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SOIL C SEQUESTRATION POTENTIAL OF EXOGENOUS ORGANIC MATTER: AN INTEGRATED LABORATORY AND MODELLING APPROACH

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To Lorena, Elena and Francesca

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On Exactitude in Science

…In that Empire, the Art of Cartography attained such Perfection that the map of a single Province occupied the entirety of a City, and the map of the Empire, the entirety of a Province. In time, those Unconscionable Maps no longer satisfied, and the Cartographers Guilds struck a Map of the Empire whose size was that of the Empire, and which coincided point for point with it. The following Generations, who were not so fond of the Study of Cartography as their Forebears had been, saw that that vast Map was Useless, and not without some Pitilessness was it, that they delivered it up to the Inclemencies of Sun and Winters. In the Deserts of the West, still today, there are Tattered Ruins of that Map, inhabited by Animals and Beggars; in all the Land there is no other Relic of the Disciplines of Geography.

- Suarez Miranda, *Viajes de varones prudentes*, Libro IV,Cap. XLV, Lerida, 1658
  translated by Andrew Hurley

La duda es uno de los nombres de la inteligencia.
Doubt is one of the names of intelligence.

- Blas Matamoro (Ed.) *Diccionario privado de Jorge Luis Borges* (1979)

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Abstract

Soil organic matter (SOM) is a key soil component as it affects nearly all properties that are significant for the agronomical and environmental functions of soils. Soil organic matter is important to warranty the crop productivity needed to satisfy the food demand of the increasing global world population and to reduce greenhouse gases emissions and the consequent adverse environmental impact caused by climate change.

The significant losses of SOM recorded worldwide in the last decades have raised concern about the necessity to recover and increase SOM levels. In particular, soil C sequestration, i.e. the long-term removal of CO_2 from the atmosphere into the soil, has been proposed as a valuable strategy to guarantee the agronomical and environmental functions of soils ecosystems.

Among the available soil management options fostering soil C sequestration, amendment is considered to be one of the more effective. The increased amount of organic residues applied to the soil in response to economical, legislative and social drivers has highlighted the need to optimize exogenous organic matter (EOM) amendment in order to increase its agronomical benefits and avoid potential adverse environmental effects.

Soil organic C (SOC) models represent a reliable solution for an efficient management of EOM amendment, for their ability to simulate future trends in SOC and the possibility to study different climate and management scenarios. However, there are no soil C models specifically developed to evaluate the C sequestration potential of amended soils.

The most widely utilized soil C model, the Rothamsted Carbon Model (RothC), does not allow C inputs to the soil deriving from crop residues and EOM to be discriminated and the quality of the organic matter entering in the soil is only defined by the ratio between decomposable and resistant organic materials. Previous research has indicated that, given the high variability in the composition and properties of EOMs, partitioning of EOM into a number of discrete pools and estimation of their functional characteristics are the main scientific challenges for reliable C modelling of amended soil.

Therefore, the main aim of this study was to devise an easy and reliable procedure for the optimization of the RothC model to improve the prediction of the long term C sequestration potential of EOM added to the soil at both local and regional scale by***:***

- developing an approach to use information derived from laboratory incubation experiments to define the size and functional properties of EOM pools.
- evaluating the relative potential of several EOMs in terms of soil organic C sequestration in relation to their chemical and physical characteristics, environmental conditions, agricultural management and future climate change.

The following procedure was adopted to achieve this goal:

- the source code of the RothC model was modified to allow assignment of 3 additional entry pools of EOM (decomposable, resistant and humic-like) with specific decomposition rates.
- an Excel version of the modified model was used to define partitioning factors and decomposition rates of EOM entry pools by fitting the cumulative respiration of soil amended with different EOMs (compost, bioenergy by-products, anaerobic digestates, meat and bone meals, animal residues, crop residues, agro-industrial wastes, sewage sludges) during laboratory incubations. The fitting was obtained minimizing the difference between simulated and measured respiration by adjusting the size and the decomposition rates of EOM pools.
- a procedure was devised for spatially explicit SOC modelling of amended soil under climate change by linking Geographic Information Systems, containing detailed information on soils, land use and climate, with the RothC model.
- the model optimized for the simulation of organic C mineralization in amended soils was run in the long term (2001-2100) simulating soil additions of different EOMs at both site and national scale (Italy) under different future climate scenarios.

The main conclusions of the study were:

- the modified Roth C model, considering discrete EOM pools with specific decomposition rate, is effective in predicting the net cumulative respiration from amended soil incubated under laboratory conditions.
- utilizing a unique set of EOM parameters for EOM type resulted in a difference of less than 10% in the prediction of long term C evolution (100 years) of amended soil in comparison to a simulation performed with EOM specific parameters.
- predicted climate change in the present century will speed up SOM decomposition leading to a generalized SOC decrease in Italian soil of 7.4%, on average, between 2001 and 2100.
- EOMs greatly differed for their long term (100 years) soil C sequestration potential (range of annual rate of C sequestration potential 0.110-0.385 t C ha^{-1} y^{-1}).
- soil C sequestration potential of compost applied for 100 years to all Italian agricultural land at a rate of 1 t C ha^{-1} y^{-1} and under climate scenario PCM B1 was 6.15 Mt C ha^{-1} y^{-1} corresponding to 4.6% of the total annual greenhouse gases emissions in Italy.
- soil C modelling of amended soil at national scale showed a great variability in long term (100 years) SOC accumulation potentials (1 order of magnitude) depending on combination of EOM type, environmental properties (soil, climate) and management options (land use and soil management).
- spatial explicit modelling of amended soils allowed areas with greater potential for soil C sequestration to be identified, therefore providing useful information to optimize resources: 100 years of application of the whole compost produced in Italy to the land with the smallest and largest potential for C sequestration resulted in a mean SOC increment of 27 and 55 t C ha^{-1}, respectively (i.e. 2-fold increment).
- soil C modelling of amended soil at regional scale could be useful to identify the relative importance of the different factors favouring organic C storage in the soil: in the present study temperature had a major impact on determining the observed SOC evolution.

The main innovative aspects of this work consist in:

- modification of the RothC model to improve the capacity of simulating SOC trends in amended soil.
- parameterization of the modified RothC by fitting respiratory curves from short term laboratory incubations of soil amended with EOM of different origin and properties.
- deployment of a procedure for spatially explicit modelling of SOC in amended soil.

Results of the present work highlighted the relevance of laboratory incubation experiments of amended soil for the improvement of SOC modelling of amended soils as a valuable tool for planning future land uses and policies aimed to foster soil C sequestration, reduce CO_2 emissions and warranty the sustainability of agricultural ecosystems.

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List of abbreviations

AD: anaerobic digestates

AR: animal residues

BE: bioenergy by-products

AW: agro-industrial wastes

BIO: soil microbial biomass

C_{mic}: soil microbial biomass C

CO: compost

CO_2-C: cumulative net CO_2-C emission

CR: crop residues

dm: dry matter

DEOM: decomposable exogenous organic matter

DPM: decomposable plant material

E: relative error

EOM: exogenous organic matter

f: OM pool partitioning factor

$f_{DEOM:}$ partitioning factor for DEOM

$f_{DPM:}$ partitioning factor for DPM

$f_{HEOM:}$ partitioning factor for HEOM

$f_{REOM:}$ partitioning factor for REOM

$f_{RPM:}$ partitioning factor for RPM

FYM: farmyard manure

fw: fresh weight

GCM: general circulation model

Gt: gigatonne = petagram = 10^{15} g

HEOM: humic-like EOM

HUM: humified organic matter

IOM: inert organic matter

IPCC: Intergovernmental Panel on Climate Change

K: OM pool decomposition rate constant

$K_{DEOM:}$ decomposition rate constant for DEOM

$K_{REOM:}$ decomposition rate constant for REOM
M: mean difference between measured and simulated data
MM: meat and bone meals
MSW: municipal solid wastes
Mt: megatonne = teragram =10^{12} g
N_{TOT}: total N
ppm: part per million
ppmv: part per million by volume
R: coefficient of correlation
REOM: resistant exogenous organic matter
RPM: resistant plant material
RMSE: root mean square error
SA: sensitivity analysis
SGDBE: soil geographical database of Europe
SI: Sensitivity index
SOC: soil organic C
SOM: soil organic matter
SMU: soil mapping unit
SPADE: soil profiles analytical database of Europe
SRES: special report on emissions scenarios
STU: soil typological unit
SS: sewage sludge
SSR: sum of squared residuals
TOC: total organic C
TPOMW: two-phases olive mill wastes
WHC: water holding capacity
WSC: water soluble C
WSN: water soluble N
WFPS: water-filled pore space
WS: wheat straw

1. Introduction

1.1 Exogenous organic matter (EOM)

1.1.1 Agronomical and environmental importance of soil organic matter

Soil organic matter (SOM) is one of the most important components of soil as it influences virtually all the properties of soil that control agricultural and environmental functions. It constitutes a great reservoir of C, N and other plant nutrients and plays an important role in improving physical, chemical and biological characteristics of the soil (Petersen et al., 2005a). Soil organic C (SOC) is the C content of SOM, which is mostly around 50 to 60%. The value of organic matter (OM) in enhancing soil quality from an agricultural point of view is well known and documented by a large number of scientific studies and experiments. Improved soil fertility by increased levels of OM allows costs and energy for tillage, irrigation and fertilization to be reduced and saved, because of improvements in important soil properties such as: soil structure, tilth, workability, water holding capacity (WHC), porosity, bulk density, cation exchange capacity, micro-organisms activity and fertilizer efficiency. An appropriate level of fertility limits exploitation of non-renewable resources (e.g. fossil fuels, phosphates) and excess of energy expenses (e.g. production of chemical fertilizers and pesticides, treatment and disposal of organic wastes). At the same time adequate SOM levels decrease soil sensitivity to erosion and compaction.

The effects of SOM on soil fertility are relevant in the perspective of the anticipated increase of world population. At the present rate of increase (1.3% per year), world population is expected to reach 7.5 billion by 2020 and 9.4 billion by 2050 (Lal, 2006a). Most of the future increase in world population will occur in developing countries where environmental resources are scarce. It has been estimated that food production must be increased by 778 million tons (or by 2.5%) per year between 2000 and 2025 to meet the needs of the increasing population (Lal, 2006b). On the other hand, the amount of productive soil area that can be dedicated to agriculture is not expected to increase due to the fact that all the soil best suited for agriculture has already been utilized. Moreover, in developed countries the top productive areas are decreasing as they are increasingly used for construction of urban and commercial areas. Consequently, the challenge to ensure sufficient food production for the increasing world population could be met only by enhancing soil fertility. To achieve this goal the presence of an appropriate SOM content is essential.

Besides the positive effects on soil fertility, SOM plays a range of key environmental functions. In particular, SOM affects the quality of waters, regulates erosion processes and maintains a high degree of biodiversity, contributing to the sustainability and the equilibrium of anthropogenic and natural ecosystems. The unparalleled increase in the atmospheric concentration of the 3 main greenhouse gases (GHG), namely CO_2, N_2O and CH_4 recorded in the last century and their negative environmental consequences on climate change has raised the attention of the scientific community on the role that SOM can exert in this context. Globally, the total quantity of organic C stored in the first 20 centimetres of soil is about 615 Gt, while the amount stored in the first meter is approximately 1550 Gt (Stockmann et al., 2013). The latter amount is roughly twice the content of C in the atmosphere (750 Gt) and 2.8 times the terrestrial biotic pool (560 Gt) (Lal, 2008). As a consequence, even slight changes in SOC content at world level present clear potential consequences for the atmospheric levels of GHG and the consequent climate change. For example, a variation of just 10% in the SOC global pool equals 30 years of anthropogenic emissions and could significantly affect concentrations of atmospheric CO_2 (Kirschbaum, 2000).

1.1.2 Losses of soil organic matter

Despite the acknowledged agronomical and environmental importance of SOM, in the last decades a significant loss of SOC has been recorded worldwide, which has mainly been attributed to the cultivation of new land and the intensification of agricultural practices (Bellamy et al., 2005; Lal, 2004; Lal, 2006b).

Cultivation of natural ecosystems (forests, pastures, etc.) and the intensification of agricultural systems are among the predominant global changes of the last century. These transformations were able to satisfy the food and fibre requirements of the world's population, but such requirements are expected to significantly increase in the 21st century due to the foreseen increase in global population. Most of the best quality land is already used for agriculture, which implies that further possible expansion would occur on marginal land, unable to sustain high yields (Tilman et al., 2002). Therefore, satisfaction of the future needs could be guaranteed mainly by intensive production practices (Powlson et al., 2001). Indeed, agricultural intensification, characterized by high mechanization, chemical inputs, high yielding varieties and irrigation, has been able to increase global food production for the last 50 years. However, concerns have been raised over both the long-term sustainability and environmental consequences of the intensification of agricultural systems and the ability to feed the rapidly growing population in the 21st century (Matson et al., 1997). In areas of East and Southeast Asia, warnings of productivity decline due to the lack of resources (water) and increased susceptibility to disease and insects pests have been observed (Matson et al., 1997; Tilman et al., 2002). Moreover, it is now clear that expansion of agricultural land and intensification can have negative environmental consequences such as increased erosion, reduced biodiversity, pollution of water and eutrophication. In particular, with concern on the C cycle, conversion of natural systems to agricultural systems and intensive agriculture has resulted in a significant depletion of the SOC pool.

Loss of organic C in cultivated soils is a worldwide phenomenon. Bellamy et al. (2005) estimated a mean C loss from soils across England and Wales of 0.6% y^{-1} between 1978 and 2003. In the Mediterranean area 74% of the land is covered by soils containing less than 2% of SOC with a decrease estimated at around 50% of the original content (Van-Camp et al., 2004). Soil in the tropics and subtropics has lost 60-80% of its SOC pool (Lal, 2006b). The global cumulative historic loss of C by cultivation is enormous and is estimated at 78 ± 17 Gt by Lal (2003) and 55 Gt by Cole et al. (1996). In the developed country, the recent growing demand for bioenergy production poses a further threat to SOM, as bioenergy crops removal may exacerbate SOM losses due to the lack of crop residues return to the soil. Traditional agricultural managements in developing countries, such as removal of crop residues and non-utilization of manure in soil, exacerbate soil C loss (Lal, 2006b).

The reduction in SOC leads to a decrease in soil fertility and the onset of several degradative processes such as erosion, desertification, compaction and nutrient deficiency (Lal, 2004). It has been estimated that roughly 2 billion ha of land are affected by degradation, which is over 30% of all land on earth (Oldeman, 1994). The EU Commission has identified OM decline as one of the main threats to soils within Europe (Jones et al., 2004). There is considerable concern that, if SOM concentrations in soils are allowed to decrease too much, then the productive capacity of agriculture will be compromised. It has been estimated that 45% of European soils have a SOC content lower than 2%, which has been suggested as a critical level (Rusco et al., 2001; Loveland and Webb, 2003).

Besides the impact on soil quality and productivity of agricultural ecosystems, SOC losses present a significant impact on atmospheric GHG levels: 1 Gt C loss is an equivalent to an atmospheric enrichment of CO_2 by 0.47 ppmv (Lal, 2007).

1.1.3 Soil C sequestration

Due to the key agronomical and environmental functions of SOM, it is of the utmost importance for the sustainability of society to restore, maintain and increase SOM levels.

In particular, the size of SOC reservoirs in soil has led to suggestions, from both scientists and politicians, that increasing the amount of SOM might be a potential strategy for tackling GHG emissions (Freibauer et al., 2004; Smith, 2004a) through the process of soil C sequestration. Soil C sequestration is defined as long-term (i.e. > 100 years) or permanent removal of CO_2 from the atmosphere into the soil (Stockmann et al., 2013). More precisely, according to Bernoux et al. (2006) “Soil C sequestration for a specific agro-ecosystem, in comparison with a reference, should be considered as the result for a given period of time and portion of space of the net balance of all GHG expressed in CO_2 equivalent computing all emissions sources at the soil-plant-atmosphere interface, but also all the indirect fluxes (gasoline, enteric emissions and so on)”. Soil C sequestration may have the potential to offset fossil-fuel emissions by 0.4-1.2 Gt C y^{-1}, corresponding to 5-15% of the global emissions (Lal, 2004). The term soil C sequestration therefore, implies a ‘lock up’ of C from atmospheric CO_2 in the soil either through accumulation of very stable C (e.g. charcoal) or by alteration of the relative magnitude of soil C pools with different residence time (Stockmann et al., 2013). When C inputs are greater than losses, SOC accumulates in the soil and after microbial decomposition and transformations into stable SOM the additional C is sequestered into the soil. The inputs of OM include plant and animal residues. The losses from the soil include decomposition, leaching and erosion of OM and burning of crop residues. The potential for increasing C storage in cropland worldwide has been estimated at about 0.6-1.2 Gt C y^{-1} or 18-36% of the annual increase in C in the atmosphere (Lal, 2004).

However, there are several indications that raise concern about the effectiveness of C sequestration in soil as a strategy to effectively address GHG emissions (Wanderer and Nissen, 2004). Soil C sequestration has a finite potential and a yearly increase in SOM can be sustained for only 50-100 years and, as soil tends to approach a new equilibrium, the increase in SOC slows down and eventually ceases (Powlson et al., 2012). In addition, this theoretical potential is further decreased by several constraints such as: land suitability, unavailability of land and resources and socioeconomic restrictions. Due to this limitation, it was estimated that only 20% of the soil C sequestration potential is realistically achievable (Freibauer et al., 2004; Smith, 2004a). Another limitation is that C sequestration is not permanent and is reversible if the soil management leading to the increased SOC is not maintained (Powlson et al., 2011b).

Therefore, soil C sequestration can play only a minor role in the reduction of GHG emissions. It is widely recognized that if CO_2 concentrations are to be stabilized at reasonable levels (450–650 ppmv), the main solution to avoid climate change is a drastic reduction in GHG emissions by finding new energy technologies that do not emit C. In fact, under the highest emission scenarios it was estimated that soil C sequestration can contribute to a reduction of only 2-5% of total GHG emissions in EU-15 (Smith, 2004a).

Notwithstanding these constraints, C sequestration still represents an attractive strategy for two main reasons.

From the exclusive point of view of climate change, it is recognized that in order to achieve acceptable levels of GHG it is necessary to obtain their sudden decrease in the next 20-30 years (IPCC - Intergovernmental Panel on Climate Change, 2000; Wanderer and Nissen, 2004). Carbon sequestration is likely to be particularly effective in reducing atmospheric CO_2 levels in the first 20-30 years of its implementation and it should be included in any set of measures aimed to reduce atmospheric CO_2 concentration, thus allowing time to be saved while technologies designed for the reduction of emissions of GHG are developed. During this critical period, C sequestration has been shown to be the most cost effective and feasible measure aimed at the reduction of GHG emissions (Marland et al., 2001).

From a wider perspective it is essential to consider that soil C sequestration is only one of the many beneficial environmental and economical implications of appropriate SOM management. Improved SOM management, necessary to achieve the sequestration of C in soil, is likely to have marked positive impacts on soil quality, ecosystem functioning and economical sustainability (Lal et al., 1998; Dumanski, 2004; Powlson et al., 2011b).

1.1.4 Soil amendment as management option to promote soil C sequestration

1.1.4.1 EOM definition and production

There are several soil management options that can be set up to recover and increase SOM and, amongst land management options, soil amendment with exogenous organic matter (EOM) is considered to be one of the more effective ways of restoring SOC and offsetting climate change (Lal, 2004; Smith 2004a, b).

Exogenous organic matter is all OM of biological origin that is returned to the soil for the purpose of growing crops, improving soil quality and restoring or reclaiming land for future use. EOM includes organic residues from agricultural, urban and industrial origin as well as the products of their processing (Marmo et al., 2004). As such EOMs include a very wide range of bio-wastes from a considerable variety of sources. EOMs may have various forms (solid, liquid, pasty) and undergo a treatment before application to the soil. Their use in agriculture depends on the agronomic value (stabilization degree, content of OM and nutrients) and the absence of risks for health and environment (content of xenobiotics and pathogens).

At European level, about 1200 million tonnes of EOMs are produced each year (with exclusion of crop residues), divided into 81% of animal origin, 9.5% of municipal wastes (sewage sludge, biowaste and green waste) and 9.5% of agro-industrial waste. However, more than 90% of EOMs applied to the soil (excluding crop residues) are of animal origin (Marmo, 2008).

In Italy, about 150 million tonnes of EOMs are produced every year divided in 87% manures, 4% agro-industrial wastes, 5% sewage sludges and 3% from municipal solid bio-wastes and green wastes.

The utilization of organic amendments is increasing due to enhanced social awareness about the importance of protecting the environment and the fact that current legislation promotes the recycling of organic wastes. Source separation of municipal solid wastes is becoming mandatory in all developed country and this generates increasing amount of organic wastes that need to be disposed in an environmental sound way. A further incentive for the agricultural recycling of organic residues is represented by the development of organic farming.

Recently, legislative and environmental drivers favoured the agricultural recycling of a wider range of organic residues. Such residues are either not usually applied to soil or novel and therefore raise the issue of their impact on soil fertility and the environment.

First, the ban in early 2000 to utilize meat and bone meal for animal production as a consequence of the appearance of Transmissible Spongiform Encephalopathies (TSEs) has suggested soil application of not infected meat and bone meal and other animal residues as a sustainable solution for their disposal.

Second, the constantly increasing interest in using renewable energy sources it is likely to produce considerable amounts of bioenergy by-products and poses the problem of their disposal. Such organic residues may still contain large amounts of organic C and a significant content of a wide range of nutritive elements. As a consequence they are very attractive as soil amendments or fertilizers and it is likely that the amount of bioenergy by-products that will be returned to the soil will significantly increase. However, bioenergy by-products are derived from a broad range of feed-stocks and present highly variable physicochemical characteristics and therefore can affect the soil ecosystem in different and unpredicted ways (Cayuela et al., 2010).

Soil amendment is often referred as a win win strategy as it allows solving the problem of organic residues disposal, restoring SOM depleted soil and building up SOC stocks (Karhu et al., 2012).

1.1.4.2 EOM decomposition

Soil organic C stocks in soil depend on the equilibrium between the OM entering in the soil (i.e. crop residues and EOM) and OM decomposition.

Soil organic matter decomposition is a complex multi stage process which is mediated by microorganisms, consisting in the breakdown of complex organic materials into simpler components and represents an important process that makes organically bound nutrients available for utilization and cycling (Franzluebber, 2004). Exogenous OM decomposition may be defined as the combination of 3 processes:

- transformation: conversion of organic C from a chemical structure to another following enzymatic attack and chemical reactions
- assimilation: incorporation of organic C into the tissues of the decomposer organisms
- mineralization: conversion of organic C in CO_2 by respiration

The rate of EOM decomposition in soil is critical to determine soil C accumulation and the effects on soil properties and nutrient cycling. EOMs decomposition after addition to the soil depends on their biochemical composition, the size and activity of soil microorganisms and by several environmental factors.

Exogenous OM of animal and vegetal origin consisting of several compounds with distinct degree of degradability: a) highly labile intercellular compounds such as proteins and sugars, b) moderately resistant structural compounds such as cellulose, hemicellulose and collagen, and c) resistant structural compounds such as lignin, polyphenols, lipids, cutin and keratin. The rate of decomposition of the whole EOM depends on the relative proportion of the different compounds (Franzluebber, 2004). Besides chemical composition, the processes that originated the by-products and the treatments they were subjected in order to transform and/or stabilize their OM are of the greatest importance in determining the susceptibility of added organic residues to microbial degradation in the soil. As an example, composted EOMs decompose slowly when added to soil because they have already undergone a significant amount of decomposition during the composting process.

Soil microorganism plays a pivotal role in EOM breakdown and transformation. More than 90% of OM is decomposed by bacteria and fungi, but also meso- and macro-fauna play an important role by creating environmental conditions conducive to microbial decomposition. Bacteria generally dominate the initial phases of decomposition, because they can develop rapidly on easily degradable compounds (i.e. soluble sugars, globular proteins). Fungi dominate in the latest phases of the decomposition process as they are able to decompose more recalcitrant material that is for the most part unavailable to bacteria.

Among the environmental factors affecting EOM decomposition, the main important are soil temperature, texture, humidity, pH and content of available nutrients.

Moreover, it needs to be considered that climate change may vary the turnover of EOMs by altering the factors that regulate their decomposition.

EOM decomposition takes place in a wide range of time and intensity of the process. The first phase of decomposition is relatively fast in the case of not stabilized EOM and results in the loss of 15-66% of the organic inputs within one or two years after soil addition (Jenkinson and Rayner, 1977). Successively, the rate of decomposition slows down with about 90% of the added EOM decomposed in a period from 10 to 100 years. Finally, in the third phase of the process the whole EOM is decomposed with a turnover time from 100 to 1000 years.

The most common parameters utilized for the evaluation of EOMs in terms of their decomposability in the soil are C and N content and their ratio (C/N). Other parameters indicative of the degree of stabilization of EOMs are extractable organic C and N and the content of compounds of biological relevance (i.e. soluble fraction, cellulose, hemicellulose, cutin and lignin). The degree of stabilization of EOMs is further evaluated by determining C and N mineralization in incubation studies of amended soils.

1.1.4.3 EOM and soil C sequestration

Regarding the role of amendment as a way to offset GHG emissions, it is important to acknowledge that soil application must represent an alternative fate to the current disposal option of EOM, as C sequestration is defined in terms of net balance of all SOC losses and gains. Since EOM was previously mostly disposed of to landfills or burned, soil amendment with EOM eliminates the corresponding emissions and this therefore constitutes a net contribution to climate change mitigation (Powlson et al., 2011b; 2012).

The rate of potential C sequestration by soil amendment in European soils has been estimated at 0.42 t C ha^{-1} y^{-1} (Smith et al., 2008) for manure/biosolid application and 0.40 t C ha^{-1} y^{-1} by Freibauer et al. (2004) for amendment, although the increase in SOC necessarily decreases with time, as a new equilibrium value is approached (Powlson et al., 2012). Arrouays et al. (2002) evaluated the potential rate for C sequestration of compost to be in the range 0.23-0.55 t C ha^{-1} y^{-1} for a period of 20 years of application. Powlson et al. (2012) evaluated at 5.1 t CO_2-eq ha^{-1} y^{-1}, the net CO_2 saving due to SOC change for an application of green compost at a rate of 36 t fresh weight ha^{-1} y^{-1}.

The prerequisite for developing policies for increasing C sequestration by organic amendments is the availability of data and/or tools that can be used to demonstrate variations in C stocks due to changed management. Measuring changes in soil C stocks by repeated measurements is expensive (Mäkipää et al., 2008) and soil C modelling could be a cost effective option for verifying changes and approaching long-term effects of amendment, which are particularly relevant to evaluate the effect of repeated applications of EOM on SOC trends (Gabrielle et al., 2005).

1.2 Soil C modelling of amended soil

1.2.1 Soil C models

Models are simplified representations of the reality with well defined boundaries (Smith and Smith, 2007). More specifically, soil C models accurately describe long-term

SOC trends under different climatic conditions and soil types (Smith et al., 1997). SOC models are predictive as they are generally used to anticipate a certain phenomenon, either for research purpose or as a tool to assist land users and decision makers in developing sustainable environmental policies.

Soil C models are generally multi-compartmental, assuming that SOC is split in various pools with in turn decay according to first order kinetic, and dynamic, i.e. environmental variables vary with time. Dynamic models can be further divided in four classes (Paustian, 1994; Battle-Aguilar et al., 2011):

- Process-orientated multi-compartment models: simulate the processes regulating the flow of energy and matter transformation. SOC pools, composed by fractions of SOM with similar chemical composition and degradability, are linked to each other by C flows and are characterized by different decomposition rates. Models in this category are the most widely utilized and include Rothamsted Carbon Model (RothC), CENTURY, NCSOIL, DAISY, CANDY and DNDC
- Organism-orientated: simulate the flow of nutrients and energy in soil through various functional or taxonomic groups of biota
- Integrated: link process to organisms orientated models
- Cohort: convert SOM in different cohorts, items sharing some particular characteristics (e.g. age, origin), which are further divided into different pools (e.g. C, N). In these models SOM decomposition is not regulated by physical and biochemical processes, as in process-based models, but microbial physiology represents the main driving factor for SOM decomposition.

To date, more than 250 models for simulating SOC trends and nutrient cycling have been developed (Manzoni and Porporato, 2009). These models differ in assumptions and processes responsible for SOM transformation, but most of them divide SOM in different pools with distinct properties and decomposition rate.

Simulation models allow studying experimental results by comparing predictions with measurements, and therefore checking the validity of the theory embedded in the models, which describes system behaviour (Cavalli and Bechini, 2011). Consequently they are an important tool to understand SOC dynamics and develop management strategies to optimize inputs for C sequestration. Soil C models have the potential to:

- compare the effects of different conditions
- quantify expected results
- describe the effect of complex factors as variations in the input
- explain how the underlying processes contribute to the observed results
- extrapolate results to other situations
- make future projections of change in SOC under different management and/or climate scenarios

In the framework of long term consequences of SOM management, models can be useful to investigate the effects of climate change and land use and management on SOM and support policy decision regarding C sequestration options. For this purpose reliable information on which management leads to the higher build up of C stocks is important and consequently, there is an urgent need to have reliable methods to measure changes in SOC and to evaluate trends in SOM content. In addition, methods leading to reliable, transparent and verifiable changes in soil C stock are at the basis of the inclusion of soil C sequestration from agricultural soils and land use changes among the measures internationally agreed under the Kyoto Protocol.

However, SOC changes in soil tend to occur slowly and in temperate regions it is common for small changes to be undetectable within one or two decades even after a major change in agricultural practices. This is partly because the changes occur against a relatively large background content of SOC and partly because spatial variability makes changes in SOC difficult to measure (Powlson, 1996).

Long term experiments are the ideal tool of detecting and quantifying slow change in SOM, but it is not feasible to conduct long term experiments covering all the possible combinations of climate and management options and providing results within a reasonable time. Soil organic C models are a reliable and practical solution to this problem as they can estimate C stocks, make projection of likely trends in SOC and estimate C storage potential for many different combinations of soil type, environment, land use, management options and climate change scenarios (Powlson, 1996). They can be used to analyse specific pedoclimatic and management scenarios, and to identify the solutions that maximise C storage in the soil (Cavalli and Bechini, 2012). Thus models represent a tool to extrapolate current knowledge both in time and space.

1.2.2 Modelling soil organic C in EOM amended soil

1.2.2.1 Application of soil C models to amended soils

In the context of predicting SOC sequestration levels that could be achieved by soil amendment, a key issue is the influence of EOM quality on the long term persistence of C added to the soil (Corbeels, 2001), as the size of the C pools and their decomposability will ultimately determine the amount of EOM C that will remain in the soil.

EOM mineralization is an extremely complex process because organic materials added to the soil contain a wide range of organic substances. The biological decomposition of EOM depends on the decomposition rate of each one of the classes of the organic compounds present in the sample, which in turn depends on their content of N, S, soluble C, lignin and various carbohydrates. Such composition is extremely variable, since organic residues may have plant and animal origin and may have undergone different stabilization treatments, such as composting, desiccation, anaerobic digestion and physical separation. Decomposition rate is also affected by soil and environmental conditions.

Process-oriented modelling offers in principle a unique mean of addressing the high variability in the properties of EOM, the effect of different pedoclimatic conditions and the complexity of mechanisms and the several factors affecting soil C mineralization. As a matter of fact, deterministic multi-compartmental C and N models have been applied also to the simulation of soil mineralization in soils amended with different EOM types. In models that simulate EOMs decomposition they are usually considered as several independent components differing in their decomposability. The aim of EOM decomposition modelling is to define the composition, size and specific rate of decomposition of such components and thereby be able to predict the rate of decomposition of any EOMs, assuming that they only differ by the relative content of those components (Antil et al., 2011).

The possibility to use multi-compartmental models to simulate SOC trends following EOM amendment in comparison to control plots is made possible by the linearity of these models, in which EOM pools decomposition are described by first order differential equations. This implies that:

- the evolution of X kg of input is X times the evolution of 1 kg of the input (addictive effect of C entering in the soil)
- the decomposition of a particular C pool is independent from the other pools
- all other conditions being the same, the simulated difference in SOC stocks between amended and control soil is exclusively attributable to EOM addition and decomposition.

The linearity of models simulating SOC accumulation due to EOM application avoids the difficult phase of estimating the initial size of SOM pools. This approach was followed by Henriksen and Breland (1999b) in a study about decomposition of crop residues in the field: as the authors were only interested in the simulated turnover of residue-derived C and N, they set to zero the initial values of the soil microbial biomass and humus pools. Similarly, Henriksen et al. (2007) found that the effect of calibrating the model with data from the control soil had a little effect on the predicted mineralization of plant residues. In their model, the only influence of soil on the simulated decomposition of crop residue would be through humus mineralization. However, the fraction of decomposed residue-derived C incorporate into humus is small and consequently, the effect of varying humus decomposition rate constant on predicted mineralization of EOM-derived material is presumably small.

However, model linearity involves a number of simplifications, including the inability to take into account the influence of priming effect, that is the change in the rate of decomposition of the native SOM due to EOM addition (Fontaine et al., 2003). Such limitation is present, for example, in the RothC (Peltre et al., 2012) and CN-SIM models (Cavalli and Bechini, 2012). A non-linear approach is possible, but more complicated to implement and requires a scale-dependent description and location of C (Monga et al., 2008).

The reliability of models in predicting long term changes in SOC following soil amendment was recently demonstrated by Karhu et al. (2012), Plaza et al. (2012) and Peltre et al. (2012) who found good correlations between modelled and measured C stocks for different types and amounts of EOM.

Table 1 reports some examples of soil C models that have been utilized to simulate SOC trends in amended soils at field scale.

Table1. Soil C models utilized for SOC simulation in amended soils.

Model	EOMs	Application rate (y^{-1})	Simulation period (y)	Reference
RothC	Chicken and dairy manure	170-670 kg N ha^{-1}	2	Abbas and Fares, 2009
RothC	Cattle and pig FYM and slurry, broiler litter	0.6-7.0 t C ha^{-1}	14	Bhogal et al., 2010
RothC	FYM, WS, SS, sawdust, compost	6.5-30 t ha^{-1}	11-52	Peltre et al., 2012
RothC	User defined	User defined	User defined	Carbo-PRO web tool, 2012
RothC	FYM	10-15 t fw ha^{-1}	25	Yokozawa et al., 2010
RothC	Waste garden compost	5-45 t ha^{-1}	15	Tits et al., 2014
C-simulator	Waste garden and household waste compost	30 t ha^{-1}	13	Tits et al., 2010
CN-SIM	FYM	2 t C ha^{-1}	52	Petersen et al., 2005
DAISY	Oilseed rape straw	8 t ha^{-1}	2	Mueller et al., 1997
DAISY	WS, maize, blue grass	6 t fw ha^{-1}	1	Mueller et al., 1998
DAISY	FYM, WS, sawdust	6.5 t dm ha^{-1}	35	Bruun et al., 2003
DAISY	MSW compost, SS, FYM, cattle slurry	200 kg N ha^{-1}	50	Peltre et al., 2013
DAISY	Compost	20 t ha^{-1}	4.5	Gerke et al., 1999
NCSOIL	MSW compost	270 t dm ha^{-1}	0.2	Mamo et al., 1999
NCSOIL	MSW compost	10-25 t dm ha^{-1}	4	Gabrielle et al., 2005
NCSOIL	FYM, Compost	2 t C ha^{-1}	7	Noirot et al., 2013
Cantis	WS	8 t dm ha^{-1} (1.2 g C kg^{-1})	1	Garnier et al., 2003
TAO	Compost, plant and animal wastes, manure	0.4-5.0 g C kg^{-1}	0.5	Pansu and Thuriès, 2003
STICS	Crop residues	2-5 g dm kg^{-1}	0.5	Nicolardot et al., 2001
Yasso07	WS, FYM, green manure	2 t C ha^{-1}	35	Karhu et al., 2012
DNDC	WS, FYM, compost	0.03-0.5 t C ha^{-1}	6	Sleutel et al., 2006b
CENTURY	WS, FYM, sawdust, green manure	2 t C ha^{-1}	30	Paustian et al., 1992
CQESTR	WS, FYM, corn stalks	6.0-7.5 t dm ha^{-1}	34	Plaza et al., 2012
3 pools model	Organic compost	20-40% w:w	5	Vidal-Beaudet et al., 2012

FYM: farmyard manure; WS: wheat straw; SS: sewage sludge; MSW: municipal solid wastes; fw: fresh weight; dm: dry matter; w: weight

However, to date no models specifically dedicated to the simulation of added EOM have been developed, with the only exception of the TAO (transformation of added organic matter) model (Thuriès et al., 2002). Furthermore some soil C model, such as the CENTURY model, does not include inputs of stabilised organic C like composted products. This evidence and the huge variability in the composition and properties of EOMs highlight the fact that existing models need to be adapted and/or calibrated in order to improve their ability to reliably simulate SOM trends in amended soils (Plaza et al., 2012).

1.2.2.2 EOM pools partitioning factors and decomposition rates

For an effective use of EOM to promote soil C sequestration there is the need to optimize and develop models capable to describe the long term decomposition of EOM in soils and produce accurate and reliable predictions (Karhu et al., 2012). In this perspective, several authors have highlighted the importance of a proper characterization of EOM to decrease the uncertainty in model predictions of SOC trends in amended soil, as the quality of amendments is the most important factor controlling their decomposition in soil (Karhu et al., 2012; Nascimiento et al., 2012). However, the quality of organic inputs is an aspect that is not adequately considered in models to date and needs further investigation (Parshotam et al., 2001).

