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Authors

Luo, Kathleen K
Huang, Guangwei
Mitchell, Alyson E

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Acceleration of lipid oxidation in raw stored almond kernels in response to postharvest moisture exposure

Kathleen K Luo,[a] Guangwei Huang[b] and Alyson E Mitchell[a]*

Abstract

BACKGROUND: Almonds are an important crop in California, and increased yields necessitate that dried in-hull almonds are stored in the field for longer periods, increasing the potential for postharvest moisture exposure (e.g., rain, fog). Processors are increasingly drying these 'wet' almonds to a moisture content of <6% using low heat before the hulling and shelling process in order to reduce mechanical damage to the nutmeat. To date, there is no information on the impact that moisture exposure and drying prior to hulling and shelling has on lipid oxidation and storage shelf life of raw almonds.

RESULTS: Raw almonds exposed to ≤8% moisture and subsequently dried (MEx) and almonds not exposed to moisture exposure (≤4% moisture; control) were stored under accelerated shelf life conditions and evaluated monthly over 12 months for free fatty acid (FFA) value, peroxide value (PV), and headspace volatiles. At 12 months of accelerated storage, MEx almonds have 1.4 times higher FFA and 3.5 times higher PV than the control, indicating significant oxidative damage. MEx almonds also demonstrated higher levels of headspace volatile compounds related to lipid oxidation (i.e., hexanal, octanal, hexanoic acid) throughout storage.

CONCLUSION: Drying almonds exposed to postharvest moisture prior to storage results in a higher degree of lipid oxidation during storage and a significant reduction in shelf life.
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Keywords: almonds; moisture; oxidation; concealed damage; shelf life; volatiles

INTRODUCTION

Climate change is causing extreme and less predictable weather patterns around the world and is significantly affecting agriculture.[1,2] California, which grows ~80% of the world's supply of almonds, is experiencing more extreme seasonal drought (summer) and heavy rain events (fall and winter), and is predicted to have higher annual rainfall with larger storm events during the next century.[3] Almonds in California are harvested from July through September, depending on variety. At hull-split, almonds are shaken from the tree, dried, then swept into windrows in the orchard for additional moisture reduction.[4] After drying in windrows, almonds are cleaned of debris and stored in stockpiles prior to processing (i.e., hulling and shelling) and final kernel storage.[4] California almond production has increased by ~50% over the past 10 years, fueled by consumer demand as almonds are a good alternative to animal protein, dairy and wheat flour, and are considered an excellent source of vitamin E.[5-9] Production now exceeds processing capabilities, and almonds are frequently left in stockpiles for longer periods, where they are more susceptible to changes in the environment. The moisture content of almonds is a critical parameter in determining optimum conditions for their handling, processing and storage, and

exposure to postharvest moisture (e.g., rain, fog) can negatively impact the quality and shelf life of almonds.

Unsaturated fatty acids are susceptible to lipid oxidation and the development of rancidity in foods. Almonds contain 44–61% lipid by weight, the majority of which are the unsaturated fatty acids oleic acid (70–80%) and linoleic acid (10–20%).[10] Lipid oxidation is initiated and accelerated by oxygen, heat, enzyme activity (e.g., lipases), moisture, and UV radiation exposure. Lipid oxidation initiates the degradation of lipids and formation of volatile compounds, which result in the unpleasant 'rancid' aroma/flavor that is the primary determinant of shelf life.[11] Common ways to evaluate the shelf life of lipid-rich foods include measuring primary lipid oxidation markers, such as peroxide values (PV) and free fatty acid (FFA) values, and/or measuring

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* Correspondence to: AE Mitchell, Department of Food Science and Technology, University of California, Davis, One Shields Avenue, Davis, CA 95616, USA. E-mail: aemitchell@ucdavis.edu

a Department of Food Science and Technology, University of California, Davis, Davis, CA, USA

b Almond Board of California, Modesto, CA, USA

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volatile compounds that are secondary or tertiary lipid oxidation products. PV measures the lipid hydroperoxides that are formed early in the oxidation process and represent the amount of active oxygen present in fat and oil.[12] A PV < 0.5 mEq kg^{-1} (milliequivalents of peroxide per kilogram of oil) is used by the almond industry to establish product acceptability. FFA values reflect the amount of fatty acids hydrolyzed from triglycerides and is a useful marker of hydrolytic rancidity. FFAs are generally considered more susceptible to lipid oxidation than triglyceride-bound fatty acids. FFA values of <1.5% are used by the almond industry to establish product acceptability. Secondary and tertiary lipid oxidation compounds (i.e., volatile organic compounds) are the 7- to 9-carbon aldehydes and alcohols, and/or the 5- to 9-carbon organic acids that are associated with rancidity flavor/aroma and are frequently used to monitor oxidative rancidity in lipid-rich foods.[11,13] All these measurements have been used to monitor the shelf life of almonds and in some cases correlated with the sensory attributes of almonds.[13,14]

Postharvest moisture exposure is reported to cause kernel browning in almonds, macadamia nuts, pecans, and hazelnuts.[15-17] Kernel browning is an undesirable attribute that is frequently associated with off-flavors and consumer rejection of nut products.[16] Rogel-Castillo et al.[16] reported that almonds with kernel browning have higher levels of volatile organic compounds related to lipid peroxidation and amino acid degradation. In macadamia nuts, the kernel browning appears at high moisture content and elevated temperature, affecting ~1% of macadamia nuts and costing the Australian macadamia industry around AU $2 million annually.[15,18] In hazelnuts, kernel browning occurs in the inner layer; which has significantly higher amounts of oil and sugar, and lower amounts of protein relative to the outer layer.[17] The kernel browning found in nuts is linked to the Maillard reaction and/or enzymatic browning.[19] In hazelnuts, enzymatic hydrolysis provides reducing sugars for the Maillard reaction.[17] In these lipid-rich nuts, lipid oxidation byproducts (e.g., carbonyl compounds) may also contribute to the Maillard reaction.[19,20]

Postharvest moisture exposure (rewetting) is shown to promote the hydrolysis of proteins, carbohydrates and lipids, and increases levels of lipid oxidation products in almond kernels.[21,22] Earlier studies have shown that almond kernels exposed to a moisture content of ≤8% and subsequently heated at high temperatures (e.g., roasting) form dark-brown centers.[16,22] This phenomenon is termed 'concealed damage' as the discoloration appears only after heating. The dark discoloration is related to increased products formed via the Maillard reaction.[4,16]

When stockpiled dried in-hull almonds are exposed to postharvest, the current industry practice is to dry these almonds to a moisture content of ≤6% by applying low heat (40–50 °C), as this reduces nutmeat damage during the hulling and shelling process (i.e., chipping and splitting).[4] This practice has the added benefit of reducing concealed damage in thermally processed almonds.[19] Although this practice reduces cosmetic damage to the nutmeat during processing, it is not understood if the initial moisture exposure increases FFAs and/or induces lipid oxidation in these nuts, which could result in decrease product shelf life.

