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Carotenoids, Phenolic Profile, Mineral Content and Antioxidant Properties in Flesh and Peel of *Prunus persica* Fruits during Two Maturation Stages

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Abstract Carotenoids and phenolic profile, antioxidant activity as well as concentrations of selected macronutrients (K, N, Mg, Ca and Na) and micronutrients (Zn, Cu and Mn) in flesh and peel of peach fruit were recorded at two harvest dates. Predominant mineral was potassium, followed by calcium, magnesium and sodium. The concentration of most micronutrients was greater in the peel than in the flesh especially in early season. The concentration of most elements in flesh and peel decreased during fruit maturation. Total carotenoids content varied with respect to the cultivar. β-cryptoxanthin and β-carotene were the major carotenoids in both tissues and flesh contain the lowest amounts. Neochlorogenic acid, chlorogenic acid, catechin, epicatechin, gallic acid, rutin, quercetin-3-*O*-galactoside, cyanidin-3-*O*-glucoside, cyanidin-3-*O*-rutinoside, were detected in both peel and flesh, with chlorogenic acid and catechin being the predominant components. Peel extracts showed markedly higher antioxidant activities, when estimated by ABTS or DPPH assays, than the flesh counterparts, consistent with the observed higher phenolic content. Overall, total phenolics levels increased at full ripening stage in both peel and flesh. The results found herein provide important data on carotenoids, phenolic and macro- and micronutrient changes during fruit growth, and emphases peach fruit as a potential functional food.

Keywords *Prunus persica* · Carotenoids · Mineral elements · Phenolic profile · Antioxidant activity · Ripening

Abbreviations

ABTS+	2,2-azinobis-3-ethylbenzothiazoline-6-sulfonic acid radical cation
DPPH•	2,2-diphenyl-1-picrylhydrazyl radical
EC_{50}	Effective concentration

Introduction

Peach (*Prunus persica* (L.) Batsch) is one of the most popular fruits in the world during summer, because of its high water and mineral content [1] and the presence of carotenoids and antioxidant molecules, such as procyanidins, anthocyanins, catechins and phenolic acids [2–4], which determine the nutritive values and, together with sugars and organic acids, contribute to the sensory quality of the fruits.

The phytochemical content of fruits is strongly influenced by different factors, such as cultivar [5–7], rootstock [8, 9], climatic conditions, agronomic practices [10, 11] and ripening stage at harvest [12, 13]. The fruit peel is usually rejected because it is thought to be indigestible or contaminated by

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sprays or human disease agents [8]. However, it is richer in nutritive compounds than the edible fleshy parts. In particular, peel of peach and nectarine contains at least twice as much phenolics [2], carotenoids and ascorbic acid as the flesh [6].

Being a potential source of bioactive compounds, peach fruit presents relevant health implications [1]. The dietary intake of peach can reduce the generation of reactive oxygen species and provide protection from a number of chronic diseases [14]. Peach shows laxative properties and is appropriate to prevent constipation and for the treatment of duodenum ulcers [6, 15]. β-carotene, α-carotene, and β-cryptoxanthin are precursors of vitamin A, essential for normal growth, reproduction, vision and resistance to infection. A severe deficiency in vitamin A can lead to xerophtalmia and irreversible blindness [16]. Furthermore, chlorogenic and neochlorogenic acids were found to be the two specific phenolic acid components of peaches and plums able to kill breast cancer cells [17].

To the best of our knowledge, information about nutritional values of peach fruit from Tunisia at different ripening stages is scarce. In a previous paper [18], we reported a genotype influence on fatty acid and volatile compounds composition of the three peach cultivars studied in the present research. Moreover, a ripening-dependent effect was observed, suggesting that the best harvesting time to achieve optimal characteristics should be the commercial ripening date. In this context, this paper aims to characterize the nutraceutical properties (carotenoids and phenolic profile, antioxidant and reducing power) and the mineral composition of flesh and peel from three peach cultivars produced in Tunisia to determine the adequate date of maturity for each variety.

Materials and Methods

Plant Material

Three peach (*Prunus persica* (L.) Batsch) cultivars ('Early May Crest', 'Sweet Cap' and 'O'Henry') were grown in the two seasons 2013–2014 at an experimental orchard (Regional Center of Agricultural Research Farm in the region of Sidi Bouzid), Center-West of Tunisia (35°2′0″N, 9°30′0″E; at 313 m a.s.l.) [18]. The study was conducted at two harvest dates. The first harvest date, named commercial ripening, represents the beginning of ripening and is performed when the fruit is fully developed and the full degree of color is almost attained but the flesh is firm and the fruit would stand shipping. This date is preferred by farmers since fruit is very resistant to marketing conditions (refrigeration, export, etc.). The second harvest date represents the full ripening of fruits from the point of view of taste, color, etc. For each ripening stage, three replicates were made. Each replicate consisted of 20 fruits collected from three trees in order to obtain a representative set of fruits. Once fruits were hand harvested, peel and flesh were separated within 24 h, lyophilised and stored at −20 °C until analysis.

