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Abstract: Soil rebuilding represents a major challenge in the recovery of abandoned quarries. In this study, we explored the possibility of using reconstructed Technosols, to achieve soil rebuilding goals at an abandoned quarry site. We first investigated the use of a mixture containing commercial manure and limestone debris (LD) as pedotechnomaterials for an "*ad hoc*" (re)constructed Technosol (CT), for the recovery of an opencast limestone quarry in one of most concentrated quarry areas in the world. In a field experiment, we tested and monitored different pedotechnosystems (PTSs) made up of constructed Technosol + pasture species + different Mediterranean plant species. Specifically, a control (CT, without any additional treatments) was compared to treatments with organic amendment (CTOA) and conventional fertilizers (CTCF). Data were collected over a 12-month period and included crop performance, plant nutritional state, soil physical-chemical parameters, and metabolites. Analysis of variance compared differences among treatments, while factor analysis (FA) interpreted multiple relationships while explaining observed variability. Results showed that CTOA had better soil physical-chemical properties, greater plant growth, and overall superior agronomic performances compared to all other treatments due to the improved substrate conditions. According to FA, these results appear related to the creation of fertile soil conditions, with most of the investigated metabolites (*i*) playing a pivotal role in observed outcomes, together with (*ii*) a clear potential in being considered as a reliable fingerprint for investigating plant responses in constructed PTSs. The proposed pedotechniques in CTOA development show a great potential for the full recovery of abandoned limestone quarries in degraded Mediterranean areas by providing an excellent medium for plant growth, facilitating environmental reclamation.

Keywords: environmental restoration; pedotechnologies; organic amendment; debris limestone; metabolomic profile

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1. Introduction

Restoration activities represent a pivotal challenge to redeem abandoned and degraded opencast quarries [1] from both environmental [2] and socio-economic perspectives [3,4]. In such areas, whatever the chosen reconversion options, soil recovery represents the main issue that must be addressed [5]. When quarries were formed, pre-existing soils were inevitably subjected to deep bio-physical-chemical alteration affecting their whole features and the complex feedback/behaviours with the surrounding environment and, in most cases, soils completely disappeared, leaving just a rough, inert rock surface [6].

Bare quarry bedrock often represents the starting surface in most environmental restoration interventions. However, this surface is a harsh environment for vegetation establishment and development, especially in limestone quarries [7,8] where the calcareous rock materials exhibit low water [9,10] and nutrient-holding capacities [11] together with a low propensity for being subjected to pedogenetic processes without further human interventions [12]. Such scenarios are exacerbated in Mediterranean areas, characterized by dry summers, where the lack of soil water availability is a major constraint in seedling survival and development [13]. All these issues are expected to be exacerbated by climate change in the coming few years [14].

Under such difficult conditions, soil rebuilding through pedotechnical practices represents the first step towards environmental reclamation, providing a suitable substrate for revegetation processes and re-establishing ecosystem services [1,2]. Pedotechnologies [15], or "pedotechnique" [16,17], are those processes deliberately planned and managed by humans aiming to create and/or modify soils in terms of genesis and features [1]. Soil materials, called pedotechnomaterials (PTM), are used to reconstruct new soils, and soil rebuilding techniques are selected according to the needs of the local ecosystem, or goals for land use.

Procedures such as the addition of mycorrhizae or water-holding polymers [18] have been specifically implemented for limestone substrate; however, despite their promising results, they are often very expensive, necessitating the use of more practical and cost-effective options [7,19]. On the other hand, many scholars have investigated the use of organic amendments (OA), often industrial and municipal by-products, for restoring soils affected by opencast mining activities in the Mediterranean region. In research conducted in Spain, Soria et al. [20] mixed the first 20 cm of degraded limestone soil with several organic amendments, i.e., stabilized sewage sludge, vegetable compost garden waste, vegetable compost from greenhouse crop residues and two mixtures thereof, in order to increase the initial soil's organic matter content to 3%. They demonstrated that among the tested OA, vegetable compost from garden waste, or from horticultural greenhouse crop waste amendments, were the best because, in the experimental conditions, they exhibited the lowest mineralization rate and the highest survival and growth rates of the introduced plants. In addition, Luna et al. [21] demonstrated that the use of compost from urban organic wastes favored native plant growth by improving the hydrological properties of degraded limestone quarry soils in south-east Spain. Such interesting outcomes confirm that OA are helpful in supporting vegetation, satisfying requirements of cost-saving as well as nutritional efficiency.

Although OA has been widely investigated as a soil amendment for soil rebuilding purposes in Mediterranean areas, there is limited understanding of the effectiveness of OA combined with mineral materials. In their protocol, specifically implemented for limestone quarries, [1] suggested that OA together with highly pedogenizable mineral materials could be a viable option for soil rebuilding purposes. Limestone debris (LD) could be an excellent PTM, since: (*i*) it is a soil-related material common in many Mediterranean soils [22]; (*ii*) it increases nutrient availability for plants [23]; (*iii*) it increases soil strength while reducing deformability [24]. These are all pivotal factors for the genesis and development of a suitable soil profile able to provide adequate conditions for plants' growth, even during the long dry season that is a feature of the Mediterranean climate.

Opencast quarrying activities are widespread along the entire Campania region of central-southern Italy, creating several concerns in terms of environmental and health hazards. More than 600 pits are localized in the Caserta province, making the area one of the most concentrated quarry areas in the world [12]. In all quarries, soil cover has been completely scalped, with limestone often present as the main rough surface. Pre-existing soils are often illegally mixed with abandoned waste materials, with landfills presenting additional commonly prohibited activities [25]. All these issues produce negative externalities amounting to USD 3.8 billion in terms of social damages [12]. For these reasons, concentrated quarry areas represent a unique paradigmatic case study on a global scale.

In the present research, we investigated the use of a mixture consisting of OA and LD for the recovery of an opencast limestone quarry in the Mediterranean region of Italy. This research was novel in that we rebuilt a Technosol (CT). Organic and mineral materials were not simply mixed, but a complete soil profile was reconstructed, with each horizon having its own properties. We began with an open-air field experiment that evaluated and compared CT behaviour under different pedotechnosystems (PTS), i.e., the whole combination of constructed Technosol + vegetation conditions. Specifically, a control (CT without any additional treatments) was compared to CT treated with an organic amendment (CTOA) and conventional fertilization (CTCF). All treatments were revegetated with a mixture of pasture and compared with four different Mediterranean species: rosemary (*Rosmarinus officinalis* L.), olive (*Olea europaea* L.), and two grape cultivars (*Vitis Vinifera* L. ssp. Sativa); all selected for profitable purposes and for their socio-cultural importance. Indeed, soil recovery is here intended as the whole processes responsible for environmental restoration and improved socio-economic conditions. Crop performance, crop nutritional status, soil physical-chemical parameters and metabolites were assessed during the 12-month experiment, crop performance, nutritional status, soil physicochemical parameters and metabolites were evaluated, the latter as plant cell markers of nutritional status [26] and environmental changes [27].

2. Materials and Methods

2.1. Study Area

The investigation was performed under field conditions with 3 months, from September until November, for: soil reconstruction (1 month), stabilization (1 month), and pasture stabilization (1 month); and then 12 months for the full experiment (*vide infra*) in an experimental area in Castel Volturno (Caserta province, southern Italy; 41°00′ N 13°58′ E, 25 m asl; Figure 1).

During the experiment, total precipitation was 905 mm and mean air temperature was 14.6 °C. December recorded heaviest rainfall (135 mm), while July was the driest month (7 mm). The warmest month was August (23.9 °C), the coldest January (6.5 °C). The dry season lasted five months, from May till to September. Overall, the site is characterized by a typical Mediterranean-oceanic to suboceanic climate [28], with soils characterized by a xeric and thermic soil moisture and temperature regime.

Opencast limestone quarries historically characterized (*vide supra*) the calcareous pre-Apennines chain of the Campania region (south-central Italy). From a geological standpoint, it is a dolomitic limestone (Jurassic) and white microcrystalline carbonate (Cretaceous) formation.

