



Article **Factors Governing Total and Permanganate Oxidizable C Pools in Agricultural Soils** from Southern Italy

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Abstract: The present investigation was aimed to quantify the three principal components of the soil carbon (C) stock, namely inorganic, organic and permanganate oxidizable, in 0–5 cm and 5–30 cm soil layers, of the main Mediterranean agricultural land coverages: olive grove, olive forest, citrus grove, vineyard, arable irrigated, arable rainfed and natural soil covered by Mediterranean scrub and garrigue. We assessed the contribution of soil properties and climatic variables on soil TOC and POxC by Pearson's correlations, multiple linear regressions, principal component analyses and variance partitioning. NAT and both olive cropping systems showed the highest TOC concentration while the other land covers showed values ranging between 8.0 and 26.6 g kg⁻¹. Soil POxC represented between 0.5% and 2.2% of the total soil C. A large number of interrelated factors govern soil C accumulation in Mediterranean agroecosystems. Rainfall and temperature had a selective effect on soil C distribution between the sampling areas, while among soil properties, texture exerted a prominent effect, resulting in positive effects from clay and negative effects from sand. Soil POxC concentration showed a similar trend to soil TOC in all land uses although on each of them represent a different TOC portion.

Keywords: soil carbon stock; soil carbon assessment; labile organic carbon; land use; Mediterranean agroecosystems

1. Introduction

Soils contain the largest C stock on Earth, storing about 2500 Gt of C in the first meter of depth, greater than the atmospheric and vegetation pools [1], with a fundamental role on global C cycle being a determining factor of soil ecosystem services such as biological, physical and chemical functions [2]. Therefore, even minimal variation of this large reserve can cause massive consequences on the biosphere from the fertility of the soil up to the greenhouse gases concentration in the atmosphere [3]. Soil C stock is generally constituted by two components, both involved in the C exchanges between soil and atmosphere: an inorganic (TIC) and an organic (TOC) C pool. If the TIC pool strictly depends on the parent material and soil forming factors, representing the most stable component, on the other side, the TOC pool, which is more labile, is influenced by several biotic and abiotic factors. Therefore, for its considerable importance, it is fundamental to understand the factors that can influence the C stock in the soil [4,5]. The relationship between TOC and biotic and abiotic factors can strongly vary across environments and is affected by land use and vegetation types, making it possible to identify specific factors that govern soil C accumulation in the agroecosystems at a regional scale (arable, natural and semi-natural) [5,6]. Among biotic factors there are vegetation type, crop residue deposition and the soil microbial community [7,8], while abiotic factors include topography, soil physicochemical



properties [9] and climate [10]. Southern Italy is a Mediterranean region where the agricultural activity is characterized by a high spatial variability, both in the type and intensity with which it is practiced, generally on soil with an organic C concentration below the critical threshold of 2% [11] and considered with a high vulnerability to global climate change and desertification risk [12]. With regard to TIC, it is present in variable shares predominantly due to calcareous soil parent material [13], while carbonates represent in many cases the dominant form of C in soil [14] resulting from dissolution and precipitation processes under xeric climatic conditions [15]. Therefore, quantifying both those C pools in Mediterranean soils is crucial to assessing the effects of management and land use as well as of climate [16]. Among soil organic C pools, studying the readily available and easily degradable forms can provide knowledge about the soil C dynamics and sequestration, allowing the future level of C stock under different environments to be predicted, representing an early and sensitive soil quality indicator [17]. Indeed, litter-derived biomolecules such as polysaccharides, lipids and proteins are quickly decomposable and rapidly supply soil food, also interacting, with soil microbiota [18]. Therefore, in addition to studying TOC variation that has long term variability, information related to this pool can help us to understand land management effects, even in the short term. The aims of this study are (a) to investigate the variability of TIC, TOC, POxC and C stocks in the typical agroecosystems of the Calabria region in order to provide baseline information at the regional scale; (b) to assess the effects of soil and climate parameters affecting TOC and POxC across agroecosystems, explaining their effects; and (c) to examine relative weight of land use, climate and soil properties in determining TOC and POxC levels in the soils of Calabria.

2. Materials and Methods

2.1. Study Area

The Calabria region is located at the southern end of the Italian peninsula and is bounded by the Tyrrhenian Sea on the western side and by the Ionian Sea on the southern and eastern sides. Most of the territory is mountainous and hilly; only 9% is represented by the plains. Agricultural areas include arable lands, tree crops, permanent meadows and pastures covering 28.7%, 45.7% and 25.6%, respectively. The main herbaceous crops are cereals, pulses and forage legumes and vegetable crops. Among the orchards, olive groves, vineyards, citrus and fruit trees are cultivated [19]. The main part of Calabria is characterized by a typically Mediterranean climate (Csa—Hot-summer Mediterranean climate) in Köppen's (1948) classification, with dry and hot summers and low average temperatures [20]. In Calabria, an average yearly rainfall of 1150 mm corresponds to noticeable seasonal contrasts and to high intraregional variability. Temperatures, generally along the coasts, never fall below 10 °C and never rise above 40 °C, but in the internal areas during the summer the maximum temperatures reach 42-44 °C. Because of its geographical location, topography and relief—with mountain ranges perpendicular to the direction of the main wet currents—Calabria is affected by rains highly variable in both time and space. The eastern side of the region is less rainy than the west side, especially as the precipitations come frequently from the west and discharge some of their rain on the Sila Plateau whilst moving towards the east. The Western coastal relief and the Serre relief receive more rainfall than the Sila Plateau, which is partially shielded from the first mountain range (Figure 1). Yearly average precipitation is >2000 mm on the Western Coastal relief and the Aspromonte Massif, whereas precipitation on the Ionian mountain slopes is 600–1000 mm, with values of ~500 mm along the coastal plains. With regards to annual maxima of high-intensity and short-duration rainfall, three homogeneous rainfall regions were delimited in Calabria, including (i) a Tyrrhenian region (25.8% of the region) along the western Tyrrhenian coast, (ii) a Central region (44.3%), comprising the mountain ranges along the main divide and (iii) an Ionian region along the eastern Ionian coast (29.9%). The Tyrrhenian rainfall region is characterized by more frequent and less severe rainfall events than the Ionian rainfall region, whereas the Central rainfall region has events with intermediate characteristics. Seasonality of the rainfall regime in Calabria is characterized by abundant rains occurring in autumn

and winter along the Tyrrhenian slopes (more than 70% of yearly total precipitation falls from October to March) and more heavily on the Ionian side. In the inland mountainous areas, from the Pollino to the Sila down to the Aspromonte, the climate is continental cold with hard and snowy winters and mild and quite rainy summers [20]. The internal central zone, which extends along the alluvial plains of the Crati and Mesina rivers, is characterized by climatic features intermediate compared to the previous ones. The Calabrian arch is part of an European-vergent chain characterized by an extensional tectonic, which is still active. Calabrian soils are highly heterogeneous and the prevailing soil orders are the following: Andisol, Vertisol, Alfisol, Inceptisol and Entisol [21,22]. A detailed description of soil properties is available in ARSSA [22].



