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A modified version of RothC to model the direct and indirect effects of rice straw mulching on soil carbon dynamics, calibrated in a Mediterranean citrus orchard.

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Abstract. Mulching of agricultural soils has been identified as a viable solution to sequester carbon into the soil, increase soil health and fight desertification; as such, it is an interesting option for carbon farming in Mediterranean areas. Models are used to project the effects of agricultural practices on soil organic carbon in the future for various soil and climatic conditions, and to help policy makers and farmers assess the best way to implement carbon farming strategies. Here, we modify the widely used RothC model to include mulching practices and their direct and indirect effects on soil organic matter input, soil temperature changes, and soil hydraulic balance. We then calibrated and validated our modified RothC (RothC_MM) using the dataset collected in a field mulching experiment described in detail in a companying article, and used the validated RothC_MM to estimate the expected soil carbon sequestration by year 2050 due to mulching for the Valencian community (Spain). Our results show that RothC_MM improved the fit with experimental data with respect to basic RothC, and was able to predict SOC and CO_2 observations taken in the field, and to model the effects of mulch on soil temperature and soil water content.

1. Introduction

The sequestration of carbon in the soil has been identified by IPCC as one of the most readily viable ways to help reduce the net CO_2 anthropic emission and thus curb global warming to 1.5 °C by 2050 (IPCC, 2018). Carbon (C) is present in soils in inorganic (SIC) and organic (SOC) forms with agriculture historically depleting SOC reserves, especially in Mediterranean areas, where 20-40% of the original SOC content has been lost after conversion to agriculture (Buyanovsky and Wagner, 1998). This loss of SOC is particularly relevant considering that agricultural soils occupy about 35% of the global land surface (Betts et al., 2007): Lal et al. (2004) estimates a global carbon debt due to agriculture of 260 Gt SOC for the top 1 m of soil, with the rate of carbon losses accelerating in the past 200 years (Sanderman et al., 2017). This means that there is a large potential to sequester carbon in the soils through conservation agricultural practices (Bossio et al., 2020), with the added benefit that increasing SOC levels will improve several ecosystem services because of the enhancement of soil structure, fertility, and resistance to erosion (Ramesh et al., 2019; Lal and Follett, 2009; Wei et al., 2021). This would be extremely important in Mediterranean lands where soil erosion and desertification are major concerns for local farmers and policy makers (García-Ruiz et al. 2012 , García-Ruiz et al. 2015, Ghaley et al., 2018, Madejón et al., 2007, Vastola et al., 2017, García-Tejero et al., 2020). Therefore, there is a wide interest to estimate accurately the effects of conservation agricultural practices on SOC trends, at least up to year 2050.

The effects of agricultural practices on SOC stocks can be estimated using dynamic mathematical models (SOC dynamic models) that try to represent the processes that incorporate (input) and mineralize (output) organic compounds in the soil. Actually, SOC is the result of the accumulation of decaying organic matter in the soil against mineralization (Lehmann and Kleber, 2015). On the one hand, SOC inputs to the soil come from aboveground decaying litter and, more importantly, from root dead remains, lysates and exudates, i.e., the so-called rhizodeposition. On the other hand, SOC outputs consist of carbon oxydized through respiration by soil organisms, as well as lost through erosion and leaching. Models simulate the inclusion of fresh organic matter in the soil as a flux toward different organic carbon pools (2-6, depending on the model). The output of carbon from each pool, including the fresh organic matter pools, is simulated by an exponential decay function, where each pool features a different turnover rate (Coleman and Jenkinson 1996, Stockmann et al. 2012). Since it has been widely observed that mineralisation rates are modified by soil temperature (T_s) and soil water content (θ_s; Bao et al., 2016, Akinremi et al., 1999, Hursh et al., 2017, Carey et al., 2016), SOC dynamic models include empirical functions used to modify the turnover rates of the carbon pools on the basis of both T_s and θ_s, which may be estimated from meteorological data (Falloon et al., 2000).

To estimate the effects of agricultural practices on SOC up to 2050 for different climates, soil types, and crops, the agricultural practices should be first included into a dedicated soil carbon cycling model and, after proper calibration, the model should be run using future climate projections (Jordon et al., 2022). How to include the agricultural practices in the model depends on the model design. In this regard, there are two main types of models (Goglio et al., 2015). On the one hand, the simple models parametrize the soil processes mostly with empirical and conceptual functions requiring, in general, few data to work, e.g., RothC (Coleman and Jenkinson, 1996), and are thus widely used throughout the world. On the other hand, the complex models try to represent the soil processes with more theoretically-sound functions, requiring large sets of data to work, e.g., CENTURY (Parton et al., 1987), and are thus used only in areas where all the required information can be gathered. The inclusion of a certain agricultural practice in simple models requires specific parameters and simple functions

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to represent the direct and indirect effects of that agricultural practice on the SOC dynamics, for instance, reduced tillage cannot be directly modelled on a simple model with no soil vertical discretization. Furthermore, simple models obtain the important θ_s data from similarly simple soil water budget functions, which are often too simplistic to adequately represent Mediterranean conditions, characterised by long droughts and short, intense precipitation events; for instance, Farina et al. (2013) showed how to modify the RothC water balance function to improve its performance in Mediterranean climate conditions.

The practice of leaving crop residues or other materials on the soil surface is called "mulching" (Kader et al., 2019), and it is especially relevant to improve soil and water conservation in orchard inter-rows ((Mulumba and Lal, 2008); (Jordán et al., 2010); (Chen et al., 2020)). In addition to improve soil tilth, nutrient availability, and weed control (Locke and Bryson, 1997), mulching also increases SOC levels (Si et al., 2018; Gu et al., 2016; Ranaivoson et al., 2017). Conservation agricultural practices can enlarge SOC stocks by directly transferring carbon to the soil, and/or indirectly, by fostering the carbon transfer to the soil from other sources, e.g., plants through rhizodeposition, and/or by decreasing the SOC mineralization rate. The direct effect is the mulch inclusion in the soil either when tilled (Dossou-Yovo et al., 2016) or carried by soil fauna. The biomass from organic mulches is a matter and energy source for soil organisms, which increases their activity, and encourages the binding of organic matter and particles of soil into macro- and micro-aggregates (Six et al. 2002), leading to an enhancement in the aggregate stability, restoration of stable C and finally, improvement in the SOC content and soil carbon sequestration (Koga and Tsuji, 2009). The indirect effects are due to changes in soil temperature and water content due to mulch application (Rahman et al., 2005), which could result in changes in root growth and soil ecology, and are especially relevant in Mediterranean climates (Warren Raffa et al., 2021, Bombino et al., 2021; Keesstra et al., 2019; Visconti et al. under review).

To date, only limited attempts have been made to include mulching in SOC dynamic models, simulating its effects on soil carbon sequestration by modelling the direct input of SOC from the biomass of organic mulches. Galdos et al. (2009) simulated the effect of straw mulch from sugarcane using the CENTURY model; the simulation was focused on understanding whether the straws left on the field contributed directly to the carbon pools and thus to increase the sugarcane production, leading to a sort of active feedback. Mondini et al. 2017 modified RothC to include additional exogenous organic matter (EOM) pools and their parameterization by fitting the respiratory curves of 30 soil treatments. Nieto et al. 2010 applied RothC to estimate the soil carbon sequestration brought by mulching in several Mediterranean olive groves. In all these studies, the models' parameters were calibrated considering only the direct effect of mulch, i.e., the increased input of carbon in the soil; the indirect effects of mulching were not considered. Moreover, none of the RothC studies on mulch adapted the model to the Mediterranean climate.

