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Effect of Extracted Walnut Pomace Cake Edible Coating and Packaging Type on Quality Parameters of Walnut (*Juglans regia* L.) Kernels During Long Storage Periods

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Abstract: Walnuts are highly valued for their rich nutritional content, but their quality degrades during storage due to oxidation and other quality reducing processes. This study investigated the use of bioactive compounds extracted from walnut pomace, a by-product of walnut oil production, to develop an edible coating that extends the shelf life of 'Milotai 10' walnut kernels. Walnut kernels were stored for eight months in four different packaging materials (PE, PP, MPP, PLA) and three treatments were used (air or without treatment, nitrogen gas, and walnut pomace extract coating). The effects of these combinations on walnut quality parameters, including polyphenol content, vitamin E, fatty acids, peroxide value, and color, were analyzed. The results show that the combination of metallized polypropylene packaging under nitrogen treatment or with atmospheric air and walnut pomace extract (MPP-A-E+) best preserves walnut quality, making it a promising option for extending shelf-life.

Keywords: walnut; packaging; edible coating; PE (polyethylene); PP (polypropylene); MPP (metallized polypropylene); PLA (polylactic acid); fatty acids; polyphenols; tocopherols

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1. Introduction

The production of walnuts (in-shell) worldwide has increased since 2012/2013. The global production of walnuts (*Juglans regia* L.) was approximately 2.66 million tons in 2023 [1]. Walnuts are grown in Asia, Europe, North Africa, United States, and South America. On the global scale, China and the United States represent more than 60% of walnut production worldwide, they are the major walnut producers.

There has been a notable increase in the consumption of walnuts in recent years, largely due to their recognized nutritional value. These health benefits are attributable to the chemical and nutritional composition of the walnut. A number of compounds have been identified in walnuts, including polyphenols, tocopherols (α, β, γ, and δ), tocotrienols, ellagic acid, and melatonin [2–9]. With respect to the polyphenol content of nuts, walnuts are the most polyphenol-rich, with an average of 1591.5 mg/100 g [10]. It is noteworthy that the kernels of walnuts are particularly rich in oil, constituting between 52 and 70%

of the kernel mass [11]. Additionally, they are a rich source of polyunsaturated essential fatty acids (PUFAs), predominantly omega-3 and omega-6 acids. The ingestion of these acids has been associated with a reduction in LDL cholesterol and an increase in HDL cholesterol [12]. For this reason, the consumption of walnuts has been demonstrated to assist in the prevention of cardiac arrhythmia, cardiovascular disease, gallstone formation, and the action of free radicals [13,14]. The walnut kernel possesses a distinctive chemical and nutritional composition. Extracts prepared with different parts of the walnut have been demonstrated to possess a range of beneficial properties, including anti-inflammatory, blood purifying, anticancer, cleansing, and detergent effects [15]. The main parts of the tree that have been extensively studied are the walnut fruit, branch, leaf, shoot, and bark. Investigation showed that the aqueous extract of walnut bark protects mice against cyclophosphamide-induced biochemical toxicity due to the polyphenols [16]. According to Kamiński et al. [17] the effects of subcritical water extraction parameters on the total polyphenols, flavonoids, and antioxidant activity of walnut bark extract were determined. The total polyphenol content extracted from the bark of the walnut ranged from 128.3 to 192.1 mg (GAE)/100 g (DM), varying according to the experimental conditions. The highest polyphenol and flavonoid contents, along with the antioxidant activity, were observed at a temperature of 131.6 °C, a raw material fraction size of 0.9 mm, and a process duration of 10 min, using subcritical water extraction. The chemical and physical properties of walnuts are influenced by storage conditions. The deterioration of walnuts is attributed to the advancement of lipid oxidation, which generates an unfavorable, rancid taste, off-flavors, and browning reactions during storage [18,19]. The process of lipid oxidation is influenced by several factors, including the temperature at which the substance is stored [20], the presence of light [21], and the levels of oxygen present [22]. The chemical composition of walnuts is significantly influenced by their processing and storage conditions, and the types of packaging materials and treatment given at the time of packaging may also affect it [23–25]. The impact of packaging with distinct modified atmospheres on the lipid oxidation of nuts was investigated in several studies. These studies employed a range of techniques, including nitrogen and carbon dioxide (CO_2) flushing, vacuum packaging, and oxygen absorber systems [26,27].

Walnut oil is produced by press extraction of walnut kernels, and the by-product of the process is walnut oil cake, which is also rich in polyphenols. The concentration of phenolics in press-cakes is generally between 10–20 g of gallic acid equivalent (GAE)/kg [28,29]. Adding natural antioxidants to lipid-rich foods is a promising strategy to prevent lipid degradation without using synthetics [30,31].

The utilization of walnut phenolics as antioxidants via a walnut protein-based coating, derived from walnut oil cake residue, has the potential to extend the shelf life of oils and walnuts. In the specific context of walnut extract, its incorporation into different oils has resulted in enhanced resistance to oxidation. For instance, the oxidation stability of walnut oil was increased by a factor of 2.4 when walnut cake extracts were added at a concentration of 518 mg phenolics per kg oil [32]. The efficacy of the ethyl acetate-soluble extract in preserving a solid foodstuff was further illustrated by the incorporation of the extract into an edible coating comprising walnut cake protein. Grosso et al. [33] investigated the shelf life of walnuts with three different treatments: without the addition of any antioxidant (control); with the addition of a walnut phenolic extract; and with the addition of butylated hydroxytoluene (BHT). According to their research, the implementation of walnut phenolics through a walnut protein-based coating was demonstrated to enhance the preservation of walnuts.

The aim of this study was to investigate the protective effect of the polyphenolic extract of walnut cake of walnut fruit 'Milotai-10′ cultivated in Hungary on the chemical properties and the content of selected biologically active components of the walnut in the cases of different packaging materials, such as polyethylene (PE), polypropylene (PP), metallized polypropylene (MPP), and polylactic acid (PLA). In order to generate more information related to the storage conditions, the walnuts were packed with air (A), nitrogen (N), and

an edible coating solution (E) that was made from walnut oil cake, at the time of packaging the walnuts in the aforementioned packaging materials.

2. Materials and Methods

2.1. Plant Material

Walnut (*Juglans regia* L.) fruits were harvested in 2023. Milotai 10 walnut variety was collected from Pálháza (48°28′18.88″ N, 21°30′34.85″ E), an area belonging to the main walnut growing region in Hungary.

