Soil redistribution and carbon dynamics in Mediterranean agroecosystems:

Radioisotopic modelling at different spatial and temporal scales

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Cover photograph: Panoramic view of the study area







Soil redistribution and carbon dynamics in Mediterranean agroecosystems: radioisotopic modelling at different spatial and temporal scales

Thesis presented by Laura Quijano Gaudes and in fulfilment of the requirements to obtain the degree of Doctor Philosophiae from the University of Zaragoza

Supervisor: Dr.ª Ana Mª Navas Izquierdo

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List of publications included in the thesis

The present thesis is a compendium of eight research papers published in international scientific journal with a referee system.

Paper I:

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Paper II:

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Paper III:

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Paper IV:

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Paper V:

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Paper VIII:

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The Final Author Versions of these Articles can be downloaded through a Open Access way from Digital CSIC, the Institutional Repository of the Spanish National Research Council

Try to learn something about everything and everything about something Thomas Henry Huxley

To my family

Preface and acknowledgments

This dissertation was prepared for the degree of Doctor Philosophiae (Ph.D.) at the Department of Earth Sciences in the Science Faculty of the University of Zaragoza, Spain.

The work for this doctoral project was done in the research group Erosion, and Soil and Water Evaluation at the Department of Soil and Water in the Experimental Station of Aula Dei, Spanish National Research Council (EEAD-CSIC) in Zaragoza, Spain. Two research stays were conducted during the Ph.D. period, a 3-month research stay in 2012 at the Department of Environmental Sciences in Basel, Switzerland under the supervision of Prof. Dr. Nikolaus J. Kuhn and a short research stay in 2013 at the Université Catholique de Louvain under the supervision of Prof. Dr. Kristof Van Oost.

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The thesis includes eight research articles done during the doctoral period. The thesis has been written in English and the abstract and conclusions sections have been also translated into Spanish.

The thesis focuses on the study and analysis of the processes related to the redistribution of soil particles in a representative experimental field of agricultural systems in Mediterranean mountain areas. This study is aimed at quantifying the soil redistribution processes and its influence on soil properties and carbon dynamics in Mediterranean mountain agroecosystems that permits a better understanding of the influence of these processes in soil properties and allows an approach to the degradation status and/or soil conditions in agro-ecosystems.

First of all, I would like to express my thanks and appreciations to my supervisor Dr.^a Ana M^a Navas Izquierdo for giving me the opportunity to accomplish this research. I would like to thank your patient guidance, encouragement and advice throughout my time as Ph.D. student. I have been fortunate to have a supervisor who brings professional integrity, passion and enthusiasm to assist me in each step to complete this thesis and respond to my queries promptly. Thank you for your constructive comments and providing the skills to enrich my understanding of Soil Science.

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Abstract

Soil erosion and associated soil redistribution is a natural process, occurring over geological time, and is essential for soil formation. However, most concerns about soil erosion are related to accelerated soil loss and degradation by human activity in agricultural lands. More than 75% of the soil losses come from agricultural land at global scale. Particularly, soil erosion is one of the most serious environmental problems in Mediterranean agroecosystems where erosion has been intensified by the long and intense history of agricultural practices, land management and specific climatic conditions such as irregular and potentially erosive precipitations. In addition, loss of the fertile topsoil with a higher content of nutrients is a threat for crop sustainability and productivity with economic costs and consequences for food security and public health impacts.

A rainfed cultivated field with representative characteristics of the Mediterranean mountain agroecosystems was selected for this research to gain knowledge on the effect of soil redistribution processes on soil status and conditions and its implications on soil carbon dynamics at field scale.

The methodology used was oriented to addressing these main research objectives (i) establish and analyze the spatial patterns of soil properties and soil nutrients as soil organic carbon and nitrogen (SOC and SON), (ii) examine the relationships between soil properties, soil nutrients, soil redistribution processes and topographic attributes, (iii) modelling soil redistribution for quantifying soil erosion and deposition rates and (iv) modelling SOC dynamics at different temporal scales.

The study soils (n=156) classified as Calcisols developed on Quaternary deposits are alkaline, non-saline and calcareous with mean values of pH, electrical conductivity and carbonates of 8.2, 0.2 dS m^{-1} and 38% respectively. Most soil samples (81%) had a silt loam texture.

The results of this thesis revealed that the spatial patterns of soil properties and soil nutrients are closely related to landscape position and topographic characteristics. Higher contents of finer soil particles (<0.05 mm soil fraction) including magnetic minerals and ¹³⁷Cs, soil organic matter and SOC and SON were recorded in the upper part of the field. On the contrary the contents of carbonate, coarse and sand fractions were inversely correlated with topographic characteristics. Spatial patterns of soil properties, ¹³⁷Cs and soil nutrients indicated that their distribution was related to similar physical processes.

A predominance of loss of ¹³⁷Cs over 70% of the total area of the field indicates that soil erosion predominates over deposition processes. Soil loss is associated to a generalized depletion of soil nutrients compared to the inventories at the reference site. Soil erosion and deposition rates derived from ¹³⁷Cs measurements with mean values of 19.7 Mg ha⁻¹ yr⁻¹ and 12.6 Mg ha⁻¹ yr⁻¹, respectively were used to calibrate WATEM/SEDEM model. Soil redistribution rates estimated from WATEM/SEDEM and Mass Balance Model III (MBM III) indicates that the main agent of soil redistribution within the field is water erosion.

The important depletion of ¹³⁷Cs, SOC and SON was associated with runoff, land use changes from forest to cultivated land and tillage practices. Tillage favors soil conditions for the neoformation of pedogenic magnetic minerals and for the decomposition of the more bioreactive carbon fraction in topsoils. Modelling approach using SPEROS-C to evaluate the effects of changes in land management on SOC stocks and carbon fluxes reported that conventional tillage practices were the main sources of exported carbon representing three times those of minimum tillage.

This thesis contributes to improve the knowledge of mechanisms that can explain why soil characteristics, land use and redistribution processes are key factors that determine the current status of soil and can be used to identify suitable locations for implementing soil conservation strategies in Mediterranean mountain agroecosystems.

Chapter 1

Introduction and objectives



Cover photograph from left to right: Panoramic view of the village of Barués located close to the study field Detailed view of Barués

1. Introduction

Agricultural soils are becoming an interesting challenge for soil science since human activity related to agriculture significantly modify soil by land use changes and land management (Pimentel et al., 1997). In the Mediterranean region, the development of agriculture and cultivation are linked to many significant changes in the landscape (Kizos and Koulouri, 2006). Steep slope areas in the Mediterranean region have been gradually transformed into stepped arable lands over the last centuries through human activity with an intensive impact on the original soil and landscape. As a consequence of these changes, agricultural soils have been modified and present different soil properties as compared to their previous and original conditions (Romanyà and Rovira, 2011).

Agriculture is the main land use in the European Union accounting for more than 47% of the total territory (Giannakis and Bruggeman, 2015). Most changes in agricultural lands during recent decades have been in response to the European Union Common Agricultural Policies (CAP) which dates back to the Treaty of Rome in 1957. The objectives of the CAP favored the rapid expansion of certain management systems and crops. In Spain, changes related to CAP in agricultural lands were characterized by the expansion of irrigation and vineyards and, to a lesser extent, almond and olive orchards at the expenses of rain fed cereals (García-Ruíz, 2010). Although CAP supports economically less favorable areas for the local population in order to avoid the agricultural abandonment of agricultural lands (Kosmas et al., 2015), this land use change has increased particularly since the 1960s as a consequence of a complex socio-economic and environmental factors as the depopulation of rural areas and the impossibility of mechanization in steep terrain (Christof et al, 2011). Since 1961, 17% of the land under annual and permanent crops in Spain has been abandoned (FAO, 2015).

In the European Mediterranean region, abandoned agricultural land is generally found in unfavorable environmental conditions such as high elevations, steep slopes, shallow soils, dry climatic conditions as well as marginal agricultural areas (MacDonald et al., 2000). Since the recent reform process of CAP initiated in 2003 and continued until 2014 many efforts have been made at the European level to promote soil conservation and to protect and enhance the soil quality and soil functions (Solazzo et al., 2015).

The Soil Science Society of America (1997) defined soil quality as the capacity of a specific type of soil to function within natural or managed ecosystem boundaries, to sustain biological productivity, maintain environmental quality, and promote plants and animal health. Thereof, soil quality would be an indicator of sustainable land management (Herrick, 2000), food security (Lal, 1999) and economic viability (Hillel, 1991). The progressive loss of soil quality due to inadequate land use management and inappropriate cultivation practices is associated to a decline of soil functions leading to effects on soil physical, chemical and biological properties (Lal, 1994) affecting soil productivity and agricultural sustainability with socio-economic implications (Nardi et al., 1996) which can be particularly critical in fragile agroecosystems as in the Mediterranean area.