The main objectives of this study were to modify the RothC model to estimate the long term changes of SOC due to mulch application in Mediterranean climate, more specifically in the inter-rows of a citrus orchard. By modifying RothC, we aimed at including a strategy to reduce atmospheric CO_2 proposed by IPCC in a simple soil carbon dynamic model, which could then be used to predict soil carbon sequestration potentials at plot and landscape scale (Metz et al., 2005). Our specific objectives were to:

- Modify RothC to include the effects of mulch on soil temperature and soil water content, especially in a Mediterranean climate;
- Calibrate and validate the modified RothC using field data, obtained in a three-year-long field experiment (Visconti et al under review);
- Use the validated, modified RothC to assess the effect of mulching on SOC trends up to year 2050.

2. Material and methods

2.1 Modifications of RothC: RothC_MM

2.1.1 The RothC model

We decided to use the RothC Rothamsted Carbon model, (RothC-26.3), implemented as described in Coleman and Jenkinson (1996). We selected this model because it requires relatively few input data, it has been tested in a wide range of conditions, and it is already used to estimate SOC stocks in various countries in its standard (Japan, Shirato and Taniyama, 2003; Switzerland, Coleman et al., 1997) or modified forms (Australia, Richards, 2001; United Kingdom, Moxley et al., 2014; Smith et al., 2020).

RothC estimates soil water content in terms of monthly top-soil water content deficit (TSMD, in mm), based on a simple soil water budget with input coming from precipitation and output from estimated potential evapotranspiration; drainage is simulated by imposing a minimum TSMD corresponding with field capacity, i.e., at a matric potential of -5 kPa. The vegetated soil is allowed to dry up to wilting point ($TSMD_{max}$), i.e., at -1.5 MPa, and the bare soil to a fraction of it (0.556 $TSMD_{max}$). A parameter used to modify the SOC pools degradation rate (*b*, see Eq. 1 below) is assumed to change linearly from a value of 1 (no effect on SOC mineralization) at matric potential values of -0.1 MPa to a minimal value of 0.2 at wilting point (-1.5 MPa). The $TSMD_{max}$, the TSMD corresponding to field capacity ($-5\ 10^{-3}$ MPa), and the TSMD corresponding to -0.1 MPa, are calculated using an empirical function based on the soil clay content.

RothC has four active and one inert SOC compartments or pools: Decomposable Plant Material (DPM), Resistant Plant Material (RPM), Microbial Biomass (BIO), Humified Organic Matter (HUM) and the Inert Organic Matter (IOM). The monthly organic inputs to the soil are divided into two compartments: DPM and RPM. Then, the output carbon from these two SOC pools flows into BIO, HUM and is lost as CO_2. From the BIO and HUM pools, the output carbon again flows into BIO, HUM and is lost as CO_2. Each active SOC pool has a different turnover time: DPM (0.165 years), RPM (2.31 years), BIO (1.69 years), HUM (49.5 years). The total output flow of CO_2 from the pools can be compared to the monthly average heterotrophic respiration from the soil.

The amount of material that decomposes in one month in any pool *i* (where *i* ={DPM, RPM, BIO, HUM}, is:

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$$Y_{deg,i} = Y_i(1 - e^{-abck_it}) \quad (1)$$

Where Y_i is the initial quantity of carbon (t C ha^{-1}) in a specific pool i, a is the rate modifying factor for temperature, b is the rate modifying factor for water content, c is the rate modifying factor for soil cover, k_i is the yearly decomposition rate constant pool i, and t is 1/12 (Coleman and Jenkinson, 1996). In RothC, weather input data controls temperature and water content modifying factors a and b, hence modelled SOC dynamic in RothC is sensitive to air temperature and soil water budget.

We modified RothC to include the direct and indirect effects of rice straw mulching application on SOC in the inter-rows of two Mediterranean citrus orchards (Visconti et al., under review). Our work was divided into 2 steps: first we modified the RothC water budget calculation to cope with the characteristic summer drought of the Mediterranean climate; then we modified RothC to include the direct and indirect effects of straw mulches on the SOC dynamics.

2.1.2 Modifications to RothC for Mediterranean climate: RothC_Med

To simulate in RothC the soil water content regime typical of semi-arid Mediterranean climates, we: first, implemented the modifications devised by Farina et al. (2013), with the modified RothC model referred to as "RothC_N" from here on; second, introduced further modifications to include more general soil water content dynamics, as observed in the field. We called RothC_Med our modification of RothC_N. Farina et al. (2013) modifications of RothC were:

- To allow the vegetated soil to become drier, reaching a matric potential of -100 MPa;
- To allow the bare soil to become drier, with $TSMD_{max}$ reaching a matric potential of -1.5 MPa (wilting point);
- The TSMD is calculated from soil texture data through pedotransfer functions, based on the Van Genuchten water retention curve function (van Genuchten, 1980);
- Parameter b still changes linearly between -0.1 and -1.5 MPa, but its minimal value can be adjusted to be either 0.2, 0.15, or 0.1.

We extended the idea of calculating the TSMD reference parameters using a soil-water retention curve, in order to translate the soil water content (volumetric, m^3 m^{-3}) time series measured in the field to TSMD and use them to calibrate the water budget function of the model. To do so, we first used pedotransfer functions to estimate the parameters of the van Genuchten function for the water retention curve of the soil: the curve can also be calibrated to fit direct observations of soil water content/soil matric potential data. With the calibrated retention curve we translated the soil water content measurements to matric potentials, and then, using Farina et al. (2013) procedure, we transformed them to TSMD values.

The further modifications we introduced to RothC water balance function were aimed at: i) fixing the water budget during long drought periods; ii) fixing the water budget for drained soils during intense rainfall; iii) include the effects of a fluctuating shallow water table on soil water content. We added a "Drought" parameter to the model to represent the minimum amount of water observed during the dry season (summer) in the field; this parameter is a maximum TSMD level which can be calibrated using soil water content timeseries. A similar "drainage" empirical parameter (here called

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"MinTSMD") was also introduced in RothC to represent the effect of soil drainage, since the soil water content data taken during heavy rainfall shows good soil drainage; this parameter is a minimum TSMD level which can be calibrated using soil water content timeseries. Finally, we introduced a sinusoidal function to fit the effect on TSMD of a yearly fluctuating shallow water table; this helped fit the soil water content observations in the Sueca mulch treatment, that showed a strong influence of a shallow water table which fluctuates yearly from 0.6 to 1 m of depth b.g.l. All the changes to the equations and algorithm for the calculation of TSMD in RothC are detailed in Supplementary Materials.

2.1.3 Modifications to RothC to include mulching: RothC_Mulch and its combination with RothC_Med (RothC_MM)

To include the direct and indirect effects of mulch in RothC, as observed in the field, we modified the model to account for: i) soil temperature changes, ii) soil water content regime changes, and iii) direct C inputs from the mulch material. We called RothC_Mulch this modified RothC; we called RothC_MM the model resulting from the combination of RothC_Med and RothC_Mulch. To represent the effect of mulch on soil temperature (either by changes in albedo or thermal barrier), we multiplied the *a* coefficient in Eq. 1 by an empirical parameter (Mulch T radiation insulation, M_T) which can be directly estimated from T_s data, in order to reduce the effect of temperature on SOC mineralization:

$$Y_{deg,i} = Y_i(1 - e^{-M_T abck_i t}) \quad (2)$$

The inclusion of a parameter that directly multiplies the effect of temperature on SOC degradation is justified by the fact that RothC assumes a linear relationship between parameter *a* and temperature over 10 ºC. To represent the effects of mulch on the soil water content regime, the TSMD in the mulch simulations was decreased by a fixed amount, thus indirectly reducing the effect on parameter *b* (Eq. 1). Finally, we introduced the "Mulch C input" variable to account for the organic carbon inputs contributed by the mulch to the soil either indirectly or directly by the straw, as done previously by Mondini et al., 2017 and Nieto et al., 2010.

