^2)
Histosoles	1745	357	0,205
Andisoles	2552	78	0,031
Inceptisoles	21580	352	0,016
Espodosoles	4878	71	0,015
Mollisoles	5480	72	0,013
Oxisoles	11772	119	0,010
Entisoles	14921	148	0,010
Ultisoles	11330	105	0,009
Alfisoles	18283	127	0,007
Vertisoles	3287	19	0,006
Aridisoles	31743	110	0,003
Misceláneos	7644	18	0,002
Total	135215	1576	0,012

3.2.3. Acumulación y distribución del carbono en el suelo.

El C presente en el suelo es el resultado entre el absorbido de la atmósfera o del material vegetal muerto y el perdido por (i) mineralización, (ii) transporte por erosión del suelo, o bien (iii) por infiltración a capas más profundas o aguas subterráneas por lixiviado (Sparks, 2011; FAO, 2015).

Su almacenamiento puede ser: a corto plazo, en forma de macroagregados (250-2000 mm); a largo plazo, en forma de microagregados (53-250 mm) y en agregados de tamaños más pequeños (< 53 mm) (Howlett *et al.*, 2011a; Nair, 2011).

En resumen, la acumulación de SOC en el suelo se genera cuando el CO_2 atmosférico queda inmovilizado con respecto a la circulación biogeoquímica durante un período de tiempo e incrementan las existencias del mismo en el suelo (Almendros, 2004). En este proceso los factores como el clima, suelo (topografía y propiedades edafológicas) y vegetación condicionan su absorción y almacenamiento (Zinn *et al.*, 2007). Además, en suelos con actuaciones humanas (cultivos, pastos y forestales) los cambios en el funcionamiento del SOC se pueden relacionar con otros factores, como el tipo de manejo del suelo, ya que modifica, degrada o mejora los suelos (FAO, 2009). Por tanto, la capacidad de captura de C en los suelos depende de:

(1) *Sus propiedades*. Diversos autores han relacionado el contenido del SOC con el tipo de suelo (Zhang *et al.*, 2007; López-Fando y Pardo, 2009), la composición mineralógica (Wang *et al.*, 2008) y con las propiedades intrínsecas de los suelos (Rodríguez-Murillo, 2001; Martínez *et al.*, 2008), especialmente con la textura (Zinn *et al.*, 2007; Lal, 2009), asociada a la estabilización del SOC por niveles de arcilla y limo (Bationo *et al.*, 2007). El SOC almacenado en partículas finas

se considera estable, con un alto grado de humificación, ya que está protegido contra la degradación y lixiviación por los pequeños poros en estos materiales. Cuando la proporción de SOC se asocia con la fracción de arena, se trata de SOC particulado. Éste no está protegido y por lo tanto es el componente más activo del SOC. Las fracciones de limo y arcilla contienen generalmente más SOC que la facción de arena (Chen *et al.*, 2015). Estas mediciones han permitido identificar la variabilidad espacial del C en función de los diferentes tipos de suelos (tabla 1) a distintas escalas geográficas y entender el proceso de secuestro de C (Venteris *et al.*, 2004; Wang *et al.*, 2010).

El aumento en los agregados del suelo es generalmente proporcional al SOC conservado y protegido en el mismo que permite que la OM funcione como una reserva de nutrientes de las plantas y energía para la microflora del suelo. La incorporación de residuos o su retención provoca un incremento significativo en los agregados totales estables de la superficie del suelo y, en menor medida, en el subsuelo (Chowdhury *et al.*, 2014).

(2) *Sus usos*. En bosque mixto y matorral de España el C almacenado está entre 11 y 12 kg m^{-2}. Sin embargo esto no ocurre con otros usos como el agrícola (alrededor de 5 kgm^{-2}) destacado por su bajo contenido (Simón *et al.*, 2010). Cabría destacar los LUC ya que éstos afectan al almacenamiento de C en el suelo (Wiesmeier *et al.*, 2015). Hay usos del suelo que pueden aumentar o reducir el C en el suelo y esto ha sido considerado en los escenarios de mitigación del cambio climático. Según Guo y Gifford (2002) el contenido del SOC se incrementa después de la conversión de bosques a pastos (+ 8 %), de cultivos a plantaciones (+ 18 %), de cultivos a bosques secundarios (+ 53 %) y de cultivos a pastos (+ 19 %). Mientras que el SOC disminuye después de la conversión de pastos a plantaciones (-10 %), de bosques a plantaciones (-13 %) y particularmente desde bosques y pastizales a cultivos (-42 % y -59 %) respectivamente.

(3) *El clima*. Cuando la temperatura media anual disminuye, se aprecia un aumento en la concentración de SOC. Las regiones con un clima frío o húmedo se caracterizan por suelos ricos en C (Stockmann et al., 2013; Batjes, 2014b). A nivel mundial, los suelos de zonas subdesérticas tienen un contenido de SOC menor a 2 kg m^{-2}, mientras que en zonas de tundra y bosque húmedo, éste asciende a más de 30 kg m^{-2} (Simón *et al.*, 2010). En los suelos españoles, al igual que otras latitudes, el clima es muy influyente en la variabilidad del SOC, principalmente en climas secos del mediterráneo, que son caracterizados por su bajo contenido en SOC, débil estructura y son propensos a la degradación (Hernanz *et al.*, 2002). En estos suelos la precipitación media anual tiene fuerte correlación con el SOC (Hontoria *et al.*, 1999). En este sentido, Hontoria *et al.* (2004) señalan que además de la precipitación intervienen otras variables que

afectan a la acumulación del C en estos suelos como es el caso de la pendiente y la temperatura.

(4) *La profundidad del perfil* también es un factor clave a considerar en la evaluación de las existencias y dinámica del SOC (Salomé *et al.*, 2010; Albaladejo *et al.*, 2013). Cuanto más profundo esté el C probablemente más antiguo sea (Stockmann *et al.*, 2013). Los factores que controlan el SOC en profundidad cobran cada vez más importancia, ya que de ellos depende no sólo su almacenamiento sino también su estabilidad. El C a una cierta profundidad puede ser fácilmente descompuesto bajo unas condiciones ambientales favorables (Schimel *et al.*, 2011). La estabilización del SOC está generalmente dividida entre los mecanismos de protección físicos y químicos (Von Lützow y Kögel-Knabner, 2010). Los físicos se vinculan a menudo a la formación estructural del suelo (es decir, a los agregados) que puede limitar la difusión de enzimas y/o catabolitos (Lawrence *et al.*, 2015), pero también puede referirse a su estado físico, como podría ser la congelación del SOC en suelos de permafrost (Harden *et al.*, 2012). La estabilización química es el resultado de la adsorción de SOC en superficies minerales o de la formación de complejos orgánicos con iones de Fe y Al disueltos procedentes de la erosión mineral del suelo (Lawrence *et al.*, 2015). A este respecto, Lorenz y Lal (2005) propusieron que se requiere de al menos un metro de profundidad para evaluar las reservas de SOC e incluso esta profundidad puede ser insuficiente para evaluar con precisión los stocks.

(5) *La topografía* (Albaladejo *et al.*, 2013; Fernández-Romero *et al.*, 2014b; Ruiz-Sinoga *et al.*, 2012). Avilés-Hernández *et al.* (2009) encontraron que a lo largo de una toposecuencia el mayor contenido de C total (raíces finas y suelo) se observó en la planicie con 208 t C ha^{-1} y el menor en la cresta con 159 t C ha^{1}.

(6) *El manejo del suelo* tiene un fuerte impacto en el contenido del SOC, como consecuencia de las diversas prácticas que incrementan o disminuyen el C en el suelo, ya que puede dar lugar a una mejor aireación, un aumento del pH y a una mayor fertilidad del suelo, favoreciendo así la actividad microbiana y la mineralización y a su vez reducir los niveles OM en el suelo (Reijneveld *et al.*, 2010). De esta manera, para Lal (2006) el uso y permanencia de estos procesos conlleva a que se hable de agroecosistemas que emiten o secuestran C. El aumento del SOC por el manejo, ha sido referido por el IPCC (2007c) como una opción para el secuestro de C que puede contribuir a la mitigación del cambio climático.

(7) *El incremento de biomasa vegetal*. El C en el suelo tiende a ser mayor con especies de hoja caduca en comparación con las coníferas debido a la rápida integración de sus hojas y raíces en el suelo (Fernández-Núñez *et al.*, 2010). Sin embargo, esta diferencia es parcialmente compensada por la mayor acumulación

de C en el árbol en el caso de las plantaciones de pino (Mosquera-Losada *et al.*, 2015). En los suelos agrícolas, el C se incrementa por los residuos que se dejan en la superficie del suelo. Estos residuos pueden ser cultivos con pastos, incorporación de cobertura vegetal en la rotación de cultivos, o la adición de residuos orgánicos como el estiércol, lodos de depuradora, etc. (Overstreet *et al.*, 2010).

Si el C es almacenado en el suelo por un largo tiempo (aumenta su tiempo medio de residencia) se denomina secuestro de C en el suelo y en este caso se produce una reducción de la actividad microbiana y una rotación de SOC en profundidad, además de aumentar las concentraciones de los complejos órgano-minerales (Stockmann *et al.*, 2013). Los principales procesos de secuestro de C en el suelo incluyen la humificación, agregación y sedimentación (Srinivasarao *et al.*, 2015). El secuestro de C puede darse en el océano, suelo, vegetación y formaciones geológicas (Sparks, 2011). No obstante cabe destacar que a nivel mundial el suelo almacena casi el doble de C que la vegetación y dos veces más que la atmósfera. Por este motivo el suelo es considerado un sumidero de C, no obstante hay incertidumbre con respecto a la cantidad y distribución del contenido del SOC (Pérez-Ramírez *et al.*, 2013). La determinación de ambas es esencial para desarrollar políticas ambientales y estrategias de manejo del suelo. Se han llevado a cabo estimaciones de su distribución a distintas escalas (figura 3 a nivel europeo) como base científica para el desarrollo de actividades conservacionistas del suelo, evaluadoras del impacto de uso del suelo y que reduzcan las emisiones.
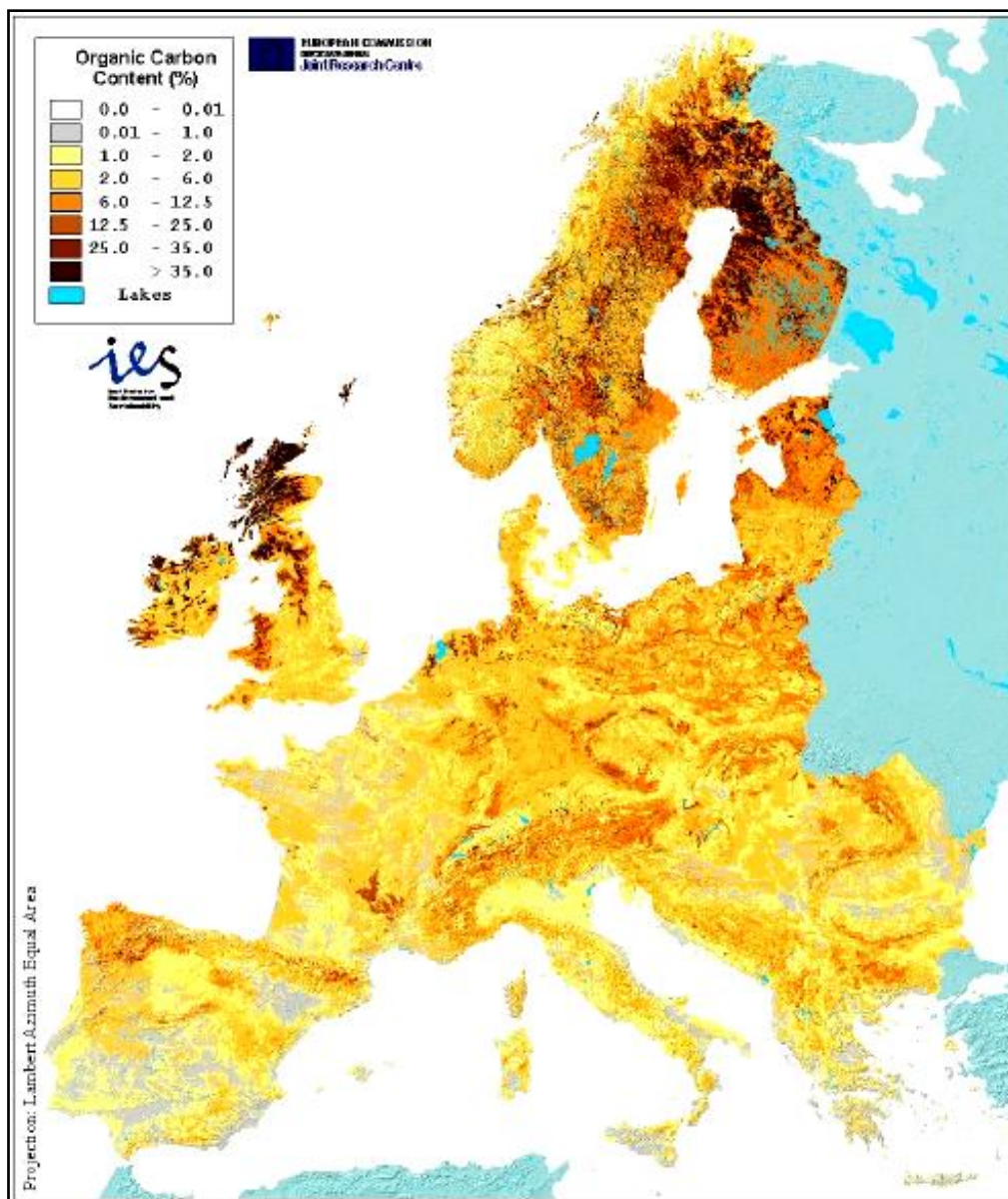
Figura 3. Distribución del SOC en el suelo. Basado en una encuesta de suelo (datos de 1960-1989) (Jones *et al.*, 2004).

3.3. MATERIA ORGÁNICA EN EL SUELO.

3.3.1. Origen, composición y procesos asociados a la materia orgánica.

La OM del suelo está compuesta por los residuos orgánicos que se originan a partir de restos vegetales, animales y biomasa microbiana en diferentes estados de descomposición o humificación (Hur *et al.*, 2013). Es la mayor reserva de C terrestre, contiene entre 52-58 % de SOC, tres veces más que los organismos vivos o la atmósfera (Fischlin *et al.*, 2007; Brevik, 2012). Este almacenamiento hace que se mejoren las propiedades físicas, químicas y biológicas del suelo (Sharma, 2011). Además del C, la OM del suelo tiene entre 34-39 % de O, 3,3-4,8 % de H y 3,7-4,1 % de N; más otros

elementos como el fósforo (P) y el azufre (S) pero en menores cantidades (Lawrence *et al.*, 2015).

Dentro de la OM del suelo se puede distinguir entre sustancias no húmicas y las húmicas. Las primeras son aquellas que presentan propiedades físico-químicas reconocibles y consisten en carbohidratos, proteínas, péptidos, aminoácidos, grasas, ceras y ácidos de bajo peso molecular. Estos componentes son atacados fácilmente por los microorganismos y permanecen en el suelo durante un período de tiempo corto. Por el contrario, las sustancias húmicas son sustancias orgánicas biogénicas, heterogéneas de origen natural, de alto peso molecular y refractarias. Su color puede ir desde amarillo a negro. Se caracterizan por ser amorfas, parcialmente aromáticas y no presentar características físico-químicas asociadas a los compuestos orgánicos (Sparks, 2011).

Los organismos del suelo contribuyen no sólo a la formación de la OM, sino también a la descomposición de la misma creando humus (material orgánico bien descompuesto, con un tamaño menor a 50 μm y que se asocia con partículas del suelo. Este incluye las sustancias húmicas (Sparks, 2011)) y abriendo una serie de poros en el suelo que permiten junto a las raíces la aireación del mismo. Además llevan a cabo una fertilización del suelo mediante el aporte de sus heces y desechos (Singh, 2015).

La humificación es la conversión de OM fresca en una forma estable de OM en el suelo o la conversión de OM en humus. La humificación y la descomposición de la hojarasca son procesos inducidos por microbios, controlados principalmente por variables específicas del sitio como la temperatura, régimen de agua del suelo, pH y nutrientes disponibles. Ellos controlan la composición de la comunidad de microorganismos y su actividad y distribución en el suelo (Swift *et al.*, 1979). Además de estas variables externas, las internas como la calidad de los recursos son también importantes ya que contribuyen a explicar las diferencias en las tasas de rotación de un reservorio de OM dado en diferentes sitios, mientras que el recurso calidad debe, además, ser responsable de las diferencias que se producen en el mismo sitio (Swift, 1987).

La mineralización es la descomposición microbiana de la OM en el suelo. Los microbios transforman los elementos orgánicos de la OM en compuestos inorgánicos (como CO_2, CH_4, NH^+_4, NO_3^-, SO_2, H_2S, HPO^{-2}_4) liberando la mitad del C en forma de CO_2. A partir de esa descomposición de la OM se produce una transformación del C presente en el suelo. El tamaño de C lábil, las condiciones ambientales y la comunidad microbiana local son factores que afectan a la mineralización (Zhao *et al.*, 2008; Li *et al.*, 2013). La tasa de mineralización de la OM humificada es dependiente del tamaño, estructura o actividad de la comunidad microbiana del suelo (Stockmann *et al.*, 2013).

Generalmente, la mayoría de la OM del suelo se presenta en forma de macro y micro agregados mediante la unión del C a partículas minerales formando pesadas fracciones de SOC (Post y Kwon, 2000). Según Six *et al.* (2004) cuando se produce una perturbación en el suelo los macro-agregados se transforman en micro-agregados, disminuyendo la estabilidad del C. Por lo tanto, la OM está relacionada directamente

con la protección de los agregados del suelo, que a su vez reduce el riesgo de erosión (Novara *et al.*, 2011). El grado, la estabilidad y la distribución del tamaño de los agregados tienen un fuerte impacto sobre la tasa de descomposición de la OM. Los agregados dependen de la fauna del suelo, raíces, agentes aglutinantes inorgánicos y variables ambientales. La liberación de polisacáridos y ácidos orgánicos durante la descomposición de OM desempeña un papel importante en la estabilización de los macroagregados (Srinivasarao *et al.*, 2015). Además de la estabilización física por la microagregación, la OM del suelo puede ser protegida de la descomposición acelerada por medio de la estabilización fisico-química mediante asociación con partículas de arcilla y por la estabilización bioquímica mediante la formación de compuestos altamente recalcitrantes (Six *et al.*, 2002; Martínez *et al.*, 2008).

Para evaluar la sostenibilidad y eficiencia del C en el suelo se requieren: medidas de secuestro, el impacto de diferentes factores de manejo, información sobre la estabilidad de la OM del suelo y el tiempo medio de residencia. La estabilización de la OM del suelo es una combinación de procesos a corto y largo plazo. Cualquier alteración en éstos pueden dar lugar a la descomposición de la OM del suelo (Schmidt *et al.*, 2011; Lal *et al.*, 2012).

3.3.2. Funciones de la materia orgánica en el suelo.

En comparación con la totalidad de la masa en peso del suelo, la OM representa una porción muy pequeña, pero está ligada directa o indirectamente a funciones muy importantes del suelo y es esencial para la maximización de la actividad biológica.

En cuanto a la mejora que la OM produce en el suelo cabe destacar que:

i)   reduce la densidad aparente del suelo. Ésta es función de la estructura del suelo, y por lo tanto tiene una estrecha correlación con su porosidad y la retención de agua (Ruehlmann y Körschens, 2009). Ésta última, junto con la disponibilidad de agua y su velocidad de infiltración aumenta cuando lo hace la OM, al igual que crece la resistencia contra la erosión hídrica y eólica.

ii)   proporciona lugares de intercambio catiónico en los suelos, mejorando su capacidad para reducir las pérdidas de nutrientes por lixiviación. Este intercambio catiónico es mayor en el humus que en la fracción de arcilla, a pesar de que la fracción en peso seco de ésta última es mayor (Sparks, 2011);

iii)   incrementa la actividad biológica ya que actúa como sustrato alimenticio. Los microorganismos estabilizan las partículas del suelo a través de la agregación dando lugar a una mejor capacidad de retención de agua en los suelos arenosos y un mejor drenaje en suelos arcillosos mediante el aumento de los poros de mayor tamaño (Sparks, 2011);

iv)   reduce la erosión, evaporación y escorrentía ya que conduce a una mayor cobertura vegetal en los suelos (Cerdà, 1998, 2000; Novara *et al.*, 2011; Zhao *et al.*, 2013) y, por lo tanto, también contribuye al aumento de la productividad de los cultivos debido a un aumento de la elasticidad y resistencia a la deformación y compactación, así como de la porosidad (Sellami *et al.*, 2008; Paradelo y Barral, 2013); y

v)   mejora la dinámica y disponibilidad de los principales nutrientes de las plantas (FAO, 2014).

Por lo tanto, la OM juega un importante papel en la mejora de la calidad física, química y biológica del suelo, contribuyendo positivamente a la fertilidad del mismo y al crecimiento de las plantas, llevando consigo el aumento de la productividad total del suelo (Srinivasarao *et al.*, 2015).

3.3.3.   Contenido de materia orgánica del suelo. Factores que influyen.

Los factores que más influyen en la formación de suelo y en su cantidad de OM son el tiempo, clima, vegetación, material parental y topografía (Sparks, 2011).

El clima es un factor muy importante debido a que determina el tipo de especie vegetal, la cantidad de material vegetal producida y el grado de actividad microbiana. La vegetación también influye fuertemente en los contenidos de OM (su presencia hace que el grado de humificación sea mayor, favoreciendo así la protección del suelo y el ecosistema en su conjunto), al igual que el material parental actúa sobre la textura (composición mineralógica, contenido en nutrientes y tamaño de las partículas). La topografía afecta al contenido de OM a través del clima, escorrentía, evaporación y transpiración. Los suelos húmedos y mal drenados son ricos en OM ya que su degradación se reduce debido a las condiciones anaeróbicas del suelo húmedo (Sparks, 2011).

Estos factores varían de unos suelos a otros, al igual que la velocidad de acumulación de OM en el suelo. Ésta última suele ser rápida al principio y disminuye lentamente. Alcanza un nivel de equilibrio que varía entre los 110 años (material parental de textura fina) y 150 años (material de arena). Este equilibrio se atribuye (1) a los ácidos orgánicos resistentes al ataque microbiano, (2) a la estabilidad del humus, debido a sus interacciones con cationes y arcillas, y (3) a la baja cantidad de nutrientes esenciales (N, P y S) que limitan la estabilidad del humus sintetizado por los organismos del suelo (Sparks, 2011).

El contenido de OM en el suelo representa un balance entre la adición y la descomposición y varía desde menos del 1 % (en suelos del desierto) hasta 100 % en suelos orgánicos, mientras que en un suelo agrícola su contenido suele oscilar entre

1-5 % en los primeros 15 cm. Los suelos mediterráneos se caracterizan por un bajo contenido en OM, normalmente alrededor del 1 % (Verheyey y De La Rosa, 2005; Kapur *et al.*, 2007; Cerdà *et al.*, 2010).

Generalmente la cantidad de OM presente en los suelos se representa por la masa en C y está determinada por el balance de dos procesos bióticos: la productividad vegetal y la descomposición de la OM. Cada uno de ellos está controlado por factores físicos y biológicos. A nivel mundial, la cantidad de OM se estima entre 1200-1500 Pg C (1Pg C= 10^{15} g C) en el primer metro del suelo (es de 2-3 veces mayor que la cantidad de OM en los organismos vivos en todos los ecosistemas terrestres) (Post, 2006). A nivel europeo, los suelos almacenan entre 73-79 Gt de C, el cual fue más de 50 veces el total de emisiones de CO_2 de los 27 estados miembros de la UE en 2009 (4,6 Gt) (EEA, 2010).

3.3.4. Técnicas empleadas en la medida de calidad de la materia orgánica.

Existen varias técnicas para determinar la cantidad y calidad de la OM, relacionadas especialmente el grado de humificación (Helal *et al.*, 2011; Tang *et al.*, 2011; Korak *et al.*, 2014). Éstas aparecen descritas a continuación.

3.3.4.1. Técnicas espectroscópicas (absorbancia, fluorescencia y DOC).

3.3.4.1.1. Carbono orgánico disuelto (DOC).

El carbono orgánico disuelto (DOC, en sus siglas en inglés) es una fuente de C fácilmente accesible para la comunidad microbiana, por eso es tan importante para los ecosistemas (Burford y Bremner, 1975). Las propiedades del suelo (pH, concentración de metales como óxidos de hierro y aluminio (Kaiser *et al.*, 1996; Kaiser y Guggenberger, 2000), arcillas y/o los minerales del suelo) (Kaiser y Zech, 2000; McDowell, 2003) son las que determinan la retención y movilidad del DOC. Según Nelson *et al.* (1997) la arcilla puede reducir el acceso de los microbios a la OM del suelo por oclusión de los agregados.

El DOC se compone de una amplia gama de moléculas que pueden ser simples (ácidos y azúcares) o sustancias húmicas complejas de gran peso molecular (Moore, 1998). Esto es en gran medida el producto al que da lugar la descomposición de la hojarasca y el humus, pero también puede originarse por los exudados de las raíces de las plantas. El DOC podría definirse de una manera resumida como el SOC que puede pasar a través de un filtro de 0,45 micras (Van den Berg *et al.*, 2012). La cantidad de DOC que puede

recuperarse del suelo depende del método de extracción seguido (e.j. HWC o carbono extraído en agua fría (CWC)).

La calidad del DOC se ve afectado por la agricultura (Chantigny, 2003). El aumento del N aumenta la concentración de DOC debido a que la actividad microbiana se ve mejorada por la fertilización nitrogenada (Freeman *et al.*, 2001). Tanto la producción como el transporte de DOC en el suelo dependen de una serie de factores, tales como: el tipo de planta, la calidad del sustrato, la actividad microbiana, la cantidad de C almacenado en el suelo, el pH, las reacciones de los metales con la OM, así como del movimiento del agua a través del suelo y su absorción por partículas minerales (Kalbitz *et al.*, 2000; Neff y Asner 2001). Todos estos están influenciados por parámetros climáticos y variables del suelo.

El DOC influye tanto en el secuestro de C como en las reservas de OM del suelo (Sandford *et al.*, 2013).

3.3.4.1.2. Absorbancia.

$SUVA_{254}$ es el cociente entre la absorbancia a 254 nm y la concentración de DOC (extraído con agua caliente, HWC). Los valores se expresan en L $mg^{-1}m^{-1}$. Este método se ha empleado en la determinación de la aromaticidad de la OM del suelo (Chow, 2006; Fuentes *et al.*, 2006). Además, es muy útil para evaluar la naturaleza de la composición general del DOC debido a su alta correlación con él (Weishaar *et al.*, 2003).

Esta técnica presenta una serie de ventajas (De la Torre, 2002):

(i)   Permite trabajar con una gran cantidad de longitudes de onda, incluso puede obtenerse un gráfico del espectro de absorción de una sustancia.

(ii)   Es de gran aplicabilidad ya que hay muchas especies absorbentes y las que no lo son pueden asociarse a otras que sí lo son formando complejos.

(iii)   Presenta una elevada sensibilidad (se pueden determinar concentraciones de hasta 10^{-5} M).

(iv)   Posee una selectividad media (es posible que aparezcan interacciones cuando hay grupos que absorben a la misma longitud de onda).

(v)   Permite la automatización del proceso cuando se lleva a cabo un análisis continuo de muestras.

(vi)   Es un sistema no destructivo (permite usar las mismas muestras para otros análisis).

Como aspecto negativo cabría destacar las interacciones por partículas que pueden interferir en el paso de luz. Las disoluciones no deben contener sólidos en suspensión (De la Torre, 2002).

3.3.4.1.3. Fluorescencia.

Esta técnica destaca por su potencial para caracterizar la OM del suelo (determinando su composición y propiedades) y estudiar las sustancias húmicas (para ello puede combinarse con la absorbancia) (Tang *et al.*, 2011). Se requieren volúmenes pequeños de muestra y es simple, rápida, no destructiva, segura y precisa.

La intensidad y posición de los picos detectados en el espectro de fluorescencia son únicas para cada característica estructural y funcional de las sustancias. Una alta intensidad de fluorescencia indica una alta humificación (Martins *et al.*, 2011; Tang *et al.*, 2011). Además, es muy sensible a la baja concentración de DOC (Birdwell y Valsaraj, 2010; Fan *et al.*, 2011).

Los índices (1) de fluorescencia (FI, en sus siglas en inglés), (2) humificación (HIX, en sus siglas en inglés) y (3) biológico (BIX, en sus siglas en inglés), junto con los valores de SUVA$_{254}$, proporcionan una evaluación de la aromaticidad, complejidad y origen del DOC (Kalbitz *et al.*, 2003).

Según McKnight *et al.* (2001), el FI fue desarrollado para evaluar las propiedades de la materia orgánica disuelta (DOM, en sus siglas en inglés) y ha sido correlacionado con la aromaticidad de ésta (Korak *et al.*, 2014). El HIX es un indicador de la biodisponibilidad de la DOM dentro de un sistema natural. Nos permite determinar el grado de humificación (o maduración) del material orgánico, ya que si éste presenta una fuerte humificación (se corresponde con una DOM aromática) es menos lábil en comparación con la que presenta un grado de humificación bajo (Zsolnay *et al.*, 1999; Ohno, 2002). El BIX permite una evaluación de la actividad biológica autóctona en muestras de suelo. Sus valores están relacionados con un origen autóctono de la DOM y la presencia reciente de ésta. Bajos valores de este índice se corresponden con una menor producción de DOM (Zsolnay *et al.*, 1999; Huguet *et al.*, 2009; Birdwell y Engel, 2010).

La DOM contiene una serie de fluoróforos diferentes y dan información sobre la estructura, grupos funcionales, configuración, heterogeneidad y características de la dinámica molecular (Guo *et al.*, 2012). El fluoróforo es un grupo funcional de la molécula que hace que ésta sea fluorescente, debido a que absorbe energía de una longitud de onda específica y la vuelve a emitir en otra determinada de mayor longitud

de onda (es decir, con menor energía). Tanto la energía emitida como absorbida dependerá del propio fluoróforo como de su ambiente químico.

En estudios de la DOM los dos principales grupos fluorescentes que se han identificados han sido; (1) sustancias húmicas y (2) otras sustancias similares a las proteínas (Singh *et al.*, 2010).

Las sustancias húmicas son una mezcla compleja de compuestos aromáticos y alifáticos derivados de la descomposición de la OM. Además se caracterizan por ácidos húmicos (precipitan cuando son tratados con soluciones ácidas de pH bajo) y fúlvicos (permanecen disueltos en soluciones ácidas), diferenciados en la solubilidad que presentan ante soluciones alcalinas y ácidas respectivamente. Ésta es la separación tradicional de las sustancias húmicas (Harvey y Boran, 1985).

Las sustancias similares a las proteínas se asocian con la presencia de actividad microbiana (alta actividad biológica) (Stedmon *et al.*, 2007).

3.3.4.1.4. Matrices de Emisión-Excitación (EEM).

Las técnicas espectroscópicas de fluorescencia, en particular el desarrollo de matrices de excitación-emisión (EEM, en sus siglas en inglés) han sufrido un cierto avance en los últimos 15 años, lo que ha permitido una investigación más exhaustiva de la fluorescencia de la DOM (Coble, 1996).

Las EEM están formadas por una serie de espectros de emisión de fluorescencia (*Em*), que van aumentando sucesivamente en función de la excitación (*Ex*), a distintas longitudes de onda. En general, las EEM abarcan una gama de *Ex* de longitudes de onda de 230 a 300 nm (longitudes de onda UV) y una emisión de 500 a 600 nm (luz visible verde-rojo). Esto hace que puedan estudiarse los compuestos fluorescentes o grupos de compuestos fluorescentes (fluoróforos como se han definido anteriormente) (Tedetti *et al.*, 2011).

Los principales fluoróforos son los húmicos y las proteínas tirosina y triptófano. Los picos húmicos se denominan A, C y M. Los A y C son los dos picos asociados al medio terrestre, estos cuentan con una alta aromaticidad. La posición del pico M con una longitud de onda más corta, presenta una menor aromaticidad y es más enriquecido en estructuras alifáticas y refleja la presencia de la OM más lábil/reciente (Coble, 1996; Coble, 2007; Hudson *et al.*, 2008).

Por otro lado, los picos de tirosina y triptófano suelen denominarse como B y T respectivamente (Reynolds y Ahmad, 1997; Baker y Spencer, 2004).

La espectroscopia de fluorescencia de las EEM es un método de caracterización de DOM que se ha utilizado para investigar el comportamiento de materiales obtenidos a

partir de fluoróforos. Dado que las ubicaciones de los picos individuales son sensibles a las condiciones físico-químicas, puede ser difícil evaluar los componentes de la DOM basados en la técnica de recolección de pico de EEM. Más recientemente, una vez obtenidas las EEM también se ha utilizado el análisis del llamado factor paralelo (PARAFAC) para caracterizar los fluoróforos en la DOM y rastrear las reacciones fotoquímicas y microbianas de la OM.

La ventaja que presentan las EEM es que dan información sobre la intensidad relativa de fluorescencia de *Ex* y de *Ex* de longitudes de onda en las diferentes regiones de una manera rápida y fácil de interpretar (Coble, 1996).

3.3.4.2. Resonancia magnética nuclear del ^{1}H (^{1}H-NMR).

La resonancia magnética nuclear (NMR, en sus siglas en inglés) es una técnica no destructiva que proporciona información valiosa sobre las propiedades estáticas y dinámicas de las moléculas, con el fin de caracterizar la OM del suelo y los procesos de humificación. Esto es posible gracias a su alto potencial para evaluar las interacciones intermoleculares.

Varios autores han propuesto el uso de la NMR como una herramienta valiosa para evaluar la degradación de la OM del suelo (Golchin *et al.*, 1994; Baldock y Preston, 1995; Preston, 1996; Knicker *et al.*, 2013). También es usada en el estudio de la relación existente entre la OM del suelo, los contaminantes y metales (Cardoza *et al.*, 2004).

Entre las diversas variantes que existen, ^{1}H-NMR se centra en el análisis de los ácidos húmicos y fúlvicos disueltos en soluciones neutras o alcalinas para caracterizar los componentes de la sustancia, y da una noción semi-cuantitativa de la proporción de grupos aromáticos, alifáticos y carboxílicos (Hemminga y Buurman, 1997). Las estructuras aromáticas condensadas muestran una mayor resistencia a la degradación del suelo y contribuyen al almacenamiento de C a largo plazo (Baldock y Smernik, 2002; Derenne y Largeau, 2001; Almendros *et al.*, 2003).

Un aspecto negativo de esta técnica es su coste económico. Además de un equipo costoso, es necesario el uso de disolventes caros, disponer de tubos de NMR, así como llevar a cabo una preparación de la muestra considerable antes de ser medida (MIT, 2008; Fernández-Romero *et al.*, 2016). Aparte del tiempo requerido para la medición de las muestras es necesario la interpretación de los datos (Cardoza *et al.*, 2004). Todo esto hace que se busquen alternativas en la caracterización de la OM del suelo.

3.3.4.3. Extracción caliente (HWC) y fría (CWC) de C en agua.

El C extraíble en agua es el componente más activo en el ciclo del C. En función de la temperatura de extracción variará su cantidad y naturaleza biológica (Bu *et al.*, 2010).

El HWC incluye microorganismos, hidratos de C solubles y otros compuestos que forman parte de la fracción lábil de la OM del suelo (Ghani *et al.*, 2003). Dada su sensibilidad a corto plazo, se ha utilizado para detectar los efectos de las diferentes prácticas de manejo y para la determinación de los efectos de las enmiendas del suelo tales como biochar o residuos agrícolas (Leifeld y Kogel-Knabner, 2005; Uchida *et al.*, 2012; Alburquerque *et al.*, 2014; Fernández-Romero *et al.*, 2014a).

HWC contiene información útil sobre la calidad del suelo. También se ha usado como indicador de cambios en la OM (Ghani *et al.*, 2003; Xue *et al.*, 2013). Uchida *et al.* (2012) en su experimento utilizaron este parámetro para detectar los efectos de diferentes prácticas de manejo. Se ha encontrado una fuerte correlación entre este parámetro y la estabilidad de los agregados (Puget *et al.*, 1999; Ghani *et al.*, 2002).

