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Modification of the RothC model to simulate soil C mineralization of exogenous organic matter

Claudio Mondini[1], Maria Luz Cayuela[2], Tania Sinicco[1], Flavio Fornasier[1], Antonia Galvez[3], and Miguel Angel Sánchez-Monedero[2]

[1]Consiglio per la Ricerca in Agricoltura e l'Analisi dell'Economia Agraria (CREA), Branch Office of Gorizia, Via Trieste 23, 34170 Gorizia, Italy
[2]Centro de Edafología y Biología Aplicada del Segura (CEBAS-CSIC), Department of Soil and Water Conservation and Waste Management, Campus Universitario de Espinardo, Apartado de Correos 164, 30100 Espinardo, Murcia, Spain
[3]Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR), Avenida de las Palmeras 4, 18100 Armilla, Granada, Spain

Correspondence to: Claudio Mondini (claudio.mondini@crea.gov.it)

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Abstract. The development of soil organic C (SOC) models capable of producing accurate predictions for the long-term decomposition of exogenous organic matter (EOM) in soils is important for the effective management of organic amendments. However, reliable C modeling in amended soils requires specific optimization of current C models to take into account the high variability in EOM origin and properties. The aim of this work was to improve the prediction of C mineralization rates in amended soils by modifying the RothC model to encompass a better description of EOM quality.

The standard RothC model, involving C input to the soil only as decomposable (DPM) or resistant (RPM) organic material, was modified by introducing additional pools of decomposable (DEOM), resistant (REOM) and humified (HEOM) EOM. The partitioning factors and decomposition rates of the additional EOM pools were estimated by model fitting to the respiratory curves of amended soils. For this task, 30 EOMs from 8 contrasting groups (compost, anaerobic digestates, sewage sludge, agro-industrial waste, crop residues, bioenergy by-products, animal residues and meat and bone meals) were added to 10 soils and incubated under different conditions.

The modified RothC model was fitted to C mineralization curves in amended soils with great accuracy (mean correlation coefficient 0.995). In contrast to the standard model, the EOM-optimized RothC was able to better accommodate the large variability in EOM source and composition, as indicated by the decrease in the root mean square error of the simulations for different EOMs (from 29.9 to 3.7 % and 20.0 to 2.5 % for soils amended with bioethanol residue and household waste compost, respectively). The average decomposition rates for DEOM and REOM pools were 89 and 0.4 yr^{-1}, higher than the standard model coefficients for DPM (10 yr^{-1}) and RPM (0.3 yr^{-1}).

The results indicate that the explicit treatment of EOM heterogeneity enhances the model ability to describe amendment decomposition under laboratory conditions and provides useful information to improve C modeling on the effects of different EOM on C dynamics in agricultural soils.

Future research will involve the validation of the modified model with field data and its application in the long-term simulation of SOC patterns in amended soil at regional scales under climate change.

1 Introduction

Exogenous organic matter (EOM) is organic material of biological origin that is applied to cultivated fields for the purpose of growing crops, improving soil quality and restoring or reclaiming land for future use (Marmo et al., 2004). Agricultural utilization of EOM is considered an effective way of restoring losses of soil organic matter (SOM) and offsetting soil degradation and climate change (Lal, 2004; Smith, 2004a, b). The reliable management of amendment requires thorough knowledge of EOM mineralization patterns, as the rate of EOM decomposition is critical in determining its effects on soil properties, nutrient cycling and C accumulation.

The prediction of EOM transformation in soil is a very difficult task as EOM mineralization is an extremely complex process that depends on several factors, such as EOM biochemical composition, EOM stabilization treatment, size and activity of soil microorganisms and pedoclimatic conditions (Franzluebbers, 2004). In particular, EOM composition is extremely variable, since organic residues may have plant or animal origins and may have undergone different stabilization treatments.

Process-oriented soil organic C (SOC) modeling represents a reliable solution for the efficient management of EOM amendment. It offers a unique means of addressing the high variability in the properties of EOM and pedoclimatic conditions and the complexity of mechanisms and factors affecting C mineralization in the field. The effectiveness of models in predicting long-term C changes in amended soils has been recently supported by the findings of Karhu et al. (2012), Noirot-Cosson et al. (2016), Peltre et al. (2012) and Plaza et al. (2012), who found good correlations between modeled and measured C stocks for different types and amounts of EOM. Some examples of C models that have been utilized to simulate SOC trends in amended soils at field scale are reported in Table 1.

As the composition and properties of amendments are the most important factors controlling their decomposition (Cavalli et al., 2014; Do Nascimento et al., 2012; Karhu et al., 2012), several authors have highlighted the importance of a proper characterization of EOM to decrease the uncertainty in model predictions of SOC trends in amended soils. Regarding the relevance of organic matter (OM) quality in SOC modeling, most 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). Exogenous organic matter is composed of substances with different properties and distinct levels of accessibility to microorganisms. The rate of EOM mineralization is mainly determined by the combination of quality and accessibility and the response intensity to environmental factors of substrates with diverse characteristics. Therefore, an accurate partitioning of EOM into a number of discrete pools and an estimation of their functional characteristics (i.e., initial C and N contents, decomposition rate) is of great importance to improve model predictions (Sierra et al., 2011; Thuries et al., 2001). Generally, C models identify two or three pools of EOM, while their decomposition rates can be fixed or variable according to the specific EOM. However, rigorous methods for establishing entry pools that account for the diversity of EOM have not been developed to date (Peltre et al., 2012). This represents one of the major problems for a reliable C modeling 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 with the C modeling of amended soils.

Several approaches have been proposed to determine EOM pool partitioning factors and decomposition rates; to date, no satisfactory method for such characterization has been found. The main approaches that have been devised so far are based on the chemical or kinetic subdivision of EOM. Partitioning based on the chemical properties of EOM is generally performed by stepwise chemical digestion (SCD) and near-infrared reflectance spectroscopy (NIRS) (Borgen et al., 2011; Peltre et al., 2011). Such methods are relatively rapid and simple, but the main disadvantage is that these operationally defined fractions do not precisely correspond to the model pools. An alternative to chemical analysis is to characterize EOM pools by the direct fitting of simulated CO_2 emissions to measured respiration curves 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 (Borgen et al., 2011; Trinoustrot et al., 2000). It is appealing because it allows for the simultaneous estimation of both pool size and decomposition rate (Scharnagl et al., 2008) that can be directly used in process-oriented models (Batlle-Aguilar et al., 2011). EOM pool characterization by fitting the CO_2 respiration from incubation was successfully achieved for NCSOIL (Corbeels et al., 1999; Gabrielle et al., 2004; Noirot-Cosson et al., 2016), CANTIS (Garnier et al., 2003; Parnaudeau, 2005) and TAO (Pansu and Thuries, 2003) models and was also performed by several other researchers (Antil et al., 2011; Borgen et al., 2011; Cavalli and Bechini, 2011). In general, the results of previous work on EOM characterization for soil C model calibration show that kinetically defined partitioning enhances the predictions of mechanistic models compared to operationally defined fractions (Borgen et al., 2011; Gabrielle et al., 2005); also, the wider applicability of EOM characterization by SCD and NIRS is obtained at the expense of accuracy.

To date, there are no soil C models specifically developed to evaluate the C accumulation potential of amended soils, with the exception of the TAO model (transformation of added organic matter; Pansu and Thuries, 2003). Furthermore, C models have not been extensively calibrated in amended soils, and the quality of organic inputs is an aspect that has not been adequately considered and needs further investigation (Parshotam et al., 2001). An example of this inadequacy is represented by the Rothamsted carbon model (RothC), one of the most well-known and widely used models simulating SOC trends (Jenkinson et al., 1991; McGill, 1996) because it requires relatively few and easily available parameters and input data. Although it has also been used on a few occasions to make predictions following the application of EOM (Yokozawa et al., 2010), its actual structure suggests that the model is not particularly suited for C simulation in amended soils. Carbon inputs to the model

Table 1. Soil C models utilized for C simulation in amended soils.

Model	EOMs	Yearly application rate	Simulation period (yr)	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	Houot et al. (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. (2005a)
DAISY	Compost	5–10 t dm ha^{-1}	50	Stöppler-Zimmer et al. (1999)
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	10–25 t dm ha^{-1}	4	Gabrielle et al. (2005)
NCSOIL	FYM, urban waste compost	2 t C ha^{-1}	13	Noirot-Cosson et al. (2016)
Cantis	WS	8 t dm ha^{-1} (1.2 g C kg^{-1})	1	Garnier et al. (2003)
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. (2006)
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)
Three-pool model	Organic compost	20–40 % w : w	5	Vidal-Beaudet et al. (2012)

EOM: exogenous organic matter; FYM: farmyard manure; WS: wheat straw; SS: sewage sludge; MSW: municipal solid waste; fw: fresh weight; dm: dry matter; w: weight.

are divided into decomposable plant material (DPM) and resistant plant material (RPM) pools, each characterized by a specific decay rate. This implies that the model does not allow C inputs derived from crop residues to be differentiated from EOM. Secondly, the quality of the OM entering the soil is only defined by the partitioning between decomposable and resistant organic materials, as the decomposition rates are fixed and constant for each pool. The insensitivity of the actual model to the variation in the quality of inputs was shown by Falloon (2001). In fact, RothC allows only a specific EOM, namely farmyard manure, to be treated separately from crop residues, but its partition coefficients and decomposition rates are fixed. This model behavior contrasts with the large variability in the decomposition rate of different EOMs and the evidence that model predictions can be improved by the identification of an EOM-specific decomposition rate, as demonstrated by Mueller et al. (2003) with the DAISY model. Similarly to RothC, the original DAISY model involves two pools of added EOM with decomposition rates that are constant for a wide range of added organic materials. Mueller et al. (2003) showed that adjusting the decomposition rates for each EOM significantly increased the model capacity to predict C mineralization in amended soils.