2.2 Calibration and validation of RothC_MM

2.2.1 Calibration/validation dataset

To calibrate and validate RothC_Med and RothC_MM we used a dataset obtained from an experiment on the application of mulch described in Visconti et al. (under review). The experiment was carried out in two citrus orchards located respectively in the experimental fields of Cajamar ADNAgroFood in Paiporta (coordinates 39º 25' 2" N, 0º 25' 4" W and altitude of 17 m a.s.l.) and Cooperativa Valenciana del Camp Unió Cristiana in Sueca (coords. 39º 12' 36" N, 0º 18' 23" W and altitude of 4 m a.s.l.), from March 2019 to January 2022. According to the Köppen-Geiger classification, the two areas are located in semiarid hot-summer Mediterranean climate (Csa, Rodríguez Ballesteros, 2016). In Paiporta the soil is classified as Typic calcixerept and in Sueca as Oxyaquic Xerofluvent according to the Soil Taxonomy (Soil survey Staff, 2014).
In each study area (Paiporta and Sueca), there were two control-bare trial plots (Bare) and two straw-mulch-covered trial plots (Mulch). The monitored variables were air temperature and relative humidity with mini-meteorological stations, and

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rainfall with rain gauges. Close to each weather station, during the first half of March 2019, two capacitance soil moisture and temperature probes (ECH2O 5TM, Decagon Devices, Inc., USA) were installed at a depth of 7 cm, one in each inter-row.

Soil CO_2 emission (soil respiration, R_s) was measured once every one-to-two months starting on March 2019 by fitting static gas-collecting chambers on two permanent-installed PVC collars per trial plot. Every soil CO_2 emission measurement lasted 30 minutes and were conducted in general between 8:00 h and 13:00 h solar time. Additionally, batches of soil samples were taken at 20 cm depth using soil augers once every three months between 2019 and 2022. The soil samples were carried to the laboratory, air-dried, grounded, and sieved through a 2-mm-mesh sieve. SOC was determined by wet oxidation with dichromate according to the Walkley and Black (1934) method. Furthermore, undisturbed soil core samples were taken at 5 cm depth in four points per trial plot to separate the roots and quantify their mass fraction. Further information regarding the experimental design, sampling and measurements is provided in Visconti et al. (under review).

2.2.2 Spin-up initialization of RothC_Med and RothC_MM

We run spin-up runs to initialise the carbon pools in RothC_Med and RothC_MM. The carbon pools of RothC do not refer to measurable quantities; thus, their initial relative relevance, i.e., which percentage of the initial SOC is in each pool, are usually estimated with a spin-up run (Nemo et al., 2017). A spin-up run is a simulation in which the carbon amount in each pool is initially set to zero and then allowed to reach equilibrium under stable yearly weather and soil management conditions. The equilibrium is usually reached after decades of simulation time; the carbon content of each pool at equilibrium is used to calculate the initial relative relevance of the carbon pools and then multiplied by the initial SOC to determine the initial amount of carbon in each pool. The inputs for the spin-up run are: the average weather conditions in the area, and the monthly soil carbon inputs from the previous land use. The soil properties are the same as in the main simulations.

We run spin-up runs for Paiporta and Sueca RothC_Med simulations, since no mulching was applied in the orchard inter-rows before the experiment started. We used the following values for the soil parameters of the RothC simulations, as measured by Visconti et al. (under review): in Paiporta, clay content 36%, soil depth 20 cm, bulk density of 1.57 kg m-3; in Sueca, clay content 32%, soil depth 20 cm, bulk density of 1.4 kg m-3. We calculated the "average year weather" inputs using monthly weather data averaged over the years 2009-2020, more specifically for air temperature (°C) and rainfall (mm), while we used the evapotranspiration (mm) estimated by Oltra (2014), obtained using Penman-Monteith method version FAO-56 Allen, (1998).

As input for the agricultural management, we used:

- DPM/RPM ratios suggested by Coleman and Jenkinson (1996) for agricultural practices, 1.44;
- Data available in the literature shows that citrus orchards were present in the area for at least 40 years before the beginning of the experiment, so the carbon input for the spin-up run was estimated from literature for Mediterranean citrus orchards (Mota et al., 2011).

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2.3 2050 projection of SOC stock

Finally, we projected the SOC stock trends to the year 2050, including the variability in the weather parameters taking into account the projection of IPCC according to which the temperature will increase by 1.5°C by 2050. To do so, we proceeded by: i) analyse the weather data (rainfall, air temperature, evapotranspiration) measured in the years 2009-2020, the same as used in the spin-up run, extracting the monthly average and standard deviation for each variable; ii) use the monthly average weather data, increasing the temperature linearly in time up to a +1.5°C by 2050, as input for the projection of the SOC trends to the year 2050; iii) use the monthly standard deviation of each variable to estimate the uncertainty for each variable; iv) run a Monte Carlo analysis (Ferrenberg and Swendsen, 1989; for a total of 10000 simulations) to perform an uncertainty analysis of the projected SOC stock trends.

3. Results

3.1 Spin-up run

The spin-up simulations took on average 830 years for the SOC pools to reach equilibrium. The relative relevance of each SOC pool, in percentage, for Paiporta and Sueca respectively, were:

- BIO= 2.18 %, 2.19 %;
- DPM= 0.91 %, 0.69 %;
- RPM= 82.99 %, 83.14 %;
- HUM= 13.92 %, 13.98 %.

These fractions were used to derive the initial conditions for our experiment simulations, multiplying them by the SOC stock measured at the beginning of the experiment, which were 28.62 t C ha^{-1} in Paiporta and 36.92 t C ha^{-1} in Sueca.

3.2 Experiment simulation

The calibration of the water budget part of the modified RothC model resulted in the following values for the new RothC_Med parameters: -47 and -40 mm for the Paiporta and Sueca "Drought" parameter, respectively; -20 mm for both Paiporta and Sueca "MinTSMD" parameter; an amplitude of 7 mm TSMD and phase shift of 2 months for the sinusoidal function used in the Sueca Bare simulation, and zero for all the parameters of the sinusoidal function in all other simulations, since the water table effect on soil water content was negligible in Paiporta and Sueca Mulch. The comparison of RothC_Med with RothC and RothC_N calibrated models for the Bare treatment shows that RothC_Med performed better than the other two versions of RothC, with RMSE between observed TSMD values and simulated one being 21.94, 30.6, and 8.51 for RothC, RothC_N and RothC_Med, respectively, in Paiporta, and 22.19, 29.59, and 8.45 for RothC, RothC_N and RothC_Med in Sueca (Fig. 1a and 1c). The results obtained for the Mulch treatment simulated using RothC_MM are shown in Fig. 1b and 1d for Paiporta and Sueca, respectively, for comparison.

