Nectarine volatilome response to fresh-cutting and storage

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I don't believe they have been able to show that any specific cultivar is better for fresh cut treatment based on their data.

Mendoza-Enano, M. L., Stanley, R., & Frank, D. (2019). Linking consumer sensory acceptability to volatile composition for improved shelf-life: A case study of fresh-cut watermelon (Citrullus lanatus). *Postharvest Biology and Technology, 154*, 137-147.

Highlights

- Nectarine volatilome investigation by chromatographic and direct injection analysis.
- Fresh-cut processing modifies the VOC profile of nectarine
- Fresh-cut nectarines emit off-flavours without any visual deterioration symptoms.
- Development of a VOC biomarkers array to predict fresh-cut nectarine storability.

Nectarine volatilome response to fresh-cutting and storage

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Abstract

The offer of fresh-cut peaches and nectarines represents a valid alternative for stone fruit commercialization and matches the increasing market demand of ready-to-eat (RTE) products.

In this study we explored the effect of fruit processing and storage on the volatilome of RTE fresh-cut nectarine. Fruit of three cultivars were sliced and packed in an industrial line and stored for 5 d at 5 °C. Volatile organic compound (VOC) evolution was assessed daily in both intact and processed fruit by an exhaustive untargeted analysis, performed by proton transfer reaction-time of flight-mass spectrometry (PTR-ToF-MS) and solid phase microextraction- gas chromatography-mass spectrometry (SPME/GC-MS).

Fresh-cut processing induced a major variation in nectarine volatilome depending on genetic differences and storage. This volatilome amelioration may be considered as an applicable strategy to enhance peach and nectarine perceived quality. Moreover, results of this study allowed the detection of a set of possible biomarkers enabling the selection of the best nectarine genotypes for processing and the prediction of the product shelf life based on the release of flavours and off-flavours.

1. Introduction

The market supply of ready-to-eat (RTE) fresh-cut fruit has increased over the last years in response to the rising demand of convenience and ready-to-use (RTE) products more aligned to the modern life-style (Cavaiuolo et al., 2015; Denoya et al., 2017). Thus, RTE fresh-cut stone fruit may represent a valuable alternative to improve the marketability of peach and nectarine (Ceccarelli, 2018), which consumption has decreased over the last decades, mostly due to the poor flavour characteristics perceived by consumers (Belisle et al., 2017; Cantin et al., 2009). However, achieving high quality fresh-cut peaches and nectarines still represents a technological challenge for the industry.

Fresh-cut processing consists of two main mechanical operations, slicing and coring, that are critical to determine the potential shelf life of the fresh-cut product (Soliva-Fortuny & Martín-Belloso, 2003). These operations induce the disruption of the cell compartmentalization releasing lytic enzymes and metabolites that trigger tissue degradation. Furthermore, wound stress, caused by cutting and slicing, may accelerate the progression of fruit maturity and senescence, enhanced by an increase of ethylene emission (Varoquaux & Wiley, 2017). The increased fruit perishability, flesh softening and surface browning are the main negative consequences of fruit fresh-cutting (Artés & Gómez, 2006) and the major impediment for the successful commercialization of RTE fresh-cut fruit (Eissa et al., 2006). Unfortunately, in the fresh-cut industry, it is still generally assumed that "if it looks good, it tastes good" (Beaulieu & Baldwin, 2002). Inconsistent or unsatisfactory aroma and flavour quality may be one of the main reasons of the slow growth for fresh-cut fruit market (Mendoza-Enano et al. 2019).

Aroma is considered a key component in determining peach consumer satisfaction (Wang et al., 2009; Belisle et al., 2017). It relies on the complex interaction of several VOC classes, including esters, C6 aldehydes, terpenes, alcohols, and lactones (Wang et al., 2009; Yang et al., 2009; Eduardo et al., 2010). The latter molecular class is reported to include some of the major contributors of the peach and nectarine aroma (Lavilla et al. 2002). Peach and nectarine aroma may easily deteriorate during cold storage (Zhang et al., 2011; Cano-Salazar et al., 2013; Ceccarelli et al., 2018) due to the insurgence of off-flavour compounds, mainly induced by chilling injury and fermentative metabolism.

Several studies were performed to extend the shelf life of processed peaches and nectarines. Most of these studies were focused on the processing suitability of different cultivars, (Giné Bordonaba et al., 2014; Denoya et al., 2017), heat treatments (Koukounaras et al., 2008), application of edible coatings (Pizato et al., 2013), inactivation of enzymatic activities by high pressure processing (Denoya et al., 2015; Denoya et al., 2016), low temperature storage, and modified atmosphere packaging (MAP) (Koukounaras et al., 2008). However, no thorough investigation has been conducted so far on the development of the flavour and off-flavour generation during processing and storage of RTE fresh-cut peaches. Packed fruit may easily ferment when the O_2 level is below an optimal concentration (Solomos, 1994), thus inducing the synthesis of ethanol, acetaldehyde, and acetic acid.

Therefore, a thorough characterization of VOC emission evolution during storage and ripening is important to monitor and predict the quality of RTE fresh-cut peaches and nectarines (Ceccarelli, 2018). To achieve these results, a deeper understanding of the influence of peach and nectarine varieties, harvest conditions, maturity, storage and shelf life with regard to flavour development is required (Colantuono et al., 2012).

In the present study, the volatilome of RTE fresh-cut nectarines was assessed daily, during refrigerated storage, by an exhaustive untargeted VOC analysis, performed by two complementary methods: PTR-ToF-MS (proton transfer reaction-time of flight-mass spectrometry) and SPME/GC-MS (solid phase microextraction- gas chromatography-mass spectrometry). The aim was to explore the effect of fruit processing (slicing, coring and packing) on VOC development during storage in relation to cultivar differences and to determine a pool of putative volatile biomarkers useful to predict the RTE fresh-cut product deterioration and its end-life.

2. Material and methods

2.1 Plant material and fruit segregation into homogeneous group

Nectarines (*Prunus persica*, L. Batch) from three cultivars, 'Western Red' (WR), 'August Red' (AR) and 'Morsiani 60' (M60), were collected from a commercial packhouse located in Faenza, Emilia Romagna, Italy.

Fruit of each cultivar was sorted into homogeneous batches, based on the fruit maturity stage, to minimise fruit biological variability. Maturity was determined with the DA-Meter (TR, Forlì, Italy), a VIS-spectrometer that measures non-destructively the chlorophyll-a content in the fruit flesh and peel (Farneti et al., 2015a). Maturity stages were expressed as Index of Absorbance Difference (I_{AD}) ranging from 0.0 to 2.0 with the lower values indicating a more advanced fruit maturity (Bonora et al., 2014). In this study, only fully ripe nectarines (I_{AD} between 0.6 and 0.4) were considered.

2.2 Experimental design

Sixty nectarines per each cultivar were collected and sorted into two batches of 30 fruit each. The first batch was fresh-cut processed, whilst the second was maintained intact. Both RTE fresh-cut and intact nectarines were stored at 5 °C for 5 d to simulate the refrigerated storage. Five biological replicates for both intact and fresh-cut fruit were daily analysed to assess quality traits and VOC emission by PTR-ToF-MS. For each cultivar, SPME/GC-MS analysis was carried out on a pooled sample at day 0, 2 and 4 to validate and support the identification of compounds in PTR-ToF-MS analysis.

Nectarines were processed in an industrial line commercially used to produce fresh-cut pome and stone fruit (Macè s.r.l., Ferrara, Italy) according to commercial standards. Prior to fresh-cut processing, each fruit was washed and dipped for 2 min in a solution of water and peracetic acid to eliminate skin contaminants. Slicing was performed by pushing the fruit longitudinally with a pneumatic plunger through a sharp corer, producing eight symmetrical slices of homogeneous thickness. Fruit core was automatically discarded whilst slices, transported by a conveyor belt, were soaked for 1 min in an antioxidant solution (2.5 g L^{-1} ascorbic acid, 2.5 g L^{-1} sodium ascorbate) to prevent surface browning. Twenty slices, of approximately 10 g each, were automatically packed into commercial polypropylene boxes heat-welded with a micro-perforated (30 µm) plastic film. Intact and fresh-cut fruit was then maintained at 5 °C until analysis.

2.3 Surface browning and colour assessment

Surface browning and flesh colour of nectarine wedges was evaluated with a Minolta CR-400 chromameter (Konica Minolta,Tokyo, Japan), using the $L^*a^*b^*$ parameters under the CIE standard illuminant D65 (Caceres et al., 2016). At each assessment, intact fruit were sliced, and fruit flesh colour was immediately measured to evaluate the colour evolution during fridge conservation. Chroma was derived from the above-mentioned chromatic parameters. Surface browning was estimated as browning index (BI), a parameter closely related to PPO (Polyphenol oxidase) activity (Denoya et al., 2017) and calculated as following (Mohammad et al., 2008):

eq.1: $$BI = 100 \times \frac{(x - 0.31)}{0.172} \text{ where } x = \frac{(a + 1.75L)}{(5.654L + a - 3.012b)}$$

2.4 Sample preparation for VOC analysis

Intact and fresh-cut nectarines, including the skin, were immediately frozen in liquid nitrogen and ground with a stainless-steel analytical mill (IKA, Staufen, Germany). For both PTR-ToF-MS and SPME/GC-MS analysis 1 g of powdered frozen fruit was transferred into a 20-mL glass vial sealed with 18 mm PTFE/silicon septa (Agilent Technologies, Santa Clara, USA). 1 mL of antioxidant solution (400 g L^{-1} of sodium chloride, 5 g L^{-1} of ascorbic acid, and 5 g L^{-1} of citric acid) was added to each vial to prevent tissue oxidation (Farneti et al., 2014). Samples were kept at -80 °C before being analysed.

2.5 VOC analysis by PTR-ToF-MS

Direct injection VOC measurement of nectarine tissue was performed in five replicates with a commercial PTR-ToF-MS 8000 apparatus (Ionicon Analytik GmbH, Innsbruck, Austria) according to the set-up described by Farneti et al., 2014. The drift tube conditions were the following: 110 °C drift tube temperature, 2.30 mbar drift pressure, 550 V drift voltage. This leads to an E/N ratio of about 140 Townsend (Td) (E corresponding to the electric field strength and N to the gas number density; 1 Td = 10^{-17} V cm^2). The sampling time per channel of ToF acquisition was 0.1 ns, amounting to 350,000 channels for a mass spectrum ranging up to *m/z* = 400. Every single spectrum is the sum of about 28.600 acquisitions lasting 35 μs each, resulting in a time resolution of 1 s. Sample measurements were performed in 60 cycles resulting in an analysis time of 60 s/sample.

