

Article

High-Temperature Influences Plant Bio-Stimulant-like Effects of the Combination Particle Film-Forming Materials-Foliar Fertilizers on Apple Trees

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Abstract: Particle film forming materials were introduced as a solution to reduce the effects of excessive solar irradiation on plant photosynthesis. Covering plant leaves with particle films leads to plant bio-stimulant-like effects: increased protection against abiotic stress and increased fruit quality. We used zeolites and diatomaceous earth carriers for foliar fertilizer, known for their application as particle film-forming material. The aim of this paper was to investigate the plant bio-stimulant-like effects of this combined two-in-one product on the yield of apple trees and their photosynthetic pigments and fruit quality. The experiments were conducted for two years, 2021 and 2022, which had different agroclimatic patterns: 2021 had a deficit of precipitation, whereas 2022 was warmer by more than +4.8 °C compared to the recorded average temperature. Applying particle film-forming material and foliar fertilizer reduces the degradation of the photosynthetic pigments by drought and excessive solar radiation by 25–30%. In the year with a deficit of precipitation there was an increased yield by an additional 11.56–12.38% and the fruit quality similarly increased. Such effects of these combined two-in-one products were limited in 2022 as the temperature was higher than normal by several degrees.

Keywords: particle film-forming materials; foliar fertilizer; plant bio-stimulant-like effects; high temperature



Citation: Sîrbu, C.E.; Deşliu-Avram, M.; Cioroianu, T.M.; Constantinescu-Aruxandei, D.; Oancea, F. High-Temperature Influences Plant Bio-Stimulant-like Effects of the Combination Particle Film-Forming Materials-Foliar Fertilizers on Apple Trees. *Agriculture* **2023**, *13*, 178. <https://doi.org/10.3390/agriculture13010178>

Academic Editors: Tommaso Frioni, Lia-Tania Dinis and Gastón Gutiérrez-Gamboa

Received: 27 October 2022
Revised: 29 December 2022
Accepted: 5 January 2023
Published: 10 January 2023



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1. Introduction

Plant bio-stimulants are a class of agricultural input defined by their main effects: enhancing/benefiting nutrient uptake and nutrient use efficiency, protecting plants against abiotic stress by increasing plant tolerance to and improving crop quality [1,2]. Plant bio-stimulants are classified as microbial and non-microbial plant bio-stimulants [1,3]. The non-microbial plant bio-stimulants are complex organic mixtures, such as humic and fulvic acids [4,5], seaweed extracts [6–8], protein hydrolysates [9,10], microalgae lysates [11–14] and inorganic elements recognized for their beneficial effects on plants, such as (soluble) silicon [15,16].

In recent decades, particle film-forming materials have been introduced as a short-term solution to reduce the effects of excessive heat and light on plant photosynthesis [17]. Several materials have been proposed for use in the formation of particle films on leaves, such as kaolin [18], zeolites [19], or diatomaceous earth [20]. Particle film-forming materials are used to cover the leaves of plants in order to mitigate solar radiation, mainly infrared (IR) and ultraviolet (UV) [17], generating a porous film that promotes gas exchange through

the stomata [21]. Particle film-forming materials protect plants against abiotic stress, such as overheating and solar injury, improving the quality of the fruit [18,22,23].

The ideal film-forming materials are (nano)porous [17]. The combination of a (nano)porous structure, active surface with high sorption capacity for ionic forms of plant nutrients and reversible dehydration have been used to produce controlled-release fertilizers that can be applied to the soil [24–26]. Such formulations release mineral nutrients in a stimuli-controlled manner, e.g., driven by concentrations in the soil solutions [27,28]. (Nano)porous materials can also determine additional effects, such as soil improvement and enhanced nutrient use efficiency [27,29,30]. Zeolites are well-known nano-carriers for soil-applied fertilizers [31,32]. Diatomaceous earth has also proven to be an efficient (nano)carrier for soil fertilizer [33]. Until now, to the best of our knowledge, the use of (nano)porous materials that form films on leaves as carriers for foliar fertilizer was primarily carried out by our group.

We proposed the utilization of the (nano)porous structure of siliceous natural nanomaterials, e.g., zeolites and diatomaceous earth, as carriers for foliar fertilizers applied to stone fruits trees, apricot and peach [34]. A combined treatment reduces the leaf temperature by up to 4.5 °C. The anti-transpirant effect of the particle film enhanced water use efficiency by up to 30%. The nutritional effects of the foliar fertilizers on the yield were amplified by the film-forming (nano)porous material by up to 8.1%. The quality of peaches and apricots increased after applying the combined film-forming particle materials and foliar fertilizers [34].

Foliar fertilizers promote the plant bio-stimulant-like effects of particle film-forming materials. As already discussed, covering the plant leaves with particle films leads to increased protection against abiotic stress and increased fruit quality [18,22,23]. Plant physiology has also been modified using film-forming material treatments, as demonstrated by the higher fixation rate of carbon dioxide, improved stomatal conductance and increased water-use efficiency [34–36]. Such effects are similar to that of plant bio-stimulants.

This paper aimed to test the plant bio-stimulant-like effects of the newly developed combination of siliceous natural nanomaterials (SNNMs), diatomaceous earth, natural zeolites and foliar fertilizer on apple trees, as a representative of seed fruit trees. The studied effects were related to enhanced tolerance to abiotic stress, e.g., photosynthesis maintained while under abiotic stress conditions, as well as yield increases and improved fruit quality. An additional objective of the study was to determine the plant bio-stimulant-like effects of the newly developed two-in-one product on an experimental field with continental temperate conditions with higher summer average temperatures.

