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Waste-Derived Fertilizer Acts as Biostimulant, Boosting Tomato Quality and Aroma

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Abstract: Tomato quality is intricately regulated by a combination of factors, including the presence of bioactive compounds referred to as secondary metabolites and various organoleptic characteristics. These attributes are notably influenced and harmonized by the specific growing conditions, with a particular emphasis on the type of fertilization employed. Traditionally, chemical fertilizers have been favored in crop cultivation due to their cost-effectiveness and ability to accelerate crop growth. However, in pursuit of sustainable and intelligent agricultural practices, there is a growing need for alternative fertilizers. In this context, the present study aimed to assess the impact of fertilizers derived from waste materials, specifically sulfur bentonite and orange residue (referred to as SB), on tomato quality. This assessment extended to examining qualitative and quantitative alterations in aroma-related volatile compounds and the antioxidant systems of tomatoes, in comparison to the conventional use of fertilizers such as horse manure (HM) and nitrogen, phosphorus, and potassium (NPK). The results obtained revealed distinct effects of different fertilizers on tomato quality. Notably, parameters such as TPRO (total protein), TCARB (total carbohydrate), LIC (lycopene content), TCAR (total carotenoid content), total phenols (TPHE), total flavonoids (TFLA), and aroma profiling exhibited significantly superior values in the group treated with sulfur bentonite (SB) fertilizer. These findings strongly suggest that the novel fertilizer functioned as a biostimulant, enhancing the nutraceutical and sensory attributes of tomatoes, with a pronounced impact on the synthesis of secondary metabolites and the aroma profile of the fruits.

Keywords: antioxidants; aroma profiling; biostimulant; fertilizer; phytochemicals; tomato

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1. Introduction

The tomato (*Solanum lycopersicum* L.) stands as one of the world's most beloved vegetables, belonging to the esteemed Solanaceae family. It claims the second spot in global vegetable consumption, following only potatoes and sweet potatoes. Moreover, it plays a significant role among canned vegetables, contributing substantially to the economic well-being of producer nations [1].

Tomatoes are celebrated for their culinary versatility and remarkable nutraceutical qualities. This adaptable fruit is savored in both its fresh and cooked forms by a diverse array of consumers. With only 30 calories per 100 g and a low fat content, it serves as a health-conscious choice. What distinguishes the tomato is its rich reservoir of antioxidants and its role as a potent source of essential vitamins (C and E), carotenoids (including lycopene and β-carotene), and a plethora of other phenolic compounds [2,3]. Owing to its substantial content of bioactive compounds, which remain largely intact during ripening and cooking and, in some cases, even become more pronounced, the tomato earns its reputation as a functional food [4].

In today's health-conscious society, consumers are increasingly drawn to vegetables replete with these bioactive compounds, celebrated for their positive impact on human

health. Scientific evidence underscores their ability to safeguard cells from oxidative harm and act preventatively against the onset of degenerative conditions such as cancer, cardiovascular diseases, diabetes, Alzheimer's, and Parkinson's [5].

The global increase in tomato production can be attributed more to enhanced yields than to an expansion of cultivated land, primarily due to the overuse of fertilizers, especially chemical ones. Tomatoes grown in chemically over-fertilized soil are more susceptible to pest diseases, necessitating extensive pesticide use, which, in turn, has adverse effects on soil and human health. Crop quality, particularly in terms of nutritional value, has now assumed precedence over sheer productivity. Consequently, there is an urgent need to identify sustainable agricultural practices that can yield high-quality produce without compromising productivity.

Crop quality is intricately linked to the content of secondary metabolites, known as bioactive compounds, as well as organoleptic aspects that are influenced and balanced by growing conditions, particularly the type of fertilization employed [6]. Typically, chemical fertilizers are favored for their cost-effectiveness and rapid crop growth due to the readily available nutrients. Prior research has demonstrated the impact of different fertilization practices on the quality of various crops. Dumas et al. [7] revealed that the use of chemical fertilizers reduced the quantity of biocompounds with antioxidant properties. Young et al. [8] found that crops like cabbage, spinach, and peppers contained more antioxidants when grown with organic fertilizers than with chemical ones. Verma et al. [9] illustrated how bioaugmented compost improved antioxidant properties in tomatoes. Jin et al. [10] showed that reducing chemical fertilizers enhanced the quality of lettuce, and Moradzadeh et al. [11] indicated that the combined use of chemical and organic fertilizers improved agro-biochemical attributes of black cumin. Additionally, Akiyama et al. [12] demonstrated that tomatoes cultivated with organic fertilizers had higher nutritional values than those with chemical fertilizers.

The growth of tomatoes is significantly influenced by the presence of sulfur and sulfur-containing compounds, which serve vital roles as signaling molecules in normal metabolic processes and under stress conditions. A significant study by Silva et al. [13] highlighted that sulfur application led to increased tomato yield and fruit production. However, there is a dearth of comprehensive information regarding how sulfur fertilization may affect tomato quality, particularly concerning bioactive compounds and aromatic profiles. Furthermore, no previous research has explored the effects of sulfur fertilization when combined with organic components on tomato quality.

Given the aforementioned knowledge gap, this current study pursues two primary objectives:

To assess how the use of sulfur bentonite in conjunction with orange residue as a biostimulant influences tomato quality and its antioxidant systems, in comparison to the effects of horse manure and NPK fertilizer.

To investigate both the qualitative and quantitative alterations in the volatile compounds responsible for tomato aroma induced by sulfur bentonite, in comparison to horse manure and NPK fertilizer.

2. Materials and Methods

2.1. Site and Soil Details

The experimental sites were located in Motta San Giovanni, Loc. Liso, Italy, in soil classified as sandy loam (according to the Food and Agriculture Organization (FAO) soil classification system [14]), comprising 11.85% clay, 23.21% silt, and 64.94% sand. The soil exhibited a slightly alkaline pH and contained 3.09% organic matter and 0.17% nitrogen. Soil amendment was conducted in triplicate within the field. The soil was divided into 1 m square parcels. Each parcel received one of the following treatments: (1) sulfur bentonite–orange pads (SB) at a rate of 476 kg S ha^{-1}, (2) nitrogen–phosphorus–potassium (NPK, 20/10/10) at 170 kg ha^{-1}, (3) horse manure (HM) at 430 kg ha^{-1}, or (4) unfertilized soil used as the control (CTR). The experiment was arranged in a randomized complete block

design with six parcels for each treatment, and the experiment was replicated for three consecutive years (2020/2021/2022). In each parcel, 3–4 tomato plants, variety Big Rio F1, per square meter were transplanted at the same growth stage, with uniform size, shape, and color. Regular watering was maintained to keep the water content at 70% of the field capacity in all parcels. Tomatoes treated with different fertilizers were harvested at the same stage of ripeness based on visual characteristics (uniform size, shape, and color). The results presented in the tables are the mean values from each parcel and across three consecutive years (n = 18).

2.2. Sample Preparation

A portion of the tomatoes treated with different fertilizers, all harvested at the same stage of ripeness (uniform size, shape, and color). The fruits were carefully mashed and homogenized and preserved in a −80 °C freezer before undergoing lyophilization, a process chosen to prevent any potential damage to the bioactive compounds and essential nutrients. The volatile fraction analyses were immediately conducted on freshly harvested fruits, which were cut into small pieces without grinding to prevent the development of secondary compounds.

2.3. Preparation of Ethanol and Water Extracts

The extracts were prepared following the method outlined by Kang [15], with minor adjustments, as detailed in Muscolo et al. [16].

2.4. Total Soluble Proteins

Soluble proteins, estimated as mg/g fresh weight (FW), were determined using the Bradford method, as reported in Muscolo et al. [16].

2.5. Total Available Carbohydrates

Total available carbohydrates were measured using the anthrone method with slight modifications, as described in Muscolo et al. [16].

2.6. Total Water-Soluble Phenols, Ascorbic Acid, Total Carotenoids, Total Flavonoids, and Vitamin E

The total water-soluble phenols were quantified using the Folin–Ciocalteu assay [17] with some minor adaptations, as reported in Muscolo et al. [16]. The absorbance was measured at 765 nm using a UV–Vis Agilent 8453 spectrophotometer (Agilent Technologies, Santa Clara, CA, USA).

Ascorbic acid was assessed in tomato powder (0.10 g) extracted with a solution of meta-phosphoric acid (3%)–acetic acid (7.98%) and centrifuged at 2365× g (4000 rpm) for 10 min. The measurement was conducted using a UV–Vis Agilent 8453 spectrophotometer (Agilent Technologies, Santa Clara, CA, USA), with absorbance at 525 nm, and ascorbic acid was detected in the supernatant using the Davies and Masten method [18].

Vitamin E was detected using the method of Prieto [19], with absorbance measured at 695 nm against the blank.

Flavonoids were estimated through the aluminum chloride colorimetric method of Djeridane et al. [20]. The absorbance was measured at 510 nm using a UV–Vis Agilent 8453 spectrophotometer (Agilent Technologies, CA, USA), and the results were expressed as rutin equivalents (mg/L) using a calibration curve.

Carotenoids (CAR) were extracted by grinding 50 mg of tomato in 25 mL of cold acetone, following the method outlined by Zhang et al. [21]. The absorbance of samples was measured at 537, 647, and 663 nm. The carotenoid content was expressed as mg g^{-1} of dry weight (dw).

2.7. Determination of Antioxidant Activities

The antioxidant activity against the DPPH radical (2,2-diphenyl-1-picryl-hydrazyl-hydrate) was determined using the method reported in Muscolo et al. [16]. The DPPH

concentration in the cuvette was adjusted to yield absorbance values of ~1.0. The absorbance changes of the violet solution were recorded at 517 nm after 30 min of incubation at 37 °C. The inhibition (I%) of radical-scavenging activity was calculated using the formula I% = [(A0 − AS)/A0] × 100, where A0 is the absorbance of the control and AS is the absorbance of the sample after 30 min of incubation. The results were expressed as Trolox equivalents (TEs).

The total antioxidant capacity (TAC) was determined as per Muscolo et al. [16]. Sample absorbance was measured at 695 nm using a UV–visible spectrophotometer. Methanol (0.3 mL) was used as a blank in place of the extract. The antioxidant activity was expressed as μg of α-tocopherol per gram of dry weight (dw) based on a calibration curve.