Each measurement was conducted automatically after 20 min of sample incubation at 40 °C by using an adapted GC autosampler (MPS Multipurpose Sampler, GERSTEL) and it lasted for 2 min (Capozzi et al., 2017).

The analysis of PTR-ToF–MS spectral data proceeded as follows. Count losses due to the ion detector dead time were corrected off-line via a methodology based on Poisson statistics. To reach a good mass accuracy (up to 0.001 Th), internal calibration was performed according to a procedure described by Cappellin et al. (2011a). Noise reduction, baseline removal and peak intensity extraction were performed according to Cappellin et al. (2011b), using modified Gaussian distributions to fit the peaks. Absolute headspace VOC concentrations expressed in μg Kg^{-1} headspace for intact and processed fruit, were statistically analysed according to ANOVA and Tukey's Honestly Significant Difference (HSD) test ($P< 0.05$) when necessary.

2.6 VOC analysis by SPME/GC-MS

Vials, containing the powdered sample and the antioxidant solution, were equilibrated at 40 °C for 10 min with constant stirring. A 2 cm solid-phase microextraction fibre (DVB/CAR/PDMS, Supelco, Bellefonte, USA) was exposed for 30 min to the vial headspace. The trapped compounds by SPME were analysed with a GC interfaced with a mass detector operating in electron ionization (EI) mode (internal ionization source; 70 eV) with a scan range of *m/z* 33 to 350

(GC Clarus 500, PerkinElmer, Norwalk, USA). Separation was carried out in an HP-INNOWax fused silica capillary column (30 m, 0.32-mm ID, 0.5-µm film thickness; Agilent Technologies, Santa Clara, USA). The initial GC oven temperature was 40 °C rising to 220 °C at 4 °C min^{-1}, the temperature of 220 °C was maintained for 1 min, then increased at 10 °C min^{-1} until it reached 250 °C, which was maintained for 1 min. The carrier gas was helium at a constant column flow rate of 1.5 mL min^{-1}. Semi-quantitative data were expressed as area units. Compounds identification was based on mass spectra matching with the standard NIST/EPA/NIH (NIST 14) and Wiley 7th Mass Spectral Libraries, and linear retention indices (LRI) compared with the literature. LRI were calculated under the same chromatographic conditions after injection of a C7–C30 n-alkane series (Supelco, Bellafonte, USA).

2.7 Data analysis

The array of masses detected by PTR-ToF-MS was reduced by applying noise and correlation coefficient thresholds. In the first case, peaks not significantly different from blank samples were removed (Farneti et al., 2015b). Regarding correlation coefficient thresholds, peaks having over 99 % correlation were excluded as putative isotopes of monoisotopic masses (Farneti et al., 2017).

Data analysis was performed with R.3.3.3 software using internal functions and the external packages “mixOmics” and “heatmap3” for multivariate statistical analysis (PCA and hierarchical clustering), “Agricolae” for ANOVA and post hoc comparisons, and “ggplot2” for graphic representations. Multivariate statistical analysis was performed on log transformed and centred data. The estimation of the optimal number of clusters was computed by performing silhouette and gap statistics.

3. Results and discussion

3.1 Untargeted nectarine volatilome assessment

The characterisation of nectarine volatilome by gas chromatographic and direct injection mass spectrometric analysis allowed the detection of all the main VOCs responsible for nectarine aroma (Tab. 1 and Tab. 2), reported in recent literature both with HS-SPME/GC-MS (Brizzolara et al., 2018) and PTR-ToF-MS (Bianchi et al., 2017) analysis.

The headspace VOC analysis of both intact and fresh-cut fruit, assessed in the three nectarine cultivars, allowed the detection of 73 compounds (Tab. 1), only one of which was not identified. Alcohols are the most representative VOC class in terms of number of compounds (14), followed by esters (13), aldehydes (10), monoterpenes (10), acids (7), lactones (6), ketones (5), hydrocarbons (2), methylphenols (2), norisoprenoids (1) and sesquiterpenes (1). Concerning VOC relative concentration (STab. 1), aldehydes (primarily hexanal, pentenal, and (E)-2-hexenal) were the most representative class in intact nectarine fruit, representing 50.6 % of total VOC profile of WR, 69.9 % for AR, and 92.2 % for M60. Monoterpenes, for the most linalool, were the second representative group accounting for 21.2 % of the total VOC content of WR, 2.5 % for AR and 1.6 % for M60. Esters (for the most hexyl acetate, isoamyl acetate and butyl acetate) were mostly representative in AR, accounting for 9.9 % of the total volatiles and 5.5 % in WR. For M60 the total ester concentration was only 0.9 % of the total VOCs. Alcohols (mostly 1-pentanol) accounted for about 7.2 % of the total VOC profile of AR and 7.7 % for WR whilst only 1.6 % for M60. The highest fraction of lactones was composed by γ-hexalactone and γ-decalactone and represented 4.7 % of the VOC profile of WR, 1.2 % for AR and 1 % for M60. Ketones concentration (for the most 1-octen-3-one and 6-methyl-5-hepten-2-one) represented 3.3 % of the WR volatiles, 2.8 % of AR and 0.8 % of M60. Sesquiterpenes, represented only by nerolidol, were mostly detected in WR, accounting for 1.8 % of the cultivar's VOC profile, while this class only amounted to 0.03 % in AR and it was not detected in M60. Hydrocarbons such as toluene and styrene accounted for 1.9 % of the total volatiles of AR, 1.3 % for WR and 0.45 % for M60. Acids (for the most isovaleric acid and pentanoic acid) accounted for 0.9 % of the VOC profile for WR and AR whilst 0.36 % for M60. β-damascenone (norisoprenoids) accounted for 0.1 % of the VOC profile in WR, 0.04 % in AR, and 0.03 % in M60.

Table 1. Volatile compounds detected by SPME/GC-MS immediately after harvest. Values are reported as percentage of total peak area per chromatogram.

					Western Red		August Red		Morsiani 60	
	ID	Formula	KI Calc	KI NIST	Intact	Processed	Intact	Processed	Intact	Processed
ACIDS										
Acetic Acid	Ac_1	$C_2H_4O_2$	1562	1449	0.11	0	0.19	0.02	0.05	0.07
Isovaleric Acid	Ac_2	$C_5H_{10}O_2$	1748	1666	0.23	0.23	0.25	0.12	0.16	0.25
Butanoic Acid	Ac_3	$C_4H_80_2$	1821	1625	0.07	0.05	0.04	0.01	0.01	0.01
Pentanoic Acid	Ac_4	$C_5H_{10}O_2$	1922	1733	0.3	0.29	0.2	0.07	0.1	0.12
2-Ethyl Hexanoic Acid	Ac_5	$C_8H_{16}O_2$	2003	1960	0	0	0.01	0	0	0
Hexanoic Acid	Ac_6	$C_6H_{12}O_2$	2025	1846	0.09	0.05	0.07	0.02	0.02	0.02
Heptanoic Acid	Ac_7	$C_7H_{14}O_2$	2198	1950	0.09	0.04	0.11	0.02	0.02	0.02
Total (%)					**0.89**	**0.66**	**0.87**	**0.26**	**0.36**	**0.49**
ALCOHOLS										
3-Pentanol	Al_1	$C_5H_{12}0$	1125	1110	0.18	0.09	0.19	0.01	0.04	0.03
1-Butanol	Al_2	C_4H_9OH	1162	1142	0.23	0.09	0.04	0.01	0.02	0.02
2+3-Methyl-1-Butanol	Al_3	$C_5H_{12}O$	1225	1208+1209	0.12	0.27	0.09	0.05	0.06	0.12
1-Pentanol	Al_4	$C_5H_{12}O$	1266	1250	2.59	2.04	1.43	0.28	0.36	0.17
Hexanol	Al_5	$C_6H_{14}0$	1366	1355	0.41	0.46	0.43	0.19	0.11	0.34
3-Octanol	Al_6	$C_8H_{18}0$	1404	1393	0	0.29	0.01	0	0	0
(Z)-2-Hexen-1-ol	Al_7	$C_6H_{12}0$	1417	1416	0.04	0.19	0.06	0.16	0.04	0.08
1-Octen-3-ol	Al_8	$C_8H_{16}0$	1460	1450	0.57	0.39	0.41	0.12	0.18	0.11
1-(2-Methoxy-1-methylethoxy)-2-propanol	Al_9	$C_7H_{16}O_3$	1486	1478	0.05	0.05	0.43	0	0.02	0.05
2-Ethyl-1-Hexanol	Al_10	$C_8H_{18}0$	1497	1491	0.34	0.49	0.49	0.24	0.09	0.2
1-(2-methoxypropoxy)-2-propanol	Al_11	$C_7H_{16}O_3$	1526	1532	0.31	0.21	1.5	0.1	0.09	0.2
1-Octanol	Al_12	$C_8H_{18}0$	1565	1557	0.37	0.43	0.34	0.2	0.15	0.08
2-phenyl isopropanol	Al_13	$C_9H_{12}0$	1763	1773	0.49	0.32	0.55	0.11	0.14	0.09
Phenol	Al_14	C_6H_60	2010	2000	0.5	0.33	0.5	0.09	0.12	0.09
Total (%)					**6.2**	**5.65**	**6.47**	**1.56**	**1.42**	**1.58**
ALDEHYDES										
Butanal	Ad_1	C_4H_80	902	877	0.52	2.26	0.33	0.14	0.12	0.35
Pentanal	Ad_2	$C_5H_{10}0$	980	979	11.83	6.99	8.89	1.13	2	0.81
Hexanal	Ad_3	$C_6H_{12}0$	1094	1083	18.33	7.11	22.78	6.98	28.14	29.42
(2E)-Hexenal	Ad_4	$C_6H_{10}0$	1230	1216	5.63	9.8	29.48	19.29	55.62	49.93
Octanal	Ad_5	$C_8H_{16}0$	1300	1289	2.69	1.82	1.82	0.35	1.48	0.41
2-Heptenal	Ad_6	$C_7H_{12}0$	1330	1323	4.13	2.38	2.57	0.28	1.09	0.59
Nonanal	Ad_7	$C_9H_{18}O$	1399	1391	3.59	2.24	1.37	0.34	2.02	0.66
(E)-2-Octenal	Ad_8	$C_8H_{14}0$	1432	1429	2.73	1.44	1.73	0.42	0.76	0.36
Decanal	Ad_9	$C_{10}H_{20}0$	1500	1498	0.73	0.71	0.36	0.13	0.76	0.24