El HWC es un método de extracción más exhaustivo que el CWC ya que con el primero se extrae una mayor cantidad de C (Gregorich *et al.*, 2003; Landgraf *et al.*, 2006). Durante la extracción de C en agua caliente se arrastran también otros nutrientes lábiles, haciendo que esta medida sea útil para la determinación de la capacidad de mineralización de otros nutrientes en el suelo.

La determinación tanto de HWC como de CWC es fácil, económica y requiere poco tiempo (Ghani *et al.*, 2002).

3.4. CAMBIO DE USO Y MANEJO EN LOS SUELOS.

3.4.1. Conversión de un suelo agrícola a pastizal o bosque y viceversa.

Las condiciones físicas de los pastizales y bosques son mejores que las de los suelos agrícolas. Por lo general, éstos últimos contienen alrededor del 3,1 % del SOC del suelo, mientras que los pastizales almacenan una mayor concentración (Stockmann *et al.*, 2013), siendo aún superior en los suelos forestales. Por eso estos suelos son tan importantes en el ciclo del C (Scharlemann *et al.*, 2014; Borchard *et al.*, 2015).

Por tanto, la conversión o LUC desde un suelo agrícola a un bosque o pastizal es beneficioso, contrariamente a lo que ocurre cuando este LUC es inverso (Huang *et al.*, 2015b; Kim y Kirschbaum, 2015; Kumar *et al.*, 2015; Sajikumar y Remya, 2015). En este último caso (de bosque a agrícola) hay una pérdida de OM que varía en función de las condiciones climáticas e hidrológicas; profundidad del perfil; drenaje; labranza; manejo; adición de fertilizantes, estiércol y residuos orgánicos al suelo (Nair *et al.*, 2011; Scharlemann *et al.*, 2014). Además, este LUC representa la segunda fuente de

emisión de C atmosférico tras la quema de combustibles fósiles causado por acción antrópica (Fu *et al.*, 2010; Scharlemann *et al.*, 2014; Guan *et al.*, 2015). Generalmente suele darse por razones económicas como ya se comentó anteriormente.

Los suelos agrícolas están sujetos a una intensa degradación (Cerdà *et al.*, 2010, Novara *et al.*, 2013) y su grado de deterioro depende fundamentalmente del clima, textura y manejo (White, 2006). Con el fin de paliar la degradación es importante el mantenimiento de la vegetación superficial para que el suelo no quede desnudo y desprotegido ante la erosión eólica e hídrica mediante el impacto de la gota de lluvia, provocando la obstrucción de los poros del suelo, la reducción de la infiltración del agua dando lugar a la escorrentía, y la aceleración de la erosión del suelo. Cuando la superficie del suelo se seca, se forma una costra que inhibe la emergencia de las plantas y la superficie desnuda después de la labranza, es propensa a la erosión eólica (White, 2006; Srinivasarao *et al.*, 2015). La cobertura vegetal reduce hasta un 93 % de pérdida de suelo (Gómez *et al.*, 2009; Repullo *et al.*, 2012). Del mismo modo, los espacios que quedan entre los distintos cultivos o entre los árboles dispuestos en hileras también deben ser cubiertos por vegetación herbácea natural o sembrada, favoreciendo el almacenamiento de SOC y mejorando de esta forma su estructura, tal y como ponen de manifiesto los cambios experimentados en los parámetros indicadores del estado estructural del suelo (densidad aparente (BD, en sus siglas en inglés), infiltración, retención de agua y trasmisión del calor o los gases) (Ordoñez *et al.*, 2007; Virto *et al.*, 2011). En esta línea, Howlett *et al.* (2011b) encontraron que la existencia de SOC en el suelo fue mayor bajo la copa de los árboles (de 5 m y a 1 m de profundidad del suelo) que en el resto del suelo sin su protección. Sin embargo, Bambrick *et al.* (2010) hallaron que la distribución espacial de los árboles y los cultivos controlan el almacenamiento de SOC en el suelo.

3.4.2. Repoblación de un suelo degradado.

La degradación se podría definir como la pérdida de utilidad del suelo a través de la reducción de la diversidad de los ecosistemas, o bien el daño ocasionado en las características físicas, sociales, culturales o económicas del suelo. Este concepto implica la disminución de la capacidad inherente del suelo para producir bienes económicos. El estado del suelo es uno de los mejores indicadores de su degradación ya que integra una variedad de procesos importantes, tales como, el crecimiento de la vegetación, el flujo superficial del agua, la infiltración, el uso y la gestión del suelo (Nair *et al.*, 2011).

La degradación del suelo supone uno de los problemas sociales, económicos y ambientales más importantes del mundo (Brevik *et al.*, 2015; Wang *et al.*, 2015) y tiene lugar en regiones subhúmedas áridas, semiáridas y secas como resultado de muchos factores, tales como las variaciones climáticas y las actividades humanas (Chen *et al.*, 2015). Es ocasionada por procesos físicos, químicos y/o biológicos. La degradación física se lleva a cabo por un deterioro de la estructura del suelo (agregados estables)

dando lugar a la formación de costras, compactación, aceleración de la escorrentía de las aguas, y erosión del suelo. Los procesos químicos incluyen la acidificación (debido a la lixiviación y el agotamiento de bases tales como calcio y magnesio, siendo común en las zonas de alta precipitación), salinización, disminución de la capacidad de retención de cationes y el agotamiento de la fertilidad. Los procesos biológicos incluyen la reducción del C total y de biomasa, además de la disminución de la biodiversidad del suelo. Estos procesos constituyen una de las principales preocupaciones y están relacionados con la eutrofización y contaminación de las aguas subterráneas, y las emisiones de GEIs (CO_2, CH_4, N_2O) (Nair *et al.*, 2011).

La desertificación es un proceso de degradación del suelo, el cual ha atraído la atención internacional generalizada debido a sus consecuencias (destrucción de los recursos y los sistemas ambientales, aumento de la pobreza, inestabilidad social y disminución del desarrollo económico) (Reynolds *et al.*, 2011). No necesariamente debe ser un proceso irreversible y permanente; si la zona no ha sido degradada más allá de su umbral ecológico podría ser restaurada (Briassoulis, 2011; Chen *et al.*, 2015). Estos procesos de restauración se caracterizan por (1) disminución de la presión impuesta por las actividades humanas excesivas, (2) restauración de las comunidades vegetales, (3) mejoras en las propiedades físico-químicas, (4) incremento tanto de la productividad como de la biodiversidad y (5) restauración del equilibrio ecológico (Su *et al.*, 2010; Su *et al.*, 2013).

3.4.3. Conversión de un cultivo con labranza a sistemas de labranza reducida.

Desde la década de 1960 se ha ido incrementando el uso de maquinaria (especialmente tractores) para llevar a cabo la gestión del suelo. Las ruedas del tractor y el tráfico del resto de vehículos producen compactación en el subsuelo (Srinivasarao *et al.*, 2015). Esto, junto con la labranza intensiva y el uso de fertilizantes químicos ha hecho que el suelo se vea dañado (Calatrava *et al.*, 2011; Montes-Borrego *et al.*, 2013), incrementando sus pérdidas de SOC debido a que éste es oxidado cuando se expone al aire por la labranza (Jaiarree *et al.*, 2014; Srinivasarao *et al.*, 2015). Además ésta afecta a los agregados del suelo haciendo que la OM quede accesible a los microorganismos (Chowdhury *et al.*, 2014).

La labranza convencional (CT, en sus siglas en inglés) llevada a cabo con arado de vertedera (deja la superficie del suelo relativamente irregular, si el suelo no es demasiado arenoso y no está demasiado seco), grada de discos (son muy efectivos para combatir las malas hierbas, entierran aproximadamente un 50 % o más de los residuos superficiales en cada operación y dejan la superficie del suelo relativamente lisa. Si se emplea tres o cuatro veces la superficie del suelo quedará desprovista de residuos y por ello el suelo se hace susceptible a la erosión), herbicidas y fertilización mineral, es muy común en los suelos agrícolas y es la causante de la degradación por erosión cuando hay

lluvias intensas, ya que a la reducida cubierta vegetal presente en estos suelos se le unen las pendientes en las que suele estar localizado, por ejemplo, el olivar (FAO, 1988; Cerdà *et al.*, 2010; Prokop y Poręba, 2012; Mandal y Sharda, 2013; Ziadat y Taimeh, 2013). Alrededor de un 36 % del olivar en Andalucía presenta unas pendientes superiores al 15 %, ya que estas laderas no son rentables para otros cultivos desde el punto de vista productivo-económico (Ibáñez *et al.*, 2014).

La labranza ha sido durante mucho tiempo una actividad agrícola clave para el suelo, debido a que lo prepara para la siembra, para incorporarle fertilizantes y residuos de cosecha, para aliviar la compactación del mismo, y para controlar las malezas (Gao *et al.*, 2015; Sainju *et al.*, 2012). No obstante, las prácticas de labranza inapropiadas conllevan una serie de aspectos negativos para el suelo (figura 4) (Srinivasarao *et al.*, 2015). Todos esto puede verse agravado por la erosión hídrica y eólica (Curaqueo *et al.*, 2011; Brunel *et al.*, 2013; Srinivasarao *et al.*, 2015). Otros aspectos negativos de la labranza son los gastos de combustible para el funcionamiento de la maquinaria, el desgaste de los equipos y el tiempo que el operario invierte en ella (Srinivasarao *et al.*, 2015).

En los últimos años cada vez más agricultores y un gran número de investigadores han propuesto alternativas a este sistema convencional de labranza, implantando uno de conservación que consiste en la reducción de las pérdidas de suelo y agua, frecuentemente porque se mantienen los residuos sobre la capa superficie mediante una labranza que no voltee el suelo. La reducción del arado aumenta la infiltración del agua y el contenido de OM hasta una profundidad de 40 cm, mejorando los agregados del suelo, ahorrando tiempo y reduciéndose la erosión, BD, emisiones de GEIs y costes de producción (Verhulst *et al.*, 2010; Jat *et al.*, 2012; Kassam y Friedrich, 2012; Kumar *et al.*, 2012; Sapkota *et al.*, 2012; Gao *et al.*, 2015). Además trae consigo una serie de beneficios sobre la calidad del suelo, su productividad y el potencial de sostenibilidad a largo plazo en términos de almacenamiento de C (Ghosh *et al.*, 2010; Grace *et al.*, 2012; Naresh *et al.*, 2012; Srinivasarao *et al.*, 2015). Los tipos de labranza de conservación son: la labranza con cobertura de rastrojo, mínima o reducida, y la labranza cero.

Figura 4. Impactos de la labranza en el suelo. Adaptado de Srinivasarao *et al.* (2015).

La *labranza con cobertura de rastrojo* se basa en la labranza sub-superficial, en la que la maquinaria corta las raíces de las plantas y retiene los residuos de los cultivos sobre la superficie. En donde hay grandes cantidades de residuos se puede usar grada de discos.

Esta labranza se lleva a cabo tantas veces como sea necesario para eliminar las malas hierbas durante el intervalo entre los cultivos. Se pueden aplicar fertilizantes en la superficie y posteriormente se incorporarán al resto del perfil mediante la labranza.

La *labranza mínima o reducida* tiene un número limitado de operaciones de campo, pero se usa tanto el arado de vertedera como las gradas de discos para preparar el suelo para la siembra, dejando una superficie rugosa y rica en nutrientes que proteja de la erosión. Principalmente consiste en una siembra manual y una eliminación de las malas hierbas mediante el uso de herbicidas. También se usan fertilizantes en éste tipo de labranza.

Por último la *labranza cero* no lleva a cabo una preparación de la superficie del suelo previo a la siembra, pero sí emplea el uso de herbicidas para combatir las malas hierbas (es imposible el uso de fertilizantes) y como su propio nombre indica el suelo no es labrado. Hay situaciones en las que la labranza no es completamente nula pero puede

clasificarse de esta manera ya que se labra menos del 25 % de la superficie para eliminar las semillas de las malezas persistentes. La eliminación de las malas hierbas conserva el agua y mejora su capacidad de infiltración, reduce los problemas de siembra y favorece el crecimiento de las plantas. Las capas de suelo sub-superficial alteradas favorecen la penetración del agua, el enraizamiento profundo y la proliferación de las raíces, y el uso del agua y de los nutrientes por las plantas (FAO, 1988).

3.4.4.   Aplicación de subproductos al suelo.

La necesidad de emplear unas prácticas agrícolas sostenibles con el fin de reducir las emisiones de los GEIs, reducir la pérdida de suelo y la escorrentía, preservar la OM en el suelo y mantener la fertilidad del mismo ha hecho que la aplicación de las técnicas de conservación ganen importancia a nivel mundial (Atkinson *et al.*, 2010; Jones *et al.*, 2012; Schulz y Glaser, 2012; Alburquerque *et al.*, 2014; Lehmann y Joseph, 2015; Puga *et al.*, 2015). Además de las mencionadas anteriormente existen otras que consisten en la adición de subproductos al suelo, procedentes de las industrias agroalimentarias cercanas, con el objetivo de:

1- reparar las propiedades físicas de los suelos, así como modificar su estructura y todo lo que ello conlleva: aireación, flujo de agua (aumentaría su cantidad, infiltración y permanencia ya que se reduce la evaporación), textura, BD;

2- restablecer las propiedades químicas de los suelos mediante variaciones en el pH, capacidad de intercambio catiónico (CEC, en sus siglas en inglés), procesos redox, disponibilidad de nutrientes, contenido de OM;

3- mejorar las propiedades biológicas del suelo dando lugar a cambios en los microorganismos y el resto de la fauna, así como en su actividad biológica (Sohi *et al.*, 2010; Herath *et al.*, 2013; Atkinson *et al.*, 2010; Lehmann *et al.*, 2011) y

4- reutilizar residuos que pueden conducir a un aumento en la productividad de los cultivos (aproximadamente un 10 %) (Horn *et al.*, 2012; IBI, 2014; Janus *et al.*, 2015; Ajayi *et al.*, 2016).

Estos residuos son:

a) Restos de poda (hojas y ramas).

Los restos de poda se añaden al suelo (figura 5) ya picados o triturados para que desaparezca el riesgo por plagas y para protegerlo de la erosión durante un tiempo prolongado. Salvo que actúe algún tipo de labranza, su descomposición y humificación

serán lentas debido a su elevada proporción en celulosa y lignina, contenido medio-bajo de humedad y alta relación C:N. Para que su descomposición sea más rápida debe añadirse el primer año de aplicación (posteriormente se habrá creado una fauna más específica encargada de ello) una fuente nitrogenada al suelo, bien de naturaleza orgánica (estiércol, purines, etc.) o inorgánica (abonos de amoniaco o urea) (Ordoñez *et al.*, 2007; Repullo *et al.*, 2012).

Figura 5. Suelo de olivar en área Mediterránea con la adición de hojas de olivo. Elaboración propia.

Los cultivos leñosos como el olivar de secano andaluz proporcionan grandes cantidades anuales de restos de poda (entre 1,3 y 3,0 t ha^{-1}). Éstos contienen altos valores de OM y humedad, y están libres de metales y patógenos (Lozano-García *et al.*, 2011). Tradicionalmente estos residuos se queman, bien como combustible en el caso de la leña gruesa, o con fin de evitar plagas llevando consigo problemas medioambientales (flameado de olivos cercanos al fuego y emisiones) (Qingren *et al.*, 2010). Una solución a esto sería su esparcimiento entre las calles de los olivos convirtiendo el residuo en recurso. Además presenta una serie de ventajas para el suelo: lo protegen de los agentes externos que causan su erosión, su degradación lenta modifica las propiedades del suelo incrementando su fertilidad de forma natural, se reduce el uso de herbicidas ya que la cubierta de restos de poda tiene un efecto sobre las malas hierbas (Ordoñez *et al.*, 2007).

Mediante una serie de estudios se ha comprobado que la adición de hojas al suelo ha incrementado el SOC y su fertilidad (Lozano *et al.*, 2011; Repullo *et al.*, 2012; Fernández-Romero *et al.*, 2014a).

b) Subproductos de industrias agroalimentarias: alperujo y vinazas.

El alperujo es un producto de desecho, de color oscuro y olor intenso, originado en el proceso de extracción del aceite de oliva (mediante dos fases). Presenta un alto contenido en grasas, azúcares, N, ácidos orgánicos, polialcoholes, pectinas, taninos y polifenoles. Además su pH es moderadamente ácido (5,4) y su conductividad es elevada (Hernández *et al.*, 2014). Se usa en la producción de energía (Lama-Muñóz *et al.*, 2014) pero también se están estudiando otras formas de aprovecharlo, tales como la aplicación directa al suelo (figura 6) determinando sus efectos sobre las propiedades del mismo. Algunos de esos estudios son los llevados a cabo por Lozano-García y Parras-Alcántara, (2013b) y Nasini *et al.* (2013) que no encontraron ningún efecto sobre el SOC, al contrario que Altieri y Esposito, (2008), que además de alperujo añadieron hojas, restos de poda y paja de trigo, entre otros para reducir la acidez y mejorar las propiedades del alperujo. Algunos efectos tóxicos en plantas y microorganismos del suelo han limitado su aplicación (Pozzi *et al.*, 2010; De la casa *et al.*, 2012).

En general los residuos de las almazaras suelen ser compostados (transformando el alperujo en abonos orgánicos de calidad) ya que su frecuente aplicación al suelo mejora su CEC, estructura, estabilidad y permeabilidad (Álvarez, 2013). Éste compost puede mezclarse con otros subproductos agrícolas (por ejemplo, la cáscara de arroz, hojas de olivar) para producir enmiendas de suelo de alta calidad (Alburquerque *et al.*, 2011; Chowdhury *et al.*, 2014). El compost maduro a partir de residuos de la almazara parece tener excelentes características, ya que está libre de fitotoxicidad y contiene alta OM (alto grado de humificación) y contenido de nutrientes (N, P, K, Na) (Serramía *et al.*, 2013; Tortosa *et al.*, 2014). Según Toscano *et al.* (2013), los subproductos de las almazaras aplicados a los olivares incrementan la producción de aceitunas (en un 9 %) y la de aceite (166-179 kg ha^{-1}).

Por su parte, la vinaza es un residuo líquido que presenta un color oscuro, alta demanda química de oxígeno y supone la mayor fuente de contaminación de la industria del etanol. Sin embargo es rico en varios nutrientes minerales esenciales para el crecimiento de las plantas y productividad de las cosechas (Darcy Dos Santos *et al.*, 2013). Al igual que ocurre con el alperujo, el uso de vinaza fresca ocasiona un impacto perjudicial sobre las propiedades físicas, químicas y biológicas del suelo, aumentando la pérdida de suelo y la disminuyendo la cobertura vegetal, probablemente debido a que contiene altas cantidades de cationes monovalente, tales como Na^{+}, que desestabilizan la estructura del suelo. Mientras que el compostaje de vinaza tuvo un efecto positivo sobre el suelo, siendo una buena estrategia para la recuperación de las zonas semiáridas (Tejada *et al.*, 2009).

Figura 6. Suelo de olivar en área Mediterránea con la adición de alperujo.Cedido por Parras-Alcántara, L.

c) Biochar.

Es un producto sólido y rico en C estable que resulta de la descomposición térmica y la combustión incompleta de la biomasa (pirólisis) en condiciones de anoxia o limitadas de oxígeno (Joseph *et al.*, 2010; Alburquerque *et al.*, 2014; Ghaffar *et al.*, 2015; Janus *et al.*, 2015). Presenta estructura predominantemente aromática y porosa, gran superficie específica, buena estabilidad química y biológica (resistente a la descomposición química y biológica), y puede potencialmente permanecer en el suelo cientos de miles de años. Es eficaz como enmienda (especialmente en el control de la acidez del suelo), absorción de contaminantes, filtración de agua de percolación del suelo, fertilidad, capacidad de retención de agua y en el secuestro de C (Roberts *et al.,* 2010; Park *et al.*, 2011; Guo *et al.*, 2014; Qiao *et* al., 2015; Ajayi *et al.*, 2016). Además, cuando el biochar se añade al suelo supone una ganancia neta de C, debido a la mejora en su capacidad de almacenamiento y a la contribución de C almacenado en las propias partículas de biochar (Woolf *et al.*, 2010; Ajayi *et al.*, 2016).

Las técnicas de HWC y $SUVA_{254}$ (comentadas en el apartado 3.3.4) son las adecuadas en la caracterización del biochar. HWC determina los efectos de las enmiendas al suelo como el biochar o residuos agrícolas y $SUVA_{254}$ es directamente proporcional a la aromatidad del biochar, lo cual significa que podría potencialmente usarse para

determinar la aromaticidad (Uchida *et al.*, 2012; Xue *et al.*, 2013; Alburquerque *et al.*, 2014; Jamieson *et al.*, 2014).

3.5. STOCK DE CARBONO (SOC Stock, (SOCS)).

3.5.1. Estudio del SOCS y factores de los que depende.

Es necesario el estudio de las reservas de SOC (SOCS) ya que su cuantificación (en forma de unidad de superficie sobre una profundidad específica) y distribución espacial son útiles para determinar la capacidad de sumidero de SOC y mejorar su captura en el suelo (Batjes, 2014b). Teniendo en cuenta los mecanismos que controlan el SOCS se puede recuperar el C en el suelo (Mishra *et al.*, 2009; Dorji *et al.*, 2014). Otra de las razones por las que es importante estudiar las reservas de SOC en profundidad es porque la contribución de las raíces de las plantas al contenido y estabilidad del SOCS es mayor que la de los residuos vegetales (Katterer *et al.*, 2011; Kell, 2011; Srinivasarao *et al.*, 2015) y por tanto el C localizado a más de 20 cm de profundidad contiene más del 50 % del total de SOCS (T-SOCS) y se considera recalcitrante e/o inaccesible a la degradación microbiana (Rumpel y Kögel-Knabner, 2010). Sin embargo, ciertos estudios basados en radiocarbono sugieren que los depósitos de C recalcitrante pueden rotar rápidamente (Schmidt *et al.*, 2011; Cusack *et al.*, 2012).

No obstante, es importante resaltar que en los estudios más recientes sobre el tema, varios investigadores señalan la necesidad de que exista un consenso a la hora de estimar los valores de SOCS y desarrollar un protocolo con el fin de poder hacer comparaciones entre los distintos estudios (Gurung *et al.*, 2015).

Los suelos contienen un SOCS de aproximadamente 1400 Pg C almacenado en sus primeros 100 cm (Kirsten *et al.*, 2015). De unos suelos a otros pueden diferir significativamente su valor debido a la influencia de una serie de factores locales. Éstos son:

a) *Topografía*: pueden establecerse distintas posiciones topográficas a lo largo de una toposecuencia. La tendencia general es la de encontrar las mayores concentraciones de SOCS en la posición topográfica más baja, mientras que en la más elevada es donde se localizan las menores concentración. Sun *et al.* (2015) encontraron esta misma tendencia para suelos agrícolas, de matorral y pastizal. Sin embargo no encontraron ningún efecto de la topografía en el SOCS para suelos forestales. Fernández-Romero *et al.* (2014b) estudiaron tres posiciones topográficas (cima, posición media y base) tanto para suelos forestales como de olivar en el área mediterránea y sus resultados coincidieron también con esa tendencia general encontrando una distribución similar de SOCS en todas las posiciones topográficas de los suelos forestales y una mayor concentración de SOCS en la posición topográfica más baja para el olivar debido

a la erosión. Schwanghart y Jarmer, (2011) encontraron los mismos resultados para suelos del sureste de España.

b) *Propiedades del suelo*: tales como la textura, CEC y pH están mal caracterizados ya que pueden interactuar con factores como la humedad y vegetación del suelo para controlar la acumulación y retención de SOC (O'Brien *et al.*, 2015). El SOCS puede variar en función de los parámetros químicos que controlan la estabilidad del SOC (Kirsten *et al.*, 2015). La actividad biológica también influye en el SOCS, ya que al reducirse la descomposición microbiana se incrementa la acumulación SOC (Von Haden y Dornbush, 2014).

c) *Uso del suelo*: Los suelos forestales son los que presentan una mayor concentración de SOCS (Dorji *et al.*, 2014). A nivel mundial, almacenan unos 818 Pg C en el primer metro de suelo en una superficie de 4,1 Mha (Jobbagy y Jackson, 2000), mientras que a nivel europeo, éste es de 22,1 t C ha^{-1} en el primer metro de suelo (De Vos et al., 2015). Las praderas o dehesas tienen unos valores similares o algo más bajos que los bosques (Poeplau *et al.*, 2011). A continuación le siguen los pastizales ya que tienen una gran capacidad de acumulación de SOC (O'Brien *et al.*, 2010; Poeplau *et al.*, 2011). Posteriormente los sistemas agroforestales, así como los suelos hortícolas (Lorenz y Lal, 2014) y por último los suelos agrícolas que son los que menor concentración poseen (Saha *et al.*, 2011; Dorji *et al.*, 2014) ya que el cultivo agota drásticamente las reservas de SOCS en la capa superficial, disminuyendo la fertilidad del suelo y afectando al ciclo global de C (O'Brien *et al.*, 2015). Los suelos agrícolas degradados cuentan con un 25% menos de SOCS que los bosques (Wang *et al.*, 2012; Sharma *et al.*, 2014).

d) *Gestión del suelo*: La aplicación de unas prácticas de manejo adecuadas incrementa el contenido de SOCS en 1 Mg ha^{-1} año^{-1}, aumentando de esta forma su producción (Dorji *et al.*, 2014; Srinivasarao *et al.*, 2015). Mediante estas prácticas puede recuperarse la vegetación nativa (bosques o pastizales perennes) y contribuir así a la recuperación de SOC ofreciendo sumideros para el aumento de CO_2 en la atmósfera (O'Brien *et al.*, 2015). Los mayores valores de SOCS se encuentran en aquellas zonas que no han eliminado sus residuos sino que los han mantenido en su capa superficial y además estaban bajo NT (Villamil y Nafziger, 2015). Cardinael *et al.* (2015) estudiaron el impacto de los sistemas agroforestales en el SOCS y encontraron que sus valores eran mayores en zonas donde se desarrollaba vegetación herbácea y además donde había una NT.

e) *El LUC* ha provocado un descenso drástico en las concentraciones de SOCS. En los últimos 20 años se han llevado a cabo estudios que estiman su contribución en el ciclo del C a escala regional y global (ya que el SOCS se redujo un 9,5 % a nivel mundial en el primer metro de suelo (7 Pg C) (Guan *et al.*, 2015). El LUC se estudia conjuntamente con la cubierta vegetal, ambos pueden variar el contenido de SOCS (Dorji *et al.*, 2014). El LUC desde un suelo forestal a

agrícola contribuye a pérdidas de hasta 12,4 Mg ha^{-1} de SOC en los primeros 50 cm del suelo (Luo y Weng, 2011; Sharma *et al.*, 2014).

3.5.2. Estimaciones del SOCS.

El SOCS depende de la concentración de C (comentado en el apartado 3.5.2), BD, espesor del horizonte y contenido en gravas (IPCC, 2003). Puede determinarse a escala regional, nacional y global (Civeira *et al.*, 2012; Kochy *et al.,* 2014; Parras *et al.*, 2015).

3.5.2.1. Densidad aparente (BD).

La BD influye en el SOCS de todo el perfil del suelo, y es particularmente crucial en la superficie, donde se almacena gran cantidad de SOC. Puede variar en función de la gestión del suelo (el uso de maquinaria pesada da lugar a la compactación, incrementando así la BD y reduciendo la porosidad). Además, la BD también puede variar a lo largo de los años como consecuencia de las diferencias en el tipo de suelo (se hinchan o se contraen), la humedad, etc. (Yang *et al.*, 2013). Generalmente la BD aumenta con la profundidad del suelo, mientras que la concentración de SOCS disminuye (Guan *et al.*, 2015).

3.5.2.2. Espesor del horizonte.

Los valores de SOCS tienden a disminuir con la profundidad (Wang *et al.* 2012; Fernández-Romero *et al.*, 2014b; Sun *et al.*, 2015). En las estimaciones de SOCS es importante tener en cuenta la profundidad que va a tomarse para el estudio, ya que puede ser genética (es decir teniendo en cuenta el espesor de cada horizonte) o secciones de control (SC) (es una medida establecida igual para todos los horizontes del perfil). Las estimaciones de SOCS pueden estar afectadas por su método de muestreo y la elección uno u otro es importante para proporcionar resultados que sean fiable, comparable y se puedan extrapolar (Lal, 2005; Parras-Alcántara *et al.*, 2015). Hay estudios usando un método y otro justificando en cada caso los beneficios de la metodología (VandenBygaart, 2006; Parras-Alcántara *et al.*, 2015). Por el contrario hay estudios que sólo contemplan SC, como por ejemplo Palmer *et al.* (2002), que controlan los cambios de SOC en la superficie de un suelo forestal. Es muy importante que el diseño del experimento esté enfocado a los objetivos que se pretenden obtener (Baritza *et al.*, 2010; Parras-Alcántara *et al.*, 2015).

3.5.2.3. Gravas.

Las gravas (2-76 mm de diámetro) consideradas una fracción inorgánica importante del suelo, influyen en el suministro de nutrientes, crecimiento de la vegetación y reducción de la cantidad de agua perdida a través de la evaporación (Koele *et al.*, 2010; Rytter, 2012; Qiu *et al.*, 2014). Qin *et al.* (2015) investigaron los efectos de las gravas en el SOC y llegaron a la conclusión de que (1) tenían efectos negativos, (2) el tamaño entre 2 mm y 20 mm era el más importante en la determinación de las propiedades del suelo y de la vegetación, (3) no eran propicias en el secuestro de nutrientes y el crecimiento de la vegetación para ambientes áridos y semiáridos y por último, (4) debían de tenerse en cuenta su contenido y tamaño en los diferentes estudios.

3.6. CALIDAD DEL SUELO (RELACIÓN DE ESTRATIFICACIÓN (SR)).

La calidad del suelo es su capacidad para funcionar dentro de los límites de los ecosistemas, para mantener la productividad animal y vegetal, mejorar la calidad del agua y aire y apoyar a la población y la salud humana (De Moraes y Lal, 2009). La superficie del suelo es la capa que reciben los fertilizantes y pesticidas aplicados a los cultivos, el impacto de la gota de lluvia y el flujo de entrada y salida de los gases (Zhang *et al.*, 2015a).

Diferentes técnicas para evaluar la calidad del suelo han sido desarrolladas y aplicadas en diferentes regiones y con distintos manejos (Das *et al.*, 2014; Beniston *et al.*, 2015; Zhao *et al.*, 2015). Aunque hay que destacar la importancia y dificultad de encontrar índices cuantitativos que sean capaces de ello en sitios determinados con precisión, de medir los efectos sobre sus propiedades durante un período de tiempo y ofrecer su comparabilidad. La calidad de éstos debe ser fácil de medir, capaz de reflejar los cambios a corto y largo plazo en las propiedades del suelo, ser sensible a los LUC, y accesible al mayor número posible de usuarios (Shukla *et al.*, 2006; Duval *et al.*, 2013). A esta dificultad se le añade las complejas interacciones existentes entre el clima, la composición y gestión del suelo y la posición del paisaje que complican la determinación de la calidad del suelo en base a un solo factor (Ogle *et al.*, 2012).

Una de las propiedades más significativas que se han investigado en el contexto de la calidad del suelo es el SOC. Científicos como Quiroga *et al.* (2005) creen que es el mejor indicador para medir la calidad y productividad. Sin embargo, otros científicos como Duval *et al.* (2013) indican que el SOC sólo no es un buen indicador, ya que los cambios que muestra son a corto plazo. Además, no siempre es el mejor indicador de los cambios en la gestión del suelo en condiciones semiáridas (Melero *et al.*, 2012; Blanco-Moure *et al.*, 2012).

Franzluebbers, (2002) estableció la relación de estratificación (SR, en sus siglas en inglés) de C como un indicador eficaz de la calidad del suelo que evalúa las características de la estratificación. La SR se define como el cociente entre el valor de

una propiedad del suelo en la superficie y el valor de la misma propiedad a mayor profundidad (Zhang *et al.*, 2015b).

La evaluación de la calidad del suelo abarca propiedades inherentes y dinámicas del mismo y todas las interacciones deben ser contabilizadas (Karlen *et al.*, 2003; Van Leeuwen *et al.*, 2015). Los factores importantes que influyen en la calidad del suelo son la labranza, rotación de cultivos, tipo de abono (si se aplica), clima y tipo de suelo (Imaz *et al.*, 2010). Una de las principales causas de la degradación del suelo es la agricultura no sostenible (Francaviglia *et al.*, 2014). Por esta razón, el tipo de labranza ha sido de gran interés con respecto a la investigación de la calidad del suelo (Lal *et al.*, 1998). En suelos con moderada a fuerte pendiente, la labranza convencional contribuye a un aumento de la erosión y degradación, reduciendo su OM (Lozano-García *et al.*, 2011). Por otra parte, la influencia de la labranza convencional en la pérdida de nutrientes conduce al deterioro de las propiedades físicas, químicas y biológicas del suelo, reduciendo así su calidad (Salvo *et al.*, 2010; Parras-Alcántara y Lozano-García, 2014). En esta línea, y como consecuencia de este efecto, varias alternativas han sido examinadas en las dos últimas décadas: la *no labranza* que ha demostrado mejorar las propiedades del suelo y reducir su erosión (Moreno *et al.*, 1997; Franzluebbers, 2002; Melero *et al.*, 2009a,b; Parras-Alcántara *et al.*, 2013) y la *labranza de conservación* que combina la mejora de las propiedades del suelo y los residuos agrícola, dos objetivos de la agricultura sostenible (Moreno *et al*., 2006; Govaerts *et al.*, 2009). Esto es especialmente importante, ya que algunas propiedades como la retención de agua, el SOC, carbonatos y contenido de nutrientes se pueden mejorar con este tipo de labranza en los suelos mediterráneos del sur de España (Moreno *et al.*, 1997). La tasa de adopción de estas alternativas ha sido lenta en Europa. Por ejemplo, sólo el 1 % de la superficie total que se gestiona con la no labranza en el mundo se encuentra en Europa. España cuenta en la actualidad con el 56 % de la superficie total de no labranza en Europa (Derpsch y Friedrich, 2010).

La SR del SOC y N con la profundidad son buenos indicadores (Franzluebbers, 2002; Sà y Lal, 2009; Corral-Fernández *et al.*, 2013). La SR de C:N se ve influida por la labranza y la incorporación de residuos de cosecha (Lozano-García y Parras-Alcántara, 2013a). Como resultado, la relación C:N y su SR se consideran buenos indicadores de calidad del suelo porque reflejan interacciones de C y N (Puget y Lal, 2005; Lou *et al.*, 2012).

Sin embargo, la SR presenta una serie de disparidades significativas vinculadas a su propia definición. El SOC, N y C:N disminuyeron en la mayoría de los suelos estudiados con el cambio de manejo del suelo y la adición de residuos de las almazaras (alperujo y hojas), sin embargo los índices de SR aumentaron con estos cambios. Los resultados pueden parecer contradictorios ya que una disminución del SOC, N y C:N debería implicar una disminución de los valores del índice de SR. Además podrían destacarse otras disparidades más del índice de SR: (i) la asignación de valores numéricos (cuantitativos) a intervalos (cualitativos), esto sin un criterio científico

concreto es muy subjetivo. Por lo tanto, los valores obtenidos se pueden entender pero no han sido verificados; (ii) el índice de SR es descriptivo (analiza la situación actual). Sin embargo, no se analiza el comportamiento de la variable estudiada con el tiempo (variable de diagnóstico); (iii) la evaluación de la calidad del suelo en base a una sola variable (índice SR) podría conducir a una simplificación de la evaluación. Sin embargo, la génesis del suelo es mucho más compleja (Brevik, 2013). Como resultado de ello, parecería lógico utilizar varias variables en lugar de una sola variable; (iv) valores muy altos de SR con la profundidad no implican el establecimiento de declaraciones precisas sobre la calidad del suelo. Por consiguiente, sería necesario determinar las diferencias de C mínimo detectable en capas más profundas (Parras-Alcántara *et al.*, 2013).