2. Materials and Methods

2.1. Plant Material and Experimental Site

The plant materials used were apples, *Malus domestica*, cv. Idared, planted at a distance of 4 × 4 m, respectively, with 625 apple trees per ha. The experiments were performed during 2021 and 2022 in the orchard of “Vasili Adamachi” experimental farm, Faculty of Horticulture, “Ion Ionescu de la Brad” Iasi University of Life Sciences. This orchard is located in northeastern Romania, Iasi county. The apple orchard from the “Vasili Adamachi” farm is a non-irrigated/rain-feed orchard.

The geographical coordinates were the following: 47°10'40–57" North latitude, 27°30'25–42" East longitude. The altitude of the orchard is 214 m. The apple orchard at the “Vasili Adamachi” farm is established on chernozem soil. The main characteristics of the soil are presented in Table 1.

The average values of the multi-annual (1975–2015) temperature, sunshine daily duration, total precipitations and wind speed for the apple orchard at the “Vasili Adamachi” farm are 9.6 °C, 7.3 h, 554.8 mm and, 4.8 m.s⁻¹, respectively. The agrometeorological data for 2020–2021 and 2021–2022 are presented in Tables S1 and S2. In the vegetation period of the 2020–2021 agricultural year (April, May, June, July and August), the level of average monthly temperatures (+17.6 °C) varied slightly around the thermal norm of

the region (+17.3 °C). In the 2021 vegetation period (April, May, June, July and August), the precipitation level was lower (254.2 mm), with a decrease of 83.3 mm compared to normal (337.5 mm), despite the highlighted periods of significant excessive rainfall in the summer of 2021. The period 2021–2022 was warmer by more than +4.8 °C than the recorded average temperature, reaching +14.5 °C for a total of 12 months. In the vegetation period, the average temperature was +6.0 °C higher than the multiyear average. Regarding precipitation, the vegetation period of 2022 was dryer by 75.0 mm compared to the period's average. Still, April and May 2022 recorded double precipitation compared to the monthly normal (average) and managed to (partially) temper atmospheric and pedological drought.

Table 1. The main characteristics of the soil from the orchard of “Vasili Adamachi” experimental farm, Faculty of Horticulture, “Ion Ionescu de la Brad”, Iasi University of Life Sciences.

Main Physicochemical and Biological Characteristics	Genetic Horizons/Soil Deep * (cm)			
	Amho (0–20 cm)	Amho (20–40 cm)	AB (40–60 cm)	Bv (60–100 cm)
Soil Texture (% colloidal clay)	40.41	42.01	42.8	44.9
Soil pH (H ₂ O)	6.05	6.31	6.88	7.01
Humus content (%)	3.181	2.021	0.091	0.072
Total nitrogen content (Nt%)	0.145	0.128	0.051	0.022
Mobile phosphorus content (ppm)	52	50	40	38
Mobile potassium content (ppm)	211	208	163	141
Base saturation (V%)	89	88	90	91

* Abbreviation of Genetic Horizons: A—Horizon (topsoil), m—continuous cementation, h—darkening due to illuviated organic matter, o—iron and aluminum oxides buildup are present; AB—transition horizon; Bv—B Horizon (subsoil), affected by argilli-pedoturbation.

2.2. Preparation and Analysis of Foliar Fertilizer with Siliceous Natural Nanomaterials (SNNMs) Carriers

Two types of siliceous natural nanomaterial, originating from Romanian quarries, were used: natural zeolites from the Rupea quarry (Zeolites Production, Rupea, Braşov) and diatomaceous earth (DE) from Pătârlagele (Sibiciu de Sus) quarry (Industria de Diatomit, Pătârlagele, Buzău, Romania). The natural zeolites from the Rupea quarry are from the clinoptilolite type zeolites class—around 85% is clinoptilolite [37]. Sibiciu de Sus DE is formed by frustules of diatoms from the *Aulacoseira* (66%) and *Actinocyclus* genera [38]. The crystalline silica accounts for less than 0.9% and the amorphous silica content is around 85% [39]. The SNNMs were prepared and activated according to the process presented in our previous paper [34]. Briefly, the following steps were followed for the generation of the SNNMs: crushing, washing, drying at 105 °C for 24 h, milling in a planetary ball mill and activation. The zeolites were activated by using a thermal treatment, the first step at 200 °C for 2 h and a second activation treatment at 250 °C for 1 h [37]. The activation of DE was performed by using an acid treatment at room temperature (0.1 M HCl for 2 h, ratio 1 g DE to 10 mL HCl solution), followed by the treatment with a basic solution, with 10 mL NaOH 0.1 M and a final washing with pure water. The washed DE was dried at 105 °C for 24 h.

Two fertilizers with activated SNNMs were prepared, NanoFert Z (with zeolites) and NanoFert D (with diatomaceous earth). The foliar fertilizers were NPK 5:25:3, with micro-elements. This foliar fertilizer's composition was selected as optimal for apple trees. The preparation process was undertaken based on the process presented in our previous paper [34]. Briefly, the soluble microelement sources, ammonium phosphate and potassium nitrate were homogenized for 15 min, mixed with chelated microelements (with EDTA—Cu, Fe, Mn, Zn) plus Boron (B) and Molybdenum (Mo), followed by a second homogenization for 15 min and grinding. The resulting composition was mixed with activated SNNMs. The same proportion of mixing SNNMs and foliar fertilizer as previously reported [34] was used: 3 kg activated SNNMs to 1 kg of foliar fertilizer mixture. The preparation process of the new two-in-one products, particle film-forming and foliar fertilizer are presented in Figure 1.