Benzaldehyde	Ad_10	C_7H_60	1522	1520	0.42	0.3	0.6	0.28	0.25	0.49
Total (%)					**50.6**	**35.05**	**69.93**	**29.34**	**92.24**	**83.26**
ESTERS										
Ethyl Acetate	E_1	$C_4H_80_2$	893	888	0.22	4.53	0.38	0.19	0.13	0.81
Isobutyl Acetate	E_2	$C_6H_{12}O_2$	1019	1012	0.15	2.55	0.16	0.25	0.08	0.35
Butyl Acetate	E_3	$C_6H_{12}O_2$	1084	1074	1.07	1.98	2.22	0.28	0.19	0.46
Isoamyl Acetate + Ethyl Benzene	E_4		1135	1122+1129	1.36	0.74	2.29	0.21	0.25	0.33
Ethyl Crotonate	E_5	$C_6H_{10}O_2$	1179	1160	0	0	0.01	0.25	0	0
Amyl Acetate	E_6	$C_7H_{14}O_2$	1190	1176	0.08	0.99	0.15	0.05	0	0.11
Ethyl Hexanoate	E_7	$C_8H_{16}O_2$	1247	1233	0	0.07	0.01	0.53	0	0
Hexyl Acetate	E_8	$C_8H_{16}O_2$	1286	1272	2.26	4.02	4.22	2.6	0.23	4.23
(Z)-3-Hexenyl Acetate	E_9	$C_8H_{14}O_2$	1329	1315	0.14	3.36	0.21	2.79	0.02	0.32
(E)-2-Hexenyl Acetate	E_10	$C_8H_{14}O_2$	1346	1333	0	2.55	0.09	2.74	0	0.39
Hexyl Butanoate	E_11	$C_{10}H_{20}O_2$	1421	1414	0.05	0.01	0.1	0.02	0	0
Ethyl Octanoate	E_12	$C_{10}H_{20}O_2$	1441	1435	0	0.65	0.01	0.07	0	0.21
Benzyl Acetate	E_13	$C_9H_{10}O_2$	1731	1720	0.16	0.15	0.13	0.02	0	0
Total (%)					**5.49**	**21.6**	**9.98**	**10**	**0.9**	**7.21**
HYDROCARBONS										
Toluene	H_1	C_7H_8	1045	1042	0.95	0.56	1.29	0.43	0.26	0.34
Styrene	H_2	C_8H_8	1269	1261	0.37	0.17	0.59	0.21	0.2	0.29
Total (%)					**1.32**	**0.73**	**1.88**	**0.64**	**0.46**	**0.63**
ISOTHIOCYANATES										
Isothiocyanato Cyclohexane	I_1	$C_7H_{11}NS$	1661	1667	1.83	1.14	2.53	0.47	0.66	0.43
Total (%)					**1.83**	**1.14**	**2.53**	**0.47**	**0.66**	**0.43**
KETONES										
Acetoin	K_1	$C_4H_8O_2$	1295	1284	0	0.08	0.01	0.01	0	0.02
1-octen-3-one	K_2	$C_8H_{14}O$	1312	1300	1.15	0.71	0.67	0.16	0.35	0.15
2,5-Octanedione	K_3	$C_8H_{14}O_2$	1339	1319	0.95	0.63	0.81	0.15	0.24	0.12
6-Methyl-5-Hepten-2-one	K_4	$C_8H_{14}O$	1347	1338	1.06	0	1.26	0	0.22	0.08
2-Undecanone	K_5	$C_{11}H_{22}O$	1598	1598	0	0.11	0.01	0.01	0	0.02
Total (%)					**3.16**	**1.53**	**2.76**	**0.33**	**0.81**	**0.39**
LACTONES										
γ-Hexalactone	L_1	$C_6H_{10}O_2$	1696	1694	3.5	4.59	0.69	0.39	0.93	0.69
γ-Octalactone	L_2	$C_8H_{14}O_2$	1907	1910	0.09	0.09	0.01	0.01	0	0.02
γ-Decalactone	L_3	$C_{10}H_{18}O_2$	2112	2138	0.63	0.64	0.31	0.12	0.06	0.09
6-pentyl-2H-Pyran-2-one	L_4	$C_{10}H_{14}O_2$	2139	2171	0.16	0.18	0.05	0.02	0	0
δ-Decalactone	L_5	$C_{10}H_{18}O_2$	2151	2194	0.13	0.16	0.07	0.03	0.01	0.02
γ-Undecalactone	L_6	$C_{11}H_{20}O_2$	2300	2259	0.33	0.19	0.11	0.03	0.01	0.01
Total (%)					**4.84**	**5.85**	**1.24**	**0.6**	**1.01**	**0.83**
METHYLPHENOLS										
4-Methyl Phenol	Mp_1	C_7H_8O	2073	2080	0.18	0.11	0.17	0.03	0.04	0.04
3-Methyl Phenol	Mp_2	C_7H_8O	2079	2091	0.73	0.53	0.77	0.14	0.22	0.17
Total (%)					**0.91**	**0.64**	**0.94**	**0.17**	**0.26**	**0.21**
MONOTERPENES										
β-Myrcene	Mt_1	$C_{10}H_{16}$	1175	1161	0.06	0.07	0.01	0.35	0	0.03
Limonene	Mt_2	$C_{10}H_{16}$	1206	1199	0.17	12.67	1.08	52.71	0.26	4.11
Linalool	Mt_3	$C_{10}H_{18}O$	1555	1547	20.65	11.05	0.99	3.06	1.21	0.73
4-Terpineol	Mt_4	$C_{10}H_{18}O$	1601	1602	0	0.04	0.01	0.07	0	0.01
HO Trienol	Mt_5	$C_{10}H_{16}0$	1616	1613	1.38	1.31	0.71	0.19	0.17	0.09

Carvone	Mt_6	$C_{10}H_{14}O$	1727	1740	0	0.12	0.01	0.04	0	0.02
Epoxylinalool	Mt_7	$C_{10}H_{18}O_2$	1767	1721	0.05	0.1	0.02	0.04	0.01	0.01
trans-Carveol	Mt_8	$C_{10}H_{16}O$	1836	1845	0	0	0.01	0.02	0	0
Geraniol	Mt_9	$C_{10}H_{18}O$	1852	1847	0.31	0.26	0.33	0.09	0.08	0.07
2,6-dimethyl-3,7-octadiene-2,6-diol	Mt_10	$C_{10}H_{18}O_2$	1953	1945	0.1	0.05	0.04	0.02	0.01	0
Total (%)					**22.72**	**25.67**	**3.21**	**56.59**	**1.74**	**5.07**
NORISOPRENOIDS										
β-Damascenone	N_1	$C_{13}H_{18}O$	1814	1823	0.1	0.03	0.04	0.01	0.03	0.02
Total (%)					**0.1**	**0.03**	**0.04**	**0.01**	**0.03**	**0.02**
SESQUITERPENES										
Neroridol	S_1	$C_{15}H_{26}O$	2035	2034	1.83	1.48	0.03	0.01	0	0
Total (%)					**1.83**	**1.48**	**0.03**	**0.01**	**0**	**0**
UNKNOWN										
Unknown	U_1	Unknown	1429	1432	0.09	0	0.18	0	0	0
Total Area (x 10ˆ6)					***245.1***	***359.6***	***182.9***	***987.18***	***583.4***	***836.8***

The PTR-ToF-MS setting adopted in this study allowed the detection of the full VOC spectra in 1 s. Only the first 30 s of the full measurement (60 s) were analysed and averaged, to avoid possible measurement inaccuracies caused by an excessive dilution of the sample headspace. The whole VOC spectra, assessed in five biological replicates per sample, were reduced from 223 to 112 masses, applying noise, and correlation coefficient thresholds. The exact chemical molecular formula was identified for 90 detected masses, while a more precise tentative identification, based on literature references, chemical standards, and correlation with SPME/GC-MS analysis, was possible for 68 masses (Tab. 2).

VOC screening by PTR-ToF-MS allowed the detection of additional compounds not detected by SPME/GC-MS analysis. Among the most representative, ethanol (*m/z* 47.049) and methanol (*m/z* 33.033) represented the highest fraction of the detected alcohols, whilst among the aldehydes, acetaldehyde (*m/z* 45.032) was the most represented in the three cultivars. Ketones, such as acetone (*m/z* 59.049), and sulfur compounds, tentatively identified as hydrogen sulfide (*m/z* 34.995), methanethiol (*m/z* 49.010) and dimethyl sulfide and/or ethanethiol (*m/z* 63.029), were also detected in the three nectarine cultivars.

Table 2. Volatile organic compounds detected by PTR-ToF-MS immediately after harvest. Values are reported as concentration (µg Kg^{-1}). * indicates compounds identified by SPME/GC-MS and [a] indicates compounds identified by Bianchi et al., 2017. For each compound, values with the same letter are no significantly different between cultivars and intact and processed fruit according to ANOVA and Tukey HSD (P< 0.05).