Figure 1. Location and main properties of the study sites. Climate indication according to Köppen classification, while soil classification was retrieved from ARSSA [22]. Numbers indicate the principal mountainous areas of Calabria; 1: Pollino Massif; 2: Western Coastal relief; 3: Sila Plateau; 4: Serre relief; 5: Aspromonte relief.

2.2. Sampling Sites

Soil samples were collected from the main agricultural land uses diffused in the Calabrian region and from one natural area: olive grove (OM) (modern olive cultivation characterized by medium size plants); olive forest (OF) (traditional olive cultivation characterized by medium large size plants); citrus grove (CT); vineyard (V); arable irrigated cropping systems (ACI); arable rainfed cropping system (ACR); natural undisturbed soil covered by Mediterranean scrub and garrigue (NAT).

Soil samples were collected from sites with an unchanged land use during the last 25–30 years assuming that main soil variables, including C stocks, have already reached an equilibrium state. The sampling sites were chosen after an extensive spatial–temporal analysis of satellite images (from 1980) and soil maps [22]. The location of the study areas, their main properties and the sampling point distribution are presented in Figure 1.

2.3. Soil Sampling

For each of the 7 land uses considered, 6 typical and representative areas, characterized by a long-term land use, were chosen, and within each area 5 points were elected for sampling. As much as possible, the sampling points within each area were selected very carefully in order to well represent the land use investigated. At each sampling point, a sampling area was identified and 3 subsamples were taken from 0–5 cm (A) and from 5–30 cm (B) soil layers by a manual auger and then thoroughly mixed to form a composite sample. Only the mineral soil was sampled after removing the superficial litter and organic material. Soil bulk density (BD) was determined by the core method [23]. Soil sampling was carried out in spring 2017. The total number of collected soil samples was 420 (Figure 1).

2.4. Sample Preparation and Analysis

After sampling, soils were transferred to the lab, air-dried and divided in two aliquots; one was sieved to pass through a 2 mm sieve whereas the other one was crushed to pass through a 500 μ m sieve. Both aliquots were stored at room temperature until further analysis. Soil sieved with the 2 mm sieve was used to determine soil pH, electrical conductivity (EC), particle size distribution (PSD) and permanganate oxidizable C (POxC), while the aliquot sieved with the 500 µm sieve was used for inorganic C (C-CaCO₃; TIC), total organic C (TOC) and N (TN). Soil pH was measured in a 1:2.5 (*w*/*v*) suspension of soil in a 0.01 M calcium chloride solution, whereas soil EC was measured in a 1:2 (w/v) suspension of soil in water, in accordance with Sparks [24]. TIC (total soil C-CaCO₃) was determined by a gas-volumetric method using a Dietrich-Fruhling calcimeter as described in Sparks [24]. TOC and TN were determined by the dry combustion method using an elemental analyzer LECO CN628 (LECO Corporation, St Joseph, MI, USA). Soil POxC was determined according to the method developed by Weil et al. [25] and Culman et al. [26]. Briefly, 2.5 g of air-dried soil were weighed into 50-mL screw-top centrifuge tubes. To each tube, 18 mL of deionized water and 2 mL of 0.2 M KMnO₄ solution (prepared in 1 M CaCl₂) were added, and tubes were vigorously hand-shaken for 2 s and then mechanically shaken at 240 rpm for 2 min using a horizontal shaker. Tubes were removed from the shaker and allowed to settle at room temperature for exactly 10 min. After 10 min, 0.5 mL of the supernatant were transferred into a second 50-mL centrifuge tube and mixed with 49.5 mL of deionized water. Finally, sample absorbance was read at 550 nm with a UV/Vis Lambda 25 (PerkinElmer, Norwalk, CT, USA) spectrophotometer using UV WinLab Software (PerkinElmer). The amount of non-labile C (NLC), not oxidized by KMnO₄, was determined as the difference between TOC and POxC [27]. Particle size distribution (PSD) was determined using an Analysette 22 MicroTec Plus (Fritsch GmbH, Markt Einersheim, Germany) laser particle sizer following the standard procedure by Walling and Collins [28]. Fourteen soil particle size classes were determined (0.9-1.4-3.3-6.0-8.1-12.1-19.9-29.6-72.4-107.8-263.7-433.4-869.0-2000.0 µm). Clay, silt and sand percentages were determined according to the USDA classification. Soil C stocks were calculated by the following equation [29]:

$$C \operatorname{stock} = TOC \times BD \times D \tag{1}$$

where C stock is the organic C stock of the investigated soil layer (Mg ha⁻¹), TOC is the concentration of TOC in the soil (%), BD is the soil bulk density (g cm⁻³) and D is the soil layer thickness (cm).

2.5. Climatic Data

Climatic and bioclimatic data were provided from Worldclim [30] and from CGIAR-CSI [31,32] with a spatial resolution of 30 s (~1 km²). Data used were the monthly and yearly averages from the period 1950–2000.

2.6. Data Calculation and Statistical Analyses

The main statistical index (mean and standard deviation) were calculated to describe each soil property involved in the TOC dynamics. Data were tested for deviation from normality (Kolmogorov-Smirnov test) and homogeneity of within-group variances (Levene's test). Statistical analysis among agroecosystems was performed in the SAS v9.2 environment (SAS inst., 2009) (proc MIXED) for soil carbon pools (TIC, TOC, POxC, NLC and C stock,). Duncan's test at p < 0.05 was used for pairwise multiple comparison between means. In order to study the relationship between the two soil layers (0–5 and 5–30 cm), TOC concentration linear regression analyses were performed in MS Excel. With the purpose of distinguishing the contribution of soil and bioclimatic factors to TOC and POxC concentrations, Pearson correlation coefficient (proc corr) and stepwise multiple linear regression (proc reg) were carried out in the SAS v9.2 environment [33], while principal component analysis (PCA) and variance partitioning (varpart) were performed using R v3.5.0 statistical software [34] with FactoMineR v1.41 [35] and vegan package v2.5-2 [36]. Pearson's correlation coefficients between soil TOC and POxC concentrations in the 0–5 and 5–30 cm soil layers and 27 soil, climatic and bioclimatic variables were calculated in order to study the relationships between the soil C stable or labile pool and pedoclimatic and bioclimatic variables. Stepwise regression analysis was used to analyze the relationship between soil TOC and POxC concentration in 0–5 and 5–30 cm soil layers and the 27 soil, climatic and bioclimatic properties. In particular, a dataset from each C pool and soil layer was randomly separated (500 bootstrap resampling interactions) into a training set (70%), used to derive the model, and an independent validation set (30%), to validate the model. The process was guided to achieve the maximum R² values and an F probability of 0.05 was set for include or remove variables. Principal component analysis (PCA) was performed using data of the 27 soil, climatic and bioclimatic variables to establish the importance of each property in determining TOC and POxC concentration among the agroecosystems. Principal component means (centroid values) were calculated for each ecosystem and the significance between means was determined using Mahalanobis distance. The relative influence of soil, land use and climate on soil TOC and POxC concentrations was assessed by using a variance partitioning. The variance partitioning was based on partial redundancy analysis (pRDA), which allows one to predict the percentage contributions of each variable (soil, land use, climate) to the total variance of the studied variables (TOC and POxC). The pRDA results consisted of variation attributed exclusively to one of the studied variables (soil, land use, climate), shared variation explained (interaction among variables) and residual variation, which is the non-explained variation by the considered factors. The statistical significance effect of each group of variables was tested by means of one-way ANOVA.