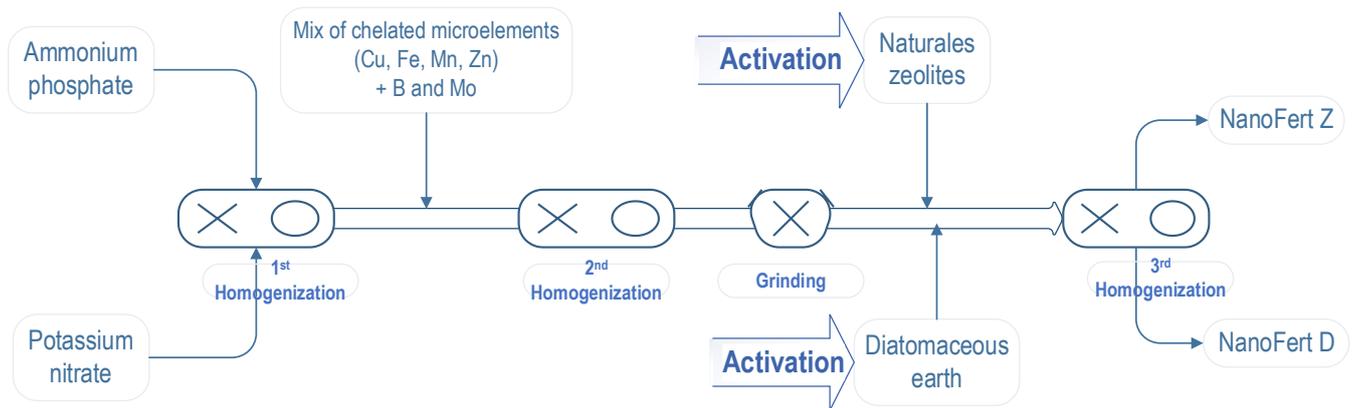


Figure 1. Presentation of the preparation process of two-in-one products, particle film-forming and foliar fertilizer, NanoFert Z (with natural zeolites) and NanoFert D (with diatomaceous earth) foliar fertilizers. Modified from Moale et al. [34]. Copyright 2021, by the authors.

Standard methods were used to analyze the resulting foliar fertilizer formulation. Standard EN SR EN 15476/2009 was used to determine the total nitrogen. The ISO 6598:1996 method was used for the gravimetric determination of phosphorus (P) after the extraction. The EN 15477:2009 method was used for the determination of potassium (K). The determination of the copper, iron, manganese and zinc was performed according to EN 16965/2018 by flame atomic absorption spectrometry (FAAS) using an ICE 3300 atomic absorption spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). Boron was determined according to the EN 17041/2018 standard, using spectrometry with azo-methine-H. All of the analyses were performed in a laboratory certified according to ISO 17025 for fertilizer analysis based on the above-mentioned standards. The calibration curves for the microelements were carried out using certified reference materials (Certipur[®] ICP, Merck Group, Darmstadt, Germany).

2.3. Application of Foliar Fertilizer with SNNMs

The experiments were performed according to a completely randomized block design schedule with four treatments and four replications per treatment and year (each replicate was conducted in five individual trees). The volume applied for each fruit tree was 2 L, corresponding to a normalized spraying volume per ha of 1250 L (per ha being 625 apple trees). The following treatments were applied: control, sprayed with water; foliar fertilizer NanoFert D, concentration 1.6% (equivalent to 5 kg/ha foliar fertilizer and 15 kg/ha diatomaceous earth); foliar fertilizer NanoFert Z concentration 1.6% (equivalent to 5 kg/ha foliar fertilizer and 15 kg/ha Rupea natural zeolites); foliar fertilizer NPK 7:30:4, with micro-elements, concentration 0.4% (equiv. to 5 kg/ha foliar fertilizer). Three treatments were applied each year, one during flowering termination, with a BBCH scale of 69 and two during the fruit growing stages, with a BBCH scale of 73–78. The first treatment, during flower termination, was applied at phenological stage 69, the second treatment at stage 73, the second fruit fall and the third treatment at phenological stage 78, with the fruit about 80% of its final size [40]. The treatments were performed with a backpack mistblower (SR 420, Stihl, Waiblingen, Germany) and conducted in the morning, between 7.00 and 10.00 when the air temperature was lower than 23 °C.

2.4. Photosynthetic Pigment Analysis

The leaf samples were collected at noon and immediately shock-frozen in liquid nitrogen, freeze-dried and stored at −20 °C until analysis. Dimethyl sulphoxide (DMSO, Merck Group, Darmstadt, Germany) was used to extract photosynthetic pigments, chlorophyll and carotenoids. The extraction was performed using excess Mg²⁺ ions in the solution [41]. Briefly, the leaf powder was mixed in microcentrifuge tubes with 1 mL DMSO and 100 mg

of magnesium hydroxide carbonate crystals. After incubation at 65 °C in the dark for 2 h, the samples were cooled and centrifuged at an RCF of $3500 \times g$. Then, 250 μL of the extracts were pipetted into a microwell plate. The optical density of the extract was determined using a microplate reader (CLARIOstar, BMG Labtech, Ortenberg, Germany) at the following wavelengths: 480 nm (carotenoids), 649 nm (chlorophyll b) and 665 nm (chlorophyll a). In the extract, the concentrations of each photosynthetic pigment (carotenoid, chlorophyll b and chlorophyll a) were calculated according to Wellburn equations [42].