The ABTS assay was conducted following the procedure described in Muscolo et al. [16]. Briefly, solutions containing 7 mmol L^{-1} ABTS•+ (final concentration) and 2.45 mmol L^{-1} ammonium persulfate (final concentration) in phosphate-buffered saline (PBS) were mixed and incubated in the dark at room temperature for 12–16 h. The absorbance of the samples was recorded at 734 nm using a UV–visible spectrophotometer. The percentage of radical-scavenging activity inhibition (I%) was calculated as I (%) = [(A0 − AS)/A0] × 100, where A0 represents the absorbance of the control and AS denotes the absorbance of the sample after 4 min of incubation. The results were expressed as μmol L^{-1} Trolox equivalents (TEs) based on a Trolox calibration curve.

2.8. Ultra-Fast Gas Chromatography Analysis

Ultra-fast gas chromatography (UFGC) analysis was carried out using the Heracles II instrument (Alpha MOS, Toulouse, France) equipped with an Odorscanner headspace autosampler (model HS 100, CTC Analytics, Zwingen, Switzerland) to automate sampling and injection. The Heracles II instrument featured two metal columns of different polarities working in parallel: a non-polar column (MXT-5: 5% diphenyl, 95% methylpolysiloxane) and a mid-polar column (MXT-1701: 14% cyanopropylphenyl, 86% methylpolysiloxane), both 10 mm in length and 0.18 mm in diameter. These columns were coupled to two flame ionization detectors (FID1 and FID2), enabling the simultaneous acquisition of two chromatograms for the identification of chemical compounds. The instrument was operated using AlphaSoft 2020 version 7.2.5 software, which included the AroChemBase module (Alpha MOS, Toulouse, France). The analysis of the volatile fraction was conducted on freshly harvested fruits, and samples were not subjected to grinding to prevent the development of secondary compounds. For each sample (6 × 3 replicates), approximately 2 mL of headspace was delivered at a rate of 125 μL/s from the autosampler to the injector, which was set to a temperature of 200 degrees Celsius. Further details of the UFGC settings can be found in Muscolo et al. [16].

2.9. Statistical Analysis

Statistical analyses were performed using one-way analysis of variance (ANOVA), and pairwise comparisons were conducted using Tukey's test. Statistically significant effects were determined at a significance level of $p \leq 0.01$. All data were analyzed using SYSTAT 13.0 for Windows (SPSS Inc., Chicago, IL, USA). Significant difference tests were employed to assess the impact of the three different fertilizers and the unfertilized soil on various measured parameters. Principal component analysis (PCA) was employed to explore relationships among different fertilizers and tomato parameters. PCA is an indispensable data analysis tool that aids in converting complex real-world datasets into manageable representative data. Additionally, PCA was applied to process the UFGC results, focusing on selecting features with the highest discriminatory power among samples. To visualize the results, the native UFGC program AlphaSoft 2020 version 7.2.5 (Alpha MOS, Toulouse, France) was utilized to generate a heat map for relative comparisons of each volatile compound.

3. Results and Discussion

Table 1 reveals that tomatoes treated with SB (sulfur and organic mix) exhibited significantly higher levels of total proteins (+40% compared to the control; +20% compared to NPK; +10% compared to HM) and carbohydrates (+30% compared to the control; +30% compared to NPK; +20% compared to HM). Additionally, lycopene content showed an impressive increase (+85% compared to the control; +36% compared to NPK; +15% compared to HM), as did carotenoid content (+40% compared to the control and NPK, and +15% compared to HM) in tomatoes cultivated with SB, surpassing HM, NPK, and control treatments (Table 1). This combination of heightened proteins and carbohydrates, along with a substantial increase in total carotenoids and lycopene in SB-treated tomatoes, enhances their nutraceutical value. These compounds collectively contribute to promoting human health and preventing various diseases, making SB-treated tomatoes a particularly nutritious choice.

Table 1. Water content (WC), dry weight (dw), fresh weight (fw), total proteins (TPRO, μg g^{-1} dw), total carbohydrates (TCARB, mg glucose g^{-1} dw), total phenols (TPHE, mg tannic acid g^{-1} dw), total flavonoids (TFLA, mg quercetin 100 g^{-1} dw), total carotenoids (CAR, mg 100 g^{-1} dw), licopene (LIC, mg 100 g^{-1} dw), total antioxidant capacity (TAC, mg alpha-tocopherol g^{-1} dw), 2,2′-diphenyl-1-picrylhydrazyl radical activity assay (DPPH•, % inhibition), vitamin A (VIT A, mg retinol 100 g^{-1} dw), vitamin C (VIT C, mg ascorbate 100 g^{-1} dw), and vitamin E (VIT E, mg alpha-tocopherol g^{-1} dw) in tomato grown in soils without fertilizer (control, CTR), with nitrogen/phosphorous/potassium (NPK), horse manure (HM), and sulfur bentonite with orange residue (SB). Data are the means ± standard errors of three replicates of three independent experiments (n = 18). * Different letters indicate significant differences per $p \leq 0.01$.

	CTR	NPK	HM	SB
WC	90.7 ^{a*}	89.2 ^{a}	90.7 ^{a}	89.7 ^{a}
Dry weight	9.3 ^{a}	10.8 ^{a}	9.3 ^{a}	10.3 ^{a}
Fresh weight	86 ^{b}	95 ^{a}	93 ^{a}	92 ^{a}
TPRO	1.2 ^{b}	1.3 ^{ab}	1.5 ^{a}	1.7 ^{a}
TCAR	17 ^{c}	16 ^{c}	21 ^{b}	24 ^{a}
LIC	14 ^{d}	19 ^{c}	23 ^{b}	26 ^{a}
TCARB	2.2 ^{b}	2.4 ^{ab}	2.6 ^{a}	2.8 ^{a}
TPHE	181.8 ^{b}	190.2 ^{b}	125.4 ^{c}	204.7 ^{a}
TFLA	361.8 ^{d}	389.9 ^{c}	511.3 ^{b}	533.3 ^{a}
VITA	132.5 ^{b}	137.3 ^{ab}	122.9 ^{c}	180.4 ^{a}
VITC	33 ^{c}	35 ^{b}	38 ^{b}	44 ^{a}
VITE	0.125 ^{a}	0.116 ^{a}	0.125 ^{a}	0.124 ^{a}
TAC	1.83 ^{b}	1.91 ^{b}	2.01 ^{b}	2.25 ^{a}
ABTS	0.018 ^{b}	0.029 ^{a}	0.032 ^{a}	0.035 ^{a}
DPPH%	43.9 ^{a}	36.6 ^{b}	45.5 ^{a}	37.2 ^{b}
DPPH	7.7 ^{b}	5.4 ^{c}	8.18 ^{a}	5.5 ^{c}

The remarkable increase in biomolecules observed in SB-treated tomatoes aligns with the findings of numerous other researchers who have emphasized the crucial role of sulfur (S) as a key nutrient for crop growth and development [22–24]. Sulfur is intricately involved in the synthesis of amino acids and proteins, making it indispensable for plant vitality. It is essential to note that a substantial proportion of soils, approximately 46%, are deficient in sulfur, and crops can only absorb a fraction of the S compared to nitrogen (N). This underscores the critical importance of sulfur fertilization, as it not only addresses this nutrient deficiency but also enhances the efficiency of nitrogen uptake, thereby maintaining a balanced nutrient profile [25–30].

The quality of tomatoes exhibited distinct responses to various fertilizers. As presented in Table 1, tomatoes treated with SB (sulfur and organic mix) outperformed other treatments, acting as a biostimulant and significantly elevating the levels of total phenols

(+10% compared to the control and NPK, and +50% compared to HM) and total flavonoids (+48% compared to the control, +38% compared to NPK, and +5% compared to HM). However, it is important to note that there were no significant differences observed in the vitamin E content among the differently treated tomatoes (Table 1). In contrast, a notable increase in the content of vitamin A (approximately 40% more than the control, NPK, and HM) and vitamin C (35% more than the control, 28% more than NPK, and 18% more than HM) was evident in tomatoes cultivated with SB fertilizer. This suggests that the combination of organic and elemental sulfur may provide a more effective nutritional boost compared to relying solely on either organic or inorganic fertilization. This enhanced nutrient availability can be attributed to the diverse range of micro and macro nutrients offered by this mixture, in contrast to mineral fertilizers, which primarily consist of only three major elements: nitrogen (N), phosphorus (P), and potassium (K), and organic fertilizers, which may lack sulfur.

Moreover, when assessing the total antioxidant capacity and ABTS levels, tomatoes fertilized with SB displayed the highest values (twice as high as the other treatments), while DPPH levels were similar to those of NPK-treated tomatoes, being the lowest among the treatments (Table 1). Two recent research articles [22,23] shed new light on the role of sulfur in the redox system. Sulfur emerges as a fundamental nutrient in the biosynthesis of secondary metabolites renowned for their high nutritional value. It has been convincingly demonstrated that sulfur exerts a positive influence on the accumulation of total phenols and flavonoids, compounds known for their potent antioxidant properties and remarkable nutraceutical value. Our data corroborate the findings of numerous other researchers, underscoring how sulfur fertilization not only augments total phenols and flavonoids in sulfur-loving crops such as garlic [30], cabbage [31], onion [32,33], and broccoli [25], but also in other species like artichoke [34] and tomato [35].

Total phenols and flavonoids possess significant antioxidant, anticancer, and antibacterial attributes. The above-mentioned compounds demonstrated efficacy as cardioprotective agents, anti-inflammatory substances, immune system boosters, and protective agents against UV radiation, thus exhibiting substantial potential for applications in the pharmaceutical and medical sectors [36–39].

The increase in total phenols and total flavonoids justified also the increase in antioxidant activities in SB-treated tomato.

The Pearson coefficient results revealed a significant positive correlation between total flavonoids, total antioxidant capacity (TAC), and, to a lesser extent, ABTS, while a negative correlation was observed with DPPH (Table 2). Total phenols did not show significant correlations with ABTS and TAC but exhibited a negative correlation with DPPH. In SB-treated tomatoes, the observed increase in carotenoids, known for their ability to prevent numerous chronic degenerative diseases through antioxidant action [40], confirmed the major role of total flavonoids, rather than total phenols, as antioxidants. Various studies have reported results showing a correlation between carotenoids, especially lycopene, and the mitigation of cancer and cardiac diseases [41,42].