			Western Red		*August Red*		*Morsiani 60*	
m/z	**Formula**	**Tentative identification**	**Intact**	**Processed**	**Intact**	**Processed**	**Intact**	**Processed**
27.026	C2H3+	Common fragment	0.21 bc	0.43 ab	0.17 bc	0.41 ab	0.08 c	0.62 a
27.034		n.i.	0.03 cd	0.19 bc	0.07 bcd	0.23 ab	0.03 d	0.39 a
27.043		n.i.	0.05 b	0.09 ab	0.05 b	0.12 ab	0.02 b	0.17 a
28.018	C [13]CH3+	n.i.	0.38 a	0.35 a	0.52 a	0.62 a	0.32 a	0.46 a
28.031	C2H4+	Ethylene	0.15 b	0.30 ab	0.26 ab	0.38 a	0.12 b	0.37 a
29.039	C2H5+	Ethanol fragment	3.74 c	50.30 ab	1.72 c	36.99 b	2.38 c	79.78 a
31.018	CH2OH+	Formaldehyde	3.39 bc	5.02 ab	3.15 bc	4.87 b	2.27 c	6.82 a
33.033	CH4OH+	Methanol	207.91 bc	375.24 ab	255.99 bc	326.32 ab	98.86 c	465.21 a
34.995	H2SH+	Hydrogen sulfide	5.37 a	3.51 a	3.57 a	5.56 a	2.90 a	5.27 a
39.022	C3H3+	Common fragment	9.97 ab	8.19 ab	6.94 b	6.67 b	3.49 b	15.30 a
41.038	C3H5+	Common fragment	36.29 a	32.65 ab	26.70 ab	32.93 ab	11.04 b	44.81 a
42.010	C2H2O+	n.i.	0.10 bc	0.25 ab	0.14 bc	0.25 ab	0.07 c	0.36 a
42.033	C2H3NH+	Acetonitrile	0.72 a	1.24 a	1.24 a	1.25 a	0.70 a	1.42 a
43.017	C [13]CH3O+	Common fragment	37.29 c	216.18 a	39.36 bc	82.36 bc	19.56 c	167.93 ab
43.054	C2[13]CH7+	Common fragment	8.13 ab	10.47 ab	9.68 ab	15.66 a	3.48 b	12.55 a
45.032	C [13]CH4OH+	Acetaldehyde	94.46 c	993.58 b	163.24 c	1447.46 b	47.42 c	2276.30 a
47.049	C [13]CH6OH+	Ethanol	19.47 c	231.60 ab	6.20 c	197.10 b	10.21 c	381.13 a
49.010	CH4SH+	Methanethiol	0.90 a	0.37 b	0.67 ab	1.03 a	0.37 b	0.54 ab
51.022		n.i.	0.32 a	0.41 a	0.20 a	0.24 a	0.17 a	0.52 a
53.038	C4H5+	n.i.	1.87 ab	1.49 ab	1.82 ab	1.76 ab	1.03 b	3.78 a
55.016		n.i.	0.07 a	0.34 a	0.23 a	0.17 a	0.08 a	0.35 a
55.054	C4H7+	Common fragment	47.47 ab	33.05 ab	50.07 ab	52.88 ab	16.43 b	94.95 a
57.033	C3H4OH+	Common fragment	13.17 ab	9.01 b	35.79 ab	17.69 ab	19.83 ab	66.73 a
57.070	C4H9+	1-Butanol*, high alcohol fragment	11.80 ab	29.52 a	5.65 b	14.64 ab	2.32 b	16.99 ab
59.049	C3H6OH+	Acetone, propanal	61.98 a	82.16 a	72.26 a	84.73 a	40.46 a	85.12 a
60.021	C2H4O2+	n.i.	0.02 bc	0.11 a	0.02 bc	0.05 abc	0.01 c	0.09 ab
61.028	C [13]CH4O2H+	Acetic acid, fragment of Acetate esters*, Acetoin*	28.73 b	320.96 a	27.95 b	80.04 b	18.84 b	182.42 ab
63.008		n.i.	0.69 a	0.56 a	1.78 a	5.85 a	0.25 a	0.72 a
63.029	C2H6SH+	Dimethyl sulfide, ethanethiol	0.69 c	5.98 bc	1.26 c	11.87 a	0.31 c	11.67 ab
65.019		n.i.	2.90 abc	2.40 abc	3.84 ab	4.28 a	0.87 c	1.52 bc
65.057	C5H5+	Ethanol cluster	0.42 b	5.84 a	0.21 b	7.39 a	0.19 b	9.63 a
66.024		n.i.	0.06 ab	0.08 ab	0.11 ab	0.12 a	0.03 b	0.04 ab
67.054	C5H7+	n.i.	1.85 bc	1.34 bc	1.96 bc	4.62 a	0.60 c	2.50 b
68.058	C4[13]CH7+	n.i.	0.17 bc	0.13 bc	0.18 bc	0.48 a	0.06 c	0.21 b
69.033	C4H4OH+	Furan	0.60 ab	0.49 ab	0.57 ab	0.70 a	0.27 b	0.62 ab
69.070	C5H9+	Aldehyde fragment, isoprene	28.61 a	17.02 ab	20.31 ab	23.26 ab	7.32 b	32.90 a
70.041		n.i.	0.05 ab	0.11 a	0.08 ab	0.07 ab	0.03 b	0.10 a
71.049	C4H6OH+	Butenal, butenone	2.67 a	1.63 ab	2.20 a	2.53 a	0.69 b	2.16 a

71.085	C5H11+	3-methyl-1-butanol + 2-methyl-1-butanol*, 3-Pentanol*, 1-Pentanol*	2.57 ab	3.43 a	1.67 ab	2.60 ab	0.64 b	3.96 a
73.028	C3H4O2H+	n.i.	1.68 bc	1.55 cd	2.48 ab	3.01 a	0.79 d	1.65 c
73.065	C4H8OH+	Butanal*, 2-methylpropanal	12.94 c	109.16 a	7.69 c	43.44 bc	5.90 c	78.20 ab
75.044	C3H6O2H+	Methyl Acetate*,propanoic acid, propanoate ester fragment	8.80 ab	19.11 a	4.45 b	8.82 ab	2.13 b	12.75 ab
75.079	C4H10OH+	2-Methylpropanol [a], butanol	0.05 b	0.22 a	0.02 b	0.09 ab	0.03 b	0.21 a
77.019		n.i.	0.16 a	0.20 a	0.19 a	0.19 a	0.14 a	0.21 a
77.048		n.i.	0.23 a	0.28 a	0.19 a	0.25 a	0.16 a	0.26 a
77.072		n.i.	0.21 a	0.21 a	0.22 a	0.24 a	0.20 a	0.26 a
79.036		Acetic acid cluster	0.02 b	1.39 a	0.04 b	0.49 ab	0.05 b	0.81 ab
79.054	C6H7+	Benzene	5.44 a	4.91 a	4.91 a	3.82 a	3.01 a	4.38 a
80.058			0.37 ab	0.36 ab	0.48 a	0.51 a	0.22 b	0.41 ab
80.990		n.i.	15.53 ab	13.00 ab	20.06 ab	23.97 a	4.32 b	7.53 ab
81.070	C6H9+	Fragment of aldehydes (Hexenals); fragment of terpenes (Linalool)	8.94 b	12.20 b	38.19 b	130.90 a	6.89 b	32.59 b
83.049	C5H6OH+	Methylfuran	1.46 a	1.02 ab	1.05 ab	1.03 ab	0.49 b	1.50 a
83.086	C6H11+	(E)-3-Hexen-1-ol, (Z)-3-Hexen-1-ol, (Z)-2-Hexen-1-ol*, Hexanal,2-Hexanone	36.01 ab	21.06 ab	38.75 ab	42.12 ab	12.04 b	72.63 a
84.053	C4[13]CH6OH+	n.i.	0.14 ab	0.10 ab	0.13 ab	0.13 ab	0.06 b	0.17 a
85.065	C5H8OH+	2-Pentenal [a]	4.76 a	2.19 a	4.02 a	4.23 a	1.63 a	4.91 a
87.044	C4H6O2H+	Butyrolactone	1.57 ab	1.51 ab	1.48 ab	1.94 a	0.59 b	1.54 ab
87.080	C5H10OH+	2-methyl butanal+3-methyl butanal, Pentanal*	5.06 ab	3.65 ab	3.99 ab	5.22 a	2.04 b	6.51 a
88.079		n.i.	0.51 a	0.60 a	0.89 a	0.99 a	0.52 a	0.96 a
89.059	C3[13]CH8O2H+	Ethyl Acetate*, Butanoic Acid*	2.27 b	79.97 a	1.13 b	13.68 b	2.40 b	39.72 ab
91.068	C7H7+	Benzyl Alcohol	0.45 bc	1.12 a	0.64 abc	0.98 ab	0.27 c	1.05 ab
93.036	C3H8OSH+	n.i.	1.73 ab	1.63 ab	2.29 a	2.47 a	0.91 b	2.61 a
93.069	C7H9+	Toluene*, Monoterpene fragment	8.55 abc	13.49 ab	4.81 bc	16.60 a	2.21 c	15.41 a
93.088		n.i.	0.22 a	0.43 a	0.15 a	0.40 a	0.08 a	0.34 a
95.018		n.i.	0.51 ab	0.48 ab	0.67 a	0.72 a	0.28 b	0.71 a
95.086	C7H11+	2-Heptenal*, Monoterpene fragment	2.88 b	2.63 b	3.62 b	18.68 a	0.65 b	3.81 b
97.028	C5H4O2H+	Furfural	1.00 ab	0.85 ab	0.81 ab	0.94 ab	0.43 b	1.42 a
97.065	C6H8OH+	2,4-Hexadienal, 2-ethylfuran	0.82 ab	0.49 bc	1.08 a	1.00 ab	0.27 c	0.72 abc
97.102	C7H13+	Heptanal, fragment	1.27 a	0.78 b	0.91 ab	1.19 a	0.24 c	0.70 b
99.080	C6H10OH+	2-Hexenal*, (2E)-Hexenal	4.31 ab	2.94 b	14.73 ab	7.95 ab	6.63 ab	22.59 a
101.060	C5H8O2H+	2,3-Pentanedione	0.59 a	0.38 ab	0.56 a	0.61 a	0.22 b	0.52 a
101.096	C6H12OH+	Hexanal*	5.14 ab	2.77 ab	5.60 ab	5.22 ab	1.71 b	10.28 a
103.075	C5H10O2H+	Isovaleric Acid*, Pentanoic Acid*	0.43 bc	0.77 ab	0.47 abc	0.76 ab	0.17 c	0.90 a
105.050	C4H8O3H+	n.i.	0.02 a	0.02 a	0.03 a	0.05 a	0.02 a	0.02 a
105.071	C8H9+	Styrene*	0.39 ab	0.39 ab	0.45 ab	0.77 a	0.24 b	0.48 ab
107.080	C8H10H+	Ethyl Benzene, Xylene	3.57 a	3.33 a	7.31 a	6.09 a	1.11 a	3.02 a
109.069	C7H8OH+	4-Methyl Phenol*, 3-Methyl Phenol*	0.08 a	0.08 a	0.12 a	0.12 a	0.09 a	0.08 a
109.103	C8H13+	n.i.	1.86 a	1.21 ab	1.79 a	1.89 a	0.43 b	1.29 a
113.024		n.i.	0.19 c	0.18 c	0.27 ab	0.31 a	0.13 c	0.20 bc
113.060	C6H8O2H+	Sorbic acid	0.20 bc	0.16 cd	0.30 ab	0.36 a	0.09 d	0.20 bc
113.096	C7H12OH+	Heptenal	1.12 a	0.64 ab	0.61 ab	0.89 a	0.18 b	0.65 ab
115.076	C6H10O2H+	Ethyl Crotonate (Ethyl (2E) -2-butenoate) *, 5-Ethyldihydro-2(3H)-Furanone*	0.38 a	0.29 ab	0.29 ab	0.31 a	0.12 b	0.37 a
115.113	C7H14OH+	Γ-Hexalactone*,Heptanone, Heptanal	0.37 ab	0.25 b	0.28 b	0.47 a	0.07 c	0.22 bc
117.091	C6H12O2H+	Isobutyl Acetate*, Butyl Acetate*, Hexanoic Acid*, ethyl butanoate	0.41 bc	1.12 a	0.51 bc	0.94 ab	0.24 c	0.72 abc
119.087	C9H11+	n.i.	0.14 bc	0.16 abc	0.15 abc	0.24 a	0.11 c	0.22 ab
121.066	C8H8OH+	Benzeneacetaldehyde [a]	0.15 bc	0.15 bc	0.24 a	0.25 a	0.10 c	0.19 ab
121.103	C9H13+	n.i.	0.40 b	0.40 b	0.40 b	0.99 a	0.23 b	0.41 b
123.083	C8H10OH+	2-phenylethanol, ethylphenol	0.08 ab	0.05 bc	0.10 a	0.10 a	0.03 c	0.08 abc
123.119	C9H15+	Nonenal	0.31 ab	0.25 b	0.32 ab	0.37 a	0.12 c	0.27 ab
125.098	C8H12OH+	Fragment of nonanal	0.60 a	0.38 a	0.44 a	0.51 a	0.11 b	0.41 a
127.113	C8H14OH+	1-octen-3-one*, 6-Methyl-5-Hepten-2-one*, (E)-2-Octenal*	1.62 a	0.90 ab	1.10 a	1.28 a	0.25 b	1.05 a
129.091	C7H12O2H+	γ-Heptalactone [a]	0.15 ab	0.16 ab	0.22 a	0.25 a	0.09 b	0.20 a
129.1293	C8H16OH+	2-octanone, Octanal*, 1-Octen-3-ol*	0.51 a	0.39 ab	0.40 a	0.56 a	0.11 b	0.35 ab
131.107	C7H14O2H+	Isoamyl Acetate+Ethyl Benzene*, Amyl Acetate*, Heptanoic Acid*	0.20 c	0.31 bc	0.42 b	0.60 a	0.14 c	0.42 b
135.114	C10H15+	HO-Trienol*, trans-Carveol*	0.23 b	0.26 b	0.33 b	0.76 a	0.16 b	0.31 b
137.134	C10H17+	(Limonene*, β-Myrcene*, Linalool*, 4-Terpineol*, Geraniol*	1.56 b	5.27 b	10.01 b	80.04 a	0.92 b	9.59 b

