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ANALYSIS OF DISTURBANCES
IN SOIL CARBON STORAGE AND DYNAMICS

PhD thesis

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Acknowledgments

Preface

The pool of carbon in soils is one of the largest near-surface stores of carbon on Earth. The amount of carbon stored in soils is about three times the amount of carbon in vegetation and twice the amount in the atmosphere. It was estimated that 1500 Pg C are contained in soil organic carbon (SOC) which is the essential component of organic matter. Soil organic carbon is important for the function of ecosystems and agro-ecosystems: on the one hand, SOC is a key indicator of soil quality affecting physical and chemical properties such as soil aggregation, soil water availability, cation exhange capacity, nutrient availability, microbial biomass C, and pH buffering; on the other hand, it is the most active soil carbon pool facilitating redistribution of carbon between atmosphere and other pools in the global carbon cycle. Organic carbon (OC) accumulation in soils reflects the balance of C inputs as organic matter (returns of plant/root residues) and C losses from the soil (as carbon dioxide, dissolved OC and loss through erosion). Carbon stocks in soils are fairly stable under undisturbed conditions (steady state). Pedosphere ecosystem disturbances change SOC level which could potentially alter the atmospheric carbon dioxide CO_2 concentration and the global climate. World soils have been a major source of atmospheric CO_2, with loss of 78± 12 Gt C since 1850, through soil cultivation, deforestation and biomass burning. In contrast soils can also be a major sink of atmospheric CO_2 with adoption of recommended management practices. However, evaluation of soil C sources and sinks is difficult because the dynamics of soil C storage and release is complex and still not well understood. The aim of this work was studying disturbance effects on soil carbon storage and dynamics in order to understand the more suitable land management practices to improve organic matter stabilization and carbon sequestration. This study was composed of three research components that examined consequence of human impact on carbon reservoirs and fluxes. The first paper investigated the effects of land cover and land-use change on the ability of a soil to store carbon and reduce CO_2 emissions using a paired-site approach; the second paper analyzed fire effects on SOC balance and distribution ; the third paper focused on the effects of soil compaction and exposure of the soil surface to rainfall and their interaction on soil CO_2 release.

INTRODUCTION

Human activities contribute to climate change by causing changes in Earth's atmosphere in the amounts of greenhouse gases, aerosols (small particles), and cloudiness. GHGs and aerosols affect climate by altering incoming solar radiation and outgoing infrared (thermal) radiation that are part of Earth's energy balance. The effect of human activity on climate has been a rising temperatures, changing precipitation patterns, sea level rise, decrease in snow and ice extent, loss of biodiversity and shifts in forest types (IPCC 2007a) (Figure 1).

CO_2 and other greenhouse gases (GHGs) have increased since the industrial revolution, and particularly faster in the last 30-50 years (Table 1). Carbon dioxide has increased from fossil fuel use in transportation, building heating and cooling and the manufacture of cement and other goods.
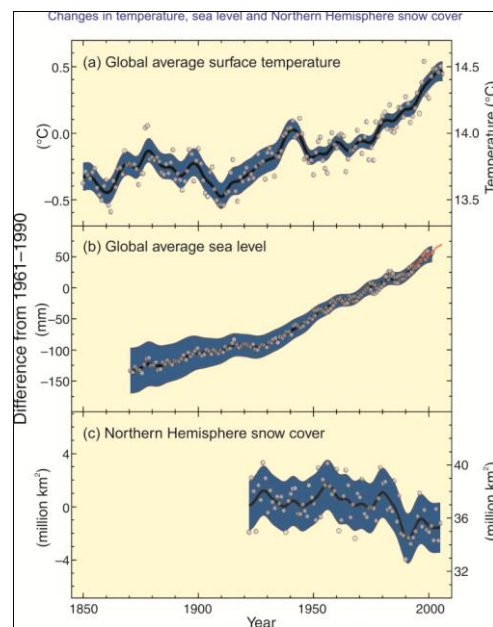
Figure 1. Observed changes in (a) global average surface temperature; (b) global average sea level from tide gauge (blue) and satellite (red) and (c) Northern Hemisphere snow cover for March-April. Smoothed curves represent decadal averaged values while circles show yearly values (IPCC, 2007b).

Table 1. Change in atmospheric concentration of trace gases since the industrial revolution at about 1750

Gas	Concentration 2001	Percent increase since 1750
Carbon dioxide	379 ppm	31
Methane	1745 ppb	151
Nitrous oxide	314 ppb	17
Chlorofuorocarbons	268 ppt	Decreasing

Ppm= parts per million, ppb= parts per billion , ppt= parts per trillion.

Deforestation releases CO_2 and reduces its uptake by plants. Carbon dioxide is also released in natural processes such as the decay of plant matter.

Methane has increased as a result of human activities related to agriculture, natural gas distribution and landfills. Methane is also released from natural processes that occur, for example, in wetlands. Methane concentrations are not currently increasing in the atmosphere because growth rates decreased over the last two decades. Nitrous oxide is also emitted by human activities such as fertilizer use and fossil fuel burning. Natural processes in soils and the oceans also release N_2O.

Halocarbon gas concentrations have increased primarily due to human activities. Natural processes are also a small source. Principal halocarbons include the chlorofluorocarbons (e.g., CFC-11 and CFC-12), which were used extensively as refrigeration agents and in other industrial processes before their presence in the atmosphere was found to cause stratospheric ozone depletion. The abundance of chlorofluorocarbon gases is decreasing as a result of international regulations designed to protect the ozone layer (IPCC, 2010).

The atmospheric level of CO_2, Methane and NO_2 are continuing to rise at an accelerating rate. The IPCC Special Report on Emission Scenarios (SRES) projects a concentration of CO_2 in 2100 range from 540 to 970 ppm (IPCC, 2001). According to various SRES scenarios, a global warming by 1.8-4.0 °C is projected by 2100 with land surface warmer than oceans, along with regional changes in precipitation and sea level rise (IPCC, 2007a).

Among anthropogenic GHGs, CO_2 is the most important and its increase is due to primarily to fossil fuel use, accounting for 57% of the global CO_2 equivalent GHG emissions. Land use change provides another significant but smaller (17.3%) contribution to global increase in CO_2 concentration (Figure 2). The CO_2 emission from land use change sectors have increased from 6.35 GT in 1970, to 9.5 GT in 2004. Over the 19th century and much of the 20th century, the terrestrial biosphere has been a net source of atmospheric CO_2 (IPCC, 2001).
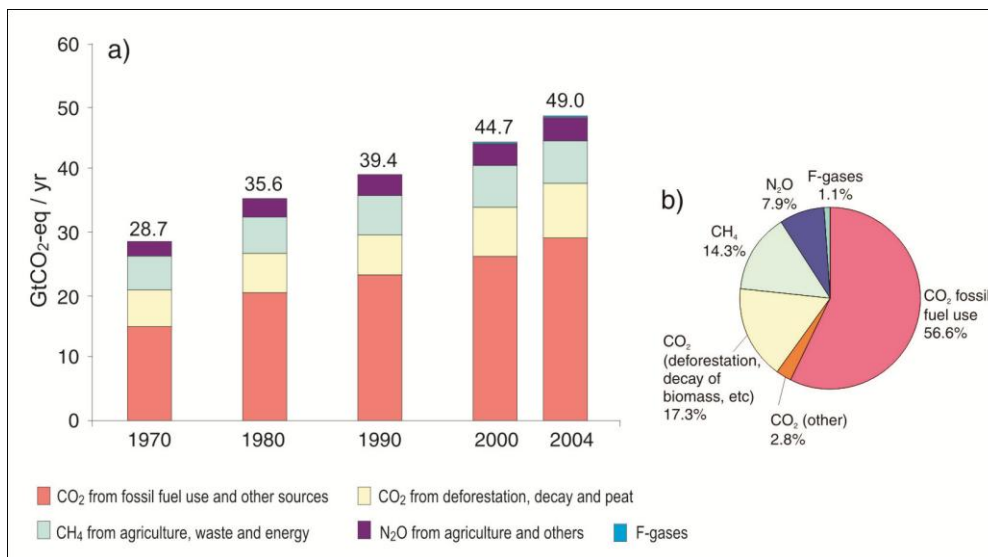
Figure 2   Global annual emission of anthropogenic GHGs from 1970 to 2004. (b) Share of different anthropogenic GHGs in total emission 2004 in terms of carbon dioxide equivalents (CO2-eq) (IPCC, 2007b).

Global Carbon Pools and Fluxes

The Earth contains 10^{23} g of Carbon, which it obtained early during its formation as planet (Schlesinger, 1995). There are four principal pools of global carbon: oceans, geological formations containing fossil and mineral carbon, atmosphere and terrestrial ecosystems (Lal et al., 1995).

Oceans contain 38.000 PgC, most of which is in the form of dissolved inorganic carbon stored at great depths where it resides for long periods of time. A much smaller amount of carbon, approximately 1.000 Pg, is located near the ocean surface. This carbon is exchanged rapidly with the atmosphere through both physical processes, such as CO_2 gas dissolving into the water, and biological processes, such as the growth, death and decay of plankton. Although most of this surface carbon cycles rapidly, some of it can also be transferred by sinking to the deep ocean pool where it can be stored for a much longer time. The largest amount of carbon on earth is stored in sedimentary rocks within the planet's crust. These are rocks produced either by the hardening of mud (containing organic matter) into shale over geological time, or by the collection of calcium carbonate particles, from the shells and skeletons of marine organisms, into limestone and other carbon-containing sedimentary rocks.
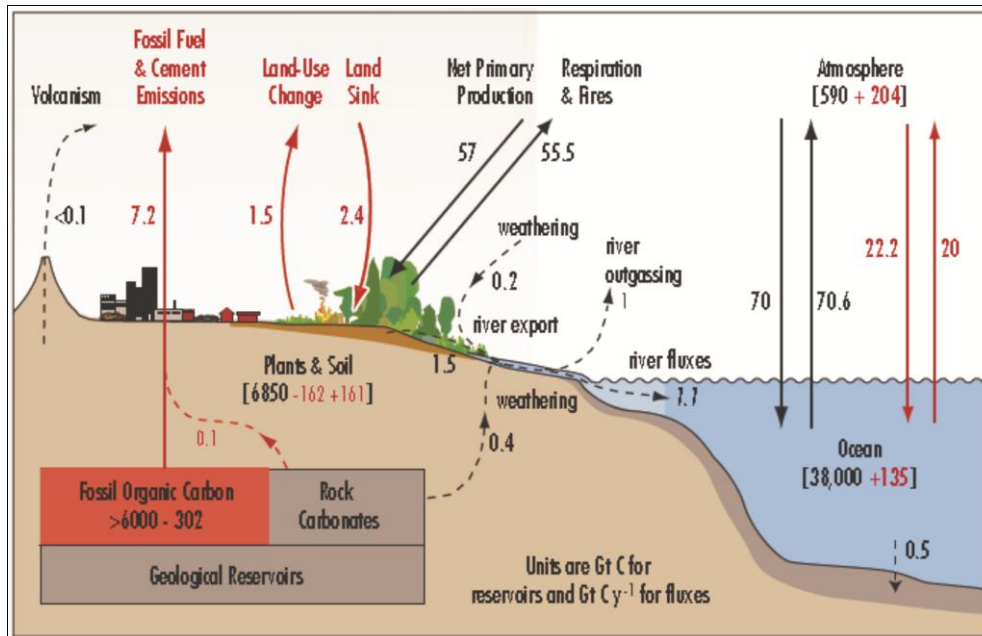
Figure 3. The Global Carbon Cycle. UNESCO-SCOPE 2006

PgC is stored in the Earth's crust as hydrocarbons formed over millions of years from ancient living organisms under intense temperature and pressure. These hydrocarbons are commonly known as fossil fuels. The atmosphere contains approximately 750 PgC, most of which is in the form of CO_2, with much smaller amounts of methane (CH_4 and various other compounds). Although this is considerably less carbon than that contained in the oceans or crust, carbon in the atmosphere is of vital importance because of its influence on the greenhouse effect and climate. The relatively small size of the atmospheric C pool also makes it more sensitive to disruptions caused by increase in sources or sinks of C from the Earth's other pools.