2.5. Assay of Apple Fruits Quality Characteristics

From each treated replicate, 10 apple fruits were sampled and analyzed for quality characteristics. The dry matter content was determined by using gravimetry. Samples weighing about 5 g were dried at 105 °C until reaching constant weight. The total soluble solids in the fruits were analyzed by using refractometry. Briefly, 100 g of grated apple pulp was homogenized in a blender with 50 mL of milli-Q water. The suspension was centrifuged at $2500 \times g$ (Universal 320 R centrifuge, Hettich, Tuttlingen, Germany) and the total soluble solids were determined using a digital refractometer (RX 5000 α , Atago, Tokyo, Japan). The juice's acidity was titrated with a solution of 0.1 N NaOH until reaching pH 8.1 (Titrino 848 Plus, Metrohm, Herisau, Switzerland) and expressed as % malic acid. L-ascorbic acid was determined using an enzymatic test kit (R-Biopharm, Darmstadt, Germany) according to the manufacturer's instructions. The total phenolic content of the apple fruits was determined with Folin-Ciocalteu reagent [43], with some modifications [44]. Briefly, 4 mL of 15% Na_2CO_3 and distilled water were added to 150 μL of the sample and 750 μL of Folin-Ciocalteu reagent, until a final volume of 15 mL was achieved. The absorbance at $\lambda = 756$ nm was measured after a 2 h incubation at room temperature. The total phenolic compounds were expressed as gallic acid (GA) equivalents, based on a calibration curve with known concentrations of gallic acid. All of the determinations were performed in triplicate. All of the reagents used were analytical-grade reagents purchased from Sigma–Aldrich (Merck Group, Darmstadt, Germany).

2.6. Statistical Analysis

The standard uncertainty for the analysis of the foliar fertilizers and the two-in-one products, SNNMs foliar fertilizers, was calculated as the standard deviation by assuming a rectangular distribution. The data from the apple orchard experiment were statistically analyzed by analysis of variance (ANOVA), using the SPSS V.21.0 software package (IBM, Armonk, NY, USA). Two-way ANOVA (treatment; year) with analysis of the interactions was also used for the yield and the fruit quality parameters. The effects of the treatments were studied using the analysis of variance (Fischer method) and Fisher's Least Significant Difference (LSD) test.

3. Results

3.1. Analysis of the Foliar Fertilizer

We prepared a new type of foliar fertilizer, which is suitable for apple foliar fertilization and the correspondent foliar fertilizers with SNNMs as nanoporous carriers (and particle film-forming material). The product containing natural zeolites was called NanoFert Z and the product containing diatomaceous earth NanoFert D.

As already discussed, the prepared foliar fertilizers were NPK 5:25:3 with microelements. This foliar fertilizer composition was confirmed to be optimal for apple fruit trees. The estimated and determined values of the fertilizer composition in the mineral nutrients are presented in Tables 2–4.

Table 2. Composition of the prepared foliar fertilizer F1, estimated value (according to receipt) and determined value.

Analyte	Unit	Estimated Value	Determined Value	Uncertainty
Nitrogen (N total)	%	2.5	2.56	±0.08
Phosphorus (as P ₂ O ₅)	%	12.5	12.09	±1.04
Potassium (as K ₂ O)	%	1.5	1.35	±0.12
Copper (Cu)	%	0.002	0.0025	±0.0003
Zinc (Zn)	%	0.025	0.0027	±0.0003
Iron (Fe)	%	0.017	0.0123	±0.0012
Manganese (Mn)	%	0.008	0.0064	±0.0008
Boron (B)	%	0.003	0.0033	±0.0003

Table 3. Composition of the prepared foliar fertilizer, NanoFert Z, estimated value (according to receipt) and determined value.

Analyte	Unit	Estimated Value	Determined Value	Uncertainty
Nitrogen (N total)	%	2.5	2.47	±0.10
Phosphorus (as P ₂ O ₅)	%	12.5	13.58	±1.04
Potassium (as K ₂ O)	%	1.5	1.65	±0.15
Copper (Cu)	%	0.002	0.0025	±0.0003
Zinc (Zn)	%	0.025	0.0032	±0.0003
Iron (Fe)	%	0.017	0.0126	±0.0013
Manganese (Mn)	%	0.008	0.0086	±0.0007
Boron (B)	%	0.003	0.0032	±0.0002

Table 4. Composition of the prepared foliar fertilizer, NanoFert D, estimated value (according to receipt) and determined value.

Analyte	Unit	Estimated Value	Determined Value	Uncertainty
Nitrogen (N total)	%	2.5	2.54	±0.13
Phosphorus (as P ₂ O ₅)	%	12.5	12.87	±1.02
Potassium (as K ₂ O)	%	1.5	1.49	±0.17
Copper (Cu)	%	0.002	0.0024	±0.0003
Zinc (Zn)	%	0.0025	0.0032	±0.0004
Iron (Fe)	%	0.017	0.0182	±0.0013
Manganese (Mn)	%	0.008	0.0090	±0.0010
Boron (B)	%	0.003	0.0033	±0.0004

The SNNMs carrier did not significantly influence the distribution and homogenization of the raw materials in the final products. The uncertainty is similar for the prepared foliar fertilizers that are mixed with film-forming materials, as for the foliar fertilizers preparation. These results demonstrate the mixing compatibility between the chosen raw materials for foliar fertilizer and the efficiency of the preparation method developed by our team.

3.2. Effects on Apple Tree Yield

The influence of applying foliar fertilizers and foliar fertilizers embedded with the particle-forming materials in the experiment organized in 2021 and 2022 is presented in Table 5.

In 2021, the effects of applying the two-in-one products, foliar fertilizer embedded within the porous structure of the particle film forming SNNMs, were more significant than in 2022. In 2021, the precipitation level was lower (254.2 mm), with a decrease of 83.3 mm compared to normal (337.5 mm) and the average monthly temperatures (+17.6 °C) varied slightly around the thermal norm (+17.3 °C). Under moderate water deficit in the soil, the particle film-forming SNNMs have an additional positive effect on the yield with respect to Fert NPK alone, which is significant in the case of DE (NanoFert D) and at the limit of statistical significance in the case of the product with zeolites (NanoFert Z).