Under controlled conditions and proper packaging (i.e., <10 °C and <65% relative humidity and/or vacuum packaging), raw almond kernels can be stored up to 2 years without experiencing the lipid oxidation that leads to consumer rejection.[14] Nonetheless, various lots of almonds, stored under optimal conditions, have a shortened shelf life, the reason for which is not always understood. In this study, we hypothesize that almonds exposed to postharvest moisture, and dried prior to kernel storage, may have a shortened shelf life due to the initiation of triglyceride hydrolysis and lipid oxidation during the rewetting phase. Understanding how this increasing practice influences product shelf life is critical towards improving inventory control and decreasing product loss and, importantly, food waste.

MATERIALS AND METHODS
Almond samples and storage
Raw Nonpareil almond kernels (from 2015 harvest year) not exposed to postharvest moisture were obtained from Blue Diamond Growers (Sacramento, CA, USA). Moisture content was measured gravimetrically at ~4% upon receiving. Almonds were then separated into a control group and a moisture-exposed group (MEx). The MEx group was exposed to moisture by incubating kernels in a KMF 240 Constant Climate Control Chamber (Binder Inc., Bohemia, NY, USA) at 38 °C and 90 ± 1% relative humidity (% RH) for 36 h. Once the moisture content of the MEx almonds was increased to 8%, the almonds were subsequently dried in a R-4 Harvest Saver Dehydrator (Commercial Dehydrator System Inc., Eugene, OR, USA) at 50 ± 1 °C for 12 h to reduce the moisture content back to 4%. MEx almonds represent crops that have been exposed to moisture (i.e., rained on) and undergo drying prior to processing. The control almonds maintained a moisture content of ~4% and did not undergo drying prior to processing. Both the control and MEx group were divided into paper bags containing 460 g each, placed in the climate control chamber at 39 ± 1 °C and 15 ± 1% RH and stored for up to 12 months. Samples were randomized and analyzed every month. Triplicate sampling was made for each group at each time point.

Chemicals
Acetic acid (high-performance liquid chromatography (HPLC) grade), chloroform (HPLC grade), hydrochloric acid (American Chemical Society (ACS) grade), potassium iodide (99.9%), sodium hydroxide (analytical grade), sodium thiosulfate (99%), and 2,2,4-trimethylpentane (HPLC grade) were purchased from Sigma-Aldrich (St Louis, MO, USA) or Fisher Scientific (Hampton, NH, USA). Authentic volatile standards (95–99%) used for identification were purchased from Sigma-Aldrich. Stable isotope internal standards n-hexyl-d$_{13}$ alcohol, octanal-d$_{16}$, and 2-methylpyrazine-d$_6$ were purchased from C/D/N Isotopes Inc. (Pointe-Claire, QC, Canada).

Analysis of conjugated dienes, free fatty acids, and peroxide value
Whole almond kernels were crushed and ground for three 1 s pulses using a laboratory mill (Waring Laboratory Equipment, Torrington, CT, USA). The oil was extracted from the ground almonds using a 12-ton Carver manual oil press (Carver Inc., Wabash, IN, USA), collected into an amber vial, and stored at −20 °C until analyzed. FFA levels and PVs were measured in the extracted almond oil according to American Oil Chemists' Society (AOCS) official methods Cd 3d-63[23] and Cd 8-53,[24] respectively.

Solid-phase microextraction (SPME) headspace volatile analysis
Almonds were ground with a laboratory mill and sieved with a size 20 Tyler sieve. An aliquot of 5 ± 0.02 g of the sieved almonds was weighed into an amber headspace vial, capped, and equilibrated at room temperature (23 ± 2 °C) for at least 4 h.

Table 1. Average value of free fatty acids and peroxide values in almonds exposed to moisture and subsequently dried (MEx) and almonds with no moisture exposure (control) over 12 months of accelerated storage

Storage month	Treatment	Free fatty acids (% oleic acid)	Peroxide value (mEq kg^{-1})
0	Control	0.09 ± 0.0a	n.d.
	MEx	0.09 ± 0.02ab	n.d.
1	Control	0.09 ± 0.01ab	0.34 ± 0.05ab
	MEx	0.10 ± 0.01abc	0.52 ± 0.21a
2	Control	0.11 ± 0.00abcd	0.46 ± 0.09ab
	MEx	0.09 ± 0.00ab	0.64 ± 0.00ab
3	Control	0.12 ± 0.00abcd	0.55 ± 0.05ab
	MEx	0.12 ± 0.00abcd	1.46 ± 0.15fgh
4	Control	0.09 ± 0.00ab	0.50 ± 0.10ab
	MEx	0.12 ± 0.00abcd	1.58 ± 0.10h
5	Control	0.12 ± 0.00abcd	0.76 ± 0.11bcd
	MEx	0.13 ± 0.01bcdef	2.01 ± 0.11i
6	Control	0.12 ± 0.00abcde	0.50 ± 0.00ab
	MEx	0.15 ± 0.02edfg	1.10 ± 0.00de
7	Control	0.11 ± 0.01abcd	1.35 ± 0.10efgh
	MEx	0.14 ± 0.00cdefg	1.22 ± 0.06efg
8	Control	0.11 ± 0.00abcd	1.39 ± 0.09efgh
	MEx	0.22 ± 0.01h	1.06 ± 0.06cde
9	Control	0.12 ± 0.01abcde	0.76 ± 0.12bcd
	MEx	0.17 ± 0.00fg	1.39 ± 0.27efgh
10	Control	0.13 ± 0.01abcdef	0.73 ± 0.06bc
	MEx	0.15 ± 0.01defg	1.13 ± 0.15defg
11	Control	0.11 ± 0.01abcd	0.56 ± 0.11ab
	MEx	0.18 ± 0.06gh	0.73 ± 0.06bc
12	Control	0.12 ± 0.00abcd	0.43 ± 0.06ab
	MEx	0.17 ± 0.01efg	1.53 ± 0.06gh

Entries followed by the same letter within a column (treatment) indicate no significant differences under Tukey's post hoc test ($P < 0.05$); n.d., not detected.

The headspace volatiles were measured and analyzed according to Luo et al.[25] Briefly, the volatiles were extracted with a 1 cm 30/50 μm StableFlex divinylbenzene/carboxen/polydimethylsiloxane fiber (Supelco Inc., Bellefonte, PA, USA) attached to an Agilent GC injector 80 (Agilent Technologies, Santa Clara, CA, USA). The volatiles were separated on a 30 m × 0.25 mm × 0.25 μm DB-Wax UI column using an Agilent 7890A gas chromatograph coupled to an Agilent 5975C mass selective detector. An external instrument standard was used to provide a response factor to correct for instrument and fiber variation. The external instrument standard contained a mixture of n-hexyl-d$_{13}$ alcohol, octanal-d$_{16}$, and 2-methylpyrazine-d$_6$ in de-volatilized ground almonds capped in a 20 mL amber headspace vial. The headspace volatile profiles were collected in scan mode (m/z range 30–300). Tentative identifications were made through NIST v.17 Mass Spectral Library Search Program. Identification was further confirmed using retention index calculation or authentic standards when available. Relative concentrations of volatiles with confirmed identification were calculated as described by Franklin et al.[11]

Statistical analyses

Statistical analyses were performed using two-way analysis of variance (ANOVA), including treatment and storage month interaction. Statistically significant differences were considered when $P < 0.05$. Tukey's post hoc test was employed to reveal the grouping for the chemical measurements. Principal component analysis

(PCA) was performed on the 48 volatiles that were significantly different ($P < 0.05$) from ANOVA results to visualize the clustering formation among samples and the relationship between volatile compounds with the samples. Agglomerative hierarchical clustering (AHC) was performed after the PCA to cluster the samples based on dissimilarity with data centered and reduced. All statistical analyses were performed using Addinsoft XLSTAT statistical and data analysis solution (version 2020.3).