The evaluation of the current status of soil conditions using chemical, biochemical and biological indicators is essential to understand and diagnose the significant changes in soils as a result of cultivation practices. The assessment of soil quality requires a set of descriptors of rapid determination (Acton and Padbury, 1993) that provide significant information about threshold

values for soil normal functioning to implement appropriate strategies for the preservation of soil and infer the consequences of land degradation in order to improve the sustainability of agricultural soils (Doran and Parkin, 1994). There is a lack of an universal soil quality assessment based on a specific assemblage of variables (Burger and Kelting, 1998; Schoenholtz et al., 2000) because soil quality indicators should be selected according to the specific processes measured and the environment and soil under study (Cantú et al., 2007) and the utility of selected soil quality indicators should be checked for each local agricultural ecosystem (Rojas et al., 2016).

The minimum data set of indicators sensitive to changes in soil quality and soil management proposed by Larson and Pierce (1991) includes soil texture, soil organic matter, soil nutrients, pH and electrical conductivity. Furthermore, soil magnetic minerals (iron oxides and oxyhydroxides) are used as indicators of environmental factors including soil degradation (Royall, 2001; Sadiki et al., 2009), anthropogenic pollution monitoring (Chaparro et al., 2006; Blundell et al., 2009), pedogenic processes related to the formation of magnetic minerals (Bidegain et al., 2009; Torrent et al., 2010) and soil redistribution processes by agricultural practices (Jordanova et al., 2011; 2012).

The formation of iron oxides in soils is a complex process that likely involves chemical, biological and physical processes (Balsam et al., 2011). Soil magnetic properties depend on the concentration and characteristics (shape, size and composition) of magnetic minerals (Mullins, 1977). The classification of magnetic components in terms of mineralogy, domain state, and concentration, is important for assessing the nature and origin of the components (Peters and Dekkers, 2003).

Magnetic susceptibility is a rapid and non-destructive technique to assess magnetic iron mineral contents (Thompson and Oldfield, 1986). *In situ* measurements of soil magnetic susceptibility using field probes have also proved to be a useful tool for mapping and screening magnetic susceptibility of topsoils in areas with low pollution impact (Kapička et al., 2001). Measurements of soil magnetic properties combined with physiographic and edaphic parameters could be useful to an approximation of the soil-forming processes in agroecosystems where pedogenesis occurs under a strong human influence (Maher, 1998) to date such studies are scarce for the Mediterranean region.

Accelerated soil degradation by anthropogenic activities, such as land use change, farm mismanagement, deforestation and overgrazing results in the loss of critical functions and ecosystem services causing not only on-site soil losses affecting crop productivity (Dercon et al., 2003) but also off-site problems of mobilization and transport of sediment and associated contaminants that can find their way into reservoirs and water bodies causing a deterioration of water (Schmitter et al., 2010). The degree of severity and geographic extent of soil degradation are diverse and complex. However, European Mediterranean agricultural soils are prone to soil degradation due to the intensive cultivation for a long period, specific climatic conditions as scarce and heavy rainfall events and drought summer followed by autumn rainfalls (Alpert et al., 2002) besides soil characteristics such as shallow soils with low soil organic matter.

The intensification of human activities and agricultural practices in Mediterranean agroecosystems is related to the loss of soil structural stability and ability to resist the destructive impacts of erosion. In addition, climate change is expected to have significant effects on European agriculture that will manifest through the increasing frequency and severity of extreme weather events and through changes in the availability of water (European Commission, 2009) with the

most severe impact on the European Mediterranean region, which exhibits a lower adaptative capacity than the Northern European agriculture (Iglesias et al., 2012)

Soil erosion is the detachment, transport and deposition of soil particles caused by one or more natural or anthropogenic erosive forces (rain, runoff, wind, gravity, tillage, land levelling and crop harvesting) (Boardman and Poesen, 2006). It is one of the major and most widespread threats on soil quality and the main cause of land degradation that has become a relevant worldwide environmental problem (Lal, 1990). Soil erosion is among the eight soil threats (i.e. soil organic matter decline, soil compaction, salinization, decline of soil biodiversity, soil sealing, landslides and soil contamination) listed within the Soil Thematic Strategy of the European Commission (European Commission, 2006) due to its impacts on food production, water quality, ecosystem services, mud floods, eutrophication, biodiversity and carbon stock shrinkage (Cerdà et al., 2009). Spain is one of the countries most severely affected by soil erosion in the European Mediterranean region (Solé-Benet, 2006).

Soil erosion, mainly due to water and to a lesser extent wind, is still the most important degradation process in European Union countries. In Spain, also water erosion is the most important type of soil erosion (Martín-Fernández and Martínez-Núñez, 2011). The main processes of water erosion include rill and interrill, gully and stream-bank erosion. Wind erosion has been reported only locally in susceptible areas of Spain. Splash (Regués et al., 1995), pipe (García-Ruiz et al., 1997) and tillage erosion (De Alba, 2003) are other types of erosion that are less represented in Spain. Soil erosion has resulted in loss of most fertile topsoil with higher organic matter contents from eroded surfaces. The severity of this problem and its expected increasing risk in cultivated landscapes as a consequence of climate change have increased concerns on soil erosion specially in Mediterranean agroecosystems, and have led to explore methods to estimate soil redistribution rates and soil loss monitoring (Walling and Quine, 1991).

Soil erosion surveys using radiotracers and modelling approaches offer a considerable potential to study soil erosion processes and quantify soil redistribution rates (Porto et al., 2003; Navas et al., 2008; 2011; Gaspar and Navas, 2013). Because of the limitations associated with traditional methods of measuring rates of soil erosion, such as erosion plots, the fallout radionuclide caesium-137 (¹³⁷Cs) has been increasingly used in recent years as an alternative approach to estimating rates of soil redistribution on both cultivated and uncultivated areas (Kachanoski, 1993; Navas et al., 2005).

Caesium-137 is an artificial radionuclide with a half-life of 30.2 years, which has been released into the stratosphere as a result of the atmospheric thermonuclear weapons tests which took place from the mid-1950s to the early 1970s or from nuclear accidents. Most of the ¹³⁷Cs fallout occurred at the beginning of the 1960s with a peak immediately preceding the Nuclear Test Ban Treaty in 1963, the year of most intensive nuclear weapon testing (He and Walling, 1997). Global fallout amounts of ¹³⁷Cs in Southern hemisphere were about one third or less than in the Northern hemisphere (UNSCEAR, 2000) because more atmospheric nuclear testing took place in the Northern hemisphere (Ritchie and McHenry, 1990). This global pattern is further complicated by ¹³⁷Cs fallout originated from the Chernobyl (April, 1986) and Fukushima (March, 2011) accidents, which increased the existing bomb derived inventories by several orders of magnitude in some locations across Europe (Dercon et al., 2012). In the Iberian Peninsula the total ¹³⁷Cs deposition

normalized on 10 May 1986 after the Chernobyl accident was the lowest in Europe, estimated <10 kBq m⁻² (De Cort et al., 1998).

The fallout input of ¹³⁷Cs from the atmosphere to the land surface occurred predominantly through wet deposition in association with precipitation. In the Ebro Basin ¹³⁷Cs spatial distribution showed a clear gradient with rainfall (Navas et al., 2007). The total ¹³⁷Cs fallout can generally be assumed to be uniform, at least at a scale where longer-term (50 year) rainfall can also be considered uniform. Once ¹³⁷Cs reaches soil's surface from atmosphere is rapidly and strongly adsorbed by fine soil particles as clay minerals and organic matter and is accumulated at or near the soil surface (Walling et al., 1995).

Redistribution of soil or sediment particles in association with ¹³⁷Cs across the landscape mainly through physical processes represent an integrated measurement of all processes leading to soil redistribution (Ritchie and McHenry, 1975). The ¹³⁷Cs fallout radionuclide has been established as an effective technique and reliable tool to obtain quantitative estimates of soil erosion and deposition (Ritchie et al, 2007) on Mediterranean agricultural landscapes (Navas and Machín, 1991; Navas and Walling, 1992; Porto et al, 2001; Mabit et al., 2008; Benmansour et al., 2013; Gaspar et al., 2013). The advantage of this technique is the potential to provide medium term spatially distributed soil redistribution rates by both water and tillage erosion that represent mean annual values for the past 50 years within agricultural landscapes (Zapata and Nguyen, 2010). One of the key issues of using measurements of ¹³⁷Cs is to establish relationships between ¹³⁷Cs loss and gain or percentage residuals for each soil sampling point and the rates of soil redistribution relative to the local reference inventory. Estimates of soil redistribution rates are based on a comparison of the ¹³⁷Cs inventory for an individual sampling point and the ¹³⁷Cs reference inventory. Lower ¹³⁷Cs inventories than the reference inventory indicating loss of radionuclide thus soil loss. Similarly, the values of ¹³⁷Cs inventories higher than the reference ones indicating soil deposition (Walling and He, 1999).