Terrestrial ecosystems contain 2100 PgC (Lal et al., 1995). Global Carbon in the pedosphere is contained in two pools: Soil Organic Carbon (SOC) and Soil Inorganic Carbon (SIC). The current SOC pool in the world soils is estimated at 1500 Pg (Eswaran et al., 1995). The SOC pool is about 2.1 times that of atmosphere pool and about 2.7 times that of the abiotic pool comprising land plants (IPCC, 2000). Estimates of the SIC pool are more tentative than those of SOC pool, but may be about 12% more than those of the SOC pool (Schlesinger, 1991; Grossman et al., 1995). Soil inorganic carbon is sequestered in carbonates. Carbonates may be present in parent rock as in limestones or calcareous

sediments, or may be pedogenically precipitated in soils. Sources of carbonate are bicarbonate and carbonates in ground or laterally moving water in soils, aerosolic dusts, or recycled from carbonatic substratum. Soil inorganic carbon does not contribute rapidly to carbon flux as organic carbon. The largest exchange occurs between the atmosphere and land plants. The pedosphere is, in fact, an interface between lithosphere and atmosphere and it interacts and supports all biotic activities. These interactions influence global carbon cycle.

The general carbon cycle is illustrated in Figure 3, which describes the different C reservoirs and the C fluxes between them. In terrestrial ecosystem, through photosynthesis, plants absorb CO_2 from the atmosphere and convert it into carbohydrates. The annual uptake carbon from atmosphere, described as gross primary productivity, amount to about 120 GtC. About half of the carbon consumed in the photosynthesis process is released through plant respiration, leaving 57 GtC in the terrestrial sink as net primary productivity (SCOPE, 2006). Under natural or undisturbed conditions, this biomass is incorporated into the soils and becomes part of the soil organic carbon (SOC) pool. The SOC pool is comprised of animal and plant residues at various stages of decomposition, chemical and microbiological breakdown products, and the bodies of microorganisms and small animals (Lal, 2008). As organic matter decomposes, CO_2 is released back into the atmosphere. Carbon dioxide emissions from agriculture and deforestation are caused by the total or partial removal of biomass from the field, increases in the mineralization rates due to changes in soil temperature and moisture and losses by leaching and erosion (Lal, 2003). However, under appropriate management, the C in the biomass of soil can be permanently stored (mean residence times may vary from 102 to 103 years), becoming a form of C sequestration (Lal, 2008; Pacala and Socolow, 2004; Schimel, 1995).

Soil organic carbon dynamics

The soil C pool comprises two components: SOC and inorganic carbon (SIC) pool (Lal., 2004 b). The SIC pool includes elemental C and carbonate minerals, such as calcite and dolomite. The SOC pool includes highly active humus and relatively inert charcoal C (Schnitzer, 1991; Stevenson, 1994; Paul and Clark, 1996).

Soil organic carbon is the elemental component of soil organic matter which includes the whole non mineral fraction of soil ranging from decayed plant and animal matter to brown to black material that bears no trace of the original anatomical structure of the material and is normally defined as "soil humus". Soil organic matter, also, includes living and dead microbial tissue, compounds synthesized by microorganisms and derivates of these materials produced as a result of microbial decay .

Although both organic and inorganic forms of carbon are found in soil, disturbances have a larger impact on the stocks of organic carbon that is the most active pool.

SOC accumulation, under undisturbed natural conditions, is in equilibrium and the input of C (litter fall, root biomass, C brought in by run-on, dust) is balanced by output (erosion, decomposition, and leaching) (Lal, 2004 a).

Soil carbon storage is primarily controlled by two fundamental processes: primary production input and decomposition. Increased primary production would result in an increased C storage, whereas increased decomposition (i.e., reduced C turnover time) would have an opposite effect. Other factor such as land use change, the conversion of natural to agricultural ecosystems, reduces the amount of C input and increases the magnitude of output. The human impact, including tropical deforestation and biomass burning, plowing (Reicosky, 2002), drainage of wetlands and low-input farming or shifting cultivation (Tiessen et al., 2001) was a major cause of CO_2 emission from soil.

The level of soil organic carbon in a particular soil is determined by many factors including climatic factors (e.i. temperature and moisture regime) and soil related factors (e.i. soil parent material, clay content, cation exchange capacity; Dawson and Smith, 2007).

Carbon sequestration

Carbon sequestration is defined as "the capture and secure storage of carbon that would otherwise be emitted to or remain in the atmposphere (DOE, 1999). The idea of carbon sequestration is either to keep carbon emission produced by human activities from reaching the atmosphere by capturing and diverting them to secure storage, or to remove carbon from the atmosphere by various means and store it. Carbon sequestration is now widely recognized as an important approach to reduce the GHGs effect. The major ways to sequester carbon include reducing consumption or using low carbon fossil fuel or clean energy, using advanced biological and chemical process to increase biomass production , or to sequester carbon in the ocean, terrestrial ecosystems or in geological formations. Some of these approaches are definitely long-term strategies that will take time and will require massive investment before this technologies can be developed and implemented. Other strategies such as terrestrial carbon sequestration in both biota and soils are usually considered short-term solutions. These short-term strategies, however, are necessary to help us buy time and allow us to develop alternatives to fossil fuels.

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The impact of fire on redistribution of soil organic matter on a Mediterranean hillslope under maquia vegetation type

Abstract

Soil organic matter (SOM) changes affect the CO_2 atmospheric levels and is a key factor on soil fertility and soil erodibility. Fire affects ecosystems and the soil properties due to heating and post-fire soil erosion and degradation processes. In order to understand fire effects on soil organic carbon (SOC) balance, research was undertaken on a fire-prone ecosystem: the Mediterranean maquia. The spatial distribution of SOC was measured in a Burnt site 6 months after a wildfire and in a Control site. Samples were collected at two different depths (0–3 and 3–10 cm) and SOC was determined. The results show that 41.8 per cent of the SOC stock was lost. This is due to the removal of the burnt material by surface wash. No significant differences in SOC content were found for the subsurface samples between burnt and control plots. Those results show that ashes and charcoal are transported by runoff downslope, and are subsequently deposited in the valley bottom, and this is the key process that contributes the burial of SOC after a forest fire. SOC redistribution by water erosion is accelerated after forest fires, and contribute to the degradation of soils located at the upper part of the hillslopes, but causes the enrichment with SOM of the soils located at the valley bottom. Buried SOC in the bottoms valley terraces will contribute to the sequestration of carbon for longer. Conservation of abandoned terraces is a key policy to avoid land degradation and climate change.

Key words: soil organic carbon (SOC); fire; mediterranean; maquia; ash; Spain

INTRODUCTION

Soil organic carbon (SOC) is an essential component of organic matter and it is the most widely used soil uality indicator (Shukla *et al*., 2006). Organic matter plays a key role in soil chemical and physical roperties, affecting bulk density, nutrient availability, structural stability, hydraulic conductivity and soil biodiversity. SOC is the largest terrestrial

carbon pool with an estimated total content of 1600 Pg C located in the first metre of depth, exceeding the terrestrial biosphere (560 Pg C) and atmosphere (750 Pg C) storage capacities Sundquist, 1993). The SOC pool is the difference between the net balance of photosynthesis and total respiration in a terrestrial ecosystem (Jenny, 1941; Schlesinger, 1977) and it is the most important reserve in the global carbon cycle. Then, changes in soil carbon emission or sequestration will affect the whole carbon cycle and subsequently the climate. Soils also are able to sequester carbon from the atmosphere and reduce the greenhouse gas concentration. The amount of SOC in an ecosystem represents a balance between the input of carbon such as litter, belowground biomass and roots, and the output of carbon due to respiration, leaching, erosion and wildfire (Tan *et al.*, 2007; Wiedinmyer and Neff, 2007) and thus it is a good indicator of the health of the ecosystem. In an undisturbed ecosystem, soil carbon is stable over time (steady-state) and soil carbon mineralization is balanced by organic matter production. Then SOC losses or gains are only found over long periods of time, and mainly due to climate change.

The loss of organic matter cause soil aggregates to break down easily and accordingly became more erodible (Wu

and Tiessen, 2002; Cantòn *et al.*, 2009). Soil organic matter (SOM) losses also deal with a reduction in soil fertility and biomass production. Stable aggregate and sustainable SOM amounts in the soils help to avoid soil erosion and desertification as soil fertility is maintained (Barthes and Roose, 2002). The soil physical properties are also improved if organic matter is present. Human disturbances such as ploughing or fires, deforestation can cause a SOC depletion and soil degradation. land degradation & development Within the soil processes, erosion causes the removal and mineralization of SOM and the global carbon flux is released into the atmosphere. Lal (1995) calculated a global CO_2 flux of 1.14 $PgCy^{-1}$ from the soil to the atmosphere. This calculation assumes that 20 per cent of the carbon displaced is easily decomposed. However, erosion, deposition and redistribution of soil may not result in a net loss of carbon at the landscape scale because it may be redeposited in neighbour areas instead of being released into the atmosphere (Van Noordwijk *et al.*, 1997; Lal *et al.*, 1998; Stallard, 1998). In fact, charcoal and wood deposit in the sediment records is widespread from recent fires and fires long ago in geological time (Scott, 2000). And, then, a loss or gain of carbon is discussed due to soil redistribution along

the slopes and within the watersheds. Most of the studies show that SOC distribution depends on topographic variations, plant inputs, decomposition, soil texture, nutrients availability, biological activity, soil moisture and or SOC erosion and deposition (Garten and Ashwood, 2002).

Water, tillage and wind erosion contribute significantly to the redistribution of soil and SOC across the landscape, with both soil and SOC being redistributed within the field/slope/watershed as well as being removed (Harden *et al.*, 1999; Smith *et al.*, 2001; McCarty and Ritchie, 2002; Ritchie and McCarty, 2003). Distribution of SOC is mainly affected by topographic variations due to soil erosion processes and slope gradient (Abrahams *et al.*, 1988). However, when vegetation cover is dense and, as a consequence, the rates of soil erosion rates are negligible (Cerdà, 1998), the distribution of SOC (even or patchy) is determined by the influence of vegetation (Jobbàgy and Jackson, 2000). Then, topography plays a secondary role. When dense natural vegetation is present, SOC distribution is mainly related to the plant distribution, but not on the slope position. Wildfire is an important component of the geomorphologic systems and its effects contribute to the increase in soil erosion, and as a consequence, soil carbon

mobilization. Although it is well known that fire contributes to extreme soil erosion rates, there is little information on the effects of fire on the carbon cycle. It is not known how SOC is redistributed along the slopes during post-fire intense erosion periods due to the lack of vegetation that control the soil and water losses and distribution. The aim of this paper is to examine, by means of paired plots, the distribution of SOC in a Control site and a recently Burnt area where intense soil losses were measured. This will shed light on the effect of fire on SOC cycle.

