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Effect of Different Foliar Particle Films (Kaolin and Zeolitite) on Chemical and Sensory Properties of Olive Oil

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Abstract: The use of kaolin foliar treatments in olive growing is a well-established approach that aims at protecting crops from the negative impacts of environmental stresses and from insect pests. The use of zeolite particle films is a far more recent technique. The experimentation was carried out on *Correggiolo* cv. cultivated in the Emilia-Romagna region (Italy). Foliar treatments were performed in summer until olive harvest. Ripening index, weight, and the oil content of olives were measured. Acidity, peroxide numbers, K232, K270 and total phenols were evaluated as well as fatty acid profiles, determined via GC-FID and phenolic compounds; vitamins and pigments were determined via HPLC-DAD. Quantitative descriptive analysis (QDA) sensory analysis and taint tests were performed. Olives treated with zeolite showed higher oil contents, and the oil obtained exhibited higher contents of total phenols, tyrosol and deacetoxy oleuropein aglycon with respect to the oils produced with kaolin and the control oil. Oils produced from kaolin-treated olives showed sensory profiles characterized by notes of berries (that are not typical of the *Correggiolo* cultivar). In the scenario of environment-friendly oil production, treatments employing zeolitite particle films represent both a valid alternative to chemical insecticide against olive fly attack and a practice that has a positive influence on the overall oil quality.

Keywords: geomaterials; kaolin; natural zeolite; olive oil quality; chabasite

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1. Introduction

Considering the threat of climate change and rising environmental temperatures, the use of rock powders (mainly kaolin and zeolite-rich tuffs) in crop protection is showing great potentialities for the agricultural sector. The foliar applications of these silicate rocks can reduce canopy temperature, preserve water content and improve pest management (fungi and insects), all this using natural and therefore eco-sustainable products. In this way, particle film application on plants contributes to agricultural productivity and directly affects the quality of productions [1].

Kaolinite ($Al_2Si_2O_5(OH)_4$) is the main constituent of kaolin, which is a commercial term that refers to a rock composed of more than 50% of this mineral [2]. Kaolinite is an aluminium–silicate clay mineral composed of a layered silicon–oxygen tetrahedron and a layered aluminium–oxygen octahedron [3,4] and characterized by a low cation exchange capacity (CEC) [5].

On the other hand, zeolites are crystalline aluminosilicates (tectosilicates) composed of a framework of linked $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra. This framework delimits cavities in the form of channels and cages in which "guest" molecules (mainly cations) and water are weakly bonded and can be reversibly exchanged. This particular structure produces the three main properties typical of most of zeolite minerals: (i) high cation-exchange capacity, (ii) reversible dehydration and (iii) molecular sieve.

Natural zeolites are often constituents of volcanic tuffs [6]; thus, analogously to kaolin, rocks whose zeolite content is greater than 50% can be classified as "zeolitite", specifying the main zeolite constituent [7].

Within the many types of natural zeolites described in the literature, clinoptilolite is the most frequent in nature, followed by mordenite, chabazite (CHA), phillipsite and erionite [7]. CHA-zeolite is particularly attractive because of its very high CEC (3.84 meq/g) and easiness in sorption and release of NH_4^+ [8,9].

Compared to kaolin, interest in the uses of zeolitites for agricultural purposes has raised in the last decade; zeolitites can be also potentially used (i) as carriers of nutrients to promote nutrient use efficiency [10] since the effect of microelement foliar application is known to influence the concentration of nutrients and chemical composition of olive fruits [11] and (ii) as pesticide carriers for controlling pests and diseases [12]. Furthermore, zeolitites are extensively used in agriculture, especially after their classification as "non-toxic" by the Inernational Agency for Research on Cancer (IARC) and as safe for human consumption by the FDA. Furthermore, the Codex Alimentarius Commission (CAC) listed zeolites as approved substances in organic food production and plant protection. The EFSA (European Food Safety Authority) approved zeolites as one of the safe compounds in food and feed additives [13].

Many studies addressed the effects of zeolitites as soil conditioners to improve soil chemical and physical properties, bringing beneficial effects in terms of plant growth and fruit quality [10,14–19] or even on the transformed product [20].

While kaolin is currently used for foliar protection and its effects have been studied, the effects of zeolitites in foliar application are still to be fully investigated, as these materials have been mainly used as soil conditioners. As of today, only a few reports in which the effect of clay particle films on plant physiology has been investigated are available, while studies which address their impacts on fruits or on processed products are even more scarce.

Particle film technology can influence some plant physiological parameters, as reported by many authors [21–23]; subsequently, this effect may influence the ripening trend as well as the chemical and sensory profiles of fruits and transformed products.

De Smedt et al. [24] reported that zeolitites particle films reduce the transpiration and improve the water-use efficiency, leading to a positive influence on yield and fruit quality. The effects of foliar rock powder applications depend on the crop species and the cultivation environment, for example, in *Vitis vinifera* zeolite reduced the damages caused by high temperatures [25]. Regarding the effect of kaolin on fruits, Schupp et al. [26] found that kaolin particle film reduces fruit size, red colour and sunburn in Fuji apple. They also observed that an early season application had no effects on fruit size or colour in Honeycrisp apple, but late season application reduced fruit size and redness. Zeolitite particle films were employed in field experiments on *Vitis vinifera* to contrast grey mould, sour rot and grapevine moth [27]. The authors reported that no differences were observed among treatments in terms of yield and berry composition, while in the transformed product (wine), an increase in phenolic compounds was observed.