Regarding EOM quality relevance in SOC modelling, most SOC models are based on the concept that decomposition can be adequately simulated by assuming different conceptual or functional pools of OM that decay according to first order kinetics with specific decomposition rate constants (Borgen et al., 2011).

Organic matter in residues can be conceptually defined as a series of fractions that comprise a continuum based on decomposition rates. These fractions have been represented in simulations as kinetically defined pools with different turnover rates. The changes in size of EOM fractions during decomposition can be mathematically described but, to establish how good are models in depicting the natural process, meaningful fractions must be first isolated from EOM and then characterized. This is very difficult to achieve, as it represents an operational separation of a continuum. In the case of SOM, due to the huge number of components, a continuous distribution of turnover times from days to millennia exists. Nevertheless, it has been demonstrated that SOM can be modelled reasonably well assuming only a few distinct pools (Towsend et al., 1997). Similarly, it could be expected for EOM to be also characterized by a continuum of decomposition rates, but that its decomposition could be reasonably simulated assuming few discrete pools.

Therefore, an accurate partitioning of EOM into a number of discrete pools and estimation of their functional characteristics (i.e. initial C and N contents, decomposition rate) is of great importance to improve model predictions (Thuries et al., 2011). However, rigorous methods for establishing entry pools that account for the diversity of EOM applied to soils have not been developed yet (Peltre et al., 2012). This represents one of the major problems for a reliable SOC modelling of amended soil as this separation is challenging and no universally recognized methodology exists to perform this task. According to Petersen et al. (2005b), the uncertainty related to the fractionation of EOM into pools is one of the major weaknesses associated to the C modelling of amended soils.

In particular, EOM is generally divided in pools using three different criteria (Mazzoleni et al., 2012).

The first one is the chemical approach defining pools by difference in EOM chemical components. This approach has the advantage that chemical compounds (i.e., water-soluble carbohydrates, holocellulose, and lignin) can be analytically determined.

The second criterion is the kinetic approach which defines pools according to their decomposition rate. For example, the RothC model distinguishes two kinetically defined pools of plant residues: decomposable (DPM) and resistant (RPM) plant materials.

The last criterion is the functional approach describing EOM as composed by metabolic (i.e. labile) and structural (i.e. resistant) pools. An example of this type of EOM characterization is represented by the CENTURY model in which EOM is partitioned in pools according to the lignin to N ratio of residues.

The characterization of EOM pools has been addressed with different approaches.

A first issue concerns the number of pools.

Most C models identify two pools with different degrees of decomposition (i.e. a rapid and a slowly decomposing pool)(Pansu et al., 2003), as in the original concept of the DAISY model (Mueller et al., 2003). This approach has been proved to be adequate in some circumstances to model C in amended soil. Double exponential decay models are an example of models with two EOM pools (e.g. O'Connell, 1997). The combination of a relative small labile pool with a larger, recalcitrant pool is a good description of the two phase decomposition of most plant residues: a rapid initial mass loss, followed by a stage with a slower loss rate. This type of models generally fits short-term decomposition trends of plant residues well. Fernandez et al. (2007) compared six different models in a study on EOM C mineralization and found that a model considering two organic pools with different degrees of biodegradability was the most appropriate to describe C mineralization kinetics for all the soils.

Nevertheless, results from several researches suggest that, at least for certain types of EOM, a better description of C mineralization is achieved by assuming at least 3 pools of EOM. Antil et al. (2011) underlined the disadvantage in the assumption that compost substrates comprise only two EOM pools, in that the soluble component that decomposes rapidly is usually very small, whereas the large insoluble component decomposes very slowly, resulting in extreme differences between the sizes and the rate constants of the two pools. Therefore compost mineralization is better estimated by partitioning EOM into three pools, which allows part of the insoluble material to decompose at an intermediate rate. Thuries et al. (2001) found that the best fit to measured CO_2 evolution data from a soil amended with a range of EOMs such as compost, manures, plant and animal residues was given by a 3 compartments model. Similarly, Kabore et al. (2011) suggested that EOMs (or at least some of them) are accurately divided into three pools: very labile, intermediary resistant and stable compounds. In the model of Henriksen and Breland (1999a), EOM is split into three biochemical compartments which are then assimilated into five SOM compartments. Adair et al. (2008) investigated litter decomposition (26 litters in 27 different sites) and found that 3 initial litter pools representing different C qualities are needed to accurately describe decomposition. Farmyard manure, the only EOM which effect on SOM can be explicitly simulated with the current version of RothC model, is split into 3 pools of different stability (decomposable, resistant and humified). A partitioning of residue in 3 different pools was also utilized by Probert et al. (2005) in modelling exercises performed with the APSIM model and by Corbeels et al. (1999), Hadas et al.

(2004) and Antil et al (2011) utilizing NCSOIL. Pansu et al. (2004), in a study about the comparison of 5 SOM models, concluded that the use of additional compartments resulted in improved long term predictions. Sierra and coauthors (2011) suggested that explicit representation of EOM heterogeneity in decomposition models, by its partitioning in different pools, is of fundamental importance to simulate processes related to long term C trends and to predict SOC stocks in amended soil. Exogenous OM is composed of substances with different chemical and physical properties and different levels of accessibility to microorganisms. The rate at which a substrate decomposes is determined by this combination between quality and accessibility. Moreover, materials with different properties will respond differently to environmental factors such as temperature and moisture, so the general response to a variation in the environment will depend on the relative proportions of substrates with different characteristics. For these reasons, representing EOM heterogeneity in models with a significant number of pools is likely to enhance the model performance.

Another important issue regarding EOM pools characterization deals with the decomposition rate of each pool. This issue has been addressed in several ways.

Some models adopt a single rate constant value for pools of native and exogenous OM. The native OM also includes the fresh plant residues produced above and underground, which constitutes the normal and cyclic input of organic C into the soil that, in steady state conditions, guarantees the stability of SOC stocks. This is the case, for instance, of RothC in which plant material and farmyard manure are both split into two pools of decomposable and resistant OM sharing the same rate constant of 10 y^{-1} and 0.3 y^{-1} for decomposable and resistant pools, respectively.

Other modelling approaches consider different decomposition rates for native and added organic pool, but assume the same decomposition rate for different EOMs. In this approach the decay rates of the two (or more) EOM pools are usually shared by all residues (Borgen et al., 2011), as in the original version of the DAISY model that assumed turnover rate of the rapidly and slowly decomposing EOM fairly constant throughout a wide range of added organic materials (Mueller et al., 2003).

A third option regarding EOM pools decomposition rates considers that such parameters are specific for each kind of EOM and different from those of native SOM. Generally, in SOC models partitioning factors are specific, while decay rate are global (shared), i.e. they are the same for each kind of pool, irrespective of the EOM considered. This implies that microbial communities responsible for EOM degradation have identical characteristics for all EOM, but this is not the case as different EOMs could selectively enhance or inhibit different components of microbial communities, resulting in altered decomposition capacity. As a matter of fact, Borgen et al. (2011) clearly showed that model predictions can be improved by identification of EOM specific decomposition rate. Similarly, in the final parameterisation of DAISY model, the turnover rate coefficients of rapidly and slowly decomposing EOM were markedly larger for grass and leguminous plant materials than the original turnover rates used for rape straw. This clearly indicates the inadequacy of the original assumption of two EOM-pools with predefined constant turnover for plant residues with very different properties (Mueller et al., 2003). Henriksen and Breland (1999a) and Henriksen et al. (2007) presented a model partitioning plant residues in 3 distinct pools (decomposable, structural, resistant) corresponding exactly to 3 chemically defined fractions. Such pools have distinct, but fixed (i.e. equal for all plant materials) decomposition rates. The only exception is represented by the structural pool which decomposition rate varies as a function of N availability for microbial growth. The need for individual adjustment of the decomposition rate invalidates the fundamental assumption that the specific decay rate constant of each defined pool maybe set a priori because it is uniform across litter qualities and support the fact that residue-specific EOM pool decomposition rate enhances the performances of the model. The fact that the approach considering EOM specific decomposition rates has been proved to be superior in terms of model simulation of C dynamics in amended soils is not surprising given the great heterogeneity of EOM composition and properties. This fact points out to the need to define specific decomposition rates for each pool of different EOMs.

On the other hand the approach addressing the issue of specific EOM pool decomposition rate implies an increased degree of model complexity and optimization requirements.

1.2.2.3 Methods to determine EOM pools partitioning factors and decomposition rates

A major limitation of current simulation models describing SOM turnover is that the conceptualized pools do not directly correspond to experimentally verifiable fractions (Cambardella, 1998). Several approaches have been proposed in order to achieve this task, but no satisfactory method to partitioning EOM have been found to date. Three main approaches have been devised so far to accomplish this task based on chemical or kinetic subdivision of EOM.

Partitioning based on the chemical properties of EOM is generally performed by stepwise chemical digestion (SCD) or near infrared reflectance spectroscopy (NIRS). An alternative to chemical analysis (or to using NIRS to predict such data) is to estimate EOM pool by model fitting to measured C and N mineralization.

1.2.2.3.1 Stepwise chemical fractionation

Chemical fractionation (stepwise chemical digestion (SCD)) is based on the fractionation of EOM in pools of different degradability meant to have a biological relevance (Shirato and Yokozawa, 2006; Henriksen et al., 2007; Borgen et al., 2011).

The most common type of chemical fractionation is based on the method of Van Soest or its modifications. The Van Soest method was initially developed to evaluate forage digestibility (Van Soest, 1963) and was then adapted to the characterization of EOM (Linères and Djakovitch, 1993). This method enables the stepwise extraction of organic materials that are assimilated to “soluble”, “cellulose-”, “hemicellulose-”, “lignin- and cutin-” like compounds. This method is relatively rapid and simple, but presents the main disadvantage that these operationally defined fractions do not precisely correspond to the model pools. This hypothesis was supported by Hadas et al. (2004) who found that the lignin content normally determined in plant residues by the Van Soest procedure was considerably lower than the optimized, kinetically defined lignin-like pool of residues. Moreover, the fraction defined by SCD may be sometimes distributed on two different pools (Thuries et al., 2002). As an example, Parnaudeau (2005), in a study on the soil decomposition of sewage sludges, found that the "soluble" fraction obtained by the Van Soest method includes also several organic compounds which are not biodegradable. The author concluded that the methods of fractionation of raw material do not appear relevant to the prediction of the decomposition of sludge. Furthermore, the hemicelluloses fraction derived from Van Soest method may be split between labile and resistant EOM fraction. This is due to the fact that hemicelluloses are a relatively large range of molecules with different degrees of degradability (heterogeneous group of linear or branched polysaccharides with a degree of polymerisation of about 100-200) (Thuries et al., 2002). A further problem is that EOM pools defined by SCD are based exclusively on material properties and therefore do not consider the possible effects of EOM interaction with soil. The relations between C mineralization and biochemical composition can be obscured by lack of available N in soil, as when residues with high C/N ratio are added to the soil (Trinsoutrot et al., 2000).

Consequently it is not obvious how data from SCD should be analyzed in order to partition residue C and N into the different EOM pools of the model (Borgen et al., 2011). In particular for models which includes 3 EOM pools, according to Antil et al. (2011) there are no availability of a chemical extractant that would fit an intermediate resistant pool.

1.2.2.3.2 Near-infrared reflectance spectroscopy (NIRS)

Near infrared reflectance spectroscopy (NIRS) measures the reflectance of samples in the spectral range between 800 and 2500 nm. The quantification of analytical characteristics based on NIRS requires multivariate statistical methods to fit the spectral response to sample properties in order to build predictive models. Once calibration has been developed, NIRS is a rapid, inexpensive and non-destructive method for sample characterization (Peltre et al., 2009). NIRS has been recently proposed as a means to rapidly determine EOM pools (Henriksen et al., 2007; Peltre et al., 2009; Borgen et al., 2011).

This is the most promising technique for its simplicity and rapidity, but, so far, NIRS predictive models of EOM characteristic have been built mainly for few and relatively homogenous EOM sets and therefore there is the need to expand the range of EOMs characterized by this technique (Peltre et al., 2009). Furthermore NIRS has the same limitation of the SCD method, i.e. the difficulty to establish a correlation between EOM pools defined by NIRS and model pools.

1.2.2.3.3 Kinetically defined EOM pools

EOM pools characteristics can also be determined by model calibration to measured C mineralization in amended soil. In this method determination of pool partitioning factors and decomposition rates is carried out by direct fitting of CO_2 respiration curves obtained from incubation experiments (Barak et al., 1990). Fitting pool parameters in this way provides kinetically defined parameters that reflect the rate of C mineralization observed for each residue (Trinoustrot et al., 2000**;** Borgen et al., 2011).

In process-based models the relationship between amount of substrate and degradation rate is well recognized. Models assume that C in decomposable EOM follows a first-order reaction kinetics equation and that EOM CO_2-C emission is proportional to the EOM C decay rate in soil. Therefore, the reaction rates can be easily estimated from laboratory experiments and directly used in process-oriented models (Battle-Aguilar et al., 2011).

Calibration of models using CO_2 evolution from incubation experiments was successfully achieved for NCSOIL (Corbeels et al., 1999), CANTIS (Garnier et al., 2003; Parnaudeau, 2005) and TAO (Thuriès et al., 2002) models. Kinetically-defined EOM pool partitioning was also performed by Hadas and Portnoy (1997), Mamo et al. (1999), Nicolardot et al. (2001), Hadas et al. (2004), Gabrielle et al. (2004, 2005), Petersen et al. (2005), Beraud et al. (2005), Gale et al. (2006), Peltre et al. (2009), Antil et al. (2011), Borgen et al. (2011), Cavalli and Bechini (2011) and Nett et al. (2011).

Kinetic definition of EOM pools has been widely applied and was shown to produce good simulations, in particular with urban wastes compost-amended soils (Hadas and Portnoy, 1997; Mamo et al., 1999). Setia et al. (2011) adopted this approach to develop a decomposition rate modifier to be included into RothC in order to simulate CO_2-C evolution from saline soils. Model parameters calibration for STICS was obtained from laboratory incubation experiments by Justes et al. (2009). The authors validated the new parameters against another set of incubation data and found satisfactory results.

Kinetically defined EOM pools provided reliable simulation of SOC in amended soil under field conditions. Gabrielle et al. (2005) demonstrated that parameterization obtained from laboratory incubations yielded a good simulation of C trends in a field study utilizing the NCSOIL model. Modelling of SOC based on partitioning of EOM by direct fitting of CO_2 evolution incubation data was in a good agreement with SOC data of 4 years field experiment involving compost and farmyard manure amendments. Kaborè et al. (2011) found a very good agreement between C accumulation rate in a field experiment and the amount of stable C estimated with TAO model calibrated with incubation data and suggest that information from laboratory incubations could be useful for model adjustment. Vidal-Beaudet et al. (2012) showed the relevance of a simplified multi-annual evolution model separating EOM into labile and stable fractions and fitted with mineralization data obtained under controlled conditions to simulate SOC dynamics in amended soil under natural conditions. The approach involving model parameterization by soil incubation data of amended soil and model application at field scale has been recently successfully adopted by Peltre et al. (2013) and Noirot-Cosson et al. (2013).

A similar approach to the direct kinetically fitting was followed by Tits et al. (2014) who determined the humification index of EOM, defined as the proportion of the added EOM still present in soil after one year in several field trials and incubation experiments. Successively, the authors established a relationship with decomposable and resistant plant material ratio (DPM/RPM) of RothC model by linear regression.

A mixed chemical and kinetic approach to EOM pool partitioning was adopted by Peltre et al. (2012). The authors first calibrated model pools on the basis of the results of some long term experiment. Successively, they calculated a linear regression between EOM partitioning factors and biochemical properties of the residues and IROC defined as the amount of EOM-C mineralized after 3 days of incubation at 28 °C. This procedure represents an intermediate between SCD and incubation fitting as the partition coefficients are based on a relationship with both chemical fractions and respiratory response of EOM.

1.2.2.3.4 Comparison between kinetically and chemically defined EOM pools

Several attempts have been performed to relate EOM pools determined chemically and by direct fitting of incubation data.

Results have shown that kinetically derived fractions do not correspond exactly to the chemically defined pools, since there is some form of overlapping as demonstrated by Parneaudeau (2005), who found that the kinetically determined stable EOM pool includes the lignin fraction, but also some soluble compound with high stability towards decomposition. Similarly, De Neve et al. (2003) failed to find a significant relationship between Van Soest fractions and C mineralization of amended soil and attributed this to the high ash content of some of the wastes. Gabrielle et al. (2004) parameterized a model for C and N mineralization (NCSOIL) with two approaches: a biochemical index based on Van Soest organic matter fractions and CO_2 data from an incubation experiment. Results clearly showed that the latter approach provided a better simulation of C and N mineralization in a compost amended soil. Simulations obtained by Borgen et al. (2011) and evaluated against an external validation dataset supported the hypothesis that kinetically defined partitioning enhances the predictions of mechanistic models compared to partitioning according to SCD. Such disagreement could be explained on the basis that net C mineralization trends result from (i) primary decomposition of residue C, (ii) incorporation of residue C into the microbial biomass developed from the residue, and (iii) secondary decomposition of microbial metabolites into which the C of the residue has been incorporated. Consequently, the relative weight of the C deriving from the residue by primary decomposition decreases during the course of decomposition. This is the main reason why only the initial rates of decomposition can be explained by the biochemical characteristics of the residues. Similarly, it is difficult to associate the decomposable and resistant pools of the model directly with the fractions measured in the residues as these two fractions also include the C of the residue that has been incorporated into the different SOM pools and is subjected to a further decomposition by the soil microorganisms (Trinsoutrot et al., 2000). There are further evidences that raise concerns about the reliability of biochemical fractionation as EOM pools partitioning method. For example, plant proteins stabilized by interaction with polyphenols or carbohydrates associated with lignin decompose more slowly than free proteins and carbohydrates. Furthermore, biochemical fractions may be differentially stabilized by interaction with soil components: proteins, for example, may be weakly adsorbed onto clay surfaces or strongly bound within organic complexes (Jans-Hammermeister and McGill, 1997).

Some authors applied a procedure that is meant to take advantage of both chemical fractionation and respiration fitting by carrying out a regression analysis of kinetically-defined partitioning parameters (dependent variable) against SCD-data (Borgen et al., 2011).

Exogenous OM soil mineralization depends not only from residue characteristics, but also from its interaction with soil properties and environmental conditions. Ideally, SOC models would take account of such interactions, so that kinetically-defined pool parameters represent only EOM properties. However, several studies have shown that SOC models are not able to fully resolve these interactions and that, on the contrary, kinetically fitted EOM pools incorporate such interactions (Cavalli and Bechini, 2012). This is not the case of SCD and NIRS optimized parameters that are exclusively based on EOM properties. As a result kinetically optimized parameters are preferable to chemically derived ones as they generally allow for a more accurate simulation of SOC trends in amended soils, even if this is might be obtained at the cost of a low generality.

1.2.2.4 Relation between laboratory studies and field conditions

Studies on C mineralization of amended soils are often preferentially conducted in the laboratory rather than in field conditions for logistic, technical and economical reasons. It is often assumed that results obtained in laboratory experiments can be extrapolated to field conditions. Nevertheless, concerns have been raised about the transferability of data collected in the laboratory to real conditions. Experiments in laboratory are carried out under controlled conditions, but environmental conditions in the field may be significantly different. For example, laboratory incubations are typically performed with sieved soil in the absence of living plants under constant conditions of temperature and soil water content. The effects of physical disturbance (e.g. soil sieving) and differences in humidity, temperature and aeration with respect to the field conditions can significantly alter the microbial decomposition of organic matter (Oburger and Jones, 2009). Laboratory studies often do not take into account many factors and interactions that can influence SOM decomposition *in situ* (e.g. diurnal variation in temperature and soil water content, diurnally regulated plant C inputs)(Glanville et al., 2013). In laboratory studies, in order to standardize conditions, EOM is usually grounded and evenly distributed, while in the field much larger size and irregular distribution of the amendment affect decomposition. Further limitations of laboratory experiments that restrict the transposition of the results to a broader scale are represented by the small size of the samples and the short incubation periods.

The above considerations imply that the results obtained in the laboratory are not necessarily expected to be similar to those obtained in the field. As a matter of fact different relationships between C mineralization in laboratory and field were reported in the literature. Lashermes et al. (2009) compared laboratory to field data in a study aimed to evaluate the amount of EOM remaining in the soil and found that EOM degradation was greater in the field than in the laboratory. This was unexpected as incubations are performed at optimal conditions for microbial activity. The authors attributed the greater mineralization to the variations in soil moisture as repeated drying and rewetting of soil-EOM mixtures enhances microbial activity and EOM mineralization. Conversely, Oburger and Jones (2009) compared C mineralization of low molecular weight C compounds in the field and in the laboratory and found a significant overestimation of field respiration. The authors attributed this to an increase in easily accessible C under laboratory conditions due to the severing of roots and hyphae in combination with additional aeration caused by the sampling procedure which might have changed the microbial metabolic activity.

However, several studies have suggested that information obtained in the laboratory may still have a significant relation with results obtained at field scale.

Glanville and co-authors (2012), employing a more systematic approach with respect to Oburger and Jones (2011), demonstrated that the contribution of low molecular weight C components to soil respiration was highly reproducible between parallel studies performed either in laboratory and in the field. The authors suggest that laboratory-based C mineralization data can be used for accurate estimation of kinetic parameters to reliably parameterize C models. Results of the work of Henriksen and Breland (1999b) support the hypothesis that decomposition is similar under laboratory and field conditions and that decay rate constants estimated under controlled conditions are directly transferrable to a field situation provided that they are adjusted by temperature and moisture response functions. Similar conclusion were drawn by Garnier et al. (2003) who demonstrated that it is possible to extrapolate data from soil incubations to field conditions.

Evaluation on how potential rates obtained in the laboratory compare to actual field rates can be useful in evaluating which are controls over field rates and constrains of microbial potentials (Schimel et al., 2006). Laboratory studies can also give important information on the relative difference between treatments and their ranking in terms of potential C sequestration. Laboratory measurement of SOC mineralization have been shown to be a sensitive indicator of SOC changes long before they could be measured in the field (Paul et al., 1999).

Fernandez et al. (2007) underlined the fact that even if carried out over short time periods, the use of laboratory methods involving incubation of soil-waste mixtures under controlled conditions can supply accurate information about C mineralization dynamics. In addition, C mineralization data obtained can be fitted to kinetic models, which allow calculating the fraction of potentially mineralizable C and its mineralization rate and, therefore, the real benefits of applying these organic wastes to soil. Hernández and Almendros (2012) found that soil C mineralization under laboratory conditions was a good predictor of C loss in the field. The results of their work suggested the possibility of predicting the sensitivity of SOC to biodegradation from laboratory incubation experiments, which results of interest for modelling global change scenarios.

The ability to realistically model the field evolution of CO_2 is based on the analytical determination of the SOC components involved in SOC dynamics. Such determination is not feasible in the field as in situ fluxes of CO_2 are too complex to allow for the determination of SOC pool sizes. These characteristics can be best determined under constant conditions in the laboratory (Paul et al., 2009). Incubation studies allow the effect of a single factor on the variable of interest to be isolated, avoiding the confounding effect of other factors and this has been shown to be of value for estimation of the response in the field and to modelling purposes.

1.2.2.5 Additional value of laboratory incubation studies

Incubation experiments for the actual measurement of EOM pool parameters despite all their merits in terms of accuracy and precisions are usually labour and time consuming. Nevertheless, the development of automated and high-throughput laboratory methods to measure soil respiration (Mondini et al., 2010; Garcia-Palacios et al., 2013) had significantly decreased the work involved in the measurement of soil respiration and increased the measurement precision and accuracy, allowing for the realization of complex experimental designs taking into account the effects of multiple factors. The time necessary for the incubation is compensated by the possibility to obtain, with relative easiness, additional information useful for a better knowledge of the EOM characteristics and the chemical and biochemical properties of the amended soil, such as N mineralization, GHG emissions, nutrient availability and microbial pool status.

Incubation experiments on C mineralization provide information about the maturity and degree of transformation of added organic materials (Vidal-Beaudet et al., 2012). Additional information for EOM characterization can be provided by high frequency measurements of soil respiration. For instance, in the study of Mondini et al. (2007) materials with similar chemical composition showed a very distinctive respiration pattern related to their different structural composition. Moreover, an accurate mineralization dynamics curve could be useful to depict specific soil to residue interaction (Cayuela et al., 2008).

Usually incubation experiments of amended soil are carried out to characterize agronomic and environmental properties of organic residues. In these experiments several parameters are measured, among these N mineralization. The N and C cycles are closely linked (Shaffer et al., 2001), therefore incubation studies on C and N mineralization trends of amended soils can be useful to provide insight on potential N mineralization of residues, as for example in the study of Song et al. (2011), who studied the relationships between CO_2 efflux and net N mineralization in a laboratory incubation experiment performed using an alpine meadow soil. The relationship between EOM C mineralization and available mineral N is difficult to establish as it is regulated by many residue, soil and environmental factors. This is reflected by the difficulty to simultaneously model EOM C and N mineralization (Cavalli and Bechini, 2012). Nevertheless, several studies have shown that characterization of amendments and short term laboratory incubations determining OM decomposition and net mineral N release were capable to provide good estimates of field available N for the first growing season. For instance, Flavel and Murphy (2006) found a significant relationship between CO_2-C evolution and gross N mineralization ($R^2 = 0.95$) in an incubation study of soil amended with different residues. Several other studies reported a good agreement on N mineralization data between laboratory and field studies, indicating that mineralization rates derived from laboratory incubations can provide an accurate estimation of in situ N mineralization (Goncalves and Carlyle, 1994; De Neve and Hofman, 1998; Haney et al., 2001).

Since the availability of easily degradable substrate and the occurrence of anaerobic conditions within the soil are important factors regulating the emission of the environmental harmful N_2O and CH_4 gases, information on C mineralization may be useful to understand the mechanisms and the environmental conditions leading to the generation of GHG. Further information on the mechanisms responsible for GHG generation can be achieved utilizing automated systems which allows to simultaneously detect the dynamics of several gases such as N_2O, CH_4, CO_2, CO and NH_3 (Mondini et al., 2010).

Soil respiration is an important aspect of soil quality and an indicator of biological soil fertility (Staben et al., 1997). The respiratory response of amended soils can be useful to evaluate potential negative effects of EOM on the microbial pool due to the presence of organic and/or inorganic pollutants or due to the generation of phytotoxic substances related to the low degree of stability of EOM. Furthermore it can be useful to detect polluted and degraded soil.

The C and N mineralization ratio has been proposed by Dilly et al. (2003) as an indicator of the biologically active C and N pools in the soil. Application of such ratio to amended soil could give information on the quality of available organic substrate, the complex connections existing between C and N mineralization of organic residues and the temporal dynamics of nutrients mobilization and immobilization.

1.3 Spatially explicit modelling of soil organic C

Soil organic C models have been successfully tested and applied under several conditions, but many SOC models, as in the case of RothC, are point based and perform simulation of SOC one site at a time.

Nevertheless, to assist land managers and policy makers to plan future land-use with the aim of restoring and increasing C stocks and for inclusion of soil C sequestration among the allowed measures within the Kyoto Protocol, more information needs to be provided by SOC modelling at the regional scale. With spatially explicit application the model is used in a similar way to when it is applied at the site scale, except that the model is run many times with different sets of inputs associated with a particular area of space, with might be a cell of a grid or a polygon representing an area of space (Smith and Smith, 2007). This can be obtained by linking Geographic Information Systems (GIS), which contain detailed information on soils, land use and climate, with a dynamic simulation model for the turnover of organic C in soil. GIS is not only necessary to format the inputs, but also to visualise the outputs and it allows for more flexible manipulation of the data and graphical display of the outputs in a spatial form (Fallon et al., 1998).

GIS-linked modelling is a useful tool for large scale studies of SOC trends, allowing actual estimates of regional soil C sequestration to be improved (Falloon et al., 1998a). Using dynamic SOC models at the regional scale allows the site characteristics, climatic conditions and land use to be taken into account and makes it possible to analyse the sensitivity of particular combinations of the soil and weather characteristics to variations in climate, land-use and management and to identify regions with most potential for C sequestration. Spatially explicit soil C model based approaches are also very flexible and amenable to a range of different scenarios. It is also important to note that the combination of the separated modelled impact of specific climate and C sequestration scenarios does not equal the simultaneous predicted effect of the same climate and C sequestration scenarios, i.e. models predict interactions between management, soil and climate that are non linear and non additive (Falloon and Smith, 2009).

To date, spatially explicit versions of SOC models have concentrated on the effects of land-use change. The integration of RothC with soil land use and climate data in a GIS environment was successfully illustrated by Falloon et al. (1998a; 2002; 2006), Smith et al. (2005, 2006) for European cropland grassland and forest, Smith et al. (2007) for European Russia, Parshotam et al. (1995) for New Zealand, Wan et al. (2011) for China and Jones et al. (2005) at global level.

However, information on the spatial variability for storage of C derived from different EOMs in contrasting soils is lacking. Indeed, experimental partitioning of CO_2 fluxes from different EOM pools allows the results of their modelling to be scaled up from point measurements to ecosystem, regional and global scales. Since SOC storage is controlled by a variety of biogeophysical, climatic, and management factors, dynamic models which integrate the main mechanisms governing SOC turnover with information on the spatial variability of such factors is the most suitable tool for predicting SOC changes at regional level due to the application of EOM with different properties.

Large scale regional modelling of SOC in amended soils could provide useful information to predict the C sequestration and GHG emissions offsetting potential of contrasting EOMs, identify the relative importance of the different factors in the SOC evolution observed and highlight the combination of factors more conducive to the soil storage of added C. This in turn would allow planning land use management and agronomical practices enhancing soil C sequestration. Because EOM availability is generally limited with respect to the land suitable for amendment, large scale spatial modelling of soil organic C can suggest ways to optimize such resources by identifying the areas with the greatest potential for the accumulation of SOC from EOM.

1.4 General aims and objectives

The main aim of this thesis was to combine laboratory data and discrete soil C modelling in order to find a simple and accurate way of predicting soil C sequestration potential of EOM at site and regional scale.

To achieve this goal the following procedure was pursued:

Firstly, the source code of the widely utilized RothC dynamic soil C model was altered in order to allow for the definition of 3 additional entry pools of exogenous organic matter: DEOM (decomposable), REOM (resistant), HEOM (humic-like substances) with specific decomposition rates. The above modifications were performed in order to improve the predictive power of the model, given the high variability in the composition and the properties of EOM that could be applied to the soil.

Secondly, a simple and reliable method was identified to estimate partition coefficients and decomposition rates of EOM pools based on kinetically defined fractions derived from fitting to respiration data of amended soil incubated in the laboratory.

Finally, a spatially explicit version of the modified RothC was deployed to assess at a national scale the potential for C storage of EOM-amended agricultural soil under different climate scenarios.

More specifically the objectives of the work were to:

- modify the RothC model to make it suitable for simulating the soil C sequestration potential of amended soils
- optimize RothC for a range of different EOMs by fitting the respiratory curve obtained from laboratory incubation of amended soils
- deploy a spatial explicit version of RothC

- assess future SOC change under climate change scenarios
- evaluate the variability of different EOMs in terms of their soil C sequestration potential
- assess at a national scale the potential for C storage of EOM added to the soil
- predict at a national scale the variability in the projected changes of SOC in EOM amended soils
- identify area with major potential for C sequestration by soil amendment
- elucidate the interaction of factors more conducive to soil C sequestration.

2. Materials and Methods

2.1 Incubation experiments

2.1.1 Soils used for incubations

The soils used for the incubation experiments of this thesis were sampled from agricultural areas in the Mediterranean area and specifically in Northern Italy and Southern Spain. The soils were sampled at 5-20 cm depth with an auger and several subsamples were pooled together to obtain a representative soil sample. Location, classification and main physico-chemical characteristics of the soils are shown in Table 2.

The soil were sieved moist through a 2 mm aperture grid and stored (5 °C) until the beginning of the experiments. Before the starting of the incubation experiments, the soils were pre-conditioned by incubation under aerobic conditions for 7 days at the same temperature and water content adopted for the incubation experiment (Tables 4 - 9).

The range of soils includes soils of widely different texture and pH. A part from Gorizia, Bueriis and Lodi, the soils were characterized by low contents of organic C and N and a reduced pool of soil microbial biomass.

The Spanish soils were all degraded soil either due to erosion processes and/or heavy metal pollution.

Table 2. Main physico-chemical characteristics of soils used for incubations.

Location	Country	Soil code	Soil use	Classification (USDA)	Sand (%)	Silt (%)	Clay (%)	pH	$CaCO_3$ (g kg^{-1})	SOC (g kg^{-1})	N_{TOT} (g kg^{-1})	SOC/ N_{TOT}	C_{mic} (μg g^{-1})
S. Martino	Italy	SM	Arable	Fluventic Eutrudept	69	28	3	8.3	740	10.5	1.2	8.8	114
Gorizia	Italy	GO	Meadow	Typic Hapludalf	37	48	15	7.8	46	25.4	2.4	10.6	795
Bueris	Italy	BU	Arable	Humic Dystruptet	6.0	48	46	7.0	-	32.0	4.5	7.1	269
Lodi	Italy	LO	Meadow	Mollic Hapludalf	67	21	12	6.7	-	22.0	2.1	10.5	205
Reana	Italy	PE	Arable	Typic Dystruptet	55	28	17	6.5	-	15.9	1.2	13.3	118
Ribis	Italy	RI	Arable	Typic Dystruptet	54	32	14	4.6	-	8.1	1.3	6.2	65
Codroipo	Italy	CO	Arable		27	58	15	7.1	-	19.0	2.0	9.5	350
Jumilla	Spain	JU	Olive orchard		52	21	27	8.0	415	10.4	1.0	10.4	119
Alquife	Spain	AL	Disused mine		53	30	17	8.5	1.3	2.5	0.9	2.8	10
Llano de la Perdiz	Spain	LL	Arable		32	17	51	7.0	0.5	9.2	1.1	8.4	146

SOC: soil organic C; N_{TOT}: total N; C_{mic}: soil microbial biomass C

2.1.2 EOMs used for incubations

The following 8 different types of EOM were considered:

Compost (CO):

VSC: compost from vine tree prunings.

HWC: compost from the separate collection of household organic wastes.

GWC: compost from green wastes.

CMC: compost from a mixture of 62% winter wheat straw + 32% cotton cardings + 6% meat and bone meal (dry weight basis). Samples were taken after 3, 9 and 92 days of composting.

CBC: compost from a mixture of 62% winter wheat straw + 32% cotton cardings + 3% meat and bone meal + 3% hoof and horn meal (dry weight basis). Samples were taken after 3, 9, 21 and 92 days of composting.

Bioenergy residues (BE):

BR: wheat starch by-product obtained after bio-ethanol production.

RSM: rapeseed meal from biodiesel production.

GWB: green waste biochar produced by continuous slow pyrolysis at 550 °C.

Anaerobic digestates (AD):

PS: digestate from anaerobic digestion of pig slurry.

OW: digestates from anaerobic digestion of different mixtures of two-phase olive mill waste (TPOMW) and liquid manure.

Meat and bone meals (MM):

Commercially available samples of meat and bone meal (MM) were selected for their incubation with soil. Two bovine (BV1, BV2), a defatted bovine (DE), a swine (SW) and a mixture of swine/bovine (SB) MMs were used in this study.

MM derived from residues of slaughtering operation that were reduced to a diameter minor than 50 mm and subjected to an autoclave treatment at 133 °C for 20 min and 0.3 MPa. Defatted MM derived from MM treated to reduce its lipid content.

The variability of MMs properties is due to their different compositions (they are obtained from a mixture of carcass trimmings*,* inedible offal, lipids and bones from different animals) and to the production process itself (temperatures, separation methods).

Animal residues (AR):

HL: hydrolysed leather, a slow release N fertiliser derived from hydrolysed animal proteins.

BLM: blood meal, organic fertiliser allowed for organic farming obtained by spray drying at low temperatures the fresh whole blood from animal processing plants.

HHM: horn and hoof meal, organic fertiliser produced by the drying of horns and hooves from animal processing plants.

Crop residues (CR):

CC: cotton carding waste, derived from the process of preparing the fibres of cotton for spinning and was supplied by Cascamificio Friulano Srl (Remanzacco, Udine, Italy).

WS: winter wheat (*Triticum aestivum L.*) straw was collected after harvesting at Reana (Udine, Italy).

Agro-industrial wastes (AW):

TPOMW: two-phase olive mill waste, semisolid sludge generated during the extraction of olive oil by the two-phase centrifugation system.

Sewage sludges (SS):

WW: wastewater sludge, sewage sludge from an urban wastewater treatment plant.

All the residues were solids, with the exception of digestates from liquid manure and TPOMW.

The main features and properties of the studied EOMs are reported on Table 3.

Table 3. Main chemical characteristics of EOMs used for incubations.

