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Humic Substances from Waste-Based Fertilizers for Improved Soil Fertility

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Abstract: This research explores how different organic waste transformation methods influence the production of humic substances (HSs) and their impact on soil quality. Using olive and orange wastes as substrates, the study compares vermicomposting, composting, and anaerobic digestion processes to determine which method produces the most humic-substance-rich products. The characterization of HSs in each product included analyses of total organic carbon (TOC), humic and fulvic acid content, humification rate, humification degree, and E4/E6 ratio, with HSs extracted using potassium hydroxide (KOH) and analyzed via Diffuse Reflectance Infrared Fourier-Transform (DRIFT) spectroscopy to assess structural complexity. The results revealed that the chemical composition of the input materials significantly influenced the transformation dynamics, with orange by-products exhibiting a higher humification rate and degree. Vermicomposting emerged as the most efficient process, producing fertilizers with superior humic content, greater microbial biodiversity, and enhanced cation exchange capacity, thus markedly improving soil quality. Composting also contributed to the stabilization of organic matter, albeit less effectively than vermicomposting. Anaerobic digestion, by contrast, resulted in products with lower levels of HSs and reduced nutrient content. Aerobic processes, particularly vermicomposting, demonstrated the most rapid and effective transformation, producing structurally complex, stable humus-like substances with pronounced benefits for soil health. These findings underscore vermicomposting as the most sustainable and efficacious approach for generating HS-rich organic fertilizers, presenting a powerful alternative to synthetic fertilizers. Furthermore, this study highlights the potential of organic waste valorization to mitigate environmental pollution and foster circular economy practices in sustainable agriculture.

Keywords: organic wastes; vermicompost; anaerobic digestion; composting; humic substances; soil fertility

1. Introduction

The intensive use of synthetic chemicals, such as fertilizers and pesticides, in agriculture to promote crop growth and protect against pests, is accelerating the mineralization of organic matter, disrupting soil structure and decreasing soil biodiversity [1]. The soil is becoming less productive and more dependent on synthetic inputs to sustain crop yields [2]. Synthetic fertilizers often supply plants with readily available nutrients, but they can cause an imbalance in the soil's nutrient profile, resulting in nutrient leaching, and reducing soil fertility [3]. Runoff from fields treated with synthetic chemicals can lead to the contamination of water bodies. This pollution can harm aquatic ecosystems, reducing biodiversity, and affecting human health through contaminated drinking water [4]. The overuse of synthetic fertilizers and pesticides to respond the increasing demand of food, is decreasing the nutritional value of crops. Studies have shown that crops grown with excessive chemical inputs often have lower levels of essential vitamins and minerals [5,6].

Additionally, the presence of pesticide residues is posing health risks to consumers and is leading to the development of resistant pest populations. These resistant pests are harder to control, requiring even more potent chemicals, which exacerbates the cycle of chemical dependency and environmental harm [7].

The diminished nutritional value of crops and the presence of chemical residues can increase the risk of diseases in humans, leading to a range of health issues, including chronic diseases and developmental problems in children [8].

Efforts to address these issues include promoting sustainable agricultural practices, such as organic farming, integrated pest management, and the use of natural fertilizers and biopesticides. These practices aim to enhance soil health, improve crop quality, and reduce the negative environmental and health impacts associated with synthetic chemicals.

With the global population reaching 8 billion in 2022 and projected to grow to 9.7 billion by 2050, the demand for food and agricultural production continues to rise, leading to increased levels of organic waste generation [9]. This waste—comprising agricultural, market, and kitchen residues—decomposes quickly, yet improper management can result in environmental challenges, notably the emission of greenhouse gases that exacerbate climate change [10]. In Italy, as the second-largest European producer of oranges and olives, about 500,000 tons of orange waste and over 2000 tons of olive oil waste are produced annually [11]. Though non-toxic, these wastes contain high levels of polyphenols, low pH, and elevated salinity, which pose environmental risks [12]. A sustainable approach is to convert these wastes into eco-friendly fertilizers through composting, which not only reduces environmental harm but also improves soil quality [13], because sustainable waste management strategies are crucial for mitigating the impact on climate change and resource waste [14].

Aerobic composting is commonly employed to manage and repurpose organic matter in waste under thermophilic conditions, driven by the heat generated from biological processes [15,16]. Throughout the aerobic composting process, microorganisms transform raw organic materials into more stable substances, primarily humic substances (HSs) [17,18]. Vermicomposting is a highly sustainable process that transforms organic wastes into nutrient-rich compost enriched with humic substances through the activity of earthworms [19]. Anaerobic digestion of wastes involves the breakdown of organic material in the absence of oxygen, resulting in the production of biogas for energy and nutrient-dense digestate, which contains digestate that is rich in humic substances [20]. The humic substances, including humic acids and fulvic acids, are critical organic components that improve soil structure by forming aggregates, enhance nutrient availability, increase soil porosity, improve nutrient retention, water-holding capacity [21,22] and boost microbial activity, creating a fertile environment for plant growth [18]. Additionally, HSs act as natural pesticides, effectively suppressing various soil-borne phytopathogens and reducing the toxicity of chemical pesticides [23,24]. These benefits stem from the diverse functional groups present in HSs, such as carboxylic, phenolic, hydroxylic, and quinolyl groups [21].

The context of this research is focused on the urgent need for sustainable agricultural practices that enhance soil quality while reducing environmental impact. With rising concerns over soil degradation and excessive reliance on synthetic fertilizers, there has been a growing focus on organic waste transformation as a promising solution for generating humic-substance (HS)-enriched fertilizers. Current literature indicates that various organic waste transformation processes—such as composting, vermicomposting, and anaerobic digestion—yield differing levels of HSs [25–27], but there has been limited comparative analysis to determine which process optimally supports soil health.

This gap—understanding which waste transformation method best produces HS-rich fertilizers—shapes the primary research question: Which organic waste transformation method yields the most humic-substance-rich products and maximally enhances soil quality? This question is important to investigate because it addresses both the efficiency of these processes in producing beneficial soil amendments and the role of different substrates in optimizing outcomes.

Thus, this study aims to evaluate how different processes influence the conversion of organic wastes into humic substances (HSs). The research hypothesis posits that the transformation methods-vermicomposting, composting and anaerobic digestion- will yield different quantities and qualities of HSs, thereby affecting soil fertility. Specifically, olive and orange wastes were selected as matrices and subjected to these three processes to determine which method yields the highest HS-rich products. Additionally, the study examined the impact of chemically vermicompost, digestate and compost on soil quality, considering both the processing method and the type of waste used. Understanding the chemical characteristic of the HSs produced, including the amount and diversity of functional groups, can play a crucial role in shaping the agronomic effects of these waste-derived organic fertilizers when applied to soils. Answering this question has significant implications: it can help refine waste management practices, promote environmental sustainability, and foster circular economy models by converting agricultural waste into valuable soil amendments

2. Materials and Methods

2.1. Feeding Materials

Raw organic materials used for composting consisted of:

(1) 90% of olive pomace obtained from traditional three phases olive oil extraction process and 10% straw, as structuring material, named Compost 1 (C1); Olive pomace contained lignin (43%), hemicellulose (11.29%), cellulose (9.55%)

(2) 90% of orange wastes coming from the orange food industry, 10% straw as structuring material and manure, named Compost 2 (C2). Orange wastes contained lignin (19%), hemicellulose (7%) and cellulose (35%).

2.2. Composting Process Set Up

The composting processes were carried on in specialized electric composters designed to promote efficient decomposition. These composters feature separate chambers, which prevent the mixing of fresh and decomposing material, allowing independent temperature regulation in each chamber to optimize microbial activity.

The experiments were conducted in triplicate for each compost mixture under specific conditions: an initial mesophilic phase of 8 days at 29 °C, followed by a thermophilic phase of 20 days at 50 °C, and concluding with a prolonged mesophilic phase of 92 days at 27 °C [28]. Afterward, the compost entered a 30-day stabilization phase at a constant 20 °C to ensure maturity. During this phase, microbial activity diminished, and easily decomposable organic matter was depleted. Moisture levels were maintained at 50%, and oxygen concentrations stayed above 15%, with daily monitoring of temperature, moisture, and oxygen using a centrally placed probe. Water was added as necessary to maintain moisture, and daily mixing ensured sufficient oxygenation, promoting the breakdown of organic matter into stable humus. Once the composting process was complete, the compost was air-dried, finely ground to pass through a 2 mm sieve, and thoroughly mixed for uniformity. Both composts reached full maturity within six months [14].

2.3. Vermicomposting Process Set Up

The vermicomposting process was conducted using a 50-liter worm bin, specifically the Vevor 5-Tray Worm Composter (model WB25101). The bin was filled with a mixture consisting of:

(1) 45% of olive wastes, 45% organic food wastes, 45% straw (45:45:10) and earthworm 20%, named vermicompost 1 (V1),

(2) 45% orange wastes, 45% organic food wastes, 45% straw (45:45:10) and earthworm 20% named vermicompost 2 (V2),

with the bedding kept loose to promote airflow and maintained at a moisture level that was slightly damp but not excessively wet. Red wigglers (*Eisenia fetida*) were introduced to the bin at a density of 1000 worms (approximately one pound) per square foot of the bin's surface area. Over the course of four months, the organic material was broken down by the worms, resulting in mature vermicompost.