OBJETIVOS

4. OBJETIVOS.

En este contexto los objetivos de esta memoria de Tesis Doctoral son:

1- Evaluar el efecto del cambio de uso (bosque mediterráneo-olivar tradicional) en el carbono y nitrógeno a lo largo de una toposecuencia (Summit, Backslope y Toeslope) además de establecer la calidad de los suelos estudiados en forma de la relación de estratificación de SOC.

2- Analizar el efecto de diferentes manejos en olivar (Cultivo tradicional (CT) usado como control, CT con la adición de alperujo, CT con la adición de hoja, no labranza (NT) con la adición de restos de poda y NT con la adición de restos de poda y cubierta vegetal) en el SOC y el carbono orgánico disuelto del C extraído en agua caliente.

3- Establecer el uso de las técnicas ópticas (absorbancia, fluorescencia y DOC, todas ellas del C extraído en agua caliente) como alternativa a la ^{1}H-NMR en la determinación de la calidad de la OM del suelo.

4- Analizar la calidad de los suelos a partir de la SR del SOC, N y C:N en olivar bajo diferentes manejos (Cultivo tradicional (CT) usado como control, CT con la adición de alperujo, CT con la adición de hoja, no labranza (NT) con la adición de restos de poda y NT con la adición de restos de poda y cubierta vegetal).

MATERIAL Y MÉTODOS

5. **MATERIAL Y MÉTODOS.**

5.1. DESCRIPCIÓN DEL ÁREA DE ESTUDIO.

El área de estudio se compone de tres zonas diferentes. La primera zona se sitúa en Torredelcampo (Jaén, España), la segunda en el Valle de los Pedroches (norte de la provincia de Córdoba, España) y la tercera en Berkshire (sureste de Inglaterra).

Los suelos estudiados en España son Calcisoles, Regosoles, Vertisoles y Cambisoles (IUSS-ISRIC-FAO, 2006).

5.1.1. Zona I.

Torredelcampo se encuentra situado a 647 m.s.n.m. Al sur y sureste del núcleo urbano se eleva el relieve hasta los 1614 m, mientras que al norte el relieve es más alomado. En relación a la distribución de pendientes, las zonas norte y central del municipio están ocupadas por pendientes que no superan el 8 %, mientras que en la zona que coincide con el núcleo urbano y las zonas externas de las Cordilleras Béticas, las pendientes son más acusadas (las mínimas son del 8 %, llegando incluso a un 40 % de máxima).

La zona de estudio está localizada sobre margas del Mioceno y margocalizas (Fernández-Romero, 2012). Además se caracteriza por poseer un clima Mediterráneo con 3-5 meses de veranos secos y calurosos (desde finales de junio a septiembre) e inviernos fríos y húmedos. En la provincia de Jaén la temperatura media anual es de 16,2 ºC y la precipitación anual, de 646,3 mm (REDIAM, 2007; AEMET, 2014).

Esta zona está tradicionalmente cubierta por bosque mediterráneo (*Quercusrotundifolia, Quercusfaginea, Quercuscoccifera, Bupleurumfruticosum, Cistusalbidus, Pinushalepensis y Pinuspinaster, Ophryslutea y Gladiolo illyricus*). Sin embargo, parte de ésta se transformó en olivar durante la década de los 40. El olivo (*Olea europaea*) de la zona de estudio presenta una variedad de aceituna Picual y se encuentra en suelos de secano. Tiene una densidad arbórea de 90 árboles ha^{-1} y cada uno de ellos posee de dos a tres troncos.

La gestión tradicional del olivar una vez recolectada la cosecha consiste en una fertilización mineral (100 kg ha^{-1} de urea (46 % N) en años alternos y aplicada durante el invierno), el uso del arado de discos (25 cm), y, a continuación, un arado de vertedera para disminuir el tamaño de los terrones del suelo en verano. Finalmente, se añade herbicida para controlar las malezas en otoño (las últimas dos prácticas se aplican exclusivamente bajo los árboles). Este manejo tradicional se conoce como laboreo convencional (figura 7).

Figura 7. Suelo de olivar con laboreo convencional. Elaboración propia.

Cada vez mayor número de agricultores está implantando técnicas de manejo alternativas al cultivo tradicional con el objetivo de mejorar la calidad de los suelos y por tanto la producción, algunas de las utilizadas en esta zona son: (i) laboreo convencional con adición de alperujo, (ii) laboreo convencional con adición de hojas de olivo, (iii) no laboreo con adición de restos de poda (figura 8), y (iv) no laboreo con adicción de restos de poda y cubierta vegetal (figura 9). En el manejo denominado como "no laboreo", no se labra el suelo ni se controlan las malezas, pero sí se aplica fertilizante mineral. Hay que resaltar que los suelos estudiados bajo estos manejos diferentes presentan propiedades físico-químicas similares.

Figura 8. Suelo de olivar sin laboreo y con adición de restos de poda. Elaboración propia.

En esta zona de estudio también se cultiva cereal (aunque su representación es minoritaria frente al olivar). En el cultivo del cereal se sigue la alternancia típica de trigo, cebada y un período de rastrojo (barbecho). El tipo de manejo es convencional, con un patrón muy similar al del olivar (figura 10).

Figura 9. Suelo de olivar sin laboreo y con adición de restos de poda y cubierta vegetal. Elaboración propia.

Figura 10. Suelo de cereal con manejo convencional. Elaboración propia.

5.1.2. Zona II.

En el Valle de los Pedroches se extiende el llamado Batolito de los Pedroches. Presenta suelos silíceos y la morfología es muy suave causada por la intensa alteración meteórica producida sobre el granito durante los climas cálidos del Plioceno. Se encuentra entre los 500 y 800 m de altitud (Zoido, 2012). Todos los suelos estudiados en la zona se dedican al cultivo de cereal (figuras 11, 12, 13 y 14), el cual presenta el mismo manejo y alternancia de cultivos que el de Torredelcampo. Esta zona se caracteriza por un clima Mediterráneo, igual que la anterior, pero en la provincia de Córdoba la temperatura media anual es de 17,6 ℃ y la precipitación anual de 536 mm (REDIAM, 2007; AEMET, 2014).

Figura 11. Cambisol con un uso de cereal (un año de cebada, un año de trigo y un año de rastrojo) en Hinojosa del Duque. Cedido por Parras-Alcántara, L.

Figura 12. Cambisol con un uso de cereal (un año de cebada, un año de trigo y un año de rastrojo) en Pozoblanco. Cedido por Parras-Alcántara, L.

Figura 13. Cambisol con un uso de cereal (un año de cebada, un año de trigo y un año de rastrojo) en Pozoblanco. Cedido por Parras-Alcántara, L.

Figura 14. Cambisol con un uso de cereal (un año de cebada, un año de trigo y un año de rastrojo) en Pozoblanco. Cedido por Parras-Alcántara, L.

5.1.3. Zona III.

Los suelos estudiados en el sureste de Inglaterra, en Berkshire (concretamente en tres zonas dependientes de la Universidad de Reading (Sonning (figuras 15 y 16), Arborfield (figura 17) y Shinfield (figura 18)) son cambisoles, bajo un clima templado caracterizado generalmente por inviernos y veranos relativamente suaves y precipitaciones durante todo el año. La temperatura media anual oscila entre 6,7 °C y 14,5 °C (con una temperatura media anual de 10,5 ºC), y la precipitación media anual es de 635,4 mm (UK MetOffice, 2014). El relieve de la zona no supera los 200 m de altitud y se trata de una gran llanura sedimentaria que apenas ha sido afectada por las perturbaciones terciarias y cuaternarias. Las margas y arcillas son predominantes en la zona (Cranfield University, 2015).

Figura 15. Cambisol en Sonning. Elaboración propia.

Los suelos muestreados en Sonning han estado cubiertos de hierba durante más de 15 años; los de Arborfield han tenido pastos permanentes hasta el otoño de 2012 y posteriormente trigo o cebada durante el invierno; y los de Shinfield han tenido una rotación de cultivos durante más de 20 años con trigo y maíz/cebada. En todos ellos se lleva a cabo una labranza convencional (durante el otoño) del mismo modo que en los cultivos anteriores.

Figura 16. Cambisol en Sonning. Elaboración propia.

Figura 17. Cambisol con uso de trigo o cebada durante el invierno en Arborfield. Elaboración propia.

Figura 18. Cambisol con una rotación de cultivos (trigo y maíz/cebada) durante más de 20 años en Shinfield. Elaboración propia.

5.2.   TOMA DE MUESTRAS Y SU PREPARACIÓN.

Las muestras de suelo se obtienen por horizontes en unos casos y por secciones de control de 25 cm en otros, en función del análisis (ver apartado 3.5.2.2).

En el laboratorio y antes de proceder a su análisis, las muestras de suelo se secan al aire en bandejas mezclándolas bien para dejar expuestas nuevas superficies. Una vez seco se rompen los agregados con un rodillo de madera, tamizándose con un tamiz de 2 mm de malla.

Los puntos de muestreo y repeticiones de cada experimento vienen comentados en cada estudio en concreto (apartado 10.1).

5.3. MÉTODOS ANALÍTICOS.

Algunos de ellos se determinan con dos métodos distintos ya que se llevan a cabo en países diferentes, habiendo solamente un tipo de medición disponible en cada caso. Este hecho no tiene influencia en el análisis, ya que no se comparan las muestras entre sí, sino que se usan para estudios separados.

5.3.1. Densidad aparente.

El procedimiento seguido es el descrito por Blake y Hartge (1986). Se recoge la muestra con un cilindro de volumen conocido. Se seca a 105 ºC hasta peso constante. Se pesa y conociendo el volumen del cilindro se calcula la BD.

5.3.2. Gravas.

Para determinar el contenido en gravas se parte de 100 g de suelo seco al aire y se pasan por un tamiz de luz de malla de 2 mm. Posteriormente se pesa la fracción de tierra fina, expresándose el resultado en g de gravas kg^{-1} de suelo.

5.3.3. Textura.

En primer lugar, la textura de los diferentes horizontes de los perfiles se realiza de acuerdo con el "Método Internacional (Pipeta Robinson)" según el Soil Survey of England and Wales (1982). La determinación abarca tres etapas diferentes: separación e inactivación de los agentes de adhesión, dispersión, y separación de la fracción gruesa mediante tamizado húmedo con tamiz de 0,05 mm. El sistema de clasificación de los grados de tamaño de partícula utilizado es el Sistema del Departamento de Agricultura de los Estados Unidos (USDA).

En segundo lugar, se lleva a cabo mediante granulometría láser, usando un Coulter LS 230 (Beckman / Coulter Inc. Brea, CA, EEUU). Esta técnica se utiliza para determinar la distribución de partículas de los sedimentos por tamaño dentro del alcance de 0,04 µm a 2000 µm. Las partículas fuera de este rango no se analizan. Las partículas de la muestra deben dispersarse mediante hexametafosfatosódico (3,3 %) y carbonato cálcico (0,7 %) en agua desionizada. El granulómetro láser indica cuando se ha añadido la cantidad óptima de muestra mediante la luz que difracta y toma como blanco o referencia agua limpia de grifo.

Figura 19. Equipo para medir la textura mediante granulometría láser. Elaboración propia.

5.3.4. pH.

La determinación del pH se lleva a cabo siguiendo el método propuesto por Williams y Stewart (descrito por Guitian y Carballas, 1976).

Dicha determinación se puede hacer en distintas relaciones suelo/agua (1:1, 1:2,5, 1:5 o en pasta saturada). Se prefirió utilizar la relación 1:2,5 con el objeto de evitar la influencia ejercida por la textura. Se realiza la medida potenciométrica después de 30 min de reposo.

5.3.5. Materia Orgánica (OM).

Se determina por gravimetría indirecta en la que se mide la pérdida de peso a causa de la combustión de la OM (versión modificada de Hieri *et al.*, 2001).

5.3.6. Carbono orgánico del suelo (SOC).

En primer lugar por una oxidación húmeda con dicromato potásico de acuerdo con el método de Walkley-Black (Nelson y Sommers, 1982).

En segundo lugar se sigue el método Thermo Fisher Scientific (patente no. 90110186·5) que consiste en eliminar todo el carbono inorgánico en forma de CO_2 por efecto de la acidificación y el calentamiento de la muestra sólida en un recipiente de plata especial

(a veces se usan capsulas de estaño debido a la presencia de mayores reacciones de las muestras en la combustión). El análisis se lleva a cabo mediante un analizador de Thermo Fisher (Thermo Fisher Scientific; Modelo de flash 2000, Waltham, MA, EE.UU.).

5.3.7. Nitrógeno.

Se determina mediante el método de Kjeldahl (Duchaufour, 1975), que consiste fundamentalmente en someter la muestra a una digestión lenta en presencia de ácido sulfúrico concentrado, utilizando una mezcla de sulfato potásico, sulfato de cobre desecado y selenio como catalizador de la digestión. A continuación se destila por arrastre de vapor, añadiéndose NaOH (35 %) desplazándose el NH_3 que se recoge en H_2SO_4. Finalmente se realiza una titulación por reducción con NaOH. Paralelamente se realiza un ensayo en blanco.

El contenido en N en la muestra se expresa en porcentaje, teniendo en cuenta que 0,1 meq de $H_2 SO_4$, equivalente a 1,4 mg de N.

La relación C:N fue calculada dividiendo la concentración SOC entre la concentración de N.

5.4. MÉTODO DE GHANI.

Se determina el carbono extraíble en agua fría (CWC) y caliente (HWC) de las muestras a temperatura ambiente y a 80 ºC, respectivamente (figura 5). Paralelamente se realizan dos ensayos en blanco.

Los análisis de DOC, absorbancia y fluorescencia se llevaron a cabo sobre el CWC y HWC, sin embargo para el de ^{1}H-RMN solo se utilizó HWC. Se usa el primer horizonte de cada suelo muestreado, ya que se considera suficiente para el objetivo de comparar estas técnicas.
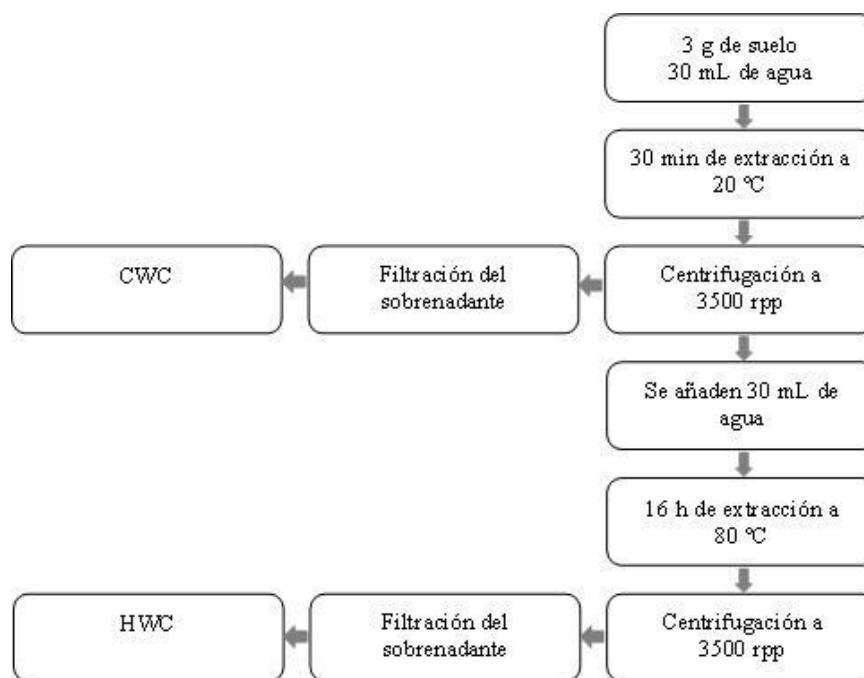
Figura 20. Descripción esquemática del procedimiento del carbono extraído en agua fría (CWC) y caliente (HWC). (Adaptado de Ghani et al., 2003).

5.5. TÉCNICAS PARA DETERMINAR LA CALIDAD DE LA MATERIA ORGÁNICA DEL SUELO.

En todas las técnicas se analizaron tres réplicas por muestra.

5.5.1. Carbono orgánico disuelto (DOC).

Previo al análisis del DOC se requiere la preparación de unos estándares para calibrar la máquina y obtener la recta de calibrado (disoluciones de carbono total mediante ftalato ácido potásico seco, y C inorgánico mediante bicarbonato sódico. Ambas disoluciones son de 1000 mg/kg cada una). Su medida se lleva a cabo usando un Shimadzu TOC 5000 (Shimadzu Corporation. Kyoto, Japón).

Figura 21. Equipo para medir el DOC (del C extraído). Elaboración propia.

5.5.2. Absorbancia.

La absorbancia se mide con un espectrómetro VarianCary 300 UV-vis (Agilent Technologies, de Santa Clara, CA, EE.UU.), desde 200 a 800 nm con intervalos de 1 nm utilizando una cubeta de 1 cm de paso de luz. Se determinó $SUVA_{254}$, que es el cociente entre la absorbancia a 254 nm y la concentración de DOC (del HWC). Los valores se expresan en mg $l^{-1}m^{-1}$.

5.5.3. Fluorescencia.

La fluorescencia se mide en un espectrofotómetro Varian Eclipse Fluorescencia (Agilent Tecnologías, Santa Clara, CA, EE.UU.) a una longitud de onda de emisión de 300 a 600 nm en incrementos de 5 nm y una excitación de 240 a 450 nm también en incrementos de 5 nm. La medición se lleva a cabo en cubetas de 1 cm de cuarzo.

Se calculan tres índices:

- FI: La relación entre las intensidades de 450 nm y 500 nm con una excitación de 370 nm, descrito por Cory *et a*l. (2010).

- HIX: se calcula mediante la siguiente fórmula:

$$\frac{\sum I435 \rightarrow 480}{\sum I300 \rightarrow 345} + \sum I435 \rightarrow 480$$

donde I es la intensidad de fluorescencia a cada longitud de onda (modificado de Zsolnay *et al*. (1999) por Ohno, (2002)).

- BIX: El cociente entre las intensidades obtenidas a 380 nm entre las obtenidas a 430 nm; con una excitación de 310 nm, descrito por Huguet *et al*. (2009).

5.5.4. Matrices de excitación-emisión.

Sus espectros se representan utilizando el programa informático RStudiov0.98.1091 (Rstudio Inc., Boston, MA, EE.UU.). Para ello se toman datos de absorbancia, fluorescencia y DOC del C extraído previamente calculados.

Las intensidades se indican en unidades Raman (RU). El llamado efecto de Raman o la dispersión de Raman se mitiga substrayendo de cada espectro los blancos que se recogen en agua ultrapura.

5.5.5. ^{1}H-NMR.

A diferencia de las medidas anteriores, se requiere una preparación previa de las muestras. Cada sub-muestra del extracto de HWC se congela y, posteriormente, liofilizada. Una vez realizado esto, se le añade óxido de deuterio como disolvente para evitar interrupciones de picos de agua en el espectro y se vuelve a congelar y liofilizar la muestra por segunda vez.

Al sólido obtenido se le añade de nuevo óxido de deuterio (100 %, densidad de 1,107 g/mL a 25 ºC) como disolvente para llevar a cabo las pruebas de ^{1}H-NMR. De esta disolución se toman entre 1,5-1,7 mL de muestra para realizar mediciones con un espectrómetro de NMR Bruker Avance III de 700 MHz (BrukerCorporation, Billerica, MA, EE.UU.). Como resultado se obtiene un espectro por muestra.

Previo a la interpretación del espectro es necesario ajustarlo localizando el pico del óxido de deuterio como una referencia de calibración colocada en 4,75 ppm del espectro.

Figura 22. Equipo para medir la ^{1}H-NMR. Elaboración propia.

5.6. DETERMINACIONES A PARTIR DE LOS RESULTADOS OBTENIDOS EN LOS MÉTODOS ANALÍTICOS.

5.6.1.   SOC Stock (SOCS).

Sus valores se expresan para una profundidad específica en Mg ha^{-1}. Se calcula como el producto de la concentración de SOC, BD, profundidad y gravas, de la siguiente manera (IPCC, 2003):

SOCstock = SOC$_{concentration}$ x BD x d x (1 - δ2 mm %) x 10^{-1}

Donde SOC es el contenido de carbono orgánico del suelo (g kg^{-1}), BD es la densidad aparente (Mg m^{-3}), d es el espesor de la sección de control o profundidad del horizonte (cm) y δ2 mm es el porcentaje fraccional (%) de gravas (tamaño mayor a 2 mm).

TSOCS: expresado en Mg ha^{-1}. Se calcula para cada suelo de acuerdo con (IPCC, 2003) de la siguiente manera:

T-SOCS= Σ$_{horizonte- control edáfico 1… n}$SOCS$_{horizonte- control edáfico}$

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5.6.2. N Stock (NS).

Al igual que el SOCS, éste se expresa en Mg ha^{-1} y su cálculo es muy similar:

Nstock = N$_{concentration}$ x BD x d x (1 -&2 mm %) x 10^{-1}

TNS: Al igual que TSOC, éste se expresa en Mg ha^{-1} y su cálculo es muy similar:

TNstock=$\Sigma_{horizonte-\ control\ edáfico\ 1\ldots\ n}NS_{horizonte-\ control\ edáfico}$

5.6.3. Relación de estratificación.

Este concepto se define por Franzluebbers (2002) para una propiedad del suelo y es la relación entre su valor en la superficie del suelo y a una profundidad inferior, manteniendo como numerador al horizonte superficial y cambiando el denominador, que es el valor de los horizontes conforme se desciende en el perfil. Así para un perfil con cuatro horizontes se definen: SR1 para SOC dividiendo el contenido de SOC de la primera sección o primer horizonte del suelo (S1) entre el contenido de SOC de la segunda sección u horizonte (S2). SR2, dividiendo el contenido de SOC de la primera sección o primer horizonte del suelo (S1) entre el contenido de SOC de la tercera sección u horizonte (S3). Y SR3 dividiendo el contenido de SOC de la primera sección o primer horizonte del suelo (S1) entre el contenido de SOC de la cuarta sección u horizonte (S4). Se ha calculado la SR para los datos siguientes: el SOC, N y C:N.

5.7. MÉTODOS ESTADÍSTICOS.

Los análisis estadísticos se realizan con los programas de software estadístico SPSS 13.0 para Windows (IBM Corporation, Armonk, NY, EE.UU.) y Minitab 16 para Windows (Minitab Inc., StateCollege, PA, EE.UU.).

El efecto de cada posición topográfica, las distintas prácticas de manejo y la profundidad sobre las variables analizadas (SOC, N, C:N, HWC, SOCS, NS) se evalúan mediante ANOVA. La significancia estadística de las diferencias en las variables entre las prácticas de uso del suelo, se someten a la prueba de Anderson-Darling para cada horizonte o combinaciones de horizontes para cada tipo de suelo.

En cuanto a la evaluación de las técnicas ópticas para la caracterización de la OM, el test de normalidad dio negativo y debieron usarse tests no paramétricos. El efecto de HWC sobre CWC se analiza usando la prueba de los rangos con signo de Wilcoxon. La correlación entre los distintos métodos analíticos se comprueba usando el Coeficiente de

Correlación de Spearman. Las regresiones lineares de estas correlaciones se representan usando SigmaPlot 12.0 para Windows (Systat Software Inc., San Jose, CA, EE.UU.).

En todos los casos, las diferencias con $p < 0,05$ se consideran estadísticamente significativas.

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RESULTADOS Y DISCUSIÓN

CAPÍTULO I

Topography and land use change effects on the soil organic carbon stock of forest soils in Mediterranean natural areas.

Topography and land use change effects on the soil organic carbon stock of forest soils in Mediterranean natural areas

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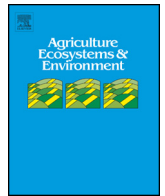
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ABSTRACT

In Mediterranean areas, through the years, natural forest (NF) areas have suffered land use change (LUC) mainly for economic reasons. This is the case of olive groves (OG) in Andalusia (south Spain), the main olive oil production area in the world. This LUC from NF to OG has caused soil erosion and the loss of soil quality. Also, this effect has been aggravated by climatic conditions and poor soil management practices. A field study was conducted to examine the effects of LUC from NF to OG in a toposequence (summit-SM, backslope-BS and toeslope-TS) and to determine soil organic carbon (SOC), nitrogen (N) and the stratification ratio (SR) of SOC in the Torredelcampo–Jaen–Spain (Mediterranean area) in a Calcisols–Regosols–Vertisols sequence.

Total SOC (T-SOC) was low for both NF and OG soils. In the case of NF, there was a pattern of decrease from the highest (SM) to the lowest topographical position (TS); whereas for OG, the highest T-SOC was found in TS (50.2 ± 1.1 g kg^{-1}). T-SOC was more than 40% higher in NF than in OG in SM and BS. The total SOC stock (T-SOCS) in NF soils remained evenly distributed in the three topographical positions. However, the trend for the OG soils was an increase of T-SOCS along the hillside (SM: 68.9 ± 4.8 Mg ha^{-1}; BS: 82.3 ± 12.3 Mg ha^{-1} and TS: 158.7 ± 15.4 Mg ha^{-1}). N followed a pattern of decrease with depth in the OG soils, but not in NF soils. As for N stock, it was higher in NF than in OG, with the exception of NF-TS and OG-TS. SR values in NF had a general trend of increasing from higher to lower topographical positions, despite the fact that T-SOC decreased from higher to lower topographical positions. This indicates that soil quality is higher in lower topographical positions even though there is less T-SOC. SR values in OG soils had a similar trend as in NF soils (but with lower values). However, T-SOC increased as well in the same way, which was opposite to the NF soils case. Therefore, soil quality was higher in lower topographical positions for both land uses.

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1. Introduction

Over the centuries, olive groves (OG) have become a landscape and socioeconomic heritage of Mediterranean areas, being a way of life and the main economic support for its inhabitants (IOC, 2012). The area covered by OG has been gradually increasing up to 9.5 million ha in the whole Mediterranean basin. This increase is produced by the replacement of Mediterranean native vegetation (Nieto et al., 2013). Actually, this land use change (LUC) has been caused by the anthropogenic action of producing crops to ensure human development. Furthermore, subsidies and the increase of olive oil prices have made this feasible (Lozano-García and Parras-Alcántara, 2013a). Andalusia, with around 15% of its cultivated area covered by this crop (more than 2 million ha), is the main production area in the EU, with approximately 40% of the OG area in the EU-28 (EUROSTAT, 2009).

This activity, although it has brought economic benefits to the region, has also created serious problems for soils, causing land degradation and accelerating soil erosion (Nieto et al., 2013; Parras-Alcántara and Lozano-García, 2014). This land degradation is especially aggravated by the Mediterranean climatic conditions and by poor environmental practices such as planting on slopes and with low tree densities or conventional tillage (CT) (Gómez et al., 2009; Lozano-García and Parras-Alcántara, 2014). This so-called CT is done with mouldboard plow, disc harrow, herbicides and mineral fertilisation. Not only has this technique increased erosion rates and water losses, but it has also decreased soil quality due to the loss of organic matter (OM) (Calatrava et al., 2011; Lozano-García et al., 2011; Lozano-García and Parras-Alcántara, 2013b).

In this line, soil management is one of the best tools for climate change mitigation and adaptation (Lal et al., 2011). The international community is concerned by the increase in greenhouse gases emissions and how these can influence climate change. As a result of this, the Kyoto protocol was signed, with the objective of mitigating and adapting to climate change using land sinks (Yimer et al., 2006). The second commitment period of this protocol (2013–2020) obliges parties to reduce greenhouse gases emissions by at least 18% compared to 1990 levels (United Nations, 2013). Little concern has been raised however, about the effect of soil degradation in climate change, which accounts for 20% of the total carbon emissions from 1850 to the end of the 20th century (Lal, 2004; Lal et al., 2011).

According to Smith (2008), LUC is the second greatest cause of carbon emissions after fossil fuel consumption. This may be linked to the fact that LUC could be the cause of soil degradation and soil organic carbon (SOC) losses, especially in Mediterranean areas (Eaton et al., 2008; Cerdà et al., 2010). Several studies have demonstrated that SOC is highly sensitive to LUC (Smith, 2008; Parras-Alcántara et al., 2013a). Climate, use and management are very influential in the carbon variability in Spanish soils (Rodríguez-Murillo, 2001; Muñoz-Rojas et al., 2012; Ruiz et al., 2012; Parras-Alcántara et al., 2013b), particularly in semiarid regions, which are characterized by low levels of soil organic matter content ($10\,g\,kg^{-1}$) (Acosta-Martínez et al., 2003). Recently, some studies showed the influence of LUC in soil physical–chemical properties such as SOC, nitrogen (N) content, pH, texture, and C:N ratio (Parras-Alcántara et al., 2013a). Other studies demonstrate some variations in soil properties related to topographic positions (Yimer et al., 2006; Hattar et al., 2010). The study of topographic positions is connected to the concept of toposequence. Gessler et al. (1996) defined a toposequence as "a spatial object that maintains flow connectivity from summit (hillslope initiation) to base (hillslope conclusion)".

If we consider SOC and N as soil quality indicators (Sharma et al., 2005; Brevik, 2009), it is necessary to explain the relationship between soil properties and topographic position. It is then necessary to establish soil quality indicators that relate properties and topographic positions. In this regard, the stratification ratio (SR) (Franzluebbers, 2002) is mostly used. The SR of SOC can be used as an indicator of soil quality and has been effectively used in other studies to monitor soil carbon and N responses to LUC, soil management and climate (Franzluebbers et al., 2007; Sá and Lal, 2009). Furthermore, an increase in this ratio can be correlated to SOC sequestration (Franzluebbers, 2002).

To the best of our knowledge, very little literature has compared the effects of LUC in natural forest (NF) areas and its relationship with topographic positions – toposequence. In addition, there seem to be few reports on stratification of SOC as affected by topography. In this context, the aims of this study are: (i) to quantify SOC and nitrogen (N) contents and their vertical distribution in OG (after LUC) and NF soils; (ii) to assess the SOC and N stocks differences in soil along a topographic gradient and their relationship with soil depth for both uses (OG and NF); and (iii) to analyze the accumulation and SR of SOC in a toposequence (summit-SM, backslope-BS, toeslope-TS) of a Calcisols–Regosols–Vertisols sequence (IUSS-ISRIC-FAO, 2006) affected by LUC in NF of a Mediterranean natural area.

2. Material and methods

2.1. Study site and experimental design

The study was carried out in Torredelcampo–Jaen (30H-414,182–4,198,827; 415,310–4,199,191; 425,903–4,177,169; 421,389–4,176,841, 647 m. a. s. l.). The underlying bedrock within the studied area consists of Miocene marl and marlaceous lime. The soils are Calcisols, Regosols and Vertisols (IUSS-ISRIC-FAO, 2006). The climate is typical Mediterranean with 3–5 months of summer drought, usually from late June to September and moderately wet cool winters. According to the nearby weather station in Torredelcampo (Jaen), the annual average temperature is 17 °C, with a maximum air temperature of 40.6 °C in August and a minimum air temperature of −5.2 °C (January). The annual average precipitation is 645.7 mm, and monthly rainfall ranges from 4.7 mm (July) to 87 mm (February). This area was naturally covered by Mediterranean forest (*Quercus rotundifolia, Quercus faginea, Quercus coccifera, Bupleurum fruticosum, Cistus albidus, Pinus halepensis and Pinus pinaster, Ophrys lutea* and *Gladiolus illyricus*). However, part of this NF was transformed into OG during the 1940s.

The experimental design consisted of studying the LUC from NF to OG in three topographical positions with the same aspect: SM, BS and TS. The NF was an unaltered natural area and the OG (Picual variety) was an unirrigated land cultivated under conventional tillage (CT) with a density of 90 trees ha^{-1} and having 2–3 trunks each. The management system in OG was: once the olives were harvested, mineral fertilization (100 kg ha^{-1} Urea (46% N) in alternate years) was applied in winter. After this, a disc harrow (25 cm) was used, and then a manual cultivator pass to diminish soil clod size in summer. Finally, herbicides were added to control weeds in autumn (the last two practices are applied solely under trees).

One observation plot per topographical position was established for each land use (NF and OG), each with an area of 400 m^2 (20 m × 20 m). In both cases (NF and OG), five sampling points per plot (SM, BS and TS) were taken. At each sampling point a soil profile was opened (Fig.1). The main topographic variables (altitude, slope and aspect) and the soil profile descriptions were recorded. The soil samples were taken from four soil sections of 25 cm (S1:0–25; S2:25–50; S3:50–75; S4:75–100) in order to establish a better comparison between the different topographical positions.

2.2. Sampling and analysis

In order to determine bulk density (BD), a sample of 3 cm diameter and 10 cm length (70.65 cm^3 core volume) was taken from each soil section (Blake and Hartge, 1986). In the laboratory, soil samples were air-dried and passed through a 2 mm sieve to remove gravels and roots. The distribution of the soil particle size was analysed by sieving and using the Robinson method (USDA, 2004). Soil pH was determined in a 1:2.5 soil to water ratio. SOC was determined by wet oxidation with dichromate according to the Walkley–Black method (Nelson and Sommers, 1982). N was determined with the Kjeldahl method (Bremner, 1996) and the C:N ratio calculated by dividing the SOC concentration by the N concentration.

Likewise, SOC stock (SOCS), expressed for a specific depth in Mg ha^{-1}, was computed as the product of SOC concentration, BD, depth and gravels, as follows (IPCC, 2003):

$$SOC stock = SOC concentration \times BD \times d \times (1 - \delta2mm\%) \times 10^{-1}$$

where SOC is the organic carbon content (g kg^{-1}), BD (Mg m^{-3}), d is the thickness of the control section (always 25 cm in our case), and $\delta2$ mm is the fractional percentage (%) of gravel larger than 2 mm size in the soil. The N stock (NS) (Mg ha^{-1}) was also computed similarly.

The total SOCS (T-SOCS) (Mg ha^{-1}) was calculated for each soil according to (IPCC, 2003) as follow:

$$T - SOCS = \Sigma_{horizon-edaphic\ controls\ 1....n} SOCS_{horizon-edaphic\ controls}$$

The total NS (T-NS) (Mg ha^{-1}) was also computed similarly.

The SR of a soil property is the ratio of its value at the soil surface to that at a lower depth as defined by Franzluebbers (2002). In this
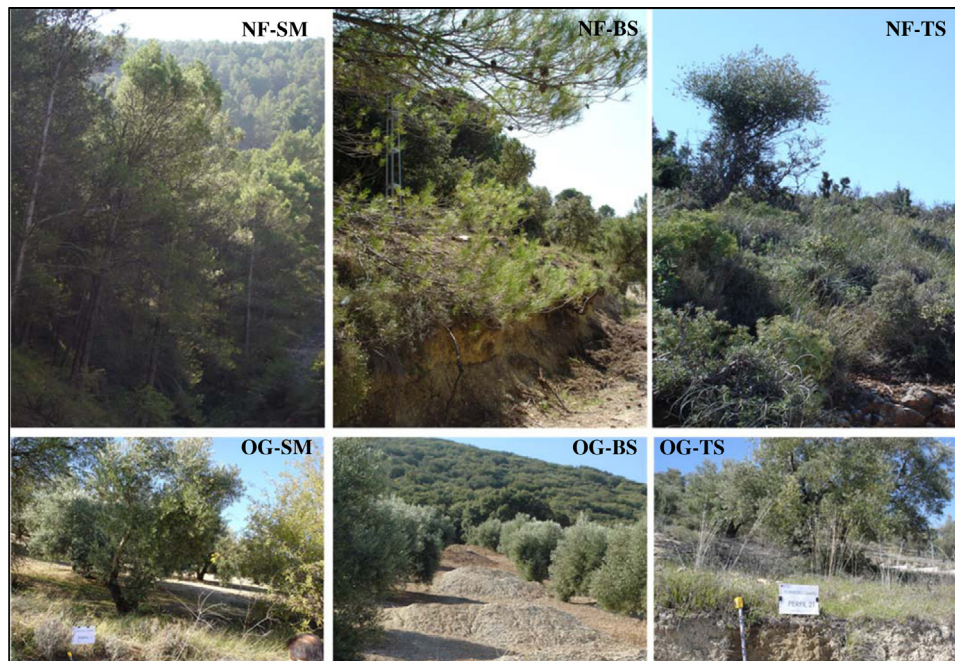
Fig. 1. The study area (Torredelcampo–Jaen–Spain). Land use change from natural forest (NF) to olive groves (OG) at summit (SM), backslope (BS) and toeslope (TS) positions.

study, three SRs (SR1, SR2 and SR3) for SOC at four different depths were calculated. The SR1 for SOC was calculated by dividing the SOC content of the soil Section 1 (S1) by that of the soil Section 2 (S2). Accordingly, SR2 and SR3 were obtained by dividing the SOC content in S1 by those of S3 and S4.