EOM type	EOM type code	EOM	EOM Code	pH	OM (%)	TOC (%)	N_{TOT} (%)	TOC/ N_{TOT}	WSC ($g\ kg^{-1}$)	WSN ($g\ kg^{-1}$)	NH_4^+ ($mg\ kg^{-1}$)	NO_3^- ($mg\ kg^{-1}$)
Compost	CO	Vine shoots compost	VSC	7.7	65.4	34.5	1.5	23.2	9.8	0.6	101	2018
		Household waste compost	HWC	8.3	64.2	34.4	2.3	14.9	5.9	0.7	226	1777
		Green waste compost	GWC	7.5	51.9	28.2	2.2	12.8	6.8	2.2	1400	800
		CC + WS + SB II_3	CMC II	7.9	90.6	42.7	1.6	27.2	23.1	2.7	627	2397
		CC + WS + SB III_9	CMC III	7.9	89.3	41.3	2.1	19.6	28.3	3.7	96	2821
		CC + WS + SB M_92	CMC M	8.1	82.2	39.9	3.5	11.3	12.4	1.8	254	2195
		CC + WS + BLM + HHM II_3	CBC II	7.7	93.3	43.5	1.7	25.7	20.3	1.9	434	1901
		CC + WS + BLM + HHM III_9	CBC III	7.9	91.2	42.9	1.9	22.0	21.9	2.4	281	2256
		CC + WS + BLM + HHM IV_21	CBC IV	7.9	87.5	42.3	2.8	15.2	23.6	2.5	134	2155
		CC + WS + BLM + HHM M_92	CBC M	7.7	83.2	40.6	3.7	10.9	11.3	3.4	59	4169
Bioenergy by-products	BE	Bioethanol residue	BR	4.2	91.9	48.5	6.2	7.8	202.5	12.8	1153	1.9
		Rapeseed meal	RSM	6.2	92.5	45.9	6.0	7.7	74.4	2.4	180	13.4
		Greenwaste biochar	GWB	7.5	98.3	86.3	0.3	345	0.1	0.0	17	0.4
Anaerobic digestates	AD	Pig slurry digestate	PS	8.5	74.6	37.9	4.4	8.7	38.7	11.6	5361	2.5
		TPOMW + manure	OW 1	8.2	75.8	43.6	3.4	13.0	23.1	1.78	17322	11048
		TPOMW + manure (55 °C)	OW 2	8.1	76.7	48.7	3.5	13.9	25.1	1.81	20118	14318
		Liquid manure	OW 3	8.2	68.6	44.1	3.1	14.5	13.6	0.94	690	7902
		TPOMW	OW 4	7.9	76.9	49.1	3.0	16.1	17.7	1.07	18744	10905
Meat and bone meals	MM	Bovine MBM 1	BV1	6.5	70.9	38.5	8.4	4.6	52.1	12.4	631	1692
		Bovine MBM 2	BV2	6.3	65.5	33.9	8.2	4.1	35.7	9.0	410	1314
		Swine MBM	SW	6.7	78.6	41.4	9.0	4.6	114.5	29.0	530	4721
		Mixed swine bovine MBM	SB	5.9	81.8	43.1	9.4	4.6	60.5	17.1	359	4165
		Defatted bovine MBM	DE	6.4	59.4	29.9	8.4	3.6	34.3	9.9	435	1714
Animal residues	AR	Hydrolyzed leather	HL	5.2	80.0	42.0	13.2	3.2	34.7	23.2	6360	3135
		Blood meal	BLM	6.7	90.8	52.6	16.4	3.2	118.9	37.9	122	3547
		Horn and Hoof meal	HHM	7.5	80.0	51.3	17.0	3.0	13.7	5.0	1887	1058
Crop residues	CR	Cotton cardings	CC	6.2	88.0	45.2	1.5	30.5	37.8	2.4	303	2005
		Wheat straw	WS	6.5	89.1	49.6	0.3	198	15.7	0.8	66	879
Agro-industrial w.	AW	Two-phase olive mill waste	TPOMW	5.3	94.1	53.0	1.3	41.1	4.1	1.1	122	0
Sewage sludges	SS	Wastewater sludge	WW	6.8	70.9	38.4	4.8	8.0	7.97	1.64	1677	2286
			Mean	*7.1*	*80.1*	*43.8*	*5.0*	*30.6*	*36.3*	*6.8*	*2670*	*3107*
			Minimum	*4.2*	*51.9*	*28.2*	*0.3*	*3.0*	*0.1*	*0.0*	*17*	*0*
			Maximum	*8.5*	*98.3*	*86.3*	*17.0*	*345*	*203*	*37.9*	*20118*	*14318*

OM: organic matter; TOC: total organic C; N_{TOT}: total N; WSC: water soluble C; WSN: water soluble N

Compost: roman numerals refer to stages of the process, numbers refer to days of composting, M: mature compost

As a whole 30 different EOMs were utilized for the incubation experiments. They were considerably distinct in terms of chemical composition, origin and stabilization/transformation processes to which they were subjected.

According to these criteria they were arbitrarily classified in 8 different EOM type: compost, bioenergy by-products, anaerobic digestates, meat and bone meals, animal residues, crop residues, agro-industrial wastes and sewage sludges (Table 3).

Most of the EOMs presented an alkaline pH, while the organic wastes with a pH < 5.2 were bioethanol residue, hydrolyzed leather and two-phase olive mill waste.

The total organic C (TOC) concentration ranged between 28.2% and 53.0%, except for green waste biochar, which had a TOC content of 86%. Green waste biochar, bioethanol residue and rapeseed meal had a concentration of organic matter higher than 91%.

Total N varied between 0.3% and 17%, mainly according to the EOM origin. As a matter of fact, vegetal derived EOM as compost, crop residues, two-phase olive mill waste and green waste biochar presented low levels of total N (0.3-2.3%). On the other side, EOM of animal origin (meat and bone meals, blood meal, horn and hoof meal) showed high values of N (8.2-17%).

As a consequence of the variability in C and N content the C/N ratio ranged between 3 (horn and hoof meal) to almost 200 (wheat straw) and 345 (green waste biochar).

The differences among EOMs were also highlighted by the content of soluble C and N. The concentration of easily available C (WSC) was extremely variable, varying from 0.1 to 203 g kg^{-1}. The EOMs showing the highest contents of easily degradable C and N were bioethanol residue and blood meal.

As a whole, high concentrations of mineral N (NO_3^- and NH_4^+) were found for liquid digestates. On the other side, bioenergy by-products were characterized by very low amounts of NO_3^-.

2.1.3 Amended soils incubation experiments

The solid residues were ground and sieved (<0.5 mm) to homogenize their particle size before application. The residues were thoroughly mixed with pre-conditioned moist soil samples (50 g dry weight basis) and aerobically incubated in the dark in 130 ml plastic jars in a thermostatic chamber. In the case of liquid residues soil were pre-incubated at such humidity that after EOM addition they were brought to the moisture content required for incubation (Tables 4 - 9).

Unamended soils were also included as a control. Each treatment was replicated two times. The moisture levels in the jars were checked weekly by measuring weight loss, and deionised water was added when necessary to maintain constant moisture.

Incubation conditions (soil type, rate of residue, soil water content, temperature and incubation time) are reported on Tables 4-9.

As a whole, more than 30 incubations were performed utilizing 30 different residues and 10 soils with contrasting properties.

2.1.4 Soil CO_2 measurement

CO_2 evolution was measured every 4 h on aliquots of moist soils by means of an automated system for gas sampling and measurement (Mondini et al., 2010). The system generally operates as an “open chamber” system in which the plastic jars (130 ml) containing the moist soil samples are continuously aerated at a constant flow rate (20 ml min^{-1}) by means of an air pump. At regular time intervals, a single jar is made a “dynamic close chamber” for a selected accumulation period (usually in the range 10-60 min) by means of two appropriate valves (Vici Valco Instruments). During the accumulation period the air is continuously recycled in the selected jar by means of a peristaltic pump. The gas concentration in the closed chamber is automatically measured at the beginning and the end of the accumulation period by a gas chromatograph (Varian, CP2003) and the difference between the final and initial measurements provides the rate of gas production for the selected accumulation time. The system is operated by dedicated software and can operate with up to 16 samples (Mondini et al., 2010)(Figure 1).

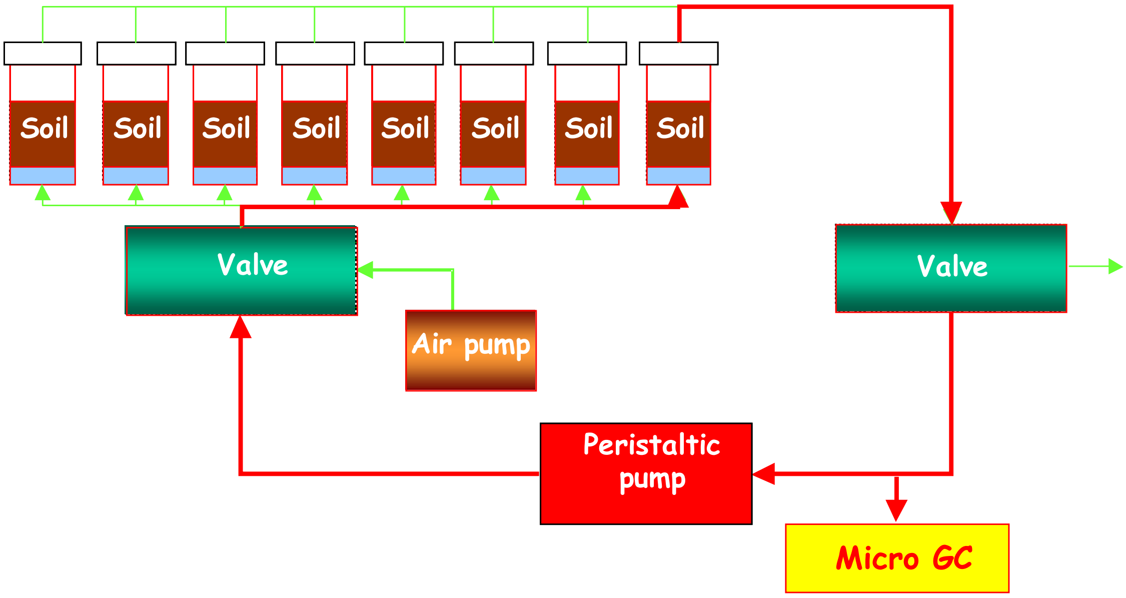

Figure 1. **Diagram of chromatographic system for soil CO_2 sampling and measurement.**

The ‘apparent’ net C mineralisation (carbon derived from the residues) was calculated as the difference between the CO_2-C produced by the residue amended soil and that produced over the same period by the unamended control soil. The results are expressed as a percentage of the added carbon.

2.2 RothC soil C modelling

2.2.1 Description of the RothC soil C model

The Rothamsted Carbon model (RothC) is the first multi-compartmental model to be developed (Coleman and Jenkinson, 1996; Jenkinson and Rayner, 1977) and is one of the most widely used models simulating SOC trends (Jenkinson et al., 1991; McGill, 1996) because it requires relatively few parameters and input data.

It describes the dynamics of SOM by splitting it into five compartments with different turnovers, namely decomposable plant material (DPM), resistant plant material (RPM), soil microbial biomass (BIO), humified organic matter (HUM) and inert organic matter (IOM). Each compartment, except IOM, follows first-order decay kinetics, i.e. each pool is considered well-mixed and chemically homogeneous and the decomposition rate is assumed to be controlled by the available substrate. The proportion of organic matter decomposed per unit time is therefore constant and equal to the decomposition (or kinetic) rate constant (K). Carbon inputs are divided into compartments of labile (DPM), resistant (RPM) and humified (HUM) organic matter, with partitioning coefficients (f) depending on the nature of the inputs. At each monthly period, part of each compartment is decomposed according to its specific decomposition rate. Part is mineralized as CO_2 and the rest is transferred to the compartments BIO and HUM. The proportion of the decomposed pool converted to CO_2 and (BIO + HUM) is determined by the clay content of the soil. The ratio CO_2/(BIO + HUM) is calculated by the equation: $CO_2/(BIO + HUM) = 1.67(1.85 + 1.60 \exp(-0.0786\ \%clay))$.The part transferred to (BIO + HUM) is divided into 46% of BIO and 54% of HUM. The rate constants are modified at each period by three multipliers, depending on the temperature, the moisture deficit of soil and the presence/absence of vegetation.

The RothC model was initially calibrated with results from several Rothamsted long-term experiments leading to partition coefficients for plant material (f_{DPM} 59% and f_{RPM} 41% of plant material-TOC) and farmyard manure (f_{DPM} 49%, f_{RPM} 49% and f_{HUM} 2% of farmyard manure-TOC) (Coleman and Jenkinson, 1996). Such partitioning has frequently been used to simulate the effect of agricultural managements (e.g. manure application) on changes in SOC stocks (Peltre et al., 2012).

The RothC model has been evaluated and optimized for a variety of ecosystems including croplands, grasslands and forests (e.g. Coleman et al., 1997; Smith et al., 1997; Falloon and Smith, 2002; Johnston et al., 2009; Powlson et al., 2011a) and in various climate regions, including semi-arid environments (Jenkinson et al., 1999; Skjemstad et al., 2004; Farina et al., 2013). It has also been used to make SOC predictions following application of exogenous organic matter (Yokozawa et al., 2010). Due to extensive previous benchmarking (e.g. Smith et al., 1997) no further model testing is presented here.

2.2.2 Modification of the RothC model

A modification to the model is proposed, involving two additional pools of EOM with different degree of decomposability (decomposable EOM, DEOM and resistant EOM, REOM). Such pools decompose with specific decomposition rates (K_{DEOM} and K_{REOM}), that may be different from those of plant input. Decomposed EOM is split in CO_2, BIO and HUM. The proportion of decomposed EOM that goes to CO_2, BIO and HUM is regulated in the same way as for the entry pools of plant residue.

Furthermore, for some materials characterized by the presence of a stable organic matter pool, part of EOM (HEOM) is directly incorporated into the HUM pool. Compost, anaerobic digestates and agro-industrial wastes were the EOMs partitioned in 3 EOM pools in this study.

The Carbon flow of the modified model is reported in Figure 2.

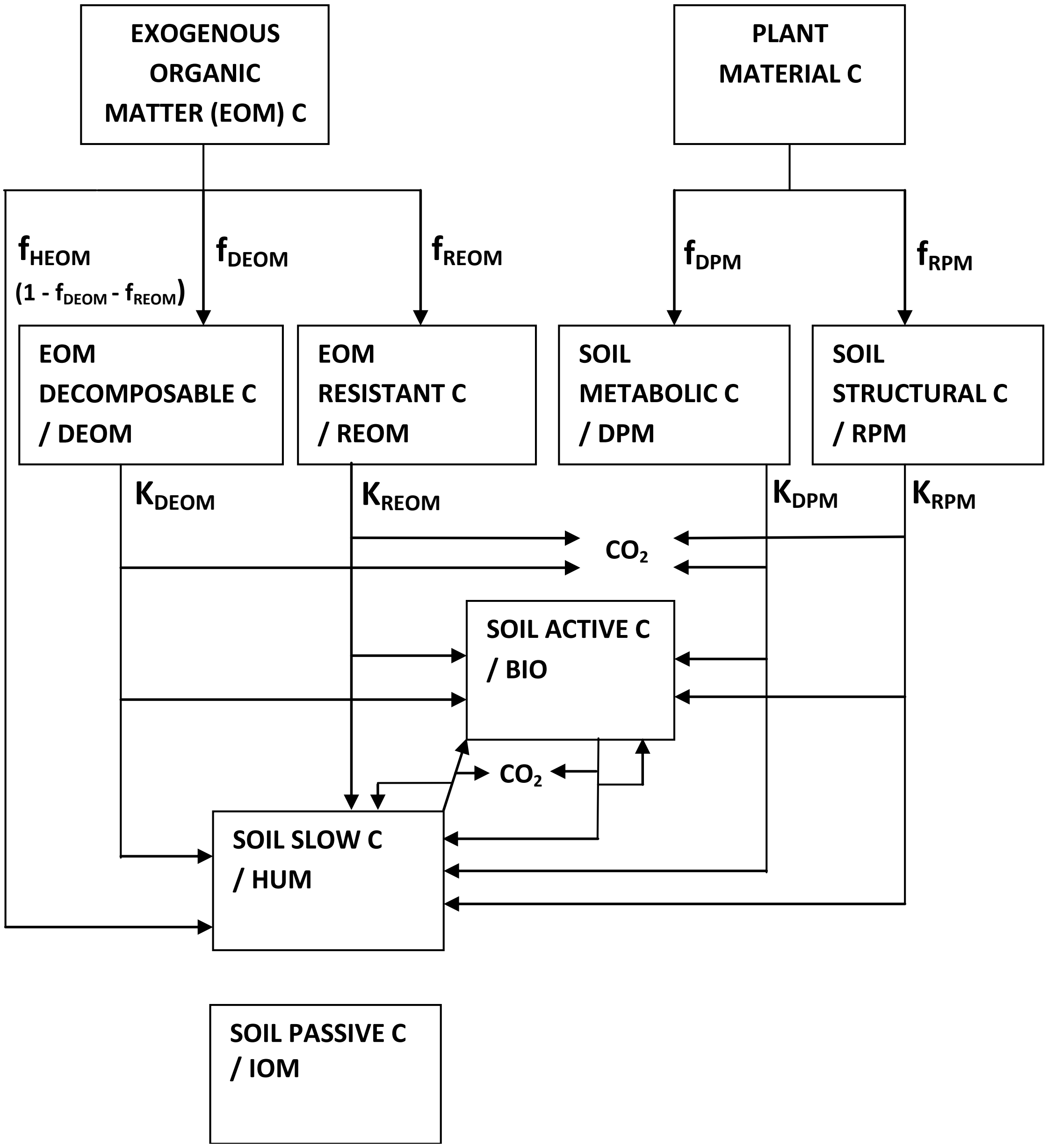

Figure 2. Structure of the modified RothC model.

2.2.3 Calibration of RothC EOM pools parameters with incubation data

Data from several incubation experiments of replicated design were applied for parameter estimation. To enable inverse modelling of the incubation trials, an Excel version of the RothC model (26.3 version) was utilized. The Excel version of the model was tested for correctness under several RothC standard scenarios.

All simulations were run as difference with the control treatment (i.e. only the CO_2 derived from EOM was simulated). Thus the initial size of the soil organic pools was virtually set to zero, including the size of the inert OM pool (IOM). This was possible because in the RothC model, the C trend of each pool is described with first order kinetics. The fate of total soil C is the sum of the fate of the C of the different pools. Therefore, the difference of CO_2 evolution between soils with and without EOM application corresponds to the CO_2 derived from the additional input of OM in the soil. It was therefore assumed that the decomposition of humified SOM was unaffected by the decomposition of added residues (i.e. no priming effect was caused by EOM application to the soil).

Inverse modelling was conducted by changing individual partition coefficients and decomposition rate constants of the EOM pools by stepwise iteration (using Excel-Solver) until maximum agreement between measured and calculated amounts of CO_2 was achieved assuming as a criteria the smallest sum of squared residuals (SSR). For each EOM and incubation conditions, an 'individual' fitting procedure was used to minimise the difference between observed and simulated values.

No default values other than the partition coefficients and the decomposition rate constants of the different C pools of EOM were taken into account for inverse modelling.

The 5 parameters considered (f_{DEOM}, f_{REOM}, f_{HEOM}, K_{DEOM}, K_{REOM}) were optimized simultaneously, considering the following constraints in order to avoid physically unrealistic parameter estimates:

$f_{DEOM} + f_{REOM} + f_{HEOM} = 1$

$f_{HEOM} < 0.3$ for anaerobic digestates and agro-industrial wastes

$K_{REOM} > 0.15\ y^{-1}$

$k_{DEOM} < 230\ y^{-1}$

f_{HEOM} was set to a maximum of 0.3 in the case of digestate according to the values found by Cavalli and Bechini (2011; 2012) after model calibration for soil amended with pig digestate. K_{REOM} was set to a minimum of 0.15 y^{-1} according to the modification proposed by Skjemstad et al. (2004). k_{DEOM} was set to a maximum of 230 y^{-1} according to maximum values found by Thuries et al. (2001) utilizing a 3 EOM pools model for 14 different plant residues, compost and manures. This constraint was not considered in the case of blood meal as the respiration curves present a very steep initial phase, an indication of a decomposable pool characterized by high degree of decomposability. This is supported by results of Thuries et al. (2001) who found a decomposition rate constant of 243 y^{-1} for the labile pool of animal residues.

2.2.4 Statistics

The accuracy of the model to simulate C mineralization was assessed according to the criteria proposed by Smith et al. (1996), utilizing the worksheet MODEVAL 2.0 for Windows (Smith et al., 1997).

The association between simulated and measured value (i.e. the percentage of total variance in the observed data that is explained by the predicted data) was evaluated by the sample correlation coefficient (R).

The percent term for the total difference between measured and simulated value, proportioned against the mean observed values, was considered by calculating the root mean square error (RMSE). The lower limit for RMSE is 0, which denotes no difference between measured and simulated values.

The consistent errors or bias in the model was evaluated by the mean difference (M) between measured and simulated data. Because M does not include a square term, simulated values above and below the measurements cancel out and so any inconsistent errors are ignored.

The error in the simulation as a proportion of the measurement was evaluated by the relative error (E), expressed as the mean error percentage over all the measurements.

2.2.5 Sensitivity analysis

To study the sensitivity of SOC values predicted by the modified RothC model towards the quality of EOM inputs over the experimental timescale a model exercise was performed utilizing weather (average climate data for 1960-2000) and land management data for the S. Martino soil.

After an equilibrium run (see section 2.3.3), the model was run for 100 years utilizing the same model inputs, but assuming a yearly addition of EOM at a rate of 1 t C ha y^{-1}. Two scenarios were simulated, i.e. addition of household compost (HWC) and mixed swine bovine meat and bone meal (SB). For each EOM model runs were performed utilizing the optimized parameters from respiration data under standard laboratory incubation conditions (defined as: 20 °C, 40% water holding capacity (WHC), 0.5% w:w application rate and 30 days incubation period) and then individually varying each parameters at arbitrary values, while maintaining constant the other parameters. A sensitivity index (SI) was calculated according to Ng and Loomis (1984) as:

Sensitivity index (SI) = % change in output variable / % change in input variable

The input variables were DEOM/REOM; DEOM/HEOM; REOM/HEOM; K_{EOM} and K_{REOM}, while the variation in SOC with respect to the baseline (SOC at equilibrium) was considered as the output variable. A large value of SI indicates that the model output variable is relatively insensitive to changes in the input variable; a small SI value indicates that the model output variable is sensitive to changes in the input variable. A SI value of 1 indicates that changes of 1% in the input value result in a change of 1% in the output variable. Negative SI values indicate that increasing the input value decreases the output value; positive SI values indicate that increasing the input value increases the output value.

2.3 Regional modelling of amended soils

2.3.1 Data sets

The geographic window, within which the study was performed, covers the area: longitude 6.750 E to 18.417 E, latitude 36.750 N to 46.917 N. The GIS platform used was ARC Map 9.3.

Information on soil properties and spatial distribution and land use classes were derived from the Soil Geographical Database of Europe (SGDBE) (European Soil Database, 2004). The database represents a digital version of the 1:1000000 Soil Map of Europe and it presents geometric and semantic components, soil information being presented in the form of Soil Map Units (SMUs), with each polygon unit on the map being assigned to a single SMU. Each SMU comprises a number of soil types or Soil

Typological Units (STUs) which are associated together within the SMU landscape, but cannot be separated spatially at the 1:1000000 map scale. The number of SMU polygons for Italy was 1314.

Mean SOC stocks in t C ha^{-1} to 25 cm depth (calculated from percentage of C content and bulk density) and the clay content in the soil upper layers were derived from SPADE2 soil profile analytical database for Europe (Hannam et al., 2009). SPADE 2 was developed to be used in conjunction with the SGDBE database, providing the soil property data for each STU. The window contained 295 representative soil profiles.

SPADE2 also provides the dominant and secondary (when present) land use class according to the Corine Land Cover nomenclature for each STU. In the database 22 different land class uses are present of which 10 were present in the STU associated with Italy. Of these, 6 represent agricultural land uses classes (grassland, arable, horticulture, vineyards, olive trees and industrial crops), covering 63.8 % of the total land.

Monthly temperature and precipitation data for Italy were extracted from CRU 1.0 (for the range 1901-2000) and TYN SC 1.2 (for the range 2001-2100) European climate databases at a $10^{'}$ x $10^{'}$ resolution downloaded from the Climate Research Unit of the University of East Anglia (Mitchell et al., 2004). The climate data for the geographic window (Italy) were extracted utilizing the TETYN software (Solymosi et al., 2008).

Monthly climate values for 2001-2100 were provided using outputs from 3 different Global Circulation Models (GCMs), namely HadCM3, PCM, and GCM2 (Mitchell et al., 2004), forced by 4 different CO_2 emissions scenarios as defined in the IPCC Special Report on Emissions Scenarios (SRES)(Nakicenovic et al., 2000) for a total of 12 different climate scenarios (Nakicenovic et al., 2000; Smith and Powlson, 2003). The emissions scenarios estimate future concentrations of GHG in the atmosphere to which climate is sensitive based on assumptions about patterns of economic and population growth, technology development and other factors.

The A1 scenario (‘world markets’) describes a future world of very rapid economic growth, global population that peaks in mid-century and declines thereafter, and the rapid introduction of new and more efficient technologies. The A1 scenario family develops into three groups that describe alternative directions of technological change in the energy system. In particular, the FI ('fossil fuel intensive') group poses emphasis on the intensive use of fossil fuels.

In the A2 scenario ('provincial enterprise') economic development is primarily regionally oriented and per capita economic growth and technological change are more fragmented and slower than in other storylines.

The B1 scenario ('global sustainability') describes a convergent world with the same global population trend as in the A1 scenario, but with rapid changes in economic structures towards a service and information economy, with reductions in material intensity, and the introduction of clean and resource-efficient technologies.

The B2 scenario ('local stewardship') describes a world with a continuously increasing global population at a rate lower than in A2, intermediate levels of economic development, and less rapid and more diverse technological change than in the B1 and A1 storylines.

Monthly potential evapotranspiration (ET) for each point of the 10' x 10' grid for the 1901-2100 period were calculated from temperature, precipitation and diurnal temperature range data according to the Hargreaves method (Allen et al., 1998).

For the modelling exercise, averaged monthly values of climatic data for the period 1901-2000 and averaged decennial values for the period 2001-2100 were utilized.

Point layers containing the meteorological data were created in ArcMap with each layer consisting of 1191 grid points (Figure 3).

Figure 3. Representation of the point layer associated to climate data for Sicily.

2.3.2 Layer linkages

An ArcMap built-in functionality was utilized to find the centre of all SMU polygons. The SMU centres were then linked through a spatial join to the nearest point of the meteorological layer, resulting in a linked soil mapping unit/meteorological layer constituted by 1314 polygons (Figure 4).

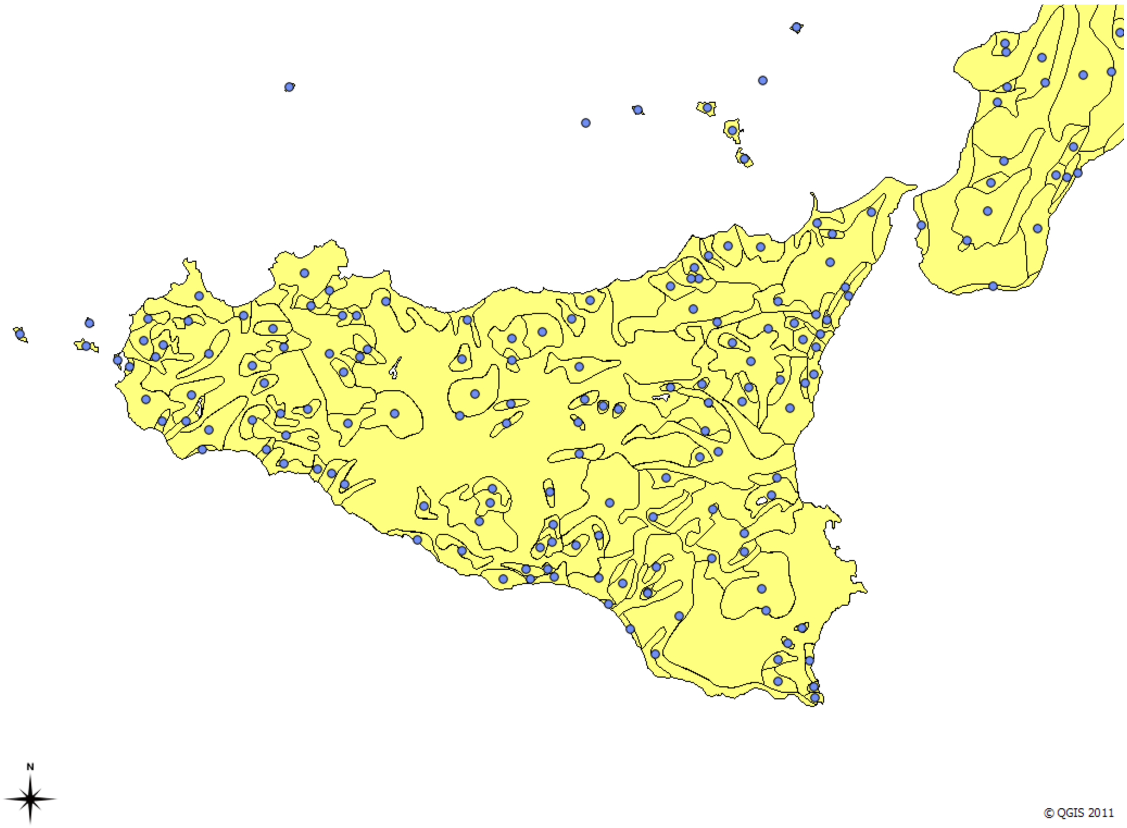

Figure 4. Linked soil mapping unit/climate layer for Sicily.

The SMU/climate layer were then linked with the soil and land use data through a query operated in MS Access utilizing information provided by the geographic and semantic components of SGDBE. This provided a linked soil, land use and meteorological database constituted by 10130 rows representing a unique combination of soil, land use and meteorology. Simulations were performed for each of the 10130 combination of climate and soil data.

2.3.3 Running the modified RothC model

RothC input and setup files were created for each one of the unique 10130 combinations of soil, land use and meteorology data. RothC was run and the model output was loaded into Excel, Access and SPSS for analysis, and into ArcMAP for visualization.

For each combination of soil, land use and climate data, the initial C content of the different SOC pools and the annual plant addition to the soil were obtained by running the RothC model to equilibrium (Coleman and Jenkinson, 1996) using average climate data for 1990-2000 and by using the clay and SOC content provided by the SPADE2 data base.

The monthly distribution of plant input was calculated in two stages. Initially, the total annual plant input was assumed to be 1 t C ha^{-1} and the proportions of plant material added to the soil in each month were set to describe the typical pattern of inputs for each land use class. After RothC was run to equilibrium, the annual C input was adjusted to give the measured soil C content provided in the soils database using the following equation:

$P_{req} = P_i \times [(C_{meas} – IOM)/(C_{sim} – IOM)]$

where P_{req} is monthly C input, P_i is the initial monthly total C addition (the sum of the proportions of the C input in the first equilibrium run is 1), C_{meas} is the measured soil C given in the soils database, C_{sim} is the simulated soil C after the equilibrium run, and IOM is the C content of the inert organic matter fraction in the soil (all in t C ha^{-1}). The size of the IOM fraction was set according to the equation given by Falloon et al. (1998b):

$IOM = 0.049 \times C_{meas}^{1.139}$

Having determined the plant additions and C contents of SOC pools, the simulations were run between 2001-2100 using the predicted climate and land use data.

Two predicted land management scenarios were chosen for estimation of C sequestration potential: annual addition of EOM at a rate of 0 (baseline) and 1 t C ha^{-1}. In the case of compost this correspond to an application rate corresponding to 9.1 t fw ha^{-1} according to the mean water and C content of green waste compost in Italy (CIC, Italian Composting Association, 2000).

The model was run for each of the 8 EOM type defined in Table 3 utilizing as a parameters the mean of the model parameters for all incubations performed with the same EOM type (Table 14). The model was run to the year 2100 for the 12 climate scenarios considered and for the two land management scenarios described above giving 24 combinations of climate x management scenarios. For each polygon, the change in SOC under the baseline run was subtracted from the change in SOC under a land management scenario including EOM addition to give the net soil C sequestration due to the change in land management.

Application of EOM was only considered for agricultural land use classes. Soils with natural land use classes were therefore excluded from the simulations. Similarly, organic soils with a SOC content > 200 t ha^{-1} were also excluded from simulation as RothC has not been parameterised for organic soils (Coleman and Jenkinson, 1996). Consequently, land for which EOM addition was simulated was 60 % of total land.

The procedure devised for spatial explicit modelling of SOC in amended soil is represented in figure 5.

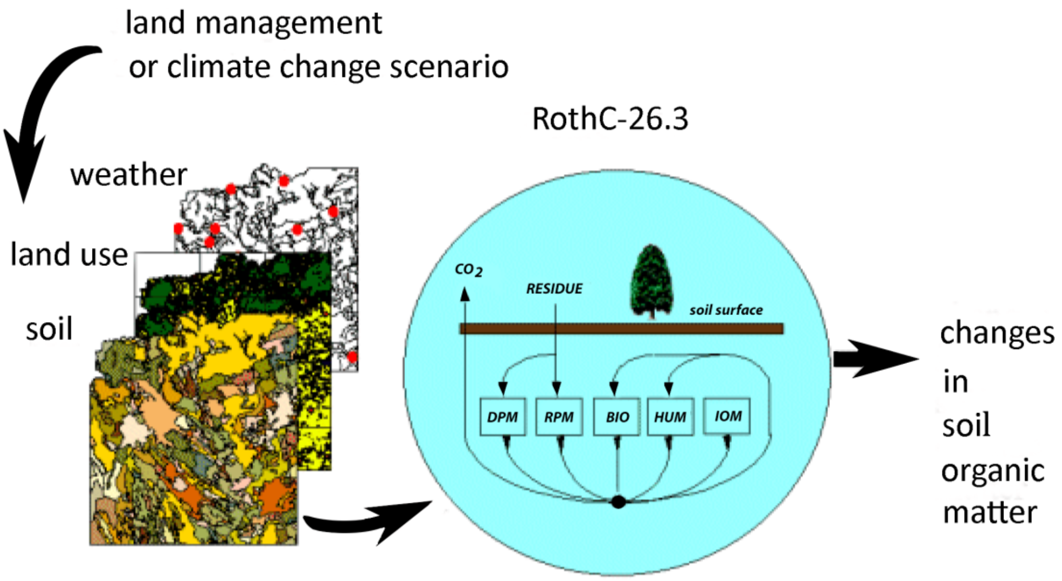

Figure 5. Diagram of the procedure devised for regional SOC modelling in amended soils (after Parshotam et al., 2005).

2.3.4 Data treatment

Model runs were performed for each combination of STU and Land Use within each SMU (10130 combinations). This was done in order to obtain the higher amount of information possible from the available data.

However, the SPADE database does not provide information on the percentage of land covered by each land use classes. Conversely these information is provided for each STUs within the corresponding SMU, but nevertheless STUs cannot be separated spatially at the 1:1000000 map scale. Therefore, for visualization it is necessary to obtain a reduction of available information at SMU level. This was obtained for SOC utilizing the following criteria:

Land use: the fraction of STU area that is occupied by their defined dominant and secondary land use was estimated according to Hannam et al. (2009). In the case of STU presenting only the dominant land use that use was attributed to 80% of the total area of the STU. In the case of STU presenting both dominant and secondary land use it was assumed that the STU is covered by 60% from the dominant land use and 30% from secondary land use.

STU: SOC content of each SMU was calculated operating a weighted average of the C content of each STU, considering the STU's percent area distributions within the SMU reported in the SGDBE database.

3 Results and Discussions

3.1 EOM soil mineralization

3.1.1 CO_2 emission trends of EOM amended soils

As a whole, the respiration pattern of 224 duplicate EOM amended soil samples was measured during laboratory incubations.

The rate of CO_2 evolution from soil was greatly affected by the type of amendment. As an example, Figure 6 shows the CO_2 evolution trends of organic materials with different degree of stabilization in two contrasting soils. In general, EOM characterized by high contents of easily degradable OM (i.e. animal residues, bioenergy by-products) caused a rapid and significant increase in the rate of CO_2 evolution that peaked within 2-3 days after the amendment and was followed by a decreasing trend.

On the other hand, the CO_2 emission patterns of more stable material (i.e. compost) were characterized by a continuously decreasing trend throughout the whole period of incubation. Some materials were characterized by a bimodal pattern of respiration rate, indicating the presence of pools of OM with different degree of degradability.