2.2. Experimental Design

The experiment started with the field reconstruction of a Technosol, i.e., a man-made soil "with strong human influence" [29] using the protocol proposed by [1]. Specifically, an "*ad hoc*" Technosol was constructed (1 month) as $\hat{}Aup_1 - \hat{}Aup_2 - \hat{}Aup_3 - 2\hat{}R$ horizontation (ˆ is for human-transported materials (HTM); "u" subscript indicate the presence of artefacts, i.e., objects or materials that have been created or modified by humans, usually for a practical purpose in habitation, manufacturing, excavation, or construction activities; "p" subscript as a clue of horizon disturbance by mechanical means, pasturing, or similar uses [30], by using an appropriate mixing of selected pedotechnomaterials (Figure 1) to ensure adequate organic carbon, total nitrogen, and available phosphorus content along the Technosol profile, such as: (*i*) the 94.5% ($\hat{}Aup_1$ horizon), 96.0% ($\hat{}Aup_2$), 98.0% ($\hat{}Aup_3$) (wt) of a limestone debris (LD; Ø $\simeq$ 4.0 mm, with few scattered fragments till to 11.0 mm) type; and, (*ii*) the remaining 5.5% ($\hat{}Aup_1$), 4.0% ($\hat{}Aup_2$), 2.0% ($\hat{}Aup_3$) (wt) of a commercial manure (CM). The horizons were composed to replace a "natural" soil horizon (Figure 1). The deepest 2ˆR horizon was formed by spolic limestone only (rock fragments), in order to replace limestone quarry conditions. Pedotechnomaterials (PTS, i.e., LD and CM) were selected [1]: (*i*) to ensure adequate organic matter and macronutrient concentrations; (*ii*) because of their admissibility by European and national regulations as mineral (LD) and organic (CM) soil amendments/fertilizers; (*iii*) they are both cheap, widespread, and easily accessible. As a matter of fact, we used one of the best-selling organic amendments, while LD is abundantly present near the investigated site.

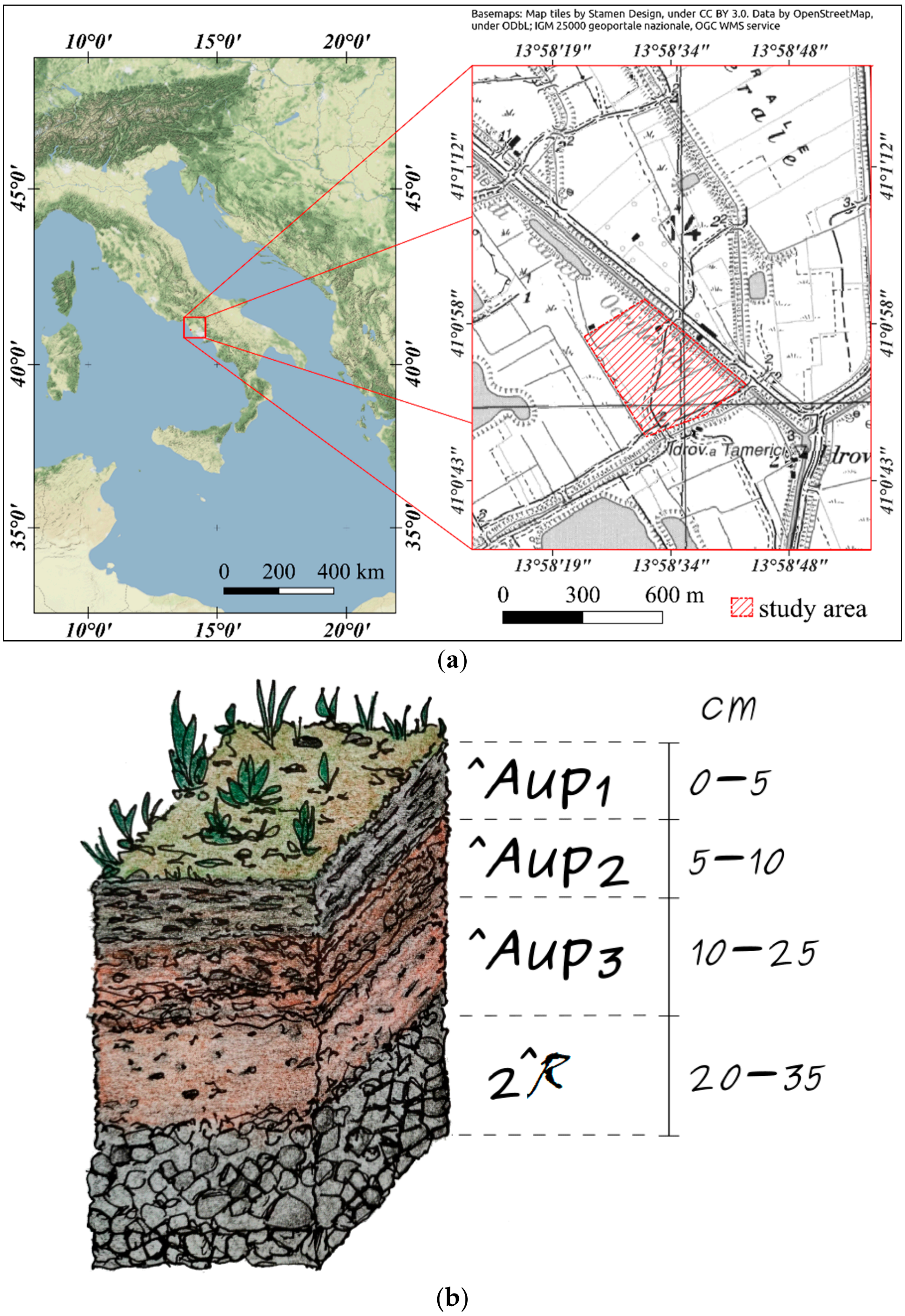

Figure 1. Study area (**a**) and schematic representation of constructed Technosol (**b**). ˆ for human-transported materials (HTM); "u" subscript indicates the presence of artefacts; "p" is for disturbance by mechanical means, pasturing, or similar uses (Soil Survey Staff, 2014).

Two main treatments, compared to a control (reconstructed Technosol without additional treatments), were investigated:

1. A (re)constructed Technosol (CT) mixed with a common commercial organic amendment (OA) at a ratio of 60:40 *w/w*: CTOA. It was mainly derived from urban organic wastes, agrozootechnical activities, composted sewage sludge, and "green wastes" such as pruning and cutting;
2. A (re)constructed Technosol (CT) treated with conventional mineral fertilization (CF) according to both plant-specific requirements and manufacturer's recommendations (*vide infra*): CTCF. It mainly consisted of NPK-based fertilizers. In particular, N was added as NO_3-N, NH_4^+-N (as ammonium nitrate), and CH_4N_2O, P as P_2O_5 (triple superphosphate), and K as K_2O (potassium oxide). Fertilizer was broadcast added at the beginning of the experiment at the recommended dose of 200 kg ha^{-1} [1]. After one month, a second CF dose was added at a rate of 300 kg ha^{-1} for rosemary and 600 kg ha^{-1} for olive and grape. At the time of vegetative wakening (spring), a third dose was added as 500 kg ha^{-1} for rosemary + pasture and 800 kg ha^{-1} for olive or grape + pasture.

After one additional month of soil stabilization and before the experiment started with vegetation planting (*vide infra*), the surface $\hat{}A_{up1}$ horizons were fully characterized (Table 1) according to official Italian official procedures [31].

Table 1. Main physical-chemical properties (*n* = 6) of surface ˆAp horizons in constructed Technosol (CT) conditions before revegetation processes (mean ± SE).

CT	pH-H_2O	EC	OC	HA + FA-C	HUM-C	NHC	N	C/N	HI	DH	HR	HU	P_{M3}	K_{M3}	WHC
		dS m^{-1}	g kg^{-1}							%			mg kg^{-1}	g kg^{-1}	%
Control	9.5 ± 0.1	0.22 ± 0.01	0.6 ± 0.0	0.05 ± 0.00	0.42 ± 0.02	0.05 ± 0.01	0.01 ± 0.00	91 ± 1	1.0 ± 0.0	80 ± 3	10 ± 0	90 ± 3	1.05 ± 0.05	0.03 ± 0.00	42 ± 1
CTOA	7.9 ± 0.1	2.76 ± 0.05	129.8 ± 1.2	28.52 ± 1.15	85.89 ± 0.18	15.40 ± 0.45	6.84 ± 0.25	19 ± 0	0.5 ± 0.0	65 ± 1	22 ± 1	88 ± 2	152.47 ± 2.55	0.38 ± 0.05	130 ± 4
CTCF	9.5 ± 0.2	0.22 ± 0.01	0.6 ± 0.0	0.05 ± 0.00	0.42 ± 0.03	0.05 ± 0.01	0.03 ± 0.01	48 ± 1	1.0 ± 0.0	80 ± 2	10 ± 0	90 ± 3	3.62 ± 0.65	0.04 ± 0.00	42 ± 1

CT = Constructed Technosol; CTCF = Constructed Technosol + conventional fertilization; CTOA = Constructed Technosol + organic amendment; EC = Electrical conductivity; OC = Organic carbon; HA + FA-C = Carbon in humic and fulvic acids; HUM-C = Carbon in humin; NHC = Non humic carbon; HI = Humification index; DH = Degree of humification; HR = Humification rate; HU = Total level of humification; P_{M3} and K_{M3} = P and K extracted with Mehlich III solution; WHC = Water holding capacity; n.d. = Non detectable.