3. Results

3.1. Soil Properties

On the upper soil layer (0–5 cm), total nitrogen ranged from 1.0 g kg⁻¹ to 2.5 g kg⁻¹ with the lowest values observed in ACI and the highest in NAT soils (Table 1).

Soil pH showed marked differences between sites reflecting soil parental material and climate conditions, ranging from acid (5.3) to neutral (7.5) conditions. The lowest values were observed on both olive cultivations (OM and OF), while the highest were detected on arable cropping system (ACI and ACR) and vineyard (V). Intermediate pH levels were under CT (6.8) and NAT (6.3) land cover (Table 1). Soil electrical conductivity (EC) varied from 151 to 293 μ S cm⁻¹ with the higher values in OM and NAT, which showed high variability among the sampling points. With regard to the deeper soil layer (5–30 cm), soil TN ranged from 0.8 to 1.7 g kg⁻¹, showing large differences from the superficial soil layer on both olive sites (–1% in OM and –0.9% in OF) and under NAT land cover (–1.5%) (Table 1). Soil BD, among the two sampled soil layers, ranged from 0.92 and 1.17 g cm⁻³ with the lowest values observed in OF and the highest in CT treatment. In general, higher values (+ 5.0%, on average) were observed in the deep soil layer (5–30 cm) than in the superficial ones (0–5 cm).

0–5 cm Soil Layer									
Land Use	TN (g kg ⁻¹)		pH (-)		EC (μS cm ⁻¹)		BD (g cm ⁻³)		
	μ	σ	μ	σ	μ	σ	μ	σ	
OM	2.3	0.4	5.7	0.6	293	174	1.01	0.05	
OF	2.5	0.4	5.3	0.5	151	72	0.92	0.02	
ACI	1.0	0.1	7.2	0.4	255	61	1.13	0.08	
ACR	1.2	0.2	7.5	0.1	229	54	1.02	0.07	
V	1.2	0.1	7.4	0.1	272	59	1.08	0.06	
СТ	1.5	0.2	6.8	0.7	236	81	1.17	0.08	
NAT	2.5	0.7	6.3	0.8	279	128	1.01	0.10	
5–30 cm Soil Layer									
OM	1.4	0.3	5.7	0.7	166	91	1.11	0.03	
OF	1.7	0.4	5.0	0.5	105	77	1.03	0.02	
ACI	0.8	0.1	7.2	0.5	191	51	1.16	0.09	
ACR	1.1	0.1	7.5	0.1	223	38	1.04	0.05	
V	1.0	0.1	7.5	0.1	230	37	1.13	0.05	
СТ	1.2	0.2	6.9	0.6	204	77	1.11	0.08	
NAT	1.0	0.2	6.2	1.1	186	99	1.14	0.09	

Table 1. Main soil properties of 0–5 cm and 5–30 cm soil layers at the experimental sites. OM: olive grove; OF: olive forest; ACI: arable crop irrigated; ACR: arable crop rainfed; V: vineyard; CT: citrus; NAT: Mediterranean scrub and garrigue. Data reported are mean (μ) and standard deviation (σ) (n = 30).

Particle size distribution, on average among both soil layers studied, showed values ranging from 2.0% to 28.9%, from 51.7% to 75.9% and from 12.6% to 22.4%, for sand, silt and clay, respectively. Soil texture varied from sandy-loam to silty-clay–loam (Table 2). The predominant textural class was silt–loam. Sand concentration was higher in NAT with respect to the other sampling sites, while lower values were registered in ACI, ACR, V and CT (Table 2).

Table 2. Distribution of soil particle sizes on the three main diametric classes (USDA) in the 0–30 cm soil layer for each land cover. OM: olive grove; OF: olive forest; ACI: arable crop irrigated; ACR: arable crop rainfed; V: vineyard; CT: citrus; NAT: Mediterranean scrub and garrigue. Data reported are mean (μ) and standard deviation (σ) (n = 30).

Land Use	Sand	l (%)	Silt	(%)	Clay (%)	
Luna Obe	μ	σ	μ	σ	μ	σ
OM	17.7	17.5	63.4	16.6	18.9	5.7
OF	27.8	20.2	51.7	14.3	20.5	6.2
ACI	2.0	4.5	75.9	4.0	22.1	2.7
ACR	9.5	11.1	71.4	9.9	19.1	1.8
V	2.0	4.5	75.6	4.6	22.4	3.8
CT	10.5	14.4	72.9	12.5	16.6	3.4
NAT	28.9	19.1	58.4	13.2	12.6	8.2

3.2. Soil C

Total soil C concentration ranged from 19.5 to 36.2 g kg⁻¹ in the 0–5 cm soil layer and from 14.4 to 27.6 g kg⁻¹ in the 5–30 cm soil layer (Figure 2).



Figure 2. Total soil C concentration and C partitioning (TIC, POxC and NLC) under different land use at 0–5 cm soil layer and 5–30 cm soil layers; 0–5 cm and 5–30 cm soil layer average value (μ); OM: olive grove; OF: olive forest; ACI: arable crop irrigated; ACR: arable crop rainfed; V: vineyard; CT: citrus; NAT: Mediterranean scrub and garrigue. Reported values are means (n = 30). Different letters indicate significant differences among agroecosystems (Duncan's test at p < 0.05).

In the superficial soil layer, the highest value was observed on NAT and the minimum on CT, while the other land uses showed values ranging between 26.2 and 31.0 g kg⁻¹. In the 5–30 cm soil layer, the highest C concentration was observed in ACR while the lowest was also observed in CT (Figure 2). On average, in the 0–5 cm soil layer, TOC was higher by +37% than in the 5–30 cm soil layer. Differences between the two soil layers were large in olive grove (OM and OF) and NAT and small

in other land uses (Figure 2). In the 0–5 cm soil layer, soil TIC ranged from 1.8 g kg⁻¹ to 20.9 g kg⁻¹. The highest inorganic C concentration was retrieved in ACI, followed by ACR and V, while the lowest values were observed under olive, both OM and OF, and CT (Figure 2). Intermediate values, around 10.0 g kg⁻¹, were retrieved on NAT soils (Figure 2). In this soil layer, TIC represented from 7% to 67% of the total soil C (Figure 3).