MATERIALS AND METHODS

Study area

The study area was located in Navalòn (Enguera), in the southwest of the province of Valencia, eastern Spain, (388550N, 008540W) at an altitude of

Figure 1. A map showing location of the study area.

850m a.s.l (Figure 1). This region has a dry Mediterranean climate with a total

annual precipitation of 537.3mm and an average annual temperature of 12.78C at Las Arenas (1961–1990) meterological station located 2 km from the study sites (Pérez Cueva, 1994). The parent material is Cretaceous Limestone.

The soil profile depth is variable—on average about 30 cm with outcrop covering 10 per cent of the north-east facing slope and with abundant rock fragments (35 per cent). The soil was classified as Xerorthent (Soil Survey Staff, 2006), with a sandy soil texture of 26 per cent clay, 26 per cent silt and 48 per cent sand for the Burnt area and 35 per cent clay, 25 per cent silt and 39 per cent sand for the Control area.

Vegetation is dominated by Pinus halepensis M., Quercus coccifera L., Rosmarinus officinalis L., Juniperus oxycedrus L., Rhamnus lycioides L., Erica multiflora L., Pistacia Lentiscus L. and Brachipodium retosum Pers. This is a typical vegetation cover developed after the removal of the Quercus ilex woodland used for fuel for millennia. Pinus halepensis was afforested during the 1980s. A toposequence with a slope angle of 15 degrees and a length of 100m was selected on a hillslope facing northeast. The sampling sites were selected with two paired plots: Burnt and Control, which had the same elevation, slope and vegetation cover and composition before the fire. The fire took

place on 8 April 2008 and affected 90 ha. During the first 3 months, the erosion rates were negligible but on 12 July 2008 a short and intense thunderstorm (15 mm/10 min) resulted in severe runoff and sediment deposition on the bottom of the slopes where abandoned agricultural terraces were present. During the following months the erosion rates were negligible.
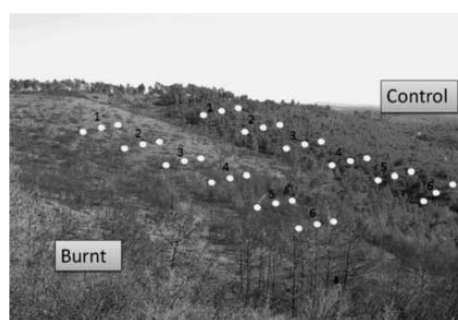
Figure 2. Sampling soil area

Soil Sampling and Analysis

Soil samples (18 at the Burnt site and 18 at the Control site at two depths) were collected in February 2009 when vegetation recovery reached 15 per cent cover at the Burnt site and the soil erosion processes were less active due to the lower rainfall intensities in winter. The vegetation cover at the Control plots was >90 per cent and no seasonal variation was found as all the species are evergreen. Figure 2 shows the soil sampling points, which move from the upper (point 1) to the lower slope tram (point 6). On both hillslopes (Burnt and Control sites) three parallel transects, 1m away, were selected.

Table I. pH in Burnt and Control site. The same letters indicate no significant statistical difference

Sampling site	Burnt		Control		Average	
1	8.03	(±0.16)	7.54	(±0.27)	7.78	(A)
2	8.05	(±0.08)	7.92	(±0.13)	7.98	(B)
3	8.12	(±0.12)	8.02	(±0.24)	8.07	(CB)
4	8.05	(±0.05)	7.95	(±0.19)	8.00	(CB)
5	8.06	(±0.10)	8.19	(±0.06)	8.12	(C)
6	8.12	(±0.09)	7.96	(±0.29)	8.04	(CB)
Average	8.07	(A)	7.93	(B)	8.00	

On each slope transect, a sample was collected every 15 m. Mineral soil samples were collected at depths of 0–3 and 3–10cm. On the Control site, the litter was removed with one's hand. The samples were composited, air-dried at laboratory temperature, and sieved through a 2mm mesh. A sample from the sediment collected by the abandoned terraces was collected in 3rd August, after the largest rainfall event that took place in 12th July and triggered a high-erosion rate. Soil organic carbon was determined by the colorimetric method after potassium dichromate digestion, following the

measured for each sample (3 samples*6 slope positions*2 sites*2 depths=72 samples).

Data Analysis

Data analysis was conducted by using the SAS statistical package1 (SAS Inst, 2002). After normal distribution of data was checked, analysis of variance was conducted, using

a factorial procedure to test the significance of the site, elevation and depth. A single ANOVA procedure was also used to test statistical differences for each elevation for site (Control and Burnt) depth and their interaction. Mean

Table II Soil Organic Carbon content along the hillslope. Numbers followed by different letters within the same row or column are significantly different at P≤ 0.05 by the least square means test.

$g\ C\ kg^{-1}$	depth	1	2	3	4	5	6	Average
Burnt	0-3	24.2	38.2	48.4	50.8	64.8	49.8	46.0
	3-10	24.1	37.2	40.2	35.6	34.4	36	34.6
Average Burnt	0-10	24.2	37.7	44.3	43.2	49.6	42.9	40.3(A)
Control	0-3	71	66.8	64	97.4	85.4	104.6	81.5
	3-10	56.2	54	45.8	60.2	60.4	65.6	57.0
Average Control	0-10	63.6	60.4	54.9	78.8	72.9	85.1	69.3(B)
Average	3-10	43.9 (A)	49.0(A)	49.6(A)	61.0(B)	61.3(B)	64.0(B)	54.8
Control-Burnt	0-3	46.8	28.6	15.6	46.6	20.6	54.8	35.5
	3-10	32.1	16.85	5.6	24.6	26	29.6	22.5

Walkley and Black method (Walkley and Black, 1934). Texture, CaCO3, pH were all

separation was achieved using the

adjusted Tukey's least significant differences (LSD).

RESULTS

Soil pH is 8.1 (±0.10) and 7.9 (±0.20) for the Burnt and Control sites respectively. There are significant differences in pH levels in the Burnt and Control sites. Soil taken from the sampling point along the slope shows that, while pH is affected at the slope surface, it is not affected by depth (Table I). At a depth of 0–10 cm, mean soil carbon content was 40.3gCkg^{-1} in soil located on the Burnt transect and 69.2gCkg^{-1} in Control one (Table II). These data show that SOC content was affected by site. The mean values for the 0–3 cm layer were 46 (24.2–64.8) g C kg^{-1} on the Burnt and 81.5 (64–104.6) gC kg^{-1} on the Control plots, meanwhile at 3–10 cm depth the values were 34.6 (24.1–40.2) g Ckg^{-1} and 57.0 (45.8–65.6) gC kg^{-1}, respectively, for the Burnt and Control transects. No statistically significant differences were found between Burnt and Control plots at 3–10 cm depth, meanwhile differences were greater and statistically significant on the 0–3 cm depth.

SOC changes along the slope were characterized by an increase from the upper to the lower slope positions. In average values, it ranges from 24.2 to 49.8 gCkg^{-1} on the Burnt and from 71 to 104.6 gCkg^{-1} on the Control one. Results show that SOC is affected by site, depth

and altitude and there is significant difference as reported in Table III.

As regard as site (Burnt/Control) data shows statistically significant differences for all sampling points except for the middle slope tram (sampling point 3). On the contrary, the effect of depth was

Table III. SOC Anova

	DF	P
site	1	<0.0001
sampling site	5	<0.0001
depth	1	<0.0001
site*sampling site	5	0.0055
site*depth	1	0.0134
sampling site*depth	5	0.0414
site*sampling site*depth	5	0.5889

determinant except for the 2nd and 3rd position. For site*depth interaction no significant differences were found for all considered sampling sites (Table IV). The SOC measurements on the sediment collected on the abandoned terraces show very high values (55.9gCkg^{-1}) ranging from 44.79 to 67.86 gC kg^{-1} in average values for each abandoned terraces (Table V). A clear increase was found from the upper to the lower abandoned terrace, which shows that ash and charcoal can be transported by runoff downslope.
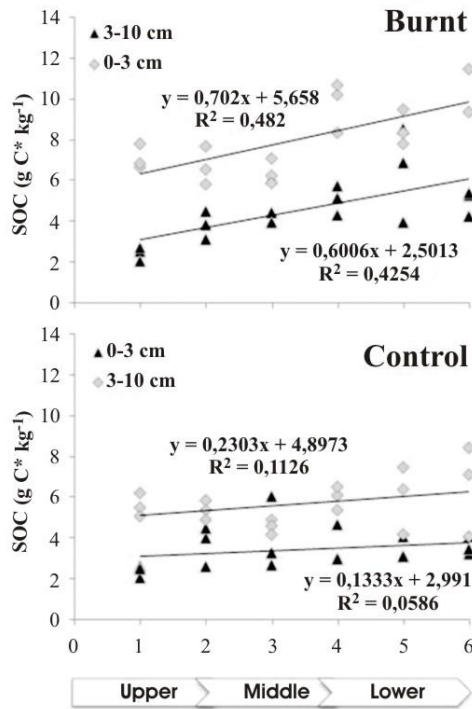
3 cm depth, meanwhile there are no differences between Control and Burnt for the 3–10 cm depth. This is because the erosion processes affects mainly the soil surface. The lower slope position reached $18.7gCkg^{-1}$ on average for the Burnt and $21.5gCkg^{-1}$ for the Control plots. In the Navalòn study area, the redistribution of the organic carbon took place during one extreme and short rainfall event in 12 July 2009, when ash was removed from the upper to the lower slope position due to the 15mm of rain in 10 min and the hydrophobic response of the soil surface in this summer dry season (see Bodì, 2009). The sediments were relocated on the lower slope tram coming from the upper

Figure 3. SOC distribution in Burnt hillslope and Control plot.

DISCUSSION

The results show that fire affects SOC distribution on the study area. No differences were found between the Burnt and Control plots underneath 3 cm depth. But differences were clear and statistically significant between surface samples (0–3 cm depth). Soil surface layer protects the soil below from high temperature during wildfire thanks to good heat insulation soil properties (De Bano, 2000), and furthermore very low change in C content from soil are reported when heated up to 1508C (Fernandez *et al.*, 1997). Figure 3 shows a significant increase on SOC from the upper to the lower slope tram for the 0–

Table IV. SOC Anova for Carbon within sampling site

Sampling site	site	depth	site*depth
1	<0.0001	0.0271	0.0287
2	0.0011	0.1703	0.2370
3	0.1394	0.0753	0.4612
4	0.0001	0.0011	0.0700
5	0.0297	0.0138	0.7674
6	0.0005	0.0078	0.1312

positions and mixed with mineral particles, mainly sand. Those sediments are now part of the organic horizon of the lower tram slope position soils, but in some terraces a 40 cm thick sediment layer with a relatively high content of organic carbon was deposited due to the surface wash coming from the slopes.

