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Investigation of the aroma of commercial peach (*Prunus persica* L. Batsch) types by Proton Transfer Reaction – Mass Spectrometry (PTR-MS) and sensory analysis

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ABSTRACT

The aim of this study was to investigate the aroma and sensory profiles of various types of peaches (*Prunus persica* L. Batsch.). Forty-three commercial cultivars comprising peaches, flat peaches, nectarines, and canning peaches (pavías) were grown over two consecutive harvest years. Fruits were assessed for chemical aroma and sensory profiles. Chemical aroma profile was obtained by proton transfer reaction-mass spectrometry (PTR-MS) and spectral masses were tentatively identified with PTR-Time of Flight-MS (PTR-Tof-MS). Sensory analysis was performed at commercial maturity considering seven aroma/ flavor attributes. The four types of peaches showed both distinct chemical aroma and sensory profiles. Flat peaches and canning peaches showed most distinct patterns according to discriminant analysis. The sensory data were related to the volatile compounds by partial least square regression. γ-Hexalactone, γ-octalactone, hotrienol, acetic acid and ethyl acetate correlated positively, and benzeneacetaldehyde, trimethylbenzene and acetaldehyde negatively to the intensities of aroma and ripe fruit sensory scores.

Chemical compounds studied in this article

Acetaldehyde (PubChem CID: 177), Benzeneacetaldehyde (PubChem CID: 998), Decahydronaphthalene (PubChem CID: 7044), γ-Hexalactone (PubChem CID: 257369), γ-Octalactone (PubChem CID: 86852), γ-Valerolactone (PubChem CID: 98323), Hotrienol (PubChem CID: 5366264), Trimethylbenzene (PubChem CID: 7247).

Keywords: canning peach, flat peach, nectarine, peach, PTR-MS, sensory analysis

1. Introduction

Peach (*Prunus persica* L. Batsch) is a fruit species from the *Prunus* genus, which also includes almonds, apricots, cherries or plums. Several traits are used to characterize its cultivars: fruit shape (round or flat), skin type (peach or nectarine), flesh color (yellow or white), texture (melting or non-melting), stone type (freestone or clingstone) or flavor (low-acid or high-acid) (Byrne et al., 2012). According to these traits, peach fruit types can be classified in peaches, nectarines, flat peaches (or nectarines), and canning peaches (also named "Pavías"). The canning peaches are clingstone and non-melting peaches usually intended for the canning industry, but also grown for fresh consumption. There has been a growing interest in both flat peaches and pavías due to their distinct quality traits for consumers (Montero-Prado, Bentayeb, & Nérin, 2013; Iglesias 2015).

The increase of peach production is not being reflected in its consumption due to several factors. One of these factors is the focus on primary quality selection traits like fruit size and appearance. Another important factor is that fruits are often harvested before the appropriate ripening time to avoid damage during harvest and postharvest manipulations, leading to the absence of the typical aroma and flavor or poor textural characteristics that compromise consumer acceptance (Reig, Iglesias, Gatius, & Alegre, 2013). Ultimately, the diversity of cultivars and their similarity in external traits (color, size, shape), together with the inexistence of a market classification based on internal quality (such as the color labels used to efficiently differentiate the sweet and non-sweet flavor of kiwifruit), are prone to affect acceptance and buying intention as consumers are often unable to differentiate most of the cultivars. This results in a continuous decrease of peach consumption in both the main producing and exporting European Union countries (Iglesias & Echeverría, 2009).

Peach quality is a complex concept and relies on diverse quality indices that have been proposed over the years. Fruit size, skin and flesh color, soluble solids content (SSC) for overall sweetness, and the ratio between SSC and titratable acidity (TA) are amongst the most common. The development of fruits that reach the maximum aroma and flavor on the tree in combination with sufficient firmness to avoid compromising management and marketing is a common objective of breeders (Iglesias & Echeverría, 2009). Peach flavor relies on chemical traits like sweetness, acidity, sugar to acid ratio or textural characteristics (Colaric, Veberic, Stampar, & Hudina, 2005; Delgado, Crisosto, Heymann, & Crisosto, 2013; Reig et al., 2013). Furthermore, other factors need to be considered to develop cultivars that match both internal and external peach quality, capable to achieve consumer acceptance, like antioxidant and nutritional compounds, volatile organic compounds (VOCs), and sensory attributes. The latter two will be addressed in the present paper.

In addition to sensory considerations, aroma and flavor are important internal fruit quality traits that reflect the diversity of biochemical processes occurring during ripening, along with appearance, texture or nutritional compounds. Aroma perception is characterized as the odor of a food product when volatile compounds enter the nasal passage and are perceived by the olfactory system (Meilgaard, Civille, & Carr, 2006). On the other hand, flavor perception is the multisensory interaction of the impressions of taste, smell, the trigeminal system, touch and visual and auditory cues, enabled by the act of eating (Auvray & Spence, 2008). The non-volatile constituents contribution to the sensory perceptions of peach fruit aroma and flavor has been widely studied (Colaric et al., 2005; Iglesias & Echeverría, 2009; Delgado et al., 2013; Reig et al., 2013). The same occurs with peach VOC emission, which is influenced by cultivar, tissue, processing, storage, ripening stage, harvest, and environmental conditions (Do, Salunkhe, & Olson, 1969; Engel, Flath, Buttery, Mon, Ramming, & Teranishi, 1988;

Horvat et al. 1990; Aubert & Milhet, 2007; Eduardo, Chietera, Bassi, Rossini, & Vecchietti, 2010). However, only a few authors have related peach fruit' aroma and flavor attributes with VOCs profile (Spencer, Pangborn, & Jennings, 1978; Cano-Salazar, López, & Echeverría, 2013; Giné-Bordonaba, Cantín, Echeverría, Ubach, & Larrigaudière, 2014).

Chemical aroma of peach fruit is mainly evaluated by gas chromatography (GC) techniques, generally preceded by steam distillation or solid phase microextraction (SPME) (Wang et al., 2009; Eduardo et al., 2010; Sánchez, Besada, Badenes, Monforte, & Granell, 2012; Montero-Prado et al., 2013; Giné-Bordonaba et al., 2014). In this study, proton transfer reaction-mass spectrometry (PTR-MS) is used to quantify the peach VOCs. Headspace PTR-MS is a highly sensitive and fast technique (pptv, parts per trillion by volume detection and < 1 min. complete spectrum acquisition) without the need of sample pre-treatment. The method is based on the reaction of a protonated agent (H_3O^+) which performs a non-dissociative proton transfer to most of the common VOCs without reacting with any of the natural components of air (Lindinger, Hansel, & Jordan, 1998).

The aim of this study was the investigation of a collection of fruits comprising peaches, flat peaches, nectarines, and canning peaches for their typological aroma profiles by PTR-MS and sensory analysis. Fruits of forty-three commercial cultivars, grown over two consecutive harvest years under Mediterranean conditions, were chosen to provide a wide species variability.

2. Material and methods

2.1. Materials

The fruits (*Prunus persica* L. Batsch) of 43 cultivars with mainly yellow flesh comprising 13 peaches, 7 flat peaches, 18 nectarines, and 6 canning peaches (Table A.1, Appendix A.) were grown at the IRTA-Mas Badia Agricultural Experimental Station (42° 03′N 3° 03′E, Girona, Spain) over the harvest years of 2012 and 2013 (N=86). Twenty fruits per cultivar and year were harvested at optimum commercial maturity from June to September, based on the range of flesh firmness (4.0–5.0 Kg/ 0.5 cm^2 measured with an 8 mm diameter probe). Four fruits per cultivar and year were selected for sensory analysis, based on similar size and homogeneous color. Flesh from three fruits was assessed for common quality indexes (Table A.2, Appendix A.): titratable acidity (TA) and soluble solids content (SSC).

Flesh from five additional fruits was pool-sampled, vacuum-packed in double-layer aluminum bags and stored at -80 ºC for further chemical determinations. The frozen samples of both harvest years were shipped under -20 ºC to the RIKILT Wageningen Research (Wageningen, The Netherlands) and stored at the same temperature until the moment of analysis.

2.2. Methods

2.2.1 Quality analysis

The titratable acidity (TA) and soluble solids content (SSC) were assessed to explore the phenotypic variation among the four fruit types in common quality traits. TA was determined through manual titration with a 0.1 M NaOH solution and using a phenolphthalein indicator until an end point of constant pH (8.0 ± 0.1). SSC was

assessed with a Quick-Brick TM 90 (Mettler-Toledo, GmbH, Germany) digital handheld refractometer as described by Bianchi et al. (2016).

2.2.2 PTR-MS profiling

Frozen samples were cut into pieces and subsequently ground, under liquid nitrogen, with a Grindomix GM 200 (Retsch, Düsseldorf, Germany) for 15 s at 10,000 rpm. Ground samples were stored at -20 ºC and analyzed within 24 h. For each sample 2.0 g of ground powder were weighted in a 250 mL screw cap glass bottle and equilibrated in a water bath at 25 ºC for 30 min. The temperature was selected to match the volatile emission in the headspace of the bottles and the conditions at which common consumers perceive the fruits. Bottles were attached to the inlet of the PTR-MS system (Ionicon GmbH, Innsbruck, Austria) where the headspace was drawn at a flow rate of 60 mL/min. The temperature of both the inlet and the drift chamber was 60 ºC. MS data between 20-160 atomic mass units (amu) was collected with a dwell time of 200 ms. Blank measurements were carried out between samples to monitor background air. The analyses were performed in independent triplicates and an averaged mass spectrum per sample was calculated after background and transmission correction. The mass spectral data (*m/z* 20-160) of the 86 peach fruits was assessed after the removal of masses *m/z* 32 (O_2^+) and *m/z* 37 (water cluster ion) from the dataset.