141.091	C8H13O2+	n.i.	0.05 c	0.05 c	0.11 ab	0.12 a	0.02 c	0.06 bc
141.129	C9H16OH+	2-Nonenal [a]	0.16 ab	0.14 bc	0.18 ab	0.20 a	0.07 c	0.17 ab
143.109	C8H14O2H+	cis-3-Hexenyl Acetate*, 2,5-Octanedione*, trans-2-Hexenyl Acetate*, 5-Butyldihydro-2(3H)-Furanone*	0.41 bc	0.39 bc	0.47 b	0.81 a	0.14 c	0.40 bc
145.124	C8H16O2H+	Ethyl Hexanoate*, Hexyl Acetate*, 2-Ethyl Hexanoic Acid*	0.15 c	0.29 c	0.32 bc	0.61 a	0.14 c	0.48 ab
149.051		n.i.	0.39 a	0.32 a	0.36 a	0.47 a	0.24 a	0.32 a
149.132	C11H17+	n.i.	0.03 b	0.05 ab	0.06 a	0.06 ab	0.04 ab	0.06 ab
153.130	C10H16OH+	HO-Trienol*, Epoxylinalool*, 2,4-Decadienal, 2,6-dimethyl-3,7-octadiene-2,6-diol*	0.14 bc	0.13 bc	0.16 abc	0.23 a	0.08 c	0.17 ab
155.103	C9H14O2H+	n.i.	0.30 b	0.31 b	0.61 a	0.66 a	0.19 c	0.28 bc
155.145	C10H18OH+	Linalool*, 4-Terpineol*	0.10 abc	0.08 bc	0.19 ab	0.20 a	0.06 c	0.13 abc
157.124	C9H16O2H+	n.i.	0.14 bc	0.14 bc	0.25 a	0.27 a	0.07 c	0.17 b
159.141	C9H18O2H+	methyl octanoate	0.22 c	0.22 c	0.37 ab	0.40 a	0.22 c	0.29 bc
163.097		n.i.	0.13 ab	0.09 ab	0.13 ab	0.20 a	0.05 b	0.09 ab
163.152	C12H19+	n.i.	0.01 b	0.02 ab	0.03 ab	0.04 a	0.02 b	0.02 ab
167.057		n.i.	0.13 ab	0.12 ab	0.16 ab	0.21 a	0.07 b	0.12 ab
169.164		n.i.	0.04 b	0.04 b	0.09 a	0.11 a	0.03 b	0.04 b
173.157	C10H20O2H+	Butanoic Acid Hexyl Ester*, Octanoic Acid Ethyl Ester*, Decanoic Acid	0.17 a	0.14 a	0.10 a	0.13 a	0.07 a	0.13 a
177.110	C13H21+	n.i.	0.02 abc	0.02 abc	0.03 ab	0.03 a	0.01 c	0.01 bc

3.2 Fresh-cut processing significantly affects nectarine volatilome

Fruit VOC profile of each nectarine cultivar was significantly modified by the fruit processing, as revealed by gas chromatographic (Fig. 1 and Tab. 1) and direct injection (Fig. 2 and Tab. 2) analysis. Based on the principal component analysis (PCA), carried out using the PTR-ToF-MS results (Fig. 2a), the first two principal components accounted for 84 % of total variance. Most of VOC differences between intact and fresh-cut fruit were described by the first principal component (PC1: 67 %), whilst differences between cultivars were mostly explained by the second component (PC2: 17 %). This variation was led by a higher concentration of several VOCs composing the volatile profile of RTE fresh-cut nectarines as shown in the PCA loading plot (Fig. 2b) and in the heatmaps of the relative fold changes carried out with either SPME/GC-MS (Fig. 1b) and PTR-ToF-MS results (Fig. 2c). VOCs were significantly grouped into three and four clusters, for SPME/GC-MS and PTR-ToF-MS analysis, respectively (Fig. 1b and 2c). The concentration of each VOC in response to fruit processing varied differently according to the cultivar. Monoterpenes, esters, and aldehydes were the VOC classes mostly affected by fruit fresh-cutting as revealed by both gas chromatographic (Fig. 1) and PTR-ToF-MS (Fig. 2) analysis.

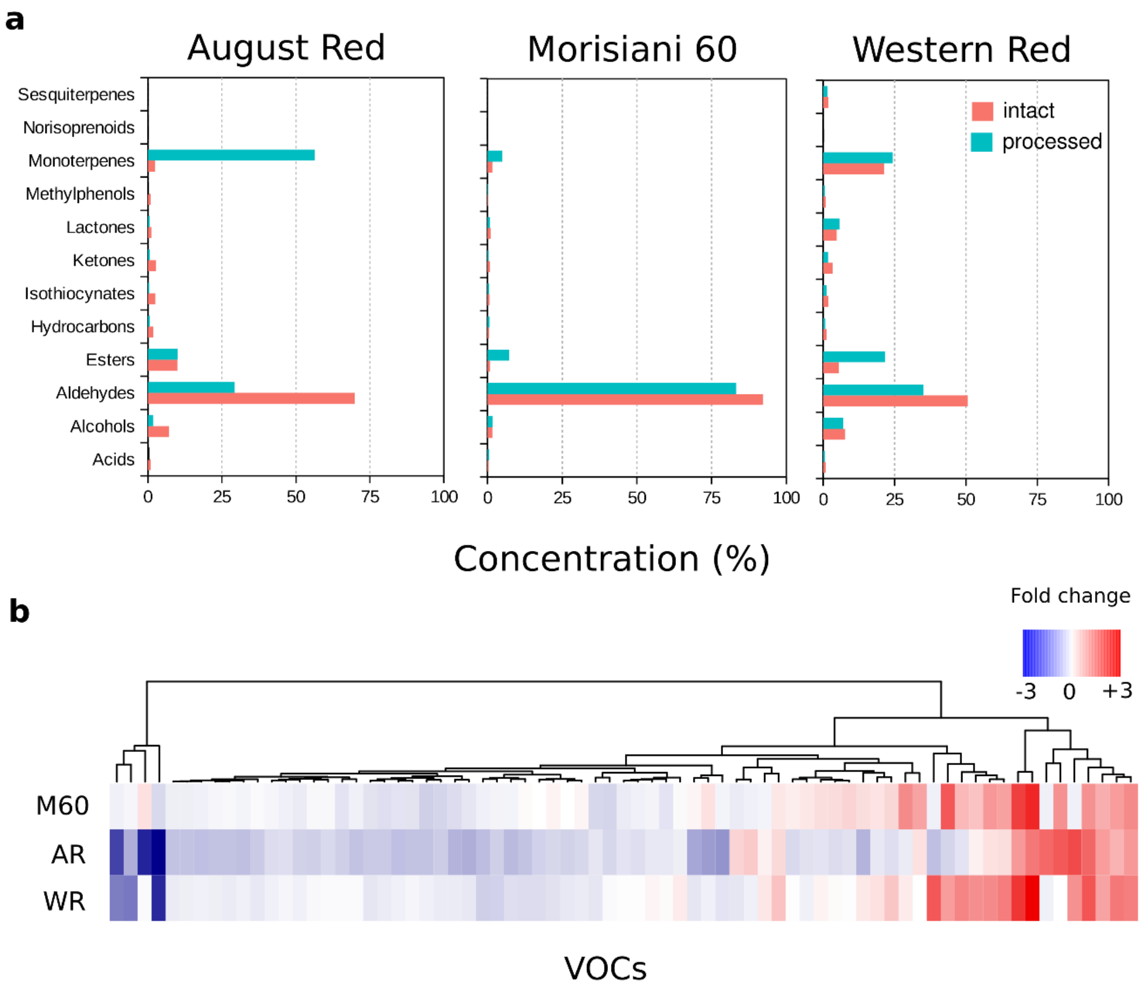

Figure 1. Analysis of unprocessed and processed nectarine VOC profile assessed by SPME/GC-MS. The bar plot of panel (a) shows the comparison of the main VOC classes of process and unprocessed fruit of the three nectarine cultivars (August Red, Morsiani 60, Western Red) detected by SPME/GC-MS analysis and reported in detail into the Table 1. Plot (b) represents the heatmap and the hierarchical dendrogram of the fold change (Log (processed/unprocessed)) of VOCs detected by SPME/GC-MS. Cluster analysis was performed using Ward's method on centred data (the high-resolution vector form of the heatmap is illustrated in SFig. 1).