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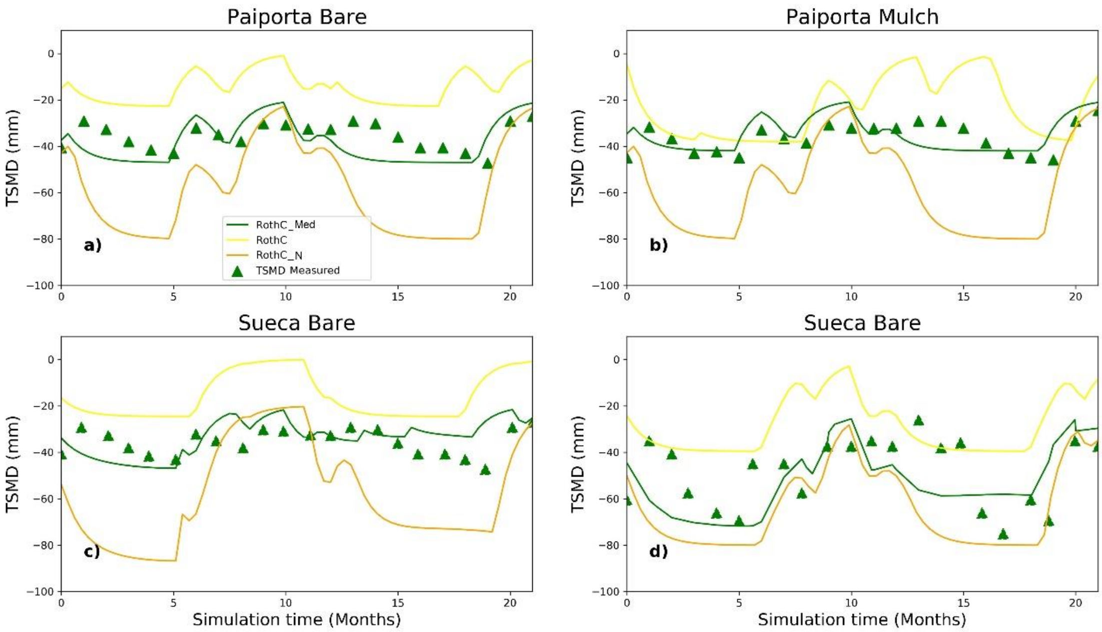

Figure 1. TSMD simulated by the basic RothC model, the RothC_N model, and the RothC_Med model after calibration for: **a)** Bare Paiporta, **b)** Mulch Paiporta, **c)** Bare Sueca, **d)** Mulch Sueca; the average soil water content measured in the field, translated to TSMD, is shown for comparison. Simulation time zero corresponds to the beginning month of the experiment (March 2019).

The Bare simulation calibration resulted in monthly C input set to 0.33 and 0.65 t C ha^{-1} month^{-1} for Paiporta and Sueca, respectively. The calibrated model generally follows the trend of the measured data (Fig. 2). The SOC stock simulated by the Bare simulation, and the prediction of the SOC stock for 2 years (from 2019 to 2021), compared with SOC stock measured, are shown in Fig. 2a and 2b. In Paiporta, the simulated SOC stock is stable in time, while in Sueca the simulated SOC stock slowly increases. More in detail, the RothC_Med estimates of the SOC stock increase during the period 2019-2021 in the Bare treatments are 2.1 and 4.9 t C ha^{-1} in Paiporta and Sueca, respectively. The simulated soil CO_2 emission in the Bare treatments follows the trend of the measurements in both Paiporta and Sueca (Fig. 2c and 2d).

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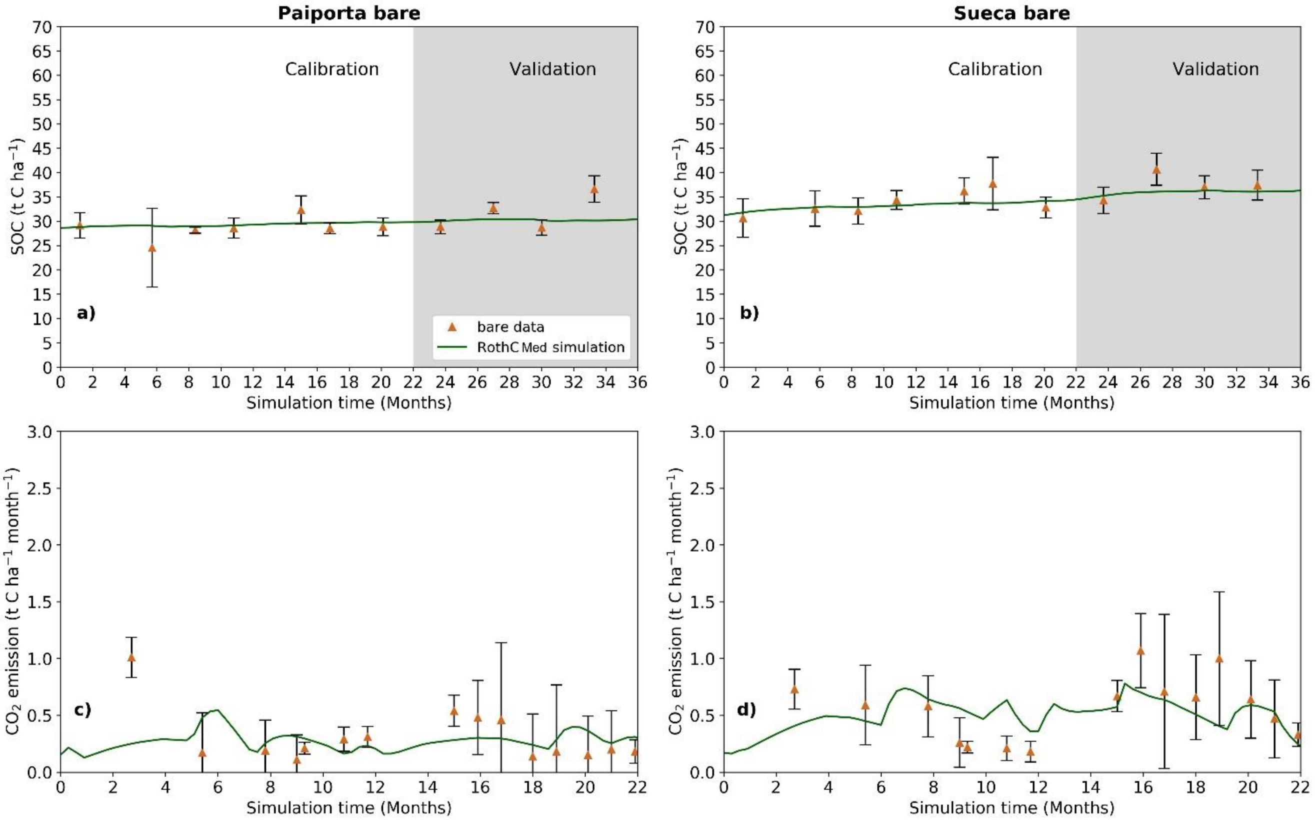

Figure 2. Simulated and measured SOC and soil CO_2 emission in the Bare simulations after calibration: **a)** SOC stock in Paiporta, **b)** SOC stock in Sueca, **c)** soil CO_2 emission in Paiporta, **d)** soil CO_2 emission in Sueca. Simulation time zero corresponds to the beginning month of the experiment (March 2019). The grey areas in **a)** and **b)** corresponds to the validation period (year 2021).