2.2.3 PTR-Tof-MS tentative identification

From the ground powder as obtained in section 2.2.1, a subset of samples was selected for volatile compounds tentative identification with a PTR-Tof-MS 8000 system (Ionicon GmbH, Innsbruck, Austria). Four samples per harvest year (n=8), one from each peach type, were chosen to provide a representative set considering the variability observed in the PTR-MS results. The procedure was identical as in section

2.2.2, with the exception that only 1.0 g ground powder was used. The chamber ionization conditions were kept as follows: drift temperature 60 °C, drift voltage 421 V and drift pressure 3.80 mbar. The instrument was operated at E/N value of 133 Townsend (1Td $=10^{-17}$ cm^2 V^{-1} s^{-1}). A further description of PTR-Tof-MS is given by Lindinger et al. (1998). Each sample measurement lasted 60 s with an acquisition rate of 1 spectrum/s. Baseline removal and spectra alignment by internal calibration of the ToF data were performed according to the procedure described by Cappellin et al. (2010). VOCs were tentatively identified based on the PTR-ToF-MS results and the existing literature after excluding the interfering ions (O_2^+, NO^+ and water clusters) and their isotopologues.

2.2.4 Sensory analysis

The fresh fruits were assessed at harvest by an 8 member trained panel, following the procedure described by Bianchi et al. (2016). Briefly, seven aroma and flavor descriptors (Table 3) were chosen during training sessions in which the panelists evaluated different commercial peach and nectarine samples. Fruits were cut in halves and the same fruit was assessed by two panelists. The pair of panelists assessing the same fruit sample changed at every tasting session according to a balanced design. In each tasting session, 4 fruits per cultivar were hand peeled and their flesh assessed in different presentation orders to block first-order and carry-over effects (MacFie, Bratchell, Greenhoff, & Vallis, 1989). Sensory evaluation was performed using a non-structured 10 cm lineal scale, in which 0 meant low intensity of the descriptor and 10 meant high intensity of the descriptor.

2.2.5 Statistical analysis

The sensory and VOCs datasets were evaluated using a two-way ANOVA, considering the type of peach (peach, nectarine, flat peach or pavía) and the harvest year as fixed factors. Due to the lack of normality detected for the majority of VOCs, a non-parametric Kruskal-Wallis test was also carried out. Since similar results were obtained in both cases (ANOVA and Kruskal-Wallis) the parametric option (ANOVA) was kept. In addition, the two-way ANOVA allows correcting the effect of the harvest year and is a robust method regarding the lack of normality (Schmider, Ziegler, Danay, Beyer, & Bühner, 2010). The interaction 'type of fruit x harvest year' was considered but then discarded because it was not significant ($p > 0.05$) for any parameter evaluated.

A Tukey's HSD post hoc test ($p \leq 0.05$) was performed to test the existence of statistical differences between the fruit typologies. The 36 significantly different VOCs ($p < 0.05$) obtained from the ANOVA results were submitted to a principal component analysis (PCA) and all the orthogonal factors obtained were used to perform a discriminant analysis (DA) to avoid possible multicollinearity issues. The impact of the VOCs over the fruits' sensory perception was assessed through a partial least square (PLS) regression model. The analyses were carried out with XLSTAT 2017 software (Addinsoft, Paris, France).

3. Results and discussion

3.1 VOC profiling

As mentioned before (section 1), the peach fruit VOC emission is influenced by factors like cultivar, storage, ripening stage or harvest conditions. It is also known that the VOC profile is affected by the different experimental conditions and methodologies used: liquid-liquid microextraction (Aubert & Milhet 2007) steam distillation (Eduardo et al., 2010) or SPME (Wang et al., 2009; Abidi 2012; Sánchez et al., 2012) coupled to gas chromatographic techniques. The comparison of the results described herein with previous works must be carefully addressed. In the present work the determinations were performed at harvest. PTR-MS high sensitivity allowed the headspace VOCs to be drawn at room temperature (25 ºC), simulating the conditions at which consumers perceive the fruits.

PTR-ToF-MS analysis allowed the tentative identification of most of the compounds (Table 4) with the exception of 11 masses (*m/z* 35, 38, 39, 44, 46, 52, 58, 62, 65, 82, 84 and 98). The ANOVA results showing the significantly different masses among peach fruit types are reported in Table 4. A burst in ethylene production regulates the onset of the ripening process in climacteric fruit. Ethylene production was observed to be different between other peach fruit traits such as acid and non-acid flavor (Iglesias & Echeverría, 2009). However, in this study ethylene was not significant between peach typologies. The masses with the highest headspace amounts were methanol, acetaldehyde and ethanol, but only the former two showed significant differences. Methanol was significantly higher in flat peaches and lower in nectarines and canning peaches. Acetaldehyde higher amounts were also observed in flat peaches together with nectarines. Spadoni et al. (2015) observed higher amounts of methanol, followed by acetaldehyde and ethanol in peaches. Other authors reported higher

concentrations of ethanol than acetaldehyde for intact tree-ripened nectarines (Takeoaka, Flath, Guntert, & Jennings, 1988).

3.1.1 Fatty acid derived compounds

Fatty acid-derived straight-chain alcohols, aldehydes, ketones, acids, esters and lactones are mainly formed by α-oxidation, β-oxidation and the lipoxygenase pathway (Schwab & Schreier, 2002).

The most abundant fatty acid related masses were *m/z* 61 and 89. Acetic acid and ethyl acetate were significantly higher in canning peaches. Acetic acid is involved in the formation of esters that contribute to the peach aroma (Salunkhe, Do, & Maga, 1976) and was previously observed among the VOCs of peaches and other *Prunus* fruits (Krammer, Winterhalter, Schwab, & Schreier, 1991). Ethyl acetate was reported as one of the major esters in peaches and nectarines (Wang et al., 2009; Rizzolo, Bianchi, Vanoli, Lurie, Spinelli, & Torricelli, 2013). Mass *m/z* 75, attributed by PTR-ToF-MS to methyl acetate (75.043) and 2-methylpropanol (75.079) was significantly higher in peaches and lower in nectarines. The former is a methyl ester of short chain fatty acids resulting from the β-oxidation pathway (Bartley, Stoker, Martin, Hatfield, & Knee, 1985) while 2-methylpropanol derives from the amino acid metabolism. Other esters observed were propyl acetate/ ethyl propanoate (103.076), butyl acetate/ methyl isovalerate (117.092), pentyl acetate/ methylbutyl acetate (131.107), hexyl acetate (145.123), and methyl octanoate (159.140) but at lower amounts (< 1 ppbv) and not significantly different among peach types. The same was observed for the two diol alcohols, 2,3-butanediol (91.074) and 1,8-octanediol (147.137). Several fragments detected were also associated with esters (*m/z* 41.038, 43.017, 43.054, 53.038, and 57.069). Mass *m/z* 99, formed by 2,5-furandione (99.010), 2-furylmethanol (99.046) and 2-hexenal (99.081), was significantly higher in nectarines and lower in peaches. The

concentration of 2-hexenal was reported to differ significantly within the part of the fruit (Aubert & Milhet 2007) or cultivar (Eduardo et al., 2010). 2,5-furandione and 2-furylmethanol are furan related compounds involved in VOCs formation, although their origin is not well established. Other furans observed at lower amounts (< 1 ppbv) were 2-ethylfuran, significantly higher in nectarines and lower in peaches and canning peaches, or 2-pentylfuran, significantly higher in flat peaches. 2,4-heptadienal and 2-nonenal were significantly higher in flat peaches and nectarines and lower in peaches and canning peaches. Formaldehyde, 2-butenal, 2-pentenal, and 1-penten-3-ol, 2-heptenal, and decanal were not significantly different for any type of fruit, although 1-penten-3-ol was found to be significantly different within the part of the fruit (Aubert & Milhet 2007).

Masses *m/z* 101 and 115 were both comprised by a lactone, γ-valerolactone (101.060) or γ-hexalactone (115.075), together with hexanal/ 3-hexenol (101.095) and heptanal (115.108), respectively. Nectarines showed significantly higher amounts of *m/z* 101 and lower of *m/z* 115, while canning peaches had the higher amounts of the latest. Other lactones found were γ-heptalactone (129.091) and γ-octalactone (143.108) but no significant differences were observed among peach fruit types. Previous studies reported γ-decalactone, and in lesser extent δ-decalactone, as the most abundant lactones in the pulp of peach and nectarine (Wang et al. 2009) while γ-hexalactone was observed to be dominant for some cultivars (Eduardo et al., 2010). Variable results can be found in the literature regarding γ-valerolactone. The amounts of this lactone were reported to increase with maturity stage and to be higher in tree ripe than artificially ripe peaches (Do et al., 1969). However, Aubert et al. (2003b) observed that γ-valerolactone was significantly higher for tree ripe than unripe nectarines but also significantly higher for unripe fruits stored in ripening chambers at 26 ºC than tree ripe ones. The *m/z* 155, associated to 2-nonen-4-olide (155.108) and linalool/ α-terpineol (discussed in section

3.1.3), was also significantly higher in nectarines and lower in canning peaches. Analogs of this lactone were previously observed in peaches and nectarines (Engel et al., 1988; Takeoaka et al., 1988; Aubert & Milhet 2007). Horvat et al. (1990) reported the lactone distribution to differ between peaches and nectarines but Wang et al. (2009) did not observe significant differences between both types of fruits. More than 10 lactones have been observed among peach fruit volatiles (Engel et al., 1988; Aubert & Milhet 2007; Eduardo et al., 2010; Abidi 2012). However, in our study only $C_5 - C_8$ γ-lactones were observed. This was in agreement with the results from Narain et al. (1990) of headspace measurements in peach. The differences with other works are prone to be due to the different methodologies of volatile assessment. These differences were observed by Takeoaka et al. (1988) who compared the volatile profiles of nectarines with both headspace and steam distillation sampling techniques and reported lower number of lactones with the former. Derail et al. (1999) compared the aroma profile of fresh peach juice and cooked pulp by simultaneous steam-distillation/extraction and observed that the increase of the amounts of lactones was thermally induced. The authors observed an increase of the flavor dilution factors of 128 times for δ-decalactone, 32 times for γ-decalactone, or 16 times for γ-jasmolactone in the cooked extracts. More recently, Rizzolo et al. (2013) detected a low proportion of lactones using a static headspace technique and reported that equilibration at 70 ºC during 30 min was enough to increase γ-decalactone and γ-dodecalactone amounts. Despite being key compounds for the peach fruit aroma definition, these lactones were not detected in the present study. The differences from previous works may be due to differences in the techniques, mainly between GC-MS and PTR-MS, and measurement conditions, such as higher temperatures used with steam distillation, solvent, SPME, and headspace extraction procedures, compared to the headspace analysis at 25 ºC.