The aim of this study was to devise an easy and effective procedure for the optimization of the RothC model to improve the prediction of EOM-C mineralization as a first step in model development for reliable SOC simulation in amended soils. Such a procedure is based on two steps:

- modification of RothC involving the introduction of additional entry pools of EOM;
- and the utilization of information derived from laboratory incubation experiments to define the size and decomposition rates of the additional EOM pools.

2 Materials and methods

2.1 Incubation experiments

2.1.1 Soils used for incubation

The soils used for the incubation experiments were sampled from agricultural areas in the Mediterranean, specifically in northern Italy and southern Spain. The soils were sampled at 5–20 cm of depth with an auger, and several subsamples were pooled together to obtain a representative sample. The location and main physicochemical characteristics of the soils are reported in Table 2.

Table 2. Main physicochemical characteristics of the soils used for incubation.

Location	Country	Soil code	Soil use	Sand (%)	Silt (%)	Clay (%)	pH	$CaCO_3$ ($g\,kg^{-1}$)	SOC ($g\,kg^{-1}$)	N_{TOT} ($g\,kg^{-1}$)	SOC / N_{TOT}	C_{mic} ($\mu g\,g^{-1}$)
S. Martino	Italy	SM	Arable	69	28	3	8.3	740	10.5	1.2	8.8	114
Gorizia	Italy	GO	Meadow	37	48	15	7.8	46	25.4	2.4	10.6	795
Bueriis	Italy	BU	Arable	6.0	48	46	7.0	–	32.0	4.5	7.1	269
Lodi	Italy	LO	Meadow	67	21	12	6.7	–	22.0	2.1	10.5	205
Reana	Italy	PE	Arable	55	28	17	6.5	–	15.9	1.2	13.3	118
Ribis	Italy	RI	Arable	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.

The soils were sieved moist through a 2 mm aperture grid and stored (5 °C) until the beginning of the experiments. Before the start of the trials, the soils were preconditioned by incubation under aerobic conditions for 7 days at the same temperature and water content adopted for the experiments.

The range of soils showed a widely different texture and pH. Apart from Gorizia, Bueriis and Lodi, the samples were characterized by low contents of organic C and N and a small pool of soil microbial biomass.

2.1.2 EOMs used for incubation

In total, 30 different EOMs were utilized for the incubation experiments. They were considerably distinct in terms of origin, chemical composition and the stabilization or transformation processes to which they were subjected. According to the above properties, they were classified into nine different EOM groups (Table 3); their main features and properties are reported in Table 4. Most of them presented an alkaline pH, while the organic waste with a pH < 5.2 included 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 86.0 %. Total N varied between 0.3 and 17 %, mainly depending on the EOM origin. Generally, vegetal-derived EOM as vine shoot compost, household waste compost, green waste compost, crop residues, two-phase olive mill waste and green waste biochar showed low levels of total N (0.3–2.3 %). On the other hand, EOM of animal origin (meat and bone meals, blood meal and horn and hoof meal) showed high values of N (8.2–17.0 %). As a consequence of the variability in C and N content, the C / N ratio ranged between 3 (horn and hoof meal), 200 (wheat straw) and 345 (green waste biochar). The differences among EOMs were also highlighted by the content of easily available C (WSC) and N (WSN), varying from 0.1 to 203 $g\,kg^{-1}$ and from 0 to 37.9 $g\,kg^{-1}$ for WSC and WSN, respectively. The EOMs showing the highest contents of easily degradable C and N were bioethanol residue and blood meal. In general, high concentrations of mineral N (NO_3^- and NH_4^+) were found for liquid digestates. Conversely, the bioenergy by-products two-phase olive mill waste and biochar were characterized by very low amounts of NO_3^-.

2.1.3 Amended soil 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 preconditioned moist soil samples (50 g dry weight basis) at the beginning of the incubation and kept under aerobic conditions in the dark in 130 mL plastic jars in a thermostatic chamber. In the case of liquid residue, soil was preincubated at such a humidity that after EOM addition they were brought to the moisture content required for incubation. Unamended soils were also included as a control. Each treatment was replicated at least twice. The moisture levels in the jars were checked weekly by measuring weight loss, and deionized water was added when necessary to maintain constant moisture. Incubation was performed for a range of temperatures (10–30 °C), soil moisture (20–40 % water holding capacity, WHC), EOM rate (0.1–0.75 %) and time (7–37 days). Details on the incubation conditions (soil type, rate of residue, soil water content, temperature and incubation time) are reported in Tables S1–S6 in the Supplement. More than 30 incubation treatments (each involving 7 treatments) were performed, utilizing 30 different residues and 10 soils with contrasting properties for a total of 224 treatments.

2.1.4 Soil CO_2 measurement

CO_2 evolution was measured every 6 h on aliquots of moist soil by means of an automated system for gas sampling and measurement (Mondini et al., 2010; Fig. 1). The “apparent” net C mineralization (C derived from the residues) was calculated as the difference between the CO_2-C emitted by the

Table 3. Description of the exogenous organic matter (EOM) used for incubation.

EOM group	EOM group code	EOM type	EOM type description	EOM type code
Compost	CO	Vine shoot compost	compost from vine tree pruning	VSC
		Household waste compost	compost from the separate collection of household organic waste	HWC
		Green waste compost	compost from green waste	GWC
		CC + WS + MM II_3	3-day-old compost from a mixture of cotton cardings, wheat straw and meat and bone meal	CMC II
		CC + WS + MM III_9	9-day-old compost from a mixture of cotton cardings, wheat straw and meat and bone meal	CMC III
		CC + WS + MM M_92	92-day-old compost from a mixture of cotton cardings, wheat straw and meat and bone meal	CMC M
		CC + WS + BLM + HHM II_3	3-day-old compost from a mixture of cotton cardings, wheat straw, blood meal and hoof and horn meal	CBC II
		CC + WS + BLM + HHM III_9	9-day-old compost from a mixture of cotton cardings, wheat straw, blood meal and hoof and horn meal	CBC III
		CC + WS + BLM + HHM IV_21	21-day-old compost from a mixture of cotton cardings, wheat straw, blood meal and hoof and horn meal	CBC IV
		CC + WS + BLM + HHM M_92	92-day-old compost from a mixture of cotton cardings, wheat straw, blood meal and hoof and horn meal	CBC M
Bioenergy by-products	BE	Bioethanol residue	wheat starch by-product from bioethanol production	BR
		Rapeseed meal	meal from biodiesel production	RSM
Anaerobic digestates	AD	Pig slurry digestate	anaerobic digestate of pig slurry	PS
		TPOMW + manure digestate	mesophilic anaerobic digestate of two-phase olive mill waste and liquid manure	OW 1
		TPOMW + manure digestate (55 °C)	thermophilic anaerobic digestates of two-phase olive mill waste and liquid manure	OW 2
		Liquid manure digestate	anaerobic digestate of liquid manure	OW 3
		TPOMW digestate	anaerobic digestate of two-phase olive mill waste	OW 4
Meat and bone meals	MM	Bovine MM 1	bovine meat and bone meal	BV1
		Bovine MM 2	bovine meat and bone meal	BV2
		Swine MM	swine meat and bone meal	SW
		Mixed swine bovine MM	mixture of swine and bovine meat and bone meal	SB
		Defatted bovine MM	defatted bovine meat and bone meal	DE
Animal residues	AR	Hydrolyzed leather	organic fertilizer derived from hydrolyzed animal proteins	HL
		Blood meal	organic fertilizer from spray drying at low temperatures fresh whole blood from animal processing plants	BLM
		Horn and hoof meal	organic fertilizer produced by drying horns and hooves from animal processing plants	HHM
Crop residues	CR	Cotton cardings	waste derived from the process of preparing cotton fibers (*Gossypium* spp., L.) for spinning	CC
		Wheat straw	winter wheat (Triticum aestivum L.) straw collected after harvesting	WS
Agro-industrial waste	AW	Two-phase olive mill waste	semisolid sludge generated during the extraction of olive oil in the two-phase centrifugation system	TPOMW
Sewage sludge	SS	Wastewater sludge	sewage sludge from an urban wastewater treatment plant	WW
Biochars	BC	Green waste biochar	biochar produced by continuous slow pyrolysis of green waste at 550 °C	GWB

CC: cotton cardings; WS: wheat straw; MM: meat and bone meal; BLM: blood meal; HHM: hoof and horn meal; TPMOW: two-phase olive mill waste. For compost, the Roman numerals refer to stages in the process, and the numbers refer to days of composting; M: mature compost.

Table 4. Main chemical characteristics of the exogenous organic matter (EOM) used for incubation.