The concentration of masses related to monoterpenes (i.e. limonene, linalool, trans-carveol, 4-terpineol, geraniol and β-myrcene), namely *m/z* 137.134, *m/z* 93.069, and *m/z* 95.086, significantly increased after processing in all cultivars. This increase due to processing was mostly evident in AR nectarines (Fig. 2c and Tab. 2). Alteration of the monoterpene volatilome composition, revealed by direct injection assessment by PTR-ToF-MS, was confirmed by SPME/GC-MS. Concentration of limonene increased after processing in all the cultivars, with the strongest fold change for AR (around 50 time higher) followed by WR and M60 (Fig. 1b and Tab. 1). The increase in monoterpenes emission may be the consequence of the mechanical wounding of the fruit, either by immediate release of pre-formed compounds sequestered in cellular compartments, or by stimulation of the enzymatic pathways leading to VOCs synthesis (Toivonen, 1997). Noticeable examples are the mevalonic acid and methylerythritol phosphate pathways to produce isopentenyl diphosphate and dimethylallyl diphosphate, as substrates for the activity of the terpene synthases enzyme (Forney, 2016).

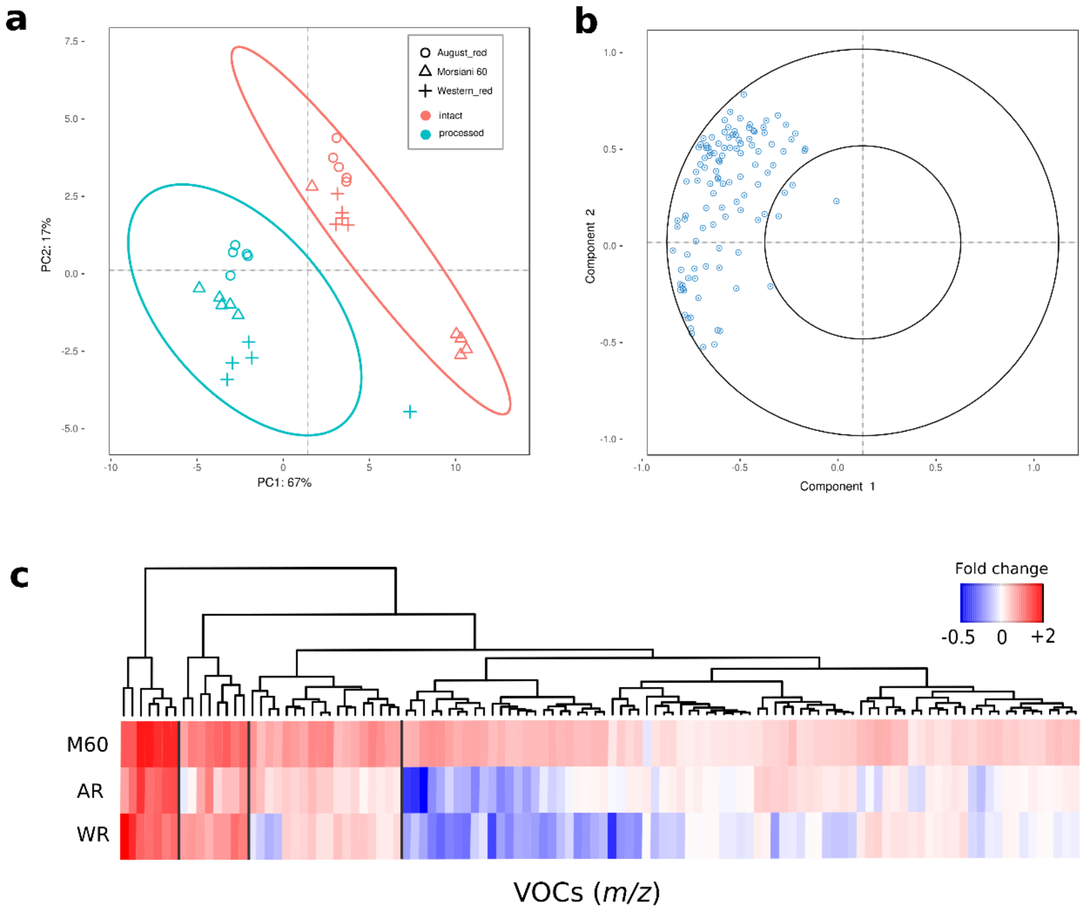

Figure 2. Analysis of unprocessed and processed nectarine VOC profile assessed by PTR-ToF-MS. Plot (a) depicts the VOC profile distribution of the three nectarine cultivars over the PCA score plot defined by the first two principal components. Plot (b) shows the projection of the VOCs identified by PTR-ToF-MS analysis (the high-resolution vector form of the loading plot is illustrated in SFig 2). Plot (c) represents the heatmap and the hierarchical dendrogram of the fold change (Log (processed/unprocessed)) of VOCs detected by PTR-ToF-MS. Cluster analysis was performed using Ward's method on centred data (the high-resolution vector form of the heatmap is illustrated in SFig. 3).

Different trends of variation in aldehyde emissions were found after fruit processing. RTE fresh-cut nectarines of all cultivars were characterized by an increased acetaldehyde (*m/z* 45.032) emission, that was almost 50 times higher for M60 processed fruit and around 10 times higher for the other two cultivars (Tab. 2 and Fig. 2c). Similarly, butanal (*m/z* 73.065) concentration was significantly increased by the cutting process, especially for WR and M60 fruit. C6-aldehydes, indicated by *m/z* 99.080 ((E)-2-hexenal) and *m/z* 101.096 (hexanal), significantly increased only in RTE fresh-cut fruit of M60 while they remained stable for the other cultivars (Tab. 2 and Fig. 2c). An increase of C6-aldehydes is generally associated with tissue disruption as a typical response to mechanical injury (Aprea et al., 2009), and it is driven by lipoxygenase (LOX) activity (Deza-Durand & Petersen, 2011). Furthermore, C6-aldehydes are part of the signalling network resulting in the activation of plant defences triggered by mechanical damages in plant tissues (Cellini et al., 2018).

Aldehydes can be further converted into the associated alcohols through the action of alcohol dehydrogenase (Forney, 2016). Indeed, in our experiment, ethanol (*m/z* 47.049) concentration significantly increased in fresh cut fruit of the three cultivars proportionally to acetaldehyde enhancement. Moreover, C6-alcohols (*m/z* 83.086), identified by SPME/GC-MS analysis as (Z)-2-hexen-1-ol and hexanol, significantly increased after processing only for M60 fruit that were also characterized by an increased concentration of C6-aldehyde. Among the remaining alcohols, methanol (*m/z* 33.033) production was significantly enhanced in fresh-cut fruit of M60 (Tab. 2 and Fig. 2c), most probably originated by the degradation of the cell wall pectin due to cell disruption (Fall and Benson, 1996).

After processing, ethyl acetate concentration (*m/z* 61.028 and *m/z* 89.059) significantly increased suggesting the conversion of ethanol to the related esters by the action of the alcohol acyltransferase (Balbontín et al., 2010). Tissue disruption by cutting also increased the emission of several other ester compounds mostly represented by the masses *m/z* 75.044, *m/z* 117.091, *m/z* 131.1076, and *m/z* 145.124, tentatively identified as methyl acetate, isobutyl acetate, butyl acetate, isoamyl acetate, amyl acetate, and hexyl acetate (Tab. 2). These esters, commonly related to fruity odours, contribute to the pleasant aroma of nectarines (Rizzolo et al., 2006; Ortiz et al., 2009). Green-odour esters such as (Z)-3-hexenyl acetate and (E)-2-hexenyl acetate (*m/z* 143,109) were also enhanced in response to fresh-cut processing.

Lactones, namely γ-hexalactone (*m/z* 115.113), γ-octalactone, γ-decalactone, δ-decalactone, and γ-undecalactone were stable after fruit processing in all cultivars (Sab. 1; Tab. 2; Fig. 1). Lactones, which are associated with pleasant and fruity notes (Rizzolo et al., 2006; Zhang et al., 2011), are key contributors to the perceived peach aroma. Therefore, their stability after fruit processing is a desirable trait that may positively affect the aroma of the processed nectarines.

One mass related to sulphur-containing compound (*m/z* 63.029) was detected by PTR-ToF-MS analysis. This mass, putatively identified as dimethyl sulfide, significantly increased after processing and may originate from amino acid breakdown and membrane deterioration. As most of sulfur compounds, dimethyl sulfide can be perceived at relatively low concentration and it can be considered as a strong off-flavour characterized by the cooked, cabbage-like odour (Mussinan & Keelan, 1994).

3.3 Effect of storage duration on fresh-cut nectarine volatilome

Fruit processing altered the nectarine colouration resulting in a drop of fruit colour brightness (L^*) in all cultivars (Fig. 3). This variation was maintained over time during postharvest storage. Higher values of a* (associated with a higher red colour degree of the fruit flesh) were induced by fruit processing in AR and WR, but not in M60 (Fig. 3b). Intact fruit showed higher values of b^* in all cultivars, suggesting a lower yellow intensity of the flesh of fresh-cut fruit (Fig. 3c). Nonetheless, in processed AR and M60 fruit, the reduction of b* values started only after 1 day of storage. The chroma index, representing colour saturation, is largely affected by b^*. Thus, the cv AR presents a slight discolouration of fruit flesh over time, regardless from the cutting process (Koukounaras et al., 2008; Allegra et al., 2015).

Similarly to Giné Bordonaba et al. (2014), any significant surface browning emerged during the five days of cold storage for all three cultivars (SFig. 4), as a possible positive effect of the antioxidant treatment applied to nectarine slices after cutting. Moreover, the dipping of fruit slices may have also inactivated from the fruit surface most of the enzymes released during cutting and slicing processes (Soliva-Fortuny & Martín-Belloso, 2003). However, based on results of Cáceres (et al. 2016), the substantial variation of L* value, measured one day after processing only in AR nectarines, can reveal an incipient flesh browning that is higher than the human perception threshold.