2.3. Pedotechnosystems Preparation

Each Technosol was first sown with a pasture grass mixture consisting of 50:50 wt.% of legumes:grasses [12], and subsequently planted with different crops of Mediterranean maquis, after 1-month stabilization. These latter were selected as both adaptable to harsh environmental conditions, their commercial use, and their socio-economic values. Specifically: rosemary (*Rosmarinus officinalis* L.) and olive (*Olea europaea* L., cv. Frantoio) transplanted at 1 and 3-years of age respectively, and grapevine (*Vitis Vinifera* L. ssp. Sativa, cv. *Trebbiano* and *Sangiovese*), grafted as cuttings.

Overall, twelve pedotechnosystems (PTS, i.e., the whole combination of Technosol + vegetation) were investigated for 12 consecutive months to cover an entire year of changes and all seasons, according to a completely randomized block design, with four replicates for each treatment, for a total of 48 (4 kind of vegetation × 3 kind of CT × 4 replicates) 5 m^2 (3 × 2 m) plots. In particular, they were made up as reported in Table 2.

Table 2. Investigated pedotechnosystems.

Constructed Technosol (CT)	Pedotechnosystems (PTS)	
	Acronym	Meaning
Control: CT without additional treatments	CTr	Pasture species + Rosemary on CT
	CTo	Pasture species + Olive on CT
	CTsg	Pasture species + Sangiovese on CT
	CTtb	Pasture species + Trebbiano on CT
CTOA: CT + organic amendment	CTOAr	Pasture species + Rosemary on CTOA
	CTOAo	Pasture species + Olive on CTOA
	CTOAsg	Pasture species + Sangiovese on CTOA
	CTOAtb	Pasture species + Trebbiano on CTOA
CTCF: CT + conventional fertilization	CTCFr	Pasture species + Rosemary on CTCF
	CTCFo	Pasture species + Olive on CTCF
	CTCFsg	Pasture species + Sangiovese on CTCF
	CTCFtb	Pasture species + Trebbiano on CTCF

2.4. Plant Characterization

Pasture shoots were harvested twice (in late spring and in the middle of winter), weighed after careful washing, and then dried (80 °C). Dry weights were used to estimate total dry matter (TDM) production (first + second harvest) as g kg^{-1} PTS. It was analysed to assess—after wet acidic digestion [32]—total N by Kjeldahl procedure, P and K concentrations by Inductively Coupled Plasma/Atomic Emission Spectroscopy AGILENT 7500 CE ICP-MS (ICP/AES).

Olive, grape, and rosemary heights (H) were measured monthly from the base of the trunk to the apical bud [2]. Tree and shrub canopy width (W) was also measured monthly. N, P, and K concentrations were assessed in dry leaves of olive, grape, and rosemary according to the methods previously described for pasture.

Metabolomics

Metabolomic analyses were conducted during the middle of summer (July). In particular, metabolites were investigated through untargeted nuclear magnetic resonance (NMR). Fifty mg of freeze-dried and powdered plant material were transferred in a microtube (2 mL). Plant samples were mixed with 1.5 mL of phosphate buffer (90 mmol; pH 6.0) in D_2O (containing 0.1% w/w trimethylsilyl propionic-2,2,3,3-d_4 acid sodium salt, TMSP) and CD_3OD (1:1), in order to obtain the NMR solvent. The obtained mixture was then: (*i*) vortexed (1 min) at room temperature; (*ii*) ultrasonicated (40 min); and finally (*iii*) centrifuged (10 min) at 13.000 rpm. Six hundred μL was transferred to a 5-mm tube and analyzed by NMR [33]. Nuclear magnetic resonance spectra were recorded according to the following parameters: T = 25 °C; Frequency = 300.03 MHz for ^1H, 75.45 MHz for ^{13}C; internal lock = CD_3OD. Each ^1H NMR spectrum was represented by 256 scans (parameters: 0.16 Hz $point^{-1}$; acquisition time = 1.0 s; relaxation delay = 1.5 s; 90° pulse width = 13.8 ls). To suppress the residual H_2O signal, a presaturation sequence was used. Free induction decays (FIDs) were Fourier transformed (LB = 0.3 Hz). An ^1H NMR processor was used to phase and correct the resulting spectra; calibration was done by TMSP at 0.0 ppm. Obtained spectra were: (*i*) bucketed (width = 0.02 ppm) with ACDLABS 12.0 ^1H NMR processor; and (*ii*) scaled to the internal standard by setting the whole area at 1 (−0.01 to 0.01 ppm). The compounds were identified upon comparison of 1H NMR data with the literature [34] and with in-house built databases. The most abundant and characteristic extracted metabolites were quantitative analyzed. Thus, buckets, corresponding to non-overlapping signals, were used to calculate each metabolite amount [35].

2.5. Physical-Chemical Characterization of Pedotechnosystems

Physical-chemical analyses, on starting (after 1 month of stabilization) and final PTS (after 12 months of plant growth), were performed on Ø < 2 mm sieved and air-dried samples. The pH-H_2O was measured on 1:2.5 soil to water mixtures; soil electrical conductivity (EC) on 1:2 soil to water suspension. Total N was measured through the Kjeldahl method, while P (P_{M3}), and K (K_{M3}) extracted with Mehlich III solution and determined by UV-spectrophotometer and ICP/AES, respectively. Organic carbon (OC) was assessed by the Spring-Klee method. Carbon in humic and fulvic acids (HA + FA-C), in humin (HUM-C) and in non-humified material (NHC), were measured according to the wet chemical procedure proposed by Dell'Abate et al. [36] and modified by Rubino et al. [37]. Such values were then used to evaluate the humification index (HI), the degree of humification (DH), the humification rate (HR), and the total level of humification (HU) [36]. The Gardner [38] procedure was used to estimate the PTS "European" maximum water holding capacity (WHC). Chromatic modifications, as clues of OC evolution and stabilization in the investigated starting and final PTS, were quantified using spectroradiometry [39]. Soil evolution was also assessed by comparing soil profiles using a 3D portable laser scanner. In particular, a picture in STL (stereolithography) format of the soil profile at the beginning of the experiment (t_0) was compared with a picture of the soil after 12 complete months (t_{12}). To make comparisons easier and to better define differences, a full spectrum height map (in grey scale colour) conversion was applied, with a scanning precision of ~0.3 mm.

2.6. Statistical Analyses

Mono-, bi-, and multivariate statistics were conducted using the R software program [40]. Significant differences ($p < 0.05$) among investigated treatments were compared through the ANOVA, by applying a post-hoc Tukey's Honestly Significant Difference (HSD) test. A factor analysis (FA) was conducted following the procedure elaborated by Capra et al. [25]: (*i*) before factor analysis, a KMO test was carried out first showing a sampling adequacy (KMO value ranges between 0.8–1.0) for each variable in the model and for the complete model; (*ii*) Box-Cox transformed data were used to calculate Pearson's product moment correlation coefficients; (*iii*) the obtained correlation matrix (CM) was used as main base for factor analysis (FA); (*iv*) FA was extracted according to the principal factor analysis (PFA) method; (*v*) a varimax rotation was applied to simplify obtained variation in a multivariate dataset with as few factors as possible.

3. Results and Discussion

3.1. Pasture Yield and Nutrient Concentrations

Overall, the control (CT) showed the worst performances ($p < 0.05$) in terms of total dry matter (TDM), N, P, and K concentrations in harvested pasture (Table 3); an exception was represented by the mineral fertilized pedotechnosystem planted with olive (CTCFo), in which the pasture grass yield was about half that recorded in CT. However, no significant difference was detected between these two PTSs. The greatest TDM amounts were always detected in all the organic amended constructed Technosols (CTOA), where the presence of a considerable amount of soil organic matter (Table 4) created favourable edaphic conditions for plant establishment and growth [41]. In particular, organic amendments likely mitigated the water deficiency stress that typically affects limestone spoils with special reference to the dry period. Conversely, the mineral fertilization, while supplying nutrients, did not improve the already scant ability of limestone debris to retain water [9,10] and so create suitable conditions for plant establishment.

Table 3. Total dry matter (TDM) and N, P, and K concentrations in pasture at the end of the experiment (mean value ± [SE], $n = 6$).