Figure 3. Total soil C compositional percentages under the different land uses at the 0–5 cm soil layer and 5–30 cm soil layer. OM: olive grove; OF: olive forest; ACI: arable crop irrigated; ACR: arable crop rainfed; V: vineyard; CT: citrus; NAT: Mediterranean scrub and garrigue. Reported values are means (n = 30).

Soil POxC, identified as the labile soil C, ranged from 0.15 to 0.60 g kg⁻¹. Higher values of POxC were observed on NAT followed by olive sites (OM and OF; 0.45 g kg⁻¹) and CT (0.43 g kg⁻¹), while the lowest concentration were retrieved on the arable cropping system, both irrigated (ACI) and rainfed (ACR) (Figure 2). Labile C average concentration ranged between 0.5% and 2.2% of the total soil C (Figure 3). No-labile C (NLC), in the 0–5 cm layer, ranged between 9.8 and 26.0 g kg⁻¹ with the higher values observed on NAT and olive sites (OM and OF) compared to the other land uses, which showed

values between the lowest limit and 15.3 g kg⁻¹ (Figure 2). Stable organic C represented from 32% to 91% of the total soil C (Figure 3). Higher values were observed on all tree crop and natural soil covers compared to arable cropping systems and vineyard (Figure 3). In the deeper soil layer, 5–30 cm, TIC concentration ranged from 1.2 to 17.2 g kg⁻¹ and showed a similar trend to the 0–5 cm layer, with the highest concentration in arable cropping systems (ACI and ACR) and vineyard and the lowest under olive grove (OM and OF) (Figure 2). TIC, in the deeper soil layer, varied from 7% to 68% of the total soil C concentration (Figure 3). Soil POxC concentration ranged from 0.10 to 0.18 g kg⁻¹ with the highest value observed on NAT, while the other land use had a similar concentration of about 0.14 g kg⁻¹. Soil NLC concentration varied between 7.9 to16.6 g kg⁻¹ (Figure 2) being from 31% to 93% of the total soil C (Figure 3). Higher values in the 5–30 cm soil layer were observed on olive grove (OM and OF) compared to the other land cover. Considering both labile and no-labile fractions, TOC ranged from 10.1 to 26.6 g kg⁻¹ in the 0–5 cm soil layer and from 8.0 to 16.7 g kg⁻¹ in the 5-30 cm soil layer (Figure 2). NAT and olive, both OM and OF, showed the highest values in the 0-5 cm soil layer (25.7 g kg⁻¹, on average), while the other land cover showed values between 12.2 and 12.9 g kg⁻¹, excluding ACI that showed a value equal to 10.1 g kg⁻¹ (Figure 2). In the 5–30 cm soil layer, TOC showed a narrower range of variation than the 0-5 cm soil layer (-32.6%), ranging between 8.0 and 16.7 g kg⁻¹, with higher values on olive grove (both OM and OF) compared to the other land cover (10.8 g kg⁻¹, on average). Different amplitude of TOC variation was observed between soil layers comparing land cover. NAT and olive grove difference mean value (-16.4 g kg^{-1} and -10.2 g kg^{-1} , respectively) were higher than other land covers (-2.5 g kg^{-1} , on average) (Figure 2). Soil POxC, on average between land uses, represented about 2.0% of TOC in the upper soil layer (0-5 cm soil layer) and 1.3% of TOC in the deeper soil layer (5–30 cm soil layer).

Considering all land covers, the relationship between the two soil layer TOC concentrations was linear and positive in the range of 0–15 g kg⁻¹ ($Y_{(TOC 5-30 \text{ cm})} = 0.83x_{(TOC 0-5 \text{ cm})} - 0.02$). Above this range, the points distribution shows an upper limit, testifying that with an increase of TOC in the 0–5 cm layer, the TOC concentration in the 5–30 cm soil layer had a minimum effect ($Y_{(TOC 5-30 \text{ cm})} + 12.8$), highlighting the presence of a significant stratification of organic matter (Figure 4).



Figure 4. Relationships between soil TOC concentration at 0–5 and 5–30 cm soil layers overall for all land uses studied (n = 420). Dotted lines represent linear regression within the interval 0–15 g kg⁻¹ ($Y_{(TOC 5-30 \text{ cm})} = 0.83x_{(TOC 0-5 \text{ cm})} - 0.02$, $R^2 = 0.96$, p < 0.001) and 15–35 g kg⁻¹ ($Y_{(TOC 5-30 \text{ cm})} = 0.020x_{(TOC 0-5 \text{ cm})} + 12.8$, $R^2 = 0.22$, p > 0.05).

Soil organic C stock in the 0–30 cm soil layer, on average among land covers, was of 42.9 Mg C ha^{-1} , with a mean contribution of 10.3 Mg C ha^{-1} from the 0–5 cm soil layer and 32.6 Mg C ha^{-1} from the 5–30 cm soil layer (Figure 5).



Figure 5. Soil organic C stock in the 0–5 cm and 5–30 cm soil layer in the different land uses. μ : overall average values; OM: olive grove; OF: olive forest; ACI: arable crop irrigated; ACR: arable crop rainfed; V: vineyard; CT: citrus; NAT: Mediterranean scrub and garrigue. Reported values are means (n = 30) \pm SE (bars). Different letters indicate significant differences among agroecosystems (Duncan's test at p < 0.05).

Land uses showed organic C stock values ranging from 29.0 to 56.6 Mg C ha⁻¹ with values ranging from 5.8 to 15.2 Mg C ha⁻¹ in the 0–5 cm layer and from 23.1 to 43.1 Mg C ha⁻¹ in the 5–30 cm layer (Figure 5). In the superficial soil layer (0–5 cm) the highest stock was retrieved in NAT soils, with intermediate levels in olive (OM and OF) and CT (12.5 Mg C ha⁻¹), and lower in the arable cropping system (ACI and ACR) and V (6.5 Mg C ha⁻¹, on average) (Figure 5). In the deeper soil layer (5–30 cm), the highest organic C stock was observed in OF (43.1 Mg C ha⁻¹) followed by CT (39.3 Mg C ha⁻¹) and OM (36.7 Mg C ha⁻¹), while concentrations between 27.9 and 29.1 Mg C ha⁻¹ were observed in ACR, V and NAT. The lowest level was observed in ACI (23.1 Mg C ha⁻¹) (Figure 5). Between land cover overall values (0–5 cm plus 5–30 cm), OF showed the highest organic C stock with 56.6 Mg C ha⁻¹ followed by OM with 50.2 Mg C ha⁻¹ and CT with 49.6 Mg C ha⁻¹. NAT showed a value of 44.3 Mg C ha⁻¹), while the lowest value was observed in ACI (29.0 Mg C ha⁻¹) (Figure 5).

3.3. Pearson's Correlations

Pearson correlations showed that both TOC and POxC, at the topsoil layer (0–5 cm) were linearly and positively related with a large number of variables (23 and 22 out of 27, respectively) comprising soil and WorldClim bioclimatic indexes (BIO01-BIO19; Ai). In the deepest sampling layer (5–30 cm) similar linear relationships only in TOC were observed and the linearity was less evident (11 out of 27) in POxC (Table 3).