Individual phenolic acids responded differently to the various fertilizations (Table 3). No significant differences were observed among the treatments for o-coumaric, 2,5 dihydroxybenzoic, and caffeic acids.

However, protocatechuic and syringic acids were only present in fertilized tomatoes compared to the control, with no differences noted between the various fertilizations. Trans-cinnamic acid was induced solely by the HM fertilizer, while trans-4-hydroxycinnamic acid exhibited the highest concentration in SB-treated tomatoes (+240% compared to the control; +420% compared to NPK; and +50% compared to HM) (Table 3).

These results suggest that the antioxidant activity found in SB-treated tomato could be related mainly and solely to trans-4-hydroxycinnamic acid.

Regarding the single flavonoids (Table 4), SB increased the synthesis of apigenin, tocopherol, vitexin, catechin, and naringin with respect to the control and the other fertilizers.

Table 2. Pearson correlation (r) between total proteins (TPRO, mg g^{-1} DW); total carotenoids (TCAR, µg 100 g^{-1} DW); lycopene (LIC, mg 100 g^{-1} DW); total carbohydrates (TCARB, mg glucose g^{-1} DW); total phenols (TPHE, µg GAE* g^{-1} DW); total flavonoids (TFLA, µg quercetin g^{-1} DW); vitamin A (VIT A, µg retinol 100 g^{-1} DW); vitamin C (VIT C, mg ascorbic acid g^{-1} DW.); vitamin E (VIT E, mg alpha-tocopherol 100 g^{-1} DW.); total anti-oxidant capacity (TAC, mg α-tocopherol/1100 g^{-1} d.w.); 2,2-diphenyl-1-picrylhydrazyl (DPPH, % inhibition); 1,1-diphenyl-2-picrylhydrazyl (DPPH radical, µM Trolox g^{-1} d.w.); and 2,2′-azino-bis-3-ethylbenzthiazoline-6-sulphonic acid (ABTS). Values in bold are different from 0 with a significance level alpha = 0.01.

Variables	TPRO	TCAR	LIC	TCARB	TPHE	TFLA	VITA	VITC	VITE	TAC	ABTS	DPPH %	DPPH
TPRO	**1**	**0.956**	**0.969**	**0.990**	0.044	**0.961**	0.700	**0.987**	0.293	**1**	0.882	−0.273	−0.273
TCAR	**0.956**	1	0.868	**0.908**	−0.028	**0.943**	0.653	**0.940**	0.559	**0.959**	0.717	−0.049	−0.048
LIC	**0.969**	0.868	1	**0.994**	−0.051	**0.953**	0.585	**0.936**	0.118	**0.969**	**0.969**	−0.315	−0.315
TCARB	**0.990**	**0.908**	**0.994**	**1**	0.014	**0.957**	0.656	**0.969**	0.178	**0.989**	**0.940**	−0.323	−0.324
TPHE	0.044	−0.028	−0.051	0.014	1	−0.232	0.735	0.199	−0.355	0.020	−0.057	−0.803	−0.801
TFLA	**0.961**	**0.943**	**0.953**	**0.957**	−0.232	1	0.481	**0.907**	0.400	**0.968**	0.865	−0.034	−0.035
VITA	0.700	0.653	0.585	0.656	0.735	0.481	1	0.804	0.050	0.684	0.494	−0.684	−0.683
VITC	**0.987**	**0.940**	**0.936**	**0.969**	0.199	**0.907**	0.804	1	0.255	**0.984**	0.843	−0.379	−0.378
VITE	0.293	0.559	0.118	0.178	−0.355	0.400	0.050	0.255	1	0.309	−0.113	0.694	0.695
TAC	**1**	**0.959**	**0.969**	**0.989**	0.020	**0.968**	0.684	**0.984**	0.309	1	0.880	−0.250	−0.249
ABTS	0.882	0.717	**0.969**	**0.940**	−0.057	0.865	0.494	0.843	−0.113	0.880	1	−0.417	−0.418
DPPH%	−0.273	−0.049	−0.315	−0.323	−0.803	−0.034	−0.684	−0.379	0.694	−0.250	−0.417	**1**	**1**
DPPH	−0.273	−0.048	−0.315	−0.324	−0.801	−0.035	−0.683	−0.378	0.695	−0.249	−0.418	**1**	**1**

Table 3. Single phenolic acids contained in differently cultivated tomato: without fertilizers (control, CTR) and with nitrogen/phosporous/potassium (NPK), horse manure (HM), and sulfur bentonite with orange residue (SB). Data are the means of three replicates of three independent experiments (n = 18). The experimental data are the mean of six replicates. Different letters in the same row indicate significant differences $p \leq 0.01$. nd = not detectable.

	CTR	NPK	HM	SB
Phenolic acids	mg/g SS	mg/g SS	mg/g SS	mg/g SS
Gallic	0.6 ^{a}	0.3 ^{b}	0.3 ^{b}	nd
Protocatechuic	nd	0.01 ^{a}	0.02 ^{a}	0.02 ^{a}
Syringic	nd	0.01 ^{a}	0.02 ^{a}	0.02 ^{a}
p-coumaric	nd	nd	0.01	nd
m-coumaric	4 ^{a}	0.6 ^{b}	nd	nd
o-coumaric	0.06 ^{a}	0.04 ^{a}	0.01 ^{a}	0.05 ^{a}
Trans-cinnamic	nd	nd	2.83 ^{a}	nd
3-hydroxycinnamic	nd	nd	nd	nd
Trans-4-hydroxycinnamic acid	0.46 ^{c}	0.3 ^{d}	1.00 ^{b}	1.58 ^{a}
Synaptic acid	0.02 ^{a}	0.04 ^{a}	0.04 ^{a}	nd
2,5 dihydroxy-benzoic acid	0.03 ^{a}	0.02 ^{a}	0.01 ^{a}	0.02 ^{a}
Caffeic acid	0.01 ^{a}	0.02 ^{a}	0.01 ^{a}	0.01 ^{a}
Chlorogenic acid	0.56 ^{b}	0.9 ^{a}	0.1 ^{a}	0.02 ^{c}
Ferulic acid	0.2 ^{b}	nd	0.34 ^{a}	nd

A recent manuscript [43] evidenced the important involvement of flavonoids in inflammatory response, highlighting their contribution to pathological pain by promoting plastic changes in the periphery and central nervous system, which in turn modify the neuronal phenotype and function. In particular, it was well demonstrated that these flavonoids diminished the neutrophil infiltration, had anti-inflammatory effect inhibiting cytokines, and antioxidant activity scavenging hydroxyl radicals; additionally, they also showed effects comparable to the corticoid prednisolone [35–38]. Pan et al. [39] evidenced that the quotidian consumption of flavonoid-rich foods was able to cause beneficial changes in the gut microbiota, diminishing the risk of cancer and normalizing vital functions at the cellular level [40]. In short, the data obtained evidenced that SB fertilization increased important phytochemical compounds in tomato, enhancing its nutraceutical value. Pearson correlation results between single phenolic acids and antioxidant activities evidenced a strong positive correlation between protocatechuic, syringic, and trans-4 hydroxycinnamic acid and ABTS and TAC (Figure 1).

Table 4. Single flavonoids contained in differently cultivated tomato: without fertilizers (control, CTR) and with nitrogen/phosporous/potassium (NPK), horse manure (HM), and sulfur bentonite with orange residue (SB). Data are the means of three replicates of three independent experiments (n = 18). The experimental data are the mean of six replicates. Different letters in the same row indicate significant differences $p \leq 0.01$. nd = not detectable.

	CTR	NPK	HM	SB
	mg/g SS	mg/g SS	mg/g SS	mg/g SS
Flavonoids				
Procyanidin 2	0.2 ^{a}	0.03 ^{b}	0.03 ^{b}	nd
Pelargonidine	0.05 ^{a}	nd	nd	nd
Cyanidine 3 O-glucoside	0.15 ^{a}	0.05 ^{b}	0.03 ^{b}	0.02 ^{b}
Catechin	0.08 ^{c}	0.15 ^{b}	0.3 ^{a}	0.3 ^{a}
Epicatechin	0.12 ^{a}	0.12 ^{a}	0.03 ^{b}	0.05 ^{b}
Delphinidin	0.54 ^{a}	0.52 ^{a}	0.1 ^{b}	0.1 ^{b}
Myricetin	1.16 ^{a}	1.42 ^{a}	nd	nd
Luteolin	0.04 ^{a}	0.03 ^{a}	0.02 ^{a}	0.03 ^{a}
Punicalagin	0.07 ^{a}	0.07 ^{a}	nd	nd
Naringin	nd	nd	nd	0.02 ^{a}
Quercetin	0.05 ^{a}	0.01 ^{a}	nd	0.02 ^{a}
Kaempferol	0.08 ^{c}	nd	2.1 ^{a}	0.16 ^{b}
Tocopherol	2.1 ^{b}	1.81 ^{c}	nd	2.99 ^{a}
Procyanidin 1	nd	0.16 ^{a}	nd	nd
Vicenin 2	0.01 ^{b}	0.08 ^{b}	0.3 ^{a}	0.08 ^{b}
Erythrocin	nd	0.05 ^{a}	nd	nd
Rutin	0.26 ^{c}	3 ^{a}	0.56 ^{b}	0.02 ^{d}