PTS	TDM	N	P	K
	g kg^{-1}			
		Rosemary		
CTr	0.03 b [0.01]	25.67 a [1.58]	0.71 b [0.18]	9.67 a [0.74]
CTOAr	0.16 a [0.02]	25.83 a [1.82]	1.79 a [0.03]	9.23 a [2.56]
CTCFr	0.05 a [0.02]	22.70 a [0.07]	1.11 b [0.06]	15.04 a [1.08]
		Olive, *cv. Frantoio*		
CTo	0.08 b [0.00]	26.82 a [2.38]	2.29 a [0.83]	10.10 a [1.54]
CTOAo	0.56 a [0.21]	27.24 a [1.34]	1.69 a [0.06]	13.71 a [1.45]
CTCFo	0.05 b [0.01]	26.09 a [0.40]	1.44 a [0.03]	10.76 a [0.50]
		Grape, *cv. Trebbiano*		
CTtb	0.02 b [0.00]	29.53 a [0.75]	2.27 b [0.08]	12.42 b [0.18]
CTOAtb	0.54 a [0.05]	32.20 a [1.40]	3.21 a [0.03]	27.87 a [3.32]
CTCFtb	0.05b a [0.00]	28.16 a [4.29]	2.99 ac [0.20]	21.68 ab [2.75]
		Grape, *cv. Sangiovese*		
CTsg	0.01 b [0.00]	12.52 a [1.28]	2.04 b [0.02]	11.02 b [0.24]
CTOAsg	0.28 a [0.04]	30.47 a [6.24]	3.13 a [0.05]	29.38 a [1.74]
CTCFsg	0.11 b [0.05]	26.05 a [6.30]	2.54 ab [0.23]	19.28 ab [3.78]

PTS = Pedotechnosystems; TDM = Total dry matter; CT = Constructed Technosol; CTCF = Constructed Technosol + conventional fertilization; CTOA = Constructed Technosol + organic amendment; o = Olive; tb = Trebbiano; sg = Sangiovese. Different letter after means values, within the same column, are for significant difference at $p < 0.05$.

Table 4. Main physical-chemical properties and humification indices in pedotechnosystems (PTS) at the end of the experiment (mean value ± [SE]; $n = 6$).

PTS	pH H_2O	EC	OC	HA + FA-C	HUM-C	NHC	N	C/N	HI	DH	HR	HU	P_{M3}	K_{M3}
		dS m^{-1}			g kg^{-1}						%		mg kg^{-1}	g kg^{-1}
							Rosemary							
CTr	9.4 a * [0.02]	0.30 b * [0.01]	0.75 b * [0.04]	0.54 b * [0.02]	0.07 b * [0.01]	0.14 b * [0.02]	0.05b * [0.00]	15.9 a * [0.7]	0.3 b * [0.1]	79.2 a * [1.5]	72.1 a * [1.9]	81.1 a * [1.2]	3.02 b [0.63]	0.07 a * [0.004]
CTOAr	8.1 b [0.04]	0.82 a * [0.03]	95.95 a * [0.94]	25.54 a [3.74]	47.14 a * [1.24]	23.27 a [4.88]	8.79 a * [0.26]	10.9 b * [0.4]	1.1 a [0.3]	52.9 b [8.9]	26.7 c [4.0]	75.8 a [5.0]	160.17 a [8.90]	0.08 a * [0.005]
CTCFr	9.3 a * [0.02]	0.36 b * [0.02]	2.44 b * [0.06]	1.41 b * [0.07]	0.30 b [0.08]	0.73 b * [0.11]	0.14 b * [0.01]	17.1 a [1.2]	0.5 b * [0.1]	66.2 ab [4.5]	57.5 b * [2.8]	70.0 a * [4.6]	1.31 b * [0.11]	0.09 a * [0.005]
							Olive, *cv. Frantoio*							
Cto	9.4 a [0.02]	0.29 b [0.02]	0.73 b [0.06]	0.09 b [0.02]	0.35 b [0.03]	0.28 b * [0.02]	0.05 b * [0.00]	13.7 a * [0.6]	3.4 a [0.7]	24.6 c * [3.8]	12.8 b [1.7]	60.4 a * [2.9]	1.33 b * [0.02]	0.08 a * [0.01]
CTOAo	8.0 b [0.04]	0.68 a * [0.06]	126.06 a [9.20]	34.09 a [3.26]	79.85 a [5.50]	12.12 a [0.54]	8.40 a [0.88]	15.2 a * [0.5]	0.4 b * [0.0]	73.5 a * [1.2]	26.9 a * [0.7]	90.3 b [0.4]	147.24 a [9.97]	0.05 a * [0.01]
CTCFo	9.3 a [0.05]	0.31 b [0.03]	1.37 b * [0.08]	0.25 b [0.06]	0.75 b [0.19]	0.37 b * [0.06]	0.18 b * [0.01]	7.5 b * [0.3]	1.6 b [0.2]	38.4 b * [2.3]	18.7 b [5.4]	71.9 a [5.9]	1.85 b * [0.19]	0.06 a [0.01]
							Grape, *cv. Trebbiano*							
CTtb	9.9 a * [0.02]	0.40 b * [0.01]	1.52 b * [0.07]	0.35 b * [0.05]	0.34 b [0.04]	0.84 b * [0.03]	0.18 b * [0.01]	8.4 b * [0.3]	2.6 a [0.4]	29.2 b * [3.5]	22.8 a * [2.7]	44.7 b * [3.3]	1.71 b * [0.06]	0.06 b * [0.001]
CTOAtb	8.3 b [0.11]	1.14 a * [0.01]	103.40 a * [3.76]	29.01 a [1.29]	55.16 a * [1.29]	19.23 a [1.87]	7.34 a [0.65]	14.3 a * [0.8]	0.7 b [0.0]	60.4 a [1.3]	28.0 a * [0.5]	81.5 a * [1.2]	193.34 a [14.77]	0.62 a * [0.01]
CTCFtb	9.6 a * [0.01]	0.37 b * [0.03]	1.42 b * [0.08]	0.50 b * [0.05]	0.39 b [0.07]	0.53 b [0.17]	0.14 b * [0.01]	10.5 b [0.5]	1.2 ab [0.5]	52.2 ab [10.6]	36.6 a * [5.5]	63.9 ab [10.0]	2.18 b * [0.09]	0.08 b * [0.001]
							Grape, *cv. Sangiovese*							
CTsg	9.6 a [0.05]	0.54 b * [0.01]	1.28 b * [0.03]	0.32 b [0.10]	0.16 b * [0.04]	0.81 b * [0.15]	0.08 b * [0.01]	16.3 a * [1.3]	4.2 a [1.8]	29.6 a [10.1]	25.4a [8.3]	37.8 b * [10.3]	2.83 b * [0.20]	0.09 b [0.02]
CTOAsg	8.1 b [0.06]	1.14 a * [0.08]	106.57 a * [1.72]	31.26 a [1.68]	51.15 a * [3.52]	24.15 a * [0.60]	9.58 a * [0.63]	11.2 a * [0.6]	0.8 a * [0.0]	56.3 a * [0.9]	29.4 a [1.9]	77.3 a * [0.9]	194.07 a [10.25]	0.64 a * [0.03]
CTCFsg	9.8 a * [0.02]	0.34 c * [0.01]	1.27 b * [0.05]	0.40 b * [0.07]	0.40 b * [0.07]	0.81 b * [0.08]	0.09 b [0.01]	14.1 a [1.9]	2.4 a [0.6]	32.9 a [6.0]	31.0 a [5.3]	36.1 b * [6.3]	3.27 b * [0.11]	0.07 b * [0.01]

EC = Electrical conductivity; OC = Organic carbon; HA + FA-C = Carbon in humic and fulvic acids; HUM-C = Carbon in humin; NHC = Non humic carbon; HI = Humification index; DH = Degree of humification; HR = Humification rate; HU = Total level of humification; P_{M3} and K_{M3} = P and K extracted with Mehlich III solution; CT = Constructed Technosol; CTCF = Constructed Technosol + conventional fertilization; CTOA = Constructed Technosol + organic amendment; o = Olive; tb = Trebbiano; sg = Sangiovese. Different letter after means values, within the same column, are for significant difference at $p < 0.05$. * Final PTSs values differ from starting conditions (Table 1) at $p < 0.05$.

From a nutritional perspective (Table 3), the highest macronutrient (N, P, K) levels were detected in pasture growth on organic amended constructed Technosols (CTOA) pedotechnosystems (PTS). The N:P:K ratio in TDM exhibited the more balanced ratio, compared to the reference data [42], in CTOA pedotechnosystems, with particular reference for those planted with both grape varieties.