Table V. Soil Organic Carbon content ($g\ C\ kg^{-1}$) on the bottom valley sediment deposition after the thunderstorm of July 12th 2008 (forest fire April 8th 2008). Samples collected August 3rd 2008. Sites (8) are abandoned terraces from the upper to the lower position

Site/samples	1	2	3	4	5	6	Average
1	42.5	48.25	43.25	47.25	45.25	42.25	44.79
2	48.5	49.25	47.25	46.5	45.87	48.2	47.60
3	52.32	54.25	42.6	59.32	46.36	46.98	50.31
4	60.28	45.25	56.32	48.25	49.35	54.25	52.28
5	59.35	62.15	64.55	52.25	48.65	49.35	56.05
6	68.25	64.25	49.35	58.35	62.54	70.25	62.17
7	67.25	68.3	58.5	69.32	64.25	69.35	66.16
8	69.45	65.25	68.32	67.25	67.58	69.3	67.86
average	58.49	57.12	53.77	56.06	53.73	56.24	55.90

Values of 40–60 per cent SOC content were measured on those sediments. Figure 4 shows an example of the sediment collected on the lower slope trams. It is widely know that fires trigger high erosion rates. This has been found by researchers from USA (Moody and Martin, 2001), Europe (Thomas *et al.*,1999) and Asia (Lavee *et al.*, 1995). The increase in soil and water losses after forest fires induce a deposition and burying of the SOC on the medium and lower slope position. And if the water erosion process is very efficient the sediments reach the valley bottom. This paper contributes with key information to understand the SOC redistribution as a consequence of forest fire. The results demonstrate that SOC is transported, deposited and then buried on the nearby foot-slopes and abandoned terraces. This

carbon reallocation will explain the high organic carbon of the soil located on the bottom of the slope. The above-mentioned increase in SOC was previously found by some authors and they reported an increase of the SOM content in areas affected by fire (Johnson and Curtis, 2001; Brye, 2006). This

Figure 4.   SOC deposition and burying in the lower slope position

increase was related to the deposition of highly organic carbon-rich material, whereas other researchers have detected

a decrease (Guinto *et al.*, 1999) and (Kavdir *et al.*, 2005) or even no significant differences on the SOM content between Burnt and Control areas (Roscoe *et al.*, 2000; Alexis *et al.*, 2007). This research found that after a forest fire, the organic carbon stock in soil was decreased in 41.8 per cent of initial carbon content at the slope position. However, all this material was buried in the valley bottom terraces (Figure 5a). Then, subsequent soil erosion processes in burn areas contribute to move SOC from slope to valley bottom. Stallard (1998) highlighted that soil erosion could have a major effect on both soil carbon pools and sequestration of soil carbon. In the study site of Navalòn, the reallocation of the SOC with the sediments on the valley bottom will result in buried and sequestered carbon (Figure 5b). Furthermore, high-soil erosion rates could strongly influence the terrestrial C balance and C budget due to the removal of the soil surface organic particles and

deposition on valley bottoms, bottom slopes, fluvial terraces, and alluvial fans (Tate *et al.*, 2000; Berhe *et al.*, 2008). Erosion and the subsequent deposition after forest fire constitute a sink for the atmospheric carbon dioxide in comparison to the prefire condition. Carbon losses by soil erosion will be replaced by the photosynthetic production of new biomass. The key factor in Mediterranean environments is the terraces located on the slopes and bottom of the valleys. When vegetation is removed (Garcìa-Ruiz *et al.*,1995; Lòpez Bermùdez *et al.*, 1998) either by forest fire or agriculture, the soil erosion is accelerated. And then the valley bottom terraces collect most of the sediments (Cerdà *et al.*, 2009). They act as sink for SOC, but they are being abandoned and probably they will be damaged by the erosion (Cerdà *et al.*, 2007). This will contribute to the land degradation in three ways: (i) soil erosion will increase, (ii) a millennia patrimony

Figure 5. (a) SOC eroded on the slopes and collected by the abandoned terraces. (b) A detailed view of the 30 cm depth deposited ash-charcoal rich material deposited on the terraces

will disappear and (iii) the SOC sinks will be transformed in CO2 sources mainly due to oxidation and erosion of the SOC-rich sediments of the terraces. Then, a policy to maintain the abandoned or active terraces in good conditions is a key question to be solved by policy-makers and farmers in order to avoid land degradation (Lòpez-Bermùdez and Albadalejo, 1990).

CONCLUSIONS

In typical Mediterranean Maquia covered landscapes, SOC rich sediments are removed from the fire-affected areas due to intense surface runoff but they are collected by the valley bottom terraces of the terraces. This sink of SOC will contribute to enrich the valley bottom soil and to sequester OC and avoid climate change. Conservation of the abandoned terraces is a key policy to avoid land degradation and climate change.

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Paired-site approach
for studying soil organic carbon dynamics in a
Mediterranean semiarid environment

Abstract

This work investigated the effects of land cover and land-use change (LUC) on the ability of a soil to store carbon (C) and reduce carbon dioxide (CO_2) emissions., in a Mediterranean area. Using a paired-site approach, we estimated the effect of land-cover change on the C stock from 1972 to 2008 in a natural reserve (Grotta di Santa Ninfa) in western Sicily. We selected 15 paired sites representative of five LUCs. We studied the effect of land use on soil organic C (SOC) content in bulk soil and in different particle-size fractions (2000–1000 µm, 1000–500 µm, 500–250 µm, 250–63 µm, 63–25 µm, and <25 µm). Laboratory incubation of the soil samples was conducted to measure CO_2 evolution in bulk soil collected at two different depths from each paired site. We found that the conversion of natural vegetation to orchards (vineyards and olive groves) resulted in SOC decreases ranging from 27% to 50%. The conversion from vineyards to arable land led to a 9% decrease in SOC, whereas the opposite caused a 105% gain. When arable land was replaced by Eucalyptus afforestation, a 40% increase in SOC was observed. SOC decline occurred mainly in coarser soil fractions, whereas the finest fractions were not influenced by land use. We calculated an overall SOC reduction of 63% in the study area, corresponding to a 58 Mg ha-1 SOC loss in less than 30 years. Our results indicate that land-use conversion, vegetation type, and management practices that control the biogeochemical and physical properties of soil could help reduce CO_2 emissions and sequester SOC.

Key Words: carbon dioxide emission, land-use change, Mediterranean environment, particle-size fraction, SOC.

INTRODUCTION

The use of land to produce goods and services represents the most substantial human alteration of the Earth system (Vitousek *et al*., 1997). The agricultural use of land alters the structure and function of

the pedosphere and its interaction with atmospheric and aquatic systems. A direct measure of human impact on the landscape is the rapid decline in carbon (C) held in biomass and in soil, and the release of carbon dioxide (CO_2) to the atmosphere. C losses from agricultural soils mainly occur because of soil management practices that increase the decomposition rates of soil organic matter and the amount of organic topsoil C that is lost through erosion (Freibaueer *et al*., 2004; Ewert *et al*., 2005; Bellamy *et al*., 2005). Moreover, the more efficient removal of agricultural products has reduced the amount of organic residue left in the field, which has increased the total output of C from ecosystems. Land-use change (LUC) is considered the second greatest cause of C emissions after fuel consumption (Watson *et al*., 2000). Globally, about 200 Pg of C were released to the atmosphere as a result of changes in land use and land cover over the past 250 years (Scholes and Noble, 2001). Long-term experimental studies have confirmed that soil organic C (SOC) is highly sensitive to LUCs in native ecosystems, such as the conversion from forest or grassland to agricultural systems, resulting in the release of 1.6 Pg C y^{-1} into the atmosphere and the loss of 40 Pg C from soil during the 1990s (Smith, 2008; Jenkinson and Rayner, 1977; Paul *et al*., 1997). Because the effects of land use on the SOC pool vary due to differences among ecosystems and

regions (Solomon *et al*., 2000; Rodríguez-Murillo, 2001; Powers, 2004; Yimer *et al*., 2007), the magnitude and effect of land use on C sequestration is soil and site-specific (Lal, 2004; Alvarez, 2005, Tiessen *et al*., 2003). For instance, pine afforestation of pasture decreased SOC in New Zealand (Groenendijk *et al*., 2002) and in the Cerrado region of Brazil (Neufeldt *et al*., 2002), but added 50% more C to grazing land in Patagonia (Nosetto *et al*., 2006). In particular, dryland soils are generally low in C (Lal, 2002), primarily because the amount of limited available water restricts plant productivity, which is the main source of SOC. In addition, a higher soil temperature, which is associated with less ground cover, increases the mineralization rate of soil organic matter.

Regional-scale information about C stocks and the relationship between C reservoirs and edaphic or climatic factors could be particularly important for identifying land-use classes and LUCs that are of particular interest in evaluating gains and losses of SOC.

Very few studies have focused on the effect of LUC on SOC and soil physical properties in typical Mediterranean crops such as vineyards and olive groves, and in natural and semi-natural vegetation. To evaluate such effects, we used a paired-site approach. Paired plots or chronosequence studies are required to verify the direction and magnitude of C fluxes that result from

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human activity on soils. Unlike chronosequence studies, which may require years or decades of monitoring to measure such changes, paired plots provide immediate results (Davis *et al.*, 2004). The goals of this work were (i) to quantify SOC stocks in five different land

Figure 1. Location of the study site.

use classes; (ii) to estimate effects of LUC on SOC dynamics; and (iii) to evaluate the contribution of different aggregate sizes on C stocks. C change at the catchment scale was also calculated to provide useful tools

for management purposes.

MATERIAL AND METHODS

Study area

The study was performed in the "Grotta di Santa Ninfa" natural reserve (longitude between 12°53'45'' and 12°55'45''E, latitude between 37°46'50'' and 37°47'50''N), in the Trapani province of southwestern Sicily (Fig. 1). The elevation ranges between 400 and 625 m above sea level. The study area has a typical Mediterranean climate, with mean annual rainfall and temperature of 860 mm and 17°C, respectively. The geology is characterized by gypsum rocks; as a consequence of the high solubility of gypsum, carsic phenomena are widespread in the area. Cambisol is the prevalent soil type. Cambisols are mainly represented by Gypsiric Cambisols, which are characterized by a low depth (70 cm); an A-By-C profile; more than 5% gypsum; a high carbonate concentration; and a sub-angular, blocky, big, well-developed

Table 1. Land use categories and class distribution in 1972 and 2008 in the Santa Ninfa Natural Reserve.

Land use	Abbreviation	1972	2008	Characteristics
Garrigue	G	62.0%	16.7%	Discontinuous shrubs formation dominated by *Thymus vulgaris* and *Micromeria graeca* grazing, with periodic burning.
Arable land	AL	33.1%	3.1%	Winter crop rotation with annual leguminous and cereal species.
Vineyard	V	4.0%	19.9%	Vineyard planted on traditional espalier.
Olive grove	OG	1.0%	1.3%	Approximately 40-year-old olive grove plantation managed with traditional tillage.
Eucalyptus afforestation	EA	-	10.1%	Approximately 40-year-old pure *Eucalyptus camaldulensis* afforestation

structure. The Cambisol group is also represented by Mollic Gypsiric Cambisol, which has a mean soil depth of 140 cm and a sub-angular blocky, medium-sized, weakly developed structure. Vertic Gleyic Gypsiric Cambisols are at depths below 110 cm and have an A-By-Bss profile type and a sub-angular to angular blocky, medium-size, strongly developed structure. The total surface area of the natural reserve is about 150 ha, and it is covered as indicated in the Table 1. Several LUCs took place between 1972 and 2008, particularly relating to afforestation activity. These changes affected areas once covered by semi-natural pre-forest vegetation, reducing the surface areas once occupied by garrigue and grassland communities (Gristina *et al.*, 2008).