The successful application of the ¹³⁷Cs approach depends heavily on the availability of reliable conversion models for converting measurements of ¹³⁷Cs redistribution to estimate of soil redistribution rates. Navas and Walling (1992) highlighted that the estimation of soil redistribution rates in Mediterranean soils was affected by the high stone content because similar ¹³⁷Cs profiles exhibited very diverse total inventories. The models proposed by Soto and Navas (2004; 2008) that estimate soil erosion and deposition rates for uncultivated and cultivated soils, respectively were specially developed for Mediterranean stony soils and tested in Mediterranean mountain areas (Navas et al., 2005, 2012). These models simulate the ¹³⁷Cs transference in soil profiles during the time in which soil is exposed to erosion processes and relate soil loss and ¹³⁷Cs loss to calculate soil redistribution rates at each sampling point. The models assume a temporary evolution of the ¹³⁷Cs concentration within the soil. It was considered a total inventory of ¹³⁷Cs equal to zero before 1954, increasing the ¹³⁷Cs inventory from this year in a quantity equal to the corresponding atmospheric deposit. Although the tests of nuclear weapons commenced in the early 1950s, the detectable quantities of ¹³⁷Cs in soils began in 1954 (Ritchie and McHenry, 1973).

Over the last years there has been a remarkable progress in the development of techniques for soil erosion assessment complementary to the existing methods such as distributed, process based models to represent soil redistribution processes. Soil erosion models are tools that estimate spatially distributed rates of soil redistribution providing scientific support for soil conservation and

water management (Merritt et al., 2003). WATEM/SEDEM is a spatially distributed soil erosion and sediment delivery model that has been applied in different landscapes as in the Loess area of central Belgium to evaluate the effectiveness of a variety of soil conservation and sediment control measures (Verstraeten et al., 2002), in Alpine mountain catchments (Van Rompaey et al., 2005), in the Southeastern Uplands of Australia (Verstraeten et al., 2007), in several mountain catchments of the Czech Republic (Krasa et al., 2010) and in the Central Spanish Pyrenees under current, past, and hypothetical future land use/land cover conditions (Alatorre et al., 2012). Validation of spatially distributed models using spatially distributed data is a vital process in model performance that rarely is undertaken (Quine, 1999). Studies using spatially distributed data of ¹³⁷Cs estimates for validating the results of spatially distributed soil erosion models including WATEM/SEDEM (Alatorre et al., 2011) at detailed scale are scarce due to the absence of spatially distributed models with ¹³⁷Cs derived soil redistribution rates can be of value to identify suitable locations for implementing soil conservation strategies in Mediterranean agroecosystems (López-Vicente et al., 2013; López-Vicente and Navas, 2009).

Information on the interaction between soil erosion and soil properties is an important requirement for sustainable management of the soil resource. According to the new approach of the Common Agricultural Policies in 2003, the definition of Good Agricultural and Environmental Conditions (GAEC) was established. The prevention of soil erosion and the maintenance of soil organic matter (SOM) were two of the GAEC requirements, which each Member State of the European Union was obliged to address through national and regional standards such as: (i) minimal soil cover maintenance, (ii) minimum land management reflecting site specific conditions to limit soil loss, and (iii) maintenance of soil organic matter level through appropriate practices including ban on burning arable stubbles (MARS, 2014). Member States are required to verify whether the farmers are compliant with the regulations and the effectiveness of GAEC on erosion and carbon budgets. However, the environmental effects of GAEC applications are still unknown. To gain a better knowledge of the effectiveness of GAEC more data, monitoring networks, remote sensing application and modelling tools are necessary (Borrelli et al., 2016).

Soil organic carbon (SOC) is the major component of SOM which is a heterogeneous mixture of organic components such as plant, animal and microbial residues in different stages of decomposition (Post and Kwon, 2000). The spatial distribution of SOC is affected by environmental factors such as soil redistribution processes, cover vegetation and land management (Boix-Fayos et al., 2009). However, soil erosion contributes significantly to the redistribution of soil nutrients as SOC because tends to remove mainly smaller, lighter particles which often contain high levels of SOM (Gregorich et al., 1998; Beguería et al., 2015).

The evaluation of soil redistribution processes and the induced depletion of soil nutrients in agroecosystems can improve the knowledge of the fate of soil nutrients due to water and tillage in cultivated soils. This is required to establish strategies to control soil erosion and implement sustainable soil management practices to prevent further soil degradation in agricultural soils. Recent studies have examined the relationships between the patterns of soil redistribution processes using the ¹³⁷Cs technique and SOC in agricultural soils (Ritchie and McCarty, 2003; Martínez et al., 2010; Navas et al., 2012). The results show that fallout ¹³⁷Cs could be used directly to determine the impacts of soil erosion on carbon (C) dynamics. Many of these studies have focused on SOC distribution in the 0–30 cm soil layer where changes in SOC are normally most dynamic.

Soil is an important component of the global carbon cycle because it is the major organic carbon pool in terrestrial ecosystems. Soils are the largest terrestrial organic carbon pool with global estimates ranging from 1115 to 2200 Pg of C (Schlesinger, 2005) and closely related to the exchange between atmosphere, biosphere and pedosphere. Soil organic carbon stock is as much as three times higher than atmospheric carbon and two times higher than in the biota (Lal, 2008). Complex processes of plant photosynthesis, soil respiration and SOC decomposition are involved in the carbon cycle in terrestrial ecosystems (Cao and Woodward, 1998). SOC together with soil organic nitrogen (SON), are recognized as fundamental indicators of soil quality and agricultural sustainability (Boix-Fayos et al, 2001; Martínez-Mena et al., 2002). Both have an important influence on soil physical, chemical and biological properties (Gregorich et al., 1994; Monaco et al., 2008).

The production of SOC within soils occurs as a result of the addition of dead plant and animal material, and its loss occurs mainly due to the decomposition and mineralisation of SOM (Polyakov and Lal, 2004). According to its chemical stability and turnover times, SOC can be divided into: (i) active carbon fraction (ACF), which has turnover rates of days to few years and is rapidly and easily decomposable (Coleman et al., 1996), and (ii) a more stable carbon fraction (SCF), with turnover rates ranging from a few years to centuries and which is highly resistant to microbial and chemical decomposition (Falloon and Smith, 2000). The distribution of SOC into different carbon fractions plays an important role in the dynamics of the global C cycle and soil carbon sequestration (Cheng et al., 2007). Therefore the characterization of SOC fractions is important to assess the processes that affect organic carbon availability for microbial decomposition and storage in soils. The oxidation of the active carbon pool determines the soil-atmosphere exchange carbon fluxes influencing the functioning of the ecosystems and nutrient cycling for maintaining the quality of soil and its productivity (Zou et al., 2005). The stable carbon pool is responsible for long-term carbon storage in soils, which contributes to SOC storage.

Soil organic nitrogen plays an important role in carbon dynamics and is closely linked to the carbon cycle through biotic processes associated with vegetative productivity and SOM decomposition (Post and Mann, 1990). SON is one of the most important nutrients for plants, and affects significantly plant growth, soil fertility and crop yield (Brady and Weil, 2002). The losses of soil nitrogen are due to the harvesting of crops, leaching, volatilisation and soil erosion (Udawatta et al., 2006).

Soil management practices can determine whether soils behave as sources or sinks of atmospheric CO_2 . The SOC is stabilized in soils by its physical protection within aggregates, resulting in longer decomposition rates of SOM (Cerdà, 1996). Moreover, soil aggregate formation is an indicator of soil stability (Blanco-Moure et al., 2012) and erodibility (Bryan, 1971). Changes in land use from forest which play an important role in carbon exchange with the atmosphere and represent primary soil carbon sinks (Zhang et al., 2011) to cultivated arable land produce a decrease in the SOC content and can reduce soil aggregation and stability, increasing the erosive processes (VandenBygaart et al., 2003). The examination of the relationships between land use change and their impact on SOC dynamics is needed to promote soil sustainability.

Agriculture plays a major role in the global fluxes of carbon dioxide modifying carbon inputs through the variation in land use, tillage and cropping practices (Bruce et al., 1999). The potential and ability of cultivated soils to stabilize carbon and its implications for soil degradation depends

on the amount of plant residues (management practices) and the degree of soil organic carbon decomposition which are vital factors in the formation and stabilization of aggregates, which in turn improve soil structure and drive soil organic carbon sequestration (Lal, 2004). Thus, SOC pool dynamics and carbon sequestration is especially of interest in agricultural mountain Mediterranean landscapes that have been intensively cultivated for several centuries (García-Ruíz and Valero-Garcés et al., 1998; Navas et al., 2014).

The capacity of soils to sequester carbon has received greater attention recently in response to worldwide concerns over the potential climatic impact of increasing CO_2 levels in the atmosphere (Davidson and Janssens, 2006). The need for strategies to mitigate the potential feedbacks to climate change in the global carbon cycle has triggered a vast amount of research (Mishra et al., 2010) to assess the effects of different agricultural practices on carbon sequestration and on the SOC dynamics (Whisler et al., 2016).

In agricultural soils, long-term monitoring of the effects of using conventional tillage and conservation agriculture measures (such as conservation crop rotations, reduced tillage, cover crops, and no-tillage), is essential to evaluate the main factors involved in terms of soil structure degradation and aggregate disruption with subsequent impacts on soil carbon sequestration (Paustian et al., 1997; Fernández-Ugalde et al., 2009).