3.2. Pedotechnosystem Behaviour and Development

The highly alkaline pH value (9.5) of limestone soil was buffered around 7.9 by the presence of the organic amendment (Table 4), creating the most optimal condition for plant establishment and growth in experimental conditions [43]. At the end of the experiment, such values ranged from 8.0 to 8.3 in all organic amended constructed Technosols (CTOA) pedotechnosystems. Such important buffering processes were not observed in constructed Technosols without treatments (Control) or in the chemically fertilized (CTCF), with values always over very alkaline limits (>9.0); a range not suitable for optimal growth of the investigated species [43] that, indeed, showed the worst performances in terms of dry matter production (Table 3). Electrical conductivity slightly increased in all investigated PTSs; however, these values did not represent a problem for plant growth (observed range of variation: 0.29–1.14 dS m^{-1}; Table 4).

The highest soil organic carbon (OC) concentrations (Table 4) were always recorded in organic amended PTSs (CTOA). No differences ($p < 0.05$) were observed between chemical fertilized (CTCF) and untreated PTSs (CT, Control), always showing lowest OC concentrations. Comparing differences with the starting conditions (Table 1), we observed a slight decrease in OC concentration in all organic amended PTSs at the end of the experiment. The opposite was true for the Control and the chemically fertilized PTSs (Table 4). Such behaviour seems to be related to time-dependent degradation processes, particularly enhanced in those constructed Technosols (CT) with a higher initial OC concentration. In such systems, OC degraded more rapidly and furnished larger amounts of nutrients for plant growth (Table 1) in comparison to CT with very low OC starting conditions. As for OC, the total humified carbon (HA + FA-C and HUM-C) showed: (i) highest values for all organic amended (CTOA) PTSs, with (ii) lowest values again featured in the Control (CT) and all PTSs treated with conventional fertilizers (CTCF).

Organic matter provides several soil benefits, such as improved soil structure and nutrient availability [44], an increase in soil fertility and plant growth [45], better root penetration with an increase in soil water content, and gas flow as well due to an augmentation in soil porosity [46]. Comparisons between the initial (Table 1) and final (Table 4) conditions of the Technosols can highlight any processes of mineralization and/or humification of organic carbon to better understand the agronomic performance of the whole pedotechnosystems. Among soil humic substances, humic and fulvic acids (HA + FA-C) are pivotal in improving soil fertility and health within short time frames [47]. Overall, humified and not humified fractions slightly decreased or increased depending on investigated PTSs and planted species, but no specific trends were observed. For example, in CTOAr pedotechnosystem, we observed a decrease in humified carbon, with a proportional increase in non-humified fractions over time. The same system planted with olive (CTOAo) does not show any significant difference at the end of the experiment vs. the starting condition, with humic substances thus being one of the few influenced by mineralization processes. Such behaviour was clearly confirmed by the C/N ratio and humification indexes (HI, DH, HR, HU) too (Table 4), thus showing that the higher soil cover assured by olive plants compared to rosemary, could have played a pivotal role in humification (prevailing under olive cover) vs. mineralization processes (under rosemary). Overall, it seems that while OA improved most soil properties, providing a remarkable amount of available nutrients (*vide infra*), it was not always involved in SOM stabilization processes in all investigated PTSs. This is also probably due to the presence of limestone gravel that is unable to bind organic matter and protect it, which is easily lost by leaching and degradation processes [12].

Previously reported soil organic carbon behaviour was clearly reflected in spectroradiometry colour analysis (Table 5), with final colours of organic amended PTSs being characterized by higher hue and chroma (from "dark grey" to "grayish brown"), both a clue of OC development and soil evolution [48]. As expected by observed OC values, all investigated macronutrients—with some exceptions—were highest in organic amended constructed Technosols (Table 4). On the other hand, untreated (CT) or mineral fertilized PTSs (CTCF) had a lower concentration of these nutrients, with N often under recommended doses for plant growth [49]. However, a general increase in total N concentration (Table 4) compared to starting conditions (Table 1), occurred more remarkably and as expected, in mineral fertilized PTSs. These data agreed with the C/N ratio, overall decreasing in the same PTSs, suggesting that OC was used as pabulum by microbial biomass with a subsequent accumulation of organic N in biomass itself. In agreement with previous outcomes (*vide supra*), it could be argued that the greatest stimulation to biomass development took place in these unamended PTSs, while in organic amended PTSs only a few stocks of organic matter were used by microbial biomass, with the rest having undergone chemical degradation or stabilization processes. Phosphorous showed higher values at the end of the experiment, compared to the beginning, in organic amended PTSs, except for CTOAo; the same trend was observed for the Control while the opposite was true for mineral fertilized PTSs. Indeed, P is subjected to up to 80% losses in terms of fixation, leaching, and volatilization [50].

Table 5. Munsell color attributes at the beginning and the end of the experiment in each investigated PTS.

PTS	$Hue_{YR\ std}$	Value	Chroma	Munsell Soil Color Description
		Starting PTS		
CTr; CTo; CTtb; CTsg; CTCFr; CTCFo; CTCFtb; CTCFsg	10.00	7.90	1.79	White
CTOAr; CTOAo; CTOAtb; CTOAsg	10.84	4.02	1.23	Dark gray
		Final PTS		
		Rosemary		
CTr	10.03	6.81	2.24	Light gray
CTOAr	10.73	4.75	1.54	Grayish brown
CTCFr	10.54	6.33	2.07	Light brownish gray
		Olive, *cv. Frantoio*		
CTo	10.03	7.42	2.17	Light gray
CTOAo	10.77	4.70	1.53	Grayish brown
CTCFo	11.60	7.37	3.97	Very pale brown
		Grape, *cv. Trebbiano*		
CTtb	10.33	8.07	1.66	White
CTOAtb	10.26	4.49	1.21	Gray
CTCFtb	10.20	7.31	1.96	Light gray
		Grape, *cv. Sangiovese*		
CTsg	10.29	7.59	2.02	White
CTOAsg	9.54	4.31	1.12	Dark gray
CTCFsg	10.12	7.48	2.04	White

CT = Constructed Technosol; CTCF = Constructed Technosol + conventional fertilization; CTOA = Constructed Technosol + organic amendment; o = Olive; tb = Trebbiano; sg = Sangiovese.

By comparing the 3D stereolithography of the soil profile (in this specific case, Technosol treated with OA) at the t_0 (before the experiment started) vs. t_{12} (at the end of the experiment, i.e., after 12 months) additional conclusions can be drawn about soil evolution (Figure 2). At the beginning of the experiment, the soil profile was still poorly differentiated in terms of detected band picks; it only showed a clear difference between the whole A horizons (^Aup$_1$ − ^Aup$_2$ − ^Aup$_3$) vs. the deep 2^R horizon. At the end of the experiment, all four constructed horizons were clearly visible and detected in terms of high differences in band picks. Surface ^Aup$_1$ and ^Aup$_2$ horizons clearly showed higher differences due to an enhanced presence in plant root growth able to create more developed horizons in terms of structure, porosity, OC concentration, etc. As expected, due to the recalcitrant nature of the substrate (limestone gravel), after only 12 months of soil development, the 2^R horizons did not show significant differences in terms of band picks. This evolution, even if observed in all investigated treatments and thus showing a strong time-dependent behaviour, was particularly enhanced in soils treated with OA. As a matter of fact, OA also seems to enhance soil evolution processes. However, on this specific topic, further investigations are under realization. Results will be presented as future steps of the research.