2.4. Digestate Process Set Up

The digestates were sourced from two biogas energy plants owned by the Fattoria della Piana cooperative in Candidoni, Calabria, Italy. Each plant operates with an installed capacity of 998 kW_e and a total volume of 3260 m^3. The plants were supplied with different feedstock compositions: the first plant received a mixture of 50% olive waste and 50% animal manure and maize silage, producing a digestate labeled as Digestate Olive (D1). The second plant was supplied with 50% orange waste, along with 50% animal manure and maize silage, yielding a digestate designated as Digestate Orange (D2).

The plant operators optimized process parameters, including temperature and retention time, to match the specific feedstock compositions. Both plants maintained a process temperature of 40 °C, with a daily loading volume of 120 m^3, a hydraulic retention time (HRT) of 60 days, and a minimum guaranteed retention time (MGRT) of 16 h at 40 °C. Following production, the digestates from both plants were analyzed to assess their chemical and biological properties, providing a basis for evaluating their suitability as humus-rich soil amendments.

2.5. Assessment of Chemical Characteristics of Composts, Vermicompost and Digestates

Chemical characterization of the initial wastes and composts was carried out according to the methodologies recommended by the ANPA manual [29]. Water soluble phenols (WSP), were detected by extracting soil in water, and determined by using the Folin–Ciocalteau reagent, following the Box Method [30]. Tannic acid was used as standard. Compost samples were extracted with bidistilled water (ratio compost/water 1:10) [31] for 24 h at 25 °C to detect ion concentration by using a chromatography system (Dionex ICS-1100). The NO_3–N was measured using a nitrate-ion selective electrode (USEPA, 2011), while NH_4-N was determined by a colorimetric method based on Berthelot's reaction [32].

2.6. Humic Substances Detection

Humic substances were extracted from the air-dried samples with 0.1 mol L^{-1} KOH (1:20 *w/v*) at room temperature for 16 h under a N_2 atmosphere and were separated from the suspended material by centrifugation at $7000 \times g$ for 20 min [33]. The humic extracts were chemically analyzed for total organic carbon, total extractable carbon, humic and fulvic acids humification rate, humification index, humification degree and E6/E4 ratio [34]. Diffuse Reflectance Infrared Fourier-Transform Spectroscopy (DRIFT) method was used to detect HS spectra. Spectra were recorded with a Nicolet Impact 400 Fourier-transform infrared spectrophotometer (Nicolet Instruments, Madison, WI, USA) and fitted with an apparatus for diffuse reflectance (Spectra-Tech, Stamford, CT, USA). Spectra were recorded with 200 scans collected at 4 cm^{-1} resolution, collected and manipulated by using the Omnic (Version 3.1) software supplied by Nicolet Instruments. For each analysis, 2 mg of dried sample was mixed with 148 mg of KBr (Fourier-transform infrared grade, Aldrich Chemical Co., Milwaukee, WI, USA) so that the mixture was homogeneous. The absorption bands of the HS were identified as described by others authors [34–37].

The CaOAc and $Ba(OH)^2$ methods [38] were used to determine the concentrations of carboxylic and total acidic functional groups, respectively [34]. The suspensions were filtered through 0.45 mm membrane filters as recommended by Perdue et al. [39]. Phenolic acidity was estimated as the difference between total and carboxyl acidity. Degree of humification (DH% = C(HA + HF) × 100/TEC) and humification rate (HR% = C(HA + HF) × 100/TOC) were calculated [40].

2.7. Soil Experiments

In this experiment a sandy-loam (11.85% clay, 23.21% silt, and 64.94% sand) soil was used [41]. The experiment was conducted from December to June with pots of 30 cm diameter each containing 9 kg of soil with a pH of 8.87 and 1.81% of organic matter and were amended with the different fertilizers whose dosage was chosen based on the carbon content and results obtained previously on various soils and different crops [12,42]. The experimental design employed a randomized block design with three replications for each treatment. This design allows the control of variability within the experimental units, enhancing the precision of treatment effect estimates.

The fertilizer amount used for each treatment and pot was:

Composts: 15 g per pot
Vermicompost: 12.5 g per pot
Digestate: 15 g per pot
Unfertilized pots have been used for comparison.

The application of fertilizers was performed uniformly to ensure consistent treatment across all experimental units. For each pot, the designated amount of fertilizer was carefully weighed and then incorporated into the soil to a dept of 7 cm, simulating typical field incorporation practices. After application, the soil was gently mixed to promote even distribution of each fertilizer within the topsoil layer, ensuring optimal contact between soil particles and the amendment.

Six months after the experiment began, in June, soil samples were collected, air-dried, and sieved through a 2 mm mesh for chemical and enzyme activity analysis. The experiments were performed in triplicates in greenhouse situated in Mediterranea University of Reggio Calabria at 25 °C day/19 °C night [43]. During the experiment, the pots were watered regularly to ensure that water content was maintained at 70% of field capacity, (Figure 1). At the end of the experiments (180 days after treatments) the differently treated soils (three replicates), were air-dried and sieved (<2 mm) prior to the chemical analysis (fully described in the section soil and pad analysis). Soil samples for the biochemical determination (microbial biomass and enzyme activities) were stored in the refrigerator at 4 °C for up to 24 h until processing. Each chemical and biological properties have been analyzed in 3 replicates. In this experiment, three pots filled with soil and treated with different fertilization types are sufficient as replicates due to the controlled environment provided by the climate chamber. In a climate chamber, variables such as temperature, humidity, and light are precisely regulated, minimizing external fluctuations and ensuring consistent conditions across all treatments. This control reduces the variability typically introduced by environmental factors, allowing for reliable comparisons between the differently fertilized pots even with a small number of replicates.

Moreover, analyzing each soil sample in triplicate further supports the experiment's validity. Triplicate analyses provide a robust measure of the soil properties within each pot, reducing the influence of random errors and increasing the reliability of the results. Together, the controlled conditions of the climate chamber and the triplicate analysis of each soil sample strengthen the experimental design, ensuring that the findings are both accurate and reproducible even with a smaller number of initial replicates.
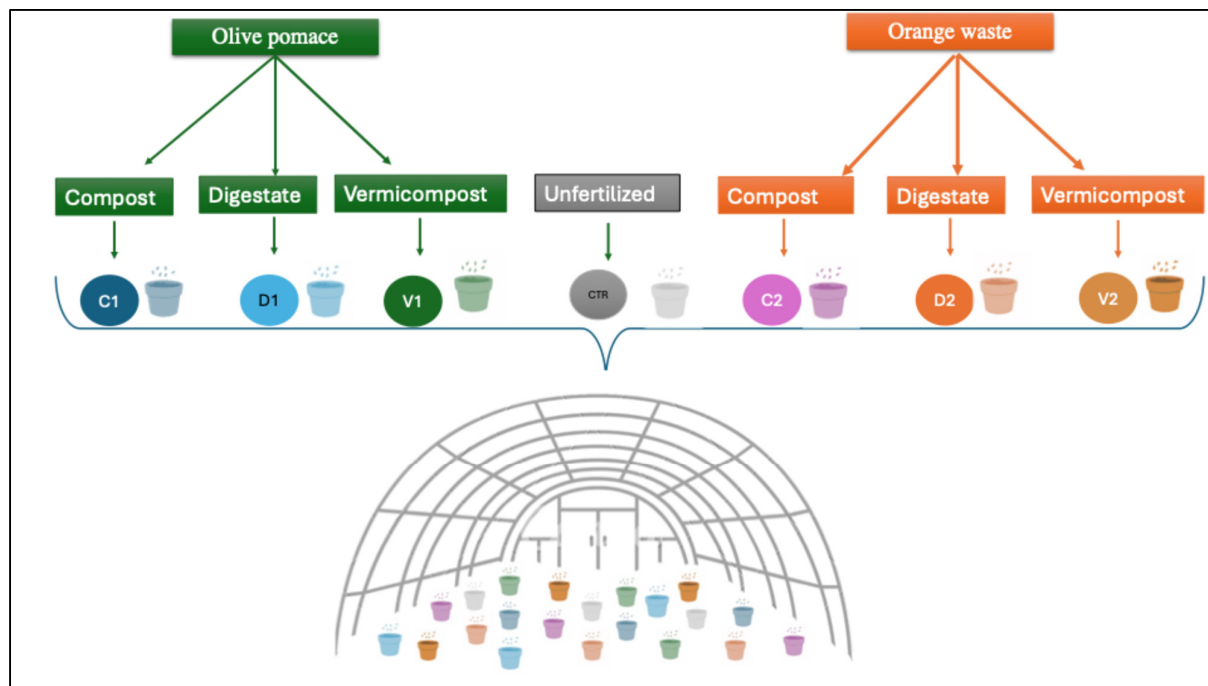
Figure 1. Experimental design in greenhouse. CTR unfertilized soil; C1 (90% wastes from olive oil + 10% straw), C2 (90% orange waste and 10% of straw), D1 (Digestate coming from olive waste 50%, and animal manure and maize silage 50%), D2 (Digestate coming from orange waste 50%, animal manure and maize silage 50%), V1 (vermicompost olive wastes: organic food waste: straw (45:45:10) earthworm 20%), V2 (vermicompost orange wastes: organic food wastes: straw (45:45:10) earthworm 20%.

2.8. Soil Analyses

Six months post-treatment, soil samples were analyzed for their physical and biological properties. Various soil parameters were measured, including pH, electrical conductivity (EC) [44], organic carbon (OC) content [45], total nitrogen (TN) content [46], and the carbon content in humic and fulvic acids [47]. Additional analyses included water-soluble phenols (WSP) [30] and cation exchange capacity (CEC) [48].