2.2. Packaging Materials

Walnut kernels were packaged with different treatments in different packaging materials. The first treatment was packed as a control without any treatment, the second treatment involved dipping in an edible coating solution (polyphenol extract of defatted walnut pellets), the third treatment had nitrogen gas flushing in the packaging. The packaging materials were PE (polyethylene), PP (polypropylene) MPP (metallized polypropylene), PLA (polylactic acid) from Sipospack Ltd. (Herceghalom, Hungary). The walnuts were packed with air (A) and nitrogen (N) and samples made with edible coating (E+) and without edible coating (E-). For the PLA packaging only control (untreated) and edible coating were used because this material could not hold the nitrogen gas appropriately. Edible coating was made from walnut pomace (pellets) using 50% methanol in 1:5 w/v ratio using a shaking waterbath (Foss Tecator 1024, Hillerød, Denmark) at 50 °C for 30 min. The extract was centrifuged at 4500 rpm for 10 min (Thermo Scientific Heraeus Megafuge 8, Hamburg, Germany) and the supernatant was filtered.

2.3. Chemicals

For the total polyphenol (TPC) measurement, gallic acid, methanol, Folin–Ciocalteu phenol reagent were purchased from Sigma Aldrich (St. Louis, MO, USA). For the fatty acid analysis, chloroform (for analysis, stabilized with ethanol) was purchased from Carlo Erba Reagents (Val de Reuil, France), methanol (for HPLC, LC-MS grade) from VWR International (Radnor, PA, USA), and isooctane (>95%) from Thermo Fisher Scientific (Waltham, MA, USA). High-purity water (>18 MΩ cm^{-1}) was prepared by a Millipore Elix Essential 3 UV Water Purification System (Merck-Millipore (Burlington, MA, USA). For determination of vitamin E, the sodium hydroxide, ethyl alcohol, ascorbic acid, hexane were obtained from Merc KGaA (Darmstadt, Germany). Glacial acetic acid, potassium iodide, sodium thiosulphate, and starch indicator for the peroxide number were purchased from Reanal Zrt. (Budapest, Hungary).

2.4. Methods

2.4.1. Total Polyphenol Content (TPC)

For the sample preparation walnut and 100% methanol was used in 1:5 w/v ratio using a shaking waterbath at 50 °C for 30 min. The extract was centrifuged at 4500 rpm for 10 min and the supernatant was filtered.

Total phenolic contents were determined using the Folin–Ciocalteu colorimetric method as described by Singleton and Rossi [34]. Briefly, 1250 µL of Folin reagent (1:10 v/v Folin:distilled water) was added in the test tube followed by 200 µL of methanol (4:1 v/v methanol:distilled water). Then, 50 µL of the sample was added and allowed to stand for 1 min, followed by the addition of 1000 µL of sodium carbonate. The results were expressed in gallic acid equivalents (mg GAE/g walnut).

2.4.2. Vitamin E

Sample preparation was carried out according to the method of SYNLAB Hungary Kft. (Budapest, Hungary). Briefly, to saponify the fat content of the walnut, 1-1 g of the homogenized sample was measured into Erlenmeyer flasks, then 5 mL of water and 5 mL of 12.5 M NaOH solution added. Then, 20 mL ethyl alcohol and 0.5 g of ascorbic acid were

added to the sample, and this was shaken at 65 °C for 90 min. After cooling the sample, 5 mL water and 5 mL hexane were added to the sample with shaking again at 25 °C for 60 min. The sample was allowed to stand for phase separation (ca. 15 min). Hexane was evaporated by nitrogen gas at 40 °C from the hexane phase and the remaining dry matter content was dissolved in methanol. Before the HPLC measurement, the sample was filtered through a 0.45 µm membrane filter before injecting 10 µL into the HPLC system.

Chromatographic separation of vitamin E components (alpha-tocopherol, gamma-tocopherol, delta-tocopherol) was performed with a reversed-phase HPLC system An Agilent (Santa Clara, CA, USA) 1200 using a 100 × 3 mm, C18, 2.6 µm particle size column (Kinetex, Phenomenex, Torrance, CA, USA). For the elution, 0.1% (*v*/*v*) formic acid in methanol (mobile phase A) and 0.1% formic acid in HPLC grade water (mobile phase B) were used as solvents at a low flow rate of 0.4 mL/min. The total gradient program was 13 min and started at 0% solvent B. Solvent B was increased linearly to 10% in 7.5 min, while from 7.5 to 13 min, solvent B was held constant.

2.4.3. Fatty Acid Profile

The sample preparation and GC-FID analysis were performed according to the method of Tormási and Abrankó [35]. A total of 4 g of ground walnuts was homogenized with 4 g of quartz sand for fat extraction. Then 1 g of each sample was centrifuged three times in an Eppendorf tube (7000 rpm, 10 min) and the released fat was removed after each round. The fatty acid composition of walnut oil was determined according to the ISO 12966-2:2017 "Rapid Method" (ISO 12966-2:2017; 2017) with some modifications [36].

An Agilent (Santa Clara, CA, USA) 6890 GC-FID system equipped with an Agilent 7683 autosampler was used to determine fatty acids. A Phenomenex (Torrance, CA, USA) Zebron ZB-FAME (60 m, 0.25 mm, 0.20 µm) column with a cyanopropyl stationary phase and a hydrogen gas (1.2 mL/min) mobile phase were used for separation. A split ratio of 50:1 and an injection volume of 1 µL were used. Fatty acids were identified by comparing the retention times of the FAME mixture and quantified using an external four-point calibration (0, 10, 20, and 40 µg/mL) and 100 µg/mL of nonadecanoic acid (dissolved in isooctane, 1 mg/mL). The following fatty acids were determined: palmitic acid (C16:0; Rt: 12.43 min), stearic acid (C18:0; Rt: 16.30 min), oleic acid (C18:1n-9c; Rt: 17.20 min), linoleic acid (C18:2n-6c; Rt: 19.04 min), α-linolenic acid (C18:3n-3c; Rt: 21.56 min). The results are expressed in relative percentages of each fatty acid.

2.4.4. Peroxide Value Determination

The ground nuts were centrifuged at 18,000 rpm for 30 min and 0.5 g of walnut oil was measured into a polished stoppered iodine flask. Then, 5 mL of glacial acetic acid and chloroform (1:1 ratio) mixture and 500 µL of saturated potassium iodide solution were added to the sample. The flask was closed and shaken for 1 min; after that 5 mL of distilled water and a few drops of starch indicator were added and it was titrated with 0.01 N sodium thiosulfate to a colorless endpoint.

2.4.5. Color Measurement

Color coordinates were determined according to C.I.E.LAB system using a tristimulus colorimeter Konica Minolta CR 410 (Minolta Canada Inc., Mississauga, ON, Canada). The color difference (ΔE*) was calculated by the following equation [37] in the case of every sample compared to the initial zero-month storage time:

$$\Delta E^*_{1;2} = \sqrt[2]{\left(L^*_1 - L^*_2\right)^2 + \left(a^*_1 - a^*_2\right)^2 + \left(b^*_1 - b^*_2\right)^2} \quad (1)$$

where L_1* and L_2* are lightness of sample and control, respectively; a_1* and a_2* are redness of sample and control, respectively; b_1* and b_2* are yellowness of sample and control, respectively.