Other factors to take into account are the use of low pressures, long equilibration or extraction times, and large quantities of sample material.

3.1.2 Amino acid derived and nitrogen-related compounds

Pyrazine (*m/z* 81.044) had higher amounts in nectarines and lower in peaches. Pyrazine was previously observed in apricots (Solís-Solís, Calderón-Santoyo, Schorr-Galindo, Luna-Solano, & Regazzo-Sánchez, 2007) and is produced by further interactions occurred after Maillard reaction, with a wide diversity of aromas depending on the side group of each pyrazine compound (Maga & Sizer, 1973; Buchbauer, Klein, Wailzer, & Wolschann, 2000). Phenol and aminobenzoic acid were also significantly higher in nectarines while benzeneacetaldehyde in flat peaches. Previously reported in *Prunus*' fruits (Krammer et al., 1991), phenol is formed by addition of a hydroxyl group to a benzene ring and is the basis of phenolic compound formation (Saltveit 2009). The valine-derived volatile 2-methylpropanol (Gonda et al., 2010) was identified at m/z 75 together with methyl acetate (Section 3.1.1). Acetonitrile, *m/z* 69 comprised by 1H-pyrazole (69.047) and isoprene (69.069), and benzyl alcohol (109.170) showed no significant differences among fruit type. 1H-pyrazole was recently reported in peaches by Brandi et al. (2011).

The compounds involved in cyanogenesis were not significantly different for any peach fruit type. Hydrogen cyanide in peach fruit is originated from the enzymatic degradation of cyanogenic glycosides, amygdalin and prunasin, together with benzaldehyde (Poulton 1993). The latest can also occur as an amino acid decomposition product and its concentration was reported to increase during maturity (Do et al., 1969) being the most abundant aldehyde observed in peaches and nectarines (Narain, Hsieh, & Johnson, 1990; Wang et al., 2009). Acetone is an end product of cyanogenesis and was

previously observed among the VOCs of several fruits including peaches (Takeoaka et al., 1988)

3.1.3 Terpene compounds and hydrocarbons

The isoprene-related compounds identified in the VOCs profile were observed at lower amounts. Myrcene and the *m/z* 155, associated to linalool/ α-terpineol (*m/z* 155.143), were significantly higher in nectarines while *m/z* 123.117, assigned to a farnesene fragment, was significantly higher in flat peaches. Canning peaches showed the lowest amounts of these compounds. Terpene compounds are formed by several isoprene units and its metabolism is in the origin of several *Prunus'* fruit VOCs (Krammer et al. 1991). Myrcene is an acyclic monoterpene precursor of linalool (Brodkorb, Gottschall, Marmulla, Luddeke, & Harder, 2010) and was reported to be the most abundant terpene in peaches and nectarines (Aubert & Milhet 2007; Wang et al., 2009; Eduardo et al., 2010). No significant differences were observed for p-cymene (135.111), carvone (151.113) and hotrienol (153.128) but these were only detected at trace amounts. Sunthonvit et al. (2007) found linalool and hotrienol to be the main terpenes in tree-ripened nectarines.

Masses *m/z* 83.086 and 85.100 were previously described as hydrocarbons (Takeoaka et al., 1988) but recently identified as fragments of diverse origins (alcohols, aldehydes, terpenes) by PTR-ToF-MS in apple fruit (Farneti et al., 2015). The former was also recently reported as dimethylbutadiene (Takeoaka et al., 1988). This compound was significantly higher in nectarines, followed by flat peaches and lower in peaches and canning peaches. Other minor hydrocarbons observed were trimethylbenzene, 1-methylcyclohexene and decahydronaphthalene, analog of naphthalene compounds previously observed among peach fruits.

3.1.4 Discriminant analysis

The subset of the 36 significantly different PTR-MS masses obtained with the ANOVA results were submitted to a principal component analysis (PCA) and the matrix of orthogonal PCs used to perform a DA (Figure 1). The PCA loadings for each VOC allowed the identification of the compounds with the higher contribution to each principal component, helping to explain the specific differences between fruit typologies observed in the DA plot. The higher positive loadings of fragments of several origins (*m/z* 43), acetic acid, ethyl acetate, and *m/z* 115 comprised by γ-hexalactone and heptanal on PC 2 were responsible for the distinction of canning peaches from the other fruits. Nectarines were differentiated from the former ones due to high positive loadings of pyrazine, γ-valerolactone together with hexanal/ 3-hexenol (*m/z* 101), *m/z* 83 and 55, *m/z* 99 comprised by 2,5-furandione, 2-furylmethanol and 2-hexenal, *m/z* 57, and *m/z* 58 on PCs 1 and 4. Peaches had intermediate characteristics between the former two, although the negative loadings of the compounds above mentioned for nectarines contributed for their negative scores, and thus, the opposed the projection of both peaches and nectarines. Flat peaches were distinguished from the rest of fruits due to the high positive loadings of *m/z* 51, methanol, *m/z* 35, and acetaldehyde on PCs 3 and 5.

The first three factors explained 100% of the variance in the PTR-MS data (45%, 37% and 18%, respectively) with 100% of correctly classified samples. The clearest separation was observed between flat peaches and canning peaches with the former ones being the most differentiated peach type. Canning peaches were also overlapped with peaches but these were only slightly overlapped with nectarines. The group formation was consistent with the sensory analysis' results detailed below, but the separation was more distinct for the volatile profiles.

3.2 Sensory analysis

ANOVA results showed that panelists detected significant differences for five out of the seven sensory attributes analyzed among types of fruits (Table 5). Aroma intensity and ripe fruit highest scores were observed for canning peaches, followed by peaches, flat peaches, and with nectarines having the lowest scores. A slightly different trend was observed for flavor intensity. Canning peaches were still equally higher scored for this attribute but were followed by flat peaches, peaches, and nectarines. Reig et al. (2013) also observed significantly higher overall flavor scores for flat peaches compared to peaches and nectarines. The relationship between the highest aroma intensity and ripe fruit attributes was reflected by the flavor intensity for canning peaches. However, with regard to flat peaches it is more likely to be due to their lower titratable acidity (TA) when compared to the other peach fruit types (Table A.2, Appendix A.). Aroma intensity and ripe fruit aroma attributes were most strongly correlated ($r = 0.91$; $p \leq 0.001$) among the sensory traits and both were similarly correlated with flavor intensity ($r = 0.68$; $p \leq 0.001$ and $r = 0.70$; $p \leq 0.001$ respectively). Flavor persistence was significantly higher scored for canning peaches and peaches, with flat peaches having the least persistent flavor and nectarines showing an intermediate behavior. This attribute was similarly related to fruit aroma ($r = 0.46$; $p \leq 0.001$) and aroma and flavor intensities ($r = 0.51$; $p \leq 0.001$ and $r = 0.54$; $p \leq 0.001$).

Aroma and flavor attributes associated with plum fruit were not significantly different for any type of peach. The stone aroma attribute showed three significantly different groups with nectarines and peaches having the highest scores and canning peaches the lowest ones. A negative relationship was observed between stone aroma and ripe fruit aroma ($r = -0.26$; $p \leq 0.05$) or aroma and flavor intensities ($r = -0.30$; $p \leq 0.01$ and $r = -0.27$; $p \leq 0.05$), suggesting that stone aroma was the dominant attribute in those fruits with lower scores of ripe or typical aroma. This relationship was also found by Spencer et al. (1978) who stated that the woody and other background aromas might

be masked by fruity aromas in peach. Nevertheless, Delgado et al. (2013) related the woody notes of the stone/pit with an aroma combination able to drive consumers' liking of peach.

Discriminant analysis (Figure 2) was performed in order to understand the differences and similarities among the fruit types perception. The first three factors accounted to explain 100% of the variance (61.4%, 30.6% and 8.0% respectively), resulting in 87% of correctly classified samples according to the confusion matrix. Ripe fruit and aroma intensity were the most discriminate attributes, followed by stone aroma and flavor intensity. Flavor persistence was the least discriminate attribute while plum aroma and flavor did not show any significant ability to discriminate between samples, in agreement with the ANOVA results for these attributes. The overlapping observed reflected the similarities between the four types of peach fruits. However, it was possible to visualize a group formation according to each peach type with the clearest separation between flat peaches and canning peaches or an opposed location of peaches and nectarines. Likewise, canning peaches were mainly grouped along with peaches while flat peaches appeared to have an intermediate behavior between peaches and nectarines.

To the best of the authors' knowledge, no studies have evaluated the sensory profile of peaches considering the relationship between the different peach fruit types. Despite the high variability observed, possibly as a result of the internal quality traits (texture, organic acids, soluble sugars), these results highlight an enhanced organoleptic perception of canning peaches and flat peaches regarding aroma and flavor intensities. This variability is prone to result from the varietal innovation of the past years, mainly concerned with peaches and nectarines and, more recently, with a higher focus over flat peaches or the significant focus over canning peaches in some Spanish breeding programs (Iglesias 2015).