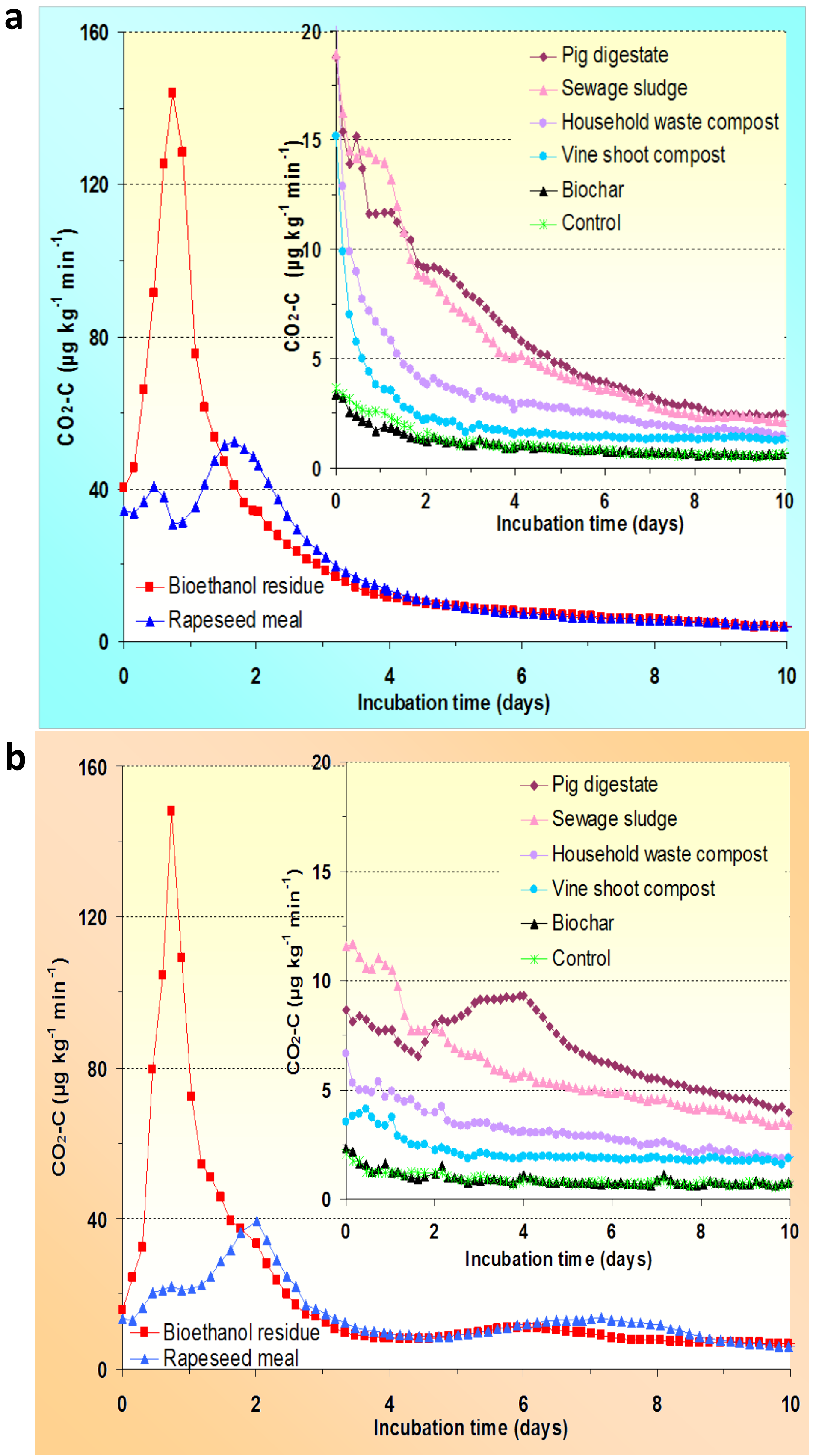

Figure 6. **Trends of CO_2 emission from S. Martino (a) and Reana (b) soils amended with EOM of different degree of degradability.**

3.1.2 Cumulative net C mineralization of EOM amended soils

The cumulative net C mineralization, i.e. the total CO_2-C derived exclusively from EOM decomposition, greatly varied as a function of the different EOMs and incubation conditions. Range and mean values of net C mineralization for the different EOM types, as defined in the material and methods section, are reported in Table 4 which summarizes results from all the incubations performed utilizing different conditions, those carried out under standard laboratory conditions (20 °C, 40% WHC, 0.5% application rate and 30 days incubation period) and those utilized for model optimization.

Table 4. Cumulative extra CO_2-C emitted in amended soil (% of added C) for EOM type for all incubations, incubations performed under standard conditions and incubations utilized for model optimization.

EOM type	All incubations				Standard conditions incubations				Incubations utilized for model optimization			
	Mean	Min	Max	n	Mean	Min	Max	n	Mean	Min	Max	n
	CO_2-C (%)				CO_2-C (%)				CO_2-C (%)			
Biochar	0.02	0.01	0.04	4	0.02	0.01	0.04	4				
Compost	3.7	0.9	11.1	34	3.0	0.9	6.6	19	3.7	0.9	11.1	34
Bioenergy by-products	12.9	6.9	16.8	20	12.8	6.9	16.8	10	13.2	6.9	16.0	17
Anaerobic digestates	3.8	0.8	7.2	27	4.0	0.8	7.1	10	3.8	0.8	7.2	25
Meat and bone meals	16.8	7.8	38.6	93	21.3	18.1	25.9	3	16.8	0.6	3.5	92
Animal residues	13.1	5.0	21.1	33	16.8	11.0	21.1	14	13.5	5.0	21.1	30
Crop residues	8.5	3.0	18.4	10	10.4	5.1	18.4	6	5.6	3.0	7.4	8
Agro-industrial wastes	10.0	6.0	17.5	3	6.3	6.0	17.5	3	6.3	6.0	6.6	2
Sewage sludges	4.8	3.8	6.0	4	4.8	3.8	6.0	4	4.8	3.8	6.0	4
Total cases				**228**				**69**				**212**

Considering all the incubations performed, extra CO_2-C varied in the range 0.01-38.6% of the C added with EOM (Table 4).

In the case of compost, incubations were performed with samples taken at different periods of the stabilization process. Considering only the stable compost, sampled at the end of the stabilization process, EOM mineralization ranged from 0.9 to 4.3%, with a mean value of 2.1% (Table 7).

According to mean values of net C mineralization obtained under standard laboratory conditions, the different EOM types can be ranked as follows (values in parenthesis are the percentage of added C emitted as CO_2-C): biochars (0.02%) < stable composts (2.0%) < composts at different degree of stabilization (3.0%) < anaerobic digestates (4.0%) < sewage sludges (4.8%) < agro-industrial wastes (6.3%) < crop residues (10.4%) < bioenergy by-products (12.8%) < animal residues (16.8%) < meat and bone meals (21.3%).

This classification is in agreement with results of similar studies on the decomposability of EOMs of different origin and nature. Thuries et al. (2001) investigated the soil C mineralization of 17 EOMs and found the following rank of mineralization rates: animal residues > plant residues > compost. Similar results were presented by Lashermes et al. (2009) in a mineralization study of 440 EOMs. In this case, the EOM type with the higher potential for soil C conservation was the anaerobic digestate, followed by composted manure. On the other side of the range of EOM degradability were animal residues.

The EOMs studied in this research were characterized by significant differences in their composition, especially in the content of the different forms of N. These differences would likely influence the behaviour of the residues once applied to the soil. So for instance, the two first generation biofuels (BR and RSM) largely differed in their water soluble C and N and extractable NH_4^+. The composted materials were characterized by different C/N ratio, extractable NH_4^+ and total P.

Besides residue properties, net mineralization was affected by incubation conditions, in particular soil characteristics, temperature of incubation and rate of EOM application.

Values of net C mineralization (expressed as percentage of added C) measured in the present study for compost amended soil are difficult to compare with those found in similar studies, as different conditions regarding temperature of incubation, application rate, soil water content, length of incubation and method of CO_2 measurement were used. Similar values to the ones recorded in this study were reported by De Neve et al. (2003), who measured CO_2-C values of 1.8, 8.1 and 8.8% of added C for green waste compost, vegetable, fruit and garden waste compost and spent mushroom compost, respectively, after 39 days of incubation at 21 °C and 80% WHC. Similarly, Thuries et al. (2001) found net mineralization of about 6% for a stable compost after 30 days of incubation at 28 °C and 75% WHC. Hadas and Portnoy (1997), after 4 weeks of incubation at 30 °C and 60% WHC, measured values of net CO_2-C of 2.5 and 6% for cattle manure and municipal solid waste (MSW) compost amended soil, respectively. Flavel and Murphy (2006) measured the following amounts of net CO_2-C: 7.7, 7.3, 11.0 and 6.9%, for straw, two green waste composts and a vermicompost, respectively, after 70 days of incubation at 15 °C and 75% WHC. Busby et al. (2007) found values in the range 0.5-1.5 and 4.8-15.5% for composted and non composted MSW amended soils, respectively after 30 days of incubation at 25 °C and 85% WHC. Hartz et al. (2000), in a study on C mineralization of 19 manures and compost, measured values in the range 5-17.5% of added C after 28 days of incubation at 25 °C and 25-kPa. Francou et al. (2008) incubated soil amended with green wastes mixed with bio-wastes and paper-cardboard for 28 days at 28 °C and 80% field capacity and recorded values of net mineralization in the range 5-12% of the added C.

The total extra CO_2-C evolved after 2 weeks in the soils amended with meat and bone meals in the present study ranged between 7.8 and 38.6% (Table 4). Comparing these results with other previous C mineralization studies of residues characterized by low values of C/N ratio, they are in the range of poultry manure (16%) or pig slurry (19%) according to a 20-day incubation study performed at 22 °C by Levi-Minzi et al. (1990). Jones (1999) studied the mineralization of a mixture of 15 ^{14}C-labelled amino acids in different soils incubated at 18 °C and found a production of CO_2-C between 10% and 25% of total added C.

Regarding by-products from bioenergy production, values of C mineralization recorded in the present study were significantly lower to the ones measured by Cayuela et al. (2010). This dissimilarity can be attributed to the different conditions utilized for the incubation, as these authors incubated the soil at higher water content (80% water filled pore space vs 40% WHC) and this might have favoured the mineralization process. Nevertheless, the organic residues showed the same relative differences in CO_2 production.

3.2 Model modification and optimization

3.2.1 Model modification

Generally soils receive two main forms of C inputs:

- Plant (crop) residues from the current land management. Such inputs contribute to maintain SOC content at equilibrium
- EOM represented by compost and/or other agricultural or industrial organic residues

The standard RothC model does not distinguish between these two inputs, i.e. the DPM and RPM pools include both plant residues and EOMs, notwithstanding their widely different nature. This limitation of the standard RothC model is highlighted by the results of Tits et al. (2014) who utilized RothC to simulate 30 years of compost addition. The quality of EOM in their work was addressed by calibrating DPM/RPM ratio with the SOC content of a long term experiment, but in this case DPM/RPM ratio encompassed not only EOM quality, but also the quality of input material (crop residues). Consequently, the calibrated DPM/RPM ratio was site specific as the ratio depended not only from compost properties, but also by the crop type and management of the site utilized for calibration. The fact that the same pool structure is used to represent organic materials that widely differ in composition and decomposition pattern (e.g. crop residues vs. compost) simplifies model structure, but is likely to generate less accurate results (Cavalli and Bechini, 2011).

The standard RothC model allows for the simulation of soil amended with farmyard manure, but its partition coefficients in DPM, RPM and HUM are fixed in the model and cannot be varied unless the user modifies the original source code. Such partition coefficients are 0.49, 0.49 and 0.02 for DPM, RPM and HUM, respectively. The decomposition rates for the DPM and RPM pools of plant residues, EOMs and farmyard manure are shared and fixed at 10 and 0.3 y^{-1}, respectively.

In the modified model, the subdivision of EOM in 3 pools, with the more stable one directly incorporated into the humus pool of SOM (Figure 2), is conceptually similar to that of the CNSIM model (Petersen et al., 2005b; Pedersen et al., 2007). In this model

EOM is partitioned in 3 pools, namely metabolic (decomposable), structural (resistant) and recalcitrant (humic-like EOM), with the latter directly incorporated into the soil humic pool. Petersen et al. (2002) indicated that OM from slurry and farmyard manure is generally assumed to contribute relatively more to SOM build-up than plant residues and this is modelled In the CNSIM model by transporting a fraction of added manure directly into the slow native OM pool. The occurrence of an EOM pool directly incorporated into the soil humic substances is supported by the findings of Peltre et al. (2013). The authors found that soil amended with farmyard manure accumulated similar proportions of C with size >50 μm and 0-50 μm, which was attributed to the presence in the manure of a fraction of labile C, together with a fraction of stabilized C directly incorporated into the humified fraction of SOC. The assumption that the stable EOM pool is directly incorporated into stable soil humus is also in agreement with the results of Nicolardot et al. (2001), who found that NCSOIL model tends to overestimate residue-derived CO_2 production and attributed this to the structure of the model that encompasses assimilation of the whole residue by the soil microflora. The authors suggest that models allowing for direct incorporation into stable SOM of a proportion of residue-C (resistant compounds such as lignin), instead of microbial incorporation, are more reliable for predicting long term C trends and that such models are more indicated to the simulation of long term SOM evolution.

The characteristic of HEOM in terms of degradability was considered to be similar to the soil HUM pool and for this reason, in the present thesis, it was assigned the same decomposition rate. This assumption was made on the evidence that certain EOM, such as composts, are characterized by the presence of substances resistant to decomposition which properties resemble those of soil humic substances and for this reason are frequently identified as humic-like substance (Sanchez-Monedero et al., 1999; Wu and Ma, 2002).

Other residues, such as olive mill wastes, have a large content of lignin whose transformation before soil application produces a stable OM. As an example, the aerobic degradation of olive mill wastewaters takes place through typical humification pathways involving polyphenol condensation and the condensation of lignin degradation moieties with N compounds, generating an effluent rich in stable OM similar to the soil humic substances (Fakharedine et al., 2006). Decomposed lignocellulosic wastes such as TPOMW have a high C sequestration potential due to the amount and quality of their humic-like substances (Serramia et al., 2010).

The reliability of the proposed model modification, i.e. the partitioning of EOM in 3 pools with specific pool parameters for each EOM, is sustained by the results of Falloon (2001), who utilized either the standard and a modified version of RothC to simulate C trends in a long term experiment (45 years) dealing with soil amendment with sewage sludge. The conventional version of RothC only accounts for additions of OM to soils in terms of either plant residues or farmyard manure. Using the standard model version and treating the sewage sludge as an input of farmyard manure to soil, resulted in a significant underestimation of SOC increases in the amended soil. A modified version of the model was then used, assuming that sewage sludge was composed of 10% DPM, 70% RPM, and 20% HUM (rather than the values of 49% DPM, 49% RPM and 2% HUM used for farmyard manure). Running the modified RothC, resulted in a much closer agreement between modelled and measured SOC trends. The specific partitioning factors for sewage sludge reflect the evidence that this organic residue is composed of a greater proportion of resistant and humified organic material and less decomposable organic material compared to farmyard manure (McGrath and Brookes, 1986). Further support to the effectiveness of the proposed modification of the model structure derives from the work of Incerti et al. (2011) who found that a model with 3 EOM pools satisfactorily described the pattern of litter decomposition. The authors compared a 3 pools model with a 2 and 1 pools models and found better description of decomposition rate by the 3 pools model. Furthermore, the authors found an enhancement of the predictive ability of the 3 pools model by varying the decomposition rate of the intermediate pool as a function of the lignin content. Accordingly, several authors have demonstrated that the performance of a dynamic C model in simulating SOC in amended soils is increased by a specific parameterization for the EOM added to the soil (Gabrielle et al., 2004; Petersen et al., 2005b; Cavalli and Bechini, 2011, 2012; Peltre et al., 2012). Heitkamp et al. (2012) showed that changing the partition coefficient between decomposable and resistant OM fractions of crop residues allowed the model predictive power to be increased. Glanville et al. (2012), in a study on decomposition of low molecular weight

C components performed either in laboratory and in the field, found a very close resemblance in the partition coefficients, while mineralization rate constants showed the greatest variation between experimental conditions. This supports the importance to parameterize not only the partition coefficient, but also the decomposition rate, since this seems an important factor causing the different behaviour of EOMs in soil. Plaza et al. (2012) concluded that the CQESTR model performance to predict SOC trends in amended soil could be improved by including additional parameters allowing for a better differentiation of EOM with contrasting degree of stability.

As a whole, these results support the hypothesis that specific EOM partitioning coefficients and decomposition rates increase model performance, as reported by Probert et al. (2005) who successfully modified the APSIM model so that any input of organic material could be specified in terms of both its fractionation into the three EOM pools of the model and the C/N ratio of each pool (previously it has been assumed that all pools have the same C/N ratio). Accordingly, the model modification proposed in the present study was based on the hypothesis that this would improve the ability of the model to simulate long term SOC trends in amended soils. This consideration was supported by the fact that preliminary tests have shown that the original model was not capable to adequately simulate the respiration of amended soil during laboratory incubations. This is not unexpected given the high variability in terms of chemical composition, origin and properties of EOM. In addition, it has to be considered that new treatments and processes for animal and vegetal residues are being developed (i.e. bioenergy process), generating new by-products which behaviour into the soil are not well known and understood (Cayuela et al., 2010).

EOM partitioning in two or three pools depends on its composition and properties. Petersen et al. (2003), in an investigation on the soil decomposition of plant residues, showed that the rate of CO_2 evolution generally peaked shortly after amendment and then gradually became fairly constant, indicating that a fraction of the added material is relatively slowly decomposable. Splitting the added organic matter between two compartments EOM1 and EOM2, the latter representing the most easily decomposable material, has been shown to represent well this mechanism.

On the other side, Cavalli and Bechini (2011) in a study on soil mineralization of liquid dairy manure found that a good agreement between the simulated and observed dynamics of CO_2 respiration (characterised by an initial rapid phase of C mineralisation and a successive slower phase of CO_2 release) was obtained by partitioning the added C input into three pools (EOM1, EOM2 and NOM) with different decomposition constants.

3.2.2 Sensitivity analysis

To test the effect of modifications carried out on the standard RothC model, a sensitivity analysis (SA) was performed to assess the effects of varying EOM model parameters on outputs. This analysis allows the parameters which have a major impact on the simulated C accumulation following EOM addition to be identified.

The analysis was performed by varying a single parameter at a time within a certain range, keeping constants the remaining. The initial values of the parameters were derived from a model parameterization under standard conditions for two EOMs, characterized by the presence or not of HEOM. More specifically the two EOMs were a mixed swine bovine meat and bone meal (SB) and a household waste compost (HWC).

In the case of SB, characterized by two EOM pools, the parameter presenting the greatest effect on the simulated SOC was K_{REOM} (Table 5; Figure 7). The SI index is negative indicating an inverse relationship between the parameter and the output. This result is in agreement with findings of Stamati et al. (2013) who demonstrated that total plant litter input and the RPM decomposition rate constant were the RothC parameters with the highest sensitivity.

Table 5. RothC EOM pool parameters sensitivity analysis for meat and bone meal amended soil.

Parameter varied	f_{DEOM}	f_{REOM}	f_{DEOM}/f_{REOM}	K_{DEOM} (y^{-1})	K_{REOM} (y^{-1})	SOC (after 100 y)	SOC-EQ	C sequestration potential (t C ha y^{-1})	SI
f_{DEOM}/f_{REOM}	0.90	0.10	9.00	27.3	0.36	42.28	5.28	0.053	-120.7
	0.80	0.20	4.00	27.3	0.36	42.58	5.58	0.056	-60.4
	0.70	0.30	2.33	27.3	0.36	42.88	5.88	0.059	-40.4
	0.60	0.40	1.50	27.3	0.36	43.17	6.17	0.062	-30.3
	0.50	0.50	1.00	27.3	0.36	43.47	6.47	0.065	-24.4
	0.40	0.60	0.67	27.3	0.36	43.77	6.77	0.068	-20.5
	0.30	0.70	0.43	27.3	0.36	44.07	7.07	0.071	-18.0
	0.21	0.79	0.26	27.3	0.36	44.34	7.34	0.073	
	0.10	0.90	0.11	27.3	0.36	44.67	7.67	0.077	-12.7
	0.01	0.99	0.01	27.3	0.36	44.93	7.93	0.079	-11.8
K_{DEOM}	0.21	0.79	0.26	1	0.36	44.53	7.53	0.0753	-37
	0.21	0.79	0.26	3	0.36	44.39	7.39	0.0739	-138
	0.21	0.79	0.26	5	0.36	44.35	7.35	0.0735	-530
	0.21	0.79	0.26	10	0.36	44.34	7.34	0.0734	-1937
	0.21	0.79	0.26	15	0.36	44.34	7.34	0.0734	-3005
	0.00	0.39	0.00	20	0.36	44.34	7.34	0.0734	-3924
	0.21	0.79	0.26	27.3	0.36	44.34	7.34	0.0734	
	0.21	0.79	0.26	40	0.36	44.34	7.34	0.0734	-8532
	0.21	0.79	0.26	50	0.36	44.34	7.34	0.0734	-12201
	0.21	0.79	0.26	60	0.36	44.34	7.34	0.0734	-17576
	0.21	0.79	0.26	70	0.36	44.34	7.34	0.0734	-19126
K_{REOM}	0.21	0.79	0.26	27.30	0.15	47.94	10.94	0.109	-1
	0.21	0.79	0.26	27.30	0.20	46.40	9.40	0.094	-2
	0.21	0.79	0.26	27.30	0.25	45.47	8.47	0.085	-2
	0.21	0.79	0.26	27.30	0.30	44.85	7.85	0.079	-2
	0.21	0.79	0.26	27.30	0.36	44.34	7.34	0.073	
	0.21	0.79	0.26	27.30	0.40	44.08	7.08	0.071	-4
	0.21	0.79	0.26	27.30	0.50	43.62	6.62	0.066	-4
	0.21	0.79	0.26	27.30	0.75	43.00	6.00	0.060	-6
	0.21	0.79	0.26	27.30	1.00	42.69	5.69	0.057	-8
	0.21	0.79	0.26	27.30	1.25	42.51	5.51	0.055	-10
	0.21	0.79	0.26	27.30	1.50	42.39	5.39	0.054	-12
	0.21	0.79	0.26	27.30	2.00	42.25	5.25	0.052	-16
	0.21	0.79	0.26	27.30	3.00	42.11	5.11	0.051	-25

EQ:	SOC at equilibrium = 36.9996 t ha^{-1}
SOC-EQ:	SOC after 100 years - SOC at equilibrium
SI (sensitivity index):	% change in output variable / % change in input variable
Added C:	1.0 t ha^{-1} y^{-1}

Values in red refer to simulation performed with initial values of the parameters derived from a model calibration under standard conditions

Moreover, SI for K_{REOM} is not constant and displays the lowest absolute values in correspondence to the lowest values of K_{REOM}. Consequently, SOC values predicted with RothC are more sensitive to differences in K_{REOM} at smaller values of the parameter.

The model output is sensitive to K_{DEOM} only at very low values (< 1). In all the optimizations performed the minimum K_{DEOM} value was 11. For values larger than 10 the sensitivity analysis showed that differences in K_{DEOM} resulted in negligible differences in the SOC accumulated. This is due to the fact that at high mineralization rates of DEOM, such pool is nearly completely mineralized before the successive EOM addition in the following year. In fact, for $K_{DEOM} = 10\ y^{-1}$ the DEOM half life, i.e. the time required for half of the pool to decompose, is $0.07\ y^{-1}$ (Six and Astrow, 2002).

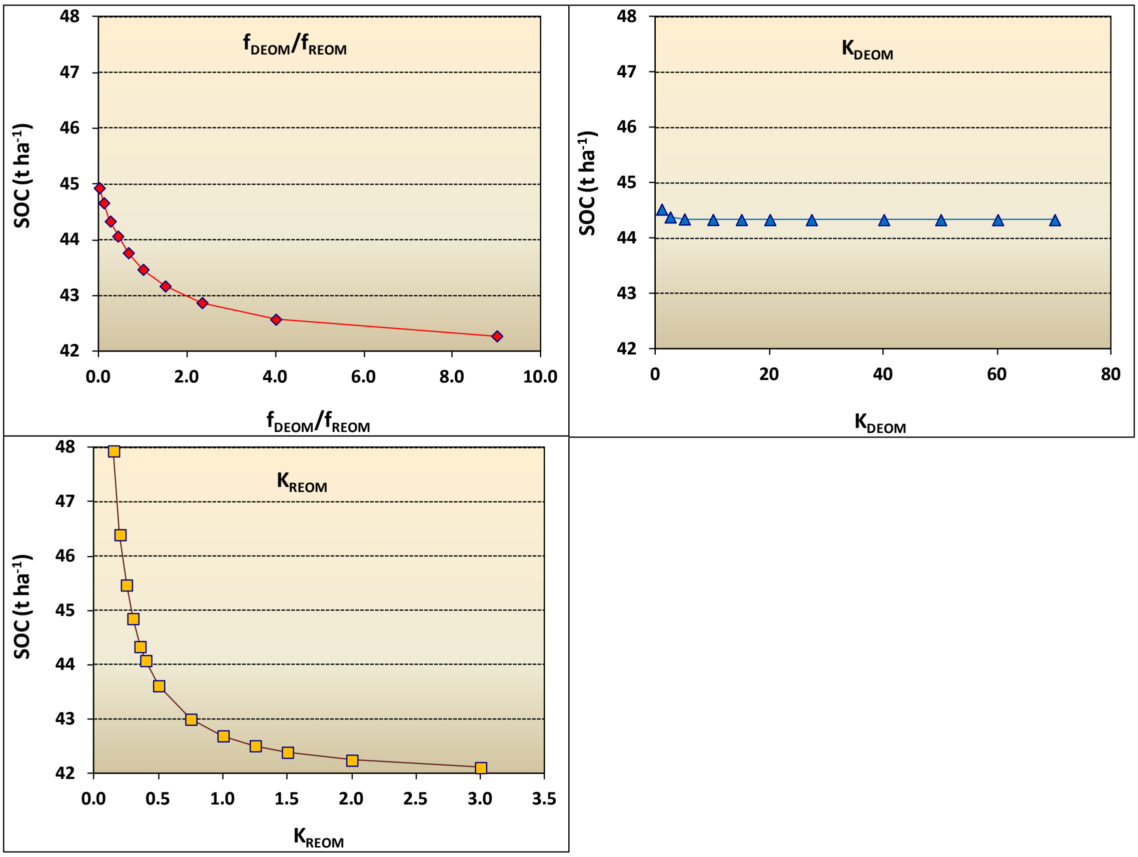

Figure 7. RothC EOM pool parameters sensitivity analysis for a meat and bone meal amended soil.

The model displayed a moderate sensitivity to variations in the f_{DEOM}/f_{REOM} ratio. Variation of the ratio from 9 to 0.11 resulted in 2.4 C t ha^{-1} increase, with larger differences at lower values of the ratio.

In the case of EOM characterized by 3 pools, typically the composted substrates, the most influential parameter on the model output was the f_{REOM}/f_{HEOM} ratio, especially at lower values (i.e. high contents of humic-like substances) (Table 6; Figure 8). This is not unexpected given the well known slow degradation rate of humic substances.

For the same reason (increase of HUM pool) the model output is also sensitive to variations in the f_{DEOM}/f_{HEOM} ratio; such sensitivity is higher at low values of the ratio.

Variations in K_{REOM} presented a moderate effect on the model output. Changing the value from 0.75 to 0.15 resulted in a SOC increase of 2.31 t C ha^{-1}, corresponding to 3.3% of the initial value.

During SA, variations in model outputs are related to variation in model inputs, highlighting the contribution of each parameter and of parameters interactions on model output variations. Therefore SA helps in selecting the most important parameters that need to be varied during parameter optimisation.

Table 6. RothC EOM pool parameters sensitivity analysis for household waste compost.

Parameter varied	f_{DEOM}	f_{REOM}	f_{HEOM}	f_{DEOM}/f_{REOM}	f_{DEOM}/f_{HEOM}	f_{REOM}/f_{HEOM}	K_{DEOM} (y^{-1})	K_{REOM} (y^{-1})	SOC (after 100 y)	SOC-EQ	C sequestration potential (t C ha y^{-1})	SI
f_{DEOM}/f_{REOM}	0.01	0.39	0.61	0.01	0.01	0.63	43	0.35	71.55	34.55	0.346	-586
	0.01	0.38	0.61	0.03	0.02	0.62	43	0.35	71.54	34.54	0.345	-631
	0.02	0.37	0.61	0.06	0.04	0.61	43	0.35	71.51	34.51	0.345	
	0.09	0.30	0.61	0.30	0.15	0.49	43	0.35	71.29	34.29	0.343	-638
	0.19	0.20	0.61	0.95	0.31	0.33	43	0.35	70.98	33.99	0.340	-975
	0.29	0.10	0.61	2.90	0.48	0.16	43	0.35	70.68	33.68	0.337	-1959
	0.34	0.05	0.61	6.80	0.56	0.08	43	0.35	70.52	33.52	0.335	-3922
f_{DEOM}/f_{HEOM}	0.53	0.37	0.10	1.43	5.30	3.70	43	0.35	47.77	10.77	0.108	-209
	0.43	0.37	0.20	1.16	2.15	1.85	43	0.35	52.43	15.43	0.154	-104
	0.33	0.37	0.30	0.89	1.10	1.23	43	0.35	57.08	20.08	0.201	-69
	0.23	0.37	0.40	0.62	0.58	0.93	43	0.35	61.73	24.73	0.247	-52
	0.13	0.37	0.50	0.35	0.26	0.74	43	0.35	66.39	29.39	0.294	-41
	0.02	0.37	0.61	0.06	0.04	0.61	43	0.35	71.51	34.51	0.345	
	0.01	0.37	0.62	0.03	0.02	0.60	43	0.35	71.97	34.97	0.350	-42
f_{REOM}/f_{HEOM}	0.02	0.88	0.10	0.02	0.20	8.80	43	0.35	49.34	12.34	0.123	-20.9
	0.02	0.78	0.20	0.03	0.10	3.90	43	0.35	53.69	16.69	0.167	-10.5
	0.02	0.68	0.30	0.03	0.07	2.27	43	0.35	58.03	21.03	0.210	-7.0
	0.02	0.58	0.40	0.03	0.05	1.45	43	0.35	62.38	25.38	0.254	-5.2
	0.02	0.48	0.50	0.04	0.04	0.96	43	0.35	66.73	29.73	0.297	-4.2
	0.02	0.37	0.61	0.06	0.04	0.61	43	0.35	71.51	34.51	0.345	
	0.02	0.28	0.70	0.07	0.03	0.40	43	0.35	75.42	38.42	0.384	-3.0
	0.02	0.18	0.80	0.11	0.03	0.23	43	0.35	79.77	42.77	0.428	-2.6
K_{REOM}	0.02	0.37	0.61	0.06	0.04	0.61	43	0.15	73.16	36.16	0.362	-12
	0.02	0.37	0.61	0.06	0.04	0.61	43	0.20	72.44	35.44	0.354	-33
	0.02	0.37	0.61	0.06	0.04	0.61	43	0.25	72.00	35.00	0.350	-40
	0.02	0.37	0.61	0.06	0.04	0.61	43	0.30	71.71	34.72	0.347	-47
	0.02	0.37	0.61	0.06	0.04	0.61	43	0.35	71.51	34.51	0.345	
	0.02	0.37	0.61	0.06	0.04	0.61	43	0.40	71.35	34.35	0.344	-70
	0.02	0.37	0.61	0.06	0.04	0.61	43	0.50	71.14	34.14	0.341	-85
	0.02	0.37	0.61	0.06	0.04	0.61	43	0.75	70.85	33.85	0.338	-126
	0.02	0.37	0.61	0.06	0.04	0.61	43	1.00	70.70	33.70	0.337	-167
	0.02	0.37	0.61	0.06	0.04	0.61	43	1.25	70.62	33.62	0.336	-209
	0.02	0.37	0.61	0.06	0.04	0.61	43	1.50	70.56	33.56	0.336	-251
	0.02	0.37	0.61	0.06	0.04	0.61	43	2.00	70.49	33.49	0.335	-336
	0.02	0.37	0.61	0.06	0.04	0.61	43	3.00	70.43	33.43	0.334	-507

EQ:	SOC at equilibrium = 36.9996 t ha^{-1}
SOC-EQ:	SOC after 100 years - SOC at equilibrium
SI (sensitivity index):	% change in output variable / % change in input variable
Added C:	1.0 t ha^{-1} y^{-1}

Values in red refer to simulation performed with initial values of the parameters derived from a model calibration under standard conditions

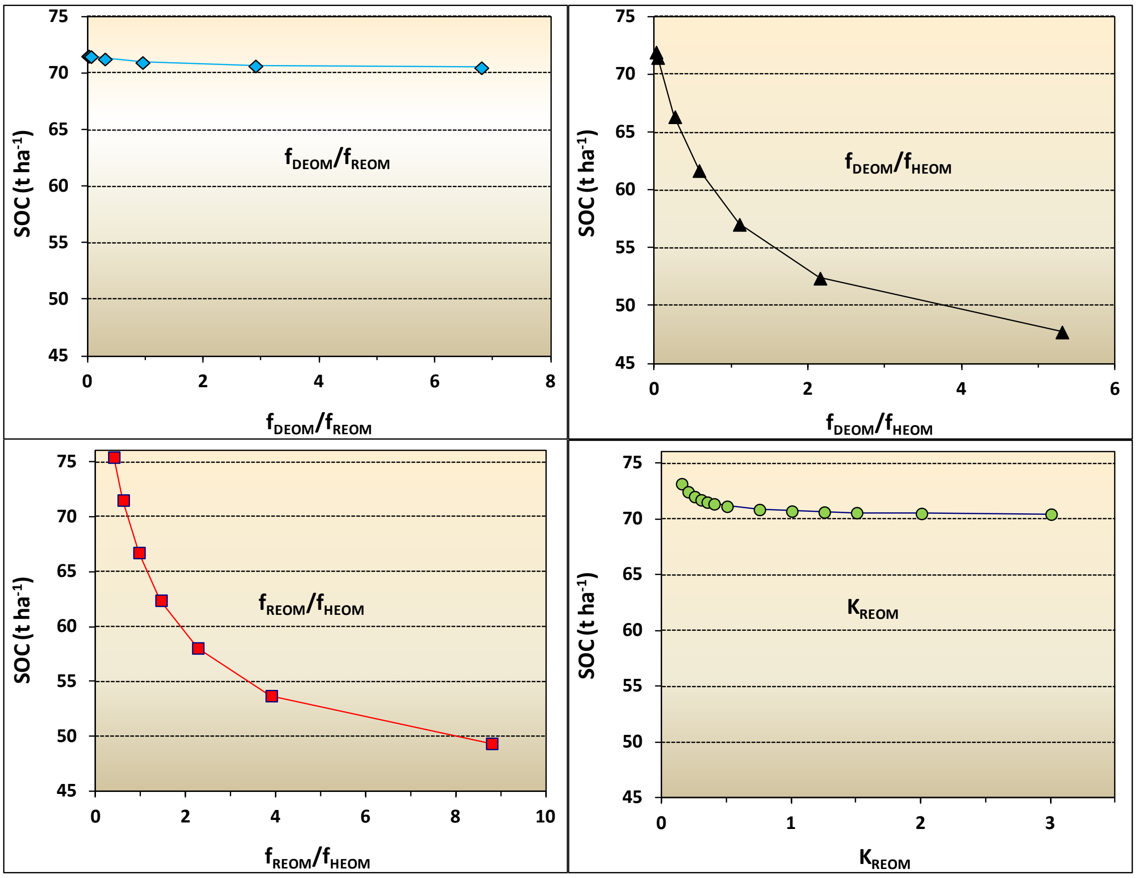

Figure 8. Roth C EOM pool parameters sensitivity analysis for household waste compost amended soil.

3.2.3 Model optimization by fitting respiration data

Model optimization is an essential step for model testing and development; its purpose is to achieve a good fit between simulated model outputs and corresponding experimental observations. This objective is achieved by exploring different combinations of parameters and identifying the solutions that provide the best agreement between measured and simulated variables.

In a preliminary test, the possibility to optimize the model following the procedure performed by Peltre et al. (2012), i.e. changing only the partition coefficients of EOM entry pools and leaving constant the decomposition rates, was investigated. Results showed that it was not possible to achieve a satisfactory fitting of the respiratory curve only by varying the proportion of DEOM, REOM and HEOM.

The optimization procedure was therefore carried out by simultaneously varying the partition coefficients for DEOM, REOM and HEOM and the decomposition rate constants for DEOM and REOM. Tables 7-12 show the incubation conditions and the model parameters obtained by fitting the model to the CO_2 measured during the different incubations. In the tables are also reported the values of the statistical indicators utilized to evaluate the model goodness of fit.

As an example of curve fitting, Figure 9 reports measured and simulated net CO_2-C evolution for meat and bone meal and hydrolyzed leather added to the S. Martino soil incubated under standard conditions.

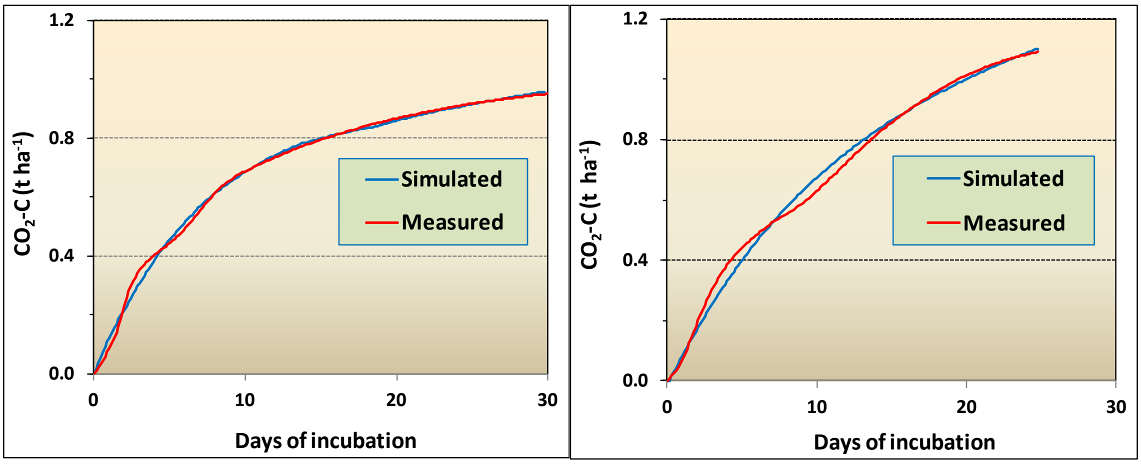

Figure 9. Examples of model fitting to measured respiration curves of meat and bone meal (left) and hydrolyzed leather (right) amended soil incubated in laboratory.