Paired sites selection

A paired-site approach was chosen to study the difference in SOC stocks after LUC, following criteria based on Conteh (1999) For the purpose of comparison, the members of a paired site were selected to be similar with respect to the type of soil,

slope, elevation, and drainage, but not to land use. The comparisons were made between adjacent patches of land with different land cover, and a known history of use.

After an extensive analysis of a spatial–temporal database that includes several layers of land use in a geographic information system, five LUCs were identified. Each LUC was replicated three times (5 land uses * 3 replicas = 15 paired sites) to statistically confirm any observed changes (Webbnet Land Resource Service, 1999). Soil type and prior and current land use are indicated for each LUC in Table 2.

The land use classes in these 15 paired sites are representative of both Sicilian agricultural landscape and human activity on the natural environment, which consists of a patchwork of agricultural areas, natural environment, and afforested areas. On-site investigations and discussions with landowners determined that no substantial differences in soil management practices have occurred over the last 30 years.

The selected land use classes were olive grove (OG), vineyard (V), arable land (AL),

Table 2. Description of five land-use changes.

Land-use change (LUC)	Soil type (FAO)	Clay	Silt	Sand	Land use 1972	Land use 2008	
		$g\ kg^{-1}$					
LUC 1	Haplic cambisol	320	400	280	V	AL	V
LUC 2	Vertic gleyic gypsiric cambisol	300	350	350	AL	EA	AL
LUC 3	Mollic gypsiric cambisol	200	450	350	G	G	V
LUC 4	Gypsiric cambisol	200	450	350	G	G	OG
LUC 5	Gypsiric cambisol	200	450	350	AL	V	AL

Eucalyptus afforestation (EA), and garrigue (G); see Table 1 for definitions.

Soil sampling and analysis

Soil sampling was conducted in the spring of 2008. As much as possible, the sampling area within each land use was chosen very carefully, to minimize the effects of spatial variability and to represent the land use investigated. Mineral soil samples were collected at depths of 0–20 cm and at 20–40 cm, after removing the forest-floor litter. At each site, three soil samplings at approximately 10-m intervals were collected along transects. The samples were gently broken to pass through a 2-mm sieve and were air dried. Aggregate separation was done by wet sieving through a series of five sieves to obtain six aggregate fractions: 2000–1000 μm, 1000–500 μm, 500–250 μm, 250–63 μm, 63–25 μm, and <25 μm. The aggregates were dried at 50°C and weighed.

SOC was determined using the Walkley–Black method (1934). The SOC content estimated as a percentage was converted to tons per hectare using the soil depth and the bulk density, which was measured using the volume of the collected sample and the weight of dry soil in the sample (Blake and Hartge, 1986).

The mean weight diameter (MWD), a measure of soil structural stability, was calculated as follows:

$$MWD = \sum nd_i + w_i,$$

where d_i is the mean diameter and w_i is the weight proportion of each size fraction.

Soil CO_2 flux was measured 3, 5, 6, 7, 9, 10, 12, 13, 19, 23, 26, 31, and 33 days after the start of incubation. Vials containing 1 g of bulk soil were wetted and incubated at constant temperature (21 ± 1°C). Five ml of gas was extracted immediately using a hypodermic needle and analyzed using an infrared gas analyzer (IRGA, model ADC.225. Mk3, manufacturer Asea Brown Boveri).

Statistical analysis

Data analysis was conducted using the SAS statistical package (SAS Inst, 2001). After normal distribution of data, analysis of variance was conducted to test the significance of LUC, fraction, depth, and their interaction by site. A single ANOVA procedure was also used to test statistical differences among land uses. A mean separation was achieved using an adjusted Tukey's least significant differences (LSD).

RESULTS and DISCUSSION

SOC stored in different land uses

The SOC content was strongly affected by land use (p ≤ 0.001). Among different land uses, the highest SOC value, at 0–40 cm depth, was found under garrigue (112 ± 22 Mg ha^{-1}), followed by *Eucalyptus* (122 ± 30 Mg ha^{-1}), vineyards (71 ± 11 Mg ha^{-1}), olive

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groves (53 ± 13 Mg ha^{-1}), and arable land. A higher variability in organic C values was found under arable land (65 ± 31 Mg ha^{-1}) due to differences in previous crops and soil management practices.

The SOC content usually varies within the soil profile, with higher values found in the topsoil (0–20 cm) than in the subsoil (20–40 cm; p ≤ 0.01, all data). Two-way ANOVA showed a significant interaction between land use and depth for total soil C. In detail, we found higher SOC content in topsoil than in subsoil for arable land and garrigue (p ≤ 0.05), whereas vineyards and olive groves showed no significant differences in SOC between the two layers. This trend may be due to the mixing of the upper soil layers during soil tillage. Surprisingly, under *Eucalyptus* the SOC content was higher in subsoil than in topsoil (p ≤ 0.1). This may be due to the translocation of C in the form of dissolved organic C; soil faunal activity, especially earthworms; and/or the effects of deep-rooting crops (Shrestha *et al*., 2004).

Our results correspond to other studies showing more organic C stocks under natural and afforested systems than under agricultural systems, mainly due to higher biomass inputs (West *et al*., 2004; Heath *et al*., 2003; Post, 2003) and low soil disturbance (Lal, 2002). In agricultural systems, yields, pruning, and crop residue are removed from fields, producing a consequent decrease of C inputs. Soil management practices using frequent tillage also reduce SOC (Lal, 1997; Schlesinger, 1986) by increasing the decomposition of organic matter.
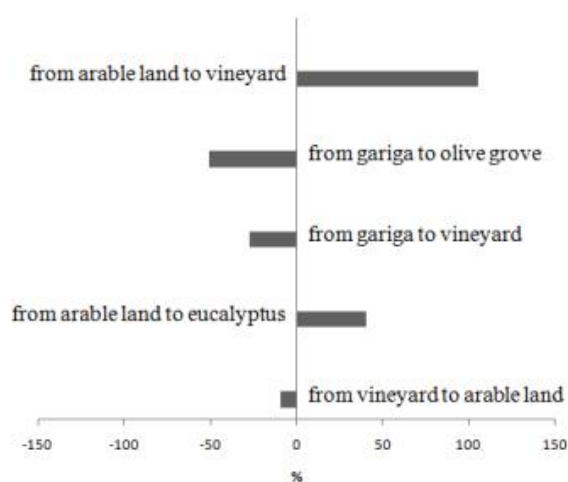

Figure 2. Percentage of soil organic carbon loss/gain as a consequence of land-use change.

Table 3. Results of analysis of variance (ANOVA) test for soil organic carbon by land-use change.

Source of variation	LUC 1 F	LUC 1 Pr > F	LUC2 F	LUC2 Pr > F	LUC 3 F	LUC 3 Pr > F	LUC 4 F	LUC 4 Pr > F	LUC 5 F	LUC 5 Pr > F
Land use	0.26	0.6119	67.75	<0.0001	56.82	<0.0001	59.32	<0.0001	59.50	<0.0001
Soil fraction	1.69	0.1402	17.90	<0.0001	50.69	<0.0001	10.12	<0.0001	2.66	0.0025
Depth	4.48	0.039	0.37	0.5469	26.86	<0.0001	24.14	<0.0001	5.52	0.0224
Land use * soil fraction	2.13	0.0643	4.82	0.0005	1.15	0.03441	3.34	0.0071	1.37	0.2425
Land use * depth	0.05	0.8191	13.03	0.0007	15.57	0.0002	0.02	0.8945	1.76	0.1905
Soil fraction * depth	0.94	0.4720	0.58	0.7433	0.32	0.9244	1.68	0.1428	0.47	0.8300
Land use * soil fraction * depth	0.67	0.6766	0.46	0.8360	0.4	0.8309	0.37	0.8971	1.14	0.3541

Effect of LUC on SOC stocks

LUC significantly affected soil C stocks at all sites, except for site number 1 (Table 3). The conversion of vineyards into arable land resulted in a 12.5% loss of SOC (p ≤ 0.61), whereas the reverse process resulted in an SOC increase of 105% (p ≤ 0.001; Fig. 2. Very few studies in the literature have examined the effect of conversion from arable land to vineyards, and vice versa, on SOC; however, in a meta-analysis, Guo and Gifford (2002) reported an average SOC increase of 18% when crop is converted to plantation.

Lower SOC losses occurred when vineyards were converted into arable land; relatively higher SOC gains occurred in the reverse process, and may be caused by differences in soil management and the age of cultivation among arable land classes. The arable land in LUC 1 was converted 30 years ago and is managed mostly with conservative tillage, whereas soil in LUC 5 has been cultivated as arable land for more than 50 years using mouldboard plough tillage.

Table 4. Soil organic carbon concentration in bulk and aggregate-size fractions.

Soil type (FAO)	Land use	Depth cm	Bulk	1000–2000	1000–500	500–250	250–63	63–25	<25
							μm		
Haplic cambisol	Vineyard	0–20	13.4	14.9	23.8	27.1	16.5	15.0	12.2
			(1.7)	(7.1)	(17.2)	(1.7)	(6.3)	0.6	1.5
		20–40	15.4	3.0	10.4	16.5	18.5	19.2	12.5
			(6.9)	(1.2)	(1.0)	(0.9)	(17.8)	(24.7)	(4.6)
	Arable land	0–20	14.7	21.5	21.2	20.5	10.4	10.0	15.8
			(4.6)	(4.2)	(6.9)	(4.8)	(2.9)	(1.8)	(6.5)
		20–40	10.5	18.9	15.7	17.7	9.7	9.1	10.6
			(1.5)	(8.7)	(3.6)	(3.3)	(2.0)	(1.8)	(1.6)
Vertic gleyic gypsiric cambisol	*Eucalyptus*	0–20	17.1	38.2	45.0	54.2	34.6	17.8	11.6
			(2.8)	(8.1)	(6.5)	(5.5)	(3.3)	(8.6)	(1.6)
		20–40	23.8	41.9	47.4	55.5	45.0	24.4	18.7
			(10.1)	(3.3)	(5.9)	(3.5)	(16.8)	(4.4)	(12.8)
	Arable land	0–20	19.2	22.7	39.0	24.3	20.4	13.4	20.4
			(10.2)	(7.4)	(12.9)	(13.1)	(2.9)	(4.0)	(16.0)
		20–40	10.0	15.5	20.6	23.3	15.9	12.0	8.5
			(1.2)	(11.8)	(12.3)	(11.2)	(4.1)	(1.9)	(1.8)
Mollic gypsiric cambisol	Garrigue	0–20	23.5	18.4	14.6	18.1	24.7	32.0	24.6
			(4.6)	(16.1)	(9.3)	(8.5)	(9.3)	(0.2)	(6.4)
		20–40	14.3	6.2	5.8	8.8	14.3	22.1	16.3
			(5.0)	(2.2)	(2.5)	(5.1)	(4.1)	(9.4)	(4.9)
	Vineyard	0–20	16.3	3.0	4.4	6.2	13.4	21.1	20.6
			(1.0)	(0.4)	(1.0)	(0.3)	(4.4)	(2.5)	(2.0)
		20–40	12.6	2.7	2.9	4.0	10.6	14.7	17.3
			(3.4)	(1.2)	(0.4)	(1.1)	(3.7)	(3.2)	(5.5)
Gypsiric cambisol	Gariga	0–20	18.9	27.8	22.2	28.4	24.0	23.8	14.8
			(3.4)	(3.9)	(2.2)	(3.5)	(5.4)	(7.2)	(2.0)
		20–40	15.2	22.5	16.5	21.0	15.1	23.3	12.8
			(4.5)	(5.7)	(3.7)	(3.6)	(8.0)	(8.4)	(4.2)
	Olive grove	0–20	9.9	15.6	25.1	24.9	14.2	10.1	7.2
			(4.0)	(2.2)	(6.4)	(5.3)	(8.4)	(4.6)	(2.2)
		20–40	7.1	14.5	16.4	12.3	7.3	7.7	6.4
			(1.6)	(2.8)	(1.3)	(9.0)	(3.5)	(2.3)	(1.1)
Gypsiric cambisol	Arable land	0–20	8.4	7.9	9.8	12.3	9.6	6.7	8.7
			(5.7)	(8.3)	(11.6)	(11.7)	(3.8)	(1.3)	(7.8)
		20–40	6.2	7.4	8.8	13.3	5.1	7.6	5.3
			(4.0)	(8.0)	(9.5)	(12.0)	(2.6)	(3.5)	(4.3)
	Vineyard	0–20	16.8	28.5	28.4	23.7	18.7	20.8	12.6
			(1.3)	(0.7)	(7.2)	(8.9)	(1.5)	(2.2)	(1.1)
		20–40	13.2	17.2	17.3	18.9	25.5	13.6	9.0
			(3.3)	(8.3)	(13.1)	(9.3)	(7.9)	(0.8)	(3.7)