RESULTS AND DISCUSSION

Lipid oxidation is a dynamic processes and multiple markers are usually used to estimate the extent of oxidation in almonds. FFA values reflect hydrolytic rancidity as FFAs are released from triglycerides by lipases in the presence of moisture. Although we expected an increase in FFA levels in MEx almonds due to hydrolysis, no significant difference was observed between the MEx and control samples for the first 7 months of accelerated storage (Table 1). This suggests that significant hydrolysis of triglycerides does not occur with short moisture exposure (here it was 36 h). Almonds typically require 48 h of soaking in water to break dormancy and another 3–5 months to germinate.[26] Interestingly, FFAs increased significantly in MEx almonds at 8, 9, 11, and 12 months of storage relative to the controls. This may result from the additional drying step these almonds underwent as compared with controls. Drying (i.e., dehydration with heat) has been

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Table 2. Average solid phase microextraction (SPME) headspace volatile concentrations (μg kg^{-1} almond) measured in moisture exposed and dried and control raw almonds at 0, 2, 4, 6, 8, 10, and 12 months of accelerated storage

| Chemical class	Treatment	Month 0 Control	Month 0 MEx	Month 2 Control	Month 2 MEx	Month 4 Control	Month 4 MEx	Month 6 Control	Month 6 MEx
Organic acids									
	Acetic acid	0.51 ± 0.06	0.57 ± 0.09	0.99 ± 0.09	2.44 ± 0.57	3.12 ± 0.49	10.42 ± 0.93	9.22 ± 1.65	14.38 ± 1.85
	Butanoic acid	0.09 ± 0.01	0.07 ± 0.00	0.04 ± 0.02	0.07 ± 0.04	0.08 ± 0.02	0.39 ± 0.05	0.24 ± 0.04	0.92 ± 0.05
	2-Methyl-pentanoic acid, anhydride	0.02 ± 0.01	0.04 ± 0.01	0.02 ± 0.01	0.71 ± 0.19	0.09 ± 0.02	3.41 ± 0.49	0.42 ± 0.02	6.41 ± 0.40
	Pentanoic acid	0.03 ± 0.01	0.03 ± 0.00	0.11 ± 0.03	0.80 ± 0.17	0.63 ± 0.16	13.99 ± 1.56	5.57 ± 0.87	32.40 ± 3.01
	Hexanoic acid	0.20 ± 0.04	0.18 ± 0.03	0.19 ± 0.00	3.22 ± 0.17	2.81 ± 1.05	87.63 ± 12.35	18.29 ± 5.10	222.06 ± 30.93
	Heptanoic acid	0.02 ± 0.01	0.03 ± 0.01	0.01 ± 0.00	0.03 ± 0.01	0.01 ± 0.00	1.70 ± 0.61	0.14 ± 0.11	6.36 ± 1.06
Alcohols									
	2-Methyl-1-propanol	0.34 ± 0.03	0.74 ± 0.07	1.96 ± 0.21	1.00 ± 0.15	1.23 ± 0.16	0.71 ± 0.08	1.10 ± 0.19	0.80 ± 0.05
	2-Methyl-1-butanol*	5.65 ± 0.64	15.39 ± 2.14	37.72 ± 5.82	30.87 ± 4.14	30.06 ± 7.86	22.82 ± 4.91	37.30 ± 9.27	31.58 ± 6.14
	3-Methyl-1-butanol*	4.90 ± 0.56	15.82 ± 1.85	34.80 ± 5.13	27.88 ± 3.56	26.96 ± 6.69	21.81 ± 4.51	33.88 ± 8.31	30.44 ± 5.72
	1-Butanol	2.74 ± 0.19	2.90 ± 0.25	8.21 ± 0.34	11.23 ± 0.16	12.59 ± 0.22	17.99 ± 1.06	23.17 ± 0.82	26.65 ± 1.51
	1-Pentanol	11.15 ± 1.00	12.57 ± 1.33	41.77 ± 2.73	85.16 ± 6.55	86.07 ± 14.30	137.89 ± 19.06	185.14 ± 25.71	276.04 ± 29.13
	2-Heptanol	0.20 ± 0.02	0.28 ± 0.06	0.21 ± 0.03	0.19 ± 0.02	0.44 ± 0.13	0.75 ± 0.31	1.38 ± 0.25	2.43 ± 0.20
	1-Hexanol	58.61 ± 2.49	68.65 ± 3.37	255.95 ± 20.00	293.91 ± 18.23	531.65 ± 100.30	512.00 ± 86.44	981.35 ± 109.08	1069.00 ± 71.16
	1-Octen-3-ol	0.38 ± 0.01	0.30 ± 0.01	1.72 ± 0.13	3.05 ± 0.30	3.27 ± 0.38	6.65 ± 1.43	9.48 ± 0.96	15.38 ± 1.25
	1-Heptanol	1.37 ± 0.03	2.03 ± 0.02	4.30 ± 0.28	14.25 ± 1.25	13.02 ± 2.31	60.03 ± 11.56	35.20 ± 2.27	116.44 ± 2.25
	2-Nonanol	0.04 ± 0.01	0.05 ± 0.01	0.03 ± 0.00	0.04 ± 0.00	0.06 ± 0.00	0.10 ± 0.01	0.18 ± 0.01	0.31 ± 0.02
	1-Octanol	0.33 ± 0.01	0.40 ± 0.01	1.10 ± 0.12	3.88 ± 0.29	4.27 ± 0.76	19.15 ± 3.45	13.18 ± 0.53	40.97 ± 0.22
	1-Acetate-1,2-propanediol	2.82 ± 0.16	0.28 ± 0.03	0.47 ± 0.04	0.34 ± 0.04	0.73 ± 0.11	0.55 ± 0.13	0.91 ± 0.28	0.76 ± 0.23
	1-Nonanol	0.75 ± 0.19	1.74 ± 0.29	1.20 ± 0.49	0.95 ± 0.07	2.20 ± 0.07	4.03 ± 0.55	6.19 ± 0.82	10.39 ± 0.22
	Benzyl alcohol	0.18 ± 0.08	0.73 ± 0.04	0.06 ± 0.00	0.12 ± 0.01	0.12 ± 0.01	0.20 ± 0.02	0.27 ± 0.02	0.39 ± 0.04
	Phenylethyl alcohol	0.17 ± 0.02	0.42 ± 0.01	0.17 ± 0.01	0.39 ± 0.01	0.29 ± 0.01	0.55 ± 0.00	0.50 ± 0.03	0.86 ± 0.10
	1-Chloro-2-propanol	690.66 ± 52.03	482.26 ± 35.62	205.67 ± 6.34	162.10 ± 1.39	178.62 ± 1.95	135.83 ± 15.14	237.97 ± 4.20	120.59 ± 5.85
	2-Chloro-1-propanol	4.73 ± 0.30	3.61 ± 0.33	1.29 ± 0.06	1.15 ± 0.05	0.99 ± 0.05	0.83 ± 0.02	1.33 ± 0.10	0.72 ± 0.03
Hydrocarbons									
	2,2,4,6-Pentamethyl-heptane*	11.39 ± 2.24	12.80 ± 1.83	5.28 ± 1.83	4.40 ± 0.74	5.50 ± 2.32	4.43 ± 1.98	4.25 ± 1.53	4.73 ± 0.74
	Decane*	49.05 ± 2.95	39.64 ± 8.09	13.83 ± 3.40	16.03 ± 6.66	21.65 ± 8.44	20.92 ± 13.95	35.22 ± 9.16	38.44 ± 6.25
	3-Ethyl-2-methyl-1,3-hexadiene	0.37 ± 0.04	0.20 ± 0.02	1.00 ± 0.13	4.45 ± 0.49	2.96 ± 0.77	9.39 ± 1.98	6.34 ± 0.70	18.18 ± 0.57
Aldehydes									
	Pentanal	0.25 ± 0.02	0.31 ± 0.15	1.26 ± 0.24	175.20 ± 25.56	14.48 ± 2.65	272.79 ± 48.87	33.93 ± 6.68	366.56 ± 52.17
	Hexanal	0.61 ± 0.17	0.40 ± 0.14	5.37 ± 0.44	287.21 ± 36.71	35.00 ± 14.64	399.58 ± 73.81	90.81 ± 13.79	573.63 ± 54.63
	Heptanal	0.41 ± 0.08	0.44 ± 0.05	1.29 ± 0.06	30.32 ± 3.80	6.71 ± 2.73	110.72 ± 23.22	22.48 ± 4.27	180.32 ± 9.55
	Octanal	0.13 ± 0.04	0.13 ± 0.03	0.57 ± 0.09	20.92 ± 2.53	5.94 ± 2.50	114.84 ± 26.66	21.30 ± 3.37	187.02 ± 1.97
	Nonanal	11.36 ± 6.31	7.83 ± 2.84	19.47 ± 1.88	56.58 ± 2.53	26.88 ± 1.15	125.69 ± 21.64	84.97 ± 18.83	224.28 ± 15.76
	(E)-2-Octenal	0.18 ± 0.03	0.20 ± 0.01	0.76 ± 0.09	4.61 ± 0.66	2.16 ± 0.47	9.18 ± 2.45	4.23 ± 0.53	18.12 ± 0.16
	Decanal	0.31 ± 0.11	0.27 ± 0.05	0.29 ± 0.02	0.98 ± 0.17	0.93 ± 0.09	6.02 ± 1.32	2.28 ± 0.24	12.29 ± 0.78
	Benzaldehyde	1.29 ± 0.02	1.57 ± 0.09	1.17 ± 0.03	1.83 ± 0.13	2.10 ± 0.12	3.36 ± 0.28	2.71 ± 0.07	4.11 ± 0.17
	(E)-2-Nonenal	0.20 ± 0.08	0.20 ± 0.02	0.14 ± 0.02	1.28 ± 0.12	0.21 ± 0.04	0.97 ± 0.28	0.52 ± 0.09	2.20 ± 0.03
	(Z)-2-Decenal	0.06 ± 0.02	0.04 ± 0.01	0.05 ± 0.01	0.26 ± 0.06	0.13 ± 0.03	1.64 ± 0.41	0.28 ± 0.03	3.30 ± 0.26
Furans									
	2-n-Butylfuran	0.22 ± 0.04	0.33 ± 0.03	0.75 ± 0.15	1.42 ± 0.33	2.05 ± 0.68	3.03 ± 0.83	4.04 ± 0.57	4.36 ± 0.73
	2-Pentylfuran	1.86 ± 0.11	1.96 ± 0.23	3.60 ± 0.39	6.23 ± 0.69	8.49 ± 2.15	12.60 ± 2.64	19.50 ± 2.42	21.94 ± 1.98
	2-Butyltetrahydrofuran	0.02 ± 0.01	0.02 ± 0.01	0.05 ± 0.01	8.50 ± 1.25	0.46 ± 0.27	12.37 ± 3.74	1.08 ± 0.24	15.02 ± 0.95