As a whole the model was able to fit very well the respiratory response of the amended soils, as indicated by the statistical indicators (Tables 7-12). The mean correlation coefficient (R) for all incubations was 0.995 and was higher than 0.945 for all but one EOM. The root mean square error (RSME) was on average 4.5%, while the relative error (E) ranged between -16.4 and 3.5% (Tables 7-12). The goodness of the fit was also underlined by the very low values of M (on average -1.2 µg CO_2-C g^{-1}). As a comparison, Cavalli and Bechini (2011) calibrated CNSIM model for five different liquid dairy manures and obtained RMSE values in the range 3-17%.

Mean values of partition coefficients of added organic C optimized for compost amended soils found in the present work (f_{DEOM}: 0.03; f_{REOM}: 0.44; f_{HEOM}: 0.53; Table 7) were in a very close agreement to values of 0.08, 0.40 and 0.52 for labile, resistant and stable EOM pools, respectively, found by Kaborè et al. (2011) for composted substrates utilizing the TAO model. Partition coefficients and decomposition rates for composted materials were also similar to those estimated by Thuries et al. (2001), utilizing a model with 3 compartment of EOM and two specific mineralization rate for labile and resistant EOM to fit measured CO_2 values. These authors found f values of 0.03, 0.18 and 0.79 for decomposable, resistant and stable EOM, and decomposition rates of 146 and 5.7 y^{-1} for decomposable and resistant EOM pools, respectively.

There was an increase of HEOM and a decrease in K_{REOM} in soil amended with compost samples of increasing age. Therefore the model parameters were in agreement with the increase in organic matter stabilization normally occurring during the composting process. Similar results were obtained by Kaborè et al. (2011) who found that the TAO model was able to quantify changes in compost EOM pools according to trends reported in the literature with increasing composting time.

The stable HEOM pool in compost substrates in the present study was on average 53% of total EOM and this was in agreement with previous works dealing with OM fractionation of composted organic materials. Lashermes et al. (2012), in a study on OM fractions of compost, found that the most recalcitrant fraction of organic C remained constant throughout the entire process representing 48% of TOC in the initial mixture and 78% of TOC in the final composts. Similar results were observed in reactors with larger volume or in industrial plants (Bernal et al., 1998; Doublet et al., 2011).

The mean percentage of HEOM in compost (53%) was similar to lignin contents reported in the literature. Lignin, assumed as proxy for the HEOM pool, in compost produced from TPOMW, manure and green wastes ranged from 30 to 54% of total organic matter (Sanchez-Monedero et al., 1999). Thuries et al. (2002) measured C lignin contents in compost up to 54% of TOC.

Lower values of humified pool for compost were reported by Peltre et al. (2012), which fitted EOM partition coefficients in the RothC DPM, RPM and HUM entry pools.

They obtained values of 0.0, 0.8 and 0.2 for DPM, RPM and HUM, respectively, for 2 compost produced by bio-wastes and green wastes and for 2 peats. Nevertheless, they set a threshold partitioning coefficient of 0.2 for the HUM pool and the fact that the optimal solution for HUM pool corresponded to the boundary fixed by the authors indicates that the optimization algorithm had sought the optimal solution outside the allowed parameter space, thus underling a structural problem of adapting the model to this data set.

In general the decomposition rate of DEOM was very high in comparison to the original decomposition rate of Roth C for DPM. For example, mean K_{DEOM} for vine compost was on average 72 y^{-1} (n = 34), a value remarkably higher than the standard value of 10 y^{-1} for decomposable plant material (DPM) utilized by the standard RothC. This indicates that also in the case of a well stabilized EOM as compost, the labile pool, albeit small, is characterized by a high degree of decomposability. This is reflected by the steep slope of the first part of the respiration curve; the model to adequately simulate the measured curve needs to impose an high value to the decomposition rate constant of the labile pool, as this parameters mainly regulates the initial slope of the cumulative respiratory curve.

In the case of incubations performed with biochar, the results of the optimization procedure were not satisfactory. Also for some soil amended with a low dose of anaerobic digestate (100 kg N ha^{-1}) it was not possible to satisfactorily fit the respiration data. Such incubations were therefore excluded from the model optimization study. The lack of fit of the model to the respiration data is mainly attributable to the fact that the OM of these materials was highly stable and released very low amounts of CO_2, close to the detection limit of the chromatography system and with a high degree of variability. RothC cannot be applied to soils containing large amounts of recent inert organic matter, such as charcoal (Falloon, 2001), material whose composition and properties resemble those of biochar. Furthermore, for highly stable materials is advisable to select high rates of EOM application in order to improve the reliability of the respiration measurement.

Table 7. Kinetic fit for EOM pools of compost.

EOM	Phase	Days	Soil	Temp °C	WHC	EOM rate %	C rate µg g^{-1}	f_{DEOM}	f_{REOM}	f_{HEOM}	K_{DEOM}	K_{REOM}	SSR µg C g^{-1}	RMSE %	R	E %	M µg C g^{-1}	CO_2-C %
VSC	M	30	SM	20	40	0.5	1725	0.02	0.39	0.59	45	0.35	42	1.3	0.9994	0.33	0.11	3.0
VSC	M	30	PE	20	40	0.5	1725	0.02	0.44	0.54	58	0.25	193	2.9	0.9972	-0.03	-0.01	2.8
VSC	M	32	LL	20	40	0.5	1725	0.00	0.44	0.56	150	0.15	137	9.5	0.9756	0.25	0.02	0.9
VSC	M	29	AL	20	40	0.5	1725	0.01	0.30	0.69	224	0.18	25	3.5	0.9957	-0.05	-0.01	1.0
HWC	M	30	SM	20	40	0.5	1720	0.02	0.37	0.61	43	0.35	40	1.3	0.9995	0.31	0.11	3.0
HWC	M	32	SM	20	40	0.5	1720	0.02	0.33	0.65	43	0.15	36	1.6	0.9990	0.19	0.06	2.6
HWC	M	32	SM	20	40	0.5	1720	0.02	0.34	0.63	41	0.15	87	2.6	0.9976	0.27	0.09	2.5
HWC	M	35	SM	30	40	0.5	1720	0.02	0.30	0.68	74	0.15	179	3.2	0.9930	0.15	0.06	2.6
HWC	M	35	SM	30	40	0.5	1720	0.01	0.35	0.64	93	0.15	334	5.6	0.9825	0.19	0.06	2.1
HWC	M	36	SM	10	40	0.5	1720	0.02	0.34	0.64	44	0.15	20	2.1	0.9995	1.53	0.28	1.6
HWC	M	36	SM	10	40	0.5	1720	0.02	0.37	0.60	35	0.15	10	1.4	0.9996	0.22	0.04	1.8
HWC	M	28	SM	20	20	0.5	1720	0.01	0.31	0.68	118	0.29	65	3.8	0.9932	-0.41	-0.09	1.6
HWC	M	28	SM	20	30	0.5	1720	0.01	0.53	0.46	127	0.19	35	3.0	0.9958	0.74	0.14	1.5
HWC	M	34	SM	20	40	0.1	344	0.02	0.28	0.70	54	0.86	6	2.3	0.9987	0.39	0.04	4.3
HWC	M	34	SM	20	40	0.25	860	0.02	0.28	0.70	54	0.39	17	2.4	0.9984	0.42	0.07	2.6
HWC	M	30	PE	20	40	0.5	1720	0.02	0.30	0.68	69	0.40	293	3.6	0.9952	-1.46	-0.50	2.8
HWC	M	32	LL	20	40	0.5	1720	0.01	0.29	0.70	222	0.16	13	1.7	0.9979	0.16	0.02	1.4
HWC	M	30	AL	20	40	0.5	1720	0.01	0.26	0.72	72	0.46	46	2.5	0.9981	0.64	0.14	2.0
GWB	M	13	PE	20	40	0.75	2115	0.01	0.52	0.47	200	0.42	21	2.7	0.9978	0.72	0.13	1.3
GWB	M	13	GO	20	40	0.75	2115	0.01	0.40	0.59	200	0.15	10	1.9	0.9983	0.28	0.05	1.0
CMC	II	37	JU	20	40	0.5	2135	0.04	0.89	0.07	38	0.31	115	0.8	0.9998	-0.02	-0.02	6.1
CMC	III	37	JU	20	40	0.5	2063	0.05	0.63	0.32	28	0.33	173	1.0	0.9997	-0.10	-0.08	6.0
CMC	M	37	JU	20	40	0.5	1993	0.002	0.31	0.69	105	0.36	48	3.1	0.9983	0.41	0.06	1.4
CBC	II	37	JU	20	40	0.5	2174	0.07	0.74	0.19	22	0.23	94	0.7	0.9999	-0.03	-0.03	6.6
CBC	III	37	JU	20	40	0.5	2124	0.07	0.59	0.34	18	0.16	651	2.1	0.9989	-0.35	-0.27	5.6
CBC	IV	37	JU	20	40	0.5	2117	0.05	0.57	0.38	16	0.23	3981	6.5	0.9952	-0.98	-0.62	4.9
CBC	M	37	JU	20	40	0.5	2031	0.01	0.35	0.64	99	0.38	113	3.1	0.9979	-0.68	-0.15	1.9
CMC	II	37	JU	30	40	0.5	2135	0.06	0.84	0.10	45	0.37	494	1.0	0.9996	0.02	0.03	9.6
CMC	III	37	JU	30	40	0.5	2063	0.06	0.62	0.32	30	0.38	590	1.3	0.9994	0.00	0.00	8.5
CMC	M	37	JU	30	40	0.5	1993	0.01	0.21	0.78	62	0.57	181	2.9	0.9982	0.21	0.07	2.7
CBC	II	37	JU	30	40	0.5	2174	0.09	0.71	0.20	21	0.33	1897	1.7	0.9990	0.18	0.30	11.1
CBC	III	37	JU	30	40	0.5	2124	0.07	0.65	0.28	21	0.37	953	1.6	0.9997	-0.02	-0.03	9.3
CBC	IV	37	JU	30	40	0.5	2117	0.05	0.55	0.40	17	0.21	2512	3.8	0.9967	0.28	0.24	6.2
CBC	M	37	JU	30	40	0.5	2031	0.01	0.26	0.73	190	0.52	283	3.2	0.9975	0.08	0.03	3.0
mean								0.03	0.44	0.53	79	0.30	403	2.7	0.9968	0.11	0.01	3.7
minimum								0.00	0.21	0.07	16	0.15	6	0.7	0.9756	-1.46	-0.62	0.9
maximum								0.09	0.89	0.78	224	0.86	3981	9.5	0.9999	1.53	0.30	11.1

WHC: water holding capacity; SSR: sum of squared residuals; RMSE: root mean square error; R: coefficient of correlation; E: relative error; M: mean difference

CO_2-C: cumulative net CO_2-C emission in amended soil; M: mature compost; roman numerals refer to phases of the composting process

For EOM code refer to material and methods section and Table 3, for soil code refer to Table 2

Table 8. Kinetic fit for EOM pools of bioenergy by-products.

EOM	Days	Soil	Temp °C	WHC	EOM rate %	C rate $\mu g\ g^{-1}$	f_{DEOM}	f_{REOM}	K_{DEOM}	K_{REOM}	SSR $\mu g\ C\ g^{-1}$	RMSE %	R	E %	M $\mu g\ C\ g^{-1}$	CO_2-C %
BR	30	SM	20	40	0.5	2425	0.12	0.88	147	0.68	30347	4.3	0.990	-1.47	-4.27	15.1
BR	30	PE	20	40	0.5	2425	0.15	0.85	145	0.37	8416	2.2	0.995	0.17	0.50	14.3
BR	34	SM	20	40	0.1	485	0.12	0.88	115	0.52	252	2.5	0.996	0.30	0.17	14.5
BR	34	SM	20	40	0.1	485	0.11	0.89	124	0.52	233	2.6	0.995	0.29	0.16	13.7
BR	32	LL	20	40	0.5	2425	0.11	0.89	113	0.29	1835	1.3	0.998	-0.01	-0.02	10.9
BR	29	AL	20	40	0.5	2425	0.20	0.80	81	0.15	152617	9.5	0.985	-0.42	-1.39	16.8
RSM	36	SM	10	40	0.5	2295	0.04	0.96	136	1.20	5211	5.0	0.993	-0.43	-0.54	8.2
RSM	36	SM	10	40	0.5	2295	0.04	0.96	186	1.36	6075	5.3	0.991	-0.26	-0.33	8.5
RSM	30	SM	20	40	0.5	2295	0.11	0.89	44	0.32	3128	2.0	0.998	-0.04	-0.09	11.8
RSM	32	SM	20	40	0.5	2295	0.15	0.85	65	0.33	3102	1.9	0.998	0.07	0.20	14.7
RSM	32	SM	20	40	0.5	2295	0.16	0.84	71	0.32	2583	1.5	0.999	0.14	0.42	16.0
RSM	35	SM	30	40	0.5	2295	0.13	0.87	108	0.18	3467	1.9	0.996	0.00	-0.01	13.5
RSM	35	SM	30	40	0.5	2295	0.14	0.86	125	0.17	5010	2.2	0.994	0.21	0.61	14.0
RSM	28	SM	20	20	0.5	2295	0.17	0.83	72	0.24	1060	1.2	0.999	-0.04	-0.12	15.1
RSM	28	SM	20	30	0.5	2295	0.15	0.85	70	0.33	822	1.1	0.999	-0.04	-0.10	14.3
RSM	30	PE	20	40	0.5	2295	0.12	0.88	90	0.32	3373	1.9	0.998	-0.14	-0.32	12.0
RSM	34	SM	20	40	0.25	1148	0.13	0.87	69	0.37	239	1.1	0.999	0.00	0.00	14.4
RSM	34	SM	20	40	0.1	459	0.13	0.87	75	0.41	78	1.6	0.999	-0.08	-0.04	14.1
RSM	32	LL	20	40	0.5	2295	0.07	0.93	49	0.15	810	1.6	0.999	-0.16	-0.19	6.9
RSM	29	AL	20	40	0.5	2295	0.11	0.89	77	0.15	92204	11.5	0.989	-6.44	-13.70	9.6
mean							0.12	0.88	98	0.42	16043	3.1	0.996	-0.42	-0.95	12.9
minimum							0.04	0.80	44	0.15	78	1.1	0.985	-6.44	-13.70	6.9
maximum							0.20	0.96	186	1.36	152617	11.5	0.999	0.30	0.61	16.8

WHC: water holding capacity; SSR: sum of squared residuals; RMSE: root mean square error; R: coefficient of correlation; E: relative error

M: mean difference; CO_2-C: cumulative net CO_2-C emission in amended soil

For EOM code refer to material and methods section and Table 3, for soil code refer to Table 2

Table 9. Kinetic fit for EOM pools of anaerobic digestates.

EOM	Days	Soil	Temp °C	WHC	EOM rate %	C rate µg g^{-1}	f_{DEOM}	f_{REOM}	f_{HEOM}	K_{DEOM}	K_{REOM}	SSR µg C g^{-1}	RMSE %	R	E %	M µg C g^{-1}	CO_2-C %
PS	36	SM	10	40	0.50	1895	0.02	0.84	0.15	40	0.86	621	5.0	0.9961	-0.58	-0.2	3.9
PS	36	SM	10	40	0.50	1895	0.00	0.70	0.30	187	1.52	727	5.4	0.9953	0.14	0.1	4.1
PS	30	SM	20	40	0.50	1895	0.08	0.62	0.30	26	0.15	345	1.5	0.9995	-0.25	-0.2	7.1
PS	32	SM	20	40	0.50	1895	0.06	0.64	0.30	38	0.21	122	1.1	0.9996	0.11	0.1	6.5
PS	32	SM	20	40	0.50	1895	0.07	0.63	0.30	52	0.21	305	1.6	0.9989	-0.40	-0.4	6.8
PS	35	SM	30	40	0.50	1895	0.05	0.65	0.30	73	0.15	1328	3.6	0.9892	-0.35	-0.3	5.8
PS	35	SM	30	40	0.50	1895	0.04	0.66	0.30	84	0.15	701	2.8	0.9951	1.47	1.2	5.4
PS	28	SM	20	20	0.50	1895	0.04	0.81	0.14	72	0.32	235	2.2	0.9986	-0.32	-0.2	5.1
PS	28	SM	20	30	0.50	1895	0.04	0.66	0.30	69	0.37	126	1.6	0.9991	-0.19	-0.1	5.0
PS	30	PE	20	40	0.50	1895	0.04	0.90	0.06	70	0.28	98	1.0	0.9996	0.05	0.0	5.3
PS	34	SM	20	40	0.10	379	0.05	0.75	0.20	55	0.43	13	1.7	0.9990	0.25	0.0	7.2
PS	34	SM	20	40	0.25	948	0.05	0.65	0.30	57	0.44	45	1.4	0.9993	0.16	0.1	6.7
PS	32	LL	20	40	0.50	1895	0.03	0.67	0.30	41	0.15	111	1.5	0.9991	-0.02	0.0	3.4
PS	29	AL	20	40	0.50	1895	0.05	0.73	0.22	47	0.16	303	2.2	0.9987	-0.12	-0.1	4.9
OW1	21	SM	20	40	0.75	325	0.00	0.70	0.30	270	0.15	7	18.8	0.9446	2.67	0.0	0.8
OW1	26	SM	20	40	1.50	649	0.01	0.83	0.16	64	0.17	5	3.0	0.9989	0.58	0.0	2.0
OW1	10	CO	20	40	1.50	649	0.01	0.78	0.21	260	0.15	9	4.81	0.9919	3.39	0.1	1.6
OW2	13	SM	20	40	0.75	347	0.01	0.83	0.16	151	0.20	2	5.1	0.9943	0.95	0.0	3.3
OW2	23	SM	20	40	1.50	693	0.02	0.79	0.19	151	0.44	1	1.6	0.9995	-0.20	0.0	3.9
OW2	7	CO	20	40	1.50	693	0.01	0.69	0.30	267	0.17	6	3.9	0.9967	0.93	0.1	1.6
OW3	26	SM	20	40	0.75	362	0.00	0.70	0.30	280	0.15	51	37.2	0.7938	1.08	0.0	0.9
OW3	22	SM	20	40	1.50	723	0.01	0.69	0.30	72	0.15	39	9.2	0.9878	-1.60	-0.1	1.8
OW3	7	CO	20	40	1.50	723	0.01	0.69	0.30	279	0.15	9	5.5	0.9903	1.18	0.1	1.2
OW4	26	SM	20	40	0.75	404	0.01	0.69	0.30	280	0.15	31	13.8	0.9645	1.75	0.1	1.4
OW4	22	SM	20	40	1.50	807	0.01	0.84	0.15	230	0.39	48	7.7	0.9892	0.24	0.0	2.8
OW4	7	CO	20	40	1.50	807	0.01	0.69	0.30	330	0.15	9	3.6	0.9943	0.55	0.1	1.7
OW4	13	PE	20	40	1.50	807	0.02	0.68	0.30	229	0.19	116	7.9	0.9793	3.16	0.5	2.1
mean							0.03	0.72	0.25	140	0.30	201	5.7	0.9849	0.54	0.0	3.8
minimum							0.00	0.62	0.06	26	0.15	1	1.0	0.7938	-1.60	-0.4	0.8
maximum							0.08	0.90	0.30	330	1.52	1328	37	0.9996	3.39	1.2	7.2

WHC: water holding capacity; SSR: sum of squared residuals; RMSE: root mean square error; R: coefficient of correlation; E: relative error; M: mean difference

CO_2-C: cumulative net CO_2-C emission in amended soil

For EOM code refer to material and methods section and Table 3, for soil code refer to Table 2

Table 10a. Kinetic fit for EOM pools of meat and bone meals.

EOM	Days	Soil	Temp °C	WHC	EOM rate µg C g^{-1}	EOM rate kg N ha^{-1}	f_{DEOM}	f_{REOM}	K_{DEOM}	K_{REOM}	SSR µg C g^{-1}	RMSE %	R	E %	M µg C g^{-1}	CO_2-C %
BV1	14	PE	20	40	961	800	0.15	0.85	89	1.15	1449	3.8	0.997	-1.05	-1.12	15.5
BV1	14	PE	25	40	961	800	0.21	0.79	90	1.41	507	1.5	0.999	-0.15	-0.23	22.1
BV1	12	BU	20	40	240	200	0.19	0.81	51	0.20	359	11.2	0.992	-6.37	-1.22	12.8
BV1	12	BU	20	40	480	400	0.17	0.83	64	0.18	1619	11.8	0.991	-6.69	-2.58	12.3
BV1	12	LO	20	40	240	200	0.31	0.69	83	0.22	359	5.1	0.997	-1.83	-0.77	24.3
BV1	12	LO	20	40	480	400	0.33	0.67	81	0.15	1377	4.7	0.996	-1.38	-1.23	25.5
BV1	13	GO	20	40	120	100	0.26	0.74	64	0.15	34	3.9	0.997	0.38	0.07	20.3
BV1	13	SM	20	40	120	100	0.27	0.73	71	0.43	102	6.0	0.996	-2.21	-0.43	23.1
BV1	13	GO	20	40	240	200	0.23	0.77	74	0.15	121	4.1	0.996	-0.67	-0.21	17.9
BV1	13	SM	20	40	240	200	0.24	0.76	65	0.35	413	7.3	0.996	-3.59	-1.15	19.8
BV1	13	GO	20	40	480	400	0.24	0.76	74	0.15	588	4.3	0.996	-0.72	-0.46	18.7
BV1	13	SM	20	40	481	400	0.24	0.76	65	0.33	1796	7.4	0.996	-3.75	-2.46	20.2
BV1	14	SM	20	40	961	800	0.16	0.84	66	0.23	6376	9.9	0.993	-6.28	-5.52	13.5
BV1	14	PE	25	40	240	200	0.18	0.82	79	0.16	36	2.3	0.998	-0.18	-0.05	15.3
BV1	14	SM	25	40	240	200	0.15	0.85	83	0.15	121	4.7	0.997	-1.90	-0.48	13.1
BV1	14	PE	25	40	481	400	0.18	0.82	77	0.49	219	2.8	0.999	-0.91	-0.53	15.9
BV1	14	SM	25	40	481	400	0.16	0.84	75	0.20	706	5.5	0.996	-2.50	-1.31	14.4
BV1	14	SM	25	40	961	800	0.22	0.78	55	0.15	2654	4.2	0.995	-0.15	-0.20	18.3
BV1	13	PE	20	40	114	100	0.14	0.86	85	1.45	6	2.2	0.999	-0.22	-0.03	15.4
BV1	13	PE	20	40	228	200	0.13	0.87	109	1.03	13	1.7	0.999	-0.005	-0.001	13.4
BV1	14	SM	20	40	114	100	0.15	0.85	82	0.45	13	3.2	0.998	-0.77	-0.09	14.3
BV1	14	SM	20	40	228	200	0.14	0.86	85	0.32	54	3.4	0.997	-0.72	-0.16	13.1
BV1	14	SM	20	40	455	400	0.14	0.86	100	0.69	440	4.4	0.997	-1.70	-0.83	14.5
BV1	14	SM	20	40	683	600	0.15	0.85	92	0.62	739	3.9	0.998	-1.56	-1.13	14.5
BV1	13	PE	20	40	455	400	0.17	0.83	88	0.89	100	2.1	0.999	-0.16	-0.08	15.9
BV1	13	PE	20	40	683	600	0.15	0.85	90	0.53	224	2.4	0.998	-0.26	-0.17	13.7

WHC: water holding capacity; SSR: sum of squared residuals; RMSE: root mean square error; R: coefficient of correlation; E: relative error; M: mean difference

CO_2-C: cumulative net CO_2-C emission in amended soil

For EOM code refer to material and methods section and Table 3, for soil code refer to Table 2

Table 10b. Kinetic fit for EOM pools of meat and bone meals.

EOM	Days	Soil	Temp °C	WHC	EOM rate $\mu g\ C\ g^{-1}$	EOM rate kg N ha^{-1}	f_{DEOM}	f_{REOM}	K_{DEOM}	K_{REOM}	SSR $\mu g\ C\ g^{-1}$	RMSE %	R	E %	M $\mu g\ C\ g^{-1}$	CO_2-C %
SB	9	BU	20	40	211	200	0.63	0.37	13	0.15	150	8.9	0.994	-4.74	-0.85	16.1
SB	9	LO	20	40	211	200	0.60	0.40	52	0.32	88	2.5	0.999	-0.66	-0.33	38.6
SB	9	SM	20	40	211	200	0.45	0.55	40	0.26	189	5.3	0.998	-2.66	-0.90	27.2
SB	16	RI	15	40	211	200	0.45	0.55	42	0.41	283	4.4	0.997	-0.82	-0.31	28.7
SB	13	RI	20	40	211	200	0.37	0.63	42	0.20	409	7.7	0.997	-3.60	-1.22	25.1
SB	16	JU	15	40	211	200	0.17	0.83	56	0.15	540	16.1	0.991	-11.18	-1.63	11.6
SB	16	PE	15	40	211	200	0.15	0.85	75	0.23	127	6.8	0.995	-2.65	-0.44	11.7
SB	18	SM	15	40	211	200	0.15	0.85	83	0.26	633	13.4	0.989	-8.08	-1.46	12.5
SB	9	GO	20	40	211	200	0.36	0.64	48	0.15	214	6.3	0.994	-0.54	-0.16	22.6
SB	13	JU	20	40	211	200	0.20	0.80	58	0.18	169	8.1	0.996	-3.98	-0.82	14.5
SB	13	PE	20	40	211	200	0.24	0.76	50	0.25	52	3.8	0.999	-1.72	-0.42	17.4
SB	27	JU	20	40	2460	2220	0.19	0.81	58	0.90	6498	1.8	0.999	-0.15	-0.52	20.0
SB	27	LO	20	40	2460	2220	0.30	0.70	77	0.30	41474	2.9	0.996	-0.35	-1.84	25.9
SB	26	SM	20	40	2460	2220	0.21	0.79	27	0.36	16202	3.9	0.997	0.75	2.11	18.1
SB	26	SM	20	40	4920	4440	0.07	0.93	101	0.92	27626	3.4	0.996	0.08	0.33	12.8
SB	26	SM	20	40	9840	8880	0.10	0.90	73	0.27	44765	2.4	0.998	-0.34	-2.58	10.2
SW	10	SM	20	40	259	200	0.34	0.66	75	0.23	889	6.7	0.996	-3.97	-1.87	26.8
BV2	14	PE	25	40	903	800	0.20	0.80	131	1.62	562	1.7	0.998	-0.06	-0.09	21.7
BV2	16	PE	15	40	193	200	0.15	0.85	93	0.16	149	7.2	0.993	-2.56	-0.43	12.2
BV2	18	SM	15	40	193	200	0.16	0.84	81	0.21	211	7.5	0.994	-2.83	-0.53	13.5
BV2	16	PE	15	40	386	400	0.16	0.84	83	0.18	538	6.7	0.994	-2.11	-0.73	12.8
BV2	18	SM	15	40	386	400	0.16	0.84	69	0.15	708	7.2	0.996	-3.55	-1.26	13.3
BV2	13	PE	20	40	226	200	0.21	0.79	77	0.50	67	3.5	0.998	-1.24	-0.35	17.7
BV2	10	SM	20	40	226	200	0.16	0.84	77	0.15	86	4.8	0.995	-0.92	-0.19	12.8
BV2	13	PE	20	40	451	400	0.22	0.78	83	0.26	636	5.4	0.997	-2.52	-1.42	17.5
BV2	10	SM	20	40	451	400	0.15	0.85	94	0.17	945	8.3	0.995	-4.58	-1.81	12.5
BV2	14	PE	20	40	903	800	0.18	0.82	94	0.22	1231	3.7	0.995	-0.45	-0.46	14.8
BV2	14	SM	20	40	903	800	0.16	0.84	75	0.18	3783	7.8	0.995	-4.71	-4.04	13.4
BV2	14	PE	25	40	226	200	0.19	0.81	105	0.35	24	1.8	0.998	-0.09	-0.03	16.2
BV2	14	SM	25	40	226	200	0.15	0.85	104	0.30	64	3.5	0.997	-1.05	-0.26	13.7
BV2	14	PE	25	40	451	400	0.19	0.81	95	0.22	129	2.1	0.998	-0.22	-0.13	16.3
BV2	14	SM	25	40	451	400	0.16	0.84	98	0.20	681	5.5	0.995	-2.23	-1.16	14.3
BV2	14	SM	25	40	903	800	0.20	0.80	81	0.18	1779	3.7	0.998	-1.70	-2.08	17.3

WHC: water holding capacity; SSR: sum of squared residuals; RMSE: root mean square error; R: coefficient of correlation; E: relative error; M: mean difference

CO_2-C: cumulative net CO_2-C emission in amended soil

For EOM code refer to material and methods section and Table 3, for soil code refer to Table 2

Table 10c. Kinetic fit for EOM pools of meat and bone meals.

EOM	Days	Soil	Temp °C	WHC	EOM rate µg C g^{-1}	EOM rate kg N ha^{-1}	f_{DEOM}	f_{REOM}	K_{DEOM}	K_{REOM}	SSR µg C g^{-1}	RMSE %	R	E %	M µg C g^{-1}	CO_2-C %
DE	9	GO	20	40	187	200	0.23	0.77	76	1.34	52	3.9	0.998	-0.96	-0.23	19.5
DE	9	BU	20	40	187	200	0.28	0.72	31	0.40	108	9.4	0.993	-4.89	-0.70	13.7
DE	12	BU	20	40	374	400	0.18	0.82	42	0.33	638	11	0.992	-5.63	-1.49	11.7
DE	9	GO	20	40	93	100	0.31	0.69	87	0.28	55	6.6	0.996	-3.57	-0.53	23.3
DE	9	SM	20	40	93	100	0.44	0.56	48	0.76	13	2.7	0.999	-0.25	-0.04	30.9
DE	9	SM	20	40	187	200	0.38	0.62	52	0.15	62	3.4	0.998	-0.58	-0.18	26.0
DE	9	LO	20	40	187	200	0.50	0.50	56	0.15	70	2.9	0.998	-0.45	-0.17	32.6
DE	9	SM	20	40	374	400	0.32	0.68	60	0.17	494	5.4	0.998	-3.36	-1.82	23.1
DE	9	GO	20	40	374	400	0.26	0.74	62	0.15	201	4.2	0.996	-0.64	-0.28	18.0
DE	12	LO	20	40	374	400	0.34	0.66	71	0.15	595	4.0	0.998	-1.34	-0.93	26.2
BV2	13	PE	20	40	87	100	0.17	0.83	85	1.66	3	1.7	0.999	0.02	0.00	18.2
BV2	14	SM	20	40	87	100	0.17	0.8301	73	0.39	7	2.8	0.998	-0.42	-0.04	15.3
BV2	14	SM	20	40	175	200	0.18	0.82	83	0.43	38	3.0	0.998	-0.73	-0.16	16.5
BV2	14	SM	20	40	349	400	0.17	0.83	88	0.63	253	3.9	0.998	-1.50	-0.63	16.5
BV2	14	SM	20	40	524	600	0.20	0.80	68	0.16	481	3.5	0.999	-1.46	-0.93	17.1
BV2	13	PE	20	40	175	200	0.17	0.83	91	1.00	7	1.4	0.999	0.00	0.00	16.1
BV2	13	PE	20	40	349	400	0.19	0.81	73	0.46	45	1.8	0.999	-0.21	-0.08	16.0
BV2	13	PE	20	40	524	600	0.19	0.81	73	0.31	85	1.7	0.999	-0.18	-0.10	15.6
BV2	9	SM	20	40	211	200	0.14	0.86	58	1.40	12	2.6	0.999	-0.23	-0.04	13.7
BV2	14	PE	25	40	844	800	0.15	0.85	121	1.36	210	1.5	0.999	0.03	0.04	17.0
BV2	16	PE	15	40	216	200	0.10	0.90	64	0.19	27	4.6	0.996	-1.11	-0.12	7.9
BV2	18	SM	15	40	216	200	0.10	0.90	74	0.20	56	5.6	0.996	-2.32	-0.30	8.5
BV2	16	PE	15	40	431	400	0.10	0.90	62	0.22	125	5.0	0.997	-1.65	-0.37	7.8
BV2	18	SM	15	40	431	400	0.12	0.88	62	0.16	268	5.8	0.997	-3.05	-0.83	9.4
BV2	13	PE	20	40	211	200	0.17	0.83	71	0.50	35	3.4	0.997	-1.08	-0.23	14.7
BV2	13	PE	20	40	422	400	0.15	0.85	62	0.17	58	2.7	0.999	-0.83	-0.29	11.8
BV2	9	SM	20	40	422	400	0.16	0.84	57	0.20	55	3.2	0.999	-1.22	-0.37	11.5
BV2	14	PE	20	40	844	800	0.12	0.88	97	0.61	213	2.3	0.998	-0.20	-0.14	11.1
BV2	14	SM	20	40	844	800	0.12	0.88	64	0.16	522	4.2	0.997	-1.61	-0.94	9.9
BV2	14	PE	25	40	211	200	0.14	0.86	96	0.35	7	1.4	0.999	0.04	0.01	12.5
BV2	14	SM	25	40	211	200	0.13	0.87	84	0.18	11	1.9	0.998	-0.17	-0.03	11.5
BV2	14	PE	25	40	422	400	0.14	0.86	96	0.38	22	1.2	0.999	0.00	0.00	12.4
BV2	14	SM	25	40	422	400	0.12	0.88	99	0.19	174	4.0	0.997	-1.65	-0.60	10.7
BV2	14	SM	25	40	844	800	0.16	0.84	74	0.19	1972	5.4	0.995	-2.87	-2.57	14.0
mean							0.21	0.79	74	0.41	1928	4.7	0.997	-1.77	-0.70	16.8
minimum							0.07	0.37	13	0.15	3	1.2	0.989	-11.18	-5.52	7.8
maximum							0.63	0.93	131	1.66	44765	16.1	0.999	0.75	2.11	38.6

WHC: water holding capacity; SSR: sum of squared residuals; RMSE: root mean square error; R: coefficient of correlation; E: relative error; M: mean difference

CO_2-C: cumulative net CO_2-C emission in amended soil

For EOM code refer to material and methods section and Table 3, for soil code refer to Table 2

Table 11. Kinetic fit for EOM pools of animal residues.

EOM	Days	Soil	Temp °C	WHC	EOM rate %	C rate $\mu g\ g^{-1}$	f_{DEOM}	f_{REOM}	K_{DEOM}	K_{REOM}	SSR $\mu g\ C\ g^{-1}$	RMSE %	R	E %	M $\mu g\ C\ g^{-1}$	CO_2-C %
HL	27	JU	20	40	0.5	2288	0.12	0.88	92	1.09	27066	5.4	0.997	-3.88	-9.59	15.8
HL	27	LO	20	40	0.5	2288	0.21	0.79	82	0.35	14820	2.5	0.997	-0.30	-1.08	19.5
HL	25	SM	20	40	0.5	2288	0.13	0.87	28	0.58	8953	3.7	0.997	-0.05	-0.09	13.5
BLM	26	SM	20	40	0.5	2874	0.04	0.96	132	1.20	35527	7.9	0.983	-1.33	-2.72	12.2
BLM	27	JU	20	40	0.5	2874	0.06	0.94	144	0.87	38469	7.3	0.980	1.34	2.90	11.0
BLM	7	JU	20	40	0.5	2874	0.15	0.85	111	0.15	16407	9.4	0.991	-3.18	-6.55	10.7
BLM	27	LO	20	40	0.5	2874	0.22	0.78	110	0.45	75279	4.3	0.989	-0.43	-2.12	20.4
BLM	26	SM	20	40	1.0	5749	0.07	0.93	99	0.16	57885	6.3	0.983	-0.85	-2.80	7.2
BLM	26	SM	20	40	2.0	11497	0.05	0.95	131	0.15	99517	5.9	0.981	-0.81	-3.67	5.0
BLM	35	JU	10	20	0.5	2631	0.07	0.93	189	0.57	12399	5.4	0.993	-1.16	-1.58	6.8
BLM	35	JU	10	30	0.5	2631	0.07	0.93	139	0.15	11499	5.8	0.987	-0.15	-0.18	5.8
BLM	35	JU	10	40	0.5	2631	0.09	0.91	111	0.15	21366	6.3	0.985	0.68	1.04	7.2
BLM	36	JU	20	20	0.5	2631	0.10	0.90	185	0.63	4693	1.9	0.998	-0.18	-0.42	11.2
BLM	36	JU	20	30	0.5	2631	0.09	0.91	189	0.60	5951	2.2	0.996	-0.15	-0.35	11.4
BLM	36	JU	20	40	0.5	2631	0.10	0.90	155	0.80	11305	2.4	0.996	-0.15	-0.44	14.9
BLM	35	JU	30	20	0.5	2631	0.12	0.88	261	0.37	4466	1.8	0.996	0.55	1.51	12.6
BLM	35	JU	30	30	0.5	2631	0.12	0.88	259	0.24	3266	1.6	0.996	-0.05	-0.14	12.1
BLM	35	JU	30	40	0.5	2631	0.13	0.87	208	0.34	4569	1.6	0.997	-0.05	-0.15	15.1
BLM	27	JU	20	40	0.5	2692	0.15	0.85	119	0.69	17033	2.9	0.995	-0.32	-1.07	15.8
BLM	27	LO	20	40	0.5	2692	0.19	0.81	247	0.82	13951	2.0	0.995	-0.10	-0.43	19.7
BLM	25	SM	20	40	0.5	2692	0.07	0.93	284	1.21	16804	3.9	0.992	-0.21	-0.53	13.9
HHM	27	JU	20	40	0.5	2975	0.40	0.60	11	0.15	116849	8.6	0.998	-6.16	-19.78	20.3
HHM	27	LO	20	40	0.5	2975	0.28	0.72	25	0.15	126675	6.3	0.994	-0.90	-3.81	21.1
HHM	25	SM	20	40	0.5	2975	0.33	0.67	14	0.15	728880	20.2	0.987	-13.64	-44.80	20.6
HHM	35	JU	10	20	0.5	2565	0.04	0.96	12	2.51	56817	21.8	0.988	-16.44	-11.77	6.3
HHM	35	JU	10	30	0.5	2565	0.08	0.92	38	0.55	53050	17.9	0.990	-13.34	-11.26	6.3
HHM	35	JU	10	40	0.5	2565	0.14	0.86	17	0.28	10226	7.0	0.998	-3.71	-3.53	6.8
HHM	36	JU	20	20	0.5	2565	0.24	0.76	15	0.15	82303	9.3	0.996	-5.36	-10.73	13.8
HHM	36	JU	20	30	0.5	2565	0.22	0.78	15	0.15	61902	7.3	0.997	-3.62	-8.05	14.4
HHM	36	JU	20	40	0.5	2565	0.24	0.76	14	0.15	79363	7.0	0.998	-4.64	-12.00	16.6
HHM	35	JU	30	20	0.5	2565	0.13	0.87	13	0.29	19209	7.1	0.998	-4.35	-6.25	10.9
HHM	35	JU	30	30	0.5	2565	0.16	0.84	23	0.23	79358	8.8	0.993	-3.86	-9.11	14.6
HHM	35	JU	30	40	0.5	2565	0.19	0.81	18	0.20	58410	6.2	0.996	-2.71	-7.73	17.3
mean							0.15	0.85	106	0.50	59826	6.6	0.993	-2.71	-5.37	13.1
minimum							0.04	0.60	11	0.15	3266	1.6	0.980	-16.44	-44.80	5.0
maximum							0.40	0.96	284	2.51	728880	21.8	0.998	1.34	2.90	21.1

WHC: water holding capacity; SSR: sum of squared residuals; RMSE: root mean square error; R: coefficient of correlation; E: relative error; M: mean difference

CO_2-C: cumulative net CO_2-C emission in amended soil

For EOM code refer to material and methods section and Table 3, for soil code refer to Table 2

Table 12. Kinetic fit for EOM pools of crop residues, agro-industrial wastes and sewage sludges.