Enzyme activity, specifically fluorescein diacetate (FDA) hydrolysis, was measured [49]. Microbial biomass carbon (MBC) was assessed using the chloroform-fumigation extraction procedure [50]. Fumigated and unfumigated soil extracts were analyzed for soluble organic carbon [45], with MBC calculated from the difference in organic C between the fumigated and unfumigated samples, applying an extraction efficiency coefficient of 0.38 [50]. Dehydrogenase (DH) activity was determined in soil sample differently amended [51].

Anions, including NO_{3-}, and cations, including NH_{4+}, were detected using ion chromatography [43], using a DIONEX ICS-1100 chromatography system (Thermo Fisher Scientific, Waltham, MA, USA). NH_4-N was calculated as the mass of the element divided by the molecular mass of the compound. Cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) were extracted and analyzed using ion chromatography after incinerating 1 g of dried sample at 550 °C for 6 h. The resulting ash was acidified with 1M HCl for 30 min at 100 °C, filtered, and analyzed with 20 mM methane-sulfonic acid as the eluent. Iron (Fe) levels were measured via atomic absorption spectrophotometry using a PerkinElmer 2380 device (Waltham, MA, USA). Calibration curves were constructed with mixed standard solutions (1, 5, 25, and 50 ppm) for each anion, ensuring accurate correlation between peak area and concentration. Cation concentrations were derived from their respective standard curves [52]. All chemicals and reagents were sourced from Panreac Quìmica SLU, Barcelona, Spain.

2.9. Statistical Analysis

Data are expressed as means of three analyses for each treatment. To analyze the effect of different fertilizers to various parameters measured, a Two-way analysis of variance ANOVA with Tukey's Honestly Significant Difference (HSD) test was conducted. This statistical approach allows for comparison across treatments while accounting for potential interaction between the types of organic waste and the transformation processes. The analyses were carried out using XLStat with significance differences at $p \leq 0.05$. To explore. Relationships among different fertilizers on soil parameter datasets we analyzed using Principal Component Analysis (PCA) with XLStat.

3. Results

3.1. Characteristics of Composts, Vermicompost and Digestates

The results on the chemical characteristics of compost, vermicompost, and digestate revealed significant variations, even within the same product category, largely due to differences in the waste materials used. Products derived from orange residues showed higher concentrations of cations, anions, carbon, nitrogen, and a higher C/N ratio (Table 1) compared to those derived from olive waste. In contrast, compost, vermicompost, and digestate produced from olive waste had the highest levels of water-soluble phenols (Table 1). These chemical differences between products made from the same type of waste but processed differently underscore the critical role of the transformation process—its specific setup and conditions—in shaping the final chemical composition, even when the waste material is the same.

Table 1. Chemical characteristic of C1, C2, D1, D2, V1, V2. The data are the mean of 3 replicates $\pm$ standard deviation ($n = 18$). Different letters in the same row indicate, significant differences among the treatments (Tukey's test, $p \leq 0.05$).

Chemical Characteristics	C1	C2	V1	V2	D1	D2
pH (H_2O)	6.3 [c] $\pm$ 0.05	7.6 [b] $\pm$ 0.5	7.49 [b] $\pm$ 0.03	7.61 [b] $\pm$ 0.02	8.5 [a] $\pm$ 0.2	8.3 [a] $\pm$ 0.8
BD (kg $\times$ m^{-3})	598 [c] $\pm$ 9.0	558 [c] $\pm$ 12	554 [b] $\pm$ 9	577 [b] $\pm$ 8	788 [a] $\pm$ 9.2	768 [a] $\pm$ 11
EC (mS $\times$ cm^{-1})	1.3 [b] $\pm$ 0.25	1.8 [b] $\pm$ 0.2	3.18 [a] $\pm$ 0.2	2.5a [b] $\pm$ 0.4	1.3 [b] $\pm$ 0.2	1.5 [b] $\pm$ 0.4
WC (%)	47 [b] $\pm$ 3.2	44 [b] $\pm$ 3	49.6 [b] $\pm$ 2	42.3 [b] $\pm$ 1	64 [a] $\pm$ 7	69 [a] $\pm$ 6
TC (%)	44 [b] $\pm$ 2.40	49 [b] $\pm$ 2.4	52.8 [a] $\pm$ 1.2	59.5 [a] $\pm$ 2	45 [b] $\pm$ 1.4	47 [b] $\pm$ 1.4
TN (%)	2.5 [ab] $\pm$ 0.22	2.7 [ab] $\pm$ 0.8	2.13 [b] $\pm$ 0.03	2.66 [ab] $\pm$ 0.02	3.7 [a] $\pm$ 0.2	2.2 [a] $\pm$ 0.9
C/N	17.6 [ab] $\pm$ 1.6	18.1 [ab] $\pm$ 1.6	19.19 [ab] $\pm$ 0.6	22.03 [a] $\pm$ 0.8	12.1 [b] $\pm$ 0.5	21.4 [a] $\pm$ 0.9
Na^+ (mg g^{-1} dw)	1.1 [c] $\pm$ 0.06	0.9 [c] $\pm$ 0.02	4.69 [a] $\pm$ 0.09	2.39 [b] $\pm$ 0.07	0.9 [c] $\pm$ 0.08	0.8 [c] $\pm$ 0.1
NH_4^+ (mg g^{-1} dw)	0.7 [b] $\pm$ 0.02	0.6 [b] $\pm$ 0.01	0.5 [a] $\pm$ 0.04	0.33 [b] $\pm$ 0.04	1.5 [a] $\pm$ 0.02	1.53 [a] $\pm$ 0.01
K^+ (mg g^{-1} dw)	17 [a] $\pm$ 1.50	18 [a] $\pm$ 1.3	7.57 [b] $\pm$ 0.2	9.65 [b] $\pm$ 0.3	0.5 [d] $\pm$ 0.02	3.6 [c] $\pm$ 0.5
Mg^{2+} (mg g^{-1} dw)	1.1a [b] $\pm$ 0.1	1.8 [a] $\pm$ 0.2	0.37 [b] $\pm$ 0.02	1.22 [ab] $\pm$ 0.04	0.53 [b] $\pm$ 0.08	0.85 [b] $\pm$ 0.06
Ca^{2+} (mg g^{-1} dw)	2.4 [a] $\pm$ 0.3	2.9 [a] $\pm$ 0.2	0.21 [b] $\pm$ 0.03	2.3 [a] $\pm$ 0.06	1.7 [a] $\pm$ 0.2	1.8 [a] $\pm$ 0.1
Cl^- (mg g^{-1} dw)	nd	nd	11.12 [a] $\pm$ 0.9	9.23 [a] $\pm$ 1.1	nd	0.48 [b] $\pm$ 0.05
NO_2^- (mg g^{-1} dw)	nd	nd	nd	0.33 $\pm$ 1.1	nd	nd
NO_3^- (mg g^{-1} dw)	0.42 [b] $\pm$ 0.002	0.51 [a] $\pm$ 0.01	nd	0.87 [a] $\pm$ 1.1	0.21 [b] $\pm$ 0.03	0.42 [a] $\pm$ 0.02
PO_4^{3-} (mg g^{-1} dw)	0.43 [b] $\pm$ 0.03	0.90 [ab] $\pm$ 0.03	1.25 [a] $\pm$ 0.01	1.44 [a] $\pm$ 0.02	0.47 [b] $\pm$ 0.06	0.63 [b] $\pm$ 0.04
SO_4^{2-} (mg g^{-1} dw)	0.27 [b] $\pm$ 0.02	0.87 [ab] $\pm$ 0.02	0.93a [b] $\pm$ 0.02	1.33 [a] $\pm$ 0.02	0.11 [b] $\pm$ 0.01	0.44 [ab] $\pm$ 0.02
WSP (mg TAE g^{-1} dw)	2.42 [ab] $\pm$ 0.06	1.0 [b] $\pm$ 0.6	2.17 [b] $\pm$ 0.03	1.77 [b] $\pm$ 0.05	5.4 [a] $\pm$ 1	2.1 [b] $\pm$ 0.5
ON/TN	93 [a] $\pm$ 5	99 [a] $\pm$ 3	95.3 [a] $\pm$ 2	96.1 [a] $\pm$ 3	92 [a] $\pm$ 8	93 [a] $\pm$ 5
NH_4^+-N/NO_3^--N	1.66 [c] $\pm$ 0.13	1.17 [c] $\pm$ 0.13	nd	0.37 [c] $\pm$ 0.05	7.14 [a] $\pm$ 0.07	3.64 [b] $\pm$ 0.05

pH (H_2O), Bulk Density (BD), Electrical conductibility (EC), Water content (WC), Total Carbon (TC); Total Nitrogen (TN), Carbon/Nitrogen ratio (C/N), Water Soluble Phenols (WSP), Organic nitrogen/total nitrogen (ON/TN), Ammonium-Nitrate-Nitrogen ratio (NH_4^+-N/NO_3^-).

A Pearson correlation matrix (Table 2) of the chemical properties of compost, vermicompost, and digestate showed that pH shows a strong negative correlation with K^+ and NH4+-N/NO_3^--N indicating that as pH increases, the concentration of potassium and the ammonium/nitrate ratio decreases. This suggests that alkaline conditions may hinder

the availability of potassium and shift nitrogen towards nitrate forms. However, EC was positively correlated with Na, Cl, and PO_4^{2-}, and WC correlated with bulk density while showing an inverse correlation with NH_4^+. TOC was linked to carbon and anions, while TN was inversely correlated with the C/N ratio. Additionally, ON/TN correlated with ammonium, and the NH_4^+-N/NO_3^--N ratio was positively correlated with potassium (Table 2). The humic characteristics of the six fertilizers further revealed that those produced from olive waste contained lower levels of carbon, humic acids, and fulvic acids compared to fertilizers derived from orange residues, humic acids were more abundant in digestate than compost and vermicompost, conversely vermicompost had the greatest percentage of fulvic acids. Fertilizers from orange waste exhibited the highest humification rate and degree, while those made from olive waste had the highest humification index (HI) and E4/E6 ratio (Table 3). A Pearson correlation matrix of the humic characteristics across the different fertilizers (Table 4) showed a positive correlation among all parameters, except for HI and E4/E6. These two were negatively correlated with the other chemical parameters but positively correlated with each other (Table 4).