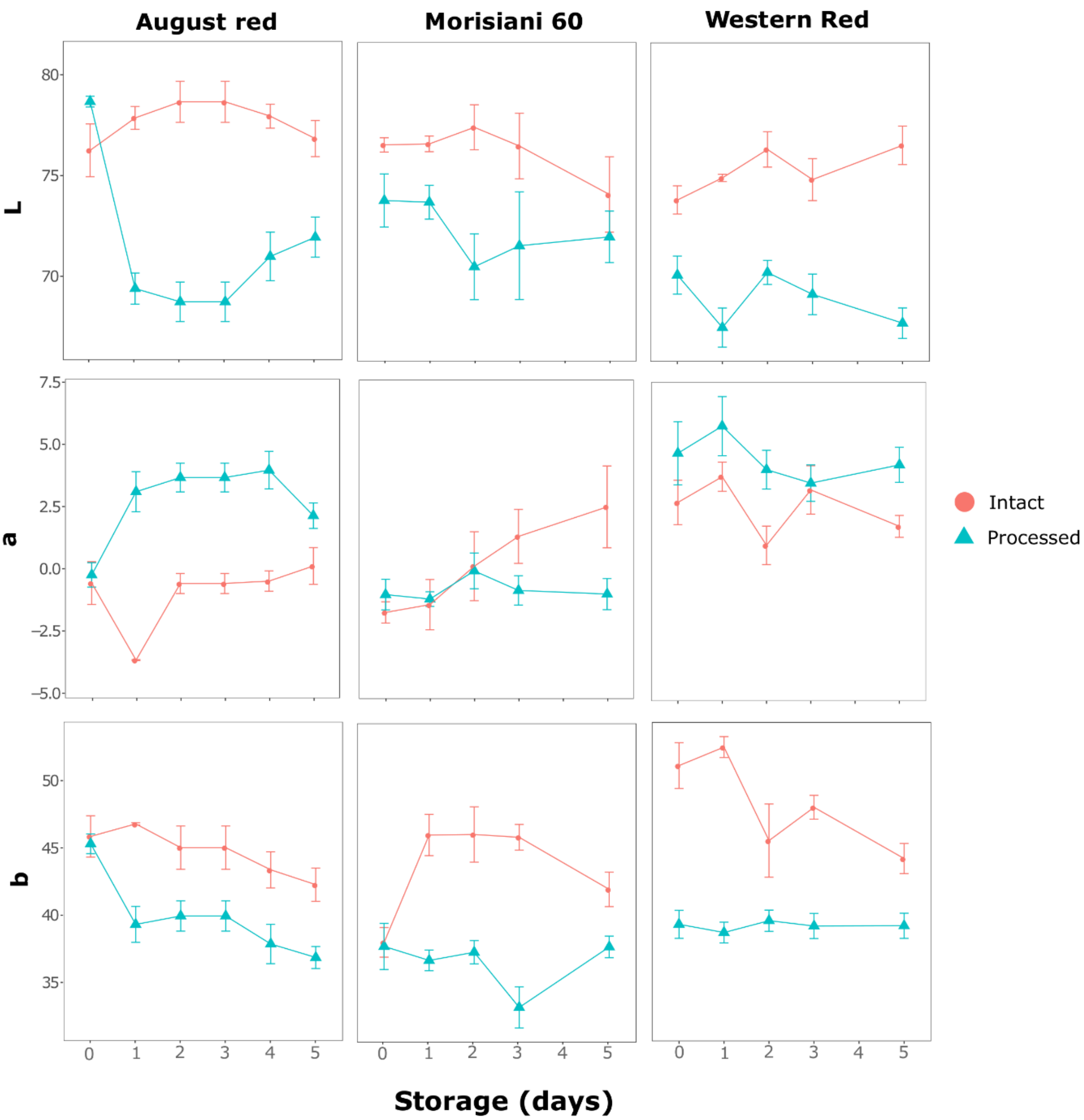

Figure 3. Chromatic evolution (Lab) during storage (5 d) of unprocessed and fresh-cut nectarine fruit assessed by tristimulus colorimeter. Each point is the average plus standard deviation of 5 biological replicates.

A principal component analysis was carried out on the SPME/GC-MS results to describe the relative effect of cultivar-dependent features, fruit processing and duration of storage on RTE fresh-cut volatilome (Fig. 4). Over 68 % of the total variability was described by the first two principal components. The volatilome of processed nectarines during storage differed substantially from that of intact ones and evolved differently during cold storage according to the cultivar. The first principal component, explaining 45.2 % of the total variability, mostly revealed differences due to fruit processing, while the second component (PC2: 23.6 %) mostly differentiated the three cultivars. Volatile profile of unprocessed nectarines resulted more stable during the storage in comparison to the fresh-cut fruit. RTE fresh-cut nectarine, indeed, enhanced the concentration of several esters, mostly ethyl acetate, isobutyl acetate, and isoamyl acetate during storage (loading plot of Fig. 4 and SFig. 5)

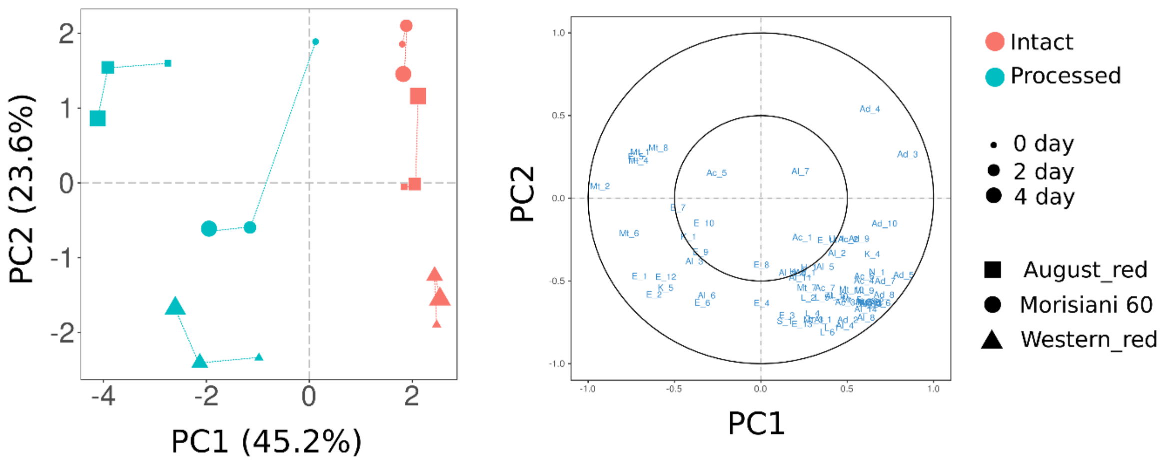

Figure 4. Analysis of unprocessed and fresh-cut nectarine VOC profile during cold storage assessed by SPME/GC-MS. Plot (a) depicts the VOC profile evolution of the three nectarine cultivars during cold storage (assessed at day 0, 2, and 4) over the PCA score plot defined by the first two principal components. Plot (b) shows the projection of the VOCs identified by SPME/GC-MS analysis.

A principal component analysis was performed also for VOC data obtained by PTR-ToF-MS (Fig. 5A). Over 80 % of the total variability was described by the first two principal components. The first principal component (corresponding to 70.1 % of the total variance) mostly discriminated the VOC emission between intact and processed fruit and the evolution during storage, similarly to the gas chromatographic analysis. Differences between cultivars were mostly evinced based on the second principal component (10.5 % of the total variance). Since most of the VOC variation in the nectarine volatilome during cold storage was expressed by these two principal components, values of PC1 and PC2, extracted from the PCA carried out with all the PTR-ToF-MS data, were considered as reliable time-related indexes to describe the volatilome evolution during storage (Fig. 5b). The modelling of PC scores to describe time-related alteration of fresh-cut products was already successfully adopted by Derossi et al. (2016) to estimate fresh-cut lettuce shelf life.

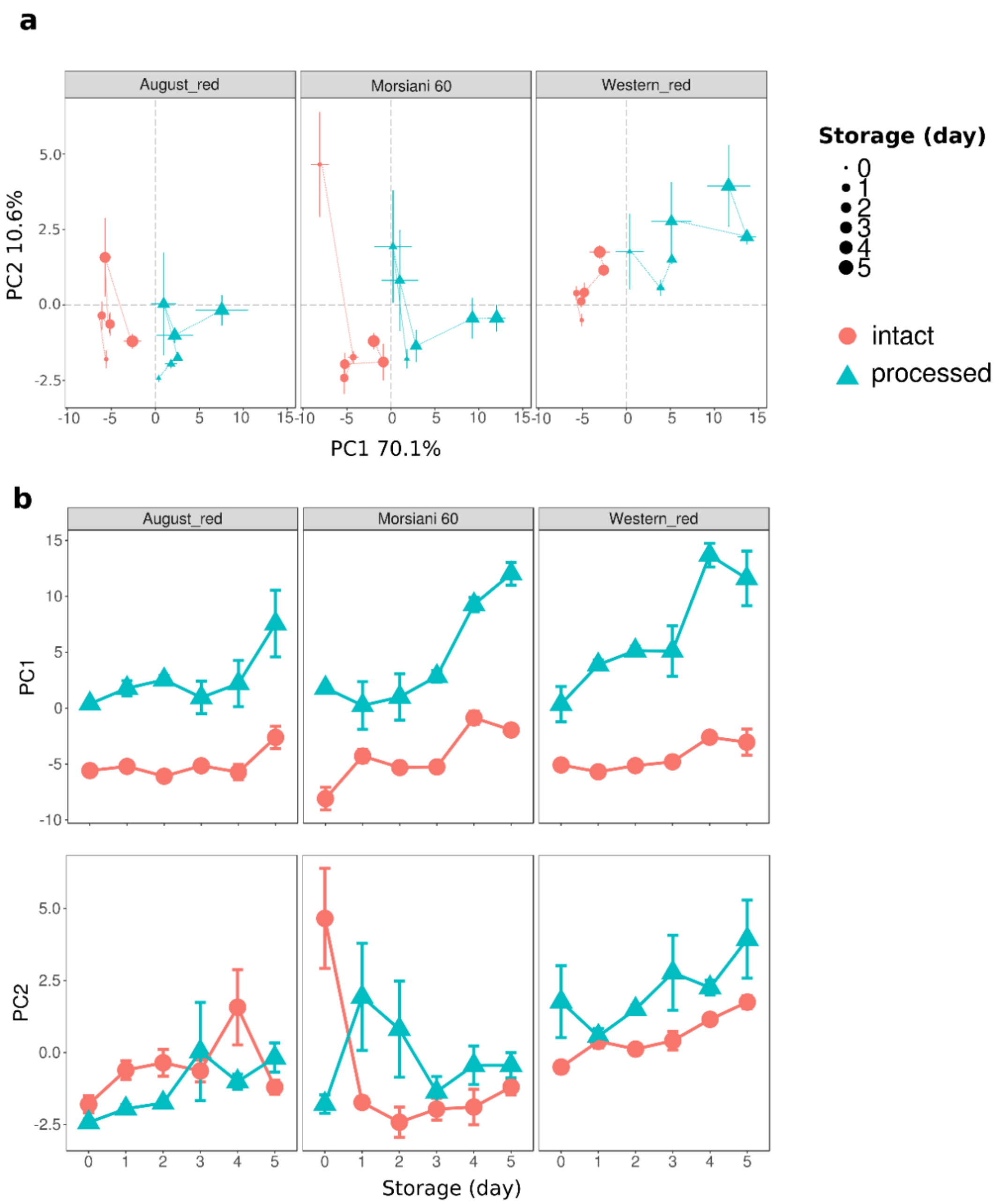

Figure 5. Analysis of unprocessed and processed nectarine VOC profile during cold storage assessed by PTR-ToF-MS. Plot (a) depicts the VOC profile evolution of the three nectarine cultivars during cold storage (daily assessed for 5 d) over the PCA score plot defined by the first two principal components. The high-resolution vector form of the loading plot is illustrated in SFig 6. Plot (b) shows the evolution of PC1 and PC2 scores (extracted from the PCA analysis of Fig. 5a) during the 5 d of storage. Each point is the average plus standard deviation of 5 biological replicates.