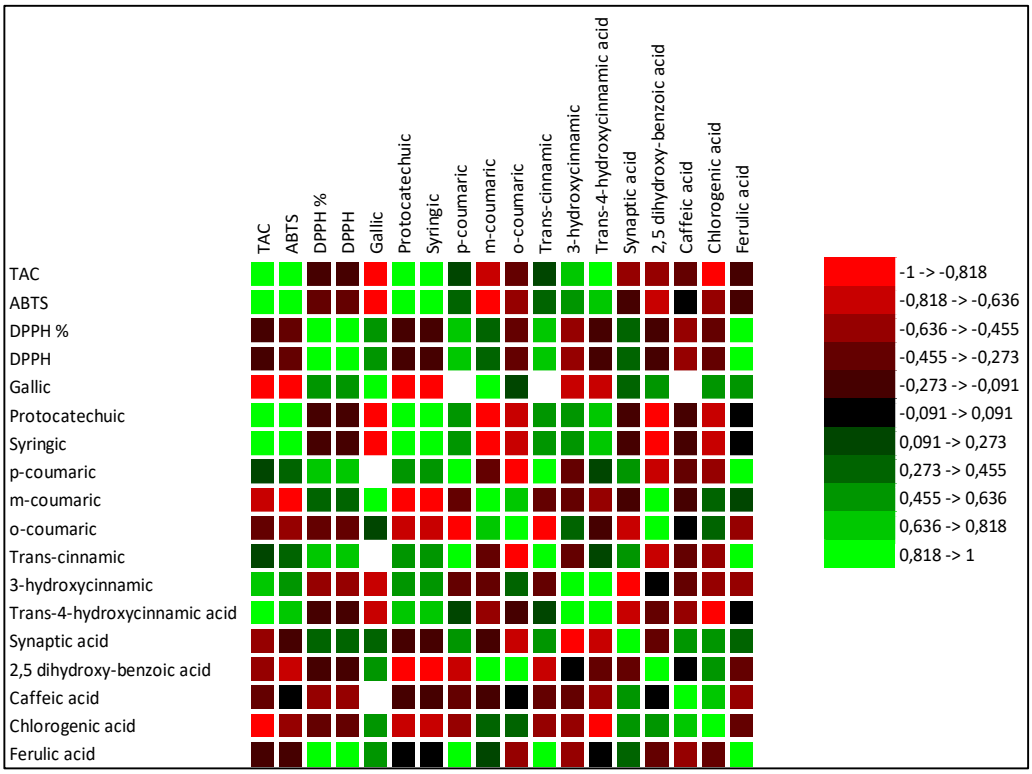

Figure 1. Pearson correlation coefficients (r) illustrating the relationships between individual phenolic acids and various antioxidant parameters, including total antioxidant capacity (TAC, mg α-tocopherol/100 g^{-1} d.w.), 2,2-diphenyl-1-picrylhydrazyl (DPPH, % inhibition), 1,1-diphenyl-2-picrylhydrazyl (DPPH radical, µM Trolox g^{-1} d.w.), and 2,2′-azino-bis-3-ethylbenzthiazoline-6-sulphonic acid (ABTS, % inhibition).

Conversely, ferulic acid correlated positively with DPPH. Regarding single flavonoids (Figure 2), only catechin, naringin, apigenin, and, at minor extent, vitexin positively and significantly correlated with TAC (Figure 2).

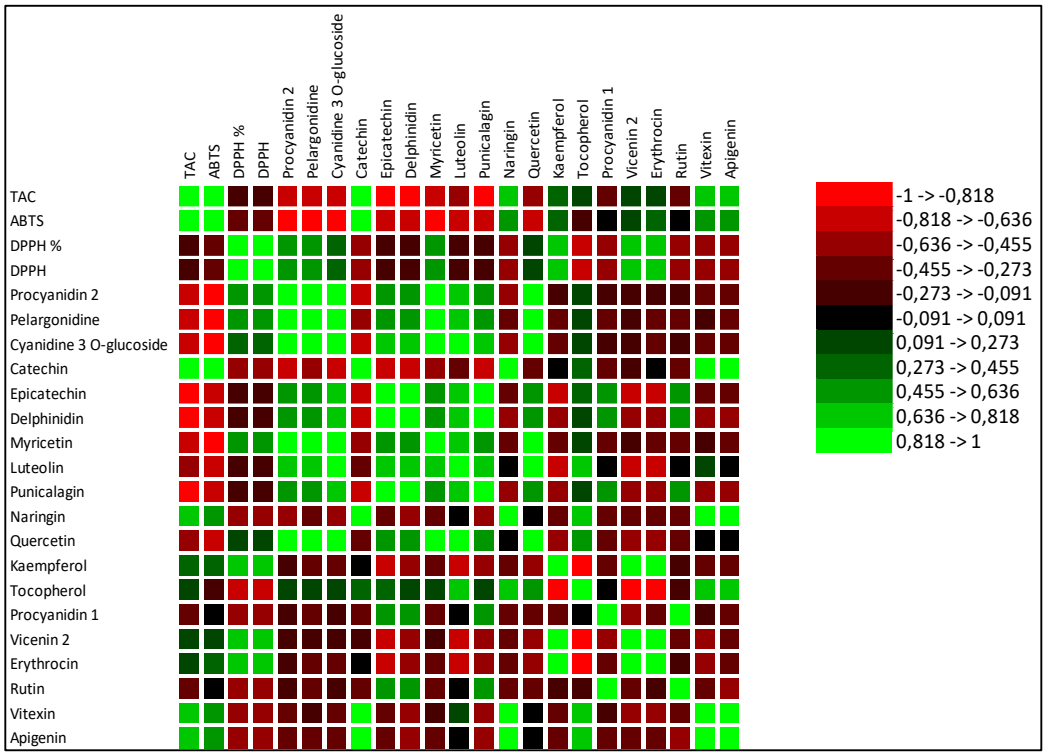

Figure 2. Pearson correlation coefficients (r) between individual flavonoids and various antioxidant parameters, including total antioxidant capacity (TAC, mg α-tocopherol*100 g^{-1} d.w.), 2,2-diphenyl-1-picrylhydrazyl (DPPH, % inhibition), 1,1-diphenyl-2-picrylhydrazyl (DPPH radical, μM Trolox g^{-1} d.w.), and 2,2′-azino-bis-3-ethylbenzthiazoline-6-sulphonic acid (ABTS, % inhibition).

ABTS correlated only with catechin; the other flavonoids were negatively or not correlated with ABTS, TAC, and DPPH activities. This result evidenced that, among the flavonoids, catechin correlated with both ABTS and TAC, activating anti-inflammatory and antioxidative responses. Considering that SB tomato contained the highest amount of trans-4 hydroxycinnamic acid, apigenin, catechin, naringin, and vitexin, its antioxidant value may be ascribed to these compounds that are positively and significantly correlated with TAC and ABTS. PCA analysis of primary and secondary metabolites evidenced positive effects of SB on vitamin A, ABTS, and total phenols (Figure 3). HM influenced the synthesis of primary metabolites, TAC, TCAR, VITE, and C (Figure 3). No positive effects were observed without fertilizations and in the presence of NPK (Figure 3).

PCA confirmed the positive correlation of SB with important single phenolic acids such as syringic, protocatechuic, and trans-4-hydroxycinnamic (Figure 4) with proven beneficial effects on human health for their antioxidant activities, as already highlighted by the Pearson correlation matrix. Single flavonoid synthesis was also affected by SB and, as reported in Figure 5, the flavonoids more affected by SB were catechin, apigenin, vitexin, and naringin—those that more correlated with the antioxidant activities.

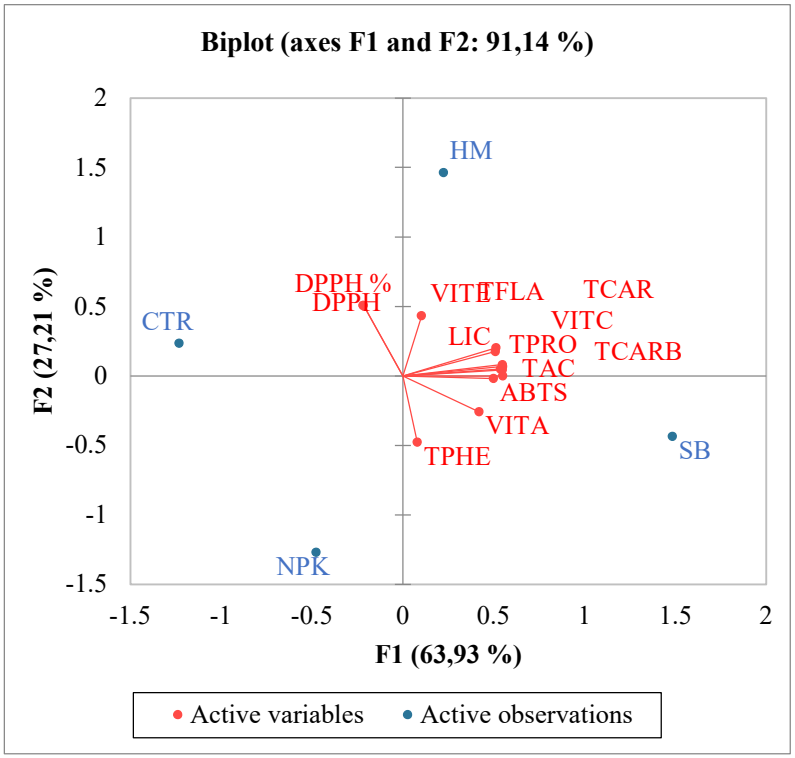

Figure 3. Principal component analysis (PCA) diagram depicting primary and secondary metabolites in tomatoes grown in distinct soil conditions: unfertilized soil (CTR) and soils enriched with various fertilizers, including nitrogen–phosphorus–potassium (NPK), horse manure (HM), and sulfur bentonite with orange residue (SB).

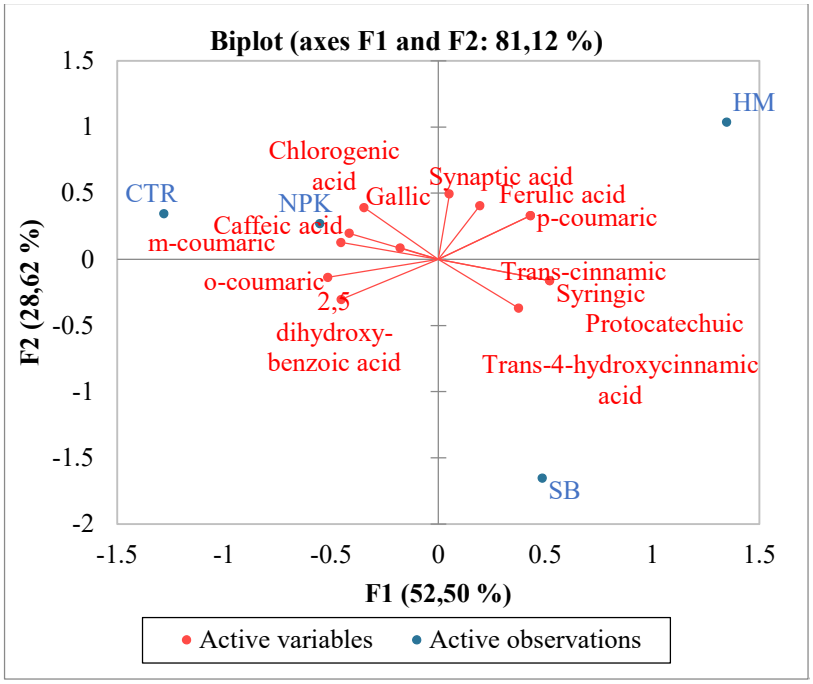

Figure 4. Principal component analysis (PCA) diagram representing individual phenolic acids in tomatoes cultivated in various soil conditions: unfertilized soil (CTR) and soils amended with different fertilizers, including nitrogen–phosphorus–potassium (NPK), horse manure (HM), and sulfur bentonite with orange residue (SB).