The Mulch simulations calibration resulted in monthly C input set to 0.61 and 0.63 t C ha^{-1} $month^{-1}$ for Paiporta and Sueca, respectively. The field observations showed that soil temperature excursion was 3% and 1% lower under mulch treatment in Paiporta and Sueca, respectively (Visconti et al. under review), so the "Mulch T insulation" parameter was set to 0.97 and 0.99 respectively. To fit the field observations of a larger soil water content, the corresponding TSMD reduction (called "Delta TSMD mulch" in the model) was set to -5 mm (as explained in Supplementary Materials). The comparison with the calibrated results from RothC and RothC_Med show that all models could fit the SOC stock observations fairly well and predicted a very similar trend, but basic RothC predicted very different CO_2 soil emission trends with respect to both RothC_Med and RothC_MM (supplementary Fig. S1). In order to fit the SOC stock and the soil CO_2 emission data, however, we had to increase the C input to the soil for RothC and RothC_Med substantially, up to 0.1 and 0.5 t C ha^{-1} $month^{-1}$ for Paiporta and Sueca, respectively.

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Fig. 3a and 3b show the comparison between the SOC stock predicted by the Mulch simulation and the SOC stock measurements, for the years 2019-2021. In Paiporta and Sueca, the simulations show a faster increase in SOC stock in the Mulch than in the Bare. The SOC stock predictions for Paiporta fairly fit measurements, even though SOC stock measurements taken in 2022 show a slight decrease in SOC stock. In Sueca, instead, the SOC stock predictions overestimate the SOC stock observations in the field. More in detail, the RothC_MM predictions of SOC increase, during the period 2019-2021 in the Mulch treatments, are 10.7 and 18.7 t C ha^{-1} in Paiporta and Sueca, respectively. The predicted soil CO_2 emission under Mulch follows the trend of the measured soil CO_2 emissions in Paiporta (Fig. 3c), but tend to underestimate measured soil CO_2 emissions in Sueca (Fig. 3d).

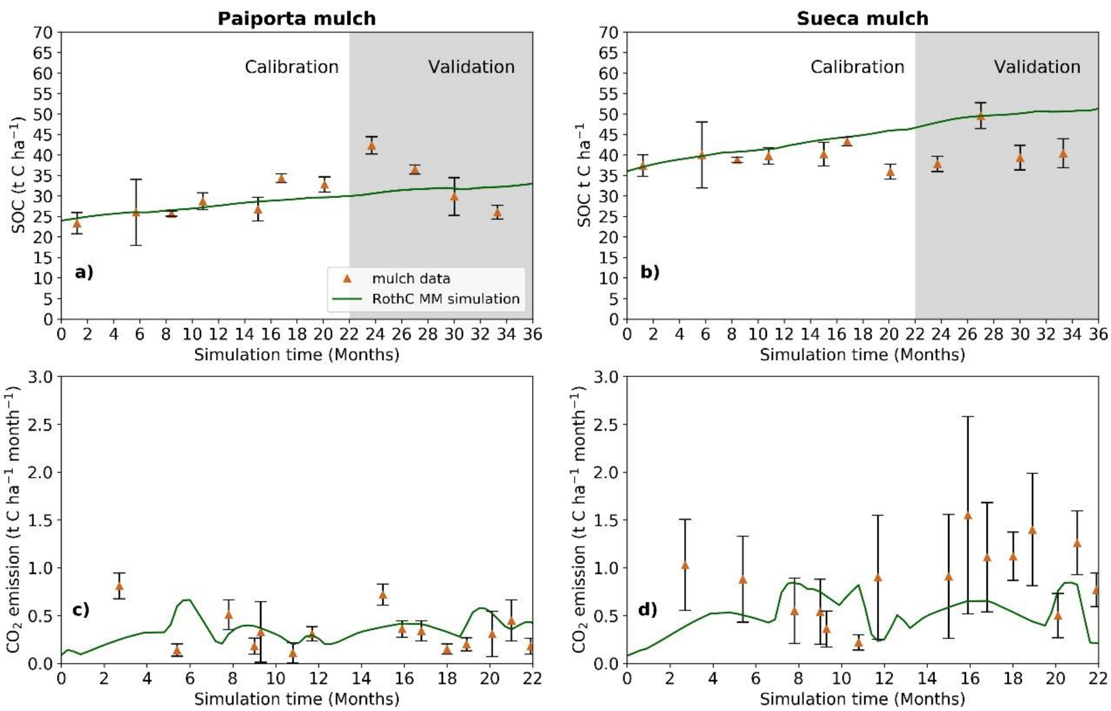

Figure 3. Simulated and measured SOC and soil CO_2 emission in the Mulch simulations after calibration: **a)** SOC stock in Paiporta, **b)** SOC stock in Sueca, **c)** soil CO_2 emission in Paiporta, **d)** soil CO_2 emission in Sueca. Simulation time zero corresponds to the beginning month of the experiment (March 2019). The grey areas in **a)** and **b)** corresponds to the validation period (year 2021).

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The linear models fit to the SOC stock data (Section 2.2.3, Supplementary material Fig. s2) had slope coefficient 2.32 in Mulch and 0.67 in Bare in Paiporta (Fig. S2a); and 1.41 in Mulch and 1.06 in Bare in Sueca (Fig. S2b; a positive slope coefficient indicates an increasing trend in the SOC stock linear model, the larger the slope coefficient the faster the increase). However, the null hypothesis could not be rejected on the basis of the Student's t-test, with p-value = 0.29 and p-value = 0.38 in Paiporta and Sueca, respectively. Thus, the slope coefficient of the linear models for Bare and Mulch are not significantly different. The RMSE of RothC_Med and RothC_MM with respect to 2021 observations of SOC were 4.86, 2.28, 11.51, 2.7 t C ha^{-1} for Paiporta Bare, Paiporta Mulch, Sueca Bare, Sueca Mulch, respectively. The linear models RMSE with respect to 2021 observations of SOC were 5.18, 2.29, 14.49, 2.53 t C ha^{-1} for Paiporta Bare, Paiporta Mulch, Sueca Bare, Sueca Mulch, respectively. The comparison between RothC_Med and RothC_MM models RMSE and linear model RMSE, thus, shows that RothC_Med and RothC_MM provide slightly better SOC stock predictions.

3.3 2050 projection of SOC stock

Fig. 4 shows the projected SOC stocks trends up to the year 2050 together with the range of variations in the predictions, with baseline calculated using average weather conditions with 1.5°C increase in air temperature, and the range of variation with the maximum and minimum SOC stock predictions related to humid/warm years and dry/cold years, respectively (the input data used to obtain the projections is shown in the Supplementary materials). The baseline simulation, shown as a line in Fig. 4, predicts a stable trend of SOC in Bare in Paiporta (Fig. 4a), and an increase in SOC in Bare in Sueca (from 50 to 84 t C ha^{-1}, Fig. 4c). The baseline prediction for Mulch shows an increase in both study areas, smaller in Paiporta (from 23 to 72 t C ha^{-1}, Fig. 4b) than in Sueca (from 36.02 to 159.14 t C ha^{-1}, Fig. 4d). In general, the projected SOC increases were larger in Mulch than in Bare treatments for both areas.