Methods

Please see electronic supplementary material as File 1and Fig. S1.

Results and Discussion

Macro and Micro Elements

The microelements (Cu, Mn and Zn) and macroelements (Ca, Mg, Na, N and K) profiles in peel and flesh of three different peach cultivars are listed in Table 1. Similar profiles were present in peel and flesh for the three peach cultivars, whereas significant differences were observed for each individual mineral. In this study, the peach fruit proved to be one of the most suitable sources of macroelements, especially potassium (Table 1). This finding is in accordance with previous results obtained for *Prunus persica* cultivars [19] where potassium levels were higher in flesh than peel. High potassium intake was positively associated with bone metabolism, lower blood pressure and reduced cardiovascular disease morbidity and mortality [20, 21]. Magnesium is generally present in high amounts in the peel of the three peach cultivars (Table 1). Only few changes were observed in the content of macroelements throughout ripening. Sodium and nitrogen were relatively less concentrated, which might be considered as a favorable result in view of the need to consume low quantities of these minerals. Zinc, copper and manganese, essential microelements for human enzymes metabolism [22], were more concentrated in peel than in flesh, with zinc and copper being the major elements in all samples (Table 1). All micronutrients, with few exceptions, were similarly concentrated during ripening.

Nutraceutical Compounds

Carotenoids Color changes that take place specially during ripening process strongly influence both visual and eating quality of peaches and nectarines. Genotypic differences markedly affect color intensity, the main pigments responsible for color (both skin and flesh) being carotenoids [23]. Total carotenoids content varied among cultivars (Table 1), with 'O'Henry' showing the highest contents. In both tissues, β-cryptoxanthin and β-carotene were the major carotenoids, even if cultivar-dependent differences were observed, in agreement with previous reports [6, 24, 25]. In particular, β-carotene was the main carotenoid in 'O'Henry', while 'Sweet Cap' presented higher β-cryptoxanthin concentration. In 'Early May Crest' differences were observed between the

Table 1 Minerals (mg 100 g^{-1} DW) and carotenoids (μg 100 g^{-1} FW) evaluated in peel and flesh from *Prunus persica* cultivars harvested at two different dates