The evaluation of $\Delta E_{1,2}$* was according to Lukács [38]. Below 0.5 it is not noticeable; between 0.5 and 1.5 slightly noticeable; noticeable between 1.5 and 3.0; 3.0 to 6.0 clearly visible; and in the case of a value above 6.0 there is great visibility.

2.4.6. Statistical Analysis

A full factorial experimental design was employed, utilizing three independent factors: type of packaging material (factor levels: PE, PP, MPP, PLA), treatment environment (factor levels: atmospheric (A), nitrogen gas (N), extract-coated (E+, E-)), and storage time (factor levels: 0, 2, 4, 6, and 8 months). Due to the porous nature of PLA, the use of nitrogen gas was not a viable option for packaging made from this material, and this combination was excluded from the study. For the fatty acid composition and peroxide value, measurements were taken only at months 0, 4, and 8, as previous studies indicated that walnuts do not go rancid quickly, making more frequent testing unnecessary. All combinations were tested in triplicate, with samples selected randomly to minimize potential experimental bias. For each combination of packaging and treatment, three replicates were set aside for measurements at fixed intervals, ensuring that replicate measurements were not derived from the same packaging. This approach assisted in the identification and exclusion of errors resulting from potential damage to the packaging or other unanticipated factors.

The dependent variables were total polyphenol content (TPC) (mg gallic acid equivalent (GAE)/100 g walnuts), tocopherol (alpha, gamma, delta) content (μg/g), fatty acid composition (percentage), and peroxide value (meq O_2/kg), which were measured at regular intervals throughout the storage period.

No special data manipulation, such as the removal of outliers or data transformation, was required. The ANOVA conditions were verified by testing the normal distribution of residuals using the Shapiro–Wilk test, and homogeneity of variance was evaluated using Levene's test. The significance level was set at $p = 0.001$. In cases where ANOVA yielded significant outcomes, pairwise comparisons were conducted. If the homogeneity of variance condition was satisfied, Tukey's post hoc test was employed; if the condition was not met, the Games–Howell post hoc test was used to explore significant differences between factor levels. The results were statistically analyzed using IBM SPSS Statistics software, version 29 (IBM Corp., New York, NY, USA, 2023).

3. Results and Discussion

3.1. Total Polyphenol Content

Table 1 shows the total polyphenol content of the samples. The initial values ranged between 13.68–16.67 mg GAE/100 g, and the data are similar to Pycia et al. [39] and Arranz et al. [40] as measured in their study. During the storage time, the TPC values showed increasing and decreasing tendencies alternately.

In the case of samples containing coating (E+), in the eighth month there was an increase of 5.3% and 4.1% for PE and PPM, while a decrease of 15.34% was observed for PP. In the case of PLA, after a temporary increase, the total polyphenol content returned to the initial value at the end of the storage period. However, without coating (E-), only the PE samples values increased, while the PP decreased by 8.5%, MPP by 12.0%, and PLA by 20.8%. A decreasing tendency was also detected in the case of the sample with nitrogen between 14.2 and 22.8%. This can be explained by transformation of polyphenols by glycosylation, which means replacing hydroxyl groups with O-glycosides or linking with C to form C-glycosides [41]. Glycosylation is one of the major modification reactions occurring in various biological processes resulting in the formation of a wide range of natural products and can affect the stability of plant polyphenols [42,43].

It can be seen that the change in total polyphenol content over time was significantly changed by the packaging materials (<0.001).

The difference between the treatments is significant from the fourth month. In the fourth month, the difference was significant in all cases, and the direction of the change was also opposite in many cases: using MPP packaging material, in a nitrogen-enriched

atmosphere (N+), or coating with walnut pomace extract (E+), in the fourth month, all the polyphenol contents of the samples that could be determined spectrophotometrically decreased significantly; in the case of the other combinations, this value increased somewhat. In the sixth month, there was a significant difference only between the atmospheric and extract coated samples and in the eighth month there was only a significant difference between the nitrogen-enriched and extract-containing samples.

Table 1. The total polyphenol content of the samples during storage (mg GAE/g).

Time (Month)	Treatment	Package Type			
		PE	PLA	MPP	PP
0	A–E-	15.42 ± 0.95 ab,A,α	15.57 ±0.31 A,αβ	16.67 ± 0.43 a,A,βγ	15.49 ± 0.25 a,A,γ
2	A–E-	16.11 ± 2.00 a,A,α	13.17 ± 1.02 A,α	13.92 ± 1.64 a,A,α	12.80 ± 0.61 a,A,αβ
4	A–E-	18.40 ± 0.68 b,B,α	18.07 ± 0.99 B,β	18.42 ± 1.02 c,B,γ	10.85 ± 0.19 a,A,α
6	A–E-	15.67 ± 1.80 a,A,α	13.17 ± 0.81 A,α	12.87 ± 0.76 a,A,α	14.28 ± 0.91 a,A,βγ
8	A–E-	16.07 ± 2.05 a,A,α	12.33 ± 0.81 A,α	14.67 ± 0.25 a,A,αβ	14.17 ± 1.52 ab,A,βγ
0	A–E+	13.68 ± 0.78 a,A,α	14.63 ± 0.60 A,α	15.31 ± 0.51 a,A,α	16.23 ± 1.03 a,A,αβ
2	A–E+	16.58 ± 1.78 a,A,α	15.30 ± 0.87 A,α	16.02 ± 2.38 a,A,α	16.81 ± 0.97 b,A,γ
4	A–E+	13.36 ± 1.44 a,A,α	16.33 ± 1.15 A,α	15.00 ± 0.59 b,A,α	12.91 ± 1.03 ab,A,α
6	A–E+	15.40 ± 0.75 a,A,α	13.93 ± 1.94 A,α	14.70 ± 1.48 ab,A,α	14.28 ± 1.78 a,A,αβ
8	A–E+	14.41 ± 0.87 a,A,α	14.63 ± 1.46 A,α	15.94 ± 1.35 a,A,α	13.74 ± 0.64 b,A,αβ
0	N–E-	16.74 ± 1.12 b,A,β	-	15.44 ± 1.58 a,A,βγ	15.06 ± 1.80 a,A,αβγ
2	N–E-	16.11 ± 2.00 a,A,α	-	12.18 ± 0.68 a,A,β	16.61 ± 1.99 a,b,Aγ
4	N–E-	12.91 ± 1.03 a,B,αβ	-	6.95 ± 0.66 a,A,α	15.22 ± 0.72 b,B,βγ
6	N–E-	16.16 ± 0.88 a,AB,αβ	-	16.16 ± 0.88 b,B,δ	11.57 ± 1.03 a,A,α
8	N-E-	13.07 ± 1.73 a,A,αβ	-	13.25 ± 0.98 a,A,βγ	11.62 ± 0.29 a,A,αβ