3.2. Effect of Composts, Vermicompost and Digestates on Soil

Soil analysis results also demonstrated significant differences across the treatments (Table 5). There was no change in soil texture and pH compared to CTR0 and CTR, but an increase in EC values and water-soluble phenols (WSP), especially with olive compost. Water content, TOC, TN, and SOM increased in compost-treated soils compared to both controls, and markers of active soil life such as MBC, FDA, and DHA were highest in soils treated with compost (Figure 2). The HC/FC ratio and CEC were also elevated in compost-treated soils (Table 5). Similar trends were observed with vermicompost treatments (Table 5), except that FDA and DHA increased only with vermicompost from orange waste (Figure 2). HC and CEC increased with both vermicomposts, but the HC/FC value increased only with orange vermicompost (Table 5).

A Pearson correlation matrix of chemical soil properties at starting of the experiments, not amended and fertilized evidenced numerous correlations. pH was always inversely correlated with the other soil parameters, EC only with WSP and TN. WC as expected was correlated with TOC, SOM, HC/FC and CEC. TOC was positively correlated with SOM, WC, and CEC, WSP showed positive correlation with MBC, TN and CEC. DHA and FDA correlated positively each other (Table 6).

PCA analysis of different fertilizers obtained with the different matrix and processes, evidenced that orange compost correlated with nutrients, both vermicompost correlated with TC, SOM and anions, while digestates correlated with WSP, WC and BD (Figure 3). The chemical characteristics of humic substances contained into the different fertilizers showed as V1 and V2 contained better quality humus as shown by TOC, TEC, CHA + CFA (Figure 4). The PCA related to potted soil differently amended, starting soil and control soil, evidenced as V1 and V2 better affected soil properties in terms of organic matter, TN, CEC HC/FC MBC and WC (Figure 5).

Table 2. Correlation matrix (Pearson (n)) of chemical characteristic of: C1, C2, D1, D2, V1, V2. Green color and its shades, in the correlation matrix, indicate a positive correlation, signifying that the variables move in the same direction. The red color and its gradients represent an inverse correlation, suggesting variables move in the opposite direction.

Variables	pH	BD	EC	WC	TC	TN	C/N	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_2^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	WSP	ON/TN	NH_4^+-N/NO_3^--N
pH	1	0.686	−0.062	0.679	0.048	0.403	−0.188	−0.153	−0.386	−0.798	−0.291	−0.197	−0.074	−0.015	0.222	0.007	−0.092	0.421	−0.146	−0.776
BD	0.686	1	−0.622	0.939	−0.521	0.472	−0.41	−0.534	−0.891	−0.775	−0.424	−0.05	−0.527	−0.288	−0.055	−0.63	−0.705	0.709	−0.74	−0.382
EC	−0.062	−0.622	1	−0.455	0.785	−0.477	0.465	0.942	0.588	0.002	−0.239	−0.613	0.955	0.368	0.069	0.897	0.785	−0.389	0.455	−0.469
WC	0.679	0.939	−0.455	1	−0.528	0.205	−0.278	−0.345	−0.909	−0.791	−0.543	−0.278	−0.418	−0.456	−0.32	−0.57	−0.669	0.574	−0.707	−0.497
TC	0.048	−0.521	0.785	−0.528	1	−0.269	0.622	0.585	0.568	0.024	0.111	−0.136	0.837	0.841	0.629	0.968	0.945	−0.439	0.525	−0.411
TN	0.403	0.472	−0.477	0.205	−0.269	1	−0.82	−0.445	−0.103	−0.326	−0.049	0.264	−0.397	0.01	0.435	−0.368	−0.415	0.776	−0.258	0.029
C/N	−0.188	−0.41	0.465	−0.278	0.622	−0.82	1	0.286	0.155	0.236	0.271	0.022	0.468	0.497	0.132	0.604	0.692	−0.813	0.379	−0.164
Na^+	−0.153	−0.534	0.942	−0.345	0.585	−0.445	0.286	1	0.444	−0.081	−0.483	−0.79	0.922	0.181	−0.138	0.714	0.551	−0.187	0.199	−0.434
NH_4^+	−0.386	−0.891	0.588	−0.909	0.568	−0.103	0.155	0.444	1	0.639	0.476	0.127	0.472	0.337	0.29	0.667	0.724	−0.512	0.854	0.261
K^+	−0.798	−0.775	0.002	−0.791	0.024	−0.326	0.236	−0.081	0.639	1	0.764	0.549	−0.112	0.018	−0.061	0.089	0.288	−0.686	0.624	0.836
Mg^{2+}	−0.291	−0.424	−0.239	−0.543	0.111	−0.049	0.271	−0.483	0.476	0.764	1	0.879	−0.34	0.229	0.34	0.081	0.333	−0.63	0.703	0.616
Ca^{2+}	−0.197	−0.05	−0.613	−0.278	−0.136	0.264	0.022	−0.79	0.127	0.549	0.879	1	−0.611	0.219	0.437	−0.258	−0.019	−0.258	0.307	0.662
Cl^-	−0.074	−0.527	0.955	−0.418	0.837	−0.397	0.468	0.922	0.472	−0.112	−0.34	−0.611	1	0.539	0.218	0.886	0.754	−0.255	0.266	−0.504
NO_2^-	−0.015	−0.288	0.368	−0.456	0.841	0.01	0.497	0.181	0.337	0.018	0.229	0.219	0.539	1	0.881	0.685	0.712	−0.229	0.257	−0.182
NO_3^-	0.222	−0.055	0.069	−0.32	0.629	0.435	0.132	−0.138	0.29	−0.061	0.34	0.437	0.218	0.881	1	0.45	0.493	0.031	0.245	−0.122
PO_4^{3-}	0.007	−0.63	0.897	−0.57	0.968	−0.368	0.604	0.714	0.667	0.089	0.081	−0.258	0.886	0.685	0.45	1	0.964	−0.509	0.622	−0.41
SO_4^{2-}	−0.092	−0.705	0.785	−0.669	0.945	−0.415	0.692	0.551	0.724	0.288	0.333	−0.019	0.754	0.712	0.493	0.964	1	−0.677	0.752	−0.226
WSP	0.421	0.709	−0.389	0.574	−0.439	0.776	−0.813	−0.187	−0.512	−0.686	−0.63	−0.258	−0.255	−0.229	0.031	−0.509	−0.677	1	−0.745	−0.243
ON/TN	−0.146	−0.74	0.455	−0.707	0.525	−0.258	0.379	0.199	0.854	0.624	0.703	0.307	0.266	0.257	0.245	0.622	0.752	−0.745	1	0.169
NH_4^+-N/NO_3^--N	−0.776	−0.382	−0.469	−0.497	−0.411	0.029	−0.164	−0.434	0.261	0.836	0.616	0.662	−0.504	−0.182	−0.122	−0.41	−0.226	−0.243	0.169	1

Table 3. Humic characteristics of the six fertilizers obtained with the different processes and biomass of C1, C2, D1, D2, V1, V2. The data are the mean of 3 replicates $\pm$ standard deviation (n = 18). Different letters in the same row indicate, significant differences among the treatments (Tukey's test, $p \leq 0.05$).

	C1	C2	V1	V2	D1	D2
TOC (%)	44 [b] $\pm$ 1.4	49 [ab] $\pm$ 1.9	53 [a] $\pm$ 2.4	59 [ba] $\pm$ 1.9	45 [b] $\pm$ 1.5	47 [b] $\pm$ 1.2
TEC (%)	17 [b] $\pm$ 1	22 [a] $\pm$ 1.4	24 [a] $\pm$ 1.1	28 [a] $\pm$ 1.5	18 [b] $\pm$ 1	20 [ab] $\pm$ 1.5
HA + FA	11 [c] $\pm$ 1	18 [b] $\pm$ 1.6	19 [b] $\pm$ 1.5 [b]	25 [a] $\pm$ 1.4	11 [c] $\pm$ 1	12 [c] $\pm$ 1
HA	6 [c] $\pm$ 0.5	10 [a] $\pm$ 1.4	8 [b] $\pm$ 0.9	9 [ab] $\pm$ 0.9	9 [ab] $\pm$ 1	10 [a] $\pm$ 1
FA	5 [d] $\pm$ 0.3	8 [c] $\pm$ 0.4	11 [b] $\pm$ 1.0	16 [a] $\pm$ 1.1	2 [e] $\pm$ 0.2	2 [e] $\pm$ 0.1
HR (%)	25 [b] $\pm$ 1.8	36 [a] $\pm$ 1.5	35 [a] $\pm$ 1	39 [a] $\pm$ 1.5	24 [b] $\pm$ 1.4	26 [b] $\pm$ 1.5
HD (%)	64 [b] $\pm$ 1.9	80 [a] $\pm$ 2.9	81 [a] $\pm$ 2.5	87 [a] $\pm$ 2	61 [b] $\pm$ 1.9	63 [b] $\pm$ 2
HI (%)	0.57 [a] $\pm$ 0.01	0.25 [b] $\pm$ 0.04	0.22 [b] $\pm$ 0.04	0.15 [b] $\pm$ 0.03	0.63 [a] $\pm$ 0.06	0.58 [a] $\pm$ 0.05
E4/E6	7.3 [a] $\pm$ 0.9 [a]	4.5 [b] $\pm$ 0.6 [b]	6.1 [a] $\pm$ 0.8	4.2 [b] $\pm$ 0.7	9.3 [a] $\pm$ 1.0	7.1 [a] $\pm$ 0.9
TA (mol kg^{-1})	9.5 [ab] $\pm$ 0.8	8.9 [b] $\pm$ 0.4	10.1 [a] $\pm$ 0.5	11.4 [a] $\pm$ 0.6	6.5 [c] $\pm$ 0.8	6.9 [c] $\pm$ 0.8
OH (mol kg^{-1})	5.4 [a] $\pm$ 0.1	2.1 [b] $\pm$ 0.5	4.9 [a] $\pm$ 0.4	4.2 [a] $\pm$ 0.4	5.1 [a] $\pm$ 0.3	4.9 [a] $\pm$ 0.2
COOH (mol kg^{-1})	4.1 [b] $\pm$ 0.5	6.8 [a] $\pm$ 0.4	5.2 [ab] $\pm$ 0.6	7.4 [a] $\pm$ 0.3	1.4 [c] $\pm$ 0.5	2 [c] $\pm$ 0.7