	Commercial ripening						Full ripening
	Sweet Cap		Early May Crest		O'Henry		Sweet Cap
	Peel	Flesh	Peel	Flesh	Peel	Flesh	Peel
Minerals							
Mg	76.87 ± 6.46^{f}	$79.07 \pm 7.56^{b,**}$	116.55 ± 11.79^{e}	107.87 ± 9.82^{a}	$90.60 \pm 8.47^{f,§}$	80.34 ± 6.22^{b}	$66.90 \pm 9.27^{q,+}$
Ca	$74.53 \pm 11.16^{f,++}$	33.13 ± 7.29^{b}	$85.95 \pm 12.51^{e,f}$	66.56 ± 12.74^{a}	$103.97 \pm 16.42^{e,++}$	$39.68 \pm 1.52^{b,**}$	$61.42 \pm 3.04^{q,++}$
Zn	1.95 ± 0.51^{e}	$1.07 \pm 0.16^{b,*}$	$1.35 \pm 0.40^{e,f}$	1.07 ± 0.03^{b}	$0.92 \pm 0.03^{f,+}$	$1.46 \pm 0.27^{a,*}$	$1.06 \pm 0.16^{q,+}$
Mn	$0.36 \pm 0.08^{f,+}$	0.07 ± 0.03^{b}	0.76 ± 0.07^{e}	$0.64 \pm 0.10^{a,*}$	$0.44 \pm 0.05^{f,++}$	0.17 ± 0.06^{b}	0.26 ± 0.03^{r}
Cu	$1.16 \pm 0.03^{f,§,++}$	$0.87 \pm 0.10^{a,*}$	0.28 ± 0.10^{f}	$0.18 \pm 0.06^{b,*}$	$4.88 \pm 1.61^{e,§§,+}$	$0.92 \pm 0.08^{a,**}$	$1.62 \pm 0.19^{p,++}$
K	$1415.01 \pm 120.31^{e,+}$	$1774.55 \pm 49.72^{a,**}$	1405.70 ± 21.44^{e}	1485.86 ± 171.50^{a}	1283.67 ± 143.76^{e}	1567.51 ± 295.38^{a}	1308.10 ± 100.67^{pq}
Na	19.01 ± 2.37^{g}	24.63 ± 4.71^{b}	33.02 ± 8.41^{f}	34.59 ± 4.95^{a}	$58.41 \pm 7.51^{e,§,++}$	16.73 ± 3.23^{b}	16.03 ± 3.46^{r}
N	6.37 ± 0.13^{e}	$5.12 \pm 0.53^{b,*}$	6.43 ± 0.28^{e}	$6.92 \pm 0.66^{a,*}$	$5.00 \pm 0.18^{f,+}$	3.82 ± 0.93^{b}	$5.97 \pm 0.36^{p,+}$
Carotenoids							
Lutein	nd	nd	$10.54 \pm 1.45^{e,§§,++}$	$2.49 \pm 1.04^{a,*}$	$7.66 \pm 0.38^{f,§§,++}$	$3.79 \pm 0.44^{a,++}$	nd
Lycopene	$221.09 \pm 42.81^{e,+}$	$22.00 \pm 5.29^{a,*}$	$45.57 \pm 2.08^{f,§§,++}$	$13.51 \pm 3.31^{b,**}$	$57.66 \pm 6.24^{f,§§,++}$	$17.86 \pm 2.55^{c,*}$	$327.90 \pm 85.89^{p,+}$
β-carotene	$385.13 \pm 49.35^{f,++}$	$61.30 \pm 8.83^{a,*}$	$653.93 \pm 84.46^{f,§§,++}$	358.10 ± 71.91	$2276.90 \pm 265.19^{e,§§,++}$	1065.65 ± 288.16^{b}	$410.13 \pm 97.00^{q,+}$
β-cryptoxanthin	$2160.77 \pm 362.88^{e,++}$	$293.30 \pm 25.73^{a,*}$	$830.15 \pm 51.32^{f,§§,++}$	$173.54 \pm 31.57^{a,**}$	$1849.42 \pm 563.72^{e,§,++}$	291.94 ± 105.75^{a}	$2352.85 \pm 597.97^{p,+}$
Total carotenoids	$2766.985 \pm 452.021^{f,++}$	$376.596 \pm 13.642^{a,*}$	$1540.18 \pm 133.43^{g,§§,++}$	$547.64 \pm 86.54^{a,b,*}$	$4191.64 \pm 760.70^{e,§§,++}$	1379.24 ± 244.83^{b}	$3090.88 \pm 776.26^{p,+}$

	Full ripening				
	Sweet Cap	Early May Crest		O'Henry	
	Flesh	Peel	Flesh	Peel	Flesh
Minerals					
Mg	47.11 ± 6.68^{z}	109.85 ± 14.16^{p}	105.04 ± 11.59^{x}	$111.98 \pm 6.13^{p,+}$	76.61 ± 10.86^{y}
Ca	23.97 ± 3.89^{y}	$87.02 \pm 13.54^{pq,+}$	55.71 ± 9.40^{x}	$93.02 \pm 19.12^{p,+}$	58.81 ± 1.81^{x}
Zn	0.68 ± 0.12^{y}	$1.58 \pm 0.25^{p,+}$	1.01 ± 0.02^{x}	1.03 ± 0.12^{q}	0.74 ± 0.17^{y}
Mn	0.11 ± 0.07^{y}	$0.64 \pm 0.01^{p,++}$	0.40 ± 0.05^{x}	$0.53 \pm 0.03^{q,++}$	0.17 ± 0.06^{y}
Cu	0.64 ± 0.05^{x}	0.41 ± 0.07^{q}	0.31 ± 0.03^{y}	0.07 ± 0.03^{r}	0.16 ± 0.08^{z}
K	1418.23 ± 89.83^{xy}	1408.23 ± 30.05^{p}	1557.80 ± 141.27^{x}	1191.38 ± 109.94^{q}	1340.84 ± 70.01^{y}
Na	19.02 ± 7.99^{x}	47.97 ± 7.89^{p}	31.46 ± 6.44^{x}	33.21 ± 5.95^{q}	29.66 ± 6.60^{x}
N	3.71 ± 0.59^{y}	4.80 ± 0.29^{p}	5.54 ± 0.07^{x}	5.22 ± 0.80^{p}	3.85 ± 0.62^{y}
Carotenoids					
Lutein	nd	nd	$5.20 \pm 1.24^{x,++}$	$12.02 \pm 2.30^{p,++}$	$5.62 \pm 0.65^{x,++}$
Lycopene	17.66 ± 4.07^{y}	$140.04 \pm 34.17^{q,++}$	25.32 ± 2.32^{x}	$36.92 \pm 4.93^{r,+}$	22.64 ± 4.48^{z}