The incorporation of crop residues has demonstrated to improve the soil structure and increase SOC accumulation (Blanco-Moure et al., 2013; Álvaro-Fuentes et al., 2014) besides helping to control erosion (García-Franco et al., 2015). Estimates of SOC stocks and their changes over the time in agricultural soils are essential to understand SOC dynamics and to identify what management practices may sequester carbon in the soil creating a carbon sink for atmospheric CO₂ over different time scales depending on how and where carbon is stored in soils (Álvaro-Fuentes and Paustian, 2011).

Over the last 30 years a number of SOC dynamics models have been developed to understand the impact of land management on SOC stocks and fluxes (e.g. CENTURY, Roth-C, ICBM, DNDC). These plant-soil models represent SOC dynamics on landscape units using various conceptual carbon pools that follow first order kinetics. Although traditionally these models omitted the impact of erosion and deposition on SOC dynamics, effort has been made to increasingly include its effect as it is the case of CENTURY5 version the EDEM model (Liu et al., 2003) or the SOrCERO model (Billings et al., 2010). Despite the progress, these models remain based on a single profile or landscape unit, not allowing the full characterization of dynamic landscapes.

To overcome this spatial limitation, combined soil erosion and SOC dynamics models are increasingly being used to understand the temporal and spatial significance of the impact of soil erosion on SOC and the carbon cycle. This is the case of the SPEROS-C model (Van Oost et al., 2005) that combines the soil erosion SPEROS model (Van Oost et al., 2003) and the SOC dynamics ICBM model (Andrén and Kätterer, 1997) and allows the spatial analysis of soil redistribution and its effect on SOC dynamics in agricultural landscapes. The model has been successfully implemented to simulate SOC dynamics at different scales (Dlugo β et al., 2012; Nadeu et al., 2014) and is, thus, a suitable tool to simulate diffusive rill and tillage induced soil redistribution processes for catchment areas up to several thousand hectares. Spatial patterns of SOC pools could be an aid for understanding the effect of land management on SOC dynamics in

agricultural soils to elucidate the lateral and vertical carbon fluxes and their relationships with soil redistribution in order to know if an agricultural system acts as a sink or source of carbon.

During the last decades, changes in land use and management have influenced the soil redistribution processes and soil properties on agricultural soils. Therefore there is an increasing need for reliable information on soil erosion in Mediterranean agricultural landscapes at detailed scale to analyze the spatial redistribution of soil and the mobilization of nutrients. The evaluation of the relationships between the spatial distribution patterns of soil properties, soil redistribution processes and soil nutrients will allow a greater knowledge of soil status and conservation to improve soil carbon sequestration and to mitigate soil degradation, which is vital to ensure sustainability of fragile Mediterranean mountain agroecosystems.

1.1. Objectives

Awareness of soil degradation and erosion affecting agricultural soils in Mediterranean mountain agroecosystems require data analysis based on field measurements on the current situation of soil functions and processes. In addition, despite growing recognition of the influences of water and tillage erosion processes on SOC dynamics, the information gap concerning the combined effect of both processes on SOC pools limit our understanding regarding the fate of eroded C.

The interaction between soil redistribution and environmental conditions (soil properties, and topography characteristics) remain a key question to be studied in agricultural fields of median mountain Mediterranean areas that occupy preferentially the valley floors.

We are faced with the following research questions: What are the main drivers and factors affecting soil and nutrient redistribution in cultivated fields located at the valley floors of a catchment? What are the main effects of soil redistribution on soil conditions in these agroecosystems?

In this research, a rainfed cereal field cultivated since the middle of the XIX century and located in the main agricultural area at the valley bottom of an ungauged catchment has been established as study site. This field was selected because of its contrasted topography and physiographic characteristics and because it exhibits common features with the agricultural systems in Mediterranean agrosystems such as the cultivation of season cereals in small fields along the valley floors.

The overall objective of this thesis focuses on the study and analysis of the processes related to soil erosion and redistribution and their effect on soil physico-chemical and magnetic properties and soil nutrients dynamics at field scale. To achieve this main goal a set of specific objectives have been defined in the same line of research as the published articles included in this thesis to fulfill a thematic unit.

The specific objectives are related to:

Soil properties

determine soil physico-chemical properties and magnetic parameters to identify the current conservation status of the soil.

- assess the relationships between the soil physico-chemical properties, magnetic parameters and topographic attributes to infer the control factors which determine their spatial variability.
- examine the influence of soil processes on the depth distribution of soil physico-chemical properties and magnetic parameters by comparing topsoil and bulk soil samples.
- assess soil magnetic parameters related to magnetic mineralogy to infer pedogenic processes and soil formation conditions.
- verify the use of portable magnetic susceptibility meter by comparing field measurements with data acquired in the laboratory for mapping and screening the contents of magnetic minerals in cultivated soils.
- create high precision digital elevation models (DEMs) and examine their suitability at different resolutions for modelling soil redistribution.

Soil redistribution patterns

- \blacktriangleright assess the spatial soil redistribution rates by applying the radiotracer ¹³⁷Cs.
- ► investigate the suitability of spatially distributed models based on empirical models for assessing soil redistribution by comparing the results with the ¹³⁷Cs derived soil redistribution rates.
- ▶ infer the main erosion process operating within the study field by modelling water and tillage erosion and quantifying both contributions separately.
- ► identify soil erosion and deposition areas to infer the implications on the spatial patterns of soil properties.
- ► assess the hydrological and erosion response of the study field during an exceptional rainfall event under fallow conditions.

Soil nutrients dynamics

- examine the relationships between the spatial patterns of soil nutrients (SOC and SON), soil properties and topographic characteristics.
- characterize soil organic carbon pools and evaluate the role of land use changes and soil redistribution processes in SOC pools dynamics.
- identify sinks and sources of soil organic carbon and nitrogen and its interplay with soil redistribution at field scale.
- evaluate the implications of land use changes on SOC depth distribution by comparing topsoil and bulk soil samples and their consequences for soil carbon sequestration.
- ▶ modelling SOC stocks and carbon fluxes to examine the effect of different land management on SOC dynamics at different temporal scales.

1.2. Research contributions

This dissertation contributes to existing studies focused on the interaction between soil redistribution processes and soil properties at field scale and its implication on soil status and quality. In this research a detailed assessment of the magnitude and impact of soil redistribution processes on soil conditions and soil organic carbon dynamics was obtained through an exhaustive field survey, subsequent soil analyses and interpretation of the results.

Soil magnetic susceptibility measurements provided a cost-efficient tool for assessing the relationships between soil redistribution processes and soil magnetic properties in cultivated Mediterranean fields aimed to explore the possibility for inferring soil conditions regarding to soil conservation status. In addition, *in situ* magnetic susceptibility measurements of topsoils have been proved a useful tool for screening the contents of magnetic minerals in cultivated soils with low magnetic signal as the study soils. A novel experimental method proposed by Chaparro and Sinito (2004) to discriminate magnetic phases has been applied in the study field to examine the soil formation conditions associated to the presence of certain magnetic mineralogy.

Papers I, II and *III* contributes to further knowledge on the application of soil magnetic properties to derive useful information on soil processes associated to soil degradation and soil redistribution in Mediterranean cultivated soils.

Paper IV is of interest for carrying a detailed field survey to characterize the hydrological response and the effects of water erosion at field scale due to an exceptional rainfall event (200–265 mm in 2.5 days) occurred in the Central Spanish Prepyrenees (October, 2012). This research contributes to fill a gap in soil erosion modelling studies for exceptional events at field scale and under fallow conditions.

The research included in *Paper V*, ¹³⁷Cs derived soil redistribution rates provided a spatially distributed dataset to implement and calibrate the soil erosion and sediment delivery model WATEM/SEDEM within the study field. The novelty of combining ¹³⁷Cs and WATEM/SEDEM models in Mediterranean agrosystems offers great potential to assess the main controls of soil erosion which is an important requirement for sustainable land management. Moreover, this study contributes to the current requirements for quantifying soil loss in arable lands to establish soil conservation strategies to prevent and control soil erosion through monitoring and long-term modelling. The sound results derived from this study also contribute to gain knowledge on the functioning of soil redistribution processes at field scale in intensively intervened agricultural landscapes by human activity. Such studies are very scarce especially in Mediterranean environments.

A novel method for the characterization and determination of SOC fraction contents using a dry combustion method assayed for this research was developed in *Paper VI*. In this study, a methodological approach was carried out to examine the relationships between the patterns of SOC and SOC fractions distribution with the land use and soil redistribution processes along a representative toposequence of Mediterranean agroecosystems with similar characteristics to the area of the study field.

The relationships between the spatial variability of soil redistribution, soil properties and the SOC pool dynamics are still poorly understood and scarcely documented in Mediterranean mountain agroecosystems. *Papers VII* and *VIII* contributes to understand the effect of soil redistribution processes on the spatial patterns of soil nutrients for developing and implementing land management strategies to preserve soil quality in Mediterranean agricultural areas.