3.3 Relationships between sensory analysis and VOCs

PLS regression was performed using the volatile compound masses and the significantly different sensory attributes among peach fruit types. The determination coefficients showed satisfactory correlations between the VOCs and the aroma intensity (R^2 = 0.58) and ripe fruit aroma (R^2 = 0.57), but lower values were observed for flavor attributes and stone aroma. The standardized regression coefficients ("β coefficients") highlighted the compounds with the higher contribution to the perception of peach fruit by reporting the relative weight of each *m/z* in the PLS model (Table 6). The greater the absolute value of a coefficient, the greater its impact over a sensory attribute.

Globally, aroma intensity and ripe fruit aroma attributes were related with the same volatile compounds and to a similar extent. These relations were also observed for flavor intensity and persistence, although to a lower extent. The highest positive contributions to the intensity and ripe fruit aromas were from *m/z* 115, comprised by γ-hexalactone and heptanal, acetic acid, hotrienol, *m/z* 143, comprised by γ-octalactone and nonanal, an unidentified compound (*m/z* 62), *m/z* 43 comprised by fragments of diverse origins, ethyl acetate, and *m/z* 75 comprised by methyl acetate and 2-methylpropanol. When an *m/z* was comprised by more than one compound, as for *m/z* 115 or 143, the impact over the sensory descriptors could not be easily attributed. However, the positive standardized regression coefficients of *m/z* 115 and 143 (both comprised by a γ-lactone and an aldehyde) allowed to relate their contribution to the intensity and ripe fruit aromas with the fruity notes of γ-lactones and not the green notes of the aldehydes, which were expected to show a negative contribution for these attributes. These results are in agreement with Spencer et al. (1978) who reported γ-lactones to be responsible for the peachy background aroma. Ethyl and methyl acetates are responsible for the fruity aroma and flavor of several fruits like apricots (Defilippi,

Manríquez, Luengwilai, & González-Agüero, 2009), apples (Karlsen, Aaby, Sivertsen, Baardseth, & Ellekjaer, 1999) or melons (Obando-Ulloa et al., 2008), among others. Acetic acid seems to be related with unpleasant attributes but its role in fruit perception is not fully understood. Our results suggest that in peach fruit it might act as an enhancer of other volatile compounds. Acids significantly affect the sensory perception of the peachy aroma attribute in mango (Malundo, Shewfelt, Ware, & Baldwin, 2001) while ethyl acetate was reported to increase in parallel with acidity in kiwifruit (Marsh, Friel, Gunson, Lund, & MacRae, 2006).

The highest negative relation with aroma intensity and ripe fruit aroma was observed for *m/z* 121, comprised by benzeneacetaldehyde and trimethylbenzene, followed by acetaldehyde, an unidentified compound (*m/z* 46), and *m/z* 139, comprised by 2-pentylfuran and decahydronaphthalene. Benzeneacetaldehyde and 2-pentylfuran are associated with immature fruit notes. Both compounds were found to be negatively correlated with ground color in peach, while the former was also negatively correlated with fruit weight, SSC, and positively correlated with firmness (Sánchez et al., 2012). Trimethylbenzene has been associated with both pleasant and unpleasant attributes in different food products but its odor description is not entirely clear. Contrarily to previous studies (Baldwin, Goodner, & Plotto, 2008), acetaldehyde had a negative impact over peach fruit perception. The high amounts of this compound might have elicited unpleasant pungent aromas (Voon, Hamid, Rusul, Osman, & Quek, 2007) while the interaction with acids enhanced the sour perception of this fruit (Baldwin et al., 2008). A naphthalene compound was reported to be negatively correlated with overall, fruity and floral peach aromas, as well as positively correlated with overcooked and woody aromas (Spencer et al. 1978). Other negative contributions were observed from 2-butanone and benzaldehyde. The latter was also previously observed to correlate negatively to SSC and positively to firmness (Sánchez et al. 2012).

The differences between sensory and volatile profiles might be due to the influence of the non-volatile constituents, such as organic acids or soluble sugars, over peach fruit sensory perception (Colaric et al., 2005). The effect of added sugars or acids is known to enhance the sensory perception of several fruit pulps or juices (Malundo et al., 2001; Marsh et al., 2006). Likewise, the interaction of certain volatiles with organic acids or sugars is reported to significantly change the perception of the aroma and flavor attributes when compared to the volatile alone (Baldwin et al., 2008). Other factors to take into account are the different sensory and instrumental release rate of certain VOCs or the possible influence of textural parameters. Ingham et al. (1995) reported significantly lower amounts of C6 aldehydes in the nose space, during *in vivo* aroma release while eating strawberries, than in headspace measurements. The influence of textural parameters on VOCs release during fruit perception was recently studied by Ting et al. (2016) using apple cultivars.

4. Conclusions

These results highlight the distinct volatile and sensory profiles associated with peach typologies. The development of new cultivars should compromise between the improvement of the sensory quality and the preservation of the typological aroma profiles. Furthermore, the lack of a greater agreement between sensory and volatile profiles, particularly for flavor attributes, indicates the need of further research concerning not only the relationship between sensory attributes and volatile compounds but also their link with the non-volatile constituents (organic acids and soluble sugars) of peach fruits.

Appendix A

Table A. 1 Fruit cultivars analyzed in this study: breeding program, peach fruit type and flesh color

Cultivar	Breeding program (origin)	Fruit type	Flesh color
African Bonnigold	ARC (South Africa)	Canning peach	Yellow
Amiga	A. Minguzzi (Italy)	Nectarine	Yellow
ASF 04.05 Nj	Agro Selection Fruits (France)	Nectarine	Yellow
Early Maycrest	Toeus (USA)	Peach	Yellow
Fercluse	INRA-Bordeaux (France)	Canning peach	Yellow
Fergaron	INRA-Bordeaux (France)	Canning peach	Yellow
Honey Glo	Zaiger Genetic Inc. (USA)	Nectarine	Yellow
IFF 1230	CREA-Forlí (Italy)	Peach	Yellow
IFF 1233	CREA-Forlí (Italy)	Peach	Yellow
IFF 331	CREA-Forlí (Italy)	Peach	White
IFF 628	CREA-Forlí (Italy)	Peach	Yellow
IFF 691	CREA-Forlí (Italy)	Peach	Yellow
IFF 800	CREA-Forlí (Italy)	Nectarine	Yellow
Lamì Nectar	A. Minguzzi (Italy)	Nectarine	Yellow
Maycrest	Minami (USA)	Peach	Yellow
Mésembrine	INRA-Bordeaux (France)	[a] Flat nectarine	Yellow
Nectabang	Agro Selection Fruits (France)	Nectarine	Yellow
Nectabelle	Agro Selection Fruits (France)	Nectarine	Yellow
Maillarqueen	Agro Selection Fruits (France)	Nectarine	White
Nectaprima	Agro Selection Fruits (France)	Nectarine	Yellow
Nectariane	Agro Selection Fruits (France)	Nectarine	Yellow
Nectareine	Agro Selection Fruits (France)	Nectarine	Yellow
Nectagala	Agro Selection Fruits (France)	Nectarine	Yellow
Nectarperle	Agro Selection Fruits (France)	Nectarine	White
Nectarcrisp	Agro Selection Fruits (France)	Nectarine	Yellow
Nectavista	Agro Selection Fruits (France)	Nectarine	Yellow
Orion	CREA-Rome (Italy)	Nectarine	Yellow
Red Valley	CIV Ferrara (Italy)	Peach	Yellow
Rubirich	Zaiger Genetics Inc. (USA)	Peach	Yellow
Spring Belle	Batistini (Italy)	Peach	Yellow
Star Nat	La Vipesa (Spain)	Flat peach	White
Summer Rich	Zaiger Genetics Inc. (USA)	Peach	Yellow
Summer Sun	ARC (South Africa)	Canning peach	Yellow
Sweet Prim	Agro Selection Fruits (France)	Peach	White
Sweet Ring	CREA-Forlí (Italy)	Flat peach	Yellow
Crispdelice	Agro Selection Fruits (France)	Peach	Yellow
Transvalia	ARC (South Africa)	Canning peach	Yellow
UFO-3	CREA-Rome (Italy)	Flat peach	White
UFO-4	CREA-Rome (Italy)	Flat peach	White
UFO-6	CREA-Rome (Italy)	Flat peach	White
UFO-7	CREA-Rome (Italy)	Flat peach	White
Venus®	CREA-Rome (Italy)	Nectarine	Yellow
Villa Giulia	CREA-Rome (Italy)	Canning peach	Yellow

[a] Mésembrine was considered a flat peach in agreement with a previous work of Reig et al. (2013).