Table 1 (continued)

	Full ripening					
	Sweet Cap		Early May Crest		O'Henry	
	Flesh		Peel	Flesh	Peel	Flesh
β-carotene	35.75 ± 5.50^{y}		$1569.65 \pm 260.41^{p,++}$	405.24 ± 133.91^{x}	$2730.95 \pm 616.09^{r,+}$	1108.50 ± 88.85^{y}
β-cryptoxanthin	181.83 ± 53.10^{y}		$1664.12 \pm 336.68^{p,++}$	330.91 ± 29.68^{x}	$814.45 \pm 289.46^{q,+}$	341.28 ± 40.92^{z}
Total carotenoids	235.23 ± 61.94^{y}		$3373.81 \pm 612.48^{p,++}$	766.67 ± 103.70^{x}	$3594.35 \pm 899.57^{q,+}$	1478.03 ± 47.62^{z}

Values are the means of three different peach samples (n = 3) ± standard deviation. Different superscripts for the same parameter mean significant differences among cultivars at $p < 0.05$, as detailed below. Different letters a–c and e-g, for the same parameter, within columns indicate significant differences $p < 0.05$ with respect to harvest period for peel. Different letters p-r and x-z, for the same parameter, within columns indicate significant differences $p < 0.05$ with respect to harvest period for flesh. Different symbols *, **, for the same parameter, within columns indicate significant differences $p < 0.05$ with respect to harvest period for flesh at each harvest $p < 0.05$. Different symbols §, §§, for the same parameter, within columns indicate significant differences $p < 0.05$ with respect to harvest period for peel at each harvest $p < 0.05$. Different symbols +,++, for the same parameter, within columns indicate significant differences between peel and flesh with respect to cultivar

two tissues, β-cryptoxanthin being more concentrated in the peel and β-carotene in the flesh. Both β-carotene and β-cryptoxanthin are vitamin A precursors, even if β-carotene seems to be a preferred substrate of enzymes involved in carotenoid absorption and conversion to vitamin A [26]. All carotenoids were less concentrated in the flesh, confirming previous results [25]. Differences between the two tissues were particularly evident in 'Sweet Cap', where flesh total carotenoids were about 86 and 92 % lower than in the peel, at commercial and full ripening, respectively. Comparing the two ripening stages, no statistical differences were found for 'Sweet Cap'; however, an increase was observed from commercial to full ripening for 'Early May Crest' and 'O'Henry' cultivars (Table 1).

Phenolics Table 2 shows the phenolic profile of peel and flesh of the three peach cultivars at the two different ripening stages. In both tissues, neochlorogenic acid was generally less concentrated than chlorogenic acid, in accordance with published findings [2, 3, 7, 24]. Cholorogenic and neochlorogenic acids are reported to be more concentrated in immature fruits [27]. A ripening dependent decrease of neochlorogenic acid was observed in 'O'Henry' peel, while chlorogenic acid underwent a decrease in the flesh of 'Early My Crest' and 'O'Henry'. Conversely, 'Sweet Cap' peel showed the highest values of both acids at full ripening (Table 2). Similar amounts of neochlorogenic acid were detected in peel and flesh of 'O'Henry' and, limited to commercial ripening, of 'Sweet Cap' fruit, while 'Early May Crest' exhibited higher concentration of neochlorogenic acid in the flesh at both ripening stages (Table 2).

In accordance with previous reports [2, 9], catechin was the main monomeric flavan-3-ol, and epicatechin was present in lower amounts in any cultivar and tissue and for any ripening stage (Table 2). Catechin showed a wide range of concentration among samples. Sweet Cap' exhibited the highest concentration in both tissues, while 'Early May Crest', particularly at commercial ripening, showed the lowest values.

Cyanidin-3-glucoside and cyanidin-3-rutinoside were quantitatively higher in peel than flesh tissue. Cyanidin-3-glucoside represented the main anthocyanin in 'Early May Crest' and 'O'Henry', while 'Sweet Cap' mainly contained cyanidin-3-rutinoside. Generally, peel anthocyanins are more concentrated in yellow-fleshed than white-fleshed cultivars [2, 5], as observed in our work for the yellow-fleshed cultivars 'Early May Crest' and 'O'Henry' (Table 2). This latter also showed good amounts of anthocyanins in the flesh, particularly at full ripening.