Glenn and colleagues [28] reported that applications of kaolin particle films reduced the environmental stress, increasing fruit weight and red colour in apple fruits. A study conducted on Balady mandarin (*Citrus reticulate*) showed that kaolin foliar application reduced fruit disorder, improved yield and fruit quality at harvest and extended storability, thanks to its effect on flesh and peel firmness [29].

Regarding the effects of foliar treatments with rock powders on fruit composition, the literature is limited and sometimes conflicting. Kahan and Damicone [30] reported that during field experiments carried out in 2005, kaolin particle films sprayed on tomato plants reduced the marketable fruit number and weight, whereas in 2006, no significant effects were observed. Studies on the influence of kaolin application on two apple cultivars under sustained deficit irrigation showed that kaolin can increase apple fruit weight and length and reduce the activity of nonenzymatic drought stress defense systems of apple trees [31].

Recently, zeolites also found interesting applications in the postharvest and storage sector. Nano zeolite-molybdates were used as a ripeness indicator in Avocado packaging [32]; moreover, the application of activated natural zeolites on snake fruits (*Salacca edulis*) was found to retard decaying process during storage [33].

Few studies have been carried out on olive fruits and on oil quality produced by olive plants treated with rock powder particle films. Khaleghi et al. [1] reported that kaolin particle films application represents a valid practice to improve and maintain olive oil quality in regions with severe water shortages.

In a study on olive trees cv *Zeity* cultivated in a sub-humid Mediterranean environment, kaolin foliar applications exerted a positive effect on olive development and the obtained oil was characterized by a lower peroxide value and lower K 232 and K 270 than the oil of untreated trees [34].

In another work [22] it was reported that kaolin and salicylic acid applications on *Olea europeae* rainfed trees determined an increase of olive yield without substantial changes in fruit and olive oil quality. Moreover, a reducing effect of kaolin film application on olive fruit fly infestation was reported, maintaining the nutritional and sensory quality of the corresponding oils [35].

A study on the effects of particle films sprayed on the canopy of olive cultivars *Picual* and *Aggizi Shami* demonstrated that kaolin and calcium carbonate influenced flowering, leaf and fruit development and oil accumulation in different ways depending on the cultivar and timing of application [36].

To our knowledge, no studies exist about the influence of zeolitite-based foliar treatments on the composition of the olives and on the chemical and sensory characteristics of the produced oils. Given the limited knowledge about the effect of kaolin and zeolitite particle films on the quality of virgin olive oil, the aim of this study is to verify if and how these two different foliar treatments affect the chemical and sensory characteristics of the oils.

2. Materials and Methods

2.1. Site Description and Treatments

The study was carried in a 15-year-old commercial olive (*Olea europeae*) cv *Correggiolo* orchard located in the Bologna hills (Italy). The study was conducted on 2 plants per thesis. The tested foliar treatments were: (1) foliar application of kaolin at a dosage of 3.0 kg/100 L of H_2O (K), (2) foliar application of italian chabasite zeolitite (hereafter named CHA-zeolitite) at a dosage of 0.6 kg/100 l of H_2O (Z) and (3) untreated control (T). Foliar applications started at the beginning of summer (18th of June) and were repeated every 20 days until the olive harvest (24th of October), according to the methods reported by Rotondi [21]. Olive sites were rainfed and the same agronomical orchard practices were applied to all treatments. The kaolinite content of the employed kaolin was 87%, while the total zeolite content of the zeolitite was 68% (of which 65% was chabazite). Both the kaolin and the CHA-zeolitite were supplied by Balco s.p.a company (Sassuolo, Italy).

2.2. Olive and Oil Analyses

Fruits fresh weight was monitored by collecting 100 olives from each thesis every twenty days (7/26, 8/6, 8/20, 9/3, 9/18, 10/5, 10/24). All productions were transformed to a similar ripening index [37] corresponding to about 50% pigmentation of the olive skin [38] with the purpose of reducing the effect of the degree of maturation on oil characteristics. Ripening index and oil content were determined at the last three application dates (18th of September and 2nd and 24th of October). The percentage of olive fly attack was also determined. Olives sampled after each foliar application were milled using a grinder (IKA MF 10 basic Microfine grinder drive, Breisgau, Germany) and oil quantity was gravimetrically determined using hexane extraction and solvent evaporation under vacuum [39]. Analysis of oil content was carried out in triplicate. After a manual harvest and being washed in containers filled with water with continuous addition of water, olive samples were processed using a low scale continuous mill (Oliomio®; Toscana Enologica Mori, Firenze, Italy) equipped with a blade crusher, a horizontal malaxator and a two phase decanter. Olive samples were processed within 24 h from collection. For each sample, the temperature (below 27 °C) and time of malaxation (20 min), the speed of the decanter (4200 rpm) and the flux of water in the separator (0.8 L h^{-1}) were standardized in order to minimize the variability due to the extraction procedures. Immediately after the extraction, oil samples were filtered through cotton filters, then poured into dark glass bottles, keeping the headspace to a minimum, and stored in a temperature-controlled cupboard set at 15 ± 1 °C until chemical analysis.