Table 5. Productive efficiency (kg/ha) after foliar fertilization with fertilizers and fertilizers combined with film-forming material applied to apple (Idared variety) in an intensive, non-irrigated orchard compared to the control—2021 and 2022.

Nr. crt.	Treatment	Dose	No. Application	Production (kg/ha) 2021	Production (kg/ha) 2022
1.	Control	-	-	10,835 ^c	7342 ^e
2.	NanoFert D	20 Kg/ha	3	16,714 ^a	10,696 ^d
3.	NanoFert Z	20 Kg/ha	3	16,625 ^{ab}	10,441 ^d
4.	Fert NPK	5 Kg/ha	3	15,373 ^b	10,386 ^d

The values marked with the same letter are not statistically different at $p < 0.05$ within the same year.

The climatic conditions in 2022 were characterized by a deficit in precipitation (75.0 mm compared to the period's average) and a significant temperature increase- +4.8 °C. Under such conditions, with a combined pedological and atmospheric drought, the protective effects of the particle film-forming SNNMs were less significant. The difference between the effects of foliar fertilizer treatment and the application of the two-in-one product, foliar fertilizer and particle film-forming materials is limited and without statistical significance. The two-way ANOVA (treatment, year) with an analysis of the interactions (Table 6, Tests of within contrasts) demonstrates the major influence of the agroclimatic conditions (years) vs. the treatment. The effect of the foliar treatments on the increased yield is statistically significant. However, the two-in-one products do not perform better than foliar fertilizer alone, as indicated by the results from 2022.

Table 6. Tests of within-subjects contrasts, two-way ANOVA (treatment, year) with analysis of interactions.

Measure: Yield (kg/ha)							
Source	Time	Type III Sum of Squares	df	Mean Square	F	Sig.	Partial Eta Squared
Year	Level 1 vs. Level 2	320,684,763.000	1	320,684,763.000	1555.908	0.000	0.995
Year × Treatment	Level 1 vs. Level 2	13,819,647.000	3	4,606,549.000	22.350	0.000	0.893
Error(Time)	Level 1 vs. Level 2	1,648,862.000	8	206,107.750			

3.3. Effects on Photosynthetic Pigments and Fruit Quality

The effects of the experimental treatments using foliar fertilizers and foliar fertilizers with particle film-forming SNNMs on the photosynthetic pigments of the leaves from the apple trees are presented in Figure 2 for 2021 and in Figure 3 for 2022.

The pattern for these two years of experimentation is similar to that observed in the case of the effect on the yield. In 2021, applying the two-in-one products, the foliar fertilizer embedded within the particle film's porous structure forming SNNMs, promotes the accumulation of photosynthesis pigments. The effect of particle film-forming SNNMs was added to the effect of foliar fertilization. The protection against photobleaching due to high solar radiation and high temperatures was 61.41%, 59.13% and 44.04% for chlorophyll *b* for NanoFert D, NanoFert Z and Fert NPK, respectively. Almost similar values were registered for chlorophyll *a*: 59.61%, 60.70% and 41.99%. For total carotenoids, the results are as follows: 60.21%, 58.33% and 41.03% for NanoFert D, NanoFert Z and Fert NPK, respectively. Foliar fertilizers support the primary and secondary metabolism of plants [45,46], stimulate the synthesis of assimilatory pigments [47–49] and support photoprotective mechanisms against reactive oxygen species formed during the harvesting of light energy [50–52]. The effects of the two-in-one product, particles film-forming material and foliar fertilizers, are similar to that of foliar fertilizers.

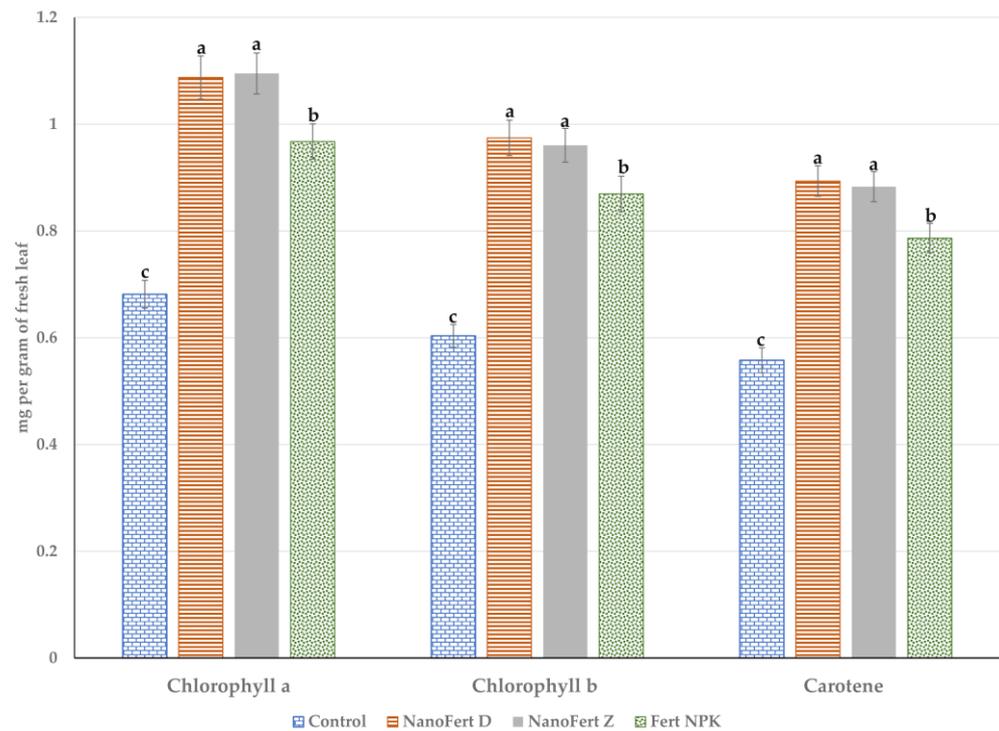


Figure 2. The effects of the experimental treatment with foliar fertilizers and foliar fertilizers with particle film-forming SNNMs on the photosynthetic pigments of the leaves from the apple trees. Orchard of “Vasili Adamachi” experimental farm, Faculty of Horticulture, “Ion Ionescu de la Brad” Iasi University of Life Sciences, 2021. Values followed by the same letter do not differ significantly at $p < 0.05$.