EOM	Days	Soil	Temp °C	WHC	EOM rate %	C rate µg g^{-1}	f_{DEOM}	f_{REOM}	f_{HEOM}	K_{DEOM}	K_{REOM}	SSR µg C g^{-1}	RMSE %	R	E %	M µg C g^{-1}	CO_2-C %
CC	26.7	LO	20	40	0.5	2529	0.09	0.91		75	1.53	2433	1.3	0.9996	0.21	0.62	17.4
CC	26.8	JU	20	40	0.5	2529	0.04	0.96		94	0.65	535	1.6	0.9993	0.21	0.24	7.2
CC	25.9	SM	20	40	0.5	2529	0.08	0.92		32	0.16	9406	6.0	0.9927	-3.23	-4.14	7.4
CC	25.9	SM	20	40	1.0	5058	0.04	0.96		72	0.31	6851	3.1	0.9959	-0.17	-0.35	5.7
CC	25.9	SM	20	40	2.0	10116	0.03	0.97		148	0.29	5785	1.8	0.9982	0.19	0.65	4.6
WS	26.7	LO	20	40	0.5	2748	0.17	0.83		26	0.94	8610	2.2	0.9990	-0.34	-1.06	18.4
WS	26.8	JU	20	40	0.5	2748	0.04	0.96		48	0.30	464	1.9	0.9991	-0.22	-0.20	5.1
WS	25.9	SM	20	40	0.5	2748	0.08	0.92		37	0.17	46962	12.9	0.9878	-6.62	-8.79	7.2
WS	25.9	SM	20	40	1.0	5495	0.05	0.95		28	0.15	14186	5.2	0.9944	-0.87	-1.56	4.8
WS	25.9	SM	20	40	2.0	10991	0.02	0.98		42	0.15	2561	1.8	0.9990	-0.02	-0.04	3.0
Agro-industrial wastes (AW)																	
TPOMW	26.7	LO	20	40	0.5	2796	0.06	0.75	0.19	230	2.40	1593	1.2	0.9995	-0.23	-0.60	17.5
TPOMW	26.5	JU	20	40	0.5	2796	0.03	0.79	0.19	119	0.81	845	1.8	0.9990	0.10	0.12	6.6
TPOMW	24.8	SM	20	40	0.5	2796	0.05	0.76	0.19	132	0.31	2978	3.3	0.9952	-1.60	-2.07	6.0
Sewage sludges (SS)																	
WW	28.8	SM	20	40	0.5	1920	0.04	0.96		45	0.31	177	1.2	0.9995	0.13	0.10	6.0
WW	28.8	PE	20	40	0.5	1920	0.04	0.96		83	0.26	203	1.5	0.9989	0.09	0.06	4.9
WW	28.8	LL	20	40	0.5	1920	0.03	0.97		62	0.15	260	2.0	0.9981	-0.10	-0.06	3.8
WW	28.8	AL	20	40	0.5	1920	0.04	0.96		62	0.15	1181	4.4	0.9975	3.49	2.19	4.5
CR	mean						0.06	0.94		60	0.47	9779	3.8	0.9965	-1.08	-1.32	8.5
	minimum						0.02	0.83		26	0.15	464	1.3	0.9878	-6.62	-8.79	3.0
	maximum						0.17	0.98		148	1.53	46962	12.9	0.9996	0.21	0.65	18.4
AW	mean						0.05	0.77	0.19	160	1.17	1805	2.1	0.9979	-0.57	-0.85	10.0
	minimum						0.03	0.75	0.19	119	0.31	845	1.2	0.9952	-1.60	-2.07	6.0
	maximum						0.06	0.79	0.19	230	2.40	2978	3.3	0.9995	0.10	0.12	17.5
SS	mean						0.04	0.96		63	0.22	455	2.3	0.9985	0.90	0.57	4.8
	minimum						0.03	0.96		45	0.15	177	1.2	0.9975	-0.10	-0.06	3.8
	maximum						0.04	0.97		83	0.31	1181	4.4	0.9995	3.49	2.19	6.0

WHC: water holding capacity; SSR: sum of squared residuals; RMSE: root mean square error; R: coefficient of correlation; E: relative error; M: mean difference

CO_2-C: cumulative net CO_2-C emission in amended soil

For EOM code refer to material and methods section and Table 3, for soil code refer to Table 2

As a whole, the results of the respiration curve fitting suggest that for a reliable simulation of C mineralization in amended soils under laboratory conditions there is not only the need to partition EOM into a number of discrete pools, but also to find specific decomposition rates for such pools.

The calibration of EOM parameters was soil and incubation condition-specific, to enable the model to find the best fit of measured data. Consequently, failures to simulate C trends can be attributed exclusively to the inadequacy of the model structure to accurately describe soil respiration. The results of the optimization procedure indicated that the modified RothC model is capable to adequately describe short term net CO_2-C evolution from amended soils, utilizing time steps of 1 day or lower, a much shorter time interval with respect to the one usually employed by the model (1 month).

3.2.4 Generality test

An interesting point concerning the applicability of the proposed method is to verify if a specific optimization can be used to simulate CO_2 evolution from different incubation conditions and/or similar EOMs.

Theoretically, kinetically defined pools would represent an intrinsic property of the residue not dependent from soil properties and environmental conditions as these interactions would be taken into account by the model. For instance, RothC considers variations in temperature and water content by a pool decomposition rate modifying factor. Furthermore, the model adjusts the output in relation to soils with different properties by considering their clay content, as this regulates both the partitioning between C evolved as CO_2 and remaining in the soil and the water retention capacity of top soil.

The results of the optimization procedure showed that EOM related parameters do not exclusively depend on residues properties, as demonstrated by the variability in partitioning factor and decomposition rate for the same EOM incubated under different conditions. This indicates that the interactions between EOM and incubations conditions can not be completely explained through the model and that the optimized parameters incorporate information about such interactions. Similar conclusions were drawn by Cavalli and Bechini (2011), who found that optimized values parameters were highly variable for the same manure applied to different soils. As an example the partitioning coefficient of decomposable EOM in their study ranged between 0.01 and 0.43 for the same manure optimized separately for 3 different soils.

However, to perform soil and environmental conditions specific optimization for each EOM is not feasible and would narrow the applicability of the method. Use of a unique set of parameters for the same EOM or EOM type would result in enhanced model generality. This would be reached at the expenses of an increase in the error between the measured and simulated C mineralization, but if the error in the SOC sequestration is kept within a reasonable limit, this would increase the range of applicability of the optimized model (Petersen et al., 2005b).

The generality of the optimized model, i.e. the possibility to use a common set of parameters for the same EOM or EOM type, was investigated with different tests.

A first test to estimate the capacity to simulate data sets different from those utilized for the calibration was performed by calculating the mean of the model parameters for:

- all incubations performed with the same EOM
- all incubations performed with the same EOM type

Incubations presenting a non satisfactory fit between simulated and measured CO_2 evolution and outliers of the model parameters were excluded from the calculation. The percentage of total incubations excluded was 6.7% of total.

Tables 13 and 14 report the mean of pool parameters, together with the coefficient of variation of standard error. Hess and Schmidt (1995) suggested a value of 50% of this parameter as threshold value for an acceptable model fit.

The mean parameter estimates, obtained from the different incubations for the same EOM, showed always a relative standard error smaller than this threshold value, with a single exception (Table 13). In the case of f_{DEOM} the coefficient of variation of the standard error was on average 15%, with a value higher than 50% in the case of stable compost CMC VII. Nevertheless, the value of f_{DEOM} for this compost was very low (0.004) and therefore the contribution of this pool to the accumulation of C in soil should be considered negligible. Ranges of relative standard error were 0.2-18.1, 0.1-20.3, 1.1-3.3 and 5.1-44.3% for f_{REOM}, f_{HEOM}, k_{DEOM} and k_{REOM}, respectively.

Also in the case of mean model parameters for EOM type (Table 14) the coefficients of variation of the standard error were always lower than the threshold indicated by Hess and Schmidt (1995).

A second criterion to evaluate the generality of the optimized model was to utilize the mean pool parameters obtained from the different incubations for the same EOM type to fit the respiration curves measured for every EOMs included in this EOM type. As expected, the goodness of the fit significantly decreased in comparison to specific EOM optimization. Assuming a threshold value of E lower than 30%, around 27% of the total incubations gave a non satisfactory fit when utilizing the mean parameters (data not shown). This is an indication that the model is not capable to fully explain the combined effects of residue composition and incubation conditions and that such interactions are incorporated, for a certain extent, in the value of the parameter.

Analysis of incubation conditions for the cases presenting an unsatisfactory fit was useful to identify which conditions resulted in an effect on C mineralization that the model was not able to completely separate from the effect of residue properties.

The main incubation conditions not resolved by the model were low temperature, soil type and rate of application.

Several incubations presenting a low fit when using mean EOM-type parameters were carried out at temperatures of 10 or 15 °C. Most of the incubations (14 out of 27, corresponding to 62.5%) carried out at these temperatures showed a bad fit. It is interesting to note that only 8% (3 out of 37) of incubations carried out at a temperature > 25 °C failed to be properly simulated by the model utilizing mean parameters. The model structure includes a rate modifying factor for temperature, which ideally takes into account the effect of the temperature on the decomposition rate. Results suggest that the rate modifying factor, under the conditions of the present study, performed satisfactorily at near standard temperatures, while it was less effective in adjusting the decomposition rate at low temperatures. The inadequacy of the temperature modifying factor incorporated in SOM models has been demonstrated in studies on the temperature dependence of SOM decomposition.

Table 13. Mean RothC EOM pool parameters for different EOMs.

EOM type	EOM	N.	Exc.	Inc.	f_{DEOM}	f_{REOM}	f_{HEOM}	K_{DEOM}	K_{REOM}	f_{DEOM}	f_{REOM}	f_{HEOM}	K_{DEOM}	K_{REOM}	f_{DEOM}	f_{REOM}	f_{HEOM}	K_{DEOM}	K_{REOM}
										Standard error (SE)					Coefficient of variation of SE (%)				
Compost	VSC	4	0	4	0.01	0.39	0.59	119	0.23	*0.005*	*0.032*	*0.03*	*42.09*	*0.04*	41.1	8.1	5.7	35.3	19.2
	HWC	14	0	14	0.02	0.33	0.65	78	0.28	*0.002*	*0.018*	*0.02*	*13.46*	*0.05*	8.5	5.3	2.7	17.3	18.8
	GWC	2	0	2	0.01	0.31	0.69	145	0.45	*0.001*	*0.043*	*0.04*	*45.50*	*0.07*	10.0	14.0	6.6	31.5	15.9
	CMC II	2	0	2	0.05	0.87	0.08	42	0.34	*0.009*	*0.025*	*0.02*	*3.18*	*0.03*	16.6	2.9	20.3	7.6	8.2
	CMC III	2	0	2	0.06	0.63	0.32	29	0.35	*0.005*	*0.006*	*0.00*	*1.20*	*0.02*	8.2	1.0	0.5	4.1	6.6
	CMC M	2	0	2	0.004	0.26	0.74	83	0.46	*0.002*	*0.047*	*0.04*	*21.77*	*0.11*	58.3	18.1	6.0	26.1	22.8
	CBC II	2	0	2	0.08	0.73	0.19	22	0.28	*0.014*	*0.015*	*0.00*	*0.24*	*0.05*	17.4	2.1	0.6	1.1	17.2
	CBC III	2	0	2	0.07	0.62	0.31	20	0.26	*0.001*	*0.031*	*0.03*	*1.47*	*0.10*	2.0	5.0	9.8	7.4	39.3
	CBC IV	2	0	2	0.05	0.56	0.39	16	0.22	*0.001*	*0.012*	*0.01*	*0.66*	*0.01*	2.2	2.2	2.6	4.0	5.1
	CBC M	2	0	2	0.01	0.31	0.69	145	0.45	*0.001*	*0.043*	*0.04*	*45.50*	*0.07*	10.0	14.0	6.6	31.5	15.9
Bioenergy by products	BR	6	1	5	0.12	0.88		129	0.47	*0.007*	*0.007*		*7.36*	*0.07*	5.8	0.8		5.7	14.4
	RSM	14	2	12	0.13	0.87		76	0.27	*0.007*	*0.007*		*6.51*	*0.03*	5.5	0.8		8.5	9.6
Anaerobic digestates	PS	14	2	12	0.05	0.70	0.25	57	0.25	*0.004*	*0.024*	*0.02*	*4.92*	*0.03*	7.4	3.5	9.1	8.6	12.9
	OW	13	0	13	0.01	0.74	0.25	220	0.20	*0.002*	*0.018*	*0.02*	*23.34*	*0.03*	13.7	2.5	7.2	10.6	13.5
Meat and bone meals	BV1	26	0	26	0.19	0.81		78	0.47	*0.011*	*0.011*		*2.68*	*0.08*	5.5	1.3		3.4	16.7
	SB	16	0	16	0.29	0.71		56	0.33	*0.043*	*0.043*		*5.51*	*0.06*	14.8	6.0		9.8	17.9
	BV2	40	4	36	0.16	0.84		81	0.29	*0.005*	*0.005*		*2.24*	*0.03*	3.3	0.6		2.8	10.3
	DE	10	0	10	0.32	0.68		59	0.39	*0.031*	*0.031*		*5.29*	*0.12*	9	5		9	31.5
Animal residues	HLM	3	0	3	0.15	0.85		67	0.67	*0.030*	*0.030*		*19.82*	*0.22*	19.7	3.6		29.4	32.5
	BLM	15	1	14	0.10	0.90		164	0.40	*0.012*	*0.012*		*14.27*	*0.07*	11.2	1.3		8.7	17.0
	BLM2	3	0	3	0.13	0.87		217	0.90	*0.034*	*0.034*		*50.12*	*0.16*	25.3	3.9		23.1	17.3
	HHM	12	2	10	0.23	0.77		16	0.19	*0.027*	*0.027*		*1.42*	*0.02*	11.7	3.6		8.6	9.6
Vegetal residues	CC	5	1	4	0.05	0.95		87	0.35	*0.012*	*0.012*		*24.14*	*0.11*	25.0	1.2		27.9	30.1
	WS	5	1	4	0.05	0.95		39	0.19	*0.011*	*0.011*		*4.34*	*0.04*	23.1	1.1		11.2	18.2
Agro-industrial w.	TPOMW	3	1	2	0.04	0.78	0.19	126	0.56	*0.011*	*0.011*	*0.0001*	*6.76*	*0.25*	28.7	1.5	0.1	5.4	44.3
Sewage sludge	WW	4	0	4	0.04	0.96		63	0.22	*0.002*	*0.002*		*7.75*	*0.04*	4.7	0.2		12.3	18.5
	Total (N.)	223	15.0	208										mean	15.0	4.2	6.0	13.5	18.6
	Total (%)	100	6.7	93.3										minimum	2.0	0.2	0.1	1.1	5.1
														maximum	58.3	18.1	20.3	35.3	44.3

N.: number of incubations; Exc./Inc.: number of incubations excluded/included from the calculation of the mean

For EOM code refer to materials and methods section and Table 3

Table 14. Mean RothC EOM pool parameters for EOM type.

EOM type	**EOM code**	**N.**	**Excl.**	**Incl.**	f_{DEOM}	f_{REOM}	f_{HEOM}	K_{DEOM}	K_{REOM}	f_{DEOM}	f_{REOM}	f_{HEOM}	K_{DEOM}	K_{REOM}	f_{DEOM}	f_{REOM}	f_{HEOM}	K_{DEOM}	K_{REOM}
										Standard error (SE)					Coefficient of variation of SE (%)				
Compost	CO	34	0	34	0.03	0.44	0.53	79	0.30	*0.004*	*0.031*	*0.034*	*11*	*0.027*	*14.6*	*6.9*	*6.4*	*13.8*	*8.8*
Bioenergy by-products	BE	20	3	17	0.13	0.87		92	0.33	*0.006*	*0.006*		*8*	*0.035*	*4.3*	*0.6*		*8.5*	*10.4*
Anaerobic digestates	AD	27	2	25	0.03	0.74	0.25	220	0.20	*0.004*	*0.018*	*0.018*	*23*	*0.027*	*14.9*	*2.5*	*7.2*	*10.6*	*13.5*
Meat and bone meals	MM	93	4	89	0.21	0.79		74	0.41	*0.011*	*0.011*		*2*	*0.039*	*5.1*	*1.4*		*2.8*	*9.5*
Animal residues	AR	33	3	30	0.15	0.85		110	0.41	*0.015*	*0.015*		*16*	*0.056*	*10.0*	*1.8*		*14.5*	*13.7*
Crop residues	CR	10	2	8	0.05	0.95		63	0.27	*0.007*	*0.007*		*15*	*0.060*	*15.7*	*0.8*		*23.2*	*22.0*
Agro-industrial wastes	AW	3	1	2	0.04	0.78	0.19	126	0.56	*0.011*	*0.011*	*0.0001*	*7*	*0.249*	*28.7*	*1.5*	*0.1*	*5.4*	*44.3*
Sewage Sludges	SS	4	0	4	0.04	0.96		63	0.22	*0.002*	*0.002*		*8*	*0.040*	*4.7*	*0.2*		*12.3*	*18.5*
	Total (N.)	224	15	209										mean	*12.2*	*2.0*	*4.6*	*11.4*	*17.6*
	Total (%)	100	6.7	93										minimum	*4.3*	*0.2*	*0.1*	*2.8*	*8.8*
														maximum	*28.7*	*6.9*	*7.2*	*23.2*	*44.3*

N.: number of incubations; Exc./Inc.: number of incubations excluded/included from the calculation of the mean

For EOM code refer to materials and methods section and Table 3

Bauer et al. (2008) showed that patterns of C loss were poorly described if the RothC temperature response function was used for the decomposition of all C pools and that data prediction was significantly improved by using different temperature response functions for the decomposition of different OM pools. These findings suggest that the temperature dependence of OM decomposition cannot be fully described with the simple approaches usually employed in most laboratory experiments and modelling approaches, but that a more complicated interplay between the temperature dependence of decomposition rates and temperature effects on the chemical recalcitrance of different organic matter fractions exists.

Some incubations with low fit were carried out with soil presenting distinctive characteristics. Several unsatisfactory fits of the respiration curve were obtained when utilizing the Spanish soils AL and LL. Both are degraded soils with extremely low values of SOM and soil microbial biomass and, especially for the AL soil, highly polluted by heavy metals. It is likely that soil degradation caused changes in the size, composition and function of soil microbial biomass affecting, in turns, the mineralization rate of EOM. The effects of heavy metal contamination on SOM decomposition are well known. In particular, heavy metals reduce microbial biomass size and substrate utilization efficiency and, consequently, impair the capacity of microorganisms to degrade the organic inputs entering the soil (Giller and McGrath, 1998).

An another soil with peculiar properties was the Bueriis soil characterized by an extremely high content of clay (46%) and silt (48%). The influence of soil texture on C mineralization has been widely studied. Several authors have previously reported greater mineralization rates for different organic materials in soils with large sand contents (Coté et al., 2000; Khalil et al., 2005). Generally, high clay contents limit microbial activity due to sorption of the decomposing substrate onto mineral particles and incorporation into soil aggregates (Khalil et al., 2005). Furthermore, the particular texture of Bueriis soil reduces soil porosity limiting air and water availability, pivotal factors in determining the rate of EOM microbial decomposition. Roth C adjusts for soil texture impact on decomposition by considering the effect of the clay content on available water content and the partitioning between CO_2 evolved and the (BIO+HUM) formed during decomposition. It is likely that this simple regulation is not sufficient to fully take into account the complex interactions of EOM with clay particles.

A fourth soil with specific properties was the Lodi soil characterized by an high content of sand (67%) and limited amount of clay (12%). Sand presents an opposite effect with respect to clay, enhancing the rate of decomposition due to the increased porosity of soil that warranties aerobic conditions which are favourable for SOM decomposition. As a matter of fact, the percentage of added C which was mineralized in this soil was significantly higher with respect to the others soils, all other incubation conditions being the same. It has to be considered that the S. Martino soil presents an even more marked sandy texture (69% soil, 3% clay) than the Lodi soil. Nevertheless, when compared to the Lodi soil, it emitted lower amount of net CO_2-C. This can be explained on the basis of the higher total N and microbial biomass C content in the Lodi soil. Both these factors may affect the rate of EOM decomposition. Incubations carried out at low soil mineral N concentrations have shown that the decomposition rate of plant residues is decreased, as N availability affects the decay rate of residue C pools. In fact, C and N cycles in soil are strongly linked due to the simultaneous assimilation of C and N by the decomposing microflora (Recous et al. 1995; Mary et al 1996). Since OM decomposition is one of the most essential soil functions controlled by soil biota, nature and abundance of soil microorganisms exert a key role in determining the rate of EOM transformation in soil (Andren et al., 2004).

Generally, the model responded well to application rates, with a few exceptions likely related to the fact that high loads of EOM may have created unfavourable conditions for microbial decomposition. In the case of meat and bone meals and blood meals, application of large N rates (800 kg N ha^{-1} or 80 t dm ha^{-1}) in the San Martino soil caused limited decomposition, which was attributed to potential toxic effect due to the release of NH_3 from highly decomposable EOMs. In fact, Tenuta and Lazarovitis (2004) demonstrated a toxic effect of NH_3 released during the mineralization of meat and bone meal applied at 2% (w/w) on the pathogen *Verticillium dahliae*. The dose applied by Tenuta and Lazarovitis (2004) corresponds with the largest meat and bone meal dose in the present study. These authors demonstrated that the accumulation of NH_3 in soil following microbial degradation of N-rich amendments depends upon soil properties. In this study, the high NH_4^+ concentration obtained after amendment with animal meals, and the chemical properties of the soil used (alkalinity, high sand concentration, low organic matter content) probably moved the equilibrium to the basic form (NH_3) and favoured its accumulation.

A low rate of decomposition was recorded in the case of plant materials added at a rate of 2% (w:w) corresponding to a field rate of 80 t dm ha^{-1}. In this case it is likely that the addition of high amounts of EOM characterized by a high C/N ratio (30 and 198 for cotton and wheat straw, respectively) to a N depleted soil (0.12%) may have reduced N availability, which resulted in the slowing down of the decomposition processes. The role of C/N ratio on C decomposition is well known. Cayuela et al. (2009) reported a rapid N immobilization in soil with a noticeable decrease of soluble N, NH_4^+ and NO_3^- concentration after addition of plant materials and suggested N as limiting factor for microbial growth, in particular for fungi and the synthesis of exracellular enzymes for polymer degradation.

Poor fits were also recorded for EOM added at low rates or for slowly decomposing substrates. This is the case of anaerobic digestates which are materials characterized by low amounts of degradable C and consequently with a slow decomposition in the soil. Consequently, the combination of low dose of application and slow degradation resulted in limited CO_2 emissions close to the detection limits of the measurement system and therefore inadequate to produce statistically robust results.

A successive evaluation on the range of applicability of the optimized model was performed by comparing the output of a long term model simulation utilizing parameters derived from a specific EOM optimization with a simulation using a common set of parameters. The simulation was performed assuming a scenario of soil amendment with different EOMs at a rate of 1 t C y^{-1} for 100 years. This evaluation was performed in two steps.

In the first step, a simulation performed with model parameters derived from an EOM amended soil incubated at standard conditions (San Martino soil, 20 °C, 40% WHC, 0.5% w:w, 30 days of incubation) was compared with a simulation carried out with mean parameters from all the incubations with the same EOM under different conditions (e.g. soil type, temperature, water content, rate of EOM application and length of incubation). The results of this comparison are reported in Table 15 and show that the difference in terms of SOC accumulation after 100 years of EOM addition was in the range -8.6 - 4.9%.

In the second step the model simulation with specific parameters was compared with the model prediction utilizing mean parameters for each of the 8 EOMs type previously defined (Table 3). In this case, the mean parameters not only reflected the different incubation conditions, but also the properties of similar type of EOM (e.g. cotton cardings and wheat straw for the crop residues EOM type). Also in this case the difference in predicted SOC content after 100 years of continuous amendment between the two model parameterization was acceptable, being in the range -9.2 - 4.7% (Table 16), i.e. the error in SOC by taking the mean values of the parameters instead of the specific ones was less than 10%.

The results of the generality tests for the optimized model provided useful information as they allowed potential model flaws to be outlined and enabled identification of knowledge gaps that may require attention for further improvements of the model.

Results of model optimization showed that the modified RothC is capable to achieve a very good fitting between measured and modelled cumulative respiration, but also that the optimized parameters depend not only on EOM properties, but also from incubation conditions, mainly temperature, soil properties and rate of application. Similar conclusions were drawn by Askri (2011). As a matter of fact, less satisfactory results were obtained when trying to identify a common set of parameters for different EOMs type, classified on the basis of their origin or chemical properties.

However, analyses performed to test the generality of the optimized parameters on the long term SOC evolution (i.e. 100 years) have shown that using a common set of parameters for each EOM type resulted in errors lower than 10%. This suggests that EOM pools parameters values are mainly determined by the properties of the residues and only for a lower extent by soil properties and other environmental factors, in agreement with findings of Antil et al. (2011) who, in a study on soil mineralization of composted manures and sewage sludges, found much larger differences among organic materials than among soils. The authors therefore assumed that rates of CO_2

release from the organic amendments were mostly typical of the materials and very little dependent on the soil or environmental conditions.

The results of the tests for the applicability of the model to different data sets clearly indicate that there is a trade off between precision and accuracy on one side and range of applicability on the other. A choice needs to be made between the capability to acceptably simulate a large number of measurement series and that to excellently simulate a few measurement data sets. However, depending on the aim of the research and/or availability of time and resources the user can decide which aspect of the simulation should prevail.

Table 15a. Results of RothC simulation of 100 years of amendment utilizing EOM specific and mean parameters.

EOM type	EOM	EOM code	f_{DEOM}	f_{REOM}	f_{HEOM}	K_{DEOM}	K_{REOM}	SOC t C ha^{-1}	Difference m-s %
Compost (CO)	Vine shoots compost (VS)	VS_CO_m	0.01	0.392	0.59	119	0.23	71.5	1.3
		VS_CO_s	0.02	0.39	0.59	45	0.35	70.6	
	Household waste compost (HW)	HW_CO_m	0.02	0.33	0.65	78	0.28	73.5	2.8
		HW_CO_s	0.02	0.37	0.61	43	0.35	71.5	
	Green waste compost (GW)	GW_CO_m	0.01	0.46	0.53	200	0.29	68.4	4.9
		GW_CO_s	0.01	0.52	0.47	200	0.42	65.2	
	CMC	CMC_CO_m	0.004	0.26	0.74	83	0.46	76.9	2.3
		CMC_CO_s	0.002	0.31	0.69	105	0.36	75.1	
	CBC	CBC_CO_m	0.01	0.31	0.68	145	0.45	74.4	2.2
		CBC_CO_s	0.01	0.35	0.64	99	0.38	72.8	
Bioenergy by-products (BE)	Bioethanol residue (BR)	BR_BE_m	0.12	0.88		129	0.47	43.9	1.6
		BR_BE_s	0.12	0.88		147	0.68	43.3	
	Rape seeds meal (RSM)	RM_BE_m	0.13	0.87		76	0.27	45.5	1.2
		RM_BE_s	0.11	0.89		44	0.32	45.0	
Anaerobic digestates (AD)	Pig slurry digestate (PS)	PS_AD_m	0.05	0.70	0.25	57	0.25	56.7	-6.5
		PS_AD_s	0.08	0.62	0.30	26	0.15	60.6	
	Two-phase olive mill waste digestate (OW)	OW_AD_m	0.01	0.74	0.25	220	0.20	57.8	5.1
		OW_AD_s	0.01	0.83	0.16	64	0.17	54.9	

s: model parameters derived from specific incubation under standard conditions

m: model parameters derived from the mean of all the incubations for the specific EOM

Simulation scenario: 100 years of EOM addition: 1 t C ha^{-1} y^{-1}

For EOM code refer to material and methods section and to Table 3

Table 15b. Results of RothC simulation of 100 years of amendment utilizing EOM specific and mean parameters.

EOM type	EOM	EOM code	f_{DPM}	f_{RPM}	f_{HUM}	K_{DPM}	K_{RPM}	SOC t C ha^{-1}	Difference m-s %
Meat and bone meals (MM)	Bovine meat and bone meal (BV1)	BV1_MM_m	0.19	0.81		78	0.47	43.8	-4.9
		BV1_MM_s	0.16	0.84		66	0.23	46.0	
	Mixed swine bovine meat and bone meal (SB)	SB_MM_m	0.29	0.71		56	0.33	44.3	-0.1
		SB_MM_s	0.21	0.79		27	0.36	44.3	
	Bovine meat and bone meal (BV2)	BV2_MM_m	0.15	0.85		84	0.36	44.5	-5.7
		BV2_MM_s	0.16	0.84		75	0.18	47.2	
	Defatted bovine meat and bone meal (DE)	DB_MM_m	0.26	0.74		68	0.50	43.5	-8.6
		DB_MM_s	0.20	0.80		68	0.16	47.6	
Animal residues (AR)	Hydrolyzed leather (HL)	HL_AR_m	0.15	0.85		67	0.67	43.2	-0.6
		HL_AR_s	0.13	0.87		28	0.58	43.5	
	Blood meal (BLM)	BM_AR_m	0.10	0.90		164	0.40	43.5	1.9
		BM_AR_s	0.04	0.96		132	1.20	42.7	
	Horn and hoof meal (HHM)	HM_AR_m	0.23	0.77		16	0.19	46.5	-1.1
		HM_AR_s	0.33	0.67		14	0.15	47.0	
Crop residues (CR)	Cotton cardings (CC)	CC_CR_m	0.05	0.95		87	0.35	44.9	-7.4
		CC_CR_s	0.08	0.92		32	0.16	48.5	
	Wheat straw (WS)	WS_CR_m	0.05	0.95		39	0.19	47.6	-1.0
		WS_CR_s	0.08	0.92		37	0.17	48.1	
Agro-industrial wastes (AW)	Two-phase olive mill waste (TPOMW)	TPOMW_AW_m	0.04	0.78	0.19	126	0.56	52.0	-2.7
		TPOMW_AW_s	0.05	0.76	0.19	132	0.31	53.5	
Sewage sludges (SS)	Wastewater sewage sludge (WW)	WW_SS_m	0.04	0.96		63	0.22	46.8	3.3
		WW_SS_s	0.04	0.96		45	0.31	45.3	

s: model parameters derived from specific incubation under standard conditions
m: model parameters derived from the mean of all the incubations for the specific EOM
Simulation scenario: 100 years of EOM addition at 1 t C ha^{-1} y^{-1}
For EOM code refer to material and methods section and to Table 3

Table 16. Results of RothC simulation of 100 years of amendment utilizing EOM specific and EOM-type parameters.

EOM type	EOM	EOM Code	f_{DEOM}	f_{REOM}	f_{HEOM}	K_{DEOM}	K_{REOM}	SOC t C ha^{-1}	Difference m-s (%)
Compost (CO)	Vine shoots compost (VSC)	VSC_CO_s	0.02	0.39	0.59	45	0.35	70.6	-3.4
	Household waste compost (HWC)	HWC_CO_s	0.02	0.37	0.61	43	0.35	71.5	-4.6
	CMC	CMC_CO_s	0.00	0.31	0.69	105	0.36	75.1	-9.2
	CBC	CBC_CO_s	0.01	0.35	0.64	99	0.38	72.8	-6.2
	Green waste compost (GWC)	GW_CO_s	0.01	0.52	0.47	200	0.42	65.2	4.7
		CO_m	0.03	0.44	0.53	79	0.30	68.2	
Bioenergy by-products (BE)	Bioethanol residue (BR)	BR_BE_s	0.12	0.88		147	0.68	43.3	3.6
	Rape seeds meal (RM)	RM_BE_s	0.11	0.89		44	0.32	45.0	-0.4
		BE_m	0.13	0.87		92	0.33	44.8	
Anaerobic digestates (AD)	Pig slurry digestate (PS)	PS_AD_s	0.08	0.62	0.30	26	0.15	60.6	-4.8
	Two-phase olive mill waste digestate (OW)	OW_AD_s	0.01	0.83	0.16	64	0.17	54.9	5.0
		AD_m	0.02	0.73	0.25	220	0.20	57.7	
Meat and bone meals (MM)	Bovine meat and bone meal (BV1)	BV1_MM_s	0.16	0.84		66	0.23	46.0	-4.4
	Mixed swine bovine meat and bone meal (SB)	SB_MM_s	0.21	0.79		27	0.36	44.3	-0.7
	Bovine meat and bone mea (BV2)	BV2_MM_s	0.16	0.84		75	0.18	47.2	-6.8
	Defatted bovine meat and bone meal (DE)	DB_MM_s	0.20	0.80		68	0.16	47.6	-7.6
		MM_m	0.21	0.79		74	0.41	44.0	
Animal residues (AR)	Hydrolyzed leather (HL)	HL_AR_s	0.13	0.87		28	0.58	43.5	1.6
	Blood meal (BLM)	BM_AR_s	0.04	0.96		132	1.20	42.7	3.6
	Horn and hoof meal (HHM)	HM_AR_s	0.33	0.67		14	0.15	47.0	-6.1
		AR_m	0.15	0.85		110	0.41	44.2	
Crop residues (CR)	Cotton cardings (CC)	CC_CR_s	0.08	0.92		32	0.16	48.5	-5.4
	Wheat straw (WS)	WS_CR_s	0.08	0.92		37	0.17	48.1	-4.6
		CR_m	0.05	0.95		63	0.27	45.8	
Agro-industrial wastes (AW)	Two-phase olive mill waste (OW)	OW_AW_s	0.05	0.76	0.19	132	0.31	53.5	-2.7
		AW_m	0.04	0.78	0.19	126	0.56	52.0	
Sewage sludges (SS)	Wastewater sewage sludge (WW)	WW_SS_s	0.04	0.96		45	0.31	45.3	3.3
		SS_m	0.04	0.96		63	0.22	46.8	

s: model parameters derived from specific incubation under standard conditions

m: model parameters derived from the mean of all the incubations for EOM type

Simulation scenario: 100 years of EOM addition at 1 t C ha^{-1} y^{-1}

For EOM code refer to material and methods section and to Table 3

3.2.5 Limitations and uncertainty of the proposed model modification and optimization

3.2.5.1 Limitations of kinetically defined EOM pools derived from incubation data

Kinetically defined pools are conceptual OM residue fractions that are determined by fitting the decomposition model to experimental data on organic residue mineralization. Such pools do not directly correspond to experimentally verifiable fractions and this may lead to uncertainties on how to transpose these conceptual pools to different types of EOM (Corbeels, 2001).

EOM pools estimated by SCD or NIRS are exclusively defined on the basis of residue properties, independently from incubation conditions. Theoretically, this could represent an advantage due to the relative simplicity and speed of these methods and would allow for a broad range of applicability of the optimized parameters as chemically defined fractions may be transposed to different EOMs.