As expected, SOC decreased when garrigue was cleared for plantations. The conversion from garrigue to vineyards and olive groves caused substantial SOC losses (23% and 50%, respectively). We observed higher litterfall on the soil surface under garrigue during the entire study period because of the higher biomass production of plantations; as a result, the soil is always covered by vegetation, which reduces erosion processes and increases organic matter stability (Barthes and Roose, 2002; Le Bissonnais *et al*., 1997). Similarly, Rodriguez-Murillo (2001) calculated that C storage in soil under olive groves (39.9 ± 28.3 Mg C ha^{-1}) and vineyards (42.5 ± 28.9 Mg C ha^{-1}) in Spain was lower than in bushland (113 ± 80 Mg C ha^{-1}). Padilla *et al*. (2010) estimated that CO_2 sequestration rates were about three times higher for shrubland than for olive groves and vineyards.

Finally, soil C stocks significantly ($p \leq 0.001$) increased (+ 40%) after the conversion from arable land to *Eucalyptus* afforestation. Studies conducted in Brazil found a 21% gain of SOC when *Eucalyptus* replaced degraded pasture (Lima *et al*., 2006).

Soil C and aggregate fractions

Regarding the different soil aggregates, the <25 μm fraction was the most abundant (mean 584 ± 119 g kg^{-1}), followed by the 25–63 μm (152 ± 32 g kg^{-1}), 63–250 μm

(159 ± 56 g kg^{-1}), 250–500 μm (42 ± 29 g kg^{-1}), 500–1000 μm (29 ± 20 g kg^{-1}), and the 1000–2000 μm fractions (33 ± 30 g kg^{-1}). In all of the fractions, small differences were found among different land uses and sites. MWD values calculated for each land use at different sites did not show significant differences. Regarding the contribution of particle-size fractions (aggregates) to bulk SOC, the following order was obtained: 0–25 μm > 25–63 μm > 63–250 μm > 500–1000 μm > 250–500 μm > 1000–2000 μm (Table. 4). The higher accumulation of SOC in the finest fraction was due to the higher mass of the silt–clay fraction in the soils, whereas the sandy fractions, in general, account for less of the total soil mass.

When the average SOC concentration of each fraction is taken into account, the 500–1000 μm and 250–500 μm fractions size showed higher SOC enrichment compared to the bulk SOC,

whereas the corresponding values of the other fractions did not differ statistically (Fig. 3).
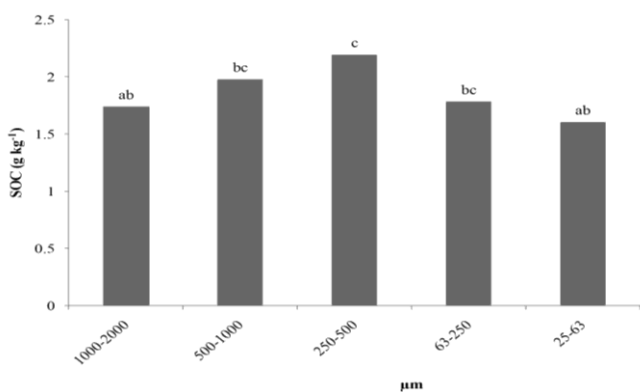

Figure 3. Soil organic carbon concentration in six different soil aggregate fractions.

The standard deviation, however, was

highest in the coarse fractions (>250 μm). This means that a wide range of SOC concentrations, from very low up to very high, were found in this fraction. As in Gerzabek *et al*. (2001), we compared the SOC mass distributions among the size fractions and found that the 250–500 μm fraction was the most enriched in SOC (C mass distribution/aggregate size distribution ratio = 1.6), whereas the smallest fraction showed no enrichment, and, in fact, a depletion of SOC (0.91; Fig. 4).

This observation runs counter to the results of other authors, who found that the silt fractions (2–63 mm) act as a medium-term sink for the introduced organic C (Gerzabek *et al*., 2001). Kong *et al*. (2005), however, reported a preferential stabilization of SOC in the microaggregate fraction. However, in vertisols in a semiarid environment, Barbera *et al*. (2010) found that this ratio decreases with decreasing particle-size fractions.

As showed in Figure 4, data variability was highest in the coarse fraction and lower in the smallest fraction, demonstrating that SOC stocks in the former fraction are less or not influenced by external factors, such as land use or site.

Effect of land use on CO_2 emission.

The magnitude of CO_2 fluxes was significantly different between land uses (p = 0.009), although all of the soils showed a

similar emission pattern during the incubation period. The soil CO_2 emission rates, averaged over 33 days, were 5.1 mg CO_2 g^{-1} C day^{-1}, 3.2 mg CO_2 g^{-1} C day^{-1}, 2.4 mg CO_2 g^{-1} C day^{-1}, and 2.0 mg CO_2 g^{-1} C day^{-1}, respectively, for olive groves, garrigue, vineyards, and arable land. We observed the lowest CO_2 emissions at the *Eucalyptus* site (0.99 mg CO_2 g^{-1} C day^{-1}). Similarly,
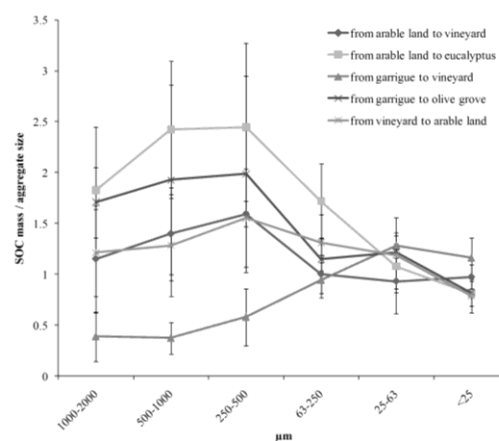

Figure 4. Soil organic carbon mass distribution/aggregate size-distribution ratio.

2001). Iqbal *et al*. (2009) mainly attribute higher CO_2 flux rates from paddies, orchards, and upland to differences in the quality of their SOC substrates as compared to woodland soil. The effect of different plant species on nutrient cycling is, in fact, determined by both the total amount of litter that is produced per unit ground area (Aerts and De Caluwe, 1997) and the nutrient release rate from litter. In particular, factors such as the

concentrations of lignin (Gallardo and Merino, 1993; Melillo *et al*., 1982), holocellulose (Berg and Staaf, 1980), cutin (Gallardo and Merino, 1993), and phenolics

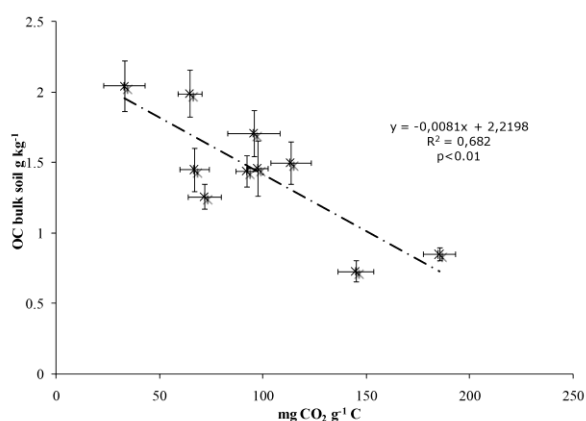(Aerts and De Caluwe, 1997), as well as physical leaf toughness (Gallardo and Merino, 1993), are mainly

Figure 5. Relationship between soil carbon dioxide emission and soil organic carbon.

responsible for the decomposition rates of organic matter.

Figure 5 clearly shows that SOC stocks in soil are the consequence of CO_2 emission rates (mg C g^{-1} C). In fact, greater amounts of mineralized organic matter cause higher CO_2 flux from soil, greater amounts of mineralized organic matter cause higher CO2 flux from soil, leading to an

SOC decrease. The ratio of CO_2 to C released during the incubation period and the SOC content in the 0–40 cm layer were lowest in *Eucalyptus* afforestation, despite its higher SOC content, indicating that this land is more efficiently storing C in soil.

CONCLUSION

This study revealed that the SOC content of surface soils is sensitive to human interference associated with land cover and LUC. Using land-use maps and the mean SOC content for each land use, we estimated the impact of LUC on SOC stocks after 30 years in a representative typical Mediterranean agro-ecosystem.

Our major findings can be summarized as follows:

- In the study area, increases in agricultural areas (vineyards, arable land, and olive groves) and decreases in natural vegetation (garrigue) profoundly affected soil C stocks;

- C reservoirs, as a consequence of landscape-use changes, decreased by 62.9% between 1972 and 2008, corresponding to an SOC loss of 58 Mg ha^{-1};

- although most SOC is stored in the finest soil fractions, SOC losses were mainly associated with coarser fractions, because the C mass distribution/aggregate size-distribution ratio did not change in the <25 μm fractions from the various land uses;

- although agriculture decreased SOC in all fractions, it did not affect the proportional weight distributions of the fractions, and thus did not modify the aggregation stability;

- SOC content in bulk soil showed a significant negative linear relationship with CO_2 emission;

- among land uses, *Eucalyptus* afforestation produced the most efficient C sequestration.

Knowledge of C stocks, and of the interplay between C stocks and edaphic or climatic factors, could also help to identify areas, types of land use, or LUCs that are of particular interest to gains and losses of SOC, and could become crucial in terms of future policies to mitigate the global greenhouse effect.