Total Organic Carbon (TOC), Total extractable Carbon (TEC); Humic acid carbon (HA); fulvic acid carbon (FA); humic acid carbon (HA) + fulvic acid carbon (FA), humification rate (HR), humification degree (HD), humification index (HI), E4/E6 (ratio of the absorbances at 465 and 665 nm), total acidity (TA), phenolic OH groups (OH), carboxylic groups (COOH).

Table 4. Correlation matrix (Pearson (n $-$ 1)) of humic characteristics of C1, C2, D1, D2, V1, V2 obtained with the different processes and biomass. Green color and its shades, in the correlation matrix, indicate a positive correlation, signifying that the variables move in the same direction. On the other hand, the red color and its gradients represent an inverse correlation, suggesting that the variables move in the opposite direction.

Variables	TOC	TEC	HA + FA	HA	FA	HR	HD	HI	E4/E6	TA	OH	COOH
TOC	1	0.992	0.970	0.235	0.933	0.889	0.900	−0.880	−0.755	0.759	−0.261	0.738
TEC	0.992	1	0.978	0.325	0.916	0.922	0.922	−0.907	−0.801	0.725	−0.360	0.760
HA + FA	0.970	0.978	1	0.235	0.964	0.965	0.971	−0.954	−0.857	0.807	−0.450	0.867
HA	0.235	0.325	0.235	1	−0.032	0.277	0.181	−0.185	−0.248	−0.354	−0.575	0.014
FA	0.933	0.916	0.964	−0.032	1	0.917	0.949	−0.931	−0.813	0.927	−0.306	0.888
HR	0.889	0.922	0.965	0.277	0.917	1	0.994	−0.992	−0.918	0.776	−0.617	0.920
HD	0.900	0.922	0.971	0.181	0.949	0.994	1	−0.997	−0.896	0.828	−0.547	0.926
HI	−0.880	−0.907	−0.954	−0.185	−0.931	−0.992	−0.997	1	0.893	−0.813	0.558	−0.918
E4/E6	−0.755	−0.801	−0.857	−0.248	−0.813	−0.918	−0.896	0.893	1	−0.759	0.687	−0.940
TA	0.759	0.725	0.807	−0.354	0.927	0.776	0.828	−0.813	−0.759	1	−0.173	0.875
OH	−0.261	−0.360	−0.450	−0.575	−0.306	−0.617	−0.547	0.558	0.687	−0.173	1	−0.628
COOH	0.738	0.760	0.867	0.014	0.888	0.920	0.926	−0.918	−0.940	0.875	−0.628	1
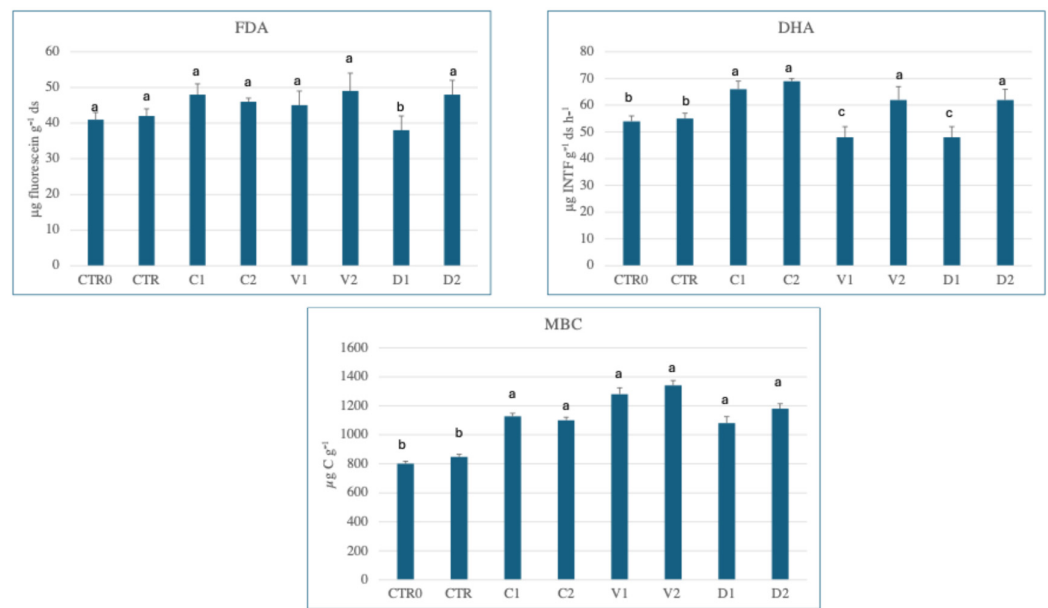
Figure 2. Fluorescein Hydrolase activity (FDA, µg fluorescein g^{-1} ds), Dehydrogenase activity (DHA, µg INTF g^{-1} ds h^{-1}), Microbial Biomass Carbon (MB µg C g^{-1} fs), of potted alkaline sandy-loam soils CTR0, and six months after the addition of C1, C2, D1, D2, V1, V2. Not amended soil was used as control (CTR). The data are the mean of three replicates ± standard deviation. Different letters significant differences among the treatments (Tukey's test, $p \leq 0.05$).

Table 5. Physical and chemical properties of potted alkaline sandy-loam soils CTR0, and six months after the addition of: C1, C2, D1, D2, V1, V2. Not amended soil was used as control (CTR). The data are the mean of three replicates ± standard deviation ($n = 24$). Different letters in the same row indicate, significant differences among the treatments (Tukey's test, $p \leq 0.05$).

	CTR0	CTR	C1	C2	V1	V2	D1	D2
pH (H$_2$O)	8.3 [a] ± 0.55	8.3 [a] ± 0.52	7.5 [a] ± 0.80	8.0 [a] ± 0.80	7.6 [ab] ± 0.40	7.3 [b] ± 0.40	7.1 [b] ± 0.40	7.4 [b] ± 0.40
EC (dS/m)	320 [c] ± 10	340 [c] ± 12	444 [a] ± 9	410 [a] ± 10	380 [b] ± 12	367 [b] ± 12	419 [a] ± 12	437 [a] ± 12
WC (%)	21.0 [b] ± 2.6	22 [b] ± 2.1	27 [a] ± 1.7	29.4 [a] ± 0.79	27.2 [a] ± 1.70	29.2 [a] ± 1.70	24 [a] ± 1.70	21 [a] ± 1.70
WSP (µg TAE g^{-1} ds)	18 [b] ± 2.0	14 [b] ± 2.8	46 [a] ± 1.7	40 [a] ± 1.60	39 [a] ± 3.3	34 [a] ± 3.1	40 [a] ± 3.26	39 [a] ± 3.26
TOC (%)	1.0 [bc] ± 0.16	0.9 [c] ± 0.16	1.7 [b] ± 0.15	2.1 [a] ± 0.15	2.1 [a] ± 0.25	2.5 [a] ± 0.25	1.3 [b] ± 0.25	1.5 [b] ± 0.25
TN (%)	0.13 [c] ± 0.01	0.14 [c] ± 0.01	0.30 [a] ± 0.02	0.33 [a] ± 0.02	0.22 [b] ± 0.04	0.23 [b] ± 0.04	0.21 [b] ± 0.04	0.25 [b] ± 0.04
C/N	7.6 [ab] ± 0.35	6.4 [b] ± 0.4	5.7 [c] ± 1	6.3 [b] ± 0.3	9.5 [a] ± 0.4	10.9 [a] ± 0.5	6.2 [b] ± 0.5	6.1 [b] ± 0.3
SOM (%)	1.72 [c] ± 0.3	1.55 [c] ± 0.27	2.92 [b] ± 0.25	3.62 [ab] ± 0.3	3.6 [ab] ± 0.13	4.3 [a] ± 0.4	2.24 [cb] ± 0.13	2.58 [cb] ± 0.4
HC (%)	0.60 [a] ± 0.06	0.61 [a] ± 0.05	0.43 [b] ± 0.02	0.44 [b] ± 0.02	0.70 [a] ± 0.01	0.75 [a] ± 0.01	0.66 [a] ± 0.01	0.65 [a] ± 0.01
FC (%)	0.40 [a] ± 0.06	0.45 [a] ± 0.08	0.26 [b] ± 0.05	0.22 [b] ± 0.05	0.38 [a] ± 0.03	0.35 [a] ± 0.05	0.62 [a] ± 0.03	0.60 [a] ± 0.03
HC/FC	1.5 [b] ± 0.12	1.33 [bc] ± 0.12	1.65 [b] ± 0.10	2 [a] ± 0.10	1.84 [b] ± 0.04	2.14 [a] ± 0.04	1.06 [c] ± 0.04	1.08 [c] ± 0.04
CEC (cmol($^+$) kg^{-1})	18.9 [b] ± 1.6	18.7 [b] ± 1.4	22 [a] ± 1.6	24 [a] ± 1.5	23 [a] ± 1.23	25 [a] ± 1.3	22 [a] ± 1.23	23 [a] ± 1.3