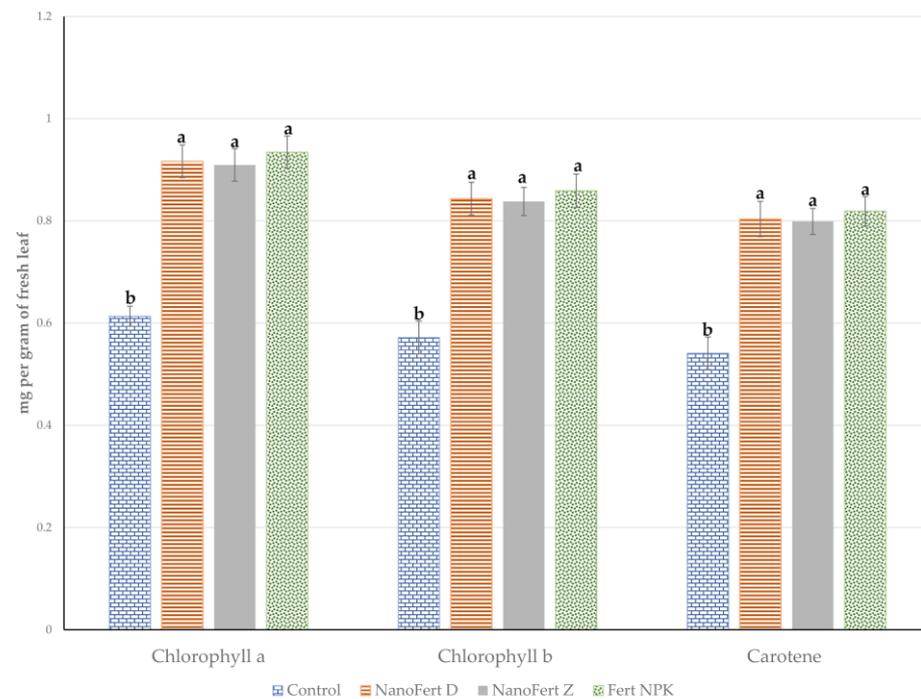


Figure 3. The effects of the experimental treatment with foliar fertilizers and foliar fertilizers with particle film-forming SNNMs on the photosynthetic pigments of the leaves from the apple trees. Orchard of “Vasili Adamachi” experimental farm, Faculty of Horticulture, “Ion Ionescu de la Brad” Iasi University of Life Sciences, 2022. Values followed by the same letter do not differ significantly at $p < 0.05$.

The effects of the applied treatments on fruit quality are presented in Table 7.

Table 7. The effect on apple fruit quality characteristics of the experimental treatment with foliar fertilizers and foliar fertilizers with particle film-forming SNNMs. Orchard of “Vasili Adamachi” experimental farm, Faculty of Horticulture, “Ion Ionescu de la Brad”, Iasi University of Life Sciences.

Quality Parameter/Treatment	2021				2022				Year Significance	Treatment Significance	Year * Treatment Significance
	Control	NanoFert D	NanoFert Z	Fert NPK	Control	NanoFert D	NanoFert Z	Fert NPK			
Dry matter (%)	13.51 ± 0.42 b	14.51 ± 0.34 a	14.27 ± 0.24 a	13.87±0.23 ab	13.28 ± 0.32 b	14.02 ± 0.28 a	13.68 ± 0.44 ab	13.92 ± 0.19 a	**	***	*
Total soluble solids (%)	12.48 ± 0.38 b	13.36 ± 0.24 a	13.22 ± 0.35 a	12.76±0.43 ab	12.32 ± 0.45 b	13.08 ± 0.32 a	12.68 ± 0.27 ab	12.68 ± 0.34 ab	*	***	*
Titrateable acidity (%)	3.21 ± 0.22 c	4.21 ± 0.09 a	3.92 ± 0.18 b	3.98±0.23 ab	3.65 ± 0.19 b	4.02 ± 0.12 a	3.78 ± 0.16 ab	3.78 ± 0.09 ab	**	***	*
Ascorbic acid (mg/kg)	10.18 ± 0.33 c	11.51 ± 0.37 a	11.22 ± 0.29 a	10.72±0.21 b	10.35 ± 0.28 b	11.14 ± 0.19 a	10.68 ± 0.27 ab	10.58 ± 0.12 ab	*	***	*
Polyphenols (mg/100 g dry matter)	517.2 ± 22.4 b	587.7 ± 34.3 a	543.2 ± 18.6 ab	527.6±18.5 b	538.4 ± 18.2 b	572.3 ± 14.3 a	532.2 ± 17.4 b	523.4 ± 17.2 b	*	***	**

The average values marked with the same letter are not statistically different at $p < 0.05$ within the same year and one quality parameter. * significant; ** very significant; *** highly significant.