The oil quality parameters, namely, acidity, peroxide number and UV spectrophotometric analysis, were determined in triplicates according to EEC reg. 2568/91 [40] and subsequent amendments.

Fatty acids profiles were evaluated according to EEC reg. 2568/91 [40] and following amendments of the Council of the European Union. The gas chromatographic equipment was a Chrompack CP 9000 (Middleburg, The Netherlands) with a flame ionization detector (FID) equipped with a Stabilwax capillary column (Restek Corporation, Bellefonte, PA, USA) with helium as the carrier gas (flow rate = 1 mL min^{-1}; split ratio of 1:20, v:v). Chromatographic parameters were as follows: injection and detection temperature 250 °C; 230 °C; column oven temperature, 240 °C. All parameters were determined in triplicate for each sample.

The phenolic fraction was extracted in triplicate using 8 g of oil; the metanolic extracts were evaporated to dryness and resuspended in 1 mL of 1:1 water:methanol solution [41].

Total phenol content of the phenolic extracts was determined via the Folin–Ciocalteau spectrophotometric method at 750 nm [42] using a Jasco V-500 Spectrophometer (Jasco, Tokyo, Japan). Results were expressed as mg gallic acid Kg^{-1} oil.

The phenolic extract was filtered on a CA membrane filter of 0.2 µm pore size before HPLC analysis. HPLC analysis was carried out using a Nexera X2 LC-30AD HPLC system (Schimadzu, Kyoto, Japan) equipped with a Nexera X2 LC-30AD pump, DGU-20A5r degassing unit, Nexera X2 SIL-30AC autosampler, CTO-20AC column oven and SPD-M30A diode array detector. The chromatographic conditions are reported in a previously published work [43]. Identification of phenolic compounds was carried out via comparison with the retention time and spectra of the standard compounds and with data literature. Hydroxytyrosol was quantified using the tyrosol calibration curve; derivatives of oleuropein and ligstroside were quantified using an oleuropein calibration curve; tyrosol, vanillin, vanillic acid, o-cumaric acid, luteolin and apigenin were quantified using the calibration curve of the relative standard.

Quantitative analysis of tocopherols, lutein and β-carotene was carried out through olive oil filtration on a PTFE membrane filter of 0.2 µm pore size (GyroDisc 25 mm, Orange Scientifc, Waterloo, Belgium) and direct injection of 20 µL in the same HPLC equipment mentioned above. Analytes were separated on a C18 column 150 mm × 4.6 mm (Inertsil ODS-2 5U, Alltech, Deerfield, IL, USA); the flow rate was 1 mL min^{-1}, the injection volume was 20 µL and the column temperature was 25 °C. The eluents used were A methanol: water 80:20 (*v*/*v*) and B methanol: tetrahydrofuran 20:80 (*v*/*v*). Quantification of analytes was carried out using their relative analytical standard's calibration curves, all purchased from Merk (Deisenhofen, Germany). Tocopherol quantification was carried out at 295 nm and β-carotene and lutein at 450 nm [38].

Sensory analyses were performed by the panel of the Agency for Agrofood Sector Services of Marche region (ASSAM), a fully-trained analytical taste panel recognized by the International Olive Oil Council (IOC) of Madrid, Spain, and by the Italian Ministry for Agriculture, Food, and Forestry Policy. A triangle test was performed with 16 judges, repeating the test two times, according with the standard [44], which provides equal to or more than 30 assessors. The judges were scheduled in groups of six to ensure full randomization within groups. Assessors were presented with vessels with three random digit codes assigned. For each subject, a tray marked with his/her number and containing three plastic vessels according to full randomization protocol was prepared.

2.3. Statistical Analysis

The data collected were elaborated using Microsoft® Excel 2007/XLSTAT© (Version 2009.3.02, Addinsoft, Inc., Brooklyn, NY, USA). The significance of differences among means at a 5% level was determined via ANOVA, followed by a Tukey's honestly significant difference (HSD) test.

In triangle tests on olive oils, significance for a difference was determined at $p = 0.05$. Principal component analysis (PCA) was used to explore chemical data distribution patterns and to visualize the "distance" between oils produced from plants subjected to different foliar treatments.

3. Results and Discussion

3.1. Chemical Properties of the Oils

Figure 1 shows the olive developments during the experimental trial and it is clear that the increase of olive fresh weight was similar under the three different treatments, and thus, the applied foliar treatments had no effects on this parameter. This result is in contrast with another report [45] where, on seven of the eight experimental sites, an increase of the fruit weight on apple fruits in the kaolin-based treatments was found.