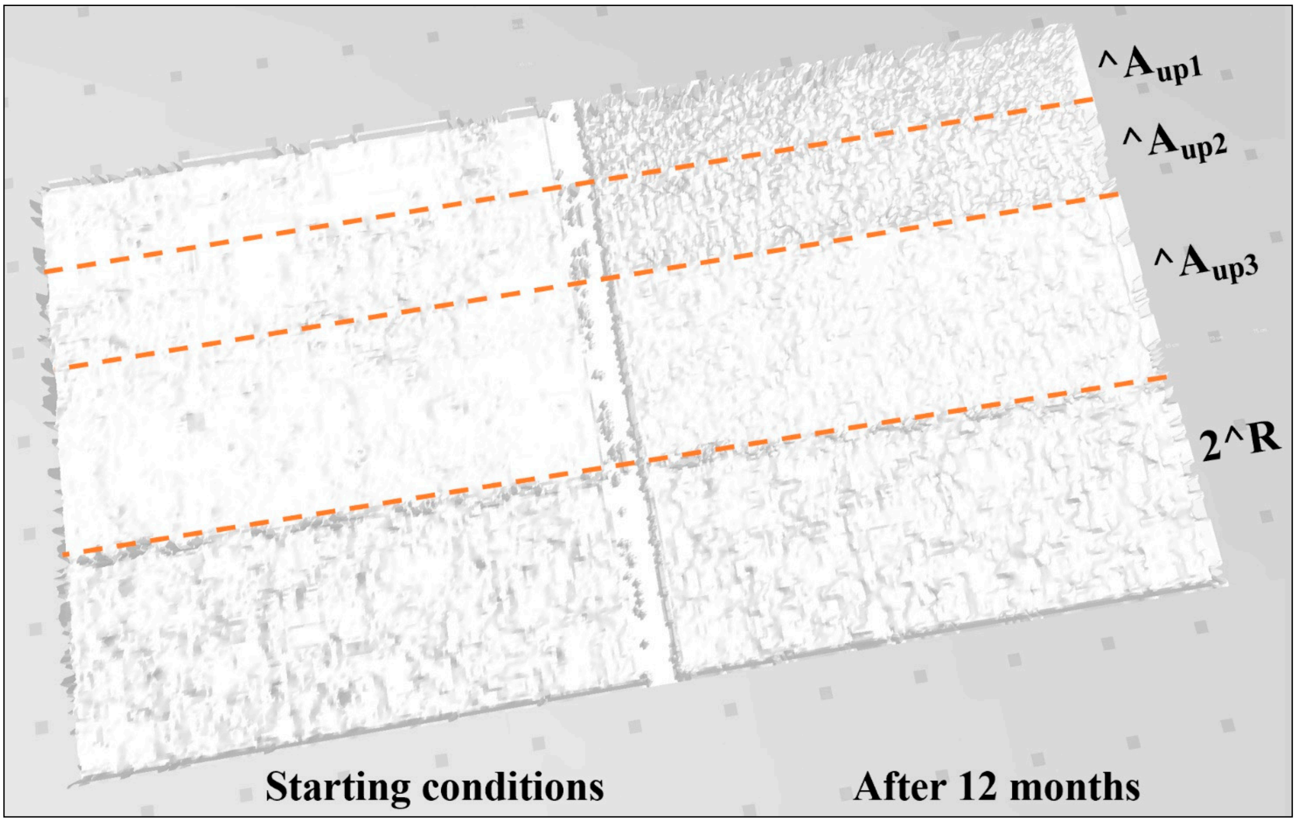

Figure 2. Comparison of soil profiles at the t_0 (before the experiment started) vs. t_{12} (after 12 months) through 3D stereolithography.

3.3. Crop Characterization and Metabolic Profile

Rosemary growth depended on PTSs (Table 6). The best plant development, in terms of both plant height (H) and canopy width (W), was observed in organic amended constructed Technosols (CTOA) pedotechnosystems. Conversely, rosemary plants in mineral fertilized PTSs died during the summer period as the conjunction of water stress—enhanced by the high porosity of limestone debris, and not mitigated by the presence of enough organic matter—and NPK mineral fertilizer might have temporarily increased osmatic processes in the investigated matrix. As a matter of fact, nutrients in chemical fertilizers are in a readily soluble form, rapidly raising the osmotic pressure, if not mitigated by any colloidal fraction [51]. The N, P, and K concentrations in rosemary leaves also provided information about plant health. Indeed, the lack of K in mineral fertilized pedotechnosystems (CTCF) was clearly reflected in the regularly observed wilting. N, P, and K concentrations did not show significant differences relating to the substrate nature, as well as the antioxidant activity. From the metabolomic analyses, it was clear that main metabolites in the extracts was rosmarinic acid, and that the complete lack in rosemary growth on mineral fertilized CT was due to the plant's early death. Usually, a low nutrient availability in soil/substratum leads to the production of huge amounts of secondary metabolites as a defensive strategy against plant pathogens, pests, herbivores, UV-light, and oxidative stress [52]. Lattanzio et al. [53] isolated rosmarinic acid in oregano shoot cultures grown under nutritional stress. In the investigated PTSs, the starting nutrient supply seemed to not significantly influence the production of such substances, rather the most nutrient rich substratum—CTOA—provided the highest concentration of rosmarinic acid. A similar trend was detected for the rosmarol, the most abundant identified abietane diterpenes.

Table 6. Rosemary morphological, nutritional, and metabolic characterization (mean value ± [SE]; n = 6) in investigated pedotechnosystems (PTS).

PTS	H	W	N	P	K	Rosmarinic Acid	Rosmanol
	cm		g kg^{-1}			g kg^{-1}	
CTr	45 a [2]	39 a [1]	11.96 a [2.21]	0.87 a [0.09]	3.77 a [1.61]	49.04 a [4.09]	29.22 a [9.20]
CTOAr	54 a [1]	48 b [2]	12.88 ab [1.02]	1.00 a [0.03]	5.51 a [1.41]	51.47 a [6.51]	35.76 a [7.31]
CTCFr	43 a [1]	32 c [1]	17.76 b [0.70]	0.90 a [0.05]	0.91 a [0.07]	Nd	23.75 a [1.06]

H = plant height; W = canopy width; nd = not detected; CT = Constructed Technosol; CTCF = Constructed Technosol + conventional fertilization; CTOA = Constructed Technosol + organic amendment; o = Olive; tb = Trebbiano; sg = Sangiovese. Different letter after means values within the same column are for significant difference at $p < 0.05$.

The agronomic performance of olive revealed a decreasing trend as CTOA ≥ CT > CTCF (Table 7). Regarding leaf macronutrient concentration, there were no statistical differences between P and K concentrations. Conversely, the presence of the organic amendment significantly increased N concentration. Overall, the leaf N, P, and K concentrations were below average for what would be expected for olive (20 g kg^{-1}, 2 g kg^{-1}, and 10 g kg^{-1}, respectively [54]). The most striking deficiency was observed for P, which represents only 25–44% of the abovementioned reference values. The P deficit may have been due to both pasture grass competition and the low P availability in limestone-base substrates where the alkaline conditions, at least at the beginning of the experiment, favoured P precipitation. For the metabolites, olive glucose, sugars, and total phenolic concentration were evaluated. These data indicate beneficial pedoconditions due to the organic amendment (CTOA). Indeed, as reported by Pedritis et al. [55], the biosynthesis of phenolic compound in several olive cultivars is induced under exposure to environmental stresses, such as salinity. Our data agreed with findings reported by Martinelli et al., [56] that showed olive drupes grown with adequate water availability had a total phenol concentration lower than drupes grown under water stress conditions.

Table 7. Olive morphological, nutritional, and metabolic characterization (mean value ± [SE]; n = 6) in investigated pedotechnosystems (PTS).

PTSs	H	W	N	P	K	Glucose	Sucrose	Glc/Suc	Phenols
	cm			g kg^{-1}		g kg^{-1}			%
CTo	117 a [11]	93 a [8]	9.38 a [0.54]	0.58 a [0.04]	6.03 a [0.46]	105.12 a [28.24]	4.76 a [0.93]	26.5 a [12.3]	4.55 a [0.72]
CTOAo	127 a [7]	98 a [8]	13.45 b [0.67]	0.69 a [0.21]	6.76 a [0.27]	74.72 a [2.73]	24.14 b [0.04]	3.1 a [0.1]	1.85 b [0.22]
CTCFo	121 a [3]	74 a [5]	11.84 a [0.59]	0.63 a [0.02]	5.59 a [0.24]	88.30 a [17.61]	9.82 c [0.76]	8.90 a [1.11]	4.93 a [0.60]

Legend as in Table 4 except for: Glc = glucose; Suc = sucrose. Different letter after means values within the same column are for significant difference at $p < 0.05$.

For both investigated grapevine cultivars (Table 8), plant height and canopy width showed the following trend CTOA > CTCF = CT, with a lack of significant difference in CTOA only for W in *Sangiovese*. In this case, grapes did not benefit greatly from organic amendments. The investigated pedotechnical treatments remarkably and significantly influenced N, P, and K concentrations in both grape cultivars. Specifically, the organic amended constructed Technosol (CTOA) showed the highest N, P, and K concentrations for *Trebbiano* and N and P for *Sangiovese*. Overall, the whole nutritional status was adequate and well-balanced for good growth and development of both cultivars [57]. NMR analysis identified caffeic acid and the flavonoids, kaempferol, quercetin and its glucoside as the main specialized metabolites. Glutamine was present only in CT and CTOA pedotechnosystems planted to *Sangiovese*. The observed sugars patter, in CT and CTCF pedotechnosystems, suggested a growth under water deficit, as has been reported in the literature for several species and various plant parts [58]. However, the accumulation of such soluble carbohydrates seems not to be severe, as highlighted by the lack of proline accumulation [59], that represent a common response of organisms to dehydration. These results suggest there were no issues in terms of salinity or nutrient deficiency [60].

Table 8. Grapevine morphological, nutritional, and metabolic characterization (mean value ± [SE]; $n = 6$) in investigated pedotechnosystems (PTS).