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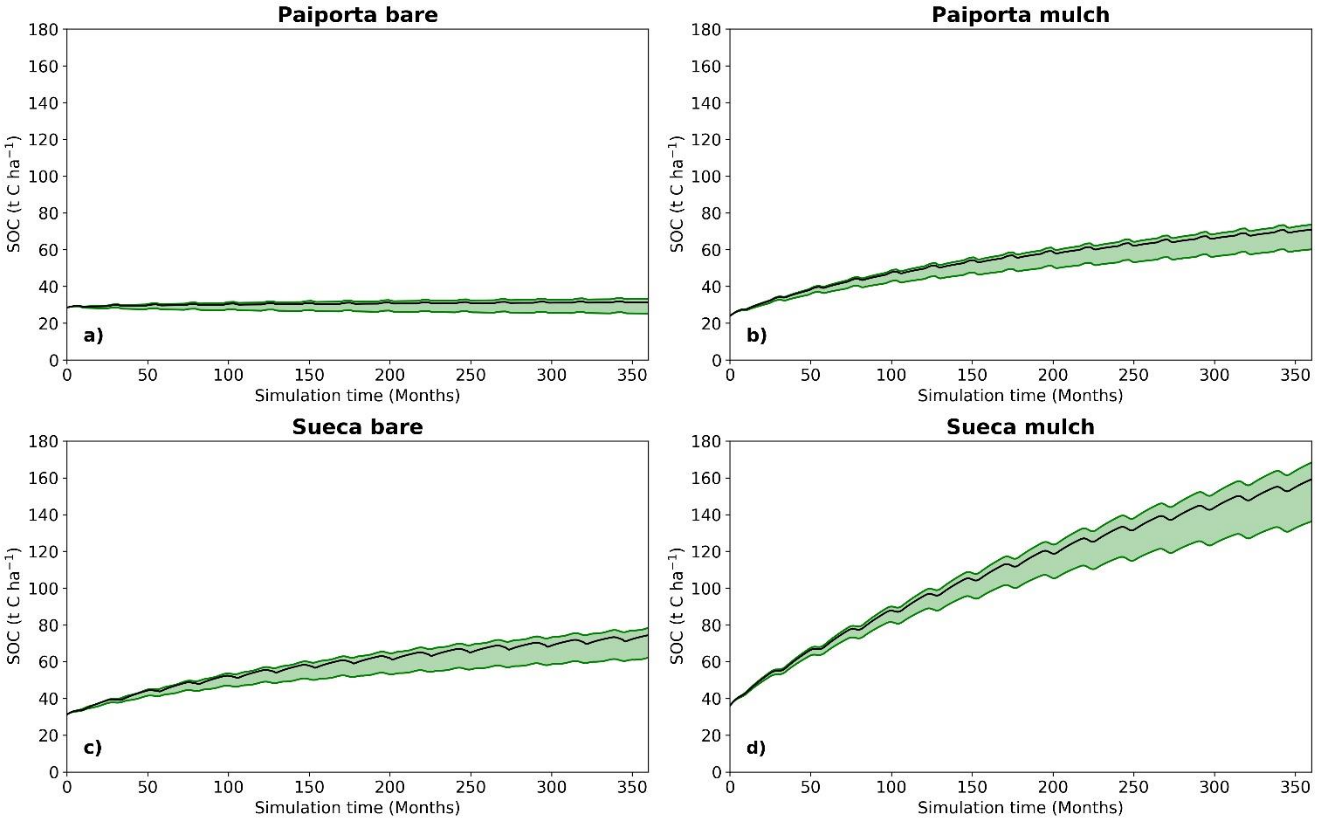

Figure 4. SOC projections with the baseline simulation to year 2050 with a 1.5°C increase in air temperature represented as a black solid line, with the related uncertainty shown, as maximum and minimum boundaries, for: **a)** Paiporta Bare, **b)** Paiporta Mulch, **c)** Sueca Bare, **d)** Sueca Mulch. The simulation time starts at 0 being March 2020, beginning of the experiment, and ends at 360 being March 2050. The weather dataset corresponding to the minimum and maximum SOC stock values simulated by the uncertainty analysis are shown in the Supplementary Materials.

4. Discussion

4.1 Calibration and validation model

The new parameters we introduced in RothC_Med, RothC_Mulch and RothC_MM are mostly empirical, but are based on direct, robust observations from the field, and as such should be calibrated using timeseries of T_s and θ_s measured in the field. The use of empirical parameters may be problematic when using RothC_MM on large scales where T_s and θ_s timeseries are not available; a physically-based description of the processes involved in the mulch effects on soil water content and energy flow would improve large spatial scale simulations. However, the use of a dedicated model for soil water and temperature, or the inclusion of mulching in a model more complex than RothC (e.g. CENTURY Parton et al., 1987),

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would increase the amount of parameters and data required to simulate SOC stock dynamics. We believe that the empirical parameters we proposed are more flexible, since they can be derived either by direct observations of T_s and θ_s measured in the field, or by estimating them using a soil water and energy flow model (e.g. Hydrus1D, Simunek et al. 2005).

The RothC_Med model fit the soil water content measured in the field much better than standard RothC, or even than RothC_N (Fig. 1a and 1b). RothC_Med was able to predict the low soil water content values reached during the long dry summer typical of a Mediterranean climate, as well as the lower than expected increase in TSMD after a rain event, due to the fact that the intense but short precipitation events in Mediterranean climates often infiltrates only the first few centimetres of soil and then quickly evaporates (Balugani et al., 2017, 2018), something that cannot be properly simulated when using monthly time steps. RothC_Med was also able to correctly predict the effects of the shallow water table on TSMD levels in Sueca Bare. However, RothC_Med predicted a faster decrease in TSMD levels at the beginning of the dry summer with respect to observations (Fig. 1); this is probably due to the fact that RothC_Med uses a simple water balance model and does not take into account the soil hydraulic conductivity effect on soil water fluxes.

When comparing simulated and measured soil CO_2 emissions, it should be kept in mind that they do not represent exactly the same thing: i) the simulated soil CO_2 emission can be taken as an estimate of soil heterotrophic respiration (R_h) only, while measured soil CO_2 emission, due to the presence of roots in the soil, is an estimate of total soil respiration (R_s, the sum of autotrophic respiration R_a and R_h); ii) the simulated soil CO_2 emission is the estimated monthly average emission of soil CO_2 from the soil, while the measurements are taken at a certain time of the day, for half an hour in a single day of the month (Visconti et al under review). Therefore, due to difference i), we would expect that the simulated R_h would, on average, underestimate measured R_s. Difference ii) is more difficult to analyse, since R_s changes daily and yearly depending on meteorological and biological conditions (Davidson et al., 1998; Ding et al., 2006; Daly et al., 2008; Jian et al., 2018). Thus accounting for both differences between simulated and measured soil CO_2 emissions, the comparison is aimed only at understanding if the simulated soil CO_2 emission is within the range measured in the field.

The calibration procedure resulted in an increase in the modelled C inputs to the soil, in a very consistent way over all Bare and Mulch simulations. Mulch C input was estimated to be 0 t C month^{-1}, since: the mulch used was dry, having been already exposed to weather while stored for one year before field application, no mulch straw was observed in the soil samples collected, and its C:N ratio was as high as 90 (Visconti et al. under review). This seems to indicate that we initially underestimated the input of organic matter in the soil. Our assumption was that mulch straw did not contribute significantly to the input of carbon to the soil; our simulations sustain this assumption, since the calibrated soil carbon input was not higher in Mulch simulations with respect to Bare simulations. The use of literature data to estimate the input of organic matter aboveground could partially explain the underestimation with respect to calibrated values. Another possible explanation is that our estimates of belowground organic carbon input for the upper soil (0-20 cm depth) was based on root mass observed in the first 5 cm of soil only.