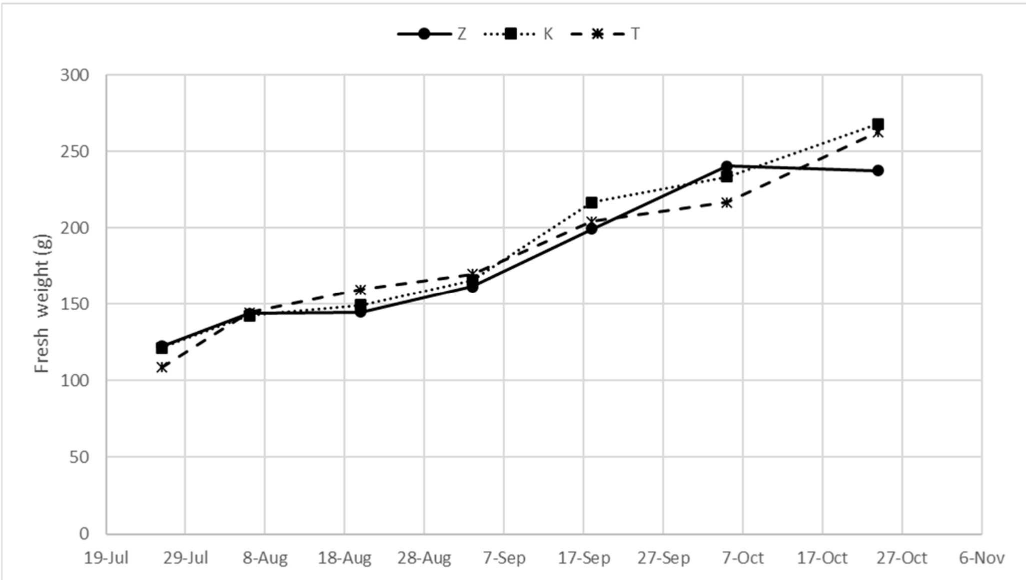

Figure 1. Olive development during the experimental trial expressed as g of fresh weight (T = untreated control, Z = zeolitite, K = kaolin).

The ripening index (RI), measured at the last three dates before harvest, was markedly lower in K with respect to the other treatments. A delay of ripening trend (RI-Z = 2.90, RI-T = 2.16 and RI-K = 1.20) was observed in the K treatment, and thus, to obtain a similar RI for all theses, it was necessary to postpone the harvest of K thesis by 20 days until the RI reached 1.80. The retarding effect of ripening had been also previously observed on tomato plants treated with kaolin [46]. Khaleghi and colleagues in their work on olive trees (cv. Zard) treated with kaolin found differences in fatty acid composition; they hypothesized that the kaolin particle modifies the surface of the olive fruit and indirectly affects gene expression and enzymatic activity involved in the fruit ripening trend and fatty acid formation [1]. Our results agree with a study where a tendency of slight delay of the maturation stage was observed on olive tree cv *Cobrancosa* via the application of kaolin during three crop seasons [22].

In Table 1, the percentage of oil extracted from olives starting from 30 days before harvest is reported. Oil quantity in olive treated with different particle films shows similar trends until 2 October, while on 24 October (corresponding to olive harvest) Z olives showed a significantly higher percentage of oil content in respect to the other thesis ($p < 0.05$). On the contrary, K olives showed the lowest percentage of oil content ($p < 0.05$), which is probably attributable to the reduction of the photosynthetic rate observed in olive treated with kaolin particles [21]. These results agree with the report of Abdel Ghani and colleagues [36], in which the authors recorded a decrease in the oil content of Picual olives harvested from olive trees treated with kaolin in three different periods (December, January and February) of the growing season.

Table 1. Percentage of oil content on olive dry weight. Data are expressed as mean of three replicates ± standard deviation. (T = untreated control, Z = zeolitite, K = kaolin).

	18-Sep.	**02-Oct.**	**24-Oct.**
T	21.89 ± 1.6 ^{ab}	29.69 ± 0.4 ^{a}	33.1 ± 0.8 ^{a}
Z	28.05 ± 1.4 ^{a}	30.1 ± 0.8 ^{a}	40.97 ± 1.2 ^{b}
K	21.13 ± 3.3 ^{b}	26.97 ± 2.4 ^{a}	24.68 ± 0.7 ^{c}
p value	0.034	0.076	<0.0001

Different letters in the same column indicate significant difference ($p < 0.05$) according to Tukey's honestly significant difference (HSD) test.

From the examination of the qualitative parameters of oils produced from the treated and untreated olive trees, it emerged that the acidity, peroxide number, K232 and K270 were not significantly influenced by K and Z treatments, while the total phenol content showed a significantly higher content in Z and K oils compared to T oil (Table 2). Similar results were detected in wines obtained with vineyard cv *Sangiovese* treated with kaolin and zeolitite [25]. Our results partially agree with the results reported by Brito and colleagues [22] where the olive oil parameters were not affected by kaolin treatment except for the K270 parameter and where the concentration of total phenolic compounds was different only in oils treated with kaolin and produced in 2015 (higher concentration of total phenolic content). Our results also agree with studies carried out on olive trees cv *Zard* where oils produced by plants treated with a larger amount of kaolin exhibited a higher concentration of total phenols compared to the control [1]. The highest concentration of total phenols was detected in Z oil although no significant differences were observed between Z and K; the same results were obtained in another work [27] where the use of zeolitite was suggested in vineyards for simultaneous control of grey mold, sour rot and grapevine moth. In that study, higher concentrations of total phenols were observed in wine obtained from zeolitite-treated plants in which the treatment was performed within 15 days of the grape harvest.