EOM group	EOM group code	EOM type	EOM type code	pH	OM (%) (%)	TOC (%) N_{TOT}	N_{TOT} ($g\,kg^{-1}$)	TOC / ($g\,kg^{-1}$)	WSC ($mg\,kg^{-1}$)	WSN ($mg\,kg^{-1}$)	NH_4^+	NO_3^-
Compost	CO	Vine shoot 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 + MM II_3	CMC II	7.9	90.6	42.7	1.6	27.2	23.1	2.7	627	2397
		CC + WS + MM III_9	CMC III	7.9	89.3	41.3	2.1	19.6	28.3	3.7	96	2821
		CC + WS + MM 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
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 digestate	OW 1	8.2	75.8	43.6	3.4	13.0	23.1	1.78	17 322	11 048
		TPOMW + manure (55 °C) digestate	OW 2	8.1	76.7	48.7	3.5	13.9	25.1	1.81	20 118	14 318
		Liquid manure digestate	OW 3	8.2	68.6	44.1	3.1	14.5	13.6	0.94	690	7902
		TPOMW digestate	OW 4	7.9	76.9	49.1	3.0	16.1	17.7	1.07	18 744	10 905
Meat and bone meals	MM	Bovine MM 1	BV1	6.5	70.9	38.5	8.4	4.6	52.1	12.4	631	1692
		Bovine MM 2	BV2	6.3	65.5	33.9	8.2	4.1	35.7	9.0	410	1314
		Swine MM	SW	6.7	78.6	41.4	9.0	4.6	114.5	29.0	530	4721
		Mixed swine bovine MM	SB	5.9	81.8	43.1	9.4	4.6	60.5	17.1	359	4165
		Defatted bovine MM	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 waste	AW	Two-phase olive mill waste	TPOMW	5.3	94.1	53.0	1.3	41.1	4.1	1.1	122	0
Sewage sludge	SS	Wastewater sludge	WW	6.8	70.9	38.4	4.8	8.0	7.97	1.64	1677	2286
Biochars	BC	Green waste biochar	GWB	7.5	98.3	86.3	0.3	345	0.1	0.0	17	0.4
			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	0.0
			maximum	8.5	98.3	86.3	17.0	345	203	37.9	20 118	14 318

EOM: exogenous organic matter; OM: organic matter; TOC: total organic C; N_{TOT}: total N; WSC: water soluble C; WSN: water soluble N; CC: cotton cardings; WS: wheat straw; MM: meat and bone meal; BLM: blood meal; HHM: hoof and horn meal; TPMOW: two-phase olive mill waste.
For compost, the Roman numerals refer to stages in the process, and the numbers refer to days of composting; M: mature compost.
For EOM group and type codes, refer to Table 3.

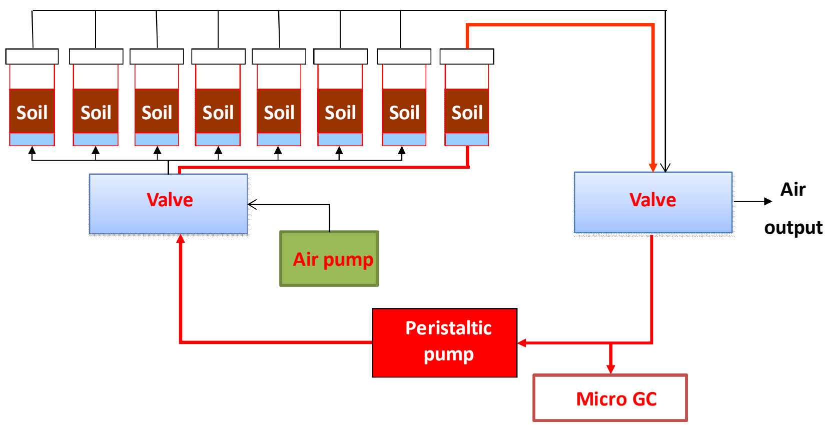

Figure 1. Diagram of the automated chromatographic system for soil CO_2 sampling and measurement.

EOM-amended soil and that produced over the same period by the unamended control soil.

2.2 RothC model modification and optimization

2.2.1 Description of the RothC model

The Rothamsted carbon model (RothC) was one of the first multi-compartmental models to be developed (Coleman and Jenkinson, 1996; Jenkinson and Rayner, 1977) and has been evaluated and optimized for a variety of ecosystems, including croplands, grasslands and forests (Coleman et al., 1997; Falloon and Smith, 2002; Smith et al., 1997), and in various climate regions, including Mediterranean and semiarid environments (Farina et al., 2013; Francaviglia et al., 2012; Skjemstad et al., 2004).

RothC describes the dynamics of SOM by splitting it into five compartments with different decomposition (or kinetic) rate constants (K), namely decomposable plant material (DPM; $K = 10\,\mathrm{yr}^{-1}$), resistant plant material (RPM; $K = 0.30\,\mathrm{yr}^{-1}$), soil microbial biomass (BIO; $K = 0.66\,\mathrm{yr}^{-1}$), humified organic matter (HUM; $K = 0.02\,\mathrm{yr}^{-1}$) 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 of time is therefore constant and equal to K.

The model considers two main types of C inputs to the soil: crop residues and farmyard manure. Crop residues are divided into the compartments DPM and RPM with partitioning factors (f) depending on the nature of the inputs. The partitioning of FYM into pools is fixed and corresponds to DPM 49 %, RPM 49 % and HUM 2 %. At each monthly time step, part of each C input pool 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 rate constants are modified at each period by three multipliers depending on the temperature, the moisture deficit of the soil and the presence or absence of vegetation. Due to extensive previous evaluations of model performance (e.g., Smith et al., 1997), no further validation of the current model is presented here.

2.2.2 Modification of the RothC model

The standard model considers C input to the system by EOM only as farmyard manure with fixed partitioning factors. In the present study, a wide range of EOMs with different characteristics was added to the soil. In agreement with the procedure adopted by Peltre et al. (2012) and Falloon (2001) for RothC simulation in amended soils, in a first stage of the study the fitting of the RothC model to the respiratory curves was assessed by varying the partitioning factors of EOM pools. To enable model fitting of the respiration data from 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.

A total of 86 simulations were performed considering soil amended with residues from different EOM groups. All the simulations were run as differences from the control treatment (i.e., only the CO_2 derived from EOM was simulated) utilizing a time step of $0.25\,\mathrm{d}^{-1}$. 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. Hence, the fate of the total soil C is the sum of the fate of the C from the different pools. Consequently, the difference in CO_2 evolution between soils with and without EOM application corresponds to the CO_2 derived from the additional input of OM to 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).

Model fitting to the measured values was conducted by changing individual partition coefficients (f_{DPM}, f_{RPM}, f_{HUM}) for the EOM pools in a stepwise iteration using Excel Solver with the Newton method until maximum agreement between the measured and simulated amounts of CO_2 was achieved, assuming as a criteria the smallest sum of squared residuals (SSR). A humified pool was attributed only to residues characterized by the presence of stable OM, such as compost, anaerobic digestates and olive mill waste. For each EOM and incubation condition, an "individual" fitting procedure was used to minimize the difference between the observed and simulated values. The three parameters were optimized simultaneously, considering the following constraints in order to avoid biologically unrealistic parameter estimates:

$$f_{DPM} + f_{RPM} + f_{HUM} = 1,$$
$$f_{HUM} < 0.3 \quad \text{for anaerobic digestates and agro-industrial waste.}$$

The partitioning factor for HUM was set to a maximum of 0.3 for digestates and agro-industrial waste according to the values found by Cavalli and Bechini (2011, 2012) after model calibration for soil amended with pig slurries stored under anaerobic conditions before use.

The capacity of the standard model to fit the C mineralization curves of amended soils was assessed by calculating the root mean square error (RMSE), i.e., the total difference between the measured and simulated values expressed as a percentage of the mean observed values.

As the results of the fitting procedure were not acceptable due to the high values of RMSE (see Sect. 3.2), a modification to the model source code was performed to improve the model ability to describe the respiratory curves of amended soil. The proposed modification involves the inclusion of two additional pools of EOM (decomposable EOM, DEOM; resistant EOM, REOM), each characterized by a specific and variable rate of decomposability. For organic residues characterized by the presence of stable OM (i.e., compost, anaerobic digestates and agro-industrial waste), a third EOM pool is introduced (humified EOM, HEOM), which is directly incorporated into the soil HUM pool. EOM added to the soil is split into the DEOM, REOM and HEOM pools according to the partitioning factors f_{DEOM}, f_{REOM} and $f_{HEOM} = 1 - f_{DEOM} - f_{REOM}$. DEOM and REOM pools decompose with specific decomposition rates (K_{DEOM} and K_{REOM}) that may be different from those of plant residues. HEOM is directly incorporated into the HUM pool and decomposes with the same decomposition rate ($K = 0.02\,\mathrm{yr}^{-1}$). Decomposed DEOM and REOM are split in CO_2, BIO and HUM. The proportion of decomposed DEOM and REOM that goes to CO_2, BIO and HUM is regulated in the same way as the entry pools of plant residue. Below is a mathematical representation of the modified model as a set of differential equations:

$$\mathrm{dDPM}/\mathrm{d}t = f_{DPM}P - K_{DPM}\mathrm{DPM}, \quad (1)$$
$$\mathrm{dRPM}/\mathrm{d}t = (1 - f_{DPM})P - K_{RPM}\mathrm{RPM}, \quad (2)$$
$$\mathrm{dDEOM}/\mathrm{d}t = f_{DEOM}E - K_{DEOM}\mathrm{DEOM}, \quad (3)$$
$$\mathrm{dREOM}/\mathrm{d}t = f_{REOM}E - K_{REOM}\mathrm{REOM}, \quad (4)$$
$$\mathrm{dBIO}/\mathrm{d}t = \alpha K_{DPM}\mathrm{DPM} + K_{RPM}\mathrm{RPM} + K_{DEOM}\mathrm{DEOM} + K_{REOM}\mathrm{REOM} + K_{HUM}(\mathrm{HUM} + (1 - f_{DEOM} - f_{REOM})E) - (1-\alpha)K_{BIO}\mathrm{BIO}, \quad (5)$$
$$\mathrm{dHUM}/\mathrm{d}t = \beta(K_{DPM}\mathrm{DPM} + K_{RPM}\mathrm{RPM} + K_{DEOM}\mathrm{DEOM} + K_{REOM}\mathrm{REOM} + K_{BIO}\mathrm{BIO}) - (1-\beta)K_{HUM}(\mathrm{HUM} + (1 - f_{DEOM} - f_{REOM})E), \quad (6)$$
$$\mathrm{dIOM}/\mathrm{d}t = 0. \quad (7)$$