Each value is expressed as mean ± standard deviation. PE (polyethylene), PP (polypropylene), MPP (metallized polypropylene), PLA (polylactic acid), A–E- (air without edible coating), A–E+ (air, with edible coating), N–E- (nitrogen without edible coating). The treatment had a significant effect ($F(2;110) = 19.12$; $p < 0.001$). The type of packaging had a significant effect ($F(3;110) = 5.06$; $p < 0.01$). Storage time had a significant effect ($F(4;110) = 8.32$; $p < 0.001$). The interaction of treatment and type of packaging had a significant effect ($F(5;110) = 8.84$; $p < 0.001$). The interaction of treatment and storage time had a significant effect ($F(8;110) = 8.13$; $p < 0.001$). The interaction of storage time and type of packaging had a significant effect ($F(12;110) = 5.18$; $p < 0.001$). The interaction of treatment, storage time and packaging had a significant effect ($F(20;110) = 9.28$; $p < 0.001$). The presence of different letters indicates that the groups in question are significantly different. Lower case Latin letters: a comparison of treatments with fixed packaging and storage time. Upper case Latin letters: a comparison of packaging materials with fixed treatment and storage time. Lower case Greek letters: comparison of storage times with fixed treatment and packaging material.

As illustrated in Table 1, the total polyphenol content across different packaging types and treatments demonstrated considerable fluctuations over the eight-month storage period. The retention of polyphenol levels was generally higher in metallized polypropylene (MPP) packaging in comparison to other packaging materials. This suggests that MPP offers superior protection against polyphenol degradation. Polyethylene (PE) also demonstrated favorable performance, maintaining higher polyphenol levels than PLA, particularly in combination with nitrogen treatment (N–E-). The nitrogen treatment (N–E-) was observed to preserve polyphenols more effectively across all treatments, with the levels in MPP remaining stable. This suggests that nitrogen may play a role in slowing down the degradation process.

In contrast, samples coated with extracts (A–E+) generally exhibited slightly lower polyphenol content. However, the coating appeared to provide some degree of protective effect in PP, with polyphenol levels only exhibiting a slight decrease from 16.81 mg/g at month two to 13.74 mg/g at month eight.

Overall, the combination of nitrogen treatment (N–E-) with metallized polypropylene (MPP) emerged as the most effective approach for preserving total polyphenol content throughout the storage period. This combination not only maintains lower degradation rates but also ensures that higher quality is retained over time. Nitrogen treatment with PE also demonstrated favorable outcomes, particularly during the initial two months of storage.

However, as storage progressed, the differences became less pronounced. Extract coating provided some initial protection, particularly in PP; however, it ultimately demonstrated limited effectiveness over extended periods, particularly by month eight, with regard to total polyphenol retention.

In the study of Yildiz and Karaca [44], walnuts were stored refrigerated and at room temperature in normal air composition and in vacuum packaging and nitrogen gas for six months. Their results showed that the total phenolic content of all samples decreased during storage. Refrigerated storage conditions had a protective effect on the phenolic content of walnuts; however, packaging under vacuum and nitrogen did not prevent the decrease of total phenolic content of walnuts at 20 °C. Ghirardello et al. [45] reported that packaging methods and storage temperature had no clearly definable effects on the total phenolic content of walnuts.

3.2. Color Parameters

Figure 1 illustrates the color difference, expressed as ΔE* values, derived from L*, a*, and b* for different packaging materials over the course of eight-months storage, with the initial month (month 0) considered as the basis for comparison. Before the storage the values of kernel color parameters among treatment and packaging materials ranged approximately from 25.94 (PLA–A–E-) to 27.33 (PP–A–E-) for L*, -1.06 (PE–A–E-) to -0.21 (PLA–A–E-) for a*, and 12.17 (PP–A–E-) to 16.27 (PLA–A–E-).

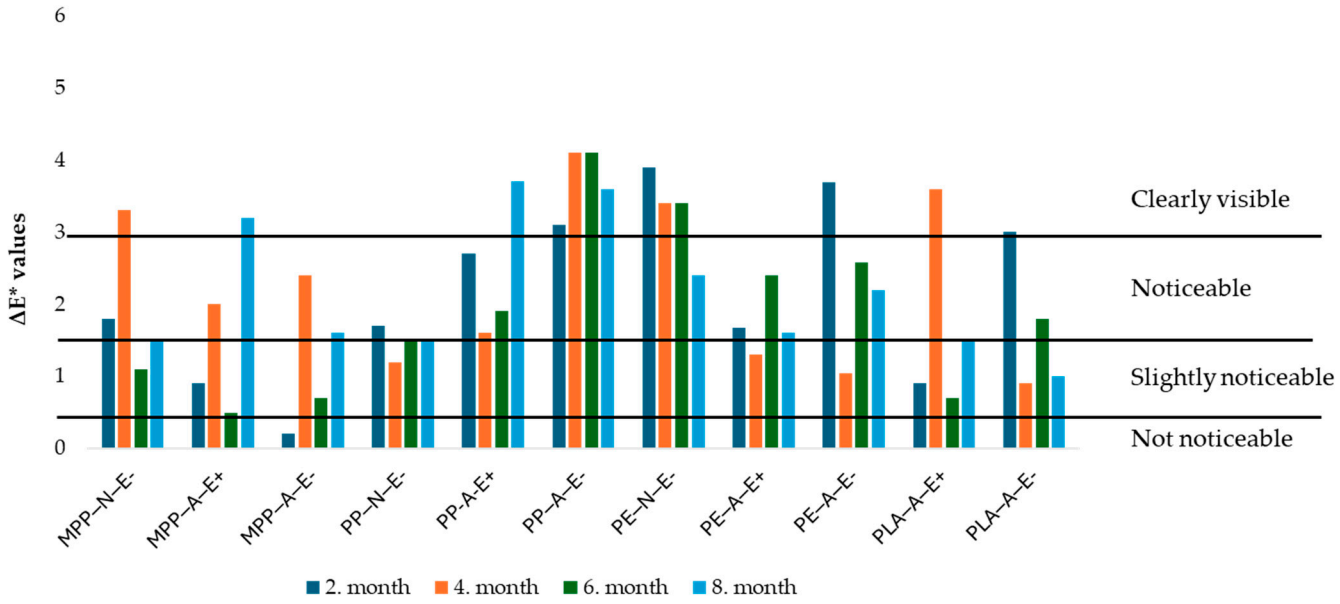

Figure 1. ΔE* values for the different packaging treatments and packaging materials for 'Milotai 10' cultivar. PE (polyethylene), PP (polypropylene), MPP (metallized polypropylene), PLA (polylactic acid), A–E- (air without edible coating), A–E+ (air, with edible coating), N–E- (nitrogen without edible coating).