pH (H$_2$O), Electrical conductibility (EC), Water content (WC), Water soluble phenols (WSP), Total Organic Carbon (TOC), Total Nitrogen (TN), Soil Organic Matter (SOM); Carbon/Nitrogen ratio (C/N); Humic content (HC), Fulvic Content (FC), Humic content/Fulvic Content ratio (HC/FC), Cation Exchange capacity (CEC).
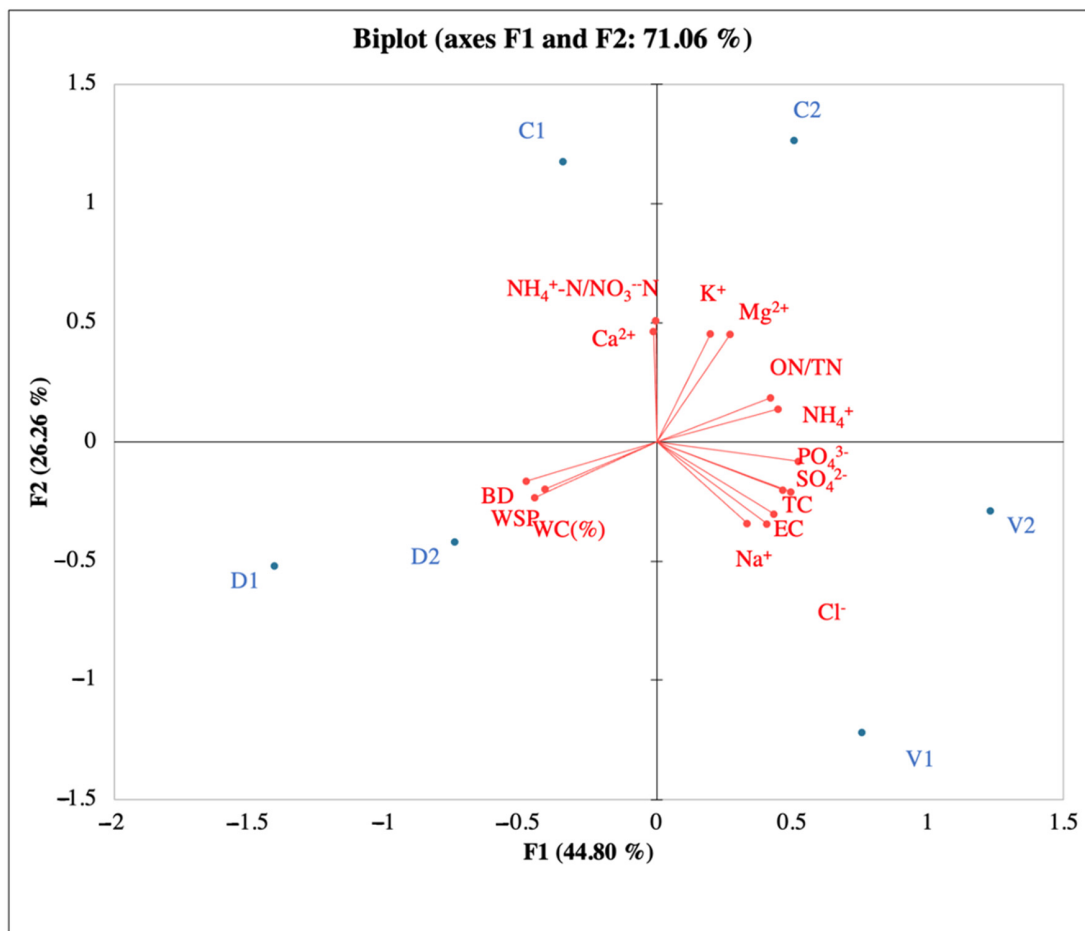
Figure 3. PCA of chemical characteristic of: C1, C2, D1, D2, V1 and V2.

Table 6. Correlation matrix (Pearson (n)) of chemical properties of potted alkaline sandy-loam soils CTR0, not amended soil was used as control (CTR) and six months after the addition of: C1, C2, D1, D2, V1 and V2. Green color and its shades, in the correlation matrix, indicate a positive correlation, signifying that the variables move in the same direction. On the other hand, the red color and its gradients represent an inverse correlation, suggesting that the variables move in the opposite direction.

| Variables	pH	EC	WC	WSP	TOC	TN	C/N	SOM	FDA	DHA	MBC	HC	FC	HC/FC	CEC
pH	1	−0.675	−0.316	**−0.767**	−0.465	−0.41	−0.146	−0.464	−0.225	0.067	**−0.764**	−0.364	−0.358	0.096	−0.639
EC	−0.675	1	0.275	**0.893**	0.296	**0.804**	−0.477	0.297	0.367	0.392	0.515	−0.348	0.077	−0.185	0.487
WC	−0.316	0.275	1	0.568	**0.888**	0.689	0.414	**0.889**	0.487	0.396	0.675	−0.155	−0.687	**0.836**	**0.845**
WSP	**−0.767**	**0.893**	0.568	1	0.604	**0.844**	−0.109	0.603	0.414	0.289	**0.74**	−0.196	−0.113	0.146	**0.738**
TOC	−0.465	0.296	**0.888**	0.604	1	0.652	0.599	1	0.693	0.38	**0.883**	0.139	−0.495	**0.795**	**0.95**
TN	−0.41	**0.804**	0.689	**0.844**	0.652	1	−0.212	0.654	0.612	0.701	0.593	−0.517	−0.46	0.38	**0.737**
C/N	−0.146	−0.477	0.414	−0.109	0.599	−0.212	1	0.597	0.261	−0.232	0.494	0.692	−0.193	0.644	0.432
SOM	−0.464	0.297	**0.889**	0.603	1	0.654	0.597	1	0.692	0.383	**0.882**	0.138	−0.495	**0.795**	**0.951**
FDA	−0.225	0.367	0.487	0.414	0.693	0.612	0.261	0.692	1	**0.724**	0.645	−0.104	−0.47	0.544	0.593
DHA	0.067	0.392	0.396	0.289	0.38	0.701	−0.232	0.383	**0.724**	1	0.175	−0.611	−0.581	0.403	0.375
MBC	**−0.764**	0.515	0.675	**0.74**	**0.883**	0.593	0.494	**0.882**	0.645	0.175	1	0.343	−0.104	0.446	**0.905**
HC	−0.364	−0.348	−0.155	−0.196	0.139	−0.517	0.692	0.138	−0.104	−0.611	0.343	1	0.568	−0.077	0.129
FC	−0.358	0.077	−0.687	−0.113	−0.495	−0.46	−0.193	−0.495	−0.47	−0.581	−0.104	0.568	1	**−0.845**	−0.309
HC/FC	0.096	−0.185	**0.836**	0.146	**0.795**	0.38	0.644	**0.795**	0.544	0.403	0.446	−0.077	**−0.845**	1	0.611
CEC	−0.639	0.487	**0.845**	**0.738**	**0.95**	**0.737**	0.432	**0.951**	0.593	0.375	**0.905**	0.129	−0.309	0.611	1
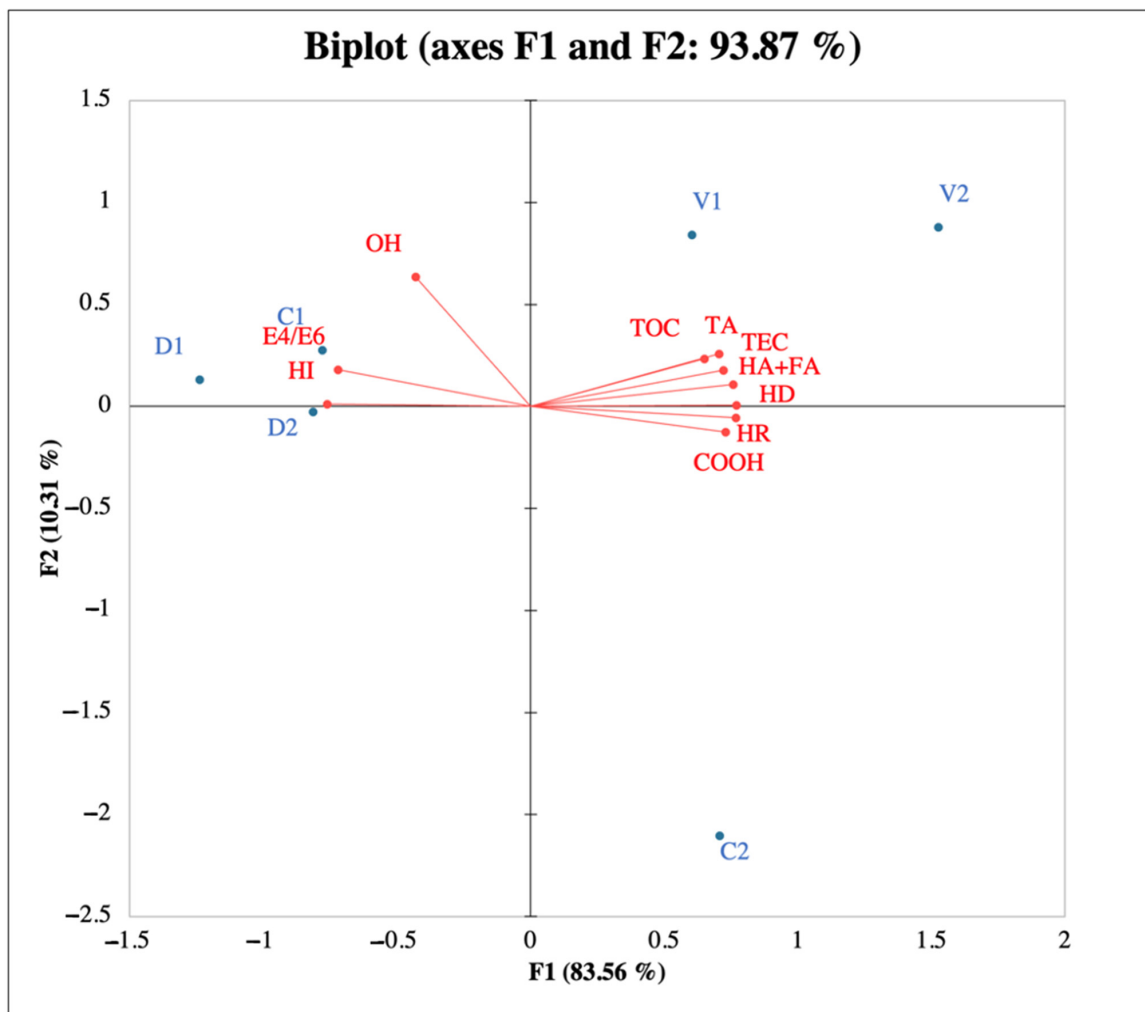
Figure 4. PCA of humic characteristics of C1, C2, D1, D2, V1 and V2.