The statistical analysis was performed using SPSS 13.0 for Windows. The effect of each topographical position on SOC and N stocks was analysed using an ANOVA analysis.

A test of data normality was done to verify the model assumptions. The statistical significance of the differences in the variables between land use and topographical position was tested using an Anderson–Darling test at each horizon or a combination of horizons for each soil type. Differences of $p < 0.05$ were considered statistically significant.

3. Results

3.1. Soil properties

According to the IUSS Working Group WRB (IUSS-ISRIC-FAO, 2006) the studied soils are classified as Calcisols (SM and BS in OG), Vertisols (TS in OG) and Regosols (in all the topographical positions in NF). Soil properties were studied at a similar thickness, so that comparisons between soils types would be easier.

As can be seen in Tables 1 and 2, the studied soils presented some differences in the physical–chemical parameters depending on the land use, the topographic position and the soil depth. The soils located in NF were characterized by high clay content (up to 70%) in the two first topographical positions (SM and BS). However, at greater depths the soils became less clayey for NF and OG (with the exception of S4 in OG). As for silt, it gradually increased from SM to TS. For OG soils, the silt fraction gradually increased from the SM to TS as in the previous case. The values oscillated from 23 to 26% in the SM, from 28 to 30% in BS, and from 33 to 44% in TS. When pH was compared, there generally were not significant differences with respect to land use (NF and OG) and topographic position; pH was between 7.9 and 9 in all cases. BD was lower in the S1 soil sections in NF than in those in OG. This occurred in all three topographic positions. However, values were very similar for both

uses in deeper sections (Table 1). Finally, the gravel content was generally higher in NF than in OG.

3.2. Soil organic carbon, nitrogen and C:N ratio

The main characteristic of the studied soils was a low concentration of SOC at depth (Table 2), with a decrease from the upper sections of soils in NF at all three topographical positions (SM: S1 32.3 g kg^{-1} – S4 10.9 g kg^{-1}; BS: S1 38.3 g kg^{-1} – S4 3.7 g kg^{-1}; TS: S1 33.4 g kg^{-1} – in S4 5.0 g kg^{-1}). As for T-SOC in NF, it was 69.0 g kg^{-1}, 65.1 g kg^{-1} and 49.2 g kg^{-1} for SM, BS and TS respectively. There was therefore a pattern of total SOC (T-SOC) decrease from the highest to the lowest topographic positions (Table 2).

OG soils had a low concentration of SOC with depth, with a decrease from the upper sections, but this decrease was less than in NF (SM: S1 11.0 g kg^{-1} – S4 6.1 g kg^{-1}; BS: S1 13.1 g kg^{-1} – S4 5.2 g kg^{-1}; TS: S1 22.3 g kg^{-1} – S4 6.7 g kg^{-1}). The decrease was gradual from one position to the following one (S1–S2, S2–S3 and S3–S4) for the BS and TS, but not in the highest topographic position (SM). Land cover therefore provides protection against soil erosion. T-SOC in each topographical position was 34.9 g kg^{-1} (SM), 35.3 g kg^{-1} (BS) and 50.2 g kg^{-1} (TS). Therefore, the pattern is an increase in T-SOC from the highest to the lowest topographical positions (Table 2).

3.3. Land use change effects on SOC

If the SOC values of both soil uses are compared, LUC effects can be evaluated. The SOC was higher in NF than in OG in the two first topographical positions (SM and BS). This increase was 49.4% and 45.8% for SM and BS respectively (Table 2). Despite this pattern, the SOC content at the TS was higher in OG than in NF.

With respect to N concentrations, these decreased with depth in NF (Table 2). As for altitude, N in NF soils did not follow a pattern, as it increased from the SM to BS (from 4.1 to 6.6 g kg^{-1}) and decreased again at the TS (3.5 g kg^{-1}). The pattern for N with depth was not clear for our OG soils. The only identified trend was that N increased with depth in OG at the TS. There was a clearer pattern

Table 1
Physical properties evaluated (average ± standard deviation) for soil types in natural forest and olive groves.

Land use	Topographical position	Soil type	SS	Depth (cm)	Gravel (%)	Sand (%)	Silt (%)	Clay (%)	BD (Mg m^{-3})
NF	Summit	RG	S1	0–25	59.9 ± 5.4 aAa	8.5 ± 1.12 aAa	22.5 ± 2.1 aAa	69.0 ± 5.7 aAa	1.0 ± 0.1 aAa
			S2	25–50	45.4 ± 3.8 bAa	7.6 ± 0.6 bAa	23.1 ± 2.9 aAa	69.3 ± 5.9 aAa	1.2 ± 0.1 bAa
			S3	50–75	38.6 ± 2.6 cAa	4.6 ± 0.9 cAa	24.8 ± 2.8 aAa	70.6 ± 6.5 aAa	1.3 ± 0.2 bAa
			S4	75–100	37.8 ± 3.7 cAa	4.8 ± 0.5 cAa	23.9 ± 2.5 aAa	71.3 ± 6.8 aAa	1.3 ± 0.1 bAa
	Backslope	RG	S1	0–25	48.2 ± 3.1 aBa	13.8 ± 1.7 aBa	21.0 ± 2.1 aAa	65.2 ± 5.4 aBa	1.0 ± 0.1 aAa
			S2	25–50	40.7 ± 4.2 bBa	18.2 ± 1.4 bBa	25.8 ± 2.0 bBa	56.0 ± 4.9 bBa	1.2 ± 0.1 bAa
			S3	50–75	34.8 ± 2.7 cBa	15.6 ± 1.3 aBa	33.1 ± 3.6 cBa	51.3 ± 2.2 bBa	1.4 ± 0.2 bAa
			S4	75–100	35.7 ± 2.9 cBa	27.7 ± 1.2 cBa	36.1 ± 3.3 cBa	36.2 ± 4.0 cBa	1.5 ± 0.2 bBa
	Toeslope	RG	S1	0–25	38.5 ± 2.8 aCa	31.7 ± 3.1 aBa	37.5 ± 2.9 aBa	30.8 ± 3.0 aCa	1.1 ± 0.1 aAa
			S2	25–50	30.0 ± 3.0 bCa	52.6 ± 3.8 bCa	28.3 ± 2.6 bBa	19.1 ± 2.0 bCa	1.5 ± 0.1 bBa
			S3	50–75	31.8 ± 4.1 bBa	53.3 ± 3.6 bCa	26.8 ± 2.1 bBa	19.9 ± 2.1 bCa	1.5 ± 0.2 bBa
			S4	75–100	33.4 ± 2.9 bBa	52.9 ± 2.7 bCa	26.8 ± 2.3 bBa	20.3 ± 1.9 bCa	1.5 ± 0.1 bBa
OG	Summit	CL	S1	0–25	46.3 ± 1.9 aAb	15.7 ± 2.1 aAb	24.9 ± 2.8 aAa	59.4 ± 4.5 aAb	1.3 ± 0.2 aAb
			S2	25–50	42.8 ± 2.9 bAa	10.6 ± 1.7 bAb	23.1 ± 3.5 aAa	66.4 ± 4.9 bAa	1.4 ± 0.1 aAa
			S3	50–75	23.6 ± 2.1 cAb	6.7 ± 1.8 cAa	26.1 ± 3.9 bAa	67.2 ± 3.8 aAa	1.3 ± 0.1 aAa
			S4	75–100	46.0 ± 2.5 aAb	14.4 ± 1.9 aAb	26.4 ± 2.1 bAa	59.2 ± 4.0 aAb	1.4 ± 0.1 aAa
	Backslope	CL	S1	0–25	30.2 ± 2.5 aBb	18.2 ± 2.7 aAb	30.2 ± 3.6 aBb	51.6 ± 2.5 aBb	1.3 ± 0.1 aAb
			S2	25–50	32.5 ± 3.8 aBb	15.3 ± 1.8 bAa	28.1 ± 1.7 aBa	43.4 ± 4.8 bBb	1.3 ± 0.2 aAa
			S3	50–75	28.6 ± 3.1 bAb	12.1 ± 2.3 cBa	27.5 ± 3.9 aAb	60.4 ± 3.2 cBb	1.4 ± 0.1 aAa
			S4	75–100	25.9 ± 4.2 bBb	14.7 ± 2.4 bAb	29.7 ± 2.5 aBb	55.6 ± 3.9 aBb	1.4 ± 0.2 aAa
	Toeslope	VR	S1	0–25	14.3 ± 1.9 aCb	28.1 ± 2.3 aBa	44.4 ± 3.2 aCb	27.5 ± 2.9 aCa	1.3 ± 0.1 aAb
			S2	25–50	8.3 ± 1.9 bCb	43.7 ± 4.3 bBb	34.9 ± 3.1 bCb	21.4 ± 3.4 bCa	1.5 ± 0.1 aAa
			S3	50–75	6.7 ± 1.2 bBb	37.4 ± 3.9 cCb	36.8 ± 3.0 bBb	25.8 ± 2.1 aCb	1.5 ± 0.1 aAa
			S4	75–100	7.3 ± 1.3 bCb	45.1 ± 3.6 bBb	33.5 ± 3.1 cCb	21.4 ± 3.7 bBa	1.5 ± 0.1 aAa

NF: Natural Forest; OG: Olive groves; SS: Soil section; BD: Bulk density.
RG: Regosols; CL: Calcisols; VR: Vertisols (IUSS-ISRIC-FAO, 2006).
Numbers followed by a different lower case letter (the first) within the same column are significantly different ($p < 0.05$) with depth, considering the same topographic position and land use. Numbers followed by a different capital letter (the second) within the same column are significantly different ($p < 0.05$) with topographic position, considering the same land use and soil section. Numbers followed by lower case letters (the third) within the same column are significantly different ($p < 0.05$) with land use, considering the same topographic position and soil section.

with altitude in OG. N was lowest at the SM (2.1 g kg^{-1}) and the highest at the TS (4.1 g kg^{-1}).

The C:N ratio in NF varied between 8.1 and 16.7 g kg^{-1}. In OG these values were between 5.8 and 20.0 g kg^{-1}. In both cases C:N did not show any pattern of increase or decrease with depth or texture. Higher BD has also been shown to be associated with more decomposed OM with lower C:N ratios (Brevik, 2000; Brevik et al., 2002). In each case, the BD at the S1 depth in NF is lower than the

Table 2
Chemical properties evaluated (average ± standard deviation) for soil types in natural forest and olive groves.

Land use	Topographical position	SS	pH H$_2$O	SOC (g kg^{-1})	Total SOC (g kg^{-1})	N (g kg^{-1})	Total N (g kg^{-1})	C/N
NF	SM-RG	S1	8.3 ± 0.3 aAa	32.3 ± 11.1 aAa	69 ± 4.2	2.5 ± 0.5 aAa	4.1 ± 0.3	12.9 ± 2.4 aAa
		S2	8.3 ± 0.2 aAa	13.8 ± 2.0 bAa		1.0 ± 0.2 bAa		14.8 ± 2.2 bAa
		S3	8.4 ± 0.5 aAa	12.0 ± 1.1 bAa		0.9 ± 0.1 bAa		13.3 ± 2.2 aAa
		S4	8.4 ± 0.8 aAa	10.9 ± 2.1 cAa		0.8 ± 0.2 bAa		12.5 ± 2.1 aAa
	BS-RG	S1	7.9 ± 0.1 aBa	38.3 ± 2.0 aBa	65.1 ± 2.1	4.3 ± 0.8 aBa	6.6 ± 0.3	8.9 ± 1.2 aBa
		S2	8.6 ± 0.5 bBa	18.2 ± 2.3 bBa		1.4 ± 0.2 bBa		12.9 ± 1.8 aAa
		S3	8.8 ± 0.2 bBa	4.9 ± 1.2 cBa		0.4 ± 0.1 cBa		12.5 ± 2.1 bAa
		S4	9.0 ± 0.1 bBa	3.7 ± 1.0 cBa		0.5 ± 0.1 cBa		8.1 ± 1.0 aBa
	TS-RG	S1	8.5 ± 0.5 aAa	33.4 ± 12.1 aAa	49.2 ± 4.7	2.3 ± 0.4 aAa	3.5 ± 0.2	14.3 ± 2.1 aAa
		S2	8.9 ± 0.1 aCa	5.7 ± 0.8 bCa		0.6 ± 0.1 bCa		10.0 ± 1.2 bBa
		S3	8.8 ± 0.2 aBa	5.1 ± 0.2 bBa		0.3 ± 0.1 cBa		16.7 ± 1.8 cBa
		S4	8.9 ± 0.5 aBa	5.0 ± 0.3 bBa		0.3 ± 0.1 bBa		16.7 ± 1.9 cCa
OG	SM-CL	S1	8.4 ± 0.6 aAa	11.0 ± 1.1 aAb	34.9 ± 1.2	0.6 ± 0.1 aAb	2.1 ± 0.1	18.3 ± 0.9 aAb
		S2	8.6 ± 0.8 aAa	12.4 ± 1.3 aAa		0.8 ± 0.2 aAa		15.0 ± 0.5 aAa
		S3	8.8 ± 0.3 aAa	5.4 ± 0.5 bAb		0.4 ± 0.1 bAb		12.5 ± 1.3 bAb
		S4	8.5 ± 0.9 aAa	6.1 ± 2.3 bAb		0.3 ± 0.1 bAb		20.0 ± 1.6 bAb
	BS-CL	S1	8.3 ± 0.3 aAa	13.1 ± 1.1 aBb	35.3 ± 0.9	0.7 ± 0.3 aAb	2.4 ± 0.9	18.6 ± 1.1 aAb
		S2	8.7 ± 0.3 aAa	10.9 ± 1.0 bBb		0.8 ± 0.3 aAb		13.8 ± 1.0 aAb
		S3	8.6 ± 0.1 aBa	6.1 ± 0.6 cBa		0.5 ± 0.2 bAa		15.0 ± 1.7 aAa
		S4	8.5 ± 0.2 aAa	5.2 ± 0.5 cBa		0.4 ± 0.1 bAa		12.5 ± 1.2 bBb
	TS-VR	S1	8.1 ± 0.3 aAa	22.3 ± 2.7 aCb	50.2 ± 1.1	1.2 ± 0.4 aBb	4.1 ± 0.2	18.3 ± 1.3 aAb
		S2	8.8 ± 0.5 bAa	14.2 ± 1.4 bAb		0.8 ± 0.1 bAa		17.5 ± 1.4 aBb
		S3	9.0 ± 0.5 bAa	7.0 ± 0.8 cAb		0.9 ± 0.1 bBb		7.8 ± 1.1 bBb
		S4	8.6 ± 0.5 aAa	6.7 ± 0.4 cAa		1.2 ± 0.1 aBb		5.8 ± 0.2 cCb

NF: Natural Forest; OG: Olive groves; SS: Soil section, SM: Summit; BS: Backslope, TS: Toeslope.
RG: Regosols; CL: Calcisols; VR: Vertisols (IUSS-ISRIC-FAO, 2006).
Numbers followed by a different lower case letter (the first) within the same column are significantly different ($p < 0.05$) with depth, considering the same topographic position and land use. Numbers followed by a different capital letter (the second) within the same column are significantly different ($p < 0.05$) with topographic position, considering the same land use and soil section. Numbers followed by lower case letters (the third) within the same column are significantly different ($p < 0.05$) with land use, considering the same topographic position and soil section.

S1 depth in OG, and the C:N ratios indicate more decomposed OM in OG. However, below the S1 depth the BD values are about the same in both NS and OG, and there are no strong C:N ratio trends. The C:N ratio was higher in OG SM than in the rest of the studied soils, regardless of the use or topographic position. Several of the studied soils in both uses had values of 12 or higher (Table 2).

3.4. Soil organic carbon and nitrogen stocks

The SOC stock (SOCS) values were very similar to each other under NF for all topographic positions (SM: 100.9 Mg ha^{-1}; BS: 102.2 Mg ha^{-1}; TS 97.0 Mg ha^{-1}). As for SOCS changes in depth, there was a decrease in all topographic positions (Fig. 2).

The trend for OG was to have the highest SOCS at the TS (158.7 Mg ha^{-1}) and the lowest at the SM (68.9 Mg ha^{-1}). Actually, SOCS at the OG TS was the highest in all studied soils (Fig. 2). As for SOCS changes with depth, there was a general decrease with depth,

with only one exception at the SM. In this case, the SOCS was higher in the second soil section (S2) than in the surface (S1) (Fig. 2).

When assessing LUC, it can be concluded that SOCS in OG was reduced at the first two topographic positions (SM: 31.7%; BS: 19.4%). However, this reduction did not occur at the TS position. In this case there was an increase of 63% (Fig. 2). The fact that NF soils were able to retain more soil (and therefore maintain a stable SOCS) could mean that soils with a higher density of tree cover have higher T-SOCS than those with lower cover.

The total NS (T-NS) in the NF was 7.6 Mg ha^{-1}, 10.2 Mg ha^{-1} and 6.9 Mg ha^{-1} for SM, BS and TS respectively. As for OG soils, T-NS increased from higher to lower topographic positions. As a result, the TS (13.4 Mg ha^{-1}) had a higher NS than the BS (5.6 Mg ha^{-1}) and SM (4.2 Mg ha^{-1}) (Fig. 3). When both soil uses are compared, NS was higher in NF than in OG, with the exception of the TS (Fig. 3). Therefore, NS differences in the studied soils due to LUC followed a similar pattern to the differences in SOCS: a reduction of N from NF
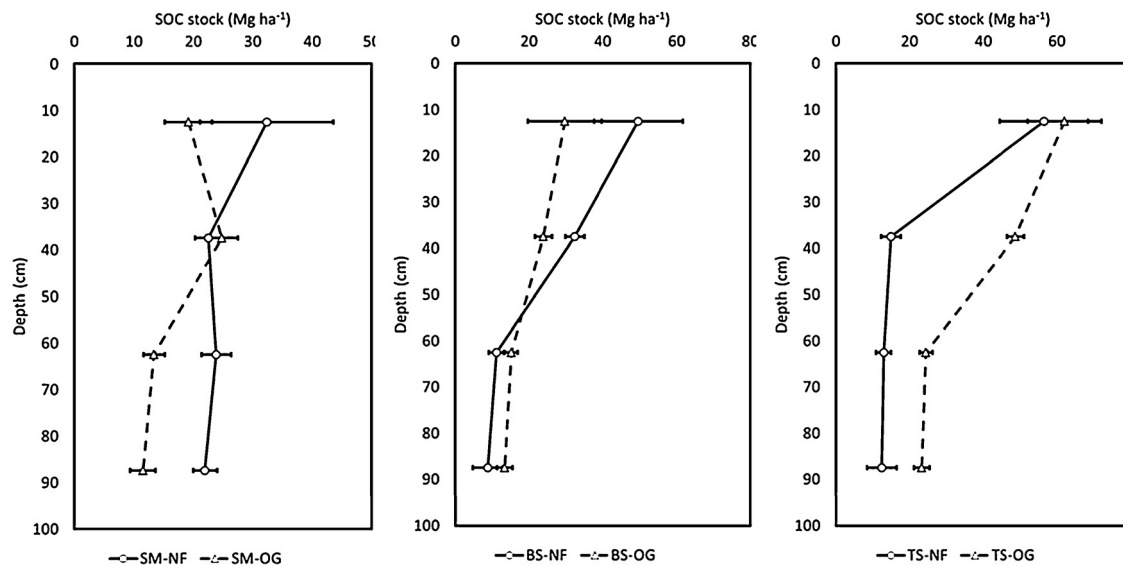
Fig. 2. Depth distribution of soil organic carbon stock (SOC-S) under natural forest (NF) and olive groves (OG) at summit (SM), backslope (BS) and toeslope (TS) positions. Data are means ± SD.
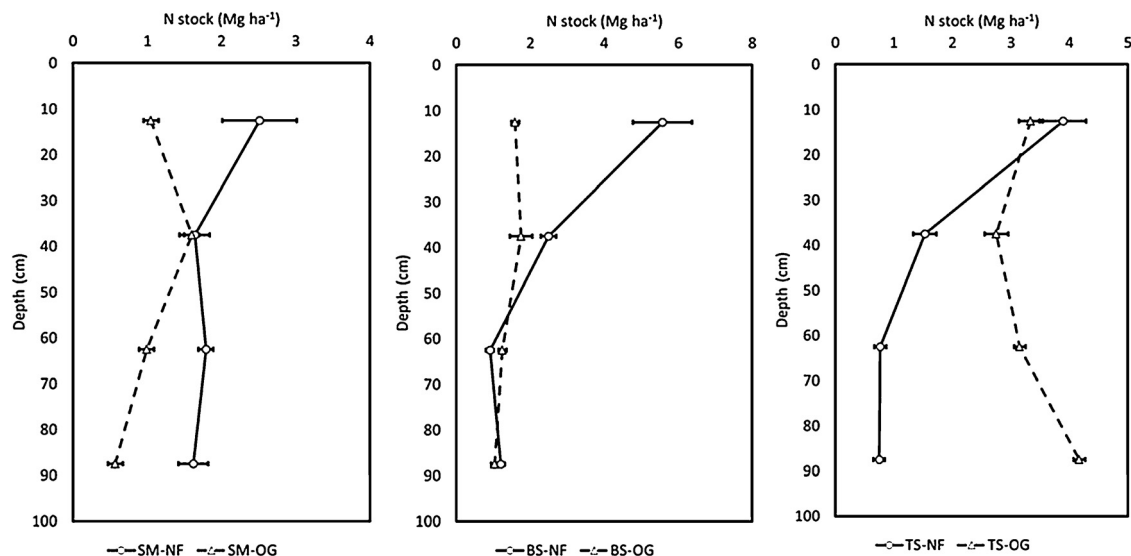
Fig. 3. Depth distribution of nitrogen stock (N-S) under natural forest (NF) and olive groves (OG) at summit (SM), backslope (BS) and toeslope (TS) positions. Data are means ± SD.

to OG in SM and BS but not in TS. These reductions were 44.3% (SM) and 44.7% (BS). The increase in N from NF to OG soils in TS was 93.23% (Fig. 3).

3.5. Stratification of SOC

In NF, the SR of SOC increased when deeper sections were taken into account at the BS (SR1 = 1.5; SR2 = 4.4; SR3 = 5.6) and TS (SR1 = 3.8; SR2 = 4.4; SR3 = 4.5), while there was an exception in the first topographical position (SM), where the SR of SOC did not change significantly between SR1, SR2 and SR3 (Fig. 4).

As for OG, the SR of SOC increased when deeper sections were considered in all the topographical positions. These values ranged from 0.8 to 1.7 in SM, from 1.2 to 2.2 in BS and from 1.3 to 2.7 in TS. SR values in OG are <2 in SM, SR1 and SR2 at the BS and SR1 at the TS. Therefore, the values with SR of SOC >2 are SR3 at the BS (2.2) and SR2 and SR3 at the TS (2.5 and 2.7 respectively).

The SR values were higher in NF than in OG soils at the BS and TS but not at the SM (with the SR1 exception), where SR2 and SR3 were higher in the OG soils.

4. Discussion

4.1. Soil properties

The studied soils presented some differences in the physical–chemical parameters. In general, with respect to clay content, NF was more clayey than OG in the superficial topographical positions, but at lower depths, the opposite was usually found (less clayey for NF and OG). As for silt, the soils had an increasing silt fraction at lower topographic positions. This is likely to be the consequence of silt's high erodibility (Durán-Zuazo et al., 2013). With respect to pH, the high values could be associated with parent material lithology and low organic carbon concentrations (Rezaei and Gilkes, 2005). Another significant feature was that BD was lower in the S1 soil sections in NF than in those in OG. This could have been caused by the higher damage and structural decline in OG caused by continuous agricultural activities. In this line, Durán-Zuazo et al. (2013) also found that BD was higher in intense agricultural land than in pine tree forest. The gravel content was generally higher in NF than in OG, caused by soil management (CT) in OG, as tillage is used to remove large stones and boulders. Similar results were obtained by Rytter (2012) when comparing arable land with NF soils in Sweden.

Fig. 4. Stratification ratio (SR) of SOC concentrations under natural forest (NF) and olive groves (OG) at summit (SM), backslope (BS) and toeslope (TS) positions. Data are means ± SD.

4.2. Soil organic carbon, nitrogen and C:N ratio

In the studied soils there was a pattern of total SOC (T-SOC) decrease from the highest to the lowest topographic position. This coincides with other authors who found an increase of SOC with altitude (Ganuza and Almendros, 2003; Leifeld et al., 2005). However, Avilés-Hernández et al. (2009) found that SOC decreased with altitude in NF soils of a toposequence in Mexico, due to different decomposition rates of the dominant vegetation species in the different topographic positions. In OG soils T-SOC decreased with altitude. Similar results were found by Durán-Zuazo et al. (2013) who argue that this exception may occur due to soil losses at the surface caused by erosion processes and demonstrates how an insufficient amount of vegetative coverage in the highest parts of mountainous areas cause higher erosion and runoff.

Many authors have concluded that low SOC concentrations in soils regardless of their use (NF or OG) and its decrease with depth could be explained by soil physical properties (texture principally). The studied soils were predominantly sandy at depth, and therefore the transformation of OM is enhanced, due to the reduction of the formation of aggregates between SOC and the mineral fraction. As a result, the SOC content is lower than with other textures (Nieto et al., 2013). González and Candás (2004) and Parras-Alcántara et al., 2013a,b obtained similar results in sandy loam soils under evergreen oak and Mediterranean high-clayey soils respectively. In addition, low SOC levels are favoured by the climatic conditions of the South of Europe (Gallardo et al., 2000).

4.3. Land use change effects on SOC

LUC affected to SOC in the first two topographical positions (SM and BS). Similar results were obtained by Albretch and Kandji (2003), who found that soils with tree coverage show an increase in carbon and nitrogen content. Also, Brevik (2013) found that SOC content in newly-forming soils was lower in soils without tree cover, and concluded that lack of litter input was likely a contributing factor. Therefore, a decrease in carbon content could be explained by the lower density of trees present after the LUC from NF to OG. In addition, OG is known to be more susceptible to erosion rates than other crops due to the relatively low tree density. This leads to exposure to raindrop, direct impact and more extreme conditions (Durán-Zuazo et al., 2013). Despite this pattern, the SOC content at the TS was higher in OG than in NF. This was due to a significant increase in T-SOC in OG at the TS (42% higher compared to BS and SM). This increase may be caused by soil erosion, and one possible explanation may perhaps be that soil erosion has led to soil loss from the higher topographic positions and accumulation at the TS. The obtained results coincide with Eaton et al. (2008) who found that LUC contributes negatively to soil carbon storage. This process is even more accelerated in Mediterranean areas (Cerdà et al., 2010).

In the case of N concentrations, these decreased with depth in NF. Similar results were obtained by Rojas et al. (2009) in Lithic Ustorthent soils in silvopastoral systems with native timber in the dry tropics. The pattern for N with depth was not clear for our OG. As for altitude, there was a clearer pattern in OG. This could be caused by soil erosion and urea (nitrogen-based fertilizer) leaching, due to the lack of vegetative cover (Sanz-Cobena et al., 2012).

The C:N ratio in both cases (NF and OG) did not show any pattern of increase or decrease with depth or texture. Higher BD has also been shown to be associated with more decomposed OM with lower C:N ratios (Brevik, 2000; Brevik et al., 2002), and may explain the differences in C:N ratios found in this study. Several of the studied soils in both uses had C:N ratio values of 12 or higher, which indicates shortage of N in the soil (Batjes and Dijkshoorn, 1999). Other studies show that elevated clay content is often
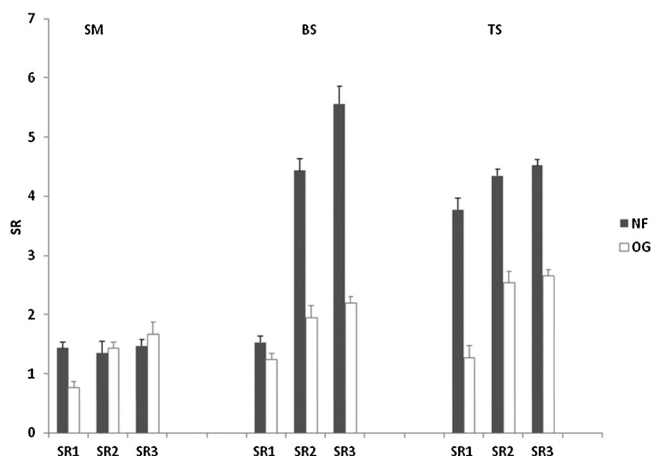
associated with more decomposed OM and with lower C:N ratio (Diekow et al., 2005; Puget and Lal, 2005; Ouédraogo et al., 2006; Yamashita et al., 2006).

4.4. Soil organic carbon and nitrogen stocks

In general, the SOCS under NF did not change for SM, BS and TS. These values were higher compared to other authors. For instance, they were around 25% higher than those of Nieto et al. (2010) in natural vegetation in a similar location (situated approximately 80 km away from our study area). Also, Muñoz-Rojas et al. (2012) obtained 55.6 Mg ha^{-1} in NF Regosols of Andalusia. These differences could be caused by a lack of anthropogenic intervention in the NF soils.

For OG the highest SOCS was found in TS and the lowest in SM, also, there was a general decrease with depth. As per the SOC case, erosion may have caused this effect by eroding the soil surface at the SM and BS, as the OG soils did not have vegetative cover that could prevent this. These values were much higher than those of Nieto et al. (2010) in Vertisols (27.1 Mg ha^{-1}) and Calcisols (26.4 Mg ha^{-1}) under CT in OG in similar areas and by Muñoz-Rojas et al. (2012) in Vertisols (58.6 Mg ha^{-1}) under permanent crops in Andalusia.

When assessing LUC, it can be concluded that SOCS was reduced at the first two topographic positions. This difference among OG and NF soils may have been caused by soil erosion and subsequent sediment accumulation (Durán-Zuazo et al., 2013). Recently, Boix-Fayos et al. (2009) found that NF with a higher density of trees has significantly higher SOCS than NF with lower density of trees in Mediterranean Cambisols and Regosols. Similar results were obtained by Nair et al. (2009). The SOCS loss at the SM and BS may have been influenced by management, as there was no tillage in NF, while in OG the soils were managed with CT. This management system could have led to a degradation process with reduction of OM and low productivity (Parras-Alcántara et al., 2013). Several authors agree that tillage reduces physical protection from erosion so that OM decomposition rates increase (Moscatelli et al., 2007; Jordán et al., 2010). Also, NF soils were always covered with vegetation, increasing OM stability, which is corroborated by Novara et al. (2012). The process of SOC loss through LUC may also have intensified due to the high temperatures and dry conditions of Mediterranean areas (JRC, 2012). Other researches have also found that LUC from NF to other uses affects the carbon balance significantly, along with soil properties (JRC, 2012). NF soils have higher input of carbon than the OG soils, especially if the latter are managed with CT (Beaufoy, 2001; Nieto et al., 2013). This reduction in carbon content may lead to disequilibrium in the nutrient intake of plants (JRC, 2012) and is therefore negative for OG, if no corrective measures are taken. In this line, García-Orenes et al. (2012) found that soil properties can recover in cases where centuries of CT caused soil degradation is remediated by moving to no tillage or straw mulch, indicating that the processes observed in this study could be reversible if the correct measures are taken.

When both soil uses are compared, NS were higher in NF than in OG, with the exception of the TS. Similar to SOCS, we can attribute this exception to soil erosion, as it causes soil loss and therefore the loss of carbon and other nutrients from the higher landscape positions. Also, a lower quality of soils is related to a lower content of essential nutrients such as N (JRC, 2012).

The similar patterns that SOC and N stocks followed were expected as most soil N is part of the SOM (Yimer et al., 2006).

4.5. Stratification of SOC

In NF, the SR of SOC increased with depth in BS and TS. A pattern of SOC SR increase with depth was found by Sá and Lal (2009) in a

dark red latosol under natural vegetation. Moreover, they indicated a positive correlation between SR of SOC and SOC sequestration. Similar values (between 4 and 5) to those obtained in this study for BS and TS were obtained by Franzluebbers (2010) and Francaviglia et al. (2014) in NF soils. This indicated higher carbon stability in these topographical positions (BS and TS). The reason for this is that high SR occurred due to high OM depositions on the surface, while SOC does not reach deeper sections of the profile at the same rate. This SOC in the surface improves aeration and soil structure (Sá and Lal, 2009). Also, it improves water infiltration and reduces nutrient loss and soil erosion, while mitigating CO_2 emissions (Franzluebbers, 2002, 2008, 2010).

With respect to SR of SOC for OG the behavior was similar to NF (increased with depth). The same pattern was obtained by Lou et al. (2012) in semiarid soils with maize crops, although these soils were not in a toposequence. According to Franzluebbers (2002), SR >2 is unusual in croplands under CT and therefore represents agricultural soils with high quality. This could be explained by the increased SOC content at the TS due to erosion and deposition processes.

According to Franzluebbers (2010), LUC is the main driver affecting SOC distribution, as NF soils are less disturbed than croplands.

5. Conclusions

Transforming a NF into cropland such as an OG led to considerable SOC loss. It also created a reduction in carbon stability; consequently lowering the soil quality. These effects were shaped by the toposequence characteristics, the climatic conditions (Mediterranean area) and increased OG soil exposure to them. Soil erosion led to an accumulation of soil at the TS of the OG soils, which mean these soils had higher T-SOC, SOCS, T-N and NS in that topographical position. NF soils were less disturbed, which increased stability, improved physical properties, and led to a more natural distribution of carbon and nitrogen across the soil sections.

SR of SOC was used to compare soil quality in both land uses. NF soils had higher values than OG soils, which represents a lower quality of soils in OG after the LUC. The results aimed to demonstrate that LUC from NF to agricultural soils (OG) is responsible for the loss of carbon and soil quality, especially when unsustainably managed. The T-SOC loss leads to the release of CO_2 to the atmosphere and NF have a higher potential for being carbon reservoirs than OG. It is therefore necessary to avoid uncontrolled LUC and maintain a sustainable balance that would prevent part of the excess of CO_2 emissions.

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CAPÍTULO II

Effects of land management on different forms of soil carbon in olive
groves in Mediterranean areas.

EFFECTS OF LAND MANAGEMENT ON DIFFERENT FORMS OF SOIL CARBON IN OLIVE GROVES IN MEDITERRANEAN AREAS

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ABSTRACT

This study analyses soil organic carbon (SOC) and hot-water extractable carbon, both measures of soil quality, under different land management—(i) conventional tillage (CT); (ii) CT plus the addition of oil mill waste *alperujo* (A); (iii) CT plus the addition of oil mill waste olive leaves (L); (iv) no tillage with chipped pruned branches (NT_1); and (v) no tillage with chipped pruned branches and weeds (NT_2)—in a typical Mediterranean agricultural area: the olive groves of Andalusia, southern Spain. SOC values in CT, A, NT_1 and NT_2 decreased with depth, but in NT_2, the surface horizon (0–5 cm) had higher values than the other treatments, 47% more than the average values in the other three soils. In L, SOC also decreased with depth, although there was an increase of 88·5% from the first (0–10 cm) to the second horizon (10–16 cm). Total SOC stock values were very similar under A ($101·9\,Mg\,ha^{-1}$), CT ($101·7\,Mg\,ha^{-1}$), NT_1 ($105·8\,Mg\,ha^{-1}$) and NT_2 ($111·3\,Mg\,ha^{-1}$, if we consider the same depth of the others). However, SOC under L was significantly higher ($p < 0.05$) at $250·2\,Mg\,ha^{-1}$. Hot-water extractable carbon decreased with depth in A, CT and NT_1. NT_2 and L followed the same pattern as the other management types but with a higher value in the surface horizon (2·3 and 4·9 mg g^{-1}, respectively). Overall, our results indicate that application of oil mill waste olive leaves under CT (L) is a good management practice to improve SOC and reduce waste. Copyright © 2014 John Wiley & Sons, Ltd.