In relation to color change for different packaging materials, a relatively minor change was observed for MPP (0.2–3.3), followed by a somewhat more pronounced alteration for PLA (0.7–3.6) and PE (1.04–3.9) after an eight-month period. The most considerable differences were identified for PP (1.2–4.1). During the experiment both increasing and decreasing trends were observed in the ΔE* values. Based on the measured color parameters, the color difference values were changed mainly due to the decrease of L* at the end of eight months, especially in the case of PP packaging material. a* and b* values were increased during the storage which are in accordance with the study of Leahu et al. and Habashi et al. [46,47]. Based on this, it can be concluded that the walnut samples had lost their color intensity.

In comparison with another study, Khir et al. [48] observed that the ΔE* values of the Tulare variety increased during the storage period, while a decreasing trend was noted for the Howard variety.

3.3. Tocopherols

Tocopherols play a considerable role in human physiology, protecting cells from the potentially damaging effects of oxygen. In foods, they primarily safeguard fats and certain natural colorants from the detrimental effects of oxygen. Scientific studies demonstrated that γ-tocopherol possesses a distinctive antioxidant and anti-inflammatory capacity in the prevention of disease [49]. Moreover, alpha-tocopherol fulfills a multitude of functions beyond its antioxidant properties. In addition to acting as an antioxidant by binding to lipid peroxyl radicals, it also exhibits pro-oxidant, cell signaling, and gene regulatory functions [50]. Walnuts are a rich source of tocopherols, predominantly gamma-tocopherol, with lesser quantities of delta- and alpha-tocopherol [44].

Figures 2 and 3 show the change in the amount of tocopherols. It can be observed that the largest amount of gamma-tocopherol is found in the samples, between 60.6–75.8% at the beginning of storage, and between 65.9–80.7% at the end of storage. This is followed by alpha-tocopherol with an amount between 21.6–35.4%, which was between 14.4–29.1% in the eighth month of storage. The smallest amount of delta-tocopherol occurs in the samples in amounts between 2.2–3.9% and 3.8–5.0% at the end of storage. The total amount of tocopherols measured at the beginning of storage was between 1135–1630 μg/g, while at the end of storage it was 779–866 μg/g. The rate of decrease during storage was between 50.2–76.3%, the highest rate in the case of the one containing nitrogen. Pycia et al. [39] measured similar vitamin E contents in Polish varieties. According to Yildiz and Karaca [44], vitamin E content decreased at the end of the experiment, alpha-tocopherol content decreased by 26.6–39.9%, the gamma-tocopherol content by 27.0–35.5%, while the delta-tocopherol by 20.8–31.5% in the case of walnut samples stored for six months in a normal air composition and packed in nitrogen gas.

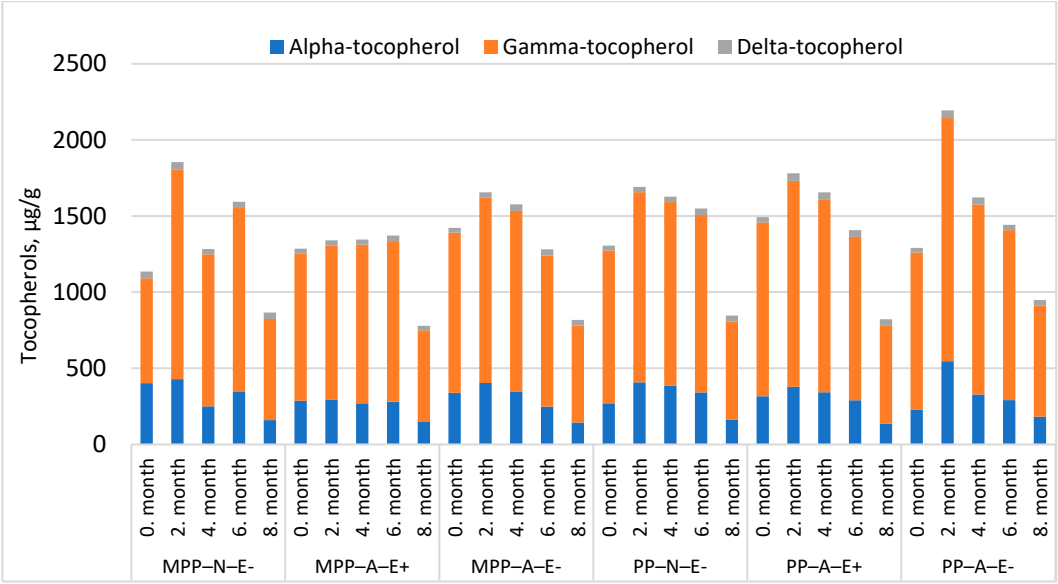

Figure 2. Tocopherol content of the MPP and PP packaging samples during storage (μg/g). MPP (metallized polypropylene), PP (polypropylene), A–E- (air without edible coating), A–E+ (air, with edible coating), N–E- (nitrogen without edible coating).