Modelling carbon fluxes in *Paper VIII* is useful for understanding SOC dynamics in Mediterranean agroecosystems and also for assessing the effects of management and land use on carbon dynamics and soil productivity. Thus this study may help to improve the current limited implementation of SOC modelling at different temporal scales in Mediterranean agroecosystems.

The results of the present study may help to improve the current scarce knowledge of SOC dynamics in intensively anthropogenized and topographical complex Mediterranean agroecosystems at field scale that can explain why soil characteristics, land use and redistribution processes are factors that determine the differences in enrichment or depletion of SOC.

The results of this dissertation could be extrapolated to similar agricultural systems because of the location and the particular topography of the study field which is a common feature of the agricultural fields in the valley floors of the Prepyrenean region.

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Chapter 2

Materials and methods



Cover photograph from left to right:

Mini disk infiltometer (Decagon Devices, Inc.) Soil moisture sensor SM200 (Delta-T Devices, Ltd)

2. Study area

The study area is a rainfed cultivated field located in the northeast of Spain in the region of Cinco Villas, Zaragoza (Figs. 1a and b). The study area is 110 km far from Zaragoza and 10 km far from Castiliscar on A-127 direction Sos del Rey Católico (Fig. 1c).



Fig. 1. (a) Location of the study area in the northeast of Spain and detailed view of the study field. (b) General view of the study area. (c) Geographic location of the study area.

The field (1.6 ha) is located in the central part of the Ebro Basin particularly in the east part of the Aragón river basin (Fig. 2a). It was selected because is a representative cultivated field of the Mediterranean mountain agroecosystems. Other reasons for selecting this field were its contrasted topography and physiographic characteristics as it is located at the bottom valley of the catchment. Most of agricultural fields in these mountain landscapes are located on valley floors. Furthermore, changes in the topography, manmade structures and past agriculture practices are well known by the owner. The average altitude is approximately 630±3.2 m a.s.l ranging from 622 to 636 m and the mean slope is 7.4% ranging from 1.1 to 19%.

The field can be considered isolated from a hydrological point of view because it is delimited by manmade infrastructures in the north and west parts by a paved trail and a narrow drainage ditch, respectively. *La* Reina gully borders the field in the east and south limits of the field. *La Reina* gully extends to the *Vandunchil* gully which is a tributary of the *Castiliscar* stream within the Aragón river basin (Figs. 2b and c).

The field has been cultivated for the last 150 years and consequently soil is thoroughly mixed within the plough layer. Conventional tillage practices have been carried out in the study field from 1959 to 1995 using a mouldboard with tractor at a ploughing depth between 25 and 30 cm. For the last 15 years (1995–2010) reduced or minimum tillage has been implemented using chisel with tractor at a ploughing depth between 15 and 20 cm and during the soil survey and sampling the

field has remained fallow. Crop rotation has not been done in the field and the main crop is winter barley (*Hordeum vulgare*) and occasionally wheat (*Triticum aestivum L*.). The vegetation bordering the field is a bottomland forest typical of riparian system in Mediterranean ecosystems with *Quercus coccifera*, *Q. ilex* and *Populus Alba*.



Fig. 2. (a) Location of the study field in the Ebro basin and within the Aragón river basin. (b) Location of the main gullies. (c) Photos of the *La Reina* gully with and without water.

The climate is continental Mediterranean characterized by cold winters and hot and dry summers. Rainfall events mainly occur in spring (April and May) and autumn (September and October) and the summer drought between the two humid periods. In the study area, the mean annual temperature is 13.4 °C and the mean annual rainfall is about 500 mm. The field has homogeneous conditions of parent material and type of soil. Soils in the study area were classified as Calcisols (FAO, 2006) developed on Quaternary deposits (Fig. 3a) which are mainly formed by alluvial deposits and characterized by a basic pH and a secondary accumulation of carbonates.

3. Methodology

3.1. Soil sampling

A total of 613 sampling sites were established on a 5x5 m grid (Fig. 3b). Soil sampling campaigns were carried out in 2009 and 2010 to collect a total of 613 topsoil samples with a 4 cm diameter manual core driller at 5 cm depth and 613 bulk core samples using a 7 cm diameter automatic core driller at 30 cm at the same sampling points where topsoil samples were collected. The sampling depth for the bulk core samples corresponded with the thickness of the plough layer. If the sampling point was considered to be at depositional site by field observations the sampling depth was increased up to 50 cm in order to ensure the sampling of the entire ¹³⁷Cs profile.

Two reference sites were selected to assess ¹³⁷Cs and soil nutrients under original vegetation cover and establish the local reference inventories of ¹³⁷Cs, soil organic carbon and nitrogen (SOC and SON) for the study field. One is adjacent to the study field and the other is separated 2 km (Fig. 3b). The two selected reference sites complied with the characteristics of a stable reference area under original vegetation cover. Both reference sites are on flat undisturbed areas under typical Mediterranean forest vegetation with *Quercus coccifera* and *Q. ilex* and are not affected by erosion

or deposition processes. Soils in the reference area were shallow and poorly developed Calcisols (FAO, 2006).

A total of 21 soil profiles were sampled until the parent material was reached, with depth ranging from 25 to 40 cm. Sampling was done using a 7 cm diameter automatic core driller. Five soil profiles were sectioned at 5 cm increment in order to examine the vertical distribution of ¹³⁷Cs, SOC and SON.

Bulk, topsoil and reference soil samples were packed, weighed, labelled and stored at 4°C prior to laboratory analysis. Samples were air-dried and passed through a 2-mm sieve to separate the coarse (>2 mm) and fine (<2 mm) fractions. Both soil fractions were weighed and the fine fraction was used for soil analyses in the laboratory.



Fig. 3. (a) Geologic map of the study area (source: IGME http://cuarzo.igme.es/geoveo2/). (b) Orthophoto of the study area showing the study field and the two reference sites. (c) Sampling sites within the study area.

3.2. Topographic attributes

A detailed digital elevation model (DEM) of the study field was generated based on elevation data measured at 5x5 m (n=617) using a Geodolite 506 total station with an angular precision of 6" and a distance accuracy of $\pm5\text{mm}\pm5\text{ppm}$ to capture the topography in detail and create a DEM at high spatial resolution. In addition, elevation was measured on 49 points located around the limits of the study field using the same total station to avoid interpolation edge effects (Fig. 3c).

First, a DEM of the study field was created at 5 m and at 1 m resolutions using the triangulated irregular network to characterize the topographic surface of the study field and derive the primary topographic attributes directly from the DEM as elevation, slope, aspect, concavity and convexity (Papers I, III, IV). A DEM with 2.5 m resolution was created using the Topo to Raster tool in ArcGIS 10.2.1 (Papers V, VII and VIII).

Triangulated Irregular Networks (TINs) represent the surface by a set of contiguous and nonoverlapping triangles connecting the original data points. The Topo to Raster tool uses an interpolation method specifically designed for the creation of hydrologically correct DEMs with a connected drainage structure. This tool is based on the ANUDEM methodology from the Australian National University. The latest version of the ANUDEM program developed by Hutchinson (1988) is included in the Spatial Analyst toolbox (Liu et al, 2009) within ArcGIS 10.2.1.

The drainage pathway of the study field is not homogeneous showing two main different directions with northeast and southeast components. Four hydrological units were identified and delineated within the study field according to field observations and topographical surveys (Fig. 4). The divides of the hydrological units were defined on the basis of the digital elevation model together with field observations. The limits of the hydrologic units were coincident with convex zones where there was divergent flow.

The hydrological units U1 and U2 were located upslope with a mean elevation of 632.2 m and 632.1 m respectively. Both units had higher mean slope values (8.5% and 9.2%, respectively), compared to U3 and U4 units located downslope. The U3 and U4 units had lower mean elevations, 631 m and 627 m, respectively, and lower mean slope values of 7.2% and 5.7%, respectively.

The topography at the northern unit U2 was characterized by a contrasting morphology of the land surface related to the development of a gully system, however the southern part was relatively flat. The three northern hydrological units (U1, U2 and U3) drained into the main ephemeral stream. These three units had a flow with a northeast component whereas the south hydrological unit (U4) had flow lines with south component draining into a single outlet point.



Fig. 4. DEM of the study field and photos in six sites with different topographic characteristics. Runoff flow lines and the four hydrological units.

3.3. Magnetic parameters

The magnetic susceptibility in soils is a fast and non-destructive technique to quantify the degree of magnetization of a soil in response to an applied magnetic field. Soil magnetic susceptibility is used to detect the presence and infer the concentration of magnetic minerals.

Volumetric magnetic susceptibility (κ) is the ratio of the induced magnetization to the applied magnetic field (Mullins, 1977). The κ is a dimensionless parameter (10⁻⁵ SI) that was measured in the field on the same 5 m grid of the soil sampling points using a MS2 susceptibility meter and a MS2D probe handle (Bartington Instruments Ltd.).