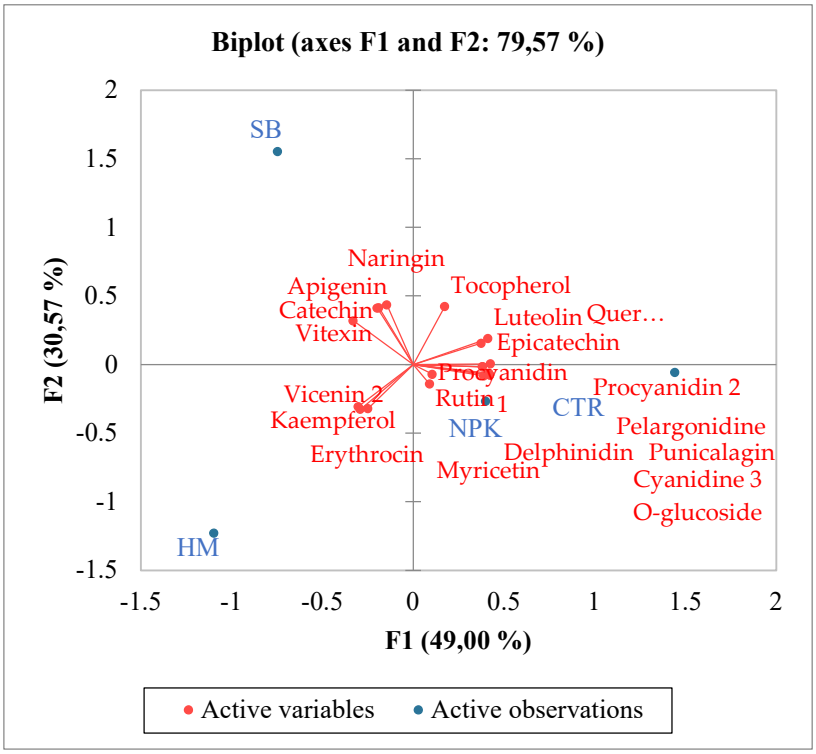

Figure 5. Principal component analysis (PCA) diagram illustrating the distribution of individual flavonoids in tomatoes cultivated under varied soil conditions: unfertilized soil (CTR) and soils enriched with different fertilizers including nitrogen–phosphorus–potassium (NPK), horse manure (HM), and sulfur bentonite with orange residue (SB).

In short, our results evidenced that SB was the fertilizer with biostimulant properties that influenced, in a prominent way, the quality of tomato fruits, increasing bioactive compounds with nutritional value and health benefit.

Regarding the aroma profiling, a comprehensive summary of discriminant chromatographic peaks and their associated sensory descriptors are reported in Table 5.

Table 5. Comprehensive summary of discriminant chromatographic peaks and their associated sensory descriptors (1-A: MTX5; 2-A: MTX 1701).

Retention Times	Name	Sensory Descriptors
13.56-1-A	acetaldehyde	Aldehydic; ethereal; fresh; fruity
49.70-1-A	3-heptanol	Green; herbaceous
61.40-1-A	ethyl hexanoate	Anise; apple; banana; berry; fruity; fruity(sweet); green; pineapple; strawberry; sweaty; sweet; unripe; waxy
66.63-1-A	(Z)-2-octenal	Earthy; fatty; fruity; green; leafy; walnut
10.68-2-A	unknown	
38.74-2-A	butane-2,3-dione	Butter; caramelized; chlorine; creamy; fruity; pineapple; pungent; spirit; strong; sweet
56.36-2-A	hexanal	Aldehydic; ethereal; fresh; fruity: green; herbaceous
90.80-2-A	1-nonanol	Dusty; fatty; floral; fresh; fruity; green; oily; orange; rose; wet

Forty-six (46) volatile compounds (Figure 6), were extrapolated from the chromatographic profiles. The volatile compounds identified in tomato were primarily aldehydes, alcohols, ketones, esters, organic acids, terpenes, and pyrazine compounds. Their relative intensities are shown as a heat map (Figure 7) .

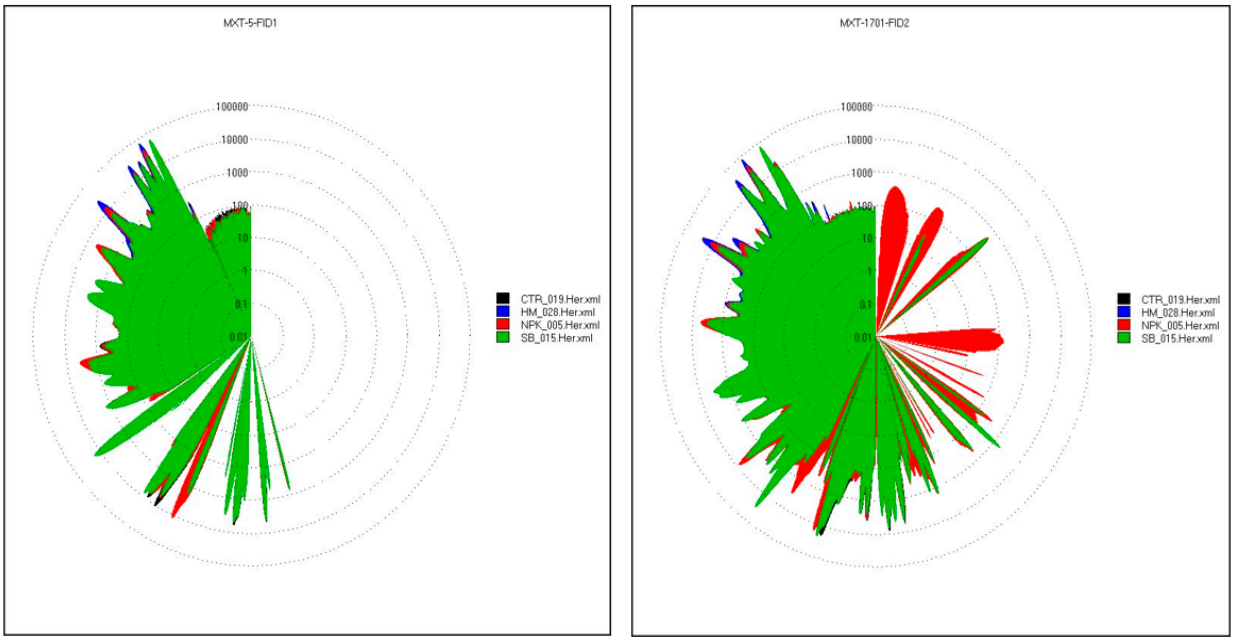

Figure 6. Odor maps or chemical fingerprints derived from UFGC analysis of tomato fruit samples cultivated in distinct soil conditions: unfertilized soil control (CONT), soil enriched with nitrogen–phosphorous–potassium (NPK), soil treated with sulfur bentonite and orange residue (SB), and soil amended with horse manure (HM).

Aldehydes were the main compounds in all samples with large intraclass variations, followed by alcohols, terpenes, and ketones. HM-treated tomato fruits had the highest concentration of aldehydes. The aromatic fraction of SB-treated tomato fruits was characterized by the highest percentage of aldehydes and a high concentration of esters and terpenes (+30%). Tomatoes fertilized with NPK were characterized by the highest percentage of aldehydes and a high concentration of both alcohols and terpenes (+20%). The pyrazine compounds were found only in tomato fruit fertilized with SB and NPK. The SB-treated tomato showed the highest percentage of both aldehydes and pyrazine compounds.

The four tomato samples were clearly distinguishable by their differences in the relative intensities of these factors. Tomato fruits treated with HM were the highest out of all samples in 1-propanol, 2-methyl-, and propanal (+20%). Tomato fruits fertilized with SB contained high levels of hexanal, followed by acetaldehyde and propanal, known to have ethereal and pungent characteristics (+22%). Tomato fruits fertilized with NPK showed relatively higher levels of propanal, 1-propanol, 2-methyl-, acetaldehyde, and ethyl hexanoate than the other treated tomatoes (+8%). Of these volatile compounds, the ethyl hexanoate is associated with fruity notes, and it plays a role in the discrimination of the NPK sample from the others (Figure 8). The tomato control showed relatively higher levels of acetaldehyde, propanal, hexanal and ethyl hexanoate than the others. Of the more than 400 volatile compounds found in ripe tomatoes, only 29 were present at concentrations greater than 1 ng L^{-1} or a one part per billion (ppb) [44]. Of these, approximately 16 had positive log odor unit values indicating a significant contribution to the tomato's aroma, including cis-3-hexenal, hexanal, 3-methylbutanal, trans-2-hexenal, trans-2-heptenal, 2-phenylacetaldehyde, β-ionone, 1-penten-3-one, β-damascenone, 6-methyl-5-hepten-2-one, cis-3-hexenol, 2-phenylethanol, 3-methylbutanol, 1-nitro-2-phenylethane, 2-isobutylthiazole, and methyl salicylate. Those volatiles that were slightly below the threshold contribute to the aromatic background [45]. The fingerprint, commonly used to distinguish food samples [46], showed evident differences between the three differently treated tomatoes compared to the control. The UFGC profiles were analyzed using PCA. In order to reduce the dataset measurements consisting of all the peak areas of each analyzed chromatogram, the most discriminant peak areas of specific compounds were extrapolated

and then treated as an input dataset for PCA analysis [47]. In Figure 9, the radar chart evidenced the clear differences between the four samples analyzed. The differences between the chromatographic finger printings fully reflected the differences in the contents of some important components.