The validation supported the ability of the RothC_MM to predict SOC trends better than a simple linear model. The RMSE values of RothC_MM models and linear models are, however, on the same order of magnitude; this is probably due to the

short time span modelled in the calibration-validation procedure: SOC values change very slowly, trends can require up to 10 years of measurements to be statistically significant (Smith, 2008), and 100-1000 years to reach equilibrium and, thus, to show that their increase is not linear in time. Moreover, the comparison with basic RothC and RothC_Med, calibrated in the same conditions, showed that: (a) using more frequent soil CO_2 emission observations it would be possible to appreciate the improvement brought on by RothC_MM with respect to basic RothC (which does predict very different trends) and RothC_Med (which predicts similar trends but lower values); (b) even if all model could properly fit the SOC stock data, RothC and RothC_Med needed much larger C input in order to do so. The last point means that using RothC to simulate a mulch experiment, without taking into account the indirect effects of mulching, would result in an overestimation of the C input. We want to stress, however, that our intention in developing the RothC_MM model was not to better fit SOC stock trends only, but to generalize RothC to account for mulch effects and estimate possible trends with different mulch materials.
The results from the calibrated and validated models show that the mulch application in Paiporta and Sueca resulted in an increase in SOC stock levels after 3 years with respect to the bare treatments (compare the trends in Fig. 2 with those in Fig. 3), even though the SOC stock measurements cannot confirm these results, as shown by the linear models analysis (subsection 3.2). Moreover, the simulations show that application of mulch has the potential to increase SOC stock more than bare treatments by year 2050, with the potential still far from reaching its maximum equilibrium (Fig. 4). However, the RothC_MM calibration and validation procedures show the effect of increasing C input (from the roots) only in Paiporta, while in Sueca the result of the calibration and validation procedure shows that the C input to the soil is similar between the Bare and the Mulch simulation. Therefore, we discuss the Sueca Mulch calibration further in section 4.2.

4.2 Analysis of Sueca Mulch simulation

The calibration of the Sueca Mulch simulation was difficult, since it was impossible to fit both SOC stock and soil CO_2 emission measurements by changing monthly C input only. Increasing monthly C input increases both simulated SOC stock and soil CO_2 emission, and vice versa. However, in the Sueca Mulch treatment the measurements show a larger soil CO_2 emission and a smaller SOC stock value with respect to the non-calibrated RothC_MM simulation; thus, the calibration constrained by both variables result in an overestimation of SOC stock and in an underestimation of the soil CO_2 emission (Fig. 2c). A better fit could be obtained by identifying a suitable parameter in RothC_MM that, when modified, would result in an opposite change in the two variables, i.e. a parameter that can increase the simulated soil CO_2 emission while simultaneously decreasing the simulated SOC stock values.
We identified three possible candidate parameters: a, b and k_i in Eq. 1, representing the temperature and the soil water content effect on SOC degradation, and the implicit rate of degradation determined by the microbial activity in the soil, respectively. Since all three values are multiplied together in Eq. 1, changing one or the other provides the same result, and, thus, we studied them at once by introducing another parameter j to reduce or increase the effects on SOC degradation:

$$Y_{deg,i} = Y_i(1 - e^{-jM_T abck_i t}) \quad (3)$$

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The two parameters M_T and j are different and have different meaning, even though both are multiplied in Eq. 3 and therefore have the same results on the calculation of $Y_{deg,i}$; just like the parameters a, b, c, or k_i have the same effect on the calculation but very different physical meaning. M_T is a parameter with a determined value that can be estimated from independent field measurements (section 2.1.3), while j is only used to study the behaviour of the model and how it could fit better the observations from the Sueca treatment.

As a thought experiment, we changed j between 0.5 and 2, halving and doubling, respectively, the degradation rate of SOC (Fig. 5). The results show that doubling the SOC degradation rate improves substantially the fit between simulated and measured values. We want to stress that the j parameter was only used to speculate on the possible causes for the strange behaviour observed in Sueca, and was not used in the calculation of the results shown in section 3.

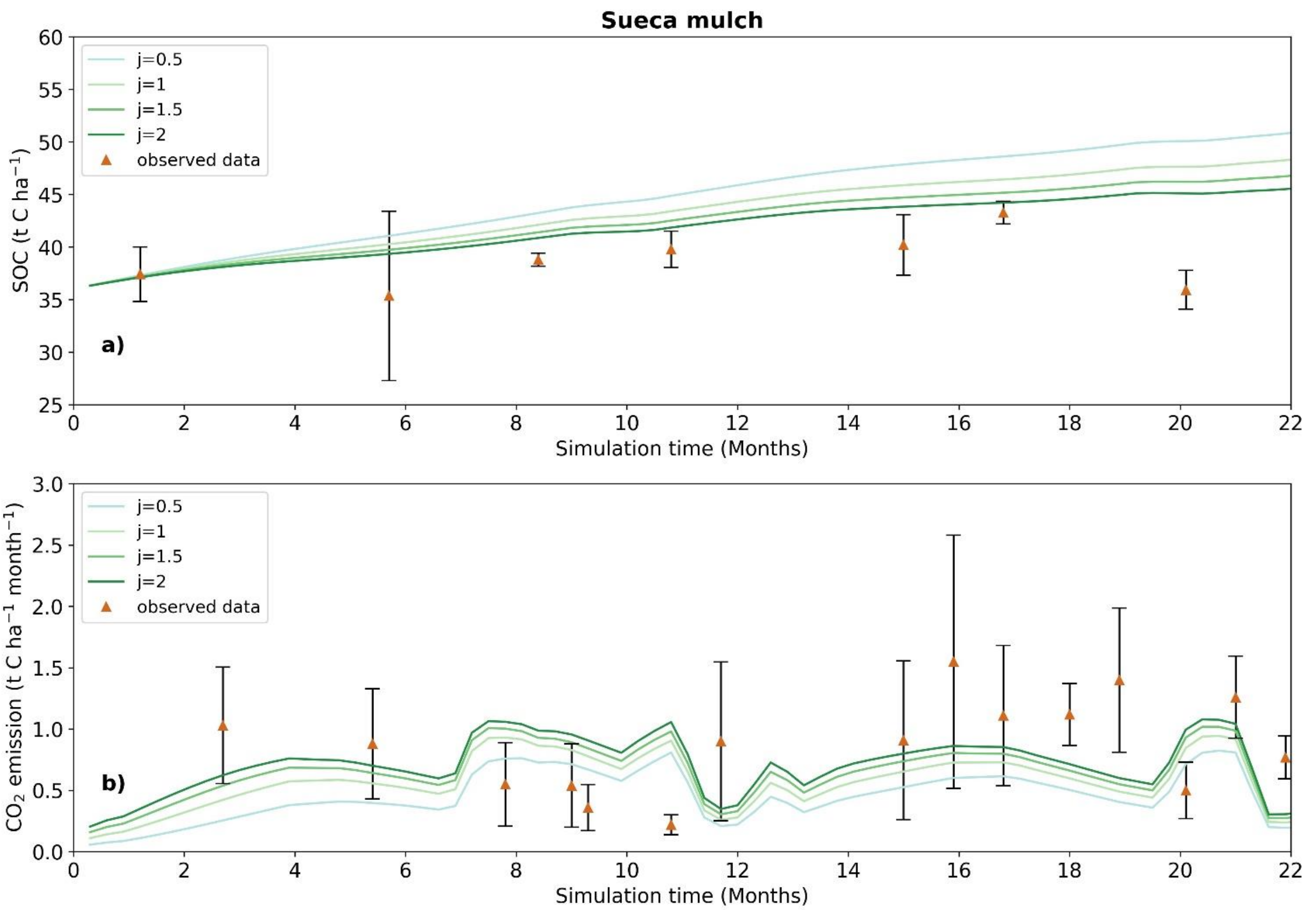

Figure 5. Variation in simulated a) SOC pools and b) soil CO_2 emission when changing the j coefficient (j=1 is the baseline simulation) for the Sueca Mulch simulation.