The MS2D sensor has a mean diameter of 185 mm and operates at 958 Hz with an alternating current producing an alternating magnetic field at 80 A m⁻¹ (Bartington Instruments Ltd., 2000). The MS2D sensor integrates the magnetic signal within an effective range of its coil. In general, the contribution comes from an area of about 270 cm² and the top 6–10 cm of the land surface. The sensitivity of the MS2D loop is 90% and 10% at 2 and 60 mm from the contact surface, respectively (Dearing, 1999) and 95% of the magnetic susceptibility signal comes from the upper 8 cm of the soil surface and the integrated volume corresponds to 4300 cm³ (Lecoanet et al., 1999).

The MS2D loop sensor was placed into contact with the soil surface next to the sampling point (n=613) where soil samples for the laboratory measurements of magnetic susceptibility were done. Before taking a reading it is necessary to remove any vegetation to avoid rough surfaces. Three readings were taken at each sampling point and the mean value was considered for data analysis. In general, the surface of the MS2D loop sensor cannot be completely in contact with the soil surface during field measurements thus the sensor is calibrated according to the surface roughness. On rough soil surface the sensor is calibrated to read 0.5 of the volumetric magnetic susceptibility value and on smooth surfaces as in the study field it is calibrated to read 0.75 of the volumetric magnetic susceptibility value so the mean value of the three readings taken at each sampling point was corrected according to the equipment recommendations (Bartington Instruments Ltd., 2000).

The mass-specific susceptibility is $\chi = \kappa/\rho$, where κ is the volumetric magnetic susceptibility (dimensionless) and ρ is the density (kg m⁻³). The χ is expressed as 10⁻⁸ m³ kg⁻¹. The χ value is proportional to the concentration of the ferrimagnetic minerals (magnetite and maghemite) in the sample, and is also sensitive to the magnetic grain size (Dearing, 1999). Mass-specific susceptibility is a magnetic concentration-dependent parameter, and their values vary according to the nature of materials, i.e. diamagnetic (~ $-6 \cdot \times 10^{-9}$ m³ kg⁻¹), paramagnetic (~ 10^{-6} m³ kg⁻¹), antiferromagnetic (~ $6 \cdot 7 \cdot \times 10^{-7}$ m³ kg⁻¹), and ferrimagnetic materials (~ $0.5 - 5.6 \cdot \times 10^{-3}$ m³ kg⁻¹) (Maher et al., 1999).

Mass-specific susceptibility was measured on the soil fine fraction of bulk (n=613) and topsoil samples (n=613) in the laboratory with a Bartington MS2 meter linked to a MS2B dual frequency sensor (Bartington Instruments Ltd.). The sensor is used with 10 ml soil sample containers and operates with an alternating current producing an alternating magnetic field at 80 A m⁻¹ (Bartington Instruments Ltd., 2000). The sensor can be operated at two different frequencies, at low frequency (0.47 kHz, χ_{LF}) and at high frequency (4.7 kHz, χ_{HF}). Soil samples were measured at each frequency for studying the frequency dependence of susceptibility. If single frequency measurements are needed, the low frequency is selected and measured.

The frequency dependence of magnetic susceptibility is expressed as percentage (χ_{FD}):

 $\chi_{FD} \% = [(\chi_{LF} - \chi_{HF}) / \chi_{LF}] \times 100$

Three measures of mass-specific susceptibility were taken from each soil sample and the average was selected for data analysis. Mass specific magnetic susceptibility at low and high frequency measurements was expressed as 10^{-8} m³ kg⁻¹.

Detailed magnetic studies using destructive measurements from the magnetic point of view, that is anhysteretic remanent magnetization (ARM) and isothermal remanent magnetization acquisition (IRM) were carried out on thirty bulk soil samples.

Bulk soil samples were selected at three different slope positions. Ten samples for each part of the slope (upslope, middle and bottom slope) were chosen in order to account for soil processes related with the topographical position along the slope that might influence soil magnetic properties. Selected soil samples were subsampled and placed on plastic containers (2.3 cm³) and fixed using sodium silicate for remanence magnetization.

Anhysteretic remanent magnetization was acquired using a partial ARM (pARM) device attached to a shielded demagnetizer Molspin Ltd., superimposing a dc bias field of 90 μ T to an alternating magnetic field (AF) of 100 mT, during its decay [100; 2.5 mT] and an AF decay rate of 17 μ T per cycle.

The remanent magnetization was measured by a spinner fluxgate magnetometer Minispin, Molspin Ltd. Anhysteretic susceptibility (κ ARM) was estimated using linear regression for ARM acquired at different DC bias fields (7.96, 47.75 and 71.58 A m–1). Related parameters, such as, King's plot (κ ARM versus κ , King et al., 1982) and the κ ARM/ κ -ratio were also calculated.

Isothermal remanent magnetization was acquired using a pulse magnetizer model IM-10–30 ASC Scientific. Each sample was magnetized by exposing it to growing stepwise dc fields, 27 forward steps from 4.3 to 2470 mT. The remanent magnetization after each step was measured using the Minispin magnetometer.

Isothermal remanent magnetization acquisition curves and SIRM were found using forward dc fields. Remanent coercivity (*H*CR, the backfield required to remove the SIRM, or IRM = 0) and *S*-ratio (= -IRM-300/SIRM, where IRM-300 is the acquired IRM at a backfield of 300 mT) were also calculated from IRM measurement, using a series of backfield demagnetization measurements allow the SIRM acquisition.

A new experimental method proposed by Chaparro and Sinito (2004) was carried out in order to discriminate magnetic phases. The method is based on the responses of different assemblages of magnetic materials when they are subjected to a pulse-magnetizing field and a demagnetizing alternating field and it separates the bulk backfield IRM curve into two individual magnetic phases experimentally.

The method is only carried out for backfield IRM measurements (Chaparro et al., 2005). First, backfield measurements without AF demagnetization are conducted [backIRM(#i), i indicates the backfield magnetization step]. Once the entire process has finished the sample is demagnetized and subsequently subjected to a dc field to acquire its corresponding SIRM again. Secondly, the residual backfield measurements are carried out, that is after each backfield magnetization step; an AF demagnetization at n mT peak value is performed. In this way a residual remanent magnetization [backIRMn(#i)] is measured at each stage of the method.

In this study separation was achieved using a high peak AF value (n = 102.5 mT) as the filter. This AF value is chosen according to the markedly different response of soft and hard magnetic materials.

From both measurements, the backIRM(#i) and backIRM102.5(#i), two magnetic phases (Phases 1 and 2), obtained by subtraction can be drawn,

Phase2(#i) = backIRM102.5(#i)

Phase1(#i) = backIRM(#i) - backIRM102.5(#i).

Based on this discrimination, it is possible to calculate the SIRM for each phase and its corresponding magnetic contribution (%) to the total SIRM, as well as, the *H*CR and *S*-ratio for each phase.

Thermomagnetic measurements were carried out on six bulk soil samples (0.4–0.5 g) using a home-made horizontal magnetic translation balance (Escalante and Böhnel, 2011) built in the Laboratory of Palaeomagnetism (Centro de Geociencias, UNAM, University of Mexico). This instrument measures the temperature dependence of high-field magnetization; basically it measures the force on specimens subjected to a magnetic gradient (Collinson, 1983), which is compensated by an electronic feedback system to hold the specimen in a fixed position. The non-uniform field was produced by an electromagnet with special shape of pole pieces, which was controlled during the experiment with a power supply at constant current. At the measuring position, the magnetic field was 500 mT and was measured using a Hall effect magnetometer. The temperature was controlled and the force recorded with a sensor that generates an output voltage. Such voltage is acquired using a PicoLog \mathbb{R} recorder. In this study, the relative values of induced magnetization (M/MRT) are of interest; hence theM/MRT-T curves are presented. Measurements were performed in air. Each sample was heated to a temperature of about 700 °C and subsequently cooled to room temperature with a controlled heating/cooling rate of 30 °C min⁻¹.

3.4. Soil physico-chemical properties

The fine fraction of soil samples was analyzed for soil texture, pH, electrical conductivity, soil organic matter, carbonates content, volumetric soil water content and soil infiltration.

Stoniness expressed as a percentage is determined by dividing the weight of the coarse fraction (>2 mm) by the weight of the total soil samples and multiplied by 100.

Particle-size analysis was carried out on bulk samples (n=613) on 5m grid and topsoil samples (n=156) on 10 m grid with a Beckman Coulter LS 13 320 laser diffraction particle size analyser using the Fraunhofer model based on Fraunhofer theory of light scattering combined with Beckman Coulter's patented Polarization Intensity Differential Scattering (PIDS) technology.

These two readings are combined to provide a continuous particle size range of $0.017-2000 \mu m$. The Fraunhofer optical model was selected because is preferred to carry out the particle size analyses in carbonate rich soils as in the study field (Murray, 2002).

Before textural analysis the organic matter was eliminated by pretreating the soil samples with H_2O_2 (10%) heated to 80 °C. The soil samples were then air dried and chemically disaggregated with 2 cc of sodium hexametaphosphate (4%) and stirred for 2 hours after which they were dispersed with ultrasound for a few minutes.