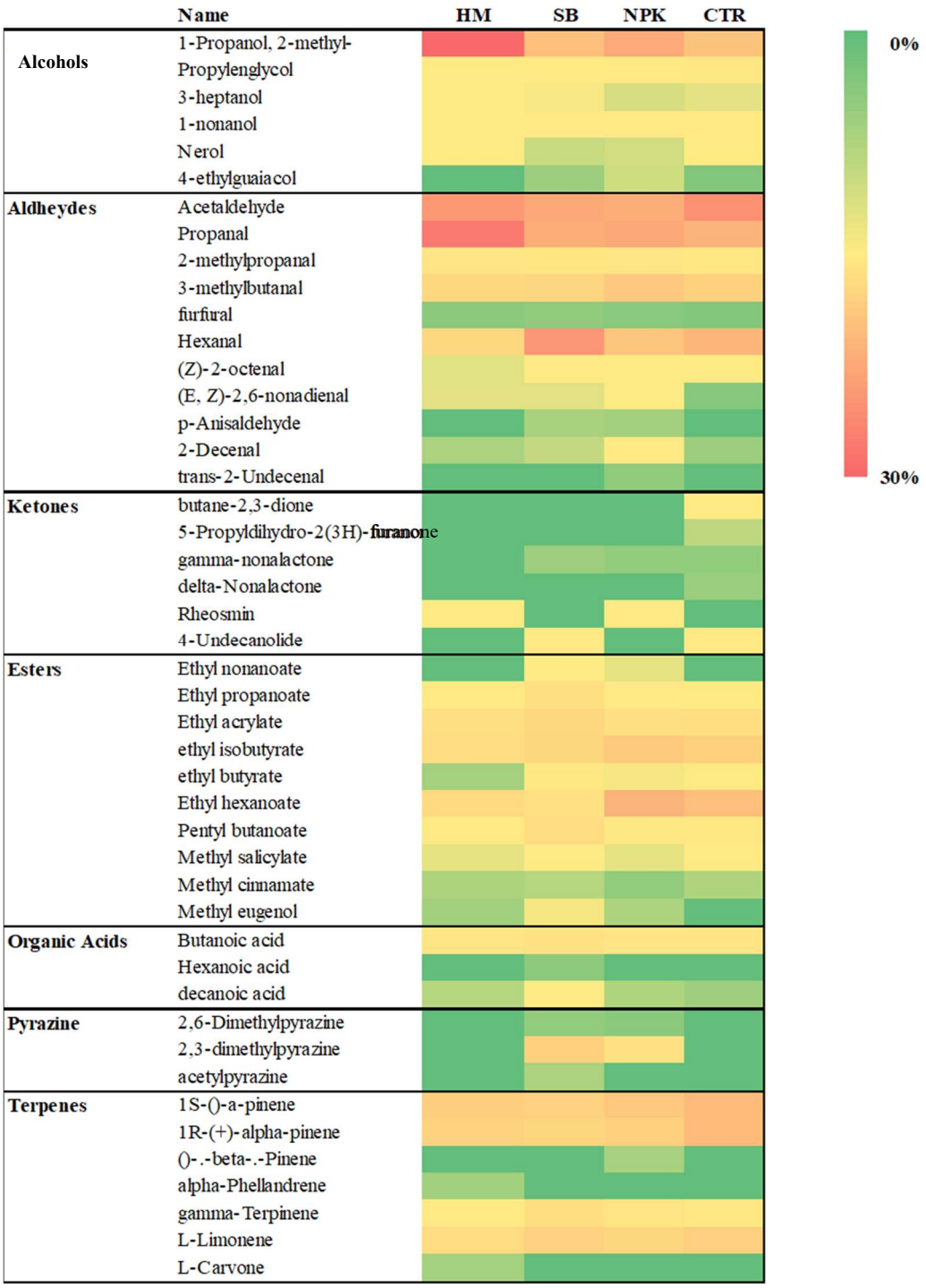

Figure 7. A heatmap displaying tomato fruit samples grown in different soil conditions: unfertilized soil control (CTR), soil with nitrogen–phosphorous–potassium fertilizer (NPK), soil treated with sulfur bentonite and orange residue (SB), and soil amended with horse manure (HM). The heatmap visualizes compound areas measured by UFGC, where green represents low peak areas and red indicates high peak areas, relative to each other.

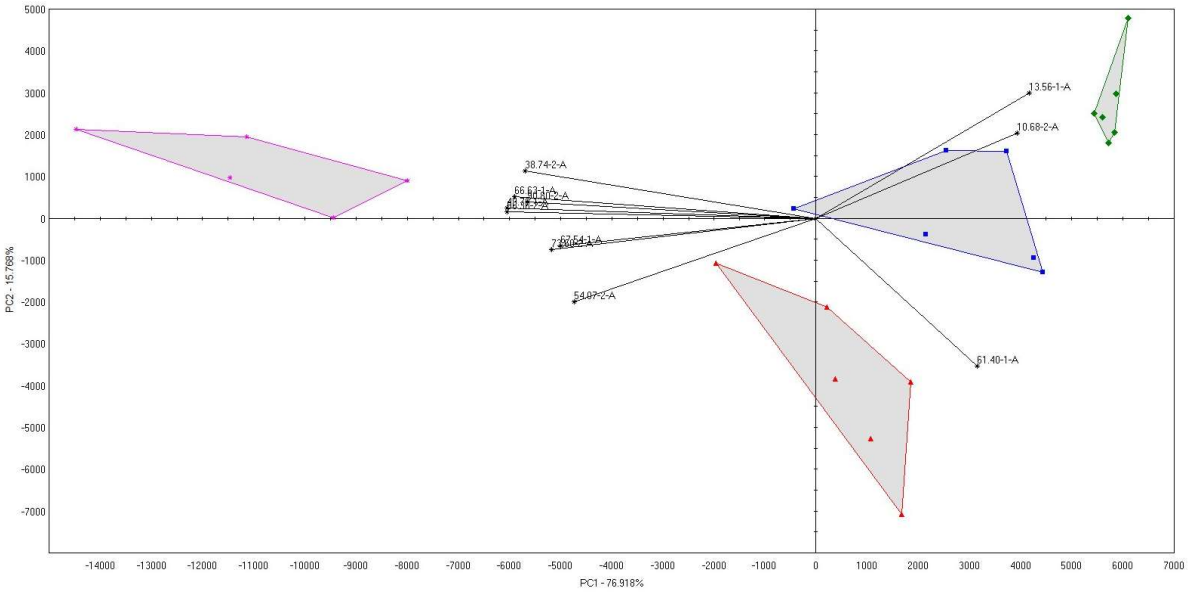

Figure 8. A PCA biplot illustrating the distribution of tomato samples cultivated in different soil conditions: unfertilized soil control (CTR), soil enriched with nitrogen–phosphorous–potassium (NPK), soil treated with sulfur bentonite and orange residue (SB), and soil amended with horse manure (HM). This biplot highlights the discrimination of odorous compounds, including acetaldehyde (13,56-1-A), 3-heptanol (49,70-1-A), ethyl hexanoate (61,40-1-A), (Z)-2-octanal (66,63-1-A), an unknown compound (10,68-2-A), butane-2,3-dione (38,74-2-A), hexanal (56,36-2-A), and 1-nonanol (90,80-2-A).

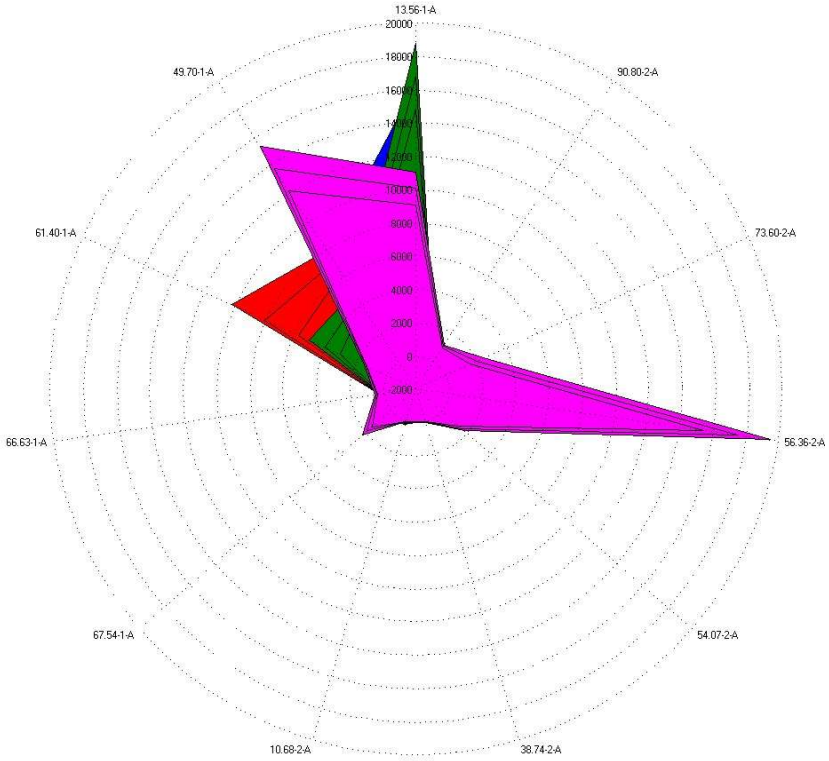

Figure 9. Radar chart illustrating discriminant peaks of tomato samples grown in different soil conditions: unfertilized soil control (CTR), nitrogen–phosphorous–potassium fertilized soil (NPK), soil with sulfur bentonite mixed with orange residue (SB), and soil with horse manure (HM). The chart discriminates based on the following odorous compounds: acetaldehyde (13,56-1-A), 3-heptanol (49,70-1-A), ethyl hexanoate (61,40-1-A), (Z)-2-octanal (66,63-1-A), unknown compound (10,68-2-A), butane-2,3-dione (38,74-2-A), hexanal (56,36-2-A), and 1-nonanol (90,80-2-A).