Since the effect of soil temperature and water content on SOC degradation rates have already been included in the M_T parameter and the RothC_Med modifications, we speculate that j may represent the effects of mulching on the Sueca soil fauna and microbial community, which is represented implicitly in RothC using the k_i parameters (Lehmann and Kleber, 2015; Cagnarini et al., 2019). The parameters k_i represent the intrinsic degradation rate of RothC pools, and are seldom modified due to the amount of data required to change them; however, it has been done in some cases (Skjemstad et al., 2004; Zimmermann et al., 2007). A proper calibration of k_i is especially important for the HUM pool, since it is the most important parameter for the determination of long term SOC stock in RothC (Cagnarini et al., 2019). Since k_i is an implicit representation of the degradation activity of the soil biota, to improve its representation in soil carbon cycling models, and explicit representation of the biological and ecological processes in the soil should be considered; various studies are already going in that direction (Allison et al., 2010; Wang et al., 2015, 2022; Sulman et al., 2018), but still need further testing before being used to predict SOC changes in field conditions.

4.3 2050 projections of SOC

The projections to year 2050 show that, in both study areas, SOC stock does not reach equilibrium even after 30 years of simulation. In Mulch simulations, in 2050 the SOC stock is expected to be increasing in both areas, even considering the variability of the parameters (Fig. 4c, 4d). In the Bare simulations, instead, the 2050 SOC stock trends are less clear: the uncertainty projection shows that SOC stock trends could be either increasing or decreasing in time in Paiporta (Fig. 4a) or slowly increasing in Sueca (Fig. 4b). In general, the uncertainty analysis conducted showed that SOC is expected to increase in all sites apart for Paiporta Bare. A way to improve our projections would be to decrease the uncertainty related to the future trends for air temperature and rainfall, e.g. using more refined climate change models for the study areas.

Our predictions show an increase in SOC stock of 62.16 t C ha^{-1} by year 2050, on average. This means that, when mulch application is considered in all citrus orchards in the Valencian Community (159 000 ha), the organic carbon sequestration is expected to reach 9.88 Mt C by year 2050; however, this assessment should be treated carefully, taking into account first the total production of rice straw in the Valencian Community and then the competition with other uses, e.g. cattle beds.

4.4 Comparison with other studies and study limitations

Throughout literature, we found two studies modelling carbon sequestration practices with straw mulch using RothC in Mediterranean region (Nieto et al., 2010; Mondini et al., 2017). Nieto et al., (2010) simulated the effect of mulch adding the organic C input of mulch in the model to compare SOC dynamics in a traditional soil management and in a mulch soil management. Mondini et al., (2017) modified RothC introducing additional pools of decomposable, and resistant exogenous organic matter to take into account the different nature of several organic amendments, including straw mulch. They conducted laboratory incubation experiments to characterize the exogenous pools of the different amendments.

Since both studies take into account only the direct effects of mulching, i.e., the increase in C input to the soil due to incorporation of the mulch biomass, the introduction of mulch in their RothC model has the effect of increasing both the simulated SOC stock and soil CO_2 emission from the soil, as explained in section 4.2. The indirect effects of mulching, as observed in the accompanying article detailing the field experiment (Visconti et al. under review), however, have the effect of increasing SOC stock while decreasing the emission of CO_2 from the soil. Our RothC_Mulch (and RothC_MM) model can simulate this indirect effect, which is particularly relevant to soil carbon sequestration practices, since it results in a net gain of carbon in the soil that is not released quickly to the atmosphere as a greenhouse gas (CO_2).

A limitation of this study is that RothC_Med and RothC_MM calibration and validation was based on data collected over a relatively short period of time (2 years for calibration and 1 year for validation). Since SOC stock changes slowly in time, to perform a proper calibration and validation, a longer dataset (around 10 years) would be preferable. For this reason, long-term field studies are suggested (and indeed required) to deliver reliable long-term sequestration projections (Smith et al., 2020); some studies are already trying to collect long-term field collected datasets in standardized platforms to help develop, calibrate and validate soil carbon models (Smith et al., 2020; LTEP-BIOCHAR, https://site.unibo.it/environmental-management-research-group/en/activities/long-term-platform).

Another limitation is that we did not account for SOC losses due to soil erosion and leaching. We do not believe that soil erosion would affect the study areas analysed here, since both Paiporta and Sueca sites are levelled terrain, lower than the surroundings (which also eliminate the issue of rain water run off). Leaching, instead, was not measured in Visconti et al. (under review), and thus was not accounted for in the present study. However, some losses of the dissolvable fraction of SOC are to be expected, due to the soil being in general well drained, as can be seen in Fig. 3 of Visconti et al. under review). Neglecting the loss of SOC due to drainage results in overestimation of the SOC degradation rate; as such, our 2050 projections of SOC stocks should be considered conservative estimates.

Finally, RothC only implicitly represent, with a single constant parameter k_i, the mineralization process carried out by the soil microbial community. This limits the validity of the model in soils with different soil microbial communities, and raises questions about the source for unexpected fitting problems, as was discussed in section 4.2. New, ecological soil models are being developed, with the aim to represent the soil microbial community mineralization process explicitly (Allison et al., 2010; Wang et al., 2015; Sulman et al., 2018); a future study should try to use these novel models to test the hypothesis of the j parameter inserted here.

5. Conclusions

Our study shows that it is possible to include both direct and indirect effects of mulching application in field conditions in a Mediterranean climate:

- Our RothC_Med model was able to fit the soil water content observations collected in the field, even in the presence of a shallow water table, with a substantial improvement on both basic RothC and the modification of RothC by Farina et al., (2013);

- Our RothC_MM model was able to estimate correctly the SOC stock and soil CO_2 emissions for the validation dataset. As far as we know, this is the first soil C dynamic model including mulching that was calibrated with SOC stock and soil CO_2 emission measurements;
- At the end of the 2019-2020 and 2050 projections simulations, the SOC stock in straw mulch-treated plots increases by, respectively, 4 t C ha^{-1} and by 23 t C ha^{-1} in Paiporta and 2.92 t C ha^{-1} and 4.76 t C ha^{-1} in Sueca; this confirms the carbon sequestration potential of mulch in a Mediterranean climate.
- RothC_MM could represent a flexible tool to assess the effect of mulch for small holder farmers of the Mediterranean countries, but it requires a long-term field studies implementation to deliver reliable long term sequestration projections. For this reason, this study represents an important step toward the assessment of the carbon sequestration potential of mulch.

Code availability.

Data availability. The dataset used in this article is detailed in "Straw mulching increases fertility and organic carbon in the inter-row topsoil of two Mediterranean citrus orchards Biology and Fertility of Soils" by Visconti et al., actually under review.

Supplement. The supplement related to this article is available online at: (insert internet link for the supplementary material sent with manuscript)

Author contributions: SP: Software, Validation, Investigation, Data Curation, Writing - Original Draft, Writing - Review & Editing, Visualization; EB: Conceptualization, Software, Validation, Formal analysis, Investigation, Writing - Review & Editing, Visualization; JMdP: Conceptualization, Methodology, Investigation, Resources, Data Curation, Writing - Review & Editing, Supervision, Project administration, Funding acquisition; DM: Methodology, Investigation, Resources, Writing - Review & Editing; FV: Conceptualization, Methodology, Investigation, Data Curation, Writing - Review & Editing, Project administration.

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Review statement.

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