'Sweet cap' presented the highest amount of total phenolics at both harvest dates, although it showed very low anthocyanin concentration. 'Early May Crest' and 'O'Henry' exhibited the lowest amount at commercial and full ripening, respectively (Table 2).

Table 2 Phenolic profile (mg kg^{-1} FW) and effective concentration (EC_{50}) values (mg kg^{-1} FW) evaluated in peel and flesh from *Prunus persica* cultivars harvested at two different dates

	Commercial ripening						Full ripening
	Sweet Cap		Early May Crest		O'Henry		Sweet Cap
	Peel	Flesh	Peel	Flesh	Peel	Flesh	Peel
Phenolic profile							
Neochlorogenic acid	$53.87 \pm 2.68^{e,\S}$	56.28 ± 4.85^{a}	$19.65 \pm 4.49^{g,++}$	50.00 ± 7.83^{ab}	$34.97 \pm 4.19^{f,\S}$	41.42 ± 5.43^{b}	$98.25 \pm 10.90^{p,++}$
Chlorogenic acid	$110.40 \pm 9.95^{e,\S\S}$	89.13 ± 1.64^{a}	63.92 ± 10.43^{g}	$85.42 \pm 14.61^{a,*}$	$89.09 \pm 5.28^{f,+}$	$55.54 \pm 7.09^{b,*}$	$206.97 \pm 17.89^{p,++}$
Total hydroxycinnamic acids	$164.28 \pm 12.51^{e,\S\S}$	145.42 ± 5.22^{a}	$83.58 \pm 12.73^{g,+}$	$135.42 \pm 19.79^{a,*}$	$124.06 \pm 9.44^{f,+}$	96.96 ± 12.51^{b}	$305.22 \pm 27.10^{p,++}$
Catechin	$117.59 \pm 4.89^{e,\S\S}$	$176.42 \pm 49.91^{a,*}$	24.18 ± 6.17^{g}	12.95 ± 4.83^{b}	55.44 ± 15.61^{f}	37.65 ± 17.34^{b}	$218.00 \pm 10.96^{p,+}$
Epicatechin	$41.16 \pm 7.76^{e,\S}$	$25.63 \pm 2.08^{a,*}$	12.65 ± 4.19^{f}	$4.17 \pm 0.54^{b,*}$	$19.37 \pm 3.26^{f,\S,++}$	8.46 ± 1.10^{b}	65.57 ± 3.87^{p}
Total flavan-3-ols acids	$158.75 \pm 12.56^{e,\S\S}$	$202.06 \pm 51.91^{a,*}$	36.83 ± 10.34^{g}	17.12 ± 5.18^{b}	74.81 ± 15.67^{f}	46.11 ± 18.34^{b}	$283.57 \pm 14.1^{(p}$
Gallic acid	$44.67 \pm 2.76^{e,\S\S}$	$30.53 \pm 4.61^{b,**}$	54.97 ± 7.58^{e}	28.60 ± 2.98^{a}	45.02 ± 15.53^{e}	31.45 ± 1.12^{b}	84.77 ± 8.32^{p}
Total hydroxybenzoic acids	$44.67 \pm 2.76^{e,\S\S}$	$30.53 \pm 4.61^{b,**}$	54.97 ± 7.58^{e}	28.60 ± 2.98^{a}	45.02 ± 15.53^{e}	31.45 ± 1.12^{b}	84.77 ± 8.32^{p}
Quercetin-3-rutinoside	$27.80 \pm 9.44^{e,+}$	2.47 ± 0.41^{a}	$12.50 \pm 5.55^{e,+}$	1.27 ± 0.35^{b}	$27.98 \pm 9.56^{e,++}$	$1.44 \pm 0.21^{b,*}$	$30.51 \pm 2.42^{p,++}$
Quercetin-3-galactoside	$52.95 \pm 10.67^{e,+}$	$16.19 \pm 1.92^{a,*}$	16.65 ± 7.79^{f}	4.31 ± 1.34^{b}	$45.49 \pm 12.28^{e,+}$	10.13 ± 6.86^{ab}	57.48 ± 10.16^{p}
Total flavonols	$80.75 \pm 20.07^{e,++}$	$18.66 \pm 2.29^{a,*}$	29.15 ± 13.34^{f}	5.58 ± 1.01^{b}	$73.47 \pm 21.69^{e,++}$	11.57 ± 6.84^{ab}	$88.00 \pm 12.35^{p,++}$
Cyanidin-3-glucoside	$1.43 \pm 0.31^{f,++}$	$0.03 \pm 0.01^{b,**}$	$30.62 \pm 8.33^{e,\S\S,++}$	0.59 ± 0.43^{b}	$38.45 \pm 8.88^{e,+}$	3.03 ± 1.66^{a}	$2.43 \pm 0.59^{r,++}$
Cyanidin-3-rutinoside	$10.10 \pm 2.83^{e,++}$	$0.09 \pm 0.04^{a,*}$	$12.59 \pm 2.81^{e,\S,++}$	0.25 ± 0.18^{a}	$15.62 \pm 4.89^{e,++}$	0.32 ± 0.32^{a}	$12.90 \pm 3.17^{q,++}$
Total anthocyanins	$11.53 \pm 3.10^{f,++}$	$0.12 \pm 0.06^{b,**}$	$43.21 \pm 10.99^{e,\S\S,++}$	0.84 ± 0.61^{b}	$54.07 \pm 13.66^{e,++}$	3.35 ± 1.98^{a}	$15.33 \pm 2.99^{r,++}$
Total phenols identified	$459.98 \pm 8.68^{e,\S\S}$	396.80 ± 57.03^{a}	$247.73 \pm 42.86^{g,\S}$	187.56 ± 23.57^{b}	$371.43 \pm 28.38^{f,++}$	189.45 ± 37.76^{b}	776.89 ± 54.93^{p}
EC_{50} values							
+ ABTS	$31.69 \pm 5.34^{f,++}$	$7.55 \pm 1.84^{b,**}$	$70.88 \pm 15.33^{e,\S,++}$	$8.02 \pm 2.24^{a,**}$	$20.23 \pm 4.92^{f,+}$	$11.87 \pm 0.94^{a,**}$	24.91 ± 4.39^{q}
+ DPPH	$19.07 \pm 2.33^{f,\S\S}$	22.83 ± 3.50^{b}	57.02 ± 21.57^{e}	$16.56 \pm 5.13^{b,**}$	$48.01 \pm 4.89^{e,\S\S,+}$	34.43 ± 3.86^{a}	49.95 ± 10.54^{p}
++Reducing power	$9.60 \pm 0.59^{f,\S\S}$	8.63 ± 2.46^{a}	$13.18 \pm 1.82^{e,++}$	$4.43 \pm 0.72^{a,**}$	$14.38 \pm 2.30^{e,\S,+}$	$5.14 \pm 0.51^{a,**}$	$16.37 \pm 1.22^{p,++}$