Table 2. Continued

Chemical class	Treatment	0 Control	0 MEx	2 Control	2 MEx	4 Control	4 MEx	6 Control	6 MEx
Oxirane	Pentyl-oxirane	0.10 ± 0.02	0.05 ± 0.01	0.48 ± 0.04	2.54 ± 0.43	1.14 ± 0.38	3.18 ± 0.99	3.53 ± 0.78	7.93 ± 1.18
Pyrazine	Methyl-pyrazine*	0.10 ± 0.01	0.12 ± 0.01	0.89 ± 0.06	1.00 ± 0.05	1.22 ± 0.08	1.38 ± 0.11	2.01 ± 0.05	1.97 ± 0.19
Ketones	2-Octanone	0.10 ± 0.01	0.65 ± 0.02	0.21 ± 0.04	1.46 ± 0.15	1.08 ± 0.27	8.26 ± 2.27	3.57 ± 0.74	19.84 ± 1.42
	1-Hydroxy-2-propanone	2.88 ± 0.27	2.72 ± 0.08	1.11 ± 0.13	1.75 ± 0.13	0.93 ± 0.21	1.83 ± 0.45	1.57 ± 0.20	1.92 ± 0.37
	1-Octen-3-one	0.28 ± 0.09	0.22 ± 0.02	1.10 ± 0.05	5.77 ± 0.48	2.76 ± 0.74	8.06 ± 1.96	6.67 ± 1.07	17.15 ± 1.57
	2-Nonanone	0.11 ± 0.02	0.12 ± 0.06	0.09 ± 0.02	0.54 ± 0.07	0.57 ± 0.18	9.02 ± 2.10	2.71 ± 0.28	22.09 ± 0.37
	3-Octen-2-one	0.37 ± 0.02	0.07 ± 0.01	1.80 ± 0.12	4.35 ± 0.39	4.57 ± 0.93	10.31 ± 1.99	12.34 ± 0.87	24.86 ± 1.13
	2-Decanone	0.05 ± 0.01	0.03 ± 0.01	0.06 ± 0.01	0.18 ± 0.03	0.17 ± 0.06	2.83 ± 0.62	0.83 ± 0.04	7.06 ± 0.17
	Acetoin	0.44 ± 0.05	0.51 ± 0.07	0.51 ± 0.08	3.34 ± 0.32	1.17 ± 0.10	3.33 ± 0.80	1.62 ± 0.69	2.29 ± 1.28
Lactones	Butyrolactone	0.57 ± 0.03	0.78 ± 0.03	0.25 ± 0.02	0.49 ± 0.02	0.42 ± 0.05	0.81 ± 0.13	0.63 ± 0.15	1.04 ± 0.23
	5-Ethyldihydro-2(3H)-furanone	0.21 ± 0.01	0.41 ± 0.02	0.55 ± 0.02	1.96 ± 0.19	2.08 ± 0.29	7.03 ± 0.95	5.13 ± 0.02	13.99 ± 0.45
	Dihydro-5-propyl-2(3H)-furanone	0.04 ± 0.00	0.06 ± 0.00	0.04 ± 0.00	0.17 ± 0.01	0.18 ± 0.02	0.99 ± 0.15	0.54 ± 0.01	2.22 ± 0.09
	5-Butyldihydro-2(3H)-furanone	0.02 ± 0.00	0.04 ± 0.00	0.05 ± 0.01	0.33 ± 0.03	0.28 ± 0.04	2.24 ± 0.42	0.91 ± 0.02	5.01 ± 0.26
	Tetrahydro-6-methyl-2H-pyran-2-one	0.02 ± 0.01	0.01 ± 0.01	0.03 ± 0.00	0.09 ± 0.01	0.09 ± 0.01	0.32 ± 0.03	0.19 ± 0.00	0.65 ± 0.04