	ТОС					POxC			
	0–5 cm		5–30 cm		0–5 cm		5–30 cm		
	r	<i>p</i> -Value	r	<i>p</i> -Value	r	<i>p</i> -Value	r	<i>p</i> -Value	
TIC	-0.46	<0.0001	-0.33	<0.0001	-0.42	<0.0001	-0.09	0.205	
pН	-0.70	< 0.0001	-0.48	<0.0001	-0.57	< 0.0001	-0.09	0.196	
EC	-0.01	0.870	-0.27	<0.0001	0.09	0.200	0.12	0.083	
BD	-0.22	0.002	-0.26	<0.0001	-0.16	0.021	-0.21	0.003	
Sand	-0.48	<0.0001	-0.23	0.001	-0.45	<0.0001	-0.15	0.029	
Silt	0.50	<0.0001	0.29	<0.0001	0.41	<0.0001	0.14	0.048	
Clay	0.26	<0.0001	0.22	0.002	0.40	<0.0001	0.13	0.046	
BIO01	-0.12	0.094	-0.01	0.901	-0.02	0.804	0.01	0.914	
BIO02	-0.22	0.001	-0.07	0.339	-0.32	< 0.0001	0.25	<0.0001	
BIO03	0.13	0.053	0.21	0.751	0.06	0.357	0.15	0.026	
BIO04	-0.53	< 0.0001	-0.40	<0.0001	-0.53	< 0.0001	0.13	0.067	
BIO05	-0.40	<0.0001	-0.19	0.007	-0.39	<0.0001	0.13	0.059	
BIO06	0.13	0.057	-0.17	0.015	0.27	<0.0001	-0.18	0.007	
BIO07	-0.43	<0.0001	-0.25	0.001	-0.49	<0.0001	0.21	0.002	
BIO08	-0.68	<0.0001	-0.52	<0.0001	-0.64	<0.0001	-0.05	0.484	
BIO09	-0.42	< 0.0001	-0.24	0.001	-0.35	< 0.0001	0.06	0.378	
BIO10	-0.34	<0.0001	-0.19	0.007	-0.26	< 0.0001	0.06	0.427	
BIO11	0.11	0.120	0.17	0.011	0.19	0.005	-0.06	0.395	
BIO12	0.51	< 0.0001	0.40	<0.0001	0.48	< 0.0001	-0.10	0.143	
BIO13	0.44	<0.0001	0.51	<0.0001	0.35	<0.0001	-0.06	0.409	
BIO14	0.57	<0.0001	0.48	<0.0001	0.54	< 0.0001	-0.09	0.186	
BIO15	-0.16	0.024	0.09	0.173	-0.28	<0.0001	0.22	0.001	
BIO16	0.44	<0.0001	0.47	<0.0001	0.36	<0.0001	-0.06	0.386	
BIO17	0.32	<0.0001	0.14	0.047	0.37	< 0.0001	-0.20	0.003	
BIO18	0.46	<0.0001	0.25	0.001	0.49	<0.0001	-0.14	0.041	
BIO19	0.40	<0.0001	0.27	<0.0001	0.32	<0.0001	-0.06	0.389	
Ai	0.46	<0.0001	0.33	<0.0001	0.44	<0.0001	-0.15	0.301	

Table 3. Pearson's coefficients and *p*-value of the correlations between soil, bioclimatic variables, TOC and POxC in the 0–5 cm and 5–30 cm soil layers. Significant values are shown in bold.

In particular, at the 0–5 cm soil layer, soil properties, excluding EC, had a significant negative effect (p < 0.001) on TOC accumulation, particularly pH (r = -0.70). TOC concentration also linearly decreased with increasing of sand (r = -0.48; p > 0.001) but increased as clay and silt increased (r = 0.50and r = 0.26, respectively; p < 0.0001), The temperature-related indexes (BIO01–BIO10), excluding the not significant BIO01, BIO03 and BIO06, showed negative linear relations with TOC at the topsoil layer; linearity was stronger versus BIO04 and BIO08 (r > 0.50; p < 0.001). In the same soil layer, TOC resulted positively and significantly related with precipitation-related indexes, from BIO12 to BIO19, resulting r > 0.40 in 7 indexes out of 9, as well as in Ai (r = 0.46) (Table 3). As observed in the top layer, in the 5–30 cm soil layer correlations between TOC and soil variables were negative and significant with TIC (r = -0.33), pH (r = -0.48), EC (r = -0.27) and BD (r = -0.26). Moreover, correlation of TOC with the textural fractions were even more significant (p < 0.0001): negative for sand (r = -0.23) and positive for silt and clay (r = 0.29 and r = 0.22, respectively). The higher significances (p < 0.001) among the many negative correlations between TOC accumulation in the 5–30 cm layer and temperature-related indexes were founded in BIO04 and BIO08 (r = -0.40 and r = -0.52, respectively). Among the pluviometric indexes many more variables highly significant related to POxC (p < 0.0001) were highlighted and, in particular, BIO13, BIO14 and BIO16 showed the highest correlation coefficients (r > 0.45). Similarly, to what found for TOC, in the 0–5 cm soil layer POxC was significantly (p < 0.001) related with soil variables TIC, pH and even with textural fractions resulting in r > 0.40 (Table 3). Furthermore, highly significant linear relationships between POxC and temperature-related indexes were also observed (p < 0.001) as in the case of BIO04, BIO07 and BIO08 (r = 0.53; r = 0.49 and r = 0.64, respectively). Additionally, for the rainfall indexes, Pearson correlations analysis showed a high significant correspondence with the POxC in the topsoil layer. In particular, a relationship with stronger linearity were observed between POxC and BIO14, BIO18 and BIO12 (r = 0.54; r = 0.49; r = 0.48, respectively) as well as with Ai (r = 0.44). With regard to the 5–30 cm soil layer, it was more difficult to find a linear correlation between variables and soil POxC concentration. A significant relation (p < 0.05) of soil particle distribution on the three principal dimensional classes appeared, while the effect of temperature and precipitation was less clear (Table 3).

3.4. Multiple Linear Regressions

MLR models calculated by the stepwise regression analysis are presented in Table 4.