Table 2. Qualitative parameters determined in oils produced under different particle treatments (T = untreated control, Z = zeolitite, K = kaolin). Different letters in the same column indicate significant difference ($p < 0.05$) according to Tukey's honestly significant difference (HSD) test.

	Acidity	**Peroxid Number**	**K232**	**K270**	**Total Phenol**
T	0.31 ± 0.03	10.43 ± 0.31	1.93 ± 0.05	0.17 ± 0.02	239.46 ± 8.48 ^{b}
Z	0.37 ± 0.03	10.75 ± 0.39	1.95 ± 0.01	0.16 ± 0.01	311.61 ± 6.08 ^{a}
K	0.30 ± 0.04	11.05 ± 0.55	1.95 ± 0.04	0.15 ± 0.01	294.54 ± 7.82 ^{a}
p-value	0.051	0.290	0.747	0.305	<0.0001

Free acidity is expressed as g/100 g of oleic acid, peroxide number as mEq O2 kg^{-1} oil, total phenol as mg/kg^{-1} of gallic acid.

The fatty acid profiles of the oils are shown in Table 3. Foliar treatments influenced the unsaturated fraction of olive oils. Linoleic acid content increased both in Z and K oils while the linolenic acid content was lower in Z and K oils with respect to the T oil. The influence of kaolin foliar treatment on the fatty acid profile was reported by Khaleghi and colleagues [1], but in their experiment the oils from kaolin-treated trees had lower PUFA and higher MUFA contents than the control. The disagreement of the results is probably attributable to the fact that their experiment was carried out in very hot and arid climates, where the leaf cover by kaolin plays a protective function; on the other hand, the positive effect of kaolin was not observed in our study because the olive trees are grown in environmental conditions (high rainfall and low temperatures) that do not lead to stress conditions [21].

Table 3. Fatty acid profiles of the oils produced under different particle treatments (T = untreated control, Z = zeolitite, K = kaolin). Different letters in the same column indicate significant difference ($p < 0.05$) according to Tukey's honestly significant difference (HSD) test.

	Palmitic Acid	Palmitoleic Acid	Stearic Acid	Oleic Acid	Linoleic Acid	Linolenic Acid
T	14.68 ± 0.13	1.41 ± 0.04	2.09 ± 0.06	71.35 ± 0.05	9.12 ± 0.06 ^{c}	0.70 ± 0.04 ^{a}
Z	14.45 ± 0.16	1.32 ± 0.04	1.93 ± 0.01	71.73 ± 0.20	9.46 ± 0.02 ^{b}	0.59 ± 0.01 ^{b}
K	15.32 ± 1.46	1.32 ± 0.26	2.10 ± 0.10	69.60 ± 1.58	10.45 ± 0.18 ^{a}	0.65 ± 0.01 ^{ab}
p-value	0.532	0.677	0.085	0.104	0.0003	0.023

The HPLC analysis of the phenolic profile showed that K and Z foliar treatments influenced the phenolic profile of oil in a different way. Oil produced from plants belonging to Z treatment exhibited a higher content of tyrosol and deacetoxy oleuropein aglycon (DAOA), while pinoresinol was significantly higher in both K and Z oils with respect to T oil (Table 4). Pinoresinol has gained interest in recent years thanks to its health-promoting contribution since it owns antitumor activity [47]. It was highlighted that the lignan content changes considerably according to several factors such as the production zone, climate, varieties of olives and oil production techniques [48]. Although phenols in olive oils have undergone extensive research, this is one of the first studies showing the change in the phenolic profile in plants subjected to foliar treatments with zeolitite and kaolin. Our results partially agree with the ones of Brito and colleagues [22], where orto-diphenols in olive oils were different in two crop seasons due to the distinctive environmental conditions that characterized the two years. Similarly, kaolin particle film might have been effective in mitigating the water stress condition in the treated plants, thus influencing the metabolism of phenolic compounds in fruits. Concerning phenolic acids, only vanillic acid was quantifiable and contained in lower concentrations in K oil than in T oil, while on the contrary, apigenin showed higher concentrations in K oil in respect to the T oil. The occurrence of flavonoid compounds in olive leaves is related to the UV-filtering capacity [49]. It was reported that in climatic conditions typical of northern Italy, such as those of this study, characterized by mild summer temperatures, the application of kaolin does not perform a mitigating action of high temperatures, but on the contrary, it determines a reduction of net photosynthesis that may result in a decrease of carbohydrate supply to the fruits, the major source of precursors for the biosynthesis of phenolic compounds [21]. It is well known that the accumulation of anthocyanin in berries is affected by high temperatures; this suggests that the foliar application of rock powders, leading to a decrease in the canopy temperature, promotes the biosynthesis of phenolic compounds [50] and decreases their enzymatic degradation [51]. Valentini and co-workers hypothesized a different mode of action of the two materials (zeolite and kaolin) on the biosynthesis and accumulation of antocyanins and stated that it is necessary to establish whether the effect of foliar treatments is linked to the temperature cooling effect or might involve a nonchemical elicitor response affecting secondary metabolism [25].