Acetaldehyde, (Z)-2-octenal, hexanal, 1-nonanol, and butane-2,3-dione were responsible for the fresh and fruity flavor. These compounds also promote the fresh feeling of the fruit and participate in the formation of the sweet character [48]. Fruity, green, and unripe flavor is related to the ethyl hexanoate and 3-heptanol. The heat map (Figure 10) showed the differences in the aroma profile of the differently treated samples. C6 volatile compounds, including hexanal, trans-2-hexene, cis-3-hexene, and corresponding alcohols, were among the most abundant volatile compounds in tomatoes, giving "green" and "grassy" notes to the fruit [49]. The highest value of hexanal was found in tomato fruits treated with SB. The PCA analysis (Figure 8) showed the first component discriminated only the samples SB and HM, while NPK and CTR were discriminated by the second ones. The SB group was absolutely different from the other groups. Odorous compounds, acetaldehyde (3,56-1-A) and an unknown (10,68-2-A), were characteristics of the HM-treated tomato and CTR groups; 3-heptanol (49,70-1-A), ethyl hexanoate (61,40-1-A), (Z)-2-octanal (66,63-1-A), butane-2, 3-dione (38,74-2-A), hexanal (56,36-2-A), and 1-nonanol (90,80-2-A) were characteristics of the SB group; and ethyl hexanoate (61,40-1-A) was characteristic of the NPK group.

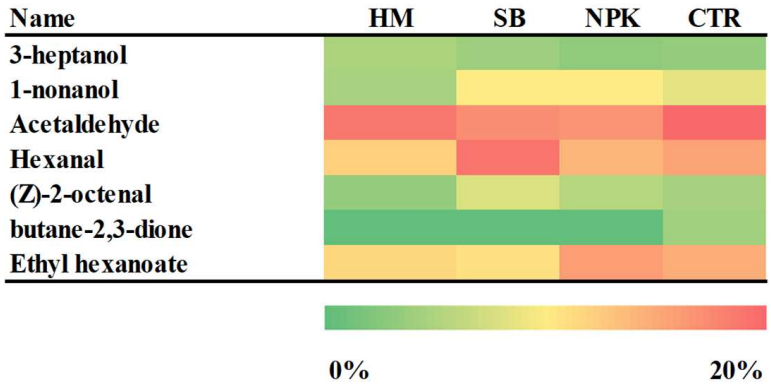

Figure 10. A heatmap displaying discriminant chromatographic peaks of tomato fruit samples grown under various soil conditions: unfertilized soil control (CTR), soil with nitrogen–phosphorous–potassium fertilizer (NPK), soil enriched with sulfur bentonite and orange residue (SB), and soil amended with horse manure (HM). The heatmap represents the peak areas measured by UFGC, with green indicating low peak area and red indicating high peak area, respectively.

In summary, the analysis of odor profiles revealed that SB-treated tomatoes had the highest percentage of C6 aldehydes, such as hexanal, often referred to as a "green" compound. Hexanal imparts a fresh, green character to the tomato aroma and can induce the activation of defense genes that enhance tolerance against fungi even at relatively low concentrations [50–54].

4. Conclusions

The fertilization of crops, either chemical or organic, has been recommended, up until now, to improve soil productivity and compensate for the lack of nutrients. As this study has shown, fertilizers from agro-industrial wastes containing both single nutrients and organic components can be used instead as improvers of soil but also as improvers of crop quality. The aromatic profiles of treated tomato, in good agreement with the secondary metabolites, have been heavily modified in intensity and composition using SB, which differently influenced the production of bioactive compounds, increasing the bioactive compounds' antioxidant activity and the main compounds responsible for the best characteristics of tomato flavor. Taken together, these results highlight that fertilizers produced by wastes can be used as biostimulants to strengthen bioactive compounds in fruits, providing a new strategy to ameliorate the nutraceutical power and profitability of crops with prominent results on the bio and green economy.

Author Contributions: Conceptualization, A.M. (Adele Muscolo) and M.R., methodology, R.D.S.; software, S.C. and A.M. (Angela Maffia); validation, A.M. (Adele Muscolo) and M.R.; formal analysis C.M. and F.M.; investigation, S.C., A.M. (Angela Maffia) and F.M. writing—original draft preparation, A.M. (Adele Muscolo); writing—review and editing, M.R.; project administration, A.M. (Adele Muscolo); funding acquisition, A.M. (Adele Muscolo). All authors have read and agreed to the published version of the manuscript.

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References

1. Food and Agriculture Organization of the United Nations (FAO). Available online: http://www.fao.org/faostat/en/#home (accessed on 1 January 2021).
2. Ilahya, R.; Hdiderb, C.; Lenucci, M.S.; Tlili, I.; Dalessandro, G. Phytochemical composition and antioxidant activity of high-lycopene tomato (*Solanum lycopersicum* L.) cultivars grown in Southern Italy. *Sci. Hortic.* **2011**, *127*, 255–261. [CrossRef]
3. Pinela, J.; Barros, L.; Carvalho, A.M.; Ferreira, I.C.F.R. Nutritional composition and antioxidant activity of four tomato (*Lycopersicon esculentum* L.) farmer' varieties in Northeastern Portugal homegardens. *Food Chem. Toxicol.* **2012**, *50*, 829–834. [PubMed]
4. Martirosyan, D.; Miller, E. Bioactive Compounds: The Key to Functional Foods. *Bioact. Compd. Health Dis.* **2018**, *1*, 36–39. [CrossRef]
5. Agarwal, S.; Rao, A.V. Tomato lycopene and its role in human health and chronic diseases. *Can. Med. Assoc. J.* **2000**, *163*, 739–744.
6. Habibi, A.; Heidari, G.; Sohrabia, Y.; Badakhshan, H.; Mohammadi, K. Influence of bio, organic and chemical fertilizers on medicinal pumpkin traits. *J. Med. Plants Res.* **2011**, *523*, 5590–5597.
7. Dumas, Y.; Dadomo, M.; Di Lucca, G.; Grolier, P. Effects of environmental factors and agricultural techniques on antioxidant content of tomatoes. *J. Sci. Food Agric.* **2003**, *83*, 369–382.
8. Young, J.W.; Mau, J.L.; Ko, P.T.; Huang, L.C. Antioxidant properties of fermented soybean broth. *Food Chem.* **2000**, *71*, 249–254. [CrossRef]
9. Verma, A.; Sharma, R.; Kumar, C.; Kaur, A.; Arora, R.; Shah, L. Nain Improvement of antioxidant and defense properties of Tomato (var. *Pusa rohini*) by application of bioaugmented compost. *Saudi J. Biol. Sci.* **2015**, *22*, 256–264. [CrossRef]
10. Jin, N.; Jin, L.; Wang, S.; Li, J.; Liu, F.; Liu, Z.; Luo, S.; Wu, Y.; Lyu, J.; Yu, J. Reduced Chemical Fertilizer Combined with Bio-Organic Fertilizer Affects the Soil Microbial Community and Yield and Quality of Lettuce. *Front. Microbiol.* **2022**, *21*, 863325. [CrossRef]
11. Moradzadeh, S.; Moghaddam, S.S.; Rahimi, A.; Pourakbar, L.; Sayyed, R.Z. Combined bio-chemical fertilizers ameliorate agro-biochemical attributes of black cumin (*Nigella sativa* L.). *Sci. Rep.* **2021**, *11*, 11399. [CrossRef]
12. Akiyama, T.; Shimo, Y.; Yanai, H.; Qin, J.; Ohshima, D.; Maruyama, Y.; Asaumi, Y.; Kitazawa, J.; Takayanagi, H.; Penninger, J.M.; et al. The tumor necrosis factor family receptors RANK and CD40 cooperatively establish the thymic medullary microenvironment and self-tolerance. *Immunity* **2008**, *29*, 423–437. [CrossRef] [PubMed]
13. Silva, M.L.d.S.; Trevizam, A.R.; Piccolo, M.C.; Furlan, G. Tomato production in function of sulfur doses application. *Rev. Bras. Tecnol. Apl. Ciências Agrárias* **2014**, *7*, 47–54. [CrossRef]
14. FAO-UNESCO. *Word Soil Map, Revised Legend*; FAO-UNESCO: Rome, Italy, 1999.
15. Kang, M.C.; Kim, S.-Y.; Kim, E.-A.; Lee, J.-H.; Kim, Y.-S.; Yu, S.-K.; Chae, J.B.; Choe, I.-H.; Cho, J.H.; Jeon, Y.-J. Antioxidant activity of polysaccharide purified from Acanthopanax koreanum Nakai stems in vitro and in vivo zebrafish model. *Carb. Polym.* **2015**, *127*, 38–46. [CrossRef]
16. Muscolo, A.; Calderao, A.; Papalia, T.; Settineri, G.; Mallamaci, C.; Panuccio, M.R. Soil salinity improves nutritional and health promoting compounds in three varieties of lentil (*Lens culinaris* Med.). *Food Biosci.* **2020**, *35*, 100571. [CrossRef]
17. Velioglu, Y.S.; Mazza, M.; Gao, L.; Oomah, B.D. Antioxidant activity and total phenolics in selected fruits, vegetables, and grain products. *J. Agric. Food Chem.* **1998**, *46*, 4113–4117. [CrossRef]
18. Davies, S.H.R.; Masten, S.J. Spectrophotometric method for ascorbic acid using dichlo-rophenolindophenol: Elimination of the interference due to iron. *Anal. Chim. Acta* **1991**, *248*, 225–227. [CrossRef]
19. Prieto, P.; Pineda, M.; Aguilar, M. Spectrophotometric quantitation of antioxidant capacity through the formation of a phospho-molybdenum complex: Specific application to the determination of vitamin E. *Anal. Biochem.* **1999**, *269*, 337–341. [CrossRef]
20. Djeridane, A.; Yousfi, M.; Nadjemi, B.; Boutassouna, D.; Stocker, P.; Vidal, N. Antioxidant activity of some Algerian medicinal plants extracts containing phenolic compounds. *Food Chem.* **2006**, *97*, 654–660. [CrossRef]
21. Zhang, B.; Deng, Z.; Tang, Y.; Chen, P.; Liu, R.; Ramdath, D.D.; Liu, Q.; Hernandez, M.; Tsao, R. Fatty acid, carotenoid and tocopherol compositions of 20 Canadian lentil cultivars and synergistic contribution to antioxidant activities. *Food Chem.* **2014**, *161*, 296–304. [CrossRef]