PTS	H	W	N	P	K	T	A	C	Gm	P	Gl	Su	Ka	Qg	Q
	cm		g kg^{-1}			g kg^{-1}									
CTtb	51 a [6]	20 a [3]	14.95 a [0.58]	1.29 a [0.06]	13.25 a [0.41]	27.18 a [7.45]	61.75 a [10.73]	27.22 a [1.43]	nd	nd	30.12 a [5.82]	97.86 a [23.17]	nd	34.71 a [1.28]	28.15 a [2.61]
CTOAtb	88 b [6]	30 b [4]	32.29 b [1.06]	1.93 b [0.07]	14.63 a [1.91]	13.13 a [4.02]	49.00 a [7.65]	15.93 a [3.66]	nd	nd	26.74 a [4.69]	65.07 a [3.21]	nd	4.64 b [3.35]	7.69 a [5.56]
CTCFtb	66 a [3]	25 a [1]	14.06 a [0.26]	1.08 a [0.03]	14.11 a [0.13]	37.74 a [9.48]	50.35 a [8.90]	24.03 a [4.86]	nd	nd	38.79 a [11.66]	115.68 a [16.60]	nd	18.09 b [1.89]	19.27 a [2.01]
CTsg	109 a [8]	30a [2]	16.40 a [1.06]	1.05 a [0.05]	20.44 a [0.37]	27.75 a [5.67]	46.58 a [0.12]	22.43 a [0.00]	8.51 a [0.39]	nd	24.12 a [2.24]	102.92 a [1.33]	6.33 [0.95]	35.80 a [6.74]	32.13 a [3.95]
CTOAsg	128 b [4]	28 a [3]	31.07 b [0.73]	1.84 b [0.12]	22.50 b [0.59]	24.26 a [0.91]	87.11 a [8.67]	15.85 a [2.84]	15.57 b [0.55]	18.63 [0.66]	32.72 a [4.29]	50.69 a [17.24]	nd	nd	3.10a [1.90]
CTCFsg	107 a [8]	35 a [4]	14.70 a [0.37]	1.31 a [0.03]	23.45 b [0.90]	32.32 a [1.37]	48.70 a [17.64]	29.27 a [5.82]	nd	nd	34.36 a [7.74]	133.79 a [32.87]	nd	35.09 a [15.43]	24.19 a [10.63]

Legend as in Table 4 except for: T = Tartaric acid; A = Aspartic Acid; C = Caffeic acid; Gm = Glutamine; P = Proline; Gl = Glucose; Su = Sucrose; Ka = Kaempferol; Qg = Quercetin 3 glucoside; Q = Quercetin. Different letter after means values within the same column are for significant difference at $p < 0.05$.

3.4. Multivariate Statistic

Factor analysis (FA) was conducted for the three main pedotechnosystems (PTSs), i.e., pasture and rosemary, pasture and olive, and pasture and grapevines (for both cultivars).

All FA showed high statistical significance, with the eigenvalues always > 1 (Tables 8–10). FA application to pasture and rosemary (Table 9) resulted in a three-component model accounting for 91% of all data variation. F1 (57%), showed most substrate parameters (WHC, pH, EC, OC, N, and K) were positively correlated with rosemary height (H) and the total dry matter (TDM) harvested for pasture species; these were all inversely correlated with C/N ratio and P concentration in the substrate together with the rosemary canopy width (W) and P concentration in harvested pasture species. This factor highlighted that C/N ratio decreased, suggesting a tendency towards mineralization rather than humification—typically featuring chemical fertilized (CTOA) pedotechnosystems. Potassium availability in the substrate increased, while P decreased due to strongly alkaline conditions leading to its immobilization and precipitation. These processes were particularly enhanced (*vide supra*) at the beginning of the experiment, before the buffering effect assured by the organic amendment, especially in CTOA pedotechnosystems.

Table 9. Factor loadings of a factor analysis for pedotechnosystem with rosemary + pasture species; extraction method: principal factor analysis (PFA); rotation method: varimax.

Parameters	**Factors**		
	F1	**F2**	**F3**
WHC	**0.901**	0.356	0.228
pH	**0.900**	0.379	0.197
EC	**0.896**	0.397	0.178
OC	**0.901**	0.342	0.244
N	**0.995**	0.071	0.021
C/N	**−0.632**	**0.548**	0.445
K_{M3}	**0.983**	0.159	0.062
P_{M3}	**−0.990**	0.019	0.070
H	**0.618**	**0.780**	0.029
W	**−0.563**	**−0.608**	−0.439
N	−0.013	**0.953**	−0.109
P	−0.445	0.313	**−0.792**
K	0.326	**0.930**	−0.073
Rosmarinic acid	−0.010	−0.052	**−0.974**
Rosmanol	0.340	**0.749**	0.083
TDM	**0.937**	0.233	−0.101
N TDM	0.051	0.132	0.173
P TDM	**−0.951**	0.159	−0.211
K TDM	0.071	0.733	−0.040
Variance (%)	57	21	13
Cumulative variance (%)	57	78	91
Eigenvalues	10.855	4.018	2.453

Bold loadings > 0.5. Orange part = substrates parameters (WHC = water holding capacity: EC = electrical conductivity; OC = organic carbon; P_{M3} and K_{M3} = P and K extracted with Mehlich III solution); Yellow part = plant parameters (H = plant heights; W = canopy diameter); Green part = pasture grass parameters (TDM = total dry matter).

Notwithstanding such low P availability in the substrate, the pasture yield and rosemary growth (H) were not negatively affected, especially for organic amended PTSs. Under P deficiency, the lower and older leaves died, and the plant mobilized available P from the oldest to the youngest leaves [61], which led to a reduction in canopy diameter (W). The concurrent reduction in P concentration in pasture may be attributable to this deficiency as well [2]. This factor can be interpreted as the role of P in investigated pedotechnosystems. F2 (21%) indicated most plant parameters, including H, N, K, and rosmanol concentration in leaves, were positively correlated to each other and with the C/N ratio in the substrate. These correlations highlighted the role of rosmanol as an indicator of favourable conditions for rosemary growth; indeed, its concentration increased with plant growth [62]. Thus, this factor can be interpreted as the role of rosmanol for rosemary growth. F3 (13%) showed P and rosmarinic acid concentration as negatively concordant in rosemary plants. Such a relationship can be explained by the fact that, in plants, P is required in relatively large amounts for the biosynthesis of primary and secondary metabolites, such as rosmarinic acid [63]. In investigated PTSs, with special reference for CT and CTCF pedotechnosystems, P availability in substratum was low due to: (*i*) extreme alkaline conditions and calcium carbonate; and (*ii*) P uptake. F3 can be interpreted as the role played by P uptake in strongly influencing secondary metabolite production.

Table 10. Factor loadings of a factor analysis for pedotechnosystem with olive tree and pasture species; extraction method: principal factor analysis (PFA); rotation method: varimax.

Parameters	**Factors**		
	F1	**F2**	**F3**
WHC	**0.965**	0.014	0.259
pH	**0.959**	−0.032	0.270
EC	**0.950**	−0.077	0.280
TOC	**0.967**	0.043	0.252
N	**0.722**	−0.008	**0.678**
C/N	0.115	0.052	**−0.942**
K_{M3}	**0.766**	−0.057	**0.628**
P_{M3}	**−0.611**	0.035	**−0.769**
H	0.267	**−0.833**	0.388
W	0.363	0.079	−0.237
N leaf	−0.225	−0.333	**−0.907**
P leaf	**0.940**	0.327	0.094
K leaf	−0.465	**−0.760**	0.050
Glu	−0.247	0.332	−0.117
Suc	**0.595**	−0.302	**0.738**
Phenols	**0.815**	**−0.501**	0.092
TDM	**0.963**	0.007	−0.119
N TDM	−0.146	**−0.969**	−0.170
P TDM	0.098	**−0.990**	−0.097
K TDM	**−0.746**	**0.610**	−0.229
Variance (%)	56	24	15
Cumulative variance (%)	56	80	95
Eigenvalues	11.728	5.068	3.079

Bold loadings > 0.5. Orange part = substrates parameters (WHC = water holding capacity: EC = electrical conductivity; OC = organic carbon; P_{M3} and K_{M3} = P and K extracted with Mehlich III solution); Yellow part = plant parameters (H = plant heights; W = canopy diameter); Green part = pasture grass parameters (TDM = total dry matter).