Chemical class	Treatment	8 Control	8 MEx	10 Control	10 MEx	12 Control	12 MEx
Organic acids	Acetic acid	7.90 ± 0.66	11.17 ± 0.50	7.75 ± 0.49	11.06 ± 0.89	7.23 ± 0.50	20.88 ± 1.50
	Butanoic acid	0.36 ± 0.06	1.19 ± 0.08	0.34 ± 0.04	1.32 ± 0.19	0.29 ± 0.06	1.67 ± 0.11
	2-Methyl-pentanoic acid, anhydride	0.46 ± 0.35	5.00 ± 0.95	0.39 ± 0.24	2.97 ± 0.96	0.21 ± 0.08	3.67 ± 0.42
	Pentanoic acid	8.38 ± 2.97	45.01 ± 5.39	9.92 ± 2.59	44.85 ± 10.30	7.19 ± 2.01	46.95 ± 6.07
	Hexanoic acid	28.11 ± 11.87	269.79 ± 32.94	44.92 ± 14.67	262.42 ± 63.10	25.98 ± 4.75	257.48 ± 37.36
	Heptanoic acid	0.32 ± 0.09	10.00 ± 0.99	0.63 ± 0.23	14.67 ± 5.93	0.23 ± 0.02	11.35 ± 1.26
Alcohols	2-Methyl-1-propanol	0.74 ± 0.18	0.50 ± 0.05	0.54 ± 0.40	0.65 ± 0.12	0.84 ± 0.12	1.72 ± 0.26
	2-Methyl-1-butanol*	28.06 ± 6.39	26.15 ± 3.95	30.58 ± 7.59	30.02 ± 5.74	24.78 ± 4.86	35.95 ± 5.06
	3-Methyl-1-butanol*	24.94 ± 5.97	24.68 ± 3.52	28.50 ± 6.51	28.94 ± 5.11	23.03 ± 5.02	35.28 ± 4.71
	1-Butanol	19.36 ± 1.15	20.86 ± 0.93	18.14 ± 1.37	21.41 ± 1.33	14.82 ± 2.05	41.01 ± 2.10
	1-Pentanol	182.95 ± 31.95	256.44 ± 31.00	212.02 ± 44.90	243.87 ± 42.24	180.39 ± 36.53	307.65 ± 28.46
	2-Heptanol	2.24 ± 0.42	3.43 ± 0.56	2.94 ± 0.89	4.91 ± 0.88	2.94 ± 0.71	6.61 ± 0.31
	1-Hexanol	911.61 ± 123.18	1038.78 ± 119.15	1014.11 ± 169.49	1040.14 ± 137.34	850.56 ± 143.08	1140.50 ± 51.12
	1-Octen-3-ol	11.05 ± 1.65	19.02 ± 2.45	14.16 ± 2.79	18.67 ± 2.60	13.64 ± 2.45	18.55 ± 0.30
	1-Heptanol	45.48 ± 8.70	140.16 ± 16.37	54.85 ± 11.15	136.84 ± 20.87	46.32 ± 9.93	139.49 ± 6.08
	2-Nonanol	0.30 ± 0.03	0.61 ± 0.05	0.45 ± 0.09	1.01 ± 0.05	0.52 ± 0.09	1.34 ± 0.13
	1-Octanol	18.40 ± 3.14	53.13 ± 6.55	22.63 ± 4.06	58.54 ± 8.00	19.92 ± 3.99	56.24 ± 1.63
	1-Acetate-1,2-propanediol	0.88 ± 0.02	0.52 ± 0.02	0.57 ± 0.04	0.42 ± 0.02	0.54 ± 0.04	0.85 ± 0.16
	1-Nonanol	7.99 ± 0.87	15.11 ± 2.04	9.50 ± 1.27	18.85 ± 2.15	9.09 ± 1.03	18.69 ± 0.21