Table A. 2 Values (Range and Mean ± Standard Deviation) of the quality indexes determined amongst the *Prunus persica* cultivars analyzed (averaged triplicates)

Parameters	**Type of fruit**			
	Peach (n=26)	Flat peach (n=14)	Nectarine (n=36)	Pavía (n=12)
TA (g malic acid/ L)				
Range	2.61 – 10.25	1.10 – 5.20	2.38 – 12.40	4.21 – 9.38
Mean ± SD	6.19 ± 2.31	2.76 ± 1.03	5.36 ± 2.65	6.99 ± 1.54
SSC (°Brix)				
Range	7.34 – 11.85	9.89 – 13.97	8.31 – 14.53	7.24 – 13.87
Mean ± SD	9.49 ± 1.21	11.47 ± 1.18	11.64 ± 1.42	10.59 ± 1.88

Appendix B

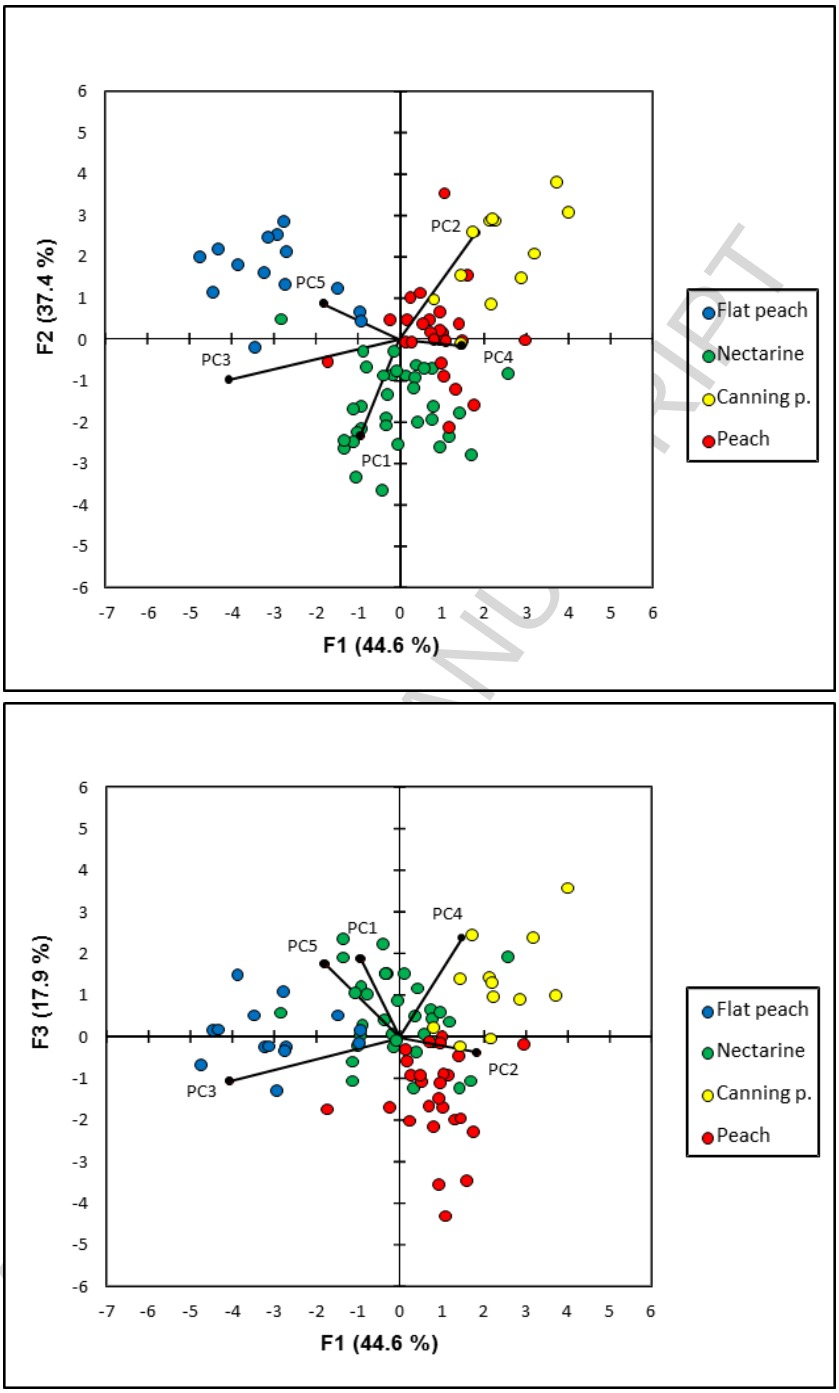

Figure B.1 Biplots of the discriminant analysis (DA) performed on the PTR-MS data of the *Prunus persica* cultivars according to their typology: Factor 1 vs Factor 2 (upper) and Factor 1 vs Factor 3 (lower).

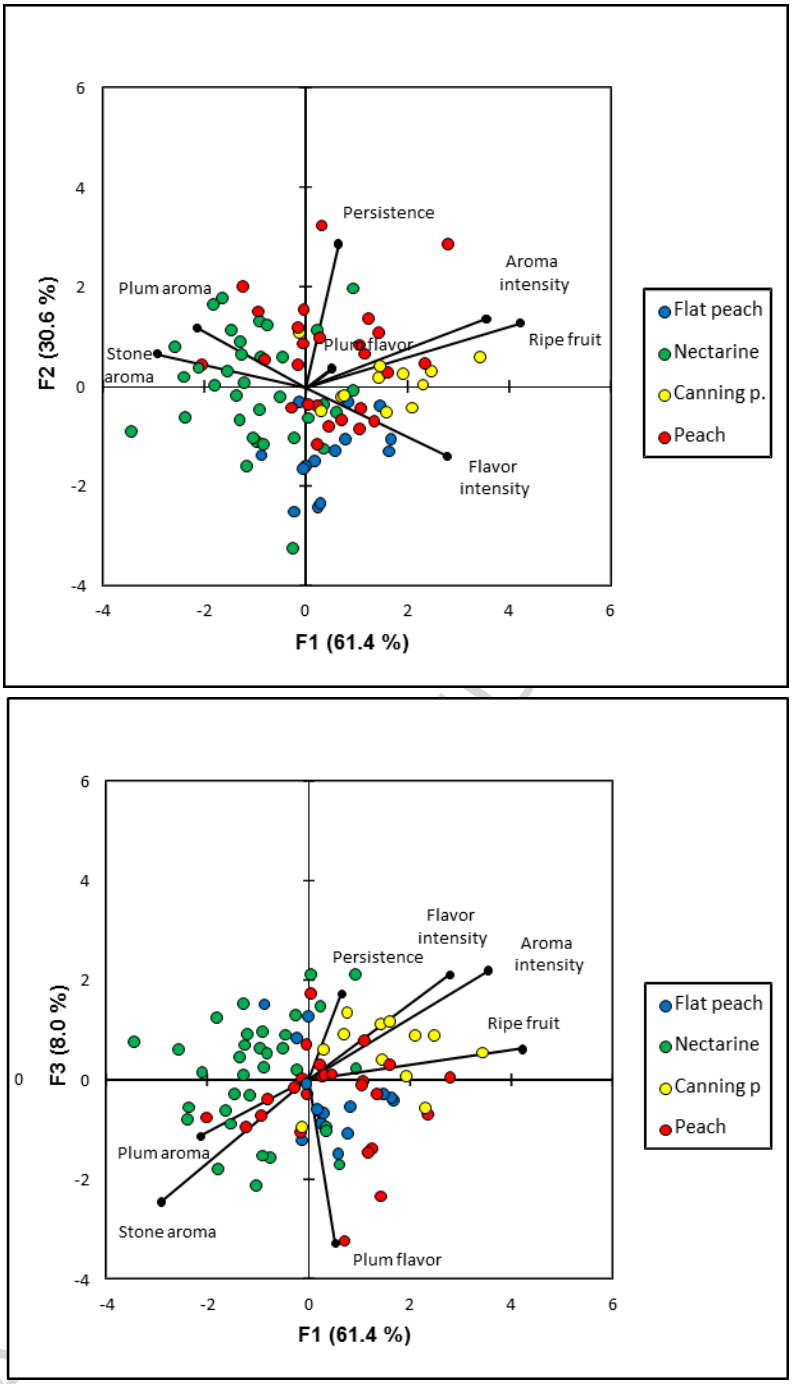

Figure B.2 Biplots of the discriminant analysis (DA) performed on the sensory data of the *Prunus persica* cultivars according to their typology: Factor 1 vs Factor 2 (upper) and Factor 1 vs Factor 3 (lower).

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Tables

Table 3. Peach sensory attributes and description used for sensory analysis.

Attributes	**Description**
Aroma	
Aroma intensity	Strength of peach overall aroma present in one sample.
Ripe fruit	Typical fruity aroma in a range from under to over ripe.
Plum aroma	Presence of plum fruit characteristic aroma.
Stone aroma	Presence of aroma associated with the stone/pit.
Flavor	
Flavor intensity	Strength of peach overall flavors detected during chewing.
Plum flavor	Presence of plum fruit characteristic taste.
Flavor persistence	Amount of flavor detected in mouth a couple of minutes after swallow.

Table 4. Tentative identification by PTR-Tof-MS (left side) of the VOCs determined by PTR-MS on the *Prunus persica* cultivars (right side): ANOVA results (Mean ± Standard Deviation) for fruit type expressed in ppbv