	TOC (g kg ⁻¹)		POxC (g kg ⁻¹)			
y	x	т	y	x	т	
0–5 cm	BD (g cm ^{-3})	-31.03	0–5 cm	pH (-)	-0.030	
	Clay (%)	2.46		$BD(g \text{ cm}^{-3})$	0.304	
	BIO03	-2.37		PSD (0.03 mm) (%)	0.011	
	BIO04	-0.02		BIO01	0.031	
	BIO08	-0.48		BIO13	0.002	
	BIO17	-0.57		BIO14	0.073	
	BIO19	-0.03		BIO17	-0.008	
	Constant	340.72		Constant	-2.737	
$R^2 = 0.86$	F = 100.0	p < 0.0001	$R^2 = 0.86$	F = 107.1	p < 0.0001	
5–30 cm	рН (-)	0.61	5–30 cm	TIC (mg kg ⁻¹)	-0.091	
	$BD(g \text{ cm}^{-3})$	-15.51		Silt (%)	0.002	
	PSD (1.4 µm) (%)	4.60		Clay (%)	0.009	
	BIO08	-0.14		BIO07	0.010	
	BIO14	-1.38		BIO09	-0.025	
	BIO18	-0.30		BIO10	0.023	
	BIO19	-0.02		BIO14	0.032	
	Constant	37.58		Constant	-2.25	
$R^2 = 0.76$	F = 59.66	p < 0.0001	$R^2 = 0.70$	F = 50.6	p < 0.0001	

Table 4. Multiple linear regression for the estimation of soil TOC and POxC concentration in the 0–5 cm and 5–30 cm soil layers (n = 210).

Stepwise linear regressions revealed the different impact of soil and bioclimatic variables on TOC and POxC stocks with high precision. In all analyses, the coefficient of determination (R^2) was never less than 0.70. MLR models allowed us to select the most relevant variables related to TOC and POxC in the two soil layers investigated. With regard to the TOC, in both soil layers, clay content, and more precisely the concentration of the finest soil particles, together with BD were the most relevant soil properties, while the indexes of thermal excursion (BIO03, BIO04), temperature on rainy period (BIO08) and the rainfall in extreme periods, hot and cold (BIO18, BIO19), were the significant bioclimatic data (Table 4). In the deeper soil layer, the incidence of temperature-related indexes was lower than in the upper one. Relatively to the soil properties, TOC accumulation was negatively correlated to soil BD and positively with the soil's finest particle content. Among bioclimatic data, TOC showed a negative correlation with all indexes, especially with those that take into account temperature and precipitation in the extreme period (BIO08, BIO17, BIO14, BIO18) (Table 4). Soil POxC was positively related to BD and fine soil particles (silt and clay) and negatively with TIC and pH. Among bioclimatic data, significant and positive relationships were observed with the precipitation in the driest month (BIO14). Furthermore, in the deeper soil layer, annual air temperature range (BIO07) showed a positive correlation, while air temperature during the wettest and driest quarter (BIO09 and BIO10) showed an opposite trend between them (Table 4).

Principal component analysis was performed in order to describe the overall pattern of sensitivity of all measured soil variables, together with bioclimatic data, to the soil TOC and POxC in the different ecosystems. PCA for TOC and POxC clearly discriminated the seven sampling areas (Figure 6).



Figure 6. Principal component analysis biplot of the seven sampled agroecosystems for soil TOC (**a**) and POxC (**b**) concentration. PC1: first component variable; PC2: second component variable. The direction and length of each line indicate the degree of association between each soil properties and bioclimatic variables with TOC and POxC values in the sampled agroecosystem. OM: olive grove; OF: olive forest; ACI: arable crop irrigated; ACR: arable crop rainfed; V: vineyard; CT: citrus; NAT: Mediterranean scrub and garrigue. Comparisons of Mahalanobis squared distances showed highly significant differences (p < 0.01) in the soil, climatic and bioclimatic variables among agroecosystems.

With regard to TOC, the first two principal components accounted for about 63% of the total variance. PC1, contributed for 46.23% of the total variance and, among soil properties, was positively correlated with clay, silt, TIC, EC and pH and negatively with BD and sand. Between the bioclimatic indexes, PC1 allowed us to discriminate the effect of temperature-related indexes compared to those related to precipitation on the study sites. PC2 explained 17.00% of variance; the soil properties with the higher influence were sand (positive), clay and silt (negative) (Figure 6). Among bioclimatic data, PC2 slightly separated the precipitation indexes from the dry and warm season from those of the wet and cold period, and temperature seasonality (BIO04) from rainfall seasonality (BIO15). PC1 separated

V and ACR from OM-OF, CT-NAT and ACI, while PC2 distinguished among ACI and V and all other land covers (Figure 6). With regard to soil POxC stock, the first two components explained about 61% of the total variance; PC1 contributed 44.39%, and PC2 contributed 16.34%. Discrimination between land cover, correlations between principal components and studied pedoclimatic variables were similar to those observed for TOC.

3.6. Variance Partitioning

Variance partitioning analysis showed that for TOC, on average between both soil layers investigated, about 80% of variation was explained by the factors considered (Figure 7).



Figure 7. Contribution of land use, bioclimatic variables and soil parameters to the proportion of explained variation (%) of TOC and POxC in 0–5 and 5–30 cm soil layers in the seven agroecosystems studied, determined from the variance partitioning. The number in each bar represents the explained variation by the corresponding factor. The interaction effect represents the proportion of variation shared between all factor, while the unexplained portion is the variation that is not possible to attribute to any considered factors (land use, climate, soil).

In particular, soil properties accounted for 15.1% of variation while a higher contribution was observed from climate, about 21.5%. Land use represented itself 9.8% of variance. With regard to the POxC, a similar incidence of each factor compared to what has been observed for TOC was observed. For both soil C pools studied, interactions between factors represented the highest proportion of explained variance, accounting for 33.4% in TOC and 32.6% in POxC. Among the soil layers investigated, both for TOC and POxC, a higher unexplained variation was observed in the deeper soil layer (5–30 cm) than in the superficial ones (0–5 cm) (24.9% vs. 15.2%, on average) (Figure 7).

4. Discussion

4.1. Soil TOC, C Stock and POxC Concentration

Measured TOC and C stock levels showed similar values compared to other studies performed in Mediterranean areas [4,10,37–42]. The average TOC content in the soils of the sampled areas was 42.9 Mg C ha⁻¹ and fell within the range of values reported for other European countries. In general, our results agree with Farina et al. [40], who found in a Southern Italy survey TOC values in rangelands higher than in croplands. This evidence partially follows the different net primary production, which is generally higher in natural ecosystems than in croplands and in trees than in annual crops [43]. With regard to the specific land uses in the present study, some differences were observed compared to other studies. In particular, the olive grove, both modern and forest, showed the largest soil C stock compared with other cropland according to Chiti et al. [37], who observed 51.5 Mg C ha⁻¹ in the 0-30 cm soil layer, and to Novara et al. [44] who reported 53 Mg C ha⁻¹ in the 0-40 cm soil layer. On the other hand, our results disagree with those obtained by Muñoz-Rojas et al. [10] in Southern Spain (16.4 Mg C ha⁻¹ in the 0–25 cm soil layer) and by Muñoz-Rojas et al. [45] in Northern Egypt (14.5 Mg C ha^{-1} in the 0–25 cm soil layer). Moreover, the value of 36.3 Mg C ha^{-1} obtained in the vineyard study site was similar to that observed in France by Martin et al. [46] and Meersmans et al. [47] (39.4 and 32.7 Mg C ha⁻¹, respectively) and in Spain by Rodríguez-Murillo [48] (42.5 Mg C ha⁻¹). Our results from arable cropping systems in the 0-30 cm soil layer were 29.0 and 34.3 Mg C ha⁻¹, respectively, from irrigated and rainfed, in agreement with data from the 0–25 cm soil layer (31.7 Mg C ha⁻¹) obtained by Muñoz-Rojas et al. [45]. Soil C stock found in our arable cropping system under rainfed conditions was higher than in irrigated systems as also observed by Mudge et al. [49]. Citrus cultivation provided values (46.9 Mg C ha⁻¹) similar to those by Chiti et al. [37] (44.1 Mg C ha⁻¹), while Mediterranean natural land cover, consisting of scrub and garrigue, showed an intermediate C stock compared to arable and woody crops (44.3 Mg C ha⁻¹) with lower values than Novara et al. [44] (112 Mg ha⁻¹), but similar to Alberti et al. [50] (47.6 Mg ha⁻¹) and Francaviglia et al. [42] (40.6 Mg ha⁻¹ in the 0–25 cm soil layer) falling within the range reported by Muñoz-Rojas et al. [10] for this land use. As observed by Li et al. [51], natural land cover showed higher TOC concentration than cropland. The higher TOC in natural areas can be associated with the larger annual addition of leaf litter combined with the absence of any soil disturbance such as tillage [52,53]. With regard to tillage, an inverse correlation among soil perturbation intensity of agroecosystems and TOC pool was retrieved, so as to highlight differences between conventionally tilled and no-till systems (CT, V, ACI, ACR vs OF, OM). These results corroborate the role of tillage on the destruction of soil structure and physical changes, which stimulate microbial activity and expose a larger organic fraction to mineralization [54,55].