Table 2. Continued

Chemical class	Treatment	Month 8 Control	Month 8 MEx	Month 10 Control	Month 10 MEx	Month 12 Control	Month 12 MEx
	Benzyl alcohol	0.30 ± 0.03	0.35 ± 0.03	0.31 ± 0.02	0.40 ± 0.02	0.27 ± 0.02	0.45 ± 0.01
	Phenylethyl alcohol	0.65 ± 0.03	1.08 ± 0.08	0.75 ± 0.14	1.36 ± 0.09	0.91 ± 0.08	1.27 ± 0.24
Hydrocarbons	1-Chloro-2-propanol	139.01 ± 6.74	69.37 ± 4.00	99.69 ± 10.53	62.95 ± 5.59	94.31 ± 8.99	113.72 ± 2.54
	2-Chloro-1-propanol	0.95 ± 0.07	0.50 ± 0.05	0.70 ± 0.11	0.44 ± 0.09	0.70 ± 0.08	0.83 ± 0.08
	2,2,4,6,6-Pentamethyl-heptane*	10.18 ± 5.55	1.42 ± 0.74	7.70 ± 5.74	6.82 ± 3.42	10.03 ± 7.33	0.51 ± 0.07
	Decane*	50.49 ± 20.81	24.80 ± 12.68	39.84 ± 22.38	44.00 ± 25.85	43.14 ± 27.06	4.75 ± 1.22
	3-Ethyl-2-methyl-1,3-hexadiene	6.06 ± 1.58	17.16 ± 2.52	6.30 ± 1.74	12.92 ± 2.51	4.15 ± 1.21	12.50 ± 1.03
Aldehydes	Pentanal	23.52 ± 15.72	229.30 ± 18.31	19.62 ± 7.89	153.51 ± 36.41	6.63 ± 7.03	164.09 ± 27.54
	Hexanal	76.30 ± 40.19	394.40 ± 51.20	59.27 ± 30.84	234.76 ± 57.43	37.18 ± 16.19	192.16 ± 28.38
	Heptanal	26.54 ± 14.24	179.29 ± 26.67	21.98 ± 10.11	132.00 ± 32.44	15.68 ± 6.02	96.69 ± 11.96
	Octanal	26.82 ± 12.69	189.88 ± 25.48	24.17 ± 9.29	148.74 ± 31.57	12.93 ± 6.01	98.21 ± 9.40
	Nonanal	74.83 ± 9.95	233.48 ± 10.93	79.21 ± 5.32	222.77 ± 24.89	93.44 ± 19.51	135.15 ± 3.35
	(E)-2-Octenal	4.27 ± 1.16	16.81 ± 2.34	5.05 ± 1.30	10.54 ± 2.01	3.33 ± 0.95	7.68 ± 0.50
	Decanal	2.43 ± 0.68	14.52 ± 2.46	2.36 ± 0.59	13.03 ± 2.37	1.51 ± 0.40	9.18 ± 0.54
	Benzaldehyde	2.78 ± 0.35	3.79 ± 0.34	2.36 ± 0.30	3.60 ± 0.34	1.84 ± 0.18	3.70 ± 0.10
	(E)-2-Nonenal	0.50 ± 0.14	2.86 ± 0.37	0.75 ± 0.28	2.70 ± 0.50	0.70 ± 0.13	1.95 ± 0.13
	(Z)-2-Decenal	0.32 ± 0.12	3.43 ± 0.45	0.38 ± 0.10	2.55 ± 0.54	0.22 ± 0.07	1.59 ± 0.14
Furans	2-n-Butylfuran	3.51 ± 1.03	4.64 ± 1.08	2.88 ± 0.94	3.90 ± 0.98	2.04 ± 0.69	3.29 ± 0.30
	2-Pentylfuran	18.19 ± 4.28	23.86 ± 4.38	17.14 ± 4.53	22.50 ± 4.20	14.22 ± 3.64	20.91 ± 1.20
	2-Butyltetrahydrofuran	0.86 ± 0.48	8.19 ± 0.53	1.31 ± 0.66	3.92 ± 0.53	0.41 ± 0.18	2.13 ± 0.28
Oxirane	Pentyl-oxirane	3.83 ± 1.09	7.54 ± 1.41	4.49 ± 1.52	5.42 ± 1.26	3.32 ± 1.01	5.89 ± 0.63
Pyrazine	Methyl-pyrazine*	1.73 ± 0.21	1.54 ± 0.21	1.35 ± 0.28	1.34 ± 0.22	1.25 ± 0.19	1.70 ± 0.03
Ketones	2-Octanone	5.45 ± 1.97	28.72 ± 5.28	5.31 ± 1.92	25.85 ± 5.43	3.63 ± 1.62	24.60 ± 2.46
	1-Hydroxy-2-propanone	1.57 ± 0.08	0.97 ± 0.05	0.70 ± 0.09	0.70 ± 0.18	0.57 ± 0.05	1.83 ± 0.41
	1-Octen-3-one	7.64 ± 2.37	17.32 ± 2.77	8.62 ± 2.42	12.45 ± 2.41	6.63 ± 1.82	10.48 ± 1.06
	2-Nonanone	4.68 ± 1.67	36.50 ± 6.29	5.36 ± 1.66	36.64 ± 7.55	4.33 ± 1.54	30.74 ± 2.42
	3-Octen-2-one	14.11 ± 2.32	26.44 ± 3.48	16.34 ± 2.78	23.15 ± 3.42	11.98 ± 1.44	21.14 ± 1.00
	2-Decanone	1.38 ± 0.48	12.36 ± 2.13	1.58 ± 0.50	13.75 ± 2.98	1.45 ± 0.61	11.80 ± 0.98
	Acetoin	0.86 ± 0.23	1.11 ± 0.07	0.54 ± 0.12	0.96 ± 0.07	0.48 ± 0.02	1.63 ± 0.40
Lactones	Butyrolactone	0.56 ± 0.02	0.83 ± 0.01	0.45 ± 0.07	0.80 ± 0.05	0.47 ± 0.04	1.64 ± 0.24
	5-Ethyldihydro-2(3H)-furanone	6.36 ± 1.45	15.37 ± 1.89	6.57 ± 1.44	14.49 ± 2.35	5.74 ± 1.32	16.58 ± 0.63
	Dihydro-5-propyl-2(3H)-furanone	0.74 ± 0.18	3.11 ± 0.47	0.89 ± 0.20	3.81 ± 0.70	0.88 ± 0.18	3.83 ± 0.21
	5-Butyldihydro-2(3H)-furanone	1.29 ± 0.38	6.65 ± 1.06	1.64 ± 0.40	8.27 ± 1.62	1.65 ± 0.35	8.16 ± 0.33
	Tetrahydro-6-methyl-2H-pyran-2-one	0.25 ± 0.07	0.77 ± 0.10	0.24 ± 0.05	0.76 ± 0.16	0.21 ± 0.06	0.80 ± 0.06

*Not significantly different.

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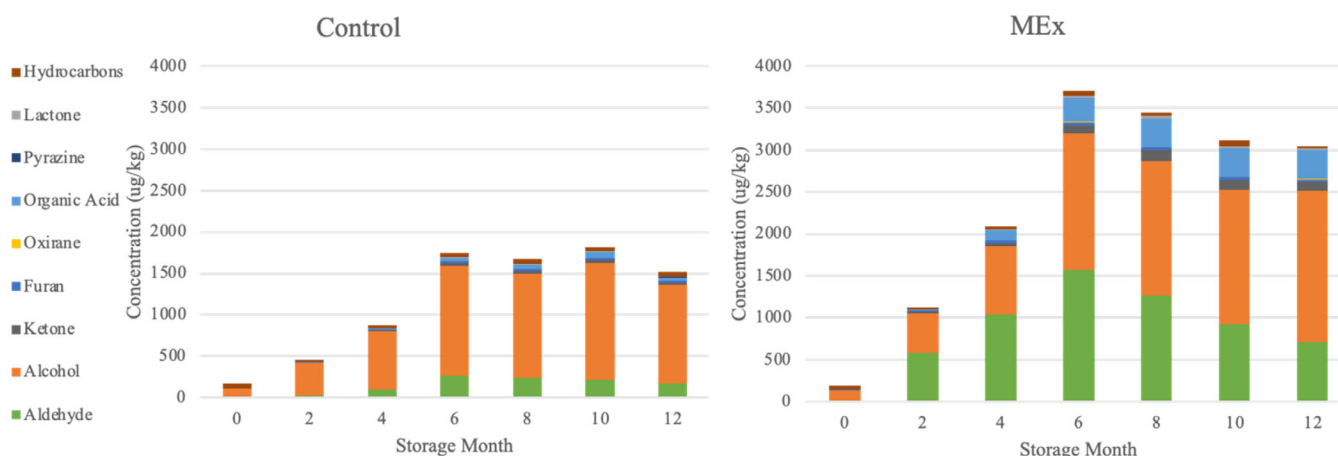
Figure 1. Concentration sum of each headspace chemical classes shown in Table 2 measured in control and MEx (exposed to moisture and subsequently dried 0samples at storage month 0, 2, 4, 6, 8, 10, and 12. 1-Chloro-2-propanol and 2-chloro-1-propanol were excluded from the alcohol concentration sum.
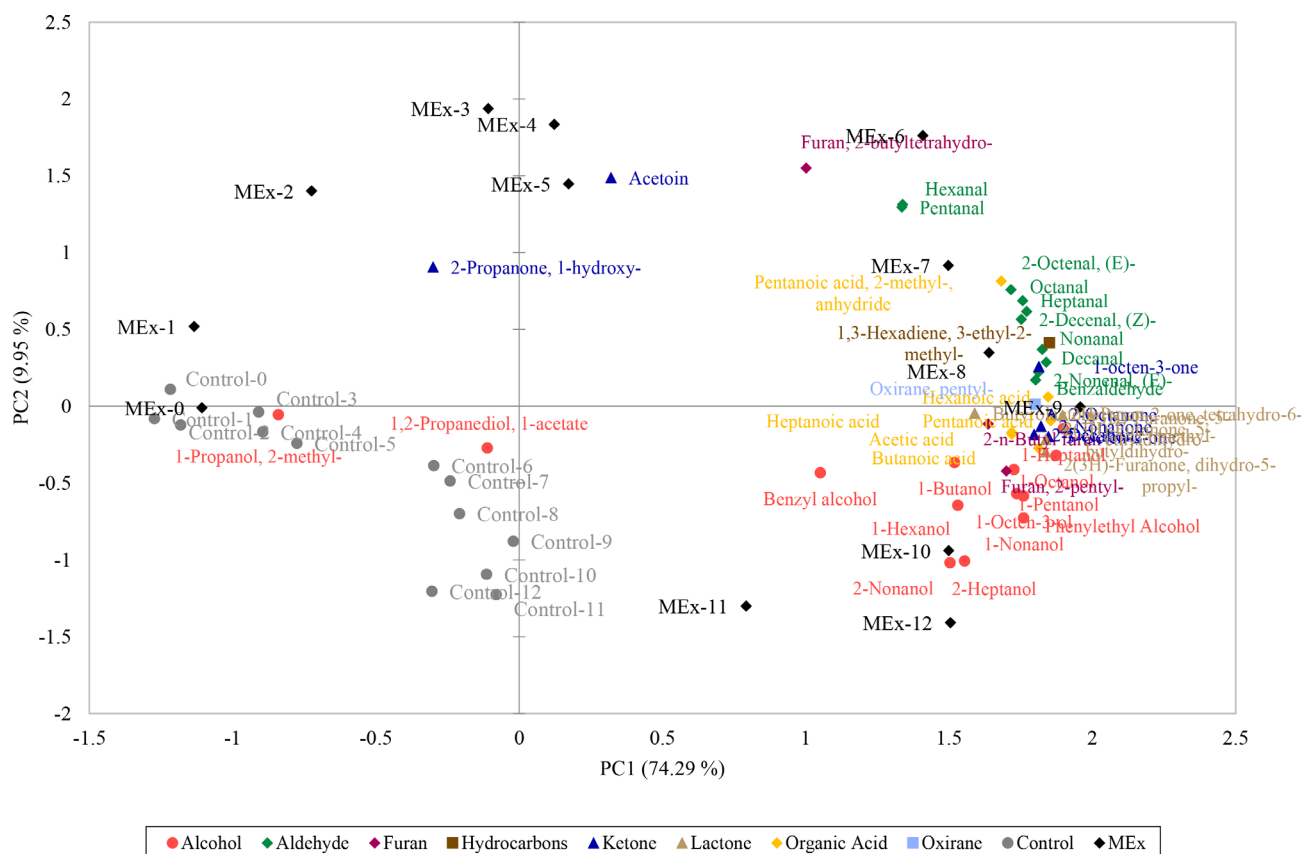