DPM is decomposable plant material, RPM is resistant plant material, HUM is humified organic matter, BIO is soil microbial biomass, DEOM is decomposable EOM, REOM is resistant EOM and IOM is inert organic matter.

f_{DPM} is the partitioning factor for DPM, f_{DEOM} is the partitioning factor for DEOM and f_{REOM} is the partitioning factor for REOM.

K_{DPM} is the decomposition rate for DPM, K_{RPM} is the decomposition rate for RPM, K_{BIO} is the decomposition rate for BIO, K_{HUM} is the decomposition rate for HUM, K_{DEOM} is the decomposition rate for DEOM and K_{REOM} is the decomposition rate for REOM.

P is plant (crop residue) input, E is EOM input, α is the transfer coefficient to BIO pool and β is the transfer coefficient to HUM pool.

The C flow of the standard and modified model is reported in Fig. 2.

An Excel version of the modified model was then utilized to perform model fitting for the same 86 respiratory curves previously simulated with the standard model. The procedure was the same with one exception: the model fitting was conducted by simultaneously changing the partitioning factors (f_{DEOM}, f_{REOM}, f_{HEOM}) and decomposition rate constants (K_{DEOM}, K_{REOM}) of the different pools of EOM, considering the following constraints in order to avoid biologically unrealistic parameter estimates:

$$f_{DEOM} + f_{REOM} + f_{HEOM} = 1,$$
$$f_{HEOM} < 0.3 \quad \text{for anaerobic digestates and agro-industrial waste,}$$
$$K_{REOM} > 0.15\,\mathrm{yr}^{-1},$$
$$K_{DEOM} < 230\,\mathrm{yr}^{-1}.$$

The criteria for setting the partitioning factor for HEOM (f_{HEOM}) to a maximum of 0.3 in the case of digestates and agro-industrial waste was the same reported for the standard model. The minimum K_{REOM} value was set at $0.15\,\mathrm{yr}^{-1}$ according to the RothC modification proposed by Skjemstad

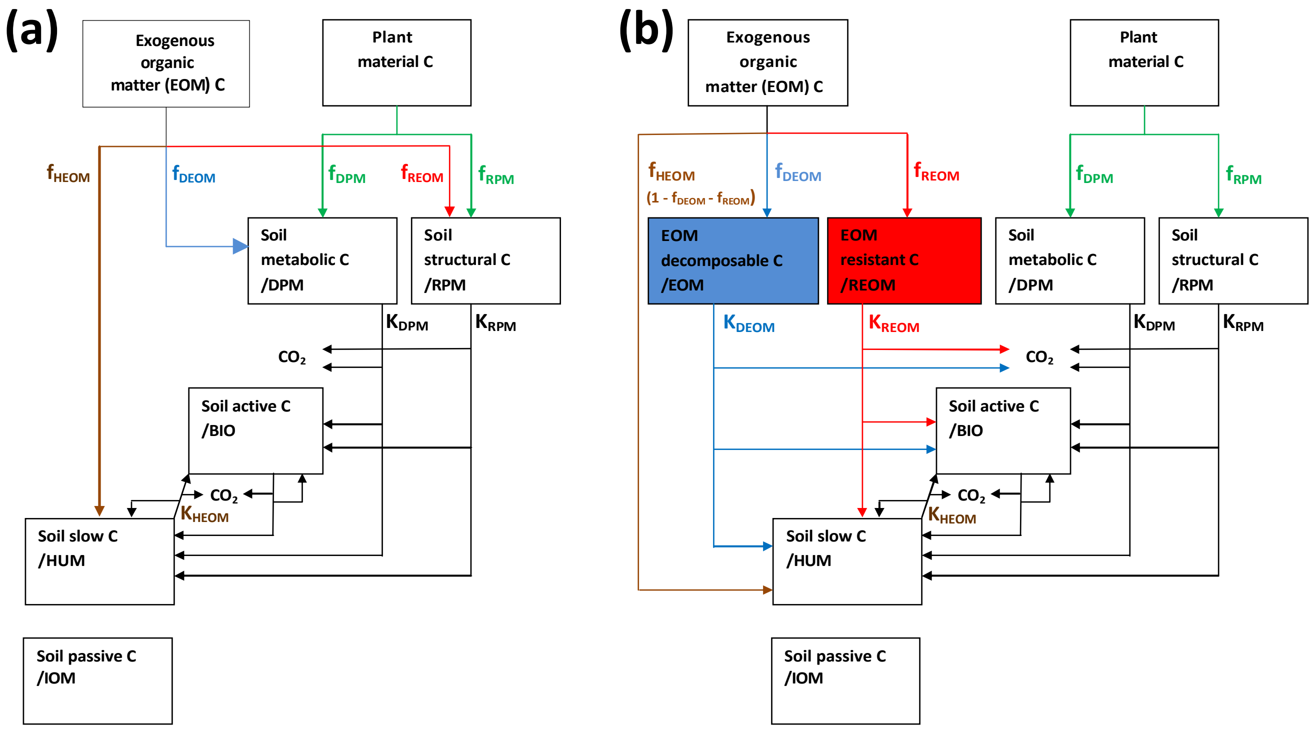

Figure 2. Structure of the standard **(a)** and modified **(b)** RothC model. DPM: decomposable plant material; RPM: resistant plant material; EOM: exogenous organic matter; DEOM: decomposable EOM; REOM: resistant EOM; HEOM: humified EOM; BIO: soil microbial biomass; HUM: humified soil organic matter; IOM: inert organic matter; f: partitioning factor; K: decomposition constant rate (yr^{-1}).

et al. (2004). K_{DEOM} was set to a maximum of $230\,\mathrm{yr}^{-1}$ in agreement with the maximum values found by Thuries et al. (2001) utilizing a three-EOM-pool model for 14 different plant residues, compost and manures. This constraint was not considered in the case of blood meal as the respiration curves presented a very steep initial phase; this is an indication of a decomposable pool characterized by a high degree of decomposability. This is supported by the results of Thuries et al. (2001) who found a decomposition rate constant of $243\,\mathrm{yr}^{-1}$ for the labile pool of animal residues.

Generally, increasing the number of variable parameters increases the precision of the model at the expense of its accuracy and generality (Snipes and Taylor, 2014). The Akaike information criterion (AIC) was developed as an aid to compare and select among different models (Symonds and Moussalli, 2011). It takes into account how well the model fits the data, but it penalizes models with greater numbers of fitted parameters. Therefore it selects the model that has a minimum number of parameters while fitting the data well. In order to select one of the two model structures, AIC was calculated according to Symonds and Moussalli (2011) as

$$\mathrm{AIC} = n\left[\ln\left(\frac{\mathrm{RSS}}{n}\right)\right] + 2k, \tag{8}$$

where n is the number of cases, RSS is the residual sum of squares and k is the number of variable parameters + 1.

According to Symonds and Moussalli (2011) a modified version of the index (corrected AIC, AICc) was calculated because of the small sample size in the present work ($n/k < 40$, where n is the number of cases and k is the number of fitted parameters in the most complex model):

$$\mathrm{AICc} = \mathrm{AIC} + \frac{2k\,(k+1)}{n-k-1}. \tag{9}$$

Further associated statistics to assess the relative strengths of each candidate model were calculated as suggested by Snipes and Taylor (2014):

$$\Delta\mathrm{AICc} = \mathrm{AICc}_{(i)} - \mathrm{AICc}_{\mathrm{best}}, \tag{10}$$

where $\mathrm{AICc}_{(i)}$ is AICc of method (i) and $\mathrm{AICc}_{\mathrm{best}}$ is the lowest AIC value.

ΔAICc is a measure of each model with respect to the best model (model with the lowest AICc). Mazerolle (2006) indicates the following interpretation of this index: $\Delta\mathrm{AICc} < 2$ suggests substantial evidence for the model, and values between 3 and 7 indicate that the model has considerably less support. A value > 10 indicates that the model is very unlikely.

$$\begin{aligned}\mathrm{ER}_{(i)} &= \text{evidence ratio}\\ &= \exp\left(-0.5 \times \Delta\mathrm{AICc}_{\mathrm{best}}\right) / \exp\left(-0.5 \times \Delta\mathrm{AICc}_{(i)}\right)\end{aligned} \tag{11}$$

$$\mathrm{LER}_{(i)} = \mathrm{Log}_{10}(\mathrm{ER}_{(i)}) \quad (12)$$

LER provides an indication of how much better the best model, i.e., the model with the lowest AICc, is in approximating the true data compared to another model. Snipes and Taylor (2014) set levels of evidence for selecting the model with the lowest AICc of "substantial", "strong" and "decisive", corresponding to LERs between model probabilities greater than 0.5, 1 and 2, respectively.