Even for olive PTSs, FA highlighted a three-component model with, again, an explained variability > 90% (Table 10). F1 (57%) can be interpreted as the influence of organic amended pedotechnosystems (CTOA) on olive performances. As a matter of fact, it showed that all substrate parameters (with the only exclusion of C/N ratio and P), were positively concordant with P concentration in olive leaves, sucrose and phenols concentration in drupe, and grass yield (TDM). Conversely, such parameters were inversely correlated with P and K concentrations in the substrate and grasses, respectively. This factor showed that with increasing soil organic matter in investigated constructed Technosols (CT), with particular reference to those organically amended (CTOA), a consequent increase in N and K macronutrients occurred. Conversely, a substrate P deficiency may have hindered plant growth and led to an increase in phenol concentrations as accumulation usually occurs under unfavourable conditions [50], e.g., in chemically fertilized PTSs (CTCF, *vide supra*). The F2 (24%) highlighted most of the previously reported and explained correlations (*vide supra*) due to competition in nutrient uptake between pasture and olive trees. The F3 (15%) showed the N and K amount in the substrate positively related to sucrose concentrations in drupes with all these parameters inversely correlated with C/N ratio and P availability in the substrate and N concentration in olive leaves. This suggests that when mineralization prevails—especially under organically amended (CTOA) pedotechnosystems—a release of available nutrients for plants in soil solution occurs, thus favouring optimal growing conditions as highlighted by an increase in sucrose concentration [51]. This factor can be interpreted to suggest that metabolites are key indicators in investigated CTOA PTSs.

Factor analysis showed that *Trebbiano* and *Sangiovese* explained 87 and 95% of the variability of a three-component model, respectively (Table 11). F1 for both cultivars (62%) exhibited a positive correlation of most substrate parameters (pH, EC, WHC, OC, N, and K) with the N, caffeic, sucrose, quercetin and its glucoside concentration in leaves, and K concentration in pasture. Furthermore, all these parameters are inversely correlated with P concentrations in both the substrate and pasture. Improving substrate conditions in terms of increasing SOM, such as in organically amended (CTOA) pedotechnosystems, would lead to improvement of several pivotal parameters. The main difference between the two cultivars occurred, as expected, in plant growth and its metabolic profile, thus underlying again the key role of metabolites as specific plant condition markers. Specifically, such improved substrate conditions: (*i*) negatively affected *Trebbiano* canopy width but not *Sangiovese* width; (*ii*) led to higher leaf P in *Trebbiano* leaves; (*iii*) led to higher aspartic and tartaric acid concentrations in *Sangiovese* leaves, along with a decrease in glutamine and proline. Overall, this factor can be interpreted to mean CTOA pedotechnosystems influenced grape performance and the ability of metabolomic profiles to precisely fingerprint the different cultivars. These findings also have important practical consequences, since the metabolic analysis can help in managing grape and, consequently, wine production in reconstructed Technosols, thus allowing the best performances in terms of quality. F2 (15% and 22%) in *Trebbiano* and *Sangiovese* cultivars related several investigated parameters. Overall, for both cultivars, the ongoing SOM mineralization (reduction of C/N ratio) seemed to play a pivotal role, being responsible for providing low P concentrations in the substrate, leading to a reduction: (*i*) in crop canopy of *Trebbiano*; (*ii*) of total dry matter (TDM) in *Sangiovese*; and (*iii*) shoot P concentration in pasture for both investigated cultivars. F2 can thus be interpreted, for both cultivars, to mean there is a competitive adsorption process associated with mineralization/humification processes. Further, there is also an ability to use the metabolomic profile to precisely fingerprint the two different cultivars. Finally, F3 (10% for both cultivars) related grape leaves and pasture parameters in different way, with most of relationships already explained in previous outcomes (*vide supra*).

Table 11. Factor loadings of a factor analysis for pedotechnosystems with *Trebbiano* and *Sangiovese* grapes + pasture species; extraction method: principal factor analysis (PFA); rotation method: varimax; bold loadings > 0.5.

Parameters	**Factors (*Trebbiano* Grape)**			**Factors (*Sangiovese* Grape)**		
	F1	**F2**	**F3**	**F1**	**F2**	**F3**
WHC	**0.974**	0.086	0.146	**0.815**	**0.507**	0.265
pH	**0.964**	0.082	0.182	**0.827**	**0.502**	0.233
EC	**0.953**	0.083	0.222	**0.836**	0.495	0.202
TOC	**0.979**	0.086	0.121	**0.807**	**0.510**	0.284
N	**0.861**	0.432	0.023	**0.609**	**0.784**	0.052
C/N	−0.057	**−0.883**	0.216	0.203	**−0.845**	0.459
K_{M3}	**0.886**	0.387	0.061	**0.634**	**0.759**	0.083
P_{M3}	**−0.785**	**−0.530**	0.020	**−0.511**	**−0.853**	0.027
H	0.268	0.333	0.125	0.210	0.196	**0.949**
W	**−0.712**	**−0.595**	−0.305	**0.917**	−0.247	0.142
N leaf	**0.976**	−0.044	0.200	**0.830**	0.283	0.421
P leaf	**0.948**	−0.192	0.090	0.479	**0.856**	0.065
K leaf	−0.127	0.033	0.339	−0.118	**−0.572**	**0.808**
Tartaric acid	−0.019	**−0.962**	−0.273	**0.751**	−0.180	0.253
Aspartic acid	−0.104	−0.246	−0.370	**0.914**	0.183	−0.263
Caffeic acid	**0.615**	0.212	0.342	**0.544**	0.219	**0.765**
Glucose	−0.308	0.073	**−0.898**	−0.174	**0.897**	0.198
Sucrose	**0.701**	0.025	0.296	**0.967**	0.092	−0.006
Kaempferol	Nd	Nd	Nd	0.109	**0.947**	−0.288
Quercetin 3 glucoside	**0.818**	**0.518**	0.012	**0.891**	0.394	−0.094
Quercetin	**0.769**	0.177	−0.163	**0.823**	**0.519**	−0.198
Glutamine	Nd	Nd	Nd	**−0.712**	0.402	**−0.546**
Proline	Nd	Nd	Nd	**−0.814**	**−0.507**	−0.265

Table 11. *Cont.*

Parameters	**Factors (*Trebbiano* Grape)**			**Factors (*Sangiovese* Grape)**		
	F1	**F2**	**F3**	**F1**	**F2**	**F3**
TDM	**−0.940**	−0.183	−0.039	−0.279	**−0.958**	−0.036
N TDM	−0.166	−0.191	**−0.951**	**−0.509**	−0.451	**0.567**
P TDM	**−0.631**	**−0.503**	0.415	**−0.721**	**−0.589**	0.363
K TDM	**0.510**	**0.571**	0.123	**0.681**	**0.612**	−0.399
Variance (%)	62	15	10	62	22	10
Cumulative variance (%)	62	77	87	62	85	95
Eigenvalues	14.904	3.594	2.429	16.843	6.045	2.830

Bold loadings > 0.5. Orange part = substrates parameters (WHC = water holding capacity: EC = electrical conductivity; OC = organic carbon; P_{M3} and K_{M3} = P and K extracted with Mehlich III solution); Yellow part = plant parameters (H = plant heights; W = canopy diameter); Green part = pasture grass parameters (TDM = total dry matter).

In summary, the FA confirmed that organic amended constructed Technosols (CTOA) are characterized by contributing to better growing conditions and agronomic performance, largely due improved substrate conditions. Additionally, the FA showed the metabolomic profiles can act as precise and reliable fingerprints for investigating plant responses in PTSs. As a matter of fact, metabolites and/or their relationships with investigated soil and plant parameters, can improve our knowledge in terms of: (*i*) constructed Technosols and investigated PTSs' response to environmental stress; thus (*ii*) providing key information for improving their management for environmental and profitable purposes.

4. Conclusions

The first, and most important, step in environmental restoration of degraded opencast limestone quarries is soil recovery. Where natural soils were totally removed, an ex-novo soil reconstruction is required. This involves the adoption of pedotechnologies aimed at managing a proper soil profile by co-utilizing both natural and human-derived mineral and organic materials. We demonstrated that a constructed Technosol containing limestone debris and organic amendment (CTOA) materials, primarily derived from "wastes" (urban organic, agrozootechnical activities, composted sewage sludge, "green wastes" such as pruning and cutting), and planted with pasture species and Mediterranean shrubs and trees showed the best soil physical-chemical and agronomic performance after only 12 months compared to a control (CT, without any additional treatments) and CT treated with commercial mineral fertilizers (CTCF). Overall, our results demonstrate that: (*i*) mineral (limestone debris) and organic waste materials are suitable for the creation of a complete soil profile reconstruction; (*ii*) the reuse of such wastes avoids their disposal in landfill areas (with the consequential negative environmental, socio-economic, and human health impacts); (*iii*) the important performances obtained by planting common and marketable Mediterranean plants suggest the possibility to adopt such pedotechnosystem to convert a degraded quarry area to an agroecosystem capable of producing economic as well as social services. Future research should aim to understand the performance of constructed Technosols using other sustainable construction materials and applied to other degraded environments.

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