Figure 2. Biplot of principal component analysis (PCA) on 46 headspace volatile compounds determined by headspace solid-phase microextraction gas chromatography–mass spectrometry for almonds that were exposed to moisture and subsequently dried (MEx) and control almonds, stored up to 12 months of accelerated storage. The first two dimensions describe 84.24% of the variables.

shown to change the microstructure of almonds, creating extra-cellular pores that allow oxygen exposure and increasing lipase contact with oleosomes.[27] The increase of FFAs after 7 months of storage in MEx almonds correlates with an increase in organic acids (i.e., hexanoic acid, heptanoic acid, and pentanoic acid) from secondary lipid oxidation (Table 2). Over 12 months of storage, FFAs never exceeded the industry rejection standard of 1.5%.

PV is a common marker used to monitor oxidative rancidity in the nut and oil industries. The PV values were consistently higher

in the MEx almonds relative to the controls beginning at 1 month (Table 1). The PVs did not exceed the industry rejection standard of 5 mEq kg^{-1} for either control or MEx samples throughout the 12 months of storage. The PVs reach maximum levels at 5 months of storage for MEx almonds (2.01 $\pm$ 0.11 mEq kg^{-1}) and 8 months of storage for the control (1.39 $\pm$ 0.09 mEq kg^{-1}). A decrease in PVs results from the decomposition of hydroperoxides into secondary lipid oxidation products (i.e., aldehydes).[28] MEx almonds have higher PVs and earlier maximum values, suggesting an
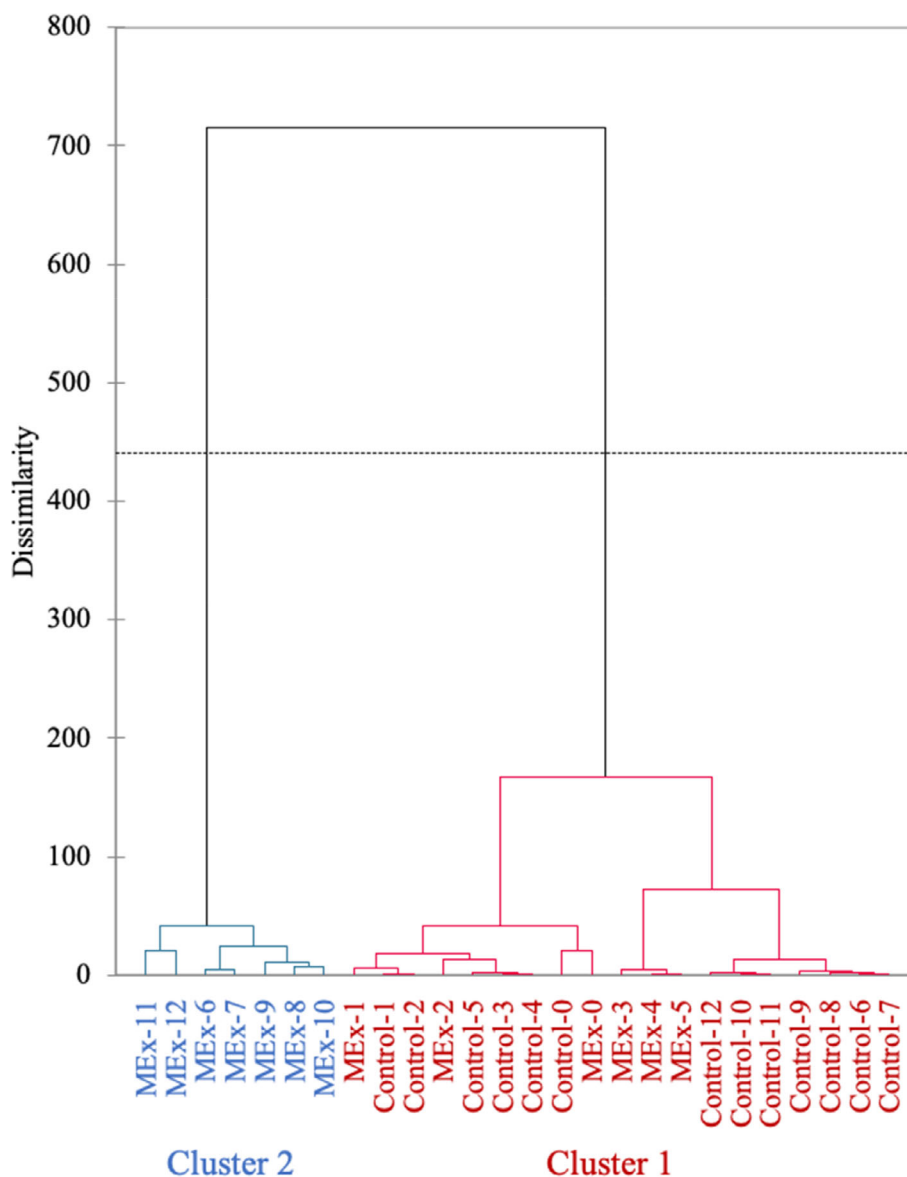
Figure 3. Dendrogram obtained from cluster analysis using the 46 headspace volatile compounds in PCA on the moisture-exposed sample and control, with the numbers indicating storage month.