2.2.3 Optimization of the modified RothC model

In the following stage of the study, the modified model was applied to the whole data set consisting of 224 cumulative respiration curves from amended soils incubated under different conditions. Biochar-amended soils ($n = 4$) were excluded from the procedure of parameter estimation due to very low values of CO_2-C emissions resulting in statistically non-robust respiration curves. Optimization was performed as described in the previous sections by finding the best combination of variable parameters that results in the best fitting of the respiratory curve.

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 and Smith, 2007). The total difference between the measured and simulated values, expressed as a percentage of the mean observed values, was considered by calculating the root mean square error (RMSE). The lower limit for RMSE is zero, which denotes no difference between the measured and simulated values. The association between the simulated and measured values (i.e., the percentage of the total variance in the observed data that is explained by the predicted data) was evaluated by the sample correlation coefficient (R). 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. The consistent errors or bias in the model was evaluated by the mean difference between the measured and simulated data (M). Because M does not include a square term, simulated values above and below the measurements cancel out, so any inconsistent errors are ignored.

3 Results

3.1 EOM soil mineralization

As an example of the rate of CO_2 mineralization from soil amended with different EOMs, Fig. 3a shows the dynamics of CO_2 evolution from the Llano de la Perdiz soil. The range and mean values of net C mineralization for the different EOM groups, as defined in the "Materials and Methods" section, are reported in Table 5, which summarizes the results from all the incubation experiments performed utilizing different conditions and incubation carried out under standard laboratory conditions (20 °C, 40 % WHC, 0.5 % application rate and a 30-day incubation period).

Considering all the incubation experiments performed, the extra CO_2-C varied in the range of 0.01–38.6 % of the added EOM-C (Table 5). According to the mean values of net C mineralization obtained under standard laboratory conditions, the different EOM groups can be ranked as follows (values in parentheses are the percentage of added C emitted as CO_2-C): biochars (0.02 %) < composts (3.0 %) < anaerobic digestates (4.0 %) < sewage sludge (4.8 %) < agro-industrial waste (6.3 %) < crop residues (10.4 %) < bioenergy by-products (12.8 %) < animal residues (16.8 %) < meat and bone meals (21.3 %).

For compost, EOM mineralization ranged from 0.9 to 11.1 % with a mean value of 3.7 % (Table 5). The total extra CO_2-C evolving from the soils amended with meat and bone meals ranged between 7.8 and 38.6 %, while for bioenergy by-products net CO_2-C production was in the range of 6.9–16.8 %. Extremely low values of C mineralization (0.01–0.04 %) were recorded for biochar-amended soil (Table 5). A significant relationship between the cumulative net CO_2-C of different EOM groups and chemical properties was found only for water soluble N ($r^2 = 0{,}70$; $P < 0.01$).

3.2 Modification of the model and optimization with incubation data

The results of the preliminary phase of the study, in which the possibility to fit soil respiratory curves using the standard model and vary the partition coefficients of EOM was investigated, are shown in Table 6, which reports the mean RMSE values for different EOM groups. In general, the fitting obtained with the standard model was not satisfactory with an average RMSE (i.e., the percentage of error between the measured and simulated values) of 21.6 % for the 86 examined incubation treatments and a maximum of 27 % in the case of bioenergy by-products. According to Smith and Smith (2007), an RMSE value lower than 10 % could represent a threshold for an acceptable simulation for a particular purpose. Consequently, the model was modified as described in Sect. 2.2.2 and the fitting procedure was performed by simultaneously varying the partitioning factors and decomposition rates of EOM. The results showed a dramatic increase in the precision of the model with an average RMSE of 2.9 % (Table 6). The calculation of AIC and related statistics (delta AICc, ΔAICc; logarithm of evidence ratio, LER) was performed to evaluate whether the increase in the complexity of the model due to the introduction of new parameters was justified by the increased goodness of fit. In particular, ΔAICc is a measure of each model relative to the best model (i.e., the model with the lowest AICc value). The results clearly show that the modified model was always the best model (ΔAICc = 0) and that the standard model was unlikely to give an effective description of respiratory curves as

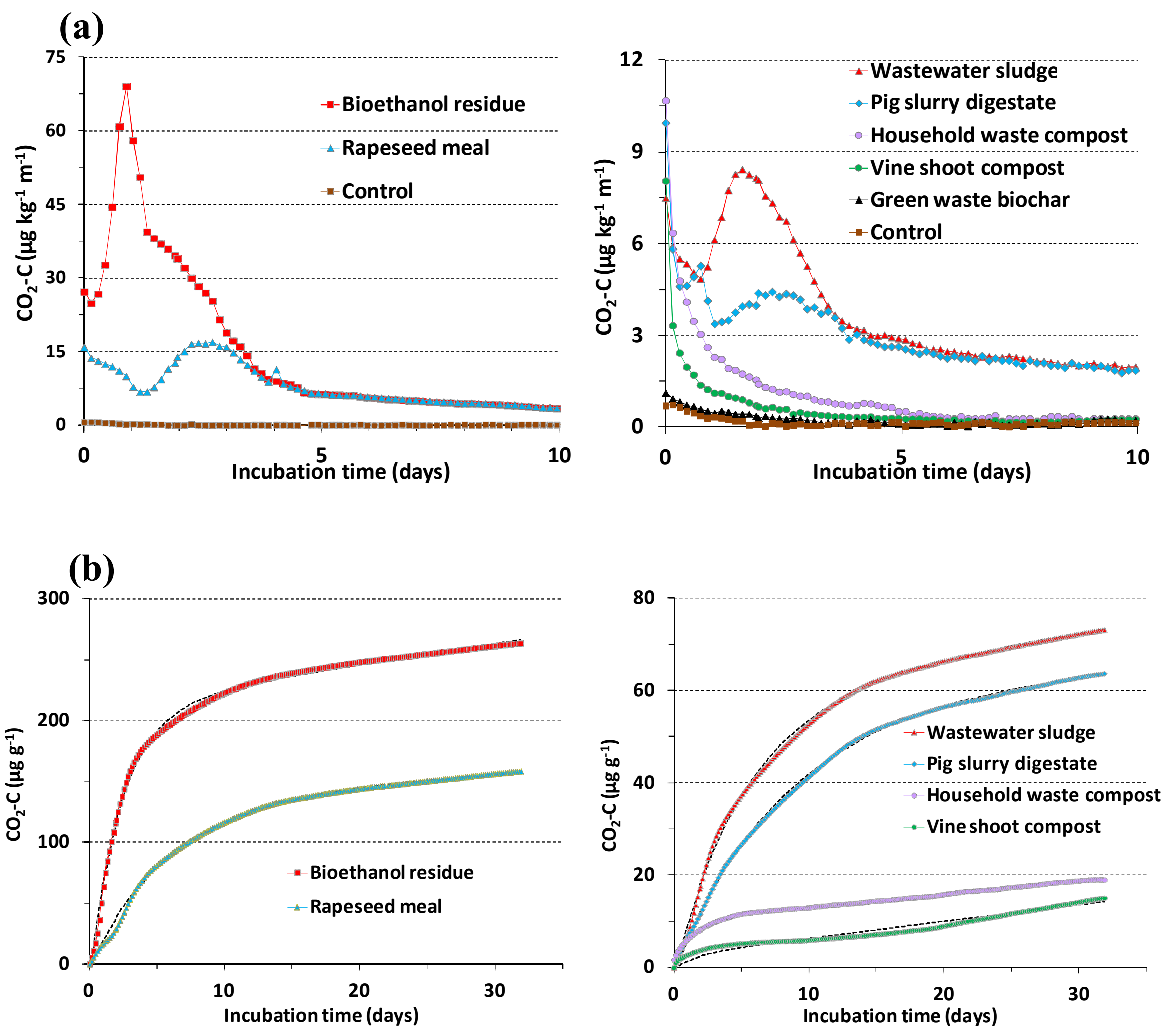

Figure 3. Rate **(a)** and net cumulative measured and simulated **(b)** CO_2 emissions from Llano de la Perdiz soil amended with different quality EOMs during a 30-day laboratory incubation. For the rate of respiration, only the first 10 days of the incubation are reported. Simulated net cumulative respiration curves are represented as dotted lines. Respiratory curves are presented on the *y* axis with a different scale for better visualization.

its ΔAICc mean value far exceeds the value of 10 indicated by Mazerolle (2006) as a threshold to support model validity.

Similarly, the evidence ratio compares the AICc of the best model with the AICc of another model and provides a measure of how much better the best model is at approximating the real data. In the present study, the average LER value clearly shows that the modified model was far better (i.e., 132 times) than the standard one, considering that a threshold LER of 2 is considered a decisive level to select the best model (Snipes and Taylor, 2014).