However, as well demonstrated by the results of this and previous researches (Cavalli and Bechini, 2011, 2012; Petersen et al., 2005b) current soil C models are not able to fully resolve the interactions of the residue with soil properties and incubation conditions. Partitioning and decomposition rate parameters obtained by fitting the measured C mineralization trajectory observed for each EOM incorporate such interactions and would lead to a more reliable simulation of SOC in amended soil. On the other hand, the wider applicability of EOM characterization by SCD and NIRS is obtained at the expense of a lower accuracy.

3.2.5.2 Uncertainty of optimized EOM parameters

The calibration procedure used a classical least squares optimization method as in most studies dealing with calibrations of SOC models (Gabrielle et al., 2004; Hadas et al., 2004; Borgen et al., 2011; Peltre et al., 2012). This method does not allow the uncertainty of model parameters or model predictions to be assessed as in Bayesian and Monte Carlo methods (Juston et al., 2010). However, it can be assumed that the uncertainty is limited since the model was run on differences in soil C between EOM amended and control soil. As a result it was not necessary to estimate the initial size of the soil C pools, which is a considerable source of uncertainty for model predictions (Christensen, 1996). In particular, RothC is especially sensitive to the estimation of IOM pool (Falloon et al., 2000). The hypothesis that avoiding estimation of SOM pools limits the uncertainty in model predictions of C mineralization in amended soils is supported by the findings of Kaborè et al. (2011) who applied the TAO model, calibrated for Mediterranean area, to a West African area without any change in the calibrated model parameters, apart from EOM partitioning obtained from biochemical characterization of the wastes, and obtained satisfactory agreement between simulated and measured values of C mineralization from an incubation experiment.

3.2.5.3 Long term SOC modelling against simulation of short term decomposition

One of the major concerns about the proposed optimization method is the fact that the classical RothC model was originally developed and validated on long-term data and not focused on the short-term turnover of easily degradable organic matter. Petersen et al. (2005b) indicated that short-term changes in SOM are very difficult to portrait, as this requires extra complexity and parameters or excessively long term incubations. This drawback is often inherent when using a relatively simple model, as in the case of RothC, to represent highly complicated processes. As a matter of fact, calibrated models with good generality for long-term data set are generally not able to simulate well short-term data series. Nevertheless, Petersen et al. (2005b) showed that satisfactory agreements between measured and simulated values could be achieved also in short term experiments by excluding some limitations from the long-term data calibration; such exclusion needs to be performed with caution as the enhancement in the model prediction ability might be reached at the cost of lower generality and biological realism.

Coppin et al. (2006) estimated the capacity of the RothC model in the prediction of C turnover on a laboratory scale and obtained a good correspondence between simulated and measured CO_2 emissions from 3 soils incubated in the laboratory for 35 days. The authors concluded that “although the RothC model was designed to predict C fluxes in soils on a large spatial and temporal scale, these results showed that it can be used within a laboratory as an experimental gauging tool". Moreover, Setia et al. (2011) adopted an approach for the optimization of RothC similar to the one presented in this study. The authors successfully utilized incubation data from amended soils to calculate a decomposition rate modifying factor specific for saline soils. Simulation of short-term changes in CO_2 respiration or N mineralization has been proved successful (Petersen et al., 2005b; Borgen et al., 2011; Cavalli and Bechini, 2011), even less satisfactory results were obtained when searching for simultaneous simulation of both processes (Cavalli and Bechini, 2012). Moreover, values for the DPM/RPM ratio usually utilized in the original RothC model (i.e. 1.44 for crop and grasses, 0.25 for deciduous or tropical wood land, 0.67 for unimproved grassland and scrubland) were estimated by fitting the RothC model to measured respiration data of plant material decaying in soil microcosms (Jenkinson and Rayner, 1997).

There are relatively few applications of RothC to investigate short term aspects of the soil C cycle, and the observed data available for such studies have largely been used in calibrating the models themselves. However, an optimization procedure based on model fitting to respiratory curves obtained from laboratory incubations of amended soil has been successfully adopted for several other soil C models (CNSIM, NCSOIL, TAO).

In non amended soils, RothC was used to simulate CO_2 respiration from a forest soil (Gu et al., 2004) and respiration data from soil incubation were utilized by Scharnagl et al. (2010) and Schadel et al. (2013) for inverse estimation of RothC pools.

Several authors have successfully used first order equations to fit respiration curves of amended soil in order to characterize and evaluate EOM (Bernal et al., 1998; Gilmour et al., 1998; Pansu and Thuries, 2003; Sleutel et al., 2005; Thuries et al., 2011). Such kind of equations regulates the C input in most of the more complex soil organic matter models such as NCSOIL, Century, DAISY, Verberne and RothC.

3.2.5.4 Discrete against cumulative respiration data

The procedure adopted to derive partition coefficients and decomposition rates of EOM pools involves fitting of simulated CO_2 to the cumulative net CO_2 measured. The main problems with fitting cumulative data are: a) experimental loss of one measured increment implies complete loss of that replication and b) errors from subsequent increments are added to those previous increments therefore accumulating errors. Fitting respiration rates (incremental data) reduces the interdependence of observation errors (Cabrera et al., 2005). Also Sleutel et al. (2005) and Hess and Schmidt (1995) made reference to the advantage of using discrete in comparison to cumulative data.

Notwithstanding the fact that the measurement system utilized in this study provided a large number of discrete and independent data, it was not possible to use incremental data as RothC output provides cumulative amounts of CO_2.

However, while the above remarks are certainly valid in case of few measurement points or measurement points taken after large time intervals, the high frequency of the measurements allowed by the automatic system used in this study (1 measurement every 4 hours) overcomes the problems related with the loss of some measurement as it permits to track with a sufficient degree of confidence a reliable trend of soil respiration.

As for the accumulation of errors the system used in this study presented a high accuracy and precision, since standard deviation was always very low.

The high number of measurements allows significant phases of the respiration curves (i.e. lag phases, peaks of maximum respiration) and outliers to be highlighted and minimize the weight that each sampling point (and the related error) has on the total cumulative respiratory response.

3.2.5.5 Incubation time and conditions

Sleutel et al. (2005) raised the question about the importance of the incubation period used to parameterize the model, as too short incubation times may lead to inaccurate evaluations of EOM pools. These authors found that an incubation time of about 50 days was the minimum period that allowed stable organic C to be estimated within less than 3% of the true value for all organic materials when using a second order model. Conversely, when utilizing a parallel first order model the minimum incubation time for reaching a satisfactory fitting for residues such as pig slurry, compost and farmyard manure was in the range 34-52 days, while for other materials (anaerobic compost, white clover residues, heifer slurry) the model could be fitted only with a longer incubation time (< 100 days). In addition, these authors found that a parallel first order model performed best in estimating stable organic C. It is worth to note that the incubations described in their work were carried out at 16 °C. One possible shortcut to reduce the incubation time is the use of higher incubation temperatures as the mineralization rates increase significantly. Consequently, higher incubation temperatures, such the one used in most of the experiments in this study (20 °C) would reduce the time needed for a satisfactory fitting. Cayuela et al. (2008), in a study on soil amended with meat and bone meals, showed that there was a Q_{10} of about 2 for incubations performed in the temperature range 15-25 °C. According to the rate modifying factor of Roth C, 30 days of incubation at 20 °C would correspond to 44 days at 15 °C in terms of the emission of the same amount of cumulative extra CO_2-C. Sleutel et al. (2005) advised against the risk that high incubation temperatures could modify the soil microbial community and the amount of labile C and suggested that mineralization studies need to be carried out at temperatures that occur in the soil for longer period. In this perspective, a temperature of 20 °C is not unrealistic for Mediterranean countries like Italy and Spain, and is not expected to give unrealistic conditions from microbial biomass.

The indications of Sleutel et al. (2005) do not agree with suggestions of Lashermes et al. (2009) who recommend incubation temperatures enabling to detect the maximum mineralization potential of the residue. However, in the latter case mineralization data are indirectly utilized together to biochemical fractions in a multivariate regression to derive EOM partitioning factors.

The results of the present study agree with the indications of Sluetel et al. (2005) to perform incubation studies at temperatures similar to those found under field conditions. As a whole, an incubation time of 30 days should be considered as a reasonable trade off between the accuracy of the information obtained in terms of C and N mineralization and EOM chemical and biochemical properties and the demand for saving costs, time and space in the laboratory. This statement is supported by the work of Gale et al. (2006) who have shown that an incubation period of 28 days at 22 °C is enough for determining whether a single or two rate decomposition constants (rapid and slow decomposition) are appropriate to represent EOM decomposition kinetics for use in C models. Hernandez and Almendros (2012) utilized an incubation period of 30 days and found a significant relationship between the average CO_2-C emitted per unit of soil weight and SOC. The authors suggest that results from laboratory incubation experiments could be representative of natural conditions and that the CO_2 released under laboratory conditions could be of interest to establish soil resilience levels based on the susceptibility to mineralization of SOC forms.

For what concerns N mineralization, Gale et al. (2006) pointed out that short-term laboratory incubations that determine net available N released from amendments after 28 days of incubation at room temperature (approximately 22 °C) have value in providing improved estimates of field plant available N for the first growing season. Justes et al. (2009), in a laboratory study of N mineralization of catch crop residue, have shown that the relationship between measured and simulated N mineralization remains the same either considering data after 28 or 156 days of incubation.

3.2.5.6 Multiple combinations of fitting parameters

In RothC, as in many other SOM models, the amount of C associated with each pool decomposes following an exponential decay. In theory these pools are of defined size that should not change with environmental conditions or with the procedure used to fit the model with the data. Cabrera et al. (1995) underlined a series of potential pitfalls in multiple pool models with exponential decay. Research has shown that pools and rate constants in the exponential models are inversely related which suggests that the same fit to available data could be obtained by increasing one parameter while decreasing the other. These observations indicate that caution should be kept in considering the estimated parameters, as different combination of pool size and decomposition rate giving a good fit to respiratory curve may result in significant differences in SOC when the model is run over long term period (100 years).

Research has also shown that increasing the incubation time can increase or decrease the size of a pool while having the opposite effect on rate constants. Moreover, increasing the number of pools may sometimes improve the goodness of fit to the incubation data, but it also increases the degree of uncertainty of the parameters.

These problems with exponential models suggest that they need to be used judiciously when trying to identify pools of defined, fixed size. One possible solution proposed by some authors to overcome such downsides is to fix rate constants, while allowing pool sizes to vary to fit the data. Thuries et al. (2001) obtained satisfactory fits to respiration curves utilizing a parallel first order 3 compartment models with fixed decomposition rates.

In this study, univocality in the optimized parameters was sought by simultaneously fitting 3 pools and 2 decomposition rate, maintaining constant incubation time and HEOM decomposition rate and by imposing constraints to partition coefficients and decomposition rates according to scientific data in order to obtain pool parameters biologically meaningful. In addition, relationships between pool size and decomposition rate were always not significant (data not shown) and this suggests that the optimized parameters reflect a unique solution.

3.2.5.7 Effect of added and native N on EOM decomposition

Results of generality test suggested that both native and residue added N might affect the rate of EOM decomposition in soil. This is not surprisingly given the close link between the C and N cycles (Shaffer et al., 2001). RothC does not consider the fate of added N, but other models allow for the effect of N on C decomposition. As an example, the C/N ratio of EOM represents the main parameters with regulates the organic residue decomposition in the PASTIS model (Garnier et al., 2003). Other C and N models have demonstrated the importance to consider N dynamics effects in regulating the decomposition of added organic matter. Moreover, several studies have shown that a satisfactory modelling of both C and N mineralization in amended soil is a very difficult task (Mueller et al., 2003; Cavalli and Bechini, 2012). Nevertheless, Karhu et al. (2012) demonstrated that the observed changes in SOC stocks in response to different organic amendments could be simulated satisfactorily well utilizing the Yasso07 model that, similarly to RothC, does not include the direct impact of N on the decomposition processes.

3.2.6 Methodological problems related to soil CO_2 measurement from laboratory incubations

A problem often overlooked by researchers dealing with soil respiration studies is potential bias introduced by the method of CO_2 evolution measurement (Heinemeyer et al., 1989).

Reliable modelling strongly relies on the quality of the input data. In the case of the present study, accurate CO_2 evolution measurements during incubation experiments are of the utmost importance as they ultimately define the EOM pool partition coefficients and decomposition rates.

Soil respiration is difficult to measure and many studies have demonstrated differences among methodologies and the biases that can be introduced if the methodologies are not correctly applied.

As a matter of fact, no standard method for measuring soil respiration exists and very few studies deal with the comparison of different respiration methods utilized in the laboratory. Furthermore, researchers are not always aware of the effects that the method adopted to measure CO_2 may have on results and the consequent interpretation of the experiment. A comparison among 3 methods of measuring C mineralization in the laboratory was carried out by Alavoine et al. (2008) who underlined the necessity to standardize measurements and to optimize incubation parameters in order to improve the accuracy of the measurement method.

The method most frequently used to measure soil respiration in the laboratory, due to its simplicity, is based on the trapping of evolved CO_2 in an alkaline solution followed by titration. However, Jensen et al. (1996) demonstrated that such method underestimates actual soil surface CO_2-flux when rates are high and overestimates CO_2 emissions when rates are low (1.6 g CO_2-C m^{-2} d^{-1}). The accuracy of methods using alkali traps compared to infrared gas analyzers for CO_2 quantification has been extensively reviewed (Ewel et al., 1987; Bekku et al., 1997; Rochette et al., 1997), with the general conclusion that alkali traps often yield underestimates of high fluxes and overestimates of low fluxes (Nay et al., 1994). This was attributed to the fact that under the last circumstance, CO_2 adsorption by the alkaline solution lowers its concentration below ambient levels, thus enhancing the flux diffusion gradient (Nay et al., 1994). The opposite is meant to happen at larger fluxes of CO_2. Concerns about the utilization of the closed chamber method with passive trapping of CO_2 for the evaluation of soil respiration were raised by Garnier et al. (2003), who found consistent lower amounts of simulated with respect to measured CO_2 and attributed such discrepancy to an overestimation due to the utilization of a close chamber method. In terms of EOM potential to build up SOC stocks, the overestimation of soil respiration at low rates by CO_2 trapping in alkaline solution appears of concern, as this method may lead to an underestimation of the soil C sequestration potential of stable EOMs, like compost and biochars.

Sanci et al. (2009), by means of a calibration system, demonstrated the validity of the closed dynamic chamber method, as the one utilized in this work, for soil respiration measurements. Furthermore, the reliability of the system employed in the present study has been proved by a series of laboratory tests (Mondini et al., 2010).

The distribution of EOM C among pools by fitting either field or laboratory C mineralization data is the reference method to initialize soil C models, as underlined by Gabrielle et al. (2004). A standardization of respiration measurements is also important because results from incubations are used to derive, modify, calibrate and make hypothesis on the structure of models. Furthermore some authors have developed equations to derive EOM pools from SCD and NIRS analyses based on regressions with pool parameters obtained by fitting respiration data (Hadas et al., 2004). As a consequence the consistency of respiration measurements can affect also the reliability of pool partitioning obtained from chemical fractionation procedures and NIRS analyses.

3.3 Long term modelling of amended soils

3.3.1 Climate change

Changes in temperature, precipitation and ET for Italy, between 2001 and 2100, predicted by the 12 different climate scenarios used for the modelling runs are reported in Table 17. The mean predicted increase in temperature in 2100 with respect to the baseline (2001) is 3.2 °C (range 1.5-6.0 °C). Evapotranspiration is also expected to increase, on average, by 14.1 mm month^{-1} (range 5.7-28.6 mm month^{-1}), while, on the whole, precipitation decreases by 1.7 mm month^{-1}. There are significant differences amongst climate scenarios, as the changes in precipitation range from negative (-7.7 mm month^{-1} for HadCM3 A1FI) to slightly positive (1.9 mm month^{-1} - CGM2 B1). The climate scenario with the greater variation with respect to the baseline is HadCM3 A1FI and the one with the lowest was PCM B1. Considering the emissions scenarios, A1FI and B1 showed the larger and smaller increase of temperature and ET, respectively.

Table 17. Variations in climate parameters for Italy between 2001 and 2100 for different climate scenarios.

Climate parameter	HadCM3				PCM				CGM2				Mean
	A1FI	A2	B1	B2	A1FI	A2	B1	B2	A1FI	A2	B1	B2	
Temperature (°C)	6.0	4.9	2.9	3.4	3.2	2.7	1.5	1.9	4.2	3.5	1.9	2.4	**3.2**
Precipitation (mm mo^{-1})	-7.7	-5.9	-4.9	0.0	-0.8	-0.4	-0.3	-1.0	-2.0	-1.3	1.9	1.8	**-1.7**
Evapotransp. (mm mo^{-1})	28.6	22.9	14.6	16.6	16.6	10.5	5.7	7.4	16.6	13.8	6.9	8.8	**14.1**

mo: month

3.3.2 Climate impacts on soil organic carbon in Italian land

Total SOC stocks in all Italian soils estimated in the present study were 1703 Mt for a depth of 25 cm, corresponding to a mean SOC content for unit area of 62.8 t C ha^{-1}. These values are in a good agreement with those estimated by Lugato et al. (2014)(1723 Mt; 56.3 t C ha^{-1}; 30 cm depth).

Results on the variation of SOC (Mt) in all Italian soils from 2001 to 2100, for the different climate scenarios and a business as usual management, are reported in Table 18. Results show, keeping land use constant, a net loss of SOC for all the climate scenarios examined. The total loss of SOC for the whole country (with exclusions of soils with SOC > 200 t ha^{-1}) was, on average, 99.25 Mt (range 48-153 Mt) corresponding to 7.44% of the initial SOC content (1334 Mt). The total amount of SOC at the beginning of the simulation in agricultural land was 748 Mt and it decreased to 694 Mt with a simulated loss of 54 Mt, corresponding to 7.2% of the content initially present.

Table 18. Losses of soil organic C (SOC) in Italian soils between 2001 and 2100 for different climate scenarios.

	HadCM3				PCM				CGM2				Mean
	A1 FI	**A2**	**B1**	**B2**	**A1 FI**	**A2**	**B1**	**B2**	**A1 FI**	**A2**	**B1**	**B2**	
SOC losses (Mt)	-132	-118	-48	-94	-84	-99	-59	-71	-153	-127	-93	-112	**-99**
% of initial SOC	-9.9	-8.9	-3.6	-7.0	-6.3	-7.4	-4.4	-5.3	-11.5	-9.5	-7.0	-8.4	**-7.4**

The range of variation in the different climate scenarios was considerable, with losses ranging from 3.6% to 11.5% of the initial SOC content, with a coefficient of variation of 31%. Considering only the climate models, the largest losses were recorded for CGM2 and the lowest for PCM. In the case of SRES scenarios, major losses were always recorded for A1FI, while the SRES scenario with the lowest losses was B1.

The percentage of SOC loss for the different agricultural land managements was larger for industrial crops (11.1%), vineyards (10.1%) and horticulture (10.0%) and smaller for grassland and arable soils at about 6.3%. Amongst non agricultural land management practices, forestry showed an average loss of 7.7%. Considering the total C losses for the different land management, larger losses were recorded in the order: forest, grassland and arable soils (forest 42.5 > grassland 26.8 > arable 17.0 Mt). This reflects the fact that the cumulated C initially present under these three land management accounted for 90.3% of the total SOC in Italy.

Contrasting data are reported in the literature concerning the effect of climate change on SOC stocks in the long period.

Lugato et al. (2014) in a recent simulation study utilizing the CENTURY model, tested against state-of-the-art top-soil data sets, found a moderate (<2.5 t C ha^{-1}), but net, decrease of SOC in the Mediterranean area by the end of 21st century. This value is within the same order of magnitude of the average per area SOC loss simulated in this study (4.4 t C ha^{-1}; data not shown). The projected overall decrease in SOC stocks in this research is in agreement with the results obtained by Smith et al. (2005), in a study on future SOC changes in all Europe (8% and 12% SOC losses for cropland and grassland, respectively). Higher SOC losses (18.4% by 2100) were predicted in Mediterranean areas by Carta (2011) in a simulation performed with RothC for the whole Sardinia island under a climate change scenario. Soil organic C changes for a business as usual scenario for Italy simulated in this study were consistent with SOC losses simulated by Muñoz-Rojas et al. (2013) using a regression model. These authors predicted SOC losses in Southern Spain for the period 2000-2100 ranging from 3.4% to 13.0%, depending on the climate scenario considered. A significant SOC decrease (0.15 t C ha^{-1} y^{-1}) was also simulated by Sleutel et al. (2006a) in Flemish cropland soils for the period 1990-2012 utilizing the DNDC model. The rise in temperature anticipated by the different climate scenarios is likely to be the main factor responsible for the anticipated increase in the rate of SOC mineralization (Davidson and Janssens, 2006). Similarly, Kirschbaum (2000) and Lal (2008b) concluded that global warming is likely to enhance rates of C decomposition.

On the other hand, Gottschalk et al. (2012) reported a moderate to null increase of SOC stocks for Europe by 2100 in a simulation study performed with RothC and attributed this to plant net primary productivity (NPP) increase equalling or prevailing losses due to higher SOC decomposition. Fuentes et al. (2012), in a study utilizing the CENTURY model for regional estimation of SOC stock changes under climate change in Northeastern Spain over an 80 years period (2007- 2087), predicted an increase in SOC storage for all the tested climate change scenarios (4.9-10.4% with respect to the initial SOC value). Lugato and Berti (2008) performed a simulation using the CENTURY model in a long term experiment located in North-Eastern Italy for the period 2008-2080 under different projected climate scenarios according to 4 GCMs. SOC changes for business as usual scenario were positive for 3 GCMs climate predictions (1.15 t C ha^{-1}) and slightly negative for the remaining climate scenario (- 0.22 t C ha^{-1}; HadCM3). These contrasting results on the long term effect of climate change on SOC stocks depend on the relative importance attributed to the increase in plant net primary productivity and organic matter decomposition, which combination ultimately determines the long term SOC balance. An agreed conclusion is that a better knowledge about the sensitivity of soil respiration to temperature is the critical element for a reliable quantification of soil C responses to climate change (Gottschalk et al., 2012).

3.3.3 Potential C sequestration and GHG offsetting of soil amendment

The results of the simulations performed at national scale with the model optimized for 8 different EOM types and 12 climate scenarios are reported in Table 19.

Table 19. Modelled soil C sequestration potential for different EOM type and climate scenarios in Italian soils amended for 100 years at a rate of 1 t C ha^{-1} y^{-1}.

GCM	SRES	EOM type										
	scenario	CO	BE	AD	MM	AR	CR	AW	SS	Mean	SD	CV
		SOC sequestration rate (t ha^{-1} y^{-1})										(%)
HADCM3	A1FI	0.375	0.116	0.253	0.106	0.108	0.129	0.197	0.141	*0.178*	*0.095*	*53.1*
	A2	0.378	0.118	0.256	0.107	0.109	0.131	0.199	0.144	*0.180*	*0.095*	*52.8*
	B1	0.395	0.126	0.271	0.114	0.117	0.141	0.210	0.156	*0.191*	*0.098*	*51.4*
	B2	0.383	0.120	0.261	0.109	0.111	0.134	0.202	0.147	*0.183*	*0.096*	*52.3*
PCM	A1FI	0.385	0.121	0.262	0.110	0.112	0.135	0.204	0.149	*0.185*	*0.097*	*52.2*
	A2	0.386	0.121	0.263	0.110	0.112	0.135	0.204	0.149	*0.185*	*0.097*	*52.3*
	B1	0.397	0.128	0.273	0.115	0.118	0.143	0.211	0.158	*0.193*	*0.099*	*51.2*
	B2	0.394	0.126	0.270	0.114	0.116	0.141	0.209	0.155	*0.191*	*0.098*	*51.5*
CGM2	A1FI	0.372	0.116	0.252	0.105	0.107	0.128	0.196	0.141	*0.177*	*0.094*	*52.9*
	A2	0.379	0.119	0.258	0.108	0.110	0.132	0.200	0.145	*0.181*	*0.095*	*52.6*
	B1	0.389	0.124	0.266	0.112	0.115	0.138	0.206	0.152	*0.188*	*0.097*	*51.7*
	B2	0.384	0.121	0.262	0.110	0.112	0.135	0.203	0.149	*0.185*	*0.096*	*52.1*
Mean		*0.385*	*0.121*	*0.262*	*0.110*	*0.112*	*0.135*	*0.203*	*0.149*	0.185		
SD		*0.008*	*0.004*	*0.007*	*0.003*	*0.004*	*0.005*	*0.005*	*0.006*			
CV (%)		*2.1*	*3.3*	*2.6*	*3.1*	*3.1*	*3.6*	*2.3*	*3.8*			

GCM: general circulation model; SRES: special report on emissions scenarios
SD: standard deviation; CV: coefficient of variation
For EOM type code refer to materials and methods section and Table 3

The contrasting EOM types significantly differed for their potential to build-up SOC stocks. Yearly C sequestration potential varied from 0.110 to 0.385 t C ha^{-1} y^{-1}. Exogenous OM quality had a great impact on the portion of added C ultimately remaining in the soil, as the same amount of added C resulted in a 3.5 fold difference in SOC sequestration potential. As expected, the largest C sequestration was predicted in compost amended soil, while the smallest was anticipated in the soil amended with meat and bone meals and animal residues. Bioenergy by-products showed values of yearly sequestration rates very similar to animal residues (0.12 t C ha^{-1} y^{-1}).

The potential of compost for soil C accumulation is widely recognized (Smith et al., 2004) and is mainly attributed to the presence of humic-like substances, whose extreme diversity and lack of regular polymeric structures impair efficient enzymatic degradation (De Nobili et al., 2001).

A good potential for SOC sequestration was recorded for anaerobic digestates (0.26 t C ha^{-1} y^{-1}) and agro-industrial waste (two-phase olive mill waste) (0.20 t C ha^{-1} y^{-1}). In the case of anaerobic digestates the degradation of cellulose, soluble starch and glucose in the acidogenic phase of the anaerobic process leads to the formation of a partially stabilized residue. The potential of two-phase olive mill waste as a C source to promote C sequestration is well recognized and mainly attributed to its high content of ligno-cellulosic substances (Sanchez-Monedero et al., 2008).

On the other side, meat and bone meals, animal residues and bioenergy by-products are the EOMs less indicated to foster C sequestration. Respiration trends in soil amended with these organic substrates showed a peak of maximum respiration 2-3 days after soil additions indicating an exponential phase of microbial growth, sustained by the high content of easily degradable substances in the organic residues (Figure 6). In fact, these EOMs can be considered as effective fertilizers, due to their significant content of nutritive elements (Cayuela et al., 2010; Galvez et al., 2012).

A significant exponential relationship was found between the cumulative respiration of amended soil under standard laboratory conditions and the mean potential for C sequestration of each EOM type (Figure 10).

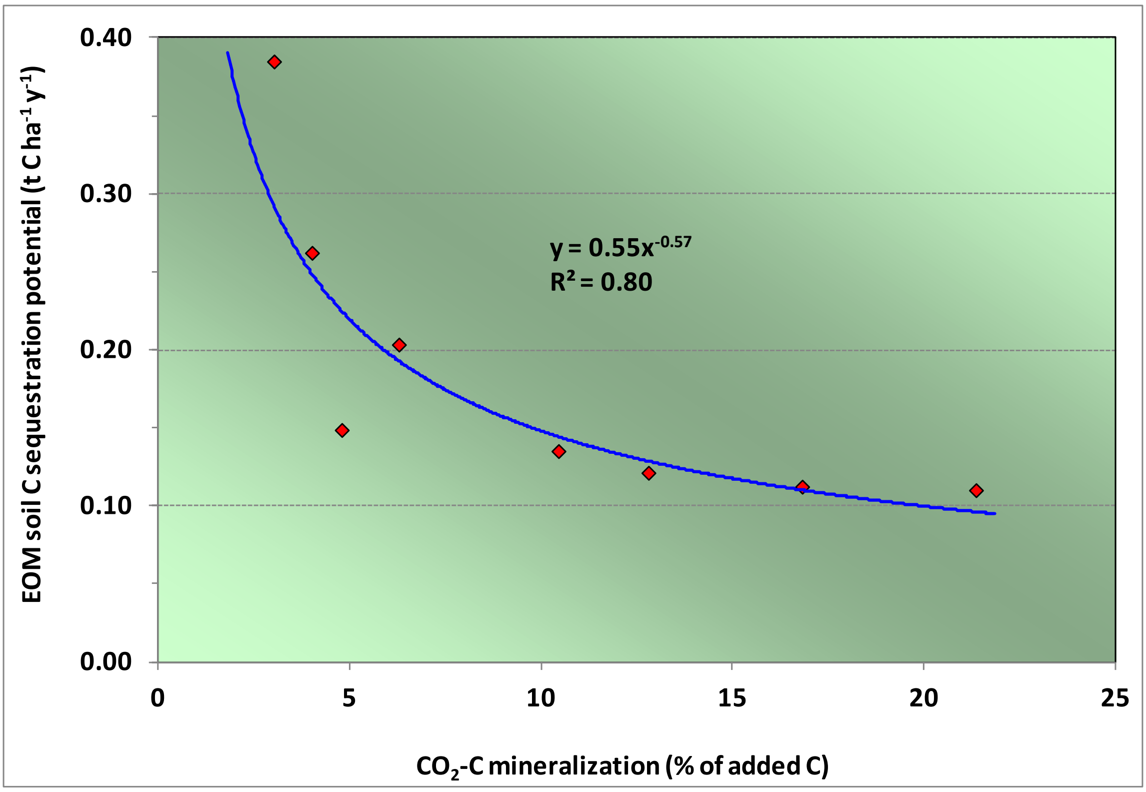

Figure 10. Relationship between net CO_2-C mineralization and soil C sequestration potential for 8 different EOM type.

These results suggest that the net C mineralization of residues during laboratory incubation is an indicator of their potential for C sequestration, but that such relationship is not linear. The occurrence of a stable C pool (humic substances-like) greatly enhances the capacity of the residue to build up SOC stocks.

The different climate scenarios had a moderate effect on the C sequestration potential predicted by the model for the different EOMs. The coefficients of variation of mean yearly sequestration potential for the 12 climate scenarios were in the range 2.1-3.8% depending on the EOM type. The variability was larger among SRES emission scenarios (c.v. range 1.9-3.5%) than among GCMs models (c.v. range 1.3-2.2%). Considering SRES emission scenarios, B1 was the one promoting the larger EOM C accumulation, while smaller sequestration potentials were recorded for A1FI. This is consistent with the anticipated consequences of these scenarios on climate change (Table 17).

A significant inverse relationship was found between the increase in temperature and evapotranspiration for each of 12 climate scenarios and the soil C sequestration potential of amended soil (Figure 11).

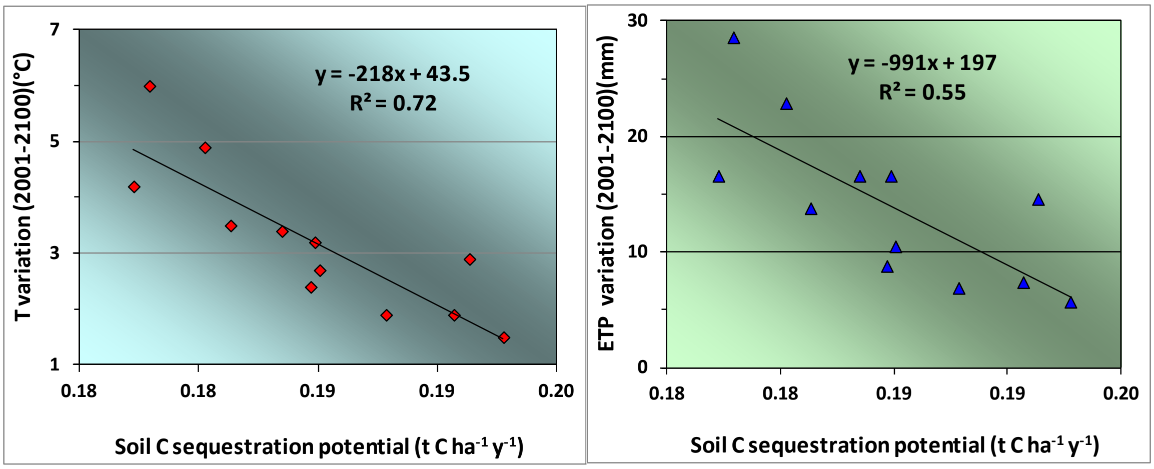

Figure 11. Correlations between changes in temperature (T) and evapotranspiration (ET) predicted by 12 different climate scenarios between 2001 and 2100 and mean C sequestration potential of amended Italian agricultural soils.

No significant relationship was found between changes in precipitation and C sequestration potential. This could be explained on the basis that changes in T and ET predicted by all 12 climate scenarios were always positive, while in the case of precipitation contrasting estimates (i.e. positive and negative variations) were provided by the different scenarios (Table 17). Furthermore, it has to be considered that an adequate soil water content increases SOM decomposition, but in the presence of an optimal temperature, i.e. the effect of precipitation on SOM mineralization is best elucidated by considering the interaction of precipitation and temperature (Smith et al., 2005), as indicated by the significant relationship between potential SOC sequestration and ET.

For each EOM type, the annual C sequestration potential reported in Table 19 is the mean of the simulations performed including all the combinations of soil, land use and climate data present at the national level for which EOM application was considered (7392 combinations). The variability in the potential to build up SOC stocks considering all combinations was enormous. As an example, in the case of compost and for climate scenario PCM B1, minimum and maximum annual SOC increases were 0.22 and 0.62 t C ha^{-1} y^{-1}. Therefore, applying the same amount of C as compost either in the best and less suitable land for C sequestration resulted in about 3-fold difference in the estimated level of SOC measured after 100 years of EOM application. Considering all the combinations between the different EOM type and the sites of application, the variability in the potential for C sequestration further increased, spanning over 1 order of magnitude (range 0.06-0.62 t C ha^{-1} y^{-1}). This range of potential C sequestration rate refers to SOC accumulation for EOM type and site with the smallest potential for C accumulation and EOM type and location with the largest capacity to build up SOC stocks.

The potential yearly C sequestration rate per unit area found in the present study for compost (0.385 t C ha^{-1} y^{-1}) is similar to the values reported by Smith et al. (2005) for compost (0.4 t C ha^{-1} y^{-1}), Smith et al. (2008) for manure/biosolid application (0.42 t C ha^{-1} y^{-1}) and Freibauer et al. (2004) for amendment (0.40 t C ha^{-1} y^{-1}) in European soils and Yokozawa et al. (2010) for Japanese arable soils (0.30 t C ha^{-1} y^{-1}). The Carbo-PRO web-tool for simulation of C sequestration in amended soil developed by INRA and based on RothC (Carbo-PRO, 2012) gives a maximum yearly sequestration potential of 0.27 t C ha^{-1} y^{-1} for a yearly application of 1 t C ha^{-1} of compost with a good degree of stability for a period of 100 years. Model parameterization of the web-model was based on biochemical properties of EOM evaluated by the Van Soest method. Thuries et al. (2002) suggest that in very stable compost part of the lignin pool can be transformed in soluble humic substances resistant to microbial degradation. Consequently, biochemical fractions based on the Van Soest method may lead to an overestimation of the labile fraction and an underestimation of the stable fraction, mainly responsible for the build up of SOC stocks.

Peltre et al. (2012) reported values of potential C sequestration in compost amended soil similar to those evaluated in the present study. However, such values were calculated considering a period of application of 20 years and it is well known that the effectiveness of strategies such as compost application in building up SOC stocks tends to decrease after several decades, as the soil approaches saturation

(Stockmann et al., 2013). The most stable compost in the study of Peltre et al. (2012) presented partition coefficients of 0, 0.8 and 0.2 for DPM, RPM and HUM respectively. These values seem not to properly reflect the nature of stable composts when considering that in mature composts lignin contents (determined with the Van Soest method) range from about 30% up to 54% of OM (Sanchez-Monedero et al., 1999; Thuries et al., 2002; Francou et al., 2008; Doublet et al., 2011). The lignin content can be assumed as a proxy for the resistant pool of EOM, as suggested by Thuries et al. (2002) who employed a model assuming 3 pools of EOM (labile, resistant and stable) in which the stable fraction was associated to the lignin fraction determined with the Van Soest method.

Sleutel et al. (2006b) reported a rate of SOC increase of 0.49 t C ha^{-1} y^{-1} for a yearly application of 10 t of compost. Such values are difficult to compare to the ones presented in this study due the very short simulation period (6 years). Nevertheless the authors underlined that DNDC only considers EOM quality in terms of C/N ratio and does not take into account the recalcitrance of OM in compost. As a consequence the authors suggest that the sequestration potential of compost in their work may have been underestimated.

Regarding the potential of soil amendment to offset GHG emissions at national level, Table 20 reports the total amount of SOC sequestered in the soil after 100 years of consecutive application of EOM at a rate of 1 t C ha^{-1} to all the area of agricultural land in Italy. Results showed a high variability in the increase of SOC stocks ranging from 175 to 615 Mt, depending on the EOM type. The percentage of increase with respect to the baseline varied from 25.1% for meat and bone meal to 88.6% for compost amended soils.

Table 20. Modelled total SOC increment (Mt) in Italian agricultural land amended for 100 years with different EOMs at a rate of 1 t C ha^{-1} y^{-1} and for different climate scenarios.