The results of the E4/E6 ratio suggested a greater degree of aromaticity for the vermicompost than compost and digestate (Table 5). The E4/E6 ratio is inversely related to the degree of condensation, lower is the value higher is the aromaticity degree.

Carboxyl groups were the major component of the total acidity for compost produced with orange waste and vermicompost produced from both olive and orange wastes. Phenolic OH were the greater components of total acidity for both digestates and for compost olive.

The DRIFT spectrum was characterized by broad bands showing great differences among compost vermicompost and digestate. Both vermicompost expressed more peaks than both compost and digestate (Figure 6).

The DRIFT spectra of compost (Figure 6) produced with olive and orange wastes showed mainly the existence of O-containing functional groups. The spectra indicated that compost from orange contained peaks at 1712 cm^{-1} (mostly CO_2H groups), at 1646 (mostly aromatic C=C), and at 1220 (mostly OH or CO_2H groups) distinct and sharp. The high intensity of these bands reflects the high solubility of this HS. These peaks were less prominent in the spectra of compost from olive waste. The peak at 831 to 1013 cm^{-1} (aliphatic C-H) were attributed mainly to C-O stretching of carbohydrates [36], as well as to aromatic CH out of plane bending. Compost C1 had a higher peak at a 1538, indicating an aromatic C=C stretch. The peak near 843 was mainly attributed to aromatic CH out of plane bending. V1 had more peaks mostly V2 coming from orange waste. In addition to the peaks detected in compost distinct and sharp were at 2444 cm^{-1} showing OH stretch of H-bounded in COOH groups. At the peaks at 1660-1645 cm^{-1} present in both vermicompost denoted

the presence of C=O stretching of Amide I, quinones and H bonded conjugated ketones. V2 in respect to V1 contained more peaks attributed mainly to C-O stretching of carbohydrates. Digestate presented less peaks than compost and vermicompost, and spectra indicated COOH groups (1712 cm^{-1}), amide I and II (1646 and 1558 cm^{-1} respectively) COO- symmetric stretching mode (1408 cm^{-1}). Peaks near the amide I (1660 cm^{-1}) were resolved clearly. The band at 1712 cm^{-1} was assigned to the C=O stretching mode of COOH groups [53]. The bands at 1409 only present in digestate D2 was due to CH2 bending and COO−symmetric stretching modes. Strong negative peaks were near, 843, and 822 cm^{-1} they were attributed mainly to C-O stretching of carbohydrates [36], as well as to C-C stretching motions of aliphatic groups and in-plane CH bending of aromatic rings. The band characteristic of aromatic rings generally found at 1514 cm^{-1}, was absent while the presence of that at 1221 cm^{-1} in D1 was due to C-O stretching vibrations in phenols and carboxyl groups.
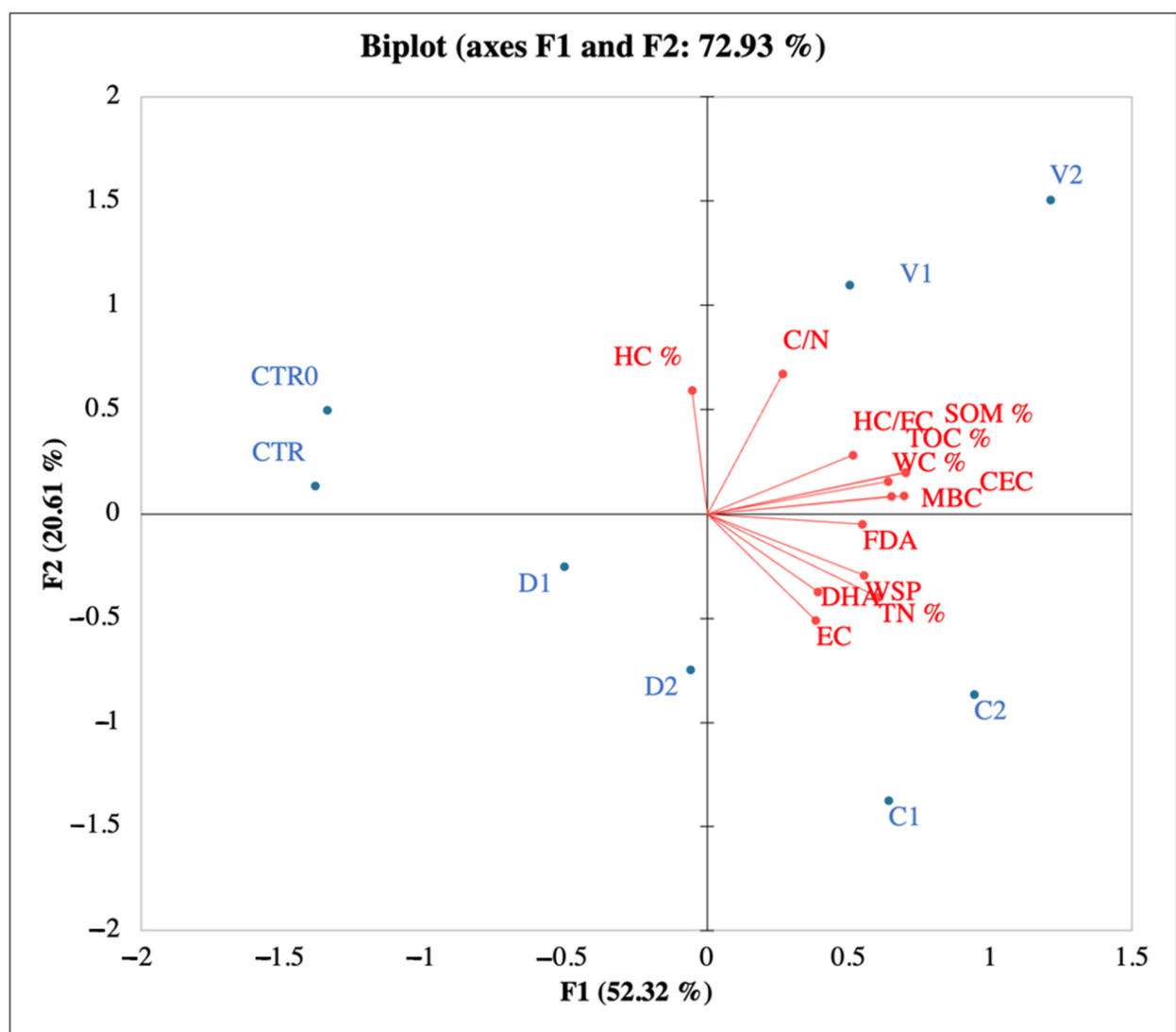
Figure 5. PCA of physical and chemical properties of potted alkaline sandy-loam soils CTR0, not amended soil was used as control (CTR) and six months after the addition of: C1, C2, D1, D2, V1 and V2.
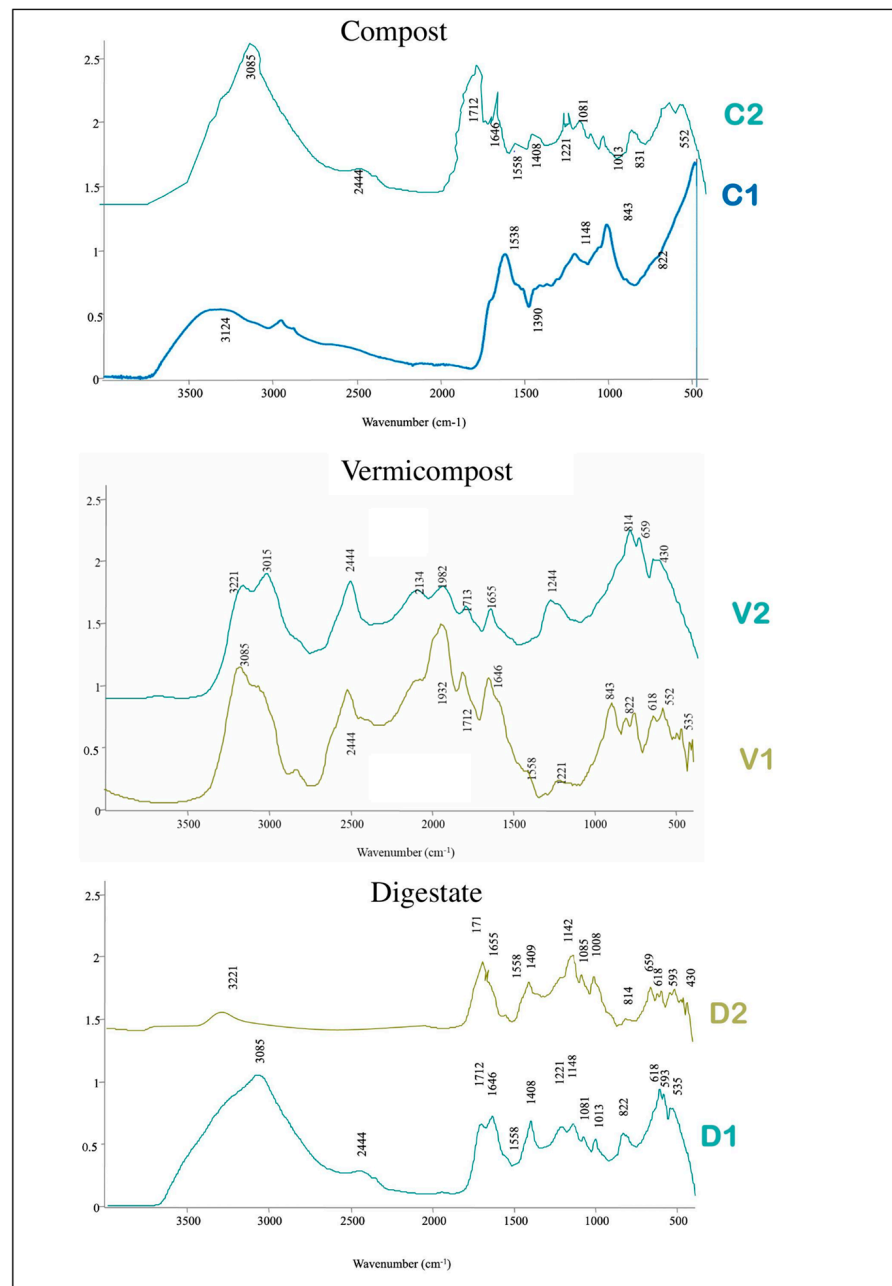
Figure 6. DRIFT spectra of compost C1, C2, D1, D2, V1 and V2.