The fitting procedure with the modified model was hence applied to all the data sets for incubation and the mean, minimum and maximum values of the statistical indicators utilized to evaluate the model goodness of fit between the measured and simulated values are reported in Table 7. Tables S1–S6 in the Supplement present the pool parameters, the incubation conditions, the net cumulative CO_2 emissions and the statistical indicators of model goodness of fit. Biochar-amended soils were omitted from the optimization procedure due to very low CO_2 emission values resulting in statistically non-robust respiratory curves.

As a whole, the modified model was able to fit the respiratory response of the amended soils very well, as reflected in the statistical indicators (Table 7; Tables S1–S6 in the Supplement). The only exceptions were represented by soils amended with a low dose of anaerobic digestate ($100\,\mathrm{kg\,N\,ha^{-1}}$). The mean correlation coefficient (R) for all incubation experiments was 0.995 and was higher than 0.945 for all but one EOM. The root mean square errors (RMSEs) for vine shoot compost, household waste compost and

Table 5. Cumulative extra CO_2-C emitted in amended soil (% of added C) for each exogenous organic matter (EOM) group for all incubation treatments and incubation performed under standard conditions.

EOM group	All incubation treatments				Standard conditions for incubation*			
	Mean	Min	Max	n	Mean	Min	Max	n
	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
Bioenergy by-products	12.9	6.9	16.8	20	12.8	6.9	16.8	10
Anaerobic digestates	3.8	0.8	7.2	27	4.0	0.8	7.1	10
Meat and bone meals	16.8	7.8	38.6	93	21.3	18.1	25.9	3
Animal residues	13.1	5.0	21.1	33	16.8	11.0	21.1	14
Crop residues	8.5	3.0	18.4	10	10.4	5.1	18.4	6
Agro-industrial waste	10.0	6.0	17.5	3	6.3	6.0	17.5	3
Sewage sludge	4.8	3.8	6.0	4	4.8	3.8	6.0	4
Total cases				228				69

* 20 °C, 40 % soil water holding capacity, 0.5 % EOM application rate and a 30-day incubation period.

Table 6. Values for the root mean square error (RMSE), ΔAICc and LER (logarithm of evidence ratio) of the respiration curve fitting performed with standard and modified RothC.

EOM group	Model	RMSE (%)	ΔAICc	LER	n
Compost	modified	3.0	0	0	18
	standard	19	586	127	
Bioenergy by-products	modified	2.7	0	0	20
	standard	27	619	134	
Anaerobic digestate	modified	1.9	0	0	13
	standard	17	557	121	
Meat and bone meal	modified	3.0	0	0	12
	standard	21	430	93	
Animal residues	modified	5.1	0	0	9
	standard	21	411	89	
Crop residues	modified	3.4	0	0	8
	standard	16	536	116	
Agro-industrial waste	modified	1.9	0	0	2
	standard	19	761	165	
Sludge	modified	1.5	0	0	4
	standard	22	1029	223	
Average	modified	2.9	0	0	86
	standard	22	616	132	

EOM: exogenous organic matter; ΔAICc: $AICc_{(i)} - AICc_{best}$; AICc: Akaike information criterion corrected for small sample size, $AICc_{(i)}$, AICc of method (i), $AICc_{best}$, lowest AICc value; n: number of cases.

Table 7. Mean, minimum and maximum values for the statistical indicators of model goodness of fit between the measured and simulated data ($n = 224$).

	RMSE %	R	E %	M $\mu g\ CO_2\text{-}C\ g^{-1}$
Mean	4.5	0.995	−1.1	−1.2
Min	0.7	0.794	−16.4	−44.8
Max	37.2	0.9999	3.5	2.9

RMSE: root mean square error; R: sample correlation coefficient; E: relative error; M: mean difference between measured and simulated data.

bioethanol residue were 4.3, 2.5 and 3.7 %, respectively; for all the cases the RMSE was 4.5 %. The relative error (E) ranged between −16.4 and 3.5 % (Tables S1–S6 in the Supplement). The goodness of fit was also underlined by the very low values of M (on average, $-1.2\ \mu g\ CO_2\text{-}C\ g^{-1}$; Table 7). As an example of curve fitting, Fig. 3b depicts the measured and simulated net cumulative CO_2-C evolution for EOMs reported in Fig. 3a.

The average decomposition rates for EOM and REOM pools were 89 and 0.4 yr^{-1}. An evaluation of pool parameters showed large variability in the composition and decomposition rates of the studied EOMs. The ranges of different parameters were 0–0.63, 0.21–0.98 and 0.06–0.78 for f_{DEOM}, f_{REOM} and f_{HEOM} and 11–330 and 0.15–2.51 for K_{DEOM} and K_{REOM}, respectively (Tables S1–S6 in the Supplement). The coefficients of variation for the parameters considering all treatments were 83, 24, 53, 69 and 95 % for f_{DEOM}, f_{REOM}, f_{HEOM}, K_{DEOM} and K_{REOM}, respectively. Pool sizes and decomposition rates were not significantly correlated.

No statistically significant relationships were found between pool parameters and the chemical properties of different EOM groups. Partition coefficients for DEOM were significantly correlated with cumulative net CO_2-C ($r^2 = 0,92$; $P < 0.01$). The calculation of mean pool parameters and associated percent of variation of standard error for all incubation experiments performed with the same EOM type (Table 8) or with the same EOM group (Table 9) always showed a relative standard error smaller than 50 %. This is a threshold value proposed by Robinson (1985) for a statistically acceptable

Table 8. Mean RothC exogenous organic matter (EOM) pool parameters for different EOM types. Values in italic font denote the standard error of the mean values.

EOM group	EOM type code	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}
					Mean value					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 waste	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	0.09	0.70	0.41	86	0.37				mean		15.0	4.2	6.0	13.5	18.6
	total (%)	100	6.7	93.3	0.004	0.26	0.08	16	0.19				minimum		2.0	0.2	0.1	1.1	5.1
					0.32	0.96	0.74	220	0.90				maximum		58.3	18.1	20.3	35.3	44.3

EOM: exogenous organic matter; N: number of incubation treatments; Exc./Inc.: number of incubation treatments excluded and included from the mean calculation; DEOM: decomposable EOM; REOM: resistant EOM; HEOM: humified EOM; f: partitioning factor; K: decomposition constant rate (yr^{-1}).
For EOM group and type codes, refer to Table 3.

estimation of the model parameters, with a single exception in the case of stable compost CMC VII (Table S1 in the Supplement).

4 Discussion

4.1 EOM soil mineralization

The ranking of the different EOM groups according to the mean values of net C mineralization was in agreement with the results of similar studies on the decomposability of EOMs of different origin and nature (Lashermes et al., 2009; Thuries et al., 2001). The values of net C mineralization (expressed as a percentage of added C) for compost-amended soil were similar to those recorded by De Neve et al. (2003), who measured CO_2-C values in the range of 1.0–8.8 % for added C for different composts. The values of mean CO_2-C respiration for meat and bone meals (16.8 %) are in agreement with other previous C mineralization studies of residues characterized by low C / N ratios; for example, 16 and 19 % were obtained from poultry manure and pig slurry after a 20-day incubation at 22 °C (Levi-Minzi et al., 1990). Regarding by-products from bioenergy production, the values of C mineralization in the present study were significantly lower than those measured by Cayuela et al. (2010). This dissimilarity can be attributed to the different conditions utilized for the incubation. Nevertheless, the organic residues showed the same relative differences in CO_2 production. The significant correlation between EOM water soluble N and mineralized added C is in agreement with previous studies showing that N availability is an important factor in regulating EOM decomposition (Trinsoutrout et al., 2000).

4.2 Model modification

The development and optimization of SOC models capable of producing accurate and reliable predictions of EOM decomposition in soils (Karhu et al., 2012) represents an essential prerequisite for their utilization as a tool for the effective management of EOM amendment. RothC considers C input into the soil in the form of EOM only as farmyard manure with fixed partitioning factors of C pools. Falloon (2001) showed that such a model structure was not adequate to simulate C dynamics in sludge-amended soils. To enhance the ability of RothC to accommodate a wider range of EOMs, some authors have proposed varying the partition coefficients attributed by RothC to EOM pools. This change resulted in much closer agreement between the modeled and measured SOC trends (Falloon, 2001; Peltre et al., 2012). Therefore, in the first stage of the study we investigated the possibility of describing the respiratory curves of amended soil utilizing the same approach. However, the results of the fitting procedure clearly showed that it was not feasible to achieve a satisfactory fitting by only varying the proportion of the EOM pools (mean RSME 21.6 %; $n = 86$; Table 6). Con-

Table 9. Mean RothC exogenous organic matter (EOM) pool parameters for different EOM groups. Values in italic font denote the standard error and the coefficient of variation of the standard error for the mean values.