acceleration of lipid oxidation with respect to controls. Although moisture exposure has been shown to increase lipoxygenase activity and lead to an increase of linoleic hydroperoxide formation,[29] this effect was not observed herein as the initial PVs were below the limit of detection for both MEx and control almonds. It is more likely that the increase in PV observed in the MEx almonds is due to low heat-induced disruption of the microstructure of almond kernels.[27] The PVs measured were comparable with other studies of raw almonds stored under different temperatures and relative humidity, with a PV ranging between 0.5 and 2 mEq kg^{-1} during 1 year of storage.[30,31]

These results suggest that the drying step – an industry practice after moisture exposure – has the greatest influence on lipid oxidation in almonds. Although the mechanical drying of 'wet' almonds can improve processing and decrease concealed damage in roasted almond products,[4,19] the process accelerates lipid oxidation and decreases raw almond shelf life. Pleasance et al.[14] proposed a consumer assessment prediction model for raw

almonds using lipid oxidation markers. The model reported that PVs and FFAs are negatively associated with the overall assessment.[14] The higher level of PVs and FFAs in MEx almonds suggest that these almonds will have a shorter shelf life than the control. However, both control and MEx almonds have lipid oxidation measurements below industry thresholds, indicating shelf stability up to 12 months in this study.

SPME headspace volatiles
A total of 53 volatile compounds belonging to the chemical classes of organic acids, alcohols, hydrocarbons, aldehydes, furans, oxirane, pyrazine, ketones, and lactones were identified in the headspace (Table 2). Two chlorinated alcohols (1-chloro-2-propanol and 2-chloro-1-propanol) were identified in the headspace in both treatments (Table 2). These propylene chlorohydrins are often present in foods that have undergone propylene oxide pasteurization such as almonds.[32,33] These propylene chlorohydrins are not considered genotoxic and have been observed in other studies of

almonds, with levels highest at the start of storage and decreasing with time.[11,34,35] Hexanol, which has been reported to be a major headspace volatile detected in Nonpareil almonds,[36] had the highest concentration in the headspace. The hexanol concentration found in MEx almonds was higher ($P > 0.05$) than controls when comparing within each month (Table 2). Levels of benzaldehyde, a key contributor to raw almond aroma, were higher in the MEx almonds relative to the controls. Benzaldehyde is a hydrolysis product of amygdalin, which ranges from 2.16 to 157.44 mg kg^{-1} in sweet commercial almond varieties.[37,38] Adding water to ground raw almonds during extraction was shown to increase levels of benzaldehyde measured in the headspace due to the hydrolysis of amygdalin.[36,37] The postharvest moisture exposure may have contributed to the hydrolysis of amygdalin and the higher concentration of benzaldehyde found in MEx almonds. Hexanal is a common quality indicator of oils as it results from the oxidation of linoleic acid and is associated with off-flavor in almonds.[39] Hexanal levels were significantly higher in MEx almonds than in control almonds at each month (Table 2), suggesting a higher degree of linoleic oxidation. The summed concentration of each class of volatile compound (e.g., organic acid, aldehyde) was plotted over the storage time (Fig. 1). The propylene chlorohydrins were not included in the summed data as they are an artifact from the pasteurization process. MEx almonds display higher total volatile concentrations relative to the control samples, with higher levels of aldehydes, alcohols, and organic acids. Higher levels of aldehydes, alcohols, and organic acids are associated with lipid oxidation and are observed in almonds.[11,34]

To better understand the possible relationship between the headspace volatiles developed during storage, a PCA analysis was performed on 46 of the 53 volatile compounds measured. ANOVA was performed on all the measured volatiles and indicated that 2,2,4,6,6-heptane, decane, 2-methyl-1-butanol, 3-methyl-1-butanol, and methyl-pyrazine were not significantly different between MEx almonds and controls ($P > 0.05$). Hence all these volatiles were excluded from the PCA analysis. 1-Chloro-2-propanol and 2-chloro-1-propanol were also excluded from the PCA analysis as they were considered artifacts generated during pasteurization. Two principal components were obtained which explain 84.24% of the variation (Fig. 2). Along PC1 (explaining 74.29% of the variance), almond samples separate into two major groups: all control samples and the 0- to 5-month MEx samples on the left, and 4- to 12-month MEx samples on the right, which are mainly driven by lipid oxidation volatiles, including 2-octanone, 1-heptanol and 1-octanol. This grouping was supported by agglomerative hierarchical clustering (Fig. 3), revealing two clusters based on dissimilarity of the headspace volatile profiles: cluster 1 (i.e., control 0–12 and MEx 0–5) and cluster 2 (i.e., MEx 6–12). Within cluster 1, control almonds after 6 months of storage and MEx almonds between 3 and 5 months of storage share similar headspace profiles. The similarity in headspace profile reflects the similarity in lipid oxidation development, suggesting that MEx almonds have a shorter shelf life than control. The separation of cluster 2 is driven by the majority of the headspace volatiles. Aldehydes found along PC1 (e.g., pentanal, heptanal, octanal, nonanal, decanal, (E)-2-octenal, (Z)-2-decenal) that correlates with cluster 2 have been reported to be products formed from the oxidation of oleic and linoleic acid through β-scission.[39] Organic acids (i.e., butanoic acid, pentanoic acid, and hexanoic acid) also correlated with cluster 2 along PC1. Most of these volatiles have been reported to be tertiary lipid oxidation products of the major unsaturated acids found in almonds.[39] Control and MEx samples separated along PC2 across storage time (Fig. 2), which is

driven by acetoin (i.e., 3-hydroxybutan-2-one) and hexanal. Acetoin is a volatile formed through sugar degradation[40] and is reported as a Maillard reaction product found in roasted almonds.[11,34,35] On the other hand, hexanal is a lipid oxidation product of linoleic acid. The correlation between higher levels of acetoin and hexanal found in MEx almonds suggested that postharvest moisture exposure followed by low-heat drying accelerates the Maillard reaction and lipid oxidation in almonds.

CONCLUSIONS

Herein we demonstrate that short-term moisture exposure followed by low-temperature drying increases markers of lipid oxidation. Although mechanical drying can be used to improve processing and decrease concealed damage in roasted almond products, it accelerates lipid oxidation and significantly decreases raw almond shelf life (up to 12 months). This information can help processors better control inventories and target these nuts for shorter storage to reduce food waste and product loss.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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