Delta and alfa tocopherols determined in Z oil were significantly higher in respect to T oil ($p < 0.05$), with the lowest content of these two tocopherols found in K oil ($p < 0.05$) (Table 5). Differently, the highest lutein contents were determined in K treatment, followed by Z treatment and then T, which showed the lowest values ($p < 0.05$) (Table 3). The oil obtained from K treatment showed a similar concentration of β carotene with respect to T oil, which exhibited the highest content (Table 5). These results disagree with another study that reported that kaolin particle films positively affected olive oil quality and composition (increase in carotenoids, chlorophylls and oleic acid) [1]. The alteration in the pigment content could be due to the photo-protective action of the kaolin, as this clay increases the reflectance [21], and therefore, a lower degradation of the pigments operated by the ROS (reactive oxygen species) may occur [52].

Table 4. Phenolic profile determined in oils produced by plants treated with different foliar treatments (T = untreated control, Z = zeolitite, K = kaolin). Different letters in the same column indicate significant difference ($p < 0.05$) according to Tukey's honestly significant difference (HSD) test.

	OhTy	Ty	Vanillic Acid	DAOA	Pinoresinol	Luteolin	Luteolin Aglycone	Apigenin
T	2.01 ± 0.26	4.15 ± 0.39 [b]	1.28 ± 0.07 [a]	117.18 ± 10.07 [b]	15.77 ± 1.03 [b]	3.29 ± 0.18	1.61 ± 0.06	0.28 ± 0.04 [b]
Z	2.24 ± 0.25	7.18 ± 0.38 [b]	1.16 ± 0.03 [ab]	297.09 ± 18.5 [a]	28.43 ± 1.67 [a]	5.55 ± 0.49	1.63 ± 0.06	0.43 ± 0.06 [ab]
K	2.04 ± 0.25	4.65 ± 0.23 [b]	0.36 ± 0.63 [b]	142.63 ± 19.21 [b]	27.47 ± 3.43 [a]	6.27 ± 2.15	1.58 ± 0.03	0.52 ± 0.07 [a]
p-value	0.514	<0.0001	0.042	<0.0001	0.001	0.066	0.483	0.007

Hydroxytyrosol (OhTy) is expressed as mg/kg tyrosol; tyrosol (TY) is expressed as mg/kg of tyrosol; deacetoxy oleuropein aglycon (DAOA) is expressed as mg/kg of oleuropein, while the other compounds are expressed as mg/kg of relative standard.

Table 5. Tocopherol and carotenoid content in oil produced under different foliar treatments (T = untreated control, Z = zeolitite, K = kaolin) Values are mean ± standard deviation. Compounds are expressed as mg of relative standard compound per kg of oil. Different letters in the same column indicate significant difference ($p < 0.05$) according to Tukey's honestly significant difference (HSD) test.

	Δ Tocopherol	β+γ-Tocopherol	α-Tocopherol	Lutein	β Carotene
T	1.72 ± 0.13 [b]	2.4 ± 0.24	146.96 ± 3.34 [b]	1.79 ± 0.01 [c]	1.36 ± 0.03 [a]
Z	2.41 ± 0.25 [a]	2.79 ± 0.18	170.56 ± 4.52 [a]	2.43 ± 0.08 [b]	1.19 ± 0.03 [b]
K	1.89 ± 0.08 [b]	2.37 ± 0.07	145.27 ± 5.15 [b]	2.77 ± 0.06 [a]	1.39 ± 0.05 [a]
p-value	0.006	0.051	0.001	<0.0001	0.001

The PCA of chemical parameters was performed considering only variables that showed significant differences between the different treatments (apigenin, lutein, pinoresinol, total phenols, β carotene α tochopherol, tyrosol and DAOA). The PCA explained 92.24% of the variability between the three oils produced from the different theses (K, Z and T) that were well-separated in the Euclidian space (Figure 2). Z oils are positioned in the right part of the graph, well separated from T oil along the principal component F1, mainly because of their higher content of tyrosol, DAOA and α and δ tocopherol. K oil was characterized by a higher lutein, pinoresinol, apigenin and total phenol content (Figure 2).

It is important to underline that in the year of study, olive fly attacks were absent, and therefore, even the oils belonging to the control thesis were irreproachable. These results show that foliar treatments affect the chemical characteristics of olive oil and moreover kaolin and zeolitite do not act in the same way.