KEY WORDS: soil organic carbon; hot-water extractable carbon; olive grove; land management

INTRODUCTION

Olive groves (OG) are one of the main agricultural systems in the Mediterranean basin, covering $9·5 \times 10^6$ ha. Spain is the main olive oil producer in the world with half of the OG area in the European Union (EUROSTAT, 2012). The area under OG cultivation in Spain and Andalusia (southern Spain) is $2·5 \times 10^6$ ha and $1·9 \times 10^6$ ha, respectively (MAGRAMA, 2013). Therefore, Andalusia is a key olive oil-producing region, with 76% of the OG area in Spain and 20% of the OG area in the European Union.

It is common to associate OG with soil degradation problems due to conventional tillage (CT) management, as the combination of sloping areas planted with a low-density tree (low vegetation cover) promotes extreme soil erosion rates by intense rainfall (Gómez *et al*., 1999; Cerdà *et al*., 2010; Prokop & Poręba, 2012; Mandal & Sharda, 2013; Ziadat & Taimeh, 2013). In general, Mediterranean soils are characterised by low organic matter (OM) content (typically around 1%) because of the low addition of carbon from plant residues under the low-density tree cover and CT management than has dominated over millennia of cultivation (Verheye & De La Rosa, 2005; Kapur *et al*., 2007; Cerdà *et al*., 2010). As a result, soil erosion is one of the main

issues of Mediterranean areas, and its control is a key factor to maintain sustainable agricultural production (Gómez *et al*., 2003; Allen *et al*., 2006; Ibáñez *et al*., 2014).

Low OM has two roles in increasing soil sensitivity to erosion. First, low OM reduces soil aggregate stability and increases the risk of soil to high erosion rates (Gómez *et al*., 2004; García-Orenes *et al*., 2009; Kocyigit & Demirci, 2012; Leh *et al*., 2013). Second, soils with high OM retain more water; the low soil organic matter (SOM) contents in OG under CT create further stress on water availability for vegetation. The climate of Mediterranean areas is characterised by dry and hot summers and wet and cold winters. Because of these dry conditions in summer and infrequent torrential rainstorms, soil water retention is essential for the survival of vegetation. This scenario is linked to low vegetative coverage, which is approximately 35% in conventional OG (Rodríguez-Lizana *et al*., 2008).

Another important problem contributing to the erosion risk is related to steep slopes. About 36% of the OG in Andalusia are planted on slopes with gradients greater than 15%, using land that is unsuitable for other crops to grow because conditions produce poor yields (Ibáñez *et al*., 2014). These conditions, along with poor management practices, such as badly managed CT (Gucci *et al*., 2012), cause land degradation, soil OM losses and therefore soil quality reduction (Shakesby *et al*., 2002; Zdruli, 2012; Siles *et al*., 2014).

Agricultural management practices in OG have traditionally been very intensive. From the 1960s, the use of machinery

(notably tractors) has further increased the damage due to the intensive tillage, along with the use of chemical fertilisers (Calatrava *et al.*, 2011; Montes-Borrego *et al.*, 2013). These practices have recently been challenged. Several studies have demonstrated the lack of sustainability for traditional OG production because soil degradation results in negative economic consequences due to lower production (Moreno *et al.*, 2006; Hervás-Martínez *et al.*, 2010).

Techniques to reduce the environmental impact in OG started to be adopted two decades ago. The purpose is to increase the soil quality, and one of its indicators is OM presence associated with soil organic carbon (SOC). Conserving and enhancing SOC has additional benefits for soil carbon dynamics, by increasing the amount of carbon sequestered in soils (Lal, 2004; Brevik, 2012; Srinivasarao *et al.*, 2014).

One of the first techniques that were used to reduce erosion was to cover the soil with protecting OM composed of recycled crop waste (e.g. crop residues such as pruned branches) (Ribeiro *et al.*, 2011; Montes-Borrego *et al.*, 2013). In OG, pruned chipped branches are used as a protective coverage against erosion. Pruning residues have been shown to provide more efficient protection against erosion than spontaneous vegetation cover, as long as this layer is of sufficient quantity, maintained through time and evenly distributed across the soil (Repullo *et al.*, 2012).

The second technique is minimum tillage along with reduced use of chemical fertilisers. This has been shown to be a good mechanism to increase soil quality (Montes-Borrego *et al.*, 2013).

The third technique is the use of organic waste residues combined with any type of tillage (Aranda *et al.*, 2011; Lozano-García & Parras-Alcántara, 2013a). Two of the most generally applied organic wastes in OG are *alperujo* and olive leaves. *Alperujo* is the solid sludge waste generated by the new two-phase method of olive oil extraction, and olive leaves are those unintentionally collected with the olives at harvest (Moreno *et al.*, 2009). Both wastes contain large quantities of OM and moisture but do not contain heavy metals or pathogenic microorganisms (Lozano-García *et al.*, 2011).

Another good indicator of soil quality is hot-water extractable carbon (HWC). Labile SOM such as HWC responds to land-use changes in the short term (Leifeld & Kögel-Knabner, 2005). Furthermore, it can be used as a sensitive indicator of SOM change (Ghani *et al.*, 2003). HWC has been specifically used to detect the effects of different management practices (Uchida *et al.*, 2012). HWC includes microorganisms, soluble carbohydrates and other compounds (Ghani *et al.*, 2003) and has been shown to correlate with soil micro-aggregate characteristics (Puget *et al.*, 1999). As a result, HWC is a widely accepted indicator of soil quality (Ghani *et al.*, 2003; Xue *et al.*, 2013).

As soil depth is crucial in the distribution of SOC stocks (SOC-S) and HWC, it is therefore important to analyse the entire soil profile, as SOC-S variability at depth is strongly influenced by vertical processes (VandenBygaart, 2006; Sombrero & de Benito, 2010), especially in temperate climates, where large amounts of SOC can accumulate below 30 cm deep (Lorenz & Lal, 2005). Most studies tend to focus on the top 30 cm or 1 m of soils and therefore substantially underestimate the change in total carbon stock.

On the basis of the foregoing, the aims of this study are twofold: (i) to analyse the SOC under different land management [CT; CT plus the addition of two oil mill wastes: *alperujo* (A) and olive leaves (L); and no tillage (NT) with chipped pruned branches (NT_1) and NT with chipped pruned branches and weeds (NT_2)] and (ii) to study the dissolved organic carbon at depth in OG with different management practices in Mediterranean areas.

MATERIALS AND METHODS

Study Site

The study was carried out in Torredelcampo, Jaén (southern Spain). The underlying bedrock consists of Miocene marl and marlaceous lime. The soils are Cambisols (IUSS-ISRIC-FAO, 2006). The climate is typical of Mediterranean areas: 3 to 5 months of hot dry summer, which occurs from June to September, and cool and moist winters. The mean annual temperature is 17 °C, with a maximum average temperature of 40·6 °C (August) and a minimum of −5·2 °C (January). The mean annual precipitation is 646 mm yr^{-1}, ranging from 4·7 mm month^{-1} (July) to 87 mm month^{-1} (February).

Experimental Design

The OG soils were studied under five different management practices. The five plots' location and characteristics are in Table I, and a view of the five plots can be seen in Figure 1. The CT plot was used as the control plot because this is the traditional management system used in OG before the alternative strategies were adopted. Four alternative management practices developed to improve the soil quality were examined. In two plots, the residues from the oil press, *alperujo* (A) and olive leaves (L), were applied on the soil surface under CT management. The other two managements were NT: NT_1 that included application of pruned olive branch chippings and NT_2 that included application of pruned olive branch chippings, and no weed control was used. All plots were planted with olive trees (*Olea europaea*) of the Picual olive variety at a density of 90 trees ha^{-1}. Each tree had two to three trunks. All five management systems had mineral fertiliser application of 100 kg ha^{-1} urea (46% N) in alternate years during the winter, after the olives had been harvested. Plots managed with CT (A, L and CT) were disc harrowed in summer (25 cm) to diminish the size of soil clods. Finally, herbicides were added in autumn to control weeds. These management practices are the most common in the OG in Andalusia.

The soils studied were very similar in their physical–chemical properties. Where there were small differences, they depended on the soil depth and management. The crop (OG) was the same at the five study sites (Table II).

The soils are characterised by around 10 to 20% gravel, although the surface horizon in L (5%) and in NT_2 (22·3%) is

Table I. Experimental design, location and characteristics

Samples	Coordinates	Management	Treatment	Beginning of treatment	Samples taken	Years of treatment
A	37°50′55″ N 03°51′56″ W	CT	Alperujo (270 Mg alperujo ha^{-1} y^{-1})	2003	Nov 2013	10
L	37°50′51″ N 03°51′54″ W	CT	Olive leaves (236 Mg olive leaves ha^{-1} y^{-1})	2003	Nov 2013	10
CT	37°50′52″ N 03°51′50″ W	CT	—	—	Nov 2013	—
NT$_1$	37°51′10″ N 03°51′44″ W	NT	Pruning residues (6 Mg ha^{-1} each 2 years)	2003	Nov 2013	10
NT$_2$	37°48′26″ N 03°53′01″ W	NT	Pruning residues (6 Mg ha^{-1} each 2 years) + vegetation cover	1999	Nov 2013	14

A, alperujo; L, olive leaves; CT, conventional tillage (control plot); NT$_1$, no tillage with chipped pruned branches (10 years); NT$_2$, no tillage with chipped pruned branches and weeds (14 years).

outside this range, a high silt content (43·8–72·7%) that provided them with a clay loam texture and a high proportion of clay (18·5–40·7%) (Table II). pH was between 6 and 8·9 in all cases, and in general, it decreased with depth. On the other hand, bulk density (BD) increased with depth.

Sampling and Analysis

Soil properties were studied at different depths along the entire soil profile, horizon by horizon, instead of by soil control sections, because soil depth is crucial to understanding the distribution and redistribution of SOC and HWC and, therefore, the total soil carbon stock. Two soil profiles were sampled in each plot.

Bulk density was determined by using a cylinder (3 cm in diameter, 10 cm in length and 70·65 cm^3 in volume) that was inserted into each soil horizon in the field (Blake & Hartge, 1986). In the laboratory, soil samples were air-dried and passed through a 2-mm sieve to remove gravel and roots. Texture was determined by laser granulometry, using a Coulter LS 230 (Beckman/Coulter Inc. Brea, CA, USA). This technique uses polarised light at three different wavelengths (450, 600 and 900 nm) to analyse the particle size distribution specifically in the 0·04 to 0·4 μm ranges. Soil pH was determined in a 1:2·5 soil-to-water ratio. SOC was determined using a Thermo Fisher Analyser (Thermo Fisher Scientific; Flash 2000 model, Waltham, MA, USA), following the Thermo Fisher Scientific method (patent no. 90110186·5). Three replications for each sampling point were performed in the laboratory (five plots × two soil profiles samples in each plot × three replications in the laboratory).

Figure 1. Images of the five plots, from left to right: control plot with conventional tillage (CT), CT and olive leaves (L), CT and alperujo (A), no tillage (NT) with chipped pruned branches (10 years) (NT$_1$) and NT with chipped pruned branches and weeds (NT$_2$). This figure is available in colour online at wileyonlinelibrary.com/journal/ldr.

Table II. Physical properties and pH evaluated for soil management types in olive groves

Place	Depth (cm)	Thickness (cm)	Horizons	Gravel (%)	Clay (%)	Silt (%)	Sand (%)	pH (H$_2$O)	BD (Mg m^{-3})
OG A	0–10	10	Ap	11·7 ± 2·2	36·9 ± 0·50	43·8 ± 1·1	19·3 ± 1·4	6·0 ± 0·55	1·3 ± 0·1
	10–65	55	Bw	12·1 ± 1·3	40·7 ± 0·12	47·2 ± 1·8	12·1 ± 0·26	6·7 ± 0·40	1·4 ± 0·1
	65–100	35	Bw/C	18·3 ± 1·3	38·1 ± 1·3	47·9 ± 0·61	14·0 ± 1·1	6·7 ± 0·62	1·4 ± 0·1
	100–115	15	C	16·5 ± 2·0	38·5 ± 1·9	46·5 ± 0·74	15·0 ± 0·9	8·1 ± 0·41	1·4 ± 0·1
OG L	0–10	10	Ap$_1$	5·0 ± 2·6	23·7 ± 0·52	46·7 ± 1·2	29·6 ± 1·6	6·2 ± 0·83	1·1 ± 0·1
	10–16	6	Ap$_2$	11·2 ± 2·3	18·5 ± 1·3	46·1 ± 0·64	35·4 ± 0·64	6·5 ± 0·46	0·6 ± 0·1
	16–65	49	Bw	12·3 ± 1·7	38·2 ± 0·47	56·2 ± 0·26	5·6 ± 0·9	6·9 ± 0·52	1·2 ± 0·1
	65–100	35	Bw/C	18·5 ± 1·8	38·0 ± 1·6	49·3 ± 1·2	12·7 ± 1·4	8·2 ± 0·74	1·3 ± 0·1
	100–115	15	C	17·0 ± 1·6	37·9 ± 0·18	48·1 ± 0·23	14·0 ± 0·23	8·1 ± 0·40	1·4 ± 0·2
OG CT	0–18	18	Ap$_1$	11·2 ± 1·8	37·1 ± 0·72	59·5 ± 1·4	3·4 ± 1·4	6·7 ± 0·33	1·3 ± 0·1
	18–65	47	Bw	18·3 ± 2·6	39·1 ± 0·63	60·7 ± 1·6	0·20 ± 0·94	7·0 ± 0·76	1·4 ± 0·1
	65–100	35	Bw/C	12·1 ± 1·4	39·8 ± 1·6	60·1 ± 0·20	0·10 ± 0·61	7·0 ± 0·43	1·4 ± 0·1
	100–115	15	C	16·5 ± 1·9	38·7 ± 1·3	60·9 ± 0·41	0·40 ± 1·41	7·9 ± 0·22	1·4 ± 0·1
OG NT$_1$	0–30	30	A	11·3 ± 2·1	31·3 ± 0·50	52·5 ± 1·7	16·2 ± 1·8	6·8 ± 0·13	1·3 ± 0·2
	30–65	35	Bw	18·5 ± 1·2	33·3 ± 0·45	53·8 ± 1·3	12·9 ± 0·33	6·9 ± 0·14	1·4 ± 0·1
	65–100	35	Bw/C	12·4 ± 2·2	31·4 ± 1·2	53·7 ± 0·47	14·9 ± 0·47	6·8 ± 0·06	1·4 ± 0·1
	100–115	15	C	12·5 ± 1·6	29·2 ± 0·21	52·9 ± 0·81	17·9 ± 1·65	8·0 ± 0·25	1·5 ± 0·2
OG NT$_2$	0–5	5	Ap$_1$	22·3 ± 2·4	21·7 ± 1·2	63·8 ± 1·6	14·5 ± 1·7	6·9 ± 0·61	1·2 ± 0·2
	5–23	18	Ap$_2$	18·2 ± 2·6	25·6 ± 1·6	72·1 ± 0·52	2·3 ± 0·74	6·8 ± 0·24	1·4 ± 0·1
	23–110	87	Bt	18·2 ± 1·1	26·2 ± 1·6	72·7 ± 1·3	1·1 ± 0·63	7·1 ± 0·35	1·4 ± 0·1
	110–135	25	Bt/C	17·8 ± 1·3	37·7 ± 1·4	55·9 ± 0·42	6·4 ± 1·5	8·8 ± 0·21	1·4 ± 0·1
	135–160	25	C1	11·1 ± 1·1	33·2 ± 0·66	46·6 ± 1·3	20·2 ± 1·4	8·9 ± 0·31	1·5 ± 0·1

The data shown are the mean value ± standard deviation ($N = 6$).
OG, olive groves; A, alperujo; L, olive leaves; CT, conventional tillage (control plot); NT$_1$, no tillage with chipped pruned branches (10 years); NT$_2$, no tillage with chipped pruned branches and weeds (14 years); BD, bulk density.

The value of *SOC-S*, expressed for a specific depth in $Mg\,ha^{-1}$, was obtained as the product of *SOC* concentration, *BD*, depth and gravel as follows (IPCC, 2003):

$$SOC - Stock = SOC\ \text{concentration} \times BD \times d \times (1-\delta 2mm\%) \times 10^{-1}$$

Where: *SOC* is the organic carbon content $(g\,kg^{-1})$, BD is the bulk density $(Mg\,m^{-3})$, *d* is the thickness, and $\delta 2mm$ is the fractional percentage (%) of gravel larger than 2 mm size.

The total *SOC-S* (*T-SOC-S*) $(Mg\,ha^{-1})$ was calculated for each soil according to IPCC (2003) as follows:

$$T - SOC - S = \Sigma_{\text{horizon } 1\ldots n}\, SOC - S_{\text{horizon}}$$

HWC was determined after applying the Ghani *et al.* (2003) method. Dissolved organic carbon in the hot water extracts was measured using a Shimadzu TOC 5000 (Shimadzu Corporation. Kyoto, Japan).

The effect of management and depth on SOC and HWC concentrations and stocks was analysed using an ANOVA (SPSS 13·0 for Windows IBM, Armonk, New York, USA). Data were tested for normality to verify the model assumptions. Differences of $p < 0.05$ were considered statistically significant.

RESULTS AND DISCUSSION

Soil Organic Carbon Concentrations

The T-SOC was similar in A, CT and NT_1 (31·3, 30·0 and $29\cdot5\,g\,kg^{-1}$, respectively). NT_2 and L had higher and significantly higher values of 49·5 and $158\cdot1\,g\,kg^{-1}$, respectively, than the other management practices (Figure 2). SOC concentrations in the surface horizon (Figure 3) were 12·2, 10·7 and $13\cdot4\,g\,kg^{-1}$ in A, CT and NT_1, respectively, and their concentration decreased with depth in the same way across the three plots. In NT_2, SOC concentration in the surface horizon was higher than in the three mentioned managements. However, the trend in depth was the same, and even the values were very similar.

L had the highest SOC concentration in the surface horizon. However, there was an important difference; the general trend was a decrease as well, although there was
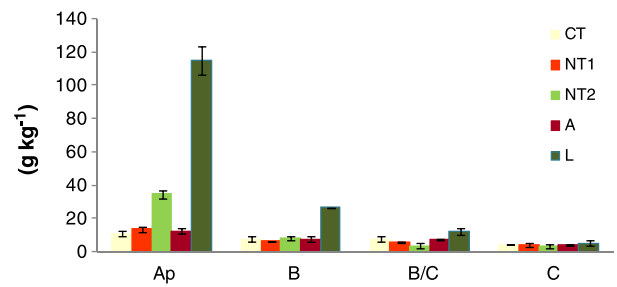
Figure 3. Soil organic carbon (SOC) of the studied soils. Mean value shown ± standard deviation ($N = 6$). CT, conventional tillage (control plot); NT_1, no tillage with chipped pruned branches (10 years); NT_2, no tillage with chipped pruned branches and weeds (14 years); A, alperujo; L, olive leaves. In the case of L, the SOC concentration in the Ap horizon is the sum resulting from the Ap_1 (0–10 cm) + Ap_2 (10–16 cm). In the case of NT_2, the SOC concentration in the Ap horizon is the sum resulting from the Ap_1 (0–5 cm) + Ap_2 (5–23 cm). This figure is available in colour online at wileyonlinelibrary.com/journal/ldr.

an increase from the first Ap horizon (0–10 cm) to the second Ap horizon (10–16 cm). In addition, the BD value for L (10–16 cm) is quite low (Table II); it was the only BD that did not fit. It was due to the high SOC content of this horizon. Here, SOC was $39\cdot8\,g\,kg^{-1}$ in the Ap_1 horizon and $75\,g\,kg^{-1}$ in the Ap_2 horizon, which represented an increase of 88·5%. Despite these differences, it is important to point out that SOC values were similar below 100 cm in all the studied management options.

Therefore, SOC decreased with depth in all treatments except for L Ap_1 and Ap_2.

Decrease in SOC concentrations with depth has been found extensively in other studies, not only for agricultural soils such as OG (Novara *et al.*, 2012; Parras-Alcántara *et al.*, 2013; Lozano-García & Parras-Alcántara, 2014) but also under other crops such as wheat, beans or maize (Hernanz *et al.*, 2009; Jemai *et al.*, 2012) and in *dehesas* and rangelands (Pulido-Fernández *et al.*, 2013; Parras-Alcántara *et al.*, 2014) and natural soils in Mediterranean areas (Rovira & Vallejo, 2007), even into soils forming in old mine lands (Brevik, 2013).

It is well known that land management can affect soil physical–chemical properties, particularly SOC. Gucci *et al.* (2012) obtained higher SOC in OG soils with NT (13·3 and $13\cdot5\,Mg\,ha^{-1}$ in the first 10 cm and the following 10 cm, respectively) than in those with CT (11·4 and $10\cdot4\,Mg\,ha^{-1}$ in the first 10 cm and the following 10 cm, respectively) at an experimental farm near Pisa (Italy) with similar conditions to ours. Our values in the treatments with NT were higher. Also, Aranda *et al.* (2011) obtained trends similar to those of Gucci *et al.* (2012) in an experiment located in OG soils of the province of Jaén (the same as our study), with higher values under NT soils with vegetative cover than in those with CT. Finally, Lozano-García & Parras-Alcántara (2013a) obtained higher SOC with a sustainable management practice (organic farming in this case) than with CT in an OG soil of a Mediterranean area, whereas Hernanz *et al.* (2009) obtained similar results but with cereal

Figure 2. Total soil organic carbon (T-SOC) of the studied soils. CT, conventional tillage (control plot); NT_1, no tillage with chipped pruned branches (10 years); NT_2, no tillage with chipped pruned branches and weeds (14 years); A, alperujo; L, olive leaves. This figure is available in colour online at wileyonlinelibrary.com/journal/ldr.

crops. In our case, NT_1 did not have significant differences ($p < 0.05$) with CT. However, NT_2 included NT and pruning residues during a longer period represented a significant increase in SOC content. This corresponds with the results of Repullo *et al*. (2012) although their treatment had not been applied for as many years as ours. Benitez *et al*. (2006) conducted a characterisation of OG soils in the provinces of Córdoba and Granada (both adjacent to the province of this study) with several combinations of soil and crop management. They generally obtained higher values in the combinations where tillage was present, rather than in those with herbicides or NT. Furthermore, Montanaro *et al*. (2009) obtained SOC values after 4 years of experiments, which were similar to the initial values in an NT treatment with pruning residues in fruit crops in a Mediterranean area, although yield was higher.

There have been several studies that have investigated the improvement/changes of soil properties after the addition of agricultural wastes. In OG soils, the most commonly applied are leaves, pruning residues and *alperujo* (including composted). López-Piñeiro *et al*. (2007) analysed the effect of watery olive husks on OG soils with irrigation in Portugal, finding that the application of this product increased SOC. Clemente *et al*. (2007) found that olive husk increased SOC in contaminated agricultural soils from a Mediterranean area. However, research in Jaén on the application of wastes (olive leaves and *alperujo*) has led to contrasting findings. Whereas *alperujo* did not seem to have an effect on SOC, olive leaves increased it (Lozano-García & Parras-Alcántara, 2013a). Other authors have also studied olive mill wastes that are similar to *alperujo*. Nasini *et al*. (2013) also found that this waste did not increase SOC although it improved OG vegetative growth. However, Altieri & Esposito (2008) found that SOC increased after the application of olive mill wastes, but these had been amended with leaves, pruning residues and wheat straw, among others to reduce its acidity and improve its properties. Finally, some authors have also investigated the potential of composting *alperujo*, to obtain its composition and properties that can be as good as those from manure or other materials (Alburquerque *et al*., 2009), increasing SOC and crop yield (de la Fuente *et al*., 2011; Fernández-Hernández *et al*., 2014) and also being a promising amendment for the bioremediation of heavy metals (de la Fuente *et al*., 2011).

Applying agricultural wastes tackles two environmental problems common in OG; the difficult management of these waste residues and improving soil properties that help to reduce erosion rates (Quinton *et al*., 2010; Lozano-García & Parras-Alcántara, 2013b). Also, Martínez-Mena *et al*. (2008) found that sediments are one of the pathways through which carbon can be lost in agricultural soils. Sediments contain two times the quantity of SOC that original soils have, which may then be eroded by various processes including water erosion (Jacinthe *et al*., 2001). As there is more sediment production in areas with OG, this leads to higher carbon losses due to erosion, compared to other areas (Martínez-Mena *et al*., 2008).

Soil Organic Carbon Stocks

The T-SOC-S values (Figure 4) were very similar in A ($101.9\,\mathrm{Mg\,ha^{-1}}$), CT ($101.7\,\mathrm{Mg\,ha^{-1}}$) and NT_1 ($105.8\,\mathrm{Mg\,ha^{-1}}$). There were significant differences in NT_2 and L. NT_2 presented a higher value than the other land management ($132.6\,\mathrm{Mg\,ha^{-1}}$), whereas L had $250.2\,\mathrm{Mg\,ha^{-1}}$. However NT_2 has a T-SOC-S value of $111.3\,\mathrm{Mg\,ha^{-1}}$, if we consider just the first 100 cm, which is the same depth as the others.

L had the highest SOC concentrations and stock. Olive leaves that were added on the surface and that subsequently became part of the second horizon added a large quantity of OM. However, no trend or pattern was found for the vertical distribution of SOC-S in our soils. Furthermore, as can be seen in Figure 5, the main differences in SOC-S content were found in the first 100 cm of all treatments (Ap, B and B/C horizons), whereas a deeper SOC-S value was relatively similar in all the studied soils.

Muñoz-Rojas *et al*. (2012) made a comprehensive analysis of various types of soil and land coverage in Mediterranean areas. The SOC-S values they obtained for Cambisols under arable cultivation and several other types of agricultural land use were 47.3 and $34.5\,\mathrm{Mg\,ha^{-1}}$, respectively. These values are lower than the values in this study, although Muñoz-Rojas *et al*. (2012) covered less depth than our study (0.75 m compared with 1 or 1.6 m in this study). T-SOC-S values in other studies in Mediterranean areas were also higher than those in Muñoz-Rojas *et al*. (2012) and similar to this study. For instance, Rodríguez-Murillo (2001) found T-SOC-S to a depth of 0.75 m ranging from 39.9 to $123\,\mathrm{Mg\,ha^{-1}}$ in several locations of peninsular Spain, and Brahim *et al*. (2010) reported a value of $101.80\,\mathrm{Mg\,ha^{-1}}$ to a depth of 1 m in Cambisols of a semi-arid Mediterranean region. The values obtained in our study are similar to those found by other authors who investigated soils from areas that normally have more OM such as Bulgaria, Belarus, Czech Republic and Hungary (an average of $118\,\mathrm{Mg\,ha^{-1}}$ in Cambisols) (Batjes, 2002) and south-west Germany ($106.6\,\mathrm{Mg\,ha^{-1}}$) (Neufeldt, 2005). Both authors studied the same depth as that used our study.
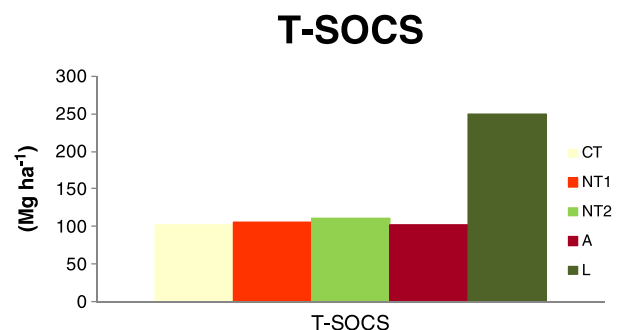
Figure 4. Total soil organic carbon stock (T-SOC-S) of the studied soils. CT, conventional tillage (control plot); NT_1, no tillage with chipped pruned branches (10 years); NT_2, no tillage with chipped pruned branches and weeds (14 years); A, alperujo; L, olive leaves. In NT_2, the T-SOC-S is the sum resulting from the first 100 cm in order to establish a better comparison with the rest of management in which the soil profiles are 100 cm in depth. This figure is available in colour online at wileyonlinelibrary.com/journal/ldr.
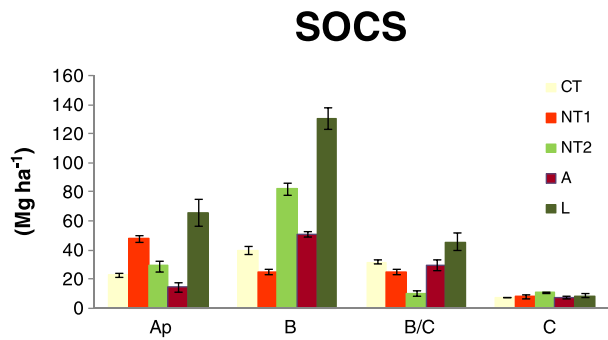
Figure 5. Soil organic carbon stock (SOC-S) of the studied soils. Mean value shown ± standard deviation ($N = 6$). CT, conventional tillage (control plot); NT_1, no tillage with chipped pruned branches (10 years); NT_2, no tillage with chipped pruned branches and weeds (14 years); A, alperujo; L, olive leaves. In the case of L, the SOC concentration in the Ap horizon is the sum resulting from the Ap_1 (0–10 cm) + Ap_2 (10–16 cm). In the case of NT_2, the SOC concentration in the Ap horizon is the sum resulting from the Ap_1 (0–5 cm) + Ap_2 (5–23 cm). This figure is available in colour online at wileyonlinelibrary.com/journal/ldr.

Figure 6. Hot-water extractable carbon (HWC) of the studied soils. Mean value shown ± standard deviation ($N = 6$). CT, conventional tillage (control plot); NT_1, no tillage with chipped pruned branches (10 years); NT_2, no tillage with chipped pruned branches and weeds (14 years); A, alperujo; L, olive leaves. In the case of L, the soil organic carbon (SOC) concentration in the Ap horizon is the sum resulting from the Ap_1 (0–10 cm) + Ap_2 (10–16 cm). In the case of NT_2, the SOC concentration in the Ap horizon is the sum resulting from the Ap_1 (0–5 cm) + Ap_2 (5–23 cm). This figure is available in colour online at wileyonlinelibrary.com/journal/ldr.

Values from Nieto *et al.* (2010) in Mediterranean soils under CT are similar to those from Muñoz-Rojas *et al.* (2012) and again lower than ours. However, in soils with pruning and cleaning residues in the same study, the values oscillated between 113·6 and 158 $Mg\,ha^{-1}$, which are closer to those of our study. The T-SOC-S of CT was within the range of values obtained by Fernández-Romero *et al.* (2014) in OG soils under CT in three topographical positions (101·7 $Mg\,ha^{-1}$ in CT and 68·9–158·7 $Mg\,ha^{-1}$ in their study). If all the values in our study are considered, our upper range is higher (250·2 $Mg\,ha^{-1}$ in L). Lou *et al.* (2012) studied agricultural soils with CT and conservation tillage. SOC and T-SOC-S values were higher with conservation tillage than with CT, although responses varied. In the experiment conducted by Lou *et al.* (2012), there seems to be a trend of uniform distribution in CT and a gradient with depth under conservation tillage.

It is worth noting that the horizon where SOC-S was the highest in L was Bw (16–65 cm), whereas the SOC-S in the same horizon were much lower in the rest of the studied management options (around 75% lower in CT, A and NT_1 and 35% lower in NT_2, but in this case, the depth of the horizon was higher). This demonstrates that the addition of olive leaves on the surface led not only to higher SOC there but also to higher and more stable SOC deeper in the soil.

Hot-water Extractable Carbon

HWC decreased with depth in all cases (Figure 6), a trend that is similar to what was obtained for SOC (Figure 3). This is similar to Wang *et al.* (2014) in agricultural soils of north-east China managed with conventional and conservation management techniques and to that of Bu *et al.* (2010) in soils under four different vegetation types of the Wuyi Mountains. Corvasce *et al.* (2006) obtained the same trend for both HWC and SOC (as in our study) in an entire soil profile in Southern Italy.

As it can be seen in Figure 6, HWC values for A, CT and NT_1 were very similar, even when horizons in the same

position are compared (e.g. the surface horizons of each treatment). These values are comparable with those of Ghani *et al.* (2003) (close to 1 $mg\,g^{-1}$ in agricultural soils of New Zealand), who actually developed the hot-water extraction method used in this study.

HWC in NT_2 decreased with depth as well. However, it had a higher HWC content in the surface horizon than A, CT or NT_1, although the values in the Bw and Bw/C horizons were similar to those of the mentioned treatments.

HWC values from the NT_1 and NT_2 can be compared with those of Chen *et al.* (2009) (0·51 $mg\,g^{-1}$) in the first 15 cm of agricultural soils, as there is not tillage either. HWC values in the surface of NT_1 were similar. However, surface values in NT_2 were much higher (1·59 $mg\,g^{-1}$) than those in NT_1 and in Chen *et al.* (2009). We believe that this was because the treatment in NT_2 had been present for longer than in NT_1 and because NT_2 had vegetative cover.

Values in L are very different from the treatments mentioned earlier and, therefore, also different from the results obtained by Chen *et al.* (2009). Total HWC was significantly higher than in the other treatments (Figure 7). Moreover, HWC was higher in each horizon type than in the same
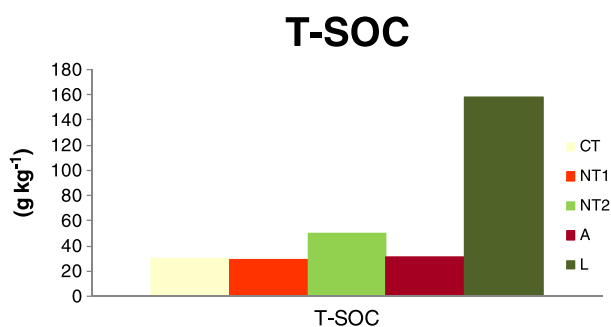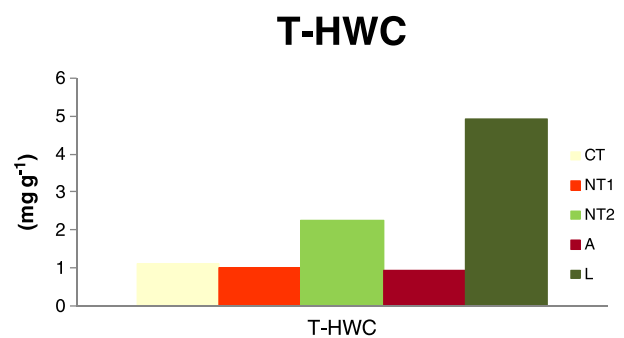

Figure 7. Total hot-water extractable carbon (T-HWC) of the studied soils. CT, conventional tillage (control plot); NT_1, no tillage with chipped pruned branches (10 years); NT_2, no tillage with chipped pruned branches and weeds (14 years); A, alperujo; L, olive leaves. This figure is available in colour online at wileyonlinelibrary.com/journal/ldr.

horizon in the rest of the treatments. As in the SOC case, HWC increased from Ap_1 ($1 \cdot 7 \, \mathrm{mg \, g^{-1}}$) to Ap_2 ($2 \cdot 4 \, \mathrm{mg \, g^{-1}}$) and decreased in deeper horizons. It is worth noting that values from L in the second horizon are very similar to those of Bu *et al*. (2010) for very similar depths ($2 \cdot 71 \, \mathrm{mg \, g^{-1}}$ in evergreen broad-leaved forest, $2 \cdot 82 \, \mathrm{mg \, g^{-1}}$ in coniferous forest and $2 \cdot 65 \, \mathrm{mg \, g^{-1}}$ for dwarf forest at a depth from 10 to 25 cm).

The addition of olive leaves to soils enabled them to have a higher quantity of HWC than in the rest of the managements. In terms of vertical distribution, HWC increased from the first to the second horizon but decreased from the second to the deepest horizon. This could be explained considering the management used in this soil: CT. As a result, the disc harrow removed soil from the third horizon (the first and second horizons have 10 and 6 cm, respectively) and poured it on the first one, creating a new surface horizon (A_0), replacing the one with the olive leaves. As these leaves do not decay, SOC is higher. This trend does not appear in the rest of the treatments (A, NT_1, NT_2 and CT), where HWC decreased with depth.

Weigel *et al*. (2011) found a strong correlation between SOC and HWC in agricultural soils under different managements in South Africa (where some areas have Mediterranean climate) and also that they were intrinsically related to each other.