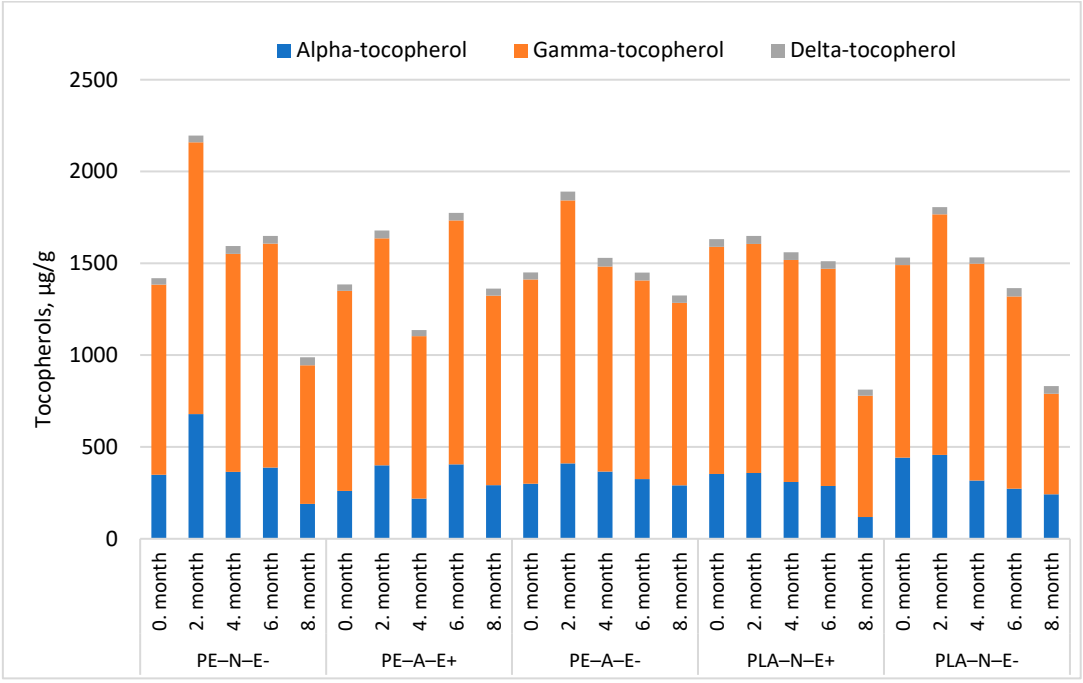

Figure 3. Tocopherol content of the PE and PLA packaging samples during storage (µg/g). PE (polyethylene), PLA (polylactic acid), A–E- (air without edible coating), A–E+ (air, with edible coating), N–E- (nitrogen without edible coating).

It can be concluded that the ratio of different tocopherols was almost constant during storage. For each sample, it can be said that the vitamin E content was the highest after two months of storage; however, in the case of the samples treated with the coating (E+), the amount of tocopherols was significantly lower ($p < 0.01$) only for the eighth month. In the case of MPP packaging with a nitrogen atmosphere (MPP–N), the amount of tocopherols fluctuates, showing an increasing and then decreasing trend. In the case of MPP and PLA uncoated atmospheric packaging (MPP–A–E- and PLA–A–E-), the values gradually decrease after an initial increasing trend, the largest between six and eight months. In the case of MPP and PLA coated atmospheric packaging (MPP–A–E+ and PLA–A–E+), on the other hand, the values initially stagnate and then also decrease significantly between the sixth and eighth months (every two months the difference between the values are not significant, but between the sixth and eighth months the difference is significant for all combinations). A more detailed statistical analysis can be seen in the Tables S1–S3 with regard to alpha-, gamma-, and delta-tocopherol content.

Elouafy et al. [51] monitored the tocopherol content of walnut oil samples at 60 °C for 60 days. During this period, alternating increasing and decreasing trends were observed for each tocopherol component. At the end of storage, the amount of all tocopherols decreased.

3.4. Fatty Acids Composition

Monounsaturated and polyunsaturated essential fatty acids are of significant nutritional importance due to their numerous beneficial physiological effects, including their role in regulating blood lipids. Walnuts are a rich source of polyunsaturated fatty acids, exceeding 70% of their total fatty acid composition [51].

The composition of fatty acids is shown in Figures 4 and 5. Amounts of 99.14–99.33% of all fatty acids are saturated palmitic acid (C16:0), stearic acid (C18:0), monounsaturated oleic acid (C18:1n9c), linoleic acid (C18:2n6c), and polyunsaturated α-linolenic acid (C18:3n3c). Linoleic acid was measured in the largest amount (57.04–60.18%) in the samples at the beginning of the experiment, and the values are similar to previous studies [52,53] between 57.32–59.09% during the eighth month of storage. This was followed by oleic acid with a

value between 20.13–27.97%, then α-linolenic acid with 8.9–11.38%. The smallest amounts of palmitic acid (5.49–6.3%) and stearic acid (2.04–3.04%) were detectable in the walnut samples. The proportion of polyunsaturated fatty acids is between 67.72–70.45%, while that of saturated is only 8.07–8.78%. Dogan and Akgul [54] investigated the fatty acid composition of different types of nuts from east Anatolia. Their results show a close similarity with the fatty acid composition of our examined Milotai 10 walnut. In the case of the four tested varieties, 49.33–54.41% linoleic acid was detected, followed by oleic acid with 22.63–27.25%, while palmitic acid was detected in the smallest amount (5.61–5.82%). Copolovici et al. [55] also showed an average of 8.8% saturated and 72.84% polyunsaturated fatty acids in the case of six walnut varieties. Moigradean et al. [56] also published similar results, with 9.5% saturated acid and 63.3% polyunsaturated fatty acids content. During storage, only minimal changes occurred in the fatty acid composition of the nut samples. This is based on the different chemical reactions, which lead to the degradation of the C-C double bonds forming secondary oxidation products. This phenomenon can cause a reduction in nutritional value of the walnut [51]. The treatments had no significant effect on any fatty acid ($p > 0.001$). For more detailed statistical analysis see Tables S4–S9.

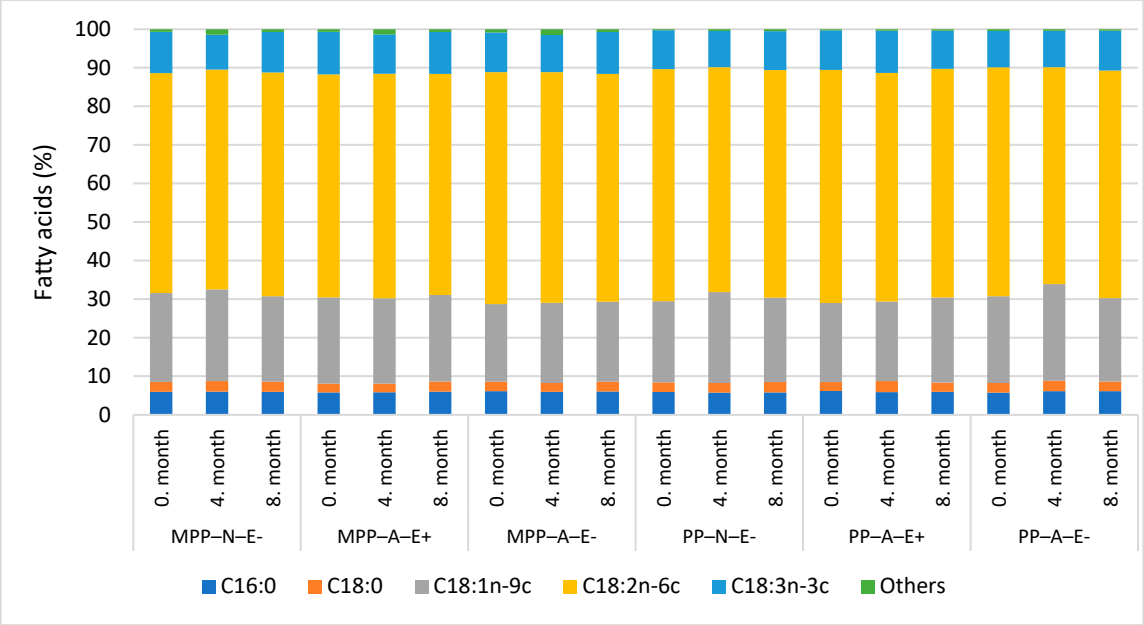

Figure 4. Fatty acid content of the MPP and PP packaging samples during storage (%). MPP (metallized polypropylene), PP (polypropylene), A–E- (air without edible coating), A–E+ (air, with edible coating), N–E- (nitrogen without edible coating).