	Full ripening				
	Sweet Cap	Early May Crest		O'Henry	
	Flesh	Peel	Flesh	Peel	Flesh
Phenolic profile					
Neochlorogenic acid	$57.50 \pm 5.52^{(x)}$	$21.81 \pm 4.45^{q,+}$	37.51 ± 15.49^{xy}	24.77 ± 4.10^{q}	28.94 ± 7.52^{y}
Chlorogenic acid	89.37 ± 4.60^{x}	64.57 ± 2.29^{q}	44.33 ± 8.36^{y}	$85.58 \pm 7.94^{q,+}$	38.35 ± 6.64^{y}
Total hydroxycinnamic acids	146.88 ± 8.41^{x}	86.38 ± 6.64^{q}	81.83 ± 21.28^{y}	$110.36 \pm 12.01^{q,+}$	67.29 ± 14.06^{y}
Catechin	188.05 ± 38.68^{x}	52.91 ± 15.35^{q}	22.58 ± 8.36^{y}	50.26 ± 18.22^{q}	25.20 ± 11.06^{y}
Epicatechin	24.30 ± 4.60^{x}	6.36 ± 0.57^{q}	2.09 ± 1.06^{y}	10.25 ± 2.38^{q}	6.45 ± 3.36^{y}
Total flavan-3-ols acids	212.35 ± 43.27^{x}	59.27 ± 15.81^{q}	24.67 ± 9.06^{y}	60.52 ± 20.59^{q}	31.65 ± 14.17^{y}
Gallic acid	42.80 ± 2.84^{x}	45.79 ± 1.24^{q}	22.86 ± 12.36^{y}	46.85 ± 3.67^{q}	37.72 ± 4.31^{y}
Total hydroxybenzoic acids	42.80 ± 2.84^{x}	45.79 ± 1.24^{q}	22.86 ± 12.36^{y}	46.85 ± 3.67^{q}	37.72 ± 4.31^{y}
Quercetin-3-rutinoside	$3.34 \pm 0.36^{++}$	$16.59 \pm 1.65^{q,++}$	1.28 ± 0.18^{y}	$15.89 \pm 5.42^{q,++}$	0.88 ± 0.25^{z}
Quercetin-3-galactoside	8.61 ± 2.35^{x}	28.36 ± 9.65^{q}	22.23 ± 18.12^{x}	30.82 ± 11.53^{q}	11.48 ± 3.73^{x}
Total flavonols	11.95 ± 2.89^{x}	44.95 ± 9.60^{q}	23.51 ± 18.30^{x}	$46.71 \pm 16.93^{q,+}$	12.36 ± 3.91^{x}
Cyanidin-3-glucoside	0.28 ± 0.03^{y}	$97.04 \pm 1.14^{p,++}$	0.57 ± 0.41^{y}	$39.44 \pm 3.23^{q,++}$	7.39 ± 5.42^{x}
Cyanidin-3-rutinoside	0.23 ± 0.04^{x}	$63.54 \pm 11.56^{p,+}$	0.11 ± 0.02^{y}	$11.48 \pm 3.08^{q,++}$	nd
Total anthocyanins	0.51 ± 0.01^{y}	$160.58 \pm 11.81^{p,++}$	0.68 ± 0.40^{y}	$50.92 \pm 6.18^{q,++}$	7.39 ± 5.42^{x}