SRES scenario	**GCM**																										
	HADCM3								**PCM**								**CGM2**										
	CO	**BE**	**AD**	**MM**	**AR**	**CR**	**AW**	**SS**	**CO**	**BE**	**AD**	**MM**	**AR**	**CR**	**AW**	**SS**	**CO**	**BE**	**AD**	**MM**	**AR**	**CR**	**AW**	**SS**	**Mean**	**SD**	**CV**
	SOC increment (Mt)								**SOC increment (Mt)**								**SOC increment (Mt)**										**(%)**
A1FI	600	184	404	168	171	204	316	223	620	193	420	176	180	215	327	236	592	182	398	166	169	201	312	220	**287**	*146*	*50.9*
A2	605	186	408	170	173	206	319	226	617	191	417	174	178	213	325	233	604	186	407	170	173	206	318	226	**289**	*147*	*50.8*
B1	634	200	432	182	186	223	336	245	633	200	432	182	186	223	335	245	620	195	421	177	181	217	328	238	**302**	*150*	*49.8*
B2	615	192	417	175	178	213	325	234	628	198	428	180	183	220	332	242	612	191	415	174	177	212	323	233	**296**	*148*	*50.2*
Mean	**613**	**191**	**415**	**174**	**177**	**212**	**324**	**232**	**625**	**196**	**424**	**178**	**182**	**218**	**330**	**239**	**607**	**188**	**410**	**172**	**175**	**209**	**320**	**229**			
SD	*15*	*7.2*	*13*	*6.1*	*6.3*	*8.6*	*8.7*	*9.9*	*7.5*	*4.0*	*6.6*	*3.4*	*3.5*	*4.8*	*4.5*	*5.5*	*12*	*5.7*	*9.9*	*4.8*	*5.0*	*6.8*	*6.9*	*7.8*			
CV (%)	*2.5*	*3.8*	*3.0*	*3.5*	*3.6*	*4.1*	*2.7*	*4.3*	*1.2*	*2.1*	*1.6*	*1.9*	*1.9*	*2.2*	*1.4*	*2.3*	*2.0*	*3.0*	*2.4*	*2.8*	*2.9*	*3.3*	*2.2*	*3.4*			

GCM: general circulation model; SRES: special report on emissions scenarios

SD: standard deviation; CV: coefficient of variation

For EOM code refer to materials and methods section and Table 3

The annual rate of GHG emissions for Italy in 2011 was estimated by the European Environment Agency (EEA, 2013) to be 133 Mt CO_2-C equivalent y^{-1}. Therefore, the range of average annual potential of C sequestration in Italy in response to the application of EOM estimated in the present work (1.75-6.15 Mt C y^{-1}) only represents 1.3-4.6% of the total annual GHG emissions in Italy. Therefore, even in the non realistic hypothesis to apply compost, which presents a high potential for C sequestration, to all the agricultural land of Italy, the contribution of soil amendment in tackling GHG emissions is limited. These results are in agreement with those of Smith (2004a) who concluded that C sequestration can play only a minor role in offsetting GHG emissions. On the other hand it is important to consider that even if soil C sequestration by EOM application has little benefit for climate change mitigation, the increase in SOC content is likely to have significant beneficial impacts on soil quality and ecosystem functioning (Powlson et al., 2011b).

The validity of the approach proposed in this study could only be validated by comparing the results of the simulation with data from long term experiments dealing with EOM amendment. Due to the lack of validation of the optimized model, the model based analysis of amended soil cannot be interpreted in terms of absolute values for certain sites and management practices. Nevertheless, it may help to quantify relative differences due to the application of different EOM type to specific sites under constant conditions in a complex system. Furthermore, the results of this study suggest a wide range of variation in C sequestration potential as a consequence of long term amendment with contrasting EOMs in sites characterized by a large range of pedoclimatic conditions and land use.

It is important to note that a sensitivity analysis performed by Falloon (2001) on the standard RothC showed that the model is relatively insensitive to variations in the quality of C inputs, as varying DPM/RPM ratio for plant inputs from 0.1 to 2.0 (i.e. 20 fold variation) resulted in a SOC decline from 29.0 to 24.3 t ha^{-1} (i.e. 16% variation). Conversely, varying both partition coefficients and constant decomposition rates in the modified model caused variations in the yearly rate of SOC accumulation up to 86%: addition of 1 t C ha^{-1} y^{-1} of either vine shoots compost or bioethanol residue for 100 years under the climate scenario CMG2 A1FI gave an annual C sequestration rate of 0.47 and 0.25 t C ha^{-1} y^{-1}, respectively.

3.3.4 Spatially explicit modelling of SOC in amended soils

The procedure adopted in this work allows the intensity in SOC changes due to variations in climate, land use and soil management to be visualized on a map. As an example, on Figure 12 is reported a map of Italy showing the expected increase in SOC stocks (expressed in t C ha^{-1}) that could be achieved in 2100 due to repeated addition of compost to all agricultural land for a specific climate scenario (PCM B1).

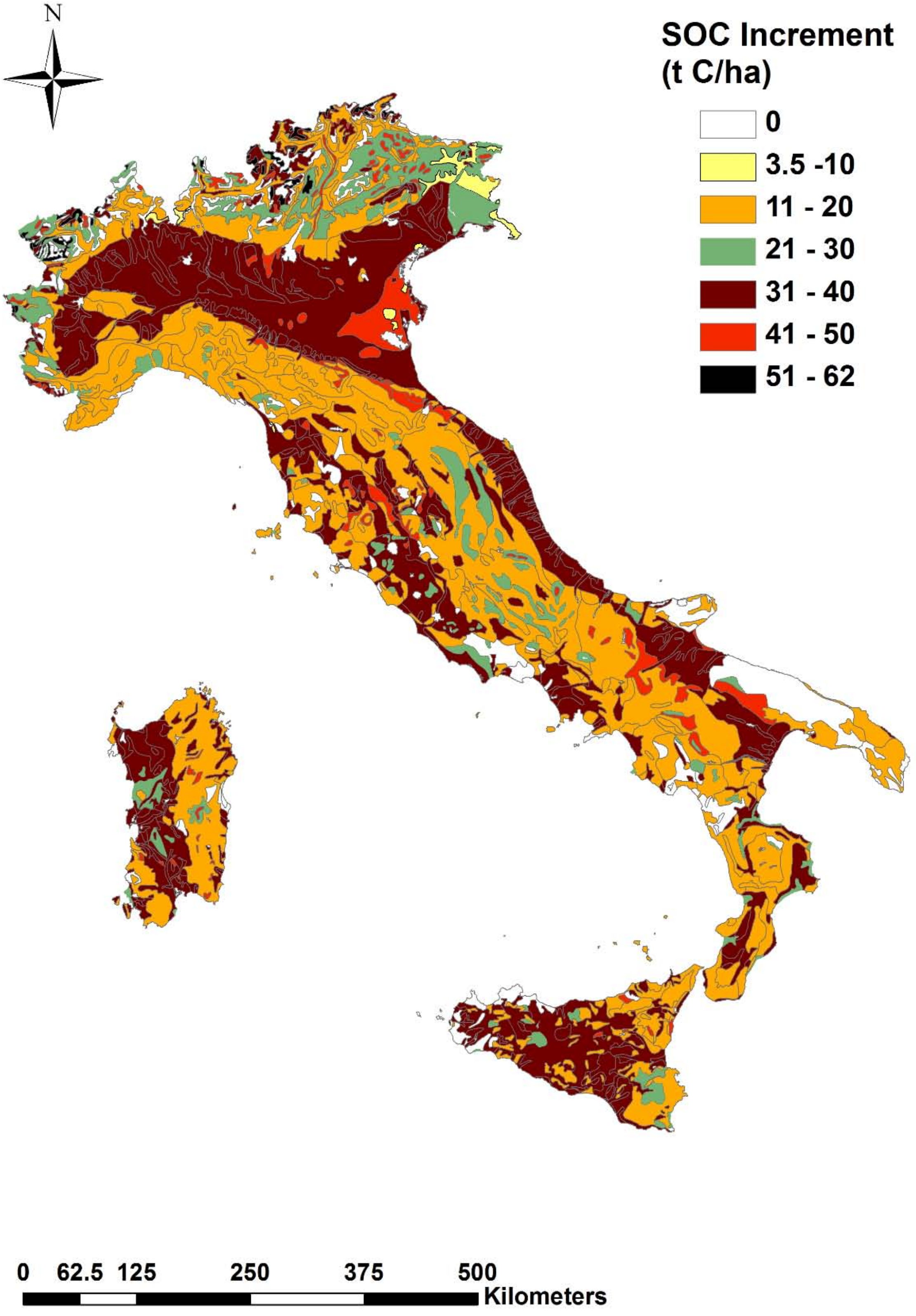

Figure 12. Map of modelled increase in soil organic C (SOC, t ha^{-1}) after 100 years of compost addition (1.0 t C ha^{-1} y^{-1}) to all the soils with agricultural land use (climate scenario PCM B1). The increase in SOC refers to the business as usual scenario in 2100.

Areas with a SOC increase of 51-62 t C ha^{-1} are all located in the mountain areas of Northern Italy characterized by grassland land use. The places on the map with the SMUs having a SOC increase in the range 41-50 t C ha^{-1} are mainly situated in the eastern portion of Po valley. The main areas with an intermediate SOC accumulation potential (31-40 t C ha^{-1}) are situated in: (i) the river Po valley, (ii) the coastal area of Emilia Romagna, Abruzzo, Marche and Apulia, (iii) the area between Apulia and Basilicata, (iv) the interior part of Tuscany, (v) central Sicily, and (vi) western part of Sardinia.

Figure 13 shows the simulated increase in SOC stocks considering compost addition only to arable soils, in order to simulate realistic compost application to the more accessible flat areas. The arable land with higher sequestration potentials is located in the North-Western part of Italy

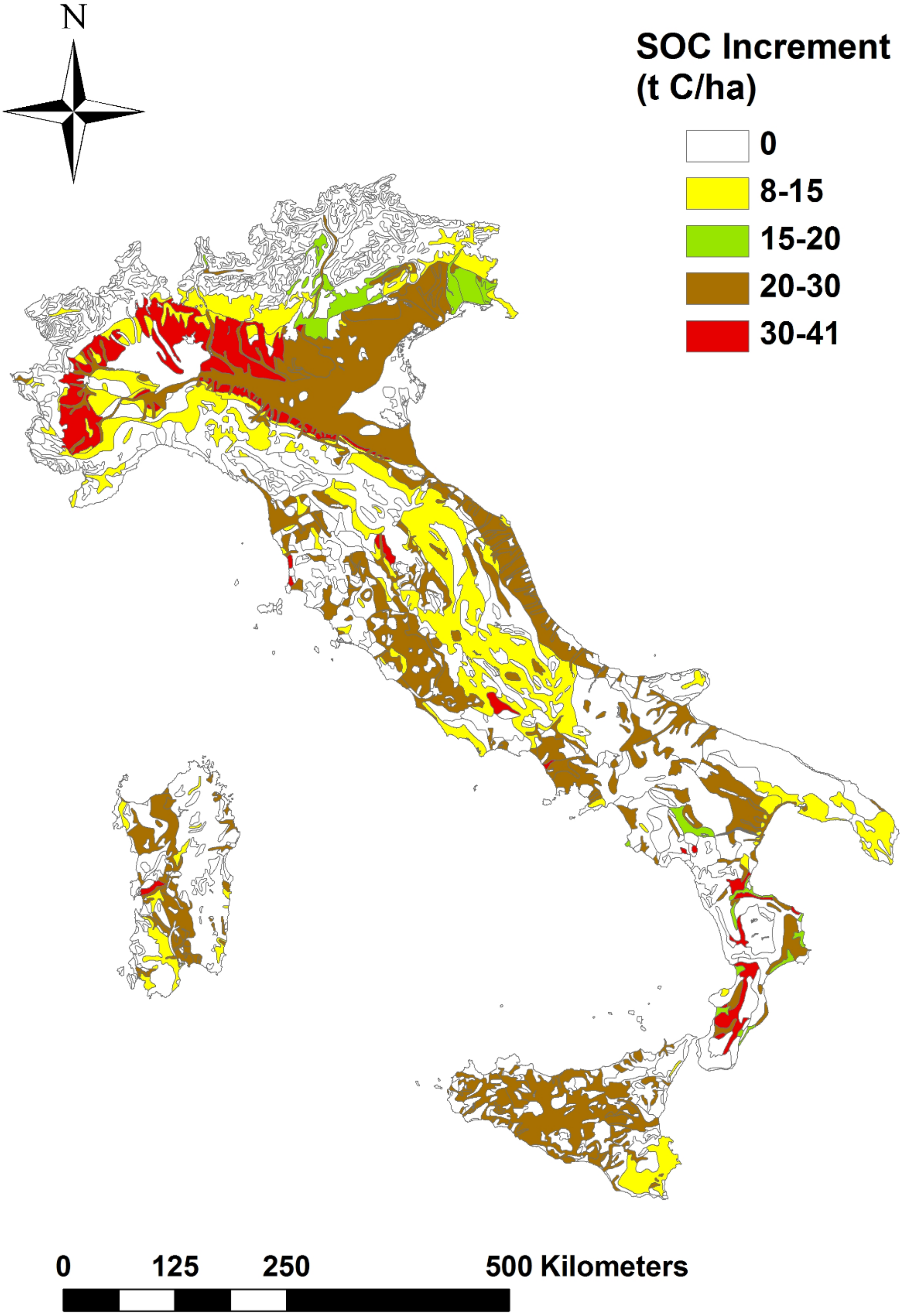

Figure 13. Map of modelled increase in soil organic C (SOC, t ha^{-1}) after 100 years of compost addition (1.0 t C ha^{-1} y^{-1}) to arable soils (climate scenario PCM B1). The increase in SOC refers to the business as usual scenario in 2100.

On the basis of the simulations performed for the whole agricultural land, further simulations were performed by applying EOMs to either the land with the greatest or lowest C storage potential. The area interested in the simulation was estimated on the basis of the predicted total production of compost in Italy in 2020 (1800000 t; CIC - Italian Composting Association, 2010). According to mean analytical data for compost produced from food wastes (CIC - Italian Composting Association, 2000) and an application rate of 1 t C ha^{-1} y^{-1}, this amount could be spread on 213750 ha of agricultural land. Therefore, model runs were performed for the climate scenario PCM B1 simulating 100 years of annual additions of different EOMs to 213750 ha of either the area with the greatest or lowest potential for C sequestration, as determined by simulations performed on the whole agricultural land. In the case of compost, results showed an average increase of SOC per unit area of 55.7 and 26.9 t C ha^{-1} for the land with the greatest and lowest C sequestration potential, respectively. In the case of meat and bone meal the simulated increases of SOC after 100 years of amendment were 18.9 and 7.2 t C ha^{-1}, respectively. Similar simulations were performed for the climate scenario CGM2 A1FI and the results for compost were 52.4 and 26.3 t C ha^{-1} and for meat and bone meal 16.5 and 6.8 t C ha^{-1} for the area with the greatest and lowest C sequestration potential, respectively (Table 21). The two climate scenarios were selected on the basis that they resulted in the largest (PCM B1) and smallest (CGM2 A1FI) C sequestration potential of added C (Tables 19; 20).

Table 21. Modelled mean SOC increments (t C ha^{-1}) after 100 years of soil amendment with different EOM type to the Italian agricultural area (213750 ha) with the largest and smallest potential for soil C sequestration.

Climate scenario	Land potential for SOC sequestration	EOM type							
		CO	BE	AD	MM	AR	CR	AW	SS
		SOC increment (t ha^{-1})							
PCM B1	Land with largest SOC sequestration potential	55.7	22.0	42.4	18.9	19.5	25.8	30.5	29.4
	Land with smallest SOC sequestration potential	26.9	7.8	17.7	7.2	7.3	8.6	14.0	9.3
	Ratio	2.1	2.8	2.4	2.6	2.7	3.0	2.2	3.2
CGM2 A1FI	Land with largest SOC sequestration potential	52.4	18.9	38.4	16.5	17.0	21.9	28.1	24.9
	Land with smallest SOC sequestration potential	26.3	7.4	17.2	6.8	7.0	8.1	13.5	8.8
	Ratio	2.0	2.5	2.2	2.4	2.4	2.7	2.1	2.8

For EOM code refer to materials and methods section and Table 3

Therefore the characteristics of the agricultural land in terms of soil properties, climate, soil use and management have a dramatic impact on the potential amount of added C stored in the soil. Considering the interaction between EOM quality and site the range of variability in C sequestration further increases. Therefore, spatially explicit modelling of SOC allows for the evaluation of the effects of the interactions between EOM and site properties.

The estimated annual production of compost for 2020 in Italy is 1800000 t. At a rate of 1 t C ha^{-1}, this could be applied to 213750 ha, representing about 1.26% of the total Italian agricultural land (17041540 ha; Sambucini et al., 2010). Considering the mean annual C sequestration rate predicted by the simulation performed with the modified RothC (0.385 t C ha^{-1} y^{-1}; Table 19) the total C that can be sequestered every year in soil by compost amendment is about 82300 t (corresponding to less than 0.1% of the annual rate of GHG emissions for Italy). This value is consistent with an amount of 98200 t of C estimated by Arrouyas et al. (2002) for France considering the actual compost production of France.

Taking into account the limited potential production of compost, it is clear that the studied scenario (compost application to all agricultural land) does not reflect a realistic option. However, the creation of a link between spatial data and a dynamic soil C cycle model represents an effective tool for land managers and policy makers to optimize the resources that are available. A simulation considering compost addition to all agricultural land, despite compost scarcity, is significant as it enables obtaining a spatial representation of the potential of land for C sequestration that can provide useful information for the best utilization of the resources. In fact, application of the estimated production of compost for 2020 to either the soil presenting the largest or the smallest C sequestration potential resulted in a 2.1 fold difference in SOC increase. Therefore maps such as those reported in Figure 12 and 13 can provide guidance as to where compost might best be applied.

The capacity of a soil to accumulate SOC depends on the complex interrelations between several factors such as climate, soil properties and land use, the relative importance of which may vary at different spatial and temporal scales. Spatially explicit modelling indicates the location of areas where the combination of these factors could result in the largest increase in SOC, and can also be useful in elucidating the role of interactions between factors in determining future SOC stocks.

A key interaction is that between temperature and precipitation. It is well known that there is a direct relationship between temperature and the rate of SOC decomposition due to the effect of temperature on microbial metabolism. Carbon mineralization in soil is also affected by soil water content, which is influenced by precipitation. In particular, both low and high water content may constrain C decomposition. Low water contents may temporarily or permanently offset the effect of temperature on decomposition by reducing the thickness of soil water films, which in turn inhibits extracellular enzyme activity and decreases substrate availability (Davidson and Janssens, 2006). Leiros et al. (1999) showed that the effect of a 2 °C temperature increase is roughly countered by a concurrent 10% decrease in soil moisture content. On the other hand, also an excessive soil water content can decrease the rate of C decomposition because of impedance to gaseous transport in the soil (Gabriel and Kellman, 2011). It is therefore important to consider how the interaction of both factors may affect SOC decomposition as demonstrated by previous studies. Smith et al. (2005) found that the most important factors regulating SOC mineralization are temperature and precipitation as in their study decomposition was faster in regions were temperature increased greatly, but soil moisture remained high enough to allow decomposition. Similarly, Fantappiè et al. (2011) found that the interaction of temperature and precipitation had a significant effect on SOC variations recorded in Italy between 1961 and 2008. In the present study, while there is a general inverse correlation between SOC increase and temperature (Figure 11), there are also some noteworthy exceptions to this behaviour, with soils that have a high potential for C sequestration located in areas characterized by high temperatures, such as Southern Italy (Figure 12). However, these areas are characterized by smaller amounts of precipitation, and the constraint exerted by low humidity on SOC decomposition could explain why areas with a significant potential for C sequestration were located in the hottest regions of Italy. The relevance of soil moisture as an important factor driving C mineralization has been highlighted by Fuentes et al. (2012) in a simulation study performed in Northeastern Spain for the period 2007-2087. The semiarid conditions prevailing in most part of the modelled area constrained microbial activity when the amount of water supplied by rainfall was reduced. This fact associated with NPP increase due to enhanced CO_2 concentration explained, according to the authors, the predicted increase in SOC stocks in the modelled area.

The combined effect of temperature and precipitation on SOC accumulation could also be seen in the SMU with the greatest SOC increases that are all located in the alpine region of Northern Italy (Figure 12), characterized by high precipitation values and low temperatures. These results are in agreement with findings of Saby et al. (2008) and Lemenih and Itanna (2004), who demonstrated a trend in SOC that is directly proportional to the mean annual precipitation and inversely proportional to the mean annual temperature.

Another important interaction in determining SOC accumulation is between land use and climate. It is well known that grassland favours C accumulation by comparison with arable soils, mainly due to greater return of plant residues, high root biomass and lack of disturbance in grassland soils. Goidts et al. (2009) reported for Southern Belgium a mean SOC content of 36.4 and 92.2 t C ha^{-1} for cropland and grassland, respectively. In this work, all the SMUs with the largest SOC increase (50-60 t C ha^{-1}, for compost amended soils) are represented by grassland and are located in areas characterized by low temperatures and high precipitation. Temperature interacts with precipitation in determining grassland distribution by adjusting water demand and consequently water availability. Increases in temperature result in enhanced soil evaporation and plant transpiration and consequently, for the same precipitation value, the water balance becomes more negative. In fact, Smit et al. (2008) found that grassland productivity was directly correlated with precipitation and inversely correlated with temperature. Therefore, the higher SOC increase per unit area recorded for grassland soil could be attributed to the combination of the higher plant inputs and the climatic conditions favouring a low rate of C mineralization.

3.3.5 Limitations and uncertainty of long term modelling of amended soil at regional scale under climate change

Regional modelling of amended soil under climate change is affected by different limitations and sources of uncertainty. Since the main aim of this study was to devise a procedure to model the C sequestration due to EOM application at both local and regional scale under climate change, limitation and sources of uncertainty related to simulations performed at site scale on unamended soils will not be discussed here. Limitations and sources of variability related to the proposed procedure for model modification and optimization were already discussed in the section 3.2.5.

3.3.5.1 Effect of increased net primary production on soil C sequestration

The predicted increase in the atmospheric CO_2 concentrations as a consequence of climate change is likely to raise the net primary production (NPP), due to the positive effect of CO_2 on photosynthesis efficiency (CO_2 fertilization effect). The increase in NPP could lead to a larger input of organic inputs in the soil enhancing soil C sequestration (Jastrow et al., 2005). It has to be considered that RothC does not present a plant module and consequently does not consider the effects that an elevated CO_2 concentration may have on plant NPP and plant residues returns to the soil, which could have considerable impacts on predicted SOC contents in future scenarios.

Nevertheless, Petersen et al. (2002) showed that a simple SOM model (C-tool) devoid of a plant growth sub-model, as in the case of RothC, was able to precisely mimic the results obtained from the complex agro-ecosystem model DAISY, therefore demonstrating that the prediction of SOM turnover can be satisfactorily performed without the need to include the complexity of an integrated soil-plant-atmosphere model.

In addition, there are evidences that the predicted positive effect of increased levels of CO_2 on soil C sequestration could be limited by several constraints. Ainsworth and Long (2005) reported that large-scale free-air CO_2 enrichment (FACE) experiments resulted in much smaller increases in crop yield than previously reported by enclosure experiments. Berthelot et al. (2001) showed that the additional C sequestration due to fertilization effect only slightly reduces the negative impact of climate on the terrestrial storage. They predicted that at global scale the additional CO_2 would lead to an extra storage in soil C of only 16 Gt by the end of the present century. The increase in NPP may be limited by lack of nutrients and water, soil fertility constraints (Lal, 2008b) and/or CO_2 levels approaching saturation (Lal, 2008b; Muñoz-Rojas et al., 2013).

3.3.5.2 Sources of uncertainty of regional modelling of amended soil under climate change

Uncertainty of SOC regional modelling are mainly associated with measurement and/or evaluation of input parameters, prediction of future climate scenarios and effect of climate change on C cycle and other factors controlling SOC stocks.

3.3.5.2.1 Input parameters

A first source of uncertainty in regional modelling is related to the measurement and/or estimation of initial parameters for the model, in particular C input from crop residues and soil properties.

A particular matter of concern for the reliability of C modelling in Mediterranean areas is the evaluation of C input from plant residues. To measure C inputs directly is difficult and costly, so several authors estimated them from yields or by inverse modelling, as in the case of the present study. RothC, when used in inverse mode, predicts how much C must enter the soil each year to maintain the measured or estimated SOC stock. However, Coleman et al. (1997) and Jenkinson et al. (1999) reported that in some dry warm regions the annual return of C required by the model was too large and unrealistic compared to the modest levels of crop yield in these regions. This unrealistically low C input is probably due to the fact that in dry warm regions the model simulates a larger soil water moisture content than the actual, resulting in higher decomposition rates of SOM. This limitation was confirmed by Farina et al. (2013) who found that accurate RothC simulations of the measured soil C in a rotation experiment in a semiarid area of Southern Italy could be obtained only if the C inputs to the soil were set to unrealistic large values. This drawback can be overcome by utilizing a modified version of the model specifically developed to improve the simulation of SOC patterns in semiarid regions by reducing SOM decomposition rates in the soil (Farina et al., 2013).

A further source of uncertainty is related to the inherent heterogeneity of soil that can result in large variability in the measured C contents and other soil properties. Sleutel et al. (2006a), in a study about regional SOC modelling in Belgium, found that the DNDC model simulated well SOC stock changes for the whole study area, although some deviations from measured values were recorded for specific area. The authors suggested that good simulation of spatial variation in SOC changes is feasible provided extensive validation and calibration of the model at the field scale. In this perspective the utilization of RothC represents a sound base as this model has been extensively validate for different climate, soil properties and management scenario (Smith et al., 1997). Moreover, it has to be underlined that the same soil and climate data sets and methodological approach utilized by Smith et al. (2007) in their work dealing with projected SOC stock in the current century for the whole Europe under climate change were utilized in the present study. Finally, an advantage in the use of RothC for spatially explicit SOC prediction is represented by the fact that the model requires relatively few and easily measured input parameters. As a consequence input data are often available at different scale and this represents a guarantee in terms of the quality of input data with respect to other models requiring input parameters more numerous and/or laborious to obtain.

3.3.5.2.2 Prediction of future climate scenario

A second source of variability in regional modelling under climate change is related to errors in the prediction of future climate scenario. Specifically for areas of complex topography, like the Mediterranean region, application of GCMs might result in considerable biases in the prediction of precipitation and temperature (Giorgi and Lionello, 2008). In particular, precipitation involves local processes of larger complexity than temperature, generally resulting in less robust projections than those for temperature (Muñoz-Rojas et al., 2013). Precipitation usually shows an orographically induced fine scale structure lacking in the global model at broader scale. Nevertheless, Giorgi and Lionello (2008) have shown that projections of a range of global and regional climate model for the Mediterranean area were generally consistent with each other at the broad scale and that the variations in climate were robust across forcing scenarios and future time periods.

3.3.5.2.3 Effect of climate change on SOC cycle and stocks

Finally, an important source of variability can be attributed to the effect of climate change to a range of anthropic and natural factors affecting SOC cycle and stocks (Fuentes et al., 2012; Lugato and Berti, 2012; Muñoz-Rojas et al., 2013).

A first source of variation is related to land management modifications that farmers could adopt to counteract the negative impacts of climate change: variations in crop rotation, crop genetics, cropping systems, land use, period of planting and harvesting, irrigation and technology (machinery, herbicides, breeding). In this study a fixed management was intentionally used to make a clearer comparison among different EOMs and better elucidate the effects of climate change in terms of C sequestration potential.

In RothC the impact of temperature on the decomposition is the same for the different pools and consequently the Q_{10} of labile and resistant pools does not change with the increasing temperature. Recent studies suggest that temperature sensitivity on SOC decomposition changes according to SOC pools and, consequently, variations in the response of different C pools to warming could not be adequately predicted by the model (Lugato and Berti, 2008). Nevertheless, there is still controversy about the relationship between temperature sensitivity of SOC decomposition and degree of stability of different C fraction and further researches are necessary to clarify this important aspect for SOC cycle (Lugato and Berti, 2008). Others possible impacts of variation in the climate are changes in residue and microbial communities composition that could affect the rate of EOM microbial decomposition. Climate change may also alter the rate and magnitude of emission of GHGs from arable land. Modelling studies by Olesen et al. (2004) showed that total GHG emission increased with increase in temperature and precipitation.

RothC is a model based on a first-order decomposition kinetics, implying a direct relation between C input and soil C stock, which could increase without limit as C input levels increase. Powlson et al. (2012) underlined that high rates of SOM accumulation can be sustained only for a limited period, albeit long, as a result of the saturation of different mechanisms ensuring EOM protection against decomposition (Six et al., 2002). This consideration is very important when the simulations are projected in the long term (Lugato and Berti, 2008) and an effect of C saturation on the potential of C sequestration cannot be excluded a priori. However, there are two reasons that give confidence on the fact that conditions for C saturation were not met for the simulations conditions selected in the present work.

First, results of some researches point out to the fact that deviations from a linear relationship between added EOM and SOC accumulation occur only for high yearly rate of C applications. For example, Heitkamp et al. (2012) showed that such deviation take place for yearly additions of 2.5 t C y^{-1}, while Gulde et al. (2008) observed an increase in SOC content with manure application rate up to 120 t fresh weight ha^{-1} y^{-1}, but no additional C sequestration was found for manure application rate of 180 t fresh weight ha^{-1} y^{-1}. Such application rates are markedly higher than the 1.0 t C y^{-1} dose utilized in the simulations of the present work.

Secondly, due to the increase in the rate of SOM decomposition caused by the anticipated climate changes, the model simulations predict a decrease in the rate of SOC accumulation in amended soil for the last decades of the 21st century and in some cases the added EOM could not compensate for the increased rate of SOC decomposition and SOC stocks begin to decrease (Mondini et al., 2012). Therefore the effect of climate change on the increase in SOM decomposition, especially in the last period of the present century, suggests that SOC stocks predicted by the model for 2100 in amended soils are likely to be far from conditions conducive to saturation.

A quantification of all sources of uncertainty was beyond the scope of the present work as the main objective of the thesis was to develop a procedure for simulation of SOC stocks in amended soil and to identify relative differences in C sequestration potential of several EOMs. Indeed, all these aspects need to be considered before application of regional modelling of amended soil as reliable, transparent and verifiable method to measure changes in soil C stock.

Nevertheless, several simulation runs were performed with EOM characterized by different values of EOM pool parameters and under different climate scenarios and such values can be taken as probability distributions for input variables, e.g. the range of values that such variables can assume. The results of the simulations performed could give an indication about the uncertainty as it possible to evaluate how, given the range of variability in the inputs, this is propagated along the model and it is translated into variability in the model output.

As an example, the variability of EOMs utilized in the present study results in an uncertainty of prediction (expressed as 90% confidence interval of the mean; Stamati et al., 2013) in C sequestration potential higher than 80%. Considering the variability in the composition within the same EOM type, uncertainty in model prediction of C sequestration rate for compost and meat and bone meal amended soil was 17.8 and 26%, respectively. These results suggest that uncertainty in the long term prediction of SOC in amended soil is large when considering the huge variability in the properties of EOMs applied to the soil, but uncertainty in model prediction is limited when considering a specific kind of EOM.

By contrast the effect of variations in climate change on C sequestration potential of amended soils presented a limited effect on the variability of the output model as uncertainty associated with different simulation performed for the same EOM type under different climate scenario was lower than 6%.

Variability in climate change prediction presented a much larger impact on the uncertainty in SOC losses simulated by the model for a business as usual land management scenario as this was higher than 51%.

The variability in the long term regional prediction of SOC trends under climate change estimated in the present study is in agreement with overall uncertainty in the model between 65.6 and 70.8% evaluated by Stamati et al. (2013) in a long term RothC simulation of C sequestration potential following conversion from cropland to set-aside.

4. Conclusions

Soil organic matter is a key soil component as it affects nearly all properties that are relevant for the agronomical and environmental functions of soils. SOM is important to guarantee the soil fertility needed to satisfy the increasing demand of food from the global world population and to offset GHG emissions and the consequent detrimental environmental consequences caused by climate change.

The significant losses of SOM recorded worldwide in the last decades have raised the concern of researchers and policy makers on the necessity to recover and increase SOM levels. In particular, soil C sequestration, i.e. the long-term (> 100 years) or permanent removal of CO_2 from the atmosphere into the soil, has been proposed as a valuable strategy to guarantee the agronomical and environmental functions of soils ecosystems. There are several soil management options that foster C sequestration and among these soil amendment is considered to be one of the more effective. The actual European legislation, promoting EOM recycling in agriculture, and the appearance of increasing amount of organic wastes from bioenergy processes have raised the attention of researchers to the need of optimizing EOM application to soil in order to increase its agronomical benefits and avoid potential detrimental environmental effects.

Soil organic C models represent a valuable tool for the optimization of soil amendment, for their capacity to predict future trends in soil organic C and the possibility to study different scenarios. However, there are no soil C models specifically developed to simulate C trends in amended soils or evaluate the C sequestration potential of different EOMs. In general, soil C models have not been extensively calibrated in EOM treated soils.

The above considerations represent the rationale from which originates the main aim of this study, that is to devise an easy and reliable procedure for the optimization of a dynamic C model to evaluate the C sequestration potential of EOM added to the soil at both local and national (Italy) scale.

For this purpose the RothC soil C model was either modified by introducing specific EOM pools and calibrated utilizing respiratory curves from laboratory incubation of amended soil and a procedure was devised for spatially explicit SOC modelling of amended soil under climate change.

The main outputs of this study were:

- the modified RothC model, considering discrete EOM pools with specific decomposition rate, is effective in simulating the net cumulative respiration from amended soil incubated under laboratory conditions
- utilizing a unique set of EOM parameters for EOM type resulted in a difference of less than 10% in the prediction of long term C evolution (100 years) of amended soil in comparison to a simulation performed with EOM specific parameters
- predicted climate change in the present century will speed up SOM decomposition leading to a generalized decrease in SOC. Despite the uncertainty associated with the different climate scenarios, the results clearly show that SOC in Italian soil will decrease significantly by 7.4%, on average, between 2001 and 2100
- results of long term (100 years) model simulations indicated that EOMs greatly differ for their soil C sequestration potential (range of annual rate of C sequestration potential 0.110 - 0.385 t C ha^{-1} y^{-1})
- soil C sequestration potential of compost applied for 100 years to all Italian agricultural land at a rate of 1 t C ha^{-1} y^{-1} and under climate scenario PCM B1 was 6.15 Mt C ha^{-1} y^{-1} corresponding to 4.6% of total annual GHG emissions in Italy
- spatial explicit modelling of amended soil indicated a high variability in long term (100 years) potential of SOC accumulation (1 order of magnitude) due to the combination of EOM type, environmental properties (soil, climate) and management options (land use and management)
- large scale spatial modelling of soil organic C can suggest ways to optimize resources by identifying the areas with the largest potential for EOM accumulation: 100 years of application of the whole compost produced in

Italy to the land with the smallest and largest potential for C sequestration resulted in a mean SOC increment of 27 and 55 t C ha^{-1}, respectively (i.e. 2-fold increment)

- spatially explicit modelling of SOC in amended soils could be useful to highlight the relative importance of the different factors in the SOC evolution observed: in the present study temperature had a major impact on determining SOC accumulation
- soil C modelling is amenable to simulate different scenarios of climate, land use and management and therefore can assist decision makers to develop strategies that favour C retention of EOMs.

The main innovative aspects of this work consist in:

- modification of the RothC model to improve the capacity of simulating SOC trends in amended soil
- parameterization of the modified RothC by fitting respiratory curves from short term laboratory incubation of soil amended with EOM of different origin and properties
- spatially explicit modelling of SOC in amended soil under climate change.

It has been shown by several authors that there are considerable differences in the turnover rates and substrate utilisation efficiencies of EOM between laboratory and field conditions. Consequently, the transfer of the optimized parameters resulting from laboratory study to field sites has to be done with caution. Hence, the potential of C sequestration of different EOMs evaluated with the procedure described in this study needs to be validated with results from long term experiments dealing with soil amendment with different EOMs. This step is essential to ensure the transferability to field conditions of the proposed procedure for the evaluation of soil C sequestration in amended soil and represents the main future development of the present work.

Nevertheless, the value of this study is relevant for the improvement of soil C modelling applied to soils amended with different EOMs. Even if the simulation results need to be validated with field data, the suggested conceptual changes to the model structure, such as the introduction of EOM separate pools and decomposition rates, may be directly transferable to field conditions. This highlights the importance of laboratory experiments on soil decomposition of EOM in providing useful information to improve the structure and the performances of existing models to simulate SOC trends in amended soils and to cover and understand main knowledge gaps in terms of environmental factors and soil processes that regulate EOM decomposition in the soil. Moreover, the results of the present laboratory based study quantify the relative differences of the different types of EOM in their potential to build up SOC stocks and therefore can be useful to identify EOM properties and environmental conditions more conducive to soil C sequestration.

Results of the present study highlight the importance of a narrower integration between laboratory incubation and field studies to enhance the capability of models to predict soil C sequestration potential of EOM and to adopt environmental and agricultural management options that favour soil C retention of EOMs.

The findings of this and similar studies will be useful to improve the reliability of soil C modelling as a valuable tool for farmers, researchers and policy makers interested to plan future land uses with the aim of increasing soil C sequestration, reducing GHG emissions and warranting the sustainability of agricultural ecosystems.

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