CONCLUSIONS

The highest T-SOC values were obtained under CT managed with an amendment of crop residues (olive leaves, L). Importantly, SOC-S under L were higher than under NT (NT_1 and NT_2). The importance of a vegetative cover in increasing SOC-S was also reflected in the fact that NT_1, without vegetation cover, had the lowest T-SOC value of our experiment, whereas NT_2, with a vegetative cover, has higher values than NT_1, CT and A. Management practices appeared to affect the top 100 cm only, as T-SOC was similar below 100 cm in all the studied soils. For total HWC, the highest value was also found in L, showing a clear relationship between SOC and HWC across all the studied soils. Both increased SOC and HWC under L indicate the possibility of improved soil quality. Therefore, we conclude that L represents the best management practice for OG to improve soil quality and reduce the erosion risk as we found greater T-SOC, HWC and T-SOC-S in soils under this treatment compared with the three other practices (including NT) and CT. This demonstrates that sustainable soil management can be achieved with CT practices when combined with modern solutions to apply one of the typical agricultural wastes of OG, thus tackling the environmental problems of reducing erosion and waste disposal. Further research is needed to assess the longer-term implications of continuing with these management practices and whether the positive effects of CT with olive leaves would be maintained through the years following extreme rainfall–erosion events and across other Mediterranean soil types.

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CAPÍTULO III

Soil quality assessment based on carbon stratification index in different
olive grove management practices in Mediterranean areas.
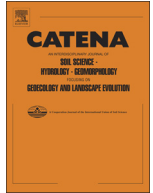
Soil quality assessment based on carbon stratification index in different olive grove management practices in Mediterranean areas

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A B S T R A C T

In Mediterranean areas, conventional tillage increases soil organic matter losses, reduces soil quality, and contributes to climate change due to increased CO_2 emissions. CO_2 sequestration rates in soil may be enhanced by appropriate agricultural soil management and increasing soil organic matter content. This study analyzes the stratification ratio (SR) index of soil organic carbon (SOC), nitrogen (N) and C:N ratio under different management practices in an olive grove (OG) in Mediterranean areas (Andalusia, southern Spain). Management practices considered in this study are conventional tillage (CT) and no tillage (NT). In the first case, CT treatments included addition of alperujo (A) and olive leaves (L). A control plot with no addition of olive mill waste was considered (CP). In the second case, NT treatments included addition of chipped pruned branches (NT1) and chipped pruned branches and weeds (NT2). The SRs of SOC increased with depth for all treatments. The SR of SOC was always higher in NT compared to CT treatments, with the highest SR of SOC observed under NT2. The SR of N increased with depth in all cases, ranging between 0.89 (L-SR1) and 39.11 (L-SR3 and L-SR4). The SR of C:N ratio was characterized by low values, ranging from 0.08 (L-SR3) to 1.58 (NT1-SR2) and generally showing higher values in SR1 and SR2 compared to those obtained in SR3 and SR4. This study has evaluated several limitations to the SR index such as the fact that it is descriptive but does not analyze the behavior of the variable over time. In addition, basing the assessment of soil quality on a single variable could lead to an oversimplification of the assessment. Some of these limitations were experienced in the assessment of L, where SR1 of SOC was the lowest of the studied soils. In this case, the higher content in the second depth interval compared to the first was caused by the intrinsic characteristics of this soil's formation process rather than by degradation. Despite the limitations obtained SRs demonstrate that NT with the addition of organic material improves soil quality.

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1. Introduction

The main agricultural system in Mediterranean areas is olive grove (OG) with 9.5×10^6 ha (Fernández-Romero et al., 2014). Olive grove soils suffer from severe erosion rates due to management techniques (conventional tillage — CT), the slope and the low tree density (Gómez et al., 2003; Cerdà et al., 2010) for millennia (Vanwalleghem et al., 2010), which resulted in soil degradation of the agriculture soils (Cerdà et al., 2009; García-Orenes et al., 2012) and high-cost of eroded soil restoration plans (Colen et al., 2015). The impact of land management and soil water erosion on soil quality is very well known (Cerdà and Doerr, 2007; Novara et al., 2013; Cerdà et al., 2014; Brevik et al., 2015; Zhang et al., 2015). Soil is essential for life inasmuch as it provides various important roles: supports, regulates, provisioned and provides cultural services (Banwart et al., 2015). This includes the provision of plant nutrients, regulation of water flow, and natural and anthropogenic compound degradation (Franzluebbers, 2002; Brevik and Sauer, 2015). All these services provided by soil are shown as a soil quality index. Soil quality is the capacity of soils to sustain biological yield, maintain the environment and improve animal and plant health (Muñoz et al., 2007). Additionally, soil quality is also important for humans, as it enables food security and economic revenue due to better and more productive crops (Lal, 1999; Imaz et al., 2010; Brevik and Sauer, 2015). It is only when soil can develop its functions with plenitude and when it is managed suitably that sustainable agriculture can be achieved and land degradation is reduced (Morugán-Coronado et al., 2013; Souza et al., 2014; Zornoza et al., 2015). Over time, scientists have developed techniques for assessing soil quality and they were applied in different regions and soil types and managements (Das et al., 2014; Beniston et al., 2015; Zhao et al., 2015) and highlighted the biological view of soil quality (Paz Ferreiro and Fu, 2014) although some socioeconomic approaches are also found (Teshome et al., 2014). Nortcliff (2002), Duval et al. (2013) and other authors highlighted the importance and challenging exercise of finding quantitative indexes that were able to define the soil quality of a particular site accurately, measuring the

combined effects on the relevant soil properties over a period and offering comparability between soils. Soil quality should be easy to measure, able to reflect short and long-term changes in soil properties, be sensitive to land use changes, and accessible to as many users as possible (Shukla et al., 2006). Moreover, specific agro-ecosystems may require different soil property measurements (Shukla et al., 2006; Imaz et al., 2010). In addition, there are complex interactions between climate, soil composition, landscape position and land management that hinder soil quality determination based on a single factor (Ogle et al., 2012). Therefore, there is no consensus with regard to the exact characteristics that a soil should have to be considered of the highest quality (Duval et al., 2013). There are two general approaches for this. The first considers that soils with the maximum quality are those in equilibrium with all their environmental components (climax soils). The second approach considers that soils with the highest productivity but lowest environmental burden are those with the maximum quality (Duval et al., 2013).

Soil quality assessment encompasses inherent and dynamic soil properties, and all interactions should be accounted for (Karlen et al., 2003; van Leeuwen et al., 2015). The more important factors that influence soil quality are tillage, crop rotation, type of manure (if applied), climate and soil type (Imaz et al., 2010). One of the main causes of land degradation is unsustainable agriculture. For this reason, the type of tillage has been of great interest with regard to soil quality investigation (Lal et al., 1998). In this respect, in soils with moderate to steep slope, CT contributes to increased soil erosion and degradation, which reduces soil organic matter (SOM) (Lozano-García et al., 2011). Furthermore, CT influences on nutrients losses and leads to the deterioration of physical, chemical and biological soil properties, thereby reducing soil quality (Salvo et al., 2010; Parras-Alcántara and Lozano-García, 2014). In this line, and as consequence of this effect, several alternatives have been examined in the last two decades. No-tillage (NT) systems have been demonstrated to improve soil properties and reduce soil erosion compared to CT (Moreno et al., 1997; Franzluebbers, 2002; Melero et al., 2009a, 2009b; Parras-Alcántara et al., 2013a). Conservation tillage has also received attention, as it combines the improvement of soil properties and agricultural wastes recycling, two objectives of sustainable agriculture (Moreno et al., 2006; Govaerts et al., 2009). This is especially important, because some properties such as water retention, soil organic carbon (SOC), carbonates and nutrient content can be improved with conservation tillage in Mediterranean soils in Southern Spain (Moreno et al., 1997). The adoption rate of these alternatives (conservation tillage) has been slow in Europe, with only 1% of the total area that is managed with NT in the world. Spain has currently 650,000 ha under this management (56% of the total area under NT in Europe) (Derpsch and Friedrich, 2010).

One of the most significant properties that have been researched in the context of soil quality is SOC. Authors such as Quiroga et al. (2005) believe that SOC is the best indicator to measure soil quality and soil productivity. However, other authors like Duval et al. (2013) indicate that SOC alone is a poor indicator of soil quality, as SOC only shows short-term changes. Also, SOC is not always the best indicator of changes in soil management in semi-arid conditions, as low soil moisture and high temperature limit SOC accumulation, which delays the effects of sustainable management practices on SOC content for several years (Chan et al., 2003; Moreno et al., 2006; Melero et al., 2012; Blanco-Moure et al., 2013). Moreover, the influence of management practices such as tillage type on SOC and other soil properties like N content can vary with soil depth, crop and site specific characteristics (Chatterjee and Lal, 2009; Du et al., 2010; Mishra et al., 2010).

In this respect, the stratification ratio (SR) of SOC and N with depth are good indicators of soil functioning (Franzluebbers, 2002; Sá and Lal, 2009; Corral-Fernández et al., 2013). Also, SR of C:N ratio is also influenced by tillage and the addition of crop residues (Lozano-García and Parras-Alcántara, 2013). As a result, C:N ratio and its SR are considered good soil quality indicators because they reflect C and N interactions in soils (Puget and Lal, 2005; Lou et al., 2012). With regard to this, authors like Franzluebbers (2002) proposed to evaluate soil quality based on the SR index, indicating that the SR of each property can be related to an aspect of soil quality. Furthermore, the SR of SOC is a good indicator of SOC sequestration rate (Franzluebbers, 2002; Moreno et al., 2006; Brye et al., 2006). Higher SR of SOC indicates that soil management enhances soil quality. This is because the top soil layer is influenced by land management but the second layer (subsequent layers) are less affected (Franzluebbers, 2002, 2010; Ferreira et al., 2012). Additionally, the time that the specific management technique has been in place affects SR of SOC as well, which is useful for medium to long-term analysis (De Oliveira et al., 2013). These indicators are especially relevant for Mediterranean areas, given the limitations to SOC accumulation that derive from climatic conditions. Also, high SR of SOC and N indexes reflect undisturbed soil and high soil quality of the surface layer, even though SOC quantities may not be high (Franzluebbers, 2002; Corral-Fernández et al., 2013).

The aim of this study is (i) to determine soil quality measured by stratification ratio index of soil organic carbon, nitrogen and C:N ratio under different management practices: conventional tillage and no tillage in olive groves in Mediterranean areas (Andalusia, southern Spain) using entire soil profiles and (ii) to indicate the stratification ratio index limitations.

2. Material and methods

2.1. Study site and experimental design

The study was conducted in Torredelcampo — Jaen (Andalusia, southern Spain) (Fig. 1). The lithological substrate consists on Miocene marl and marlaceous lime. The area has a Mediterranean climate, with three to five months of hot and dry summers (June to September) and moderately wet, cool winters. The mean annual temperature is 17 °C, with a maximum temperature of 40.6 °C (August) and a minimum of −5.2 °C (January). The average precipitation is 645.7 mm/year, and the monthly rainfall ranges from 4.7 mm (July) to 87 mm (February). The studied soils were Cambisols (CM) according to the classification developed by the IUSS Working Group (IUSS-ISRIC-FAO, 2006). These were very similar in their physical-chemical properties, with slight differences with respect to management type, and characterized by gravel content variability (5–22%), silt (44–73%) and clay (19–41%), basic-acid pH (6–8.9) and similar values with respect to bulk density (BD) (1.4 Mg m^{-3}) (Fernández-Romero et al., 2014).

The study consisted of studying the effect of five different management practices in unirrigated OG soils (Table 1). All plots had olive trees (*Olea europaea* variety *Picual*), with a tree density of 90 trees ha^{-1} (10 m of separation between trees) with 2–3 trunks each. A mineral fertilizer (Urea, 46% N) was applied in alternate years during winter, just after the harvest, in addition to this, a broad-spectrum herbicide was added in autumn to control weeds under trees in all management systems.

2.2. Sampling and analysis

Soil properties were studied at different depths in the entire profile, horizon by horizon, instead of using soil control sections to reduce the effect of mixing of materials that are not from the same horizons (Parras-Alcántara et al., 2015). Four soil profiles were sampled in each plot. Three replicates for each sampling point were made (5 plots × 4 soil profiles samples in each plot × 3 replications per horizon in the laboratory).

Soil samples were air-dried at constant room temperature (25 °C), and passed through a 2 mm sieve to remove gravels and roots. The analytical methods are described in Table 2.
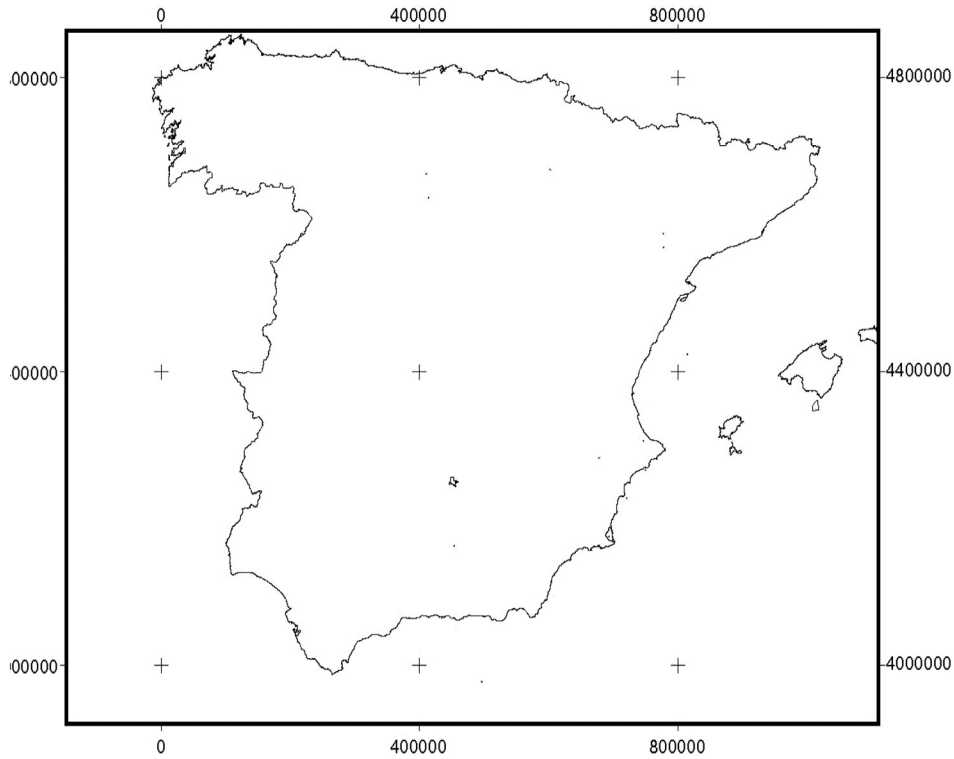
Fig. 1. Study area (Torredelcampo-Jaen-Andalusia, southern Spain).

2.3. Statistical analysis

The statistical analysis was performed using SPSS Inc., 2004 (SPSS 13.0 for Windows, IBM Corporation, Armonk, NY, USA). The statistical significance of the differences in the variables between horizons and management were tested using the Anderson-Darling test at each horizon or a combination of horizon for each soil management. Differences with $p < 0.05$ were considered statistically significant. The effect of management and depth on SOC, N and C:N ratio was analyzed using an ANOVA.

3. Results

3.1. Soil organic carbon, nitrogen and C:N ratio

SOM was evenly distributed along the profile in soils under CT, reaching the deepest layers (Table 3).This is caused by a high clay content that led to a higher SOC stock in A and L. The Bw horizon had the highest SOC stock values in both cases. Also, SOM remained stored in the surface without reaching deeper layers in NT1. However, this did not occur under NT2, despite being also managed with NT. NT2 did not follow the same pattern due to having the plant roots of the vegetative cover in deeper soil layers. As for N stock, it followed the same trend as SOC stock (Table 3).

In all cases, pH and BD increased with depth (Fig. 2). However, SOC and N decreased with depth (Table 3). C:N ratio increased with depth in our soils under CT, whereas it decreased for our soils under NT.

3.2. Stratification of soil organic carbon

The SRs of SOC at the surface compared to deeper layers increased for all treatments, ranging from 0.53 (L-SR1) to 8.13 (L-SR4) (Table 4 and Fig. 3).In addition to this, SR of soils under NT was always higher than under CT.

Normally, SR1 and SR2 values were very similar and no significant differences (p < 0.05) were found between them with the exception of L (0.53-SR1; 1.51-SR2). If deeper layers are considered, significant

Table 1
Experimental design. Characteristics.

	A	L	CP	NT$_1$	NT$_2$
Treatment code	Alperujo (oil mill waste) 270 Mg ha^{-1} year^{-1}	Olive leaves (oil mill waste) 236 Mg ha^{-1} year^{-1}		Pruning residues (OG) 6 Mg ha^{-1} each 2 years	Pruning residues (OG) 6 Mg ha^{-1} each 2 years + natural vegetation cover
Management	CT	CT	CT	NT	NT
Years of treatment	8	8		10	14
Beginning of treatment	2003	2003		2003	1999

A: alperujo (oil mill waste); L: olive leaves (oil mill waste); CP: control plot; NT$_1$: no tillage with chipped pruned branches; NT$_2$: no tillage with chipped pruned branches and weeds; OG: olive groves.

CT: conventional tillage (annual passes with a disk harrow and cultivator in spring, followed by a tine harrow in summer); NT: no-tillage.

All samples collected were taken in November 2013, also, a mineral fertilizer (urea, 46% N) was applied in alternate years during winter, just after the harvest, in addition to this a broad-spectrum herbicide was added in autumn to control weeds under trees in all management systems.

Table 2
Methods used in field measurements, laboratory analysis and for calculations in this study.

Parameters	Method
Field measurements	
Bulk density (Mg m^{-3})	Cylindrical core sampler[a]; Blake and Hartge (1986)
Laboratory analysis	
Particle size distribution	Laser granulometer (LS230, Beckman Coulter Inc., Brea, CA, USA)
	Classified according to USDA (2004)[b]
pH	Glass electrodes in a solution with soil:water ratio of 1:1 (Peech, 1965)
Soil organic carbon	Thermo Fisher Scientific method (patent n. 90110186.5)[c]
Nitrogen	Thermo Fisher Scientific method (patent n. 90110186.5)[c]
Parameters calculated from study data	
SOC stock (Mg ha^{-1})	(SOC concentration × BD × d × (1-δ_2 mm%) × 0.1)[d]; Intergovernmental Panel on Climate Change (IPCC) (2003)
Total SOC stock (Mg ha^{-1})	$\sum_{horizon}$ SOC Stock$_{horizon}$; Intergovernmental Panel on Climate Change (IPCC) (2003)
N stock (Mg ha^{-1})	(N concentration × BD × d × (1-δ_2 mm%) × 0.1)[d]; Intergovernmental Panel on Climate Change (IPCC) (2003)
Total N stock (Mg ha^{-1})	$\sum_{horizon}$ N Stock$_{horizon}$; Intergovernmental Panel on Climate Change (IPCC) (2003)
Stratification ratio	Franzluebbers (2002)

[a] 3 cm diameter, 10 cm length and 70.65 cm^3 volume. (Beckman/Coulter Inc. Brea, CA, USA).
[b] Particles larger than 2 mm were determined by wet sieving and smaller particles were classified according to USDA standards (USDA, 2004).
[c] Thermo Fisher Analyzer (Thermo Fisher Scientific; Flash 2000 model, Waltham, MA, USA).
[d] Where SOC is the organic carbon content (g Kg^{-1}), d the thickness of the soil layer (cm), δ_2 mm is the fractional percentage (%) of soil mineral particles >2 mm in size in the soil, and BD the soil bulk density (Mg m^{-3}).

differences (p < 0.05) were found between SR1 and SR3 and SR4 as well as between SR2 and SR3 and SR4 in all the managements studied. The SR index increased gradually reaching 8.13 (L-SR4) (Table 4).

When the management type was analyzed on a level-by-level basis (comparison of all SR1 in each treatment and the same for all SR2, SR3 and SR4), significant differences (p < 0.05) were found between CP and L, compared to NT1 and NT2, ranging between 0.53 (L) and 3.12 (NT2). The highest values (>2) were found in NT systems: NT1 and NT2 (2.16 and 3.12) respectively (Table 4 and Fig. 3). With respect to SR2, similar values to SR1 were found in all cases except in L (1.51).This difference (0.53-SR1; 1.51-SR2) was caused by tillage, as olive leaves (olive mill by-products) are transported to deeper layers by disk harrow in CT. As for SR3, values ranged from 2.54 to 7.22, with significant differences (p < 0.05) between CP and NT2 and the other management practices (NT1, L and A; without significant differences between them). The highest SR of SOC index values (SR1, SR2 and SR3) were found in NT2; showing how NT systems with pruning residues + natural vegetation cover give stability to soils and enhance their C sequestration rate. For SR4, the highest value was found in L (8.13-SR4).If CP is compared to the NT systems (NT1 and NT2), SRs of SOC are higher in NT1 and NT2 in all cases, with significant differences (p < 0.05) between these management systems (Table 4).

An important issue was to evaluate the proportion of SR index values that were >2 in the studied soils, as this value is considered the threshold of soils with good quality (for agricultural soils). In this respect, 65% of the total SR values were >2 in the studied soils (3.05 A-SR3; 3.32 L-SR3; 8.13 L-SR4; 2.54 CP-SR3 and all SRs in NT$_1$ and NT$_2$) (Table 4). As shown in Fig. 3, the addition of alperujo and olive leaves to soils under CT improved SOC quantity in the surface horizons compared to deeper horizons. Moreover, L showed a much higher SOC content in the first and second horizon than in deeper horizons. The lower value of SR1 (0.53) in L was due to the significantly higher SOC in the second horizon than in the first horizon, due to SOM translocation under CT.

3.3. Stratification of nitrogen

The SR of N increased with depth in all cases, ranging between 0.89 (L-SR1) and 39.11 (L-SR3 and L-SR4) (Fig. 3). With regard to the SR index changes with depth for each management type, no significant differences (p < 0.05) were found between SR1 and SR2 with the exception

Table 3
Soil properties evaluated (average ± standard deviation-SD) in Cambisols of the study area for different management types.

Management	Depth (cm)	Thickness (cm)	Horizons	SOC (g kg^{-1})	SOCS (Mg ha^{-1})	T-SOCS (Mg ha^{-1})	N (g kg^{-1})	NS (Mg ha^{-1})	T-NS (Mg ha^{-1})	C:N
A	0–10	10	Ap	12.20 ± 1.40Ad	14.49	101.91	1.10 ± 0.03Ac	1.31	0.57.68	11.08
	10–65	55	Bw	7.60 ± 1.32Bb	50.76		0.59 ± 0.04Bc	3.95		12.86
	65–100	35	Bw/C	7.40 ± 0.52Bb	29.47		0.57 ± 0.06Bb	2.28		12.94
	100–115	15	C	4.00 ± 0.47Cb	7.19		0.08 ± 0.01Ca	0.14		50.00
L	0–10	10	Ap1	39.81 ± 1.62Ab	39.81	250.23	3.13 ± 0.03Aa	3.13	15.45	12.72
	10–16	6	Ap2	75.03 ± 0.41Ba	25.72		3.51 ± 0.03Aa	1.20		21.38
	16–65	49	Bw	26.42 ± 0.22Ca	130.33		2.16 ± 0.03Ba	10.68		12.21
	65–100	35	Bw/C	12.00 ± 0.69Da	45.69		0.08 ± 0.00Cc	0.30		150.00
	100–115	15	C	4.90 ± 1.70Ea	8.68		0.08 ± 0.00Ca	0.14		61.25
CP	0–18	18	Ap	10.71 ± 1.62Ad	22.91	101.69	1.82 ± 0.01Ab	3.89	13.08	5.89
	18–65	47	Bw	7.56 ± 0.54Bb	39.70		1.00 ± 0.01Bb	5.23		7.59
	65–100	35	Bw/C	7.53 ± 1.41Bb	31.65		0.91 ± 0.02Ba	3.82		8.28
	100–115	15	C	4.21 ± 0.21Cb	7.43		0.08 ± 0.00Ca	0.14		52.63
NT1	0–30	30	Ap	13.41 ± 0.14Ad	47.73	105.82	1.50 ± 0.03Ab	5.35	14.31	8.91
	30–65	35	Bw	6.22 ± 0.12Bc	25.12		1.09 ± 0.00Bb	4.40		5.71
	65–100	35	Bw/C	5.69 ± 0.43Bc	24.94		1.01 ± 0.03Ba	4.41		5.66
	100–115	15	C	4.20 ± 1.26 Cb	8.03		0.08 ± 0.00Ca	0.15		52.50
NT2	0–5	5	Ap1	25.98 ± 1.74Ac	12.14	132.58	2.81 ± 0.03Aa	1.31	13.00	9.26
	5–23	18	Ap2	8.34 ± 0.79Be	17.09		0.99 ± 0.05Bc	2.04		8.39
	23–110	87	Bw	8.30 ± 1.61Bb	82.06		0.93 ± 0.03Bb	9.17		8.95
	110–135	25	Bw/C	3.60 ± 0.44Cd	10.56		0.08 ± 0.00Cc	0.24		45.00
	135–160	25	C1	3.30 ± 1.32Cb	10.73		0.08 ± 0.00Ca	0.24		45.00

SOC: soil organic carbon; SOCS: soil organic carbon stock; T-SOCS: total soil organic carbon stock; N: nitrogen; NS: nitrogen stock; T-NS: total nitrogen stock; C:N: C:N ratio.
CP: control plot; A: alperujo (oil mill waste); L: olive leaves (oil mill waste); NT1: no tillage with chipped pruned branches; NT2: no tillage with chipped pruned branches and weeds.
Numbers followed by capital letters within the same column are significant differences (p < 0.05) at different depths, considering the same management. Numbers followed by lower-case letters within the same column mean significant differences (p < 0.05) between the same SR considering different managements.

Fig. 2. Texture (Sand, Silt and clay proportions), pH and bulk density of the different soil management types in olive groves. Average values and standard deviation in each soil horizon.

of L (SR1-0.89 and SR2-1.45). For deeper SR (SR3 and SR4), significant differences ($p < 0.05$) were found with respect to surface SR (SR1 and SR2), with very high values of SR, ranging between 13.75 and 39.11 for A-SR3 and L-SR3-SR4 respectively (Table 4).

When comparing management types (A, L, CP, NT1 and NT2), the SR index ranged from 1.86 to 13.77 (A), from 0.89 to 39.11 (L), from 1.82 to 22.74 (CP), from 1.38 to 18.75 (NT1) and from 2.84 to 35.12 (NT2) (Table 4 and Fig. 3). The analysis of SR1 indicated that L (0.89) and NT1 (1.38) had lower values compared to CP (1.82). However, A and NT2 had higher values than CP (A: 1.86 and NT2: 2.84). In the case of SR2, SR of N values were lower than in CP in all cases except in NT2 (2.84). However, when deeper layers were considered, SR3 was higher in L (39.11) and NT2 (35.12) compared to CP (22.74). In addition, significant differences ($p < 0.05$) were found with respect to CP for those two management practices (L and NT2).

Approximately half of the SRs of N indexes were >2 (A-SR3:13.77; L-SR3 and SR4: 39.11; CP-SR2:2.00; CP-SR3:22.74; NT1-SR3:18.80; and in all cases for NT2). It is usually considered that soils with a SR < 2 are degraded soils. As can be observed in Fig. 3, the trend in the studied soils was that SR indexes when deeper layers were considered were much higher compared to values at upper depths.

This is due to the much lower N in deeper soil horizons compared to the surface (Table 4).

An important feature is that SR decreased generally in all managements with respect to CP with the exception of NT2 (all SRs) and L-SR3 and L-SR4, which increased. This indicates that the behavior of NT2 and L was very different compared to the rest of the studied soils.

3.4. Stratification of C:N ratio

The SR of C:N ratio was characterized by low values, ranging from 0.08 (L-SR3) to 1.58 (NT1-SR2) and generally showing higher values in SR1 and SR2 compared to those obtained in SR3 and SR4. Moreover, no significant differences ($p < 0.05$) were found between SR1 and SR2 for all management types except L. An important feature was the effect of management compared to CP, considering that SR of C:N ratio values were much higher in the studied soils under NT (NT1 and NT2) compared to CP. This was especially noticeable in NT1, with values that doubled those of CP (Table 4). In general, these low values of SR of C:N ratio were caused by high SR of SOC values in the surface while SR of N was higher with depth.

Table 4
Stratification ratios of soil organic carbon concentration, total nitrogen concentration and C:N ratios in Torredelcampo—Jaén (Mediterranean areas) in olive groves with conventional tillage and no-tillage. Data are mean ± SD.

Tillage	Relations	SOC-SR	N-SR	C:N-SR
CP	SR1 (Ap/Bw)	1.41 ± 0.03Ac	1.82 ± 0.73Ab	0.77Ac
CT	SR2 (Ap/Bw-C)	1.42 ± 0.05Ac	2.00 ± 0.56Ab	0.71Ac
(n = 4)	SR3 (Ap/C)	2.54 ± 0.08Bc	22.74 ± 8.56Bb	0.11Bb
A	SR1 (Ap/Bw)	1.60 ± 0.04Ac	1.86 ± 0.39Ab	0.86Ac
CT	SR2 (Ap/Bw-C)	1.65 ± 0.04Ac	1.93 ± 0.87Ab	0.85Ac
(n = 4)	SR3 (Ap/C)	3.05 ± 0.07Bb	13.75 ± 3.56Bc	0.22Ba
L	SR1 (Ap1/Ap2)	0.53 ± 0.01Ad	0.89 ± 0.09Ad	0.60 Bd
CT	SR2 (Ap1/Bw)	1.51 ± 0.04Bc	1.45 ± 0.28Bc	1.04Ab
(n = 4)	SR3 (Ap1/Bw-C)	3.32 ± 0.06Cb	39.11 ± 14.16Ca	0.08Dc
	SR4 (Ap1/C)	8.13 ± 1.23 Da	39.11 ± 12.23Ca	0.21Ca
NT1	SR1 (Ap/Bw)	2.16 ± 0.45Ab	1.38 ± 0.34Ac	1.56Aa
NT	SR2 (Ap/Bw-C)	2.36 ± 0.09Ab	1.49 ± 0.65Ac	1.58Aa
(n = 4)	SR3 (Ap/C)	3.19 ± 0.31Bb	18.75 ± 7.64Bb	0.17Ba
NT2	SR1 (Ap1/Ap2)	3.12 ± 0.22Aa	2.84 ± 1.21Aa	1.10Ab
NT	SR2 (Ap1/Bw)	3.13 ± 0.16Aa	3.02 ± 1.38Aa	1.03Ab
(n = 4)	SR3 (Ap1/Bw-C)	7.22 ± 2.45Ba	35.12 ± 13.97Ba	0.21Ba
	SR4 (Ap1/C1)	7.87 ± 1.98Ca	35.12 ± 14.21Ba	0.22Ba

SOC-SR: stratification ratio of soil organic carbon; N-SR: stratification ratio of nitrogen; C:N-SR: stratification ratio of the C:N ratio.
CP: control plot; A: alperujo (oil mill waste); L: olive leaves (oil mill waste); NT1: no tillage with chipped pruned branches; NT2: no tillage with chipped pruned branches and weeds. CT: conventional tillage; NT: no-tillage.
n = sample size; SD: standard deviation.
Numbers followed by capital letters within the same column are significant differences (p < 0.05) at different depths, considering the same management. Numbers followed by lower-case letters within the same column mean significant differences (p < 0.05) between the same SR considering different managements.

4. Discussion

4.1. Stratification of soil organic carbon

Franzluebbers (2002) proposed that SR of SOC might be a better indicator of soil quality compared to total SOC, because SR is the quotient of the SOC content at the soil surface to that at the bottom of the arable layer.

Land management change (LMC) and the addition of pruning residues and oil mill wastes to these soils improved soil quality because they produced changes in the physical and chemical properties (Fernández-Romero et al., 2014). In addition, the highest C content in the top layer (Table 3) is due to C input from biomass residue (Parras-Alcántara et al., 2013b).

The SR of SOC index values increased from surface to depth (Fig. 3). This coincides with Corral-Fernández et al. (2013), Lozano-García and Parras-Alcántara (2013) and Parras-Alcántara and Lozano-García (2014), the first in Mediterranean evergreen oak woodland with different management types, the second in Mediterranean OG with olive mill by-products, and the third in OG in Mediterranean rangelands. All these authors studied CM in all cases, which is the same soil in our study.

The studied soils showed that the addition of both residues (pruning and oil mill wastes) and LMC increased SR values with respect to CP. In addition, several of these values were higher than 2 or even higher than 7 (8.13 — L-SR4; 7.22 — NT2-SR3 and 7.87 — NT2-SR4). However, in other cases, SR indexes were lower than 2 (in SR1 and SR2 for A, L and CT), with values between 0.53 (L-SR2) and 1.65 (A-SR2) (Table 4). The SR indexes of SOC in NT2 were the highest in SR1, SR2 and SR3 showing how the NT system with pruning residues and weeds gives stability to soils and enhances their C sequestration rate. In this respect, Álvarez et al. (2014) found values close to 1.7 and 2 for SR1 and for SR2 respectively in NT systems with and without cover crop for agricultural soils under different management options in semiarid conditions in Argentina. These values are slightly lower than obtained by us, although the behaviour of soils is similar to our study. These differences could be attributed to the fact that we studied entire soil profiles, whereas Álvarez et al. (2014) studied soil control sections (0–5, 5–10, 10–20 cm…etc.). In this line, sampling by pedogenic horizon — entire soil profile is a better method because the sampling is based on natural properties of the soil, as opposed to soil control section, which does not account for soil properties and can therefore lead to the mixing of materials that are not from the same horizons (Parras-Alcántara et al., 2015). Moreover, these values can be compared with our soils under NT (NT1 and NT2), showing that the addition of organic material led
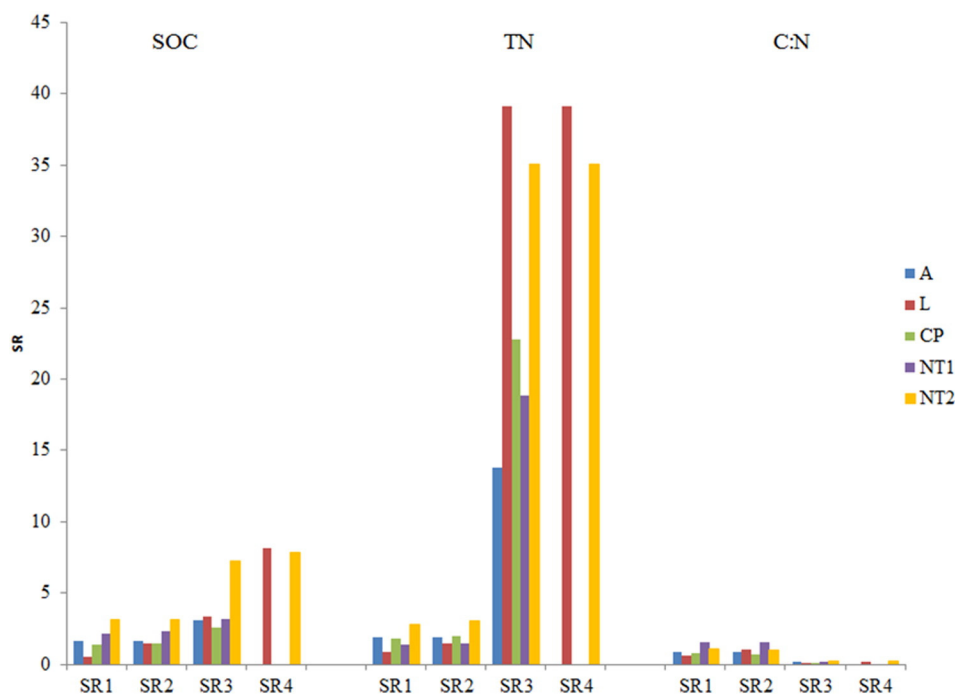
Fig. 3. Stratification ratios (SR) of SOC concentrations, N concentrations and C:N ratios. SOC: soil organic carbon; TN: total nitrogen; C:N: carbon:nitrogen ratio. CP: Control plot; A: CT with alperujo-oil mill waste; L: CT with olive leaves–oil mill waste; NT1: NT with pruning residues-OG; NT2: NT with pruning residues-OG + natural vegetation cover. CT: conventional tillage; NT: no-tillage; SR1, SR2, SR3 and SR4: stratification ratios.

to significant improvements in NT1 and NT2. Other authors such as Spargo et al. (2008) studied the addition of organic material to NT in agricultural soils of Virginia (USA) to assess whether the SR of SOC would increase compared to NT without this material. Although all NT treatments gave SRs > 2, those with organic material were higher.