Table 2 (continued)

	Full ripening					
	Sweet Cap	Early May Crest		O'Henry		
	Flesh	Peel	Flesh	Peel	Flesh	
Total phenols identified	414.49 ± 51.90^{x}	$396.97 \pm 19.75^{p,++}$	153.55 ± 22.38^{y}	$315.35 \pm 55.78^{p,+}$	156.41 ± 35.32^{y}	
EC_{50} values						
+ ABTS	$31.80 \pm 3.80^{y,*}$	$44.26 \pm 1.33^{p,+}$	$63.54 \pm 5.02^{x,*}$	$10.21 \pm 3.20^{r,+}$	$43.46 \pm 10.57^{y,*}$	
+ DPPH	26.55 ± 1.43^{z}	$38.99 \pm 0.81^{pq,+}$	63.62 ± 5.23^{x}	33.50 ± 2.43^{q}	41.32 ± 7.79^{y}	
++Reducing power	11.30 ± 1.27^{x}	9.69 ± 0.46^{q}	8.75 ± 0.28^{y}	8.83 ± 0.29^{q}	9.01 ± 0.99^{y}	

Values are the means of three different peach samples (n = 3) ± standard deviation. Different superscripts for the same parameter mean significant differences among cultivars at $p < 0.05$, as detailed below. Different letters a–c and e-g, for the same parameter, within columns indicate significant differences $p < 0.05$ with respect to harvest period for peel. Different letters p-r and x-z, for the same parameter, within columns indicate significant differences $p < 0.05$ with respect to harvest period for flesh. Different symbols *, **, for the same parameter, within columns indicate significant differences $p < 0.05$ with respect to harvest period for flesh at each harvest $p < 0.05$. Different symbols §, §§, for the same parameter, within columns indicate significant differences $p < 0.05$ with respect to harvest period for peel at each harvest $p < 0.05$. Different symbols +,++, for the same parameter, within columns indicate significant differences between peel and flesh with respect to cultivar. ABTS+ (2,2-azinobis-3-ethylbenzothiazoline-6-sulfonic acid radical cation); DPPH• (2,2-diphenyl-1-picrylhydrazyl radical). + EC50 (mg kg^{-1} FW): effective concentration at which 50 % of DPPH or ABTS radicals are scavenged. ++ EC_{50} (mg kg^{-1} FW): effective concentration at which the absorbance is 0.5

Two different flavonols were quantified: quercetin-3-rutinoside and quercetin-3-galactoside, which is consistent with previous works [2, 3, 12]. Their contents differed between peel and flesh and were dependent on cultivar and ripening stage (Table 2). As for the other phenolics, the peel contained significantly higher flavonol concentration than the flesh (2- to 7-fold), the highest concentration being found in 'Sweet Cap' and 'O'Henry'. These results are in accordance with previous reports in a wide range of both peach and nectarine round cultivars [5, 6].

Overall, no clear trend was observed in phenolic content with ripening, in accordance with previous findings [2]. Peel total phenols of 'Sweet Cap' and 'Early May Crest' increased with ripening, while no change occurred in the flesh. In 'Sweet Cap' peel such an increase was due to the higher concentration of hydroxycinnamic acids (86 %), flavan-3-ols (79 %) and hydroxybenzoic acids (90 %) in respect to commercial ripening, while 'Early May Crest' showed an increased concentration of flavan-3-ols (61 %), flavonols (54 %) and anthocyanins (272 %). Other works found significant decrease in phenolic compounds during fruit ripening [12].