Fatty acid analysis revealed stable levels across all packaging materials and treatments, with minor fluctuations in palmitic (C16:0), stearic (C18:0), oleic (C18:1n-9c), linoleic (C18:2n-6c), and linolenic (C18:3n-3c) acids. Nitrogen treatment (N–E-) demonstrated slightly better preservation of fatty acid composition, particularly in PE and MPP packaging. Atmospheric treatment and PLA packaging showed minor increases in peroxide value, indicating mild oxidation, but overall, the fatty acid content remained stable across all treatments.

In conclusion, the findings suggest that fatty acids are largely preserved in walnuts across all packaging types, with nitrogen-treated MPP and PE demonstrating the most effective maintenance of fatty acid stability. The atmospheric treatment resulted in slight oxidation, as evidenced by a minor increase in peroxide value, but this effect was not considerable over the storage period.

A similar result was also reported by Elouafy et al. [51]. Walnut oil samples were stored at 60 °C for 60 days and only a minimal change was observed in the amount of fatty

acids during storage, mainly in the case of linoleic acid. During the storage, the same trend was observed, i.e., small increasing and decreasing phases changing continuously.

The omega-6/omega-3 (linoleic acid/linolenic acid) ratio was between 5.23 and 6.04. In the case of PLA packaging, the values decreased by the end of the eighth month, so the packaging material had effects on the fat content, but the air composition had no effects.

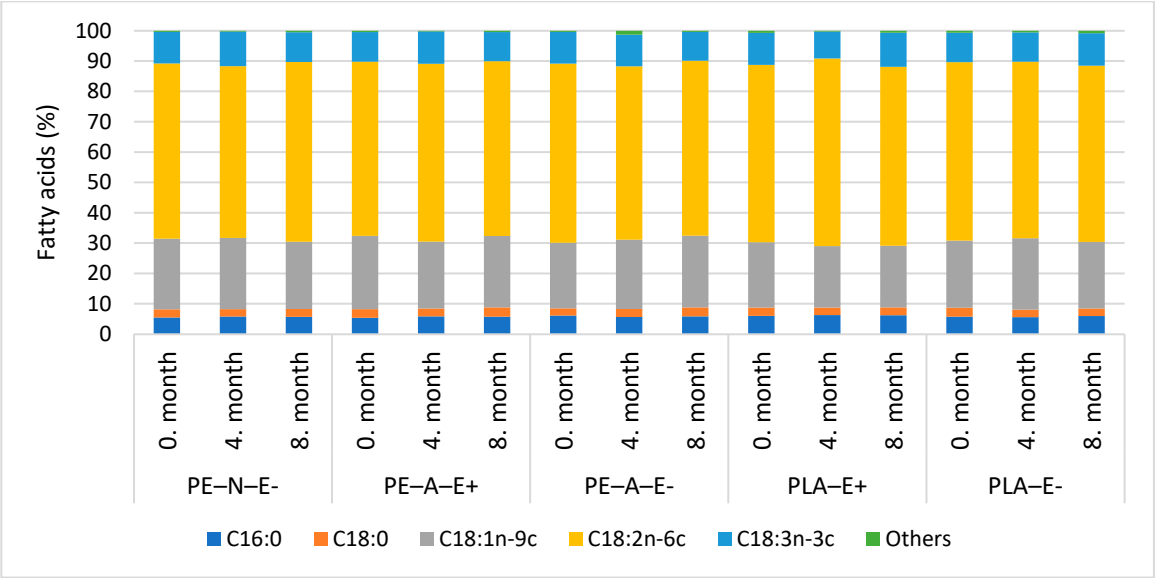

Figure 5. Fatty acid content of the PE and PLA packaging samples during storage (%). PE (polyethylene), PLA (polylactic acid), A–E- (air without edible coating), A–E+ (air, with edible coating), N–E- (nitrogen without edible coating).

3.5. Peroxide Value

The peroxide value is a widely utilized quality parameter for the monitoring of lipid oxidation and the determination of oil quality. It provides quantitative results regarding the level of primary oxidation products present in oils and fats. In vegetable oils, the peroxide value reflects the extent of oxidation and, consequently, the degree of rancidity [57].

Table 2 illustrates the change in peroxide value observed in both the coated (E+) and uncoated samples (E-). The values exhibited a range of 0.67 to 4.99 milliequivalents of oxygen per kilogram (meqO_2/kg). Regardless of the coating application, air composition, and packaging material, both increasing and decreasing trends in peroxide values were observed. The use of nitrogen gas resulted in a reduction in peroxide values for all samples, regardless of the packaging material (0.69–3.49 meqO_2/kg) compared to the samples stored in an atmospheric environment (0.73–4.99 meqO_2/kg). The lowest peroxide values were observed for the combined application of metalized polypropylene and nitrogen gas (MPP–N–E-).

The application of nitrogen treatment was demonstrated to be the most effective method for preserving the quality of walnuts, resulting in minimal degradation across a range of storage conditions and packaging materials, particularly those composed of polyethylene (PE) and polypropylene (PP). While extract coating provides some initial protection, its effectiveness diminishes over time, particularly in PLA, where significant quality loss occurs. The most rapid deterioration in quality is observed in cases where atmospheric treatment is employed, particularly in the case of PM (metallized polypropylene), which exhibits high initial values indicating a faster rate of degradation. Over time, the differences between packaging materials become less pronounced, with polyethylene (PE) and polypropylene (PP) offering comparable levels of protection by time point 8. In conclusion, nitrogen treatment is the most reliable method for maintaining walnut quality,

while extract coating and packaging material selection play a secondary role in long-term preservation.

Table 2. Peroxide value of the samples during storage (meqO_2/kg).