If we compared CT with NT, SR of SOC values were higher in NT1 and NT2 in all cases, showing significant differences (p < 0.05) between management systems (Table 3). This is due to the accumulation of SOC in the top soil layer caused by soil surface coverage and root distribution change in NT (Lou et al., 2012).

Several authors found that SRs of NT systems were >2, whereas SRs of CT were <2 (Díaz Zorita and Grove, 2002; Hernanz et al., 2009; Du et al., 2010; López-Fando and Pardo, 2011). Also, Dikgwatlhe et al. (2014) found much higher SRs under NT compared to CT in agricultural soils in north China in all cases except for SR4; which coincides with the results of Ernst and Siri-Prieto (2009) in Uruguayan agricultural soils. As outlined by Spargo et al. (2008), NT soils with organic material have higher SRs of SOC than NT soils without this material. This could be an explanation of the significant difference (p < 0.05) of NT1 and NT2 with respect to CT. Parras-Alcántara and Lozano-García (2014) found SR1 values in CT > 2 in CM in OG soils of Mediterranean areas of southern Spain. Those values doubled the values of our soils under this management, reaching values of 3.74-SR1. These differences are due to our soils being under countryside OG, whereas those studied by Parras-Alcántara and Lozano-García (2014) were OG in Mediterranean rangelands.

On the other hand, all SR values found by Álvarez et al. (2014) were <2 regardless of the treatment, although those under NT were higher than those under reduced tillage. In this sense, Mrabet et al. (2001) found similar values to ours for CT (1.2-SR1) in semi-arid agricultural soils in Morocco. As can be observed in Fig. 3, the addition of oil mill wastes (alperujo and olive leaves) to CT soils improved the quantity of C in the surface horizon compared to deeper horizons. Moreover, L showed a much higher SOC content in the first and second horizons compared to deeper horizons. The lower values (0.53-SR1) in L were due to the significantly higher SOC in the second horizon than in the first horizon, due to SOM translocation under CT.

Many authors have used the SR index as an indicator of soil quality changes due to LMC (CT versus conservative tillage). Moreno et al. (2006) found that SRs of SOC were >2 in agricultural soils of a Mediterranean area under conservation tillage, but for CT, the SR of SOC values were close to 1, which is lower than ours. In this line, if we compared conservation tillage soils (Moreno et al., 2006) to L and A; SRs are higher in their soils, probably driven by the absence of moldboard plowing and a reduced number of tillage operations. This could demonstrate that tillage reduces the positive effects of the addition of organic material on soils.

Mrabet (2002) studied the effects of conservation tillage and CT in agricultural soils of Africa, and found that SR of SOC was >2 for both management types (CT and conservation tillage) when deeper horizons were considered. In our study area, CT showed higher SR of SOC when deeper horizons were considered, but not as much as Mrabet (2002), who found SR values of 3.2 considering the deepest section (calculated with soil control sections each 5 cm). In this sense, Mrabet (2002) found values close to ours for NT2 in soils under conservation tillage (8.4 for their soils and 7.22 and 7.87 in SR3 and SR4 — NT2). Nevertheless, not all authors have found significant differences between CT and conservation tillage. For instance, Madejón et al. (2007) found a slight increase in the SR of SOC in conservation tillage as compared to CT in agricultural soils of southwest Spain. Also, Melero et al. (2009b) found no significant differences in SR of SOC between these two management techniques in agricultural soils of the same climate and area. In this regard, Franzluebbers (2005) indicates that SR of SOC values considering deeper horizons in Mediterranean soils are affected by how C is incorporated, as residues accumulate in the subsurface horizon. Also, C decomposition rates are lower in deeper horizons than in upper horizons

(Lorenz and Lal, 2005).As shown in Table 4, significant differences (p < 0.05) were found between the two management systems (CT and NT). This would suggest that the management system has an effect on C accumulation in soils. Furthermore, the supply of OM from the surface to deeper horizons is ensured under NT, which led to an accumulation of C in soils under this system.

4.2. Stratification of nitrogen

The SRs of N of our soils (A, L, NT1 and NT2) were characterized by increases with depth and for being influenced by the management type (CT and NT). Similar results were obtained by Corral-Fernández et al. (2013)in Mediterranean evergreen oak woodland with CT and organic tillage, as well as by Lozano-García and Parras-Alcántara (2013) in OG with the addition of oil mill wastes under CT; and Parras-Alcántara et al. (in press, 2013) for land use change and LUM in OG with NT, CT and organic farming. In all cases, these variations were justified by the management type, and LMC (CT to natural forest). This improved soil quality because this change caused alterations in the physical and chemical properties and the soil biotic community. In addition, the SR of N depended on SOC concentrations. Consequently, the highest N content in the top layer is due to C input from biomass residues (Table 4).

The SR of N was higher under NT (NT1 and NT2) compared to CT, having a similar behavior as the SR of SOC. In this line, Sá and Lal (2009) and Lou et al. (2012) reported that NT or minimum tillage increased the SR of N compared to CT, arguing that higher SRs in organic farming compared to CT is a result of the accumulation of SOC in the surface due to soil surface coverage and root distribution change in organic tillage. In addition, Lozano-García and Parras-Alcántara (2013) obtained high SRs of N when olive mill by-products were applied in Mediterranean OG.

The highest SR1 value was found in NT_2 (2.84), which were 33% higher than the second highest value (A-SR1: 1.86). This shows that NT_2 implied more differences between N content in the surface compared to deeper horizons than in the rest of the managements. Parras-Alcántara and Lozano-García (2014) obtained values of 2.45 in SR1 for CM under CT. These values are higher than our values under CP (SR1-1.82),and these differences could be due to a smaller residue return and dandification due to lithology. Also, Parras-Alcántara et al. (2013b) found values close to 1.8 (SR1) in Mediterranean OG in CM under CT, which is similar to our SR1 values under CP (1.82).

As with SR of SOC, L presented a particular case with the lowest SR1 (0.89) of all the studied management practices. This unusually higher N concentration in the Bw horizon compared to the Ap horizon could be attributed to the combined effect of tillage and the addition of olive leaves over the years, where tillage mixed the soil and poured deeper layers of soil on top of the previous surface horizon (the one that contained leaves).

It is usually considerer that soils with a SR <2 are degraded soils, a fact that has been studied for N and is also applicable to this nutrient (Franzluebbers, 2002; Parras-Alcántara and Lozano-García, 2014), but the specific circumstances of L have to be considered, given the reasons for a higher N content in the second horizon outlined above. If lower depths are observed, L had significantly higher SR, the second highest values of all the studied soils (SR3 and SR4 with 39.11).

4.3. Stratification of C:N ratio

C:N ratio is a soil fertility indicator because of its close relationship with SOC and N. Also, C:N ratio is influenced by agricultural management practices (Liang et al., 2011). In this line, the management type had an effect on the SR of C:N ratio of our soils. The highest values were found in NT (NT1 and NT2) compared to CT. This may have partially been caused by a higher quantity of organic residue relative to root inputs, which led to a higher soil C:N ratio (Puget and Lal, 2005). Under

NT, the input of residue could have been concentrated on the surface due to the soil surface vegetative cover, thus C:N ratio was stratified, showing a declining trend with increasing depth. This change in C:N ratio suggests that the degree of SOC decomposition decreases toward the surface (Lou et al., 2012).

As can be observed in Fig. 3 and Table 4, the SR of C:N ratio was normally higher in NT1 and NT2, indicating that soils under NT were influenced by the accumulation of organic residue on the surface as commented above and as also found by Parras-Alcántara and Lozano-García (2014).

With respect to CT (A and L), the addition of oil mill wastes had an effect on the input of organic material. In addition to this, the mixing effect of the moldboard plow and disk harrow may have homogenized the distribution of residues or slightly stratified it in L, thereby leading to a decline with depth. By contrast, A had an increased SR1 of C:N compared to L, possibly as a result of the high N content of olive leaves (Fernández-Escobar et al., 1999).On the other hand, Parras-Alcántara et al. (2013b) found SRs of C:N ratio uniformly distributed over the entire soil entire profile in OG with CT of Mediterranean areas of Southern Spain. We obtained similar results in A, NT1 and NT2.

4.4. Limitations to the SR method

As indicated by Parras-Alcántara et al. (2013b), SR indexes have significant disparities linked to the definition of SR (a soil property value on the soil surface divided by the value of the same property at a lower depth). For the studied soils, SOC, N and C:N ratio decreased in some cases with LMC and the addition of oil mill wastes (alperujo and olive leaves) (Table 3). However, the SR indexes increased (Fig. 3) when LMC and oil mill wastes were applied. These results may seem contradictory because a decrease of SOC, N and C:N ratio should involve a decrease in the SR index values.

Apart from that, we can also point out other disparities of the SR index: (i) allocating numerical values (quantitative) at intervals (qualitative) without a specific scientific criterion is very subjective. Therefore, the values obtained can be understood but not verified; (ii) the SR index is descriptive (it analyzes the current situation). However, the behavior of the variable studied over time is not analyzed (diagnostic variable); (iii) the assessment of soil quality based on a single variable (SR index) could lead to an oversimplification of the assessment. However, soil genesis is much more complex (Brevik, 2013), which documents differences in soil genesis at a single research site due to differences in conditions at different parts of the study site. As a result, it would seem logical to use several variables instead of a single variable; (iv) very high SR values with depth do not imply establishing accurate statements about soil quality. It would therefore be necessary to determine the minimum detectable carbon differences in deeper layers.

5. Conclusions

SOC, N and C:N ratios were studied under different management techniques (A, L, NT1 and NT2) in agricultural (OG) soils (CM) in Mediterranean areas, in order to assess soil quality changes. The SRs of these properties were assessed. The SR index values were higher under no-tillage (NT) for all the properties assessed, which could be considered as an improvement of soil quality.

As for A and L (addition of oil mill wastes combined with CT), the positive effects of both were only significant in SR3 and SR4, but not in SR1 and SR2. This is particularly relevant for L, with the lowest SR1 of SOC within all the studied management techniques. Given the particular case of L, with the second horizon containing significantly higher SOC and N due to its intrinsic formation process, it can be considered that the SR method has some limitations. This is because the first horizon had lower SOC and N than the one immediately below. This is not likely to be because it is degraded but because the second horizon had an addition of organic material (leaves), which was then buried by tillage. As

a result, the second horizon does not naturally belong to the soil, but is also a result of the management technique, which makes it interesting to assess SR3 and SR4. SR of N had similar trends, with the highest values in NT1 and NT2. SR of C:N ratio did not have significant trends, apart from higher SRs (generally) in NT1 and NT2. Despite the limitations outlined above, the SRs obtained demonstrate that NT with the addition of organic material is positive for soil and that it improves its quality. More research will be needed to assess the longer-term implications of these management practices and whether SR1 and SR2 will change in L, if tillage is limited or once the technique is more established (medium to long term).

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CAPÍTULO IV

Evaluation of optical techniques for characterising soil organic matter quality in agricultural soils.
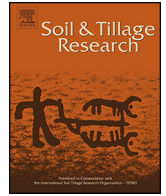
Evaluation of optical techniques for characterising soil organic matter quality in agricultural soils

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ABSTRACT

Soil organic matter (SOM) is one of the main global carbon pools. It is a measure of soil quality as its presence increases carbon sequestration and improves physical and chemical soil properties. The determination and characterisation of humic substances gives essential information of the maturity and stresses of soils as well as of their health. However, the determination of the exact nature and molecular structure of these substances has been proven difficult. Several complex techniques exist to characterise SOM and mineralisation and humification processes. One of the more widely accepted for its accuracy is nuclear magnetic resonance (NMR) spectroscopy. Despite its efficacy, NMR needs significant economic resources, equipment, material and time. Proxy measures like the fluorescence index (FI), cold and hot-water extractable carbon (CWC and HWC) and SUVA-254 have the potential to characterise SOM and, in combination, provide qualitative and quantitative data of SOM and its processes. Spanish and British agricultural cambisols were used to measure SOM quality and determine whether similarities were found between optical techniques and ^{1}H NMR results in these two regions with contrasting climatic conditions. High correlations ($p < 0.001$) were found between the specific aromatic fraction measured with ^{1}H NMR and SUVA-254 (Rs = 0.95) and HWC (Rs = 0.90), which could be described using a linear model. A high correlation between FI and the aromatics fraction measured with ^{1}H NMR (Rs = −0.976) was also observed. In view of our results, optical measures have a potential, in combination, to predict the aromatic fraction of SOM without the need of expensive and time consuming techniques.

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1. Introduction

1.1. The importance of organic matter

Soil organic matter (SOM) is composed of organic residues that are originated from plant and animal remains and microbial products at different stages of decomposition or humification (Hur et al., 2013). Additionally, it is one of the main global carbon pools, storing three times more carbon than living organisms or the atmosphere (Fischlin et al., 2007; Brevik, 2012). Aside from carbon sequestration, SOM is also a measure of soil quality because of the beneficial function it has on a variety of soil processes. For instance, it reduces erosion and, therefore, increases crop production by increasing the elasticity and resistance to deformation and compactability as well as porosity and water retention (Sellami et al., 2008; Paradelo and Barral, 2013). Increased water retention decreases potential runoffs by improving water infiltration in to soils and provides a store of water for plant uptake, buffering against moisture and rainfall fluctuations (Lal, 2004). This is of importance considering that the lack of water retention leads to a change in the hydrological patterns of agricultural areas and promotes the quantity and severity of floods and water-led erosion. Also, SOM leads to an increased vegetative cover, which ultimately reduces soil erosion (Cerdà, 1998, 2000; Novara et al., 2011; Zhao

et al., 2013). Carbon mineralisation is crucial in SOM dynamics and along with carbon input, determines how much carbon accumulates in soil and releases nutrients that are essential for plant growth. Factors that affect mineralisation are the size of labile carbon, environmental conditions and the local microbial community (Zhao et al., 2008; Li et al., 2013). SOM and soil assemblage; SOM decomposition and transport by organisms contribute to soil stabilisation and the improvement of soil structure (Brevik et al., 2015). Moreover, SOM quantity has been directly related to the preservation of soil aggregates, which in turn reduces soil erodibility (Novara et al., 2011). Also, the direct processing of SOM along with its decomposition contribute to the improvement of soil chemical properties and stability (Brevik et al., 2015). Therefore, optimal quantities of SOM improve structure, water retention, and nutrient holding capacity of soils, which has an effect in multiple aspects of the soil system. These are essential considering the wider context of Earth System, as SOM conservation techniques have been proven to improve the fertility of degraded soils of a wide variety of ecosystems that are the main resource of large communities of developing areas of our planet, as well as have an influence on biogeochemical cycles and climate change mitigation (Batjes, 2014; Saha et al., 2014; Srinivasarao et al., 2014).

1.2. SOM carbon fractions and their importance

SOM has been conceptualised as containing three pools, with different residence/turnover times (Trumbore, 2000). These pools are the active SOM (living biomass of microorganisms and partially decomposed residues; associated with 1 year turnover); the slow SOM (resistant plant material; associated to a turnover from years to centuries); and passive SOM (humic substances and inert organic matter), which has been traditionally associated with longer residence time (thousands of years) and more stability. Some authors consider that the inert organic matter should not be considered as part of the passive pool, but as a fourth pool (Trumbore, 1997; Ohno, 2002; Agren and Bosatta, 2002; Sparks, 2003; Bell and Lawrence, 2009; Dungait et al., 2012). Although the traditional view has been that decomposition led to complex molecules that were very stable as a result of their structure; it has recently been known that environmental conditions, organo-mineral associations and other processes influence more in SOM stability than structure, which only plays a secondary role. As a result of this new view, recent research has found that humic substances, which have always been considered high molecular mass polymers, could be simpler than originally thought (Kleber and Johnson, 2010; Schmidt et al., 2011). Still, their structure is on discussion and the separation of SOM into fractions with different turnovers remains a major challenge (Kleber, 2010; Schmidt et al., 2011; Schrumpf and Kaiser, 2015).

Non-humic substances are composed by microbial biomass, decomposable plant material (active SOM); and resistant plant material, mainly waxes, lignified tissues and polyphenols (slow SOM) (Dungait et al., 2012). Microbial biomass has been used for comparing natural and degraded ecosystems and as an early indicator of soil processes, fertility and health (García-Gil et al., 2000; Brevik, 2009; Chen et al., 2013).

1.3. Current SOM quality measurements. Challenges

Measures such as % organic matter measured by loss of ignition (LOI) are useful, popular and inexpensive methods to determine bulk SOM (Luke et al., 2009; Salehi et al., 2011). However, some studies have concluded that bulk SOM measurements cannot be used, on their own, as a representative indicator of carbon in soil due to their limitations (Koarashi et al., 2005; Salehi et al., 2011).

Humic substances have also been measured to determine soil quality, as their presence has been associated with a higher quality of soils as stated in Section 1.2. Their study is relevant in agricultural soils, as they increase crop yield and root dry weight, although this response is not fully understood (Rose et al., 2014). Therefore, the determination and characterisation of humic substances gives essential information of the maturity and stresses of soils as well as of their health.

Traditionally, alkali and acid abstraction methods have been used, to later interpret the chemistry of the extracted functional groups (Olk and Gregorich, 2006). Afterwards, these were combined with other complex techniques that enabled scientists to obtain new information on the structure and dynamic associations of humic substances (Sutton and Sposito, 2005; Schmidt et al., 2011). Despite these advances, SOM dynamics and cycling still have many questions to answer, with models differing in SOM fluxes results for the future, due to their sensitivity to SOM turnover time assumptions (Schmidt et al., 2011). There are a number of powerful but complex and expensive techniques that have been used for the study of soil fluxes (Helal et al., 2011). The economic resources needed, along with the time required to prepare the samples and conduct the analyses, make its use with a large number of samples difficult and delays experiments, while more work is still needed to accurately determine and define the molecular structures and linkages between the SOM components (Weishar et al., 2003; Helal et al., 2011 Helal et al., 2011).

Nuclear magnetic resonance (NMR) spectroscopy is a non-destructive technique that is valuable for the characterisation of SOM and humification processes, providing information on static and dynamic properties of molecules. This is due to its high performance to assess intermolecular interactions. The relationship between SOM, contaminants and metals can also be studied with NMR (Cardoza et al., 2004). Of the various variants that exist, ^{1}H NMR spectroscopy was used in this study. This technique analyses humic and fulvic acids dissolved in neutral or alkaline solutions to characterise the components of the substance, and gives a semi-quantitative notion of aromatic, aliphatic and carboxylic groups (Hemminga and Buurman, 1997). One of the main drawbacks of this technique is the quantity of economic resources that are necessary for its regular application in research laboratories/centres. This is due to the expensive deuterated solvents and NMR tubes, as well as the expensive equipment and significant sample preparation that are required (Weishar et al., 2003 Cardoza et al., 2004; MIT, 2008). Also, the technique is time consuming not only when measuring, but when interpreting 2-D or 3-D data resulting from it (Cardoza et al., 2004). Simpler methods for the characterisation of SOM are required.

1.4. Proxy measures. Opportunities to improve the ability to characterise SOM quality

Water extractable carbon is the most active component in the carbon cycle. Its quantity and biological nature is affected by the extraction temperature (Bu et al., 2010). Hot-water extractable carbon (HWC) contains simple compounds such as microorganisms, soluble carbohydrates and other compounds that account for the labile fraction of SOM (Ghani et al., 2003). HWC responds to land use changes in the short term and has been used to detect the effects of different land management practices and for determining the effects of soil amendments such as biochar or agricultural residues (Leifeld and Kogel-Knabner, 2005; Uchida et al., 2012; Alburquerque et al., 2014; Fernández-Romero et al., 2014). For these reasons, it has been proven useful to obtain information about soil quality (Ghani et al., 2003; Xue et al., 2013).

Fluorescence has become popular because of its potential to characterise SOM and study humic substances, as it is non-

destructive, simple, non-separative and accurate. As a result, it has been used for determining the compositional and structural properties of SOM (Chen et al., 2003; Senesi and D'Orazio, 2005; Sun et al., 2007; Kwiatkowska et al., 2008; Henderson et al., 2009; Hur and Kim, 2009; Tang et al., 2011). The intensity and position of the peaks detected in the spectra are unique to each substance structural and functional characteristics. For instance, higher fluorescence intensities are related to a higher humification (Martins et al., 2011).

The fluorescence index (FI) was developed to assess different properties of dissolved organic matter (DOM). It was defined by McKnight et al. (2001) as the ratio of emission intensities at 450–500 nm excited at 370 nm. The 450 nm point was chosen for specific characteristics of the experiment. Later, Cory et al. (2010) modified the ratio to 470–520 nm to reflect corrections specific to the instruments used. This index has been correlated to the aromaticity of DOM (Korak et al., 2014).

Fluorescence spectroscopy can be used in combination with UV–vis spectroscopy to characterise humic substances, as absorbance measures transitions from the ground state to the excited state, as opposed to fluorescence spectroscopy (Skoog et al., 2007). Its spectra are usually uniform and provide with qualitative data when a specific wavelength is selected (Hassouna et al., 2012). Also the specific absorbance at 254 nm (SUVA-$_{254}$) has been recognised as a method to determine SOM aromaticity (Fuentes et al., 2006; Chow 2006). This parameter is very useful for assessing the nature of the general composition of dissolved organic carbon (DOC), due to its high correlation with it (Weishar et al., 2003).

Considering what has been described in Sections 1.3 and 1.4, both the fluorescence and NMR techniques can be used in combination to determine the humic substances properties and the degree of aromaticity; while HWC could contribute further to the understanding of soil quality, given its usefulness to detect the biodegradation of soil biochemical properties (Ghani et al., 2003; Saab and Martin-Neto, 2007; González-Pérez et al., 2007).

As an illustrative and additional way to characterise and represent some of the analyses conducted and the results obtained, excitation–emission matrix (EEM) spectra have been plotted. These provide information on the relative intensity of fluorescence at different excitation and emission wavelengths regions in a fast manner that is also easy to interpret (Coble, 1996). Several peaks have been identified that are used to describe EEM fluorescence spectra. Peak A and C refer to humic peaks. Peak A is referred to as UVC-excited and is located at an excitation wavelength (λ_{Ex}) between 240 and 260 nm and an emission wavelength (λ_{Em}) between 400 and 460 nm. Peak C, also referred to as UVA-excited; is located at a λ_{Ex} between 320 and 360 nm and a λ_{Em} between 420 and 460 nm. There are also peaks that indicate biological activity material (peaks B and T, which are defined as tyrosine-like and

tryptophan-like peaks, respectively). B has λ_{Ex} of 270–280 nm and λ_{Em} of 300–315 nm whereas T has λ_{Ex} between 270 and 280 nm and λ_{Em} of 345–360 nm (Birdwell and Engel, 2010).

1.5. Aim/objective of this study

The aim of this study was to evaluate the use of fluorescence spectroscopy to measure SOM quality (specifically the grade of humification). The specific objectives were: (1) characterise water extractable SOM quality using liquid state ^{1}H NMR; (2) characterise the quality of water extractable organic matter using fluorescence spectroscopy and UV–vis; (3) compare measures of quantity and quality of water extractable organic matter with the specific organic matter fractions measured by ^{1}H NMR like aromaticity. If robust relationships and similarities between optical measures and ^{1}H NMR are found, there may be potential for fluorescence spectroscopy as a fast and more cost-effective method of organic matter characterisation.

2. Materials and methods

2.1. Field sites description

Cambisols were sampled in two regions with contrasting climatic conditions; Andalusia (South Spain) and Berkshire (South East England) (Table 1). Berkshire has a temperate climate, characterised generally by relatively mild winters and summers and rainfall throughout the year. The annual mean temperature ranges from 6.7 °C and 14.5 °C (30 years, annual mean temperature: 10.5 °C) and the average annual rainfall is 635.4 mm (UK Met Office, 2014).

Andalusia has a Mediterranean climate, which is characterised by hot and dry summers contrasted with cool and wet winters. In the province of Cordoba (Hinojosa del Duque and Pozoblanco), the annual mean temperature is 17.6 °C and the average annual rainfall is 536 mm (Aemet, 2014). As for the province of Jaen (Torredelcampo), its annual mean temperature is 16.2 °C and the average annual rainfall is 646.3 mm (REDIAM, 2007).

In Berkshire, samples were collected from University of Reading Farms at Sonning, Arborfield and Shinfield. The site sampled at Sonning (GS-UK-1) has been covered with grass for over 15 years. Arborfield (CC-UK-1) was permanent pasture until autumn 2012, and has been subsequently drilled with wheat or winter barley. Shinfield (CC-UK-2) has been in an arable rotation for over 20 years and sown with either winter wheat, maize or spring barley.

In Andalusia, soil samples were collected between the provinces of Jaen (Torredelcampo) and Cordoba (Hinojosa del Duque, Pozoblanco) that were managed with conventional tillage of cereals and olive crops. CC-ES-3 was managed with a wheat-barley-fallow cycle, whereas the other sites (CC-ES-1 and CC-ES-2)

Table 1
Sample points, land use and locations.

Crop	Sample location	Abbreviation[a]	Coordinates
Grass	Sonning Farm (UK)	GS-UK-1	51°28′44″N, 0°53′52″W
Cereal	Aborfield farm (UK)	CC-UK-1	51°24′53″N, 0°54′32″W
	Shinfield farm (UK)	CC-UK-2	51°24#4−5#N, 0°57′14″W
	Hinojosa del Duque (Cordoba, Spain)	CC-ES-1	38°33′05″N, 05°09′46″W
	Pozoblanco (Cordoba, Spain)	CC-ES-2	38°20′58″N, 04°31′37″W
	Torredelcampo (Jaen, Spain)	CC-ES-3	37°50′50″N, 03°51′14″W
Olive grove	Torredelcampo (Jaen, Spain)	OG-ES-1	37°50′55″N, 03°51′56″W
	Torredelcampo (Jaen, Spain)	OG-ES-2	37°50′51″N, 03°51′54″W
	Torredelcampo (Jaen, Spain)	OG-ES-3	37°50′52″N, 03°51′50″W

[a] GS-UK: soil covered with grass, United Kingdom; CC-UK: cereal crops from United Kingdom; CC-ES: cereal crops from Spain; OG-ES: olive grove from Spain.

were covered by wheat crops throughout the year. OG-ES-1, OG-ES-2, and OG-ES-3 were covered by olive grove.

2.2. Sample collection and preparation

Soil samples were collected from each horizon. Total soil depths are included in Table 2. Only the first horizon from each soil (specified in Section 2.3) was used for the analyses. Samples were air dried and sieved with a 2 mm sieve.

2.3. Analytical methods

Cold and hot water extractable carbon were determined following Ghani et al. (2003). This consists in a cold and a hot extraction of the supernatant of the samples (room temperature and 80 °C, respectively). To do this, 30 ml of ultrapure water was added to 3 g of soil. Then, there was a 30-min extraction in a shaker at 20 °C. After this, the sample was centrifuged during 20 min at 3500 rpm. Once this was done, the supernatant was extracted (cold extraction) and analysed (DOC). The resulting pellet was used for the rest of the steps. 30 ml of ultrapure water were added to the pellet, which was then shaken on a vortex to mix the ultrapure water with the pellet. The sample was then left in a bath at 80 °C during 16 h. The sample was centrifuged at 3500 rpm during 20 min and was filtered with a 0.45 μm cellulose nitrate filter (hot extraction). The filtered supernatant was analysed for DOC, fluorescence, absorbance and NMR.

The techniques that were compared in this study were applied to the first horizon of each soil sample, as this was considered sufficient for the purposes of comparing these techniques. This horizon was at different depths depending on the soil sample (at 12 cm in GS-UK-1; 10.5 cm in CC-UK-1; 5.7 cm in CC-UK-2; 15 cm in CC-ES-1; 20 cm in CC-ES-2; 30 cm in CC-ES-3; 10 cm in OG-ES-1; 10 cm in OG-ES-2 and 18 cm in OG-ES-3).

Fluorescence of all the hot water extracts was measured in a Varian Eclipse Fluorescence spectrophotometer (Agilent Technologies, Santa Clara, CA, USA) at an emission wavelength from 300 to 600 nm at 5-nm increments and an excitation of 240–450 nm at 5-nm increments. All samples were run in 1 cm quartz cuvettes and in triplicate.

FI was calculated as the ratio of intensities at 450 over 500 nm with an excitation of 370 nm, as described by Cory et al. (2010). McKnight et al. (2001) introduced this index approach for the characterization of the fulvic and fraction of DOM.

The humification index (HIX) was calculated with the following formula:

$$\frac{\sum I_{435 \to 480}}{\sum I_{300 \to 345}} + \sum I_{435 \to 480}$$

where I is the fluorescence intensity at each wavelength (modified from Zsolnay et al., 1999 by Ohno, 2002).

The biological/autochthonous index (BIX) has been calculated as the ratio of intensities at 380 nm over 430 nm with an excitation of 310 nm, as described by Huguet et al. (2009). This index assesses the relative contribution of autochthonous DOM in water and soil samples.

A subsample of the HWC extract was frozen and subsequently freeze-dried to remove all the water present. Deuterium oxide was added as a solvent to avoid disruptions in the spectrum, as other solvents have a proton signal that causes disruptions, as demonstrated by Cardoza et al. (2004), prior to a second freezing and a second freeze-drying. This second stage of freezing-freeze-drying was used to avoid that H_2O peaks interfered in the spectra. After that, deuterium oxide (100%, density of 1.107 g/ml at 25 °C) was added again as a solvent to conduct the NMR tests. NMR was measured in 1.5–1.7 ml of sample with a Bruker Avance III 700 MHz NMR spectrometer (Bruker Corporation, Billerica, MA, USA). The deuterium oxide peak was used as a calibration reference and placed in 4.75 ppm.

Absorbance of all the hot water extracts was measured with a Varian Cary 300 UV–vis spectrometer (Agilent Technologies, Santa Clara, CA, USA), from 200 to 800 nm with 1 nm intervals using a 1 cm cuvette.

SUVA-$_{254}$ has been used for this study. This is the absorbance at 254 nm divided by the DOC concentration (of the hot water extracts). Values are expressed in $l\,mg^{-1}\,m^{-1}$.

DOC of the cold and hot water extracts was calculated with a Shimadzu TOC 5000 total organic carbon analyser (Shimadzu Corporation, Kyoto, Japan). Standards were calculated using Stock solutions of 1000 ppm.

% organic matter measured by LOI was calculated using a modified version of Hieri et al. (2001). A soil sample of 10 g was heated at 105 °C for 24 ho. Then, the sample was weighted again (w_1) and heated in a Muffle furnace at 550 °C for 16 h to ignite the organic matter. The sample was weighted after this (w_2) and the % of organic matter was obtained by weight difference between w_1 and w_2.

Soil pH was determined in 1:2.5 soil to water ratio. Texture was determined by laser granulometry, using a Coulter LS 230 (Beckman/Coulter Inc., Brea, CA, USA). This technique uses polarised light at three different wavelengths (450 nm, 600 nm and 900 nm) to analyse the particle size distribution specifically in the 0.04 μm to 0.4 μm range.

EEM fluorescence spectra were obtained by collecting a series of emission scans of λ_{Ex} 240–450 nm at 5 nm intervals and λ_{Em} 300–600 nm, also at 5 nm intervals. EEM spectra were plotted using RStudio v0.98.1091 (Rstudio Inc., Boston, MA, USA).

Table 2
Basic physical and chemical properties for soils studied under grass (GS), cereal crops (CC) and olive grove (OG).

Land use	Location	Sample point[a]	Horizon	Depth first horizon (cm)	Total soil depth (cm)	Soil texture	Clay (%)	Silt (%)	Sand (%)	pH (H$_2$O)	% OM (LOI)
GS	UK	GS-UK-1	A	0–12	60	Silty sand	1.70	22.3	76.0	3.58	10.51
CC	UK	CC-UK-1	Ap	0–10.5	19	Silty sand	2.50	32.7	64.8	5.66	6.99
		CC-UK-2	Ap	0–5.7	13.3	Sandy silt	8.20	46.3	45.5	6.95	5.96
CC	Spain	CC-ES-1	Ap	0–15	100	Silty sand	4.1	23.6	72.3	6.06	4.30
		CC-ES-2	Ap	0–20	82	Silty sand	2.00	13.0	85.0	6.05	4.82
		CC-ES-3	Ap	0–30	50	Silty sand	33.7	63.8	2.50	6.98	6.83
OG	Spain	OG-ES-1	Ap	0–10	38	Silty sand	36.9	58.5	4.60	5.53	6.52
		OG-ES-2	Ap$_1$	0–10	16	Silty sand	23.7	56.7	19.6	6.15	15.57
		OG-ES-3	Ap$_1$	0–18	38	Silty sand	37.1	59.5	3.40	6.74	7.41

[a] GS-UK: soil covered with grass, United Kingdom; CC-UK: cereal crops from United Kingdom; CC-ES: cereal crops from Spain; OG-ES: olive grove from Spain; LOI: loss of ignition.

Intensities are reported in Raman units (RU). Raman scattering was mitigated subtracting blanks that had been collected on ultrapure water from each spectrum.

2.4. Statistical methods

Data were tested for normality to verify the model assumptions. As the data failed the normality test, non-parametric tests were used. The effect of the hot water extraction in the extractability of carbon (compared to the cold water extraction) was analysed using a Paired Sample Wilcoxon Signed Rank Test. The correlation between the different analytical methods was tested using the Spearman Rank and assessing the significance of the resulted Spearman Correlation Coefficient (Minitab 16 for Windows. Minitab Inc., State College, PA, USA). Linear regressions of the Spearman correlations were also plotted (SigmaPlot 12.0 for Windows. Systat Software Inc., San Jose, CA, USA). Differences of $p < 0.05$ were considered statistically significant.

3. Results and discussion

3.1. Soil characteristics

The majority of CC-UK soils had sandy texture, with a relatively high proportion of silt (Table 2). The only exception was CC-UK-2, although the sand proportion was quite close to that of silt. This texture was similar to that of CC-ES-1 and CC-ES-2, although CC-ES-3 had a higher proportion of silt and higher proportion of clay than of sand. All the OG soils presented a texture of a majority of silt (56.7–59.5%), followed by clay. It is worth considering that silt is the most erodible fraction (Table 2).

pH in the UK soils was generally acid, although GS-UK-1 and CC-UK-1 had values between 3.58 and 5.66 and CC-UK-2 had values close to 7. ES soils had generally higher values, ranging from 5.53 to 6.98 (Table 2). Some authors have related pH and measurement of aromatics (Weishar et al., 2003). GS-UK-1 has the lowest pH (3.58) and is the one with the highest aromatics content and highest HWC.

3.2. Total extractable carbon by cold and hot extractions

CWC and HWC measurement results are in Table 3. HWC extracted significantly more carbon ($P < 0.01$) than CWC, thus proved to be a more exhaustive extraction method. The increases in the values ranged from 161 to 605%. This was equivalent to higher values by a factor between 3 and 7, respectively. The most significant increase was obtained in GS-UK-1. Gregorich et al. (2003) obtained a similar trend in maize-cropped soils of Ottawa, Canada, and found HWC exceeding CWC by a factor of two. Moreover, Landgraf et al. (2006) found that HWC had higher carbon concentrations than CWC by a factor that varied from 4 to 6 in surface horizons of forest soils in SE Germany.

A correlation analysis was run to assess whether the C extractability differed between the different soils and locations. The correlation resulted to be high (Rs = 0.91, $p < 0.01$). Wang and Wang (2007) found a similar correlation ($r = 0.93$, $p < 0.01$) in forest oxisols of Southern China. Klose and Makeschin (2003) also found that HWC and CWC increased with the same proportion in forest soils of NE Germany. On the other hand, Ghani et al. (2003) found a positive but poor correlation.

HWC and CWC data were compared with SOM (measured by LOI) to assess which of the two extraction methods would imply a higher correlation with the organic matter from the samples (Table 4). HWC implied a higher correlation with SOM measured with LOI (Rs = 0.70, $p < 0.05$) than CWC (Rs = 0.55). Despite the fact that the correlation between CWC and SOM was lower than that of HWC; other authors have found even poorer correlations. For instance, Van Miegroet et al. (2005) found a r^2 of 0.2 in forest soils in Utah, USA.