Although not following a definite pattern, the evolution of samples during storage occurs mostly on the second principal component (PC2) variation (Fig. 4b). As previously observed, PC2 also allows to discriminate volatilome differences between cultivars in both fresh-cut and unprocessed fruit. Overall differences in volatile emission between intact and RTE fresh-cut fruit existed immediately after processing and remained stable until three days of storage, but drastically increased after 4 and/or 5 d of cold storage. On the other hand, unprocessed fruit revealed less marked volatilome alteration during the five days of storage (Fig 5b). The increase of PC1 values in the last days of storage is associated with a pool of VOCs that increased in the same period (Fig. 6 and SFig. 7). Most of these compounds are related to fermentative metabolites such as ethanol (*m/z* 47.049) and acetaldehyde (*m/z* 45.032), but also to the burst in ethylene (*m/z* 28.031) production (Fig. 6). The accumulation of fermentative metabolites during fruit maturation and senescence induced the synthesis of other aroma volatiles such as acetate esters and ethyl esters (Larsen & Watkins, 1995; Ortiz et al., 2009), as confirmed by the parallel increase of ethyl acetate identified by the molecular masses *m/z* 89.059 (Fig. 6) and *m/z* 61.028, methyl acetate (*m/z* 75.044), and ethyl crotonate (*m/z* 115.076) (Sfig. 7). Esters are generally associated with fruity and floral aromas and therefore this increase may positively contribute to the pleasant aroma of nectarines. The accumulation of these compounds is common during ripening and can be enhanced by several factors, including chilling injury, temperature, and fermentation, consequent to the exposure of the fruit to low oxygen concentration (Pesis, 2005). In our experimental conditions, the packaging process of fruit slices may have induced a depletion of O_2 and/or an accumulation of CO_2 (Jacxsens et al., 2000), resulting in the production of fermentative off-flavour metabolites causing aroma spoilage during the last days of refrigerated storage. Other off-flavour compounds increased starting from the fourth day of storage in processed fruit, such as dimethyl sulfide (*m/z* 63.029) (fig. 6) and C5 acids (isovaleric acid or pentanoic acid, *m/z* 103.075; Sfig. 7). The variation of the PC1 was also determined by the increase of an array of other VOCs detected by PTR-ToF-MS analysis such as formaldheyde (*m/z* 31.018), 1-butanol (*m/z* 57.07), furan (*m/z* 69.033), 2-methyl-1-butanol (*m/z* 71.085), butanal (*m/z* 73.065), 2-methyl-propanol (*m/z* 75.079), butyrolactone (*m/z* 87.044), benzyl alcohol (*m/z* 91.068), and styrene (*m/z* 105.05).

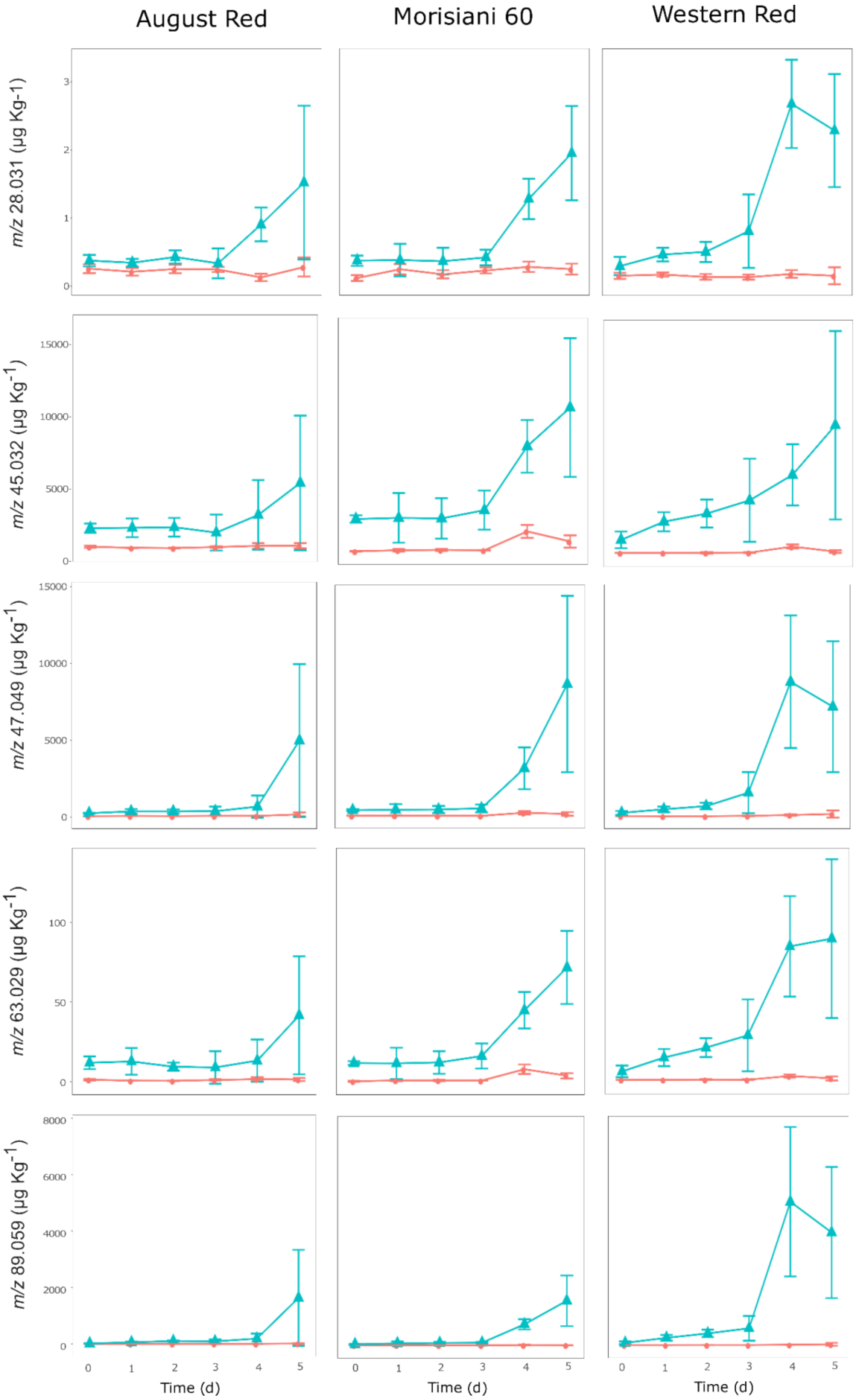

Figure 6. Storage evolution of five masses (out of 112 detected in total by PTR-ToF-MS). These masses have been selected to monitor the fruit spoilage level: ethylene (*m/z* 28.031), acetaldehyde (*m/z* 45.032), ethanol (*m/z* 47.049), dimethyl sulfide (*m/z* 63.029), and ethyl acetate (*m/z* 89.059). All data are shown as the average and standard deviation of 5 biological replicates. The storage evolution of all the detected masses is reported in the SFig. 7.

4. Conclusions

The lack of flavour, caused by incorrect conservation and harvesting practices which are not tailored on each specific cultivar, is one of the main reasons contributing to consumers' dissatisfaction and a decline in the per capita consumption of peaches (Belisle et al., 2017; Cantin et al., 2009). Results of this study revealed that fresh-cut processing induced a substantial variation in the volatile profile of the nectarines through enhancement of different VOC classes, especially for esters and monoterpenes. This volatilome modification, due to fresh-cutting, may be considered as a valuable and applicable strategy to enhance peach and nectarine perceived quality and, consequently, consumer satisfaction. A practical application of the proposed approach is the fast massive screening of cultivars, selecting those richer in desired volatile compounds to submit to sensory analysis, reducing the efforts and the cost of the sensory evaluation (Corollaro et al 2014).

However, the volatilome of fresh-cut nectarines was less stable during storage, resulting in a shorter shelf-life based on off-flavour emission. Since visual appearance of fresh-cut fruit did not show any significant deterioration during storage, consumers could be misled in the perception of the product quality and freshness at purchase, as surface appearance is the main parameter driving consumers to purchase the fresh-cut fruit. At consumption, the higher concentration of off-flavour metabolites, such as ethanol, acetaldehyde or dimethyl sulfide, could ruin the eating experience, therefore undermining the consumers likelihood of repurchase the product.

Thus, a reliable quality management system based on the use of biomarkers is necessary to control RTE fresh-cut product. This comprehensive volatilome investigation based on direct injection analysis (PTR-ToF-MS) and gas chromatographic analysis (SPME/GC-MS) allowed the detection of an array of putative VOC biomarkers that could be used during all stages of the fresh-cut industry: from the selection of the genotypes most suitable for fresh-cutting, to the final prediction of the product spoilage. However, in consideration of the high cost of commercial mass spectrometry equipment, we advise the possible employment of these biomarkers to develop innovative electronic gas sensors (Mascini et al. 2018) and smart labels. The application of smart labelling may play a key role in identifying changes in the headspace of the packaging due to the accumulation of off-flavour volatiles. For instance, smart labels sensitive to ethanol and/or dimethyl sulfide could be used as marker indicating that fruit is incurring in fermentation and therefore to flavour spoilage.

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Author contribution

FS and BF conceived the experiment. ID and ACel contributed to design the experiments and performed the classical postharvest analysis. BF and ACec analysed the data and performed the statistical analysis. BF and ACec drafted the manuscript. IK BF and FB processed and analyzed PTR-ToF-MS data. BF and EA processed and analyzed GC-MS data. FS supervised the work. All authors critically contributed to the review of the manuscript and discussion of the data.

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Captions supplementary material

SFigure 1. High-resolution vector form of the heatmap illustrated in Fig. 1b.

SFigure 2. High resolution vector form of the loading plot illustrated in Fig. 2b.

SFigure 3. High-resolution vector form of the heatmap illustrated in Fig. 2c.

SFigure 4. Browning index evolution of fresh-cut nectarine fruit during storage.

SFigure 5. VOC differences of unprocessed and fresh-cut nectarine fruit assessed by SPME/GC-MS analysis during storage. Data are reported as relative percentage content.

SFigure 6. High-resolution vector form of the loading plot of the PCA illustrated in Fig. 4a.

SFigure 7. VOC differences of unprocessed and fresh-cut nectarine fruit assessed by PTR-ToF-MS analysis during storage. All data concentration (μg kg^{-1}) are shown as the average and standard deviation of 5 biological replicates