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Effects of soil compaction, rain exposure and their interaction on Soil Carbon Dioxide emission

Abstract

Soils release more carbon, primarily as carbon dioxide, per annum than current global anthropogenic emissions (Luo and Zhou, 2006). Given that soils emit carbon dioxide through mineralization and decomposition of organic matter and respiration of roots and soil organism (Houghton, 2007), evaluation of the effects of abiotic factors on microbial activity is of major importance in the context of mitigation greenhouse gases emissions. Previous studies demonstrate that soil CO_2 emission is significantly affected by temperature and soil water content. A limited number of studies have illustrated the importance of bulk density and soil surface characteristics as a result of exposure to rain on CO_2 emission, however, none examine their relative importance. Therefore, this study investigated the effects of soil compaction and exposure of the soil surface to rainfall and their interaction on CO_2 release. We conducted a factorial soil core experiment with three soil types, three different bulk densities (1.1 g cm^{-3}, 1.3 g cm^{-3}, 1.5 g cm^{-3}) and three difference exposures to rainfall (no rain, 30 minutes and 90 minutes of rainfall). The results demonstrated CO_2 release varied significantly with bulk density, exposure to rain and time. The relationship between rain exposure and CO_2 is positive: CO_2 emission was 53% and 42% greater for the 90 min and 30 min rainfall exposure, respectively, compared to those not exposed to rain. Bulk density exhibited a negative relationship with CO_2 emission: soil compacted to a bulk density of 1.1 g cm^{-3} emitted 32% more CO_2 than soil compacted to 1.5 g cm^{-3}. Furthermore we found that the magnitude of CO_2 effluxes depended on the interaction of these two abiotic factors. Given these results, understanding the influence of soil compaction and raindrop impact on CO_2 emission could lead to modified soil management practices which promote carbon sequestration.

Key Words: Soil Carbon Dioxide flux, Rain exposure, Soil Compaction.

INTRODUCTION

The total global emission of carbon dioxide from soils is 68–75 Pg CO_2 C year^{-1} (Mosier, 1998). This is one of the largest fluxes in the global carbon cycle and small changes in the magnitude of soil CO_2 flux can have a major influence on atmospheric CO_2 levels (Schlesinger and Andrews, 2000). Soils, with microbial catabolism, release more C for annum than current global antropogenic emissions (Luo and Zhou, 2006) and therefore could play a key role in mitigating GHG's emissions. Soils emit carbon dioxide through mineralization and decomposition of organic matter and respiration of roots and soil organism (Houghton 2007), but act as carbon sinks as they are able to accumulate carbon through photosynthesis. Studying and measurements of soil CO_2 is essential to understanding the C cycle in terrestrial ecosystem.

Many factors influence CO_2 fluxes between the soil and the atmosphere through influencing microbial process in the soil and the physical movement of CO_2 between the soil and atmosphere. Soil physical factors (Smith, 2003)and environmental variables such as, air temperature, photosynthetically active radiation (PAR) and air humidity, significantly affect ecosystem CO_2 exchange (Lloyd and Taylor, 1994; Davidson et al., 1998; Liu et al., 2006). According to Xu and Qi (2001), 70% of the temporal variation of

soil CO_2 efflux can be interpreted by a combination of soil temperature and moisture content. The release of CO_2 from soil organic matter by heterotrophic respiration, and, where roots are present, the release by autotrophic root respiration, generally increase exponentially with temperature (Anderson, 1973; Edwards, 1975; Ewel et al., 1987a; Fang et al., 1998; Longdoz et al., 2000). High soil water contents have been shown to impede the diffusion of CO_2 in soil (Linn and Doran, 1984; Doran et al., 1990; Skopp et al., 1990) but, alternatively, a low soil water content can inhibit soil microbial activity and root respiration (Davidson et al., 1998; Xu and Qi, 2001a, b: Curiel Yuste et al., 2003).

Soil compaction increases soil bulk density, compresses larger pores to smaller pores, thus decreases soil porosity and the infiltration capacity (Huang et al.). Consequently soil bulk density has been shown to impact CO_2 efflux, influencing soil microorganism survival and their microbial activity (Jensen et al., 1996). The numbers of soil bacteria, fungi and actinomycetes decreased by 26-39% with increased soil bulk density (Li et al., 2002) and the microbial activity, monitored by changes in soil CO_2 flux, decreased with an increase in soil bulk density (i. e., Liebig et al., Pengthamkeerati et al.). Alternatively, Shestak and Busse (2005) attributed reduced CO_2 flux in compacted soil to

reduced gas diffusivity rather than to any direct influence on the function of the soil microbial community. Furthermore, several studies have show an increase in CO_2 following rewetting due to mineralization of organic matter exposed after the physical breakdown of soil aggregates which occurs due to compaction and rainfall exposure (Beare *et al*., 1994; Denef *et al*., 2001) and subsequent mineralization of microbial C (Mikha *et al*., 2005),

It is not well documented how soil bulk density and rain exposure controls soil carbon dioxide flux. Therefore we undertook laboratory core experiments to investigate the effects of soil compaction and rain exposure on CO_2 flux at constant and not constant soil moisture. we hypothesize that soils with different bulk densities and rainfall exposures emit different quantities of CO_2 due to impacts on microbial activity and survival, CO_2 diffusivity, aggregate breakdown and the degree of surface sealing as a result of exposure to rainfall.

MATERIALS AND METHODS

We undertook controlled laboratory experiments, thus eliminating bias associated with spatial variability, and interactions between soil compaction, rainfall and other climatic conditions associated with field studies (Greacen and Sands, 1980). We used a factorial design with three contrasting soil types, three bulk densities and three different rain exposures, each was replicated five times resulting in 135 soil cores in total. The three soils were: a clay (59% clay, 24% silt, 17% sand), a silt (3% clay, 32% silt, 65% sand), and a sand (86 % clay, 37 %silt, 10 % sand) with the same organic matter content. The soil was sieved to 5 mm and compacted in 5 mm layers using a standard weight into 64.5 mm diameter 60 mm tall plastic pipe with geotextile fixed across the base. Each of the three soils were compacted to densities of 1.1 g cm^{-3}, 1.3 g cm^{-3}, or 1.5 g cm^{-3}, which are representative of agricultural soils. Our rain exposures were no rain and 30 minutes or 90 minutes under a rainfall simulator. To minimize differences in moisture content the difference in water volume between the 90 minute and 30 minute and no exposure rainfall treatments was carefully added to the surface of the no exposure and 30 minute exposures using a syringe. After the rainfall treatment the cores were incubated in open toped Kilner jars at 22 ±1°C.

Soil CO_2 efflux and water content were measured 1, 2, 5, 6, 9, and 10 days after the start of the incubation. A lid with a rubber gas sampling septa was fitted to each of the Kilner jars and five ml of gas was extracted immediately using a hypodermic needle and analyzed using an infrared gas analyzer (IRGA) (model ADC.225. Mk3, manufacturer Asea Brown

Boveri). Two further samples were then taken after 60 and 120 minutes to allow the rate of CO_2 emission to be determined. The volume of CO2 produced from the cores was converted to µg/g soil/minute using the universal gas law as used by Jassal *et al*. 2004 and Certini *et al*. 2003.

For the silt soil CO_2 emission was also measured under constant soil moisture conditions. For this experiment 22 mm diameter, 90 mm tall plastic pipe was used. The same bulk densities (1.1 g cm^{-3}, 1.3 g cm^{-3}, 1.5 g cm^{-3}) were used but the cores were either not exposed to rainfall or exposed for 90 minutes. Soil cores were incubated at constant temperature (22 ± 1 °C) for nine days and CO_2 emission and O_2 consumption were measured every 80 minutes using respirometer (Columbus Instruments Micro-Oxymax).

Data analysis was conducted using SAS statistical package (SAS Inst, 2001). The data were checked for normalcy and multivariate analysis of variance (MANOVA) was conducted to test the effects of bulkd density, exposure to rainfall and their interactions on CO_2 emission.

RESULTS AND DISCUSSION

Soil carbon dioxide emission during incubation at constant temperature.

Soil CO_2 emission is affected by soil texture, rain exposure and soil bulk density (Tab. 1). The clay soil had the highest emission compared to sand and silt soil: the average of Carbon dioxide emission rate was 0.063±0.044 µg CO_2 g^{-1} min^{-1}, 0.017±0.010 µg CO_2 g^{-1} min^{-1} and 0.010 ± 0.004 µg CO_2 g^{-1} min^{-1} respectively for clay, silt and sand soil. Cumulative CO_2 emission over 9 days from the clay-textured soil was six times greater than for the silt soil and three times greater than for the sand soil. These results concur with Rastogi *et al*. (2001) who observed that CO_2 evolution from fine-textured soil could be approximately twice as high as that from coarse textured soil. This occurs because fine textured soils have higher water holding capacities, which potentially prolong the availability of water in surface layers, thus maintain favorable condition for microbial soil respiration (Feiziene *et al*., 2010).

Soil CO_2 efflux significantly decreased (p<0.001) with increased soil bulk density. On average soil CO_2 emission rate decreased by 27% and 37% as soil bulk density increased from 1.1 g cm^{-3} to 1.3 g cm^{-3} and 1.5 g cm^{-3} respectively. Similar observations were also reported by Liebig *et al*. (1995) and Pengthamkeerati *et al*. (2005) who found a significant negative correlation of soil bulk density with soil CO_2 efflux. This occurs as increases in soil bulk density reduces gas diffusivity (Smith *et al*., 2000) which is linked with oxidation rate (Ball *et al*., 1997) and consequently rates of soil respiration and CO_2 emission (Van der Linden *et al*., 1989; Yoo and Wander, 2006).

CO_2 emission rate during the 9 day incubation period decreased with soil compaction for all soils except for clay soil (Tab. 2). In clay soil the highest average of CO_2 emission rate was founded in samples compacted to 1.3 g cm^{-3}, followed by 1.1 g cm^{-3} and 1.5 g cm^{-3}. In the first 24 hours of incubation, CO_2 emission from all soils decreased with increase of compaction.

Table 1. Results of analysis of variance (ANOVA) test for soil carbon dioxide emission rate during incubation at constant temperature

Source of variation	F	Prob>F
Soil	876.09	<0.0001
BD	16.31	<0.0001
Rain	119.48	<0.0001
Replicas	0.85	0.4947
soil*BD	9.00	<0.0001
soil*rain	45.99	<0.0001
soil*BD*rain	8.61	<0.0001

However, the effect of bulk density on soil CO_2 emission resulted in statistically significant differences on days 2 and 5 (Figure 1).
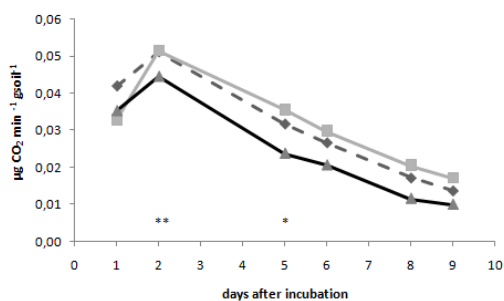

Figure 1. Average of soil carbon dioxide emission rate during incubation period. The black line, the grey line and dotted line indicate soil compacted to 1.5 g cm^{-3}, 1.3 g cm^{-3}, 1.1 g cm^{-3}, respectively(***= p<0.0001; * p<0.1)

Soil CO_2 emission significantly increased with increased rain exposure time (Tab. 1) on days 1, 2 and 5 (figure 2).
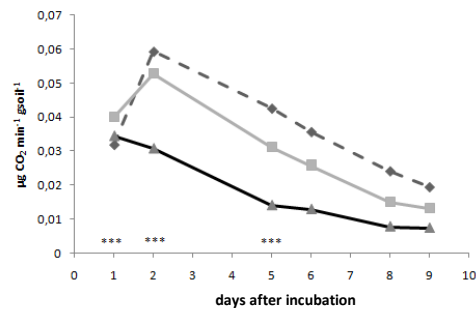

Figure 2. Average of carbon dioxide emission rate during incubation period. The black line, the grey line and dotted line indicate soil exposed to rainfall for 0', 30' and 90', respectively. (***= p<0.001).