The results demonstrate similar patterns for the two experimental years. In 2021, applying SNNMs with foliar fertilizer significantly improved several quality characteristics of apple fruits, especially in the case of NanoFert D, a product made with diatomaceous earth (DE). In 2022, the effects on fruit quality were lower, with some effects still being present on the apple fruits harvested from the trees treated with NanoFert D.

The two-way ANOVA (treatment, year), with analysis of the interactions, revealed the limitation of the plant bio-stimulant-like effect on the crop quality of the two-in-one products, NanoFert D and NanoFert Z.

4. Discussion

Particle film technology aims to protect plants against biotic and abiotic stress. Due to its greater benefits, the film-forming technology was mainly applied to horticultural crops. In the years since its introduction, the application of particle film-forming materials to leaves demonstrated effects that are also related to improved fruit and vegetable quality [53–56].

Protection against abiotic stress and improved crop quality traits are agricultural functions that characterize plant bio-stimulants [1,2,57]. Plant bio-stimulants are a class of agricultural inputs that have been developed by the agrochemicals industry in the last 50 years and were introduced into the academic community 10 years ago during the 1st Bio-stimulant World Congress, which represented a milestone in plant bio-stimulant acceptance in the scientific community, held in 2012, in Strasbourg [58]. Another agricultural function of plant bio-stimulants is enhancing nutrient uptake and nutrient use efficiency [59,60]. This agricultural function still needed to be systematically investigated for the particle film-forming materials. Therefore, the beneficial effect of particle film-forming material on the performance of the treated plant should also involve enhanced nutrient uptake.

The ideal film-forming materials are porous [17]. Porous nanomaterial was described recently as the “main vein of agricultural nanotechnology” [52]. Despite their porosity and use as particle film-forming materials, siliceous natural nanomaterials (SNNMs), e.g., zeolites and diatomaceous earth, were not used as slow-release matrices/carriers for foliar fertilizer. Our approach was to use SNNMs as film-forming materials and as a slow-release matrix for foliar fertilizers to demonstrate the possibility of particle film-forming materials enhancing nutrient uptake [34]. Before mixing them with foliar fertilizers, we activated the SNNMs. Using the activation treatment, we enhanced the cation exchange capacity of natural zeolites and diatomaceous earth (DE). After activation, the zeolite exchange capacity (CEC) exceeded 2.5 meq/g and the CEC of diatomaceous earth reached almost 0.75 meq/g [34]. Kaolin, one of the main materials used in particle film technology, is less suitable as a carrier for foliar fertilizer. Kaolinite, the main clay mineral constituent of kaolin, has a relatively low CEC—0.38 meq/g [61]. Other particle film forming materials, for example, chabazite zeolite (CHA), have even higher CEC [62]. Formulations based on copper and chabazite zeolites were used to control plant diseases, e.g., grape downy mildew [63] and grapevine gray mold and sour rot [54], and not in combination with foliar fertilizers, for the foliar nutrition of the treated plants.

Foliar fertilizers emphasize the plant bio-stimulant effects of particle film-forming materials. The resulting two-in-one products, foliar fertilizers embedded in SNNMs, combine particle film-forming technology with foliar fertilization and complement plant protection effects against abiotic stress and plant nutrition. Due to their association with foliar fertilizers, the effects of particle film-forming materials became similar to those of plant bio-stimulants.

In our previous test on stone fruits during 2020 and 2021, we demonstrated the plant bio-stimulant effects for the two-in-one products, foliar fertilizers embedded in SNNMs. The anti-transpirant effect of the particle film enhanced water use efficiency by up to 30%. The nutritional effects of the foliar fertilizers on yield were amplified by the film-forming (nano)porous material by up to 8.1%. Peach and apricot fruit quality increased after applying the combined film-forming particle materials and foliar fertilizers [34].

The similarities between the particle film-forming materials and plant bio-stimulants are not only related to agricultural functions. These similar final effects on the treated plants also result from the similar response at the plant cellular level. High temperatures decrease the efficiency of photosynthetic machinery [64]. In apples, heat events significantly reduce the efficiency of photosystem II and increase non-photochemical quenching [65]. Non-photochemical quenching generates reactive oxygen species [66]. Excessive reactive oxygen species are quenched by antioxidant systems at a non-destructive level under normal conditions [67]. However, high temperatures and high light intensity produce ROS levels that have adverse effects on plants [68]. Increases in the leaf temperature inactivated Rubisco (D-ribulose 1, 5-bisphosphate carboxylase-oxygenase), the first enzyme of the Calvin cycle, reducing CO₂ assimilation [63,69]. Heat stress also determines other adverse effects on chloroplasts, such as impairment of protein translation, chlorophyll breakdown and inactivation of PSII [19]. The drought stress amplifies the effects exerted by the heat stress on the photosynthetic pigments of fruit trees. Drought stress determined the accumulation of reactive oxygen species, leading to photosynthetic pigment peroxidation and photoinhibition [70].

Plant bio-stimulant applications reduce reactive oxygen species (ROS) formation in the treated plants, maintaining the ROS pool at a physiological level [71]. The foliar application of microbial plant bio-stimulants based on a *Trichoderma* consortium protects *Passiflora caerulea* (a shadow plant) from the damage induced by high light intensity [72]. The foliar application of plant bio-stimulants based on plant extracts rich in phytohormones, brassinosteroids, amino acids, or nitrophenolates (NP) resulted in a lower accumulation of ROS-stress-related markers (malondialdehyde and proline) in rice under heat stress [73]. The application of glycine-betaine on the sweet cherry tree (*Prunus avium*) improved water status, increased antioxidant activity and the polyphenol content and protected the photosynthetic pigments from photodegradation [74]. A plant bio-stimulant based on a magnesium–polyphenolic compound stimulated the accumulation of the pigments involved in heat dissipation by the xanthophyll cycle [75].