4. Discussion

Aerobic and anaerobic transformation of organic wastes is a complex process driven by a diverse community of microorganisms, which utilize nitrogen (N) and carbon (C) for their metabolic activities [54,55]. Bacteria, fungi, and actinomycetes are the primary microbial agents driving these transformation processes, each contributing with varying intensity based on multiple factors [56,57]. Critical parameters influencing microbial activity include temperature [58], moisture content, oxygen availability [59], and chemical composition of the raw materials. Our findings highlighted substantial differences in the chemical composition of the two raw materials, which significantly affected transformation processes and microbial dynamics. Additionally, the comparison of different transformation processes showed also that both aerobic methods—composting and vermicomposting—produced fertilizers of better quality compared to digestate obtained through anaerobic processes. Data evidenced that olive wastes underwent to both anaerobic and aerobic transformation processes produced by-compounds richer in water soluble phenols with less carbon and

nutrients such as potassium magnesium, phosphate and sulphate, in respect to the orange by-products. Conversely, orange by-products contained HS with a greater amount of HA+FA, higher humification rate and degree and lower humification index and E4/E6 ratio. Based on the findings that humification index (HI), and humification rate are effective measures to evaluate the extent of humification in organic materials, relating the humification index decrease and the humification rate increase to the maturity of the organic matter [60], our data demonstrated a greater maturity of humic matter in all orange by-products. Additionally, referring to the type of process used, the aerobic processes resulted more appropriate than anaerobic in transforming both raw materials with a less production of reduced compounds, and a more microbial biodiversity involved in the transformation process [61]. Vermicomposting generated bioavailable fulvic acids and smaller quantities of highly active humic acids, promoting rapid nutrient cycling and supporting plant growth. In contrast, composting produced a larger quantity of stable humic acids, which can contribute to long-term soil structure and fertility. Digestate, while yielding fewer humic substances overall, provided low-molecular-weight fulvic acids that can offer immediate nutrient availability when applied to soil. Each of these processes, therefore, delivers a unique profile of humic components, allowing for strategic selection based on specific agricultural or environmental goals. Considering both aerobic processes, vermicomposting resulted to produce the best fertilizer quality with both the matrices. The decrease in E4/E6 ratio with the concomitant increase in the peaks of hydroxy O-H in the humic structures of compost and vermicompost as well as the observed increase in the band characteristic of aromatic rings generally found at 1514 cm^{-1}, and the enhanced stretching vibration of aromatic C=C and C=O (1650 cm^{-1}) also indicated an enhanced oxidation degree of humic substances, and the appearance of C-O-C (1244 cm^{-1}) in vermicompost and compost indicated the high structural stability of humic substances, accompanied by the enhancement of humification degree. This is consistent with the results of the elemental analysis which demonstrated a greater number of carboxylic groups in HS contained in compost and vermicompost. COOH (carboxyl) groups in humic substances provides a clearer understanding of how these functional groups contribute to soil health by enhancing nutrient retention, promoting cation exchange capacity, and fostering beneficial microbial activity. These interactions ultimately improve soil structure, fertility, and resilience, making COOH groups a key factor in the positive effects of humic substances on soil. Data on soil evidenced that nevertheless, the addition of all the by-products improved SOM, MBC and enzymatic activities in respect to control, the greatest increase was observed with both vermicompost, followed in ranking by compost and digestate. A greater cation exchange capacity was also observed in soil treated with vermicompost in respect to the other treatments and this can be related to the greatest COOH groups of humic substances contained into it. The Pearson data evidenced a good correlation of humic characteristics of V1, V2 and C2 with the main indicators of soil quality. It is well known that the earthworms fragment the organic waste substrates, stimulate microbial activity greatly and increase rates of mineralization, rapidly converting the wastes into humus-like substances with a finer structure than composts but possessing a greater and more diverse microbial activities. The consistent improvements in soil quality observed with the use of vermicompost appeared to be primarily due to their humic substance content, rather than changes in nutrient levels. Vermicomposting is a faster transformation process able to accelerate the production of humus, which not only improve soil health but also offer a sustainable alternative to synthetic fertilizers. As reported by Fornes et al. [62] one of the most significant factors affecting the quality of products such as composts and vermicompost is the original raw materials. In this study, emerged that vermicomposting and composting are superior to anaerobic digestion in producing humus-rich fertilizers primarily because of the differences in oxygen availability, microbial activity, and organic matter breakdown during these processes, which directly impact humus formation. Oxygen facilitates the activity of aerobic microorganisms that efficiently decompose organic matter and transform it into humic substances. This oxygen-rich environment enhances humification, the process by which organic matter breaks down into

stable humic substances, which are crucial for soil health. In contrast, anaerobic digestion occurs in oxygen-deprived conditions, which supports anaerobic bacteria but limits the diversity and activity of organisms that contribute to humus formation. Consequently, anaerobic digestion produces fewer humic substances and a less stable organic product, resulting in a fertilizer with lower humus content and reduced soil enhancement properties. The results of this study that compared the characteristics of composts and vermicompost as aerobic by-products and digestate as anaerobic by-product, obtained in parallel, using the same organic wastes processed with the same processes, gave new insight on their use.

5. Conclusions

The study demonstrated that transforming organic wastes, specifically olive pomace and orange waste, through different processing methods significantly alters the chemical and humic composition of the resulting fertilizers, with each method providing distinct advantages for soil health. All tested fertilizers, regardless of substrate or processing technique, exhibited high levels of humic substances (HSs), which positively influenced key soil parameters, including microbial biomass, enzymatic activity, and cation exchange capacity.

Among the methods examined, vermicomposting emerged as the most effective, yielding fertilizers with enhanced humic stability, nutrient retention, and strong associations with improved soil quality indicators. Fertilizers derived from vermicomposted olive pomace and orange wastes were particularly effective in increasing microbial diversity and soil structural stability, reinforcing vermicompost's superior role in promoting long-term soil fertility and health.

In conclusion, the aerobic and anaerobic processing of organic wastes like olive pomace and orange wastes not only reduces landfill burden and greenhouse gas emissions but also reintegrates valuable organic matter into the soil, fostering sustainable agricultural systems. This process offers a viable, eco-friendly alternative to synthetic fertilizers, with potential to enhance soil health and productivity.

Future research should expand the range of organic waste types and assess the long-term impacts on soil health and fertility. Additionally, exploring the influence of varying environmental conditions on transformation processes and microbial communities could provide deeper insights. Investigating the synergistic effects of combining different organic waste types during processing may further improve fertilizer quality and maximize soil health benefits.

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