The pH and electrical conductivity (EC, dS m^{-1}) were measured on saturated paste extracts of soil-water ratio, 1:2.5 and 1:5, respectively using a pH-meter and conductivity meter. The pH and EC were determined on soil samples (n= 156) on the 10 m grid.

Soil organic matter content (SOM, %) was determined in bulk soil samples (n=156) on the 10 m grid by dichromate oxidation and subsequent titration with ferrous ammonium sulphate using a Mettler Toledo titrimeter with selective electrode (Guitian and Carballas, 1976).

Total carbonate content $(CO_3^{2^-}, \%)$ was analysed in bulk soil samples (n=156) on the 10 m grid and in topsoil samples (n=613) on 5 m grid using a pressure calcimeter (CSIC, 1976). Dry soil sample (1 g) was treated with 10 ml of dilute hydrochloric acid (50%) in a sealed container connected to the pressure calcimeter. As a result of the carbonate-acid reaction the released CO_2 gas is measured volumetrically. The pressure calcimeter is calibrated with a fixed amount of pure calcimeter has a manometer composed by a glass tube into a U-shape filled with mercury or water. The glass tube is positioned with the curved region at the bottom. The gas from the reaction exerts a force on the liquid (mercury or water depends on the carbonates content) and the difference in the heights of the columns is a measure of the pressure of the gas.

Volumetric soil water content was measured in the field (θ_0) on the 10 m grid (n=156) using the soil moisture sensor SM200 (Delta-T Devices, Ltd.) for evaluating the water regime in the soil. The sensor is a frequency domain reflectometry probe which measures soil dielectric with a 100 MHz waveform. The sensor consists of a durable plastic body (the length of 6.7 cm and diameter of 4 cm) and two stainless steel rods (length of 5.1 cm, diameter of 0.25 cm). The sensor was inserted into the soil when acquiring the measurement next to the same 10 m grid of sampling points established to collect the soil samples for laboratory analysis. Three measurements were carried out and its average value has been considered for data analysis.

Soil water retention characteristics are estimated by determining volumetric soil water content at saturation (θ_s), field capacity (θ_{FC}) and permanent wilting point (θ_{PWP}) in the laboratory using water saturated porous plates (Richards, 1947). The field capacity and the permanent wilting point were measured using the pressure membrane apparatus Soil Moisture Equipment Co., Santa Barbara California models 1200 and 1000, respectively. Volumetric soil water content at 1, 0.33 and 15 atmospheres, respectively.

Soil samples were placed in retaining rubber rings (4.6 cm in diameter and thickness 1.1 cm) on the porous pressure plate and were wetted from below with distilled water for 24 hours. Before placing soil samples on pressure plate, it was saturated by submerging in distilled water for 24 hours.

After saturation to determine volumetric soil water content at saturation, soil samples were weighed and dried for 24 hours in a furnace at 105 °C and re-weighed. To determine volumetric soil water content at field capacity and permanent wilting, saturated soil samples were placed into a pressure chamber in which the air pressure is 0.33 and 15 bars, respectively. Pressure was applied for 24 hours and after removal the pressure soil samples were weighed and dried for 24 hours in a furnace at 105 °C and re-weighed.

The Mini disk Infiltometer is a quick way to test undersaturated hydraulic conductivity and infiltration rates. The Mini Disk Infiltometer (Decagon Devices, Inc.) is a small, compact and simple field instrument for measuring soil undersaturated hydraulic conductivity. The infiltrometer was placed on a smooth soil surface vertically. Record water volume infiltrated at regular time intervals. Collected data were used as cumulative infiltration *versus* time. Water begins to leave the lower chamber and infiltrate into the soil at a rate determined by the hydraulic properties of the soil.

Soil organic carbon content (%) was measured by dry combustion method using a LECO RC-612 multiphase carbon analyser (Leco Corp., St. Joseph, MI). The dry combustion method is based on thermal oxidation of the sample at an established temperature (Nelson and Sommers, 1996). LECO devices consist of a furnace where a sub-sample of <2 mm soil (0.1500 g) previously grounded with a mortar and pestle is introduced and combusted into flow oxygen. Soil organic carbon content was measured at 550 °C. The CO₂ gas evolved after combustion was determined by infrared analysis (Bremner, 1996).

The characterization of SOC carbon fractions was carried out using LECO, RC-612 multiphase carbon analyzer. The temperature of the furnace was stepped at 350 °C and 550 °C to oxidize the active (ACF) and stable carbon fractions (SCF), respectively. Because the decomposition of the most thermally labile components of SOC is released at approximately 300–350 °C and the decomposition of more refractory and stable carbon occurs at higher temperatures (420–550 °C) (López-Capel et al., 2008).

Soil nitrogen content (%) was measured with the dry combustion method using a LECO CN TruSpec carbon and nitrogen analyser which operates on the same principle of the LECO RC-612 multiphase carbon analyser consist of a furnace where a sub-sample of <2 mm soil (0.1500 g) previously grounded with a mortar and pestle is introduced and combusted into flow oxygen. Soil nitrogen was measured by determining the NOx gas evolved after combustion at 950 °C by a thermal conductivity detector (LECO, 2006). The SOC, SOC fractions and SON contents were converted into contents per surface area expressed as inventories or stocks (kg m⁻²) multiplying the content by the mass of the fine fraction and dividing by the surface of the core sampler.

The massic activity of ¹³⁷Cs was measured using a high resolution, low background, low energy, hyperpure coaxial gamma-ray detector coupled to an amplifier and multichannel analyser. The detector has an efficiency of 50%, and a 1.9 keV resolution (shielded to reduce background), and was calibrated using standard soil samples in the same geometry as the measured samples. Gamma emission of ¹³⁷Cs was measured at 661.6 keV with counting times over 30,000 s and the analytical precision of the measurements is around 5% (95% level of confidence). The content of ¹³⁷Cs in the soil sample is expressed as a concentration or massic activity (Bq kg⁻¹) and as activity per unit area or inventory (Bq m⁻²). The inventory was calculated using the mass of the fine fraction and the cross section of the core sampler (Navas et al., 2005).

3.5.Data analysis

Classical descriptive parameters including mean, minimum, maximum, coefficient of variation (CV), standard deviation (SD), and skewness were determined by using SPSS 19.0 (Chicago, IL,

USA) for Windows. The distribution of variables was evaluated by using the Kolmogorov-Smirnov test.

The statistical significance of the relationships between soil properties, physiographic factors and soil redistribution rates were assessed using the Pearson's correlation coefficients and linear regression analyses.

Analysis of variance (ANOVA), Fisher Least Significant Difference tests and Kruskal–Wallis tests were performed to analyse the difference between the means of different groups. Tukey's mean difference was used at the 5% probability level to separate the effects.

Factor analysis was used to reduce and simplify the representation of the relationships between a set of interrelated variables. The number of factors was determined using the eigenvalue-one criterion, which determines that factors with eigenvalues greater than 1 are to be extracted. The applicability of the factor analysis in the data sets used in this study was verified by applying Bartlett's sphericity and Kaiser–Meyer–Olkin (KMO) tests.

Confusion matrices were computed to compare the measured and simulated soil redistribution rates. The confusion matrix allows computing a number of useful prediction statistics when applied to simulation model output (Beguería, 2006).

Statistical analysis of NS model efficiency and linear regression were carried out using R Statistical Software v.3.1.2 (R Core Team, 2014). Plots were created using the R package ggplot2 (Wickham, 2009).

Soil texture data are compositional and require special considerations before the application of standard multivariate analysis (Loosvelt et al. 2013). For this purpose clay, silt and sand contents were transformed based on the additive log-ratio methodology proposed by Aitchison (1982; 1986). Statistical analyses from untransformed and transformed data have been compared to select the most significant correlations.

The analysis of the spatial distribution from the primary topographic attributes (slope, aspect and concavity-convexity) and soil properties was made using ESRI ArcGIS software 10.2.1. The ordinary kriging method was used to interpolate all the topographic and soil properties analysed in this study into a continuous map.

Kriging is a geo statistical interpolation method that utilizes a variogram which depends on the spatial distribution of data rather than on actual values. Kriging weights are derived using a datadriven weighting function to reduce the bias toward input values, and it provides the best interpolation when good variogram models are available.