3.2. Sensory Profiles of the Oils

QDA sensory analysis evidenced that no significant differences between intensities of all sensory attributes (olive fruity, bitterness, green notes, pungency and other pleasant notes) were found among the three treatments (Figure 3A); similar results were reported in another work where it was stated that kaolin treatment on olive tree cv *Carolea* did not affect the sensory quality of olive oils [35]. In a previous work we reported the influence of kaolin and zeolitite particle film on organoleptic properties of olive oil, but in those experiments the sensorial quality was impaired by the different levels of olive fly infestation [21]. Even if the main sensorial attributes did not show significant differences among the tested oils, it is important to underline that the "typology" of pleasant notes exhibited some significant differences. The prevalent pleasant note that was perceived in all oils was almond as it is indeed the typical attribute of *Correggiolo* oil. Different minor pleasant flavours were instead perceived in Z, T and K oils: in Z oil, the minor pleasant flavours were represented by grassy notes, in T oil artichoke notes were perceived while in K oil the tasters perceived notes of berries that are not typical of the *Correggiolo* cultivar. These differences in the pleasant flavours were perceived in the same way, both olfactorily and gustatorily (Figure 3B).

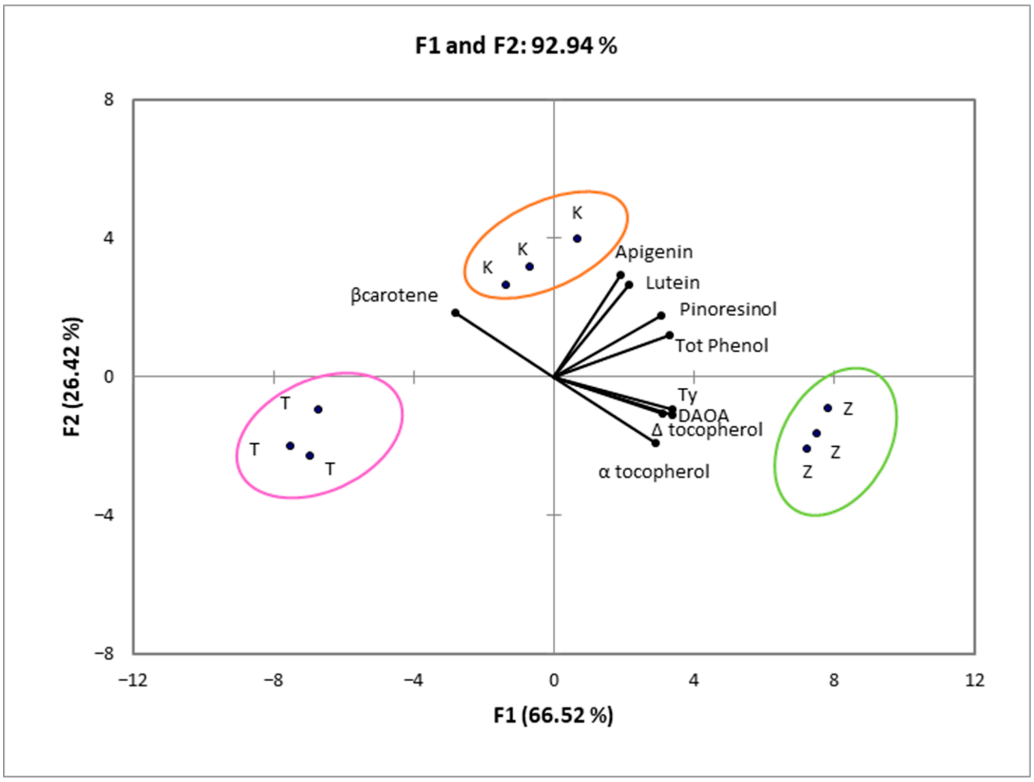

Figure 2. PCA analysis of chemical parameters determined in oils produced by plants sprayed with different particle film. K = kaolin, Z = zeolitite, T = untreated control.