m/z	[a] **Tentative identification**	**Sum formula**	**Fruit type**			
			Peach (n=26)	Flat peach (n=14)	Nectarine (n=34)	Canning peach (n=12)
28.017	**Hydrogen cyanide**	CH_2N^+	1.3 ± 1.3	1.5 ± 1.2	1.1 ± 0.8	1.0 ± 0.6
28	N.I.					
29.037	Ethylene	$C_2H_5^+$	12.5 ± 6.5	17.9 ± 13.8	13.4 ± 6.8	16.2 ± 15.4
31.018	**Formaldehyde**	CH_3O^+	8.8 ± 4.6	11.3 ± 8.4	7.7 ± 2.8	8.4 ± 4.9
33.033	Methanol [20]	CH_5O^+	1219.7 ± 1332.8^{ab}	1486.8 ± 1928.4^{a}	531.8 ± 338.8^{b}	428.0 ± 154.8^{b}
35	N.I.		2.5 ± 2.8^{ab}	3.0 ± 4.1^{a}	1.1 ± 0.7^{b}	0.9 ± 0.3^{b}
38	N.I.		3.3 ± 0.5	3.2 ± 0.4	3.3 ± 0.5	3.6 ± 0.5
39	N.I.		14.7 ± 3.4^{b}	15.8 ± 3.7^{ab}	19.3 ± 8.2^{a}	14.6 ± 2.4^{b}
41.038	Fragment (alcohol, ester) [21] [23]	$C_3H_5^+$	19.5 ± 8.9	20.3 ± 10.9	24.6 ± 13.5	18.9 ± 10.6
42.033	**Acetonitrile**	$C_2H_4N^+$	3.2 ± 3.2	17.5 ± 42.4	23.6 ± 56.5	7.2 ± 6.2
43.017	Fragment (ester) [21] [23]	$C_2H_3O^+$	82.5 ± 64.8^{b}	54.5 ± 30.6^{b}	56.2 ± 25.9^{b}	183.1 ± 215.5^{a}
43.054	Fragment (alcohol, ester, acetate) [21] [23]	$C_3H_7^+$				
44	N.I.		2.3 ± 1.6^{b}	2.0 ± 0.8^{b}	2.2 ± 1.3^{b}	4.5 ± 4.8^{a}
45.034	Acetaldehyde [3] [15] [18] [20]	$C_2H_5O^+$	1208.9 ± 720.5^{b}	1802.5 ± 890.1^{a}	1328.7 ± 424.9^{ab}	909.4 ± 518.9^{b}
46	N.I.		27.6 ± 16.8^{b}	41.2 ± 20.7^{a}	30.3 ± 9.9^{ab}	20.9 ± 12.1^{b}
47.049	Ethanol [3] [5] [15] [18] [20] [14]	$C_2H_7O^+$	265.9 ± 113.5	346.9 ± 239.4	265.0 ± 107.0	328.4 ± 257.0
51.023	Fragment	$C_4H_3^+$	7.2 ± 7.8^{ab}	8.6 ± 11.0^{a}	3.2 ± 2.0^{b}	2.6 ± 0.8^{b}
51	N.I.					
52	N.I.		0.1 ± 0.1^{a}	0.1 ± 0.2^{a}	< 0.1^{b}	< 0.1^{ab}
53.038	Fragment (ester) [23]	$C_4H_5^+$	1.0 ± 1.0^{b}	1.6 ± 1.3^{ab}	2.6 ± 3.2^{a}	0.9 ± 0.7^{b}
55.054	Fragment (aldehyde) [23]	$C_4H_7^+$	48.1 ± 43.9^{b}	74.3 ± 58.1^{ab}	124.0 ± 154.2^{a}	46.0 ± 31.3^{b}
57	N.I.		39.4 ± [13].9^{b}	66.2 ± 44.7^{ab}	143.6 ± 206.4^{a}	51.1 ± 45.7^{ab}
57.069	Fragment (alcohol, ester) [21] [23]	$C_4H_9^+$				
58	N.I.		1.5 ± 1.4^{b}	2.4 ± 1.5^{ab}	5.0 ± 7.0^{a}	1.8 ± 1.5^{ab}
59.049	Acetone [3]	$C_3H_7O^+$	15.8 ± 7.0	15.3 ± 5.9	17.2 ± 7.1	18.7 ± 17.1
61.028	Acetic acid [6] [14]	$C_2H_5O_2^+$	56.6 ± 59.1^{b}	16.7 ± 19.7^{b}	19.4 ± 15.5^{b}	180.2 ± 241.7^{a}
62	N.I.		1.4 ± 1.3^{b}	0.5 ± 0.5^{b}	0.6 ± 0.4^{b}	4.3 ± 5.7^{a}
63.044	**Ethylene glycol** [21]	$C_2H_7O_2^+$	2.0 ± 1.0	2.5 ± 1.3	2.1 ± 0.7	2.3 ± 1.8
65	N.I.		2.2 ± 1.1	2.9 ± 2.2	2.1 ± 0.9	2.8 ± 2.3
69.047	1H-Pyrazole [12]	$C_3H_5N_2^+$	3.9 ± 1.3	4.3 ± 1.9	4.9 ± 1.9	3.9 ± 0.9

m/z	[a] **Tentative identification**	**Sum formula**	**Fruit type**			
			Peach (n=26)	Flat peach (n=14)	Nectarine (n=34)	Canning peach (n=12)
69.069	**Isoprene** [23]	$C_5H_9^+$				
71.049	2-Butenal [5]	$C_4H_7O^+$	1.1 ± 1.3	1.1 ± 0.8	1.1 ± 0.5	1.3 ± 0.9
73.064	2-Butanone [3]	$C_4H_9O^+$	3.7 ± 4.9	3.9 ± 2.3	2.4 ± 1.1	2.5 ± 1.2
75.043	Methyl acetate [3] [18]	$C_3H_7O_2^+$	14.2 ± 24.6^{a}	2.5 ± 3.6^{ab}	1.8 ± 2.0^{b}	5.8 ± 6.0^{ab}
75.079	2-Methylpropanol [3]	$C_4H_{11}O^+$				
81.044	**Pyrazine**	$C_4H_5N_2^+$	7.5 ± 5.3^{b}	12.8 ± 8.9^{ab}	25.7 ± 30.8^{a}	8.1 ± 6.3^{ab}
82	N.I.		0.6 ± 0.5^{b}	1.0 ± 0.7^{ab}	1.9 ± 2.2^{a}	0.6 ± 0.5^{b}
83.086	Hydrocarbon [3]/ Fragment [21]/ Dimethylbutadiene [20]	$C_6H_{11}^+$	25.0 ± 23.7^{b}	42.1 ± 35.5^{ab}	73.4 ± 92.1^{a}	24.0 ± 18.2^{b}
84	N.I.		1.6 ± 1.6^{b}	2.7 ± 2.3^{ab}	4.7 ± 6.1^{a}	1.6 ± 1.2^{b}
85.064	2-Pentenal [5] [10]	$C_5H_9O^+$	1.5 ± 1.2	1.1 ± 0.7	3.0 ± 5.5	0.9 ± 0.5
85.100	Hydrocarbon [3]/ Fragment (alcohol) [21]	$C_6H_{13}^+$				
87.044	2,3-Butanedione [3] [5] [19]	$C_4H_7O_2^+$	1.0 ± 0.6	1.3 ± 0.3	1.2 ± 1.0	0.9 ± 0.3
87.080	1-Penten-3-ol [3] [5] [9]	$C_5H_{11}O^+$				
89.059	Ethyl acetate [5] [10] [18] [19] [22]	$C_4H_9O_2^+$	5.6 ± 7.6^{b}	1.8 ± 3.2^{b}	1.3 ± 1.1^{b}	21.6 ± 31.7^{a}
91.074	2,3-Butanediol [22]	$C_4H_{11}O_2^+$	0.1 ± 0.2	< 0.1	< 0.1	0.1 ± 0.2
95.049	Phenol [5] [6]	$C_6H_7O^+$	0.3 ± 0.2^{b}	0.4 ± 0.3^{ab}	0.5 ± 0.3^{a}	0.2 ± 0.2^{b}
97.065	2-Ethylfuran [5] [15]	$C_6H_9O^+$	0.2 ± 0.1^{b}	0.3 ± 0.1^{ab}	0.4 ± 0.2^{a}	0.2 ± 0.1^{b}
97.101	**1-Methylcyclohexene** [13]	$C_7H_{13}^+$				
98	N.I.		0.2 ± 0.2^{b}	0.3 ± 0.2^{ab}	0.7 ± 1.0^{a}	0.2 ± 0.2^{ab}
99.010	2,5-Furandione [12]	$C_4H_3O_3^+$	5.7 ± 5.6^{b}	10.2 ± 7.6^{ab}	23.0 ± 33.9^{a}	7.7 ± 7.4^{ab}
99.046	2-Furylmethanol [2]	$C_5H_7O_2^+$				
99.081	2-Hexenal [2] [5] [9] [10] [11] [15] [19]	$C_6H_{11}O^+$				
101.060	γ-Valerolactone [1] [5] [8]	$C_5H_9O_2^+$	1.1 ± 1.1^{b}	2.3 ± 2.0^{ab}	3.7 ± 5.1^{a}	1.1 ± 1.1^{ab}
101.095	Hexanal/ 3-Hexenol [2] [3] [5] [9] [10] [11] [19]	$C_6H_{13}O^+$				
103.076	Propyl acetate [3] [5] [19]/ Ethyl propanoate [3] [5]	$C_5H_{11}O_2^+$	0.1 ± 0.1	0.1 ± 0.0	0.1 ± 0.1	0.1 ± 0.1
107.049	Benzaldehyde [1] [2] [3] [5] [7] [10] [11] [12]	$C_7H_7O^+$	4.3 ± 6.9	4.4 ± 4.8	3.4 ± 3.7	2.3 ± 1.5
109.070	Benzyl alcohol [1] [3] [5] [6] [7] [11] [19]	$C_7H_9O^+$	0.3 ± 0.1	0.3 ± 0.1	0.3 ± 0.1	0.3 ± 0.1
111.080	2,4-Heptadienal [15] [17] [14]	$C_7H_{11}O^+$	0.1 ± 0.1^{b}	0.2 ± 0.1^{a}	0.2 ± 0.1^{a}	0.1 ± 0.0^{b}
113.095	2-Heptenal [10] [15] [19]	$C_7H_{13}O^+$	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	< 0.1
115.075	γ-Hexalactone [2] [3] [5] [9] [10] [11] [12]	$C_6H_{11}O_2^+$	0.5 ± 0.3^{b}	0.4 ± 0.1^{bc}	0.3 ± 0.2^{c}	0.8 ± 0.3^{a}
115.108	Heptanal [10] [20] [22]	$C_7H_{15}O^+$				
117.092	Butyl acetate [3] [5] [10] [19]/ Methyl isovalerate [1] [3]	$C_6H_{13}O_2^+$	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.0	< 0.1