EOM group	EOM group code	N	Exc.	Inc.	Mean value f_{DEOM}	f_{REOM}	f_{HEOM}	K_{DEOM}	K_{REOM}	Standard error (SE) f_{DEOM}	f_{REOM}	f_{HEOM}	K_{DEOM}	K_{REOM}	Coefficient of variation of SE (%) f_{DEOM}	f_{REOM}	f_{HEOM}	K_{DEOM}	K_{REOM}
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 waste	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 sludge	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*

EOM: exogenous organic matter; N: number of incubation treatments; Exc./Inc.: number of incubation treatments excluded and included from the mean calculation; DEOM: decomposable EOM; REOM: resistant EOM; HEOM: humified EOM; f: partitioning factor; K: decomposition constant rate (yr^{-1}).
For EOM codes, refer to Table 3.

sequently a modification of the model was proposed based on the hypothesis that its performance would be enhanced by setting specific EOM decomposition rates different from those of plant residues. This corresponds to the introduction of two new pools of organic C entering into the soil, as decomposable and resistant EOMs are considered to have different properties in terms of degradability with respect to the corresponding plant residues pools. The results of the fitting procedure performed with the modified model demonstrated a remarkable improvement in the goodness of fit of the respiratory curves (average RMSE 2.9 %; $n = 86$; Table 6). The introduction of new parameters (such as the decomposition rate of decomposable and resistant EOM in the present study) generally decreases the bias between the simulated and measured values, but this is obtained with an increase in the complexity of the model. Too many parameters could result in a greater variance in the output of the model due to the uncertainty associated with the parameter estimation. Moreover, a model with too many parameters holds the risk of overfitting, i.e., of modeling the random noise in the data rather than the true values. This causes a decrease in the predictive performance or generality of the model when applied to different data sets as an over-fitted model is too dependent on the data utilized for its calibration. An ideal model would fit the data well with a minimum number of parameters. Calculation of ΔAICc and the evidence ratio (Table 6), which are the statistics derived from AIC, clearly showed that the modified model was far better in comparison to the standard one in terms of the simulation of respiration curves from amended soil. According to the AIC-derived indexes, the benefit obtained by the modified model in terms of decreased bias between the measured and simulated data overcompensates for the increase in model complexity due to the introduction of new parameters.

In addition to the results for RMSE and AIC, the reliability of the model modification was supported by the findings of previous work indicating the limitation of RothC in amended soil and the increase in model performance obtained by setting specific decomposition rates for EOM. The standard RothC model has been shown to be insensitive to the variation in the quality of EOM inputs and is therefore not adequate for the simulation of soils amended with EOMs characterized by a huge variability in chemical structure and degradability (Tits et al., 2014). This limitation has been attributed to the fact that it does not distinguish between crop residues and EOM, despite their widely different nature; this is highlighted by the results of Tits et al. (2014). The authors simulated 30 years of compost addition, and the quality of EOM in their work was addressed by calibrating the DPM / RPM ratio with the SOC content; however, this ratio encompassed not only EOM quality, but also the quality of the input materials (crop residues). Consequently, the calibrated DPM / RPM ratio was site specific, as this ratio depended not only on compost properties, but also on 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 the model structure, but it is likely to generate less accurate results (Cavalli and Bechini, 2011).

The results of previous work also suggest that for a reliable simulation of C mineralization in amended soils there is not only the need to partition EOM into a number of discrete pools, but also to differentiate the quality of EOM from that of crop residues. In particular, Cavalli et al. (2014) underline the relevance of assessing different decomposition rates for crop residues and EOM pools, as in the modified RothC, since they found that EOM degradable and resistant pools always decomposed more rapidly than the analogue crop residue pools. Similarly, Borgen et al. (2011) clearly showed that model predictions can be improved by the identification of an EOM-specific decomposition rate. Mueller et al. (2003) demonstrated the inadequacy of the original assumption in the DAISY model for two EOM pools with predefined constant turnover. Henriksen and Breland (1999) and Henriksen et al. (2007) presented a model partitioning plant residues in three distinct pools (decomposable, structural, resistant) that have distinct but fixed (i.e., equal for all plant materials) decomposition rates. The only exception is represented by the structural pool in which the 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 may be set a priori because it is uniform across litter qualities and supports the fact that the residue-specific EOM pool decomposition rate enhances the performance of the model. Further support for the effectiveness of the proposed modification to the model structure presented in this study is derived from the work of Incerti et al. (2011) who found that a model with three EOM pools satisfactorily described the pattern of litter decomposition. In addition, the authors found an enhancement of the predictive ability of the three-pool model by varying the decomposition rate of the pool with intermediate degradability as a function of the lignin content. Accordingly, Cavalli and Bechini (2012) and Petersen et al. (2005b) have demonstrated that C simulation in amended soils is increased by a specific EOM parameterization. Finally, it has to be noted that models with a similarly complex structure as in the proposed modified RothC (five different pools of C input to the soil and specific decomposition rates for decomposable and resistant EOM) have already been proposed and successfully validated for amended soils (NC-SOIL, Noirot-Cosson et al., 2016; CN-SIM, Petersen et al., 2005a; Cavalli and Bechini, 2012).

4.3 Model optimization

The results of the respiration curve fitting for the whole data set show that the modified model was able to adequately fit the respiratory response of amended soil, as demonstrated by the average value of RMSE for vine shoot compost (4.3 %), household waste compost (2.5 %), bioethanol residue (3.7 %) and each of the 224 respiratory curves examined in this study (4.5 %). As a comparison, Cavalli and Bechini (2011) calibrated the three EOM pools in the CNSIM model for a reduced range of incubation conditions (three soils and five liquid dairy manures) and obtained an average RMSE of 8.7 %. The results 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 the EOM parameters was specific to soil and incubation conditions to enable the model to find the best fit for the measured data. Consequently, failure 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 model, encompassing additional EOM pools with specific parameters, is able to accommodate the large variability of the tested EOMs in terms of composition and properties. Such variability in EOM quality is indicated by the extended range of values characterizing each pool parameter. These findings support the hypothesis that explicit treatment of EOM heterogeneity would improve the performance of the RothC model. The lack of correlation between the chemical properties of residues and pool parameters is in agreement with the evidence that operationally defined fractions do not precisely match kinetically defined pools. This is mainly due to the fact that the distinct components of organic residues interact with soil components and this modifies their decomposability along the incubation period (Trinsoutrout et al., 2000). Kinetically defined pools take into account such interactions and this represents an advantage in terms of simulation accuracy with respect to the operationally defined pools. The significant relationship between cumulative CO_2 and f_{DMP} could be explained by the fact that most of the mineralized EOM-C emitted during incubation is derived from the degradable pool.

The calculation of mean pool parameters for EOM type and EOM group (Tables 8 and 9) indicated that the uncertainty associated with the parameters was always lower than the suggested threshold for the statistically acceptable estimation of the parameter (standard error of the mean < 50 %; Robinson, 1985). These results indicate that the parameter values mainly reflect the EOM properties and that the model is capable of keeping the effects of incubation conditions (i.e., type of soil, temperature, soil water content, rate of EOM application) to a minimum. This is in agreement with previous work suggesting that EOM quality is the most important factor affecting organic residue decomposition in soil (Cavalli et al., 2014; Do Nascimento et al., 2012; Karhu et al., 2012;). Low variability associated with mean parameters for an EOM group is an indication that this common set of parameters could be utilized to simulate SOC patterns in soil amended with the different EOMs belonging to a specific group with an acceptable error.

4.4 Potential limitations of the proposed model modification and optimization

Soil organic C modeling is subject to several potential drawbacks and limitations. Due to the aim of this work, only aspects specifically related to the proposed procedure for model modification and optimization will be discussed. These are the suitability of short-term incubation to assess EOM pool parameters, issues of model validation in long-term field conditions and problems associated with the simultaneous fitting of multiple parameters.

4.4.1 Suitability of short-term incubations to assess EOM pool parameters and model validation under field conditions

One of the major concerns about the proposed optimization method is the suitability of short-term incubations to adequately characterize EOM in terms of pools of different decomposability. It has been suggested that short-term incubations are appropriate only to estimate the mineralization of the more decomposable pools. On the other hand, long-term incubations, while providing a more accurate characterization of EOM, are highly demanding in terms of laboratory work, time and space. To date, an agreed minimum incubation period to obtain reliable evaluations of EOM pools has not been established. Sleutel et al. (2005) underlined that such a period depends on the EOM type and the kind of model used to fit the data. They found that for a specific EOM, a reliable estimation was obtained within only 16 days at 16 °C and that a second-order model required a minimum incubation time of about 50 days at 16 °C for the estimation of EOM stable organic C within less than 3 % of the true value for all organic materials. For a parallel first-order model, a minimum incubation period of 42 days at 16 °C was necessary to obtain a reliable estimation of pig slurry and compost pools. Such EOMs represent well-stabilized materials for which the incubation time is likely to be more important for a reliable parameter estimation with respect to more degradable EOMs. Such minimum incubation periods are consistent with the incubation time utilized for most of the experiments in this study, when considering the different incubation temperature. It is important to note that one possible shortcut to reduce the incubation time needed for a satisfactory fitting is the use of higher temperatures, as the mineralization rates significantly increase. According to the rate modifying factor for temperature utilized in RothC, an incubation period of 30 days at 20 °C corresponds to a period of 42 days at 16 °C to mineralize an equal amount of CO_2.

To verify the suitability of the incubation period utilized in this work (30 days) for a satisfactory curve fitting and test the dependence of EOM pool parameters on the incubation time, we have utilized an independent data set from a laboratory incubation performed at 15 and 25 °C for 300 days with a corn- and soybean-residue-amended soil. We calibrated the EOM pool parameters by considering the whole incubation period (300 days) and a shorter incubation time (30 days for incubation at 25 °C and 50 days for incubation at 15 °C). The results showed that the standard error associated with parameters obtained at different incubation times was acceptable (smaller than 50 % of the parameter value; Robinson, 1985). To estimate the error in SOC prediction associated with a set of parameters calibrated at different incubation times, we performed long-term RothC simulations (100 years) involving an annual addition of $1\,\mathrm{t\,ha^{-1}}$ of EOM-C and utilizing such a different set of parameters. The results showed that the difference in the yearly rate of SOC sequestration was always lower than 7 %. We obtained similar results utilizing another set of independent data from a 60-day incubation of soil amended with cow manure, pig slurry and anaerobic digestates. In this case the difference in C sequestration potential utilizing sets of parameters obtained after 30 and 60 days of incubation was lower than 5 %.