Since TIC stock can play an important role in C cycling and climate change [56], estimates of inorganic C stocks is of considerable importance [57]. Indeed, in three different areas (i.e., vineyard and both arable crops) soil inorganic C represented more than half of the total C content, reaching in some cases two thirds of the total soil C stock. Nevertheless, arid and semi-arid climatic conditions could greatly contribute, as soil-forming factors, to the formation of carbonate, as also argued by Tan et al. [58]. Further, together with the geological, pedogenetic and climatic processes, a negative relationship between TOC and TIC could be established as a result of carbonate dissolution during TOC decomposition [17].

Labile soil C stock, like POxC, comprises several easily decomposable substrates (i.e., polysaccharides, a fraction of microbial biomass) and was proposed as a reliable soil variable to predict soil nutrient availability and long-term soil C dynamics [26,59]. With regard to the upper soil layer (0-5 cm), Mediterranean scrubs, tree crops and vineyard showed higher concentrations than arable crops areas. This is consistent with previous studies that reported POxC levels in uncultivated and forest soils higher than in cultivated soils [60]. This suggests that different quantities and qualities of biomass input, as well as its degradation process, can have a significant effect on soil POxC levels. In particular, among the studied ecosystems, tree crops with deeper roots and larger above-ground C-inputs, such as leaf litter, can greatly contribute to soil C accumulation [53], whereas in croplands, residue removal and intensive tillage practices stimulate soil C mineralization and promote rapid labile C oxidation [61]. Moreover, the highest supply of organic matter in the surface layer was coupled with a more active C mineralization processes, which contributed to the release of C labile, as argued by Hiederer [62]. In the deeper soil layer, on the contrary, differences among systems were reduced as a probable result of superficial litter effect disappearance. On average, soil POxC accounted for 2.0% and 1.3% of TOC in the 0–5 and 5–30 cm soil layers, respectively, falling into the range of 1%–5% presented by several authors [26]. Finally, a good correlation between soil POxC and NLC globally for both soil layers was found ($R^2 = 0.62$), confirming the good aptitude of this parameter to predict the TOC stabilization process in the soil according with Hurisso et al. [59]. As revealed also from POxC data, Calabrian agroecosystems showed different patterns of TOC stratification along the soil profile. Although TOC

concentration was always higher in the topsoil (0–5 cm) than in subsoil, the reduction in concentration between the two layers was a function of land use. As referred for POxC, TOC stratification can be ascribed to several factors, namely residue deposition on topsoil, soil disturbance and crop management, especially tillage [63]. This evidence was observed also by several authors [44,64,65]. In particular, as shown in Figure 5, a linear relationship between top and subsoil C concentration was attained for the range 0–15 g kg⁻¹. This occurred in four out of seven land uses (namely CT, V, ACI, ACR). These four land uses are characterized by a higher soil disturbance compared to olive grove and undisturbed scrubs areas. Indeed, citrus and vineyard, as well as arable crop, are subjected to regular and repeated soil tillage during cropping season, while olive trees in Calabria are generally managed by no till use. This confirms that tillage can be the main factor responsible for TOC gradients along the profile in agricultural soils [66,67] and could contribute to subsoil C storage [42,65], especially under Mediterranean climatic conditions where water transport is limited. Among agroecosystems, the amount of C stock per cm of depth, calculated as the ratio between the C stock divided by soil layer depth, showed higher concentration in topsoil than in subsoil, confirming that in addition to a faster mineralization, in deeper layers a more efficient immobilization process also occurs [41,62,66,68].

4.2. Main Factors Affecting C Accumulation

A wide range of local site variables can be related to TOC distribution on agroecosystems linked to soil properties or climate that determine the processes of organic matter from its formation, to transformation, until the stabilization into the soil [65]. Among soil properties, as observed by Pearson correlation coefficients and the MLR approach, a great contribution to soil organic matter derived from silt and clay particles that showed a significant influence on both total and labile forms. Primarily, fine soil particles had a positive effect on soil water holding capacity and thus on plant biomass production [69]. After that, as argued by Kiem et al. [70], TOC dynamics are slowed down by silt and clay due to physical mechanisms of protection against oxygen diffusion and the attack of soil microorganisms, absorbing organic matter on soil structure and stabilizing it [9]. This double action mechanism has been supported by different C surveys around the world [5,68,71]. Another soil property that can play an important and significant role on C dynamics is pH; varying from each sampling areas and affecting soil reduction and oxidation processes into the soil can determine the fate of C substrate addressing to accumulation or mineralization [72] and vice versa. Indeed, in our soil survey, C accumulation in acid and sub-acid soil (OM, OF, CT, NAT) was higher than under neutral pH (ACI, ACR, V), thus confirming the negative correlation between soil pH and TOC content, as also observed by other authors [73], who related higher pH values to higher microbial mineralization activity. Soil pH, furthermore, is an important factor revealing TIC distribution across land uses and soil acidification processes [5]. Together with the pH, EC can play an important role in TOC distribution, addressing organic matter decomposition affecting soil functioning such as microbial activity and hydrology [74]. As a result of soil texture and management practices, bulk density represents an important physical variable affecting soil C sequestration as it controls macro and microporosity distribution and hence the microbial access to soil water and air volumes. Shifts to this ratio can have a significant effect on soil C decomposition and immobilization processes, establishing a negative correlation between BD and TOC [75]. Climate variables give a great contribution in explaining TOC distribution across land use at the regional scale [76]. Del Grosso et al. [77] observed that temperature and precipitation parameters can explain more than 50% of TOC regional variability. As revealed from our analysis, in the complex interaction between climate and soil C, a clear and contrasting trend between temperature and precipitation was observed. The role of temperature on TOC depends on its influence on the soil microbial community and organic matter decomposition. Indeed, low temperature inhibits microbial activity and can lead to reduced C mineralization, increasing C stock [78,79]. This effect was confirmed in our study by the negative Pearson correlations found between TOC and the temperature-related indices used. However, although some authors reported that an increase of temperature can result in higher plant growth and productivity associated with