m/z	[a] **Tentative identification**	**Sum formula**	**Fruit type**			
			Peach (n=26)	Flat peach (n=14)	Nectarine (n=34)	Canning peach (n=12)
119.107	**Hexylene glicol**	$C_6H_{15}O_2^+$	< 0.1[b]	< 0.1[ab]	< 0.1[a]	< 0.1[ab]
121.066	Benzeneacetaldehyde [5] [11] [12] [15] [14]	$C_8H_9O^+$	0.2 ± 0.1[b]	0.3 ± 0.1[a]	0.2 ± 0.1[ab]	0.2 ± 0.1[ab]
121.100	Trimethylbenzene [3] [5]	$C_9H_{13}^+$				
123.117	Fragment (farnesene) [23]	$C_9H_{15}^+$	0.2 ± 0.1[bc]	0.2 ± 0.1[a]	0.2 ± 0.1[ab]	0.1 ± 0.1[c]
127.112	6-Methyl-5-hepten-2-one [3] [5] [9] [10] [16] [20] [22]	$C_8H_{15}O^+$	0.1 ± 0.0	0.1 ± 0.0	0.2 ± 0.1	0.1 ± 0.0
129.091	γ-Heptalactone [2] [3] [5] [9] [11] [15]	$C_7H_{13}O_2^+$	< 0.1	< 0.1	< 0.1	< 0.1
129.127	Octanal [9] [10] [15] [20] [22] [14]	$C_8H_{17}O^+$				
131.107	Pentyl acetate/ Methylbutyl acetate [1] [3] [5] [9] [19] [20]	$C_7H_{15}O_2^+$	< 0.1	< 0.1	< 0.1	< 0.1
135.111	*p*-Cymene [3] [5] [15] [17] [22] [14]	$C_{10}H_{15}^+$	< 0.1	< 0.1	< 0.1	< 0.1
137.133	Myrcene [3] [15] [22]	$C_{10}H_{17}^+$	1.4 ± 1.4[ab]	2.1 ± 2.4[ab]	2.5 ± 2.7[a]	0.6 ± 1.0[b]
138.064	**Aminobenzoic acid**	$C_7H_8NO_2^+$	0.1 ± 0.2[ab]	0.2 ± 0.2[ab]	0.3 ± 0.3[a]	0.1 ± 0.1[b]
139.113	2-Pentylfuran [3] [4] [10] [15] [20]	$C_9H_{15}O^+$	0.1 ± 0.1[b]	0.2 ± 0.1[a]	0.1 ± 0.1[b]	0.1 ± 0.0[b]
139.145	**Decahydronaphthalene**	$C_{10}H_{19}^+$				
141.129	2-Nonenal [5] [10] [15] [14]	$C_9H_{17}O^+$	0.1 ± 0.1[b]	0.2 ± 0.1[a]	0.1 ± 0.1[ab]	0.1 ± 0.0[b]
143.108	γ-Octalactone [2] [3] [9] [10] [11] [16] [19]	$C_8H_{15}O_2^+$	0.3 ± 0.1	0.2 ± 0.0	0.3 ± 0.1	0.3 ± 0.1
143.143	Nonanal [4] [10] [11] [16] [19] [20]	$C_9H_{19}O^+$				
145.123	Hexyl acetate [3] [5] [9] [10] [11] [17] [20]	$C_8H_{17}O_2^+$	0.2 ± 0.2	0.1 ± 0.0	0.1 ± 0.1	0.1 ± 0.0
147.137	**1,8-Octanediol**	$C_8H_{19}O_2^+$	< 0.1	< 0.1	< 0.1	< 0.1
151.113	Carvone [12] [22]/ Thymol [14]	$C_{10}H_{15}O^+$	< 0.1	< 0.1	< 0.1	< 0.1
153.128	Hotrienol [2] [3] [9] [20]	$C_{10}H_{17}O^+$	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.0
155.108	**2-Nonen-4-olide**	$C_9H_{15}O_2^+$	0.2 ± 0.2[ab]	0.2 ± 0.2[ab]	0.3 ± 0.3[a]	0.2 ± 0.1[b]
155.143	Linalool [11] [16] [19] [20] / α-Terpineol [3] [7] [9] [10]	$C_{10}H_{19}O^+$				
157.159	Decanal [10] [19] [20] [22]	$C_{10}H_{21}O^+$	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0
159.140	Methyl octanoate [3] [19]	$C_9H_{19}O_2^+$	< 0.1	< 0.1	< 0.1	< 0.1

Values with different letter within row indicate significant differences by Tukey's HSD post hoc test ($p \leq 0.05$).

N.I. (not identified): compounds not identified by PTR-Tof-MS. Bold compounds not previously reported among peach fruit VOCs.

[a] References: [1] Do et al., 1969; [2] Engel et al., 1988; [3] Takeoka et al., 1988; [4] Horvat et al., 1990; [5] Narain et al., 1990; [6] Krammer et al., 1991; [7] Aubert et al., 2003a; [8] Aubert et al., 2003b; [9] Aubert & Milhet 2007; [10] Wang et al., 2009; [11] Eduardo et al., 2010; [12] Brandi et al., 2011; [13] Pereira et al., 2011; [14] Abidi 2012; [15] Sánchez et al., 2012; [16] Eduardo et al., 2013; [17] Montero-Prado et al., 2013; [18] Rizzolo et al., 2013; [19] Giné-Bordonaba et al., 2014; [20] Spadoni et al., 2015; [21] Farneti et al., 2015; [22] Dabbou et al., 2016; [23] Ting et al., 2016.

Table 5. ANOVA results (Mean ± Standard Deviation) of the aroma and flavor attribute scores amongst the *Prunus persica* cultivars

Attributes	**Type of fruit**			
Aroma	Peach (n=26)	Flat peach (n=14)	Nectarine (n=34)	Canning peach (n=12)
Aroma intensity	5.06 ± 1.01^{b}	4.65 ± 0.79^{bc}	4.38 ± 0.93^{c}	5.93 ± 1.00^{a}
Ripe fruit	4.32 ± 1.12^{ab}	3.87 ± 0.95^{bc}	3.25 ± 0.78^{c}	5.08 ± 1.22^{a}
Plum aroma	1.39 ± 0.56	1.18 ± 0.38	1.50 ± 0.50	1.07 ± 0.46
Stone aroma	1.48 ± 0.62^{a}	1.30 ± 0.51^{ab}	1.69 ± 0.74^{a}	0.86 ± 0.43^{b}
Flavor				
Flavor intensity	4.77 ± 0.80^{b}	5.15 ± 0.51^{ab}	4.58 ± 0.77^{b}	5.48 ± 0.79^{a}
Plum flavor	1.68 ± 0.62	1.58 ± 0.45	1.44 ± 0.51	1.41 ± 0.52
Flavor persistence	4.53 ± 0.77^{a}	3.91 ± 0.52^{b}	4.36 ± 0.78^{ab}	4.66 ± 0.35^{a}

Values with different letter within row indicate significant differences by Tukey's HSD post hoc test ($p \leq 0.05$).

Table 6. Partial least square (PLS) regression results: standardized regression coefficients indicating the relative contribution of the volatile organic compounds (VOCs) to the sensory attributes of peach fruits [a]

m/z	VOCs	Aroma intensity	Ripe fruit	Stone aroma	Flavor intensity	Persistence	[b] Organoleptic description
43.017	Fragment (ester)	0.07**	0.06*		0.05**	0.05**	
43.054	Fragment (alcohol, ester, acetate)						
44	N.I.	0.05*	0.05*		0.04*	0.05*	
45.034	Acetaldehyde	-0.08*	-0.06*		-0.06*	-0.08*	Pungent, ethereal, fruity [3]
46	N.I.	-0.08*	-0.06*		-0.06*	-0.08*	
57	N.I.	-0.04*	-0.04**	0.02*	-0.03*	-0.02*	
57.069	Fragment (alcohol, ester)						
58	N.I.	-0.04*	-0.04**	0.02*	-0.03*	-0.02*	
61.028	Acetic acid	0.08**	0.07**		0.06**	0.06**	Sour pungent, cider vinegar, acidic tangy [3]
62	N.I.	0.07**	0.07**		0.06**	0.06**	
63.044	**Ethylene glycol**					-0.04*	
73.064	2-Butanone	-0.06*				-0.07*	Chemical, slightly fruity, green [3]
75.043	Methyl acetate	0.07*	0.07*		0.05*	0.07*	Fruity, slightly bitter [3]
75.079	2-Methylpropanol						Wine [3], Pungent [6], Licorice, alcoholic, chemical [8]
81.044	**Pyrazine**	-0.03*	-0.04*		-0.02*		Green, earthy, nutty, woody [2]
82	N.I.	-0.03*	-0.03*		-0.02*		
85.064	2-Pentenal	0.02*				0.02*	Fruity, strawberry [4] Green [6]
85.100	Hydrocarbon/ Fragment (alcohol)						
89.059	Ethyl acetate	0.06**	0.06**		0.05**	0.05**	Ethereal, fruity, sweet [3]
97.065	2-Ethylfuran	-0.04*	-0.04*		-0.03*		Rubber, pungent, acid [4], Sweet-ethereal, burnt [6]
97.101	**1-Methylcyclohexene**						
98	N.I.	-0.04*	-0.04**	0.02*	-0.03*	-0.02*	
99.010	2,5-Furandione	-0.04*	-0.04**	0.02*	-0.03*	-0.02*	Faint acrid [3]