The ability to estimate reliable SOM pools utilizing short-term incubation data also depends on the accuracy in tracking the cumulative respiratory curve. The high measurement frequency of the automatic system used in this study (one measurement every 6 h) improves the precision of the cumulative curve in comparison to standard methodologies (i.e., alkali trapping) characterized by a limited number of sampling points. A high number of measurements allows outliers to be more easily identified and eliminated. A further source of uncertainty is related to the fact that cumulative curves accumulate errors associated with each sampling point. The system used in this study is characterized by high precision; as a percent, relative standard deviation of the mean for CO_2 measurements is typically less than 0.5 % (Mondini et al., 2010). This minimizes the weight that each sampling point has on the total cumulative respiratory response in comparison to traditional measurements with alkali trapping, usually taken at large sampling intervals. We consider the accuracy of the measurement system utilized in this work to compensate for the possible limitations associated with short incubation times in comparison to incubation performed for longer periods, but with less accurate and frequent measurements.

The reliability of short incubation times in performing an acceptable characterization of EOM pool parameters is also supported by other research. Mueller et al. (2003) used an incubation time of 52 days at 9 °C to calibrate EOM pools for the DAISY model. It is important to note that an incubation period of 30 days at 20 °C, as carried out in our work, would correspond to an incubation period of 86 days at 9 °C to mineralize the same amount of CO_2. De Neve et al. (2003) incubated waste for 39 days at 21 °C to estimate the amount of stable C, a parameter that can be used directly as an input in some C sequestration simulations models. Gale et al. (2006) showed that an incubation period of 28 days at 22 °C was sufficient for determining decomposition rate constants to represent EOM decomposition kinetics to be used in C models. Peltre et al. (2013) calibrated EOM pool parameters of the DAISY model utilizing respiration curves from amended soil incubated at 15 °C for 56 days. Saviozzi et al. (2014) performed an incubation of 25 days at 25 °C to infer the labile and recalcitrant EOM-C pool parameters. Similar conclusions concerning the suitability of short-term incubations to obtain reliable EOM characterization were drawn by Beloso et al. (1993), Pedra et al. (2007) and Garcia et al. (1992) utilizing incubation periods of 21, 28 and 42 days, respectively.

Overall, an incubation time of 30 days with measurements performed with an accurate system could be considered a reasonable trade-off between the accuracy of the information obtained in terms of C mineralization and the demand for saving costs, time and space in the laboratory.

The suitability of short-term incubations in estimating reliable EOM pools does not imply that the parameters derived from short-term laboratory incubation can be automatically transposed to field conditions to simulate the long-term C dynamics of amended soils. Laboratory incubations are usually performed with sieved soil under optimal constant conditions for microbial activity that could result in quite different EOM mineralization rates with respect to those for structured soil in a variable field environment. Therefore the assimilation of laboratory data into existing models need to be carefully evaluated against field data (Schimel et al., 2006). Nevertheless, several authors have demonstrated that model parameterization obtained in laboratory incubations can be utilized to provide a reliable simulation of EOM mineralization under field conditions (Gabrielle et al., 2005; Kaboré et al., 2011; Noirot-Cosson et al., 2016; Vidal-Beaudet et al., 2012). This could be explained by the fact that EOM composition and properties are the main factors regulating their mineralization in the soil (Cavalli et al., 2014; Do Nascimento et al., 2012; Karhu et al., 2012).

The data requirements for model validation under field conditions make this task currently unfeasible to a large degree. As the main objective of the proposed model modification is to increase the ability to capture the large variability in EOM quality, validation at a real scale would require data from long-term field experiments dealing with a large range of EOM with contrasting properties. This is problematic due to the limited amount of suitable data available. While there are several ongoing long-term experiments dealing with manure, straw and sludge amendment, there are relatively few experiments reporting C data for soils amended with compost from source-separate collection and anaerobic digestates. In the case of new EOMs, such as meat meals and bioenergy by-products, there is a lack of field-scale experiments. There are no long-term field experiments dealing with EOMs characterized by different degrees of stability (i.e., compost at different stages of the composting process) that would allow an improved validation of important model parameters such as pool partitioning factors (f_{DEOM}, f_{REOM}, f_{HEOM}) and K_{REOM}.

Another opportunity for enhanced validation would be the assessment of the model ability to discriminate the effects of soil texture on EOM mineralization. Cavalli et al. (2014) reported no significant differences in EOM decomposition among soils with contrasting texture and attributed this to the soil structure disturbance caused by sample preparation in incubation experiments that can reduce the physical protection of the applied EOM and decrease textural effects that might be more explicit under field conditions. Unfortunately, experiments concerning EOM application to soils with contrasting texture are very few.

The establishment of field experiments dealing with EOM characterized by contrasting properties and degrees of transformation under different environmental and management options would allow for a proper evaluation of model performances in simulating long-term SOC dynamics.

4.4.2 Simultaneous fitting of multiple 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 a defined size that should not change with environmental conditions or the procedure used to fit the model with the data. Cabrera et al. (2005) underlined 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; this is a situation formally called equifinality or non-identifiability. 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. The possibility to obtain a non-identifiable set of parameters also increases with a decreasing amount of incubation data. These problems with exponential models suggest that they need to be used judiciously in trying to identify pools of a defined and fixed size; different combinations of pool size and decomposition rate with a good fit to the respiratory curve may result in significant differences in SOC when the model is run over a long-term period.

A possible solution to avoid this pitfall is to have independent controls to constrain the parameter estimates (Ahrens et al., 2014). Unfortunately, we did not have such controls for all the incubation data. Nevertheless, we are confident that the optimized parameters represent a univocal set of values. First of all, a unique identification of the optimized parameters was sought by maintaining a constant HEOM decomposition rate and imposing constraints on partition coefficients and decomposition rates according to scientific data in order to obtain biologically meaningful pool parameters. As for the influence of incubation time on pool estimates, we have found a consistent set of parameters between calibrations performed after 30 and 300 days of incubation. Regarding the impact of few measurements points, this does not apply to our curves characterized by high-frequency measurement. Even if from a theoretical point of view there is the possibility to obtain different sets of parameters leading to an accurate simulation, this is limited by the shape of the cumulative curve. For example, the first part of the curve, describing the fast release of CO_2 from the most degradable C, can be adequately described only by a specific combination of K_{DEOM} and f_{DPEOM} values. Finally, a significant correlation between pool size and decomposition is an indication of model over-parameterization and the likelihood of obtaining accurate simulations with different combinations of parameters. In the present work, such relationships were never significant and this suggests that the optimized parameters are likely to reflect a unique solution. Simultaneous fitting of several parameters is not unusual in model calibration. As an example, Mueller et al. (2003) and Cavalli and Bechini (2012) simultaneously fitted five and six parameters, respectively.

5 Conclusions

The effective management of organic amendment requires the development of C models able to take into account the quality of added EOM. The main innovative aspects of this work consist of the modification of the RothC model to include additional EOM pools and their parameterization by model fitting to the respiratory curves of amended soils. The results of the study show that the modified and optimized model was able to adequately describe EOM mineralization curves obtained under laboratory conditions and support the hypothesis that defining EOM-specific partitioning factors and decomposition rates improves the simulation ability of the model in amended soils.

Due to the effect of different environmental conditions between laboratory and field conditions, the validation of the modified model with field data represents a necessary step in the model development as a tool to evaluate SOC storage in EOM-amended soils in the long term. However, the conceptual changes to the model structure and the potential usefulness of the model are justified through its ability to simulate detailed experimental data. We consider the capacity of the model to adequately describe the mineralization curves of EOM under laboratory conditions to represent an essential prerequisite for a reliable C modeling of amended soils; it demonstrates the ability of the model to resolve the large variability in EOM composition and properties. Furthermore, information derived from the fitting procedure could be useful in identifying knowledge gaps in environmental factors and soil processes that regulate EOM decomposition in the soil and suggest further ways to improve the model.

The findings of the present research indicate that laboratory experiments on EOM decomposition could be useful in improving the simulation of C dynamics in amended soils.

Data availability. We provide the non-textual resources underlying the research as a Supplement.

The Supplement related to this article is available online at https://doi.org/10.5194/bg-14-3253-2017-supplement.

Author contributions. CM conceived and designed the experiments, analyzed the data, wrote the paper, prepared figures and/or tables and reviewed drafts of the paper.

MLC conceived, designed and performed the experiments, analyzed the data, and reviewed drafts of the paper.

TS performed the experiments and reviewed drafts of the paper.

FF conceived and designed the experiments, performed the experiments and reviewed drafts of the paper.

AG performed the experiments and reviewed drafts of the paper.

MASM conceived, designed and performed the experiments and reviewed drafts of the paper.

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Disclaimer. This publication reflects the author's views, findings and conclusions and the European Commission is not liable for any use that may be made of the information contained therein.

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