Particle film-forming material also reduce reactive oxygen species formation in leaves [76]. Kaolin application regulates secondary metabolism in grapes, enhancing accumulation of polyphenol compounds and boosting antioxidant capacity [77]. Phenylpropanoid and flavonoid pathways are stimulated in grapes by kaolin application [78]. Particle film determine a fine-tuning of the heat dissipation by xanthophyll cycle [79].

The main difference between plant bio-stimulants and particle film-forming materials is related to the mode of action. One of the main modes of action of particle film-forming material is reducing the leaf temperature by modifying the light reflection characteristics, especially IR light [80,81]. Our combined treatment reduces the leaf temperature of stone fruit trees, apricot and peach by up to 4.5 °C [34]. The two-in-one products, NanoFertD and NanoFertZ, shield the photosynthesis pigments from degradation due to excessive (UV and IR) solar radiation. Similar shielding effects were reported for other particle film-forming products [79,82]. In 2022, higher temperatures resulted from more intense solar radiations, combined with the decrease in precipitation, limiting the protective effects of the particle film-forming material on photosynthesis pigments. A decrease in the leaf temperature has several beneficial physiological effects. The mode of action of plant bio-stimulants is chemical/molecular priming, i.e., the preparedness/pre-activation of the metabolic pathways related to plant defense [83,84]. Molecular priming was demonstrated to be an efficient approach to controlling plant abiotic stress [85]. However, despite the different modes of action, the agricultural functions of plant bio-stimulants and particle film-forming materials are very similar. Particle film-forming materials, especially in combination with foliar fertilizers, have plant bio-stimulant-like effects on treated plants.

The results of our experiments using two-in-one products, foliar fertilizers embedded in SNNMs, on non-irrigated apple fruit trees were collected across two years under different forms of stress. 2021 was characterized by a moderate water/precipitation deficit during the apple vegetation period, with a temperature in the normal range. Applying

the SNNMs combined with foliar fertilizers benefits nutrient uptake (higher yield), increases the protection of the photosynthetic pigments against inactivation and increases fruit quality. The year 2022 was characterized by a higher temperature (+4.8 °C) during the vegetation period, combined with a precipitation deficit. The average temperature was higher than the multiyear average by +8.6 °C, +10.0 °C and +7.2 °C in June, July and August 2022, respectively. Under such agrometeorological conditions, SNNM applications with foliar fertilizer could no longer exert the whole range of effects similar to those of plant bio-stimulants. The climatic conditions (higher temperatures/higher solar radiation and water deficit) limited the influence of the particle film-forming material on phytonutrients accumulation in apple fruits. The only exception is the accumulation of polyphenols in the case of NanoFert D. In this case, it could be speculated that this effect is the result of soluble silicon species slowly being released from the diatomaceous earth [20]. Additionally, the DE porosity, more complex than on zeolites, could be related to the enhanced effects of the DE observed in some situations. Under normal temperature conditions, particle-forming materials combined with foliar fertilizers exert similar effects with plant bio-stimulant: enhanced nutrient use efficiency, increased protection against abiotic stress and improved fruit quality. High-temperature conditions limit plant bio-stimulant-like effects of the particle-forming materials combined with foliar fertilizers. More investigations are necessary to find solutions for such high-temperature conditions.

5. Conclusions

The application of particle film-forming materials on crops can demonstrate plant bio-stimulant-like effects, such as protecting the treated plants against abiotic stress and increasing crop-quality traits. The agricultural functions of particle film-forming materials were more similar to those that define plant bio-stimulants when such particle film-forming materials are combined with foliar fertilizers. This two-in-one combination evidences the function related to enhanced nutrient uptake and nutrient use efficiency.

The effects of particle film-forming materials and plant bio-stimulants are also similar at the physiological, cellular and biochemical levels. However, the mode of action is different. Particle film-forming materials reduce the leaf temperature and plant bio-stimulants determine a molecular priming of the plant metabolic pathways related to defense.

Our present study reveals that high temperatures limit the plant bio-stimulant-like effects of the two-in-one combination, particle film-forming materials and foliar fertilizers. One potential solution for such high-temperature conditions are complementary/compatible combinations with plant bio-stimulants.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/agriculture13010178/s1>, Table S1. The agrometeorological data for 2020–2021, Iasi agrometeorological station; Table S2. The agrometeorological data for 2021–2022. Iasi agrometeorological station.

Author Contributions: Conceptualization, F.O. and T.M.C.; methodology, C.E.S., D.C.-A. and M.D.-A.; validation, T.M.C., C.E.S. and F.O.; formal analysis, C.E.S.; investigation, C.E.S., M.D.-A. and D.C.-A.; resources, F.O.; writing—original draft preparation, C.E.S.; writing—review and editing, F.O. and D.C.-A.; visualization, D.C.-A.; supervision, F.O. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Romanian Ministry of Agriculture and Rural Development, project Research on the biological activity of some nanomaterial-based products on major pest and pathogens of fruit trees and assessment of the ecotoxicological impact of these on useful entomofauna—ADER 7.3.9. and by the Romanian Ministry of Research, Innovation and Digitalization, project PN.19.23.01.01 Integrated platform for smart valorization of the biomass- Smart-Bi, Nucleu Programme ChemEmergent. The APC was funded by project ADER 7.3.9.

Institutional Review Board Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: Authors thanks to Industriile de Diatomit, Pătârlagele, Buzău, Romania and Zeolites Production, Rupea, Braşov, Romania for the donation of natural zeolites and diatomaceous earth used for experiments. Additionally, the authors thank Bogdan Trică for his support with the statistical analysis.

Conflicts of Interest: The authors declare no conflict of interest.

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