22. Narayan, O.P.; Kumar, P.; Yadav, B.; Dua, M.; Atul Kumar Johri, A.K. Sulfur nutrition and its role in plant growth and development. *Plant Sign. Behav.* **2022**, 2030082. [CrossRef]
23. Zenda, T.; Liu, S.; Dong, A.; Duan, H. Revisiting Sulphur—The Once Neglected Nutrient: It's Roles in Plant Growth, Metabolism, Stress Tolerance and Crop Production. *Agriculture* **2021**, *11*, 626. [CrossRef]
24. Ranadev, P.; Revanna, A.; Bagyaraj, D.J.; Shinde, A.H. Sulfur oxidizing bacteria in agro ecosystem and its role in plant productivity—A review. *J. Appl. Microbiol.* **2023**, *134*, lxad161. [CrossRef] [PubMed]
25. Chowdhury, M.A.H.; Sultana, T.; Rahman, M.A.; Saha, B.K.; Chowdhury, T.; Tarafder, S. Sulphur fertilization enhanced yield, its uptake, use efficiency and economic returns of *Aloe vera* L. *Heliyon* **2020**, *18*, e05726. [CrossRef] [PubMed]
26. De Pascale, S.; Maggio, A.; Pernice, R.; Fogliano, V.; Barbieri, G. Sulphur fertilization may improve the nutritional value of *Brassica rapa* L. subsp. *sylvestris*. *Eur. J. Agron.* **2007**, *26*, 418–424. [CrossRef]
27. Yanar, D.; Geboloğlu, N.; Yanar, Y.; Aydin, M.; Çakmak, P. Effect of different organic fertilizers on yield and fruit quality of ındeterminate tomato (*Lycopersicon esculentum*). *Sci. Res. Essays* **2011**, *6*, 3623–3628. [CrossRef]
28. Ibañez, T.B.; de Melo Santos, L.F.; de Marcos, A.; Igor, L.; Ribeiro, V.; Ribeiro, F.V.; dos Reis, A.R.; Adônis Moreira, A.; Heinrichs, R. Sulfur modulates yield and storage proteins in soybean grains. *Soil Plant Nutr.* **2021**, *78*, 1–9. [CrossRef]
29. Degryse, F.; Baird, R.; da Silva, R.C.; Holzapfel, C.B.; Kappes, C.; Tysko, M.; McLaughlin, M.J. Sulfur Uptake from Fertilizer Fortified with Sulfate and Elemental S in Three Contrasting Climatic Zones. *Agronomy* **2020**, *10*, 1035. [CrossRef]
30. Thangasamy, A.; Kalyani, G.; Pranjali, H.; Ghodke, S.; Ahammed, T.P.; Manjusha, J.; Kaushik, B.; Major, S. Effects of sulfur fertilization on yield, biochemical quality, and thiosulfinate content of garlic. *Sci. Hortic.* **2021**, *289*, 110442. [CrossRef]
31. Nawirska-Olszanska, A.; Biesiada, A.; Kita, A. Effect of Different Forms of Sulfur Fertilization on Bioactive Components andv Antioxidant Activity of White Cabbage (*Brassica Oleracea* L.). *Appl. Sci.* **2021**, *11*, 8784. [CrossRef]
32. Judita, B.; Petra, K.; Alena, V.; Ján, T.; Matyáš, O. The role of sulphur on the content of total polyphenols and antioxidant activity in onion (*Allium cepa* L.). *Potravinarstvo* **2014**, *8*, 284–289.
33. Muscolo, A.; Papalia, T.; Settineri, G.; Mallamaci, C.; Panuccio, M.R. Sulfur bentonite-organic-based fertilizers as tool for improving bio-compounds with antioxidant activities in red onion. *J. Sci. Food Agric.* **2019**, *100*, 785–793. [CrossRef] [PubMed]
34. Montesano, V.; Negro, D.; Sonnante, G.; Laghetti, G.; Urbano, M. Polyphenolic Compound Variation in Globe Artichoke Cultivars as Affected by Fertilization and Biostimulants Application. *Plants* **2022**, *11*, 2067. [CrossRef] [PubMed]
35. Tietel, Z.; Yermiyahu, U.; Bar-Tal, A. Sulfate Fertilization Preserves Tomato Fruit Nutritional Quality. *Agronomy* **2022**, *12*, 1117. [CrossRef]
36. Tungmunnithum, D.; Thongboonyou, A.; Pholboon, A.; Yangsabai, A. Flavonoids and Other Phenolic Compounds from Medicinal Plants for Pharmaceutical and Medical Aspects: An Overview. *Medicines* **2018**, *25*, 93. [CrossRef]
37. Mutha, R.E.; Tatiya, A.U.; Surana, S.J. Flavonoids as natural phenolic compounds and their role in therapeutics: An overview. *Futur. J. Pharm. Sci.* **2021**, *7*, 25. [CrossRef]
38. Di Lorenzo, C.; Colombo, F.; Biella, S.; Stockley, C.; Restani, P. Polyphenols and Human Health: The Role of Bioavailability. *Nutrients* **2021**, *13*, 273. [CrossRef]
39. Tchonkouang, R.D.N.; Antunes, M.D.C.; Vieira, M.M.C. Potential of Carotenoids from Fresh Tomatoes and Their Availability in Processed Tomato-Based Products. In *Carotenoids—New Perspectives and Application*; Martínez-Espinosa, R.M., Ed.; IntechOpen: London, UK, 2022. [CrossRef]
40. Mozos, I.; Stoian, D.; Caraba, A.; Malainer, C.; Horbańczuk, J.O.; Atanasov Atanas, G. Lycopene and Vascular Health. *Front. Pharmacol.* **2018**, *9*, 521. Available online: https://www.frontiersin.org/articles/10.3389/fphar.2018.00521 (accessed on 23 May 2018). [CrossRef]
41. Arballo, J.; Jaume, A.; John, W.E. Lycopene: A Critical Review of Digestion, Absorption, Metabolism, and Excretion. *Antioxidants* **2021**, *10*, 342. [CrossRef]
42. Ferraz, C.R.; Carvalho, T.T.; Manchope, M.F.; Artero, N.A.; Rasquel-Oliveira, F.S.; Fattori, V.; Casagrande, R.; Verri, W.A., Jr. Therapeutic Potential of Flavonoids in Pain and Inflammation: Mechanisms of Action, Pre-Clinical and Clinical Data, and Pharmaceutical Development. *Molecules* **2020**, *25*, 762. [CrossRef]
43. Feng, X.; Weng, D.; Zhou, F.; Owen, Y.D.; Qin, H.; Zhao, J.; Huang, Y.; Chen, J.; Fu, H.; Yang, N.; et al. Activation of PPARgamma by a Natural Flavonoid Modulator, Apigenin Ameliorates Obesity-Related Inflammation Via Regulation of Macrophage Polarization. *EBioMedicine* **2016**, *9*, 61–76. [CrossRef]
44. Pan, L.; Ye, H.; Pi, X.; Liu, W.; Wang, Z.; Zhang, Y.; Zheng, J. Effects of several flavonoids on human gut microbiota and its metabolism by in vitro simulated fermentation. *Front. Microbiol.* **2023**, *14*, 1092729. [CrossRef] [PubMed]
45. Rosa, S.I.; Rios-Santos, F.; Balogun, S.O.; Martins, D.T. Vitexin reduces neutrophil migration to inflammatory focus by down-regulating pro-inflammatory mediators via inhibition of p38, ERK1/2 and JNK pathway. *Phytomedicine* **2016**, *23*, 9–17. [CrossRef] [PubMed]
46. Li, X.; Han, Y.; Zhou, Q.; Jie, H.; He, Y.; Han, J.; He, J.; Jiang, Y.; Sun, E. Apigenin, a potent suppressor of dendritic cell maturation and migration, protects against collagen-induced arthritis. *J. Cell Mol. Med.* **2016**, *20*, 170–180. [CrossRef]
47. Yang, H.; Huang, J.; Mao, Y.; Wang, L.; Li, R.; Ha, C. Vitexin alleviates interleukin-1beta-induced inflammatory responses in chondrocytes from osteoarthritis patients: Involvement of HIF-1alpha pathway. *Scand. J. Immunol.* **2019**, *90*, e12773. [CrossRef] [PubMed]

48. Kopustinskiene, D.M.; Jakstas, V.; Savickas, A.; Bernatonien, J. Flavonoids as Anticancer Agents. *Nutrients* **2020**, *12*, 457. [CrossRef] [PubMed]
49. Buttery, R.G.; Ling, L.C. Volatile Components of Tomato Fruit and Plant Parts. In *Bioactive Volatile Compounds from Plants*; Teranishi, R., Buttery, R.G., Sugisawa, H., Eds.; American Chemical Society: Washington, DC, USA, 1993; pp. 23–34.
50. Wang, L.; Baldwin, E.A.; Bai, J. Recent Advance in Aromatic Volatile Research in Tomato Fruit: The Metabolisms and Regulations. *Food Bioprocess Technol.* **2016**, *9*, 203–216. [CrossRef]
51. Zhan, P.; Tian, H.; Sun, B.; Zhang, Y.; Chen, H. Quality control of mutton by using volatile compound fingerprinting techniques and chemometric methods. *J. Food Qual.* **2017**, *2017*, 9273929. [CrossRef]
52. Muscolo, A.; Papalia, T.; Settineri, G.; Mallamaci, C.; Carabetta, S.; Di Sanzo, R.; Russo, M.T. Effect of organic fertilizers on selected health beneficial bioactive compounds and aroma profile of Topepo sweet pepper. *Foods* **2020**, *9*, 1323. [CrossRef]
53. Korčok, M.; Vietorisová, N.; Martišová, P.; Štefániková, J.; Mravcová, A.; Vietoris, V. Aromatic Profile of Hydroponically and Conventionally Grown Tomatoes. *Appl. Sci.* **2021**, *11*, 8012. [CrossRef]
54. Wakai, J.; Kusama, S.; Nakajima, K. Effects of trans-2-hexenal and cis-3-hexenal on post-harvest strawberry. *Sci. Rep.* **2019**, *9*, 10112. [CrossRef]