Antioxidant Activities

Antioxidant activity was assessed by free radical scavenging (DPPH• and ABTS•+) and reducing power assays (Table 2). The data were normalized and expressed as EC_{50} values (mg kg-1 FW) for comparison. Differences related to cultivar, tissue and ripening stage were observed. For any cultivar, ABTS• scavenging activity was higher in the peel than in the flesh at commercial ripening, in accordance with the findings of Loizzo et al. [4] in fruits of *Prunus persica*, var. platycarpa. However, an opposite trend was shown at full ripening, when 'Early May Crest' and 'O'Henry' showed higher activity in the flesh (Table 2). All the cultivars exhibited the highest flesh ABTS• scavenging activity at full ripening, while no change was observed in the peel, except for 'Early May Crest', whose activity decreased with ripening (Table 2). At both stages, the highest peel antioxidant activity was observed in 'Early May Crest' and the lowest in 'O'Henry'. In the flesh, cultivar-dependent differences were less evident, with Sweet Capuse' showing the lowest activity at both stages.

Some discrepancies can be found between phenolic concentration and ABTS• scavenging activity. At both ripening dates, peel was a richer source of phenols than flesh. However, at full ripening, except for 'Sweet Cap', antioxidant activity was higher in the flesh. Moreover, at commercial ripening, 'Early May Crest' showed the highest antioxidant activity among the different cultivars, but it contained the lowest total phenolic concentration. This discrepancy could be related to differences in the concentration of single phenolics, known to possess different antioxidant capacity, as well as to phenolics

not measured in the present work, such as proanthocyanidins, which are present in high levels in *Prunus* sp. [28, 29].

DPPH$^{\bullet}$ scavenging activity showed no clear trends during ripening as well as between the two tissues (Table 2). The only differences between flesh and peel activity were observed in 'O'Henry' and 'Early May Crest' fruits, at commercial and full ripening, respectively. DPPH$^{\bullet}$ scavenging activity increased in 'Sweet Cap' peel and 'Early May Crest' flesh at full ripening while, at this stage, it decreased in 'O'Henry' peel. Among the cultivars, 'Sweet Cap' displayed the lowest activity at commercial ripening in the peel and at full ripening in the flesh. At full ripening the highest DPPH$^{\bullet}$ antioxidant activity in the flesh was shown by 'Early May Crest', similarly to what observed for ABTS$^{\bullet}$ scavenging.

Reducing potential differed among the cultivars (Table 2). As for DPPH$^{\bullet}$ scavenging activity, the lowest reducing power of the peel at commercial ripening was displayed by 'Sweet Cap', which at full ripening exhibited instead the highest activity in both tissues. No cultivar-dependent difference was observed in the flesh at commercial ripening. During ripening, flesh activity generally underwent an increase while in the peel it showed an opposite trend in 'Sweet Cap' (increase) and 'O'Henry' (decrease). Peel reducing potential was higher than flesh one in 'Early May Crest' and 'O'Henry' fruit at commercial ripening and in 'Sweet Cap' at full ripening (Table 2).

Summarizing data recorded by the three different assays, it emerges that at commercial ripening 'Early May Crest' peel has always the highest antioxidant activity, while at full ripening 'O'Henry' peel displays the lowest antioxidant activity among the tested cultivars. Generally, peel activity is higher than flesh at commercial ripening while at full ripening differences between tissues are less clear. Finally, flesh antioxidant activity tends to increase during ripening, while in the peel this trend is only shown by 'Sweet Cap' fruit.

Conclusion

Evaluation of the nutritional value of fruit during the ripening process can help to estimate the optimal date for harvesting to achieve the best quality for both fresh consumption and processing. Carotenoids levels were higher in the peel than in the flesh at commercial ripening, while phenolics, particularly total hydroxycinnamic acids, total flavonols and total anthocyanins, were more concentrated in the peel irrespective of the harvesting stage. 'O'Henry' was the richest in carotenoids despite a ripening-dependent decrease in the peel, whereas 'Sweet Cap' had the highest phenols content, which further increased in the peel during ripening. The micronutrients content was balanced, which can be considered as a positive fact with respect to ideal quality of fruit, suggesting the peel peach as a potential source of high-value components for functional foods and nutraceutical applications, as well as for nutritional and pharmaceutical purposes.

Compliance with Ethical Standards

Conflict of Interest We declare not conflict of interest.

Human and Animal Rights This article does not contain any studies with human or animal subjects.

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