Figure 3. *Cont.*

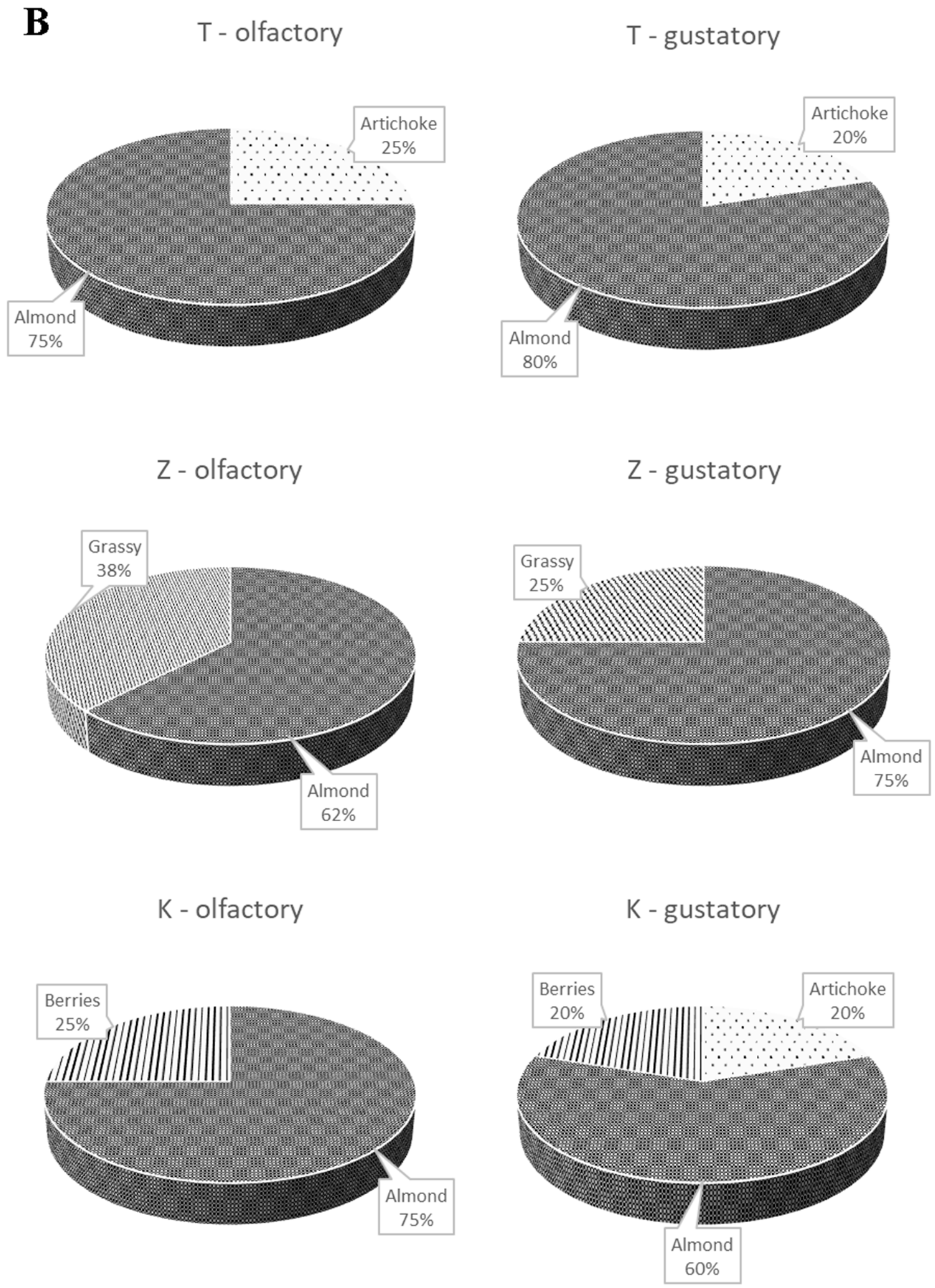

Figure 3. (**A**) Sensory profiles of olive oils produced by plants treated with particle films of CHA-zeolitite (Z), kaolin (K) and untreated plants (T). (**B**) Gustatory and olfactory pleasant flavors of olive oils produced by plants treated with CHA-zeolitite (Z), kaolin (K) and untreated plant (T).

These differences in the typology of pleasant flavours were also corroborated by the results of the triangular test sensory analysis carried out to evaluate if the foliar treatments could determine sensory differences in comparison to T oil. The minimum number of correct responses required to conclude that there is a perceptible difference is 20 (α 0.001). The oil produced with plants treated with CHA-zeolitite particle film (Z) did not differ from the T oil (8 correct answers); in fact, the difference between grassy notes and artichoke was not statistically perceived by assessors. The oil produced by plants treated with kaolin particle film (K) was judged to be different from the untreated T oil (22 correct answers). The triangular test does not allow identification of how the K oil differs from the T oil; we highlighted that, using QDA results, no sensory defects or off-flavor were reported by assessors, leading us to argue that the perceived difference due to kaolin treatments does not produce any negative sensory effect. It is plausible that tasters perceived the berry note which was not found in T oil.

4. Conclusions

With this study, we investigated the chemical and sensorial quality of olive oils obtained from plants subjected to particle film treatments using silicate rock powders (kaolin and zeolite-rich tuffs) during a year in which the olive fly attacks were absent and therefore even the oils belonging to the control thesis were irreproachable. In a cold and humid environment (such as our experimental conditions), kaolin did not exploit its mitigant effect on high temperatures, confirming its unsuitability in such a climate with respect to zeolitites. The tendency of K to form a continuous layer on the surface of leaves and olives (as previously observed by other work [21]) influenced the plant transpiration rate and the olive ripening trend, which showed a marked delay. During olive ripening, important substances were synthetized, and these substances affect the chemical and organoleptic properties of oils. On the contrary, particle films of zeolitite are more recommended in cool environments typical of Northern Italy. The oils produced maintained the sensory profile typical of the *Correggiolo* cultivar with an improvement in the nutritional composition, thanks to their higher content of some phenolic substances.

The positive effects of the use of zeolitite on olive oil quality represent a further advantage in addition to those reported in another work in comparison to kaolin application [21].

Particle film technology against pests and diseases can represent a useful tool for farmers to protect their crop production and at the same time reduce the environmental impact. Results presented in this study clarify the effect of kaolin and zeolitite foliar treatments on chemical and sensory characteristics of olive oils.

The latest consumer trends and government protocols have shifted toward organic materials to replace synthetic chemical products. In the scenario of sustainable and environment-friendly olive oil production, treatments employing zeolitite particle films represent both a valid alternative to chemical insecticide against olive fruit fly attack and an agricoltural practice that has a positive influence on the overall quality of the final product.

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