The average CO_2 emission rates over the 9 days were 0.035± 0.014 µg CO_2 g^{-1} min^{-1}, 0.030 ± 0.015 µg CO_2 g^{-1} min^{-1}, 0.018 ± 0.012 µg CO_2 g^{-1} min^{-1} for soil exposed to rainfall simulator for 90 mins, 30 mins and not exposed respectively. As water addition enhances microbial metabolism, resulting in an increase of soil CO_2 emission (Birch 1958, Orchard and Cook 1983), differences in CO_2 emission found between samples exposed to different rain exposure times could be attributed to changes in soil moisture due to the formation of surface seals (MCINtyre 1958 ab) and to deposition of clays from suspension at the end of the rainfall event (Tackett and Pearson 1965, Pagliai *et al*., 1983, Norton 1987, Onofiok and Singer 1984, Norton 1987, Remley and Bradford, 1989)

Seals reduce evaporation, thus maintain favorable conditions for soil respiration. This explains the higher water content after 8 days in the soil cores exposed to

rain for 90' (Figure 3) and consequently the higher CO_2 emission rates.
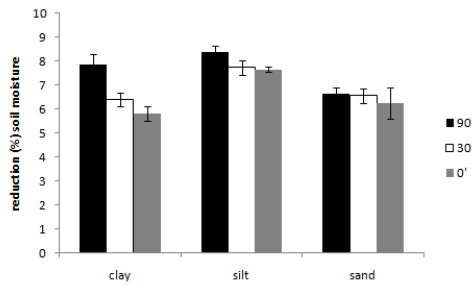

Figure 3 Soil Moisture reduction(%) between the first and ninth day after incubation.

In addition physical alteration of soil aggregates due to raindrop impact may have increased CO_2 emission by increasing substrate availability and enhancing access to non–biomass labile organic carbon (van Gestel *et al*., 1991; Van Gestel *et al*. 1993, Wu and Brooks 2005).

Other factors such as pre rain soil moisture (Lee *et al*., 2002; Borken *et al*., 2002; Xu *et al*., 2004; Sponseller 2007), soil organic layer (Borken *et al*. 1999; Savage and Davidson 2001) size of the organic carbon pool (Franzluebbers *et al*. 2000), and wetting intensity (Orchard and Cook, 1983; Liu *et al*., 2002, Borken *et al*. 2003) also impact soil moisture. However the same volume of water was added to each soil core regardless of the rainfall exposure time and the soil was homogenised.

All interactions (soil*bulk, soil*rain, soil*rain*bulk) terms were significant (Tab. 1). Soil CO_2 flux rate from soil exposed to rainfall for 90 mins was 171.7%, 181.5% and 32.3 % higher for clay, silt and sand soil, respectively, compared to no rain

exposure. The interaction between soil*bulk density was also significant (p<0.001) with soil CO_2 efflux with increasing bulk density was 17.76%, 20.76% and 41.73% lower for clay, silt and sand soil respectively, compared to the lowest bulk density.
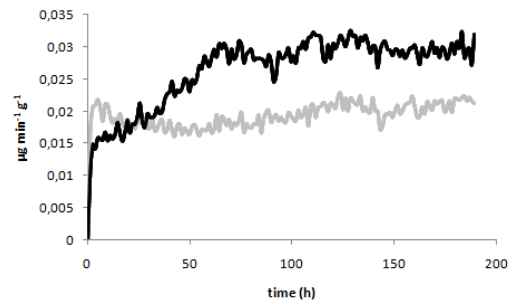

Figure 4. Carbon dioxide rate from soil exposed to rain simulator for 90' (black line) and soil no exposed (gray line).

For all cores there was a rapid and substantial increase in soil respiration occurred on 1 day after the simulated precipitation pulses and followed by a gradual decline, as well as found by several studies (Kieft *et al*., 1987; Appel *et al*., 1998; Fierer and Schimel, 2003; Sponseller, 2007, Chen *et al*. 2008). Significant increase in soil respiration following a rain event could be a result of degassing of stored CO_2 from past microbial and plant CO_2 efflux (Liu *et al*., 2002). This is a fast process that happens after few hours of water addition (Smart and Penuelas, 2005). Given that in our study CO_2 emission was measured 24 h after water addition, we attribute it to microbial metabolism which takes several hours to days to occur (Steenwerth *et al*., 2005, Chen *et al*., 2008)

Soil Carbon dioxide emission during incubation at constant temperature and soil moisture

Soil CO_2 emission rate under constant soil moisture and temperature varied significantly with bulk density, rain exposure and their interaction (Tab. 4). As expected, an increase of soil compaction level reduces soil CO_2 emission. Average CO_2 emission rates were 0.025 ± 0.002 µg min^{-1} g^{-1}, 0.024 ± 0.002 µg min^{-1} g^{-1} and 0.019 ± 0.004 µg min^{-1} g^{-1}, respectively for soil compacted to 1.1 g cm^{-3}, 1.3 g cm^{-3} and 1.5 g cm^{-3} As for the constant soil moisture experiments soil CO_2 emission was higher for the soil exposed to rainfall.

Figure 4 illustrates CO_2 efflux during eight days of incubation for soil exposed and not exposed to rainfall. Cumulative CO_2 emission in soil exposed to rain was 26% less compared to unexposed soil. One possible explanation for the CO_2 flux enhance after rainfall may be related to aggregate breakdown due to raindrop impact. It could be hypothesized that this breakdown of soil aggregate during rainfall event, resulted in the prompt exposure of previously encapsulated SOC, which became available for decomposition. Reicosky (2003), in a field experiment attributed an increase in CO_2 emissions from intensively tilled areas to the increase in surface area caused by aggregate breakdown.

The interaction between rain exposure and bulk density was significant. The effect of soil compaction on CO_2 emission rate reduction was greater in soil exposed to rainfall simulator (9%), compared to no rain exposure treatment (33%).

CONCLUSION

This study revealed that soil respiration is strongly affected by abiotic factor such as soil texture, soil compactio, rain exposure, and their interaction.

Our major findings were:

- CO_2 emission from clay-textured soil was six and three times greater than silt and sand soil, respectively.

- Soil compaction changes water content and soil aeration resulting in a decrease in soil CO_2 emission.

CO_2 emission is greater in soil exposed to rainfall than the soil not exposed. This is attributable to soil aggregate breakdown causing: (I) exposure of encapsulated SOC and (II) formation of soil surface seal which reduces evaporation, and thus maintains favorable conditions for soil respiration. Both effects contribute to enhance soil CO_2 emission after rain exposure in the first experiment, while in the second incubation experiment, at constant soil moisture, soil CO_2 emission increase is only attributable to enhance access to non–biomass labile organic carbon.

Table 2. Soil carbon dioxide emission during incubation at constant temperature.

		Clay						Silt						Sand					
Bulk density	Rain exposure	Days after incubation																	
(g cm^{-3})	(min)	1	2	5	6	8	9	1	2	5	6	8	9	1	2	5	6	8	9
1.1	90'	0.078	0.128	0.070	0.058	0.044	0.032	0.014	0.026	0.042	0.039	0.022	0.015	0.010	0.020	0.019	0.012	0.012	0.011
		(0.009)	(0.038)	(0.005)	(0.003)	(0.010)	(0.002)	(0.006)	(0.009)	(0.016)	(0.017)	(0.011)	(0.008)	(0.001)	(0.003)	(0.003)	(0.003)	(0.002)	(0.001)
	30'	0.112	0.109	0.047	0.039	0.023	0.013	0.013	0.026	0.037	0.034	0.012	0.011	0.015	0.018	0.018	0.010	0.009	0.008
		(0.020)	(0.034)	(0.020)	(0.010)	(0.010)	(0.004)	(0.004)	(0.009)	(0.012)	(0.012)	(0.005)	(0.006)	(0.007)	(0.002)	(0.002)	(0.001)	(0.002)	(0.001)
	0'	0.104	0.104	0.041	0.029	0.023	0.016	0.017	0.018	0.001	0.007	0.000	0.006	0.014	0.011	0.011	0.010	0.009	0.010
		(0.013)	(0.029)	(0.009)	(0.010)	(0.010)	(0.008)	(0.004)	(0.004)	(0.010)	(0.005)	(0.005)	(0.004)	(0.001)	(0.001)	(0.001)	(0.001)	(0.001)	(0.002)
1.3	90'	0.068	0.145	0.102	0.092	0.069	0.065	0.011	0.035	0.035	0.029	0.017	0.010	0.010	0.016	0.015	0.010	0.010	0.007
		(0.007)	(0.039)	(0.009)	(0.003)	(0.023)	(0.015)	(0.004)	(0.006)	(0.004)	(0.002)	(0.009)	(0.006)	(0.003)	(0.002)	(0.002)	(0.001)	(0.001)	(0.001)
	30'	0.082	0.135	0.073	0.065	0.044	0.036	0.011	0.030	0.032	0.023	0.012	0.013	0.010	0.016	0.015	0.010	0.009	0.008
		(0.014)	(0.031)	(0.027)	(0.023)	(0.011)	(0.011)	(0.005)	(0.005)	(0.005)	(0.009)	(0.005)	(0.006)	(0.003)	(0.002)	(0.002)	(0.001)	(0.002)	(0.002)
	0'	0.079	0.059	0.022	0.024	0.019	0.011	0.013	0.020	0.019	0.014	0.005	0.006	0.011	0.011	0.010	0.009	0.006	0.004
		(0.011)	(0.010)	(0.008)	(0.008)	(0.011)	(0.004)	(0.003)	(0.007)	(0.006)	(0.006)	(0.005)	(0.007)	(0.003)	(0.001)	(0.001)	(0.001)	(0.001)	(0.00)1
1.5	90'	0.078	0.138	0.062	0.053	0.032	0.022	0.009	0.021	0.033	0.029	0.011	0.014	0.010	0.010	0.010	0.007	0.005	0.003
		(0.017)	(0.045)	(0.008)	(0.004)	(0.001)	(0.001)	(0.003)	(0.005)	(0.006)	(0.003)	(0.006)	(0.004)	(0.002)	(0.001)	(0.001)	(0.002)	(0.001)	(0.001)
	30'	0.100	0.111	0.032	0.029	0.018	0.017	0.009	0.022	0.017	0.016	0.007	0.009	0.009	0.009	0.009	0.006	0.003	0.004
		(0.020)	(0.024)	(0.008)	(0.006)	(0.005)	(0.005)	(0.002)	(0.007)	(0.010)	(0.004)	(0.005)	(0.006)	(0.001)	(0.000)	(0.000)	(0.001)	(0.001)	(0.000)
	0'	0.051	0.030	0.006	0.006	0.004	0.005	0.014	0.016	0.008	0.012	0.004	0.008	0.008	0.009	0.008	0.005	0.001	0.002
		(0.010)	(0.006)	(0.011)	(0.002)	(0.002)	(0.002)	(0.004)	(0.004)	(0.005)	(0.003)	(0.002)	(0.004)	(0.002)	(0.001)	(0.001)	(0.001)	(0.000)	(0.001)

Values are the mean (n = 5) with standard deviation in parentheses.

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