3.3. Quality of cold-water extractable carbon using UV–vis and fluorescence

Cold-water extractable carbon (CWC) data was compared with UV–vis and fluorescence spectroscopy, using SUVA-$_{254}$ and FI, respectively. The Spearman rank correlation was calculated to evaluate the quality and reproducibility of CWC using optical techniques (Table 4).

There were high correlation patterns between CWC and SUVA-$_{254}$ (Rs = 0.82, $p < 0.05$) although not between CWC and FI (Rs = −0.29), where the slight correlation that could be appreciated was inverse. Chow (2006) obtained a worse correlation between CWC and SUVA-$_{254}$ ($R^2 = 0.38$), whereas that of Van Miegroet et al. (2005) was even lower ($R^2 = 0.01$). As Weishar et al. (2003) point out; some authors have found conflicting conclusions when using SUVA-$_{254}$ to determine the aromaticity of DOC.

Table 3
Results of the analyses and indexes calculated for the UK and ES soils. Mean values shown ± standard deviation.

Land use	Location	Samples[a]	SUVA-$_{254}$ ($1\,mg^{-1}\,m^{-1}$)	FI	BIX	HIX	CWC ($mg\,g^{-1}$)	HWC ($mg\,g^{-1}$)	^{1}H NMR		
									% Aliphatics (0.5–3.00 ppm)	% Carbohydrates (3.00–4.2 ppm)	% Aromatics (6.00–8.00 ppm)
GS	UK	GS-UK-1	4.50 ± 0.15	1.45 ± 0.05	2.31 ± 0.21	0.37 ± 0.05	0.41 ± 0.0	2.89 ± 0.0	37.79 ± 4.91	56.23 ± 4.85	5.98 ± 0.44
CC	UK	CC-UK-1	3.01 ± 0.13	1.66 ± 0.02	3.20 ± 0.12	0.64 ± 0.03	0.32 ± 0.0	1.54 ± 0.0	42.73 ± 1.75	52.53 ± 1.69	4.74 ± 0.65
		CC-UK-2	1.49 ± 0.10	1.84 ± 0.01	3.90 ± 0.15	0.23 ± 0.03	0.20 ± 0.0	0.74 ± 0.0	46.51 ± 0.03	49.58 ± 0.04	3.91 ± 0.07
CC	Spain	CC-ES-1	0.38 ± 0.05	2.03 ± 0.01	0.54 ± 0.05	0.79 ± 0.03	0.14 ± 0.0	0.43 ± 0.0	43.03 ± 0.04	54.57 ± 0.05	2.40 ± 0.09
		CC-ES-2	0.65 ± 0.02	1.92 ± 0.01	0.45 ± 0.05	0.38 ± 0.04	0.10 ± 0.0	0.26 ± 0.0	35.44 ± 1.09	61.09 ± 1.40	3.47 ± 0.46
		CC-ES-3	0.35 ± 0.03	1.61 ± 0.01	4.30 ± 0.07	0.35 ± 0.02	0.08 ± 0.0	0.30 ± 0.0	44.16 ± 3.72	53.20 ± 3.92	2.64 ± 0.20
OG	Spain	OG-ES-1	0.93 ± 0.11	1.81 ± 0.02	0.43 ± 0.02	0.63 ± 0.05	0.12 ± 0.0	0.56 ± 0.0	48.22 ± 0.12	47.52 ± 0.18	4.26 ± 0.23
		OG-ES-2	2.51 ± 0.43	1.73 ± 0.01	0.35 ± 0.02	0.54 ± 0.03	0.62 ± 0.0	1.70 ± 0.0	57.57 ± 1.31	38.10 ± 0.82	4.33 ± 0.5
		OG-ES-3	0.47 ± 0.03	1.93 ± 0.02	0.54 ± 0.08	0.81 ± 0.03	0.12 ± 0.0	0.45 ± 0.0	52.20 ± 3.11	43.90 ± 3.12	3.90 ± 0.04

[a] GS-UK: grass cover, United Kingdom; CC-UK: cereal crops from United Kingdom; CC-ES: cereal crop from Spain; OG-ES: olive grove from Spain; LOI: loss of ignition; SUVA-$_{254}$: specific absorbance at 254 nm; FI: fluorescence index; BIX biological/autochthonous index; HIX: humification index; CWC: cold-water extractable carbon; HWC: hot-water extractable carbon; NMR: nuclear magnetic resonance.

Table 4
Spearman rank correlation coefficient of the studied soils. Bold values indicate significance (at least $p < 0.05$).

	% OM (LOI)	Aromatics	Aliphatics	Carbohydrates	SUVA-$_{254}$	FI	BIX	HIX	HWC	CWC
% OM (LOI)	X	**0.700**	0.383	−0.483	0.533	**−0.600**	−0.113	0.033	**0.7**	0.546
Aromatics	**0.700**	X	0.017	−0.233	**0.950**	**−0.633**	−0.104	−0.100	**0.900**	**0.737**
Aliphatics	0.383	0.017	X	**−0.95**	−0.133	0.167	−0.312	0.217	0.200	0.146
Carbohydrates	−0.483	−0.233	**−0.95**	X	−0.083	−0.083	0.312	−0.283	−0.35	−0.271
SUVA-$_{254}$	0.533	**0.950**	−0.133	−0.083	X	−0.517	−0.104	−0.167	**0.883**	**0.821**
FI	**−0.600**	**−0.633**	0.167	−0.083	−0.517	X	-0.337	0.517	−0.533	−0.287
BIX	−0.113	−0.104	−0.312	0.312	−0.104	−0.337	X	−0.437	−0.054	−0.171
HIX	0.033	−0.100	0.217	−0.283	−0.167	0.517	−0.437	X	−0.083	0.029
HWC	**0.7**	**0.900**	0.200	−0.35	**0.883**	−0.533	−0.054	−0.083	X	**0.912**
CWC	0.546	**0.737**	0.146	−0.271	**0.821**	−0.287	−0.171	0.029	**0.912**	X

LOI: loss of ignition; SUVA-$_{254}$ specific absorbance at 254 nm; FI: fluorescence index; BIX: biological/autochthonous index; HIX: humification index; HWC: hot-water extractable carbon; CWC: cold-water extractable carbon.

3.4. Quality of hot-water extractable carbon using UV–vis and fluorescence

HWC data was compared with SUVA-$_{254}$ and FI to assess whether it had higher correlation than CWC. As it can be seen in Table 4, there is a high correlation (Rs = 0.88, $p < 0.001$) between HWC and SUVA-$_{254}$ whereas that of HWC with FI is not as significant (Rs = −0.53). In both cases, HWC was more significantly correlated to the results obtained with fluorescence and SUVA-$_{254}$ than CWC.

3.5. EEM spectra general characteristics

A set of reference fluorescence spectra has been represented in Fig. 1. As it can be seen in Fig. 1a and b, the two soils with the highest % aromatics measured with ^{1}H NMR as well as high SUVA-$_{254}$ and HWC values (GS-UK-1 and CC-UK-1) showed strong peaks C (10-12 RUs), which indicate UVA-excited humic peaks as described by Coble (1996). They also showed weak peaks A.

On the other hand, Fig. 1c represents the soil with the highest FI, but lowest % aromatic measured with ^{1}H NMR as well as comparatively low values of SUVA-$_{254}$ (CC-ES-1). The EEM spectrum of this soil is very different from the ones represented in Fig. 1a and b, with a strong peak A or UVC-excited (8 RUs), and weak peaks C and T. The presence of the latter indicates biological activity.

3.6. Relationship between optical measures and NMR

The aromaticity of isolated fulvic acid samples was calculated as the ratio of the area of aromatic hydrogen region to the total area of the ^{1}H NMR spectrum (% aromaticity). An analogous method was used to calculate the ratio of the area of aliphatic hydrogen and carbohydrate hydrogen regions.

As it can be seen in Fig. 2, the aromatic hydrogen region is situated in a chemical shift of 6–8 ppm by frequency. On the other hand, the carbohydrate hydrogen and aliphatic hydrogen regions are situated in a chemical shift of 3–4.2 ppm and 0.5–3 ppm, respectively. For Fig. 2, the two soils with the highest % aromatics were chosen for representation purposes (GS-UK-1 and CC-UK-1).

Results of these measurements can be found in Table 3, along with the results from the optical techniques. Correlation analyses were conducted comparing the results from all of them (Table 4).

The largest carbon fraction of the UK soils was carbohydrates. The same trend was found in the CC-ES soils, but not in the OG-ES soils, where the largest carbon fraction was aliphatics.

The proportion of aromatics of the UK soils ranged from 3.91% to 5.98%, whereas for the CC-ES and OG-ES soils, it ranged from 2.40% to 3.47% and 3.90% to 4.33%, respectively. As these were taken from samples in the first horizon of each soil, the low level of aromaticity can be explained by the fact that plant residues may have accumulated in the surface, while microorganisms did not have enough capacity to decompose them. As Cardoza et al. (2004) point out, NMR is a powerful tool for investigating humic substances interactions at the molecular level.

Aromatics have positive correlations for SUVA-$_{254}$, CWC and HWC but are inversely correlated to FI. Correlations are high for aromatics compared with SUVA-$_{254}$ and HWC (Figs. 3 and 4). Rs of 0.95 and 0.90, respectively; $p < 0.001$), but not as good for FI (Fig. 5). The correlation between aromatics and CWC, although significant, is not as strong as the one with HWC (Rs = 0.74, $p < 0.05$). Weishaar et al. (2003) found that SUVA-$_{254}$ is a good predictor of the humic fraction (higher SUVA-$_{254}$ indicates higher humic acid content and molecular weight in DOM solutions) and the general chemical properties of HWC, although it does not predict the reactivity of HWC from different types of source materials nor information of the individual molecules of samples
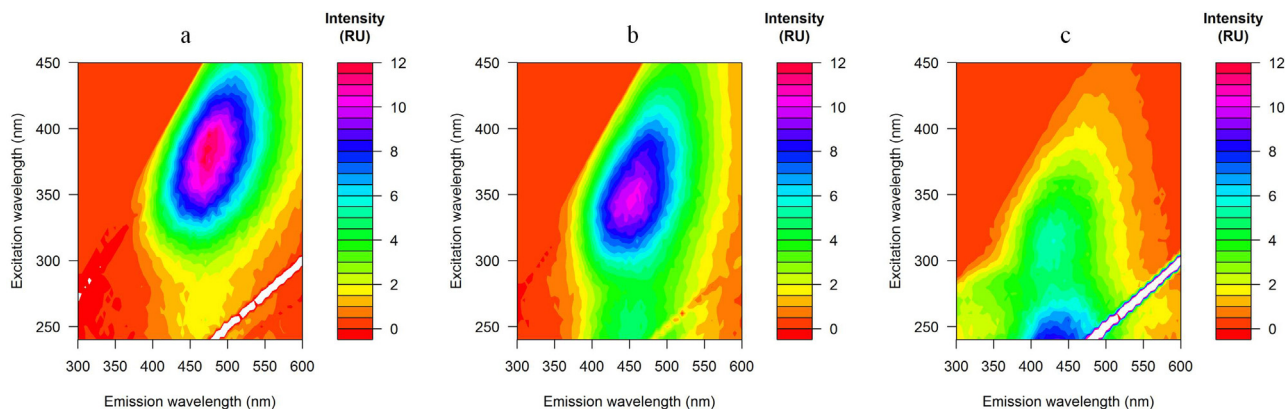
Fig. 1. EEM plots from: (a) GS-UK-1; (b) CC-UK-1; (c) CC-ES-1.
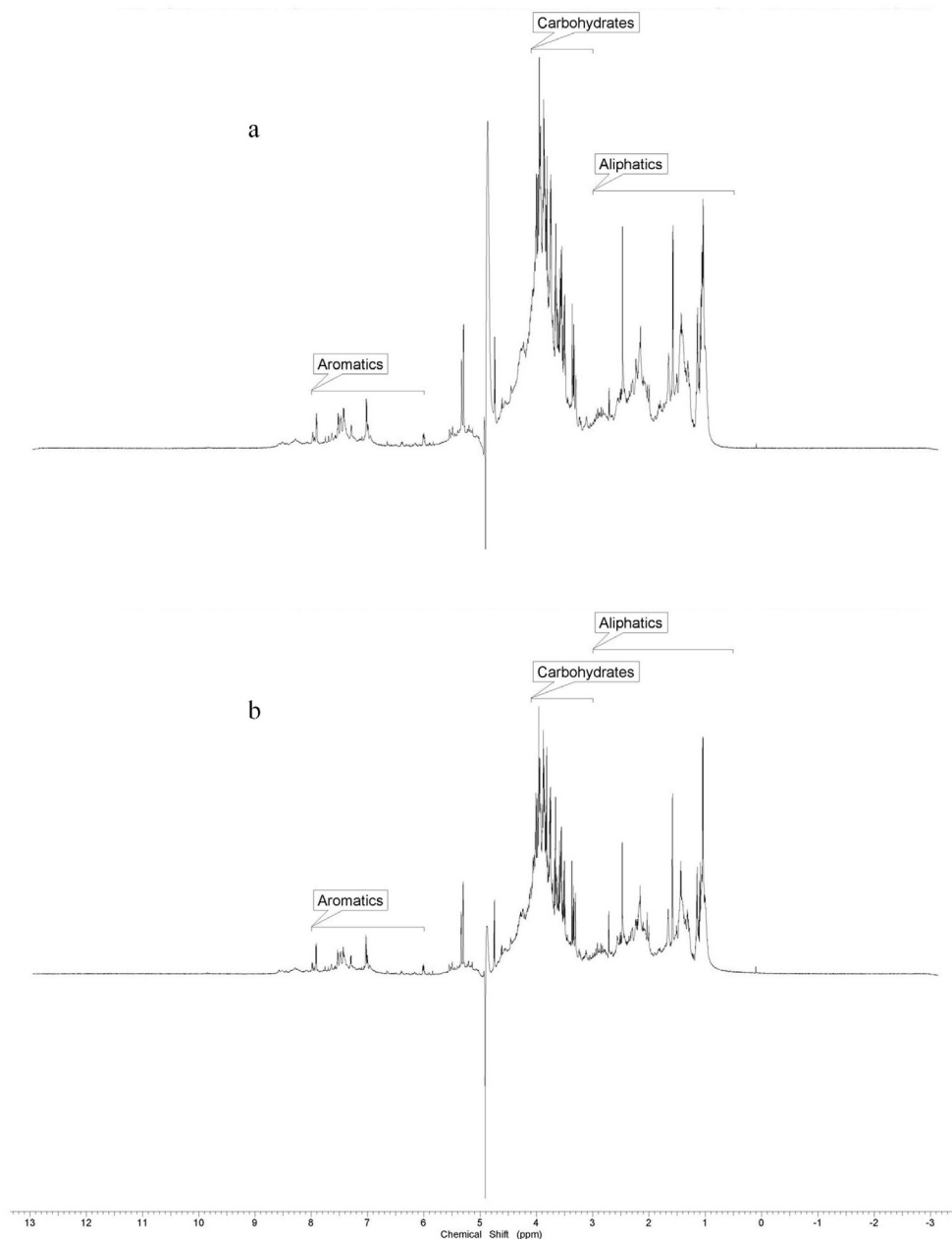
Fig. 2. Liquid state ^{1}H NMR spectra from: (a) GS-UK-1; (b) CC-UK-1.

unless these are humic substances (Chin et al., 1997; Chin et al., 1997). They obtained a good correlation between SUVA-$_{254}$ and aromaticity determined by ^{13}C NMR ($R = 0.97$), which was slightly higher than ours. Yeh et al. (2014) also found a high correlation between SUVA-$_{254}$ measurements and the aromatic fraction of samples of organic matter of river sediments of Taiwan. Jamieson et al. (2014) found that higher SUVA-$_{254}$ implied higher aromaticity in biochar from sugar maple, thus demonstrating that this effect is currently studied when characterising organic material with a high recalcitrance and that is able to retain carbon for thousands of years, due to its stability (Lehmann, 2007).

According to McKnight et al. (2001) and other authors (Rodríguez et al., 2014; Wei et al., 2014), there is a correlation between the FI values and those from methods that indicate the aromaticity of humic substances such as the ratio of the aromatic carbon region area in the total NMR spectra and SUVA-$_{254}$. This pattern was observed in our soils, with negative correlations

between FI and these 2 parameters (Rs = −0.63 and Rs = −0.52, respectively), although only the trend with the aromatic carbon region area in the total NMR spectra was statistically significant ($p < 0.05$).

Kim et al. (2006) and Rodríguez et al. (2014) indicated that differences in the FI higher than 0.1 would imply significant differences in the aromaticity of the samples. If this assumption is applied to our case, CC-UK-2 has differences in its aromaticity with GS-UK-1 but not with CC-UK-1. CC-ES-2 has a different aromaticity than CC-ES-1 and CC-ES-3. In the same way, OG-ES-1 has differences with OG-ES-2 and OG-ES-3. When all the types are compared, there are combinations of differences in the aromaticity but a single pattern cannot be obtained.

Given the results above, the regressions between the aromatic carbon region measured with ^{1}H NMR and SUVA-$_{254}$ and HWC are powerful. The equations we obtained can explain very significantly the relationship between these variables ($p < 0.001$ for the results
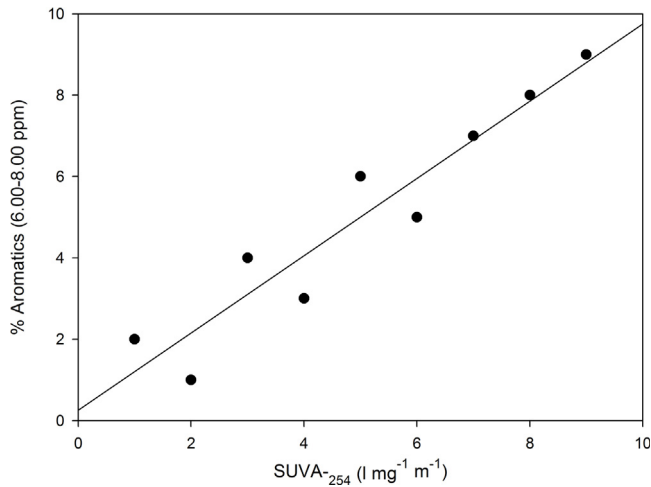
Fig. 3. Correlation between % aromatics and SUVA-$_{254}$. A linear regression model was calculated to explain the relationship between the variables. The equation was y [% aromatics] $= 0.250 + 0.950\, x$ [SUVA-$_{254}$], $p < 0.001$

of ^{1}H NMR predicted with SUVA-$_{254}$ and $p < 0.01$ if they are predicted using HWC). These equations (Fig. 3 and Fig. 4) could therefore be used to predict the aromaticity of water-extractable carbon.

The regression of the aromaticity measured with ^{1}H NMR with FI, although significant ($p < 0.05$), did not have the same level of confidence as the one with HWC and SUVA-$_{254}$. As it can be seen in Fig. 5, an outlier was identified in the regression analysis (FI value of CC-ES-3). Fig. 5 shows how the regression model improved when the outlier was removed from the analysis (Rs = −0.98). The linear regression equation that resulted after the elimination of the outlier is able to explain the ^{1}H NMR values using FI with a very high significance ($p < 0.001$).

However, according to McKnight et al. (2001), the FI would not be sufficient to estimate aromaticity and other techniques are necessary (e.g. SUVA-$_{254}$), as geological processes can alter aromaticity without changing the FI.

SUVA-$_{254}$ did not demonstrate a particularly strong correlation with FI (Rs = −0.52, Table 4). The correlation was negative (higher SUVA-$_{254}$ led to lower FI) which coincides with authors like Kothawala et al. (2012) with minerals soils collected across Canada although their trend is less clear than in the study of other authors
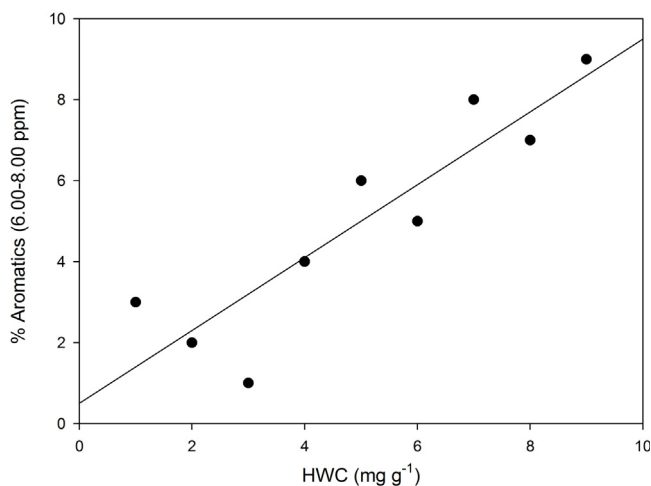
Fig. 4. Correlation between % aromatics and HWC. A linear regression model was calculated to explain the relationship between the variables. The equation was y [% aromatics] $= 0.500 + 0.900\, x$ [HWC], ($p < 0.01$)
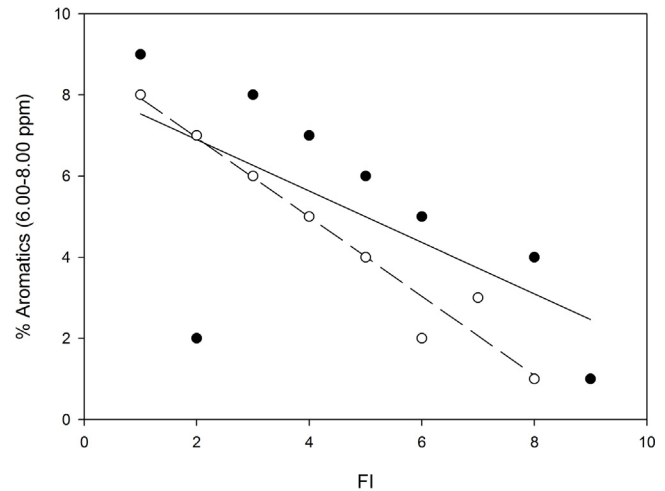
Fig. 5. Correlation between % aromatics and FI. A linear regression model was calculated to explain the relationship between the variables. The equation was y [% aromatics] $= 8.17 − 0.633\, x$ [FI], ($p < 0.05$), represented by the solid line. The removal of an outlier resulted in the equation: y [% aromatics] $= 8.89 − 0.976\, x$ [FI], which explained the relationship with a higher significance ($p < 0.001$). The second equation is represented by the dashed line.

such as Williams et al. (2010), where the slope is more pronounced. The correlation of Williams et al. (2010) was similar to ours ($r = −0.57$ in their study and Rs = −0.52 in ours), although the statistical analysis in their case was the Pearson correlation, as their data followed a normal distribution. Hassouna et al. (2012) found a negative correlation as well, with slightly higher correlation in Mediterranean calcareous soils ($r = −0.69$). As in the case described in Fig. 5, if the same outlier was removed, the correlation improved significantly (Rs = −0.98) and the equation of the linear regression explained with a very high degree of significance ($p < 0.001$) the relation between SUVA-$_{254}$ and FI. Analogously, the same outlier could be removed in the analysis of HWC vs. FI, obtaining a significant correlation between them (Rs = −0.88). A linear regression model explains significantly ($p < 0.01$) the relationship between HWC and FI and therefore similar conclusions can be stated as in the case of the correlation of SUVA-$_{254}$ to FI.

Given the strong intrinsic relationships between the results of SUVA-$_{254}$, HWC and FI; and how they are able to predict the proportion of aromaticity measured with ^{1}H NMR, we can conclude that UV–vis absorbance and fluorescence spectroscopy can be used to characterise the aromaticity of carbon and may be a plausible substitute for ^{1}H NMR, given that they are more cost-effective. Other authors such as Zornoza et al. (2008, 2015),) demonstrated the effectiveness of spectroscopy (near infrared reflectance spectroscopy in their study) as an accurate, cost- and time-effective method for predicting and/or estimating soil biogeochemical properties and other soil parameters.

Correlations between aliphatics and the data from the optical measures and CWC/HWC were poor (Table 4), although slight trends can be observed for SUVA-$_{254}$, FI and CWC. In these cases, the correlation was positive for FI and CWC but negative for SUVA-$_{254}$.

Correlations were also poor between carbohydrates and the data from the optical measures and HWC/CWC, with only one trend detected. This was the inverse correlation (Rs = −0.35) between HWC and carbohydrates.

BIX and HIX did not correlate well with any of the other parameters (Table 4), with very few trends detected. Of the trends detected, HIX was positively correlated with FI (Rs = 0.52). It is worth noting that BIX was positively correlated with

carbohydrates but inversely correlated to aliphatics (Rs = 0.31 and −0.31, respectively), whereas the trend was the contrary for HIX (Rs = −0.28 and 0.22). A similar trend than ours was also found by Kalbitz et al. (2003) between HIX and carbohydrates in forest soils, arable soils and a fen area; although theirs was stronger ($r^2 = 0.81$). Williams et al. (2010) studied the correlation between HIX and SUVA-$_{254}$ in watershed from mixed land use in Canada. They obtained a positive correlation ($r = 0.74$), whereas our correlation was negative. On the other hand, Yeh et al. (2014) did not find a clear trend between SUVA-$_{254}$ and HIX. The significance of our comparison between SUVA-$_{254}$ and HIX values is extremely low and therefore robust conclusions on this issue cannot be stated. Bu et al. (2010) compared HWC and HIX in various soils with different vegetation types in Wuyi Mountain (SE China), obtaining a poor negative correlation, just like ours. However, Kalbitz et al. (2003) found a strong correlation between the aromatic fraction of DOM and HIX ($r^2 = 0.80$).

Yeh et al. (2014) calculated BIX as well, obtaining that higher SUVA-$_{254}$ values implied lower BIX values, which coincides with our comparison in this case, although its significance is not relevant enough to establish a robust conclusion.

Plotting the results from Birdwell and Engel (2010) for FI, HIX, and BIX did not led to significant correlations, which is similar to our results and, along with the authors commented above, demonstrate that a number of studies have found difficulties when correlating HIX and BIX to other parameters.

4. Conclusions

Different techniques to measure the quantity and quality of SOM were tested in cambisols from very different climatic locations and under different cropping systems. HWC extracted a higher amount and carbon than CWC, and correlated better with the %SOM (LOI) than CWC.

SUVA-$_{254}$ and HWC correlated significantly with the proportion of aromatics measured with ^{1}H NMR, demonstrating their complementary nature. Linear regression models fitted to the data were able to explain the relationship between the specific fraction of aromatics measured with ^{1}H NMR and SUVA-$_{254}$ and HWC, and therefore allow the aromatic fraction to be estimated at lower cost using SUVA-$_{254}$ and HWC.

A linear regression model was also able to explain the relationship between ^{1}H NMR measurements and FI, after an outlier was removed.

BIX and HIX were not useful indexes for our purposes, as they did not correlate well to the carbon fractions measured with ^{1}H NMR or with FI, SUVA-$_{254}$, or HWC.

The EEM spectra showed a difference in the peak types that appeared in the CC-UK soils and in the CC-ES soil. The fact that Fig. 1a and b showed a stronger peak C and Fig. 1c showed a stronger peak A indicated subtle qualitative differences in their humic fractions. This could have been caused by the different soil management (more intense agricultural activity in CC-ES-1). More work will be needed to confirm this.

In view of our results, optical measures have a potential, in combination, to predict the aromatic fraction of SOM without the need of expensive and time consuming techniques like ^{1}H NMR; which could be very useful when the equipment is not available or in instances when a high number of samples need to be analysed simultaneously.

Acknowledgments

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CONCLUSIONES

8. CONCLUSIONES.

Las conclusiones que se derivan de la presente memoria de Tesis Doctoral son:

PRIMERA. Desde el punto de vista metodológico, las técnicas ópticas estudiadas (absorbancia, fluorescencia y medición del carbono orgánico disuelto) presentan un fuerte potencial para cuantificar y caracterizar las fracciones de la materia orgánica a bajo precio y en un período corto de tiempo, a diferencia de técnicas como $^{1}H^{-}NMR$.

SEGUNDA. El efecto del cambio de uso (forestal-olivar tradicional) provoca una reducción en el carbono y en el nitrógeno; además de una pérdida en la calidad de los suelos, estimada a partir de la relación de estratificación.

TERCERA. A partir del cambio de uso la capacidad de almacenar carbono en el suelo se ve afectada por la topografía, produciéndose un aumento de la misma en las posiciones topográficas más bajas. Esto fue debido a que en éstas se produce acumulación-sedimentación superficial de la materia orgánica procedente de las posiciones topográficas más elevadas.

CUARTA. En relación a las diferentes técnicas de manejo comparadas en olivar (laboreo convencional, laboreo convencional con la adición de alperujo, laboreo convencional con la adición de hoja de almazara, no laboreo con la adición de restos de poda y no laboreo con la adición de restos de poda y cubierta vegetal) se observa que la adición del subproducto hoja de almazara en olivar con laboreo convencional mejora las propiedades químicas del suelo (carbono orgánico del suelo, stock de carbono orgánico y carbono extraíble en agua caliente) además de reducir el riesgo de erosión hídrica, en relación a los otros manejos incluido el no laboreo.

QUINTA. La aplicación de la relación de estratificación como índice de calidad indica, en término generales, que el olivar con no laboreo es el suelo que presenta mejor calidad; y, en términos particulares, que el manejo convencional con la adición de subproductos agrícolas mejora la calidad de los suelos en profundidad (SR3 y SR4).

CONCLUSIONS

9. CONCLUSIONS.

The conclusions of this PhD thesis are the following:

FIRST. From a methodological point of view, the studied optical techniques (absorbance, fluorescence and measurement of dissolved organic carbon) present a strong potential for the quantification and characterisation of organic matter fractions at low cost and in a short period of time, as opposed to ^{1}H-NMR.

SECOND. Land use effects (forest to traditional olive grove) lead to a carbon and nitrogen content reduction; along with a loss of soil quality, which was estimated using the stratification ratio.

THIRD. After land use change, the carbon storage capacity of soils is affected by topography. This capacity increases in the lowest topographical positions, given that there is a surface accumulation and sedimentation of organic matter originating from the upper topographical positions.

FOURTH. With regard to the different management techniques compared in olive grove soils (conventional tillage with *alperujo*, conventional tillage with the addition of olive tree leaves from the oil mill, no-tillage with the addition of olive tree prunings, and no-tillage with the addition of olive tree prunings and vegetative cover), it was observed that the addition of olive tree leaves to soils under conventional tillage improves chemical properties (soil organic carbon, soil organic carbon stock and hot-water extractable carbon) and reduces the risk of water erosion in these soils, compared to the other management techniques studied, including no-tillage.

FIFTH. The use of the stratification ratio as soil quality index indicates that olive grove soils under no-tillage present the highest quality in general terms. In specific terms, the addition of agricultural by-products to olive grove soils under conventional tillage improves soil quality at depth (SR3 and SR4).

PRODUCCIÓN CIENTÍFICA DE LA TESIS DOCTORAL / SCIENTIFIC PRODUCTION OF THE PhD THESIS

10. PRODUCCIÓN CIENTÍFICA DE LA TESIS DOCTORAL.

10.1. ARTÍCULOS DE INVESTIGACIÓN / RESEARCH PAPERS.

- Título: Topography and land use change effects on the soil organic carbon stock of forest soils in Mediterranean natural areas.

  - Autores: M.L. Fernández-Romero, B. Lozano-García, L. Parras-Alcántara.

  - Revista (año, vol., pág.): Agriculture, Ecosystems and Environment 195 (2014) 1-9 (DOI:10.1016/j.agee).

  - Base de Datos Internacional o Nacional (caso de CC.JJ., CC.SS. y Humanidades) en las que está indexada: ISI Web of Knowledge. Journal Citation Index.

  - Área temática en la Base de referencia: Agriculture, multidisciplinary; ecology; environmental sciences.

  - Índice de impacto de la revista en el año de publicación del artículo: 3,402.

  - Lugar que ocupa/ Nº de revistas del área temática: Agriculture, multidisciplinary: 1 of 56. Ecology: 36 of 145. Environmental sciences: 36 of 223.

- Título: Effects of land management on different forms of soil carbon in olive groves in Mediterranean areas.

  - Autores: María Luisa Fernández-Romero, Beatriz Lozano-García, Luis Parras-Alcántara, Chris D. Collins, Joanna M. Clark.

  - Revista (año, vol., pág.): Land degradation & development (DOI: 10.1002/ldr.2327).

  - Base de Datos Internacional o Nacional (caso de CC.JJ., CC.SS. y Humanidades) en las que está indexada: ISI Web of Knowledge. Journal Citation Index.

  - Área temática en la Base de referencia: Environmental sciences; soil science.

  - Índice de impacto de la revista en el año de publicación del artículo: 3,089.

  - Lugar que ocupa/ Nº de revistas del área temática: Environmental sciences: 50 of 223. Soil Science: 3 of 34.

- Título: Evaluation of optical techniques for characterising soil organic matter quality in agricultural soils.

  - Autores: M.L. Fernández-Romero, J.M. Clark, C.D. Collins, L. Parras-Alcántara, B. Lozano-García.

  - Revista (año, vol., pág.): Soil & Tillage Research 155 (2016) 450-460 (DOI: 10.1016/j.still).

  - Base de Datos Internacional o Nacional (caso de CC.JJ., CC.SS. y Humanidades) en las que está indexada: ISI Web of Knowledge. Journal Citation Index.

  - Área temática en la Base de referencia: Soil science.

  - Índice de impacto de la revista en el año de publicación del artículo: 2,622.

  - Lugar que ocupa/ Nº de revistas del área temática: 9 of 34.

- Título: Soil quality assessment based on carbon stratification index in different olive grove management practices in Mediterranean areas.

  - Autores: M.L. Fernández-Romero, L. Parras-Alcántara, B. Lozano-García, J.M. Clark, C.D. Collins.

  - Revista (año, vol., pág.): Catena 137 (2016) 449-458 (DOI: 10.1016/j.catena).

  - Base de Datos Internacional o Nacional (caso de CC.JJ., CC.SS. y Humanidades) en las que está indexada: ISI Web of Knowledge. Journal Citation Index.

  - Área temática en la Base de referencia: Geosciences, multidisciplinary; soil science; water resources.

  - Índice de impacto de la revista en el año de publicación del artículo: 2.820

  - Lugar que ocupa/ Nº de revistas del área temática: Geosciences, multidisciplinary: 32 of 175. Soil science: 5 of 34. Water resources: 8 of 83.

10.2. PARTICIPACIÓN EN CONGRESOS / CONGRESS CONTRIBUTIONS.

a) Comunicaciones orales / Oral communications.

- Título: Land use change from forest to olive grove soils in a toposecuence in Mediterranean areas (South of Spain).

  - Autor: María Luisa Fernández-Romero, Luis Parras-Alcántara, Beatriz Lozano-García.

  - Congreso: European Geosciences Union (EGU) General Assembly 2014 (27 April - 2 May), Vienna (Austria); 05/2014.

- Título: Land management effects on soil carbon in olive groves of Mediterranean areas.

  - Autor: Maria Luisa Fernández-Romero, Luis Parras-Alcántara, Beatriz Lozano-García, Joanna Clark, Chris Collins.

  - Congreso: European Geosciences Union (EGU) General Assembly 2015 (12-17 April), Vienna (Austria); 04/2015.

b) Comunicaciones en forma de póster / Poster contributions.

- Título: Assessment of fluorescence EEM vs. Liquid-state ^{1}H-NMR spectroscopy for the characterization of natural OM in agricultural soils from the UK and Spain.

  - Autor: Maria Luisa Fernández, Chris Collins, Joanna Clark, Luis Parras-Alcántara, Beatriz Lozano-García.

  - Congreso: European Geosciences Union (EGU) General Assembly 2014 (27 April-2 May), Vienna (Austria); 05/2014.

- Título: Evaluation of soil organic carbon changes in forest soils from Mediterranean natural areas.

  - Autor: Maria Luisa Fernández-Romero, Luis Parras-Alcántara, Beatriz Lozano-García.

  - Congreso: European Geosciences Union (EGU) General Assembly 2015 (12-17 April), Vienna (Austria); 04/2015.

10.3. OTROS.

First prize (Winner) at Soil Research Centre Scientific Photograph Competition (figura 23). University of Reading. September, 2013.

Figura 23. Cambisol con cárcavas provocadas por la erosión debido a una gestión inadecuada y un aumento de las precipitaciones (Olivar en el área Mediterránea). Elaboración propia.