Time (Month)	Treatment	Package Type			
		PE	PLA	MPP	PP
0	A–E-	0.74 ± 0.09 a,A,α	0.92 ± 0.03 a,B,α	3.46 ± 0.03 c,C,β	1.07 ± 0.10 a,D,α
4	A–E-	1.05 ± 0.04 b,B,αβ	0.99 ± 0.01 a,B,α	0.79 ± 0.16 a,A,α	2.74 ± 0.12 c,C,β
8	A–E-	1.22 ± 0.49 β	1.05 ± 0.16 α	1.13 ± 0.37 α	1.04 ± 0.17 α
0	A–E+	3.61 ± 0.27 b,C,γ	1.50 ± 0.17 b,A,β	2.08 ± 0.20 b,B,γ	1.93 ± 0.16 b,B,α
4	A–E+	0.99 ± 0.16 b,A,α	4.99 ± 0.11 b,D,γ	1.54 ± 0.28 b,B,β	2.29 ± 0.05 b,C,β
8	A–E+	1.80 ± 0.25 b,B	0.89 ± 0.10 a,A,α	1.00 ± 0.11 a,A,α	1.90 ± 0.23 b,B,α
0	N–E-	3.49 ± 0.52 b,B,β	**	0.96 ± 0.12 a,A	1.06 ± 0.10 a,A,β
4	N–E-	0.79 ± 0.03 α	**	0.69 ± 0.15	0.91 ± 0.02 α
8	N–E-	0.85 ± 0.02 α	**	0.95 ± 0.10	0.79 ± 0.05 α

PE (polyethylene), PP (polypropylene), MPP (metallized polypropylene), PLA (polylactic acid), A-E- (air without edible coating), A–E+ (air, with edible coating), N–E- (nitrogen without edible coating). Each value is expressed as mean ± standard deviation. The treatment had a significant effect ($F(2;110) = 270.437$; $p < 0.001$). The type of packaging had a significant effect ($F(3;110) = 10.96$; $p < 0.001$). Storage time had a significant effect ($F(4;110) = 174.20$; $p < 0.001$). The interaction of treatment and type of packaging had a significant effect ($F(5;110) = 99.35$; $p < 0.001$). The interaction of treatment and storage time had a significant effect ($F(8;110) = 20.74$; $p < 0.001$). The interaction of storage time and type of packaging had a significant effect ($F(12;110) = 181.77$; $p < 0.001$). The interaction of treatment, storage time and packaging had a significant effect ($F(20;110) = 143.452$; $p < 0.001$). The presence of different letters indicates that the groups in question are significantly different. Lower case Latin letters: a comparison of treatments with fixed packaging and storage time. Upper case Latin letters: a comparison of packaging materials with fixed treatment and storage time. Lower case Greek letters: comparison of storage times with fixed treatment and packaging material. **: no sample.

Yildiz and Karaca [44] stored walnuts refrigerated and at room temperature for six months in a normal air composition and packed in nitrogen gas. The initial value was 0.24–0.28 meqO_2/kg, and the maximum during storage was 1.15 meqO_2/kg. Most of the walnut samples showed similar changes in peroxide values: they increased first, then decreased to a minimum in the third month of storage, and they increased again. According to Yildiz and Karaca [44], it can be concluded from the results that the rate of degradation was faster than the formation of peroxides in the third month of storage. A similar fluctuating trend was observed by several researchers during the storage of walnuts. This may be due to the unstable nature of peroxides and their simultaneous formation and degradation in vegetable oils. According to Ding et al. [58], the unstable lipoxygenase activity may also be the cause of the fluctuating tendency of peroxide values. Elouafy et al. [51] investigated the peroxide value during the storage of walnut oil samples at 60 °C for 60 days. Their results were between 1.19–3.75 meqO_2/kg. During the storage, similar changes were observed in the tendency of the peroxide value to the results of our study, i.e., increasing and decreasing phases followed each other. According to the standards of most companies, the peroxide value should be lower than 1 meqO_2/kg; however, in the study of Buransompob et al. [59] walnuts with a peroxide value of less than 3 meqO_2/kg are also of acceptable quality. In addition, Mexis et al. [60] states, that based on the results of sensory tests, walnuts can be consumed with a peroxide value of up to 10 meqO_2/kg.

Oleic acid can be an indicator for the peroxide value, because walnuts with higher oleic acid content have the longest shelf life. This relationship can be used for the oil stability prediction [61]. This observation is mostly valid between our data, especially for the MPP–A–E+ (8-months), PP–N–E- (4 months), and PE–N–E+ (0 and 8-months).

4. Conclusions

In recent decades, there has been an increasing effort in the direction of such research, of which the results can contribute to the development of circular food systems. This also

appears in the legislation and legislative strategies, thus supporting industry participants to use processing that is more beneficial for the environment [62].

In this research, we examined one of the possible uses of walnut pellets (rich in phenolic compounds), a byproduct of walnut oil production. Across all analyses—total polyphenol content, tocopherol levels, fatty acid composition, color parameters, and peroxide values—nitrogen treatment combined with metallized polypropylene (MPP–N) consistently outperformed other packaging types and treatments in preserving walnut quality over time. PE also demonstrated favorable results under nitrogen treatment, particularly in the early months, but showed more degradation by the end of the study. We can conclude that for the longer storage period of walnuts (min. eight months), the most suitable combination is MPP atmospheric packaging and coating with nut pomace extract (MPP–A–E+), since most of the properties can be preserved in this case in the greatest quantity. Extract coatings were less effective during longer storage for PLA, which showed significant degradation for all variables. Atmospheric treatment led to rapid quality deterioration, especially in MPP, emphasizing the importance of a controlled atmosphere in preserving walnut quality. Nitrogen treatment and MPP packaging are recommended as the most reliable combination for long-term walnut storage.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/app142210120/s1, Table S1: Statistical analysis of Alpha-tocopherol concentration (μg/g); Table S2. Statistical analysis of Gamma-tocopherol concentration (μg/g); Table S3. Statistical analysis of Delta-tocopherol concentration (μg/g); Table S4. Statistical analysis of Palmitic C16:0 [%]; Table S5. Statistical analysis of Stearic C18:0 [%]; Table S6. Statistical analysis of Oleic C18:1n-9c [%]; Table S7. Statistical analysis of Linoleic C18:2n-6c [%]; Table S8. Statistical analysis of Linolenic C18:3n-3c [%]; Table S9. Statistical analysis of Other fatty acids [%].

Author Contributions: Conceptualization, M.M. and P.K.; methodology, J.T., L.S.-D., J.K., D.S. and L.A.; software, J.T., L.S.-D., J.K., D.S. and L.A.; validation, J.T., L.S.-D., J.K., D.S. and L.A.; formal analysis, J.T., L.S.-D., J.K., D.S. and L.A.; investigation, J.T., L.S.-D., J.K., D.S. and L.A.; resources, M.M.; data curation, J.T., L.S.-D., J.K. and L.A.; writing—original draft preparation, M.M. and P.K.; writing—review and editing, I.D. and B.S.-N.; visualization, I.D.; supervision, M.M.; project administration, M.M.; funding acquisition, M.M. All authors have read and agreed to the published version of the manuscript.

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