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Soil magnetic susceptibility and surface topographic characteristics in cultivated soils



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Cover photograph from left to right:

T-type yellow plastic markers at each sampling point on a 5x5 m grid Geodolite 506 total station

Magnetic susceptibility in topsoils and bulk cores of cultivated Calcisols



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Cover photograph from left to right:

Manual core driller for collection of topsoil samples Automatic core driller for collection of bulk samples Relevant magnetic and soil parameters as potential indicators of soil conservation status of Mediterranean agroecosystems



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Cover photograph from left to right:

MS2 susceptibility meter and MS2B dual frequency sensor (Bartington Instruments, Ltd.) MS2 susceptibility meter and MS2D probe handle (Bartington Instruments, Ltd.) Severe soil erosion during a 3-day exceptional rainfall event: combining modelling and field data for a fallow cereal



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Cover photograph from left to right:

La Reina gully during the extreme rainfall event in October 2012 Ephemeral gully in the study field after extreme rainfall event in October 2012 Estimating erosion rates using ¹³⁷Cs measurements and WATEM/SEDEM in a Mediterranean cultivated field



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Cover photograph from left to right: Rills in the study field Soil hole after soil sampling Lateral and depth patterns of soil organic carbon fractions in a mountain Mediterranean agrosystem



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Cover photograph from left to right: Sectioned bulk soil sample LECO RC-612 multiphase carbon analyser (Leco Corp.) Spatial patterns of SOC, SON, ¹³⁷Cs and soil properties as affected by redistribution processes in a Mediterranean cultivated field (Central Ebro Basin)



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Cover photograph from left to right:

Soil bulk core collected at reference site Plastic containers for gamma-ray analysis Modelling the effect of land management changes on soil organic carbon stocks in a Mediterranean cultivated field



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Cover photograph from left to right:

Quartz boats for soil organic carbon analysis Crop residues in the study field

Chapter 11

Conclusions



Cover photograph from left to right: View of the study field during summer and spring, respectively

Conclusions

Research in a rainfed cultivated field located in the valley floor of a median mountain Mediterranean agroecosystem encompassing *in situ* measurements of soil properties (i.e. elevation and magnetic susceptibility) quantification of edaphic parameters, fallout ¹³⁷Cs measurements and modelling together with field observations at detailed scale, have provided the basis for assessing the relationships between soil properties, soil redistribution processes and soil nutrient dynamics to infer its current soil conditions and status of soil degradation.

Topographic factors are linked to soil drainage and translocation of soil particles thus similar processes that affect the redistribution of soil particles from upslope to downslope positions control the spatial variability of the soil properties within the field.

The spatial analysis of the terrain attributes derived from a high-resolution digital elevation model (DEM) in combination with the application of geostatistical interpolation are useful tools to infer the spatial distribution of soil properties.

The main cause for the spatial variability of magnetic minerals is the redistribution of fine soil components by runoff supported by the direct and statistically significant correlations between finer soil particles (<0.05 mm), magnetic minerals and SOM and by their similar general trends and spatial variability patterns.

The enrichment of pedogenic fine-grained ferromagnetic particles in the upper soil layers is associated with specific soil formation conditions within the plough layer. Soil iron components are good markers of pedogenic processes and can provide an approximation of soil forming environment.

In situ magnetic susceptibility measurements proved to be a useful tool for screening and mapping the contents of magnetic minerals in cultivated soils with low magnetic signal as the study soils to obtain a preliminary reference of the spatial distribution of magnetic minerals in the soil surface layers as a proxy of soil processes.

Soil erosion predominates over deposition within the field. As much as 63% of the sampling points were identified as eroded by ¹³⁷Cs inventory values below the reference inventory (1507 Bq m⁻²). Over 70% of the study field is eroded (average: 19.7 Mg ha⁻¹ yr⁻¹) whereas in the rest the ¹³⁷Cs average soil deposition rates were lower (12.6 Mg ha⁻¹ yr⁻¹). The spatial patterns of WATEM/SEDEM soil redistribution rates with mean erosion of 3.9 Mg ha⁻¹ yr⁻¹ and mean deposition of 5.8 Mg ha⁻¹ yr⁻¹ occurring in 35% of the grid cells of are in good spatial agreement with the ¹³⁷Cs derived estimates.

Constraints for estimating the rainfall erosivity factor (R -factor) due to the limited rainfall records available for the study area underestimates real rainfall and therefore the simulated soil losses. Other limitations in terms of the representation of erosion processes in response to individual rainfall events implies a level of uncertainty for modelling the relationships between rainfall, runoff and erosion particularly in mountain Mediterranean agroecosystems characterized by extreme rainfall events with high contribution to soil loss.

To overcome these soil redistribution modelling limitations this study confirms the potential of using medium term soil redistribution rates derived from ¹³⁷Cs estimates to assess and reduce uncertainties in WATEM/SEDEM model calibration.

The efficiency of the WATEM/SEDEM simulations is highly dependent on resolution and quality of the DEM. Lower performance of WATEM/SEDEM simulations with optimal model parameters in three of the four hydrological units within the study field is related with topographic changes from human activity and impact of heavy machinery. Topographic changes in agricultural fields which are not directly related to water and/or tillage soil redistribution processes may not allow the successful implementation of a topography driven model as WATEM/SEDEM.

The main factor controlling soil redistribution processes within the field is water erosion compared with almost negligible soil redistribution rates by tillage estimated with ¹³⁷Cs using the MBM III model. These results were in line with the optimal values of tillage transport coefficient obtained after calibration of the WATEM/SEDEM model by using ¹³⁷Cs derived soil redistribution rates.

After repeated pulses of rainfall, runoff redistributes soil particles through the gully system that drains the field into the main stream. Removal of finer soil particles by water erosion processes in association with ¹³⁷Cs and relatively rich organic fractions occurred at the end of the gully system and at some points along the edge of the field close to the main stream evidenced by the high soil erosion rates found in the north part of the field (>20 Mg ha⁻¹ yr⁻¹). Enriched sediment in carbonate, coarse and sand fractions are deposited at the end of the gully system whereas finer soil particles are exported out of the field to the main ephemeral stream by runoff.

The *in situ* soil redistribution map which includes small rills and ephemeral gullies within the study field after the 3-day exceptional rainfall event (~235 mm) that affected the study area in October 2012 allows a detailed description of the processes of soil erosion and sediment redistribution suggesting that exceptional rainfall events had important implications on soil redistribution within the field by activating the ephemeral gully system and intensifying erosion processes by water.

Similar redistribution processes affect the spatial patterns of ¹³⁷Cs and soil organic carbon (SOC) within the field whereas the spatial distribution of soil organic nitrogen (SON) was less coincident. The important depletion of soil nutrients compared to the reference inventories is associated with land use changes from forest to cultivated land, tillage practices and soil erosion by runoff.

The analysis of SOC dynamics comparing different land uses along a mountain Mediterranean toposequence revealed that in forest subsoils the relative contribution of the stable carbon fraction was higher than in cultivated soils suggesting that forest soils function as a carbon sink for the fraction which has slow turnover rates.

Vertical distributions of ¹³⁷Cs and SOC are mainly due to physical processes related to redistribution processes and tillage practices. Soil homogenization and mixing by tillage in the plough layer influence the depth distribution of soil properties and SOC dynamics. In cultivated

soils the contribution of stable carbon fraction to SOC is higher compared to forest within the first 20 cm.

In the field, soils were characterized by higher contents of the active carbon fraction (ACF) than of the stable carbon fraction (SCF) and both carbon fractions were higher in topsoil than subsoils as was the case with ¹³⁷Cs and SON contents.

The effect of soil redistribution processes on SOC dynamics is evidenced by the differences between the relative contributions of ACF and SCF to SOC in eroded and depositional points. The higher contributions of ACF to SOC in bulk and topsoil samples at depositional points suggested that, primarily, the smaller and lighter particles of soil enriched in the most bioreactive carbon fraction are removed preferentially downslope by physical processes related to water erosion. Furthermore, at eroded points, the soil loss led to the exposure of relatively enriched subsoil in the stable carbon fraction.

The spatial patterns of modelled SOC stocks using SPEROS-C model and the stocks measured for the last 150 years were in good agreement. However, the best model performance was obtained in the hydrological unit with contrasted topography (U2) which highlights the model's sensitivity to topography. Modelled SOC stocks were lower and significantly different at eroded sites than at depositional ones indicating that the model is able to reproduce the relation between soil and SOC redistribution.

The magnitude of simulated lateral carbon fluxes was related to the type of land management practices. Conventional tillage resulted in the highest carbon losses with a value of 0.14 g C m⁻² yr⁻¹, compared to the period of minimum tillage using chisel (0.04 g C m⁻² yr⁻¹). Multiple scenario analysis showed that the incorporation of crop residues into soil by reduced tillage practices was a good management for increasing SOC in topsoils favoring soil organic carbon sequestration.

Modelling SOC stocks and fluxes in Mediterranean agroecosystems using SPEROS-C is a powerful tool to evaluate agricultural management practices which have a key role in carbon sequestration.

The results of this study could be extrapolated to similar Mediterranean agricultural systems because of the location and characteristics of the study field (i.e. topography, land management, cultivation of season cereal) that are common features of the Mediterranean mountain agroecosystems that occupy the valley floors. In these agroecosystems, maintaining and improving soil quality is an essential component of long-term soil sustainability with environmental and economic consequences.

This study helped to improve the current scarce knowledge of SOC and SOC fractions dynamics in Mediterranean agroecosystems and to highlight the need for further research into mechanisms that can explain the relationships between the spatial variability of soil properties, soil redistribution and soil nutrient patterns and dynamics.

The complexity of mountain Mediterranean agroecosystems as a result of the long history of human impact in relation to changes in land use and management together with the specific climatic conditions of this area, poses significant challenges to predict their responses to multiple driving forces. Further research to mitigate soil degradation in Mediterranean agroecosystems is needed to develop erosion control strategies at the field scale.



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