a higher litter deposition, we hypothesize that in the study areas the temperature did not represent a limiting factor for plant production. The precipitation effect can be directly associated with an increase of net primary production of agroecosystems, thus increasing organic matter deposition in soil [71]. According to Deng et al. [76], in our study a positive correlation among TOC and annual precipitation was retrieved. However, a similar correlation has not been observed by other authors in Italy [38,50], which is probably due to the low annual rainfall that never exceeds 1000 mm in our sampling areas. Indeed, in arid and sub-arid agroecosystems, precipitation can stimulate plant production more than the microbial decomposition processes [64]. That was also confirmed by the positive correlation between Ai and measured TOC, as also observed by Delgado-Baquerizo et al. [80] and Rial et al. [81]. Therefore, our study agrees with Conforti et al. [71], who highlighted cool and wet climatic conditions as more favorable to C accumulation in Calabrian soils. Effects from climate variables were also confirmed by the relations between TOC and some bioclimatic parameters, as highlighted by Pearson coefficients and MLR analysis. An in-depth analysis of MLR highlighted an interacting effect between temperature and rainfall, related to the rainfall in dry and warm period represented by BIO14, BIO17 and BIO18 indexes, showing a negative relation with TOC concentration. This evidence points out what was said above, indicating also how the association between higher temperature and rainfall, and therefore high soil water contents, can stimulate soil microbial activity and hence organic matter depletion. Besides, based on the rainfall seasonality and distribution [82], these indicators can also lead to suppose a great effect of short rain events during late summer and autumn that can cause rapid variation of soil water content and related soil respiration flushes [83]. The climate effect was higher in the upper soil layer than in the deeper one, as also reported by Wagai et al. [84] and Willaarts et al. [39]. Soil physico-chemical variables as well as climatic factors showed a different impact on the soil organic pool of specific land uses. The principal component analysis allowed us to strongly discriminate the studied agroecosystems by climate characteristics indicating in climate the major factor explaining TOC distribution [39]. Indeed, OF, OM, CT, NAT and ACI were clearly separated from V and ACR by bioclimatic indexes, pointing out also a separation between temperature and rainfall indices. This evidence can result from the different distribution of land uses within the Calabrian region with OF, OM, CT, NAT distributed along the Tyrrhenian coast, whereas V and ACR are sites along the Ionian coast, confirming the trend observed by Versace et al. [85] and Capra et al. [86] among these areas, with higher rainfall along Tyrrhenian than Ionian coast and an opposite trend with regard to temperature regime, with consequences on TOC stock. Moreover, this discrimination can also be imputable to the finer soil texture observed in ACR and V, represented by long PC2, although to a lesser extent than climate parameters. The minor differences observed between olive tree areas (both OM and OF), NAT and ACI can be related to differences on climate of these agricultural districts and their soil textures. Among arable cropping systems (ACI and ACR), PCA evidenced a high discrimination between them. Indeed, these areas showed great differences in climate and their management. A significant differentiation was caused by the BIO17 index, representing the precipitation in the summer, indicating higher seasonal aridity in ACR than in ACI. Moreover, these differences can be exacerbated by irrigation in ACI. Needless to say, irrigation can play an important role in promoting TOC decomposition.

4.3. Contribution of Each Group of Edaphic Factor to C Soil Stocks

The variation partitioning analysis demonstrated that large parts (amounts) of TOC and POxC, in both layers investigated, could be explained by the combined effects of soil properties and climate variables. The relative contribution of soil properties and climate to TOC and POxC was also mediated by land use. Among the edaphic factors, climatic parameters help to explain the higher proportions of variations, although better in the surface than in the deeper soil layer. The greater weight of climate than other factors in determining C stock in the soils was also recognized by some authors [64], whereas others pointed out the reduction of the climate effect from surface to deep soil layers [39]. Not in accordance with our findings, other authors [4] reported in a Mediterranean environment

a higher contribution of soil variables than climate; however, this discrepancy could be related to the higher investigated surface and soil heterogeneity found among sampling areas. Land use and management had a secondary role explaining, on average, about 10.5% of SOC and POxC variation, showing similar values observed by Rabbi et al. [87]. Beside the aforementioned factors, however, the interaction between them could explain about a third of all variance. This evidence confirms how TOC accumulation and organic matter decomposition are the result of several different complex interactions, leading us to suppose that relatively small changes, especially with regard to climate parameters, can have a considerable effect on soil TOC and POxC deriving from a direct and indirect effect. The unexplained variance, larger in deeper than in surface soil layers, can indicate the influence of several factors not considered in the present work (such as soil discontinuity, micro-topography, exposure, local drainage, specific management) that can drive TOC variation at the agroecosystem scale [39,53].

5. Conclusions

Soil TIC, TOC and POxC distribution on most common land use across the Calabrian region, as well as the relationship with soil properties and climate variables, were studied. In particular, with regard to the first objective, our results highlighted that the agroecosystem where the most common tree crops of the region (olive and citrus) are grown can reach higher organic C stocks in the soils, combining their economical gaining with high landscape and environmental values. On the contrary, vineyard and arable crops showed lower values. Soil POxC levels highlighted a similar trend to soil TOC in all land uses, showing greater percentage incidence in the upper soil layer than in the deep one. Therefore, POxC can represent a simple and reliable indicator, especially in the superficial soil layer, of land-use change and management practice effects on soil C stock, discriminating between easily degradable and recalcitrant soil C forms. With regard to the second and the third objectives of this study, a large number of interrelated factors govern soil C accumulation in Calabrian agroecosystems. Among these factors, the considered soil properties and climate variables exert a synergistic and significant effect on total and labile soil C stock. In particular, rainfall and temperature have a selective effect on soil C distribution on the two sides of the Calabrian region, while among soil properties a prominent effect was observed from textural properties. In particular, if the Tyrrhenian side was characterized by higher TOC accumulation due to higher precipitation and colder temperature, the Ionic side of the region, on the contrary, revealed a lower accumulation of organic C due to the higher temperatures and lower precipitation. Within this context, land use and soil properties compared to climatic variables might predict a lower amount of the variability of soil C dynamics. Hence, it is relevant to investigate how climate change can affect soil C dynamics on the agricultural systems in Mediterranean areas. Further research is therefore needed to assess the effect of conservative practices in most common Calabrian agroecosystems, especially in those that show the lowest C stock values, in order to increase soil organic C concentration and contrast climate change.

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