99.046	2-Furylmethanol						Warm, oily, burnt, sweet, caramel [3]
99.081	2-Hexenal						Almond, herbal, apple, plum [3] Green, banana-like [1]
107.049	Benzaldehyde	-0.05*	-0.04*		-0.04*	-0.06*	Bitter almond [3] [8]
115.075	γ-Hexalactone	0.12***	0.11**		0.09**	0.11***	Coconut, fruity [1], vanilla-like, warm, herbaceous, sweet [3]
115.108	Heptanal						Fatty, harsh, pungent, green, citrus [3] [8]
121.066	Benzeneacetaldehyde	-0.08*	-0.07*		-0.06*	-0.08*	Harsh, hawthorn, floral, pungent, bitter, sweet [3]
121.100	Trimethylbenzene						Musty [5]
123.117	Fragment (farnesene)		-0.05*				
137.133	Myrcene					0.04*	Woody, resinous, musty, balsamic, ethereal [8]
138.064	**Aminobenzoic acid**					0.04*	
139.113	2-Pentylfuran	-0.06*	-0.06*		-0.05*	-0.06*	Fatty, butter, warm, sweet [8]
139.145	**Decahydronaphthalene**						
143.108	γ-Octalactone	0.08*	0.07*		0.06*	0.08*	Coconut [1], creamy, apricot, peach, sweet [3]
143.143	Nonanal						Fatty, wax, citrus, green, melon skin, floral [3] [8]
153.128	Hotrienol	0.09*	0.08*		0.07*	0.09*	Sweet, tropical, fennel, ginger [6]
155.108	**2-Nonen-4-olide**					0.04*	Overripe orange, oak [7]
155.143	Linalool/ α-Terpineol						Sweet, fruity, floral, tea-like [1] [6]/ Floral, sweet [6]
	R^2	0.58	0.57	0.07	0.34	0.44	

[a] Significance: standardized regression coefficients ("β coefficients") were significant at $p \leq 0.05$ (*), $p \leq 0.01$ (**) and $p \leq 0.001$ (***). Only significant coefficients are shown. N.I. (not identified): compounds not identified by PTR-Tof-MS. Bold compounds not previously reported among peach fruit VOCs

[b] References: [1] Derail et al. 1999; [2] Buchbauer et al., 2000; [3] Burdock 2001; [4] Jordán et al., 2002; [5] Longchamp et al. 2009; [6] Narain et al. 2010; [7] Stamatopoulos et al., 2014; [8] Bonneau et al. 2016.

Figure captions

Figure 1. Scores (upper) and loadings (lower) plot of the discriminant analysis (DA) performed on the PTR-MS data of the *Prunus persica* cultivars according to their typology: peaches (red spheres), nectarines (green pyramids), flat peaches (blue cubes), and canning peaches (yellow cylinders).

Figure 2. Scores (upper) and loadings (lower) plot of the discriminant analysis (DA) performed on the sensory data of the *Prunus persica* cultivars according to their typology: peaches (red spheres), nectarines (green pyramids), flat peaches (blue cubes), and canning peaches (yellow cylinders).

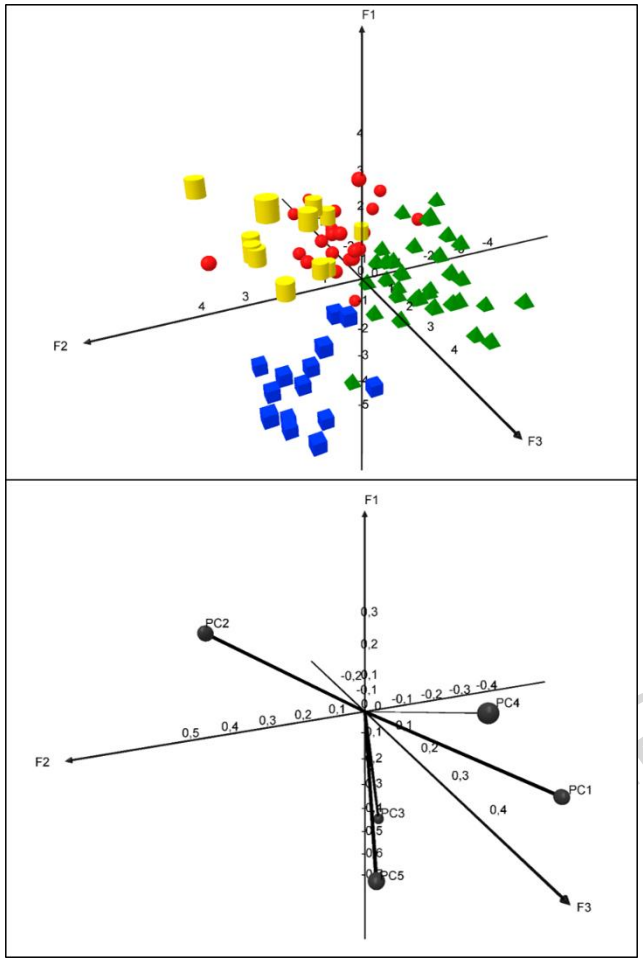


Figure 1

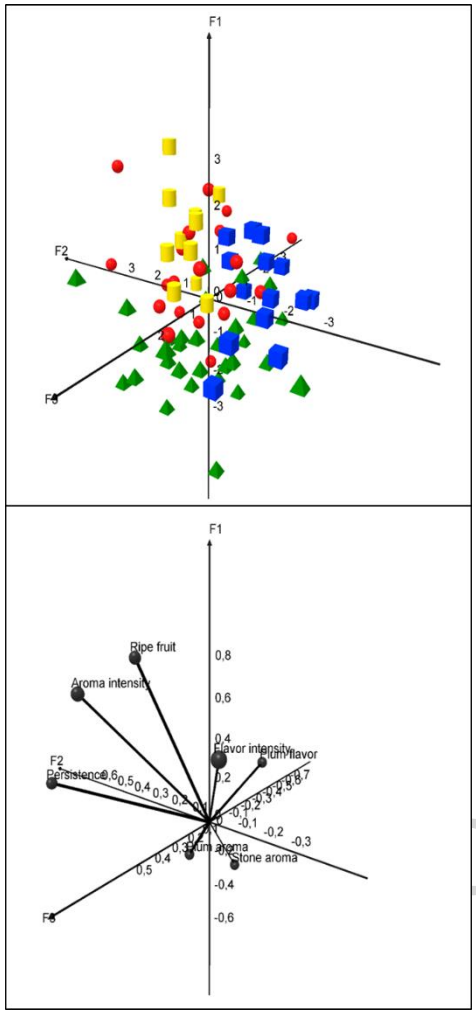
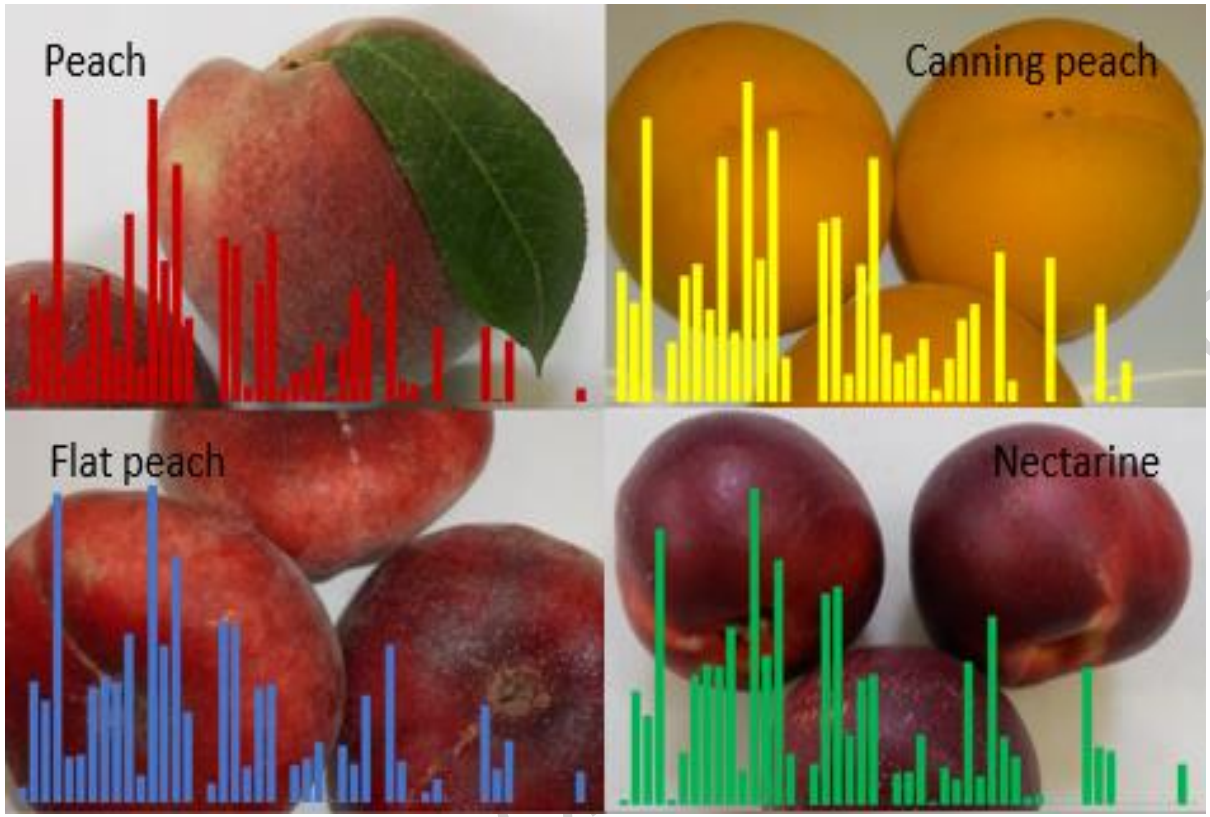


Figure 2



Graphical abstract

Highlights

- Peach, flat peach, nectarine, and canning peach have distinct aroma profile.
- PTR-MS is useful to differentiate the volatile profiles of the peach typologies.
- Canning peach and flat peach show an enhanced aroma and flavor perception.
- The improvement of peach quality should consider the typological aroma profiles.